Supporting Information

Thermally-Induced Intramolecular [2 + 2] Cycloaddition of Allene-Methylenecyclopropanes: Expedient Access to Two Separable Spiropolycyclic Heterocycles

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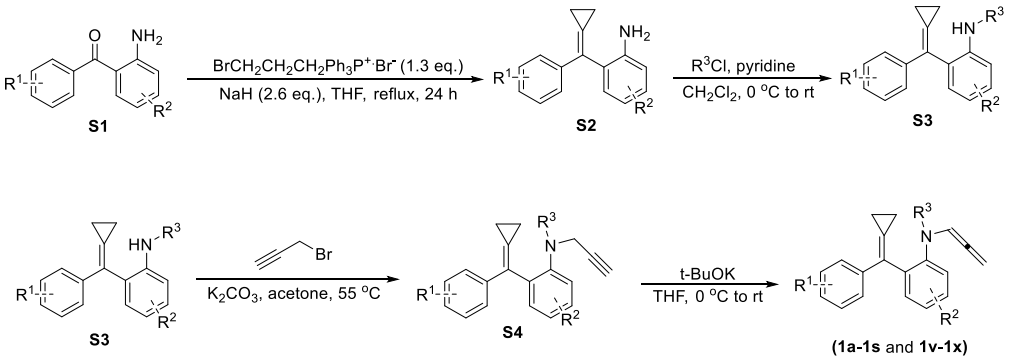
CONTENTS

1. General Remarks

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. NMR spectra were recorded with Varian and Agi spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR) and 376 MHz (^{19}F NMR) in $CDCl_3$, respectively. Chemical shift was reported in ppm down field from internal TMS. Organic solvents used were dried by standard methods when necessary. Commercially available reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI and HRMS was measured on a HP-5989 instrument. The 8 W Blue LED (Manufacturer: Liangyuan-Light Factory, Model: PAR 38, Wavelength: 425 nm) was directly got from the supermarket.

2. General Procedure for the Synthesis of Substrates

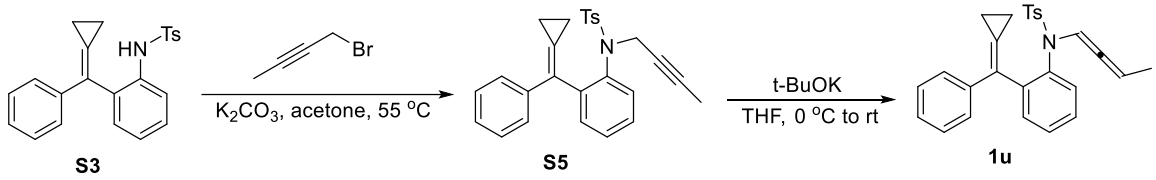


The procedure of preparing substrates **1** was slightly modified by the previous literature.[1] A solution of 3-bromopropyltriphenylphosphonium bromide (5.96 g, 13 mmol) and NaH (624 mg, 26 mmol) in THF (15 mL) was stirred at 65 °C in an oil bath under Ar for 12 h. Afterwards compound **S1** (10 mmol) in THF (10 mL) was added and the reaction solution was stirred at 65 °C in an oil bath for another 12 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 80/1) to afford the products **S2** in moderate yields.

A solution of compounds **S2** (4.0 mmol) in CH_2Cl_2 (15.0 mL) was stirred at 0 °C in an ice bath. Then pyridine (8.0 mmol) and the corresponding acyl chloride (6.0 mmol) were added in one portion, respectively; the resulting mixture was warmed to room temperature and stirred overnight. Upon completion, the mixture was washed with $CuSO_4$ solution and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 30/1) to afford the products **S3** in moderate yields. A solution of compound **S3** (2.5 mmol) and K_2CO_3 (5.0 mmol) in acetone (15.0 mL) was stirred at 55 °C, then, propargyl bromide (5.0 mmol) was added dropwise. Upon completion, the mixture is cooled and filtered through a celite, the solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the products **S4** in good yields.

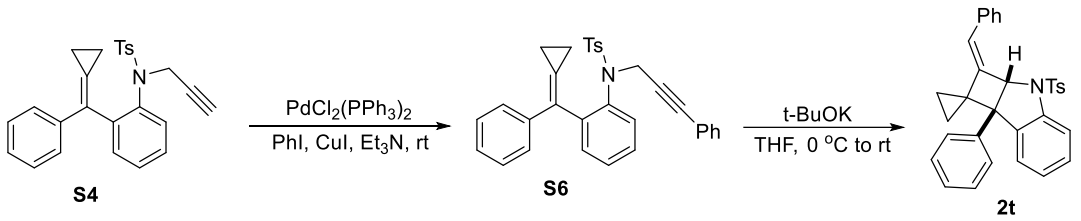
A solution of compound **S4** (2.0 mmol) in THF (15.0 mL) was stirred at 0 °C in an ice bath under Ar. Then t-BuOK (0.3 eq.) was added dropwise, and the resulting mixture was warmed to room temperature and stirred overnight. The solvent was removed under vacuum and the residue was

purified by a flash column chromatography on silica gel (PE/EA = 30/1) to afford the products **1a-1q**, and **1v-1x** in moderate yields.



S3 **S5** **1u**

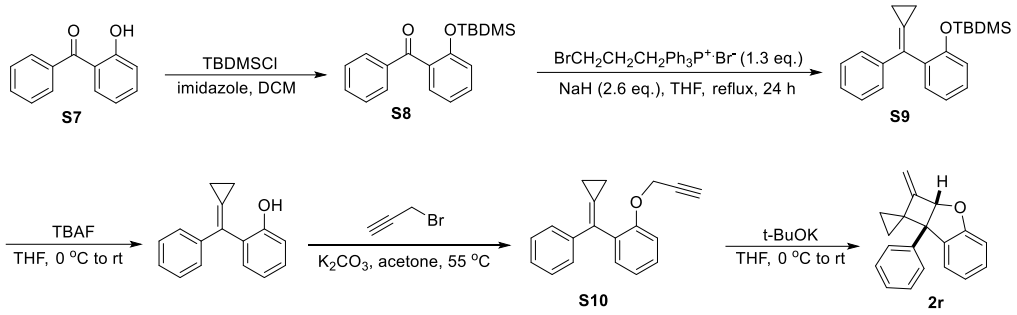
A solution of compound **S3** (2.5 mmol) and K_2CO_3 (5.0 mmol) in acetone (15.0 mL) was stirred at 55 °C, then, 1-bromide-2-butyne (5.0 mmol) was added dropwise. Upon completion, the mixture is cooled and filtered through a celite, the solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the product **S5** in good yield. A solution of compound **S5** (2.0 mmol) in THF (15.0 mL) was stirred at 0 °C in an ice bath under Ar. Then t-BuOK (0.3 eq.) was added dropwise, the resulting mixture was warmed to room temperature and stirred overnight. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 30/1) to afford the product **1u**.



S4 **S6** **2t**

To a 50-mL oven-dried Schlenk tube containing a magnetic stirrer bar was mixed with **S4** (3.0 mmol), $PdCl_2(PPh_3)_2$ (2 mol%) and CuI (4 mol%). Then deoxidized Et_3N (20 mL) is added under Ar. Subsequently, PhI (3.3 mmol) was added dropwise and the resulting mixture was stirred at room temperature. Upon completion, the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 10/1) to afford the product **S6** in good yield. A solution of compound **S6** (2.5 mmol) in THF (15.0 mL) was stirred at 0 °C in an ice bath under Ar. Then t-BuOK (0.3 eq.)

was added dropwise, and the resulting mixture was warmed to room temperature and stirred overnight. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 30/1) to afford the product **2t**.

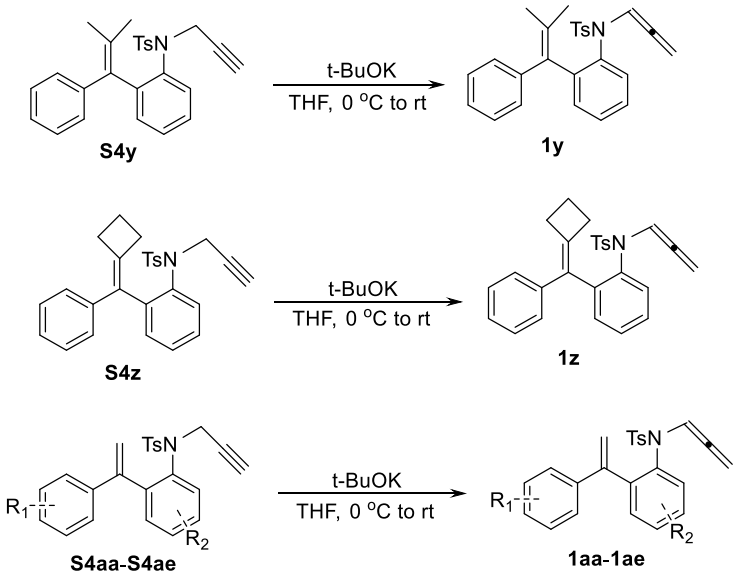


S7 (10.0 mmol) was dissolved in DCM (30 mL) and then cooled to 0 °C, to which was added imidazole (12.0 mmol) and the corresponding TBDMSCl (12 mmol). Then, the reaction mixture was stirred at room temperature until the reaction was complete upon monitored by TLC analysis. Then, the reaction mixture was extracted by DCM/H_2O and the organic phase was dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 30/1) to afford the product **S8** in good yield. A solution of 3-bromopropyltriphenylphosphonium bromide (4.83 g, 10.4 mmol) and NaH (0.50 g, 20.8 mmol) in THF (15 mL) was stirred at 65 °C in an oil bath under Ar for 12 h. Afterwards compound **S8** (8 mmol) in THF (10 mL) was added and the reaction solution was stirred at 65 °C in an oil bath for another 12 h. Upon completion, the reaction mixture was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 30/1) to afford the product **S9** in moderate yield.

A solution of **S9** (5.0 mmol) in THF (15 mL) was stirred at 0 °C. TBAF (6.0 mmol, 1.90 g) dissolved in THF (5 mL) was added to the mixture. Then, the resulting solution was stirred at room temperature until TLC analysis showed the complete consumption of substrate (about 0.5 h). Aqueous saturated NH_4Cl was added to neutralize TBAF. Next, the resulting mixture was extracted by EtOAc/H_2O and the organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was used in the next step without further purification. A solution of the

above crude product (5.0 mmol) and K_2CO_3 (10.0 mmol) in acetone (15.0 mL) was stirred at 55 °C, then, propargyl bromide (5.0 mmol) was added dropwise. Upon completion, the mixture is cooled and filtered through a celite, and then the solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 10/1) to afford the product **S10** in good yield.

A solution of compound **S10** (4.0 mmol) in THF (20.0 mL) was stirred at 0 °C in an ice bath under Ar. Then t-BuOK (0.3 eq.) was added dropwise, and the resulting mixture was warmed to room temperature and stirred overnight. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 30/1) to afford the product **2r**.

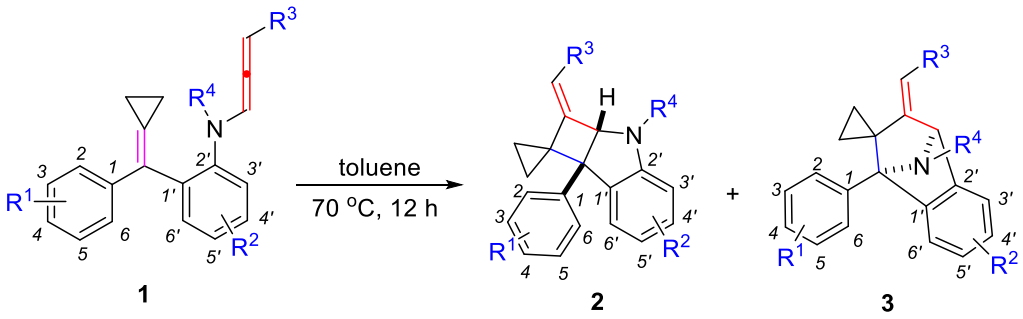


Compounds **S4y-S4ae** were prepared according to the previously reported literature.[1][2]

A solution of compound **S4** (4.0 mmol) in THF (20.0 mL) was stirred at 0 °C in an ice bath under Ar. Then t-BuOK (0.3 eq.) was added dropwise, the resulting mixture was warmed to room temperature and stirred overnight. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (PE/EA = 30/1) to afford the products **1y-1ae** in good yields.

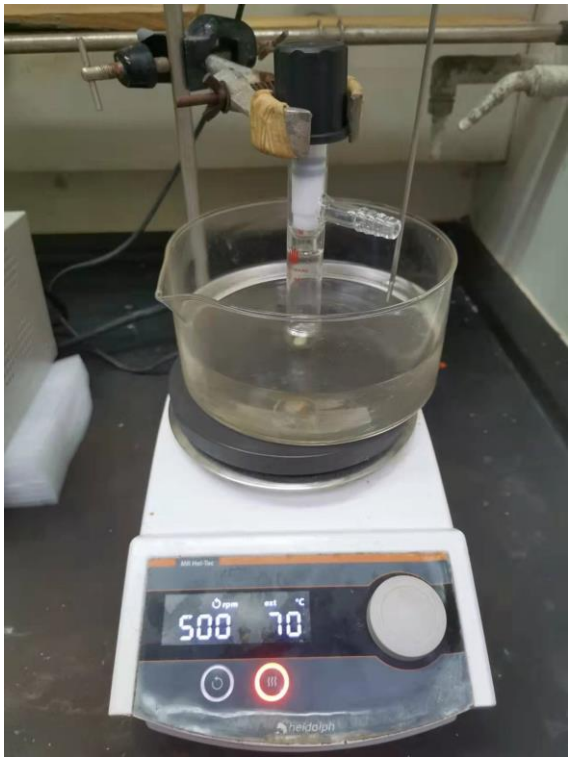
3. General Procedure for the Synthesis of Products

3.1 Method



A 10 mL flame-vacuum dried screwed-tube equipped with a magnetic stirring bar was charged with **1** (0.2 mmol) and toluene (2.0 mL) under argon atmosphere. The reaction mixture was stirred at 70 °C for 12 hours in a pre-heated oil bath. After the reaction was finished up, the reaction mixture was cooled to ambient temperature. Then, organic solvent was removed under reduced pressure and the resulting residue was purified through a silica-gel column chromatography (eluent: petroleum ether / ethyl acetate = 20 / 1) to provide the desired products **2** and **3**.

3.2 Reaction Setup



4. Mechanistic Investigations

4.1 Computational Methods, Coordinates and Energies

4.1.1 Computational Details

All DFT calculations were performed with Gaussian 16 program.[2] The geometries of all minima and transition states have been optimized at M06-2X/6-31G(d) level of theory. 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 or first-order saddle points on the respective potential energy surfaces. All transition states were characterized by one and only one imaginary frequency pertaining to the desired reaction coordinate. Thermochemical corrections to 298.15 K have been calculated for all minima from unscaled vibrational frequencies obtained at this same level. The solvent effect was estimated by the IEFPCM method with radii and nonelectrostatic terms for SMD salvation model in toluene. Solution-phase single point energy calculations were performed at M06-2X/6-311+G(d,p) level based on the gas phase optimized structures. The possible conformers for each species were searched manually, and the best conformer was used to calculate the reaction energy profile.

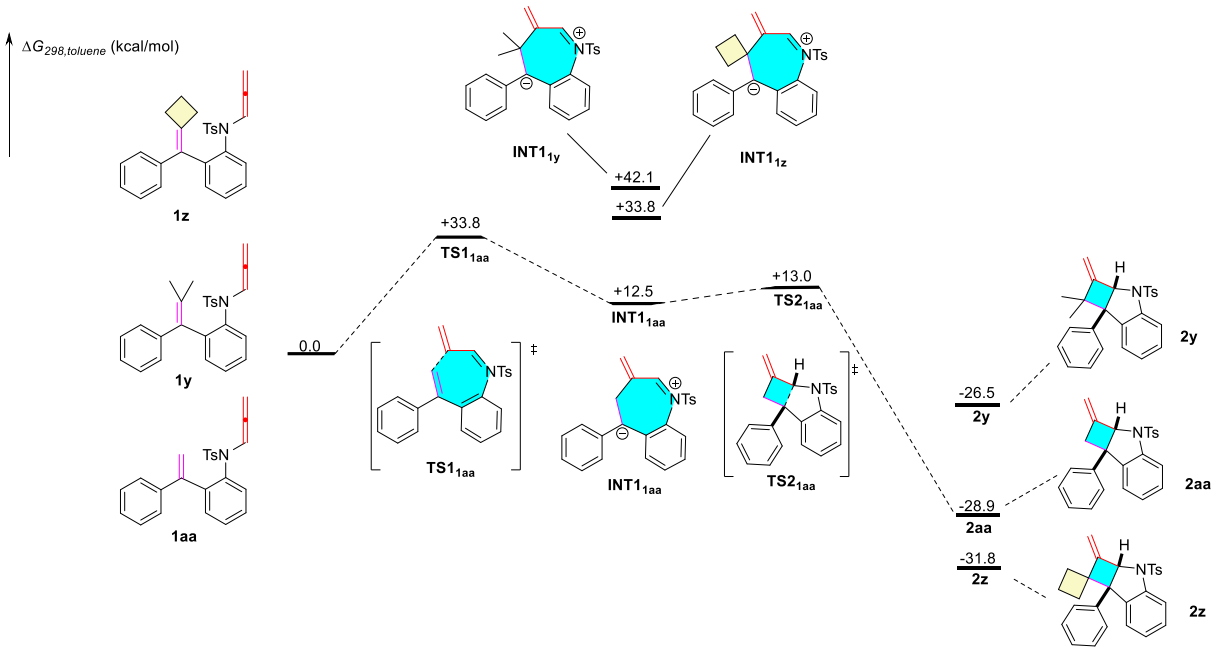


Figure S1. A theoretical investigation of controlling experiment.

4.1.2 Computational Coordinates and Energies

Table S1. The total energies, enthalpies and free energies of all species in toluene shown in Figure 2.[a]

	E_{tot} (E_h)	$H_{298,\ toluene}$	$G_{298,\ toluene}$
1z	-1646.578439	-1646.093821	-1646.184002
INT1$_{1z}$	-1646.5354	-1646.051041	-1646.133925
1y	-1608.522401	-1608.04453	-1608.132282
INT1$_{1y}$	-1608.463913	-1607.986518	-1608.068854
1aa	-1529.930774	-1529.51291	-1529.594758
1a	-1607.275455	-1606.821684	-1606.90827
TS1$_{1a}$	-1607.236099	-1606.783385	-1606.863961
INT1$_{1a}$	-1607.278374	-1606.823086	-1606.907788
TS2$_{1a}$	-1607.278659	-1606.824349	-1606.905036
TS2$_{side}$	-1607.257441	-1606.804766	-1606.886718
INT2$_{side}$	-1607.301566	-1606.845464	-1606.930079
TS3$_{side}$	-1607.27272	-1606.818253	-1606.89954
3a	-1607.349241	-1606.892392	-1606.971376
2a	-1607.349946	-1606.893707	-1606.972791
2y	-1608.577404	-1608.097457	-1608.178651
2z	-1646.64499	-1646.158041	-1646.238875
2aa	-1529.989761	-1529.569503	-1529.644429
Ts1$_{1a-1}$	-1607.178639	-1606.727859	-1606.809615
1r	-808.396784	-808.085293	-808.149477
TS1$_{1r}$	-808.368097	-808.057674	-808.117583
INT1$_{1r}$	-808.397725	-808.084998	-808.143609
TS2$_{1r}$	-808.396297	-808.084608	-808.142158
2r	-808.462397	-808.148637	-808.208052
TS1$_{1aa}$	-1529.879407	-1529.463043	-1529.542326

INT1$_{1aa}$	-1529.918867	-1529.499383	-1529.577414
TS2$_{1aa}$	-1529.918824	-1529.500335	-1529.57664

Calculated at SMD(toluene)/M06-2X/6-311+G(d,p)//M06-2X/6-31G(d)

1z

Opt @ M06-2X/6-31G(d)

SCF Done: E(M062X) = -1646.578439a.u.

Zero-point correction = 0.455579 Hartree/Particle

Sum of electronic and thermal Free Energies = -1646.184002a.u.

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INT1$_{1z}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1646.535400a.u.
Zero-point correction = 0.457060Hartree/Particle
Sum of electronic and thermal Free Energies = -1646.133925a.u.

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H,5.19533500,1.69797100,0.34179300

1y

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1608.522401a.u.
Zero-point correction = 0.448850Hartree/Particle
Sum of electronic and thermal Free Energies = -1608.132282a.u.

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C,3.82592300,1.48643100,2.36406900
C,4.63911300,-0.78266000,1.66115300
H,4.77212400,2.01849100,2.20187600
H,3.01324600,2.21216000,2.30773000
H,3.86659900,1.08895800,3.38590500
H,5.62687100,-0.36206000,1.88534000
H,4.33945800,-1.36080800,2.54466100
H,4.73626100,-1.46880500,0.81935600
H,6.12329200,0.23387800,-0.00817300

H,5.44349400,0.47826600,1.60591000
C,-2.27137300,1.29116300,-0.22426100
C,-3.54832100,1.27128800,0.71002000
C,-2.57536000,2.80009800,-0.50269300
C,-3.94463900,2.66996400,0.19363100
H,-3.27626500,1.27484900,1.76727000
H,-4.24965700,0.45586500,0.51898600
H,-1.88338500,3.44631200,0.04085100
H,-2.58335300,3.10940200,-1.55155900
H,-4.14832000,3.41057600,0.96999400
H,-4.79216000,2.65646900,-0.49438500

INT1$_{1y}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1608.463913a.u.
Zero-point correction = 0.450134Hartree/Particle
Sum of electronic and thermal Free Energies = -1608.068854a.u.

S,-0.28973100,-2.05364200,-1.45345300
O,-0.38011900,-1.78160600,-2.87578600
O,-0.57080200,-3.37259600,-0.91489800
N,-1.42233900,-0.95424500,-0.72238600
C,-1.56827100,-1.04756200,0.72369900
C,-2.03990500,-2.18679900,1.36907500
C,-2.02779300,-2.18537300,2.76112300
C,-1.57308000,-1.06516500,3.46199200
C,-1.15344100,0.07851500,2.78850500
C,-1.15793100,0.10109900,1.38867900
C,-0.91547500,1.23430200,0.45831000
C,-2.35662400,-0.38427000,-1.52143100
C,-2.96936300,0.82712900,-1.14848100
C,-2.18013300,1.79965700,-0.12589900
C,-3.17865000,2.02013000,1.04506500
C,-2.03718900,3.15912600,-0.84117000
C,-4.17846300,1.19909400,-1.63318700
C,0.41853900,1.75355500,0.31402800
C,0.86775000,2.48613800,-0.81792600
C,2.14881000,3.01763500,-0.88779800
C,3.05837600,2.83765600,0.15156500
C,2.66744800,2.06376400,1.24685400
C,1.39897200,1.51600000,1.31691700
C,1.25817500,-1.50452500,-0.82701600
C,2.01270300,-0.61417700,-1.58885200
C,3.26496300,-0.24250500,-1.12257700

C,3.75917700,-0.73485700,0.08903000
C,2.96798600,-1.60880900,0.83945800
C,1.71361900,-2.00446200,0.39097300
C,5.12331800,-0.31903900,0.57154600
H,-2.35704300,-3.05298700,0.79973800
H,-2.36548600,-3.06346500,3.30165500
H,-1.57087200,-1.07867100,4.54777600
H,-0.85674300,0.96557200,3.34095400
H,-2.45707300,-0.78703400,-2.52271300
H,-3.42184000,1.08823700,1.55842100
H,-2.75377600,2.72131600,1.77139800
H,-1.34760300,3.81281000,-0.29989200
H,-1.69206400,3.05826700,-1.87133800
H,-4.82900900,0.48855900,-2.13115300
H,-4.55320400,2.21138900,-1.52957700
H,0.21265100,2.61261500,-1.66861200
H,2.43881000,3.57630700,-1.77372700
H,4.05081900,3.27577600,0.10532300
H,3.36856600,1.87658900,2.05691900
H,1.14496700,0.90201100,2.17357800
H,1.62625100,-0.24378200,-2.53237900
H,3.86241900,0.45939900,-1.69689500
H,3.34006500,-1.98703600,1.78752400
H,1.10223300,-2.69968400,0.95784000
H,5.30567900,0.73575200,0.34637800
H,5.90661000,-0.90623700,0.07951700
H,5.22506000,-0.46446700,1.65016300
H,-4.11142700,2.43501200,0.65003400
H,-3.00964100,3.65781800,-0.87841300

1aa

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1529.930774a.u.
Zero-point correction = 0.391802Hartree/Particle
Sum of electronic and thermal Free Energies = -1529.594758a.u.

C,2.86394600,-0.72547400,-0.04230200
C,2.87126900,-2.02307200,0.48007500
C,2.77477200,-3.12341800,-0.36326800
C,2.66484000,-2.94180000,-1.73960900
C,2.64373500,-1.65436600,-2.26742200
C,2.73773000,-0.55221200,-1.42469700
C,2.22475000,1.68052500,0.50828300
C,0.83860100,1.63601100,0.28752100

C,2.87149300,2.91516600,0.39085700
C,0.13437200,2.78894500,-0.05009200
C,2.17195600,4.06531800,0.04192800
C,0.80018800,4.00088700,-0.18830300
C,2.99980100,0.45478500,0.85102400
C,3.81203700,0.45192700,1.91480500
N,0.12939800,0.40896700,0.48795400
S,-0.60336100,-0.37621500,-0.81570100
O,-0.30055100,0.43827700,-1.97864500
O,-0.27103500,-1.78437500,-0.74528400
C,-2.34061100,-0.22205300,-0.46900800
C,-3.04011500,0.86684500,-0.98328300
C,-2.97107400,-1.18690200,0.30916600
C,-4.39122800,0.99643400,-0.68894700
C,-4.32400200,-1.03625200,0.59663400
C,-5.04947200,0.05228600,0.10688100
C,-6.52222000,0.19040100,0.39382500
C,0.18596200,-0.19496800,1.76633100
C,-0.07309000,-1.43672900,2.09815900
C,-0.32144600,-2.64362800,2.52674400
H,2.92372900,-2.15867400,1.55724300
H,2.76883900,-4.12531500,0.05573400
H,2.57671200,-3.80144500,-2.39666100
H,2.53789300,-1.50374600,-3.33709800
H,2.70139200,0.45181600,-1.83866800
H,3.94504100,2.95157300,0.55000300
H,-0.94030600,2.72281000,-0.18690900
H,2.69885100,5.00904400,-0.05737000
H,0.24651100,4.89350800,-0.46085200
H,4.43324000,-0.40766900,2.14646600
H,3.87824900,1.31090800,2.57597600
H,-2.52926100,1.58083400,-1.62213400
H,-2.40719000,-2.04367600,0.66351500
H,-4.94952700,1.83876600,-1.08886400
H,-4.82811600,-1.78178400,1.20564100
H,-7.11639900,-0.20727200,-0.43626900
H,-6.80411100,-0.35759600,1.29628500
H,-6.80302100,1.23877300,0.52636000
H,0.47299700,0.51169200,2.54099700
H,-1.31965300,-2.95137500,2.83278000
H,0.46165000,-3.39766100,2.56898100

1a

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1607.275455a.u.
Zero-point correction = 0.425599Hartree/Particle
Sum of electronic and thermal Free Energies = -1606.908270a.u.

C,2.50394800,-0.84453900,-0.51533300
C,2.56819400,-2.12275800,0.04905800
C,2.34309200,-3.24968200,-0.73192800
C,2.05070800,-3.11553000,-2.08731200
C,1.97834600,-1.84780000,-2.65573200
C,2.19994900,-0.71837500,-1.87488400
H,2.77468700,-2.22034100,1.11103900
H,2.38274200,-4.23616500,-0.27930300
H,1.86388800,-3.99635000,-2.69380300
H,1.73264900,-1.73286900,-3.70675100
H,2.12125600,0.27066300,-2.31803300
C,1.99405200,1.60739000,-0.00609600
C,0.59125700,1.60210000,-0.06577000
C,2.66011100,2.81162000,-0.25261900
C,-0.11264900,2.76125800,-0.38298200
C,1.96028600,3.96755200,-0.57994400
H,3.74497300,2.81877100,-0.20744100
C,0.56961900,3.94048300,-0.65566900
H,-1.19739100,2.72661100,-0.39671700
H,2.49986600,4.88745500,-0.78204000
H,0.01611900,4.83843600,-0.91054400
C,2.75751200,0.36651300,0.30706300
C,3.65064800,0.38095600,1.29257500
C,4.67010600,-0.32212600,2.07087500
C,4.30568600,1.13616000,2.36219100
H,5.63158400,-0.52544300,1.60529400
H,4.35613700,-1.07098300,2.79405200
H,3.74726500,1.34684900,3.27159000
H,5.03280300,1.90041200,2.09883700
N,-0.12471100,0.41198300,0.28243000
S,-1.02714400,-0.41675600,-0.87999800
O,-0.85857400,0.33546700,-2.11022800
O,-0.71577000,-1.82818400,-0.78322100
C,-2.70420900,-0.20406000,-0.32740900
C,-3.43973300,0.88022800,-0.79875400
C,-3.25306300,-1.12004200,0.56368100
C,-4.74136800,1.05621100,-0.34682000
H,-2.99759800,1.55441000,-1.52600400
C,-4.55653600,-0.92334500,1.00822200

H,-2.66710400,-1.97588000,0.88273000
C,-5.31506800,0.16243300,0.56392100
H,-5.32749400,1.89553800,-0.71161600
H,-4.99655700,-1.63029900,1.70649900
C,-6.73843000,0.34712200,1.02278700
H,-6.99592600,1.40691000,1.09877300
H,-7.43549900,-0.11169100,0.31290900
H,-6.90462100,-0.11787400,1.99775800
C,0.07923500,-0.13344600,1.57196300
C,-0.15519500,-1.35283300,1.99338900
C,-0.36963500,-2.53242100,2.50801200
H,-1.32871600,-2.80307600,2.94589200
H,0.39982800,-3.30131200,2.49215400
H,0.46796400,0.60376600,2.27038000

$TS1_{1a}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1607.236099a.u.
Zero-point correction = 0.426391Hartree/Particle
Sum of electronic and thermal Free Energies = -1606.863961a.u.

C,-1.99551200,0.38310800,0.60591900
C,-3.09367200,0.00539400,1.39580400
C,-3.07315000,0.16444800,2.77214300
C,-1.95760800,0.72478100,3.39377600
C,-0.90197400,1.17352700,2.61600800
C,-0.90853800,1.04405200,1.21868900
C,0.08511400,1.77797100,0.42152400
C,-1.44504000,0.54808200,-1.91749900
C,-0.41970900,1.39476800,-2.07793300
C,-0.46524500,2.64163500,-0.49279800
C,-1.65947500,3.50580200,-0.48492600
C,-0.31338500,4.03102900,-0.96869800
C,0.60410200,1.68920000,-2.87925300
C,1.51531900,1.51610900,0.51119600
C,2.42884900,2.22594500,-0.29018900
C,3.79034700,1.94531200,-0.23534700
C,4.27371500,0.96442000,0.62582000
C,3.37844900,0.25054000,1.42396400
C,2.01776100,0.50921000,1.35617000
H,-3.95566400,-0.43245300,0.91010100
H,-3.93401600,-0.14175100,3.35733400
H,-1.93333400,0.85451600,4.47112200
H,-0.06225900,1.68784100,3.07565300

H,-1.92390300,0.18505100,-2.82050500
H,-2.41944600,3.34731600,-1.24391400
H,-2.03607000,3.83132700,0.48141900
H,0.24024500,4.71498200,-0.33052200
H,-0.21647000,4.22987300,-2.03240000
H,1.21639700,0.89236900,-3.29310000
H,0.91041900,2.70623200,-3.10269400
H,2.06641000,3.00996000,-0.94416400
H,4.47788300,2.50531900,-0.86201900
H,5.33865900,0.75839500,0.67878000
H,3.74326000,-0.52271700,2.09467400
H,1.32794100,-0.08187000,1.94985900
N,-2.05363400,-0.02361700,-0.76616800
S,-2.02175300,-1.75832900,-0.95672200
O,-2.88210500,-2.35588100,0.04310900
O,-2.24618000,-2.00678400,-2.36875600
C,-0.33893000,-2.13834800,-0.55110200
C,-0.03531600,-2.58557600,0.72995800
C,0.65187900,-1.93975600,-1.51226700
C,1.29269200,-2.86580900,1.04035600
H,-0.83101600,-2.72235000,1.45570100
C,1.97046900,-2.20539600,-1.17426800
H,0.38251200,-1.60022300,-2.50751400
C,2.30718400,-2.68128500,0.09861800
H,1.54436000,-3.23086400,2.03254600
H,2.75495800,-2.04920600,-1.90980100
C,3.74309400,-2.99644700,0.42500500
H,3.87779700,-3.18456800,1.49334100
H,4.07706900,-3.88706600,-0.11800600
H,4.39551000,-2.16649300,0.13598900

INT1$_{1a}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1607.278374a.u.
Zero-point correction = 0.428685Hartree/Particle
Sum of electronic and thermal Free Energies = -1606.907788a.u.

S,2.36548100,-1.21977400,-1.24343900
O,2.20105200,-1.49086000,-2.65728100
O,3.47891300,-1.77599300,-0.50852900
N,0.84210400,-1.76443900,-0.45725100
C,0.78446700,-1.37903000,0.89986500
C,1.84979700,-1.68980100,1.76963900
C,1.97425700,-1.01659800,2.96706500

C,1.04307400,-0.02214900,3.32053000
C,-0.05163700,0.21738900,2.51951100
C,-0.26908600,-0.50921400,1.32245500
C,-1.49959600,-0.52934200,0.60725600
C,-0.18159600,-1.82981000,-1.34537800
C,-1.56787300,-2.11718900,-1.13779200
C,-1.98584000,-1.90744900,0.26760500
C,-1.88150200,-3.03032300,1.26578500
C,-3.22816300,-2.51301000,0.85169300
C,-2.40176000,-2.28812200,-2.18845500
C,-2.29681000,0.63046700,0.28405200
C,-3.57516300,0.49652600,-0.30178900
C,-4.31978400,1.61460400,-0.66372800
C,-3.82839800,2.89784600,-0.44893300
C,-2.55945900,3.05111200,0.11745500
C,-1.80138400,1.94559100,0.46235900
C,2.20969500,0.51017600,-0.92159400
C,1.28369100,1.23568600,-1.66928400
C,1.06442100,2.56511700,-1.33960200
C,1.75369500,3.16673200,-0.27952100
C,2.67137700,2.40712900,0.45115100
C,2.90716300,1.07223800,0.14123600
C,1.51139400,4.61510800,0.05377200
H,2.57348300,-2.44164000,1.48514300
H,2.78999400,-1.26437100,3.63821000
H,1.14787100,0.50784700,4.26226500
H,-0.83232700,0.89768800,2.84702800
H,0.15844300,-1.82709500,-2.37547200
H,-1.57278800,-4.00128800,0.89191700
H,-1.51846400,-2.78035800,2.25788900
H,-3.77763800,-1.90741100,1.56499600
H,-3.84588600,-3.13704300,0.21233100
H,-2.04675300,-2.23413100,-3.21262900
H,-3.45776800,-2.47583900,-2.03308300
H,-3.98492500,-0.49288300,-0.46674200
H,-5.30007200,1.47778700,-1.11117800
H,-4.41867000,3.76727100,-0.72005800
H,-2.15696400,4.04761900,0.28063700
H,-0.79766200,2.08457800,0.85323000
H,0.74360200,0.76582700,-2.48512500
H,0.33277100,3.14110000,-1.89902100
H,3.20070500,2.86243500,1.28314100
H,3.60016700,0.46838800,0.71721200
H,0.45261100,4.86889800,-0.04883400

H,2.07263500,5.26565000,-0.62582000
H,1.82560200,4.84715200,1.07409800

$TS2_{1a}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1607.278659a.u.
Zero-point correction = 0.428542Hartree/Particle
Sum of electronic and thermal Free Energies = -1606.905036a.u.

S,2.34444700,-1.15584400,-1.30625900
O,2.14590300,-1.41122200,-2.71864800
O,3.48928100,-1.69342100,-0.60547000
N,0.87076000,-1.75647900,-0.48728800
C,0.84164800,-1.38949200,0.87741200
C,1.91693000,-1.70004300,1.72947000
C,2.03513700,-1.04851300,2.94190200
C,1.08928800,-0.08165100,3.32246900
C,-0.01238200,0.16158500,2.52761500
C,-0.21397900,-0.53580900,1.31495800
C,-1.43999700,-0.55599400,0.58131500
C,-0.19961200,-1.78219700,-1.33068000
C,-1.55992200,-2.18261700,-1.09709500
C,-1.95536600,-1.94329700,0.30712500
C,-1.85178900,-3.03293700,1.34141700
C,-3.19623200,-2.50658800,0.93363400
C,-2.39650500,-2.42163100,-2.12855900
C,-2.24128400,0.60504800,0.26885100
C,-3.51860100,0.47341900,-0.31875400
C,-4.25648900,1.59361700,-0.68620400
C,-3.75889900,2.87583600,-0.47513200
C,-2.49399400,3.02620300,0.09952200
C,-1.74517800,1.91714100,0.45590900
C,2.16198700,0.56689500,-0.95814800
C,1.21158700,1.28670600,-1.67668400
C,0.96248400,2.60362500,-1.31141400
C,1.63632200,3.19069400,-0.23609900
C,2.59266300,2.44062400,0.45730800
C,2.86135900,1.12341700,0.10864700
C,1.29079300,4.58467300,0.21760100
H,2.65407800,-2.42909200,1.42076400
H,2.86168300,-1.29233600,3.60126600
H,1.18849200,0.42715300,4.27639000
H,-0.80100100,0.82531800,2.87014500
H,0.09598600,-1.71211400,-2.37254400

H,-1.56620600,-4.02079300,0.99456600
H,-1.46671600,-2.75690000,2.31833300
H,-3.72155900,-1.86579200,1.63445400
H,-3.83710800,-3.14028800,0.32738300
H,-2.05581800,-2.38175300,-3.15816400
H,-3.44161800,-2.65068600,-1.95439400
H,-3.92812300,-0.51534800,-0.48933100
H,-5.23471000,1.46020500,-1.13914200
H,-4.34253700,3.74667200,-0.75599000
H,-2.08495400,4.02135100,0.25646900
H,-0.74481700,2.04985800,0.85772400
H,0.68032100,0.82763900,-2.50428500
H,0.21508200,3.17565700,-1.85310000
H,3.12516300,2.89149100,1.29019900
H,3.58501400,0.52626400,0.65311400
H,0.98714600,5.21426900,-0.62188300
H,2.13110400,5.06168200,0.72788100
H,0.45333500,4.55124800,0.92594600

TS2$_{side}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1607.257441a.u.
Zero-point correction = 0.427244Hartree/Particle
Sum of electronic and thermal Free Energies = -1606.886718a.u.

S,1.62000800,-1.01723300,-0.94494000
O,1.16828700,-0.33460100,-2.14613200
O,1.65395600,-2.46524900,-0.82593700
N,0.66233800,-0.48454700,0.30763400
C,0.10852400,0.77424700,0.53689300
C,0.98479400,1.85786100,0.84965800
C,0.50590500,3.11932900,1.03814600
C,-0.89806300,3.36824300,0.96517800
C,-1.76208700,2.36132500,0.67250300
C,-1.32406100,1.00613300,0.40849300
C,-2.25535000,0.00239900,0.14701300
C,0.23728200,-1.12832900,1.47020100
C,-1.04519000,-1.74497900,1.46000200
C,-1.87667700,-1.42979400,0.22981900
C,-2.76117700,-2.49327000,-0.36587600
C,-1.47296600,-2.16730500,-1.04703500
C,-1.56691500,-2.45808800,2.48096000
C,-3.66471300,0.34237900,-0.14653700
C,-4.70941700,-0.24491700,0.58364100

C,-6.03401800,0.06298700,0.30138700
C,-6.34362100,0.95315800,-0.72678300
C,-5.31798500,1.53445300,-1.46686500
C,-3.98999200,1.23288700,-1.17909100
C,3.25004200,-0.41198900,-0.57016400
C,3.84459400,0.52711100,-1.40275400
C,5.11129200,1.00609600,-1.07776400
C,5.77979400,0.55938300,0.06341600
C,5.15280900,-0.38641100,0.88498500
C,3.89351900,-0.87996500,0.57453100
C,7.16344000,1.05630700,0.39340000
H,2.04757600,1.64345500,0.91321900
H,1.18894100,3.93586700,1.25083600
H,-1.27700800,4.36414700,1.17030700
H,-2.82804600,2.55707200,0.67183800
H,0.74683000,-0.87641900,2.39711400
H,-2.82260900,-3.43974200,0.15990600
H,-3.68356100,-2.17576500,-0.83781300
H,-1.49540300,-1.58610000,-1.96353500
H,-0.65264300,-2.87109800,-0.96666600
H,-0.95797200,-2.77024300,3.32368900
H,-2.60404700,-2.77621200,2.46754400
H,-4.46350600,-0.93667300,1.38501100
H,-6.82861700,-0.39117800,0.88543800
H,-7.37943200,1.18881800,-0.95015600
H,-5.55038800,2.21986700,-2.27612400
H,-3.18807100,1.67539200,-1.76365800
H,3.31178800,0.87464700,-2.28180800
H,5.58679900,1.74139200,-1.72114700
H,5.66381200,-0.73967800,1.77673100
H,3.41001400,-1.62241000,1.20333800
H,7.28759900,1.19830800,1.47066000
H,7.37500200,2.00452200,-0.10605000
H,7.91991400,0.33289400,0.06934900

INT2$_{side}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1607.301566a.u.
Zero-point correction = 0.429605Hartree/Particle
Sum of electronic and thermal Free Energies = -1606.930079a.u.

S,2.09407500,1.65090500,-0.46492900
O,2.63648200,2.55560000,0.54687700
O,1.85291200,2.11652400,-1.81863400

N,0.65851600,0.93050100,0.06190000
C,-0.52269100,1.74439600,0.46005000
C,-0.43604100,3.22239200,0.39137200
C,-1.42480200,3.93583600,-0.16406600
C,-2.61672300,3.29320100,-0.70078100
C,-2.80304700,1.96427900,-0.59211300
C,-1.82745100,1.10685800,0.07058800
C,-2.06020000,-0.20107400,0.35124900
C,0.32266300,1.01447900,1.47760500
C,-0.23522200,-0.21585800,2.08365400
C,-1.07429500,-1.01534000,1.13959700
C,-1.32617100,-2.47166200,1.44062900
C,-0.34540700,-2.11371300,0.37536300
C,-0.00940200,-0.51286300,3.36295800
C,-3.28075600,-0.88624500,-0.15422700
C,-4.27196000,-1.33130600,0.72850400
C,-5.40846300,-1.97401300,0.24981500
C,-5.56696400,-2.18907000,-1.11847800
C,-4.58529100,-1.75502000,-2.00442800
C,-3.44917500,-1.10698800,-1.52501400
C,3.11429800,0.19986000,-0.49818500
C,4.06356300,0.01069400,0.49649800
C,4.83708300,-1.14760000,0.47175700
C,4.66670100,-2.10438000,-0.52930800
C,3.70000600,-1.88240200,-1.51994200
C,2.92149100,-0.73479800,-1.51418700
C,5.51320700,-3.35026900,-0.56622800
H,0.46153900,3.69125900,0.78223900
H,-1.34520600,5.01713600,-0.21695900
H,-3.37157100,3.91051600,-1.17696200
H,-3.71112500,1.50522400,-0.96760000
H,0.96454500,1.64415900,2.09291500
H,-0.93775100,-2.85771100,2.37614600
H,-2.27488400,-2.89724100,1.13619000
H,-0.63789300,-2.25394200,-0.66081800
H,0.71648300,-2.21526200,0.57735400
H,0.64004900,0.10701600,3.97380600
H,-0.46646600,-1.37006300,3.84540900
H,-4.14399900,-1.16276400,1.79459100
H,-6.17367600,-2.30581300,0.94491000
H,-6.45338200,-2.69287400,-1.49110400
H,-4.70208700,-1.91970900,-3.07118100
H,-2.68156300,-0.75897200,-2.21142500
H,4.19283100,0.76476400,1.26588800

H,5.58606000,-1.30837700,1.24209800
H,3.56314700,-2.62128800,-2.30522400
H,2.17340800,-0.55254700,-2.27950200
H,4.89267000,-4.24385400,-0.68273300
H,6.10136600,-3.45914600,0.34791500
H,6.20782900,-3.32183000,-1.41239900

TS3$_{side}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1607.272720a.u.
Zero-point correction = 0.428822Hartree/Particle
Sum of electronic and thermal Free Energies = -1606.899540a.u.

S,-1.33952300,-1.93770200,-1.33141400
O,-1.78535900,-3.20575600,-0.73022300
O,-1.37141500,-1.77999000,-2.78338200
N,0.11040700,-1.48488400,-0.80269900
C,1.96529200,-1.92424100,0.45704100
C,2.81767700,-3.00116000,0.25545200
C,4.16970900,-2.77524300,0.02081900
C,4.68544100,-1.47278200,-0.06626000
C,3.84512100,-0.38926000,0.08766400
C,2.48248100,-0.60417300,0.39949400
C,1.56382600,0.47032900,0.58978700
C,0.46503100,-2.01123100,0.50980500
C,-0.02527600,-1.11810400,1.63355000
C,0.37232300,0.29583500,1.38436000
C,0.18066700,1.37861300,2.48810800
C,-0.72808800,1.37229400,1.33935500
C,-0.78668600,-1.54417300,2.63824900
C,1.87007200,1.78826600,-0.01447700
C,2.66040500,2.75467200,0.60912600
C,2.91057900,3.96214400,-0.03981500
C,2.37765800,4.19927700,-1.30326100
C,1.59662300,3.22702000,-1.92681300
C,1.33988300,2.01770700,-1.29035600
C,-2.50031200,-0.70203900,-0.72304100
C,-3.30585000,-0.97098500,0.37998800
C,-4.15307200,0.01935500,0.86968100
C,-4.20967800,1.28248100,0.26917100
C,-3.40104300,1.52741900,-0.84501900
C,-2.55268300,0.54312200,-1.34371700
C,-5.15415200,2.33535400,0.79204700
H,2.41581600,-4.00932400,0.26035700

H,4.83572100,-3.62097200,-0.12295000
H,5.73922100,-1.32076000,-0.27267400
H,4.22605400,0.62316400,0.00112500
H,0.12821800,-3.04222300,0.67326500
H,-0.13520400,0.96805700,3.44071900
H,0.93774900,2.15191600,2.54672200
H,-0.62078300,2.14653000,0.58780000
H,-1.72429700,0.95540100,1.45097700
H,-1.08318300,-2.58745100,2.69035500
H,-1.17263500,-0.88868900,3.41510900
H,3.08663300,2.55955700,1.58995500
H,3.52538400,4.71415400,0.44414200
H,2.57529900,5.14053200,-1.80593900
H,1.18902900,3.40681200,-2.91638900
H,0.74547600,1.23512800,-1.75732400
H,-3.26717600,-1.95844400,0.82909500
H,-4.79050300,-0.19091900,1.72590800
H,-3.44790600,2.49849400,-1.33237400
H,-1.94531500,0.71733300,-2.22746200
H,-4.92031400,3.31973400,0.37847700
H,-5.10997000,2.40362900,1.88335000
H,-6.18929600,2.09873000,0.52249800

3a

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1607.349241a.u.
Zero-point correction = 0.431377Hartree/Particle
Sum of electronic and thermal Free Energies = -1606.971376a.u.

S,0.19230500,-0.19886500,2.22176300
O,-0.21589700,1.01875900,2.90003500
O,0.46017100,-1.41795700,2.97240000
N,-1.07436800,-0.62013900,1.15831800
C,-3.35026400,-3.05901600,0.04689500
C,-2.46145400,-2.07368300,0.05112900
C,-1.12072900,-2.06014400,0.75924000
C,-0.08076300,-2.11847800,-0.34792700
C,0.76095100,-3.13457900,-0.75562600
C,1.66145900,-2.86852300,-1.79274400
C,1.69104700,-1.61279000,-2.38807700
C,0.81437700,-0.59561800,-1.98718200
C,-0.08398300,-0.85754700,-0.96544800
C,-1.18097600,-0.04875300,-0.23437300
C,-2.52154000,-0.74692100,-0.63461300

C,-3.82543300,-0.01660400,-0.77359800
C,-3.14000200,-0.56986600,-1.98696100
C,-1.25956000,1.44997500,-0.34301300
C,-0.97069500,2.09888300,-1.54699200
C,-1.11388100,3.47982900,-1.66396600
C,-1.56203300,4.22999500,-0.58214600
C,-1.89833900,3.58484000,0.60615200
C,-1.76435100,2.20504200,0.72219700
C,1.64177300,0.20256300,1.27074800
C,2.57308400,-0.79753700,1.00261700
C,3.66265100,-0.49766200,0.19822600
C,3.83037900,0.78345400,-0.34078900
C,2.89529000,1.77258000,-0.03019600
C,1.79813100,1.49428200,0.78002100
C,4.99747600,1.07325900,-1.24838000
H,-4.27678500,-2.98577400,-0.51724200
H,-3.18606500,-3.97215300,0.60943500
H,-1.00315400,-2.74088300,1.59837300
H,0.74418200,-4.10399700,-0.26585500
H,2.35267000,-3.63904800,-2.11995800
H,2.41397300,-1.40669800,-3.17200300
H,0.89987500,0.38040600,-2.44847400
H,-4.70091900,-0.52988100,-0.38776300
H,-3.82347400,1.06066400,-0.64244800
H,-2.67475000,0.14323600,-2.66218600
H,-3.53829300,-1.46082500,-2.46303300
H,-0.65435600,1.52908500,-2.41208000
H,-0.87742900,3.96479200,-2.60601500
H,-1.66551600,5.30713000,-0.66874500
H,-2.27248100,4.15580600,1.45005100
H,-2.03295000,1.70743900,1.64619600
H,2.43151800,-1.78937900,1.41858300
H,4.39235700,-1.27153700,-0.02620000
H,3.02636700,2.77649700,-0.42465700
H,1.07531800,2.26388500,1.03238400
H,5.93851500,0.74091000,-0.79993600
H,5.08008500,2.14103900,-1.46434200
H,4.88511700,0.54379200,-2.20114100

2a

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1607.349946a.u.
Zero-point correction = 0.430480Hartree/Particle
Sum of electronic and thermal Free Energies = -1606.972791a.u.

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S,-0.29559400,-2.32645500,-1.30328400
 O,-0.33022500,-2.15571100,-2.74485100
 O,-0.55333300,-3.60581000,-0.66760200
 N,-1.46013100,-1.25761900,-0.69255400
 C,-1.58080600,-1.18107800,0.73147400
 C,-1.93840200,-2.22215800,1.58137700
 C,-2.02105200,-1.94786600,2.94494700
 C,-1.77862400,-0.66474700,3.43685100
 C,-1.43872100,0.37131100,2.56790800
 C,-1.32621700,0.10963700,1.20626600
 C,-1.01589400,1.05406700,0.06763800
 C,-1.35596600,0.12904800,-1.16497500
 C,-2.67581700,0.86512900,-1.32096800
 C,-2.25959100,1.89863600,-0.32802900
 C,-3.14343500,2.72195800,0.55485400
 C,-2.33343300,3.38838700,-0.51592100
 C,-3.77732500,0.60061800,-2.00735900
 C,0.33033600,1.74099500,0.09000500
 C,0.71453600,2.50743100,-1.02026900
 C,1.94481200,3.15151200,-1.05588800
 C,2.81654200,3.05362800,0.02897500
 C,2.44859000,2.29271400,1.13235500
 C,1.22060900,1.63198300,1.15856700
 C,1.25859000,-1.70583000,-0.70845500
 C,2.00594700,-0.85327500,-1.51896800
 C,3.19239900,-0.32731100,-1.02627700
 C,3.63879000,-0.64242900,0.26082300
 C,2.86781100,-1.49718100,1.05290100
 C,1.67533800,-2.03364500,0.57921100
 C,4.93655400,-0.07382900,0.77101800
 H,-2.13498000,-3.20976100,1.18183700
 H,-2.29386700,-2.74378800,3.63069200
 H,-1.86587800,-0.46912100,4.50081700
 H,-1.25473600,1.37202000,2.95014600
 H,-0.69096500,0.21079000,-2.02736600
 H,-4.21500300,2.61591900,0.41410800
 H,-2.83043300,2.85811000,1.58571700
 H,-1.47148000,3.97356900,-0.20907000
 H,-2.84127900,3.74318000,-1.40793200
 H,-3.83935600,-0.27790900,-2.64189900
 H,-4.65286700,1.24169000,-1.94588300
 H,0.03362800,2.60058400,-1.86368100
 H,2.22123500,3.73756900,-1.92727000
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H,3.77343300,3.56716200,0.01034100
H,3.12369400,2.19832700,1.97866000
H,0.96767800,1.01195300,2.01214200
H,1.66286100,-0.62681300,-2.52367100
H,3.77838700,0.34724300,-1.64462100
H,3.20609300,-1.74710200,2.05491700
H,1.07986600,-2.70795100,1.18675300
H,5.78850600,-0.65102900,0.39517000
H,4.97754700,-0.09289200,1.86341000
H,5.06337600,0.96079300,0.43835700

2y

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1608.577404a.u.
Zero-point correction = 0.453188Hartree/Particle
Sum of electronic and thermal Free Energies = -1608.178651a.u.

S,-0.37600300,-2.25711400,-1.38512800
O,-0.36875800,-2.00790400,-2.81634000
O,-0.71120200,-3.55483800,-0.82715800
N,-1.51063200,-1.17346700,-0.73956000
C,-1.58543800,-1.11995800,0.68709900
C,-1.95334200,-2.17006700,1.52137400
C,-1.97784000,-1.93266500,2.89318400
C,-1.67586900,-0.67016400,3.40487800
C,-1.33225700,0.37591100,2.55021000
C,-1.26599700,0.15141100,1.17649300
C,-0.95344900,1.11115100,0.03989100
C,-1.41748700,0.22649800,-1.17378500
C,-2.74096200,0.96590300,-1.14625500
C,-2.19493600,2.07973600,-0.26563600
C,-3.06540400,2.49111900,0.91618900
C,-1.84089700,3.32362000,-1.08622500
C,-3.95020200,0.63904000,-1.57316200
C,0.45185100,1.69065500,0.03686500
C,1.01122700,2.17968900,-1.15360700
C,2.27086100,2.76636500,-1.17997500
C,3.02227800,2.86541200,-0.01138400
C,2.50236100,2.35020200,1.17031400
C,1.23653400,1.76633800,1.19160300
C,1.18856100,-1.74861500,-0.71861200
C,2.03825800,-0.97224400,-1.50015300
C,3.22211700,-0.50339100,-0.94385000
C,3.55572200,-0.78796000,0.38229800

C,2.68707900,-1.57774400,1.14223400
C,1.50569200,-2.06805000,0.60139900
C,4.83850600,-0.26536700,0.97294800
H,-2.19933000,-3.13759900,1.10001500
H,-2.25683300,-2.73546500,3.56830300
H,-1.72683800,-0.49455200,4.47466800
H,-1.13796000,1.36499500,2.95546800
H,-0.85288600,0.31084100,-2.10491600
H,-3.42219600,1.62765000,1.48061300
H,-2.51146100,3.15254900,1.59341900
H,-1.17252400,3.98967300,-0.53065500
H,-1.36858800,3.08118300,-2.04042200
H,-4.11578200,-0.27849100,-2.13013100
H,-4.81296300,1.26685100,-1.36662500
H,0.46257100,2.09258000,-2.08580700
H,2.66772000,3.13997300,-2.11934400
H,4.00468200,3.32834800,-0.02580900
H,3.08410300,2.39421300,2.08686700
H,0.87357400,1.34639700,2.12186900
H,1.76743500,-0.74674800,-2.52696200
H,3.88831200,0.11264300,-1.54146300
H,2.94006300,-1.80998200,2.17321200
H,0.83781100,-2.69113400,1.18731900
H,5.67431300,-0.93643900,0.74576000
H,4.76733400,-0.17940900,2.06063300
H,5.08030900,0.72025100,0.56504700
H,-2.76445600,3.86552900,-1.31375300
H,-3.93806200,3.04521900,0.55364200

2z

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1646.644990a.u.
Zero-point correction = 0.460335Hartree/Particle
Sum of electronic and thermal Free Energies = -1646.238875a.u.

S,0.48564200,-2.35290400,-1.36962000
O,0.40112000,-2.14509300,-2.80443700
O,0.58451700,-3.67729100,-0.78306900
N,-0.92342500,-1.66494900,-0.72833200
C,-1.04261000,-1.65531900,0.69729700
C,-1.09175100,-2.77278000,1.52300100
C,-1.23377200,-2.56210900,2.89315200
C,-1.35029000,-1.27302200,3.41346200
C,-1.31546100,-0.16419400,2.56831100

C,-1.14512300,-0.35328300,1.19994500
C,-1.10549200,0.66567000,0.08135600
C,-1.22915800,-0.29328700,-1.15837900
C,-2.71028800,0.02909900,-1.20415100
C,-3.73727100,-0.60598900,-1.74821000
C,0.02560200,1.66877800,0.11167800
C,0.24834800,2.47347100,-1.01581700
C,1.26282000,3.42249900,-1.03540500
C,2.08267100,3.59153900,0.07994900
C,1.88379800,2.78950400,1.19771700
C,0.87112000,1.83075500,1.21031800
C,1.81664800,-1.36048700,-0.74077900
C,2.31582700,-0.32010900,-1.52095200
C,3.31576700,0.48988200,-0.99941400
C,3.81720200,0.27459200,0.28755900
C,3.29605200,-0.77505900,1.04908800
C,2.29612900,-1.59898100,0.54522200
C,4.91050100,1.15556100,0.83189000
H,-1.01364900,-3.76711200,1.09983700
H,-1.27117400,-3.41714800,3.56077700
H,-1.48044700,-1.13164700,4.48163400
H,-1.41455000,0.83854300,2.97498600
H,-0.66542000,-0.02096900,-2.05352700
H,-3.58236500,-1.49567300,-2.35160100
H,-4.76090500,-0.27401000,-1.59505700
H,-0.38587100,2.35468200,-1.89145600
H,1.41140400,4.03360100,-1.92068500
H,2.87026500,4.33943200,0.07308000
H,2.52669900,2.89800700,2.06707700
H,0.75630400,1.19252500,2.07976300
H,1.92934100,-0.16507700,-2.52348800
H,3.70568100,1.31151800,-1.59398000
H,3.67896500,-0.94965100,2.05100500
H,1.89774200,-2.42300100,1.12881000
H,5.89327800,0.81092600,0.49163400
H,4.91712500,1.15133800,1.92526100
H,4.78306600,2.18727700,0.49120000
C,-2.55441600,1.18989700,-0.24323700
C,-3.66086900,1.43365400,0.80008000
C,-2.85539500,2.60102000,-0.81601500
C,-4.24161900,2.51098900,-0.14269100
H,-3.25022500,1.88630200,1.70876500
H,-4.27888700,0.57294700,1.06883300
H,-2.22709500,3.35816000,-0.33692900

H,-2.81366900,2.72387300,-1.90178000
H,-4.64196200,3.42084100,0.30927100
H,-4.98886400,2.09074200,-0.82099600

2aa

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1529.989761a.u.
Zero-point correction = 0.396467Hartree/Particle
Sum of electronic and thermal Free Energies = -1529.644429a.u.

S,-1.12609500,-1.89077800,-1.22275900
O,-1.10519500,-1.78083300,-2.67050300
O,-1.78087100,-2.99039100,-0.53741700
N,-1.88726100,-0.48204900,-0.67421100
C,-1.97714300,-0.29565900,0.74159200
C,-2.63477700,-1.12609000,1.64284200
C,-2.64249500,-0.74985900,2.98451300
C,-2.03707600,0.43539100,3.40463100
C,-1.39561900,1.26362700,2.48451900
C,-1.35029800,0.88677100,1.14700200
C,-0.73911200,1.61216500,-0.03122300
C,-1.37302500,0.78525500,-1.20981600
C,-2.41010400,1.88450700,-1.35702600
C,-1.61323000,2.83189100,-0.48072200
C,-3.61600500,1.89038700,-1.90107400
C,0.76263900,1.80388900,-0.00296800
C,1.39777700,2.34313000,-1.13067400
C,2.77217700,2.54384300,-1.15468700
C,3.54541800,2.21646600,-0.04103100
C,2.92881400,1.67061200,1.07870000
C,1.55115900,1.45479800,1.09387200
C,0.54527100,-1.78030300,-0.63413000
C,1.52606700,-1.24581900,-1.46742900
C,2.82011900,-1.11534000,-0.98250900
C,3.14346900,-1.51020700,0.31942300
C,2.13928000,-2.03926800,1.13414600
C,0.83635800,-2.17826400,0.66805300
C,4.55656200,-1.37284000,0.82139000
H,-3.11671400,-2.03314100,1.29820100
H,-3.14610900,-1.38183500,3.70922000
H,-2.07560600,0.71956400,4.45134900
H,-0.93156400,2.19291200,2.80549200
H,-0.74536000,0.62428600,-2.08960400
H,-3.99158200,1.01289100,-2.41924400

H,-4.26723300,2.75688400,-1.83463200
H,0.80777500,2.60739800,-2.00596300
H,3.23998400,2.96306800,-2.04045900
H,4.61829300,2.38531800,-0.05037200
H,3.52113600,1.39783800,1.94803100
H,1.09347600,0.99827800,1.96512700
H,1.27225300,-0.95659000,-2.48249400
H,3.59157900,-0.68989400,-1.61858700
H,2.38091200,-2.34797600,2.14766100
H,0.05611500,-2.60164300,1.29274000
H,5.17785600,-2.20250600,0.46660600
H,4.59287500,-1.37304300,1.91407400
H,5.00666700,-0.44304900,0.46064800
H,-1.02921000,3.56296100,-1.04970900
H,-2.15602000,3.35036100,0.3145390

$TS1_{1a-1}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1607.178639a.u.
Zero-point correction = 0.423938Hartree/Particle
Sum of electronic and thermal Free Energies = -1606.809615a.u.

S,0.26840100,-2.25222100,-1.32291300
O,0.29183300,-2.03707200,-2.75701400
O,0.18277300,-3.57254300,-0.72617600
N,-1.10169700,-1.40198400,-0.80109000
C,-1.42260900,-1.29540100,0.59544700
C,-1.58340100,-2.39523000,1.42982700
C,-1.92475800,-2.17957400,2.76572000
C,-2.13651600,-0.89153100,3.24495700
C,-1.99532000,0.20428600,2.39079800
C,-1.62835100,0.02129300,1.06256900
C,-1.41486700,1.16342000,0.09828300
C,-1.49324600,-0.19627000,-1.42768000
C,-2.86311700,-0.01833700,-1.64627700
C,-2.46817500,1.94730300,-0.36569600
C,-3.79467300,2.42122800,0.02290200
C,-2.78371600,3.35076100,-0.64937700
C,-3.97636200,-0.56400600,-1.19483300
C,-0.05309700,1.78825300,0.07771500
C,0.33087900,2.61007200,-0.99238900
C,1.54146700,3.29169800,-0.96838900
C,2.39096600,3.17489600,0.13108300
C,2.03130300,2.34019200,1.18426300

C,0.82940200,1.63757800,1.15274000
C,1.66794100,-1.42645700,-0.61581500
C,2.33424400,-0.46427900,-1.37360500
C,3.44861700,0.15569100,-0.82957600
C,3.89534800,-0.16360700,0.45776300
C,3.20054300,-1.12274000,1.19653400
C,2.08613900,-1.76612100,0.66629000
C,5.10306600,0.53405700,1.02482100
H,-1.44669600,-3.39376900,1.03128100
H,-2.04938600,-3.03212300,3.42565200
H,-2.42288600,-0.73569000,4.28004200
H,-2.16076700,1.21341900,2.75885200
H,-0.73608600,0.35727100,-1.97455500
H,-4.65712100,2.10239100,-0.55804700
H,-3.99389700,2.55470900,1.08478200
H,-2.28921600,4.12367500,-0.06218100
H,-2.99985100,3.63965800,-1.67469900
H,-4.01316600,-1.17481200,-0.28586700
H,-4.93379700,-0.36957700,-1.67681400
H,-0.33926300,2.72186100,-1.84110800
H,1.81675300,3.92576000,-1.80589900
H,3.32794600,3.72379600,0.16000600
H,2.69251500,2.22438300,2.03902200
H,0.56833400,0.98238700,1.97779600
H,1.99209100,-0.23457500,-2.37755500
H,3.97772700,0.90974100,-1.40602000
H,3.54120300,-1.37811900,2.19617800
H,1.55959800,-2.53460000,1.22325900
H,6.01532200,0.22373300,0.50457200
H,5.23013100,0.31484800,2.08785000
H,5.01088500,1.61894500,0.90477100

1r

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -808.396784a.u.
Zero-point correction = 0.293144Hartree/Particle
Sum of electronic and thermal Free Energies = -808.149477a.u.

C,1.02945400,0.39866400,-0.69960600
C,2.26029100,0.94290300,-0.30834400
C,3.45348900,0.43441100,-0.80605400
C,3.44248600,-0.63670000,-1.69883800
C,2.22700600,-1.18938500,-2.08801000
C,1.03116600,-0.67727500,-1.59276800

H,2.27661400,1.75898200,0.40640600
H,4.39707000,0.87064600,-0.49046600
H,4.37505600,-1.03822900,-2.08310500
H,2.20553000,-2.02585800,-2.77978900
H,0.08792300,-1.11692400,-1.90277200
C,-1.48950500,0.12256200,-0.23757700
C,-1.55371500,-1.19097900,0.25432000
C,-2.64726100,0.64832100,-0.82308200
C,-2.71680300,-1.94784200,0.14114000
C,-3.81631400,-0.09560400,-0.93224200
H,-2.60433200,1.65846500,-1.21894300
C,-3.84753800,-1.40390700,-0.45582400
H,-2.70823300,-2.95809700,0.53631500
H,-4.69366800,0.33944300,-1.39969400
H,-4.75128500,-1.99896100,-0.54115200
C,-0.24875600,0.95075100,-0.17689800
C,-0.33863200,2.19088400,0.30115400
C,0.29164200,3.47585700,0.60657500
C,-1.19002600,3.22515300,0.89101200
H,0.55136400,4.13766900,-0.21674200
H,0.96094400,3.54349800,1.46143600
H,-1.49637300,3.11935800,1.92923700
H,-1.91748900,3.73206800,0.26172400
C,0.15749600,-1.14153700,1.85598100
C,1.43115600,-1.30806300,2.09838000
C,2.70303500,-1.45603200,2.34559100
H,3.07402800,-2.24876000,2.99131600
H,3.43731500,-0.79246200,1.89248600
H,-0.48084300,-0.49648700,2.45597300
O,-0.47320600,-1.81718100,0.83103900

$TS1_{1r}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -808.368097a.u.
Zero-point correction = 0.293531Hartree/Particle
Sum of electronic and thermal Free Energies = -808.117583a.u.

C,-2.19501000,-0.03788000,-0.39574100
C,-3.44037300,-0.67784500,-0.49565300
C,-3.61515300,-1.95172100,0.00422600
C,-2.54101200,-2.61155700,0.61750800
C,-1.32408300,-1.97143300,0.73473100
C,-1.11728900,-0.65668600,0.25942900
C,0.12954700,0.05580400,0.52892500

C,-1.17319000,1.96423000,-1.44608800
C,0.11922000,2.03851400,-1.09023900
C,0.00603300,1.39171900,0.82458400
C,-0.94344600,2.19897700,1.61101200
C,0.55899100,2.43291600,1.71252900
C,1.35420600,2.33968200,-1.48169900
C,1.43778100,-0.55239400,0.25868600
C,2.62373600,0.09674000,0.64252600
C,3.86959100,-0.43929300,0.33422300
C,3.96641600,-1.63195500,-0.37533200
C,2.80116100,-2.27593000,-0.78900800
C,1.55679800,-1.74097400,-0.48546700
H,-4.24254400,-0.14642700,-0.99658300
H,-4.57987600,-2.44009300,-0.08754500
H,-2.66920900,-3.61166300,1.01837700
H,-0.49931100,-2.45874100,1.24681000
H,-1.58786700,2.73077000,-2.09412700
H,-1.52757900,2.96094900,1.10411800
H,-1.44957100,1.70702300,2.43730600
H,1.07112100,2.11152600,2.61590500
H,0.94826700,3.34830200,1.27427800
H,1.72954300,2.02498100,-2.45063900
H,2.05378300,2.84366500,-0.82062100
H,2.56735700,1.02422600,1.19968600
H,4.76887800,0.08059600,0.65069500
H,4.93887400,-2.05103900,-0.61440000
H,2.86239500,-3.19427500,-1.36515400
H,0.66271100,-2.23676500,-0.84816000
O,-2.18631500,1.18518500,-1.01060600

INT1$_{1r}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -808.397725a.u.
Zero-point correction = 0.296176Hartree/Particle
Sum of electronic and thermal Free Energies = -808.143609a.u.

C,-2.18162800,-0.00396600,-0.46132200
C,-3.47561700,-0.55143800,-0.51459800
C,-3.71107300,-1.79545100,0.02063700
C,-2.64750200,-2.52073200,0.60107600
C,-1.38644000,-1.97994100,0.66306100
C,-1.10562100,-0.66967600,0.17905600
C,0.13464000,0.00498400,0.35110100
C,-0.97584100,1.86718800,-1.49113600

C,0.13489500,2.15576500,-0.66966600
C,0.02820400,1.45474800,0.65186000
C,-0.95697200,1.96127500,1.66866800
C,0.51834200,2.09152500,1.91948800
C,1.20944500,2.87886500,-1.07344800
C,1.43530800,-0.59070200,0.14940700
C,2.61279800,0.14372200,0.41206100
C,3.87002900,-0.39442000,0.15074800
C,3.99751200,-1.67287800,-0.37696600
C,2.84350700,-2.40830100,-0.66785800
C,1.59063200,-1.87660800,-0.42523900
H,-4.25525200,0.01821000,-1.00922600
H,-4.70738100,-2.22282000,-0.01673100
H,-2.83398300,-3.50081500,1.02849500
H,-0.58605000,-2.51390900,1.16598300
H,-1.16097600,2.44587400,-2.39151000
H,-1.51052200,2.86259300,1.42405900
H,-1.50750500,1.22052600,2.23995100
H,0.96562500,1.43681600,2.66022700
H,0.96468200,3.07923700,1.85302900
H,1.34150200,3.17721400,-2.10780600
H,1.97123200,3.17692900,-0.36333200
H,2.54081500,1.13418100,0.84251300
H,4.75599800,0.19496900,0.36795500
H,4.97909700,-2.09254600,-0.57318300
H,2.92784800,-3.39725400,-1.10870900
H,0.70959700,-2.44012500,-0.71404000
O,-2.02530500,1.10714400,-1.22740600

$TS2_{1r}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -808.396297a.u.
Zero-point correction = 0.295659Hartree/Particle
Sum of electronic and thermal Free Energies = -808.142158a.u.

C,-2.17355500,0.00753000,-0.54324900
C,-3.48224200,-0.48755600,-0.57100800
C,-3.75668300,-1.68555700,0.05752100
C,-2.72769500,-2.40312400,0.69378200
C,-1.44283000,-1.90123400,0.72412400
C,-1.13196200,-0.64861300,0.14459800
C,0.12064600,0.04005800,0.24269000
C,-0.72820300,1.65216000,-1.57999000
C,0.18788600,2.19005900,-0.62945200

C,0.02503300,1.47528100,0.66238100
C,-0.97857800,1.93913800,1.68174100
C,0.49095900,2.01181200,1.98238500
C,1.21539300,3.00113700,-0.96486700
C,1.41706800,-0.58338600,0.09220500
C,2.60021800,0.12291100,0.39540000
C,3.84967500,-0.45399800,0.18701700
C,3.95854400,-1.74433600,-0.31777600
C,2.79710100,-2.45461800,-0.63711100
C,1.55131900,-1.88332100,-0.44938000
H,-4.24207000,0.06681900,-1.11102600
H,-4.76681300,-2.08146800,0.04347100
H,-2.95067300,-3.34395200,1.18643300
H,-0.65723800,-2.42721900,1.25880000
H,-0.70817700,2.03458700,-2.59864500
H,-1.50155600,2.86779800,1.47717600
H,-1.56643300,1.17868800,2.18647800
H,0.89864700,1.29551600,2.68838500
H,0.96702000,2.98795400,1.99613200
H,1.38125100,3.31439700,-1.99027600
H,1.91421400,3.34886400,-0.21311100
H,2.53638100,1.12280800,0.80610500
H,4.74444300,0.11171700,0.42930800
H,4.93450400,-2.19423600,-0.47026600
H,2.87019900,-3.45545500,-1.05219700
H,0.66083700,-2.42731500,-0.74853800
O,-1.90838800,1.05430400,-1.36428700

2r

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -808.462397a.u.
Zero-point correction = 0.297402Hartree/Particle
Sum of electronic and thermal Free Energies = -808.208052a.u.

C,-1.96441300,-0.51496500,-0.86611200
C,-3.15927100,-1.21735000,-0.91252800
C,-3.43382200,-2.09006300,0.14070200
C,-2.54284700,-2.24731500,1.20192700
C,-1.34541900,-1.52862600,1.22590400
C,-1.05359600,-0.66155400,0.18137800
C,0.11778400,0.25983700,-0.05403400
C,-0.39268300,1.01588100,-1.34235300
C,-0.63224200,2.25665200,-0.49632500
C,-0.03248800,1.60678400,0.70610900

C,-0.45192900,1.80344700,2.13153900
C,0.91470100,2.22925400,1.69267100
C,-1.20937700,3.42459600,-0.74282400
C,1.49361200,-0.36166800,-0.12137700
C,2.60014000,0.46354600,-0.36449900
C,3.87945100,-0.06853600,-0.47254900
C,4.07935300,-1.44113100,-0.33645500
C,2.98811800,-2.27079400,-0.10376500
C,1.70476900,-1.73640100,-0.00132400
H,-3.84538800,-1.08113000,-1.74076000
H,-4.36167700,-2.65372100,0.13176800
H,-2.78101400,-2.92838600,2.01211400
H,-0.64394800,-1.65218900,2.04740200
H,0.31886600,1.11997600,-2.16479100
H,-1.20345900,2.56444400,2.31968900
H,-0.53739800,0.91363800,2.74830100
H,1.76191100,1.62918300,2.01160500
H,1.11782100,3.28994900,1.57453600
H,-1.60869100,3.65845100,-1.72474900
H,-1.31534500,4.18039300,0.03160700
H,2.45156900,1.53564500,-0.47133500
H,4.72204600,0.58916900,-0.66361900
H,5.07809300,-1.85882300,-0.41679800
H,3.13038900,-3.34282000,-0.00603400
H,0.86023600,-2.39813200,0.16034100
O,-1.56288000,0.36309900,-1.83072300

$TS1_{1aa}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1529.930774a.u.
Zero-point correction = 0.391802Hartree/Particle
Sum of electronic and thermal Free Energies = -1529.594758a.u.

C,2.24423300,-0.67433900,-0.16570900
C,3.05645500,-1.57145200,-0.85011800
C,4.33756200,-1.15396100,-1.20111600
C,4.78426400,0.12175600,-0.85734400
C,3.95391400,1.00109800,-0.16438800
C,2.65801400,0.60983700,0.16870000
C,1.65331800,1.37426400,0.95992200
C,0.48478000,-1.25066800,1.52367200
C,1.03896000,-0.62910500,2.62513200
C,1.64945900,1.03900700,2.33469200
C,1.27815600,-1.08058500,3.86458600

C,0.58564100,2.08682800,0.30052200
C,-0.56579300,2.51655900,0.99734100
C,-1.56064300,3.24795300,0.35946800
C,-1.45730800,3.56336500,-0.99414300
C,-0.33506100,3.12783400,-1.70636500
C,0.66427000,2.40195800,-1.07754500
H,2.69235100,-2.56328700,-1.10148800
H,4.99222500,-1.83121600,-1.73967100
H,5.78755800,0.43194600,-1.13239800
H,4.29768500,1.99426500,0.10949800
H,-0.44266300,-1.80494500,1.62534900
H,1.35155900,-2.13932300,4.08972400
H,1.47544200,-0.38850600,4.68019000
H,-0.68405200,2.27493300,2.04854400
H,-2.43003500,3.56914900,0.92712500
H,-2.23291100,4.14022000,-1.48805100
H,-0.24217100,3.35552100,-2.76419800
H,1.52520300,2.06458400,-1.64692900
N,0.88716200,-1.00907300,0.23441800
S,-0.09397200,-1.63038000,-1.05451500
O,0.30352200,-0.86687000,-2.21942600
O,0.01683300,-3.08058900,-1.02954800
C,-1.73521400,-1.18893600,-0.56960000
C,-2.57891300,-2.17572700,-0.06423800
C,-2.15808900,0.12357300,-0.74995900
C,-3.87765000,-1.82477200,0.28095700
H,-2.21672500,-3.19354300,0.04129200
C,-3.46196200,0.44963000,-0.39699000
H,-1.48564300,0.86943500,-1.16397000
C,-4.33522300,-0.51227500,0.11895900
H,-4.54995400,-2.58068200,0.67718900
H,-3.80057500,1.47382600,-0.52729200
C,-5.75618700,-0.15093700,0.46441700
H,-5.83818400,0.89924700,0.75544900
H,-6.41244200,-0.30784900,-0.39875200
H,-6.13497200,-0.76738500,1.28372900
H,2.64715900,0.88906500,2.73986800
H,1.02983700,1.63837100,3.00279200

INT1$_{1aa}$

Opt @ M06-2X/6-31G(d)

SCF Done: E(M062X) = -1529.918867a.u.

Zero-point correction = 0.394950Hartree/Particle

Sum of electronic and thermal Free Energies = -1529.577414a.u.

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C,1.28450000,-1.02355300,1.11943800
 C,2.42251800,-0.73134200,1.89809900
 C,2.30797600,0.10664400,2.98814000
 C,1.06238900,0.66819300,3.32249000
 C,-0.06904300,0.30742100,2.62341700
 C,-0.01400100,-0.61545100,1.55146800
 C,-1.15940900,-1.24236200,0.97579700
 C,0.46294800,-2.15636200,-0.93118100
 C,-0.66287700,-2.93952000,-0.53745800
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 C,-2.36028200,-0.55293300,0.57409900
 C,-3.50725900,-1.25593100,0.14432100
 C,-4.63393900,-0.58110900,-0.31680100
 C,-4.66293400,0.80793900,-0.36216800
 C,-3.53411800,1.52343600,0.05037900
 C,-2.40471300,0.86149800,0.49722900
 H,3.38212000,-1.14793900,1.62354900
 H,3.18445600,0.32516300,3.58924200
 H,0.97899500,1.33180700,4.17763700
 H,-1.04789100,0.64674600,2.94954400
 H,0.71237100,-2.18149400,-1.98651200
 H,-1.24228000,-3.44816800,-2.52799600
 H,-2.30749600,-4.12313300,-1.16791300
 H,-3.52582400,-2.33869300,0.17886500
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 H,-5.54658500,1.32961000,-0.71545000
 H,-3.53557900,2.60987700,0.00763300
 H,-1.52019500,1.43083500,0.76731400
 N,1.42952300,-1.55736900,-0.18187900
 S,2.51847100,-0.55923700,-1.19946600
 O,3.79083000,-0.44890000,-0.52240700
 O,2.43194700,-1.11277000,-2.53555500
 C,1.63250000,0.96687100,-1.10467300
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 C,0.05800100,3.22295900,-0.76861700
 H,1.50557900,3.80515300,0.71539500
 H,-1.20171400,2.36700200,-2.29005800
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C,-0.82733500,4.41877100,-0.53553900
H,-0.23847600,5.33277600,-0.41818400
H,-1.52854100,4.56247300,-1.36092900
H,-1.41203000,4.28550500,0.38230000
H,-0.29581200,-3.11358800,1.58580800
H,-1.99169900,-3.26685200,1.13039900

$TS2_{1aa}$

Opt @ M06-2X/6-31G(d)
SCF Done: E(M062X) = -1529.918824a.u.
Zero-point correction = 0.394681Hartree/Particle
Sum of electronic and thermal Free Energies = -1529.576640a.u.

C,1.26082400,-1.04862700,1.11667700
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C,1.06517700,0.63977300,3.32371200
C,-0.07180400,0.30210100,2.62095500
C,-0.02984200,-0.61672300,1.54619300
C,-1.18319400,-1.22311300,0.96153200
C,0.39901500,-2.15092600,-0.92973200
C,-0.72481100,-2.93843600,-0.53215200
C,-1.11593800,-2.73358600,0.89735300
C,-1.51230600,-3.53341900,-1.45690600
C,-2.37318500,-0.51303600,0.56146600
C,-3.53402300,-1.19681100,0.13871600
C,-4.65054100,-0.50344100,-0.31941100
C,-4.65488000,0.88577200,-0.36794200
C,-3.51190800,1.58204100,0.03800400
C,-2.39211600,0.90153000,0.48169600
H,3.35529600,-1.21160800,1.62153500
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H,0.99242600,1.30212700,4.18077700
H,-1.04498600,0.65914500,2.94519800
H,0.63354900,-2.16486600,-1.98882400
H,-1.30777600,-3.45165300,-2.51950400
H,-2.37956400,-4.11009600,-1.15628200
H,-3.57088200,-2.27904400,0.17509300
H,-5.52774300,-1.05999100,-0.63624000
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S,2.49750300,-0.60953800,-1.20320400

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C,-0.23402800,2.27966100,-1.68886400
H,0.20313100,0.36601900,-2.58554700
C,0.15391400,3.24495500,-0.75307900
H,1.62682000,3.78167000,0.72169400
H,-1.13955600,2.42918100,-2.26963900
C,-0.69832100,4.46404900,-0.51800400
H,-0.09622500,5.31426100,-0.18770300
H,-1.23940500,4.75245400,-1.42263400
H,-1.44076400,4.26214400,0.26324000
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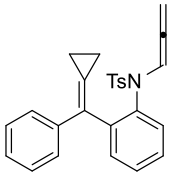
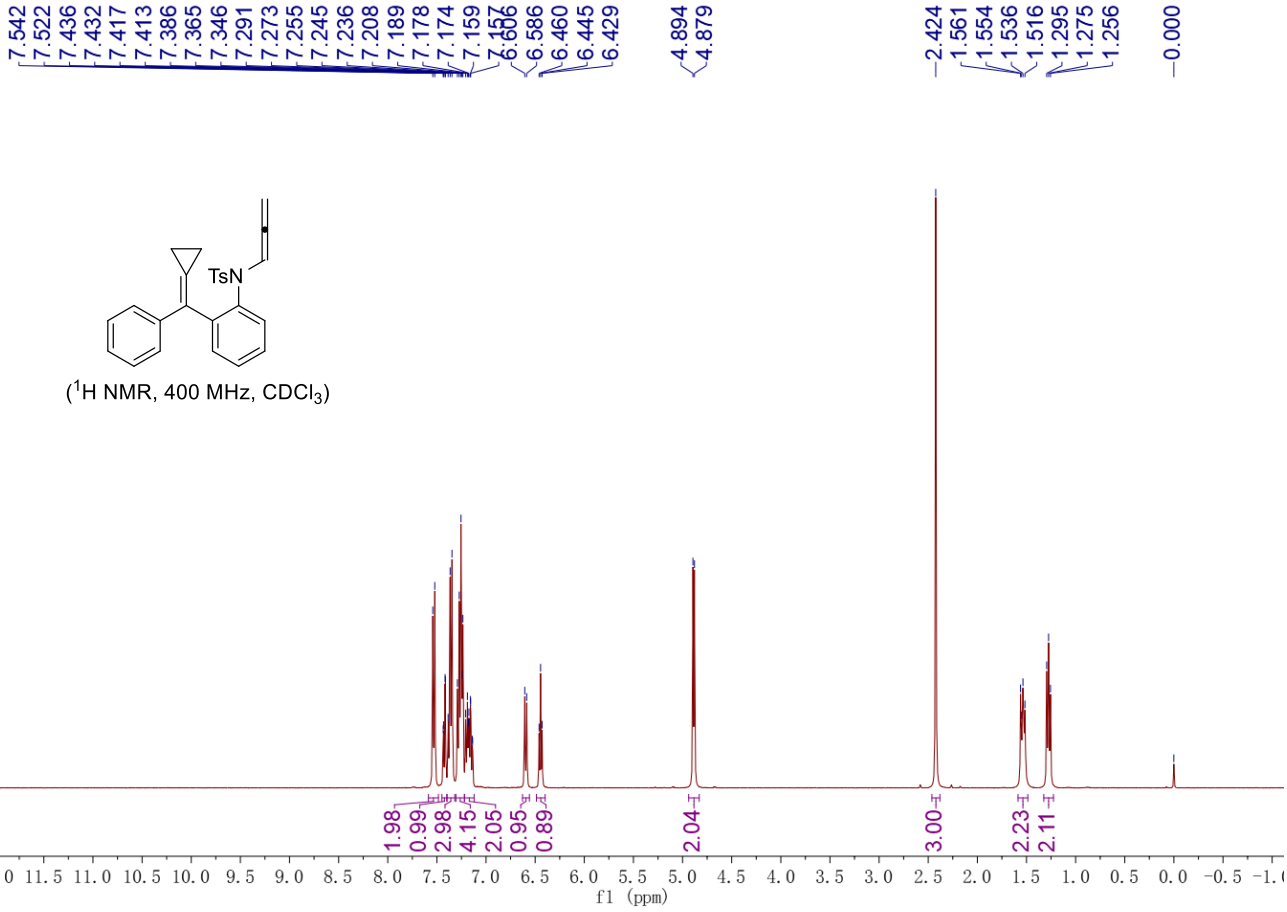
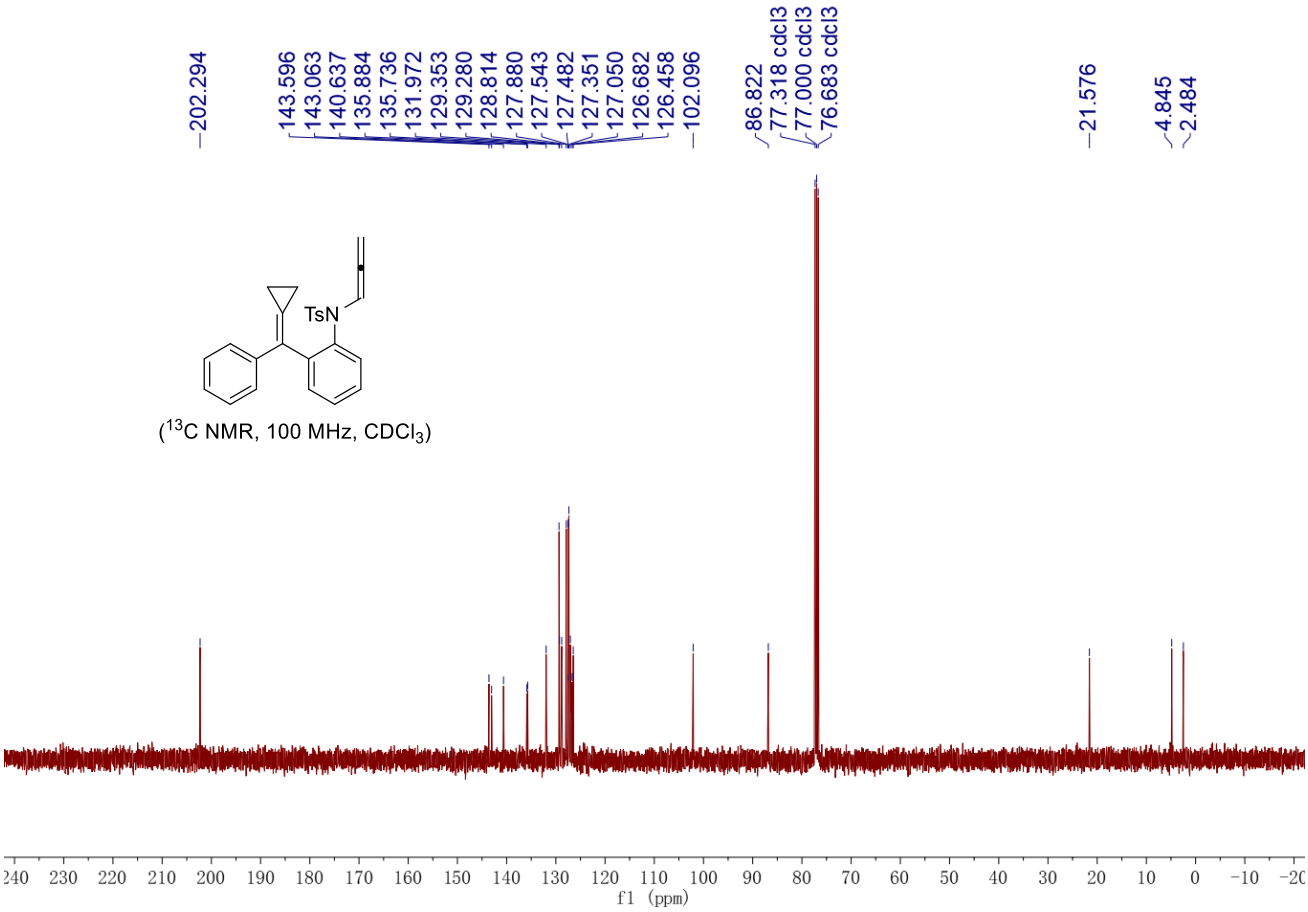
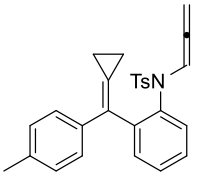
5. Characterization Data of Substrates



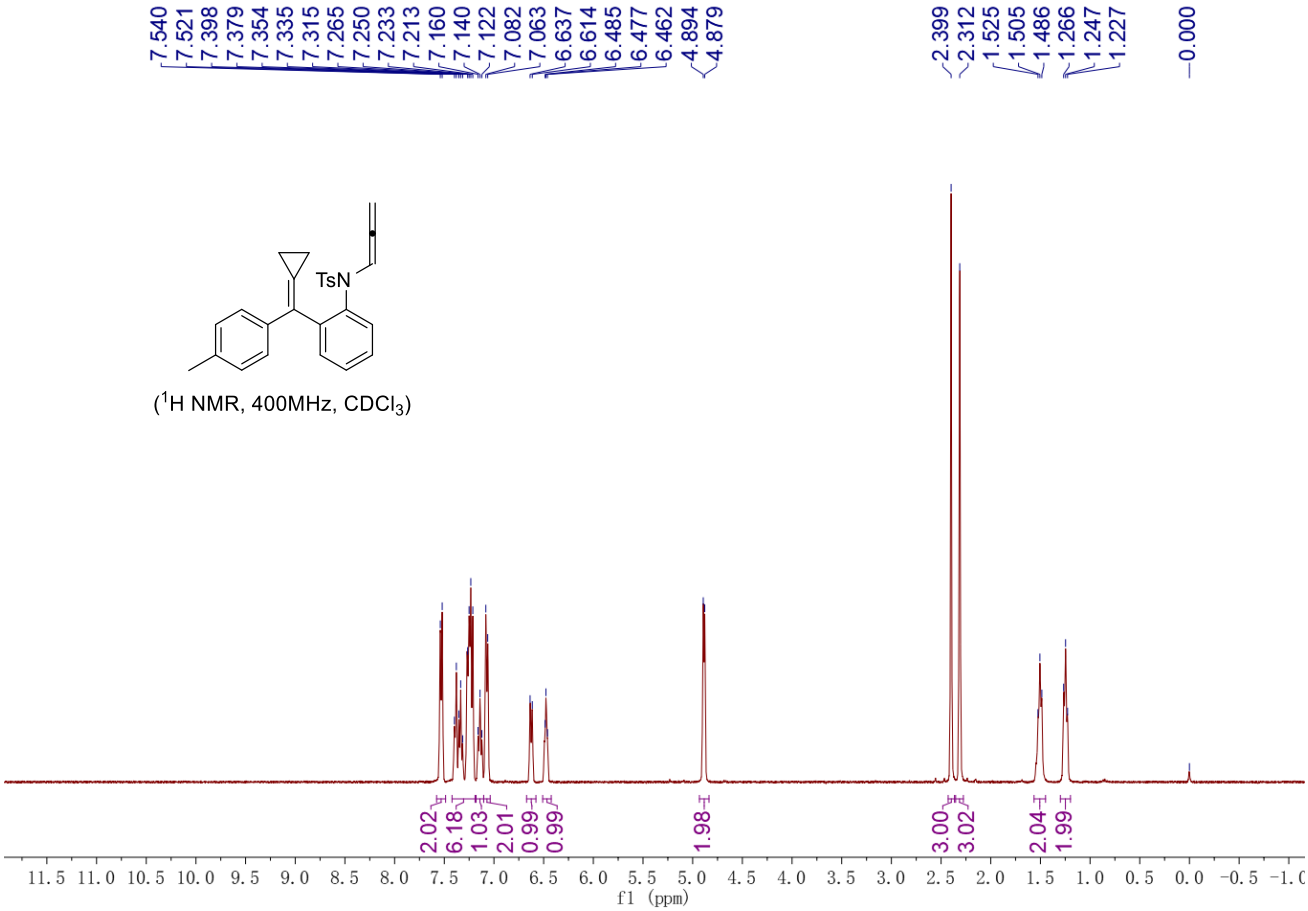
4-methyl-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1a**): Yield: 677 mg, 82%, yellow solid, m.p. 148-150 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.32 (m, 4H), 7.31 – 7.22 (m, 4H), 7.22 – 7.12 (m, 2H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.44 (t, *J* = 6.0 Hz, 1H), 4.89 (d, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 1.59 – 1.49 (m, 2H), 1.32 – 1.23 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.3, 143.6, 143.1, 140.6, 135.9, 135.7, 132.0, 129.4, 129.3, 128.8, 127.9, 127.5, 127.5, 127.4, 127.0, 126.7, 126.5, 102.1, 86.8, 21.6, 4.8, 2.5; IR (neat): ν 3042, 2974, 1595, 1491, 1362, 1162, 966, 880, 769 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 436.13417, found: 436.13389.

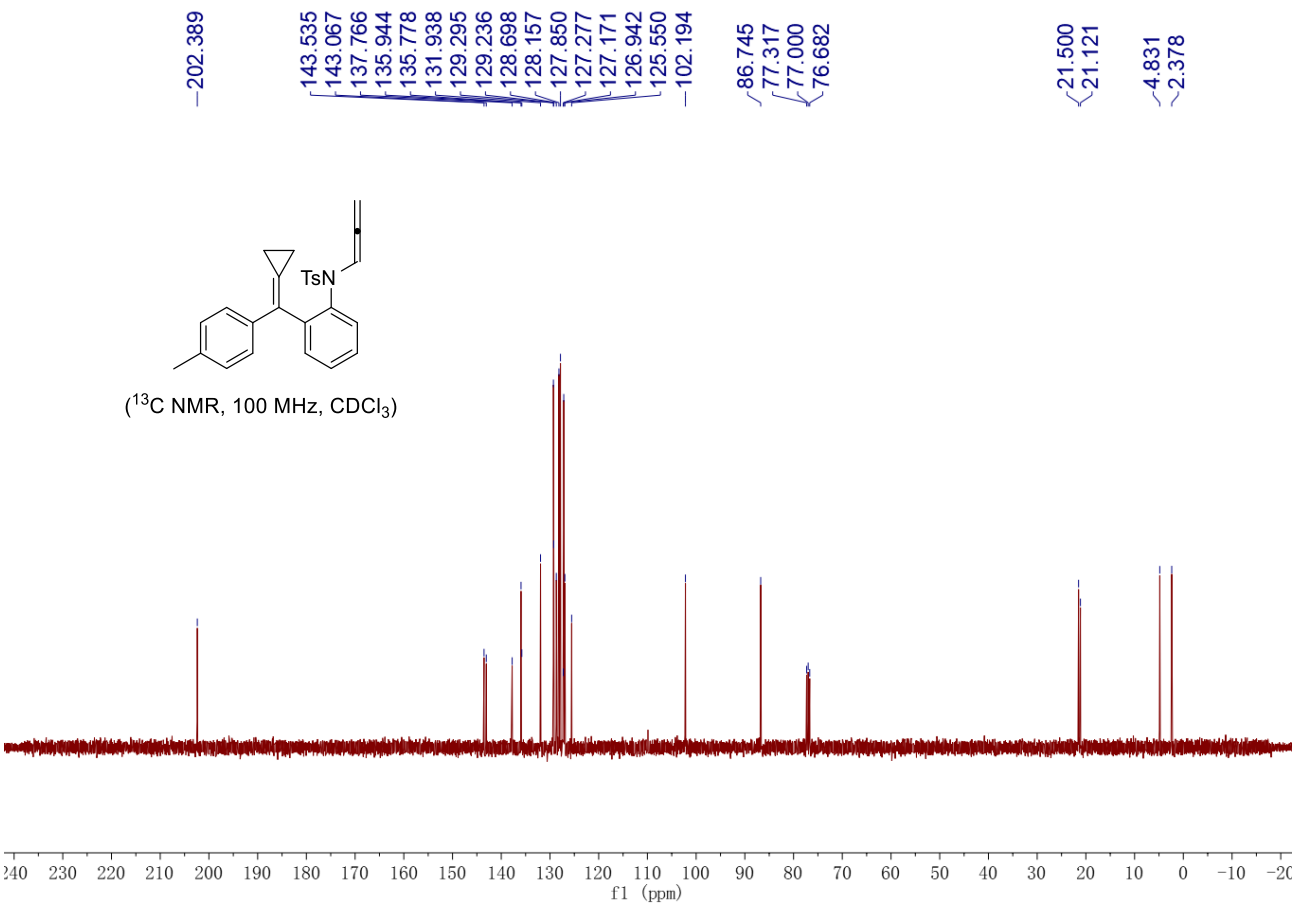


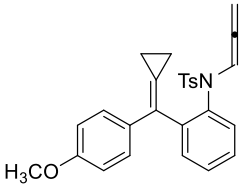

202.294
143.596
143.063
140.637
135.884
135.736
131.972
129.353
129.280
128.814
127.880
127.543
127.482
127.351
127.050
126.682
126.458
102.096
86.822
77.318 cdcl3
77.000 cdcl3
76.683 cdcl3
21.576
4.845
2.484
TsN
(^{13}C NMR, 100 MHz, $CDCl_3$)
f1 (ppm)



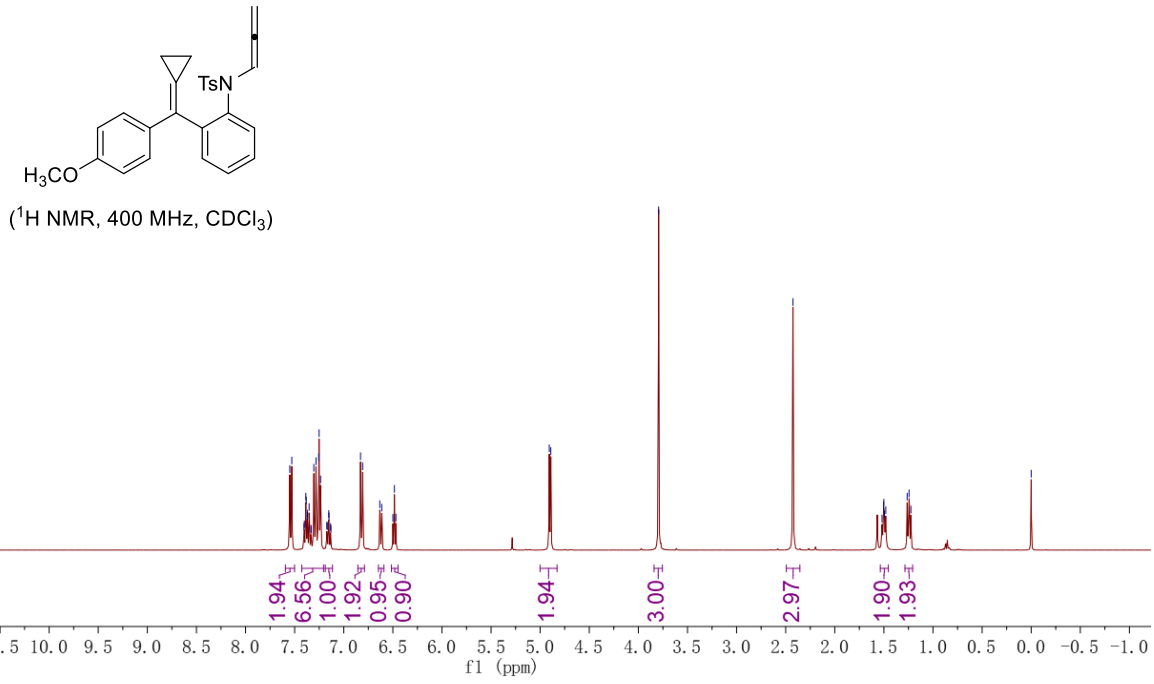
4-methyl-*N*-(2-(cyclopropylidene(p-tolyl)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1b**): Yield: 649 mg, 76%, yellow solid, m.p. 147-149 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.42 – 7.19 (m, 6H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 1H), 6.51 – 6.42 (m, 1H), 4.89 (d, *J* = 6.0 Hz, 2H), 2.40 (s, 3H), 2.31 (s, 3H), 1.56 – 1.45 (m, 2H), 1.30 – 1.20 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.4, 143.5, 143.1, 137.8, 135.9, 135.8, 131.9, 129.3, 129.2, 128.7, 128.2, 127.8, 127.3, 127.2, 126.9, 125.6, 102.2, 86.7, 21.5, 21.1, 4.8, 2.4; IR (neat): ν 3063, 3019, 2961, 1432, 1356, 1265, 1026, 969, 813, 755 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.14998.

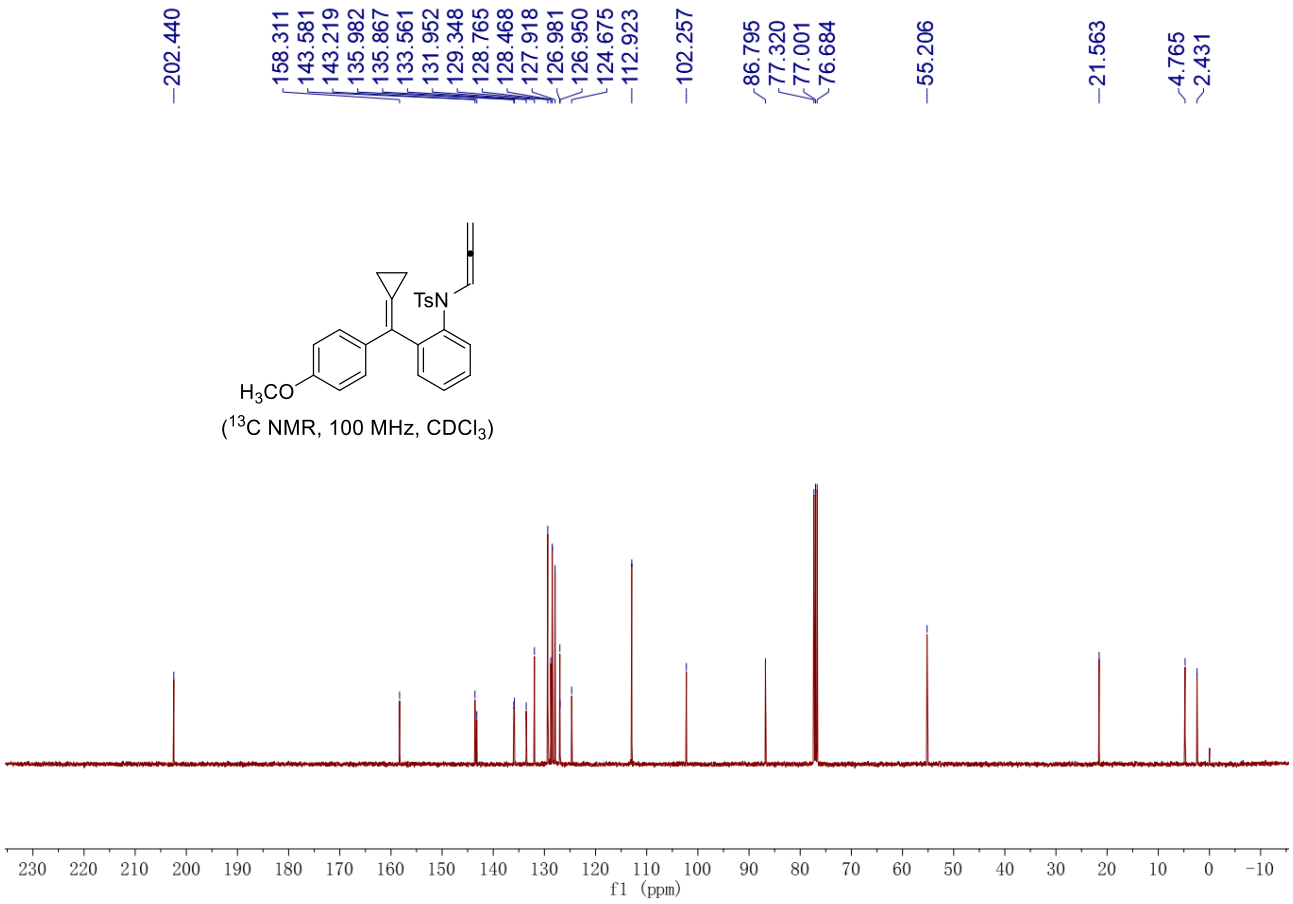


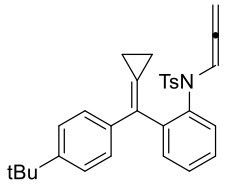

202.389
143.535
143.067
137.766
135.944
135.778
131.938
129.295
129.236
128.698
128.157
127.850
127.277
127.171
126.942
125.550
102.194
86.745
77.317
77.000
76.682
21.500
21.121
4.831
2.378
TsN
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)



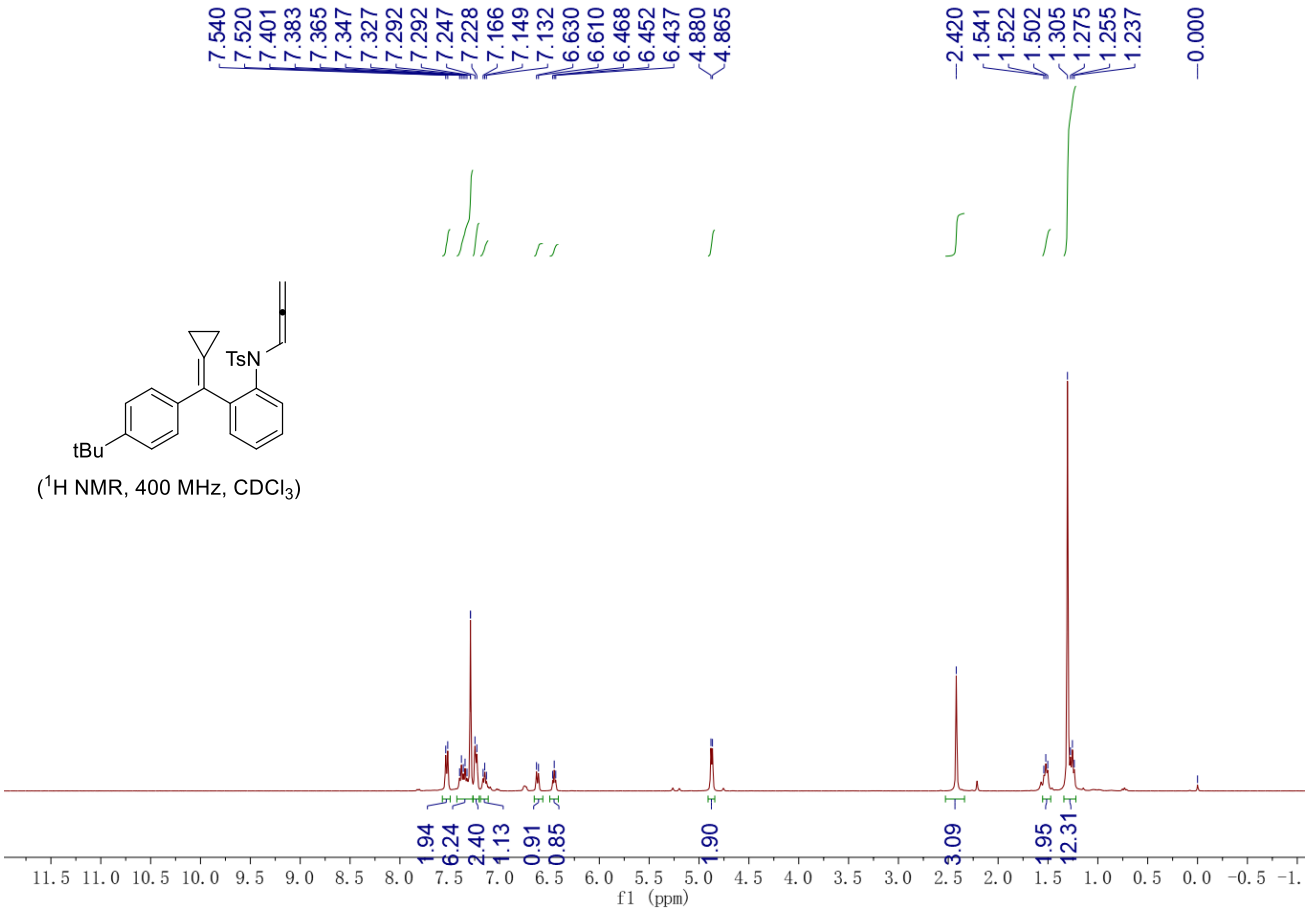
4-methyl-*N*-(2-(cyclopropylidene(4-methoxyphenyl)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1c**): Yield: 718 mg, 81%, yellow solid, m.p. 137-139 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.20 (m, 7H), 7.15 (td, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.48 (t, *J* = 6.0 Hz, 1H), 4.90 (d, *J* = 6.0 Hz, 2H), 3.79 (s, 3H), 2.43 (s, 3H), 1.54 – 1.46 (m, 2H), 1.29 – 1.21 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.4, 158.3, 143.6, 143.2, 136.0, 135.9, 133.6, 132.0, 129.3, 128.8, 128.5, 127.9, 127.0, 127.0, 124.7, 112.9, 102.3, 86.8, 55.2, 21.6, 4.8, 2.4; IR (neat): ν 2956, 2912, 2849, 1594, 1509, 1430, 1247, 1026, 969, 818 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 466.14497, found: 466.14474.

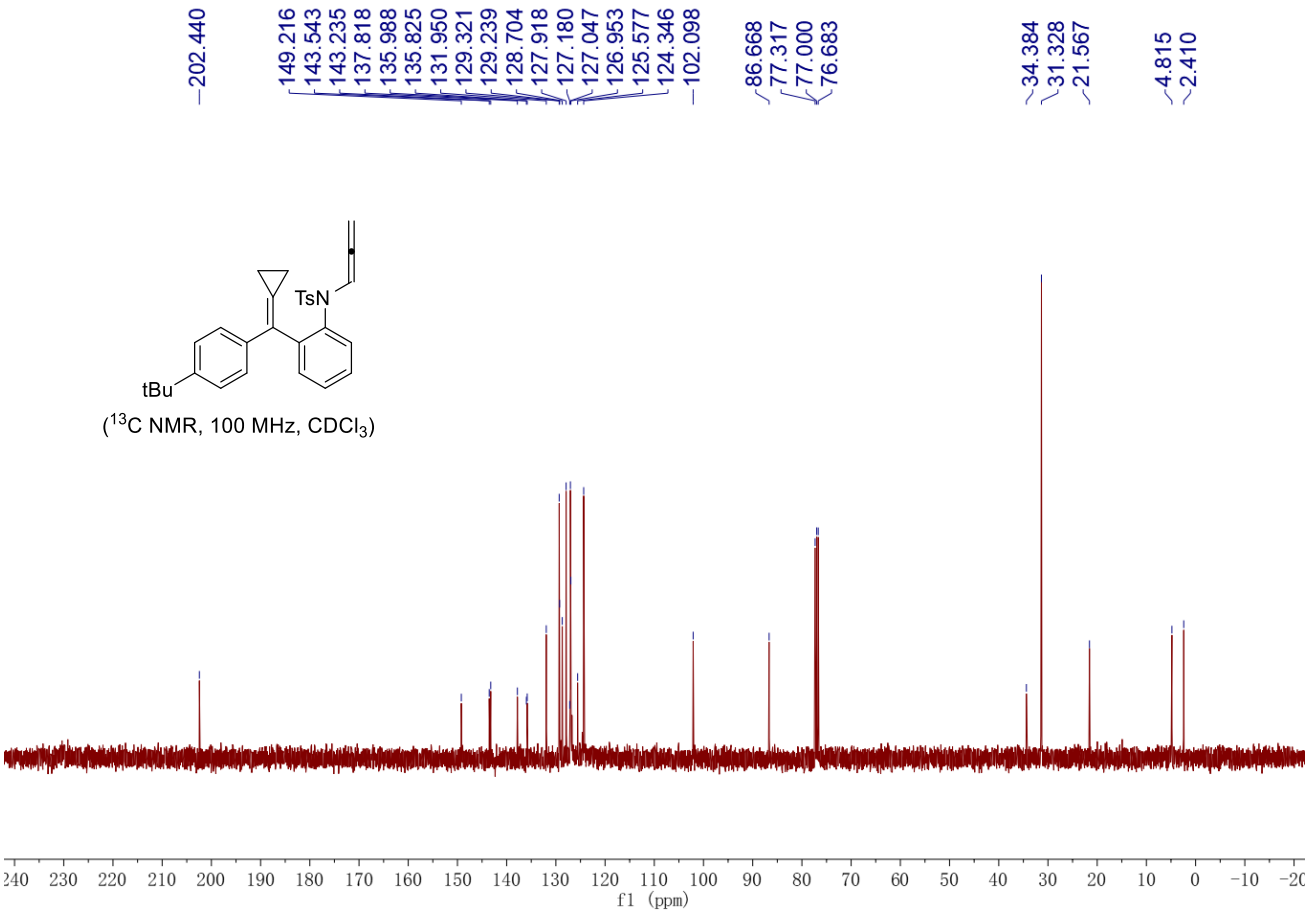


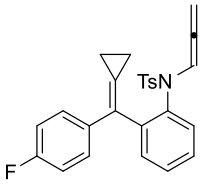

202.440
158.311
143.581
143.219
135.982
135.867
133.561
131.952
129.348
128.765
128.468
127.918
126.981
126.950
124.675
112.923
102.257
86.795
77.320
77.001
76.684
55.206
21.563
4.765
2.431
TsN
H3CO
(13C NMR, 100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



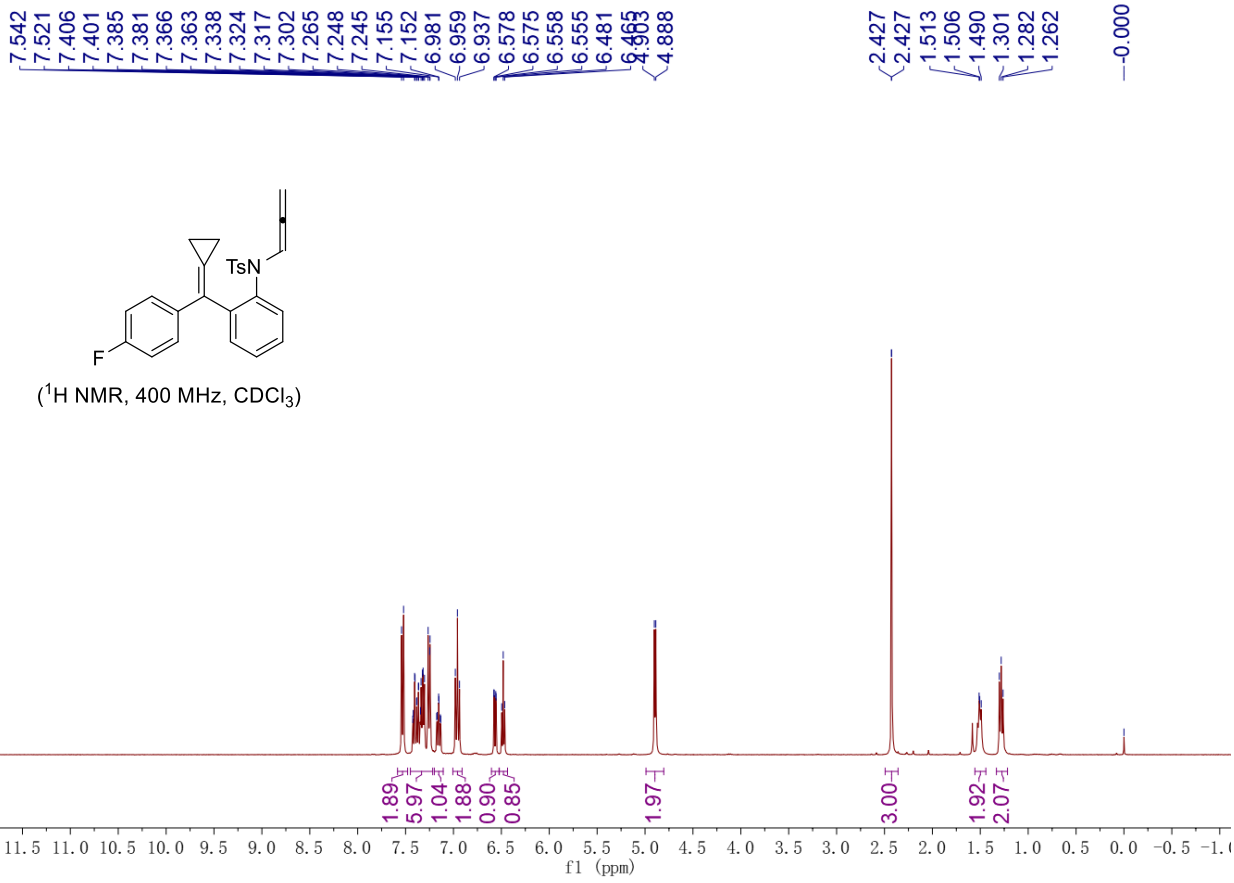
4-methyl-*N*-(2-((4-(tert-butyl)phenyl)(cyclopropylidene)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1d**): Yield: 778 mg, 83%, yellow oil; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.20 (m, 8H), 7.15 (t, *J* = 6.8 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.45 (t, *J* = 6.0 Hz, 1H), 4.87 (d, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 1.55 – 1.47 (m, 2H), 1.24-1.34 (m, 12H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.4, 149.2, 143.5, 143.2, 137.8, 136.0, 135.8, 131.9, 129.3, 129.2, 128.7, 127.9, 127.2, 127.0, 127.0, 125.6, 124.3, 102.1, 86.7, 34.4, 31.3, 21.6, 4.8, 2.4; IR (neat): ν 3037, 2959, 2859, 1445, 1360, 1156, 1090, 963, 813, 756 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 492.19677, found: 492.19640.

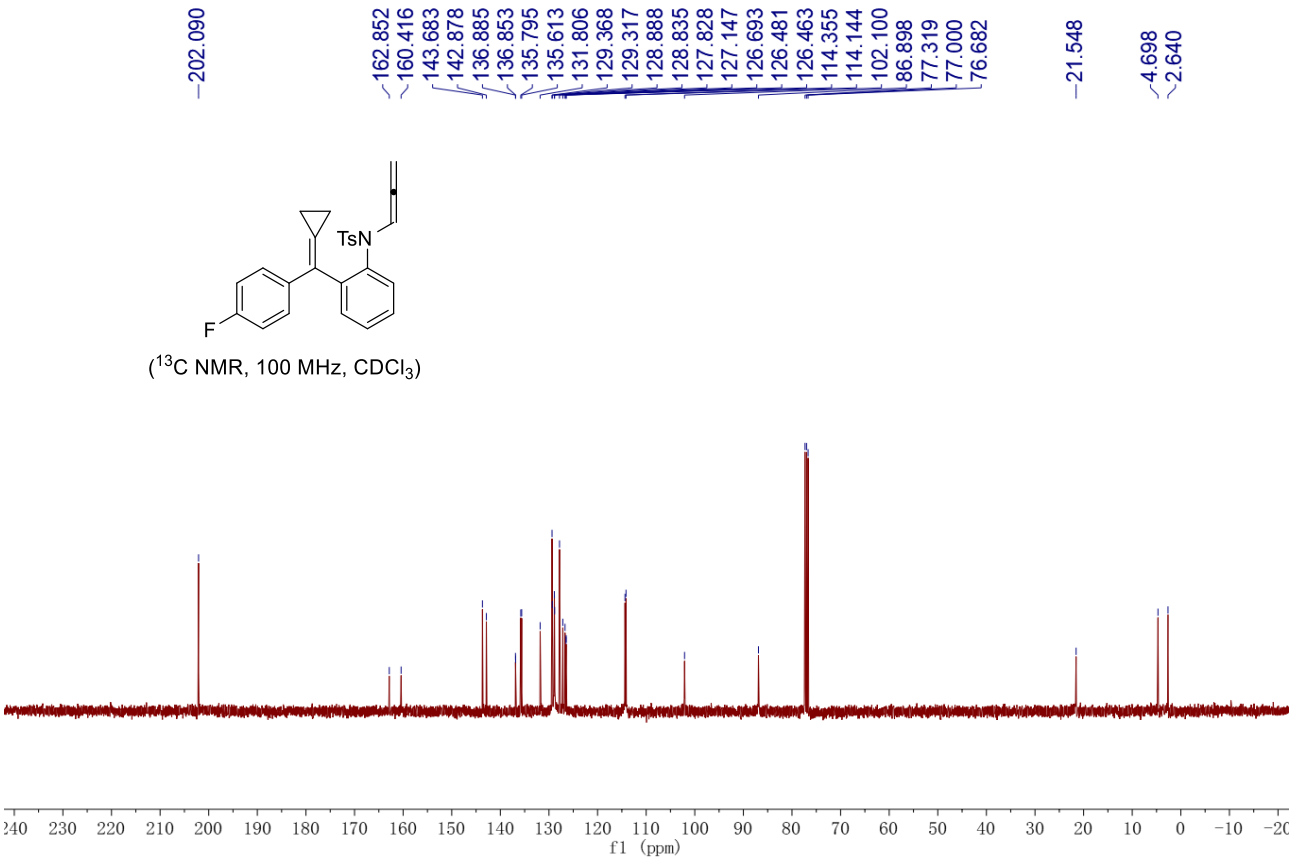



202.440
149.216
143.543
143.235
137.818
135.988
135.825
131.950
129.321
129.239
128.704
127.918
127.180
127.047
126.953
125.577
124.346
102.098
86.668
77.317
77.000
76.683
34.384
31.328
21.567
4.815
2.410
TsN
tBu
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

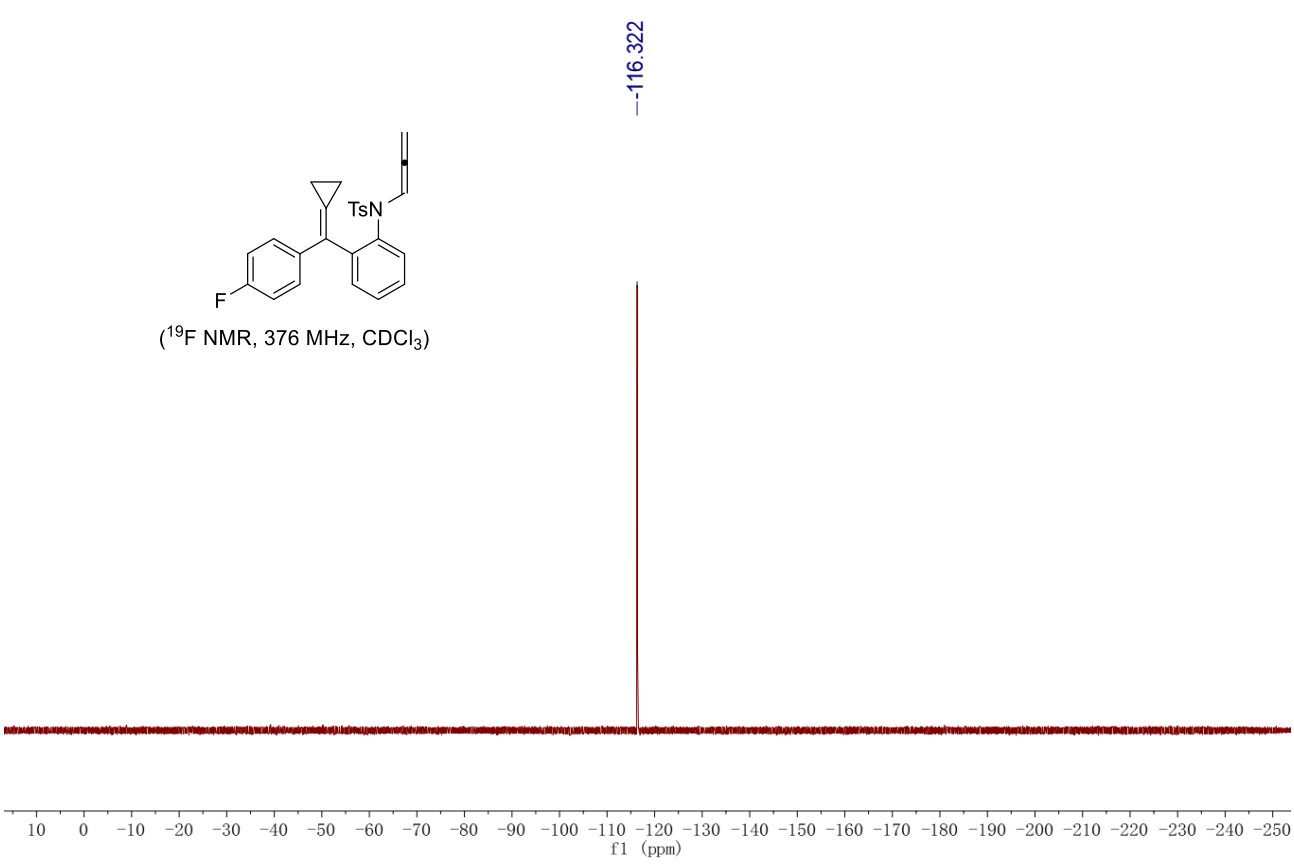


4-methyl-*N*-(2-(cyclopropylidene(4-fluorophenyl)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1e**): Yield: 663 mg, 77%, yellow solid, m.p. 152-154 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.22 (m, 6H), 7.15 (td, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 6.96 (t, *J* = 8.8 Hz, 2H), 6.57 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 6.48 (t, *J* = 6.0 Hz, 1H), 4.90 (d, *J* = 6.0 Hz, 2H), 2.49 – 2.36 (m, 3H), 1.56 – 1.44 (m, 2H), 1.33 – 1.22 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.1, 161.6 (d, *J* = 243.6 Hz), 143.7, 142.9, 136.9, 136.8, 135.7, 135.6, 131.8, 129.3, 129.3, 128.8 (d, *J* = 5.3 Hz), 127.8, 127.1, 126.6, 126.4 (d, *J* = 1.8 Hz) 114.2 (d, *J* = 21.1 Hz) , 102.1, 86.9, 21.5, 4.7, 2.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.3; IR (neat): ν 3066, 3026, 2964, 1594, 1506, 1355, 1261, 1088, 965, 836, 829 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 454.12475, found: 454.12465.

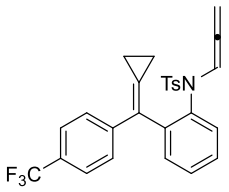




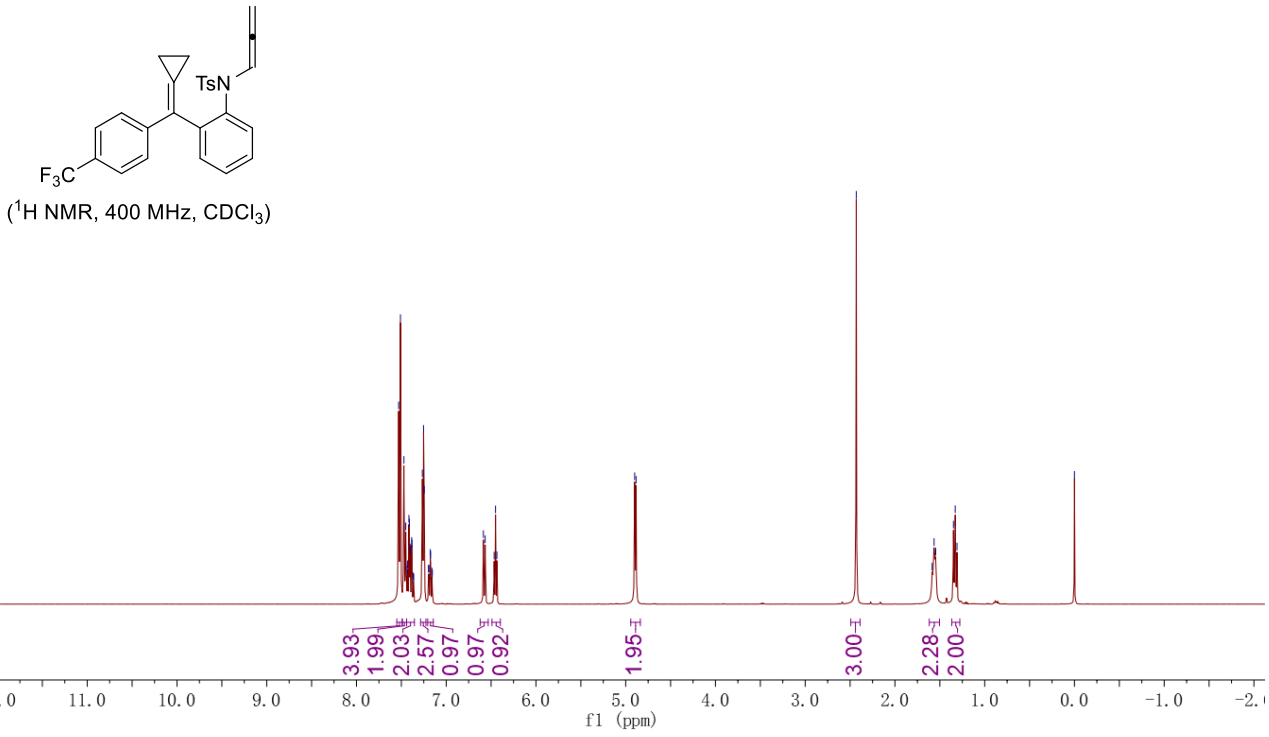
(^{13}C NMR, 100 MHz, $CDCl_3$)

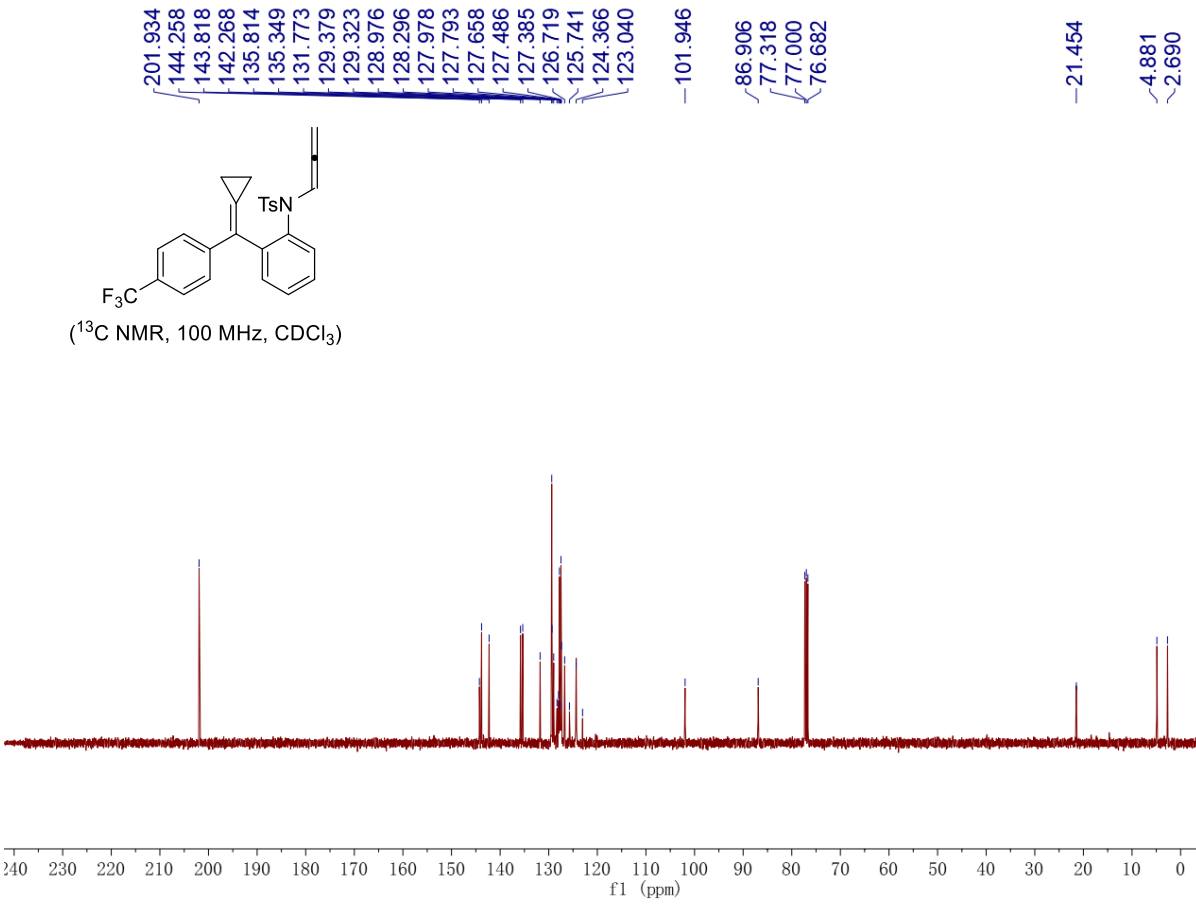


(^{19}F NMR, 376 MHz, $CDCl_3$)

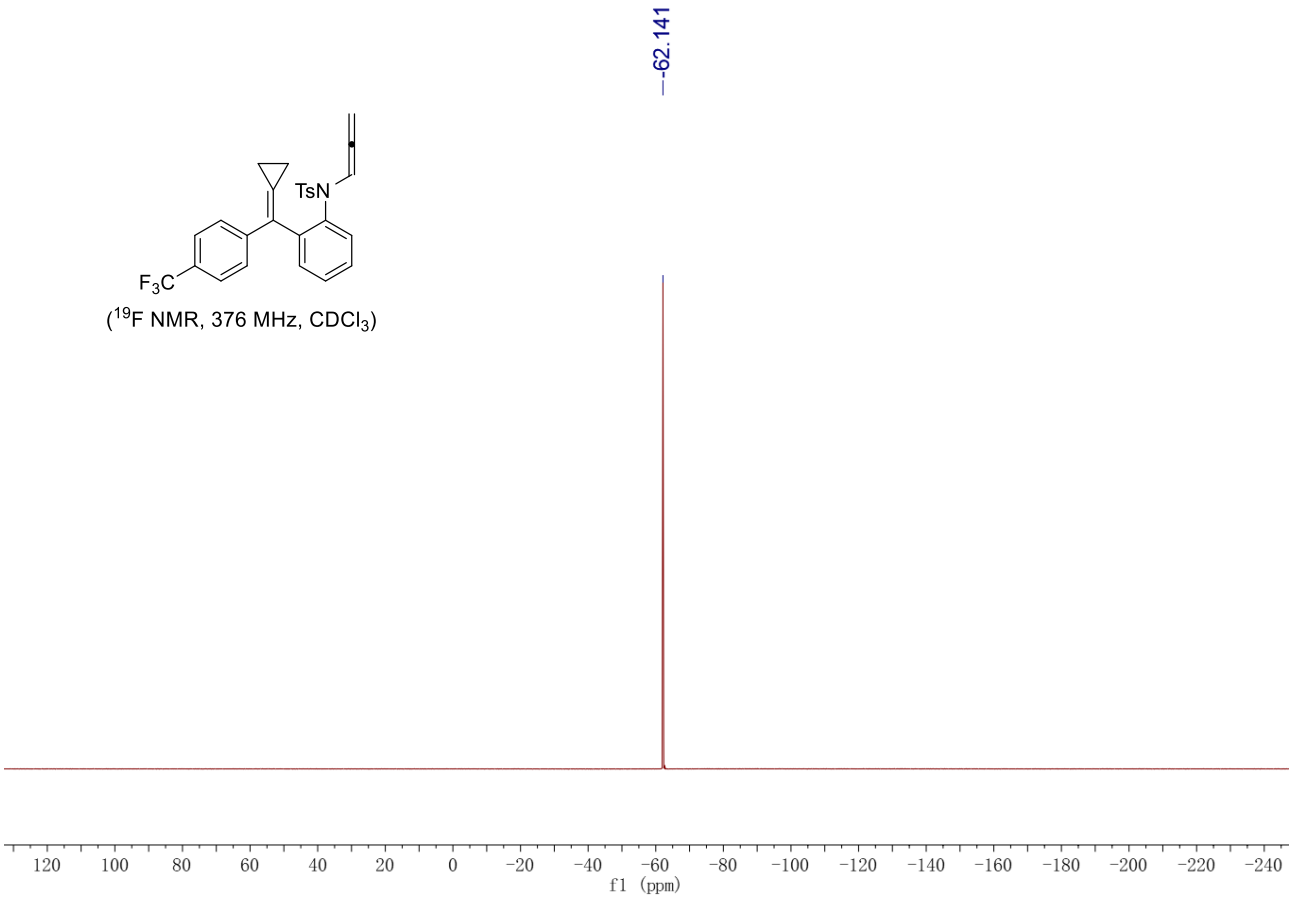


4-methyl-*N*-(2-(cyclopropylidene(4-(trifluoromethyl)phenyl)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1f**): Yield: 702 mg, 73%, yellow oil; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52 (d, *J* = 8.0 Hz, 4H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.35 (m, 2H), 7.29 – 7.23 (m, 3H), 7.18 (td, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.45 (t, *J* = 6.0 Hz, 1H), 4.89 (d, *J* = 6.0 Hz, 2H), 2.43 (s, 3H), 1.62 – 1.50 (m, 2H), 1.37 – 1.28 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 201.9, 144.2, 143.8, 142.2, 135.8, 135.3, 131.7, 129.4, 129.3, 128.9, 128.1 (q, *J* = 31.9 Hz), 127.7, 127.4, 127.3, 126.7, 125.7, 124.4 (q, *J* = 270.1 Hz), 124.3 (q, *J* = 3.5 Hz), 123.0, 101.9, 86.9, 21.4, 4.9, 2.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.14; IR (neat): ν 3068, 3036, 2961, 1613, 1479, 1361, 1158, 1069, 662 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 504.12156, found: 504.12200.

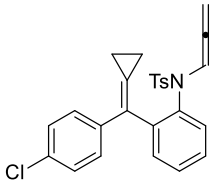




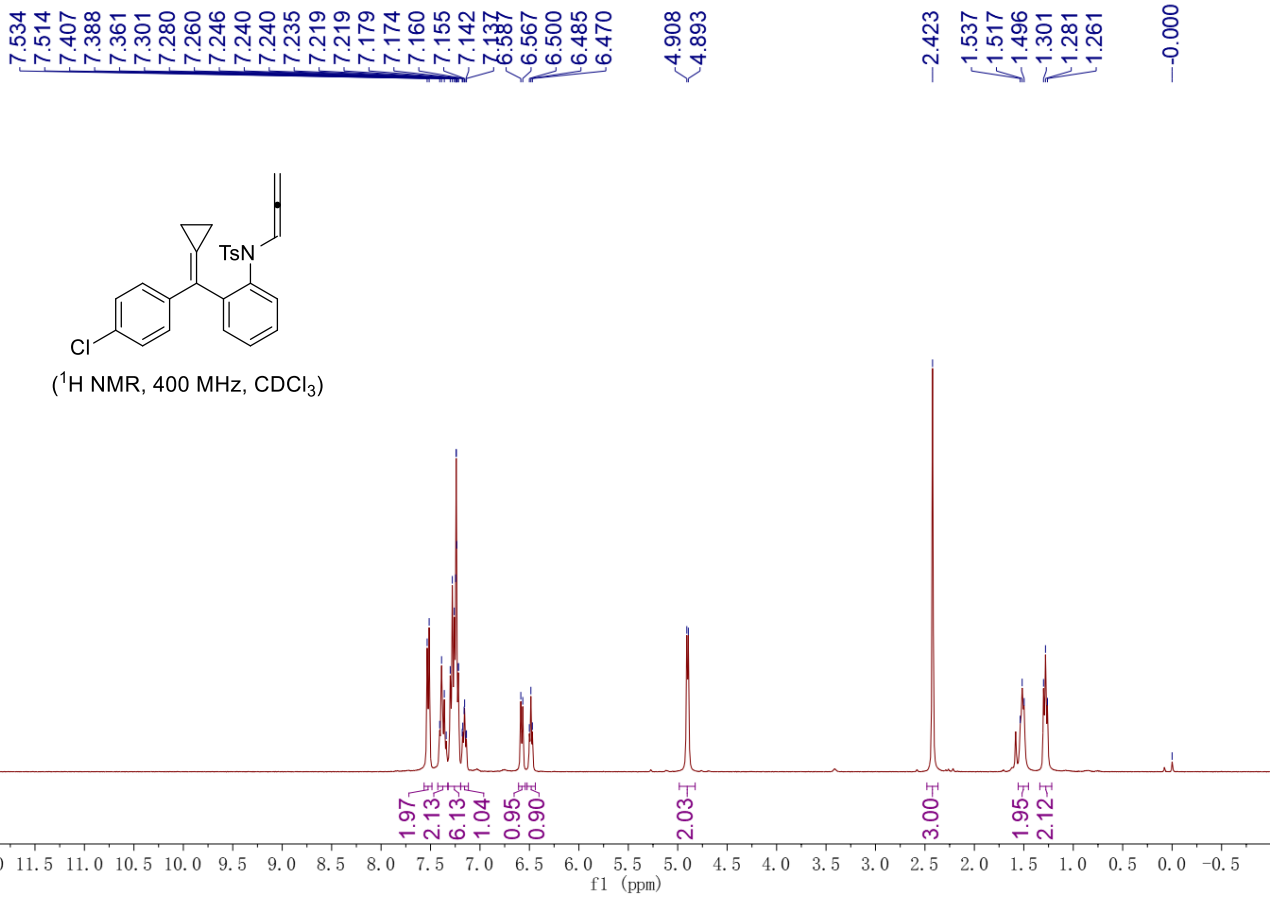
(^{13}C NMR, 100 MHz, $CDCl_3$)

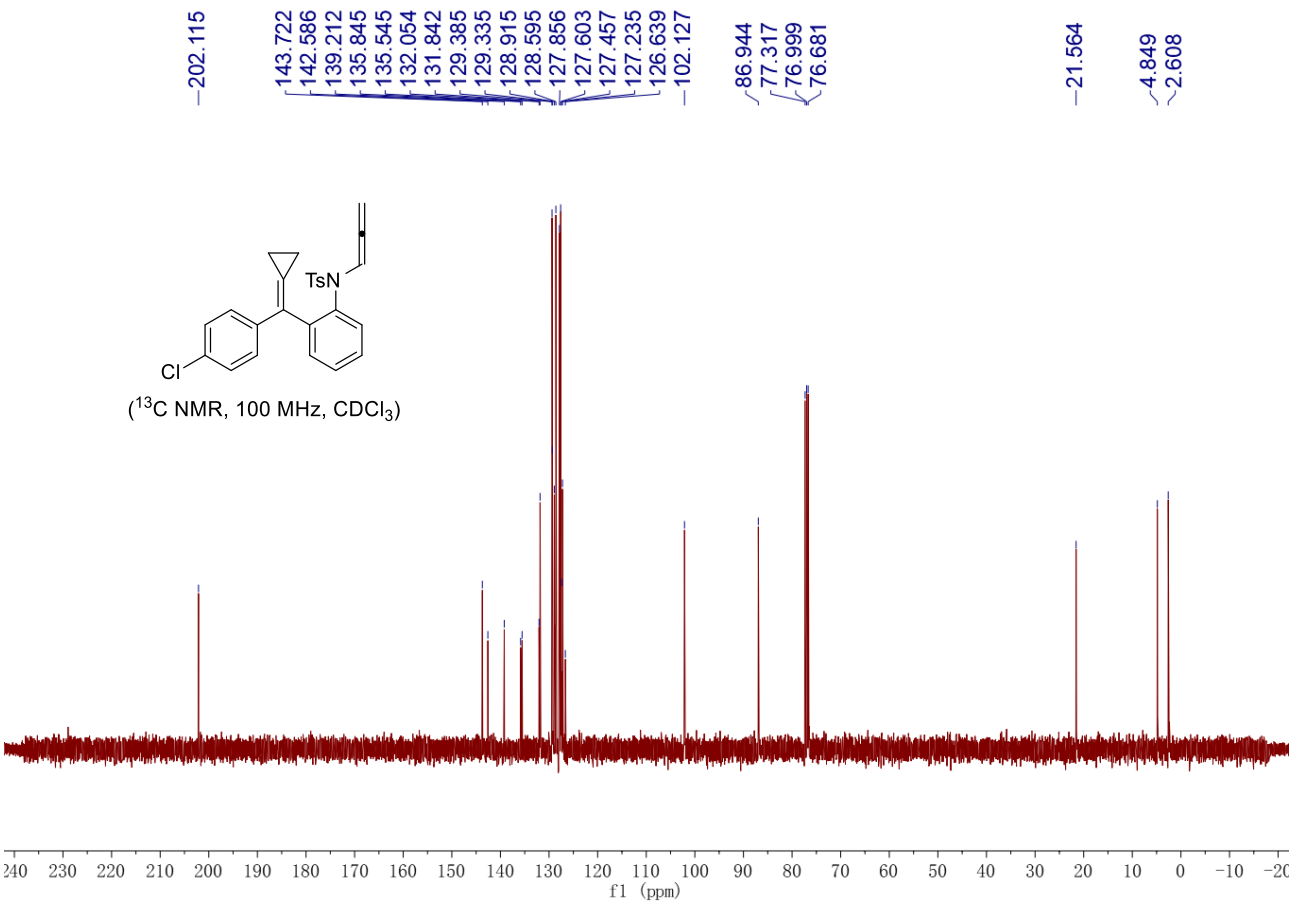


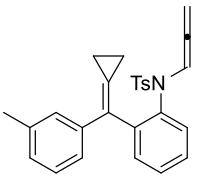
(^{19}F NMR, 376 MHz, $CDCl_3$)



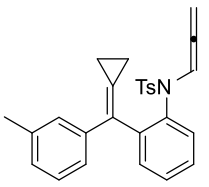
4-methyl-*N*-(2-((4-chlorophenyl)(cyclopropylidene)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1g**): Yield: 706 mg, 79%, yellow solid, m.p. 156-158 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.33 (m, 2H), 7.32 – 7.20 (m, 6H), 7.16 (td, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.49 (t, *J* = 6.0 Hz, 1H), 4.90 (d, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 1.56 – 1.45 (m, 2H), 1.34 – 1.22 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.1, 143.7, 142.6, 139.2, 135.8, 135.5, 132.1, 131.8, 129.4, 129.3, 128.9, 128.6, 127.9, 127.6, 127.5, 127.2, 126.6, 102.1, 86.9, 21.6, 4.8, 2.6; IR (neat): ν 3051, 3021, 2961, 1487, 1356, 1149, 1026, 889, 762 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 470.09520, found: 470.09614.



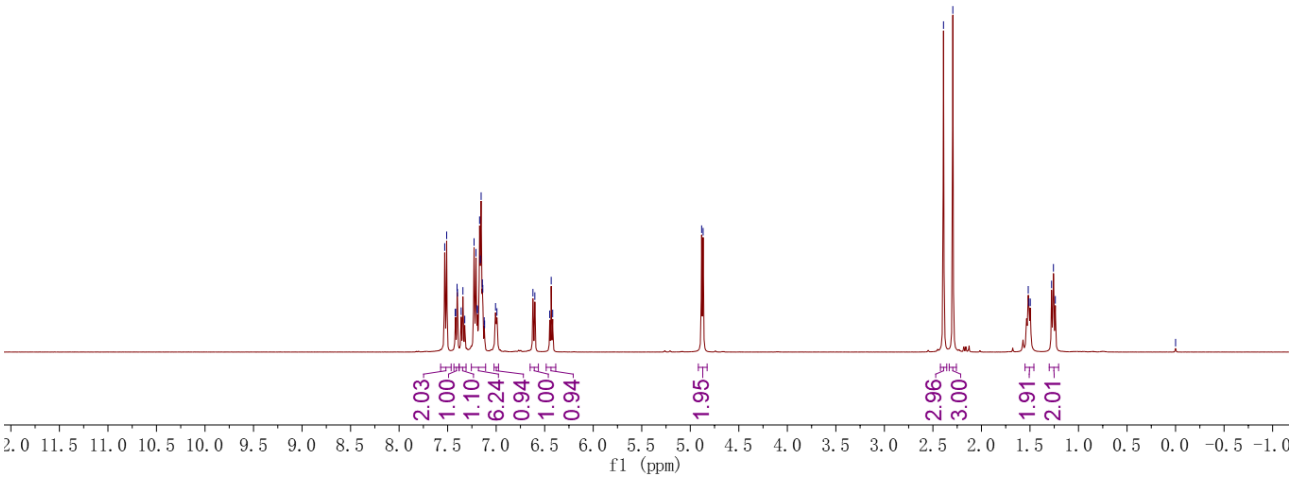

202.115
143.722
142.586
139.212
135.845
135.545
132.054
131.842
129.385
129.335
128.915
128.595
127.856
127.603
127.457
127.235
126.639
102.127
86.944
77.317
76.999
76.681
21.564
4.849
2.608
TsN
Cl
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

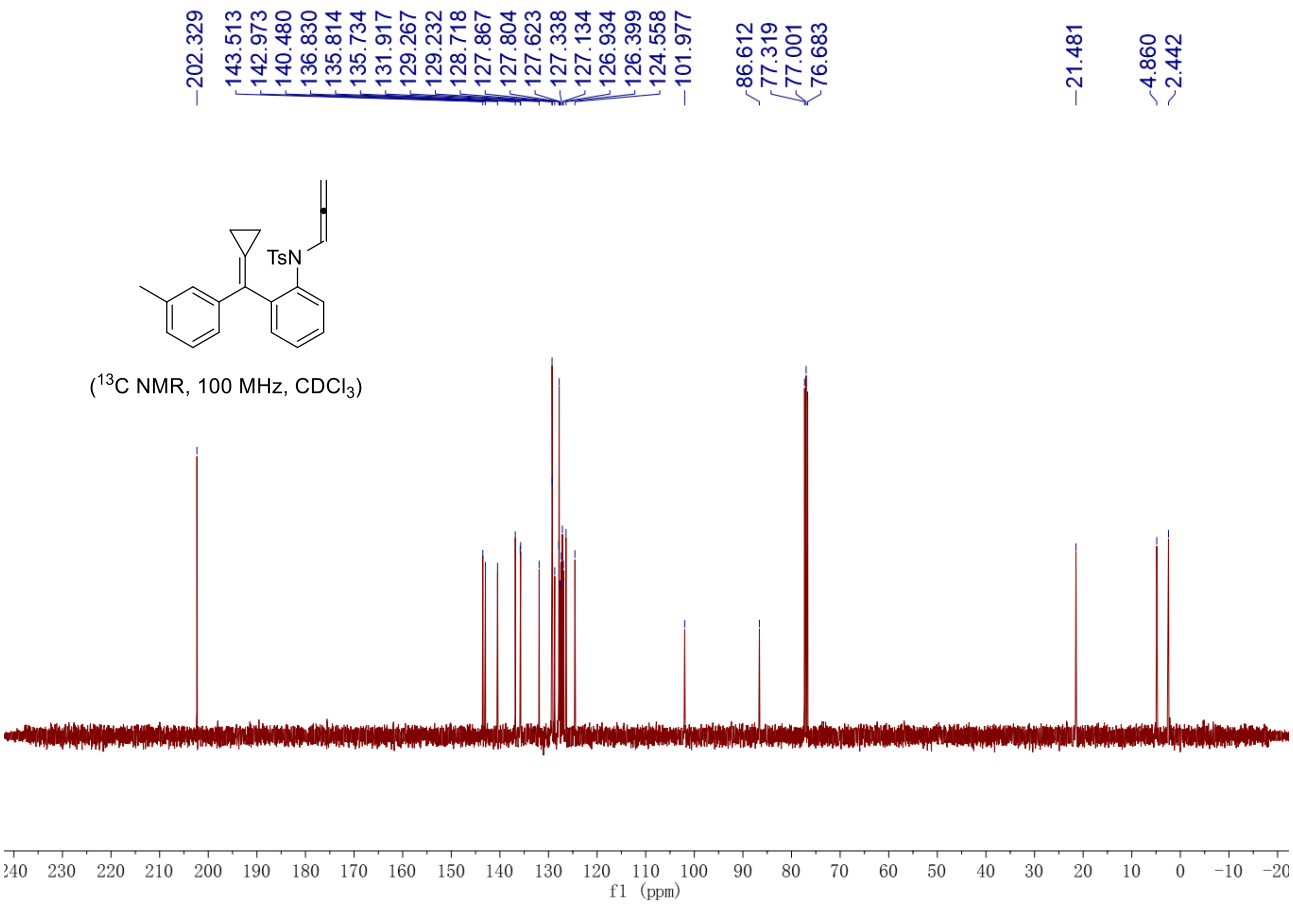


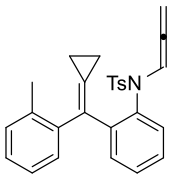
4-methyl-*N*-(2-(cyclopropylidene(m-tolyl)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1h**): Yield: 777 mg, 81%, yellow solid, m.p. 147-149 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52 (d, J = 8.0 Hz, 2H), 7.41 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.26 – 7.11 (m, 6H), 7.00 (d, J = 6.0 Hz, 1H), 6.61 (d, J = 7.6 Hz, 1H), 6.43 (t, J = 6.0 Hz, 1H), 4.88 (d, J = 6.0 Hz, 2H), 2.39 (s, 3H), 2.29 (s, 3H), 1.55 – 1.46 (m, 2H), 1.30 – 1.21 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.3, 143.5, 143.0, 140.5, 136.8, 135.8, 135.7, 131.9, 129.3, 129.2, 128.7, 127.9, 127.8, 127.6, 127.3, 127.1, 126.9, 126.4, 124.6, 102.0, 86.6, 21.5, 4.9, 2.4; IR (neat): ν 3060, 3018, 2974, 1594, 1484, 1437, 1346, 1157, 1088, 801, 704 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.15039.



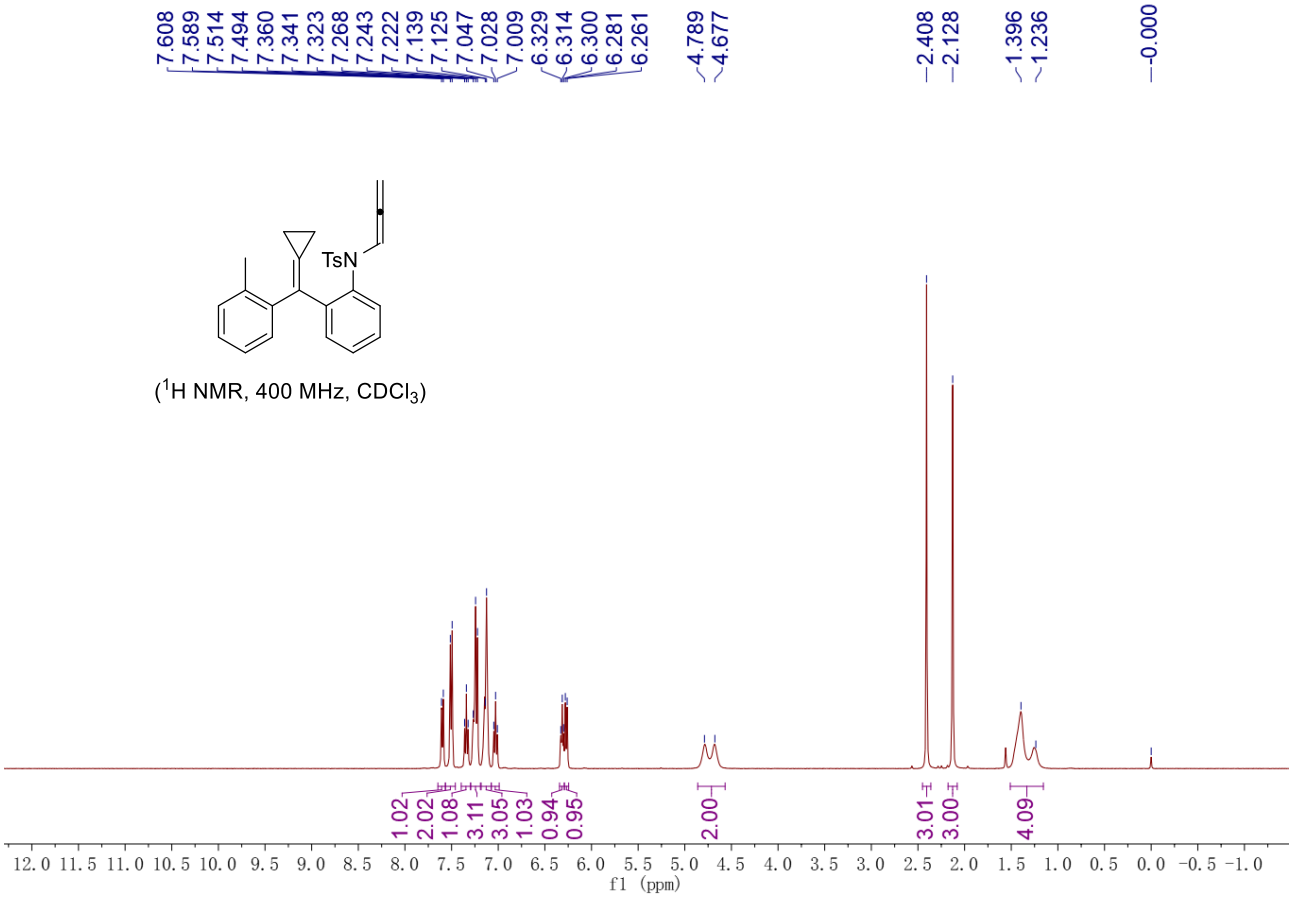
(^{1}H NMR, 400 MHz, $CDCl_3$)

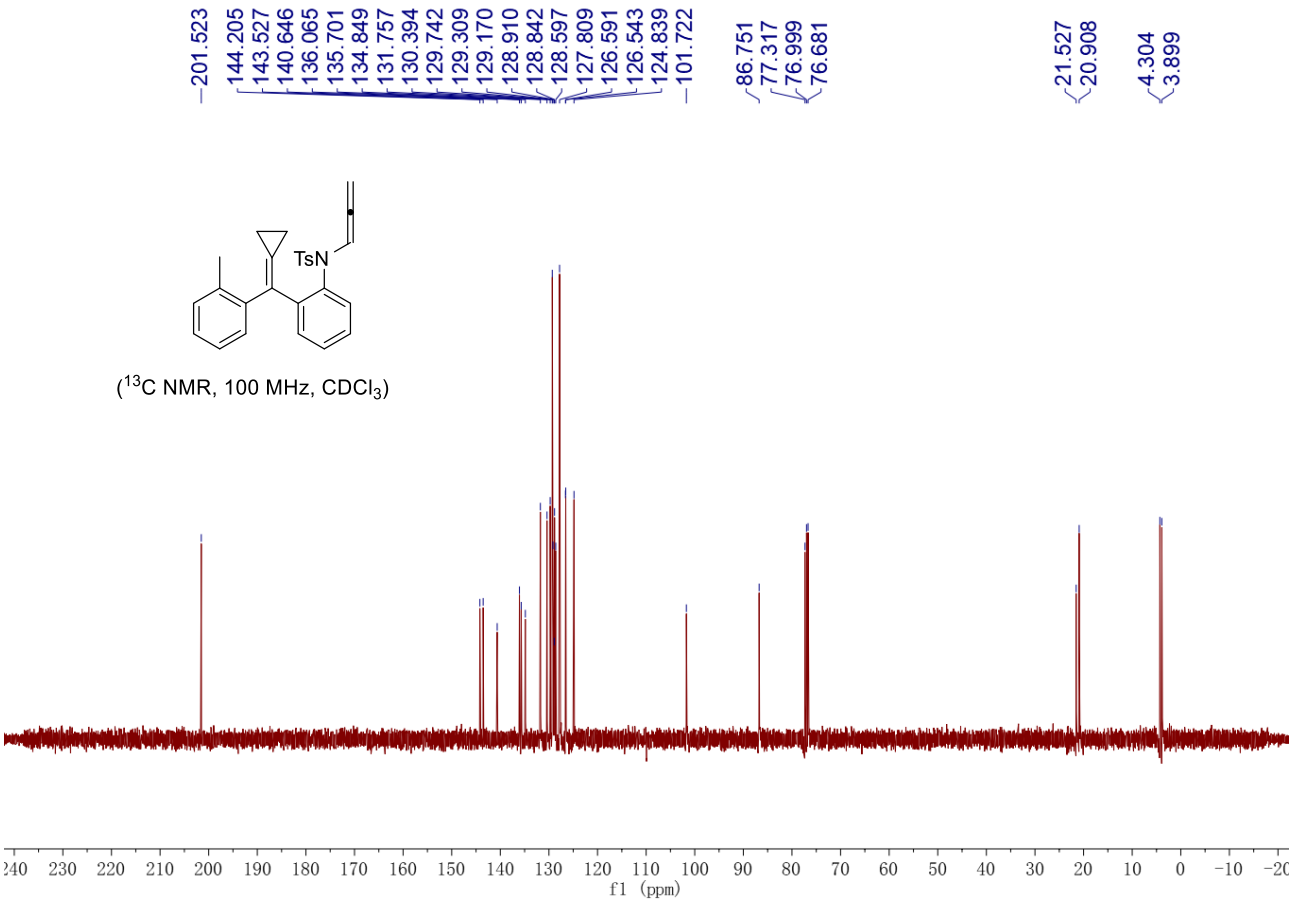


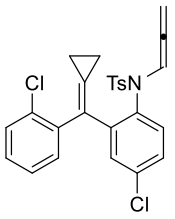

202.329
143.513
142.973
140.480
136.830
135.814
135.734
131.917
129.267
129.232
128.718
127.867
127.804
127.623
127.338
127.134
126.934
126.399
124.558
101.977
86.612
77.319
77.001
76.683
21.481
4.860
2.442
TsN
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)



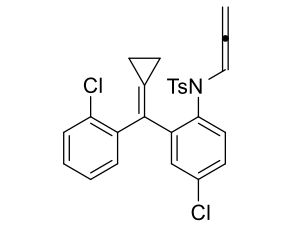
4-methyl-*N*-(2-(cyclopropylidene(o-tolyl)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1i**): Yield: 649 mg, 76%, yellow solid, m.p. 161-163 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.19 (m, 3H), 7.18 – 7.07 (m, 3H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.31 (t, *J* = 5.6 Hz, 1H), 6.27 (d, *J* = 8.0 Hz, 1H), 4.79 (m, 1H), 4.68 (m, 1H), 2.41 (s, 3H), 2.13 (s, 3H), 1.51 – 1.16 (m, 4H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 201.5, 144.2, 143.5, 140.6, 136.1, 135.7, 134.8, 131.8, 130.4, 129.7, 129.3, 129.2, 128.9, 128.8, 128.6, 127.8, 126.6, 126.5, 124.8, 101.7, 86.8, 21.5, 20.9, 4.3, 3.9; IR (neat): ν 3050, 2979, 2906, 1594, 1482, 1353, 1165, 1089, 764, 722 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.15064.



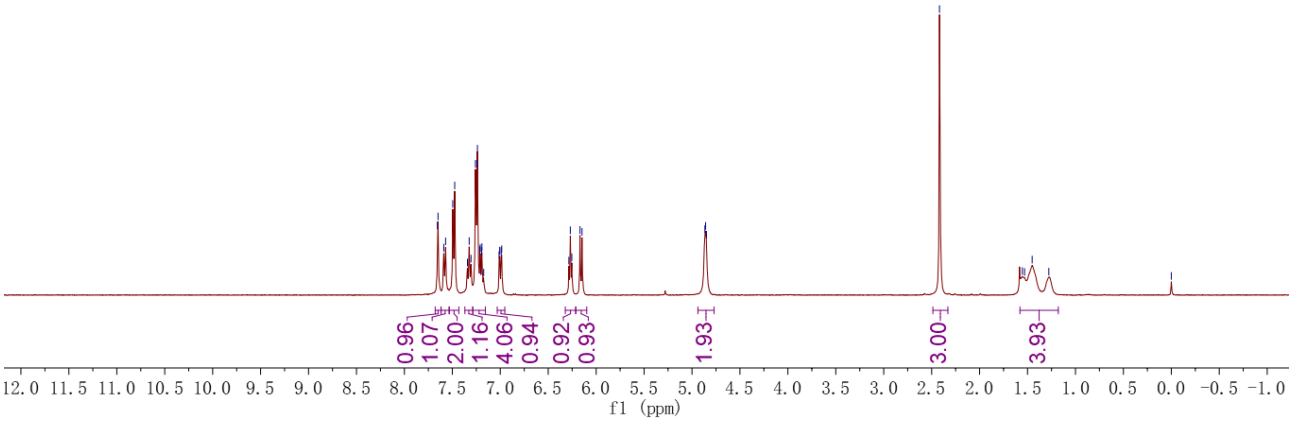

201.523
144.205
143.527
140.646
136.065
135.701
134.849
131.757
130.394
129.742
129.309
129.170
128.910
128.842
128.597
127.809
126.591
126.543
124.839
101.722
86.751
77.317
76.999
76.681
21.527
20.908
4.304
3.899
TsN
(^{13}C NMR, 100 MHz, $CDCl_3$)
f1 (ppm)

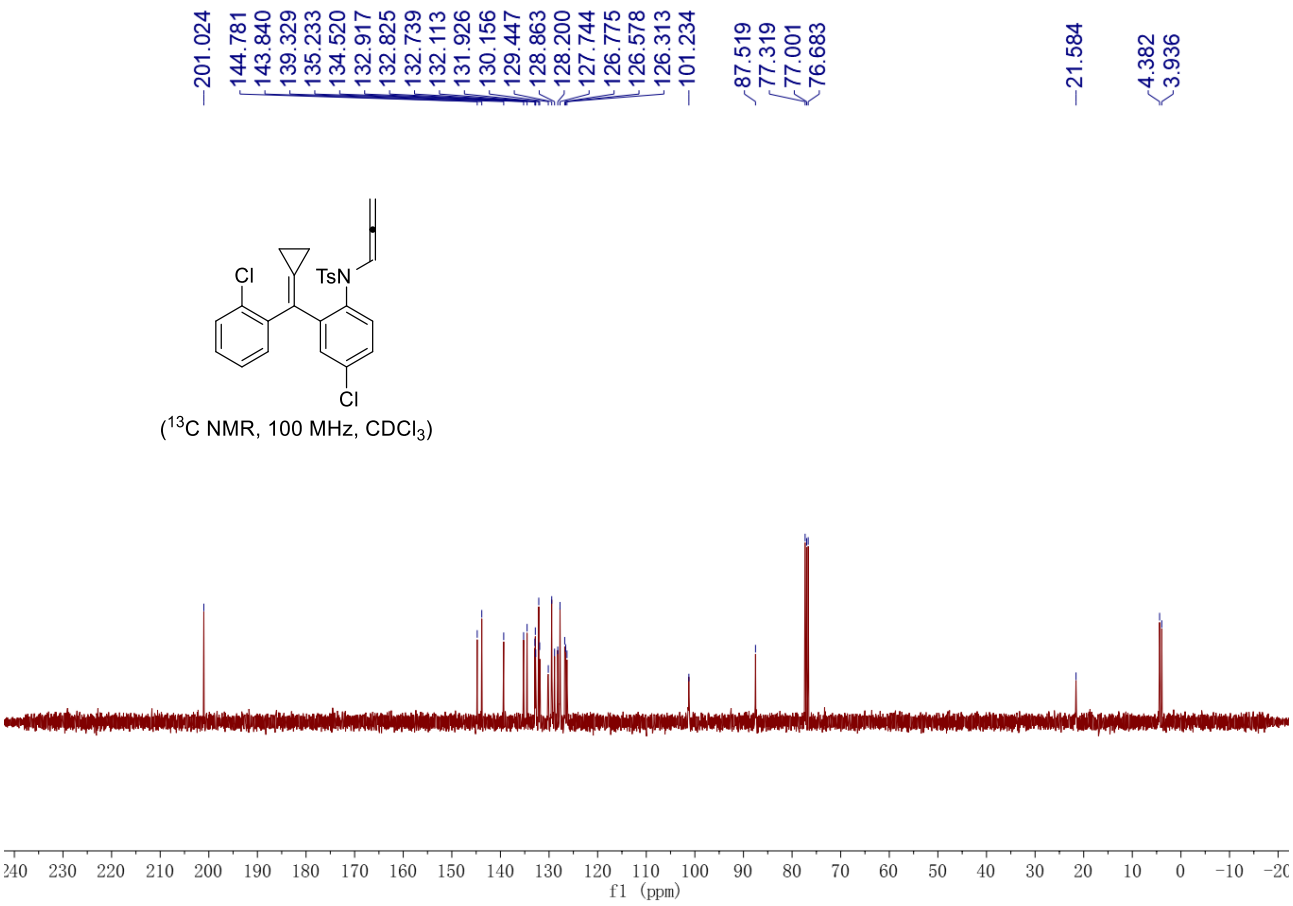


4-methyl-*N*-(4-chloro-2-((2-chlorophenyl)(cyclopropylidene)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1j**): Yield: 692 mg, 72%, yellow solid, m.p. 160-162 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 (d, *J* = 2.8 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.29 – 7.16 (m, 4H), 7.00 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.27 (t, *J* = 6.0 Hz, 1H), 6.16 (d, *J* = 8.4 Hz, 1H), 4.94 – 4.77 (m, 2H), 2.42 (s, 3H), 1.58 – 1.18 (m, 4H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 201.0, 144.8, 143.8, 139.3, 135.2, 134.5, 132.9, 132.8, 132.7, 132.1, 131.9, 130.2, 129.4, 128.9, 128.2, 127.7, 126.8, 126.6, 126.3, 101.2, 87.5, 21.6, 4.4, 3.9; IR (neat): ν 3047, 2984, 1600, 1476, 1440, 1355, 1165, 1086, 1025, 884, 782 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 504.05623, found: 504.05686.

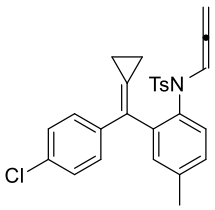


(^{1}H NMR, 400 MHz, $CDCl_3$)

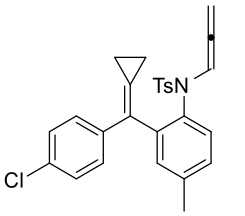




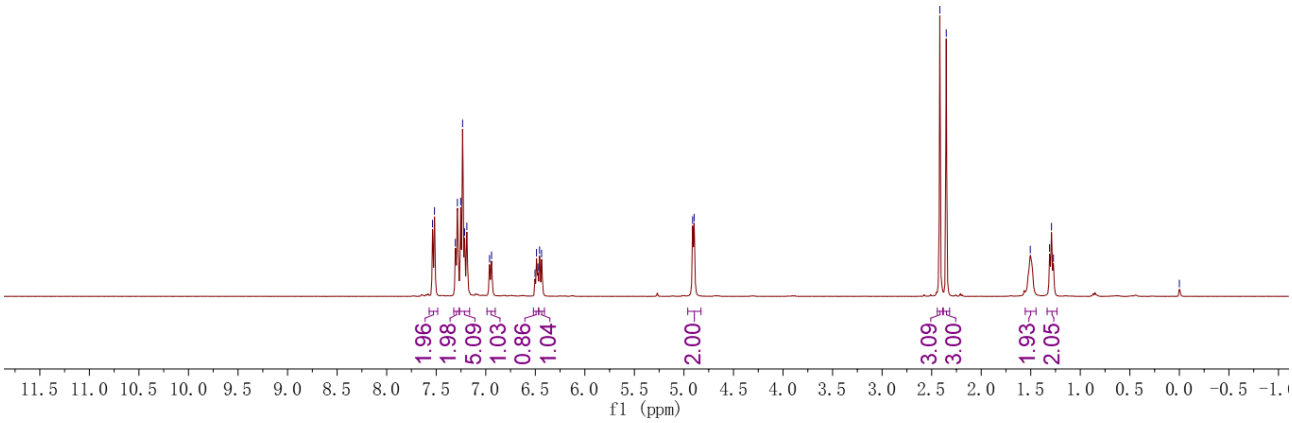
(^{13}C NMR, 100 MHz, $CDCl_3$)

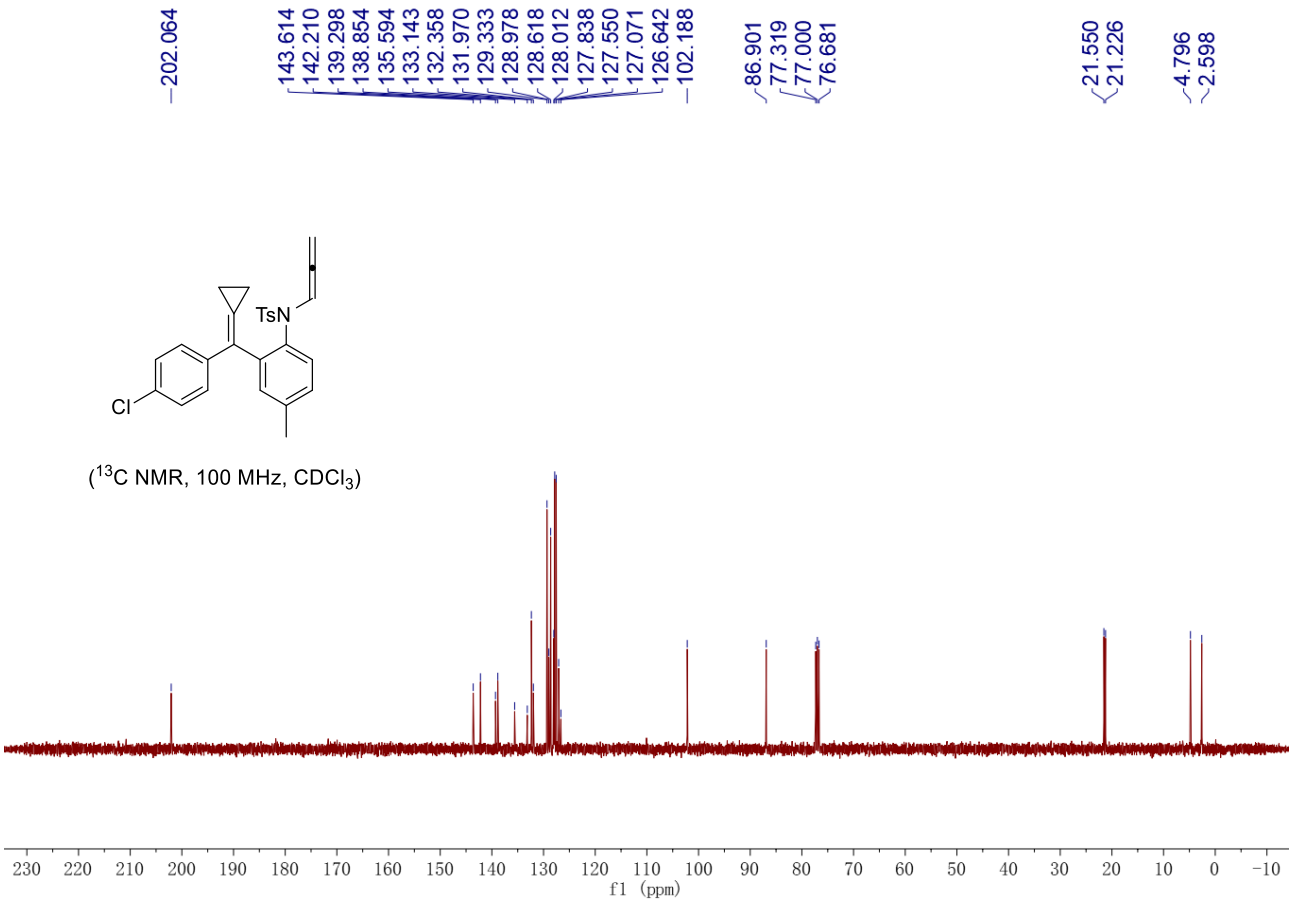


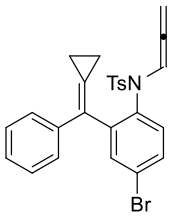
4-methyl-*N*-(2-((4-chlorophenyl)(cyclopropylidene)methyl)-4-methylphenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1k**): Yield: 710 mg, 77%, yellow solid, m.p. 161-163 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.16 (m, 5H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.49 (t, *J* = 6.0 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 4.90 (d, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 2.35 (s, 3H), 1.56 – 1.45 (m, 2H), 1.33 – 1.24 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.1, 143.6, 142.2, 139.3, 138.9, 135.6, 133.1, 132.4, 132.0, 129.3, 129.0, 128.6, 128.0, 127.8, 127.6, 127.1, 126.6, 102.2, 86.9, 21.5, 21.2, 4.8, 2.6; IR (neat): ν 3055, 2964, 2922, 1589, 1488, 1363, 1166, 1089, 963, 829, 797 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 484.11085, found: 484.11173.



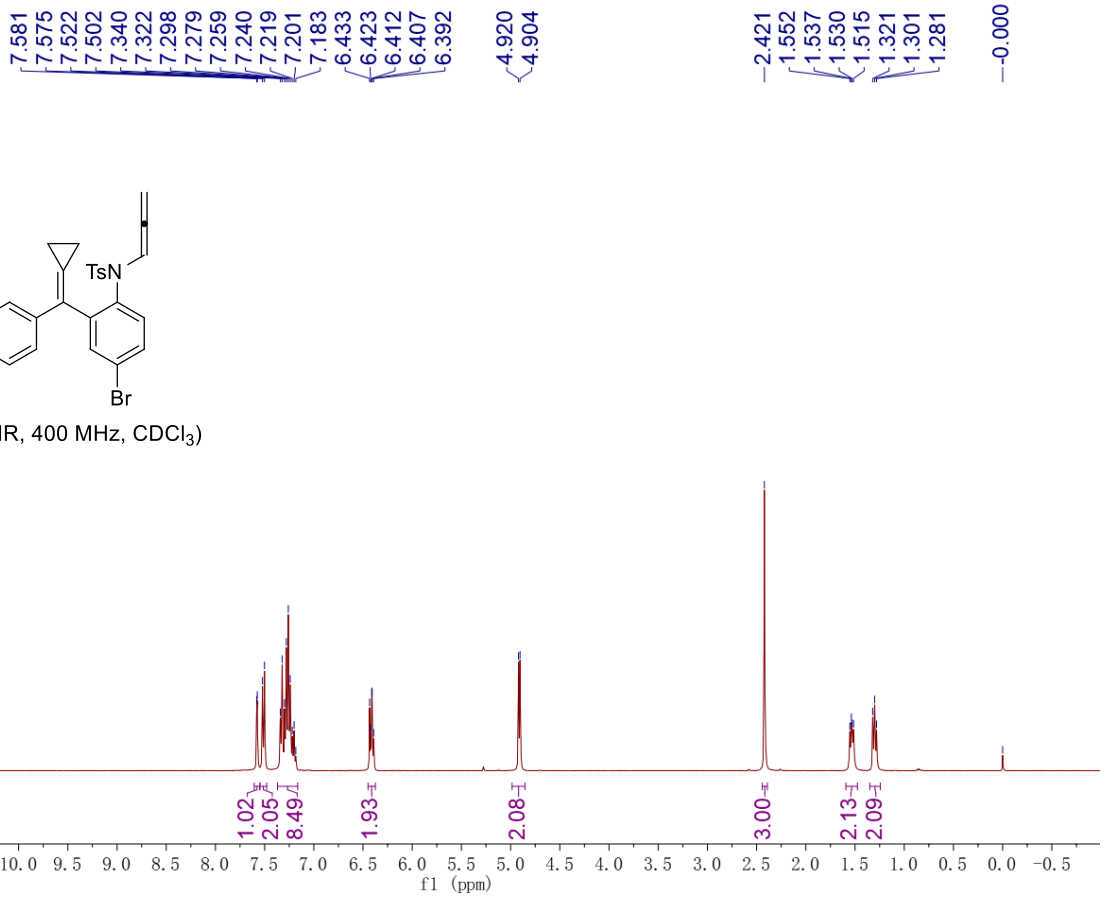
(^{1}H NMR, 400 MHz, $CDCl_3$)

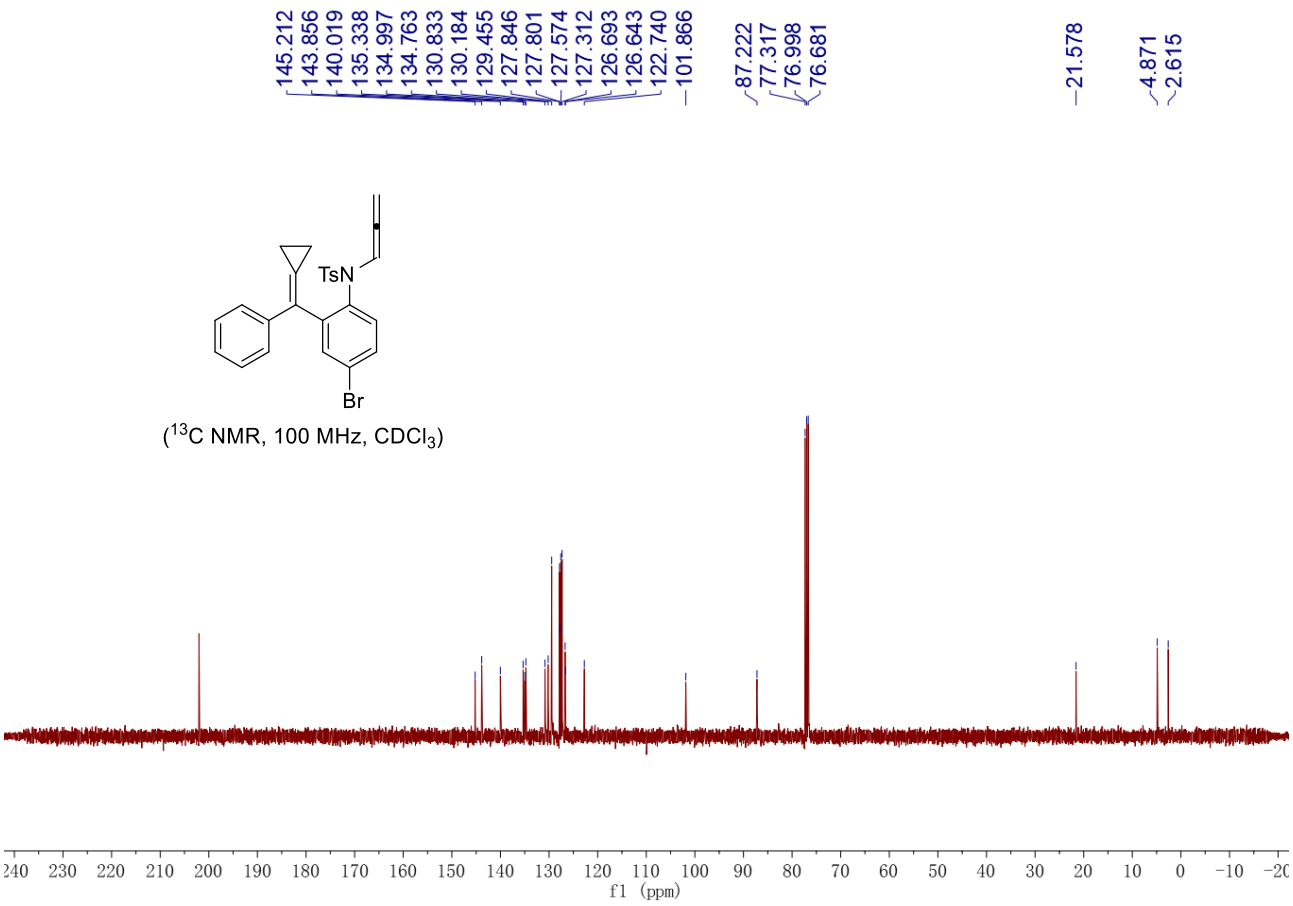


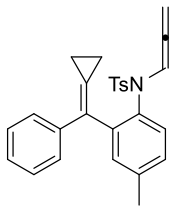

202.064
143.614
142.210
139.298
138.854
135.594
133.143
132.358
131.970
129.333
128.978
128.618
128.012
127.838
127.550
127.071
126.642
102.188
86.901
77.319
77.000
76.681
21.550
21.226
4.796
2.598
TsN
Cl
(^{13}C NMR, 100 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



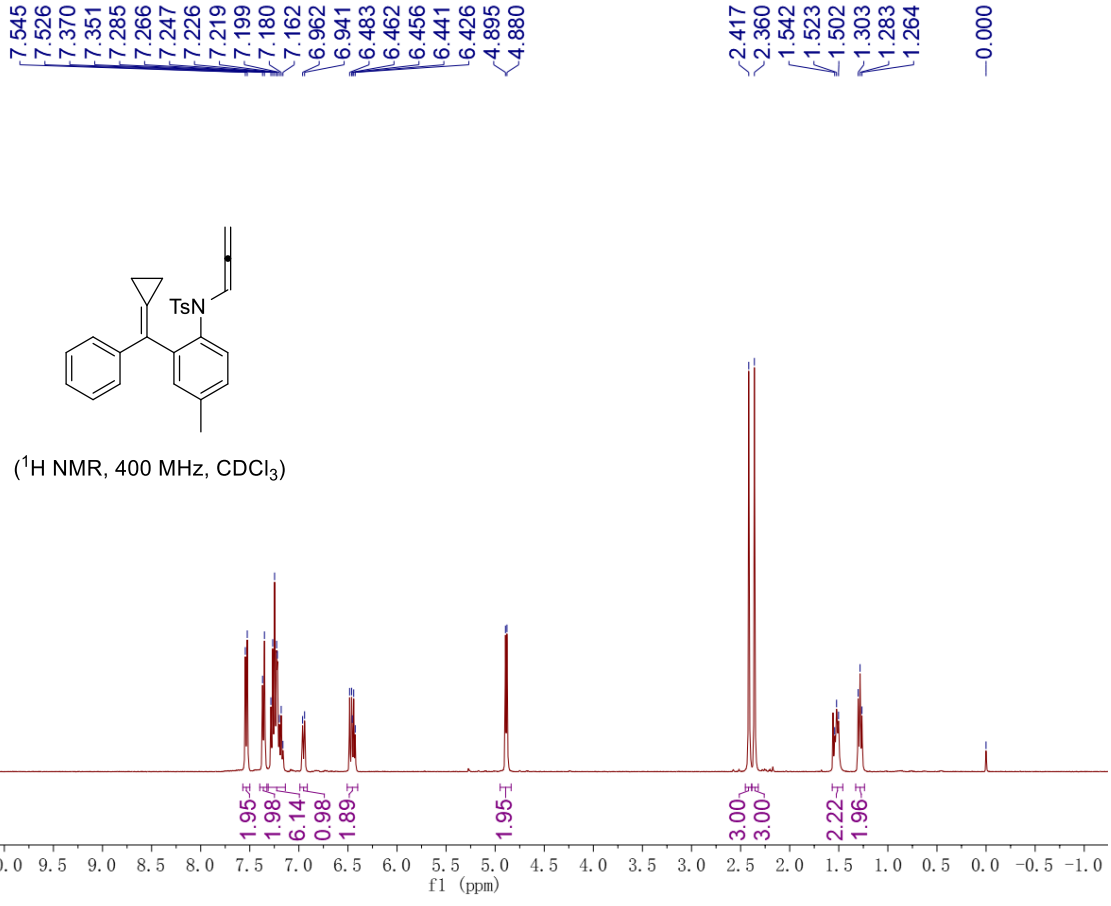
4-methyl-*N*-(4-bromo-2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1l**): Yield: 815 mg, 83%, yellow solid, m.p. 168-170 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, *J* = 2.4 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.16 (m, 8H), 6.42 (d, *J* = 8.0 Hz, 1H), 6.41 (t, *J* = 6.4 Hz, 1H), 4.91 (d, *J* = 6.4 Hz, 2H), 2.42 (s, 3H), 1.59 – 1.48 (m, 2H), 1.35 – 1.24 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.0, 145.2, 143.9, 140.0, 135.3, 135.0, 134.8, 130.8, 130.2, 129.5, 127.8, 127.8, 127.6, 127.3, 126.7, 126.6, 122.7, 101.9, 87.2, 21.6, 4.9, 2.6; IR (neat): ν 3057, 2966, 2924, 1594, 1479, 1440, 1359, 1270, 1166, 967, 760 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 514.04468, found: 514.04478.

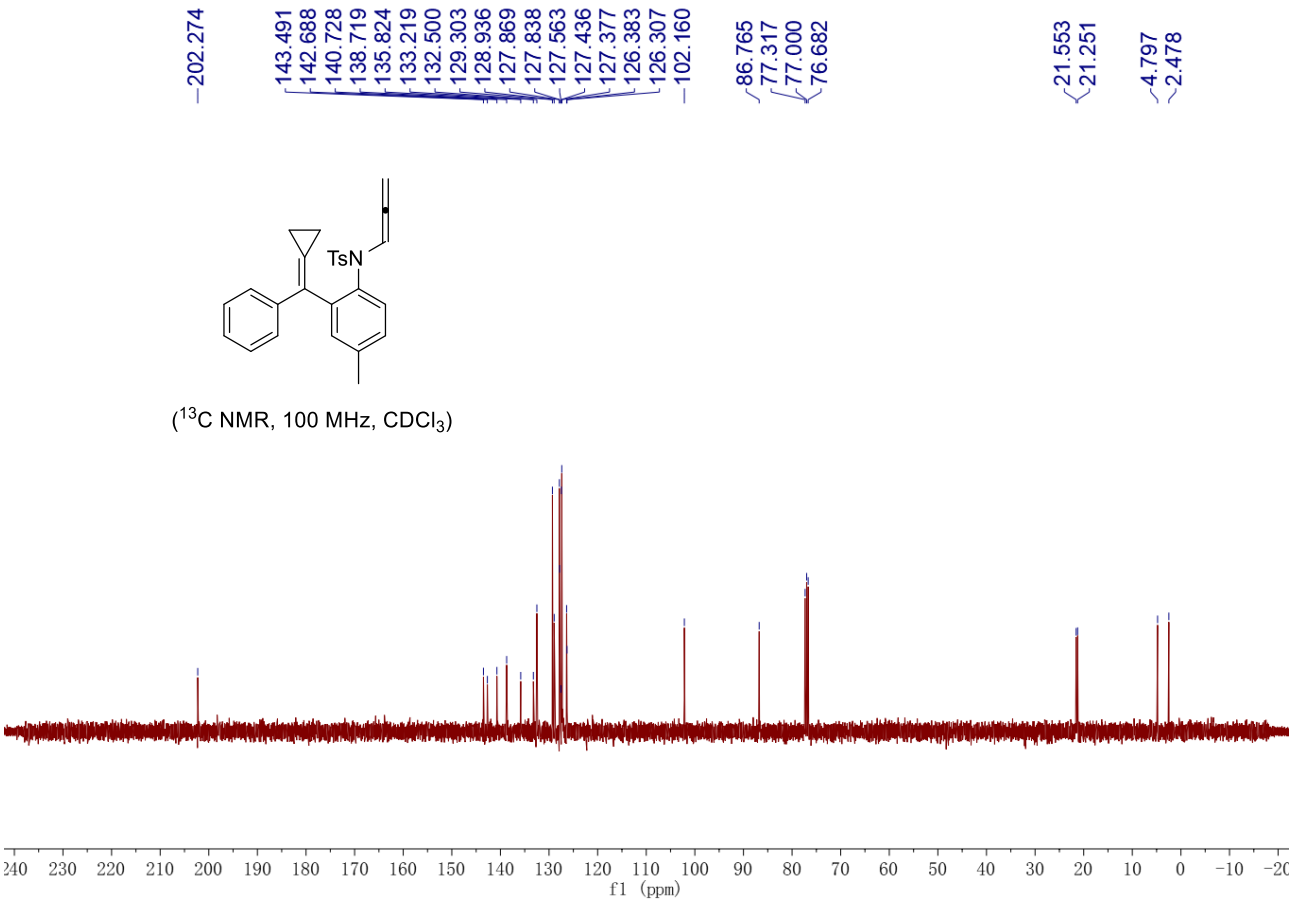



145.212
143.856
140.019
135.338
134.997
134.763
130.833
130.184
129.455
127.846
127.801
127.574
127.312
126.693
126.643
122.740
101.866
87.222
77.317
76.998
76.681
21.578
4.871
2.615
TsN
Br
(13C NMR, 100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

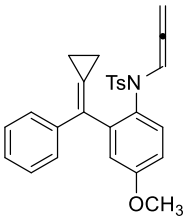


4-methyl-*N*-(2-(cyclopropylidene(phenyl)methyl)-4-methylphenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1m**): Yield: 700 mg, 82%, yellow solid, m.p. 178-180 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.31 – 7.14 (m, 6H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.47 (d, *J* = 8.4 Hz, 1H), 6.44 (t, *J* = 6.0 Hz, 1H), 4.89 (d, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 2.36 (s, 3H), 1.55 – 1.46 (m, 2H), 1.32 – 1.24 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.3, 143.5, 142.7, 140.7, 138.7, 135.8, 133.2, 132.5, 129.3, 128.9, 127.9, 127.8, 127.6, 127.4, 127.4, 126.4, 126.3, 102.2, 86.8, 21.6, 21.3, 4.8, 2.5; IR (neat): ν 3055, 2984, 2919, 1605, 1492, 1432, 1343, 1166, 1089, 946, 812 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.15055.

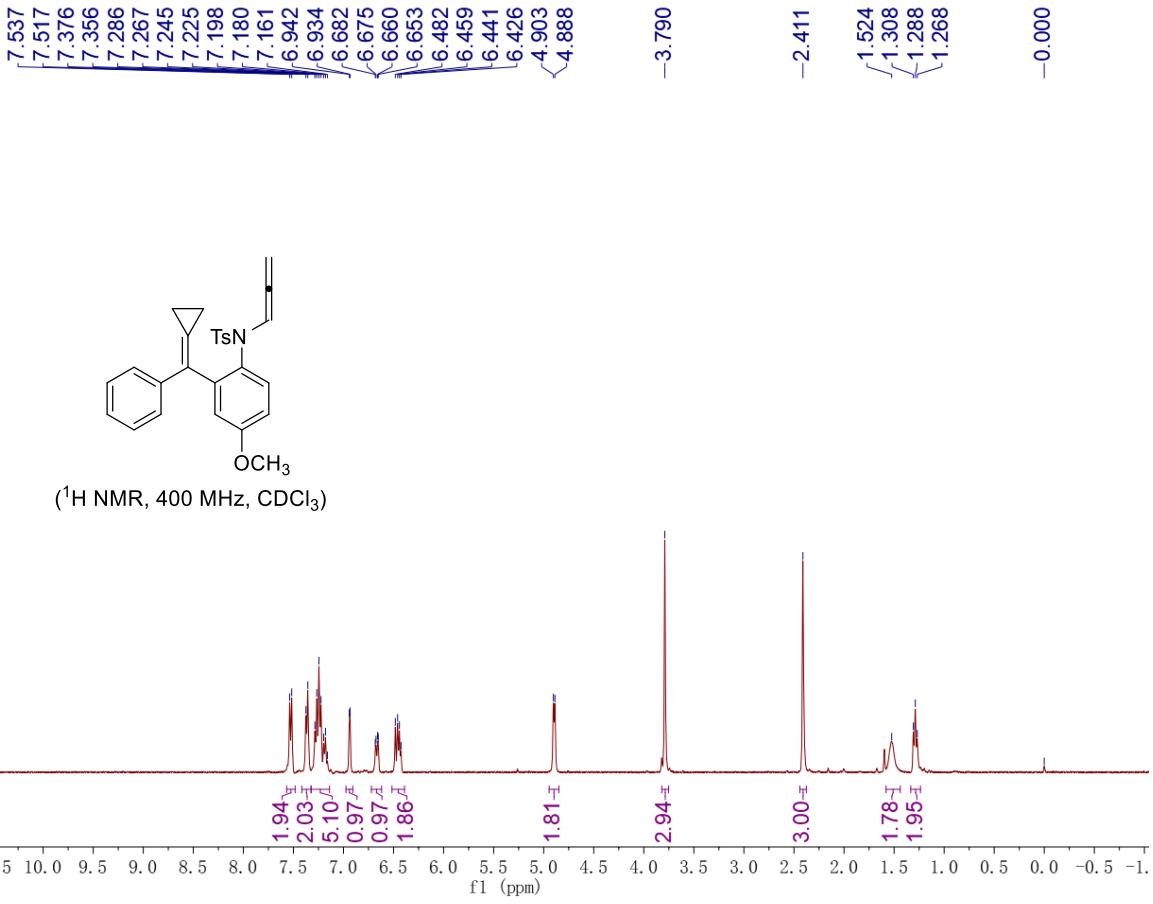


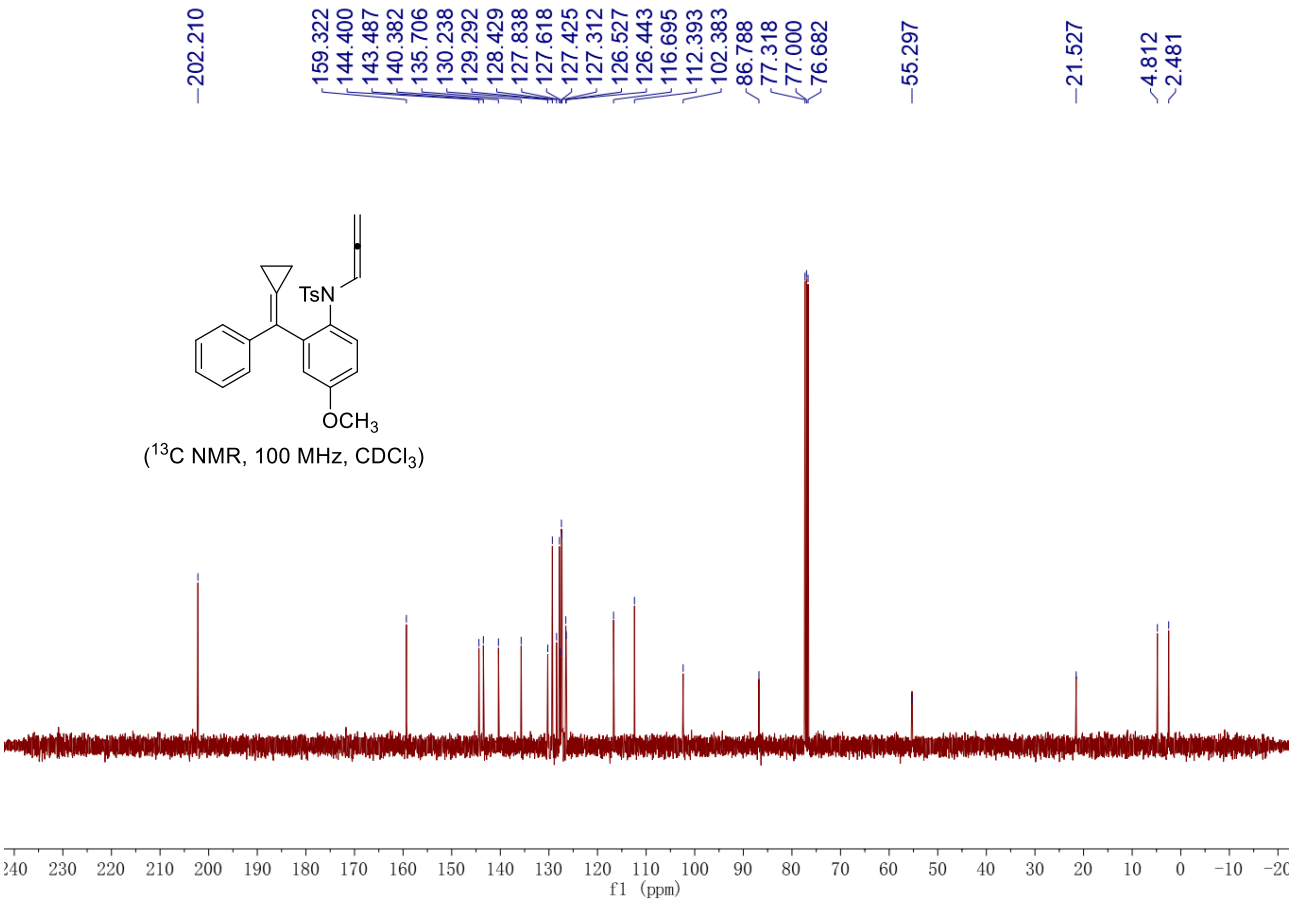


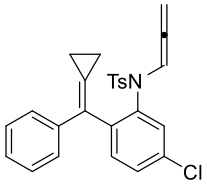
(^{13}C NMR, 100 MHz, $CDCl_3$)



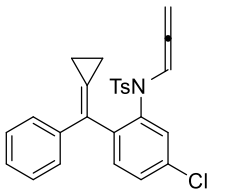
4-methyl-*N*-(2-(cyclopropylidene(phenyl)methyl)-4-methoxyphenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1n**): Yield: 709 mg, 80%, yellow solid, m.p. 146-148 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.14 (m, 5H), 6.94 (d, *J* = 2.8 Hz, 1H), 6.67 (dd, J_1 = 9.2 Hz, J_2 = 2.8 Hz, 1H), 6.47 (d, *J* = 9.2 Hz, 1H),6.44 (t, *J* = 6.0 Hz, 1H), 4.90 (d, *J* = 6.0 Hz, 2H), 3.79 (s, 3H), 2.41 (s, 3H), 1.58 – 1.44 (m, 2H), 1.33 – 1.24 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.2, 159.3, 144.4, 143.5, 140.4, 135.7, 130.2, 129.3, 128.4, 127.8, 127.6, 127.4, 127.3, 126.5, 126.4, 116.7, 112.4, 102.4, 86.8, 55.3, 21.5, 4.8, 2.5; IR (neat): ν 3039, 2974, 1589, 1492, 1356, 1232, 1167, 966, 811 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 466.14474, found: 466.14487.



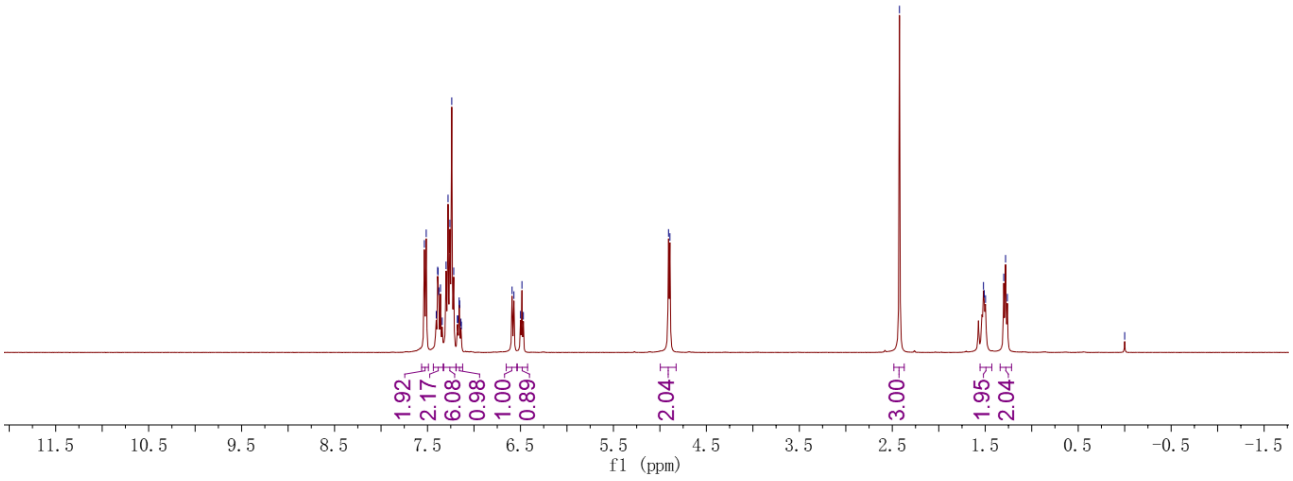

202.210
159.322
144.400
143.487
140.382
135.706
130.238
129.292
128.429
127.838
127.618
127.425
127.312
126.527
126.443
116.695
112.393
102.383
86.788
77.318
77.000
76.682
55.297
21.527
4.812
2.481
TsN
OCH3
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

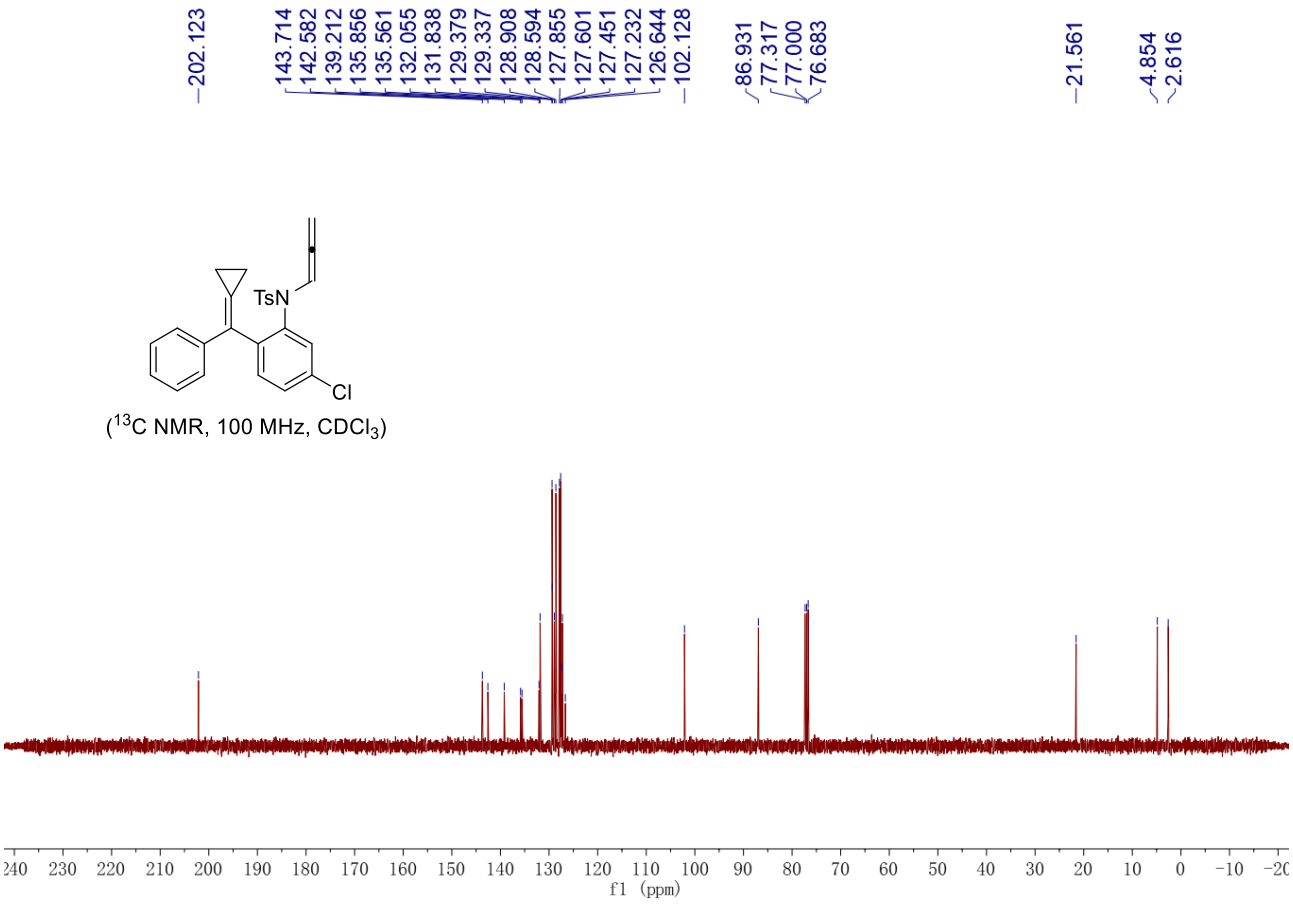


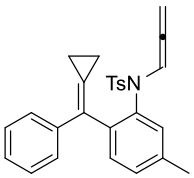
4-methyl-*N*-(5-chloro-2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1o**): Yield: 662 mg, 74%, yellow solid, m.p. 154-156 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.33 (m, 2H), 7.33 – 7.19 (m, 6H), 7.16 (td, *J* = 7.5, 2.0 Hz, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 6.48 (t, *J* = 6.1 Hz, 1H), 4.90 (d, *J* = 6.1 Hz, 2H), 2.42 (s, 3H), 1.56 – 1.43 (m, 2H), 1.34 – 1.22 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.1, 143.7, 142.6, 139.2, 135.9, 135.6, 132.1, 131.8, 129.4, 129.3, 128.9, 128.6, 127.9, 127.6, 127.5, 127.2, 126.6, 102.1, 86.9, 21.6, 4.9, 2.6; IR (neat): ν 3055, 3029, 2964, 1599, 1490, 1356, 1260, 1165, 1092,1025, 887, 816 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 470.09520, found: 470.09466.



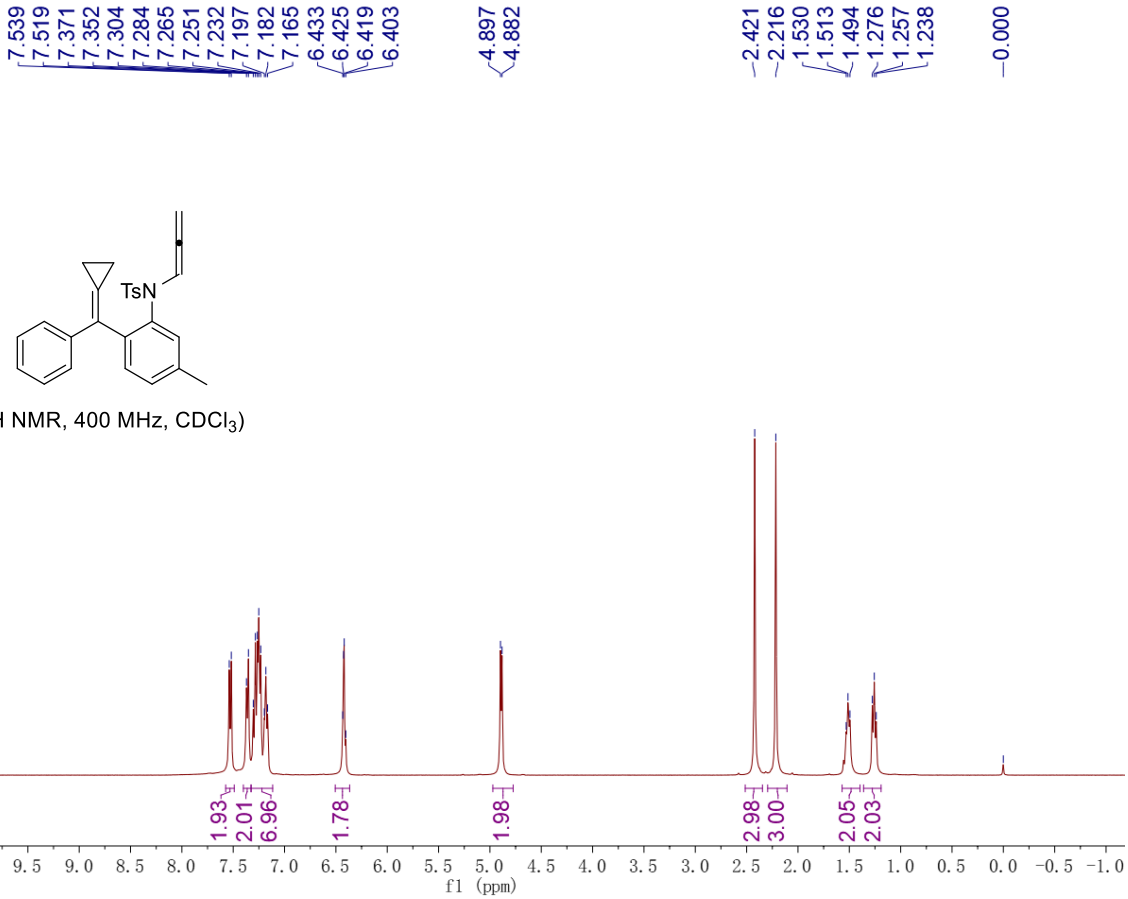
(^{1}H NMR, 400 MHz, $CDCl_3$)

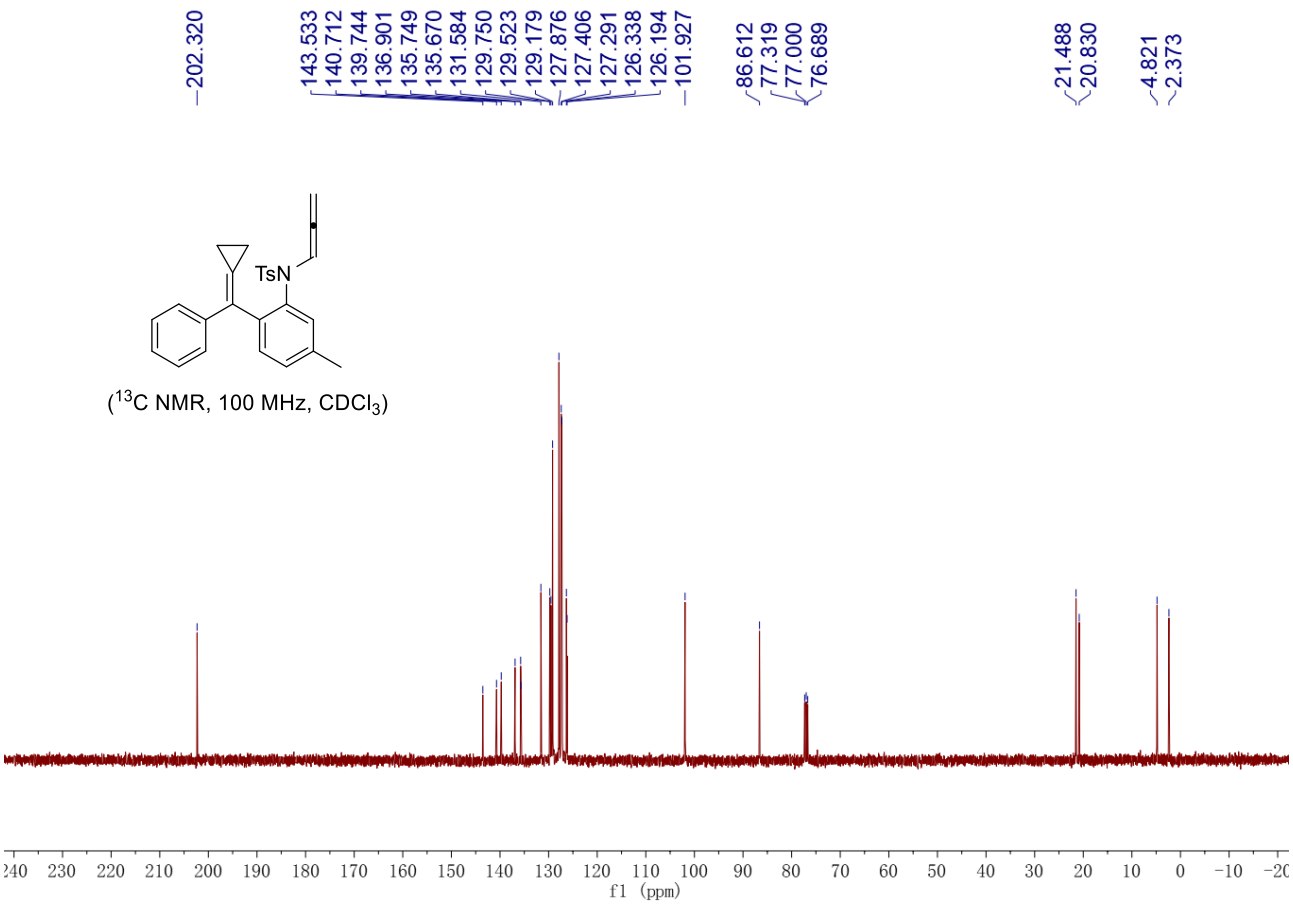


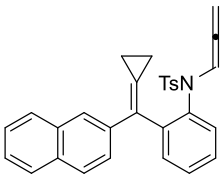

202.123
143.714
142.582
139.212
135.856
135.561
132.055
131.838
129.379
129.337
128.908
128.594
127.855
127.601
127.451
127.232
126.644
102.128
86.931
77.317
77.000
76.683
21.561
4.854
2.616
TsN
Cl
(13C NMR, 100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)



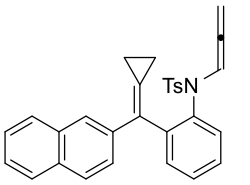
4-methyl-*N*-(2-(cyclopropylidene(phenyl)methyl)-5-methylphenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1p**): Yield: 717 mg, 84%, yellow solid, m.p. 156-158 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.33 – 7.12 (m, 7H), 6.51 – 6.37 (m, 2H), 4.89 (d, *J* = 6.2 Hz, 2H), 2.42 (s, 3H), 2.22 (s, 3H), 1.57 – 1.40 (m, 2H), 1.36 – 1.19 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.3, 143.5, 140.7, 139.7, 136.9, 135.7, 135.7, 131.6, 129.7, 129.5, 129.2, 127.9, 127.4, 127.3, 126.3, 126.2, 101.9, 86.6, 21.5, 20.8, 4.8, 2.4; IR (neat): ν 3039, 2966, 2919, 1594, 1487, 1442, 1358, 1168, 969, 812 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.15070.



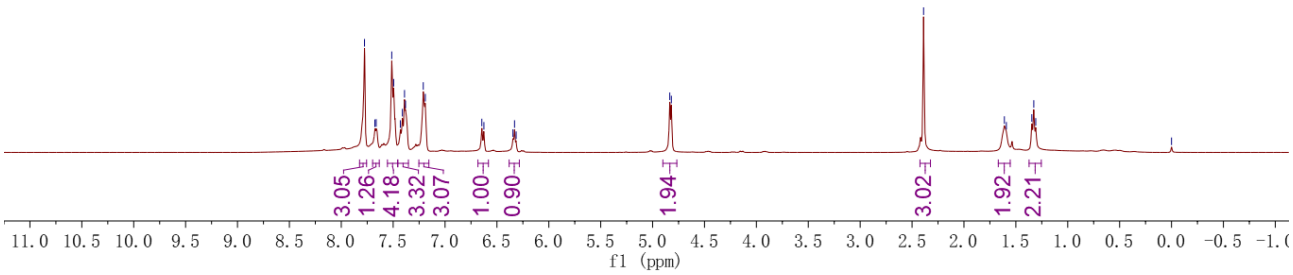

202.320
143.533
140.712
139.744
136.901
135.749
135.670
131.584
129.750
129.523
129.179
127.876
127.406
127.291
126.338
126.194
101.927
86.612
77.319
77.000
76.689
21.488
20.830
4.821
2.373
TsN
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

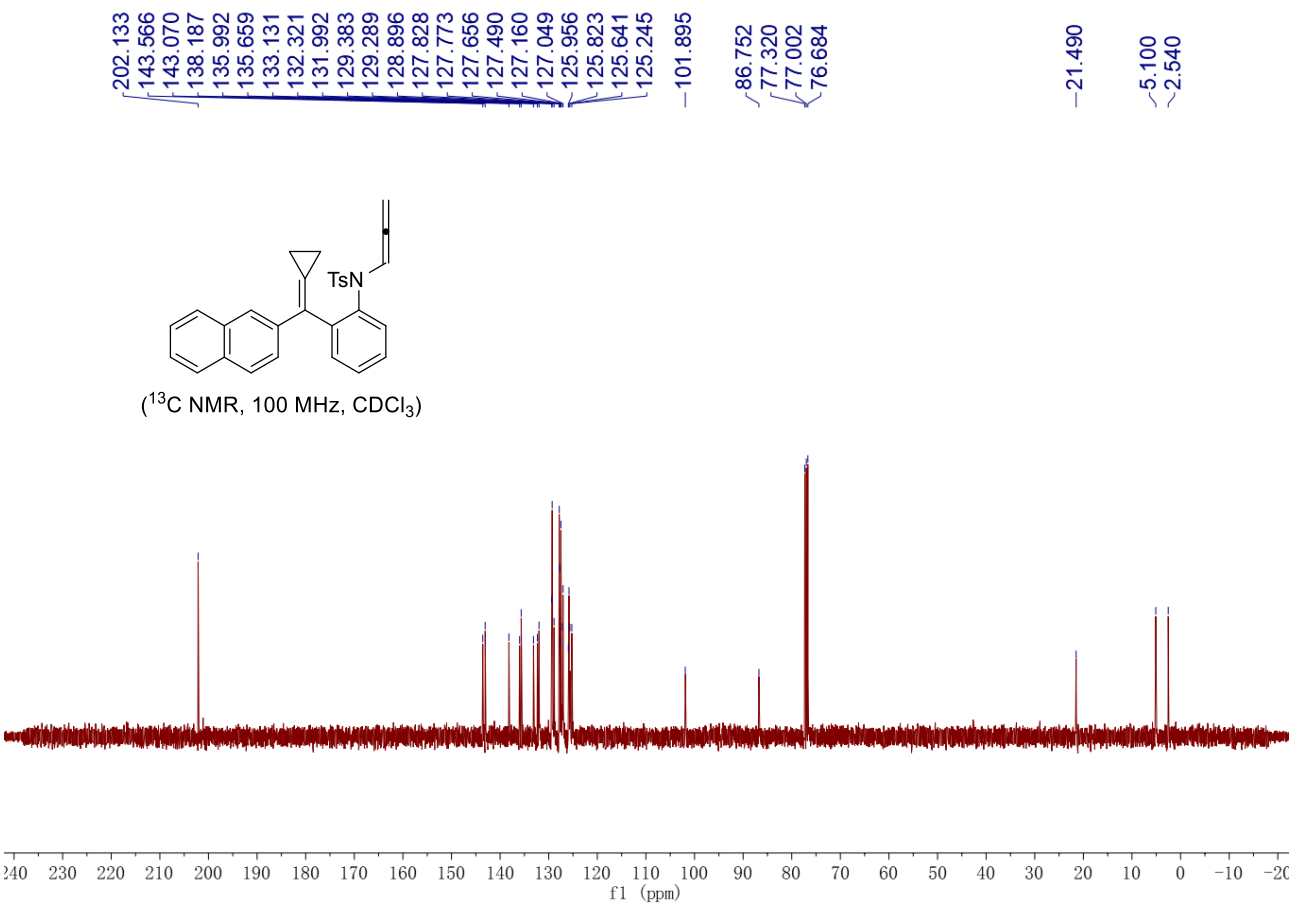


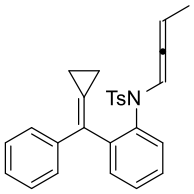
4-methyl-*N*-(2-(cyclopropylidene(naphthalen-2-yl)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1q**): Yield: 722 mg, 78%, yellow solid, m.p. 158-160 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.82 – 7.76 (m, 3H), 7.67 (d, *J* = 5.2 Hz, 1H), 7.56 – 7.46 (m, 4H), 7.46 – 7.35 (m, 3H), 7.20 (m, 3H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.33 (t, *J* = 6.1 Hz, 1H), 4.83 (d, *J* = 6.1 Hz, 2H), 2.39 (s, 3H), 1.67 – 1.55 (m, 2H), 1.37 – 1.25 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.1, 143.6, 143.1, 138.2, 136.0, 135.7, 133.1, 132.3, 132.0, 129.4, 129.3, 128.9, 127.8, 127.8, 127.7, 127.5, 127.2, 127.0, 126.0, 125.8, 125.6, 125.2, 101.9, 86.8, 21.5, 5.1, 2.5; IR (neat): ν 3044, 2968, 1592, 1490, 1432, 1358, 1167, 1141, 879, 812 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 486.14982, found: 486.15047.



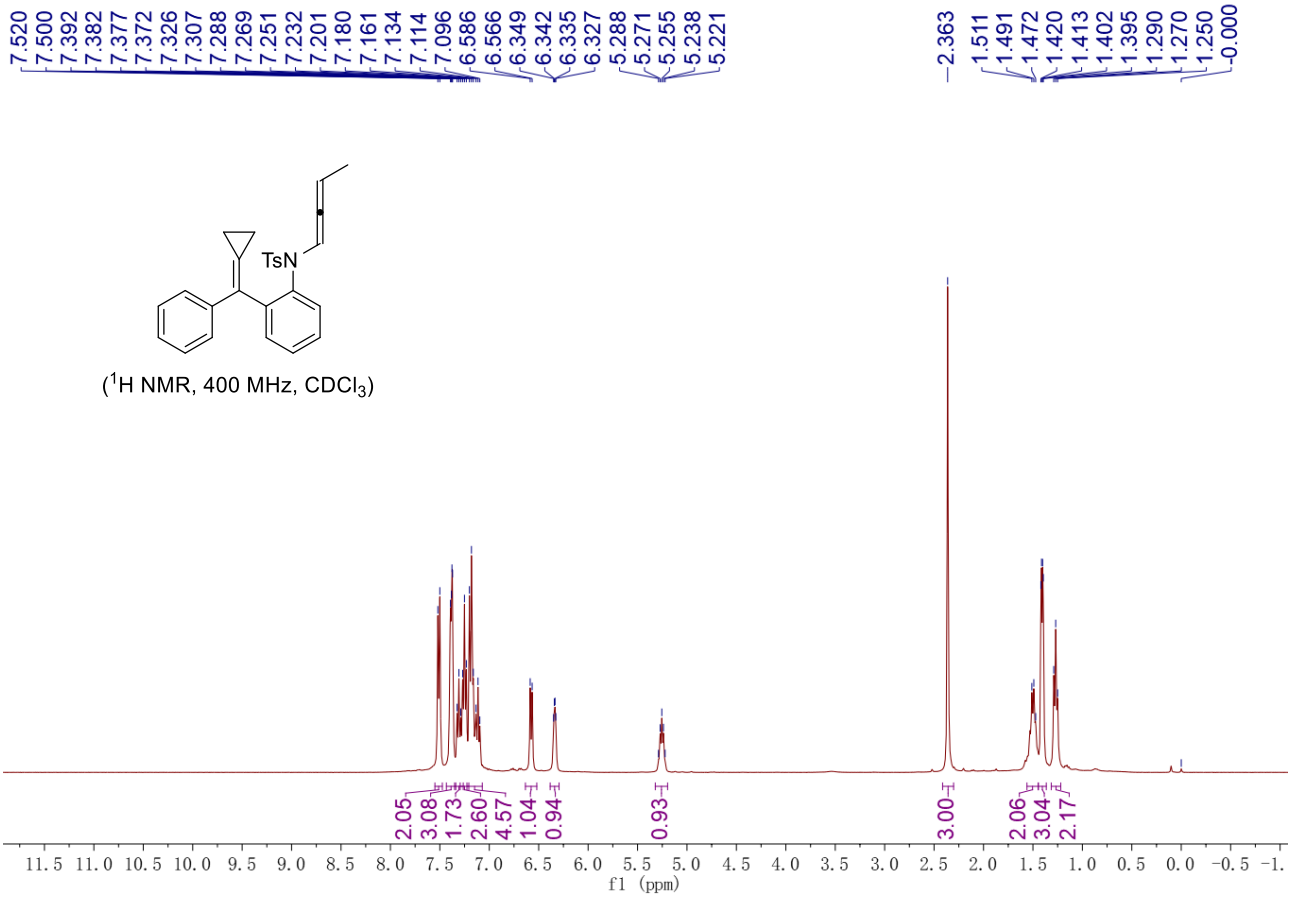
(^{1}H NMR, 400 MHz, $CDCl_3$)

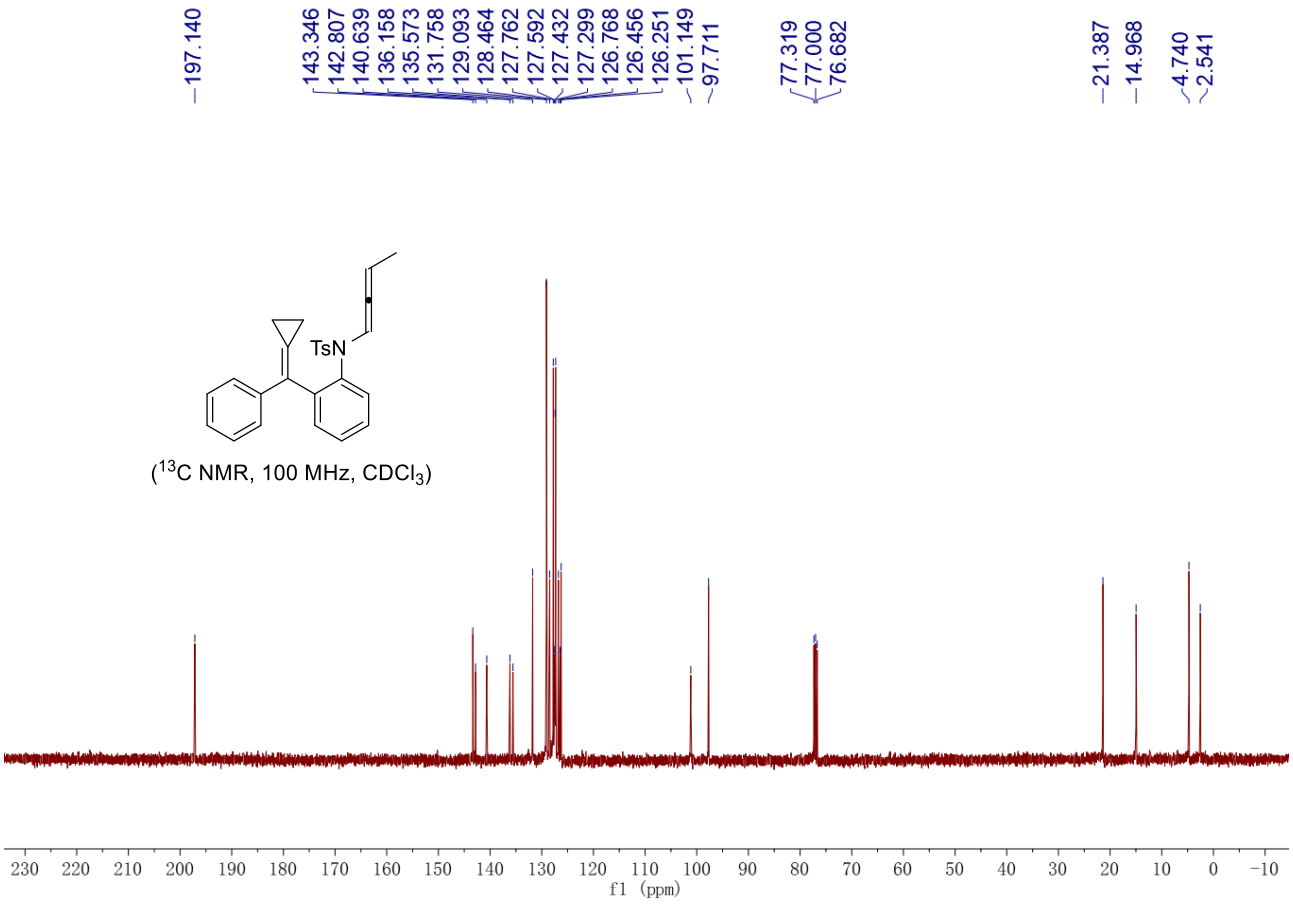


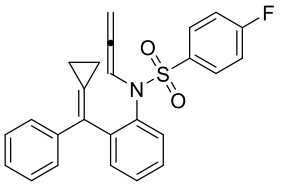

202.133
143.566
143.070
138.187
135.992
135.659
133.131
132.321
131.992
129.383
129.289
128.896
127.828
127.773
127.656
127.490
127.160
127.049
125.956
125.823
125.641
125.245
101.895
86.752
77.320
77.002
76.684
21.490
5.100
2.540
TsN
(13C NMR, 100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)



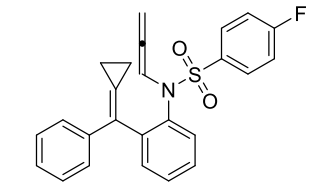
***N*-(buta-1,2-dien-1-yl)-*N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-4-methylbenzenesulfonamide** (**1u**): Yield: 615 mg, 72%, yellow solid, m.p. 137-139 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.34 (m, 3H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 2H), 7.22 – 7.08 (m, 4H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.34 (dq, J_1 = 6.4 Hz, J_2 = 2.8 Hz, 1H), 5.25 (dq, J_1 = 7.2 Hz, J_2 = 6.4 Hz, 1H), 2.36 (s, 3H), 1.56 – 1.45 (m, 2H), 1.41 (dd, J_1 = 7.2 Hz, J_2 = 2.8 Hz, 3H), 1.31 – 1.22 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 197.1, 143.3, 142.8, 140.6, 136.2, 135.6, 131.8, 129.1, 128.5, 127.8, 127.6, 127.4, 127.3, 126.8, 126.5, 126.3, 101.1, 97.7, 21.4, 15.0, 4.7, 2.5; IR (neat): ν 3047, 2972, 2917, 1597, 1495, 1443, 1353, 1166, 1030, 863, 754 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.15066.



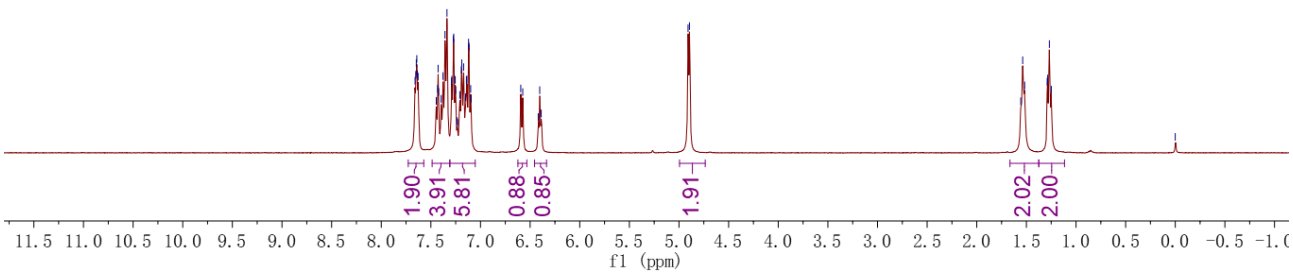

197.140
143.346
142.807
140.639
136.158
135.573
131.758
129.093
128.464
127.762
127.592
127.432
127.299
126.768
126.456
126.251
101.149
97.711
77.319
77.000
76.682
21.387
14.968
4.740
2.541
TsN
(13C NMR, 100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

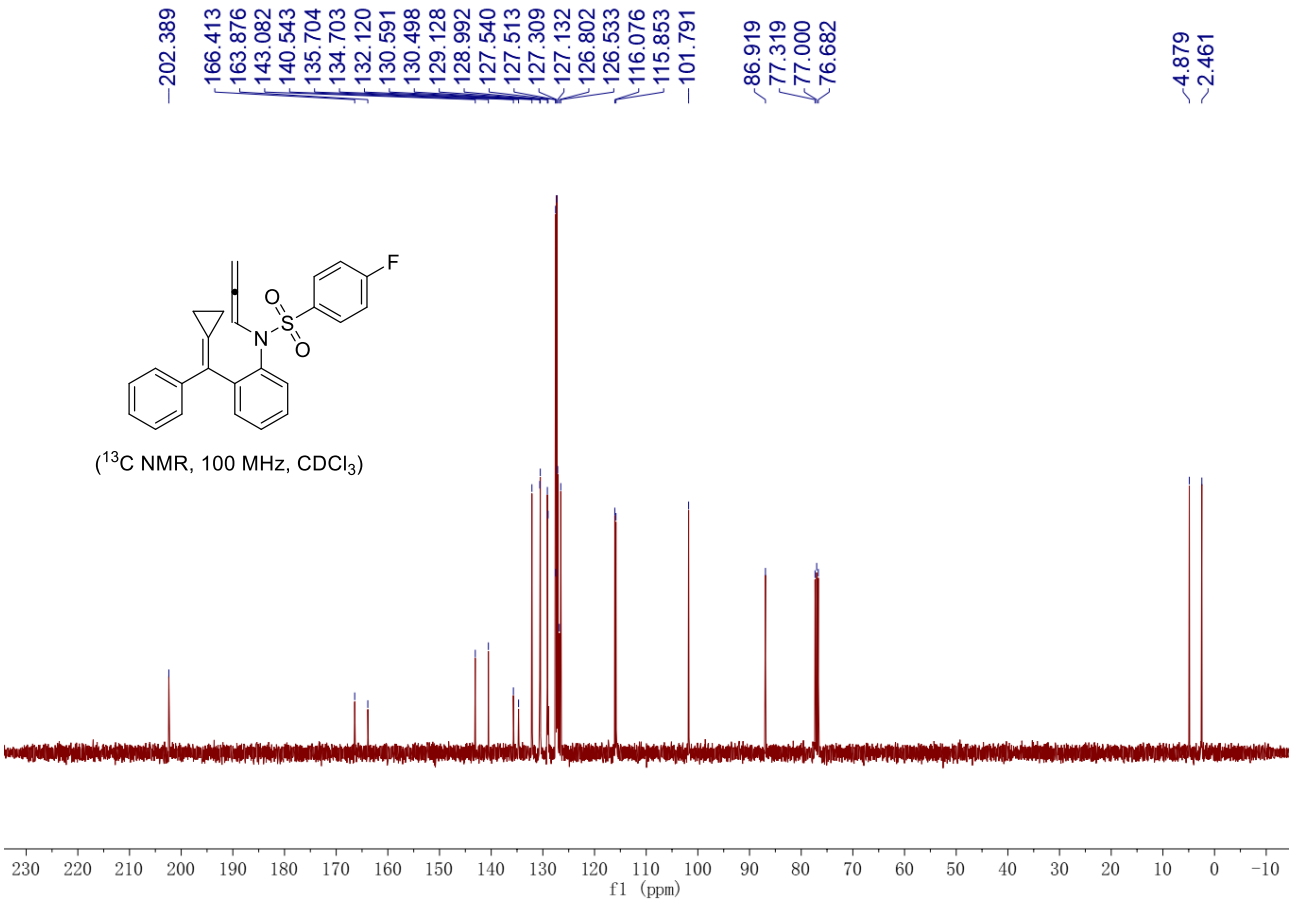


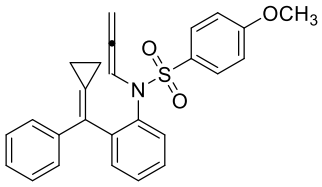
***N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-4-fluoro-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide** (**1v**): Yield: 659 mg, 79%, yellow solid, m.p. 166-168 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 – 7.57 (m, 2H), 7.49 – 7.31 (m, 4H), 7.31 – 7.05 (m, 6H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.40 (t, *J* = 6.0 Hz, 1H), 4.90 (d, *J* = 6.0 Hz, 2H), 1.67 – 1.37 (m, 2H), 1.37 – 1.12 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.4, 165.1 (d, *J* = 253.7 Hz), 143.1, 140.5, 135.7, 134.7, 132.1, 130.5 (d, *J* = 9.3 Hz), 129.1, 129.0, 127.5, 127.5, 127.3, 127.1, 126.8, 126.5, 116.0 (d, *J* = 22.3 Hz), 101.8, 86.9, 4.9, 2.5.IR (neat): ν 3076, 3052, 2964, 1589, 1494, 1440, 1359, 1170, 1162, 1022, 897, 836 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 440.10910, found: 440.10982.



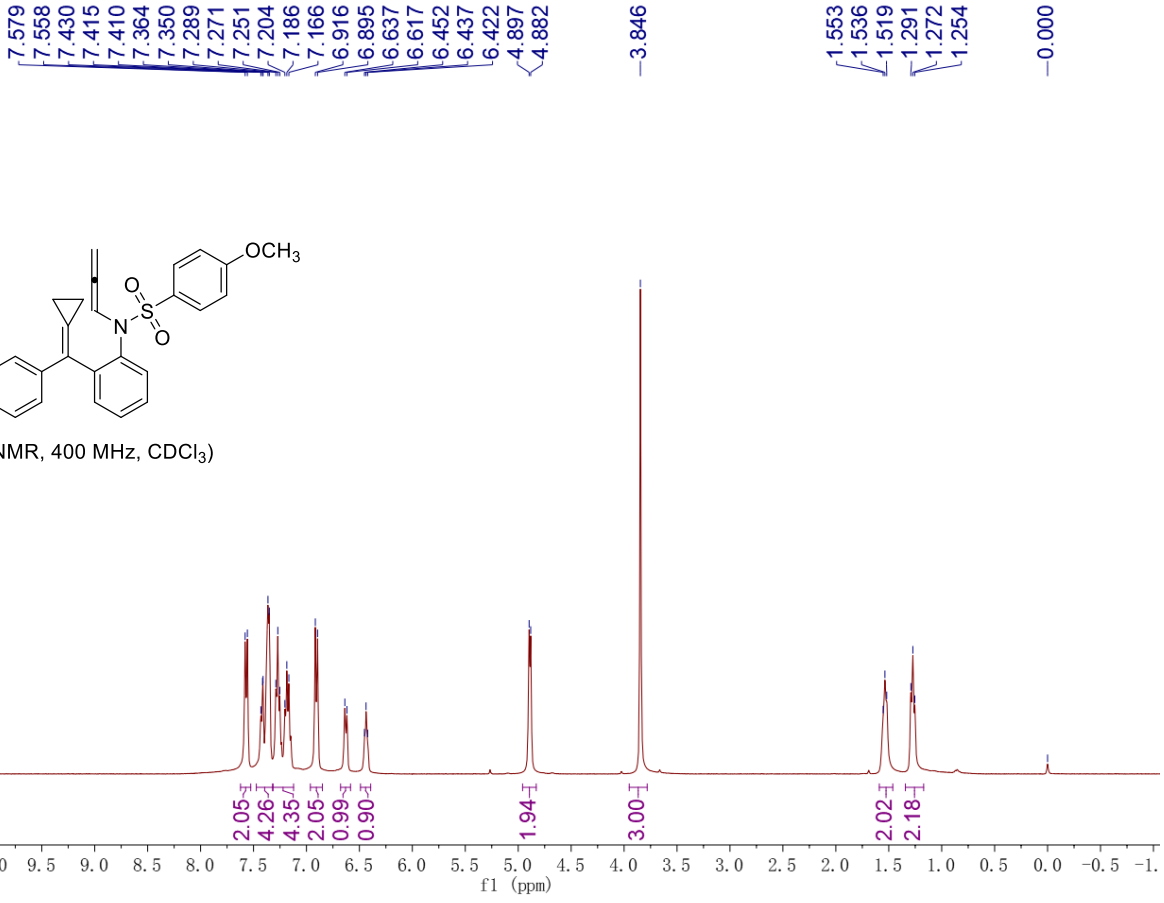
(^{1}H NMR, 400 MHz, $CDCl_3$)

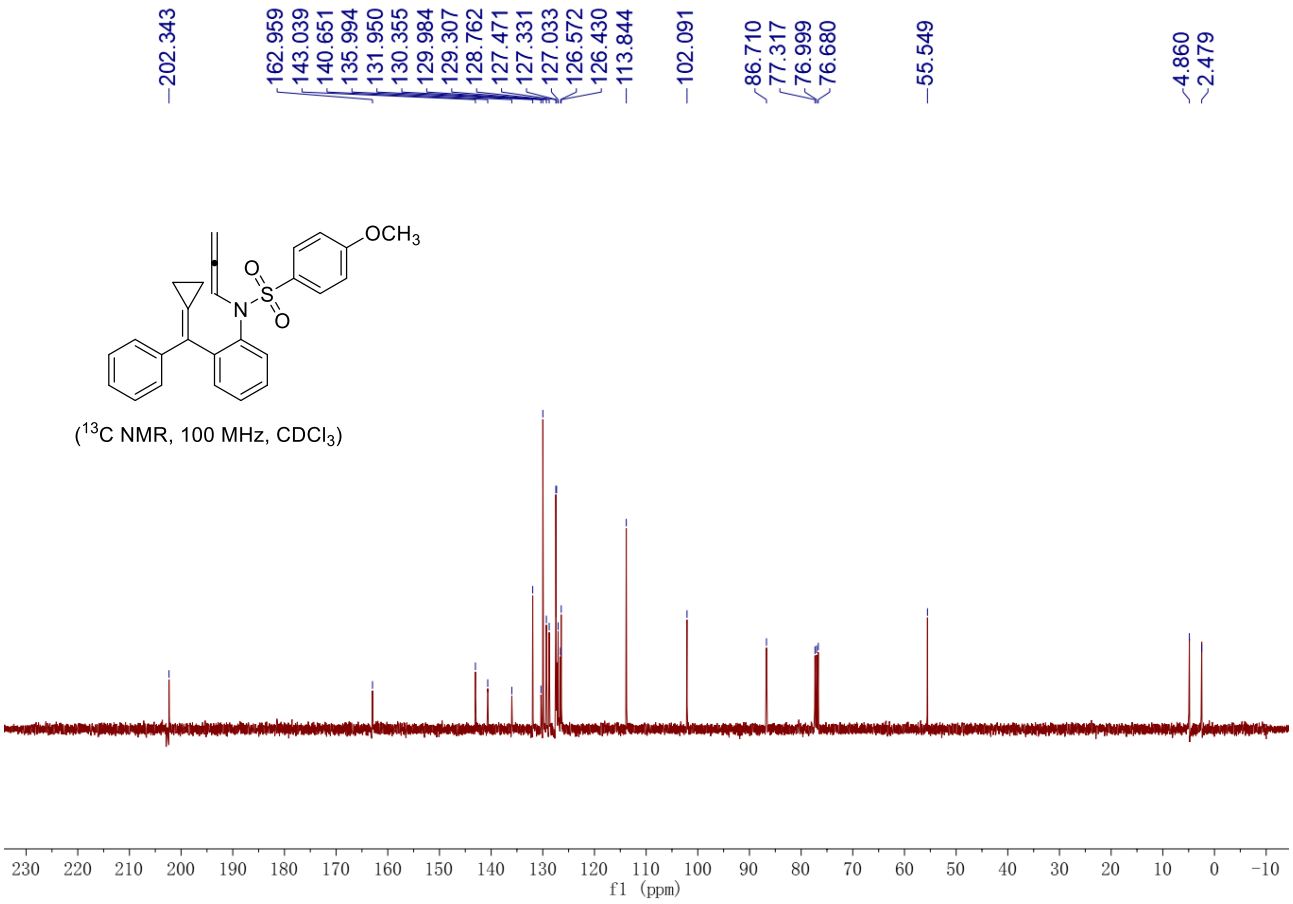


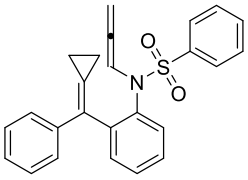

202.389
166.413
163.876
143.082
140.543
135.704
134.703
132.120
130.591
130.498
129.128
128.992
127.540
127.513
127.309
127.132
126.802
126.533
116.076
115.853
101.791
86.919
77.319
77.000
76.682
4.879
2.461
F
O
S
O
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



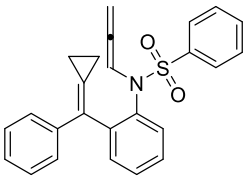
***N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-4-methoxy-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide** (**1w**): Yield: 703 mg, 82%, yellow solid, m.p. 141-143 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.32 (m, 4H), 7.32 – 7.12 (m, 4H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.44 (t, *J* = 6.0 Hz, 1H), 4.89 (d, *J* = 6.0 Hz, 2H), 3.85 (s, 3H), 1.59 – 1.46 (m, 2H), 1.29-1.25 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.3, 163.0, 143.0, 140.7, 136.0, 131.9, 130.4, 130.0, 129.3, 128.8, 127.5, 127.3, 127.0, 126.6, 126.4, 113.8, 102.1, 86.7, 55.5, 4.9, 2.5; IR (neat): ν 3045, 2974, 1589, 1497, 1361, 1262, 1153, 1092, 1027, 828, 755 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 452.12909, found: 452.12968.



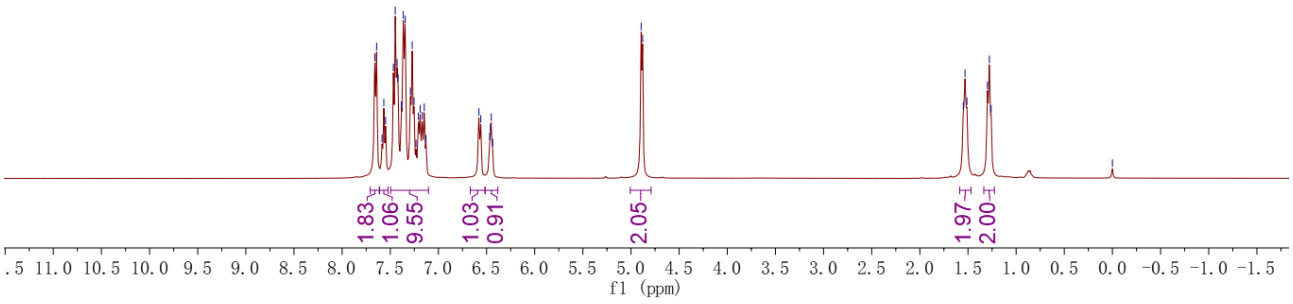

202.343
162.959
143.039
140.651
135.994
131.950
130.355
129.984
129.307
128.762
127.471
127.331
127.033
126.572
126.430
113.844
102.091
86.710
77.317
76.999
76.680
55.549
4.860
2.479
OCH3
O
S
O
N
(13C NMR, 100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

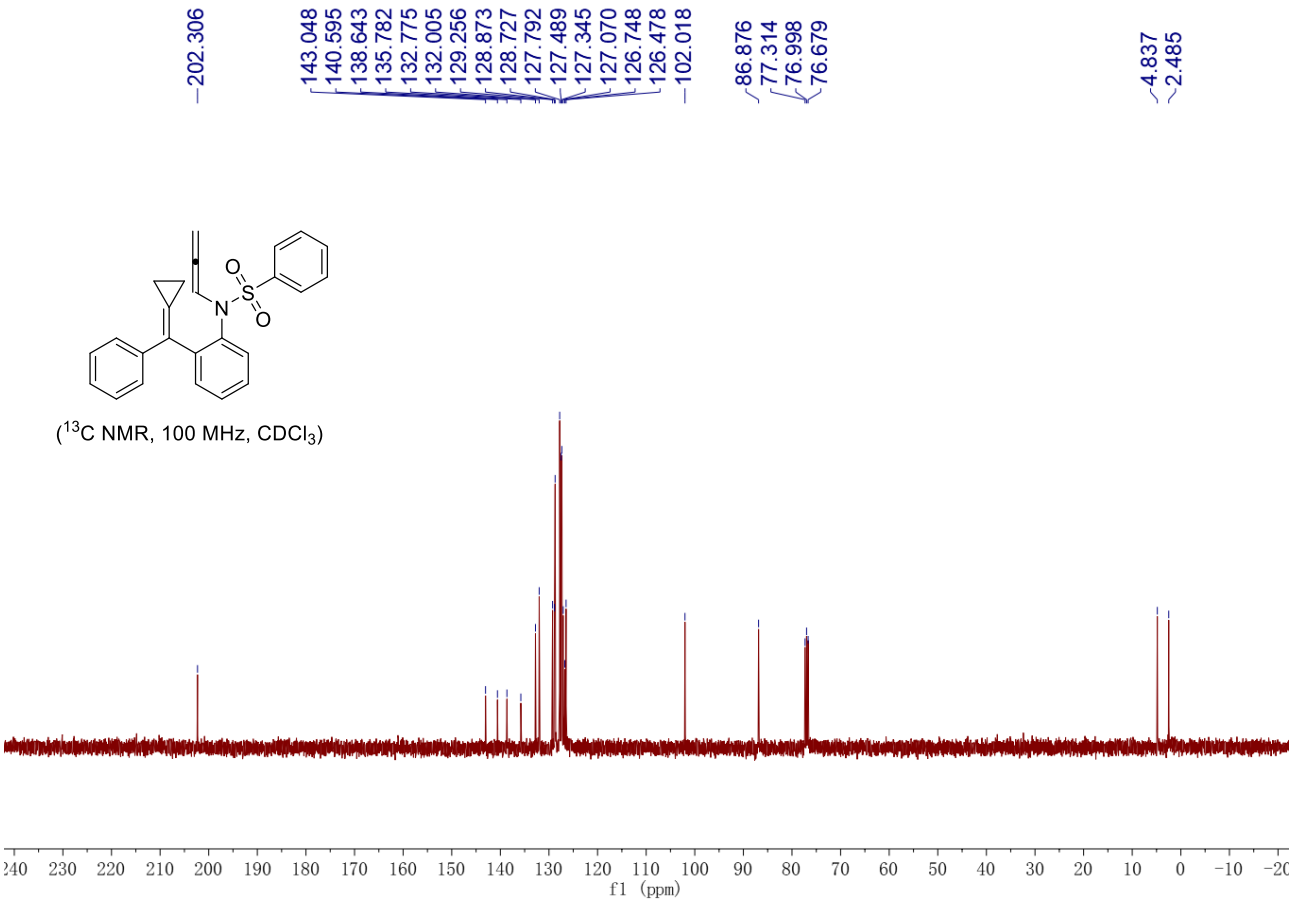


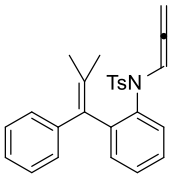
***N*-(2-(cyclopropylidene(phenyl)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide** (**1x**): Yield: 614 mg, 77%, yellow solid, m.p. 149-151 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.50 – 7.10 (m, 10H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.52 – 6.38 (m, 1H), 4.89 (d, *J* = 6.0 Hz, 2H), 1.59 – 1.47 (m, 2H), 1.34 – 1.23 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.3, 143.0, 140.6, 138.6, 135.8, 132.8, 132.0, 129.3, 128.9, 128.7, 127.8, 127.5, 127.3, 127.1, 126.7, 126.5, 102.0, 86.9, 4.8, 2.5; IR (neat): ν 3050, 3026, 2969, 1599, 1490, 1440, 1355, 1343, 1169, 1091, 1023, 941, 894, 753 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 422.11852, found: 422.11798.



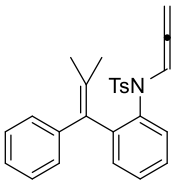
(^{1}H NMR, 400 MHz, $CDCl_3$)



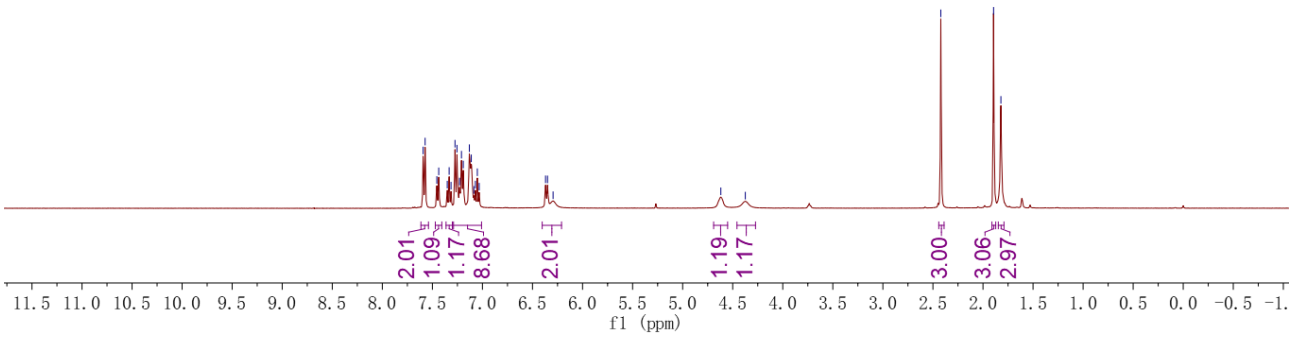

202.306
143.048
140.595
138.643
135.782
132.775
132.005
129.256
128.873
128.727
127.792
127.489
127.345
127.070
126.748
126.478
102.018
86.876
77.314
76.998
76.679
4.837
2.485
O
S
O
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

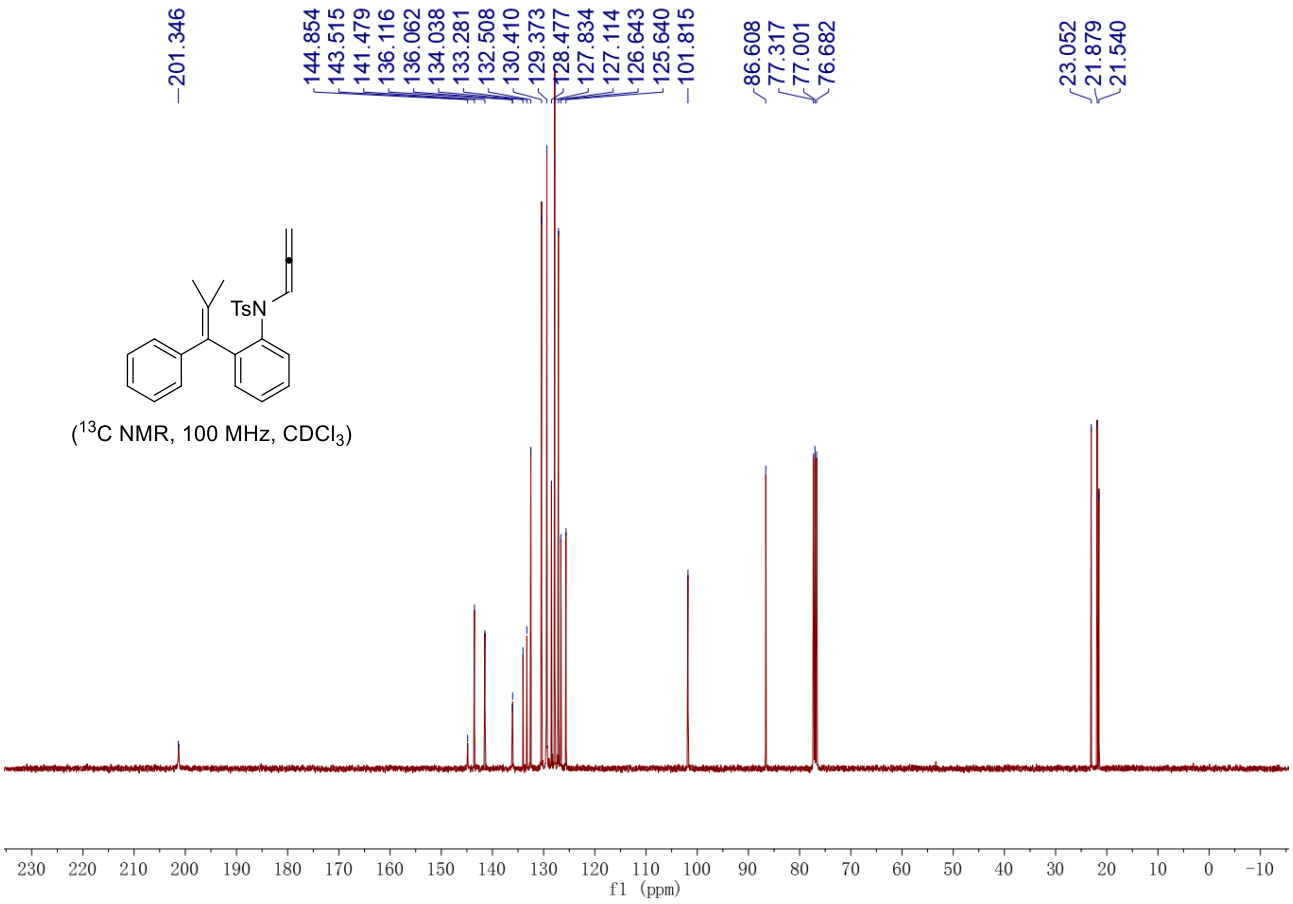


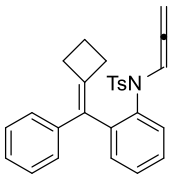
4-methyl-*N*-(2-(2-methyl-1-phenylprop-1-en-1-yl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1y**): Yield: 689 mg, 83%, yellow solid, m.p. 154-156 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.01 (m, 9H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.29 (s, 1H), 4.62 (s, 1H), 4.37 (s, 1H), 2.42 (s, 3H), 1.89 (s, 3H), 1.82 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 201.3, 144.9, 143.5, 141.5, 136.1, 136.1, 134.0, 133.3, 132.5, 130.4, 129.4, 128.5, 127.8, 127.1, 126.6, 125.6, 101.8, 86.6, 23.1, 21.9, 21.5; IR (neat): ν 3045, 2985, 2906, 1435, 1347, 1164, 1088, 1020, 963, 813 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 438.14982, found: 438.14968.



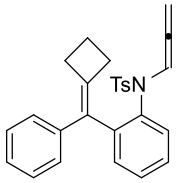
(^{1}H NMR, 400 MHz, $CDCl_3$)



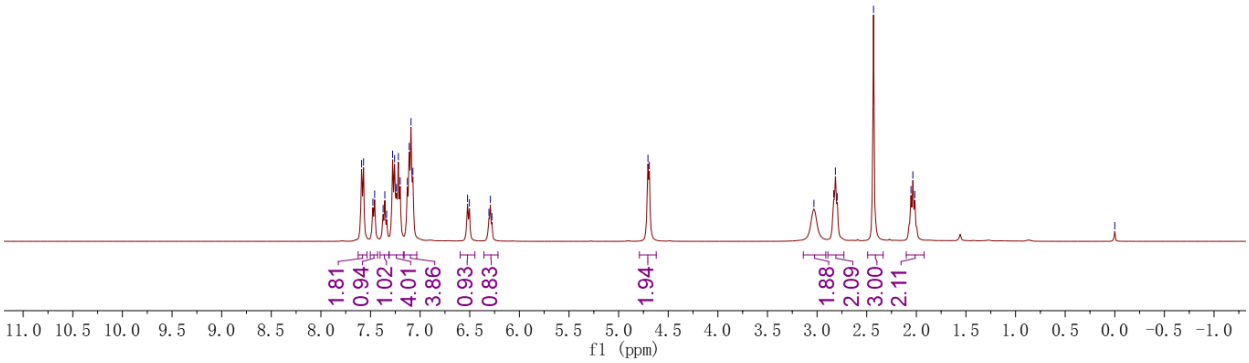

201.346
144.854
143.515
141.479
136.116
136.062
134.038
133.281
132.508
130.410
129.373
128.477
127.834
127.114
126.643
125.640
101.815
86.608
77.317
77.001
76.682
23.052
21.879
21.540
TsN
(13C NMR, 100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

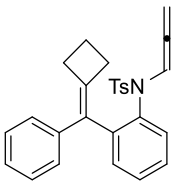


4-methyl-*N*-(2-(cyclobutylidene(phenyl)methyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1z**): Yield: 683 mg, 80%, yellow solid, m.p. 178-180 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.31 – 7.17 (m, 4H), 7.16 – 7.03 (m, 4H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.29 (t, *J* = 6.0 Hz, 1H), 4.70 (d, *J* = 6.0 Hz, 2H), 3.14 – 2.91 (m, 2H), 2.89 – 2.73 (m, 2H), 2.43 (s, 3H), 2.10 – 1.92 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.0, 143.5, 143.1, 142.0, 139.9, 136.1, 136.0, 132.2, 130.3, 129.5, 129.4, 128.7, 128.1, 127.8, 127.3, 126.9, 125.7, 101.7, 86.6, 31.9, 31.2, 21.5, 17.1; IR (neat): ν 3068, 2985, 2909, 1597, 1474, 1443, 1346, 1158, 1088, 899, 771 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14582, found: 450.15053.

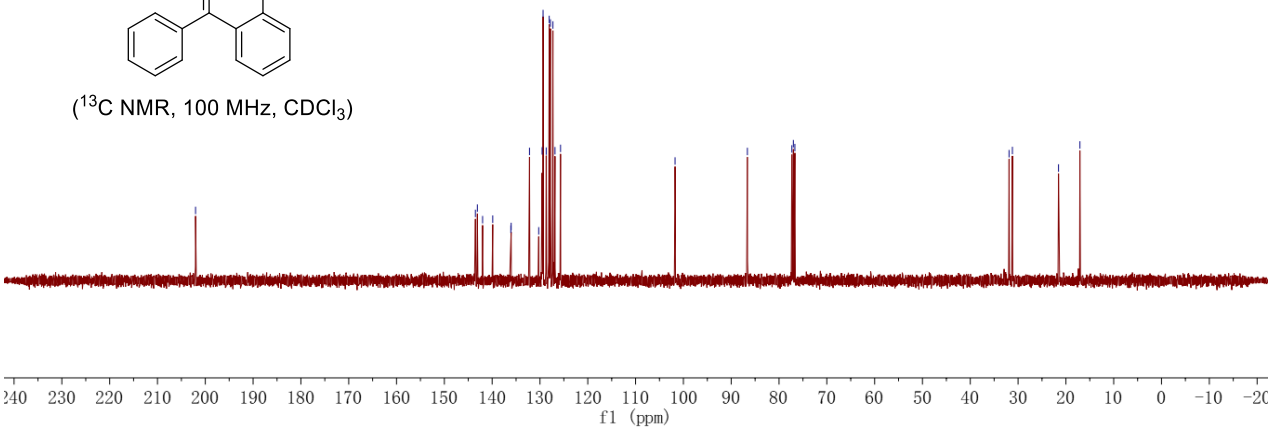


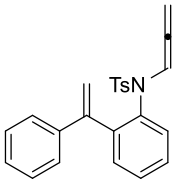
(^{1}H NMR, 400 MHz, $CDCl_3$)



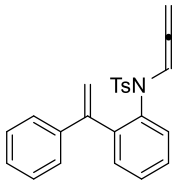


(^{13}C NMR, 100 MHz, $CDCl_3$)

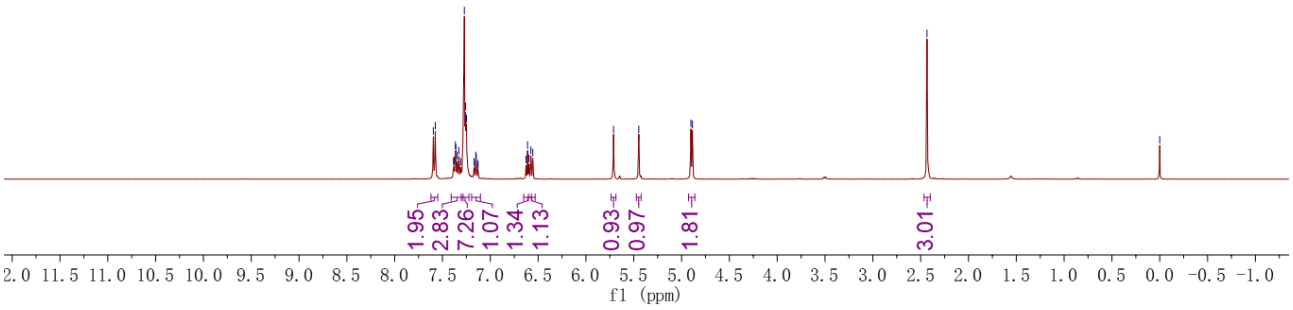


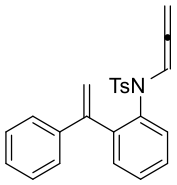


4-methyl-*N*-(2-(1-phenylvinyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1aa**): Yield: 642 mg, 83%, yellow solid, m.p. 144-146 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 (d, J = 8.4 Hz, 2H), 7.41 – 7.30 (m, 2H), 7.30 – 7.22 (m, 7H), 7.15 (td, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 6.61 (t, J = 6.0 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 5.71 (s, 1H), 5.45 (s, 1H), 4.89 (d, J = 6.0 Hz, 2H), 2.43 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.1, 146.7, 143.7, 143.5, 141.3, 135.9, 135.6, 131.6, 129.5, 129.4, 128.8, 127.9, 127.7, 127.5, 127.5, 127.4, 117.1, 102.6, 87.0, 21.6; IR (neat): ν 3055, 2969, 1589, 1440, 1359, 1168, 1088, 1025, 959, 871, 770 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 410.11852, found: 410.11906.

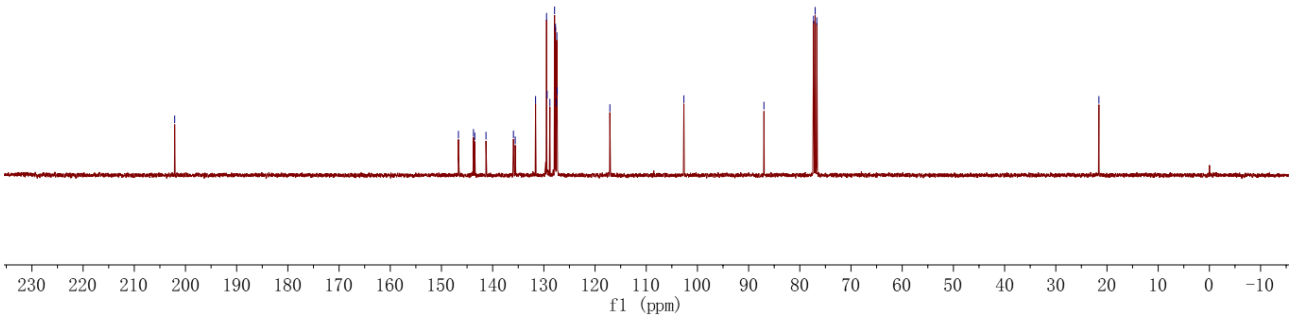


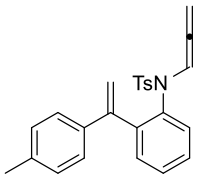
(^{1}H NMR, 400 MHz, $CDCl_3$)



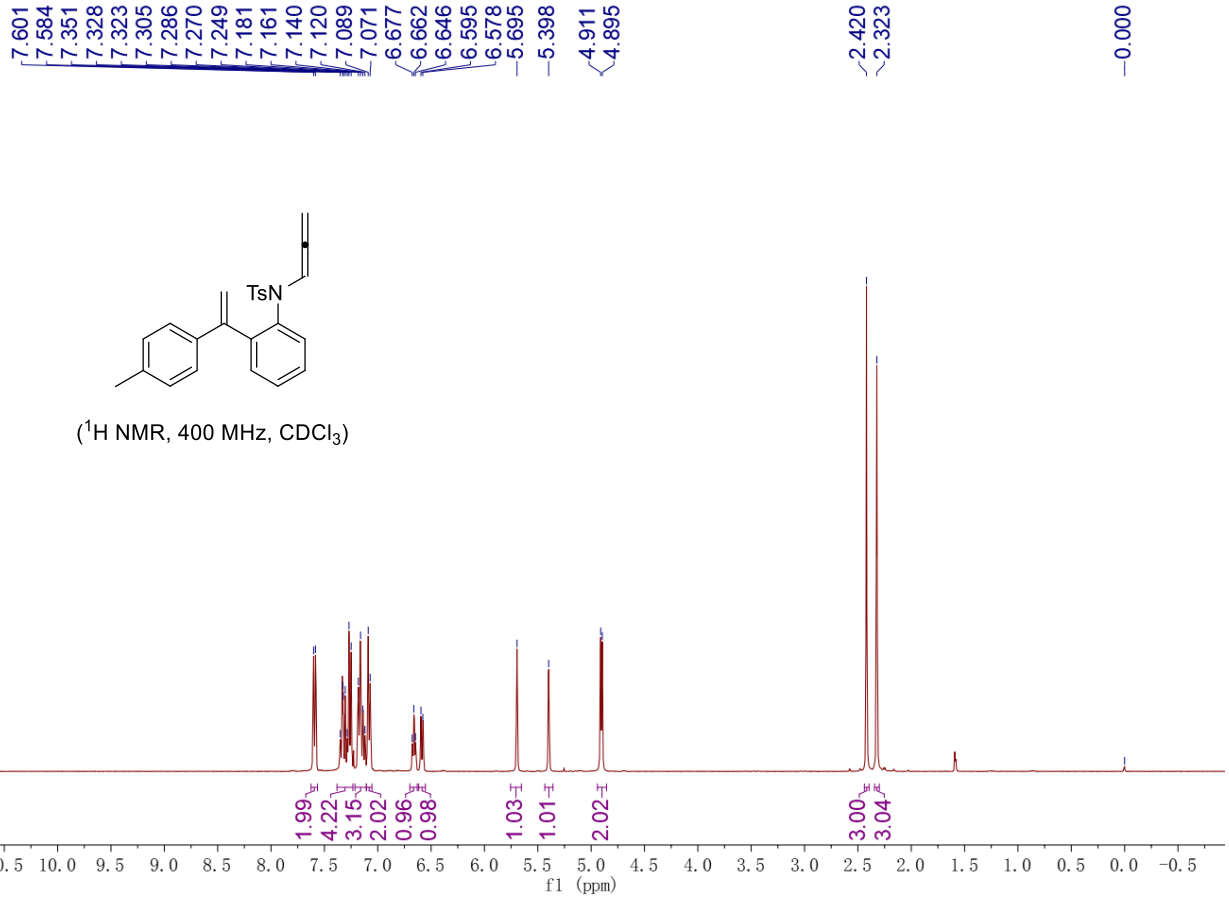


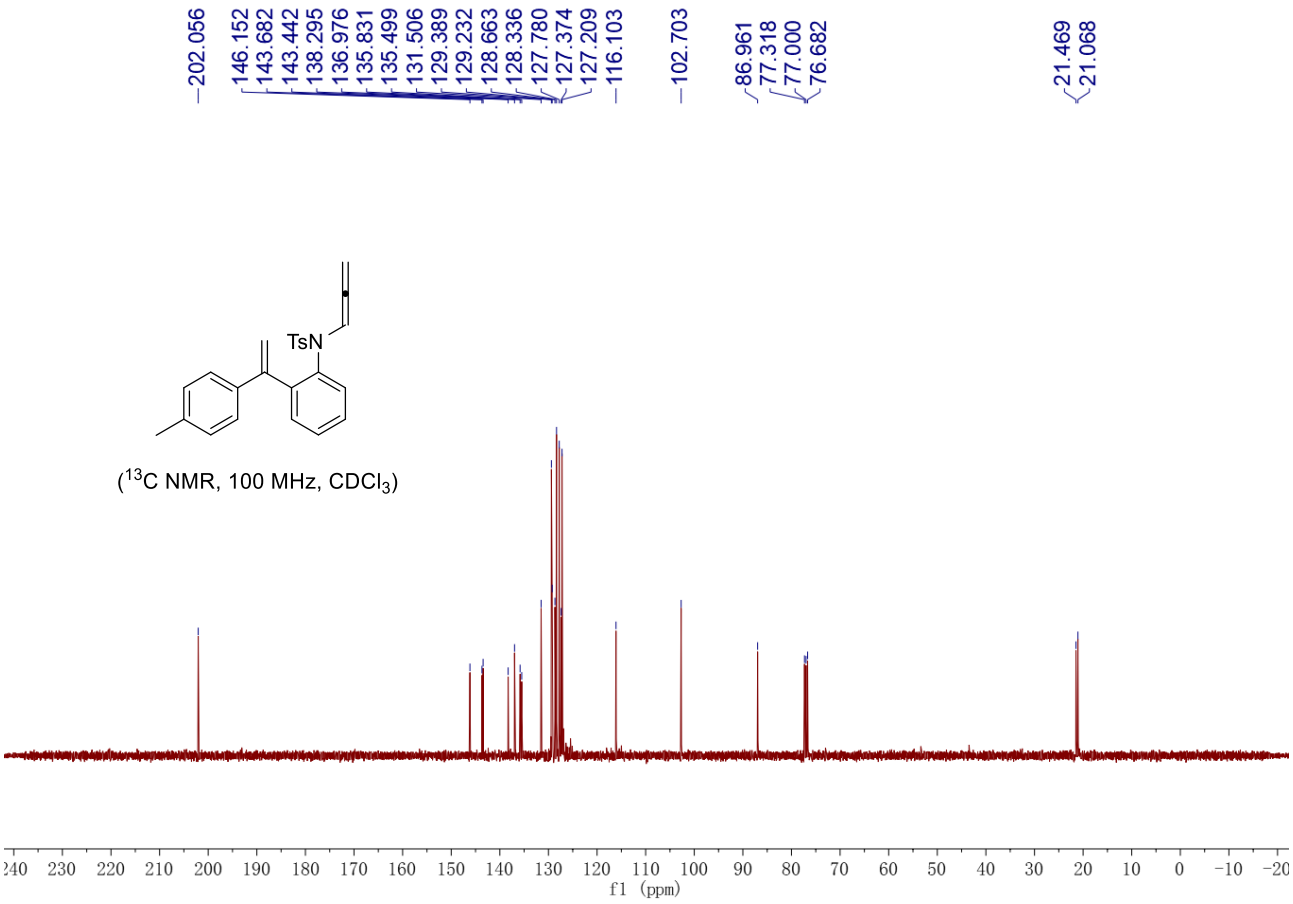
(^{13}C NMR, 100 MHz, $CDCl_3$)

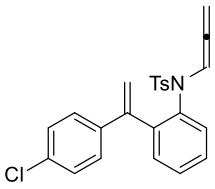




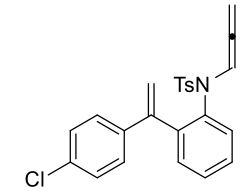
4-methyl-*N*-(2-(1-(p-tolyl)vinyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1ab**): Yield: 674 mg, 84%, yellow solid, m.p. 157-159 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 (d, *J* = 6.8 Hz, 2H), 7.38 – 7.23 (m, 4H), 7.21 – 7.11 (m, 3H), 7.08 (d, *J* = 7.2 Hz, 2H), 6.66 (t, *J* = 6.1 Hz, 1H), 6.59 (d, *J* = 6.8 Hz, 1H), 5.69 (s, 1H), 5.40 (s, 1H), 4.90 (d, *J* = 6.1 Hz, 2H), 2.42 (s, 3H), 2.32 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 202.1, 146.2, 143.7, 143.4, 138.3, 137.0, 135.8, 135.5, 131.5, 129.4, 129.2, 128.7, 128.3, 127.8, 127.4, 127.2, 116.1, 102.7, 87.0, 21.5, 21.1; IR (neat): ν 3018, 2950, 2921, 1600, 1508, 1456, 1351, 1164, 1089, 1061, 936, 810, 733 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 424.13417, found: 424.13515.



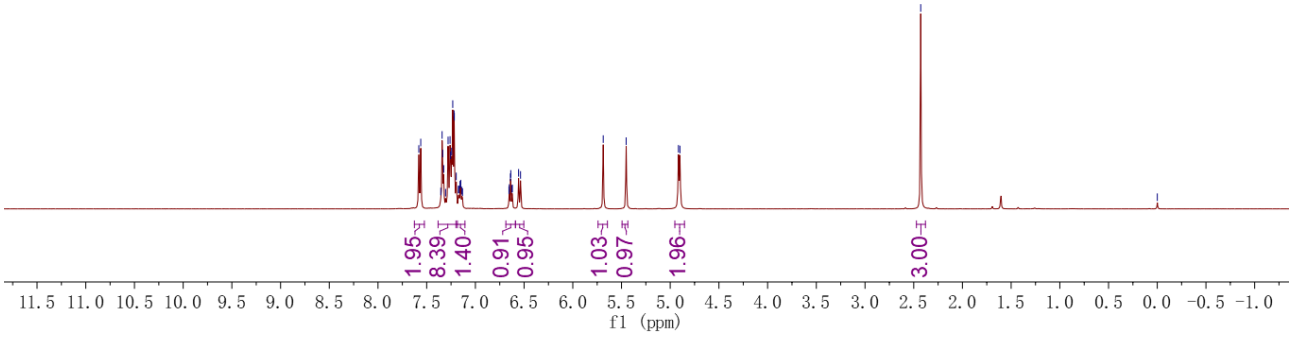

202.056
146.152
143.682
143.442
138.295
136.976
135.831
135.499
131.506
129.389
129.232
128.663
128.336
127.780
127.374
127.209
116.103
102.703
86.961
77.318
77.000
76.682
21.469
21.068
TsN
(13C NMR, 100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

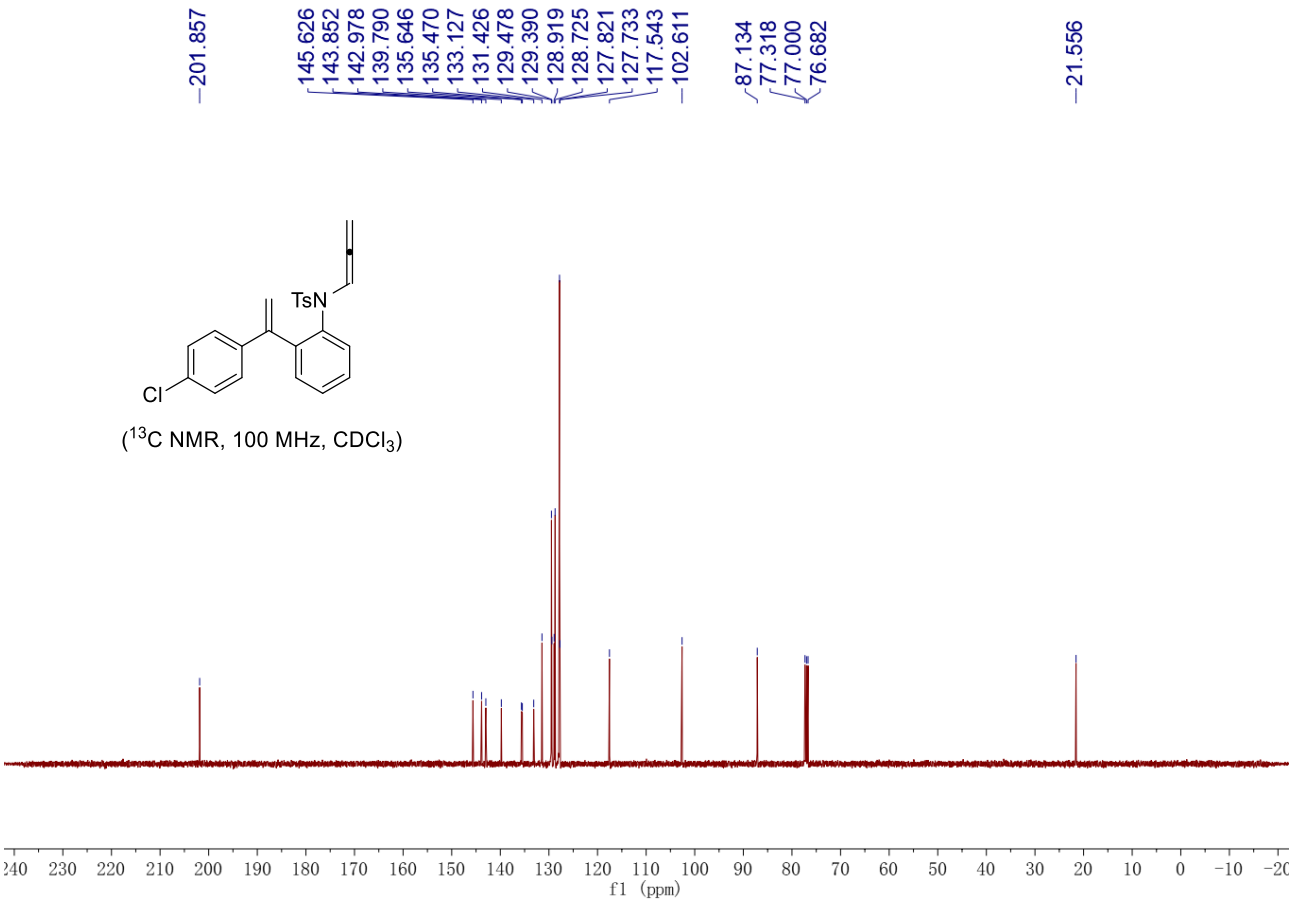


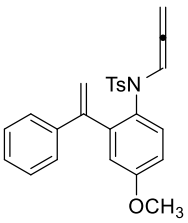
4-methyl-*N*-(2-(1-(4-chlorophenyl)vinyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1ac**): Yield: 657 mg, 78%, yellow solid, m.p. 135-137 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.57 (d, J = 8.0 Hz, 2H), 7.38 – 7.18 (m, 8H), 7.15 (td, J_1 = 7.2 Hz, J_2 = 2.8 Hz, 1H), 6.64 (td, J_1 = 6.4 Hz, J_2 = 1.2 Hz, 1H), 6.55 (d, J = 8.0 Hz, 1H), 5.69 (s, 1H), 5.45 (s, 1H), 4.91 (d, J = 6.4 Hz, 2H), 2.43 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 201.9, 145.6, 143.9, 143.0, 139.8, 135.6, 135.5, 133.1, 131.4, 129.5, 129.4, 128.9, 128.7, 127.8, 127.7, 117.5, 102.6, 87.1, 21.6; IR (neat): ν3071, 2966, 1610, 1597, 1487, 1437, 1361, 1165, 1091, 960, 834, 767 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 444.07955, found: 444.07917.



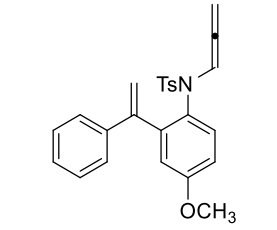
(^{1}H NMR, 400 MHz, $CDCl_3$)



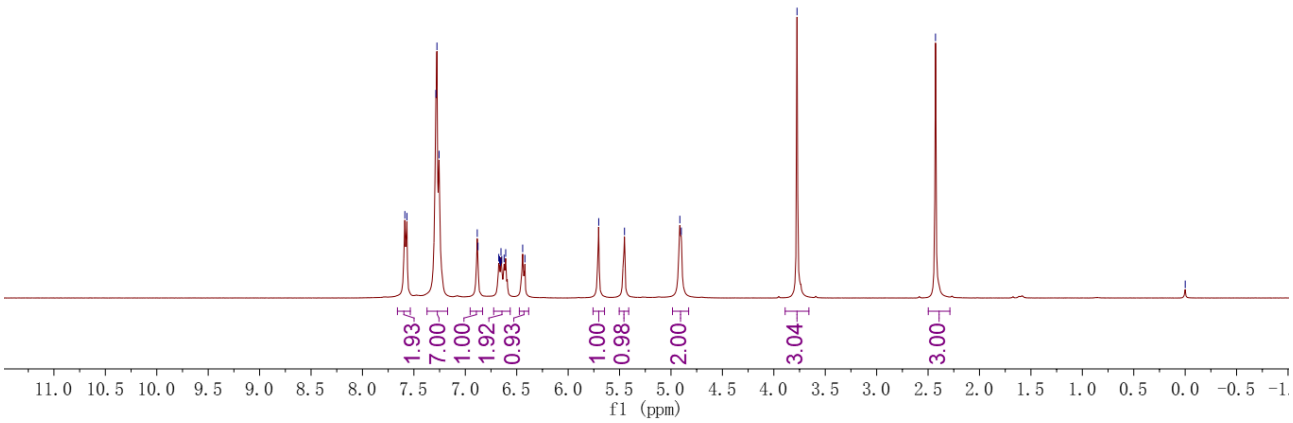

201.857
145.626
143.852
142.978
139.790
135.646
135.470
133.127
131.426
129.478
129.390
128.919
128.725
127.821
127.733
117.543
102.611
87.134
77.318
77.000
76.682
21.556
TsN
Cl
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

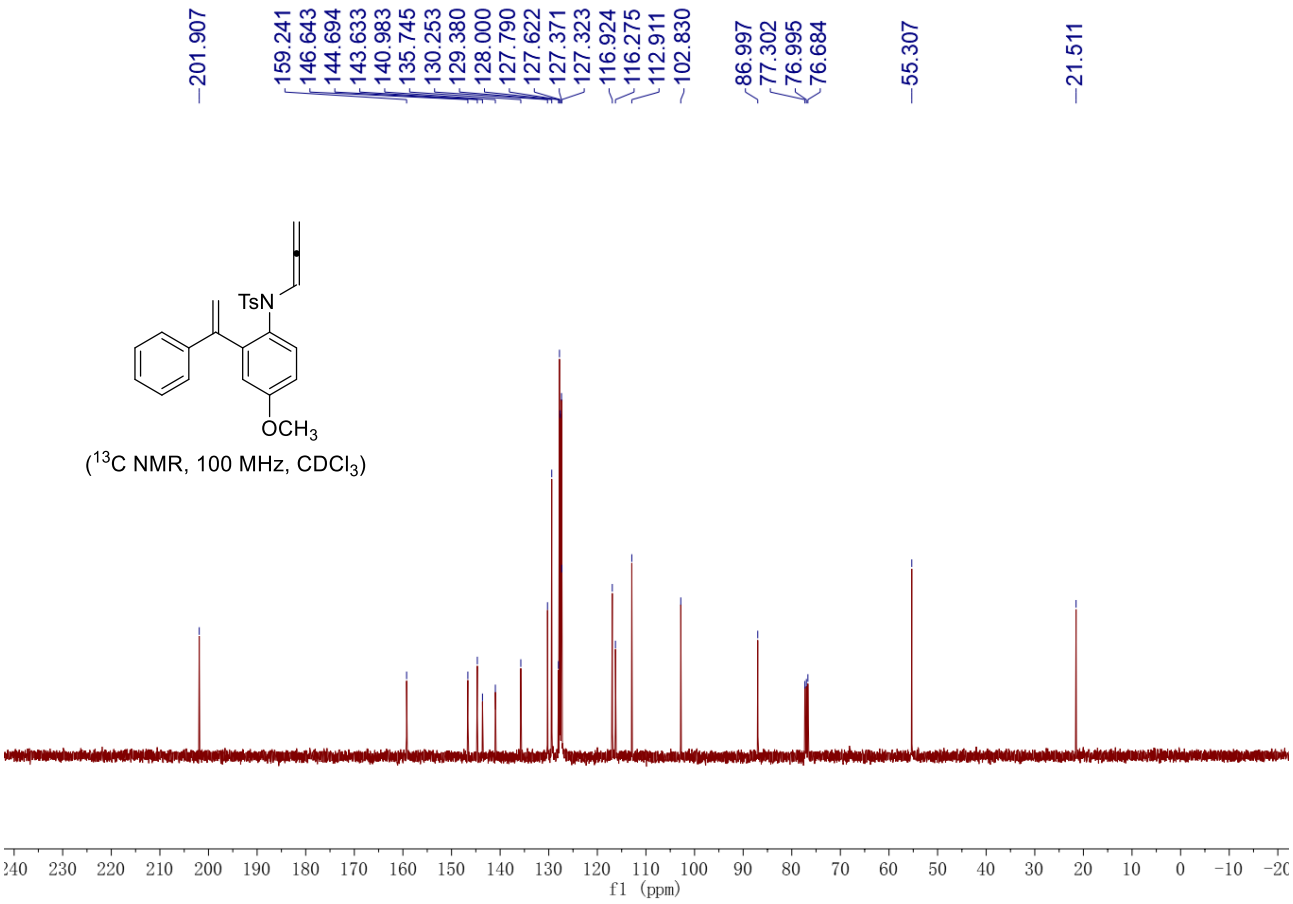


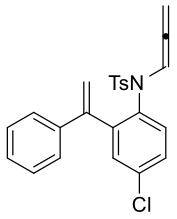
4-methyl-*N*-(4-methoxy-2-(1-phenylvinyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1ad**): Yield: 676 mg, 81%, yellow solid, m.p. 159-161 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.17 (m, 7H), 6.88 (d, *J* = 3.2 Hz, 1H), 6.72 – 6.56 (m, 2H), 6.43 (d, *J* = 8.8 Hz, 1H), 5.70 (s, 1H), 5.45 (s, 1H), 4.91 (d, *J* = 6.0 Hz, 2H), 3.77 (s, 3H), 2.43 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 201.9, 159.2, 146.6, 144.7, 143.6, 141.0, 135.7, 130.3, 129.4, 128.0, 127.8, 127.6, 127.4, 127.3, 116.9, 116.3, 112.9, 102.8, 87.0, 55.3, 21.5; IR (neat): ν 3079, 3032, 2956, 1594, 1484, 1358, 1234, 1168, 1041, 941, 895, 702 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 440.12909, found: 440.12907.



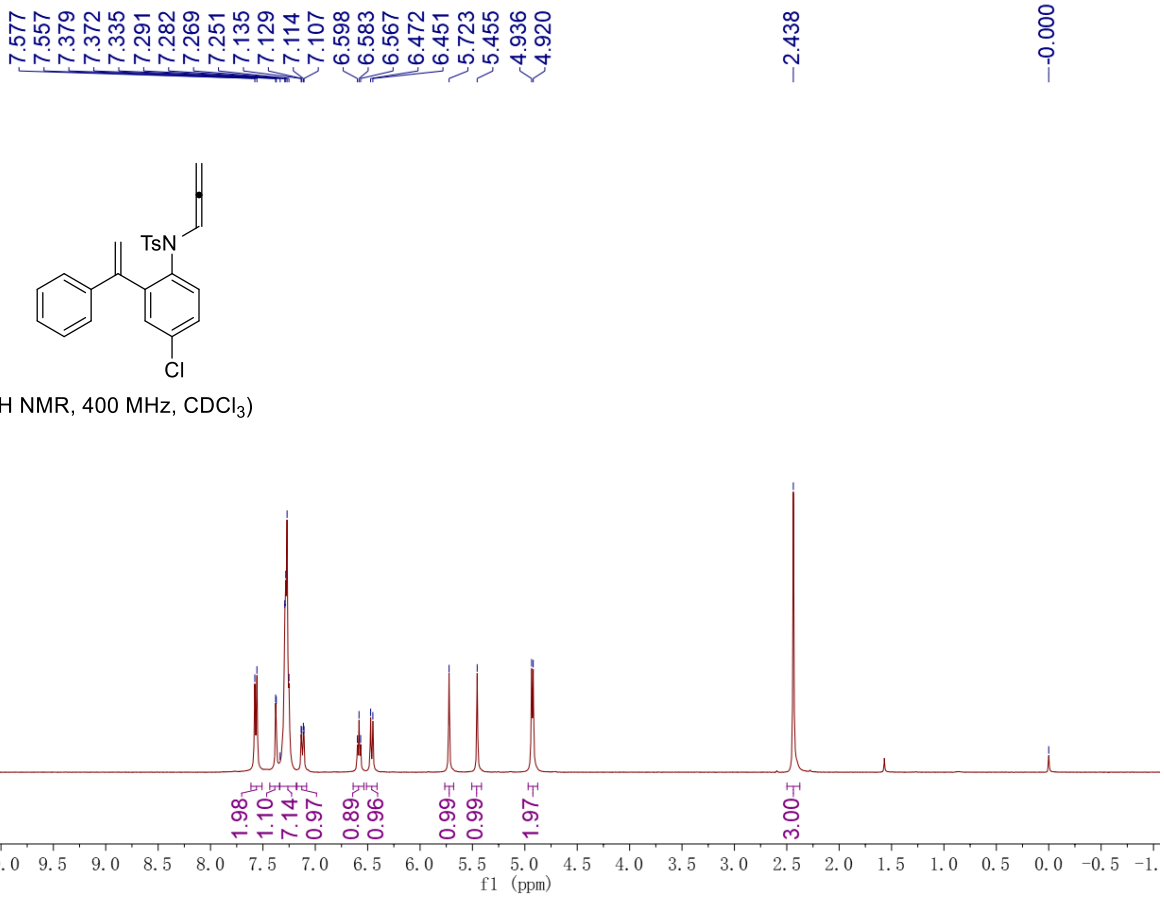
(^{1}H NMR, 400 MHz, $CDCl_3$)

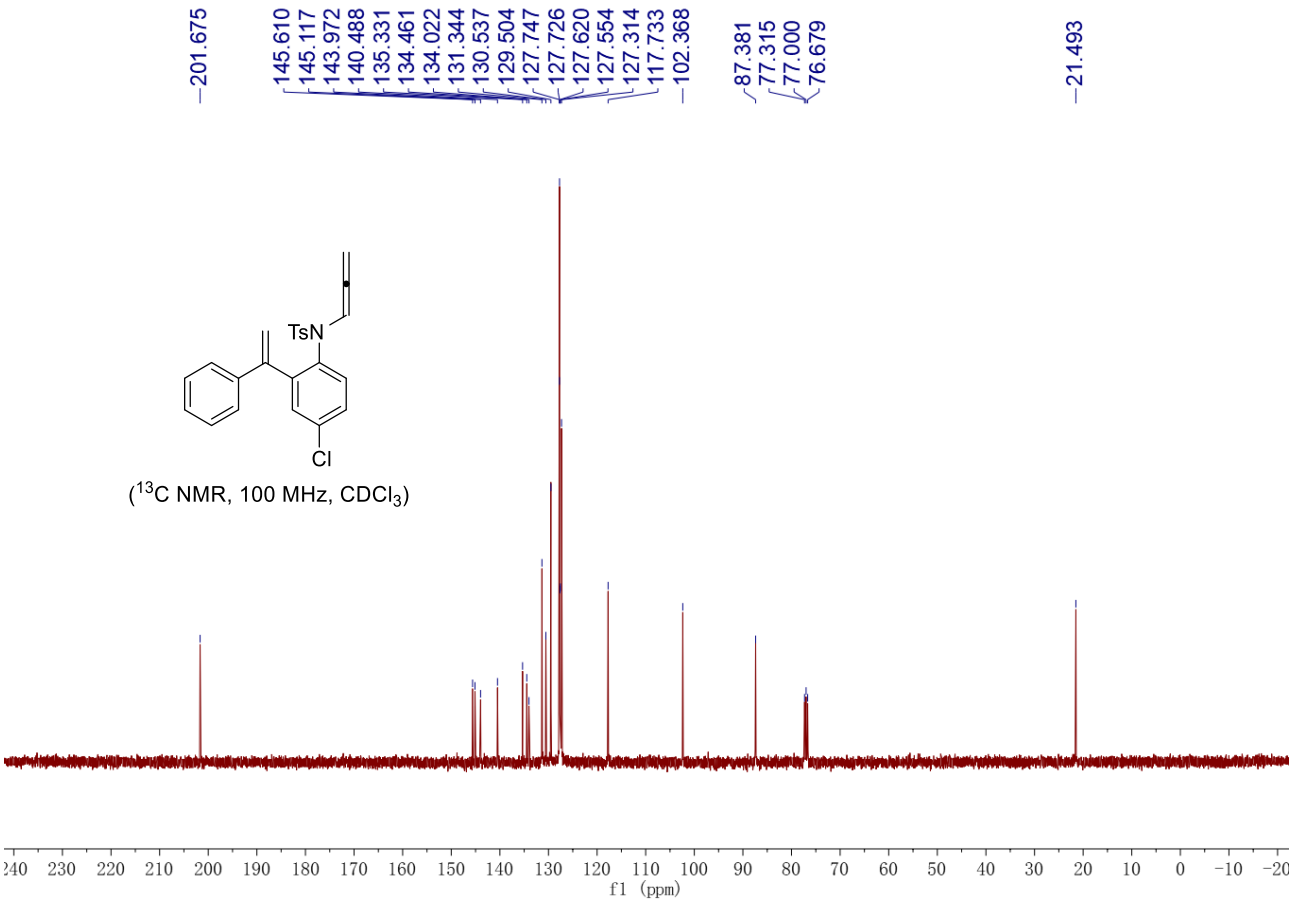


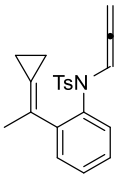

201.907
159.241
146.643
144.694
143.633
140.983
135.745
130.253
129.380
128.000
127.790
127.622
127.371
127.323
116.924
116.275
112.911
102.830
86.997
77.302
76.995
76.684
55.307
21.511
TsN
OCH3
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)



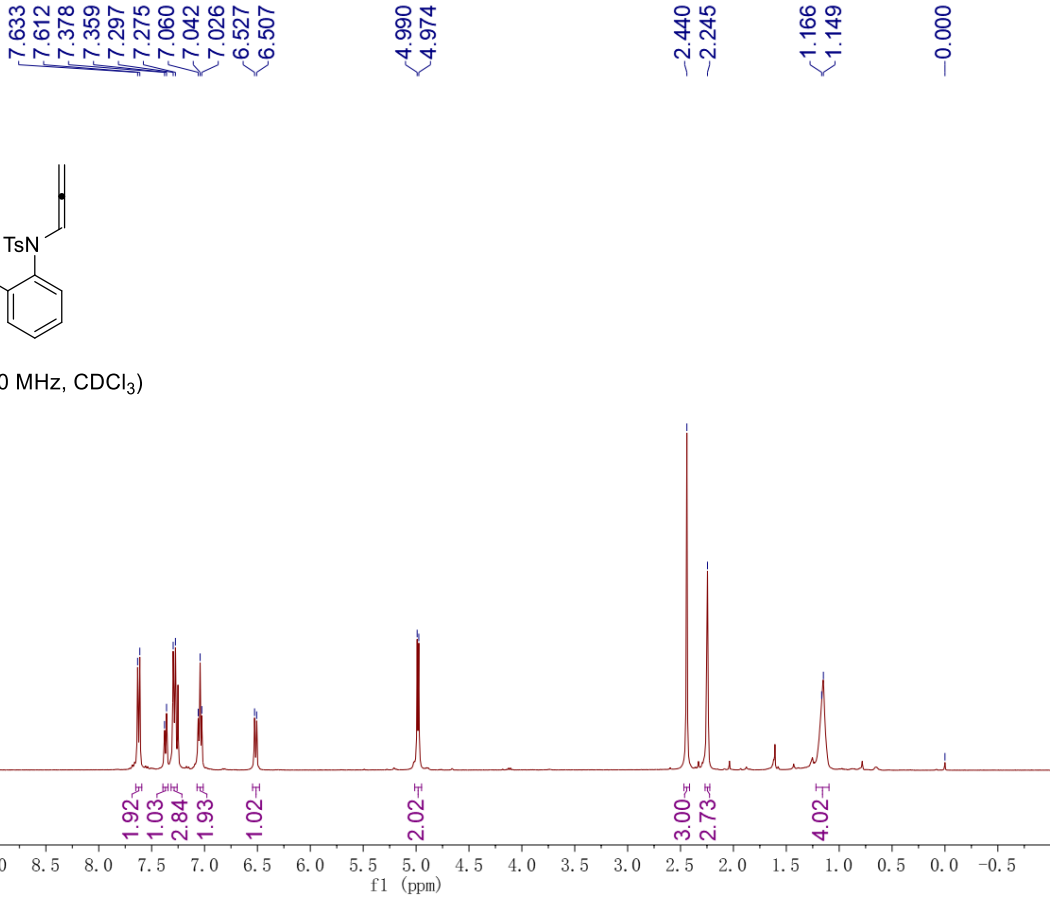
4-methyl-*N*-(4-chloro-2-(1-phenylvinyl)phenyl)-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1ae**): Yield: 632 mg, 75%, yellow solid, m.p. 154-156 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.34 – 7.18 (m, 7H), 7.12 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.58 (t, *J* = 6.0 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 1H), 5.72 (s, 1H), 5.45 (s, 1H), 4.93 (d, *J* = 6.0 Hz, 2H), 2.44 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 201.7, 145.6, 145.1, 144.0, 140.5, 135.3, 134.5, 134.0, 131.3, 130.5, 129.5, 127.7, 127.7, 127.6, 127.6, 127.3, 117.7, 102.4, 87.4, 21.5; IR (neat): ν 3094, 3050, 2972, 1594, 1477, 1435, 1358, 1268, 1167, 1157, 1087, 960, 815, 777 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 444.07955, found: 444.07954.

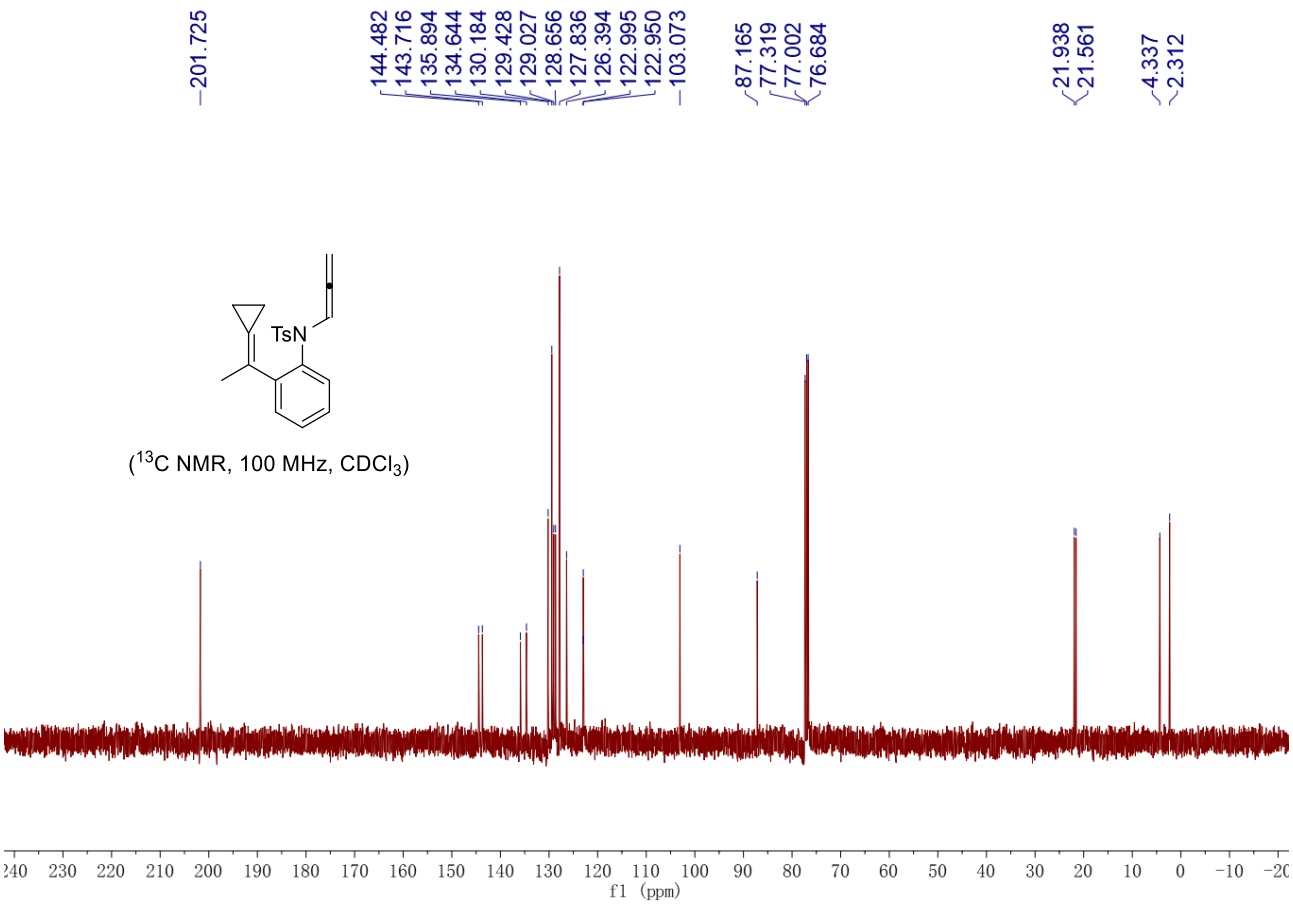



201.675
145.610
145.117
143.972
140.488
135.331
134.461
134.022
131.344
130.537
129.504
127.747
127.726
127.620
127.554
127.314
117.733
102.368
87.381
77.315
77.000
76.679
21.493
TsN
Cl
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

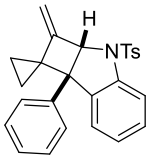


N-(2-(1-cyclopropylideneethyl)phenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (1af): Yield: 632 mg, 61%, yellow oil; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 3H), 7.04 (m, 2H), 6.52 (d, *J* = 8.0 Hz, 1H), 4.98 (d, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 2.25 (s, 3H), 1.22 – 1.10 (m, 4H).; ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 201.7, 144.5, 143.7, 135.9, 134.6, 130.2, 129.4, 129.0, 128.7, 127.8, 126.4, 123.0, 123.0, 103.1, 87.2, 21.9, 21.6, 4.3, 2.3; IR (neat): ν 3052, 2969, 2912, 1735, 1594, 1440, 1356, 1164, 1090, 755, 734, 704 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]+: 374.11852, found: 374.11789.

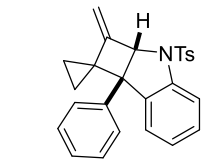



201.725
144.482
143.716
135.894
134.644
130.184
129.428
129.027
128.656
127.836
126.394
122.995
122.950
103.073
87.165
77.319
77.002
76.684
21.938
21.561
4.337
2.312
TsN
(^{13}C NMR, 100 MHz, $CDCl_3$)
f1 (ppm)

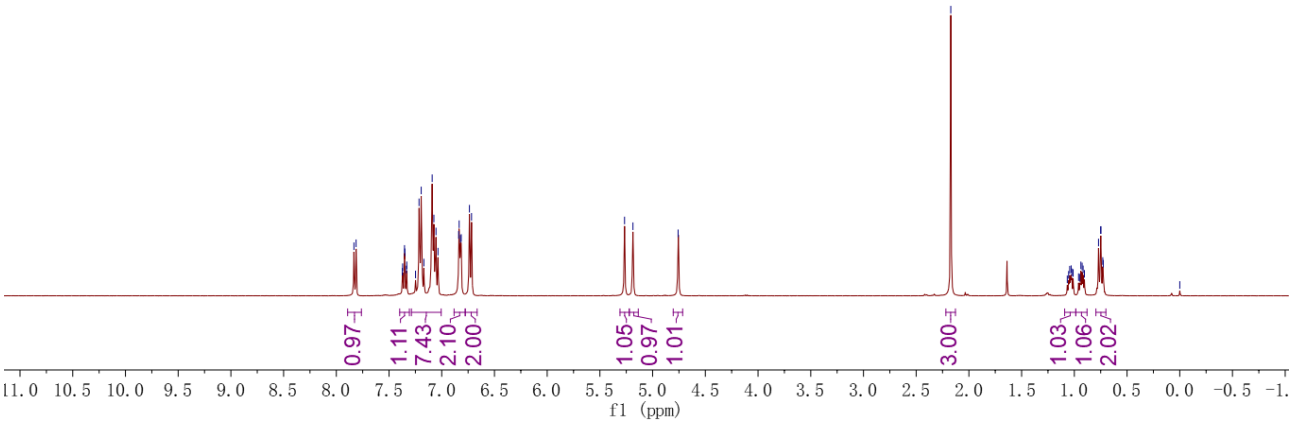
6. Characterization Data of Products.

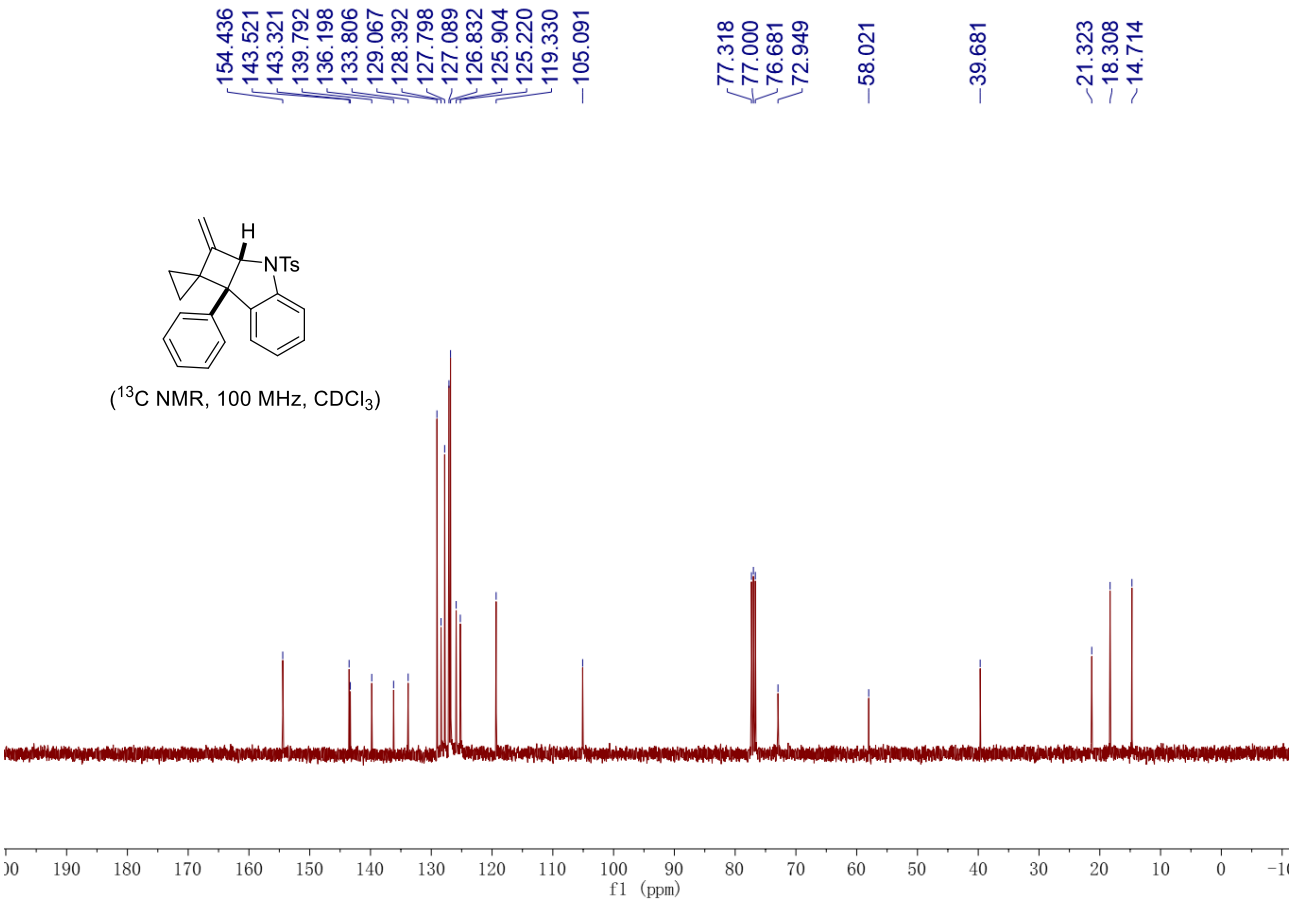


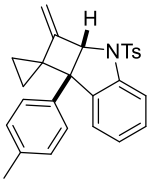
2-methylene-7b-phenyl-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2a**): Yield: 54 mg, 65%, white solid, m.p. 152-154 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.82 (d, J = 8.0 Hz, 1H), 7.35 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.29 – 7.01 (m, 7H), 6.88 – 6.78 (m, 2H), 6.73 (d, J = 8.0 Hz, 2H), 5.27 (s, 1H), 5.19 (s, 1H), 4.76 (s, 1H), 2.17 (s, 3H), 1.04 (m, 1H), 0.93 (m, 1H), 0.80 – 0.70 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 154.4, 143.5, 143.3, 139.8, 136.2, 133.8, 129.1, 128.4, 127.8, 127.1, 126.8, 125.9, 125.2, 119.3, 105.1, 72.9, 58.0, 39.7, 21.3, 18.3, 14.7; IR (neat): ν 3055, 2959, 2917, 2844, 1591, 1453, 1353, 1171, 1085, 1052, 962, 890, 742, 669 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 436.13417, found: 436.13434.



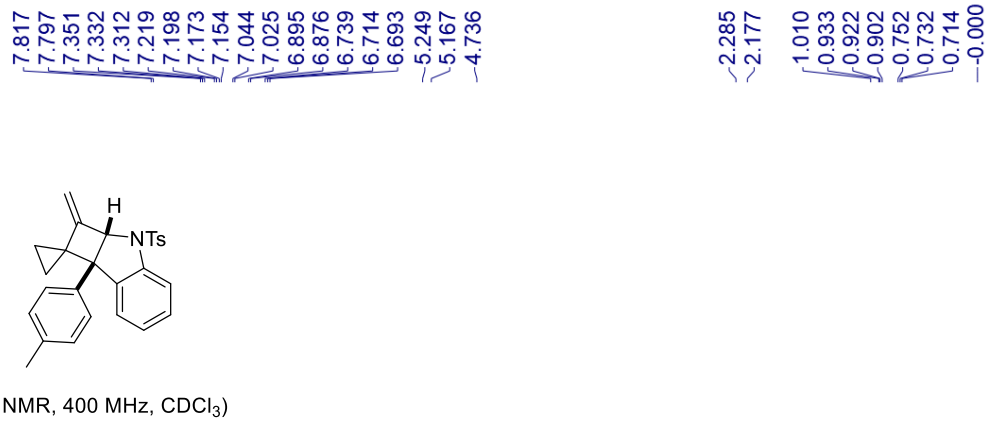
(^{1}H NMR, 400 MHz, $CDCl_3$)

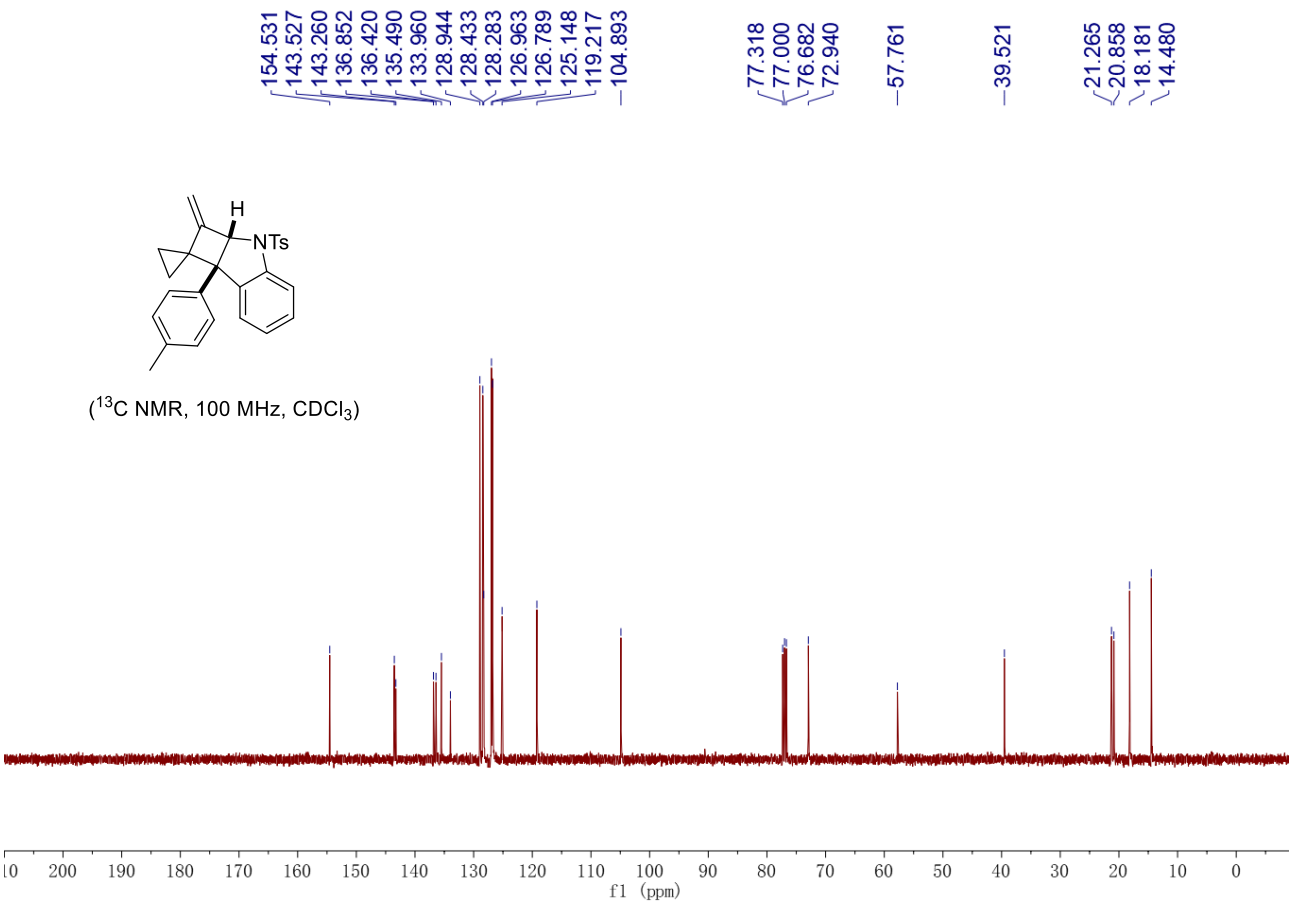


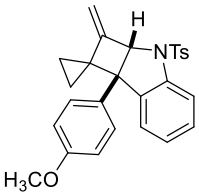

154.436
143.521
143.321
139.792
136.198
133.806
129.067
128.392
127.798
127.089
126.832
125.904
125.220
119.330
105.091
77.318
77.000
76.681
72.949
58.021
39.681
21.323
18.308
14.714
H
NTs
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)



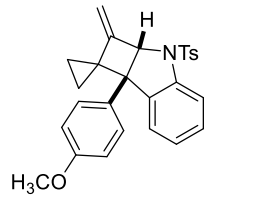
2-methylene-7b-(*p*-tolyl)-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2b**): Yield: 59 mg, 68%, white solid, m.p. 192-194 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.25 – 7.13 (m, 3H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.77 – 6.64 (m, 4H), 5.25 (s, 1H), 5.17 (s, 1H), 4.74 (s, 1H), 2.29 (s, 3H), 2.18 (s, 3H), 1.07 – 0.88 (m, 2H), 0.80 – 0.67 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 154.5, 143.5, 143.3, 136.9, 136.4, 135.5, 134.0, 128.9, 128.4, 128.3, 127.0, 126.8, 125.1, 119.2, 104.9, 72.9, 57.8, 39.5, 21.3, 20.9, 18.2, 14.5; IR (neat): ν 3073, 3024, 2992, 2919, 1594, 1456, 1353, 1184, 1169, 1088, 931, 819, 758 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.15064.



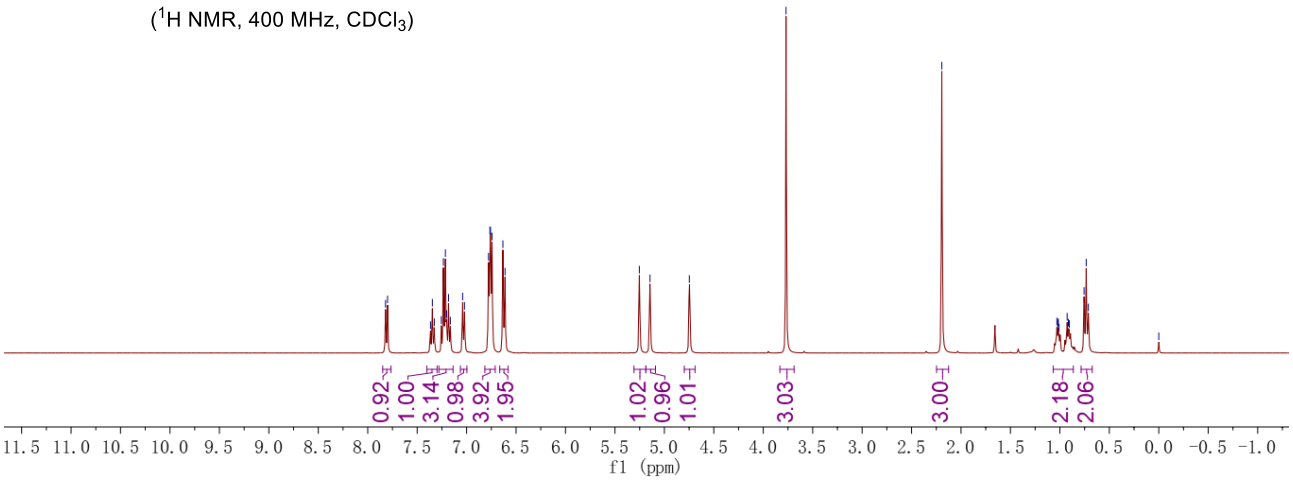

154.531
143.527
143.260
136.852
136.420
135.490
133.960
128.944
128.433
128.283
126.963
126.789
125.148
119.217
104.893
77.318
77.000
76.682
72.940
57.761
39.521
21.265
20.858
18.181
14.480
H
NTs
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

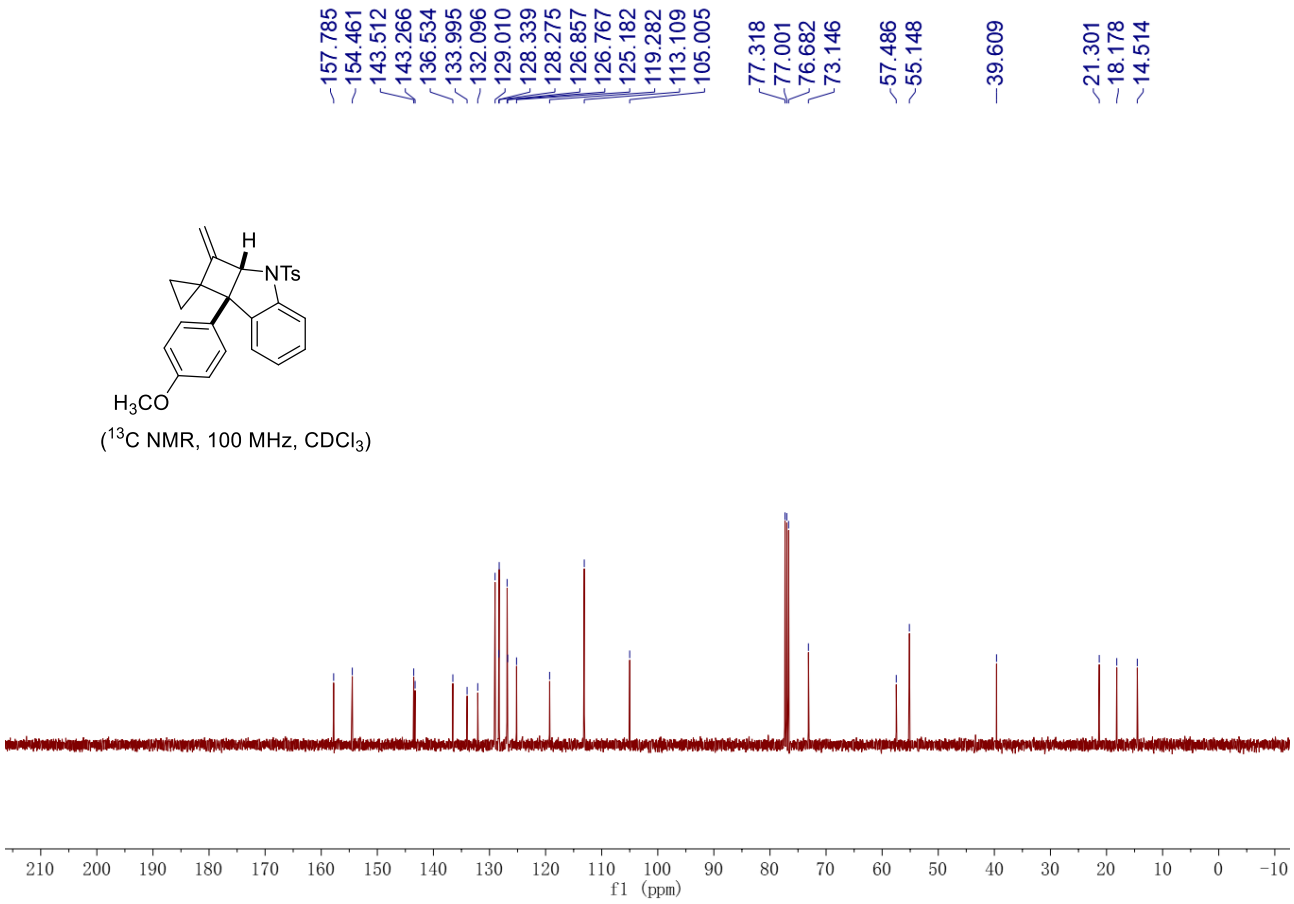


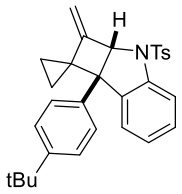
7b-(4-methoxyphenyl)-2-methylene-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2c**): Yield: 66 mg, 74%, white solid, m.p. 196-198 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.28 – 7.14 (m, 3H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.82 – 6.71 (m, 4H), 6.62 (d, *J* = 8.8 Hz, 2H), 5.25 (s, 1H), 5.15 (s, 1H), 4.75 (s, 1H), 3.77 (s, 3H), 2.19 (s, 3H), 1.07 – 0.86 (m, 2H), 0.79 – 0.67 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 157.8, 154.5, 143.5, 143.3, 136.5, 134.0, 132.1, 129.0, 128.3, 128.3, 126.9, 126.8, 125.2, 119.3, 113.1, 105.0, 73.1, 57.5, 55.1, 39.6, 21.3, 18.2, 14.5; IR (neat): ν 3052, 2959, 2904, 1607, 1510, 1456, 1351, 1251, 1087, 1032, 881, 764, 660 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 466.14474, found: 466.14485.



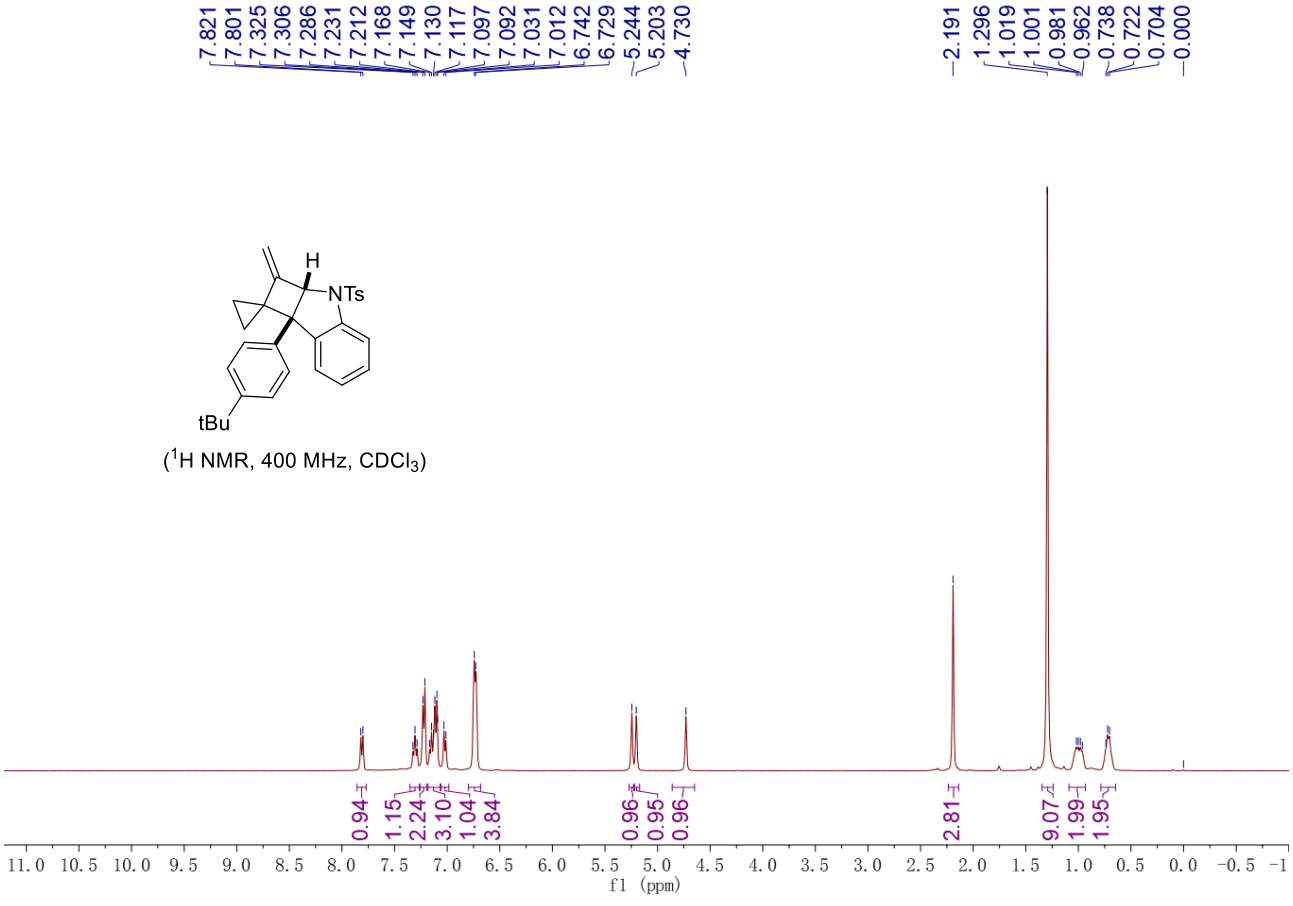
(^{1}H NMR, 400 MHz, $CDCl_3$)

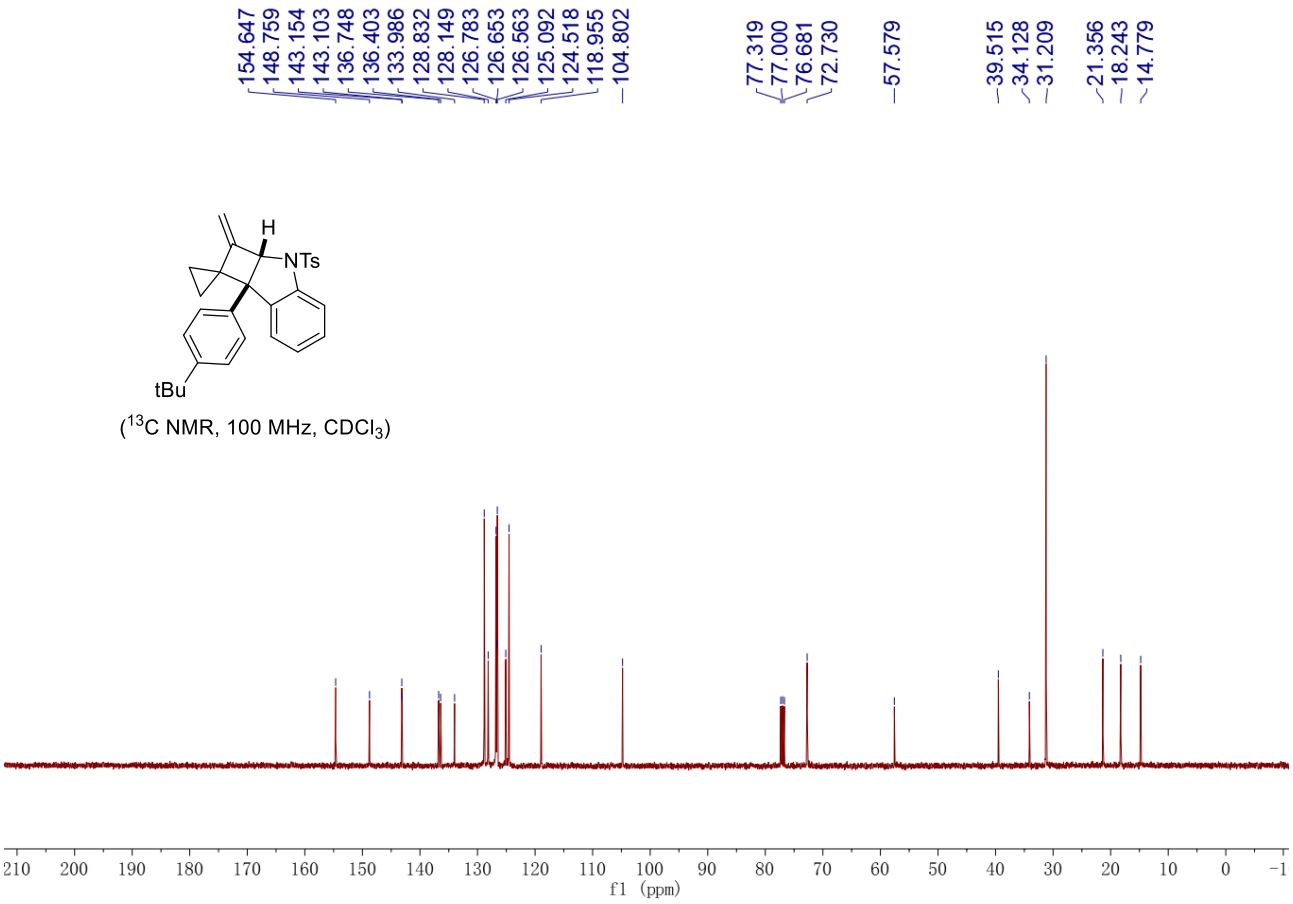


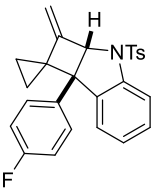

157.785
154.461
143.512
143.266
136.534
133.995
132.096
129.010
128.339
128.275
126.857
126.767
125.182
119.282
113.109
105.005
77.318
77.001
76.682
73.146
57.486
55.148
39.609
21.301
18.178
14.514
H
NTs
H3CO
(13C NMR, 100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



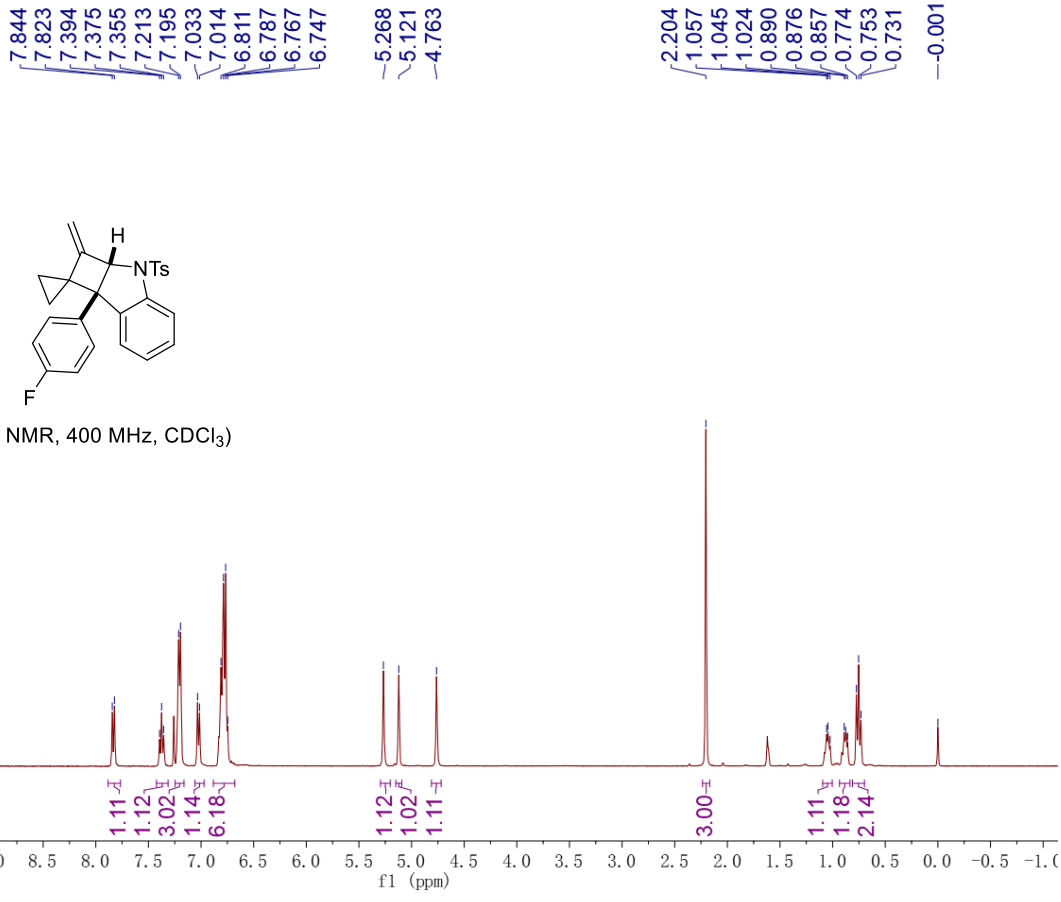
7b-(4-(tert-butyl)phenyl)-2-methylene-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1, 1'-cyclopropane] (**2d**): Yield: 60 mg, 64%, pale yellow oil; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.19 – 7.07 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.80 – 6.68 (m, 4H), 5.24 (s, 1H), 5.20 (s, 1H), 4.73 (s, 1H), 2.19 (s, 3H), 1.30 (s, 9H), 1.09 – 0.93 (m, 2H), 0.79 – 0.65 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 154.6, 148.8, 143.2, 143.1, 136.7, 136.4, 134.0, 128.8, 128.1, 126.8, 126.7, 126.6, 125.1, 124.5, 119.0, 104.8, 72.7, 57.6, 39.5, 34.1, 31.2, 21.4, 18.2, 14.8; IR (neat): ν 3068, 2964, 2859, 1597, 1456, 1355, 1089, 876, 755, 659 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 492.19677, found: 492.19746.

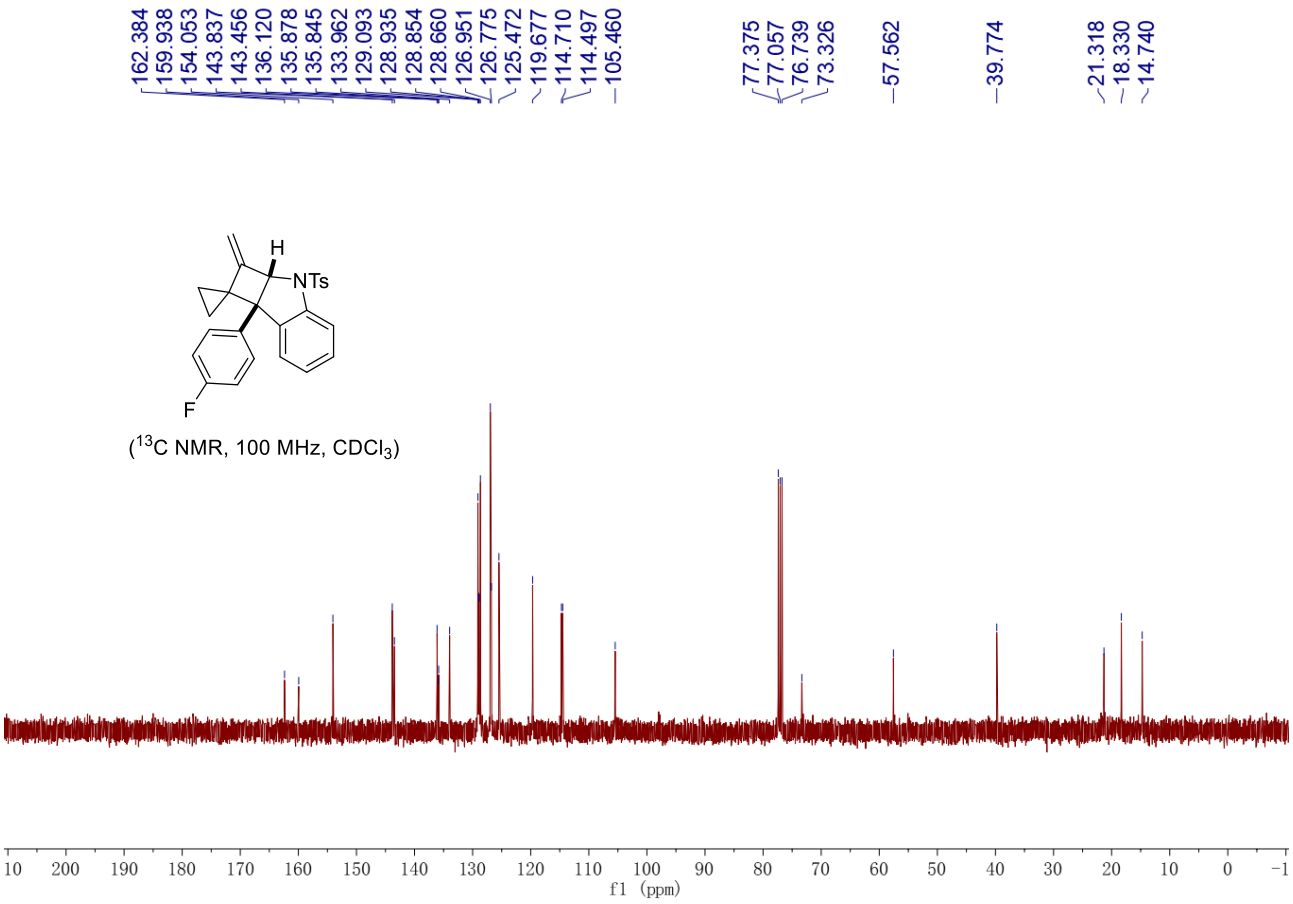


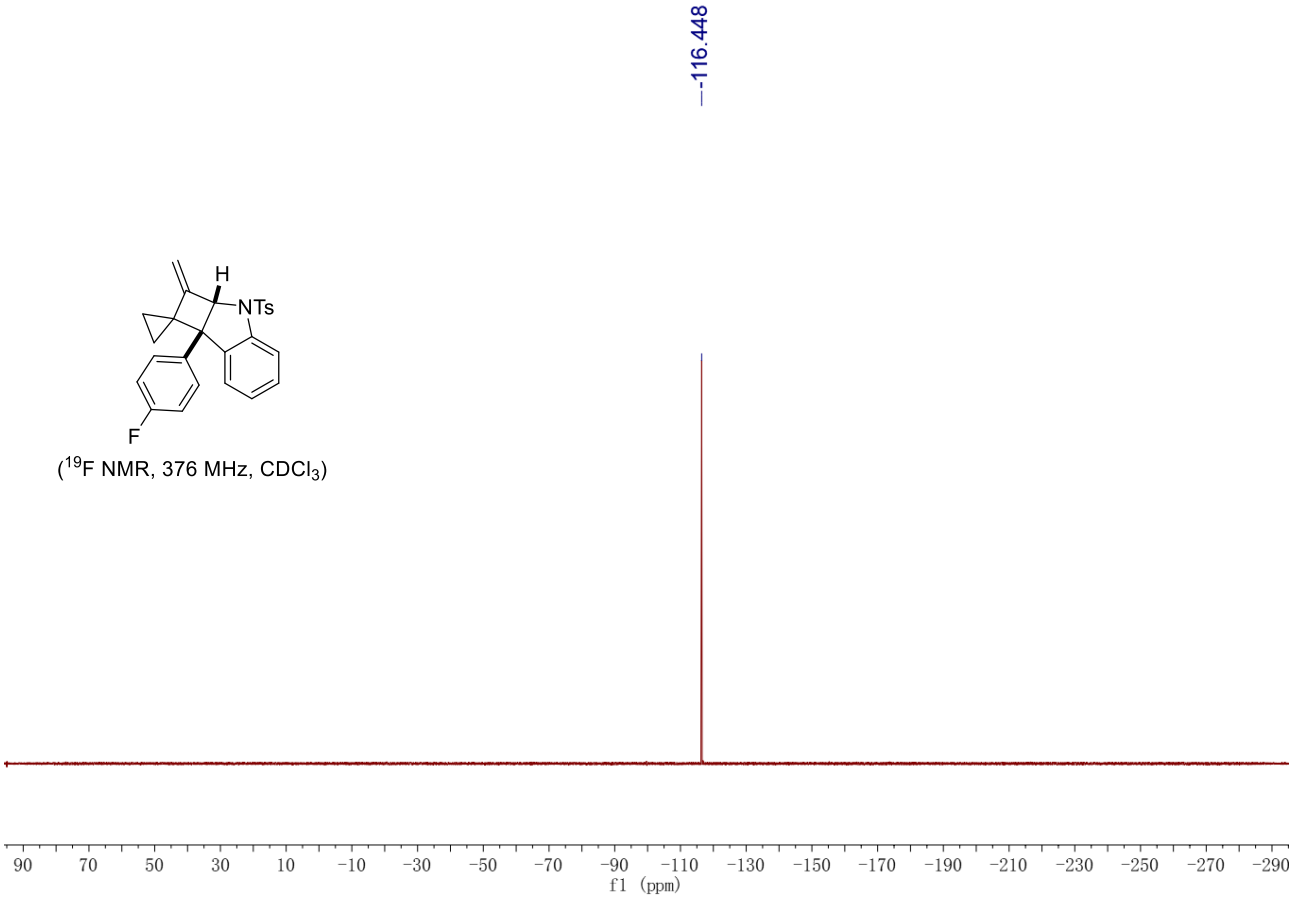

154.647
148.759
143.154
143.103
136.748
136.403
133.986
128.832
128.149
126.783
126.653
126.563
125.092
124.518
118.955
104.802
77.319
77.000
76.681
72.730
57.579
39.515
34.128
31.209
21.356
18.243
14.779
H
NTs
tBu
(13C NMR, 100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

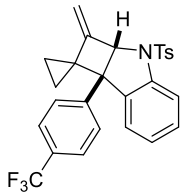


7b-(4-fluorophenyl)-2-methylene-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2e**): Yield: 56 mg, 65%, white solid, m.p. 177-179 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.83 (d, *J* = 8.4 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.25 – 7.16 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.88 – 6.68 (m, 6H), 5.27 (s, 1H), 5.12 (s, 1H), 4.76 (s, 1H), 2.20 (s, 3H), 1.09 – 1.00 (m, 1H), 0.93 – 0.84 (m, 1H), 0.81 – 0.70 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 161.2 (d, *J* = 244.6 Hz), 154.1, 143.8, 143.5, 136.1, 135.9 (d, *J* = 3.3 Hz), 134.0, 129.1, 128.9 (d, J = 8.1Hz), 128.7, 127.0, 126.8, 125.5, 119.7, 144.6 (d, J = 21.3 Hz), 105.5, 73.3, 57.6, 39.8, 21.3, 18.3, 14.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.4; IR (neat): ν 3060, 2985, 1594, 1500, 1352, 1218, 1171, 1085, 1051, 890, 657 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 454.12475, found: 454.12582.

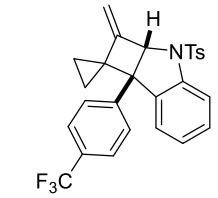



162.384
159.938
154.053
143.837
143.456
136.120
135.878
135.845
133.962
129.093
128.935
128.854
128.660
126.951
126.775
125.472
119.677
114.710
114.497
105.460
77.375
77.057
76.739
73.326
57.562
39.774
21.318
18.330
14.740
H
NTs
F
(13C NMR, 100 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

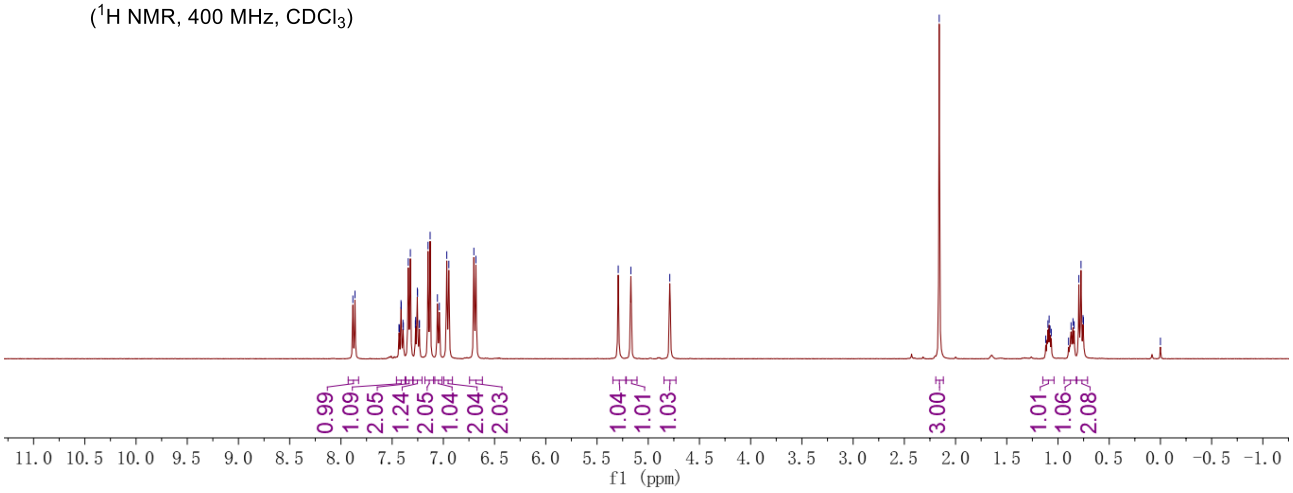

-116.448
H
NTs
F
(19F NMR, 376 MHz, CDCl3)
90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −250 −270 −290
f1 (ppm)

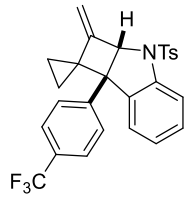


2-methylene-3-tosyl-7b-(4-(trifluoromethyl)phenyl)-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2f**): Yield: 62 mg, 64%, white solid, m.p. 173-175 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.41 (dt, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.25 (dt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 5.29 (s, 1H), 5.17 (s, 1H), 4.79 (s, 1H), 2.16 (s, 3H), 1.15 – 1.04 (m, 1H), 0.94 – 0.82 (m, 1H), 0.82 – 0.71 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 153.6, 143.9, 143.5, 135.5, 133.5, 129.0, 128.8, 128.2 (q, *J* = 32.2 Hz), 127.5, 126.9, 126.8, 125.4, 124.7 (q, J = 3.1 Hz), 124.3 (q, *J* = 270.1 Hz), 120.1, 105.8, 73.2, 57.9, 39.8, 21.0, 18.4, 14.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3; IR (neat): ν 3068, 2989, 2921, 1670, 1615, 1453, 1354, 1324, 1115, 1068, 877, 739, 658 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 504.12156, found: 504.12154.

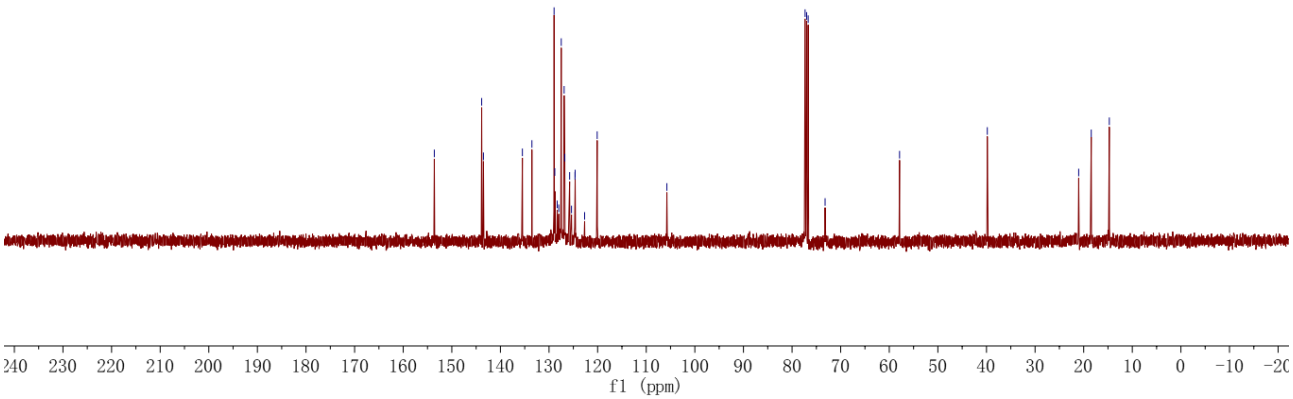


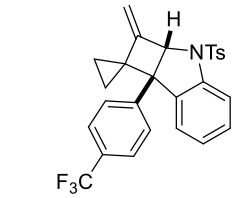
(^{1}H NMR, 400 MHz, $CDCl_3$)



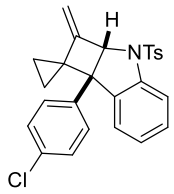


(^{13}C NMR, 100 MHz, $CDCl_3$)

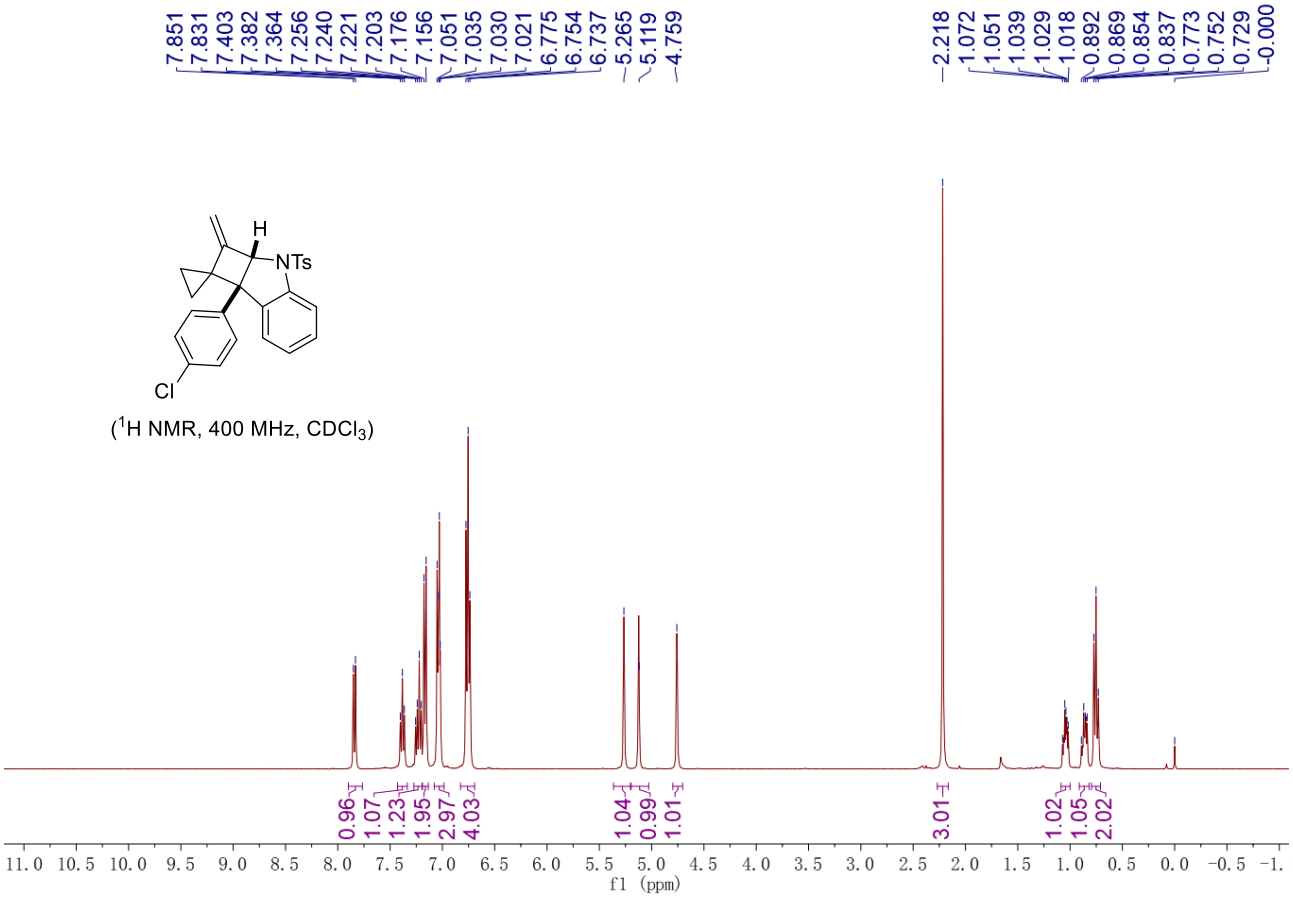


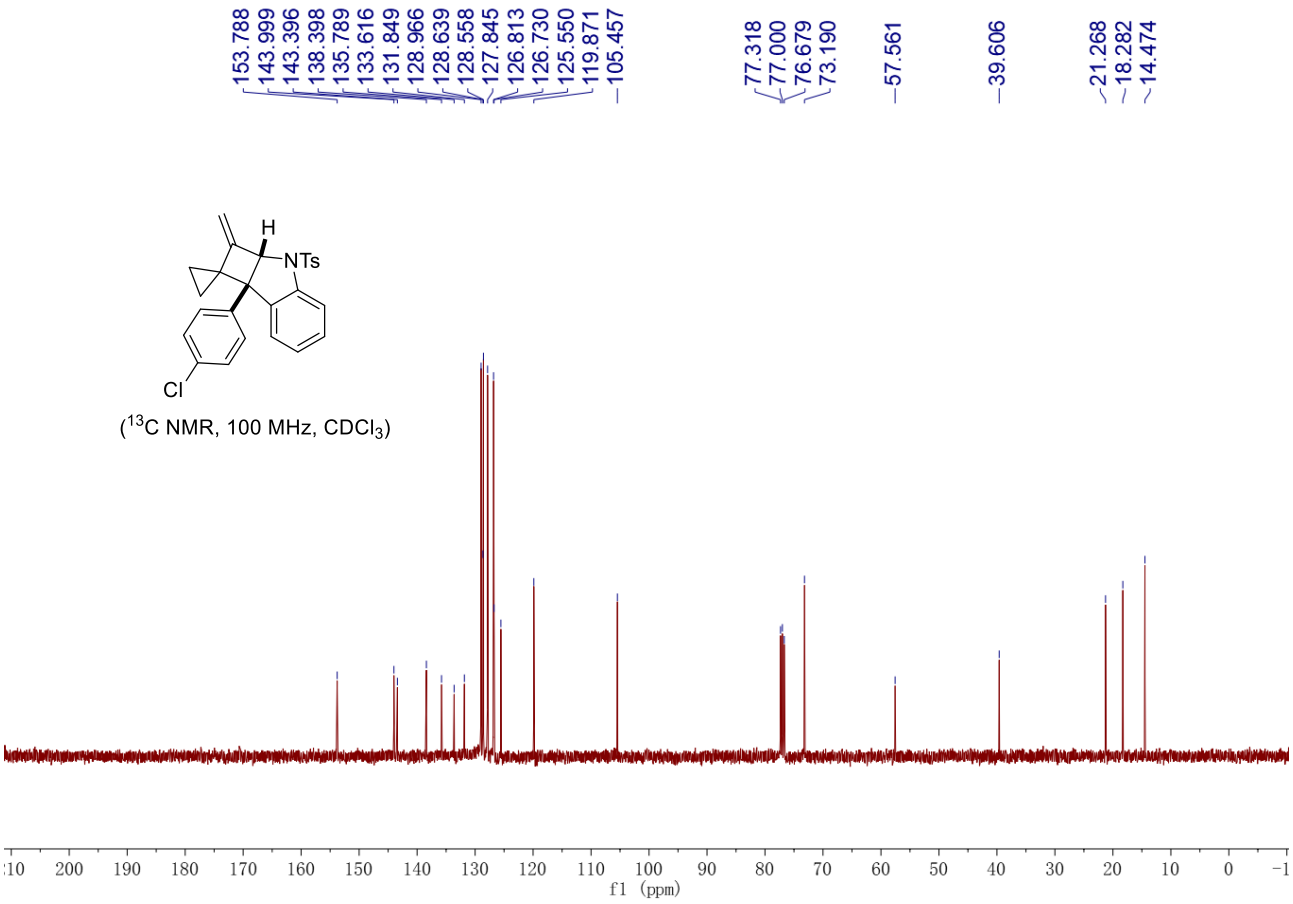


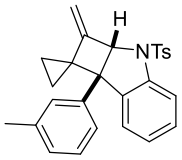
(^{19}F NMR, 376 MHz, $CDCl_3$)



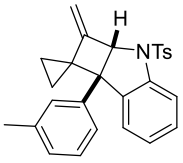
7b-(4-chlorophenyl)-2-methylene-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2g**): Yield: 58 mg, 65%, white solid, m.p. 177-179 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.08 – 6.98 (m, 3H), 6.83 – 6.69 (m, 4H), 5.26 (s, 1H), 5.12 (s, 1H), 4.76 (s, 1H), 2.22 (s, 3H), 1.09 – 1.00 (m, 1H), 0.91 – 0.82 (m, 1H), 0.79 – 0.71 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 153.8, 144.0, 143.4, 138.4, 135.8, 133.6, 131.8, 129.0, 128.6, 128.6, 127.8, 126.8, 126.7, 125.5, 119.9, 105.5, 73.2, 57.6, 39.6, 21.3, 18.3, 14.5; IR (neat): ν 3068, 3026, 2953, 1597, 1492, 1450, 1354, 1169, 1088, 1051, 1011, 929, 824, 757, 676 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 470.09520, found: 470.09659.



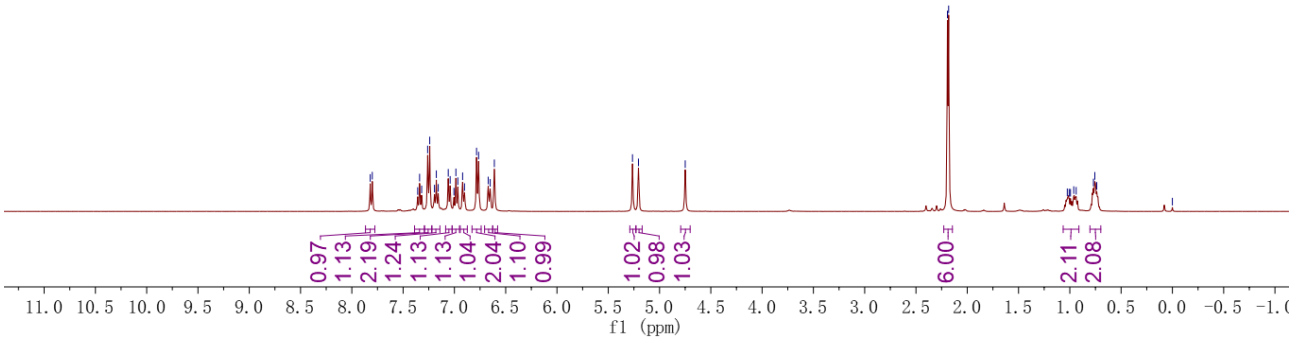

153.788
143.999
143.396
138.398
135.789
133.616
131.849
128.966
128.639
128.558
127.845
126.813
126.730
125.550
119.871
105.457
77.318
77.000
76.679
73.190
57.561
39.606
21.268
18.282
14.474
H
NTs
Cl
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

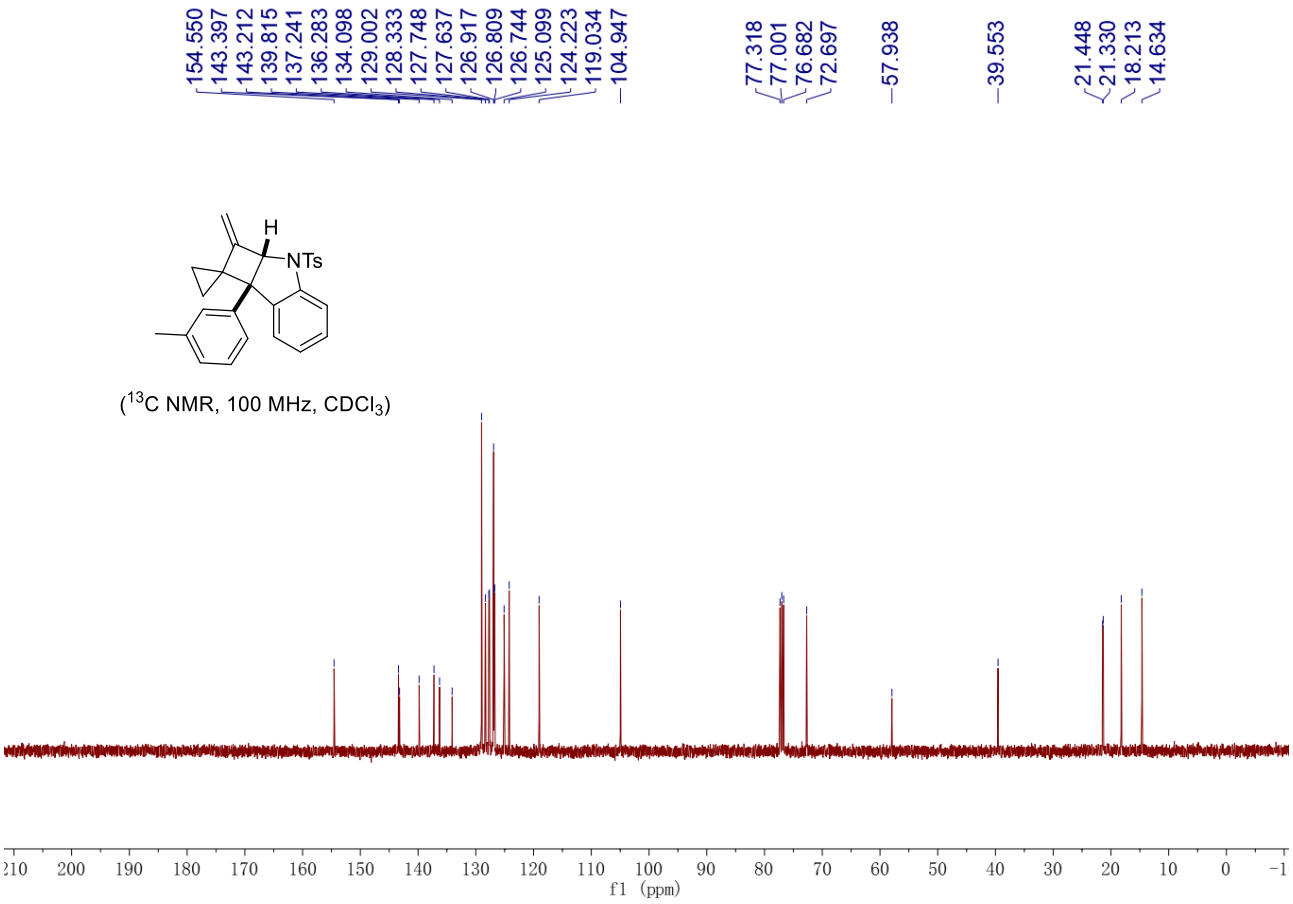


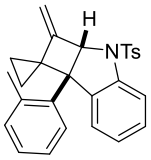
2-methylene-7b-(m-tolyl)-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cycloprop ane] (**2h**): Yield: 56 mg, 65%, white solid, m.p. 193-195 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 5.26 (s, 1H), 5.21 (s, 1H), 4.75 (s, 1H), 2.19 (s, 3H), 2.18 (s, 3H), 1.06 – 0.91 (m, 2H), 0.80 – 0.70 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 154.5, 143.4, 143.2, 139.8, 137.2, 136.3, 134.1, 129.0, 128.3, 127.7, 127.6, 126.9, 126.8, 126.7, 125.1, 124.2, 119.0, 104.9, 72.7, 57.9, 39.6, 21.4, 21.3, 18.2, 14.6; IR (neat): ν 3039, 2976, 2913, 1681, 1597, 1456, 1351, 1164, 1087, 1060, 888, 780, 670 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.15012.



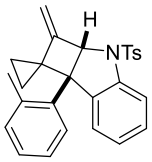
(^{1}H NMR, 400 MHz, $CDCl_3$)



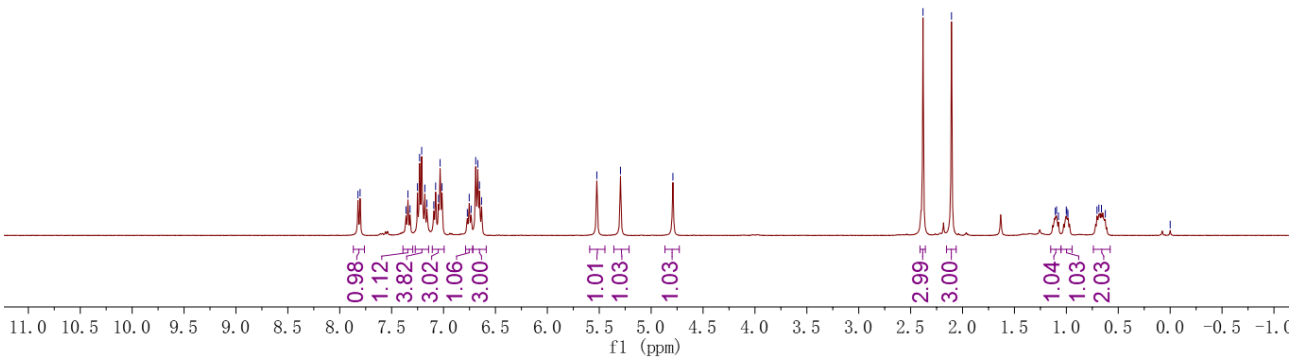

154.550
143.397
143.212
139.815
137.241
136.283
134.098
129.002
128.333
127.748
127.637
126.917
126.809
126.744
125.099
124.223
119.034
104.947
77.318
77.001
76.682
72.697
57.938
39.553
21.448
21.330
18.213
14.634
H
NTs
(13C NMR, 100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

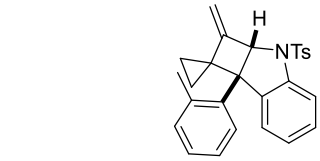


2-methylene-7b-(o-tolyl)-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2i**): Yield: 26 mg, 30%, white solid, m.p. 191-193 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.27 – 7.14 (m, 4H), 7.11 – 6.99 (m, 3H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.72 – 6.59 (m, 3H), 5.52 (s, 1H), 5.30 (s, 1H), 4.79 (s, 1H), 2.38 (s, 3H), 2.11 (s, 3H), 1.15 – 1.05 (m, 1H), 1.05 – 0.94 (m, 1H), 0.74 – 0.58 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 154.1, 143.6, 142.8, 137.8, 137.0, 135.8, 133.6, 132.1, 129.0, 128.1, 127.5, 126.6, 126.2, 124.9, 124.9, 119.6, 105.9, 70.1, 58.6, 39.6, 21.3, 19.1, 15.5; IR (neat): ν 3057, 2992, 2911, 1683, 1597, 1461, 1350, 1166, 1155, 1090, 1067, 892, 704, 662 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.15016.

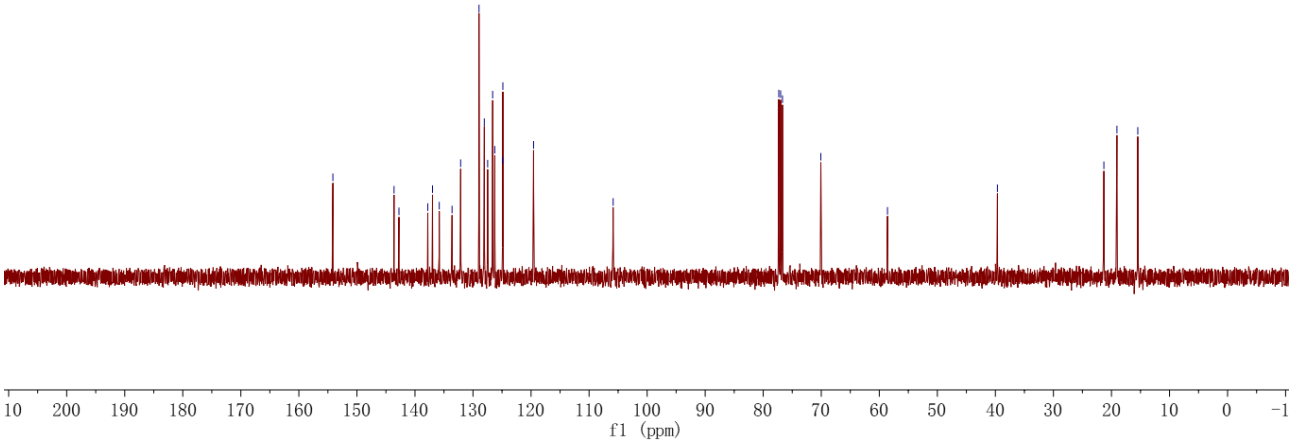


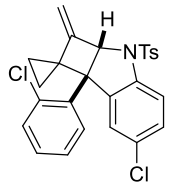
(^{1}H NMR,400 MHz, $CDCl_3$)



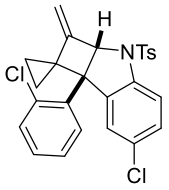


(^{13}C NMR, 100 MHz, $CDCl_3$)

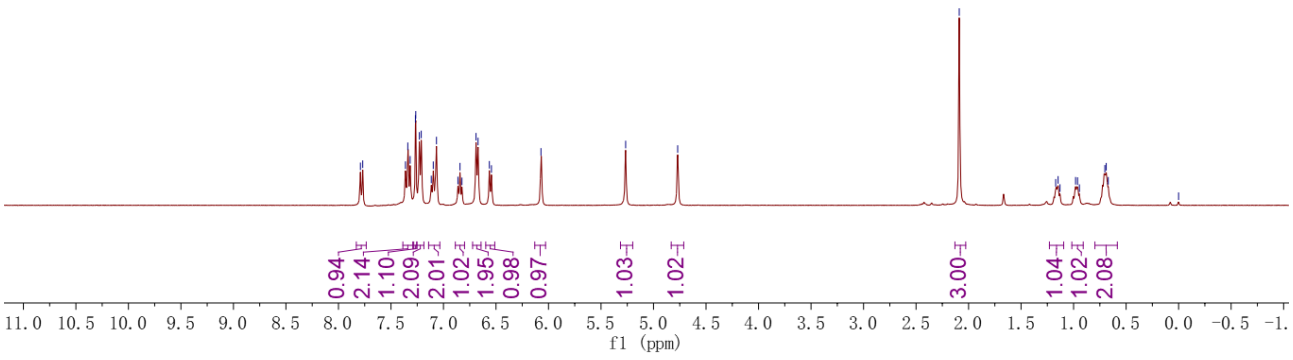


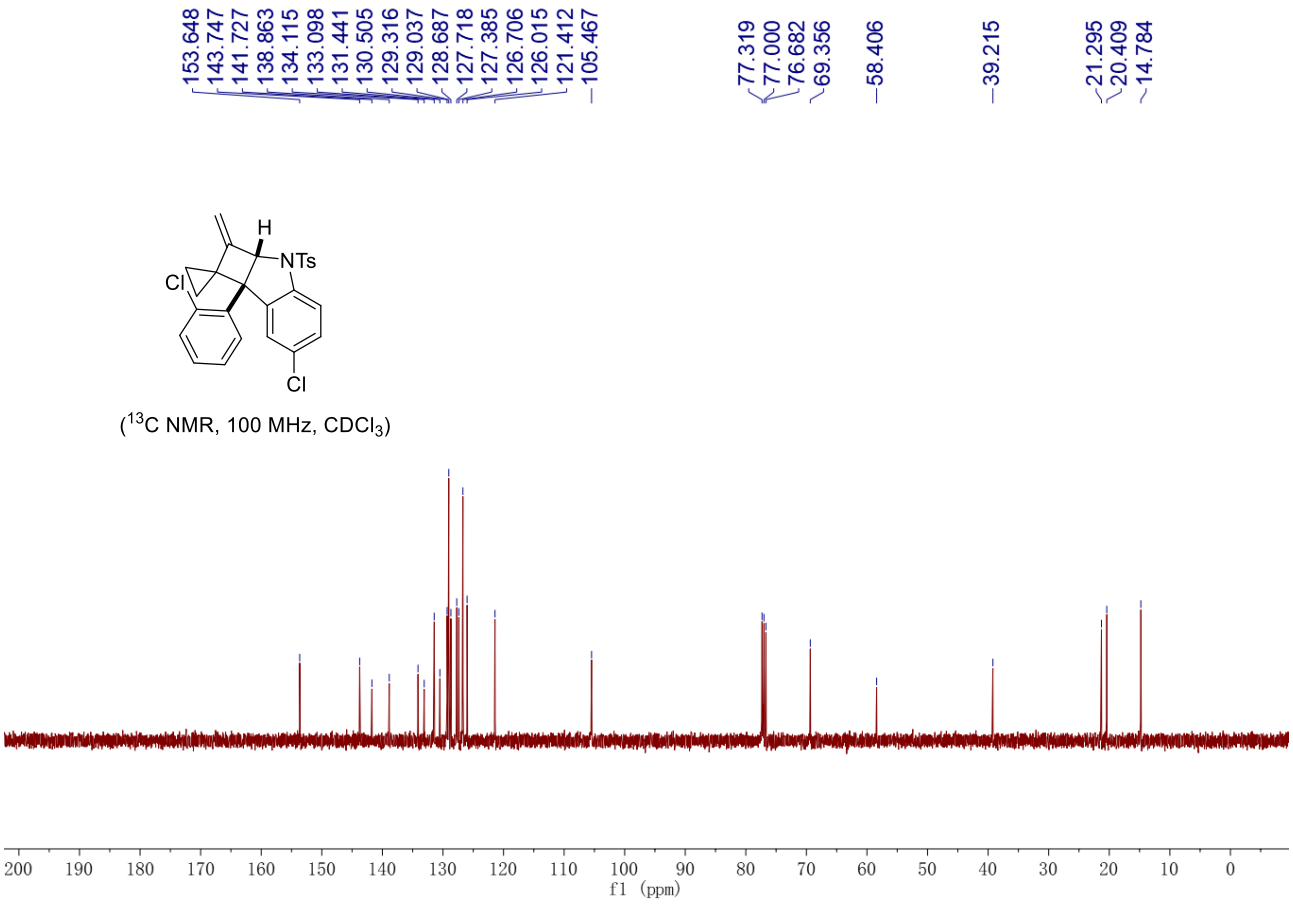


6-chloro-7b-(2-chlorophenyl)-2-methylene-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2j**): Yield: 36 mg, 38%, white solid, m.p. 173-175 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.78 (d, *J* = 8.8 Hz, 1H), 7.34 (t, *J* = 8.8Hz, 2H), 7.27 (d, *J* = 1.2 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 2H), 7.14 – 7.03 (m, 2H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 2H), 6.55 (d, *J* = 8.0 Hz, 1H), 6.07 (s, 1H), 5.27 (s, 1H), 4.77 (s, 1H), 2.09 (s, 3H), 1.23 – 1.09 (m, 1H), 1.02 – 0.91 (m, 1H), 0.80 – 0.58 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 154.1, 143.6, 142.8, 137.8, 137.0, 135.8, 133.6, 132.1, 129.0, 128.1, 127.5, 126.6, 126.2, 124.9, 124.9, 119.6, 105.9, 70.1, 58.6, 39.6, 21.3, 19.1, 15.5; IR (neat): ν 3068, 3044, 2984, 1678, 1594, 1463, 1353, 1065, 1039, 888, 766, 660 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 504.05623, found: 504.05680.

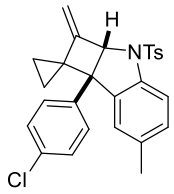


(^{1}H NMR, 400 MHz, $CDCl_3$)

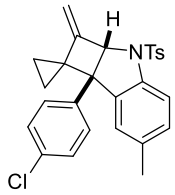




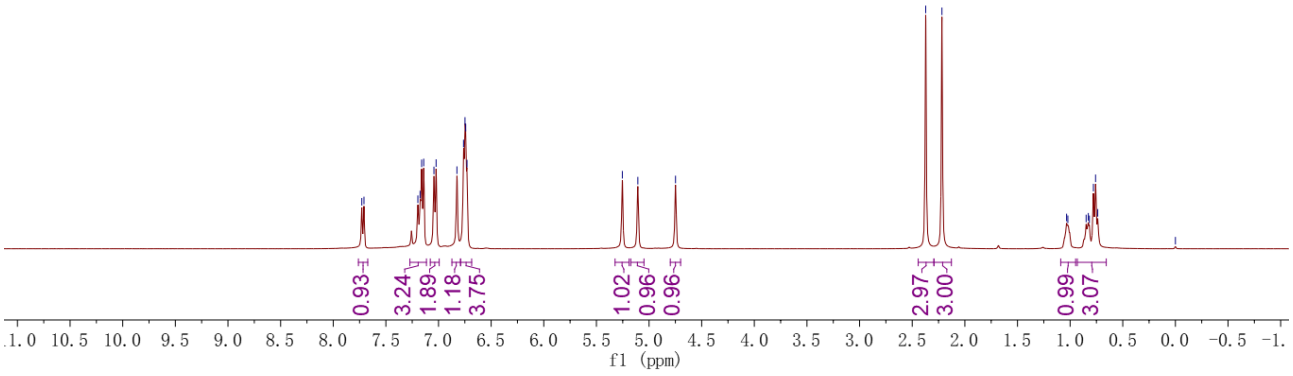
(^{13}C NMR, 100 MHz, $CDCl_3$)

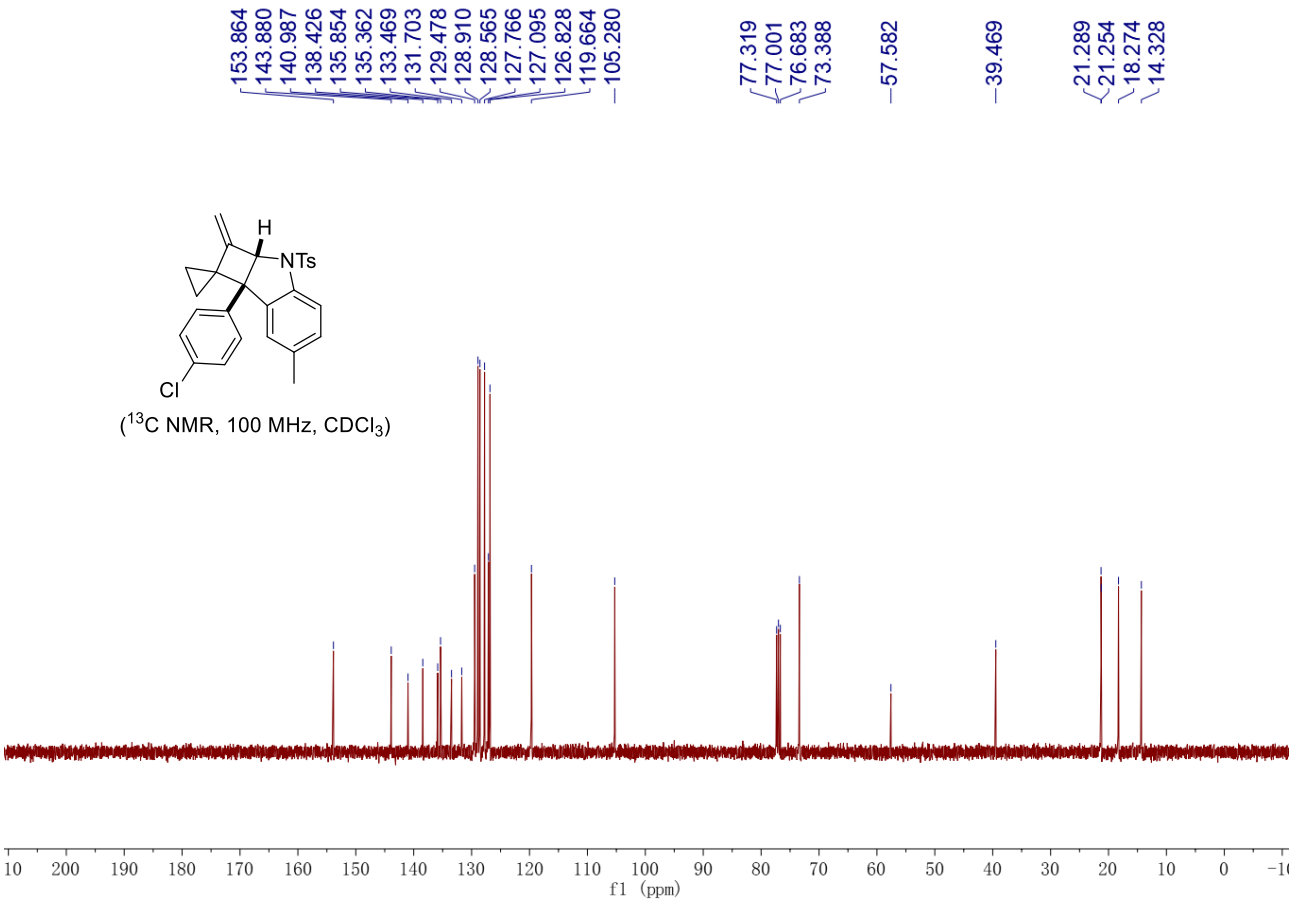


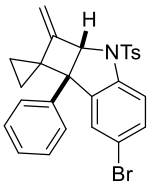
7b-(4-chlorophenyl)-6-methyl-2-methylene-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2k**): Yield: 56 mg, 61%, white solid, m.p. >200 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.27 – 7.11 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.83 (s, 1H), 6.79 – 6.69 (m, 4H), 5.25 (s, 1H), 5.11 (s, 1H), 4.75 (s, 1H), 2.37 (s, 3H), 2.22 (s, 3H), 1.09 – 0.95 (m, 1H), 0.93 – 0.66 (m, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 153.9, 143.9, 141.0, 138.4, 135.9, 135.4, 133.5, 131.7, 129.5, 128.9, 128.6, 127.8, 127.1, 126.8, 119.7, 105.3, 73.4, 57.6, 39.5, 21.3, 21.3, 18.3, 14.3; IR (neat): ν 3071, 2990, 2917, 1675, 1597, 1479, 1352, 1161, 1078, 875, 675 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 484.11085, found: 484.11090.



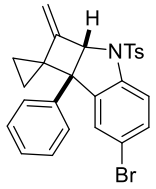
(^{1}H NMR, 400 MHz, $CDCl_3$)



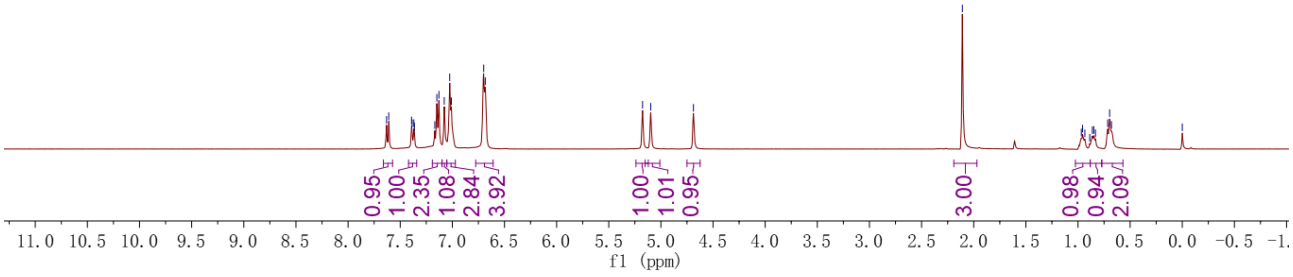

153.864
143.880
140.987
138.426
135.854
135.362
133.469
131.703
129.478
128.910
128.565
127.766
127.095
126.828
119.664
105.280
77.319
77.001
76.683
73.388
57.582
39.469
21.289
21.254
18.274
14.328
H
NTs
Cl
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

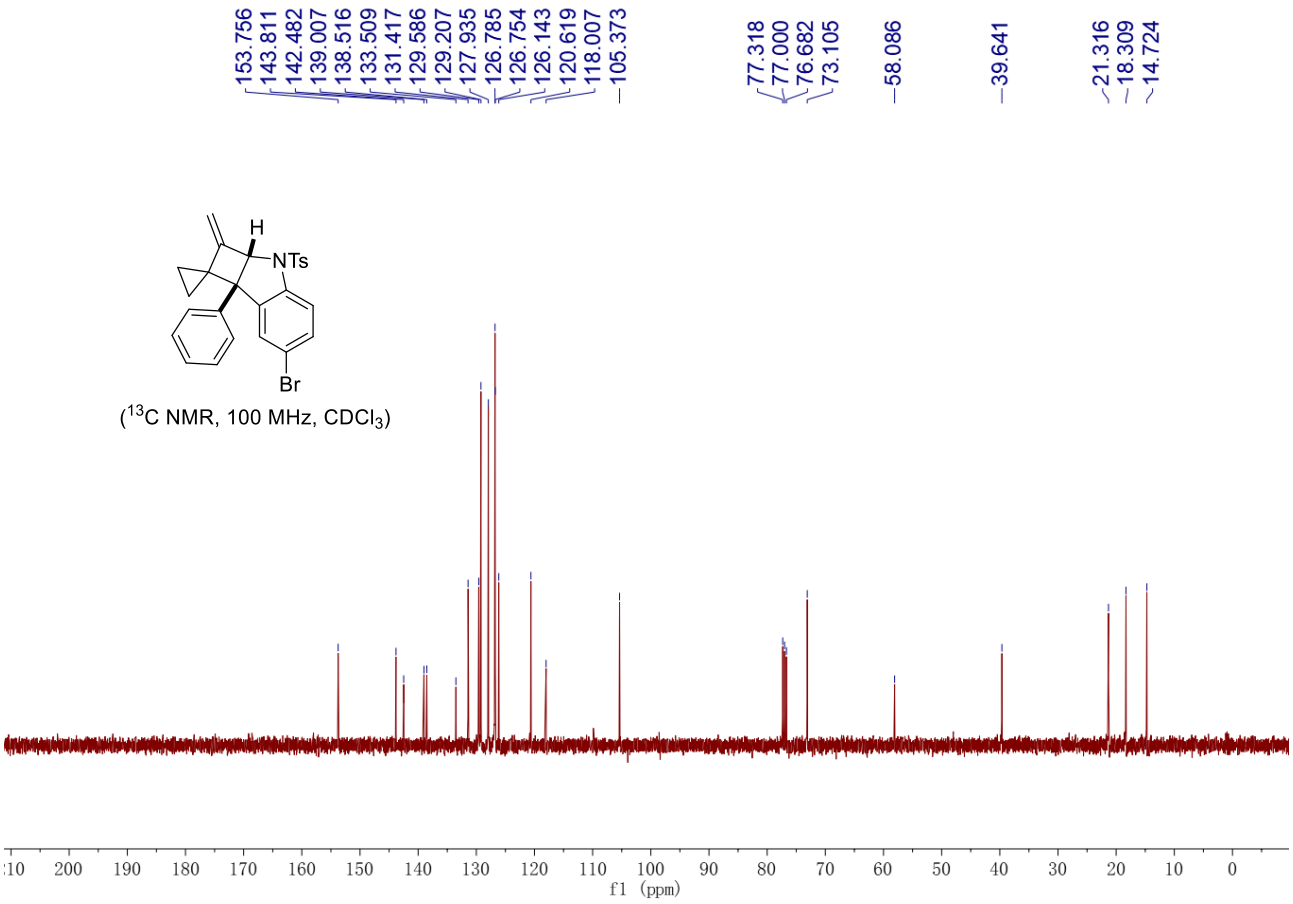


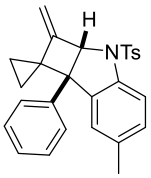
6-bromo-2-methylene-7b-phenyl-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2l**): Yield: 66 mg, 67%, white solid, m.p. 189-191 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, J = 8.4 Hz, 1H), 7.38 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.19 – 7.10 (m, 2H), 7.08 (s, 1H), 7.05 – 6.97 (m, 3H), 6.78 – 6.61 (m, 4H), 5.18 (s, 1H), 5.10 (s, 1H), 4.69 (s, 1H), 2.11 (s, 3H), 1.02 – 0.88 (m, 1H), 0.88 – 0.77 (m, 1H), 0.77 – 0.57 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 153.8, 143.8, 142.5, 139.0, 138.5, 133.5, 131.4, 129.6, 129.2, 127.9, 126.8, 126.8, 126.1, 120.6, 118.0, 105.4, 73.1, 58.1, 39.6, 21.3, 18.3, 14.7; IR (neat): ν 3063, 2979, 2908, 1686, 1600, 1471, 1355, 1170, 1087, 1059, 1013, 870, 702, 655 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 514.04468, found: 514.04566.



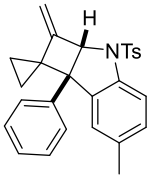
(^{1}H NMR, 400 MHz, $CDCl_3$)



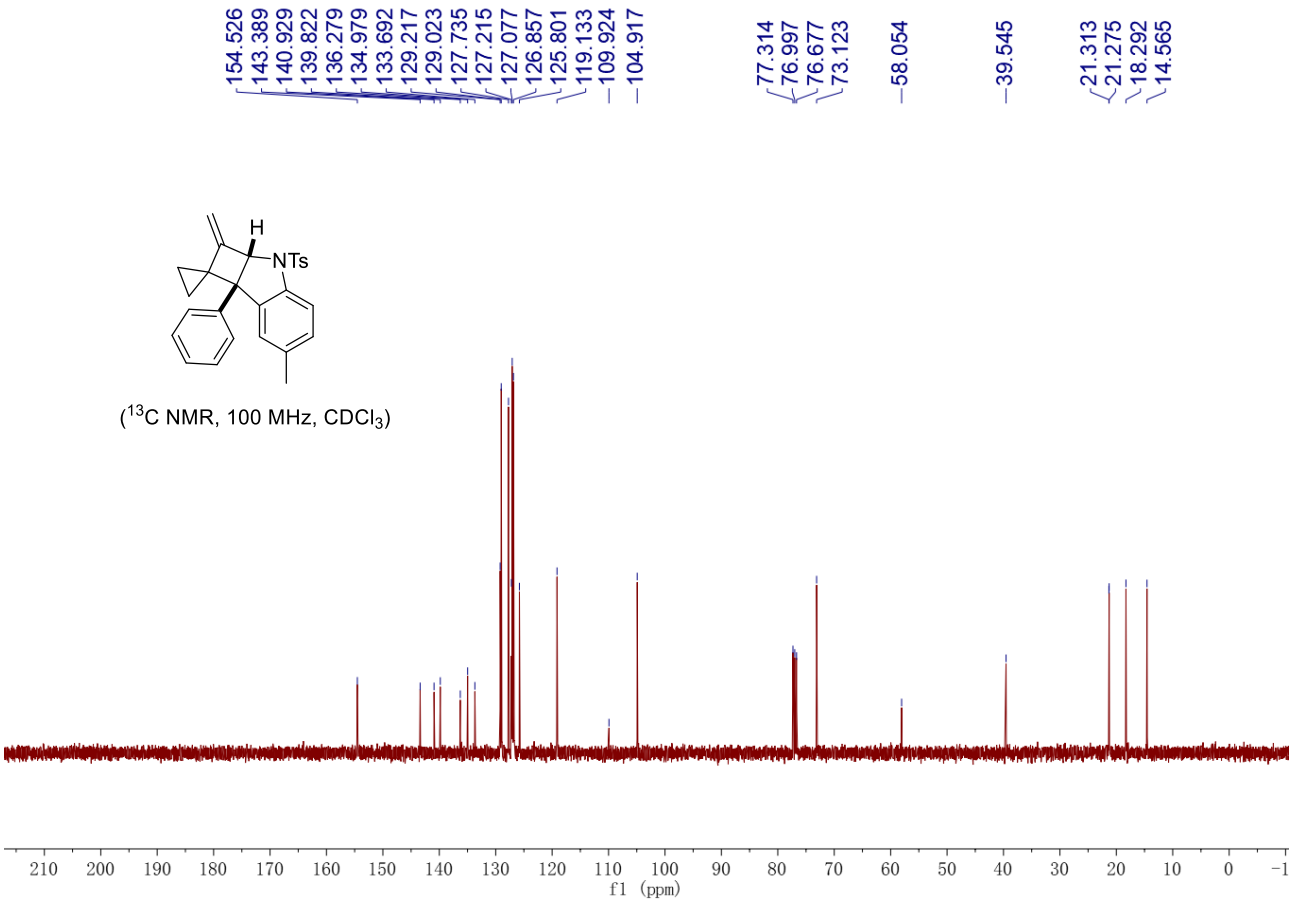

153.756
143.811
142.482
139.007
138.516
133.509
131.417
129.586
129.207
127.935
126.785
126.754
126.143
120.619
118.007
105.373
77.318
77.000
76.682
73.105
58.086
39.641
21.316
18.309
14.724
H
NTs
Br
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

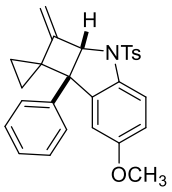


6-methyl-2-methylene-7b-phenyl-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2m**): Yield: 56 mg, 65%, white solid, m.p. >200 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.70 (d, *J* = 8.4 Hz, 1H), 7.26 – 7.13 (m, 3H), 7.12 – 7.02 (m, 3H), 6.89 – 6.76 (m, 3H), 6.72 (d, *J* = 7.6 Hz, 2H), 5.26 (s, 1H), 5.17 (s, 1H), 4.74 (s, 1H), 2.35 (s, 3H), 2.17 (s, 3H), 1.06 – 0.96 (m, 1H), 0.96 – 0.86 (m, 1H), 0.81 – 0.70 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 154.5, 143.4, 140.9, 139.8, 136.3, 135.0, 133.7, 129.2, 129.0, 127.7, 127.2, 127.1, 126.9, 125.8, 119.1, 109.9, 104.9, 73.1, 58.1, 39.5, 21.3, 21.3, 18.3, 14.6; IR (neat): ν 3065, 2976, 2911, 1670, 1592, 1479, 1352, 1170, 1157, 1097, 1059, 932, 873, 763, 669 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 450.14982, found: 450.15051.

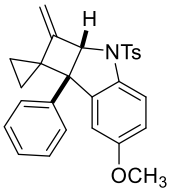


(^{1}H NMR, 400 MHz, $CDCl_3$)

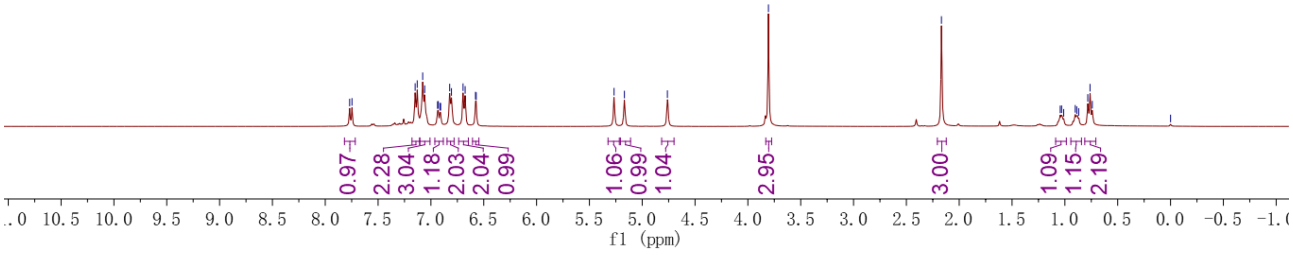

154.526
143.389
140.929
139.822
136.279
134.979
133.692
129.217
129.023
127.735
127.215
127.077
126.857
125.801
119.133
109.924
104.917
77.314
76.997
76.677
73.123
58.054
39.545
21.313
21.275
18.292
14.565
H
NTs
(^{13}C NMR, 100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)



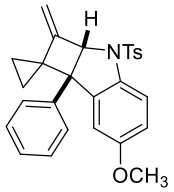
6-methoxy-2-methylene-7b-phenyl-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2n**): Yield: 51 mg, 58%, white solid, m.p. 189-191 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.76 (d, *J* = 8.8 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.11 – 7.01 (m, 3H), 6.92 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 6.81 (d, *J* = 6.4 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 2.7 Hz, 1H), 5.27 (s, 1H), 5.17 (s, 1H), 4.76 (s, 1H), 3.81 (s, 3H), 2.17 (s, 3H), 1.09 – 0.99 (m, 1H), 0.94 – 0.84 (m, 1H), 0.81 – 0.71 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 157.6, 154.4, 143.4, 139.5, 137.9, 136.7, 133.3, 129.0, 127.8, 127.1, 127.0, 125.8, 120.6, 113.5, 112.5, 105.1, 73.6, 58.4, 55.6, 39.7, 21.4, 18.5, 14.6; IR (neat): ν 3071, 3019, 2969, 1672, 1604, 1484, 1348, 1025, 852, 700, 678 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 466.14474, found: 466.14458.



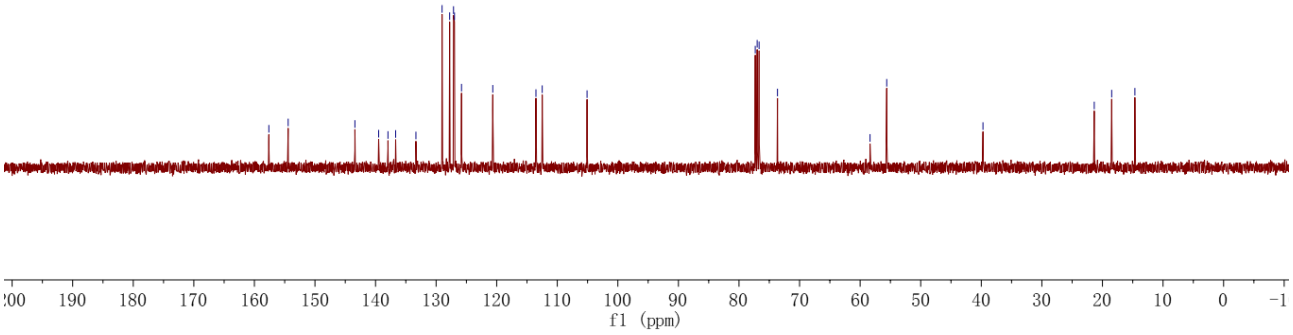
(^{1}H NMR, 400 MHz, $CDCl_3$)

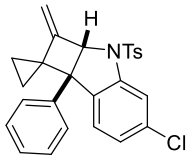


157.612
154.425
143.405
139.490
137.948
136.684
133.335
129.019
127.766
127.130
126.972
125.808
120.644
113.521
112.486
105.082
77.318
77.000
76.682
73.648
58.368
55.610
39.722
21.351
18.473
14.644

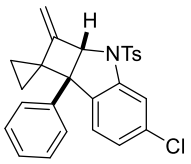


(^{13}C NMR, 100 MHz, $CDCl_3$)

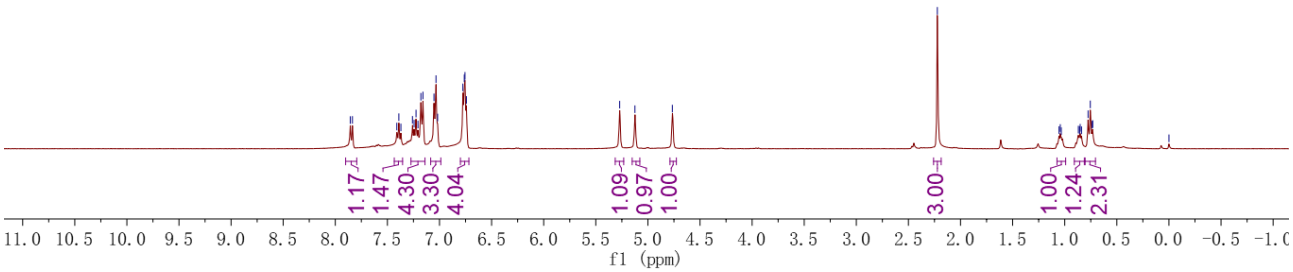


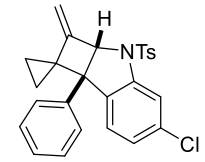


5-chloro-2-methylene-7b-phenyl-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2o**): Yield: 61 mg, 68%, white solid, m.p. 173-175 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.27 – 7.14 (m, 3H), 7.08 – 6.99 (m, 3H), 6.80 – 6.72 (m, 4H), 5.27 (s, 1H), 5.12 (s, 1H), 4.77 (s, 1H), 2.22 (s, 3H), 1.07 – 0.99 (m, 1H), 0.91 – 0.80 (m, 1H), 0.80 – 0.70 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 153.8, 144.0, 143.4, 138.4, 135.8, 133.7, 131.9, 129.0, 128.7, 128.6, 127.9, 126.9, 126.7, 125.6, 119.9, 105.5, 73.2, 57.6, 39.6, 21.3, 18.3, 14.5; IR (neat): ν 3060, 2987, 2925, 1591, 1490, 1353, 1170, 1089, 1011, 886, 757, 676 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 470.09520, found: 470.09616.

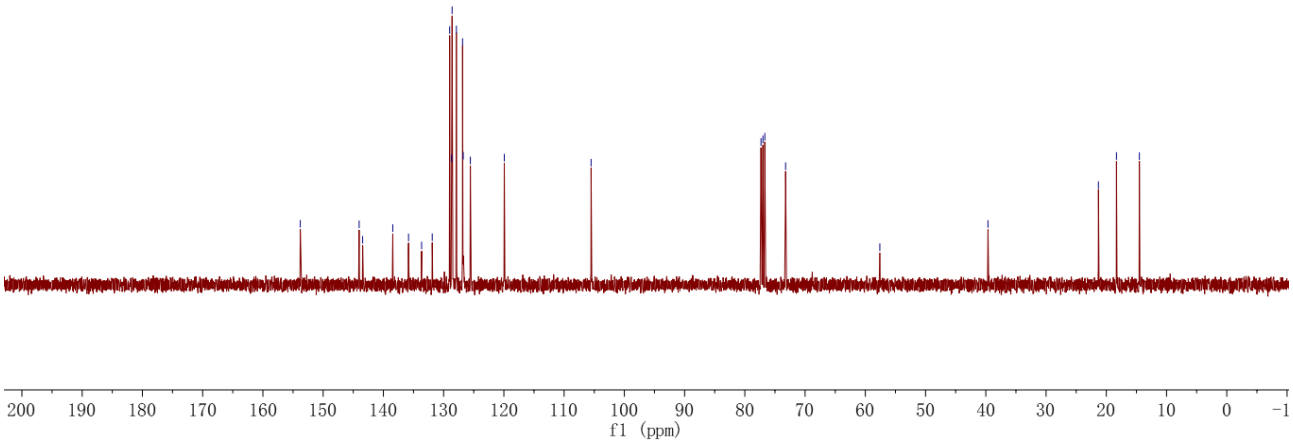


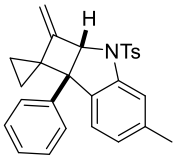
(^{1}H NMR,400 MHz, $CDCl_3$)



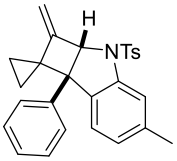


(^{13}C NMR, 100 MHz, $CDCl_3$)

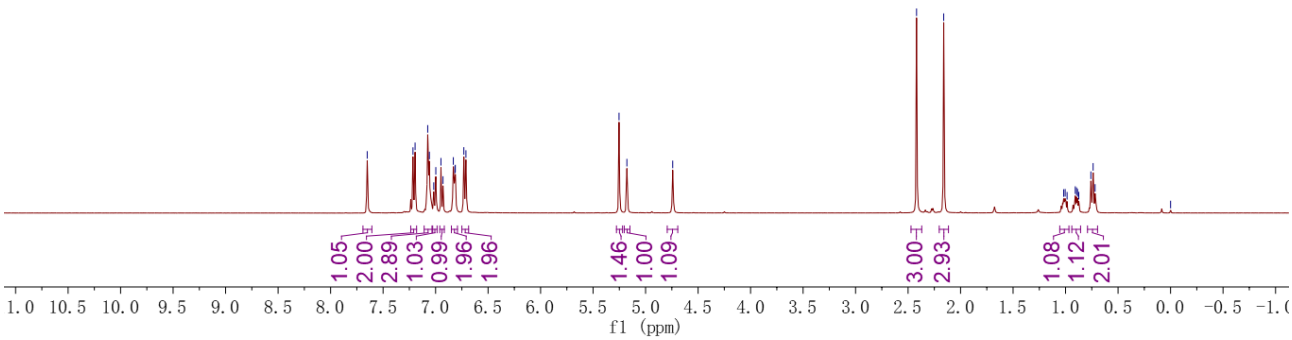


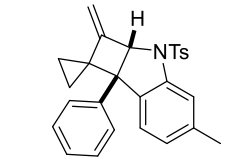


5-methyl-2-methylene-7b-phenyl-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2p**): Yield: 56 mg, 65%, white solid, m.p. >200 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.11 – 7.03 (m, 3H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.85 – 6.79 (m, 2H), 6.72 (d, *J* = 8.0 Hz, 2H), 5.25 (s, 1H), 5.18 (s, 1H), 4.74 (s, 1H), 2.42 (s, 3H), 2.16 (s, 3H), 1.06 – 0.97 (m, 1H), 0.94 – 0.86 (m, 1H), 0.79 – 0.70 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 154.6, 143.4, 143.4, 139.8, 138.5, 133.8, 133.2, 129.0, 127.7, 127.0, 126.7, 126.4, 126.2, 125.8, 119.8, 104.9, 73.1, 57.7, 39.5, 21.6, 21.3, 18.3, 14.5; IR (neat): ν 3050, 2981, 2916, 1678, 1592, 1497, 1348, 1168, 1064, 898, 757, 674 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.15029.

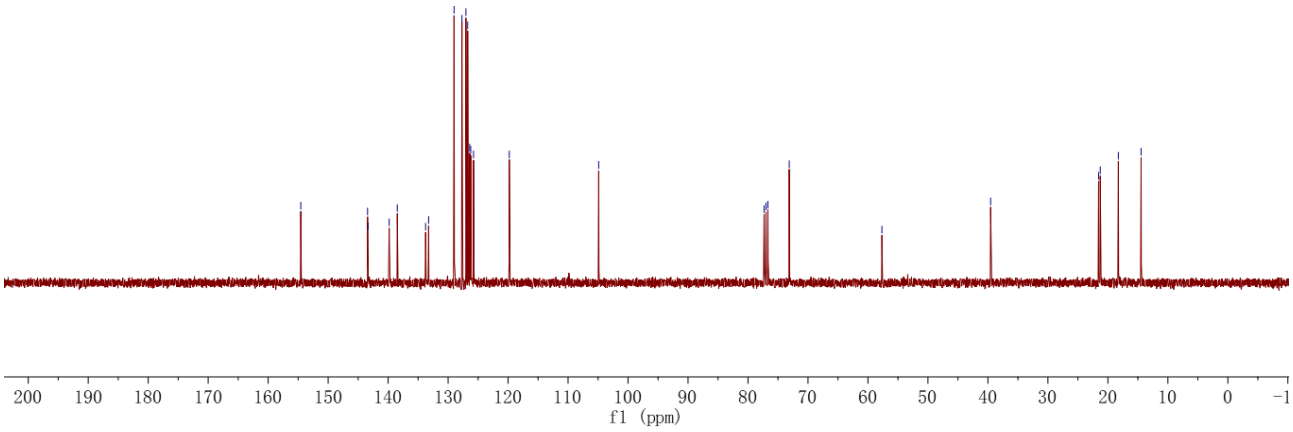


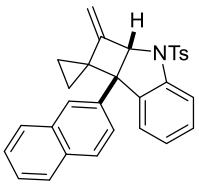
(^{1}H NMR, 400 MHz, $CDCl_3$)



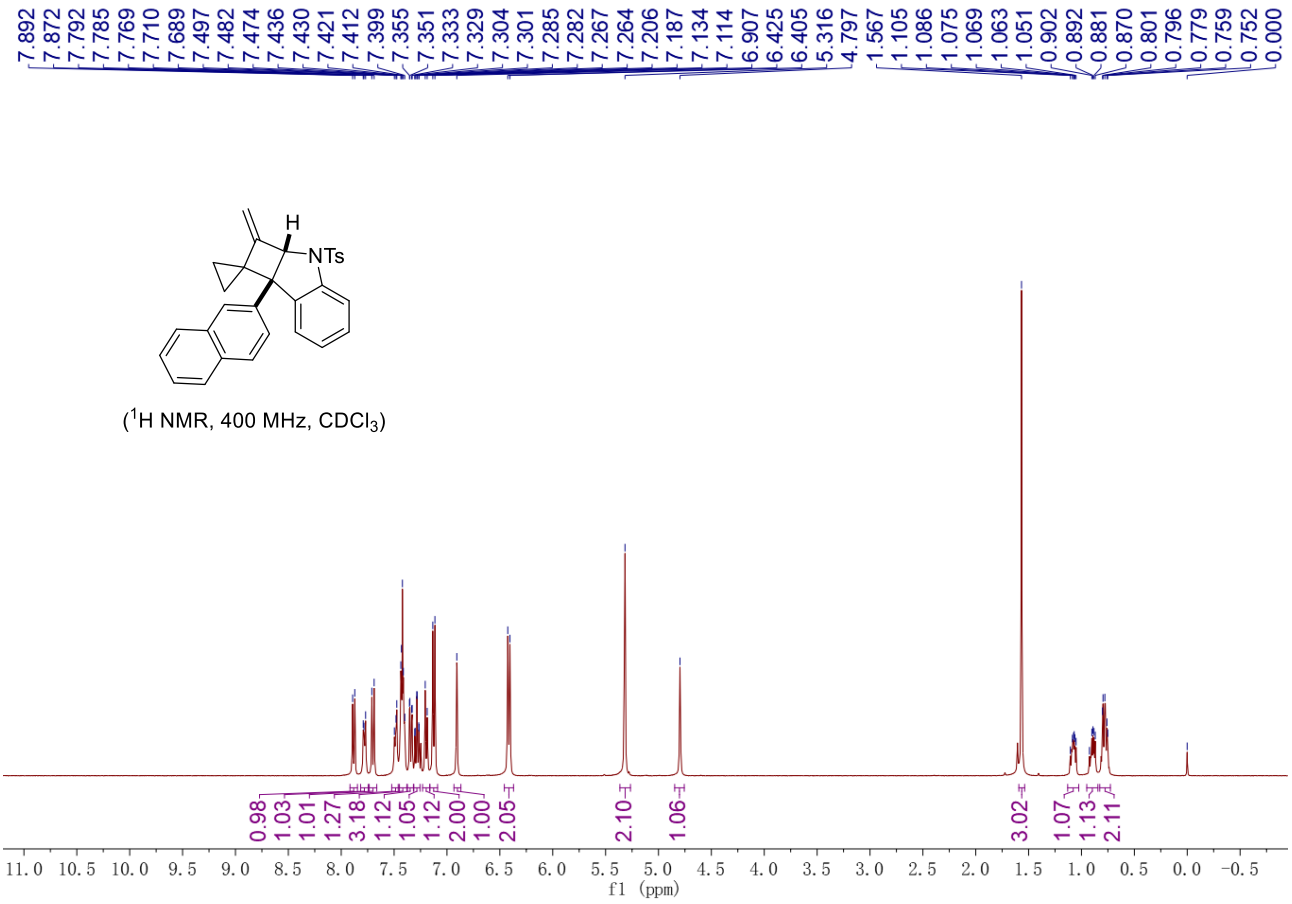


(^{13}C NMR, 100 MHz, $CDCl_3$)

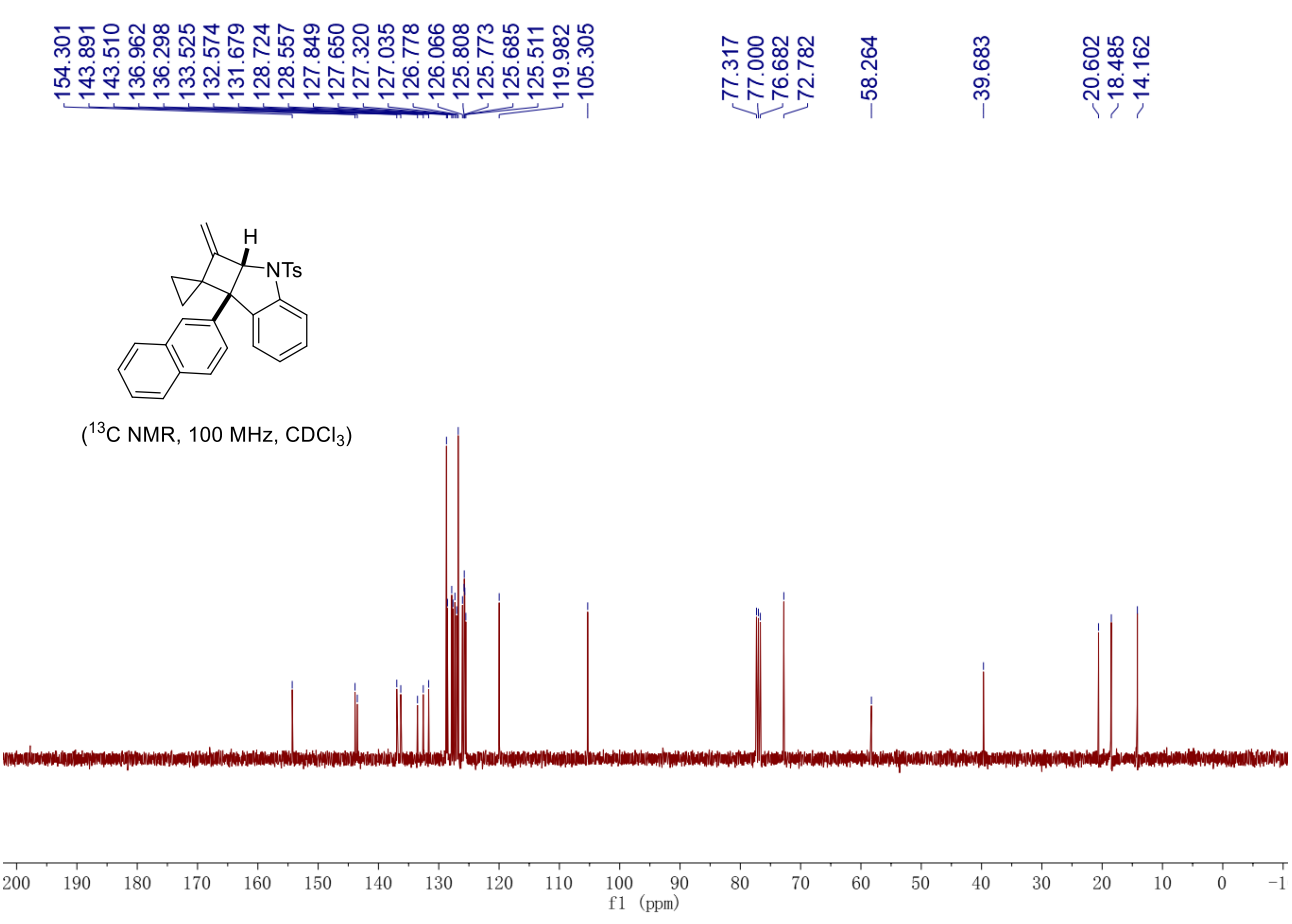




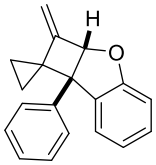
2-methylene-7b-(naphthalen-2-yl)-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2q**): Yield: 65 mg, 70%, white solid, m.p. >200 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.74 (m, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.52 – 7.45 (m, 1H), 7.45 – 7.37 (m, 3H), 7.34 (dd, J_1 = 8.6 Hz, J_2 = 1.6 Hz, 1H), 7.28 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.91 (s, 1H), 6.41 (d, *J* = 8.0 Hz, 2H), 5.32 (s, 2H), 4.80 (s, 1H), 1.57 (s, 3H), 1.13 – 1.03 (m, 1H), 0.95 – 0.84 (m, 1H), 0.83 – 0.73 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 154.3, 143.9, 143.5, 137.0, 136.3, 133.5, 132.6, 131.7, 128.7, 128.6, 127.8, 127.7, 127.3, 127.0, 126.8, 126.1, 125.8, 125.8, 125.7, 125.5, 120.0, 105.3, 72.8, 58.3, 39.7, 20.6, 18.5, 14.2; IR (neat): ν 3057, 2981, 1686, 1589, 1450, 1350, 1165, 1088, 1061, 886, 757 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 486.14982, found: 486.15059.



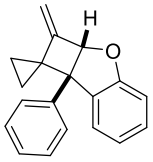
(^{1}H NMR, 400 MHz, $CDCl_3$)



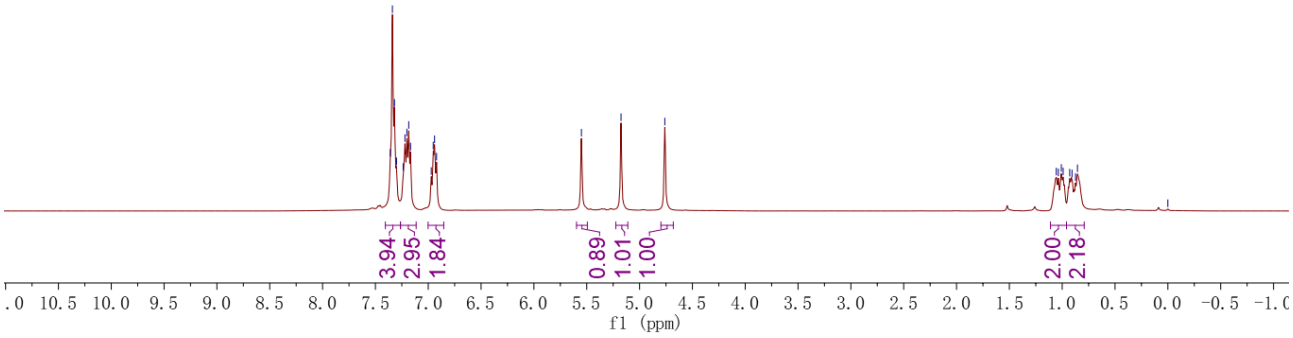
(^{13}C NMR, 100 MHz, $CDCl_3$)

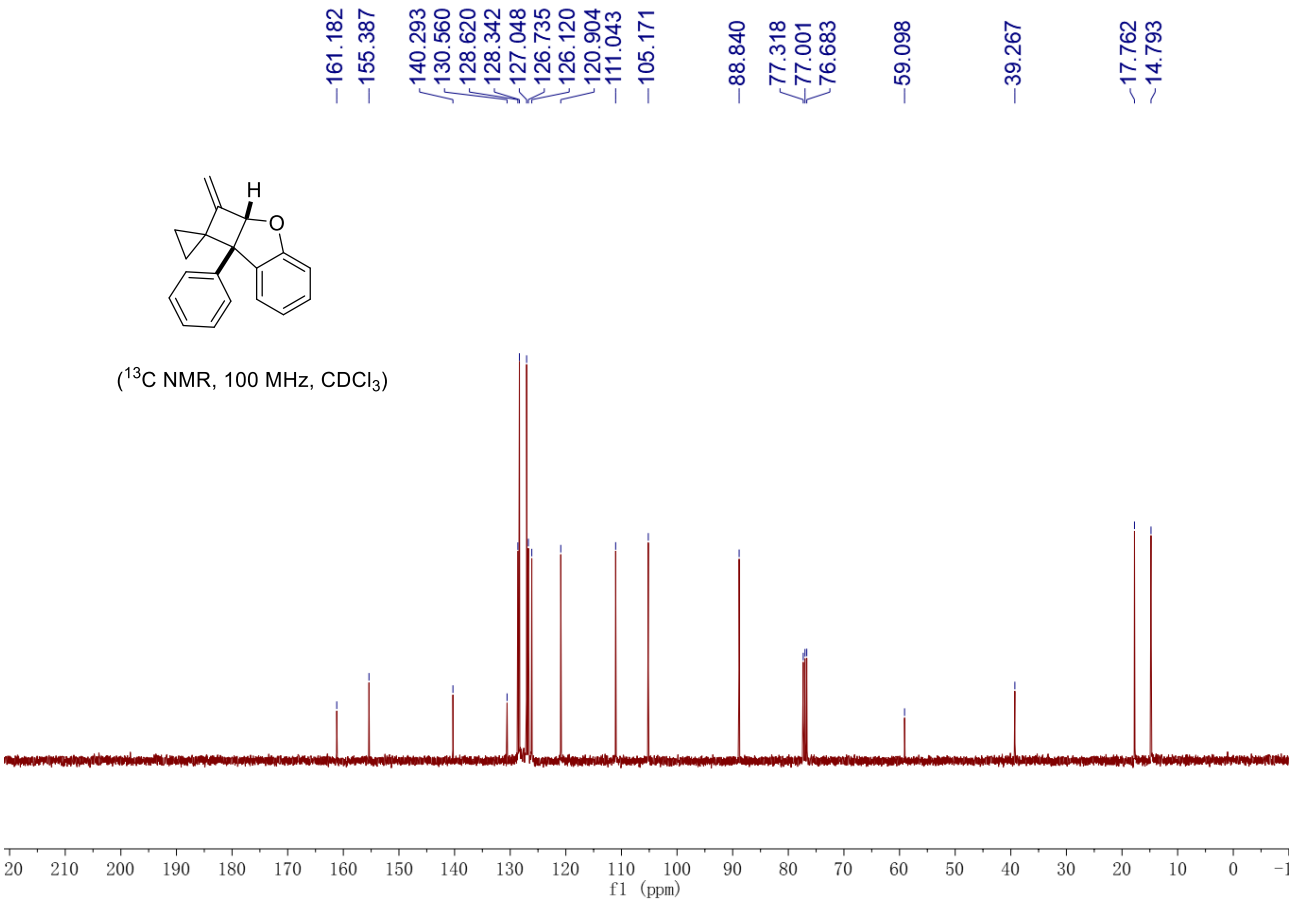


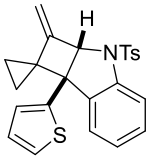
2-methylene-7b-phenyl-2a,7b-dihydro-2H-spiro[cyclobuta[*b*]benzofuran-1,1'-cyclopropane] (**2r**): Yield: 43 mg, 82%, white solid, m.p. 89-91 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.41 – 7.26 (m, 4H), 7.26 – 7.11 (m, 3H), 7.00 – 6.85 (m, 2H), 5.55 (s, 1H), 5.18 (s, 1H), 4.76 (s, 1H), 1.11 – 0.96 (m, 2H), 0.96 – 0.79 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 161.2, 155.4, 140.3, 130.6, 128.6, 128.3, 127.0, 126.7, 126.1, 120.9, 111.0, 105.2, 88.8, 59.1, 39.3, 17.8, 14.8; IR (neat): ν 3058, 2961, 2859, 1591, 1471, 1207, 1041, 1024, 760, 699 cm^{-1}; HRMS (EI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 260.1196, found: 260.1190.



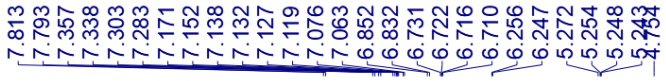
(^{1}H NMR, 400 MHz, $CDCl_3$)

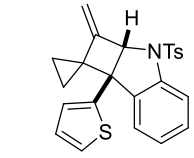



161.182
155.387
140.293
130.560
128.620
128.342
127.048
126.735
126.120
120.904
111.043
105.171
88.840
77.318
77.001
76.683
59.098
39.267
17.762
14.793
H
O
(^{13}C NMR, 100 MHz, $CDCl_3$)
f1 (ppm)

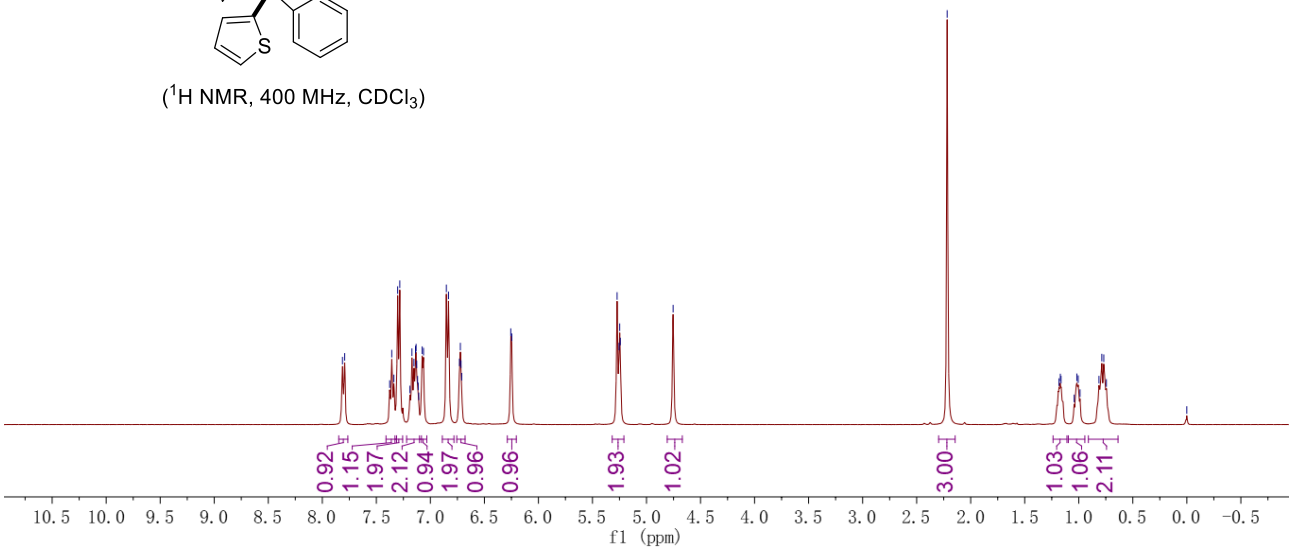


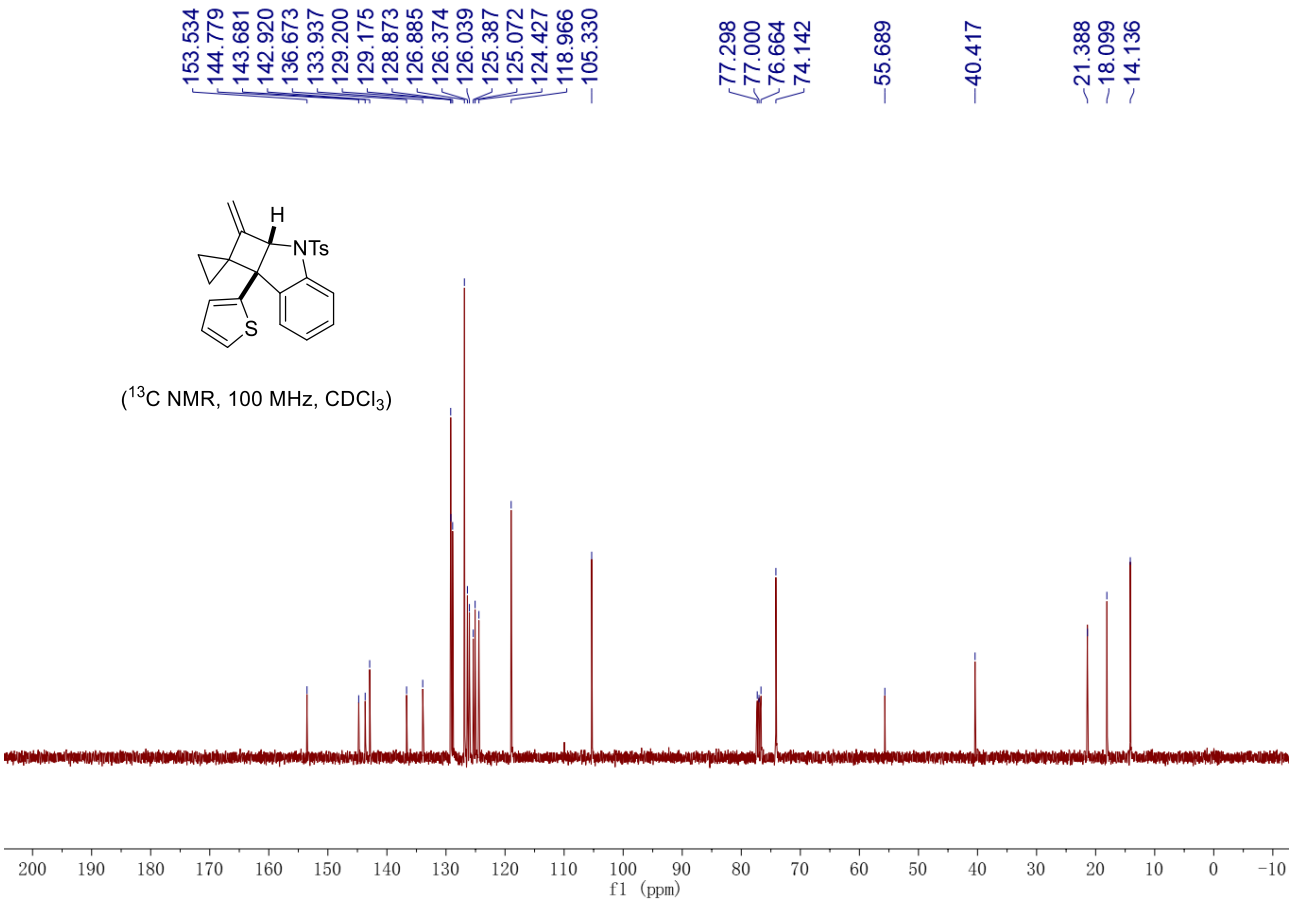
2-methylene-7b-(thiophen-2-yl)-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2s**): Yield: 63 mg, 75%, white solid, m.p. 164-166 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.08 (m, 2H), 7.07 (d, *J* = 5.2 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.76 – 6.68 (m, 1H), 6.25 (d, *J* = 3.4 Hz, 1H), 5.32 – 5.21 (m, 2H), 4.75 (s, 1H), 2.22 (s, 3H), 1.24 – 1.11 (m, 1H), 1.10 – 0.94 (m, 1H), 0.91 – 0.64 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 153.5, 144.8, 143.7, 142.9, 136.7, 133.9, 129.2, 129.2, 128.9, 126.9, 126.4, 126.0, 125.4, 125.1, 124.4, 119.0, 105.3, 74.1, 55.7, 40.4, 21.4, 18.1, 14.1; IR (neat): ν 3063, 2998, 2914, 1597, 1463, 1347, 1166, 1087, 1063, 882, 759, 683 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 442.09059, found: 442.09130.

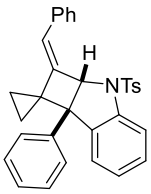




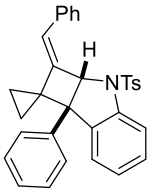
(^{1}H NMR, 400 MHz, $CDCl_3$)



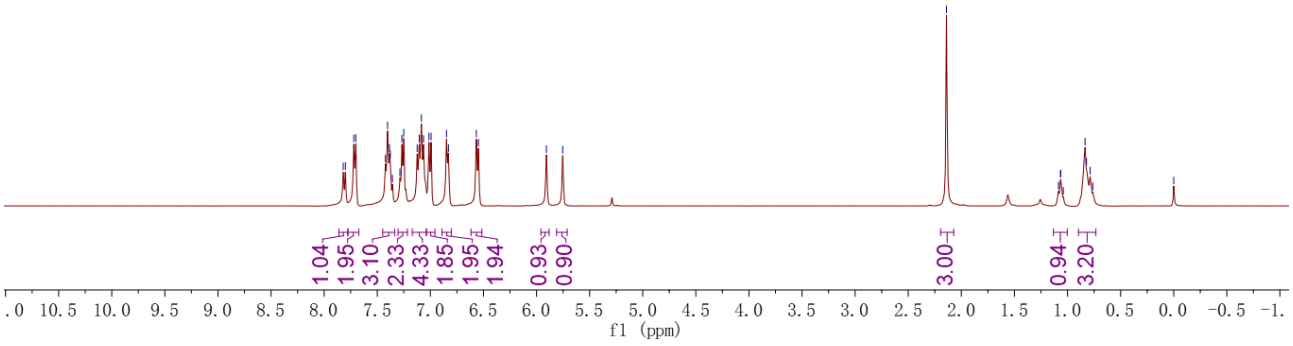

153.534
144.779
143.681
142.920
136.673
133.937
129.200
129.175
128.873
126.885
126.374
126.039
125.387
125.072
124.427
118.966
105.330
77.298
77.000
76.664
74.142
55.689
40.417
21.388
18.099
14.136
H
NTs
S
(13C NMR, 100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

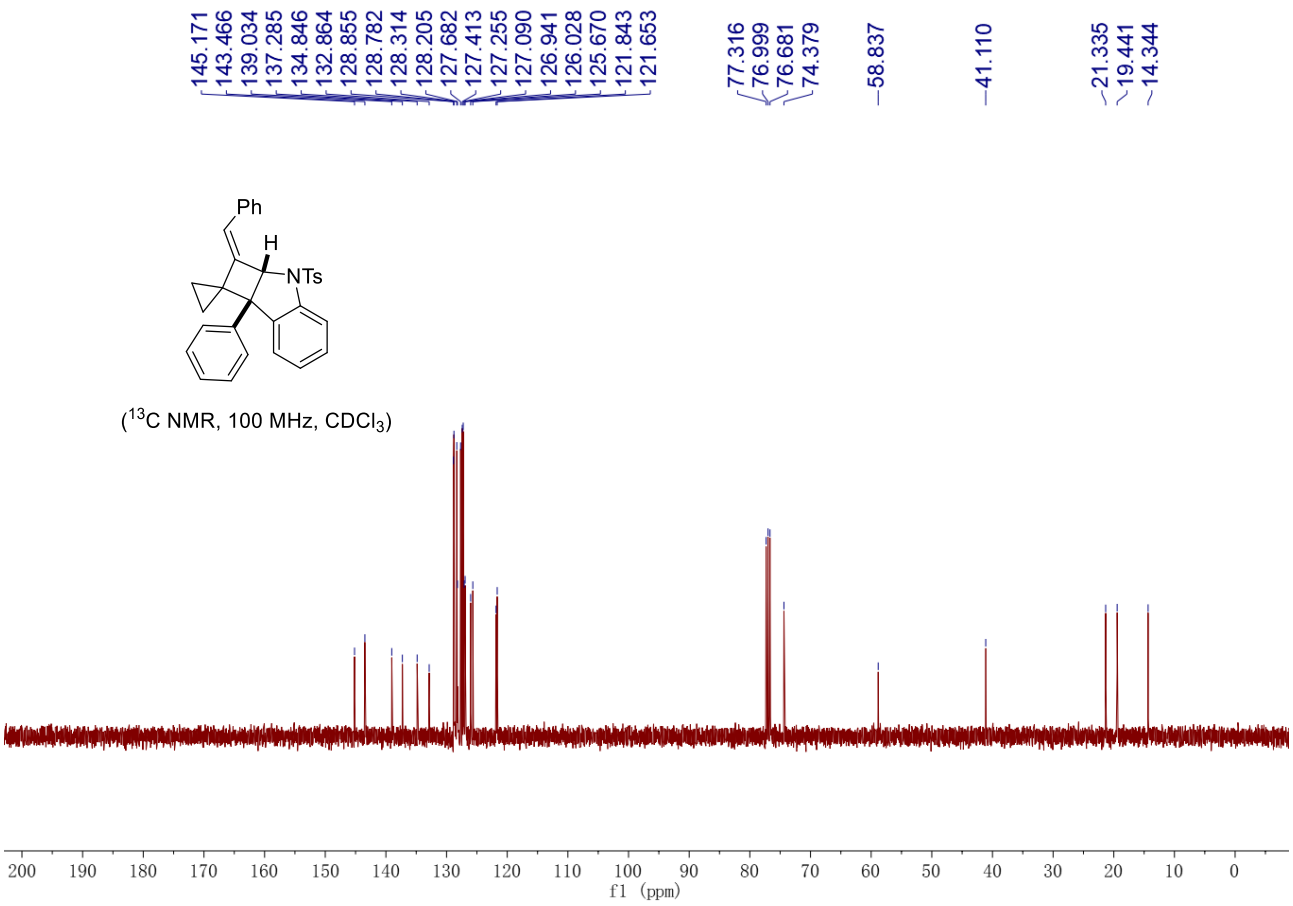


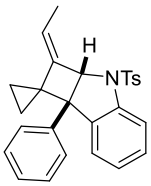
2-((Z)-benzylidene)-7b-phenyl-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2t**): Yield: 62 mg, 63%, white solid, m.p. >200 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.34 (m, 3H), 7.30 – 7.22 (m, 2H), 7.17 – 7.04 (m, 4H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 7.2 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 2H), 5.91 (s, 1H), 5.75 (s, 1H), 2.14 (s, 3H), 1.13 – 1.00 (m, 1H), 0.90 – 0.73 (m, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 145.2, 143.5, 139.0, 137.3, 134.8, 132.9, 128.9, 128.8, 128.3, 128.2, 127.7, 127.4, 127.3, 127.1, 126.9, 126.0, 125.7, 121.8, 121.7, 74.4, 58.8, 41.1, 21.3, 19.4, 14.3; IR (neat): ν 3050, 3024, 2919, 2852, 1589, 1453, 1350, 1167, 1088, 811, 752, 676 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 512.16547, found: 512.16534.



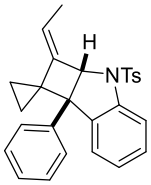
(^{1}H NMR, 400 MHz, $CDCl_3$)



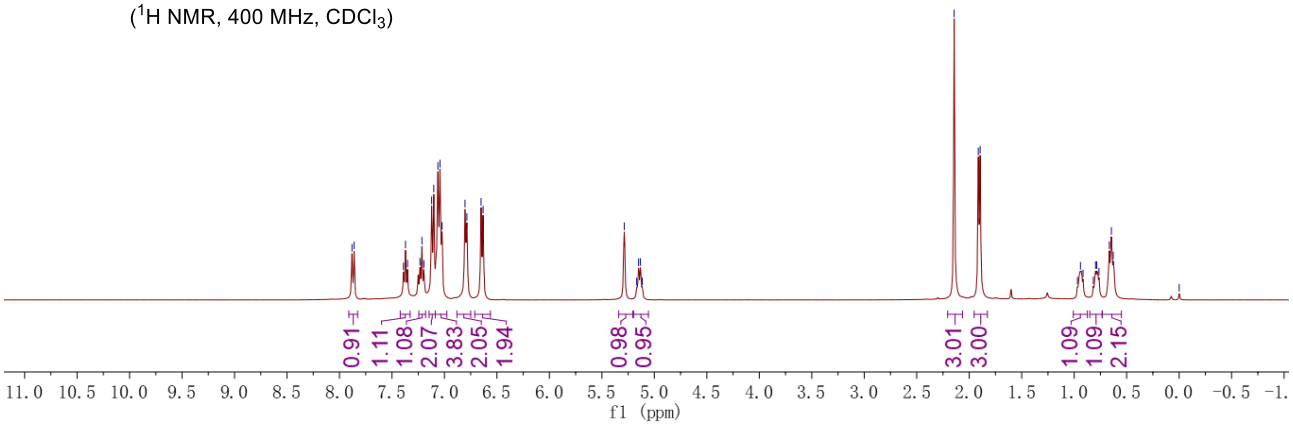

145.171
143.466
139.034
137.285
134.846
132.864
128.855
128.782
128.314
128.205
127.682
127.413
127.255
127.090
126.941
126.028
125.670
121.843
121.653
77.316
76.999
76.681
74.379
58.837
41.110
21.335
19.441
14.344
Ph
H
NTs
(13C NMR, 100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

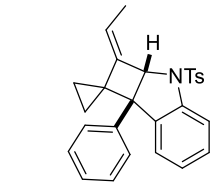


(Z)-2-ethylidene-7b-phenyl-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2u**): Yield: 26 mg, 30%, white solid, m.p. >200 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.09 – 6.98 (m, 4H), 6.80 (d, *J* = 7.2 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 2H), 5.29 (s, 1H), 5.14 (q, *J* = 7.2 Hz, 1H), 2.14 (s, 3H), 1.90 (d, *J* = 7.2 Hz, 3H), 1.01 – 0.87 (m, 1H), 0.85 – 0.73 (m, 1H), 0.73 – 0.55 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 143.5, 143.4, 143.2, 139.9, 136.8, 133.3, 129.0, 128.3, 127.7, 127.3, 127.0, 126.9, 125.7, 125.5, 120.4, 117.3, 72.8, 57.8, 39.4, 21.4, 18.0, 14.1, 13.3; IR (neat): ν 3047, 2979, 2919, 1594, 1456, 1351, 1168, 1153, 1089, 1059, 812, 757, 672 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 450.14982, found: 450.14975.

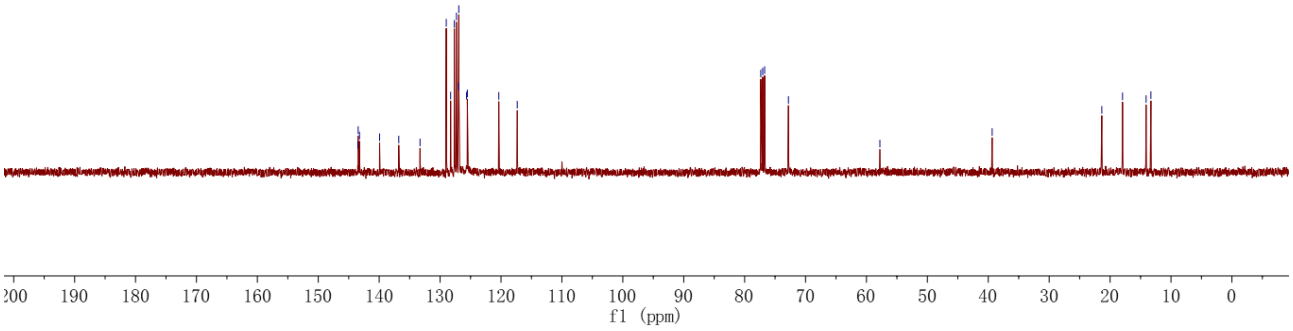


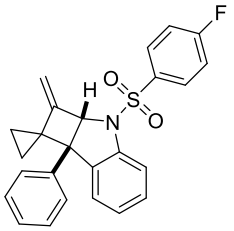
(^{1}H NMR, 400 MHz, $CDCl_3$)



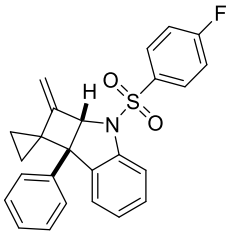


(^{13}C NMR, 100 MHz, $CDCl_3$)

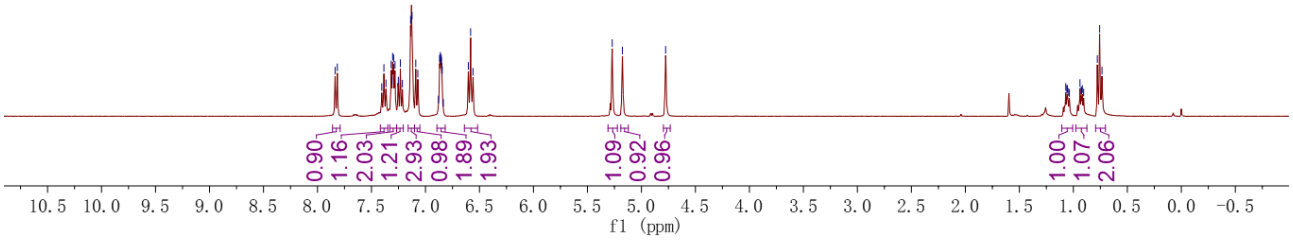


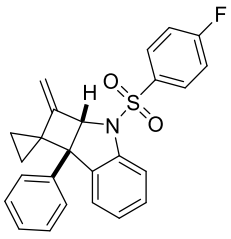


3-((4-fluorophenyl)sulfonyl)-2-methylene-7b-phenyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2v**): Yield: 54 mg, 65%, white solid, m.p. 169-171 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.83 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.16 – 7.10 (m, 3H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.58 (t, *J* = 8.4 Hz, 2H), 5.27 (s, 1H), 5.18 (s, 1H), 4.78 (s, 1H), 1.11 – 1.01 (m, 1H), 0.98 – 0.87 (m, 1H), 0.79 – 0.70 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 165.2 (d, *J* = 253.5 Hz), 154.1, 143.1, 139.7, 136.3, 132.8 (d, *J* = 3.1 Hz), 129.6 (d, *J* = 9.5 Hz), 128.5, 128.0, 127.1, 127.1, 126.3, 125.7, 119.7, 115.7 (d, *J* = 22.4 Hz), 105.4, 73.3, 58.0, 39.8, 18.5, 14.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.0; IR (neat): ν 3047, 2974, 2927, 1589, 1492, 1359, 1239, 1172, 1153, 1087, 893, 782, 677 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 440.10910, found: 440.10913.

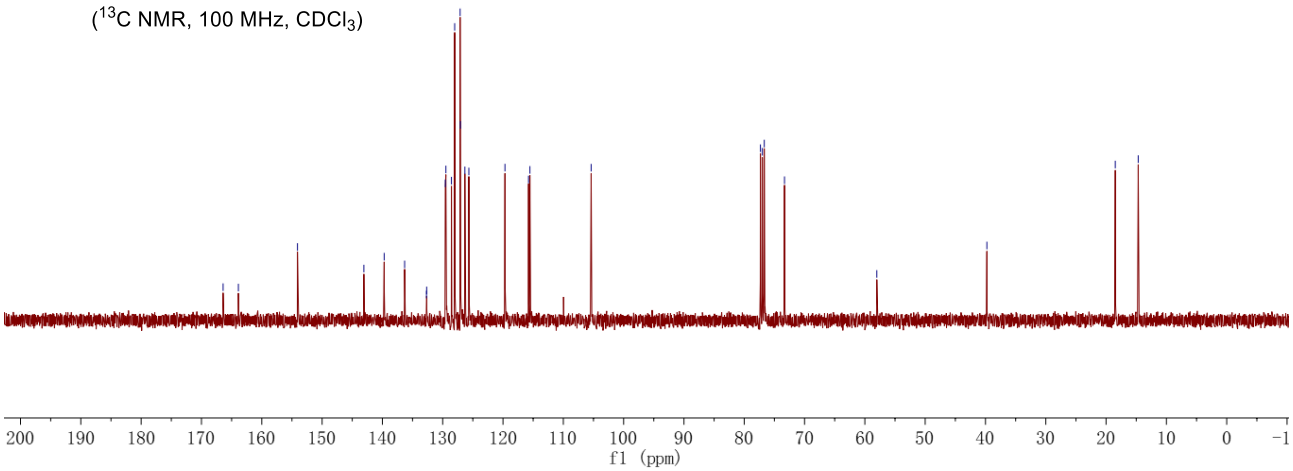


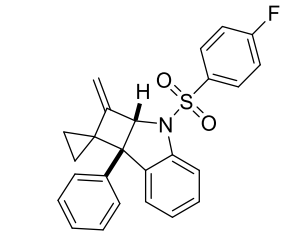
(^{1}H NMR, 400 MHz, $CDCl_3$)



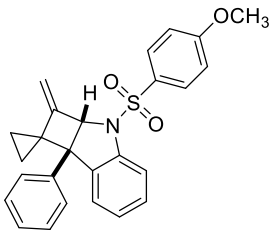


(^{13}C NMR, 100 MHz, $CDCl_3$)

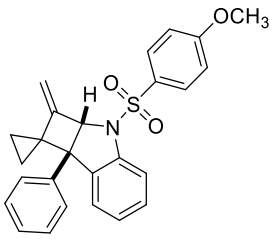




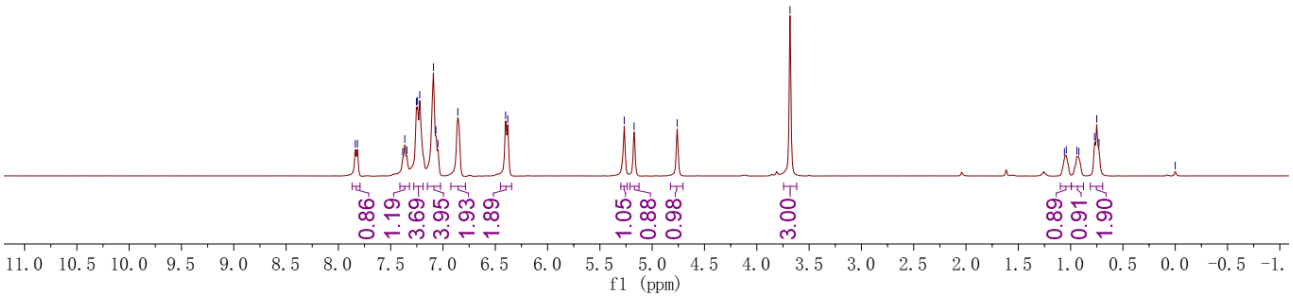
(^{19}F NMR, 376 MHz, $CDCl_3$)

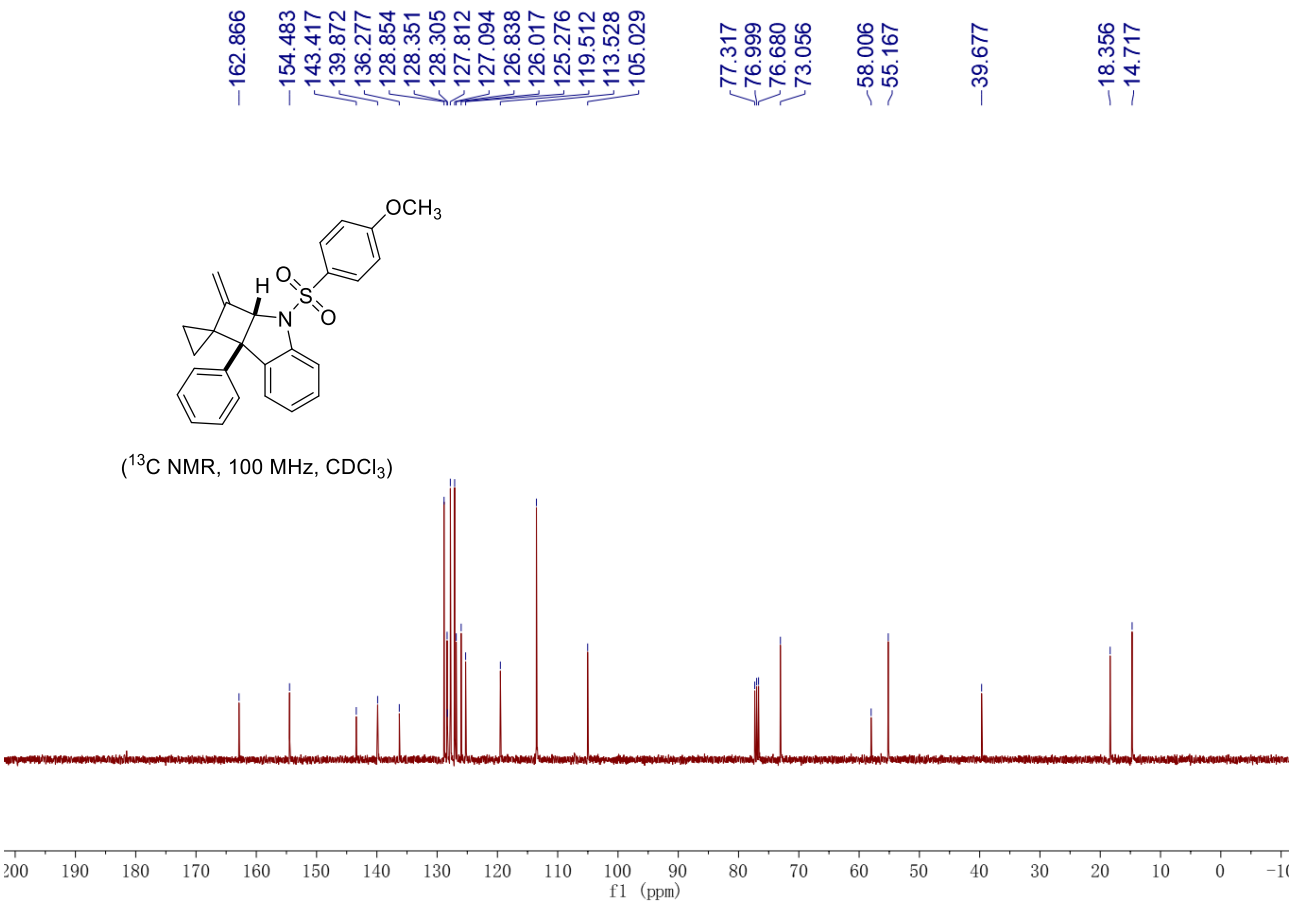


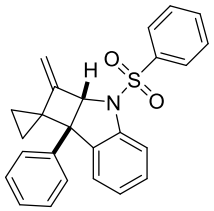
3-((4-methoxyphenyl)sulfonyl)-2-methylene-7b-phenyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2W**): Yield: 54 mg, 63%, white solid, m.p. 177-179 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.28 – 7.19 (m, 3H), 7.08 (m, 4H), 6.86 (m, 2H), 6.39 (d, *J* = 8.4 Hz, 2H), 5.27 (s, 1H), 5.17 (s, 1H), 4.76 (s, 1H), 3.68 (s, 3H), 1.05 (m, 1H), 0.93 (m, 1H), 0.75 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 162.9, 154.5, 143.4, 139.9, 136.3, 128.9, 128.4, 128.3, 127.8, 127.1, 126.8, 126.0, 125.3, 119.5, 113.5, 105.0, 73.1, 58.0, 55.2, 39.7, 18.4, 14.7; IR (neat): ν 3066, 2979, 2961, 1589, 1492, 1349, 1262, 1088, 1028, 834, 759, 679 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 452.12909, found: 452.12975.



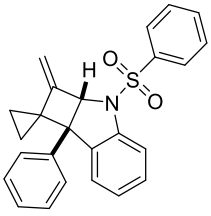
(^{1}H NMR, 400 MHz, $CDCl_3$)



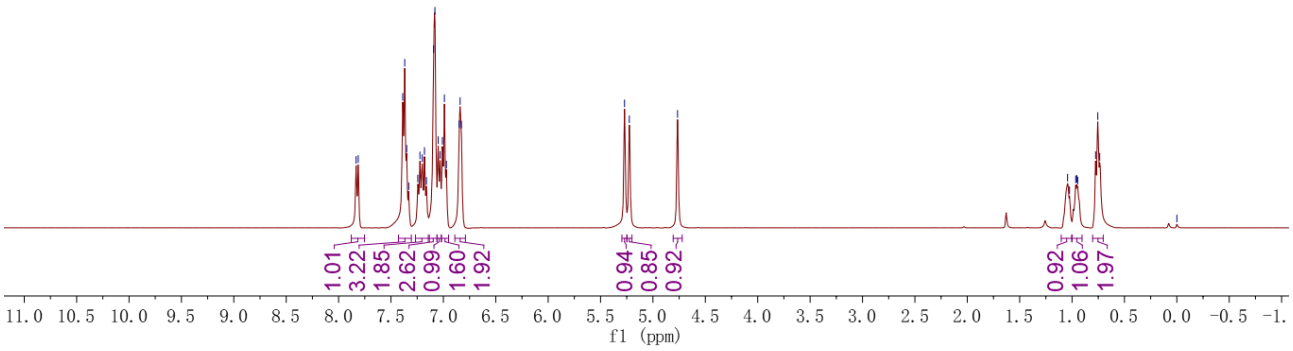

162.866
154.483
143.417
139.872
136.277
128.854
128.351
128.305
127.812
127.094
126.838
126.017
125.276
119.512
113.528
105.029
77.317
76.999
76.680
73.056
58.006
55.167
39.677
18.356
14.717
OCH3
H
O
S
O
N
O
(13C NMR, 100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

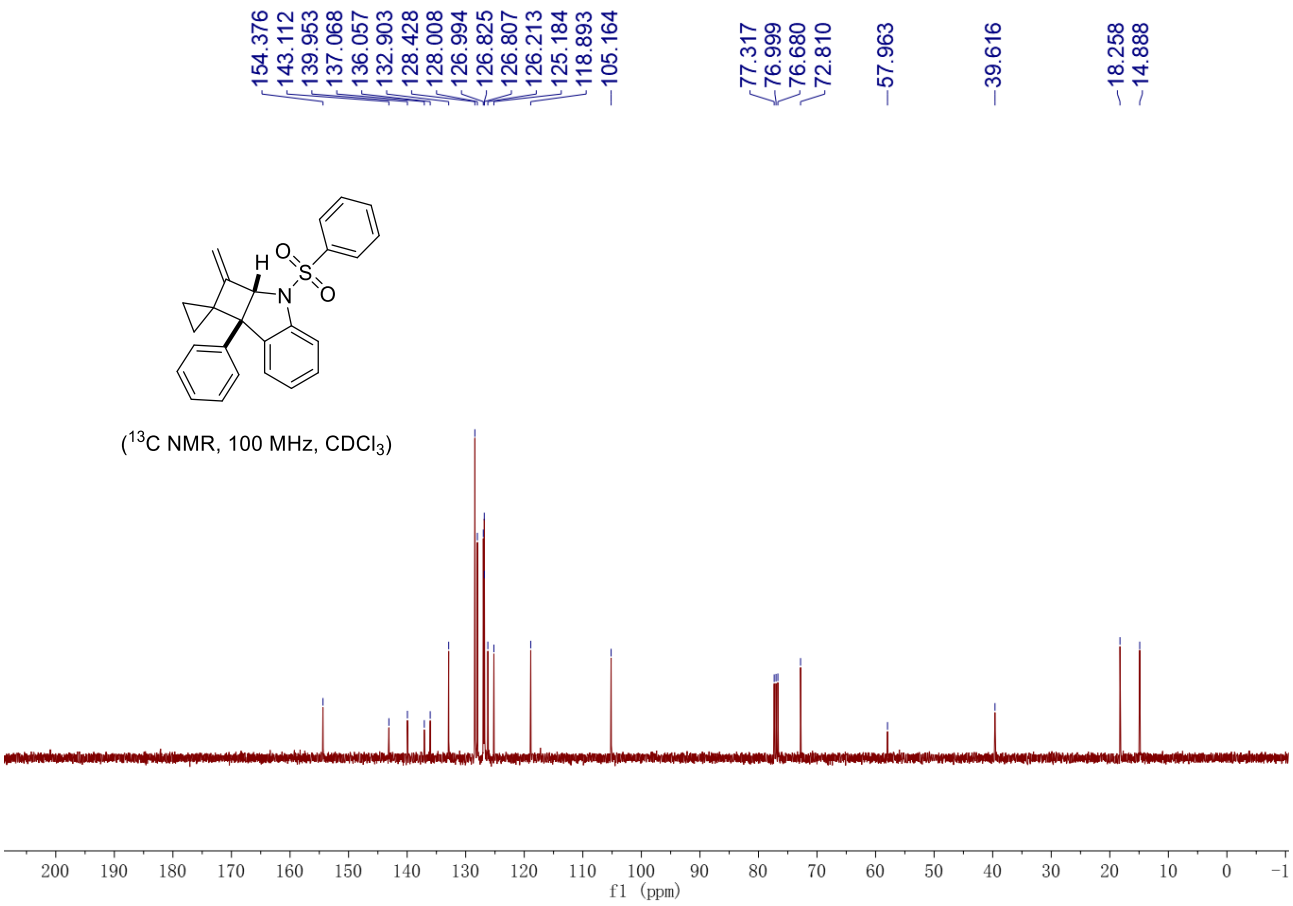


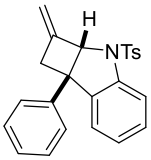
2-methylene-7b-phenyl-3-(phenylsulfonyl)-2,2a,3,7b-tetrahydrospiro[cyclobuta[*b*]indole-1,1'-cyclopropane] (**2x**): Yield: 52 mg, 65%, white solid, m.p. 171-173 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.82 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.31 (m, 3H), 7.27 – 7.14 (m, 2H), 7.09 (m, 3H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 8.0 Hz, 2H), 6.89 – 6.79 (m, 2H), 5.27 (s, 1H), 5.23 (s, 1H), 4.77 (s, 1H), 1.10 – 1.00 (m, 1H), 1.00 – 0.91 (m, 1H), 0.80 – 0.70 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 154.4, 143.1, 140.0, 137.1, 136.1, 132.9, 128.4, 128.0, 127.0, 126.8, 126.8, 126.2, 125.2, 118.9, 105.2, 72.8, 58.0, 39.6, 18.3, 14.9; IR (neat): ν 3058, 3003, 2922, 1597, 1448, 1352, 1168, 1089, 1050, 1027, 914, 890, 740, 685 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 422.11852, found: 422.11780.



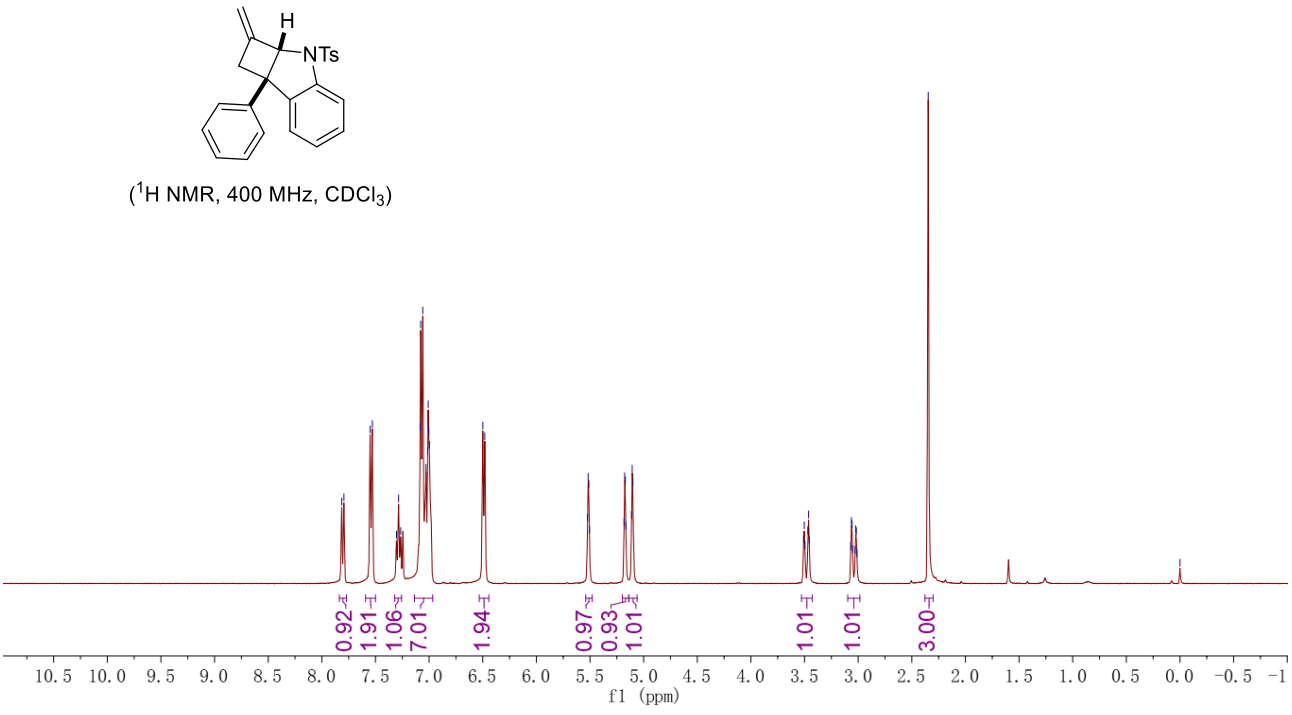
(^{1}H NMR, 400 MHz, $CDCl_3$)

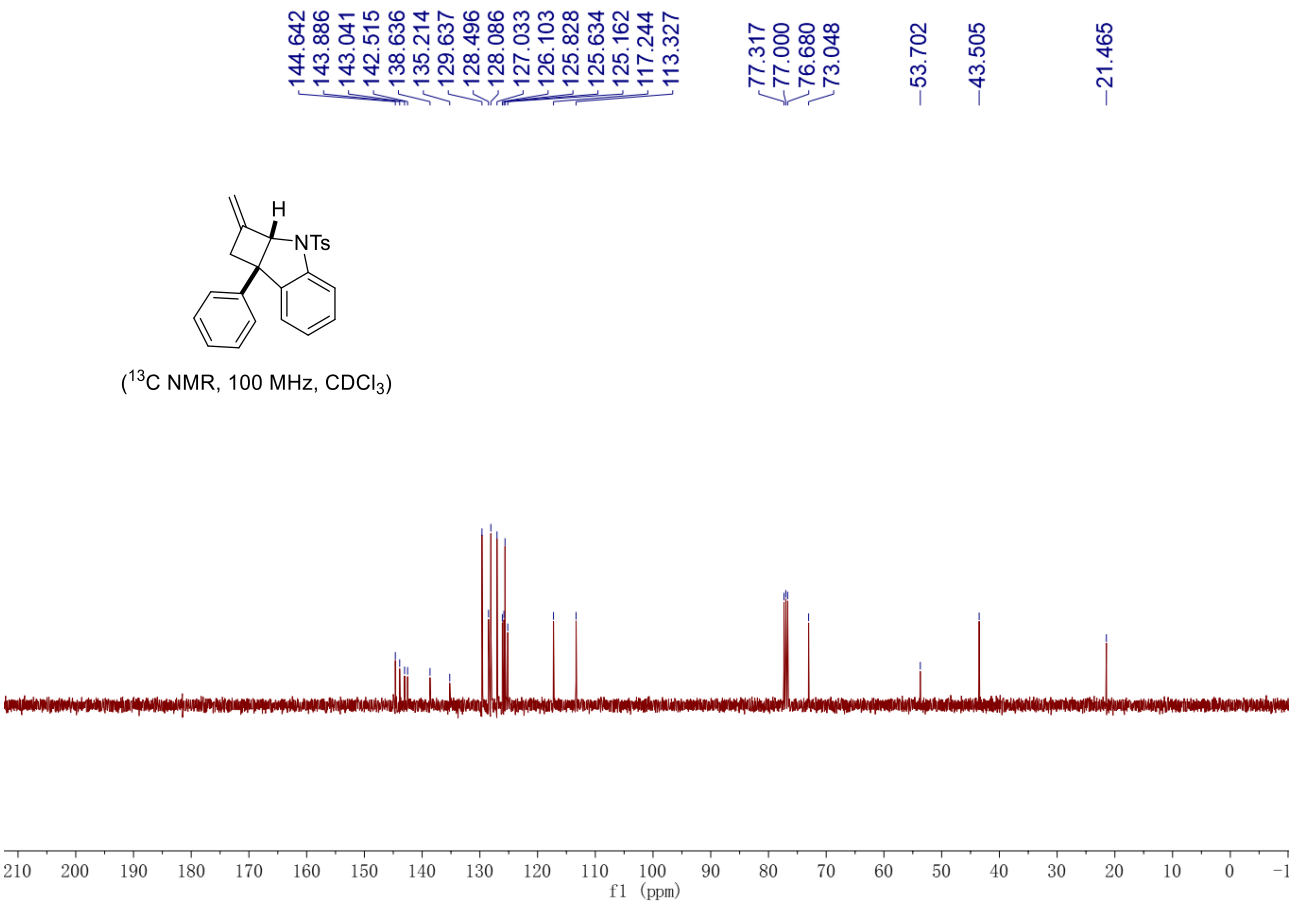



154.376
143.112
139.953
137.068
136.057
132.903
128.428
128.008
126.994
126.825
126.807
126.213
125.184
118.893
105.164
77.317
76.999
76.680
72.810
57.963
39.616
18.258
14.888
H
O
S
O
N
(^{13}C NMR, 100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

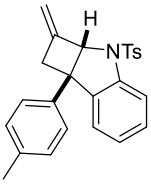


2-methylene-7b-phenyl-3-tosyl-2,2a,3,7b-tetrahydro-1*H*-cyclobuta[*b*]indole (**2aa**): Yield: 63 mg, 81%, white solid, m.p. 152-154 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.14 – 6.97 (m, 7H), 6.49 (d, *J* = 7.2 Hz, 2H), 5.51 (dd, J_1= 2.8Hz, J_2 = 2.4 Hz, 1H), 5.20 – 5.14 (m, 1H), 5.14 – 5.06 (m, 1H), 3.48 (dt, J_1= 16 Hz, J_2 = 2.8 Hz, 1H), 3.04 (dq, J_1 = 16 Hz, J_2 = 2.4 Hz, 1H), 2.35 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 144.6, 143.9, 143.0, 142.5, 138.6, 135.2, 129.6, 128.5, 128.1, 127.0, 126.1, 125.8, 125.6, 125.2, 117.2, 113.3, 73.0, 53.7, 43.5, 21.5; IR (neat): ν 3052, 3026, 2925, 1597, 1471, 1356, 1091, 1028, 758, 678 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 410.11852, found: 410.11897.

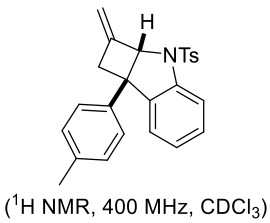




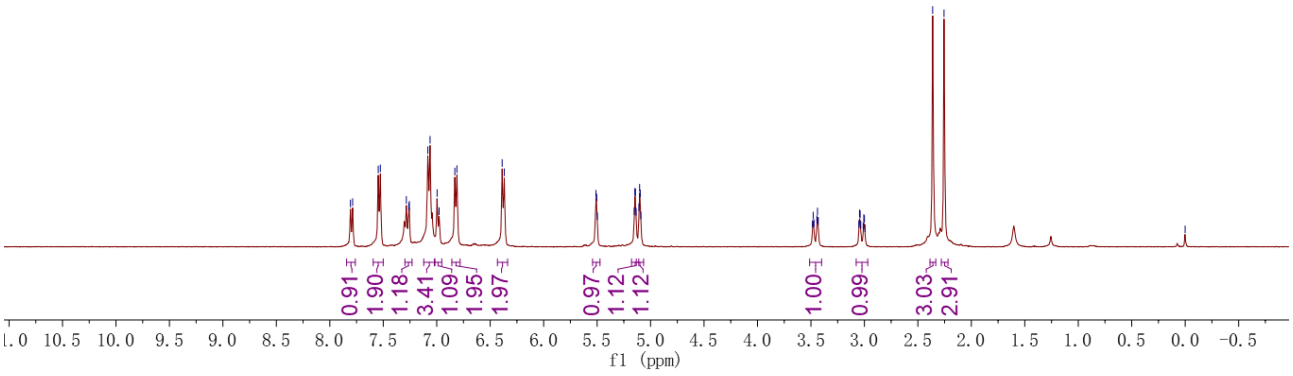
(^{13}C NMR, 100 MHz, $CDCl_3$)

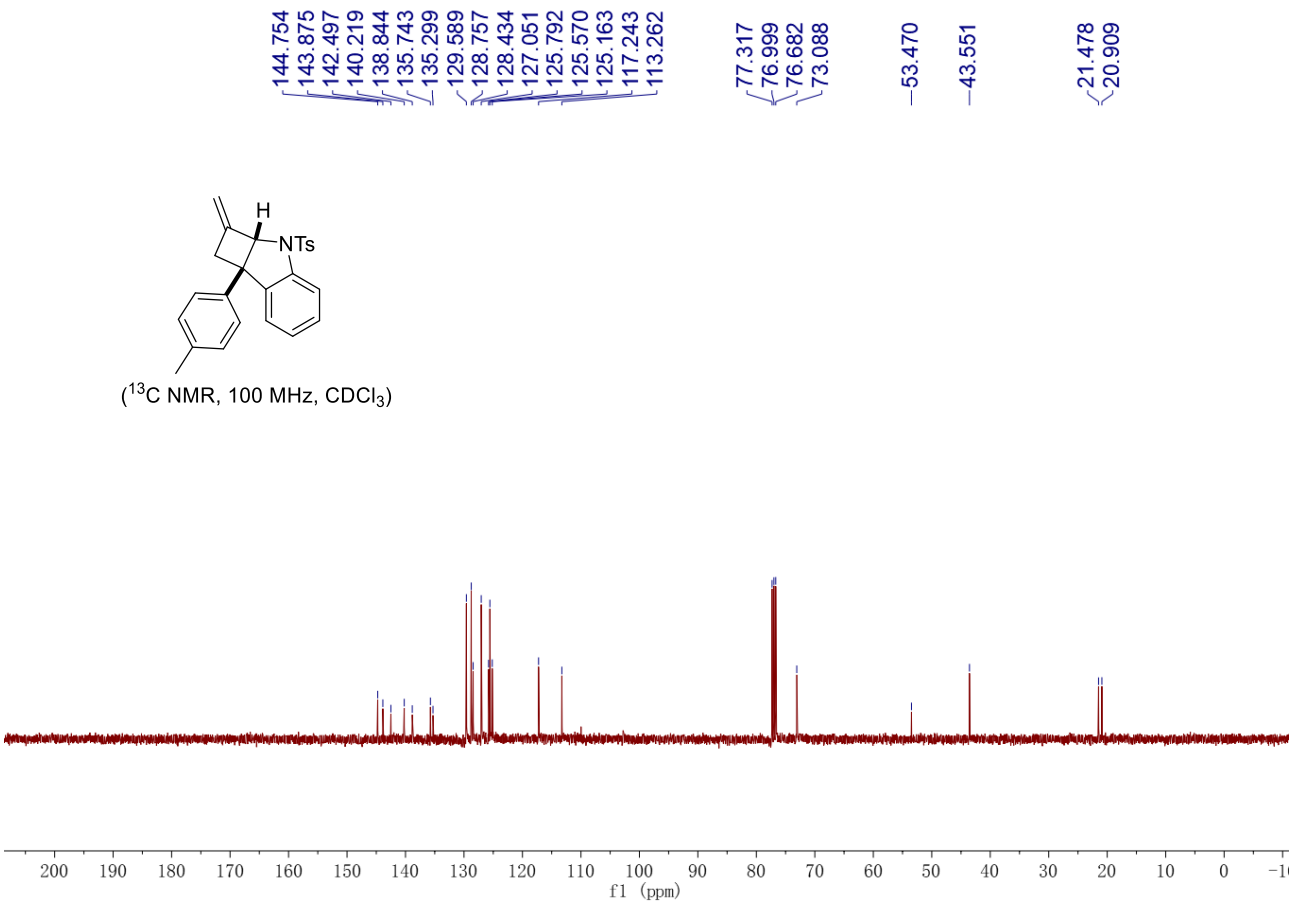


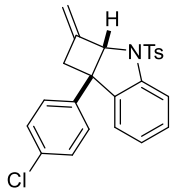
2-methylene-7b-(*p*-tolyl)-3-tosyl-2,2a,3,7b-tetrahydro-1*H*-cyclobuta[*b*]indole (**2ab**): Yield: 68 mg, 85%, white solid, m.p. 156-158 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.31 – 7.23 (m, 1H), 7.07 (m, 3H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.38 (d, *J* = 8.0 Hz, 2H), 5.51 (dd, J_1 = 2.8 Hz, J_2 = 2.4 Hz, 1H), 5.14 (q, *J* = 2.4 Hz, 1H), 5.10 (q, *J* = 2.4 Hz, 1H), 3.46 (dt, J_1 = 16.0 Hz, J_2 = 2.8 Hz, 1H), 3.02 (dq, J_1 = 16.0 Hz, J_2 = 2.4 Hz, 1H), 2.36 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 144.8, 143.9, 142.5, 140.2, 138.8, 135.7, 135.3, 129.6, 128.8, 128.4, 127.1, 125.8, 125.6, 125.2, 117.2, 113.3, 73.1, 53.5, 43.6, 21.5, 20.9; IR (neat): ν 3026, 2945, 2924, 2845, 1589, 1508, 1450, 1351, 1086, 1055, 935, 810, 763, 684 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 424.13417, found: 424.13473.



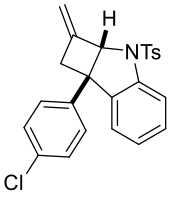
(^{1}H NMR, 400 MHz, $CDCl_3$)



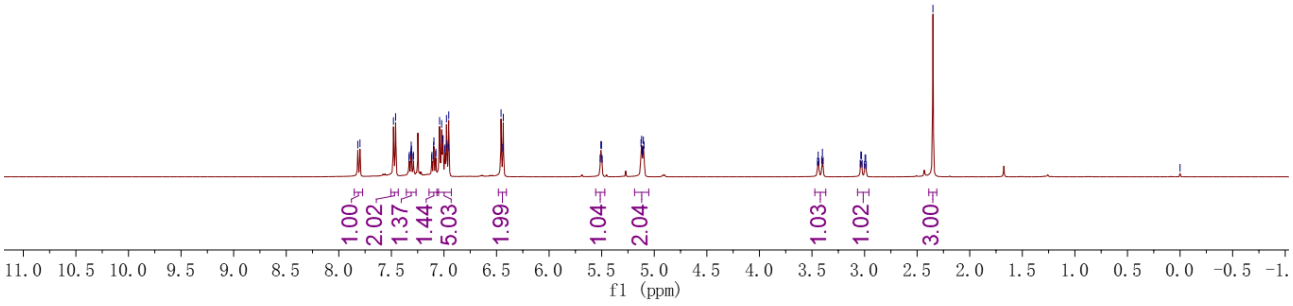

144.754
143.875
142.497
140.219
138.844
135.743
135.299
129.589
128.757
128.434
127.051
125.792
125.570
125.163
117.243
113.262
77.317
76.999
76.682
73.088
53.470
43.551
21.478
20.909
H
NTs
(13C NMR, 100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

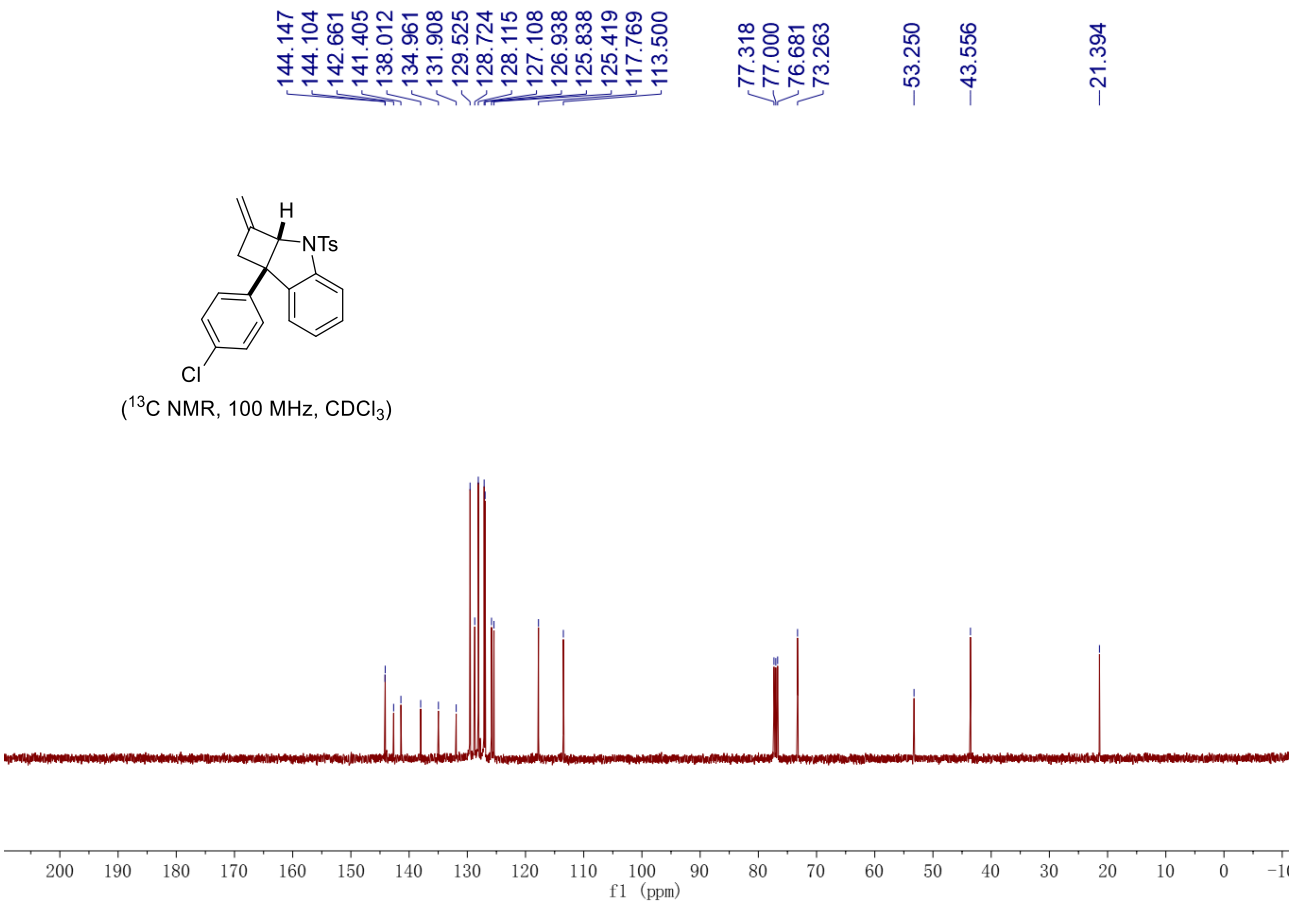


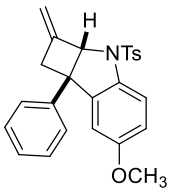
7b-(4-chlorophenyl)-2-methylene-3-tosyl-2,2a,3,7b-tetrahydro-1*H*-cyclobuta[*b*]indole (**2ac**): Yield: 60 mg, 71%, white solid, m.p. 129-131 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.31 (m, 1H), 7.10 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.07 – 6.93 (m, 5H), 6.48 – 6.41 (m, 2H), 5.51 (dd, J_1 = 2.8 Hz, J_2 = 2.4 Hz, 1H), 5.19 – 5.05 (m, 2H), 3.42 (dt, J_1 = 16.0 Hz, J_2 = 2.8 Hz, 1H), 3.01 (dq, J_1 = 16.0 Hz, J_2 = 2.4 Hz, 1H), 2.35 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 144.1, 144.1, 142.7, 141.4, 138.0, 135.0, 131.9, 129.5, 128.7, 128.1, 127.1, 126.9, 125.8, 125.4, 117.8, 113.5, 73.3, 53.3, 43.6, 21.4; IR (neat): ν 3066, 2953, 2917, 1594, 1487, 1350, 1163, 1089, 1070, 933, 820, 742, 658 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 444.07955, found: 444.07866.



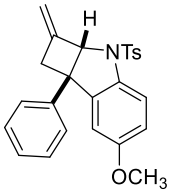
(^{1}H NMR, 400 MHz, $CDCl_3$)



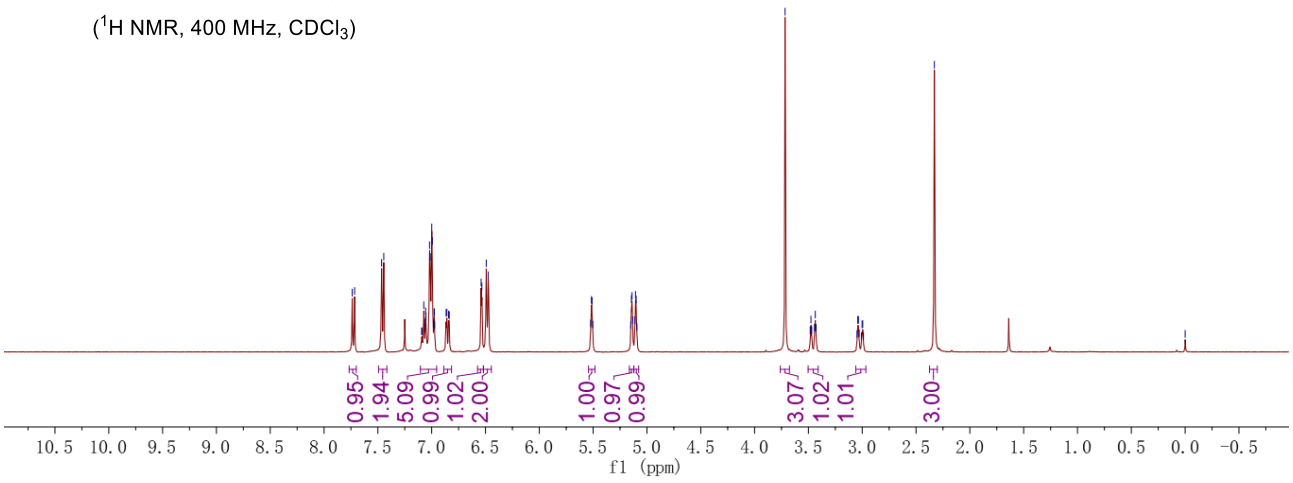

144.147
144.104
142.661
141.405
138.012
134.961
131.908
129.525
128.724
128.115
127.108
126.938
125.838
125.419
117.769
113.500
77.318
77.000
76.681
73.263
53.250
43.556
21.394
H
NTs
Cl
(13C NMR, 100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

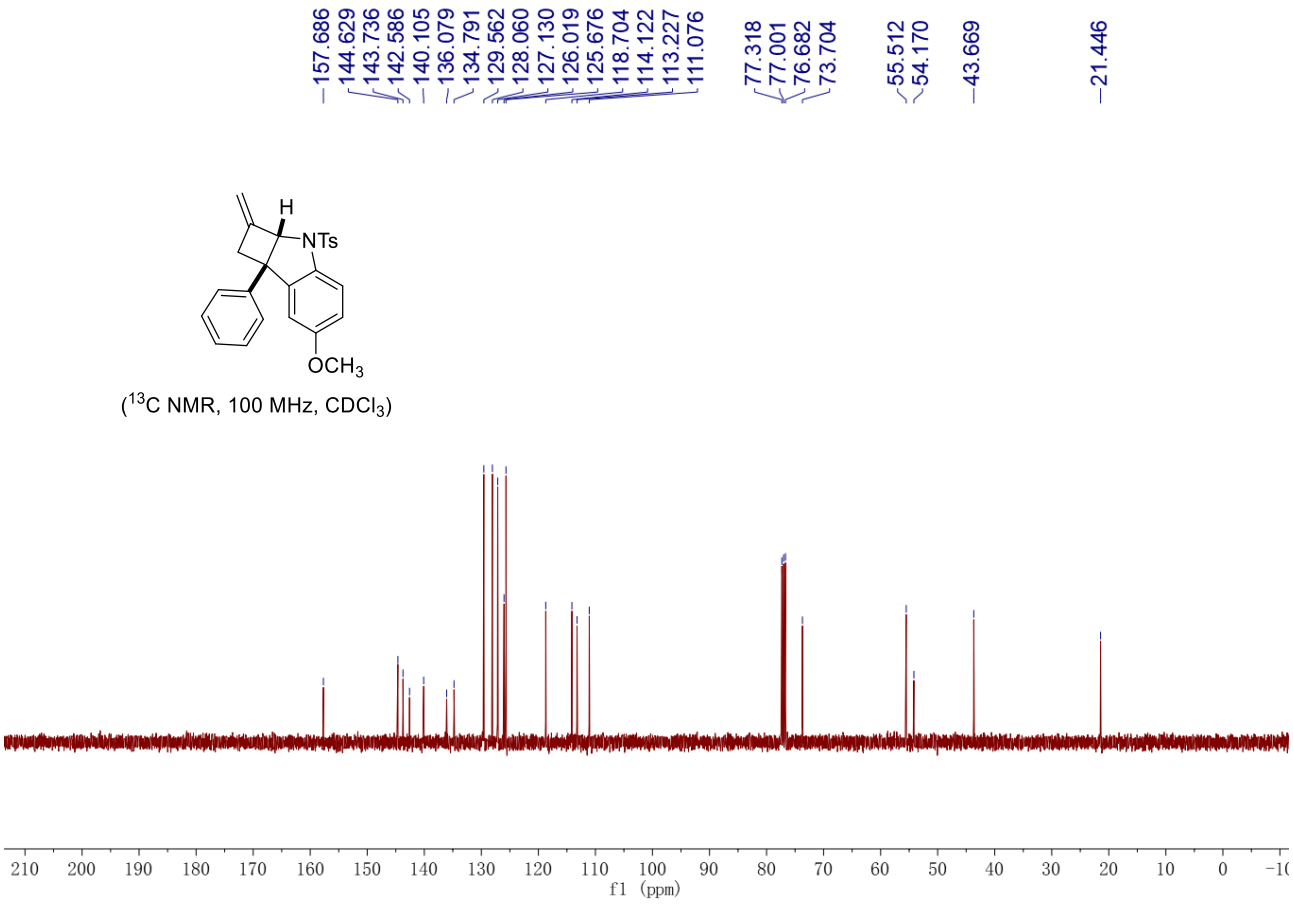


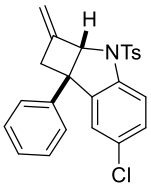
6-methoxy-2-methylene-7b-phenyl-3-tosyl-2,2a,3,7b-tetrahydro-1*H*-cyclobuta[*b*]indole (**2ad**): Yield: 51 mg, 61%, white solid, m.p. 151-153 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.11 – 6.95 (m, 5H), 6.85 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 6.54 (d, *J* = 2.8 Hz, 1H), 6.48 (d, *J* = 7.2 Hz, 2H), 5.51 (dd, J_1= 2.8Hz, J_2 = 2.4 Hz, 1H), 5.16 – 5.12 (m, 1H), 5.12 – 5.08 (m, 1H), 3.72 (s, 3H), 3.46 (dt, J_1= 16.0 Hz, J_2 = 2.8 Hz, 1H), 3.02 (dq, J_1 = 16.0 Hz, J_2 = 2.4 Hz, 1H), 2.33 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 157.7, 144.6, 143.7, 142.6, 140.1, 136.1, 134.8, 129.6, 128.1, 127.1, 126.0, 125.7, 118.7, 114.1, 113.2, 111.1, 73.7, 55.5, 54.2, 43.7, 21.4; IR (neat): ν 3050, 2956, 2917, 1597, 1482, 1351, 1210, 1165, 1077, 1027, 902, 812, 699 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 440.12909, found: 440.12864.



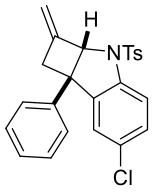
(^{1}H NMR, 400 MHz, $CDCl_3$)



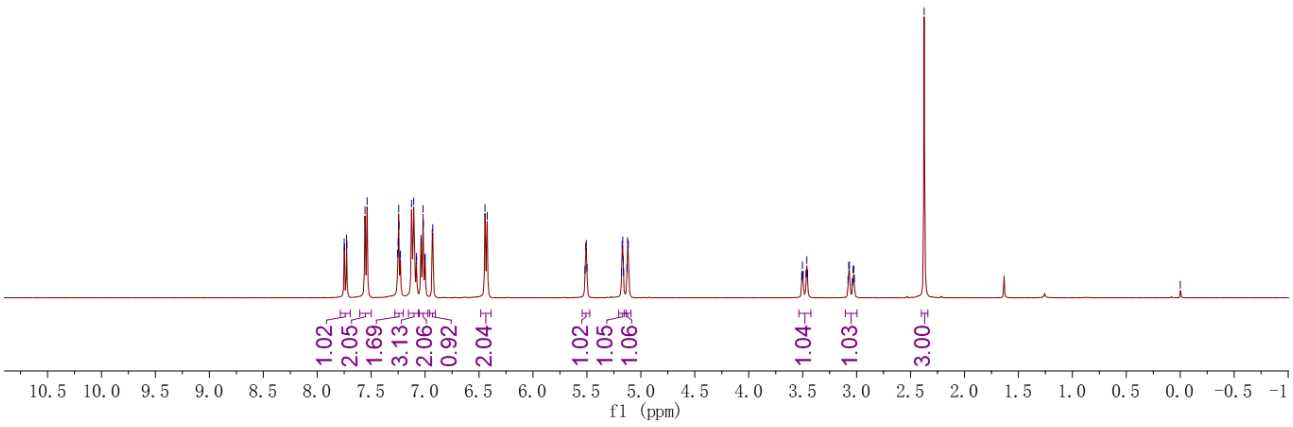

157.686
144.629
143.736
142.586
140.105
136.079
134.791
129.562
128.060
127.130
126.019
125.676
118.704
114.122
113.227
111.076
77.318
77.001
76.682
73.704
55.512
54.170
43.669
21.446
H
NTs
OCH3
(13C NMR, 100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

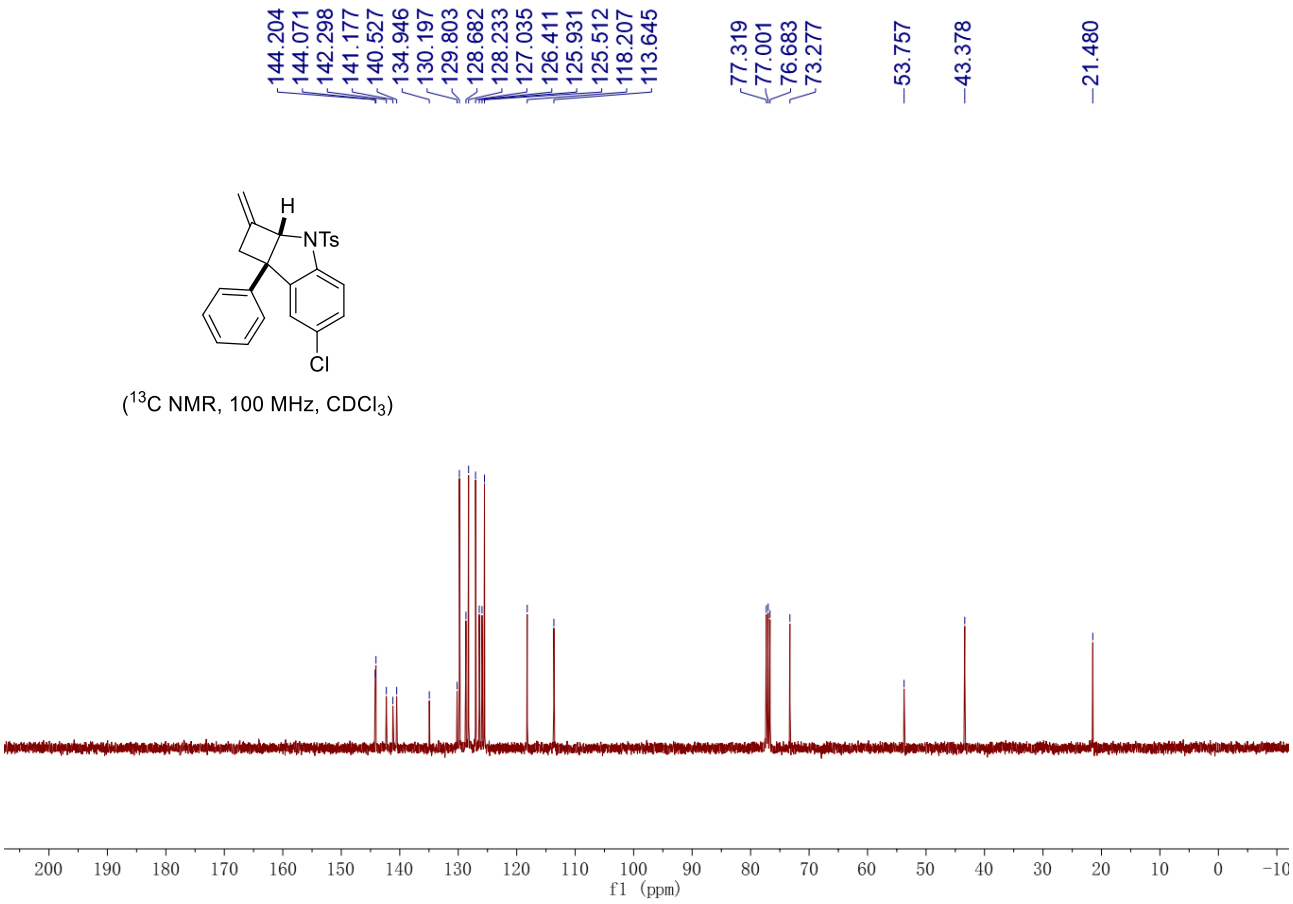


6-chloro-2-methylene-7b-phenyl-3-tosyl-2,2a,3,7b-tetrahydro-1*H*-cyclobuta[*b*]indole (**2ae**): Yield: 66 mg, 78%, white solid, m.p. 152-154 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.74 (dd, J_1 = 8.8 Hz, J_2 = 1.2 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.24 (m, 2H), 7.15 – 7.05 (m, 3H), 7.02 (td, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 2H), 6.93 (d, J = 2.0 Hz, 1H), 6.43 (d, J = 8.4 Hz, 2H), 5.51 (dd, J_1 = 2.8 Hz, J_2 = 2.4 Hz, 1H), 5.17 (m, 1H), 5.12 (m, 1H), 3.48 (dt, J_1 = 16.0 Hz, J_2 = 2.8 Hz, 1H), 3.05 (dq, J_1 = 16.0 Hz, J_2 = 2.4 Hz, 1H), 2.37 (s, 3H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 144.2, 144.1, 142.3, 141.2, 140.5, 134.9, 130.2, 129.8, 128.7, 128.2, 127.0, 126.4, 125.9, 125.5, 118.2, 113.6, 73.3, 53.8, 43.4, 21.5; IR (neat): ν 3058, 2969, 2922, 1597, 1463, 1354, 1164, 1090, 897, 697 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 444.07955, found: 444.07914.

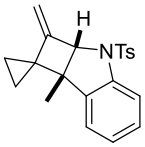


(^{1}H NMR, 400 MHz, $CDCl_3$)

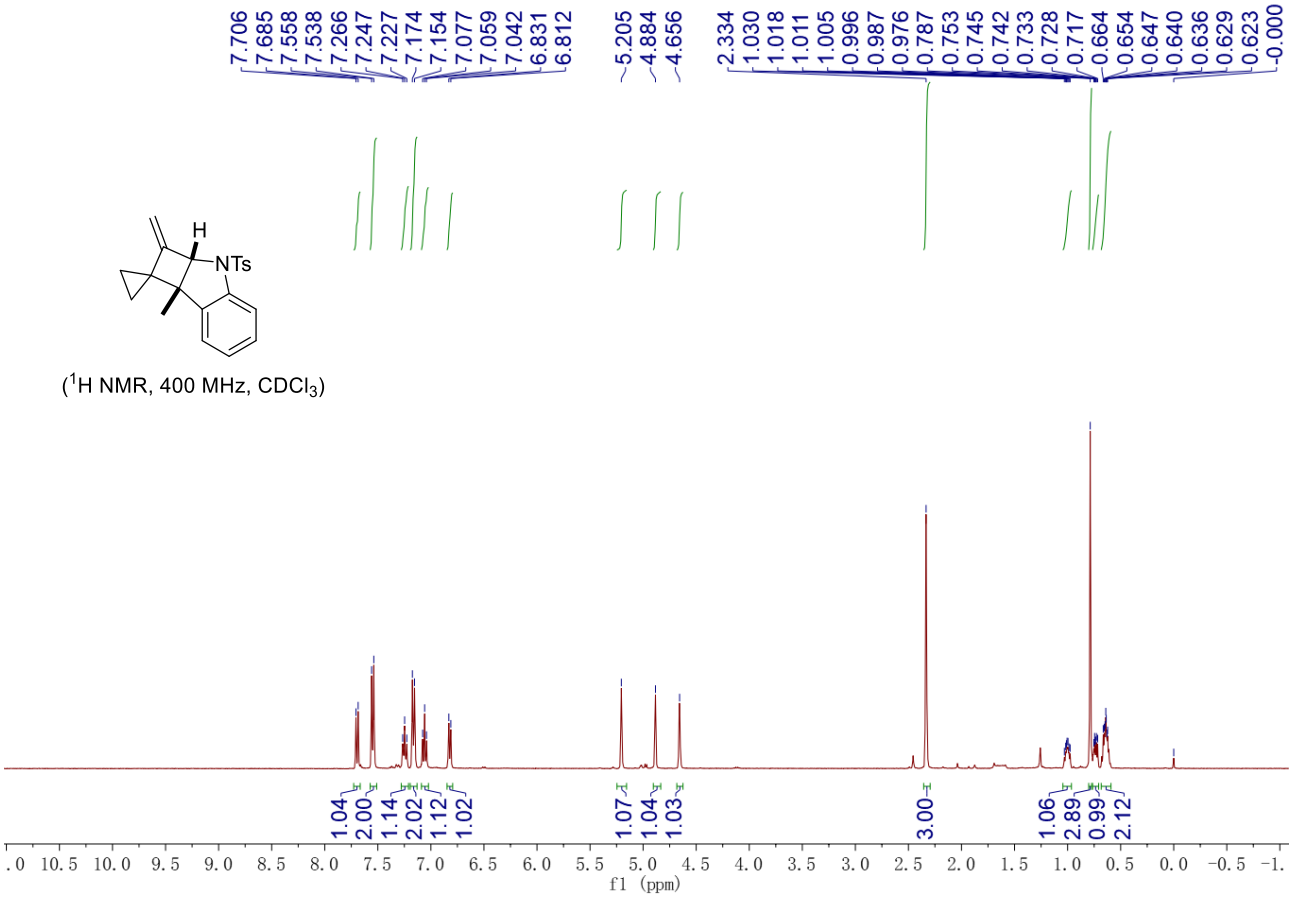


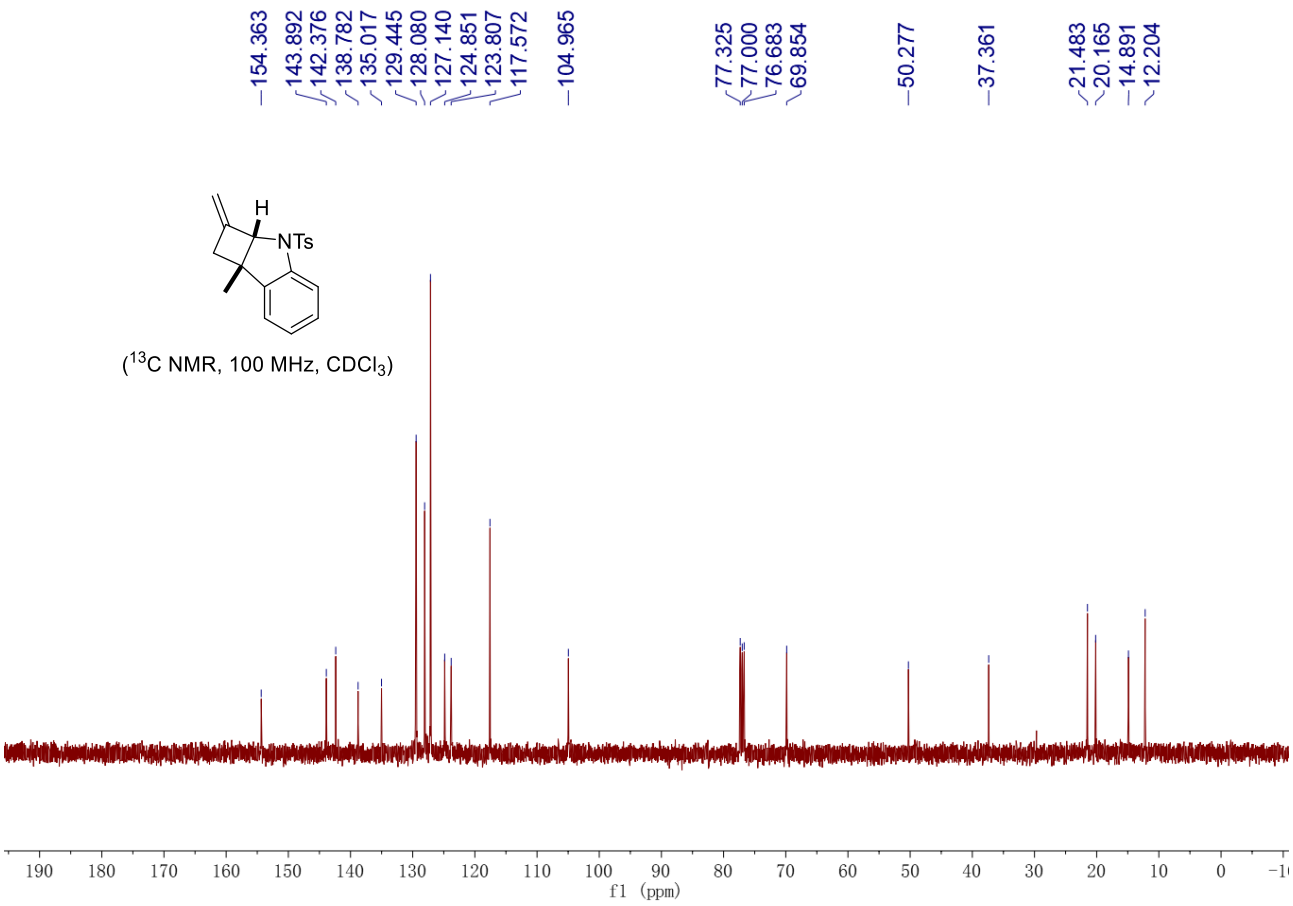


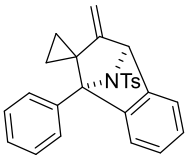
(^{13}C NMR, 100 MHz, $CDCl_3$)



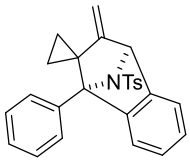
7b-methyl-2-methylene-3-tosyl-2,2a,3,7b-tetrahydrospiro[cyclobuta[b]indole-1,1'-cyclopropane] (2af): Yield: 37 mg, 53%, white solid, m.p. 140-142 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 5.21 (s, 1H), 4.88 (s, 1H), 4.66 (s, 1H), 2.33 (s, 3H), 1.04 – 0.96 (m, 1H), 0.79 (s, 3H), 0.76 – 0.71 (m, 1H), 0.68 – 0.59 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 154.4, 143.9, 142.4, 138.8, 135.0, 129.4, 128.1, 127.1, 124.9, 123.8, 117.6, 105.0, 69.9, 50.3, 37.4, 21.5, 20.2, 14.9, 12.2.; IR (neat): ν 3034, 2956, 2912, 1675, 1599, 1469, 1349, 1163, 1074, 896, 754, 659 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]+: 374.11852, found: 374.11936.



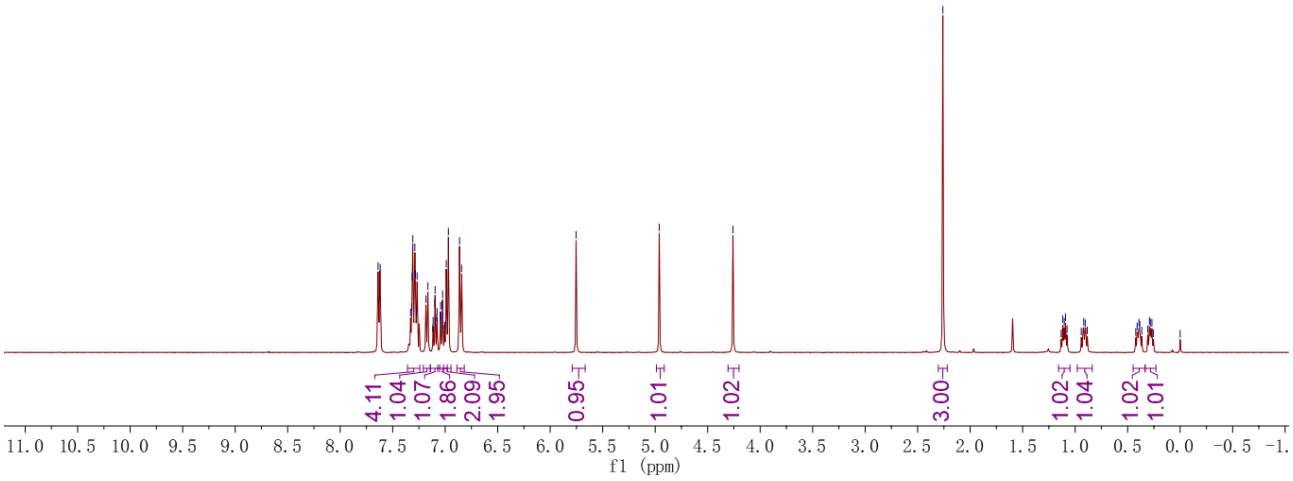

154.363
143.892
142.376
138.782
135.017
129.445
128.080
127.140
124.851
123.807
117.572
104.965
77.325
77.000
76.683
69.854
50.277
37.361
21.483
20.165
14.891
12.204
H
NTs
(^{13}C NMR, 100 MHz, $CDCl_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

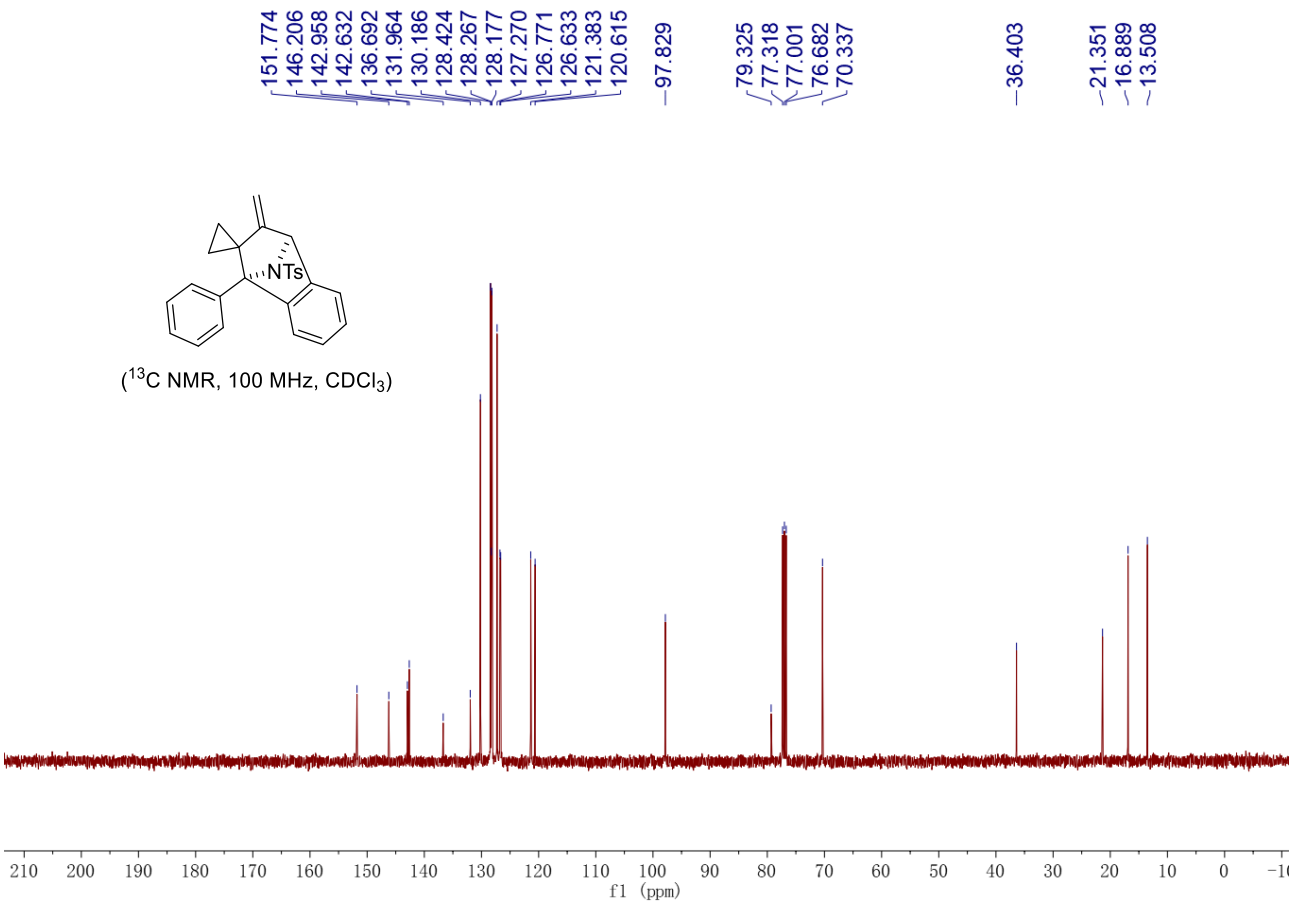


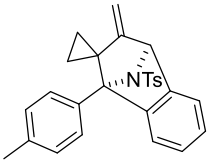
***N*,4-dimethyl-*N*-(3'-methylene-1'-phenyl-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)benzenesulfonamide (3a)**: Yield: 21 mg, 25%, white solid, m.p. >200 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.24 (m, 4H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.10 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.07 – 6.99 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 5.75 (s, 1H), 4.96 (s, 1H), 4.26 (s, 1H), 2.26 (s, 3H), 1.16 – 1.05 (m, 1H), 0.98 – 0.84 (m, 1H), 0.45 – 0.33 (m, 1H), 0.33 – 0.23 (m, 1H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 151.8, 146.2, 143.0, 142.6, 136.7, 132.0, 130.2, 128.4, 128.3, 128.2, 127.3, 126.8, 126.6, 121.4, 120.6, 97.8, 79.3, 70.3, 36.4, 21.4, 16.9, 13.5; IR (neat): ν 3042, 2917, 2841, 1591, 1461, 1341, 1157, 1083, 1023, 983, 867, 678 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 436.13417, found: 436.13421.



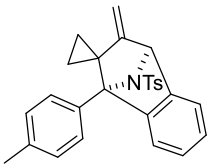
(^{1}H NMR, 400 MHz, $CDCl_3$)



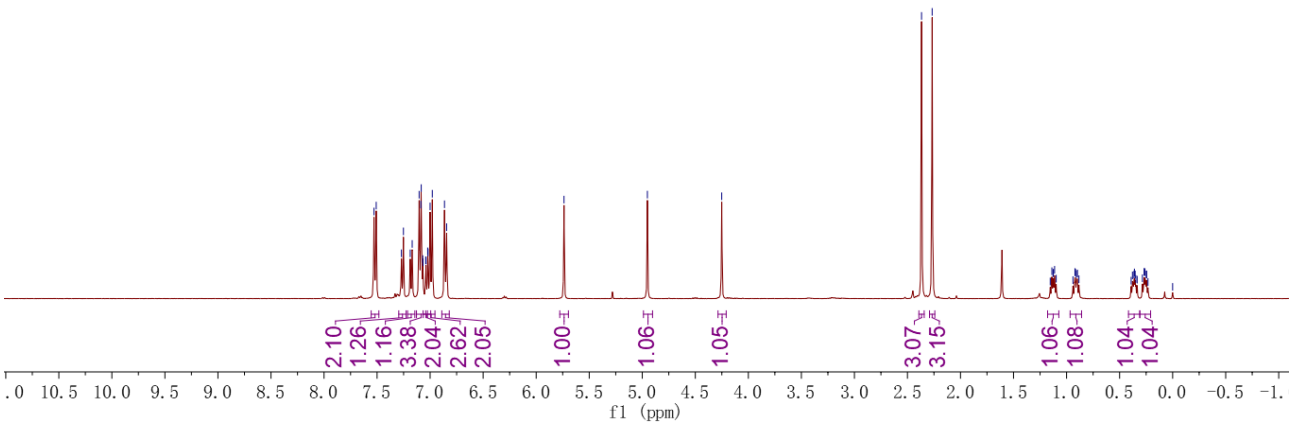

151.774
146.206
142.958
142.632
136.692
131.964
130.186
128.424
128.267
128.177
127.270
126.771
126.633
121.383
120.615
97.829
79.325
77.318
77.001
76.682
70.337
36.403
21.351
16.889
13.508
NTs
(^{13}C NMR, 100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

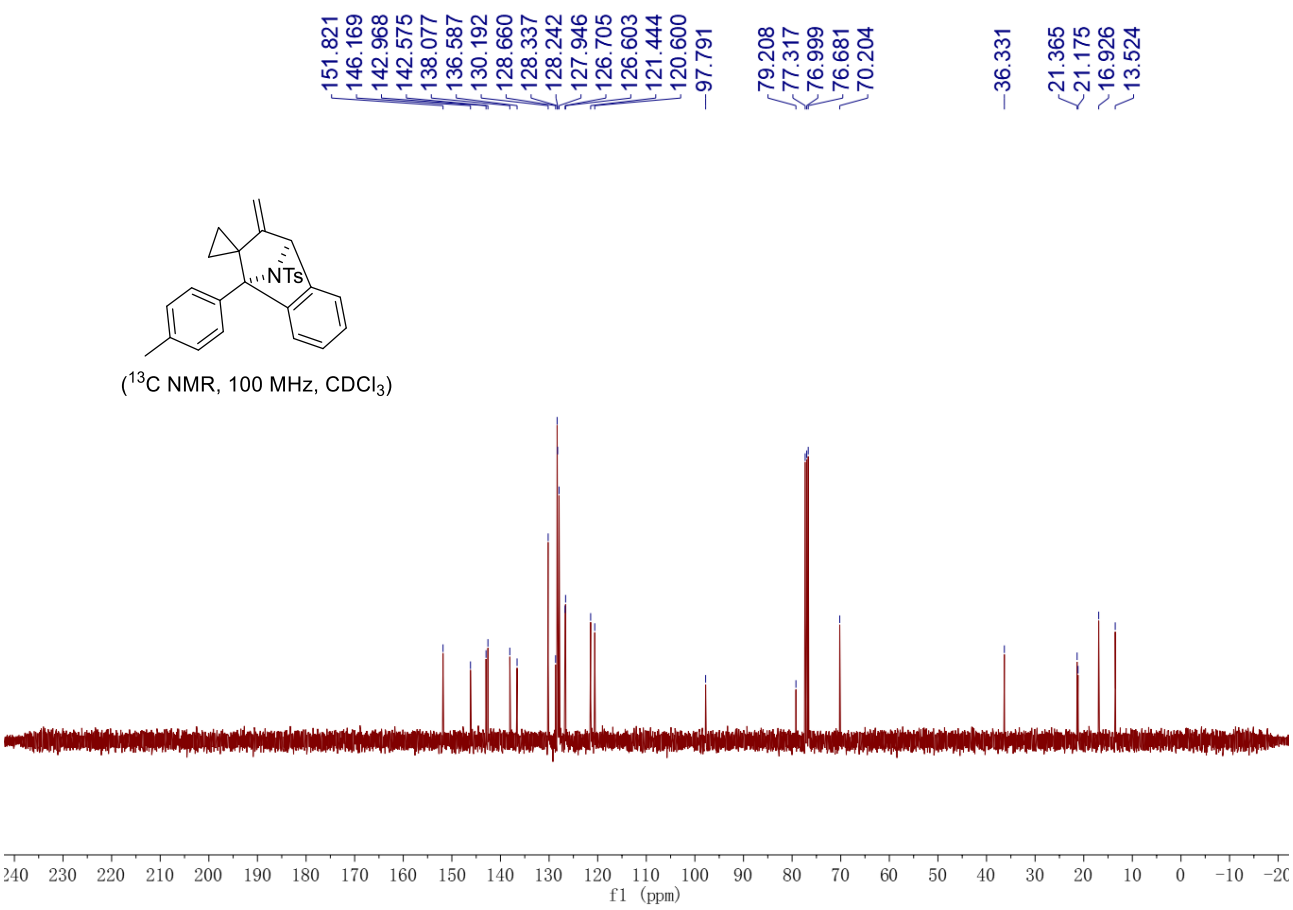


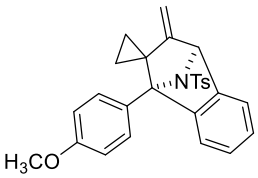
***N*,4-dimethyl-*N*-(3'-methylene-1'-(p-tolyl)-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)benzenesulfonamide (3b)**: Yield: 21 mg, 24%, white solid, m.p. 195-197 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.13 – 7.04 (m, 3H), 7.03 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 3H), 6.85 (d, *J* = 8.0 Hz, 2H), 5.74 (s, 1H), 4.95 (s, 1H), 4.25 (s, 1H), 2.37 (s, 3H), 2.27 (s, 3H), 1.18 – 1.07 (m, 1H), 0.97 – 0.86 (m, 1H), 0.42 – 0.31 (m, 1H), 0.31 – 0.21 (m, 1H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 151.8, 146.2, 143.0, 142.6, 138.1, 136.6, 130.2, 128.7, 128.3, 128.2, 127.9, 126.7, 126.6, 121.4, 120.6, 97.8, 79.2, 70.2, 36.3, 21.4, 21.2, 16.9, 13.5; IR (neat): ν 3060, 2995, 2922, 1599, 1453, 1342, 1089, 1022, 986, 878, 735, 690 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.14883.



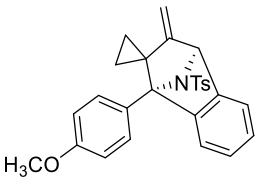
(^{1}H NMR, 400 MHz, $CDCl_3$)



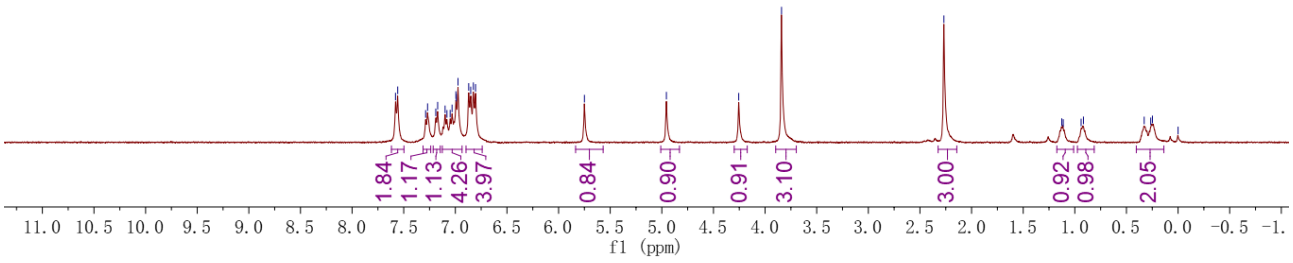

151.821
146.169
142.968
142.575
138.077
136.587
130.192
128.660
128.337
128.242
127.946
126.705
126.603
121.444
120.600
97.791
79.208
77.317
76.999
76.681
70.204
36.331
21.365
21.175
16.926
13.524
NTs
(13C NMR, 100 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

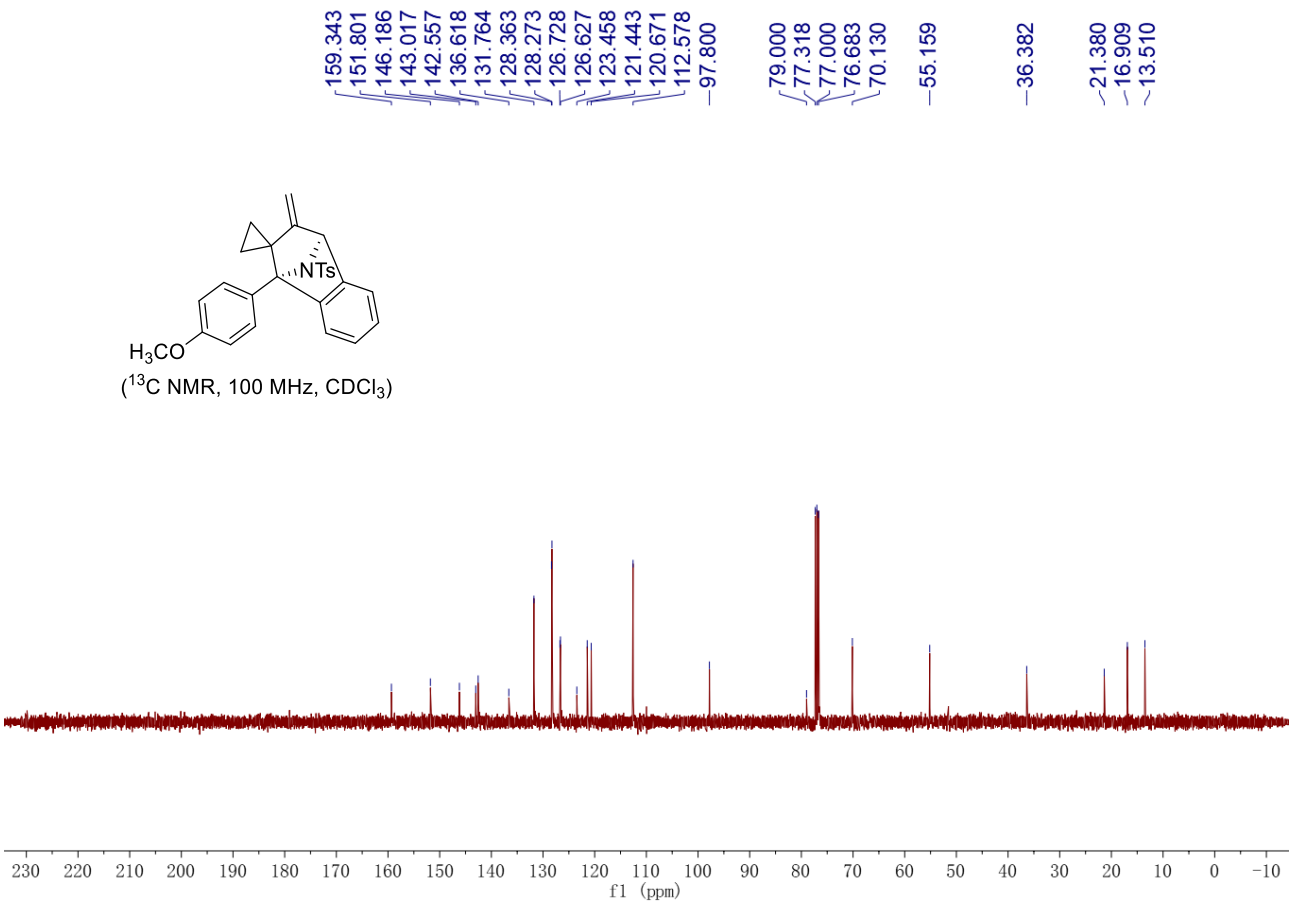


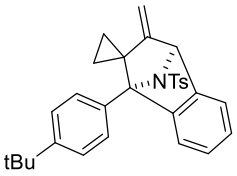
***N*-(1'-(4-methoxyphenyl)-3'-methylene-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)-*N*,4-dimethylbenzenesulfonamide (3c)**: Yield: 17 mg, 19%, white solid, m.p. 191-193 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.57 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.13 – 6.93 (m, 4H), 6.84 (m, 4H), 5.75 (s, 1H), 4.96 (s, 1H), 4.26 (s, 1H), 3.84 (s, 3H), 2.27 (s, 3H), 1.17 – 1.01 (m, 1H), 0.97 – 0.81 (m, 1H), 0.40 – 0.14 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 151.8, 146.2, 143.0, 142.6, 138.1, 136.6, 130.2, 128.7, 128.3, 128.2, 127.9, 126.7, 126.6, 121.4, 120.6, 97.8, 79.2, 70.2, 36.3, 21.4, 21.2, 16.9, 13.5; IR (neat): ν 2990, 2930, 2841, 1589, 1510, 1458, 1343, 1302, 1249, 1100, 1089, 833, 754, 651 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 466.14474, found: 466.14511.



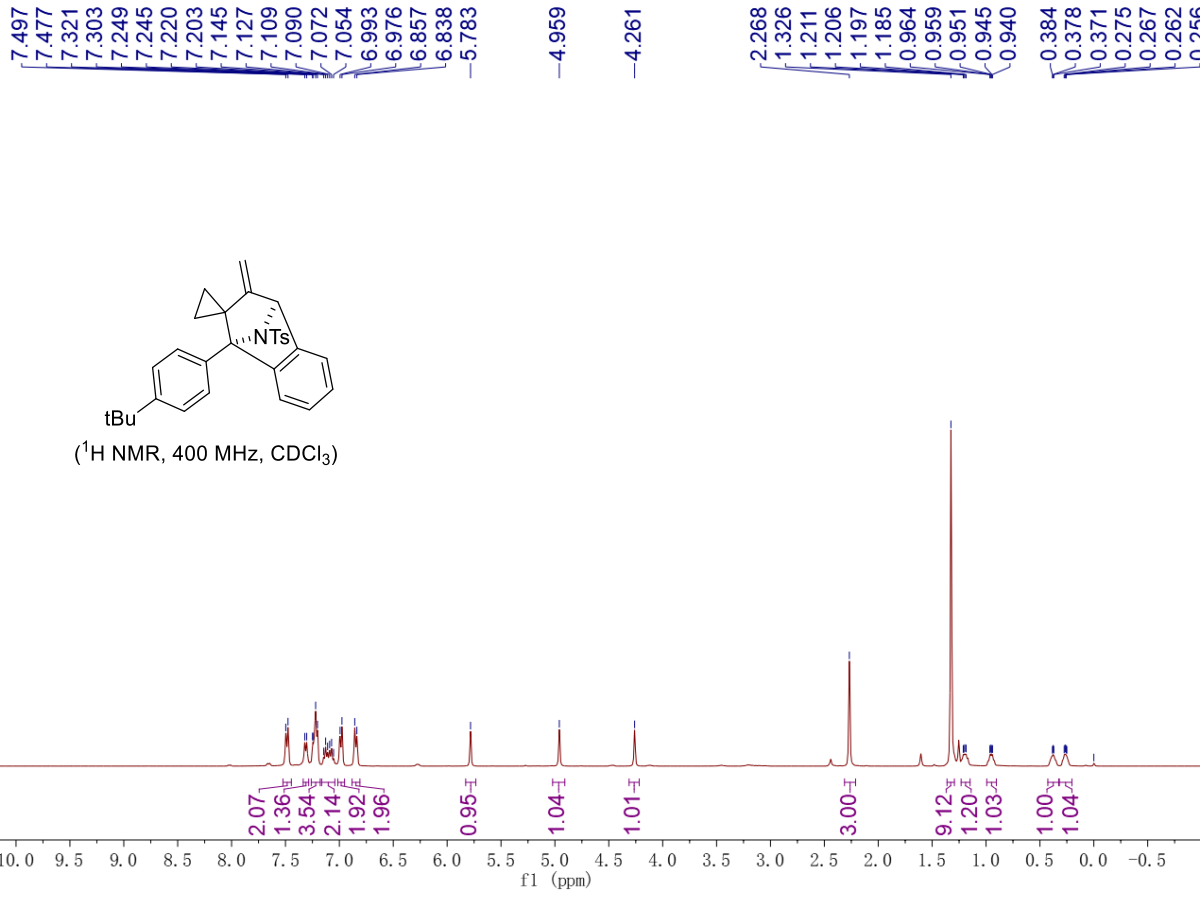
(^{1}H NMR, 400 MHz, $CDCl_3$)

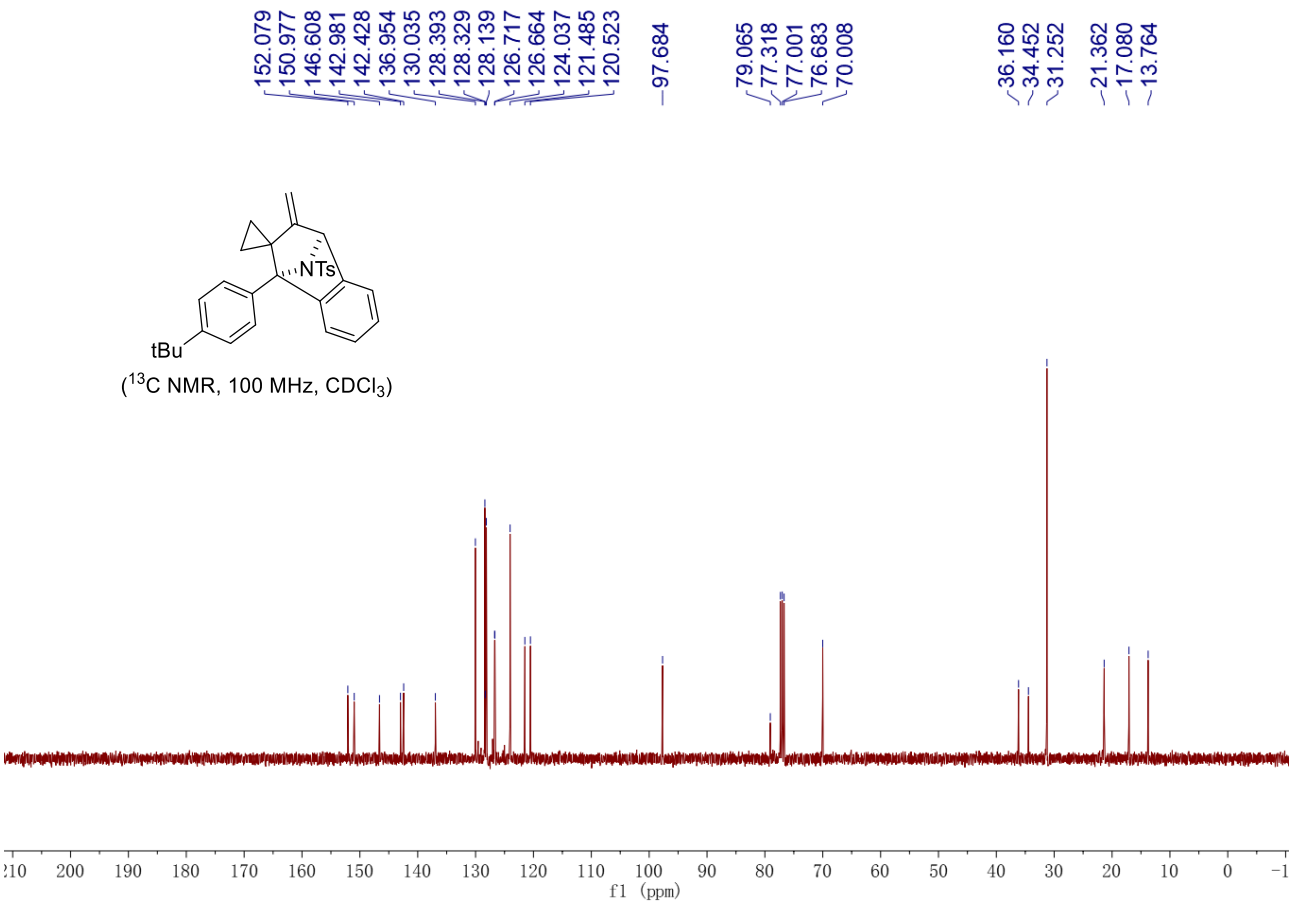


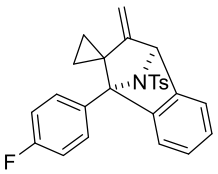

159.343
151.801
146.186
143.017
142.557
136.618
131.764
128.363
128.273
126.728
126.627
123.458
121.443
120.671
112.578
97.800
79.000
77.318
77.000
76.683
70.130
55.159
36.382
21.380
16.909
13.510
NTs
H3CO
(13C NMR, 100 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



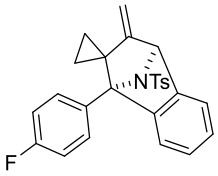
***N*-(1'-(4-(tert-butyl)phenyl)-3'-methylene-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)-*N*,4-dimethylbenzenesulfonamide (3d)**: Yield: 16 mg, 17%, pale yellow oil; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.26 – 7.18 (m, 4H), 7.16 – 7.04 (m, 2H), 6.98 (d, *J* = 6.8 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 2H), 5.78 (s, 1H), 4.96 (s, 1H), 4.26 (s, 1H), 2.27 (s, 3H), 1.33 (s, 9H), 1.23 – 1.15 (m, 1H), 0.99 – 0.90 (m, 1H), 0.43 – 0.33 (m, 1H), 0.32 – 0.20 (m, 1H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 152.1, 151.0, 146.6, 143.0, 142.4, 137.0, 130.0, 128.4, 128.3, 128.1, 126.7, 126.7, 124.0, 121.5, 120.5, 97.7, 79.1, 70.0, 36.2, 34.5, 31.3, 21.4, 17.1, 13.8; IR (neat): ν 3050, 2964, 2867, 1597, 1453, 1340, 1089, 913, 811, 732, 667 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 492.19677, found: 492.19707.



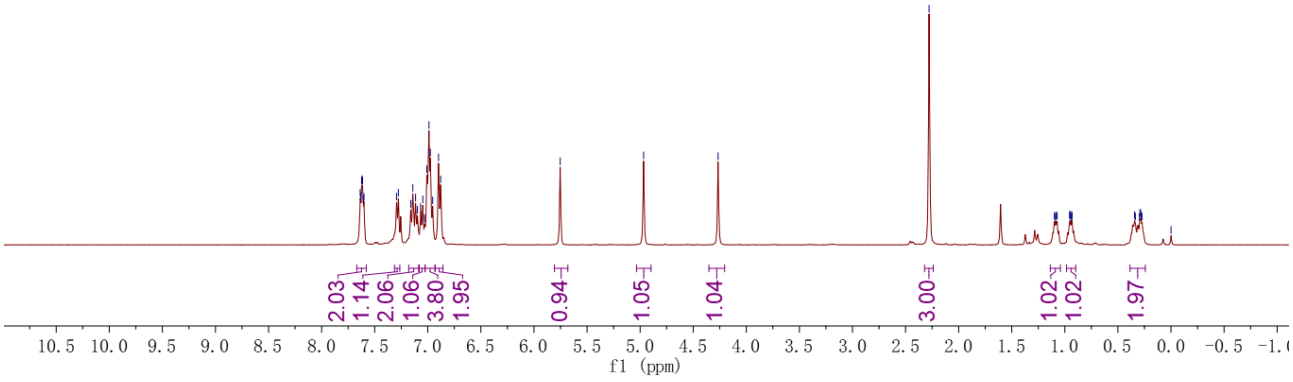

152.079
150.977
146.608
142.981
142.428
136.954
130.035
128.393
128.329
128.139
126.717
126.664
124.037
121.485
120.523
97.684
79.065
77.318
77.001
76.683
70.008
36.160
34.452
31.252
21.362
17.080
13.764
NTs
tBu
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

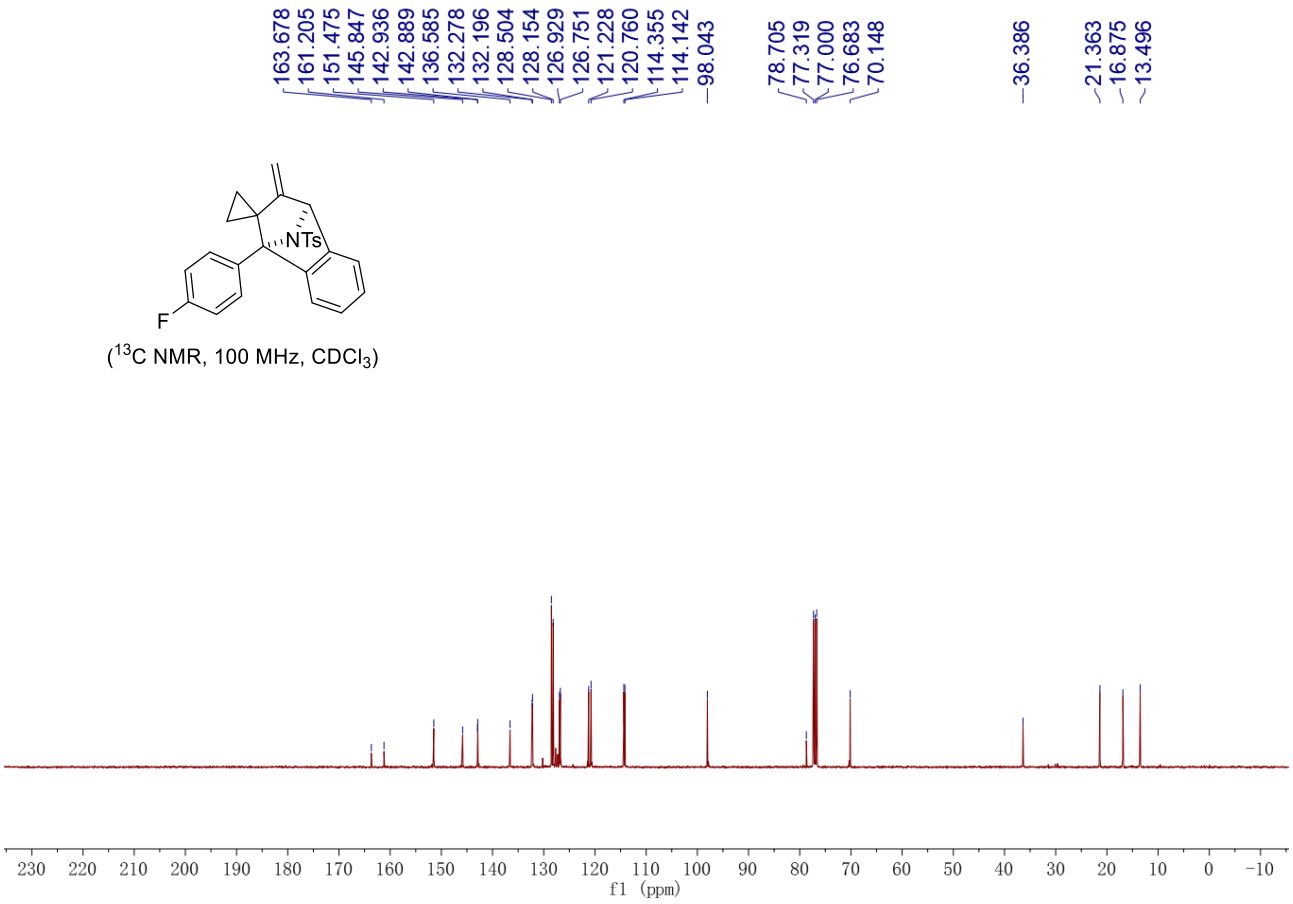


***N*-(1'-(4-fluorophenyl)-3'-methylene-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)-*N*,4-dimethylbenzenesulfonamide (3e)**: Yield: 18 mg, 21%, white solid, m.p. > 200 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.67 – 7.58 (m, 2H), 7.29 (d, *J* = 6.8 Hz, 1H), 7.18 – 7.09 (m, 2H), 7.08 – 7.03 (m, 1H), 7.02 – 6.93 (m, 4H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.75 (s, 1H), 4.97 (s, 1H), 4.27 (s, 1H), 2.28 (s, 3H), 1.14 – 1.04 (m, 1H), 0.98 – 0.90 (m, 1H), 0.39 – 0.24 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 162.5 (d, *J* = 247.3 Hz), 151.5, 145.8, 142.9, 142.9, 136.6, 132.3 (d, *J* = 8.2 Hz), 128.5, 128.2, 126.9, 126.8, 121.2, 120.8, 114.1 (d, *J* = 21.3 Hz), 98.0, 78.7, 70.1, 36.4, 21.4, 16.9, 13.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.9; IR (neat): ν 3066, 3026, 2964, 1594, 1506, 1355, 1261, 1088, 965, 836, 829 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 454.12475, found: 454.12371.

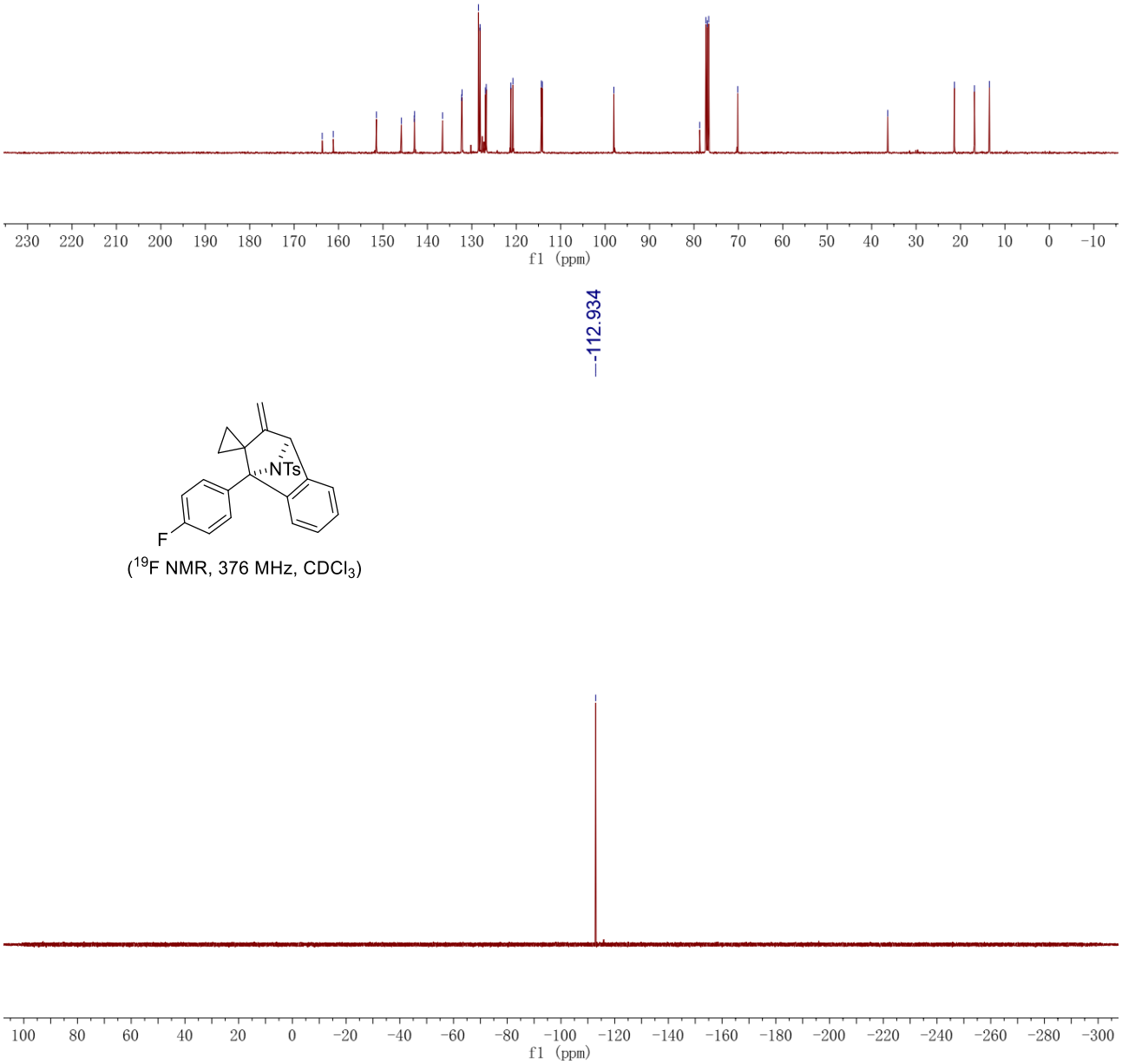


(^{1}H NMR, 400 MHz, $CDCl_3$)

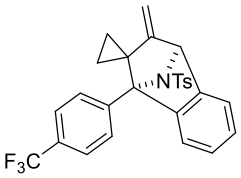




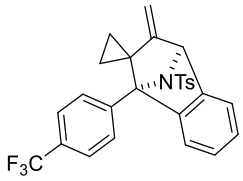
(^{13}C NMR, 100 MHz, $CDCl_3$)



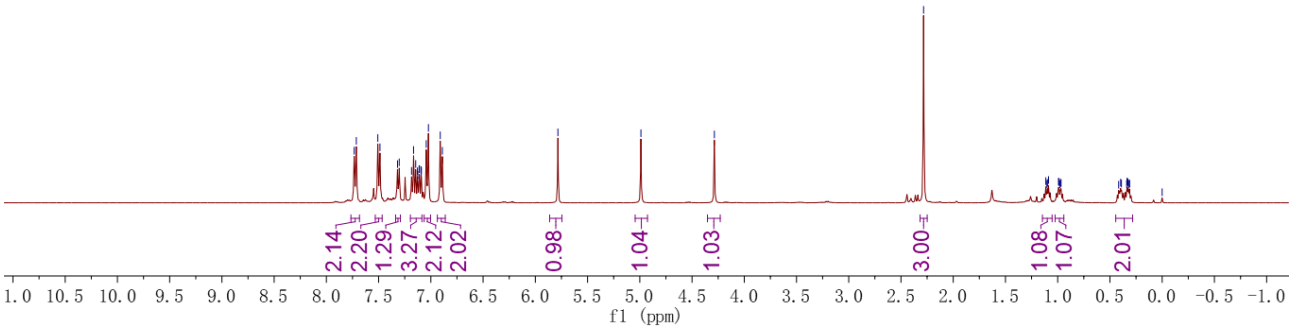
(^{19}F NMR, 376 MHz, $CDCl_3$)

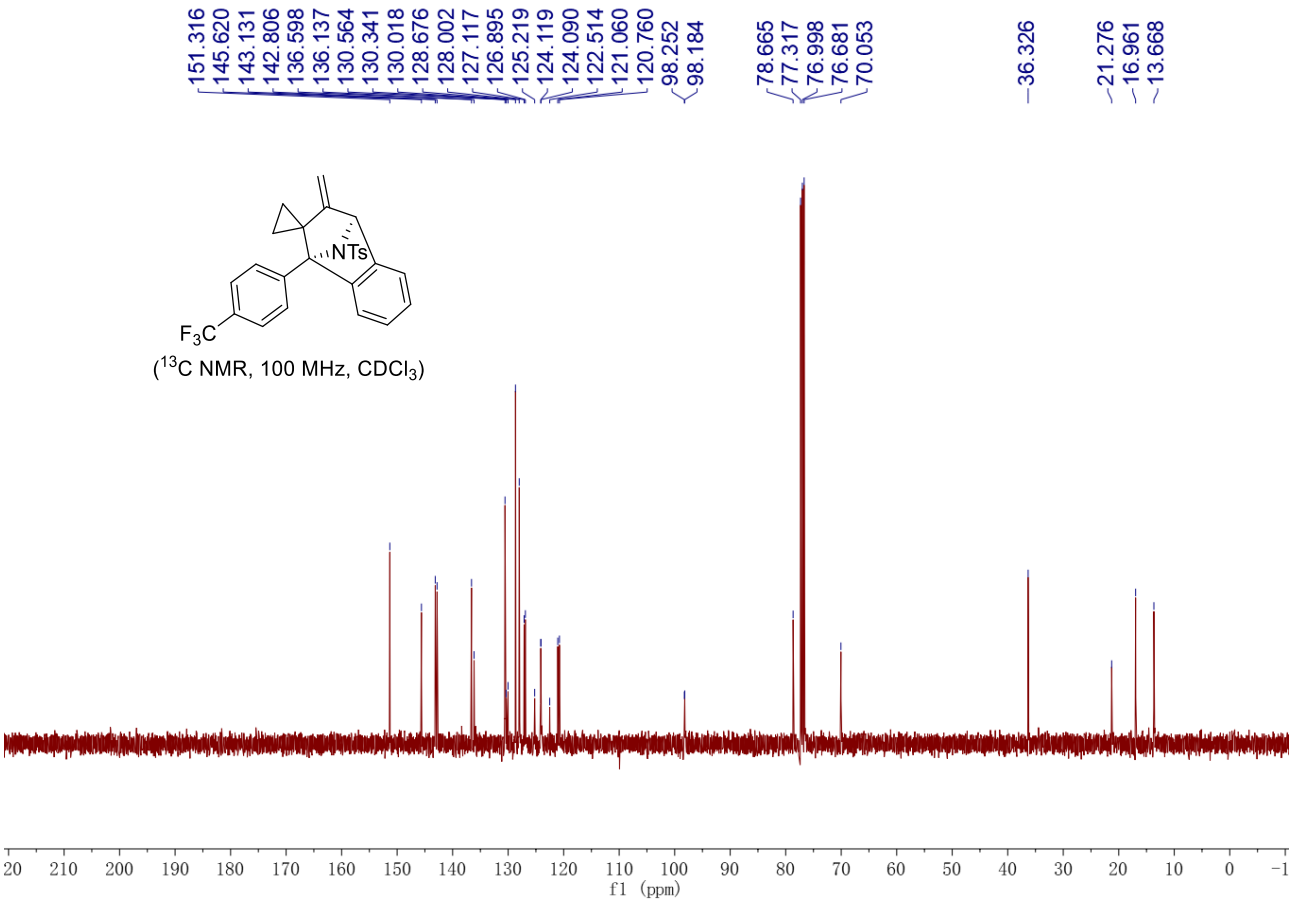


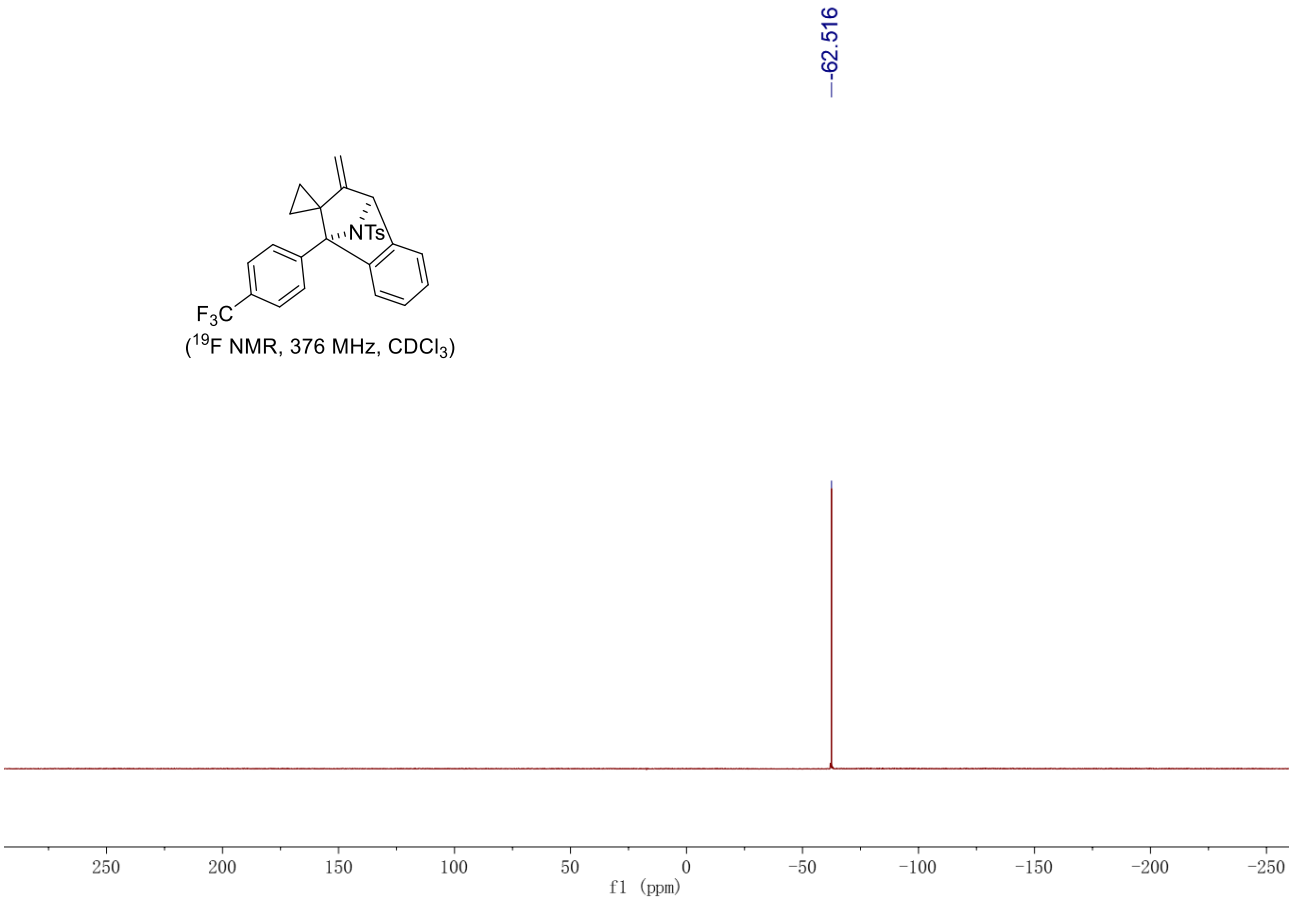
***N*,4-dimethyl-N-(3'-methylene-1'-(4-(trifluoromethyl)phenyl)-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)benzenesulfonamide (3f)**: Yield: 18 mg, 19%, white solid, m.p. 160-162 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 6.4 Hz, 1H), 7.20 – 7.09 (m, 3H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 5.78 (s, 1H), 4.99 (s, 1H), 4.29 (s, 1H), 2.28 (s, 3H), 1.15 – 1.05 (m, 1H), 1.02 – 0.94 (m, 1H), 0.44 – 0.28 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 151.3, 145.6, 143.1, 142.8, 136.6, 136.1, 130.6, 130.2 (q, *J* = 32.2 Hz), 128.7, 128.0, 127.1, 126.9, 124.1 (q, *J* = 2.9 Hz), 123.8 (q, *J* = 270.5 Hz), 121.1, 120.8, 98.3, 98.2, 78.7, 70.1, 36.3, 21.3, 17.0, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5; IR (neat): ν 3073, 2919, 1670, 1597, 1456, 1329, 1156, 1113, 881, 681 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 504.12156, found: 504.12118.

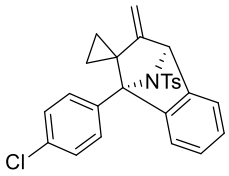


(^{1}H NMR, 400 MHz, $CDCl_3$)

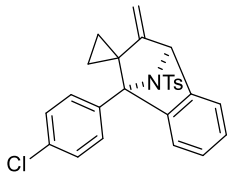



151.316
145.620
143.131
142.806
136.598
136.137
130.564
130.341
130.018
128.676
128.002
127.117
126.895
125.219
124.119
124.090
122.514
121.060
120.760
98.252
98.184
78.665
77.317
76.998
76.681
70.053
36.326
21.276
16.961
13.668
NTs
F3C
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

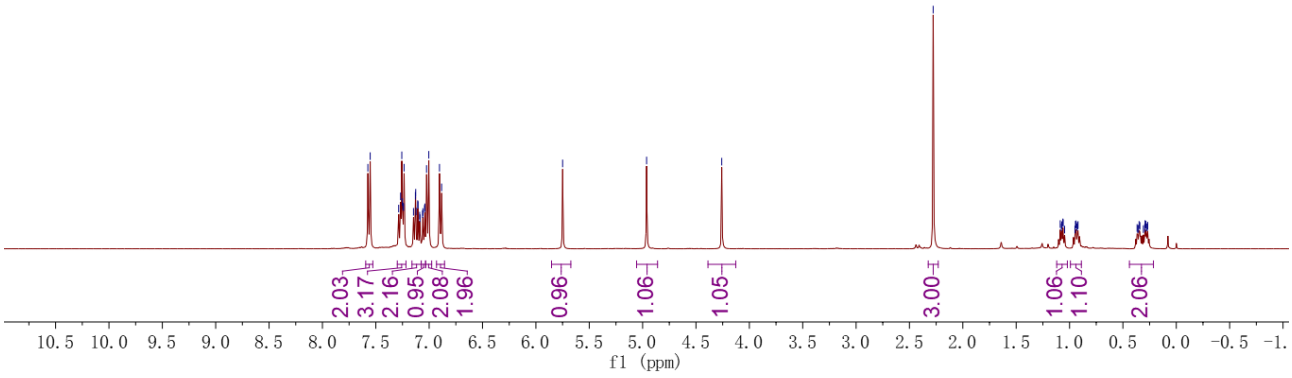

-62.516
NTs
F3C
(19F NMR, 376 MHz, CDCl3)
f1 (ppm)

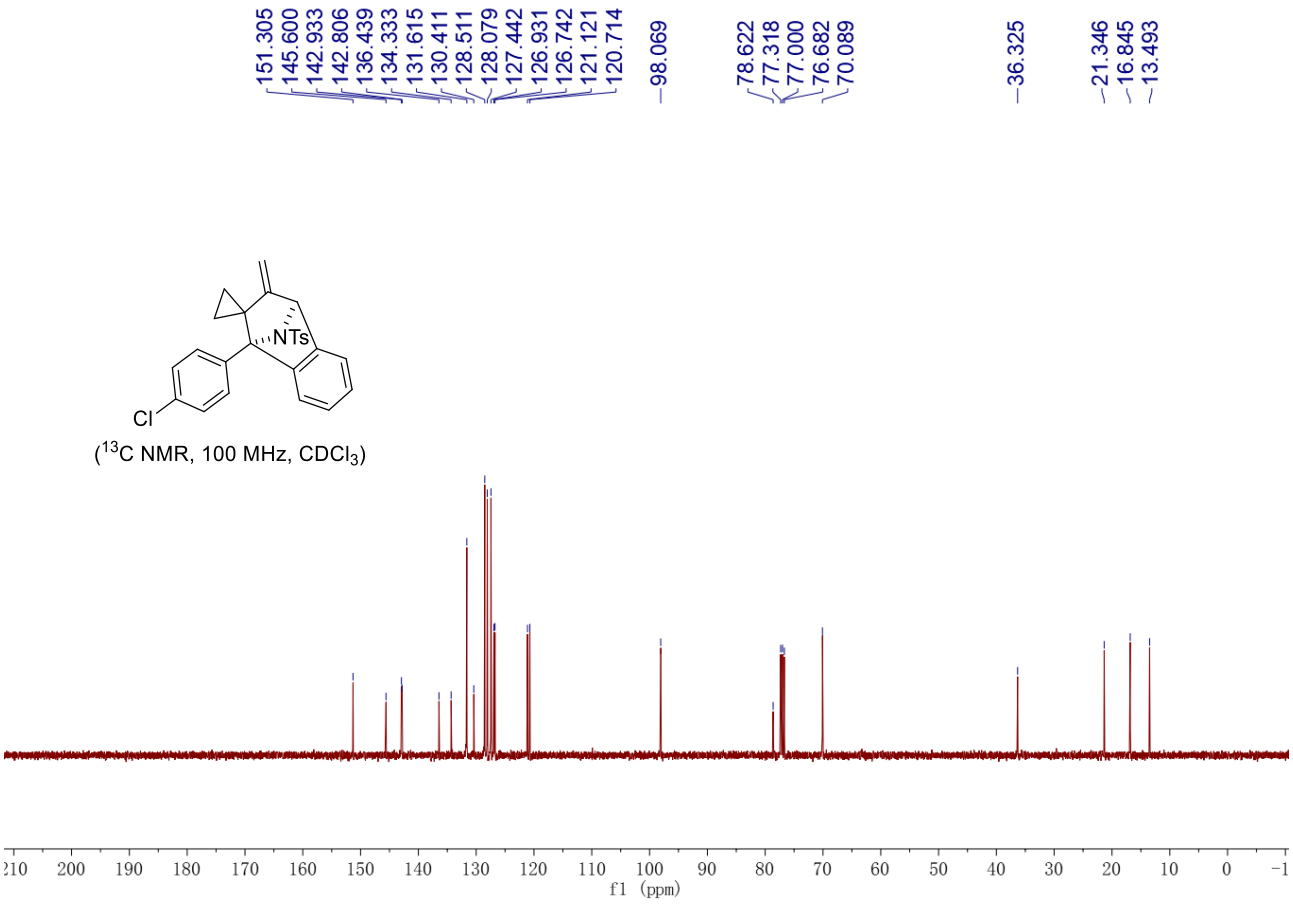


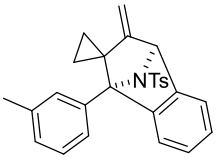
***N*-(1'-(4-chlorophenyl)-3'-methylene-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)-*N*,4-dimethylbenzenesulfonamide (3g)**: Yield: 20 mg, 22%, white solid, m.p. > 200 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.30 – 7.22 (m, 3H), 7.16 – 7.08 (m, 2H), 7.05 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.75 (s, 1H), 4.96 (s, 1H), 4.26 (s, 1H), 2.28 (s, 3H), 1.12 – 1.02 (m, 1H), 0.99 – 0.89 (m, 1H), 0.44 – 0.21 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 151.3, 145.6, 142.9, 142.8, 136.4, 134.3, 131.6, 130.4, 128.5, 128.1, 127.4, 126.9, 126.7, 121.1, 120.7, 98.1, 78.6, 70.1, 36.3, 21.3, 16.8, 13.5; IR (neat): ν 3045, 2985, 2925, 1612, 1508, 1340, 1226, 1159, 990, 837, 743, 687 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 470.09520, found: 470.09568.



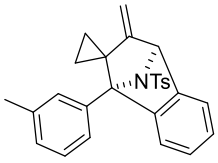
(^{1}H NMR, 400 MHz, $CDCl_3$)



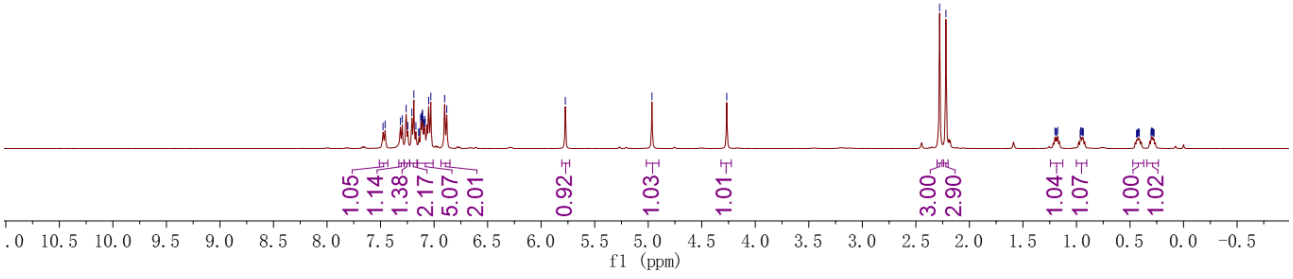

151.305
145.600
142.933
142.806
136.439
134.333
131.615
130.411
128.511
128.079
127.442
126.931
126.742
121.121
120.714
98.069
78.622
77.318
77.000
76.682
70.089
36.325
21.346
16.845
13.493
NTs
Cl
(13C NMR, 100 MHz, CDCl3)
f1 (ppm)

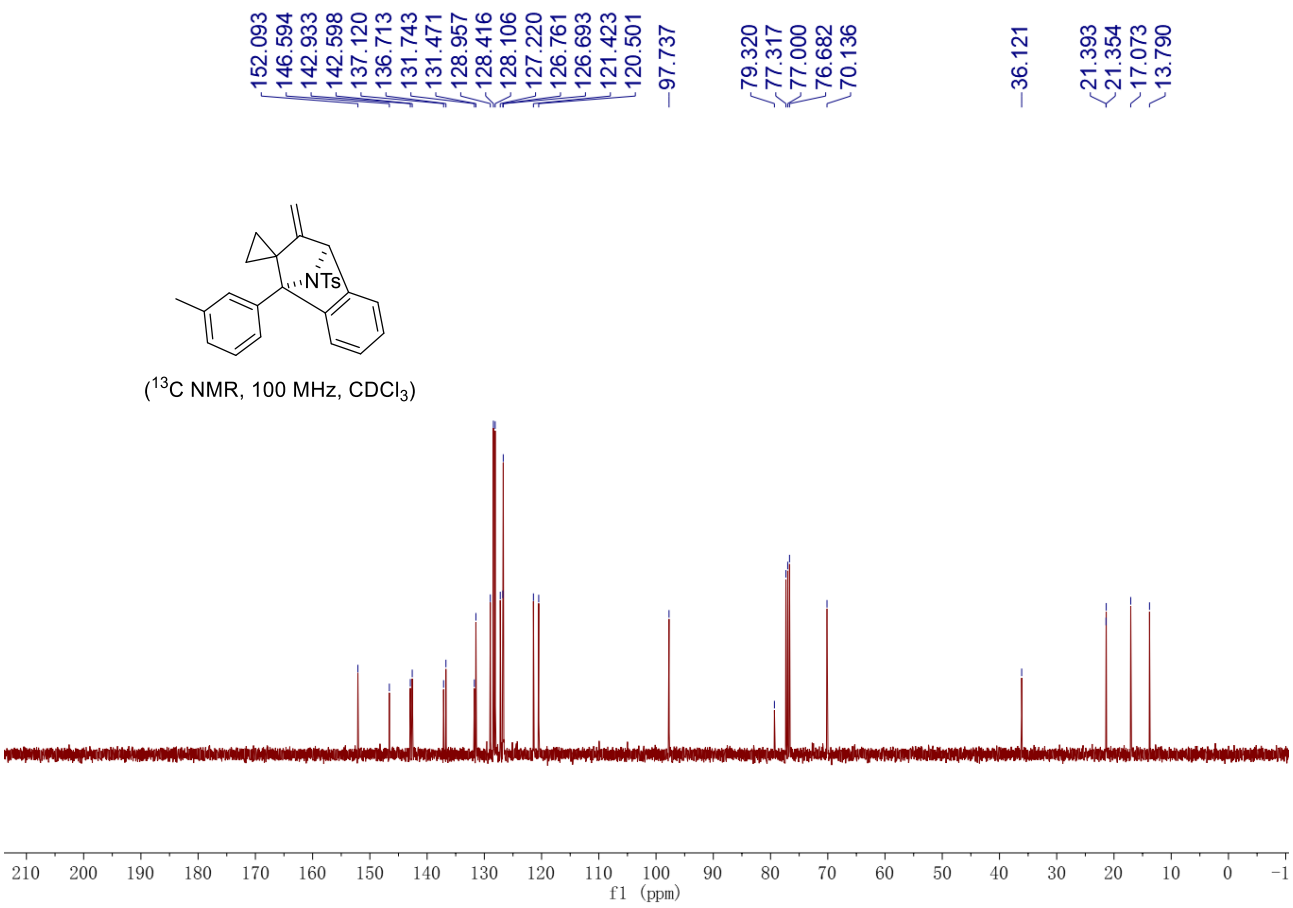


***N*,4-dimethyl-N-(3'-methylene-1'-(m-tolyl)-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)benzenesulfonamide (3h)**: Yield: 17 mg, 20%, white solid, m.p. 195-197 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 6.8 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.15 – 7.01 (m, 5H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.77 (s, 1H), 4.97 (s, 1H), 4.27 (s, 1H), 2.28 (s, 3H), 2.22 (s, 3H), 1.24 – 1.13 (m, 1H), 1.00 – 0.90 (m, 1H), 0.47 – 0.37 (m, 1H), 0.34 – 0.23 (m, 1H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 152.1, 146.6, 142.9, 142.6, 137.1, 136.7, 131.7, 131.5, 129.0, 128.4, 128.1, 127.2, 126.8, 126.7, 121.4, 120.5, 97.7, 79.3, 70.1, 36.1, 21.4, 21.4, 17.1, 13.8; IR (neat): ν 3065, 3034, 2916, 1665, 1594, 1458, 1324, 1153, 1091, 958, 874, 734, 653 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 450.14982, found: 450.15064.

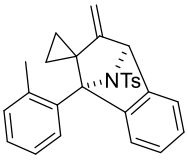


(^{1}H NMR, 400 MHz, $CDCl_3$)

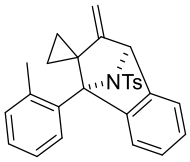




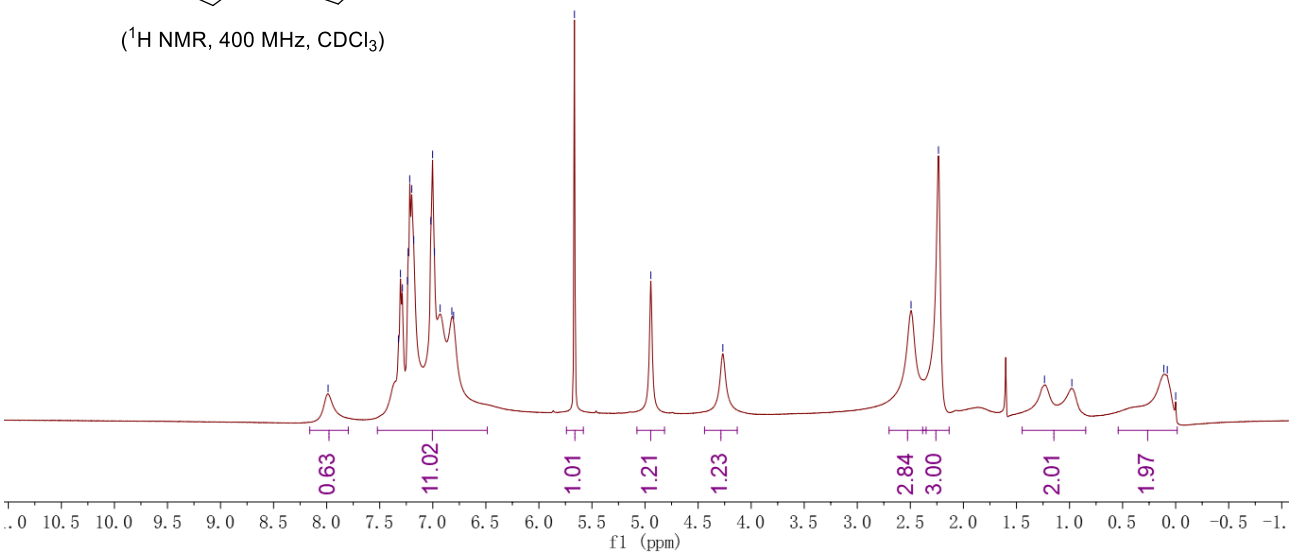
(^{13}C NMR, 100 MHz, $CDCl_3$)

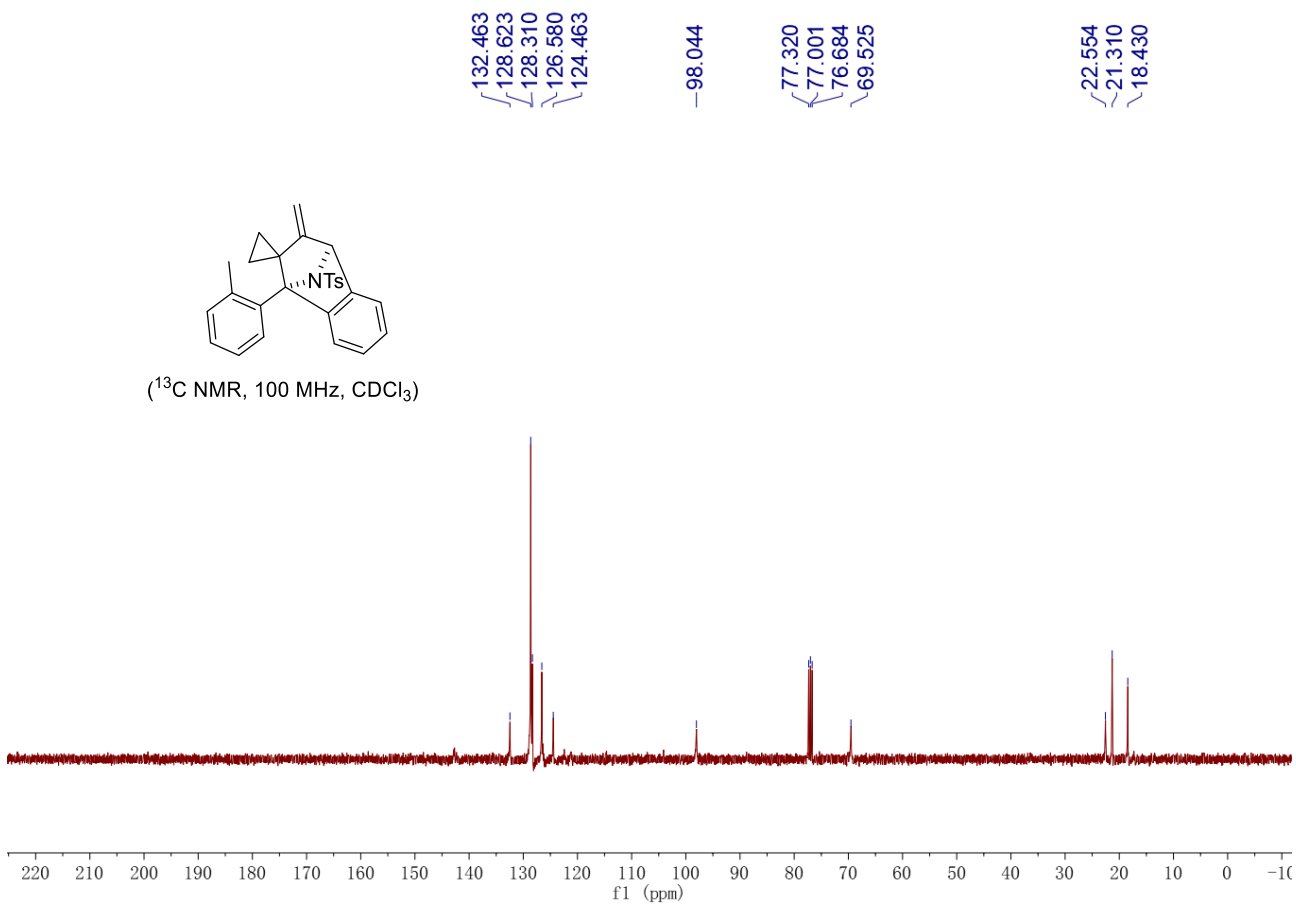


***N*,4-dimethyl-*N*-(3'-methylene-1'-(o-tolyl)-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)benzenesulfonamide (3i)**: Yield: 43 mg, 51%, white solid, m.p. 155-157 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.99 (s, 1H), 7.52 – 6.49 (m, 11H), 5.67 (s, 1H), 4.95 (s, 1H), 4.27 (s, 1H), 2.49 (s, 3H), 2.24 (s, 3H), 1.45 – 0.85 (m, 2H), 0.54 – 0.01 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 132.5, 128.6, 128.3, 126.6, 124.5, 98.0, 69.5, 22.6, 21.3, 18.4; IR (neat): ν 3058, 2922, 2846, 1675, 1599, 1458, 1340, 1158, 1087, 991, 876, 772, 692 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.15029

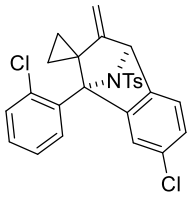


(^{1}H NMR, 400 MHz, $CDCl_3$)

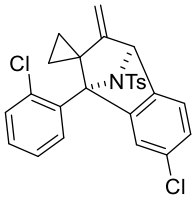




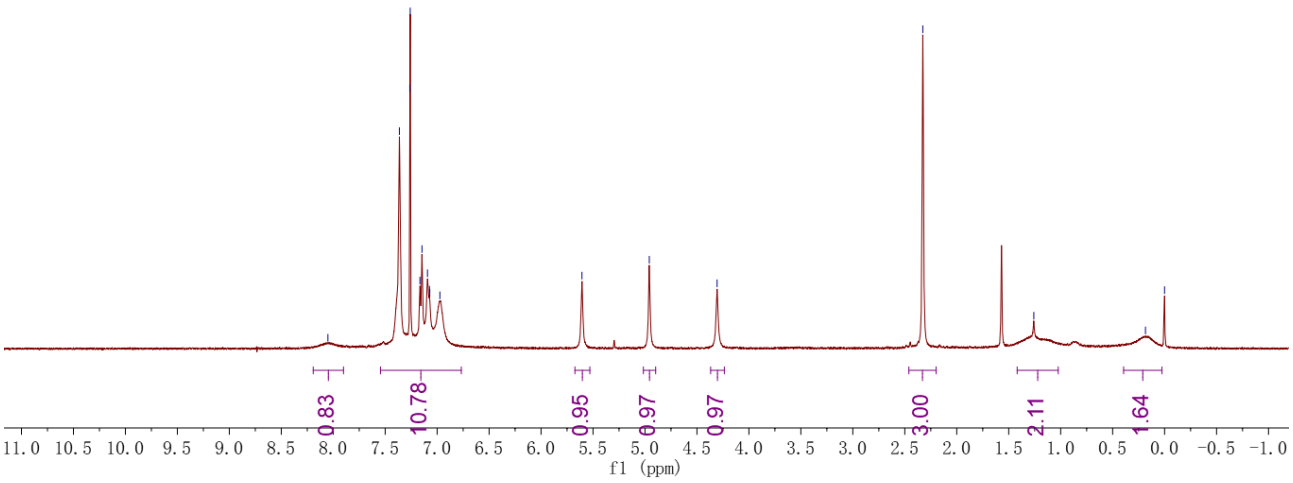
(^{13}C NMR, 100 MHz, $CDCl_3$)

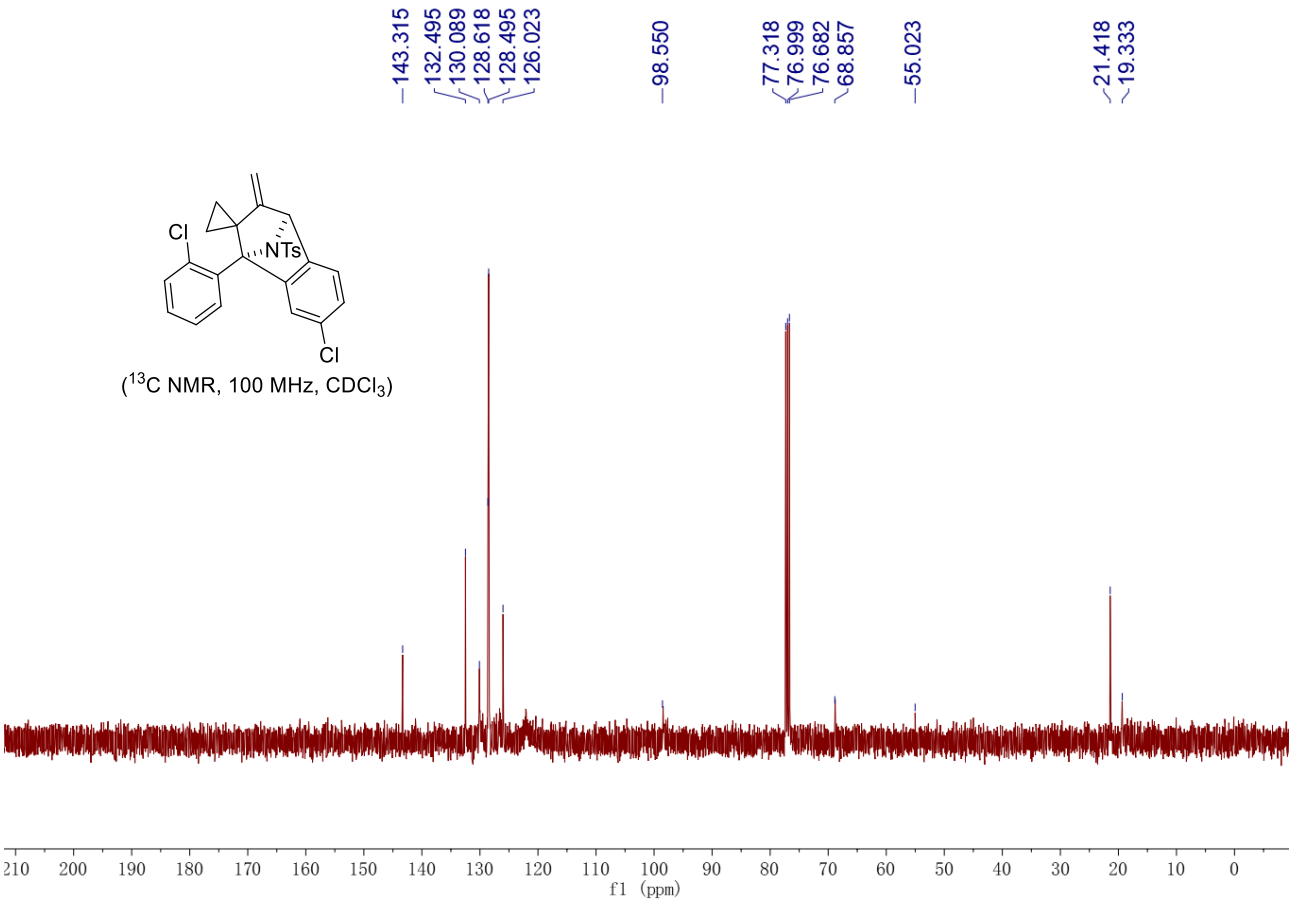


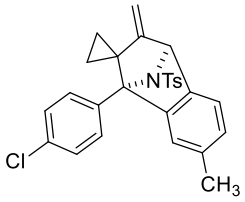
***N*-(7'-chloro-1'-(2-chlorophenyl)-3'-methylene-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)-*N*,4-dimethylbenzenesulfonamide (j)**: Yield: 39 mg, 41%, white solid, m.p. > 200 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.05 (s, 1H), 7.55 – 6.77 (m, 11H), 5.61 (s, 1H), 4.96 (s, 1H), 4.31 (s, 1H), 2.33 (s, 3H), 1.42 – 1.02 (m, 2H), 0.39 – 0.03 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 143.3, 132.5, 130.1, 128.6, 128.5, 126.0, 98.6, 68.9, 55.0, 21.4, 19.3; IR (neat): ν 2951, 2921, 2846, 1646, 1591, 1471, 1343, 1158, 1083, 889, 689 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 504.05623, found: 504.05619.



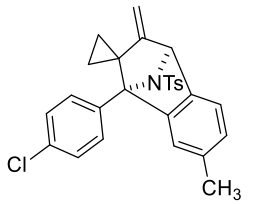
(^{1}H NMR, 400 MHz, $CDCl_3$)



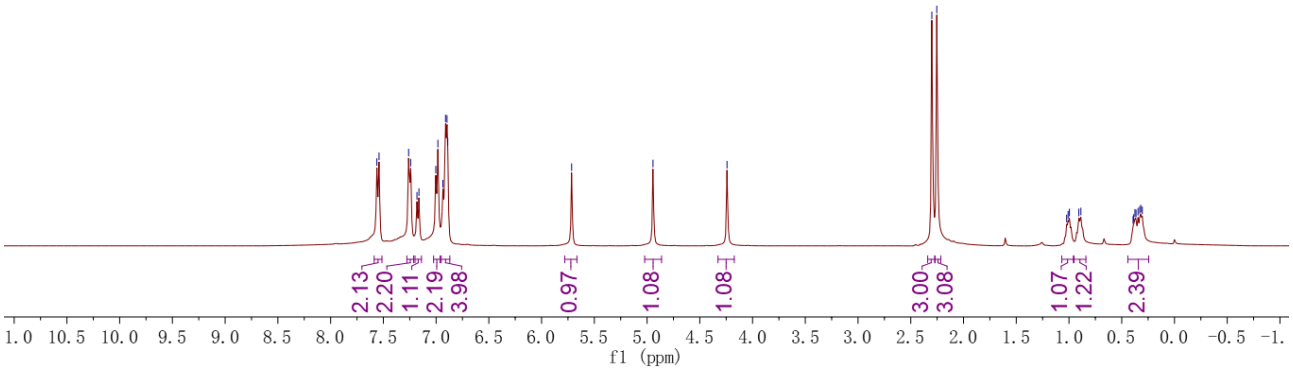

143.315
132.495
130.089
128.618
128.495
126.023
98.550
77.318
76.999
76.682
68.857
55.023
21.418
19.333
Cl
NTs
Cl
(13C NMR, 100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

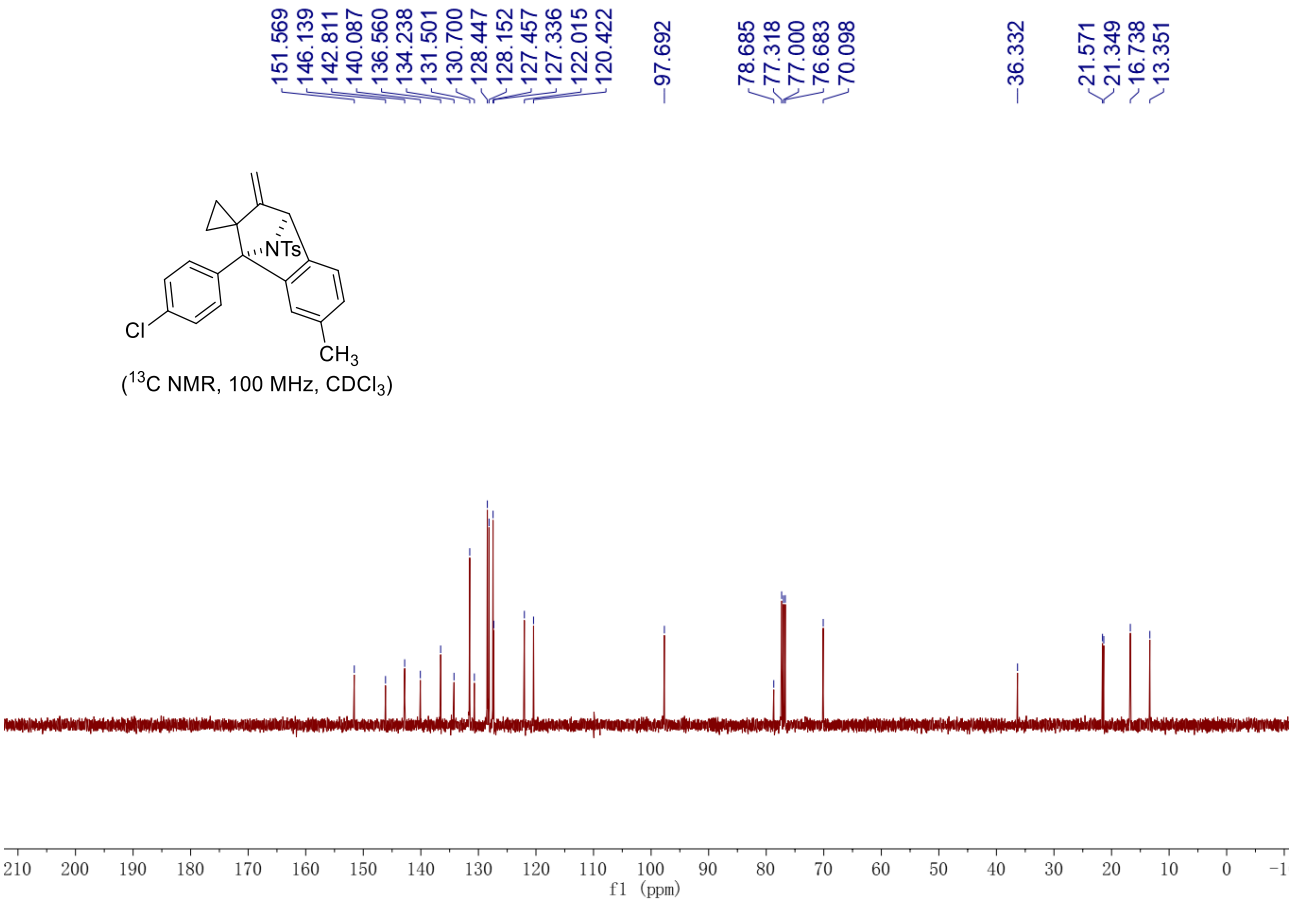


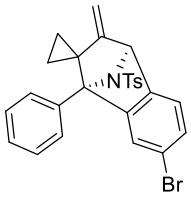
***N*-(1'-(4-chlorophenyl)-7'-methyl-3'-methylene-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)-*N*,4-dimethylbenzenesulfonamide (3k)**: Yield: 21 mg, 23%, white solid, m.p. > 200 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.95 – 6.87 (m, 4H), 5.72 (s, 1H), 4.94 (s, 1H), 4.24 (s, 1H), 2.30 (s, 3H), 2.25 (s, 3H), 1.07 – 0.96 (m, 1H), 0.95 – 0.84 (m, 1H), 0.44 – 0.24 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 151.6, 146.1, 142.8, 140.1, 136.6, 134.2, 131.5, 130.7, 128.4, 128.2, 127.5, 127.3, 122.0, 120.4, 97.7, 78.7, 70.1, 36.3, 21.6, 21.3, 16.7, 13.4; IR (neat): ν 3073, 2917, 2849, 1664, 1591, 1495, 1332, 1155, 1003, 808, 652 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 484.11085, found: 484.11051.



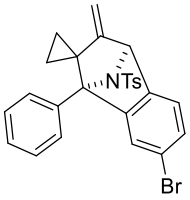
(^{1}H NMR, 400 MHz, $CDCl_3$)



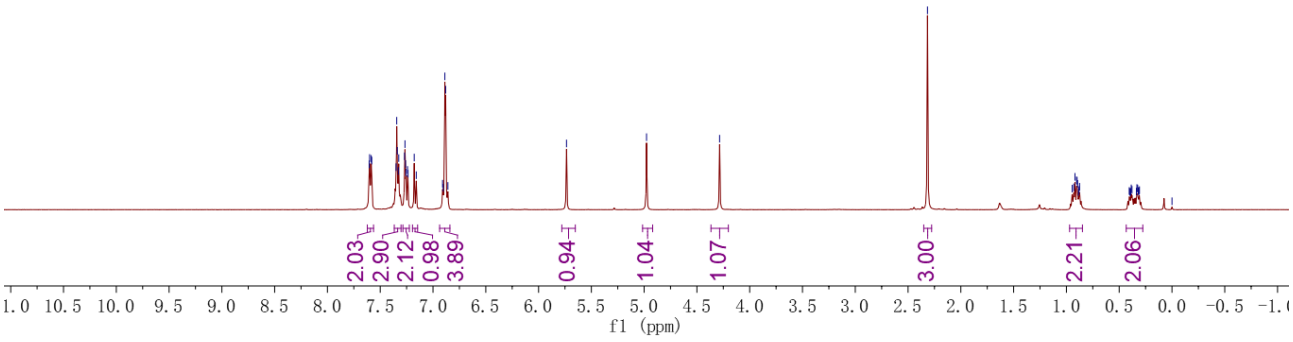

151.569
146.139
142.811
140.087
136.560
134.238
131.501
130.700
128.447
128.152
127.457
127.336
122.015
120.422
97.692
78.685
77.318
77.000
76.683
70.098
36.332
21.571
21.349
16.738
13.351
NTs
Cl
CH3
(13C NMR, 100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

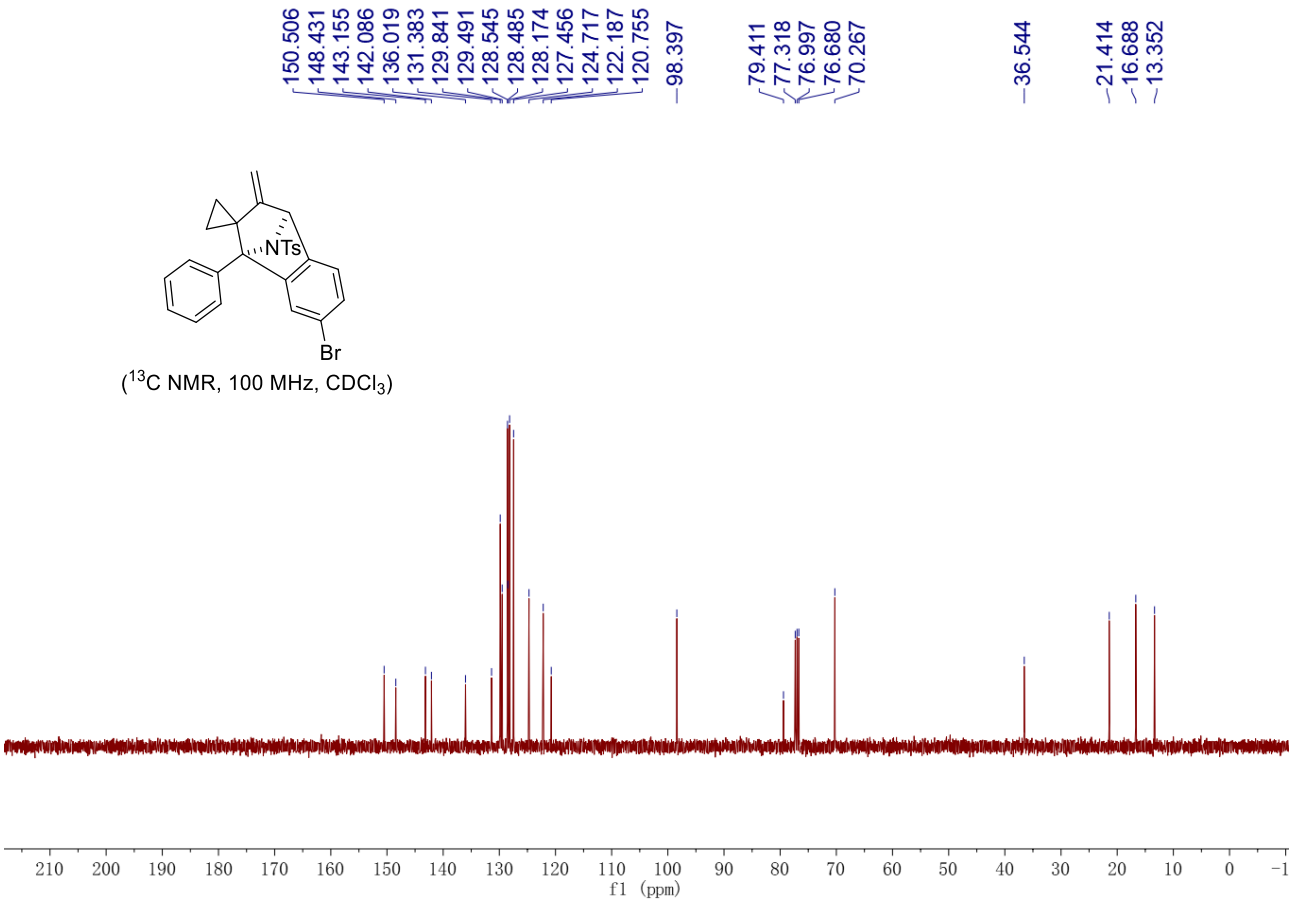


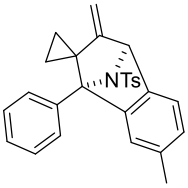
***N*-(7'-bromo-3'-methylene-1'-phenyl-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)-*N*,4-dimethylbenzenesulfonamide (3l)**: Yield: 21 mg, 21%, white solid, m.p. >200 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 – 7.56 (m, 2H), 7.37 – 7.30 (m, 3H), 7.28 – 7.22 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.94 – 6.84 (m, 4H), 5.74 (s, 1H), 4.98 (s, 1H), 4.29 (s, 1H), 2.32 (s, 3H), 0.97 – 0.85 (m, 2H), 0.43 – 0.28 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 150.5, 148.4, 143.2, 142.1, 136.0, 131.4, 129.8, 129.5, 128.5, 128.5, 128.2, 127.5, 124.7, 122.2, 120.8, 98.4, 79.4, 70.3, 36.5, 21.4, 16.7, 13.4; IR (neat): ν 3055, 2921, 2843, 1775, 1668, 1592, 1453, 1340, 1155, 1085, 863, 731, 663 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 514.04468, found: 514.04511.



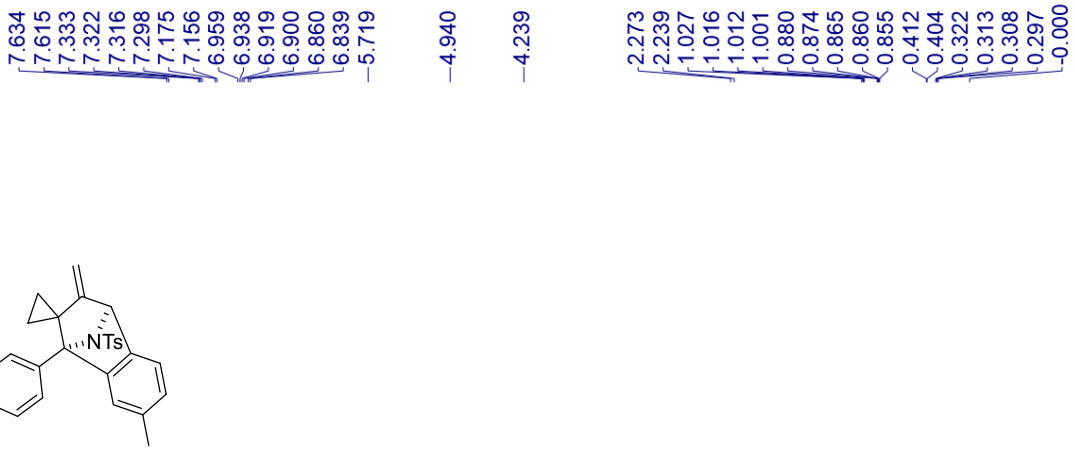
(^{1}H NMR, 400 MHz, $CDCl_3$)



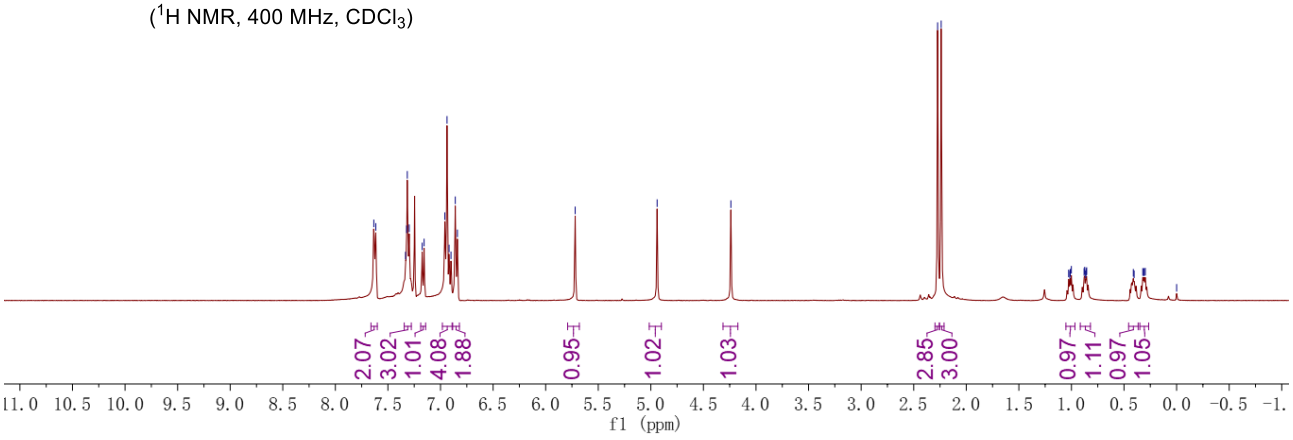

150.506
148.431
143.155
142.086
136.019
131.383
129.841
129.491
128.545
128.485
128.174
127.456
124.717
122.187
120.755
98.397
79.411
77.318
76.997
76.680
70.267
36.544
21.414
16.688
13.352
NTs
Br
(13C NMR, 100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

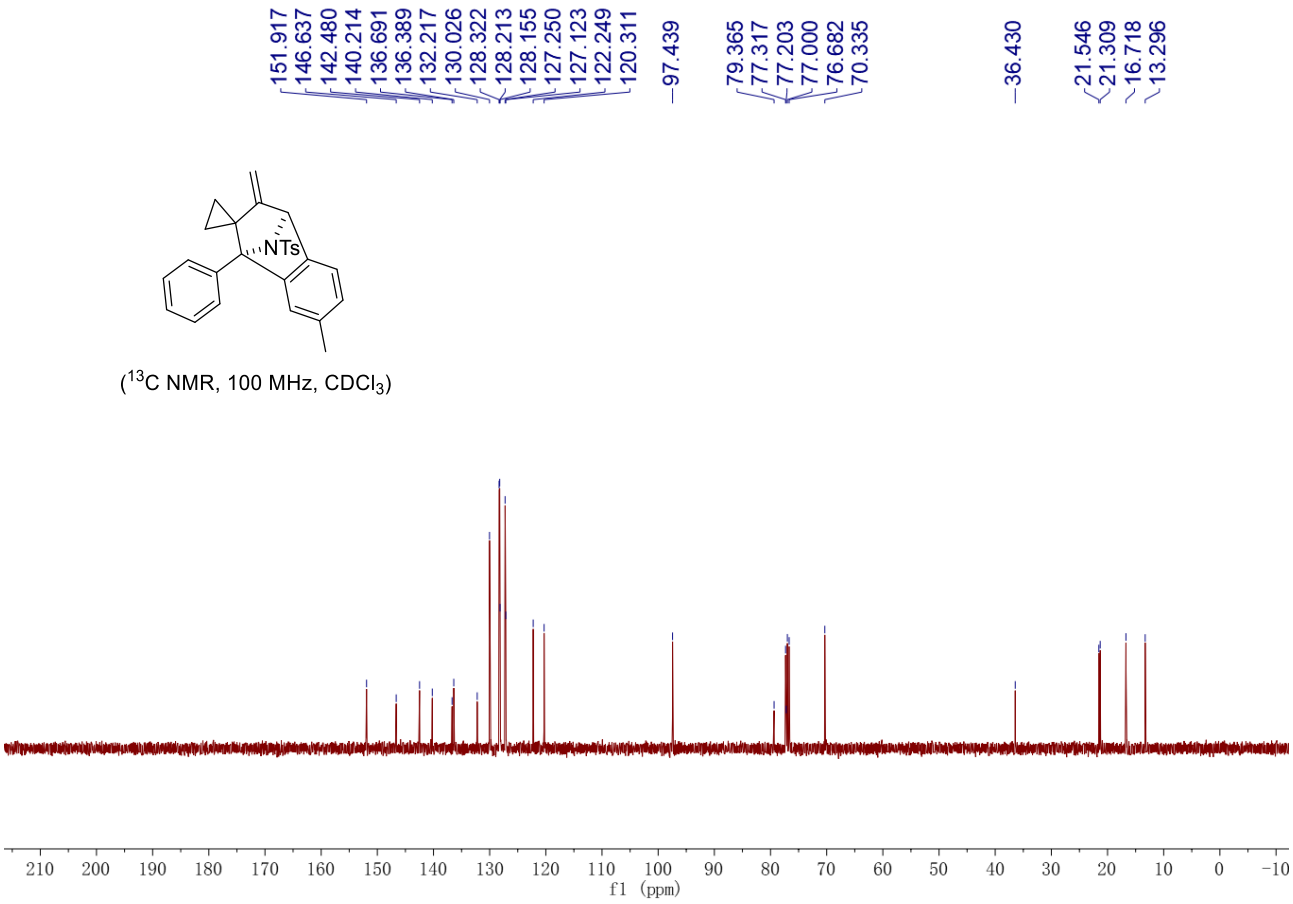


***N*,4-dimethyl-*N*-(7'-methyl-3'-methylene-1'-phenyl-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)benzenesulfonamide (3m)**: Yield: 23 mg, 27%, white solid, m.p. 181-183 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.98 – 6.89 (m, 4H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.72 (s, 1H), 4.94 (s, 1H), 4.24 (s, 1H), 2.27 (s, 3H), 2.24 (s, 3H), 1.05 – 0.97 (m, 1H), 0.92 – 0.82 (m, 1H), 0.46 – 0.37 (m, 1H), 0.35 – 0.27 (m, 1H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 151.9, 146.6, 142.5, 140.2, 136.7, 136.4, 132.2, 130.0, 128.3, 128.2, 128.2, 127.3, 127.1, 122.2, 120.3, 97.4, 79.4, 70.3, 36.4, 21.5, 21.3, 16.7, 13.3; IR (neat): ν 3052, 2924, 2856, 1772, 1594, 1445, 1342, 1157, 1087, 872, 703, 666 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 450.14982, found: 450.14922.

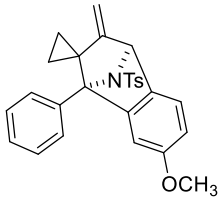


(^{1}H NMR, 400 MHz, $CDCl_3$)

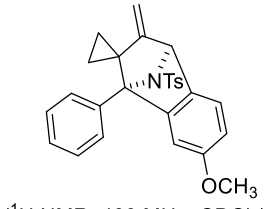




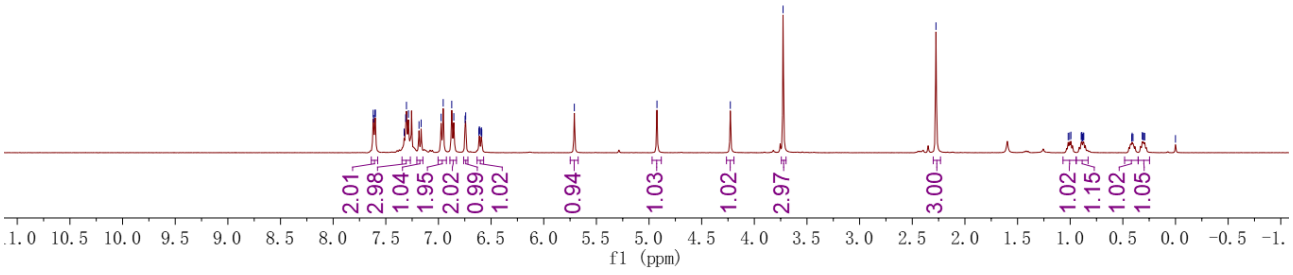
(^{13}C NMR, 100 MHz, $CDCl_3$)

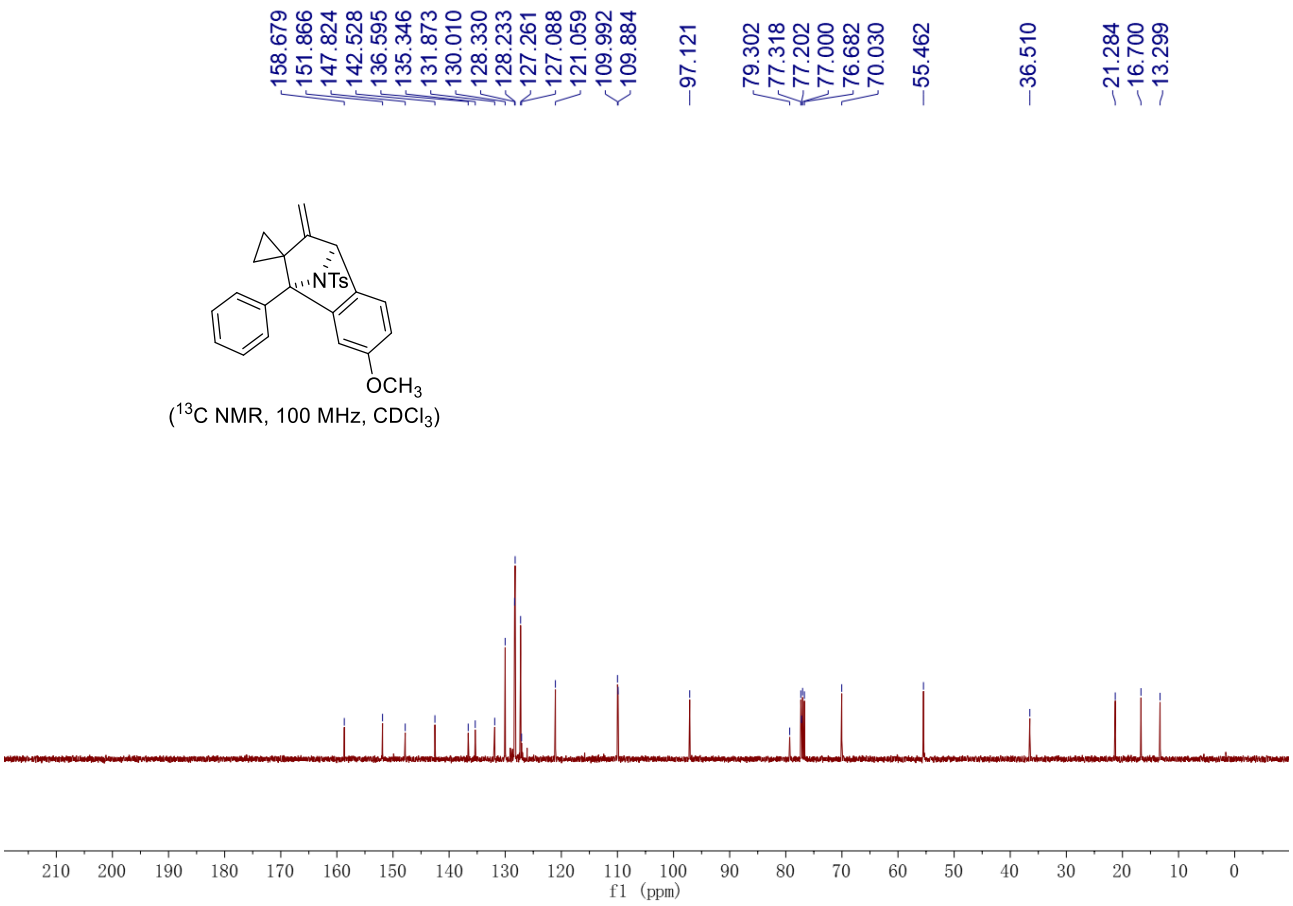


***N*-(7'-methoxy-3'-methylene-1'-phenyl-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)-*N*,4-dimethylbenzenesulfonamide (3n)**: Yield: 22 mg, 25%, white solid, m.p. > 200 °C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.64 – 7.58 (m, 2H), 7.35 – 7.27 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 2.4 Hz, 1H), 6.60 (dt, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 5.71 (s, 1H), 4.92 (s, 1H), 4.23 (s, 3H), 3.73 (s, 3H), 2.27 (s, 3H), 1.07 – 0.94 (m, 1H), 0.94 – 0.83 (m, 1H), 0.48 – 0.35 (m, 1H), 0.35 – 0.25 (m, 1H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 158.7, 151.9, 147.8, 142.5, 136.6, 135.3, 131.9, 130.0, 128.3, 128.2, 127.3, 127.1, 121.1, 110.0, 109.9, 97.1, 79.3, 70.0, 55.5, 36.5, 21.3, 16.7, 13.3; IR (neat): ν 3071, 2977, 2914, 1670, 1589, 1471, 1341, 1283, 1152, 1084, 979, 870, 729, 670 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 466.14474, found: 466.14390.

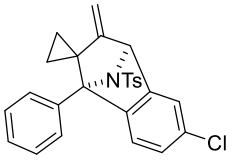


(^{1}H NMR, 400 MHz, $CDCl_3$)

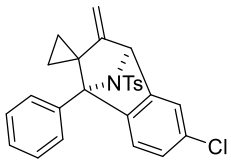




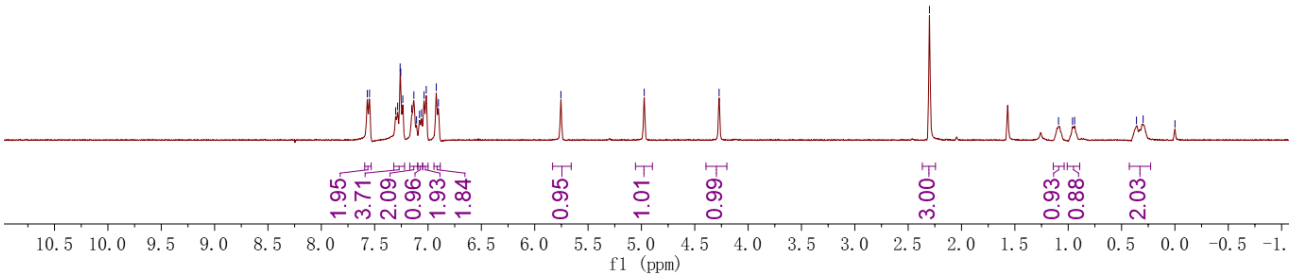
(^{13}C NMR, 100 MHz, $CDCl_3$)

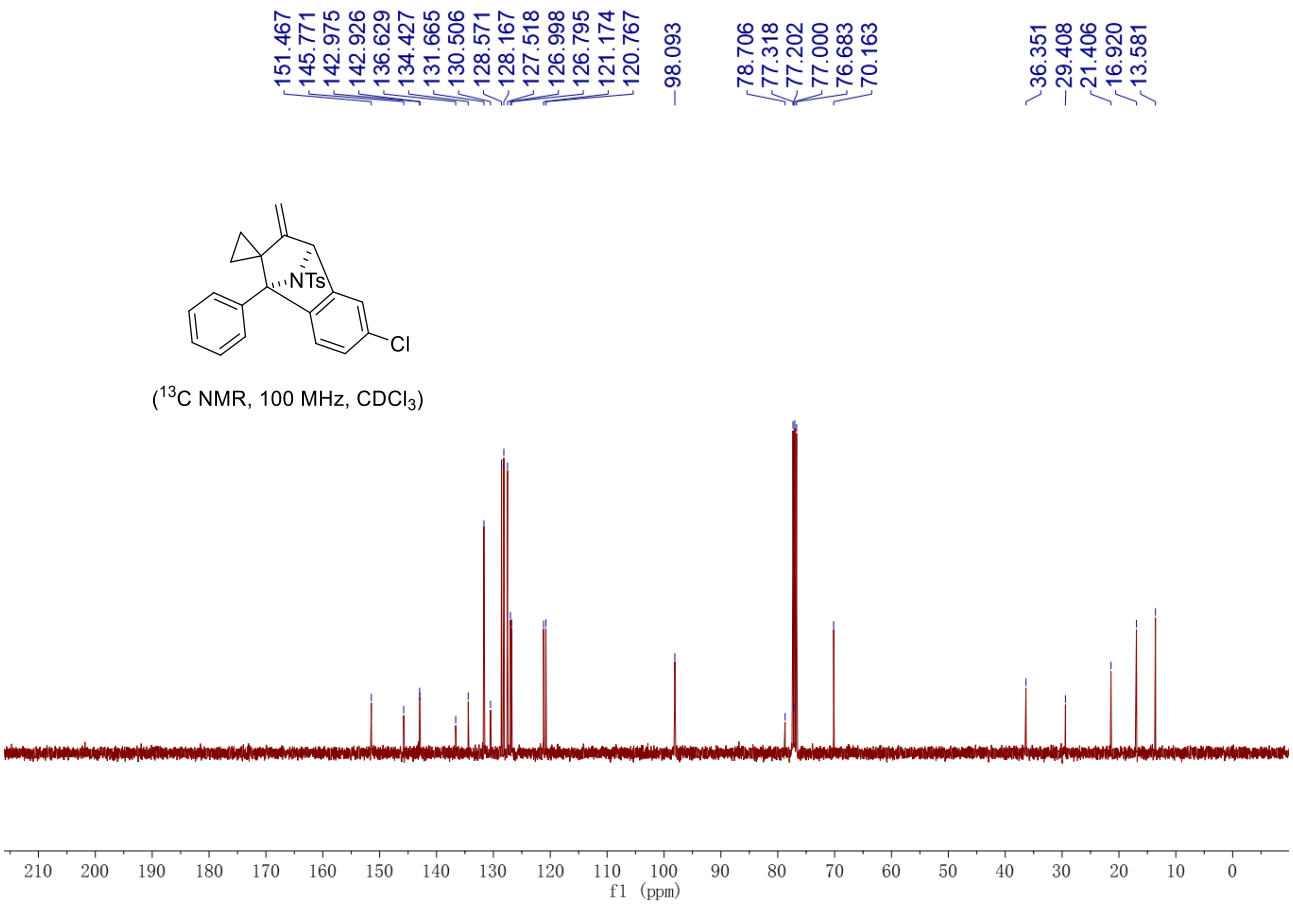


***N*-(6'-chloro-3'-methylene-1'-phenyl-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)-N,4-dimethylbenzenesulfonamide (3o)**: Yield: 18 mg, 20%, white solid, m.p. > 200 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.22 (m, 3H), 7.17 – 7.10 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.75 (s, 1H), 4.97 (s, 1H), 4.27 (s, 1H), 2.30 (s, 3H), 1.09 (m, 1H), 1.01 – 0.89 (m, 1H), 0.43 – 0.23 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 151.5, 145.8, 143.0, 142.9, 136.6, 134.4, 131.7, 130.5, 128.6, 128.2, 127.5, 127.0, 126.8, 121.2, 120.8, 98.1, 78.7, 70.2, 36.4, 29.4, 21.4, 16.9, 13.6; IR (neat): ν 3068, 2922, 2849, 1670, 1599, 1492, 1342, 1158, 1089, 1015, 830, 654 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 470.09520, found: 470.09463.

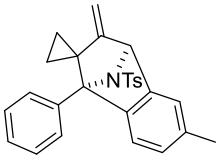


(^{1}H NMR, 400 MHz, $CDCl_3$)

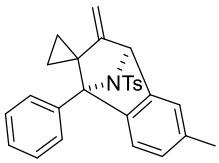




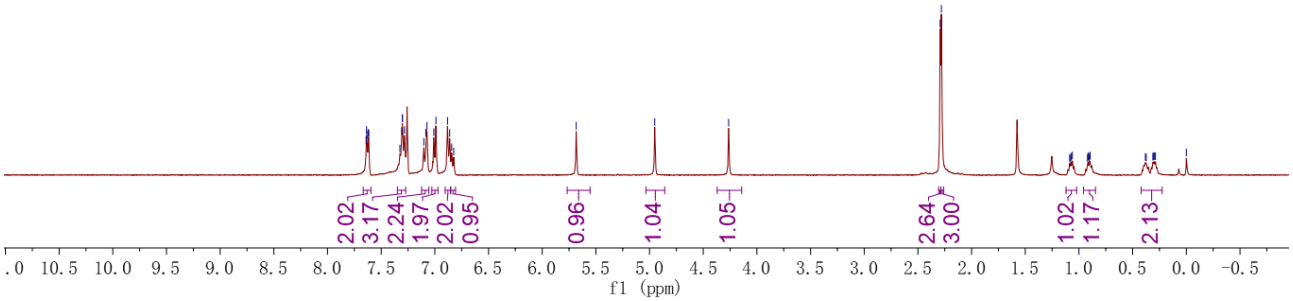
(^{13}C NMR, 100 MHz, $CDCl_3$)

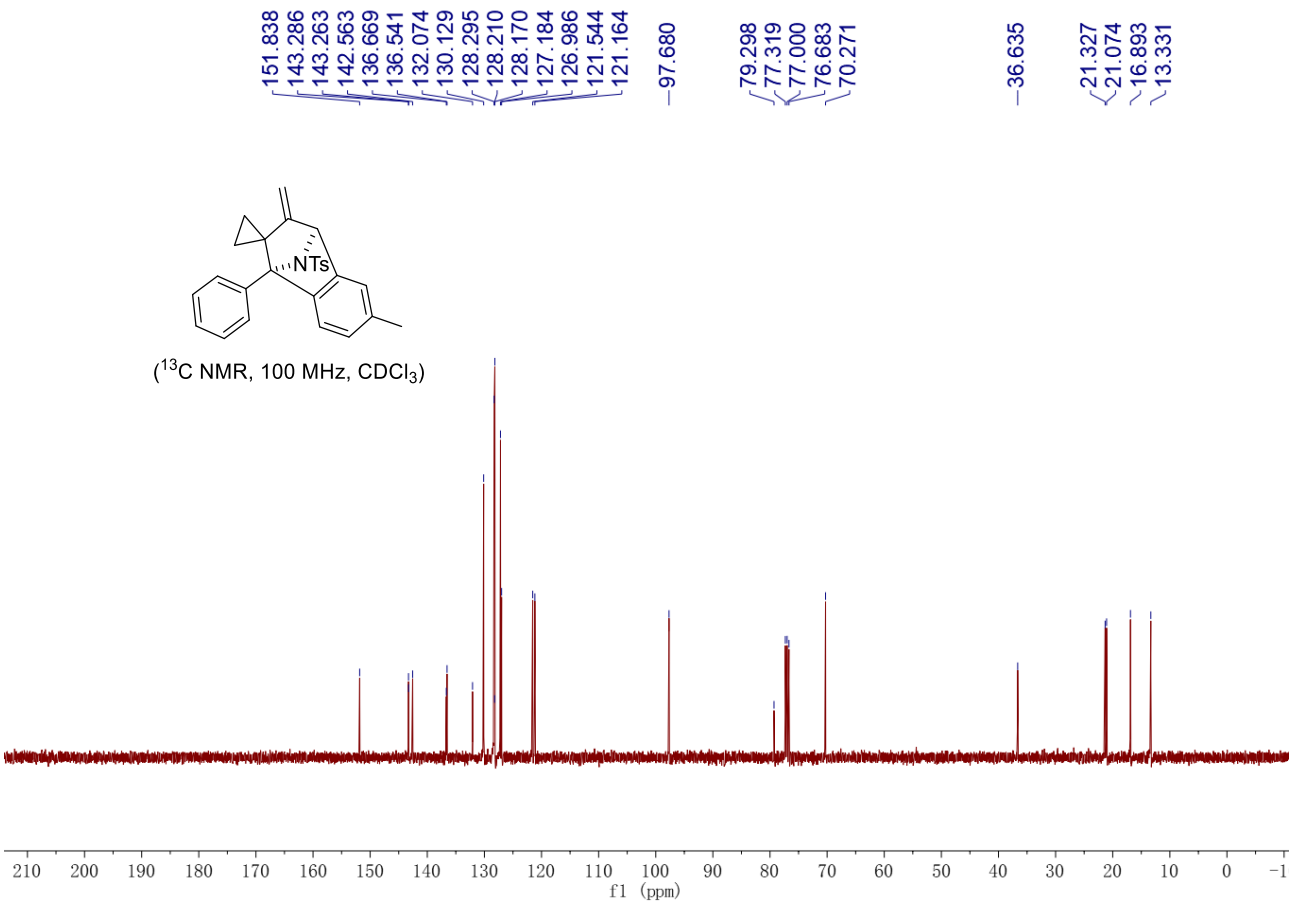


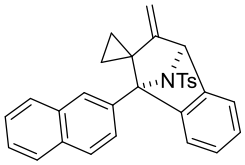
***N*,4-dimethyl-*N*-(6'-methyl-3'-methylene-1'-phenyl-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)benzenesulfonamide (3p)**: Yield: 22 mg, 26%, white solid, m.p. 161-163 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.67 – 7.60 (m, 2H), 7.35 – 7.27 (m, 3H), 7.12 – 7.06 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 5.68 (s, 1H), 4.95 (s, 1H), 4.26 (s, 1H), 2.29 (s, 3H), 2.28 (s, 3H), 1.12 – 1.02 (m, 1H), 0.96 – 0.85 (m, 1H), 0.42 – 0.23 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 151.8, 143.3, 143.3, 142.6, 136.7, 136.5, 132.1, 130.1, 128.3, 128.2, 128.2, 127.2, 127.0, 121.5, 121.2, 97.7, 79.3, 70.3, 36.6, 21.3, 21.1, 16.9, 13.3; IR (neat): ν 3047, 2916, 2848, 1665, 1594, 1448, 1341, 1159, 1088, 880, 732, 691 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.14933.



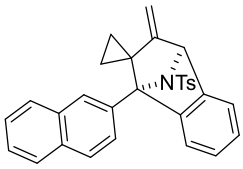
(^{1}H NMR, 400 MHz, $CDCl_3$)



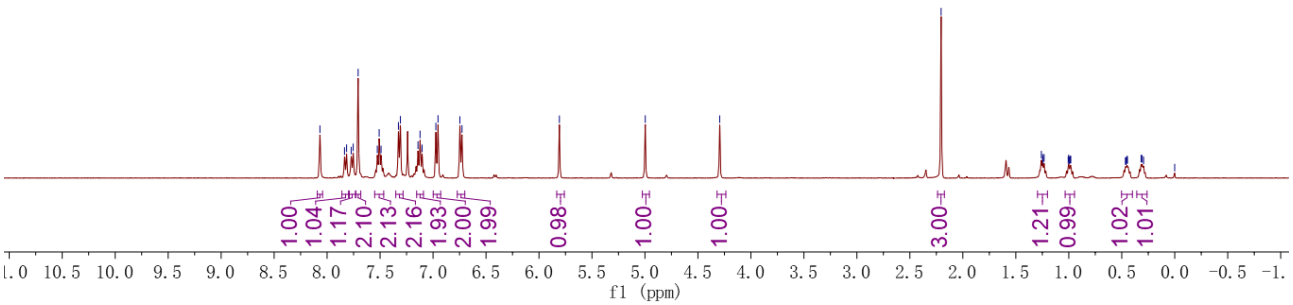

151.838
143.286
143.263
142.563
136.669
136.541
132.074
130.129
128.295
128.210
128.170
127.184
126.986
121.544
121.164
97.680
79.298
77.319
77.000
76.683
70.271
36.635
21.327
21.074
16.893
13.331
NTs
(13C NMR, 100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

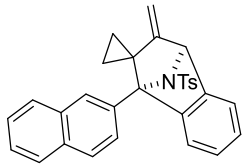


***N*,4-dimethyl-*N*-(3'-methylene-1'-(naphthalen-2-yl)-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)benzenesulfonamide (3q)**: Yield: 19 mg, 20%, white solid, m.p. >200 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.07 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.71 (s, 2H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.12 (t,*J* = 7.6 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 2H), 5.81 (s, 1H), 5.00 (s, 1H), 4.29 (s, 1H), 2.21 (s, 3H), 1.30 – 1.20 (m, 1H), 1.03 – 0.95 (m, 1H), 0.50 – 0.40 (m, 1H), 0.36 – 0.26 (m, 1H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 151.9, 146.2, 143.0, 142.7, 136.6, 132.9, 132.2, 129.6, 128.8, 128.7, 128.4, 128.3, 128.2, 127.4, 126.9, 126.8, 126.7, 126.5, 125.9, 121.5, 120.7, 97.9, 79.3, 70.1, 36.3, 21.3, 17.1, 13.8; IR (neat): ν 3047, 2984, 2916, 1668, 1589, 1456, 1324, 1152, 1091, 958, 873, 741, 661 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 486.14982, found: 486.15015.

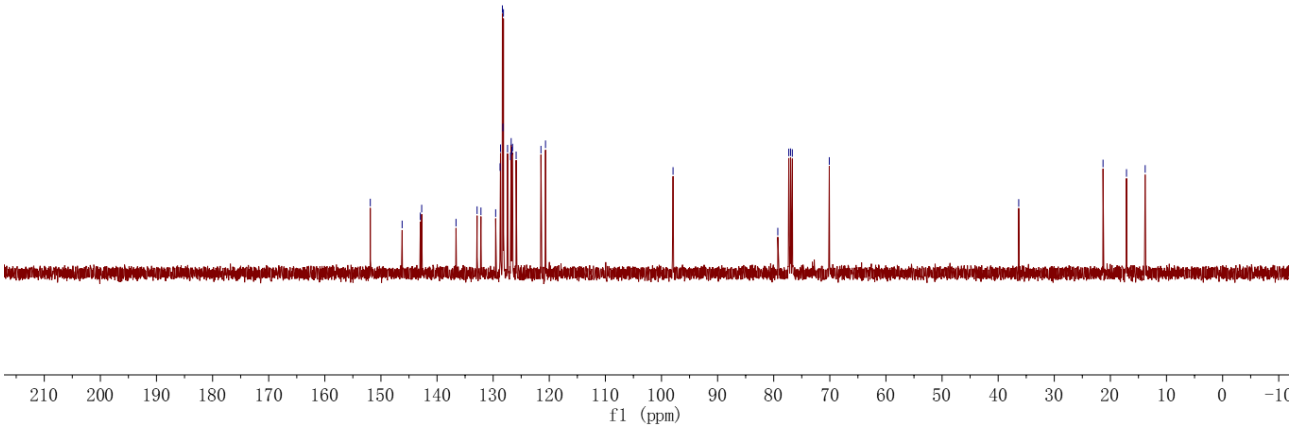


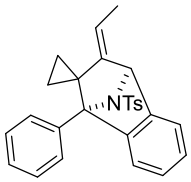
(^{1}H NMR, 400 MHz, $CDCl_3$)



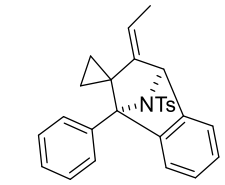


(^{13}C NMR, 100 MHz, $CDCl_3$)

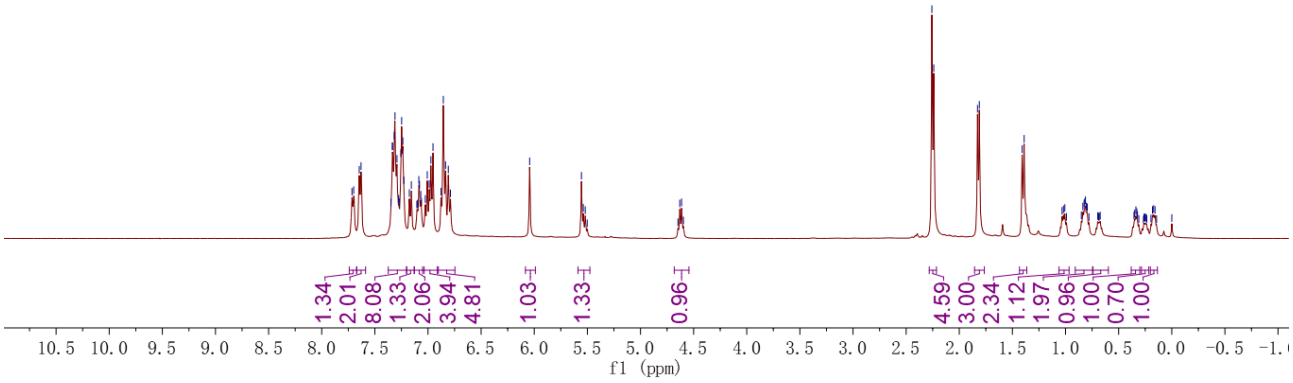


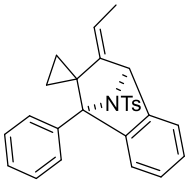


***N*-(3'-ethylidene-1'-phenyl-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)-*N*,4-dimethylbenzenesulfonamide (3u)**: Yield: 15 mg, 18%, white solid, *Z*:*E* = 1.5:1; m.p. 197-199 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.71 (d, *J* = 6.4 Hz, 1.34H), 7.64 (d, *J* = 6.8 Hz, 2H), 7.37 – 7.20 (m, 8.08H), 7.17 (d, *J* = 7.6 Hz, 1.33H), 7.08 (td, J_1 = 7.6 Hz, J_2 = 2.8 Hz, 2H), 7.05 – 6.91 (m, 3.94H), 6.90 – 6.75 (m, 4.81H), 6.04 (s, 1H), 5.59 – 5.48 (m, 1.33H), 4.62 (q, *J* = 6.8 Hz, 1H), 2.28 – 2.21 (m, 4.5H), 1.82 (d, *J* = 6.8 Hz, 3H), 1.40 (d, *J* = 7.6 Hz, 2.34H), 1.06 – 0.97 (m, 1H), 0.91 – 0.75 (m, 2H), 0.74 – 0.60 (m, 1H), 0.38 – 0.29 (m, 1H), 0.29 – 0.21 (m, 0.7H), 0.22 – 0.12 (m, 1H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 146.2, 145.2, 144.1, 142.8, 142.6, 142.5, 142.2, 139.5, 136.6, 136.3, 132.0, 131.7, 130.5, 130.2, 128.4, 128.3, 128.3, 128.2, 128.2, 127.2, 127.1, 126.7, 126.6, 126.4, 126.3, 121.6, 121.4, 120.4, 120.0, 113.1, 108.1, 80.6, 79.3, 72.3, 66.1, 37.1, 35.7, 21.4, 16.2, 14.0, 13.4, 12.6, 11.7, 9.2; IR (neat): ν 3058, 2982, 2919, 1594, 1453, 1339, 1156, 1087, 814, 680 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 450.14982, found: 450.15006.

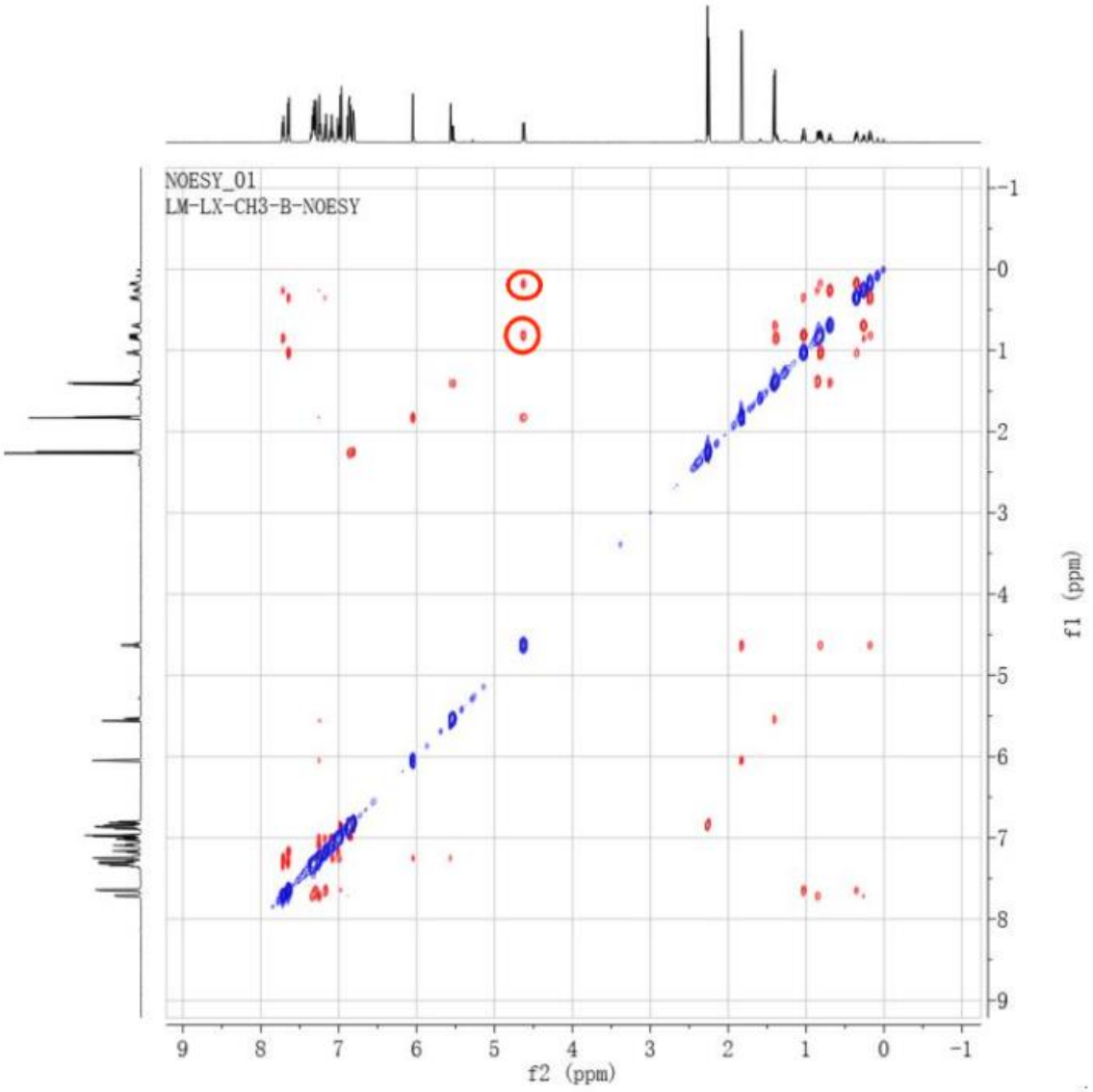


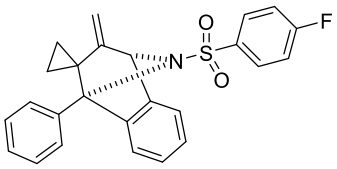
(^{1}H NMR, 400 MHz, $CDCl_3$)



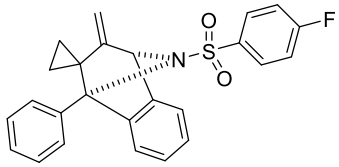


(^{13}C NMR, 100 MHz, $CDCl_3$)

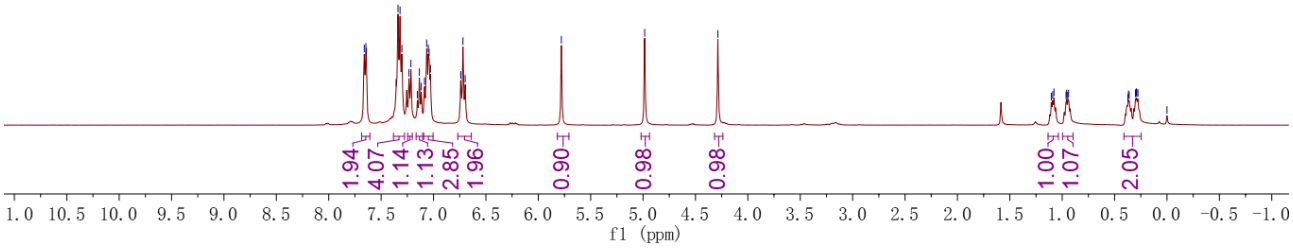

NOESY_01
LM-LX-CH3-B-NOESY
f2 (ppm)
f1 (ppm)

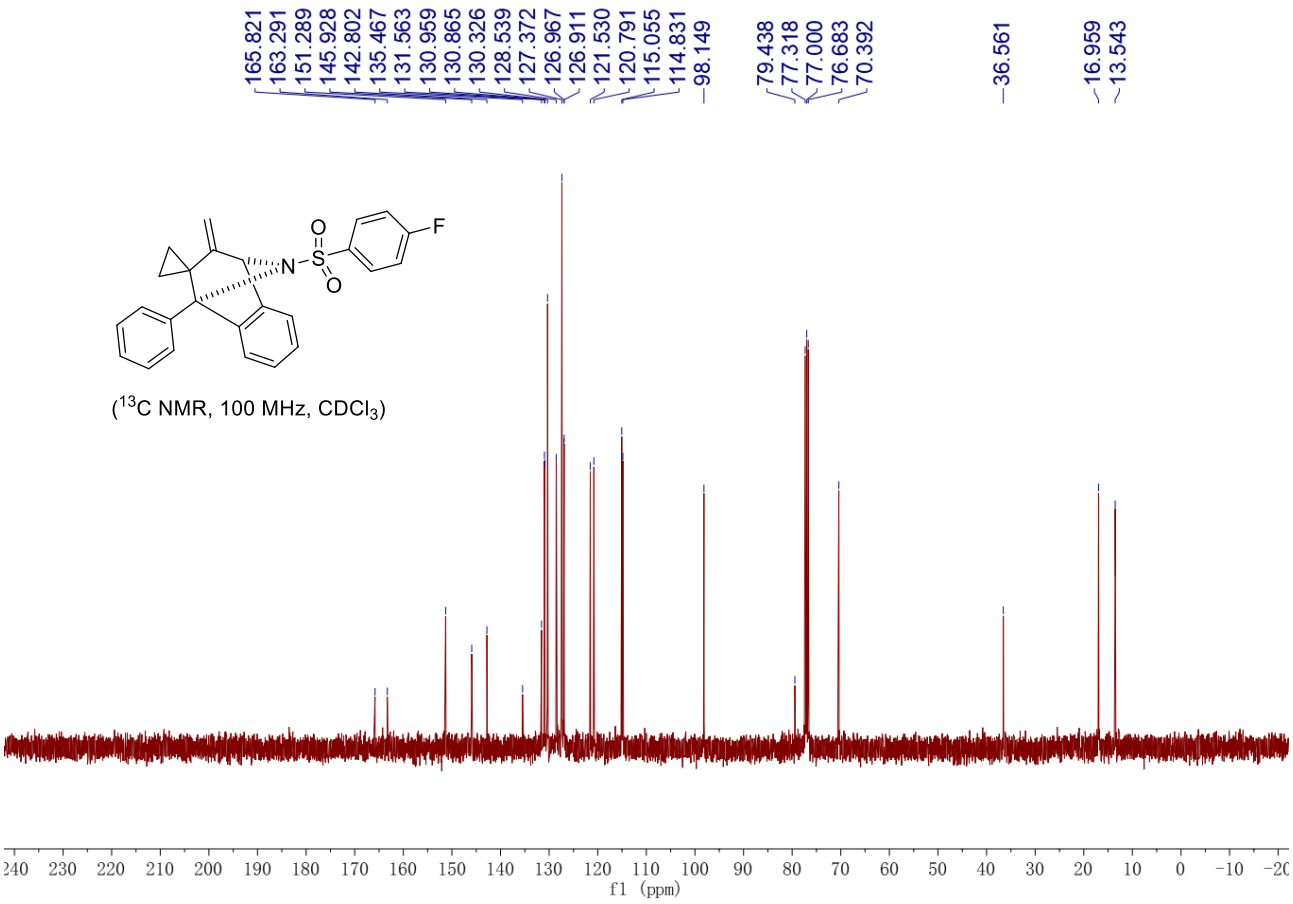


9'-((4-fluorophenyl)sulfonyl)-3'-methylene-1'-phenyl-3',4'-dihydro-1'*H*-spiro[cyclopropane-1, 2'-[1,4]epiminonaphthalene] (3v): Yield: 13 mg, 16%, white solid, m.p. 197-199 ºC; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.69 – 7.61 (m, 2H), 7.38 – 7.28 (m, 4H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.09 – 7.00 (m, 3H), 6.72 (t, *J* = 8.4 Hz, 2H), 5.78 (s, 1H), 4.98 (s, 1H), 4.29 (s, 1H), 1.13 – 1.04 (m, 1H), 1.00 – 0.90 (m, 1H), 0.41 – 0.25 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 164.6 (d, *J* = 253.0 Hz), 151.3, 145.9, 142.8, 135.5, 131.6, 130.9 (d, *J* = 9.4 Hz), 130.3, 128.5, 127.4, 127.0, 126.9, 121.5, 120.8, 114.9 (d, *J* = 22.4 Hz), 98.1, 79.4, 70.4, 36.6, 17.0, 13.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.0; IR (neat): ν 3060, 2972, 2925, 1766, 1662, 1450, 1341, 1156, 1087, 1025, 878, 757, 688 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 440.10910, found: 440.10925.

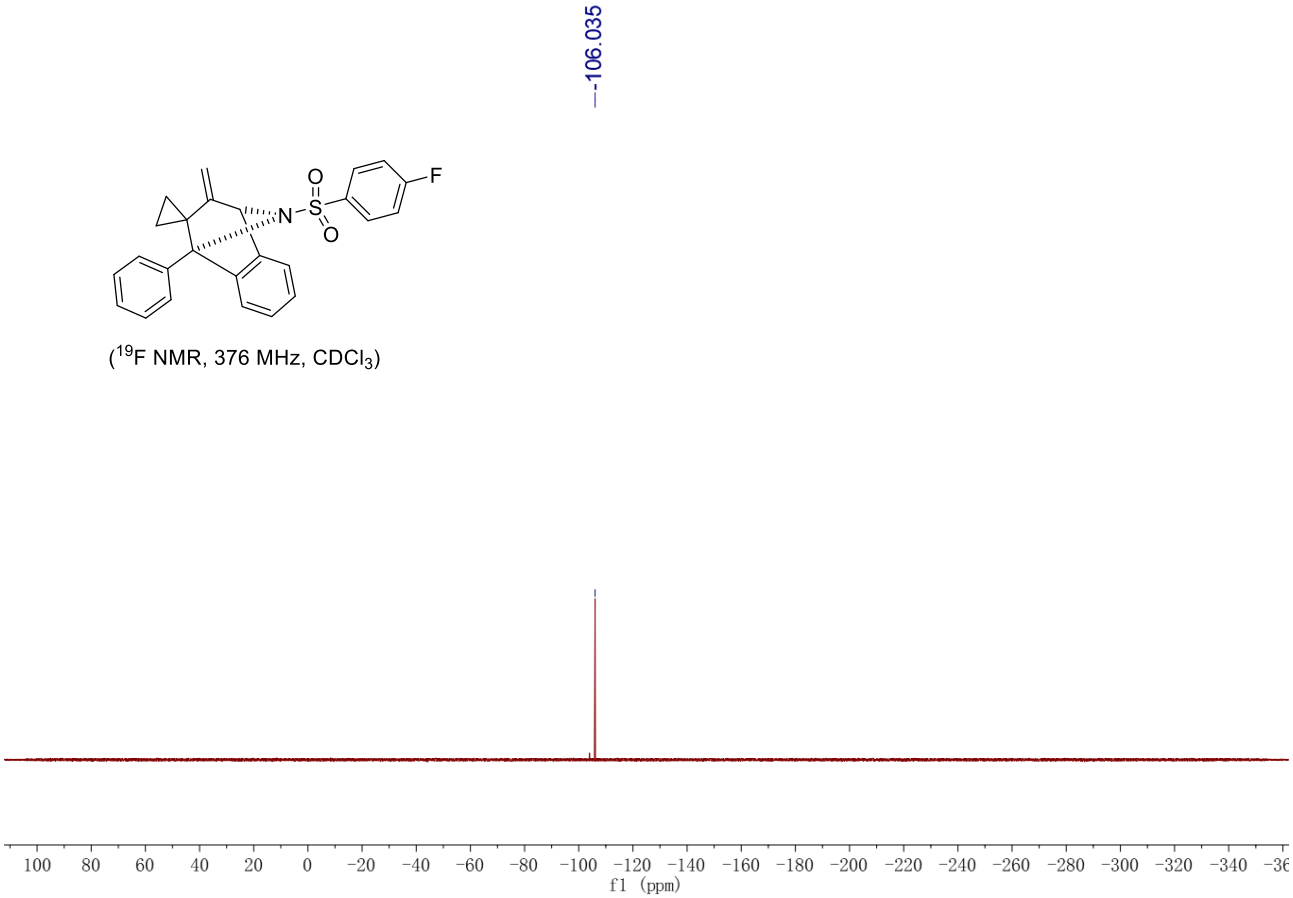


(^{1}H NMR, 400 MHz, $CDCl_3$)

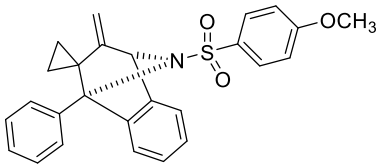




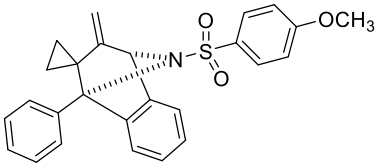
(^{13}C NMR, 100 MHz, $CDCl_3$)



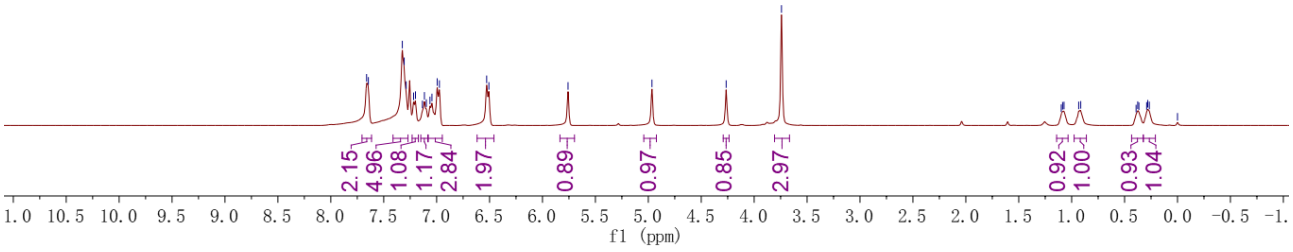
(^{19}F NMR, 376 MHz, $CDCl_3$)

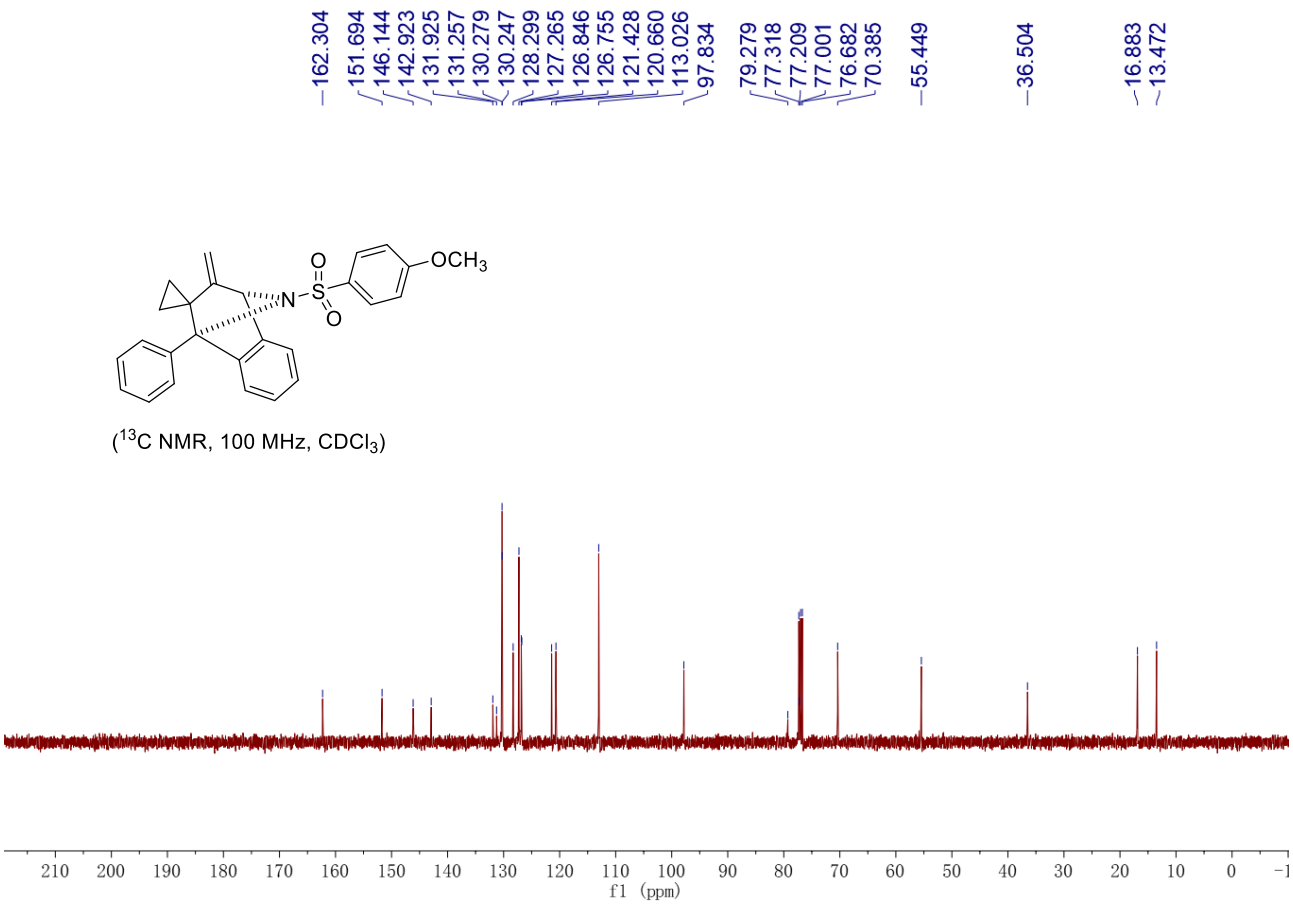


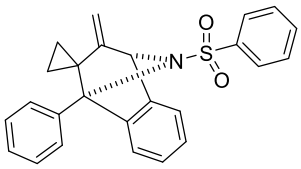
9'-((4-methoxyphenyl)sulfonyl)-3'-methylene-1'-phenyl-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-[1,4]epiminonaphthalene] (3w): Yield: 19 mg, 22%, white solid, m.p. 187-189 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 (d, *J* = 6.8 Hz, 2H), 7.41 – 7.27 (m, 5H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.08 – 6.95 (m, 3H), 6.52 (d, *J* = 8.4 Hz, 2H), 5.76 (s, 1H), 4.97 (s, 1H), 4.26 (s, 1H), 3.74 (s, 3H), 1.14 – 1.03 (m, 1H), 0.98 – 0.86 (m, 1H), 0.43 – 0.32 (m, 1H), 0.32 – 0.21 (m, 1H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 162.3, 151.7, 146.1, 142.9, 131.9, 131.3, 130.3, 130.2, 128.3, 127.3, 126.8, 126.8, 121.4, 120.7, 113.0, 97.8, 79.3, 70.4, 55.4, 36.5, 16.9, 13.5; IR (neat): ν 3045, 2985, 2917, 1667, 1594, 1492, 1340, 1257, 1088, 866, 695 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ $[M+Na]^+$: 452.12909, found: 452.12960.



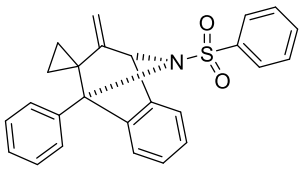
(^{1}H NMR, 400 MHz, $CDCl_3$)



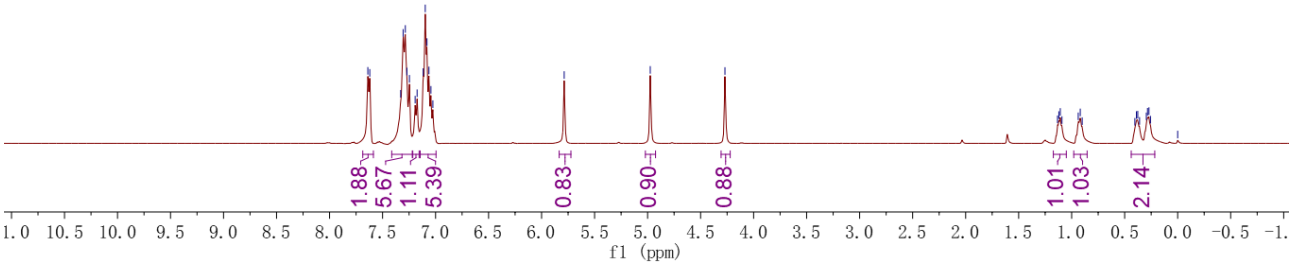

162.304
151.694
146.144
142.923
131.925
131.257
130.279
130.247
128.299
127.265
126.846
126.755
121.428
120.660
113.026
97.834
79.279
77.318
77.209
77.001
76.682
70.385
55.449
36.504
16.883
13.472
OCH3
O
S
N
O
(13C NMR, 100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

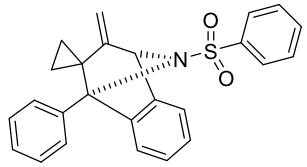


3'-methylene-1'-phenyl-9'-(phenylsulfonyl)-3',4'-dihydro-1'*H*-spiro[cyclopropane-1,2'-[1,4]epiminonaphthalene] (3x): Yield: 23 mg, 29%, white solid, m.p. 149-151 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.22 (m, 6H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.15 – 7.00 (m, 5H), 5.79 (s, 1H), 4.97 (s, 1H), 4.27 (s, 1H), 1.17 – 1.05 (m, 1H), 0.98 – 0.85 (m, 1H), 0.44 – 0.22 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 151.6, 146.1, 142.8, 139.5, 131.9, 131.7, 130.2, 128.3, 128.1, 127.8, 127.3, 126.8, 126.8, 121.4, 120.6, 97.9, 79.3, 70.3, 36.4, 16.9, 13.5; IR (neat): ν 3058, 2925, 2852, 1777, 1590, 1492, 1361, 1238, 1088, 838, 697 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]$^{+}$: 422.11852, found: 422.11807.

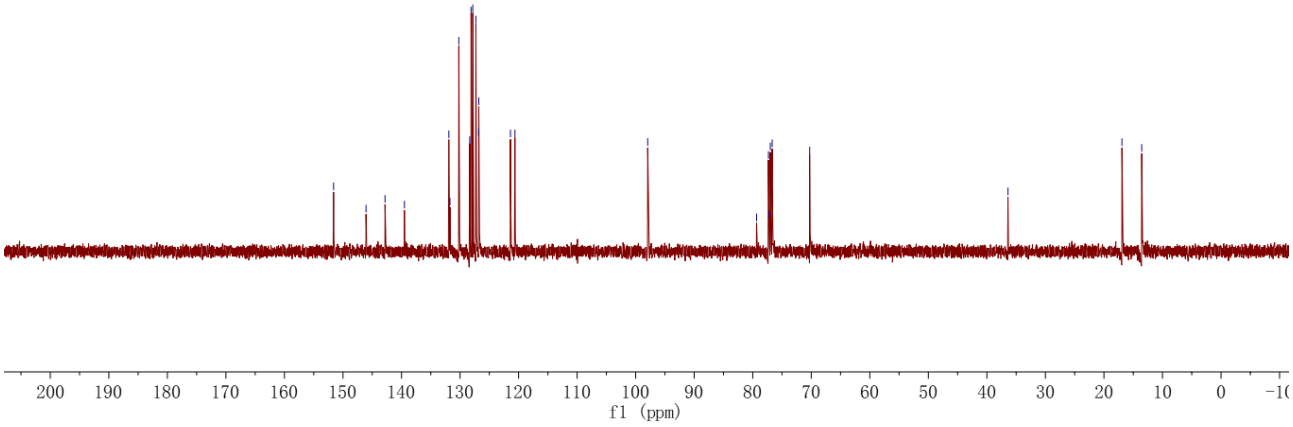


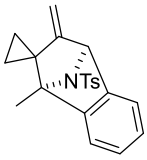
(^{1}H NMR, 400 MHz, $CDCl_3$)



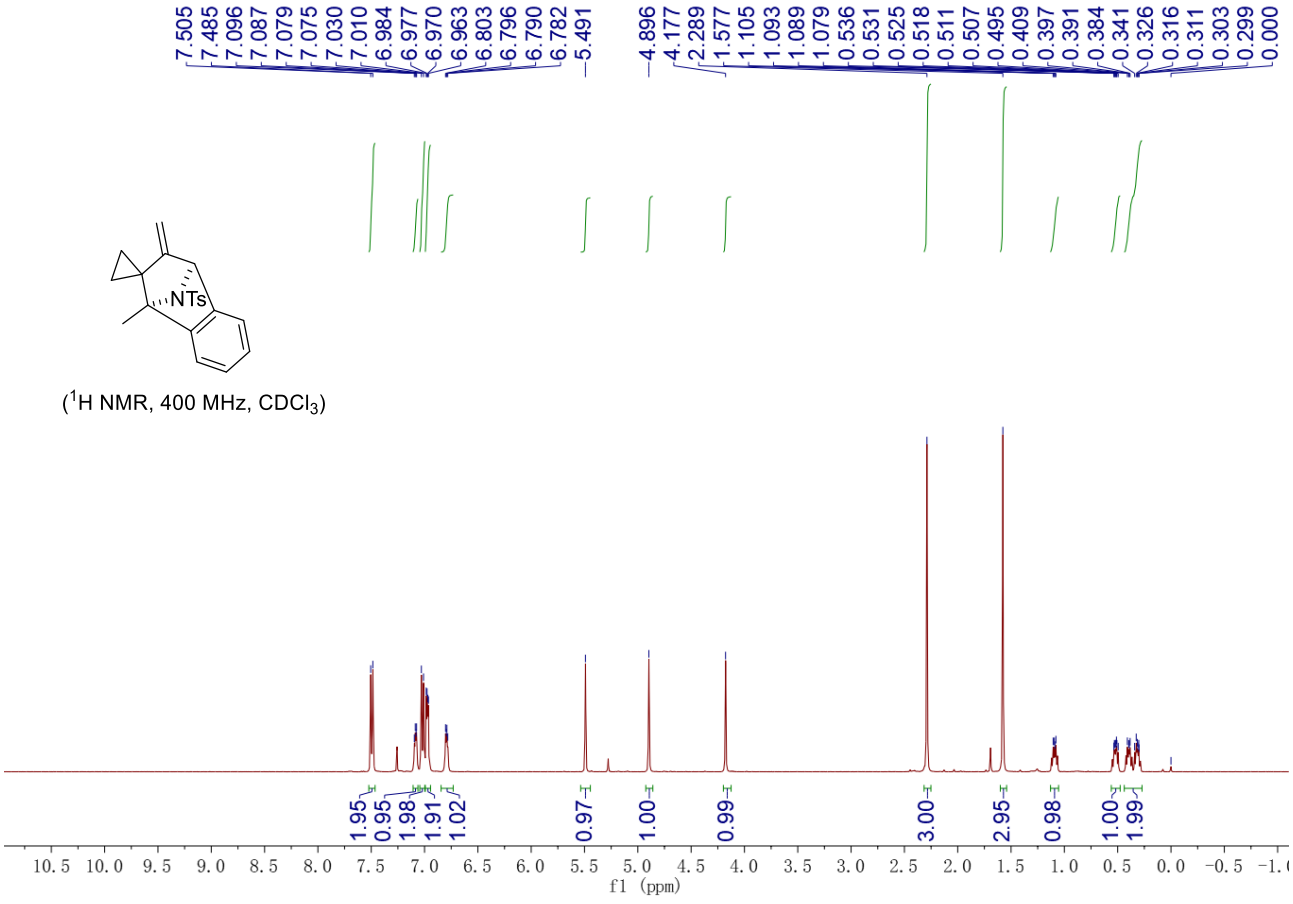


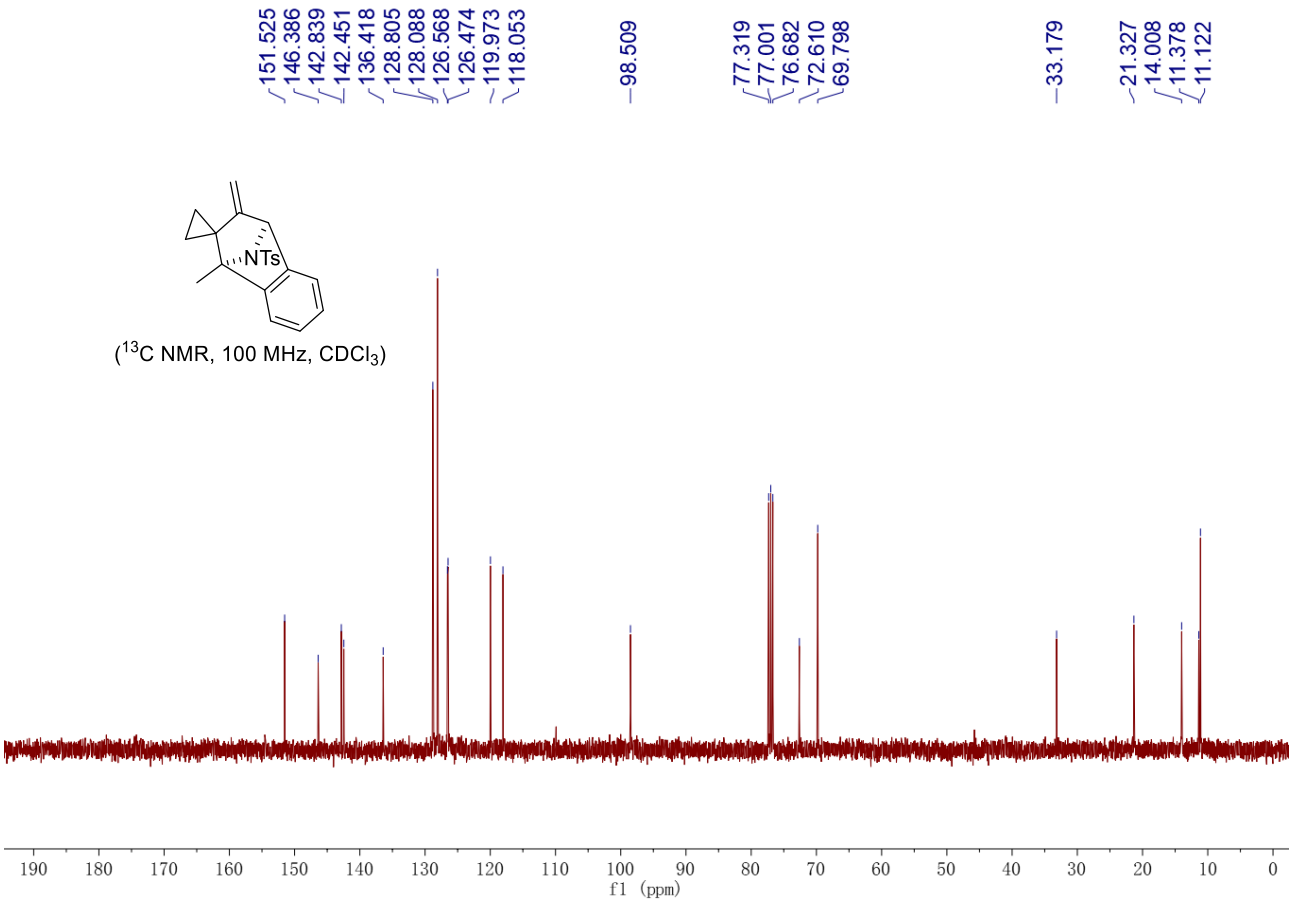
(^{13}C NMR, 100 MHz, $CDCl_3$)



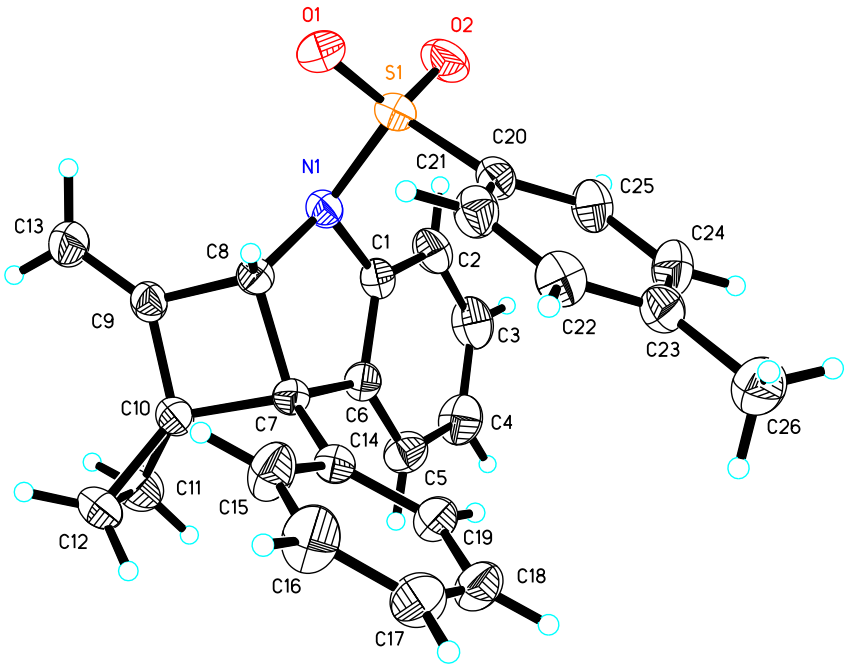


***N*,4-dimethyl-*N*-(1'-methyl-3'-methylene-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphthalen]-1'-yl)benzenesulfonamide (3af)**: Yield: 23 mg, 32%, white solid, m.p. 181-183 ^{o}C; Eluent: PE/EA = 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.11 – 7.06 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.99 – 6.94 (m, 2H), 6.85 – 6.73 (m, 1H), 5.49 (s, 1H), 4.90 (s, 1H), 4.18 (s, 1H), 2.29 (s, 3H), 1.58 (s, 3H), 1.13 – 1.05 (m, 1H), 0.56 – 0.48 (m, 1H), 0.44 – 0.27 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$, TMS) δ 151.5, 146.4, 142.8, 142.5, 136.4, 128.8, 128.1, 126.6, 126.5, 120.0, 118.1, 98.5, 72.6, 69.8, 33.2, 21.3, 14.0, 11.4, 11.1; IR (neat): ν 3076, 3000, 2935, 1670, 1594, 1461, 1331, 1159, 1089, 773, 656 cm^{-1}; HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NO_2Na$ [M+Na]+: 374.11852, found: 374.11823.




151.525
146.386
142.839
142.451
136.418
128.805
128.088
126.568
126.474
119.973
118.053
98.509
77.319
77.001
76.682
72.610
69.798
33.179
21.327
14.008
11.378
11.122
NTs
(13C NMR, 100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7. X-ray Data

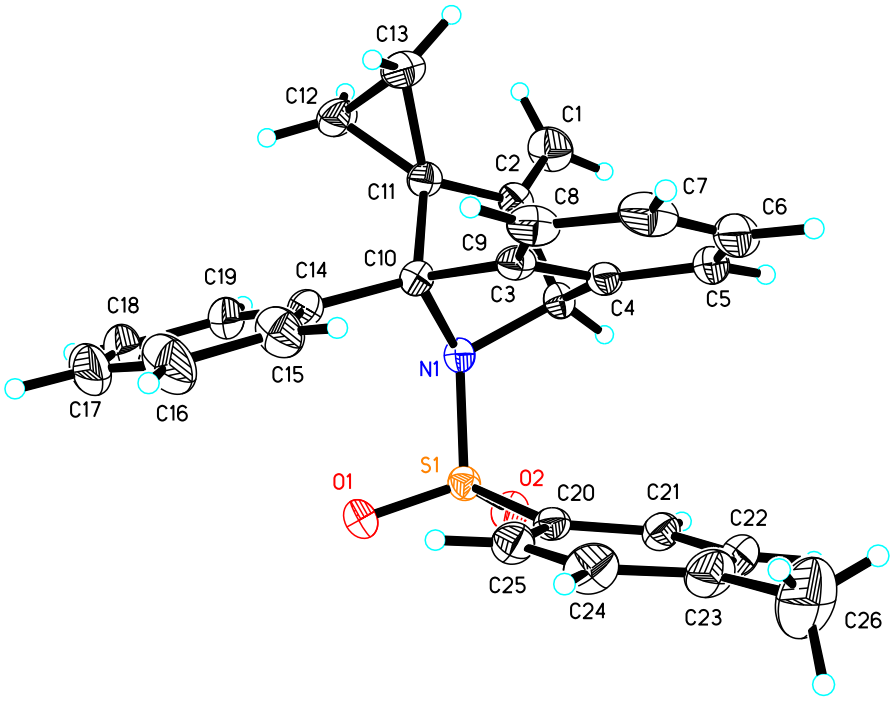


Single crystals of **2a** were grown in dichloromethane and hexanes. Dichloromethane (2.0 mL) was added to **2a** (25 mg in a 4 mL vial) followed by 2 drops of hexanes. The 5 mL vial was capped and placed at room temperature in the experimental cabinet for 2 days, whereupon crystals formed.

A colorless crystal of **2a** was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 293(2) K, on a Rigaku AFC7R diffractometer. The crystal data of **2a** have been deposited in CCDC with number 2053911 and displayed at 30% ellipsoid contour probability level.

Table S2. Crystal data and structure refinement for 2a.

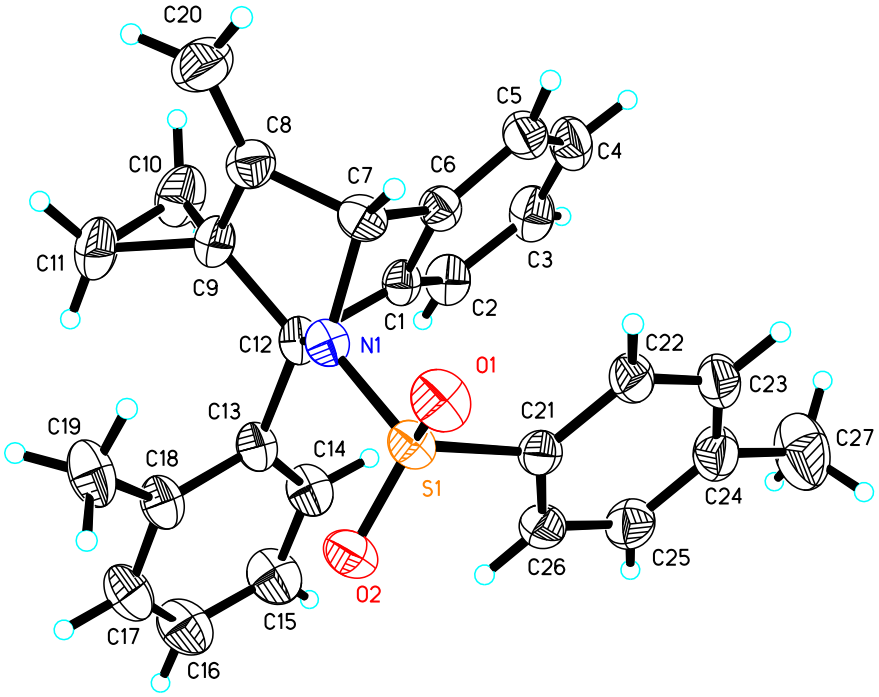
Identification code	**2a**	
Empirical formula	$C_{26}H_{23}NO_2S$	
Formula weight	413.51	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.9811(3) Å	a = 90°
	b = 18.8774(5) Å	b = 106.4060(10)°
	c = 13.1287(4) Å	g = 90°
Volume	2135.21(11) $Å^3$	
Z	4	
Density (calculated)	1.286 Mg/m^3	
Absorption coefficient	0.174 mm^{-1}	
F(000)	872	
Crystal size	0.200 x 0.150 x 0.120 mm^3	
Theta range for data collection	2.599 to 26.000°	
Index ranges	-11<=h<=9, -23<=k<=23, -15<=l<=16	
Reflections collected	22842	
Independent reflections	4162 [R(int) = 0.0350]	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6505	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	4162 / 0 / 281	
Goodness-of-fit on F2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.1060	
R indices (all data)	R1 = 0.0535, wR2 = 0.1152	
Extinction coefficient	0.021(3)	
Largest diff. peak and hole	0.237 and -0.273 e.$Å^{-3}$	



Single crystals of **3a** were grown in dichloromethane and hexanes. Ethyl acetate (2.0 mL) was added to **3a** (30 mg in a 4 mL vial) followed by 2 drops of hexanes. The 5 mL vial was capped and placed at room temperature in the experimental cabinet for 4 days or longer if necessary, whereupon crystals formed. A colorless crystal of **3a** was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 293(2) K, on a Rigaku AFC7R diffractometer. The crystal data of **3a** have been deposited in CCDC with number 2098330 and displayed at 30% ellipsoid contour probability level.

Table S3. Crystal data and structure refinement for 3a

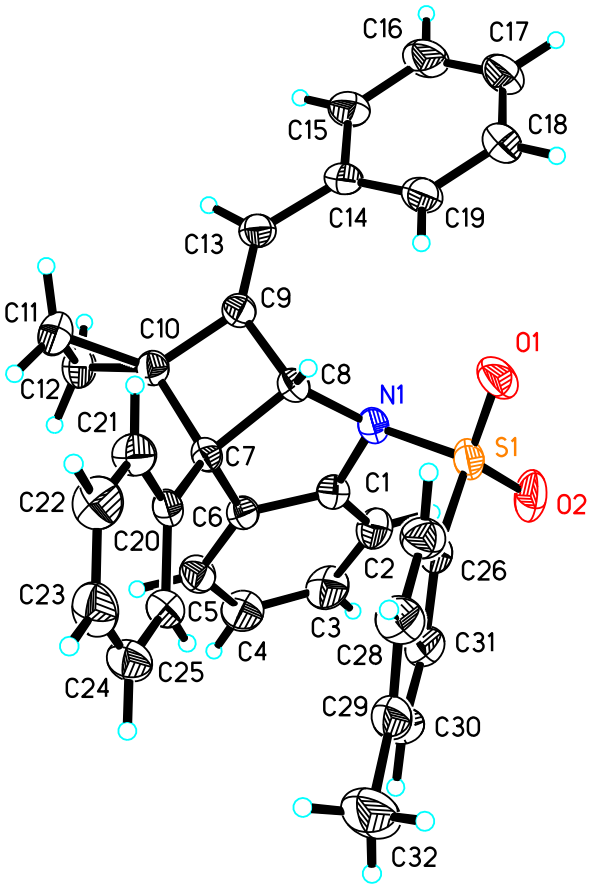
Identification code	**3a**	
Empirical formula	$C_{26}H_{23}NO_2S$	
Formula weight	413.51	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.2784(4) Å	a = 90°
	b = 8.8889(3) Å	b = 99.1490(10)°
	c = 21.1110(7) Å	g = 90°
Volume	2089.51(12) $Å^3$	
Z	4	
Density (calculated)	1.314 Mg/m^3	
Absorption coefficient	0.178 mm^{-1}	
F(000)	872	
Crystal size	0.200 x 0.150 x 0.120 mm^3	
Theta range for data collection	2.997 to 25.999°	
Index ranges	-13<=h<=13, -10<=k<=10, -26<=l<=26	
Reflections collected	41384	
Independent reflections	4073 [R(int) = 0.0701]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5417	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	4073 / 0 / 273	
Goodness-of-fit on F2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.1068	
R indices (all data)	R1 = 0.0461, wR2 = 0.1135	
Extinction coefficient	0.023(3)	
Largest diff. peak and hole	0.306 and -0.397 e.$Å^{-3}$	



Single crystals of **3i** were grown in dichloromethane and hexanes. Ethyl acetate (2.0 mL) was added to **3i** (20 mg in a 4 mL vial) followed by 2 drops of hexanes. The 5 mL vial was capped and placed at room temperature in the experimental cabinet for 3 days or longer if necessary, whereupon crystals formed. A colorless crystal of **3i** was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 293(2) K, on a Rigaku AFC7R diffractometer. The crystal data of **3i** have been deposited in CCDC with number 2115147 and displayed at 30% ellipsoid contour probability level.

Table S4. Crystal data and structure refinement for 3i

Identification code	**3i**	
Empirical formula	$C_{27}H_{25}NO_2S$	
Formula weight	427.54	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.5309(4) Å	a = 90°
	b = 9.3578(3) Å	b = 96.3810(10)°
	c = 20.9960(9) Å	g = 90°
Volume	2251.51(14) $Å^3$	
Z	4	
Density (calculated)	1.261 Mg/m^3	
Absorption coefficient	0.167 mm^{-1}	
F(000)	904	
Crystal size	0.200 x 0.150 x 0.120 mm^3	
Theta range for data collection	2.924 to 26.000°	
Index ranges	-14<=h<=13, -11<=k<=11, -25<=l<=25	
Reflections collected	22194	
Independent reflections	4397 [R(int) = 0.0443]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6393	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	4397 / 0 / 291	
Goodness-of-fit on F2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.1013	
R indices (all data)	R1 = 0.0490, wR2 = 0.1101	
Extinction coefficient	0.051(4)	
Largest diff. peak and hole	0.206 and -0.345 e.$Å^{-3}$	



Single crystals of **2t** were grown in dichloromethane and hexanes. Ethyl acetate (2.0 mL) was added to **2t** (30 mg in a 4 mL vial) followed by 2 drops of hexanes. The 5 mL vial was capped and placed at room temperature in the experimental cabinet for 4 days or longer if necessary, whereupon crystals formed. A colorless crystal of **2t** was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 293(2) K, on a Rigaku AFC7R diffractometer. The crystal data of **2t** have been deposited in CCDC with number 2124437. Displayed at 30% ellipsoid contour probability level.

Table S5. Crystal data and structure refinement for 2t.

Identification code	**2t**	
Empirical formula	$C_{32}H_{27}NO_2S$	
Formula weight	489.60	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.0253(3) Å	a= 90°
	b = 15.0177(6) Å	b= 97.7000(10)°
	c = 18.9324(8) Å	g = 90°
Volume	2542.95(17) $Å^3$	
Z	4	
Density (calculated)	1.279 Mg/m^3	
Absorption coefficient	0.158 mm^{-1}	
F(000)	1032	
Crystal size	0.200 x 0.150 x 0.120 mm^3	
Theta range for data collection	2.560 to 25.997?	
Index ranges	-11<=h<=11, -18<=k<=18, -18<=l<=23	
Reflections collected	25697	
Independent reflections	4968 [R(int) = 0.0365]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6416	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4968 / 0 / 327	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.0953	
R indices (all data)	R1 = 0.0570, wR2 = 0.1061	
Extinction coefficient	0.0119(19)	
Largest diff. peak and hole	0.191 and -0.314 $e.Å^{-3}$	

8. References

1) K. Chen, R. Sun, Q. Xu, Y. Wei, M. Shi, Thermal induced intramolecular [2 + 2] cycloaddition of allene-ACPs, *Org. Biomol. Chem.*, 2013, **11**, 3949-3953.

2) (a) K. Chen, Z.-Z. Zhu, J.-X. Liu, X.-Y. Tang, Y. Wei and M. Shi, Substrate-controlled Rh(ii)-catalyzed single-electron-transfer (SET): divergent synthesis of fused indoles, *Chem. Commun.*, 2016, **52**, 350-353; (b) X.-S. Ning, X. Liang, K.-F. Hu, C.-Z. Yao, J.-P. Qu and Y.-B. Kang, Pd-tBuONO Cocatalyzed Aerobic Indole Synthesis, *Adv. Synth. Catal.*, 2018, **360**, 1590-1594.