Supporting Information

Acid-promoted intra- and intermolecular [2+2] cycloaddition of indoles with aryl alkynes to access cyclobutene-fused indolines

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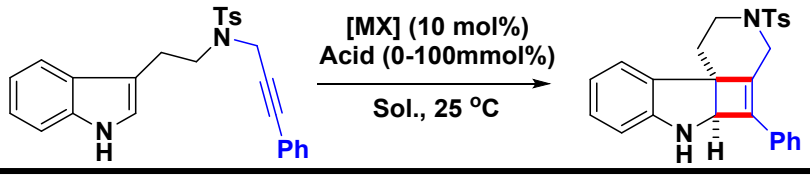
Contents of Supplementary Information

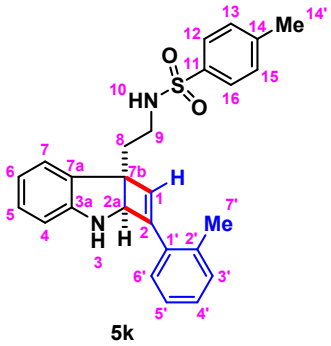
Table S1. Reaction Development and Optimization [a]



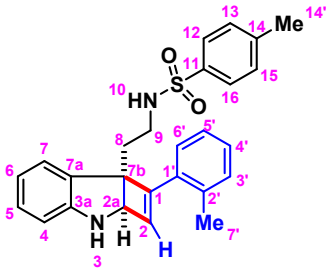
Entry	[MX]	Acid	Sol.	Time	Conv. [c]	Yield [d]
1	$Cu(NO_3)_2·3H_2O$	--	$CHCl_3$	10 h	--	N.R [e]
2	$CuCl_2$	--	$CHCl_3$	10 h	--	N.R [e]
3	Fe_2O_3	--	$CHCl_3$	10 h	--	N.R [e]
4	$CuBr_2$	--	$CHCl_3$	10 h	--	N.R [e]
5	CuBr	--	$CHCl_3$	10 h	--	N.R [e]
6	$CoCl_2$	--	$CHCl_3$	10 h	--	N.R [e]
7	$Fe_2(SO_4)_3$	--	$CHCl_3$	10 h	--	N.R [e]
8	$Fe(OAc)_2$	--	$CHCl_3$	10 h	--	N.R [e]
9	$Fe(NO_3)_3·9H_2O$	--	Toluene	10 h	--	N.R [e]
10	$Fe(NO_3)_3·9H_2O$	--	1,4-Dioxane	10 h	--	N.R [e]
11	$Fe(NO_3)_3·9H_2O$	--	MeOH	10 h	--	N.R [e]
12	$Fe(NO_3)_3·9H_2O$	--	EtOH	10 h	--	N.R [e]
13	$Fe(NO_3)_3·9H_2O$	--	DCM	10 h	24%	5%
14	$Fe(NO_3)_3·9H_2O$	--	DCE	10 h	--	trace
15	$Fe(NO_3)_3·9H_2O$	--	CH_3CN	10 h	--	trace
16	$Fe(NO_3)_3·9H_2O$	--	DMF	10 h	--	N.R [e]
17	$Fe(NO_3)_3·9H_2O$	--	THF	10 h	--	N.R [e]
18	$Fe(NO_3)_3·9H_2O$	--	HFIP	10 h	13%	3%
19	$Fe(NO_3)_3·9H_2O$	$TsOH·H_2O$	TFE	10 h	91%	70%
20	$Fe(NO_3)_3·9H_2O$	TfOH	TFE	2 h	100%	88%
21	$Fe(NO_3)_3·9H_2O$	HCl	TFE	3 h	100%	88%
22	$Fe(NO_3)_3·9H_2O$	HNO_3	HFIP	2 h	100%	90%
23 [b]	--	TfOH	DCE	10 h	--	N.R [d]

[a] All the reactions were conducted with **1a** (0.1 mmol, 1.0 eq.) in the presence of the metal catalyst (0.01 mmol, 10 mol%) with/without acid (0.1 mmol, 1.0 eq.) in the specific solvent (1 mL) at the room temperature for 2-10 h, unless otherwise noted; [b] Reaction condition: 0.1 mmol of **1a** using 1.2 eq. of TfOH in 0.4 M DCM with 4 Å MS under nitrogen; [c] The conversions were determined by HPLC; [d] The yields were determined by HPLC; [e] No reaction.

Table S2. The assignments of compounds 5k and 6k



5k



6k

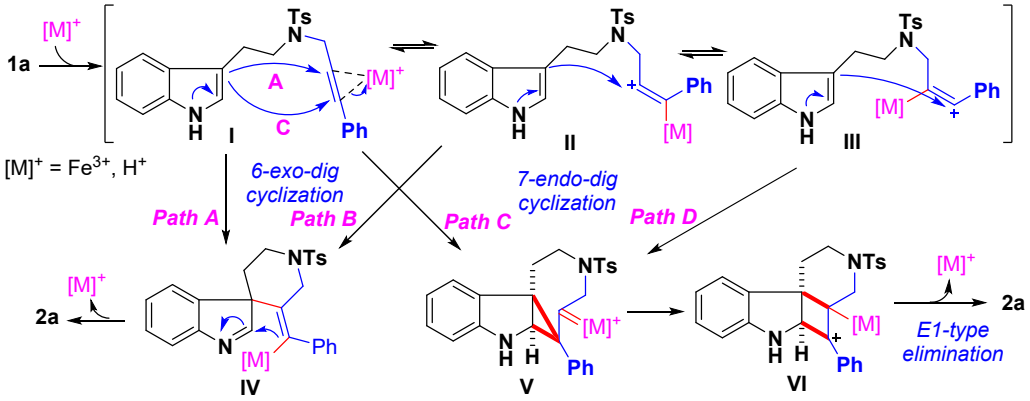
Position	5k		6k	
	δ_C(ppm)	δ_H (ppm, multi., *J* in Hz)	δ_C(ppm)	δ_H (ppm, multi., *J* in Hz)
1	137.1	6.39 (d, *J* = 1.8 Hz, 1H)	142.9	-
2	143.1	-	141.7	6.71 (d, *J* = 1.4 Hz, 1H)
2a	65.1	**4.73 – 4.70 (m, 1H)**	64.0	**5.90 (d, *J* = 1.4 Hz, 1H)**
3	-	6.20 (d, *J* = 2.8 Hz, 1H)	-	-
3a	152.3	-	141.1	-
4	109.6	6.44 – 6.39 (m, 1H)	113.3	7.78 (d, *J* = 7.9 Hz, 1H)
5	127.0 (127.7)	6.90 (td, *J* = 7.6, 1.6 Hz, 1H)	128.9	7.41 (ddd, *J* = 7.7, 1.4 Hz, 1H)
6	116.5	6.52 (t, *J* = 7.4 Hz, 1H)	127.1	7.36 (dd, *J* = 7.5, 1.2 Hz, 1H)
7	122.8	6.96 (d, *J* = 7.3 Hz, 1H)	124.6	7.48 (dd, *J* = 7.5, 1.3 Hz, 1H)
7a	131.1 (130.9)	-	134.7	-
7b	56.1	-	54.8	-
8	33.6	2.12 – 1.92 (m, 2H)	31.7	2.21 – 2.10 (m, 2H)
9	39.9	2.91 – 2.66 (m, 2H)	39.5	2.79 – 2.70 (m, 2H)
10	-	7.58 (t, *J* = 5.6 Hz, 1H)	-	7.51 (t, *J* = 5.7 Hz, 1H)
11	137.4	-	137.0	-
12/16	126.5	7.69 – 7.62 (m, 2H)	126.5	7.61 – 7.54 (m, 2H)
13/15	129.5	7.35 (d, *J* = 7.9 Hz, 2H)	129.6	7.32 (d, *J* = 8.0 Hz, 2H)
14	142.5	-	142.6	-
1’	130.9 (131.1)	-	129.8	-
2’	136.8	-	136.9	-
3’	130.6	7.25 – 7.15 (m, 1H)	130.6	7.20 – 7.16 (m, 1H)
4’	127.7 (127.0)	7.25 – 7.15 (m, 1H)	127.1	7.61 – 7.54 (m, 1H)
5’	125.6	7.25 – 7.15 (m, 1H)	125.8	7.24 – 7.20 (m, 1H)
6’	127.4	7.49 – 7.42 (m, 1H)	128.6	7.24 – 7.20 (m, 1H)
7’	21.4	2.26 (s, 3H)	21.5	2.25 (s, 3H)
14’	20.9	2.35 (s, 3H)	20.9	2.35 (s, 3H)

The careful comparisons of the NMR data between the regioisomers **5** and **6** revealed that there is a diagnostic signal in ^{1}H-NMR. Specifically, the δ_H of C2a-H in compounds **5a-5p** normally appears at 4.5- 4.9 ppm. In contrast, the δ_H of C2a-H in

their congeners **6a-6p** normally appears at 5.6- 5.7 ppm. Presumably, the significant high-field shifts observed in **5a**-**5p** were attributed to the fact that C2a-H of **5a**-**5p** locates in the shielding region of phenyl group. No shielding effect presents in compounds **6a**-**6p**.

These assignments were further validated by the extensive 2D-NMR analysis of **5k** and **6k**, along with the X-ray crystal structure analysis of **5k**. The NMR signal assignments of **5k** and **6k** were shown in the table S2.

Scheme S1. Plausible reaction mechanism (exemplified by **1a**)



Based on the results, as well as the previous reports (*J. Am. Chem. Soc*. 2017, **139**, 10302-10311, *J. Am. Chem. Soc*. 2018, **140**, 5860-5865), the plausible mechanism was proposed and outline in Scheme S1 (exemplified by **1a**). Both $Fe(NO_3)_3$ and HNO_3 act as the acids to activate the aryl alkyne, thereby forming complex **I**. It may equilibrate to the cationic vinyl intermediates **II** or **III**, which then evolve through four distinct reaction pathways (paths **A**-**D**). Specifically, both paths **A** and **B** undergo 6-*exo*-dig cyclization from complex **I** and the cationic intermediate **II** respectively, thereby providing the intermediate **IV**. It then proceeds with nucleophilic cycloaddition to give the product **2a** and regenerate the acid catalyst. In contrast, for paths **C** and **D**, it proceeds through 7-*endo*-dig cyclization to form the intermediate **V**, which then undergoes 1,2-migration to form intermediate **VI**. The final E1-type elimination affords the product **2a** and close the catalytic cycle.

At current stage, we cannot determine whether the reaction proceeds through the intermediate **I** or intermediates **II**/**III**. Since both 6-*exo*-dig cyclization and 7-*endo*-dig cyclization are favored based on the Baldwin's ring-closing rules (*J. Chem. Soc., Chem. Comm.*, 1976, **18**, 734-736), all the paths **A**-**D** are possible. Considering the stability of the intermediates, as well as the fact that the electron-requisite of the aryl alkynes, path **B** is less possible.

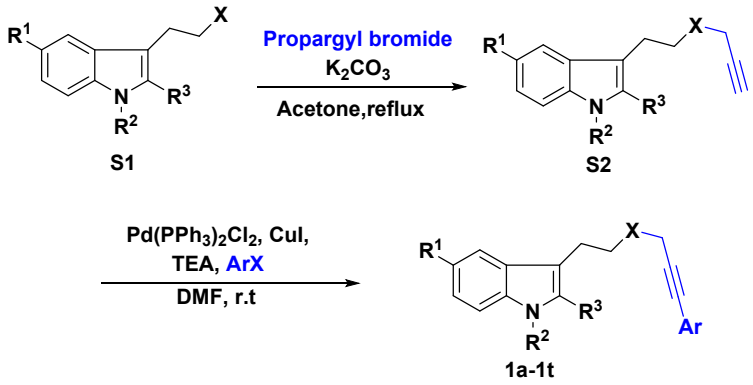
Notably, the results show that the combination of $Fe(NO_3)_3$ and HNO_3 is necessary to achieve optimal reaction efficiency and selectivity. Presumably, both $Fe(NO_3)_3$ and HNO_3 can serve to activate the alkyne moiety and promote the transformation of intermediate **IV** or **V** to **2a**. The stoichiometric amount of HNO_3 renders the reaction

faster and prevents $Fe(NO_3)_3$ from poisoning by the chelating nitrogen groups of the starting materials or products.

1. General information.

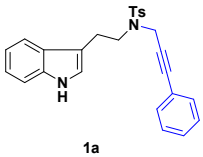
All reactions were performed under air atmosphere using flame-dried glassware unless otherwise noted. CH_2Cl_2 was distilled from calcium hydride and tetrahydrofuran (THF) from sodium metal. All reagents were commercially available and used without further purification unless otherwise indicated. Analytical thin-layer chromatography (TLC) was carried out on precoated 0.25 mm thick silica gel GF254 plates. Visualization of the developed chromatogram was performed by a UV light or by a solution of ceric ammonium molybdate, or $KMnO_4$, followed by heating. All compounds were purified by flash column chromatography using silica gel (300–400 mesh). Solvents for extraction and flash column chromatography were reagent grade. Yields reported were for isolated, spectroscopically pure compounds. Optical rotations were measured on an SGW®-3 polarimeter (Shanghai INESA optical instrument Co. Ltd) using a thermostable optical glass cell (0.1 dm path length and solution concentrations (*c*) in g/100 mL). ^1H, ^{13}C and ^{19}F–NMR experiments were performed on a Bruker AM-400 and DRX-500 NMR spectrometer at ambient temperature. The residual solvent protons (^1H) or carbons (^{13}C) were used as internal standards (δ_H = 7.26 ppm and δ_C = 77.16 ppm for $CDCl_3$). ^1H NMR data are presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant and integration). The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; sept, septet; qt, quartet of triplets; dd, doublet of doublets; dt, doublet of triplets; AB, AB quartet; m, multiplet and combinations thereof. ^{13}C NMR spectra with proton decoupling were described with the aid of an APT sequence, separating methylene and quaternary carbons (e, even) from methyl and methine carbons (o, odd). ESI-MS and HR-ESI-MS were taken on API STAR Pulsar at Central South University.

2. General procedure for the synthesis of compounds 1a- 1t.



Step 1: To a stirring solution of tryptamine derivatives **S1** (1 eq.) in acetone (0.3 M) were added potassium carbonate (1.1 eq.) and propargyl bromide (1.1 eq.) successively, which was then heated to reflux at 60 ℃. Upon the completion of the reaction as indicated by TLC, the reaction was quenched by the addition of the saturated aqueous NH_4Cl. The aqueous phase was extracted with ethyl acetate. The combined organic layers were then washed with brine and dried over anhydrous Na_2SO_4, which was concentrated under reduced pressure in vacuum. The crude product was purified with flash column chromatography on silica gel to afford **S2**.

Step 2: A Schlenk tube quipped with a magnetic stirring bar was charged with **S2** (2 mmol, 1 eq.), $Pd(PPh_3)_2Cl_2$ (0.1 mmol, 5 mmol%) and CuI (0.2 mmol, 10 mmol%) under nitrogen, which were added then DMF (2.0 mL, 1M) and Et_3N (4 mmol, 2 eq.) successively *via syringe*. The resulting mixture was stirred at 25 ℃ for 10 min. Then the aryl halide (3 mmol, 1.5 eq.) was added *via syringe*. Upon the completion of the reaction as indicated by TLC, the reaction was quenched with the saturated aqueous NH_4Cl. The aqueous phase was extracted with ethyl acetate. The combined organic layers were then washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified with flash column chromatography on silica gel to afford **1**.



1a

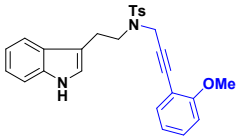
***N*-(2-(1*H*-indol-3-yl)ethyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzene**

sulfonamide (1a): white solid (1.58 g of **1a** was obtained from 1.45 g starting material, 90% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 8.11 (s, 1H), 7.84 – 7.76 (m, 2H), 7.67 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.39 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.35 – 7.17 (m, 6H), 7.14 (d, *J* = 2.4 Hz, 1H), 7.13 – 7.10 (m, 2H), 7.08 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 4.44 (s, 2H), 3.78 – 3.43 (m, 2H), 3.17 (dd, *J* = 9.1, 6.5 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 143.5, 136.2, 135.8, 131.6, 129.5, 128.5, 128.2, 127.8, 127.3, 122.4, 122.2, 122.1, 119.5, 118.7, 112.3, 111.3, 85.8, 81.9, 47.1, 37.6, 24.3, 21.4.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{24}N_2O_2S[M+H]^+$, 429.1631, found 429.1630.



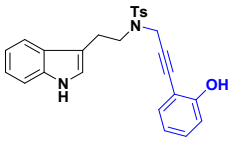
1b

***N*-(2-(1*H*-indol-3-yl)ethyl)-*N*-(3-(2-methoxyphenyl)prop-2-yn-1-yl)-4-methyl benzenesulfonamide (1b)**: yellow solid (550.0 mg of **1b** was obtained from 705.3 mg starting material, 60% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 8.12 (s, 1H), 7.82 – 7.76 (m, 2H), 7.70 – 7.64 (m, 1H), 7.37 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.33 – 7.25 (m, 1H), 7.23 – 7.16 (m, 3H), 7.13 (d, *J* = 2.3 Hz, 1H), 7.05 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.96 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.88 – 6.81 (m, 2H), 4.50 (s, 2H), 3.79 (s, 3H), 3.66 – 3.58 (m, 2H), 3.21 – 3.13 (m, 2H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 160.0, 143.3, 136.2, 135.8, 133.5, 129.9, 129.5, 127.8, 127.3, 122.3, 122.0, 120.2, 119.4, 118.8, 112.4, 111.4, 111.2, 110.5, 86.0, 82.3, 55.6, 47.1, 37.9, 24.3, 21.4.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_3S$ $[M+H]^+$, 459.1737, found 459.1737.



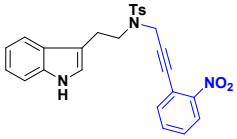
1c

***N*-(2-(1*H*-indol-3-yl)ethyl)-*N*-(3-(2-hydroxyphenyl)prop-2-yn-1-yl)-4-methyl benzenesulfonamide (1c)**: yellow solid (302.2 mg of **1c** was obtained from 373.0 mg starting material, 64% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 8.09 (s, 1H), 7.79 – 7.73 (m, 2H), 7.60 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.28 – 7.18 (m, 4H), 7.11 (d, *J* = 2.3 Hz, 1H), 7.11 – 7.07 (m, 1H), 7.06 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.90 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.83 (td, *J* = 7.5, 1.1 Hz, 1H), 5.53 – 5.45 (m, 1H), 4.39 (s, 2H), 3.62 (dd, *J* = 8.7, 6.5 Hz, 2H), 3.14 (dd, *J* = 8.7, 6.5 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 157.0, 144.0, 136.2, 135.5, 131.8, 130.7, 129.7, 127.6, 127.2, 122.3, 122.2, 120.1, 119.5, 118.6, 114.9, 112.1, 111.3, 108.4, 89.3, 80.1, 47.2, 37.6, 24.5, 21.5.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{24}N_2O_3S[M+H]^+$, 445.1580, found 445.1581.



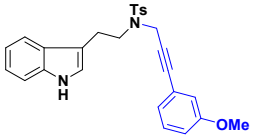
1d

***N*-(2-(1*H*-indol-3-yl)ethyl)-4-methyl-*N*-(3-(2-nitrophenyl)prop-2-yn-1-yl)benzene sulfonamide (1d)**: yellow solid (381.0 mg of **1d** was obtained from 343.2 mg starting material, 83% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 8.13 (s, 1H), 8.01 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.51 (td, *J* = 7.6, 1.4 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.25 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.20 – 7.15 (m, 4H), 7.09 (t, *J* = 7.4 Hz, 1H), 4.46 (s, 2H), 3.71 – 3.64 (m, 2H), 3.17 (t, *J* = 7.6 Hz, 2H), 2.27 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 149.4, 143.5, 136.2, 135.7, 134.8, 132.7, 129.5, 128.9, 127.8, 127.3, 124.6, 122.4, 122.1, 119.4, 118.7, 117.6, 112.2, 111.2, 90.5, 80.9, 47.1, 37.7, 24.3, 21.4.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{23}N_3O_4S[M+H]^+$, 474.1482, found 474.1482.



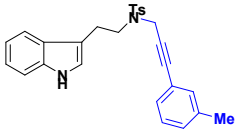
1e

***N*-(2-(1*H*-indol-3-yl)ethyl)-*N*-(3-(3-methoxyphenyl)prop-2-yn-1-yl)-4-methyl benzenesulfonamide (1e)**: yellow solid (703.4 mg of **1e** was obtained from 709.3 mg starting material, 76% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 8.14 (s, 1H), 7.83 – 7.76 (m, 2H), 7.66 (dq, *J* = 8.0, 0.9 Hz, 1H), 7.38 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.23 – 7.16 (m, 2H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.08 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.87 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 6.72 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.66 (dd, *J* = 2.7, 1.4 Hz, 1H), 4.43 (s, 2H), 3.79 (s, 3H), 3.65 – 3.57 (m, 2H), 3.20 – 3.12 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 159.2, 143.5, 136.2, 135.8, 129.6, 129.2, 127.8, 127.3, 124.1, 123.2, 122.3, 122.1, 119.5, 118.7, 116.8, 114.6, 112.3, 111.3, 85.6, 81.8, 55.3, 47.1, 37.5, 24.4, 21.4.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_3S[M+H]^+$, 459.1737, found 459.1740.



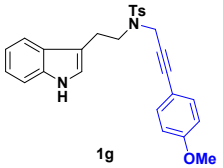
1f

***N*-(2-(1*H*-indol-3-yl)ethyl)-4-methyl-*N*-(3-(m-tolyl)prop-2-yn-1-yl)benzene sulfonamide (1f)**: yellow solid (751.1 mg of **1f** was obtained from 704.5 mg starting material, 85% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 8.11 (s, 1H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.17 – 7.11 (m, 3H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 6.0 Hz, 2H), 4.44 (s, 2H), 3.62 (t, *J* = 7.9 Hz, 2H), 3.16 (t, *J* = 7.9 Hz, 2H), 2.36 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 143.4, 137.8, 136.2, 135.9, 132.2, 129.5, 129.3, 128.6, 128.1, 127.8, 127.3, 122.3, 122.1, 122.0, 119.5, 118.7, 112.3, 111.2, 85.9, 81.5, 47.0, 37.6, 24.3, 21.4, 21.2.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_2S[M+H]^+$, 443.1788, found 443.1787.



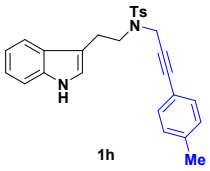
1g

***N*-(2-(1*H*-indol-3-yl)ethyl)-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methyl benzenesulfonamide (1g)**: yellow solid (639.9 mg of **1g** was obtained from 717.9 mg starting material, 68% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 8.13 (s, 1H), 7.83 – 7.75 (m, 2H), 7.66 (dq, *J* = 7.9, 0.9 Hz, 1H), 7.38 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.21 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.11 – 7.04 (m, 3H), 6.83 – 6.76 (m, 2H), 4.42 (s, 2H), 3.82 (s, 3H), 3.65 – 3.56 (m, 2H), 3.20 – 3.11 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 159.7, 143.4, 136.2, 135.9, 133.0, 129.5, 127.8, 127.3, 122.3, 122.1, 119.4, 118.7, 114.3, 113.8, 112.3, 111.3, 85.7, 80.5, 55.3, 47.0, 37.6, 24.4, 21.5.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_3S[M+H]^+$, 459.1737, found 459.1739.



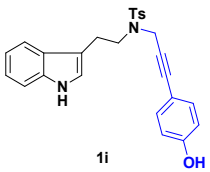
1h

***N*-(2-(1*H*-indol-3-yl)ethyl)-4-methyl-*N*-(3-(*p*-tolyl)prop-2-yn-1-yl)benzene sulfonamide (1h)**: yellow solid (13.0 mg of **1h** was obtained from 352.45 mg starting material, 73% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ_H 10.90 – 10.87 (m, 1H), 7.76 – 7.71 (m, 2H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 3H), 7.24 (d, *J* = 2.3 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.06 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.01 – 6.96 (m, 2H), 6.91 (td, *J* = 7.4, 6.8, 1.0 Hz, 1H), 4.45 (s, 2H), 3.48 – 3.42 (m, 2H), 3.06 – 3.00 (m, 2H), 2.31 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ_C 143.9, 138.9, 136.7, 135.9, 131.6, 130.1, 129.5, 127.9, 127.4, 123.6, 121.5, 119.0, 118.8, 118.5, 111.9, 111.0, 85.6, 82.5, 47.5, 37.5, 24.2, 21.4, 21.4.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_2S[M+H]^+$, 443.1788, found 443.1789.



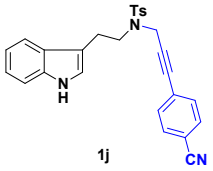
1i

***N*-(2-(1*H*-indol-3-yl)ethyl)-*N*-(3-(4-hydroxyphenyl)prop-2-yn-1-yl)-4-methyl benzenesulfonamide (1i)**: white solid (378.1 mg of **1i** was obtained from 373.4 mg starting material, 80% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ_H 10.89 – 10.86 (m, 1H), 9.85 (s, 1H), 7.76 – 7.70 (m, 2H), 7.52 (d, J = 7.9 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.23 (d, J = 2.4 Hz, 1H), 7.06 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 6.95 – 6.88 (m, 3H), 6.72 – 6.67 (m, 2H), 4.42 (s, 2H), 3.46 – 3.40 (m, 2H), 3.05 – 2.98 (m, 2H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ_C 158.4, 143.8, 136.7, 135.9, 133.4, 130.1, 127.9, 127.4, 123.6, 121.5, 118.8, 118.5, 115.9, 112.2, 111.9, 111.0, 85.9, 80.8, 47.5, 37.5, 24.2, 21.4.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{24}N_2O_3S[M+H]^+$, 445.1580, found 445.1582.



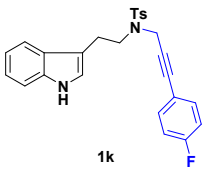
1j

***N*-(2-(1*H*-indol-3-yl)ethyl)-*N*-(3-(4-cyanophenyl)prop-2-yn-1-yl)-4-methyl benzenesulfonamide (1j)**: white solid (501.0 mg of **1j** was obtained from 528.8 mg starting material, 74% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 8.18 (s, 1H), 7.77 (d, J = 7.9 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 7.9 Hz, 2H), 7.39 (d, J = 8.3 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 7.8 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.13 (s, 1H), 7.07 (t, J = 7.8 Hz, 1H), 4.42 (s, 2H), 3.60 (t, J = 7.8 Hz, 2H), 3.15 (t, J = 7.9 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ_C 143.6, 136.3, 135.8, 132.1, 131.9, 129.6, 127.8, 127.2, 127.0, 122.4, 122.2, 119.5, 118.5, 118.3, 112.0, 111.9, 111.4, 86.9, 84.0, 47.3, 37.6, 24.4, 21.5.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{23}N_3O_2S[M+H]^+$, 454.1584, found 454.1584.



1k

***N*-(2-(1*H*-indol-3-yl)ethyl)-*N*-(3-(4-fluorophenyl)prop-2-yn-1-yl)-4-methyl**

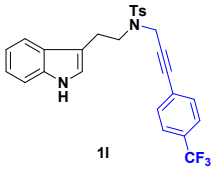
benzenesulfonamide (1k): yellow solid (266.0 mg of **1k** was obtained from 352.45 mg starting material, 57% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ_H 10.91 – 10.86 (m, 1H), 7.77 – 7.70 (m, 2H), 7.54 – 7.48 (m, 1H), 7.38 – 7.31 (m, 3H), 7.24 (d, J = 2.4 Hz, 1H), 7.22 – 7.11 (m, 4H), 7.06 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 6.91 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 4.45 (s, 2H), 3.49 – 3.40 (m, 2H), 3.07 – 2.98 (m, 2H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ_C 162.4 (d, J = 247.6 Hz), 143.9, 136.7, 135.8,134.1, 134.0, 130.2, 127.9, 127.4, 123.6, 121.5, 118.8, 118.5, 116.2 (d, J = 22.3 Hz), 112.0, 110.9, 84.4, 83.0, 47.6, 37.4, 24.2, 21.4.

^{19}F NMR (471 MHz, Chloroform-d) δ -110.4.

HR-ESI-MS(m/z): calcd. for $C_{26}H_{23}FN_2O_2S[M+H]^+$, 447.1537, found 447.1539.



1l

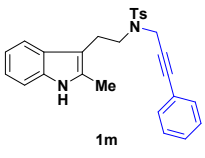
***N*-(2-(1*H*-indol-3-yl)ethyl)-4-methyl-*N*-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)benzenesulfonamide (1l)**: yellow solid (350.0 mg of **1l** was obtained from 352.45 mg starting material, 70% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ_H 10.90 (s, 1H), 7.77 – 7.72 (m, 2H), 7.72 – 7.67 (m, 2H), 7.52 (dd, J = 7.9, 1.1 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.31 – 7.26 (m, 2H), 7.25 (d, J = 2.4 Hz, 1H), 7.06 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 6.92 (ddd, J = 7.9, 7.0, 1.0 Hz, 1H), 4.51 (s, 2H), 3.53 – 3.44 (m, 2H), 3.10 – 3.00 (m, 2H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ_C 144.0, 136.7, 135.8, 132.4, 130.2, 129.3, 129.0, 127.9, 127.4, 126.3, 125.8 (q, J = 3.9 Hz), 125.4, 123.7, 123.0, 121.5, 118.8, 118.5, 112.0, 110.9, 86.2, 84.0, 47.7, 37.4, 24.2, 21.3.

^{19}F NMR (471 MHz, Chloroform-d) δ -62.9.

HR-ESI-MS(m/z): calcd. for $C_{27}H_{23}F_3N_2O_2S[M+H]^+$, 497.1505, found 497.1510.



1m

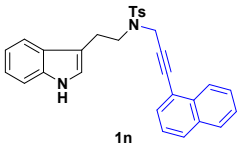
4-methyl-*N*-(2-(2-methyl-1*H*-indol-3-yl)ethyl)-*N*-(3-phenylprop-2-yn-1-yl)

benzenesulfonamide(1m): yellow solid (807.6 mg of **1m** was obtained from 743.0 mg starting material, 90% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.89 (s, 1H), 7.80 – 7.75 (m, 2H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.20 (m, 6H), 7.15 – 7.10 (m, 3H), 7.05 – 6.98 (m, 1H), 4.45 (s, 2H), 3.56 – 3.39 (m, 2H), 3.14 – 3.05 (m, 2H), 2.41 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 143.4, 135.9, 135.2, 132.0, 131.6, 129.5, 128.5, 128.4, 128.2, 127.7, 122.2, 121.1, 119.4, 117.8, 110.3, 107.9, 85.7, 82.0, 47.0, 37.9, 23.7, 21.4, 11.6.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_2S[M+H]^+$, 443.1788, found 443.1787.



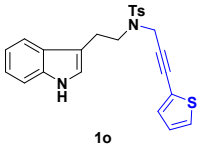
1n

***N*-(2-(1*H*-indol-3-yl)ethyl)-4-methyl-*N*-(3-(naphthalen-1-yl)prop-2-yn-1-yl) benzenesulfonamide (1n)**: yellow solid (752 mg of **1n** was obtained from 704.9 mg starting material, 79% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 8.07 (s, 1H), 7.87 – 7.80 (m, 5H), 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.44 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.21 – 7.17 (m, 1H), 7.16 (s, 1H), 7.15 (d, *J* = 1.6 Hz, 2H), 7.02 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 4.60 (s, 2H), 3.78 – 3.64 (m, 2H), 3.22 (dd, *J* = 9.0, 6.5 Hz, 2H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 143.5, 136.2, 135.8, 133.0, 133.0, 130.7, 129.6, 128.9, 128.2, 127.7, 127.3, 126.8, 126.4, 125.9, 125.0, 122.3, 122.1, 119.9, 119.5, 118.7, 112.3, 111.2, 86.8, 83.9, 47.1, 37.8, 24.5, 21.3.

HR-ESI-MS(*m/z*): calcd. for $C_{30}H_{26}N_2O_2S[M+H]^+$, 479.1788, found 479.1789.



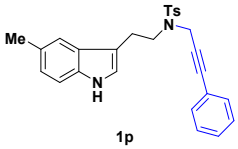
1o

***N*-(2-(1*H*-indol-3-yl)ethyl)-4-methyl-*N*-(3-(thiophen-2-yl)prop-2-yn-1-yl) benzenesulfonamide (1o)**: yellow solid (580.0 mg of **1o** was obtained from 704.9 mg starting material, 67% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 8.17 (s, 1H), 7.82 – 7.76 (m, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.26 – 7.22 (m, 2H), 7.15 – 7.09 (m, 2H), 6.99 (dd, *J* = 3.7, 1.2 Hz, 1H), 6.95 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.45 (s, 2H), 3.64 – 3.56 (m, 2H), 3.16 (dd, *J* = 9.2, 6.4 Hz, 2H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 143.6, 136.3, 135.6, 132.4, 129.7, 127.7, 127.4, 127.3, 126.9, 122.4, 122.1, 119.5, 118.7, 112.2, 111.3, 86.0, 79.0, 47.2, 37.8, 24.4, 21.6.

HR-ESI-MS(*m/z*): calcd. for $C_{24}H_{22}N_2O_2S[M+H]^+$, 435.1195, found 435.1198.



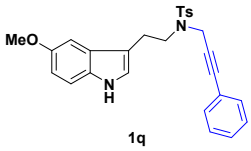
1p

4-methyl-*N*-(2-(5-methyl-1*H*-indol-3-yl)ethyl)-*N*-(3-phenylprop-2-yn-1-yl) benzenesulfonamide (1p): yellow solid (667.9 mg of **1p** was obtained from 732.9 mg starting material, 75% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 8.07 (s, 1H), 7.83 – 7.78 (m, 2H), 7.44 – 7.40 (m, 1H), 7.33 – 7.24 (m, 6H), 7.15 – 7.08 (m, 3H), 7.04 (dd, *J* = 8.3, 1.6 Hz, 1H), 4.47 (s, 2H), 3.66 – 3.58 (m, 2H), 3.18 – 3.10 (m, 2H), 2.36 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 143.5, 135.7, 134.6, 131.6, 129.6, 128.7, 128.5, 128.2, 127.8, 127.5, 123.7, 122.6, 122.2, 118.3, 111.7, 111.0, 85.8, 81.9, 47.1, 37.5, 24.3, 21.4, 21.4.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_2S[M+H]^+$, 443.1788, found 443.1789.



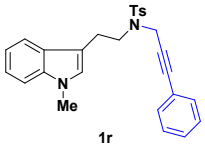
1q

***N*-(2-(5-methoxy-1*H*-indol-3-yl)ethyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl) benzenesulfonamide (1q)**: yellow solid (545.4 mg of **1q** was obtained from 573.72 mg starting material, 79% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 8.16 – 8.12 (m, 1H), 7.86 – 7.78 (m, 2H), 7.33 – 7.29 (m, 1H), 7.28 – 7.23 (m, 5H), 7.14 – 7.09 (m, 4H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.43 (s, 2H), 3.78 (s, 3H), 3.65 – 3.59 (m, 2H), 3.15 (dd, *J* = 9.1, 6.4 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 154.0, 143.5, 135.8, 131.5, 131.4, 129.6, 128.5, 128.2, 127.8, 127.7, 123.2, 122.2, 112.4, 112.1, 112.0, 100.3, 85.7, 82.0, 55.8, 47.1, 37.7, 24.6, 21.4.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_3S[M+H]^+$, 459.1737, found 459.1736.



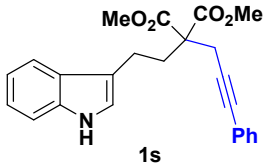
1r

4-methyl-*N*-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-*N*-(3-phenylprop-2-yn-1-yl) benzenesulfonamide (1r): yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.81 – 7.75 (m, 2H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.28 – 7.22 (m, 5H), 7.11 (dt, *J* = 7.0, 1.5 Hz, 2H), 7.06 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.99 (s, 1H), 4.43 (s, 2H), 3.77 (s, 3H), 3.62 – 3.55 (m, 2H), 3.17 – 3.11 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 143.4, 137.0, 135.9, 131.5, 129.5, 128.4, 128.1, 127.8, 127.7, 127.0, 122.2, 121.6, 118.9, 118.8, 110.8, 109.3, 85.7, 82.0, 47.2, 37.6, 32.6, 24.3, 21.4.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}O_2S[M+H]+$, 443.1788, found 443.1789.



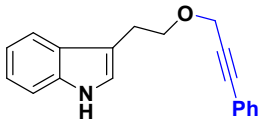
1s

Dimethyl 2-(2-(1*H*-indol-3-yl)ethyl)-2-(3-phenylprop-2-yn-1-yl)malonate (1s): brown oil (266.4 mg of **1s** was obtained from 254.9 mg starting material 84% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 8.03 (s, 1H), 7.68 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.37 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.31 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.20 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.08 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 3.77 (s, 6H), 3.25 (s, 2H), 2.84 – 2.75 (m, 2H), 2.66 – 2.57 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 170.9, 136.3, 131.7, 128.2, 128.0, 127.3, 123.2, 122.0, 121.4, 119.3, 119.0, 115.2, 111.1, 84.4, 83.7, 57.3, 52.8, 32.7, 23.9, 20.2.

HR-ESI-MS(*m/z*): calcd. for $C_{24}H_{23}NO_4[M+H]^+$, 390.1700, found 390.1701.



1t

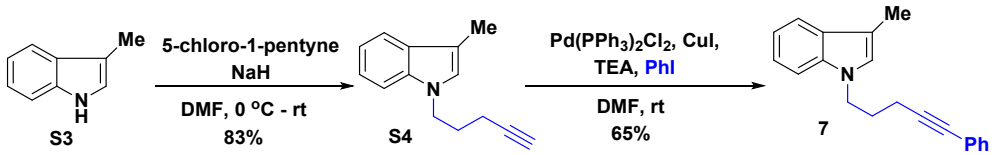
3-(2-((3-phenylprop-2-yn-1-yl)oxy)ethyl)-1*H*-indole (1t): 82.6 mg of **1t** was obtained from 77.4 mg starting material, 77% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 8.02 (s, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.32 (m, 3H), 7.26 – 7.21 (m, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 2.3 Hz, 1H), 4.46 (s, 2H), 3.95 (t, *J* = 7.2 Hz, 2H), 3.16 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 136.2, 131.8, 128.4, 128.3, 127.6, 122.7, 122.1, 122.0, 119.3, 118.9, 112.8, 111.1, 86.2, 85.4, 70.3, 58.9, 25.7.

HR-ESI-MS(*m/z*): calcd. for $C_{19}H_{17}NO[M+H]^+$, 276.1383, found 276.1386.

3. Typical procedures for the synthesis of compound 7



Step 1: To solution of 3-methylindole **S3** (2.59 g, 20 mmol) in DMF (40 mL, 0.5 M) at 0 ℃ was add sodium hydride (60%, 960 mg, 24 mmol). The mixture was allowed to warmed to the room temperature and stirred for 30 another minutes, which was then added 5-chloro-1-pentyne (2.46 g, 24 mmol) dropwise. Upon the completion as indicated by TLC, the reaction was cooled to 0 ℃ and quenched with the saturated aqueous NH_4Cl. The aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over the anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (petroleum ether) to afford 3-methyl-1-(pent-4-yn-1-yl)-1*H*-indole **S4** as colorless film (3.22 g, 83% yield).

Step 2: A Schlenk flash quipped with a magnetic stirring bar was charged with **S4** (295.9 mg, 1.5 mmol), $Pd(PPh_3)_2Cl_2$ (53.2 mg, 0.075 mmol) and CuI (28.5 mg, 0.15 mmol) under nitrogen. Then DMF (1.5 mL, 1M) and Et_3N (303 mg, 3 mmol) was added *via syringe*. The mixture was stirred at 25 ℃ for 0.5 h, which was then followed by the addition of iodobenzene (459.02 mg, 2.25 mmol) *via* syringe. Upon the completion as

indicated by TLC, the reaction mixture was quenched by the saturated aqueous NH_4Cl. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over the anhydrous Na_2SO_4. The solvent was removed under the reduced pressure. The crude product was purified by the flash column chromatography (petroleum ether) on silica gel to give **7** as a white solid (268.5 mg, 65% yield).

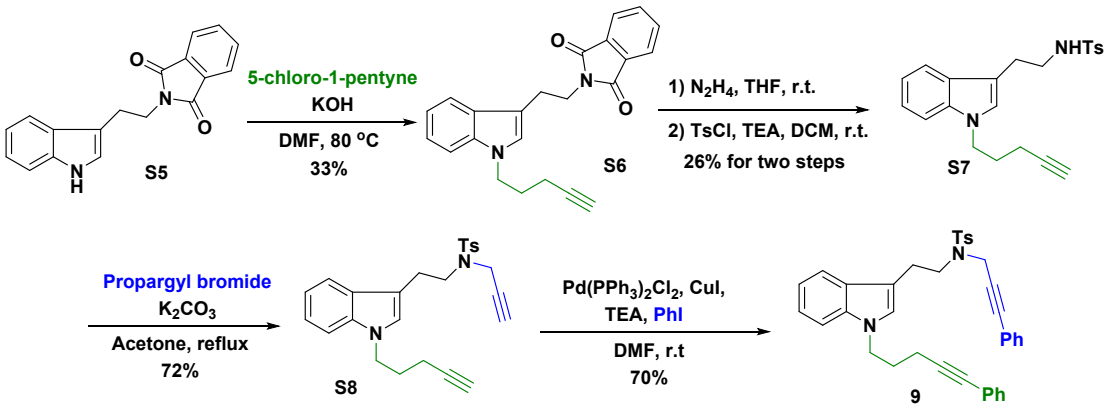
3-methyl-1-(5-phenylpent-4-yn-1-yl)-1*H*-indole (7):

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.64 (d, J = 7.9 Hz, 1H), 7.50 (dt, J = 7.4, 2.3 Hz, 2H), 7.43 (d, J = 8.2 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.27 (t, J = 7.8 Hz, 1H), 7.18 (t, J = 7.1 Hz, 1H), 6.99 (s, 1H), 4.32 (td, J = 6.7, 2.0 Hz, 2H), 2.46 – 2.42 (m, 2H), 2.40 (s, 3H), 2.14 (td, J = 6.8, 2.0 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 136.4, 131.6, 128.9, 128.4, 127.9, 125.7, 123.7, 121.5, 119.1, 118.6, 110.4, 109.2, 88.8, 81.8, 44.6, 29.2, 16.9, 9.6.

HR-ESI-MS(*m/z*): calcd. for $C_{20}H_{19}N[M+H]^+$, 274.1590, found 274.1589.

4. Typical procedures for the synthesis of compound 9



Step 1: To a suspension of **S5** (580 mg, 2 mmol) and potassium hydroxide (280 mg, 5 mmol) in DMF (10 mL, 0.2 M) at room temperature was added 5-chloro-1-pentyne (309 mg, 3 mmol). The mixture was heated to 80 ℃ and stirred at this temperature. Upon the completion as indicated by TLC, the reaction was quenched with water. The aqueous phase was extracted with ethyl acetate, then the combined organic layers were washed with brine, dried over the anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford **S6** as white solid (469.8 mg, 33% yield).

Step 2: To solution **S6** (460 mg, 1.3 mmol) in THF (5 mL, 0.25 M) at room temperature was added hydrazinium hydroxide solution (1 mL). The mixture was stirred for 24 h. The suspension was filtered. The filtrate was diluted with 20% aqueous NaOH solution and was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over the anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was then dissolved in CH_2Cl_2 (5 mL), which was followed by the addition of Et_3N (197 mg, 1.95 mmol) and TsCl (267 mg, 1.4 mmol) at 0 ℃ successively. Then the mixture was allowed to warmed to the room temperature. Upon the completion as indicated by TLC, the reaction was quenched with water. The aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over the anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford **S7** as a white solid (126.2 mg, 26% yield).

Step 3: To a stirring solution of **S7** (60 mg, 0.16 mmol) in acetone (2 mL, 0.08 M) were added potassium carbonate (55.2 mg, 0.4 mmol) and propargyl bromide (38 mg, 0.32 mmol), which was then heated to reflux at 60 ℃. Upon the completion as indicated by TLC, the reaction was quenched by the saturated aqueous NH_4Cl. The aqueous phase was extracted with ethyl acetate. The combined organic layers were then washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified with flash column chromatography on silica gel to afford **S8** as a yellow film (47.8 mg, 72% yield).

Step 4: A Schlenk flash quipped with a magnetic stirring bar was charged with **S8** (224 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (17.55 mg, 0.025 mmol) and CuI (9.5 mg, 0.05 mmol) under nitrogen, then DMF (2 mL, 0.25 M) and Et_3N (101 mg, 1 mmol) was added *via* syringe. The reaction was performed at 25 ℃ for 0.5 h, then iodobenzene (153 mg, 0.75 mmol) was added *via* syringe. Upon the completion as indicated by TLC, the reaction mixture was quenched by the addition of the saturated aqueous NH_4Cl. The reaction mixture was extracted with ethyl acetate, then wash the combined organic phases with brine, and dry the organic phases over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. And the crude product was purified by flash column

chromatography on silica gel to give **9** as a white solid (200.6 mg, 70% yield).

4-methyl-*N*-(2-(1-(5-phenylpent-4-yn-1-yl)-1*H*-indol-3-yl)ethyl)-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (9): m.p.: 67~69 ℃.

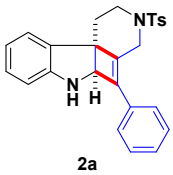
^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.81 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 7.9 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.43 (d, J = 8.2 Hz, 1H), 7.36 (dd, J = 5.0, 2.0 Hz, 3H), 7.35 – 7.21 (m, 6H), 7.17 – 7.04 (m, 4H), 4.47 (s, 2H), 4.32 (t, J = 6.7 Hz, 2H), 3.66 – 3.57 (m, 2H), 3.22 – 3.13 (m, 2H), 2.43 (t, J = 6.7 Hz, 2H), 2.35 (s, 3H), 2.14 (p, J = 6.7 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 143.4, 136.3, 135.8, 131.6, 131.6, 129.6, 128.5, 128.4, 128.2, 127.9, 127.8, 126.2, 123.6, 122.2, 121.7, 119.1, 119.0, 111.1, 109.6, 88.6, 85.8, 82.0, 81.9, 47.3, 44.8, 37.6, 29.1, 24.4, 21.5, 16.9.

HR-ESI-MS(*m/z*): calcd. for $C_{37}H_{34}N_2O_2S[M+H]^+$, 571.2414, found 571.2409.

5. Typical procedures for the synthesis of compounds 2a-2t

A Schlenk flask equipped with a magnetic stirring bar was charged with **1** (0.2 mmol, 1.0 eq.), $Fe(NO_3)_3·9H_2O$ (0.01 mmol, 5 mol%) under air. Then a solution of HNO_3 (68%, 0.2 mmol, 1.0 eq.) in TFE (2 mL) was added dropwise *via* syringe. The reaction was performed at 25 ℃ for the indicated time. Upon the completion as indicated by TLC, the reaction was quenched by Et_3N. Then the mixture was filtered through the celite. After the removal of the solvent under the reduced pressure, the residue was purified by column chromatography to give compound **2**.



2a

5-phenyl-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta[1,2-*b*]indole (2a)

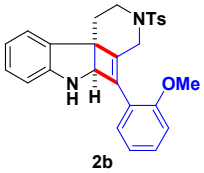
The reaction was performed at 25 ℃ for 6 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 8: 1). The title compound was obtained as a white solid (39.8 mg of **2a** was obtained from 41.1 mg starting material, 97% yield), m.p.： 90~94 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.66 (d, J = 8.3 Hz, 2H), 7.36 (td, J = 7.0, 1.5 Hz, 2H), 7.30 – 7.24 (m, 3H), 7.22 (d, J = 8.0 Hz, 2H), 7.06 (dd, J = 7.5, 1.2 Hz, 1H),

7.00 (td, J = 7.7, 1.3 Hz, 1H), 6.66 (td, J = 7.5, 1.1 Hz, 1H), 6.60 – 6.54 (m, 1H), 4.58 (d, J = 13.9 Hz, 1H), 4.53 (d, J = 1.1 Hz, 1H), 3.85 (dt, J = 13.6, 4.5 Hz, 1H), 3.71 (dd, J = 13.8, 1.3 Hz, 1H), 3.24 (ddd, J = 13.1, 11.2, 3.6 Hz, 1H), 2.41 (s, 3H), 2.25 (dt, J = 13.6, 3.8 Hz, 1H), 2.16 (ddd, J = 13.6, 11.2, 4.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 152.7, 143.7, 139.6, 137.8, 134.8, 132.5, 132.4, 129.8, 128.9, 128.4, 128.3, 127.7, 126.6, 123.6, 119.1, 112.2, 66.2, 52.5, 44.7, 43.7, 33.7, 21.7.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{24}N_2O_2S[M+H]^+$, 429.1631, found 429.1638.



2b

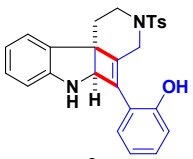
5-(2-methoxyphenyl)-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta [1,2-*b*]indole (2b)

The reaction was performed at 25 ℃ for 6 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 7: 1). The title compound was obtained as a white solid (64.0 mg of **2b** was obtained from 71.7 mg starting material, 89% yield), m.p.: 89~92 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.71 – 7.66 (m, 2H), 7.29 (td, J = 7.8, 1.7 Hz, 1H), 7.25 (dd, J = 7.6, 1.7 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.11 (dd, J = 7.5, 1.3 Hz, 1H), 7.02 (td, J = 7.7, 1.3 Hz, 1H), 6.97 (td, J = 7.5, 1.1 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H), 6.68 (td, J = 7.5, 1.0 Hz, 1H), 6.58 (d, J = 7.8 Hz, 1H), 4.70 (d, J = 14.1 Hz, 1H), 4.52 – 4.48 (m, 1H), 3.96 – 3.85 (m, 4H), 3.77 (dd, J = 14.1, 1.3 Hz, 1H), 3.31 (ddd, J = 13.2, 11.3, 3.7 Hz, 1H), 2.42 (s, 3H), 2.25 (dt, J = 13.6, 3.8 Hz, 1H), 2.15 (ddd, J = 13.6, 11.2, 4.9 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 157.0, 152.5, 143.3, 140.5, 135.1, 133.7, 132.9, 129.6, 129.4, 128.3, 128.2, 127.5, 123.5, 121.6, 120.6, 118.7, 111.7, 110.9, 67.1, 55.2, 52.1, 44.9, 44.6, 33.5, 21.5.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_3S$ $[M+H]^+$, 459.1737, found 459.1740.



2c

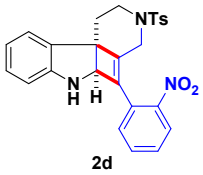
2-(3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta[1,2-*b*]indol-5-yl) phenol (2c)

The reaction was performed at 25 ℃ for 5 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 6: 1). The title compound was obtained as a gray solid (59.8 mg of **2c** was obtained from 61.1 mg starting material, 98% yield), m.p.: 100~106 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 7.78 – 7.73 (m, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.27 (dd, J = 7.6, 1.7 Hz, 1H), 7.20 (ddd, J = 8.7, 7.3, 1.7 Hz, 1H), 7.16 (t, J = 7.6 Hz, 2H), 6.98 – 6.95 (m, 1H), 6.94 – 6.89 (m, 2H), 6.87 (td, J = 7.4, 1.2 Hz, 1H), 4.68 (dd, J = 13.5, 1.2 Hz, 1H), 4.46 (d, J = 1.4 Hz, 1H), 3.97 (dtd, J = 12.8, 4.4, 1.2 Hz, 1H), 3.39 (dd, J = 13.4, 1.5 Hz, 1H), 3.17 (ddd, J = 12.8, 8.8, 6.3 Hz, 1H), 2.49 (s, 3H), 2.36 – 2.33 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 154.9, 150.3, 143.8, 143.2, 136.3, 134.6, 134.3, 129.9, 129.9, 128.4, 128.4, 127.6, 123.6, 122.7, 120.2, 119.8, 116.9, 116.7, 68.5, 54.5, 44.7, 43.4, 33.7, 21.6.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{24}N_2O_3S[M+H]^+$, 445.1580, found 445.1586.



2d

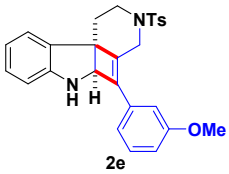
5-(2-nitrophenyl)-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta[1,2-*b*]indole (2d)

The reaction was performed at 50 ℃ for 2 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1). The title compound was obtained as a yellow solid (47.5 mg of **2d** was obtained from 87.0 mg starting material, 54% yield), m.p.: 81~86 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.83 (dd, J = 8.1, 1.3 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.56 (td, J = 7.6, 1.3 Hz, 1H), 7.45 (td, J = 7.8, 1.4 Hz, 1H), 7.30 (dd, J = 8.6, 7.0 Hz, 3H), 7.10 (dd, J = 7.5, 1.2 Hz, 1H), 7.06 (td, J = 7.7, 1.3 Hz, 1H), 6.71 (td, J = 7.5, 1.0 Hz, 1H), 6.61 (dd, J = 7.8, 0.9 Hz, 1H), 4.62 (d, J = 1.0 Hz, 1H), 4.42 (d, J = 14.0 Hz, 1H), 3.91 – 3.84 (m, 1H), 3.76 (dd, J = 14.0, 1.2 Hz, 1H), 3.31 (ddd, J = 13.4, 10.5, 4.2 Hz, 1H), 2.47 (s, 3H), 2.34 – 2.14 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 152.2, 147.9, 146.3, 143.9, 134.6, 134.3, 132.6, 131.6, 131.4, 129.8, 128.7, 128.6, 127.4, 126.4, 124.3, 123.7, 119.1, 112.0, 68.6, 53.6, 44.4, 43.3, 33.6, 21.6.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{23}N_3O_4S[M+H]^+$, 474.1482, found 474.1487.



2e

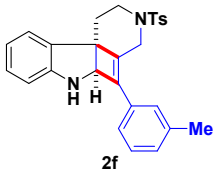
5-(3-methoxyphenyl)-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta [1,2-*b*]indole (2e)

The reaction was performed at 25 ℃ for 4 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1). The title compound was obtained as a white solid (46.9 mg of **2e** was obtained from 54.7 mg starting material, 86% yield), m.p.: 80~82 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.69 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.4 Hz, 1H), 7.04 (td, *J* = 7.6, 1.2 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.87 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.81 (t, *J* = 2.0 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 4.60 (d, *J* = 13.8 Hz, 1H), 4.54 (s, 1H), 3.85 (s, 4H), 3.75 (d, *J* = 13.9 Hz, 1H), 3.28 (ddd, *J* = 13.8, 11.1, 3.6 Hz, 1H), 2.45 (s, 3H), 2.28 (dt, *J* = 13.7, 3.9 Hz, 1H), 2.19 (ddd, *J* = 13.7, 11.1, 4.7 Hz, 1H).

^{13}C NMR (126 MHz,Chloroform-*d*) δ_C 159.9, 152.6, 143.6, 139.9, 137.6, 134.8, 133.7, 132.2, 129.9, 129.7, 128.3, 127.6, 123.5, 119.2, 119.0, 113.5, 112.3, 112.1, 66.1, 55.3, 52.4, 44.6, 43.5, 33.6, 21.6.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_3S[M+H]^+$, 459.1737, found 459.1742.



2f

5-(m-tolyl)-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta[1,2-*b*]indole (2f)

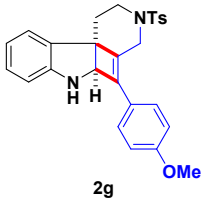
The reaction was performed at 25 ℃ for 2 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 7: 1). The title compound was obtained as a white solid (42.8 mg of **2f** was obtained from 54.3 mg starting

material, 79% yield), m.p.: 86~90 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.70 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.24 (m, 3H), 7.15 – 7.07 (m, 4H), 7.03 (td, *J* = 7.7, 1.3 Hz, 1H), 6.69 (td, *J* = 7.4, 1.1 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 4.61 (d, *J* = 13.9 Hz, 1H), 4.55 (d, *J* = 1.1 Hz, 1H), 3.88 (dt, *J* = 13.2, 4.5 Hz, 1H), 3.74 (dd, *J* = 13.8, 1.2 Hz, 1H), 3.27 (ddd, *J* = 13.1, 11.2, 3.6 Hz, 1H), 2.45 (s, 3H), 2.39 (s, 3H), 2.28 (dt, *J* = 13.6, 3.8 Hz, 1H), 2.19 (ddd, *J* = 13.7, 11.2, 4.8 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 152.6, 143.6, 139.3, 138.4, 137.9, 134.7, 132.4, 132.3, 129.7, 129.0, 128.7, 128.3, 127.6, 127.1, 123.8, 123.5, 119.0, 112.1, 66.0, 52.3, 44.6, 43.6, 33.5, 21.6, 21.5.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_2S[M+H]^+$, 443.1788, found 443.1793.



2g

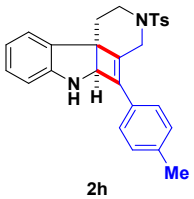
5-(4-methoxyphenyl)-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta [1,2-*b*]indole (2g)

The reaction was performed at 25 ℃ for 5 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 6: 1). The title compound was obtained as a white solid (63.2 mg of **2g** was obtained from 68.5 mg starting material, 92% yield), m.p.: 89~93 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.72 – 7.67 (m, 2H), 7.28 – 7.24 (m, 4H), 7.08 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.03 (td, *J* = 7.6, 1.3 Hz, 1H), 6.95 – 6.91 (m, 2H), 6.69 (td, *J* = 7.4, 1.1 Hz, 1H), 6.60 (dd, *J* = 7.9, 1.0 Hz, 1H), 4.58 (d, *J* = 13.7 Hz, 1H), 4.52 (d, *J* = 1.1 Hz, 1H), 3.85 (s, 4H), 3.71 (dd, *J* = 13.7, 1.2 Hz, 1H), 3.26 (ddd, *J* = 13.1, 11.3, 3.5 Hz, 1H), 2.45 (s, 3H), 2.27 (dt, *J* = 13.7, 3.7 Hz, 1H), 2.17 (ddd, *J* = 13.6, 11.2, 4.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 159.5, 152.7, 143.5, 137.4, 136.8, 134.8, 132.6, 129.7, 128.2, 127.9, 127.6, 125.3, 123.5, 119.0, 114.3, 112.1, 66.1, 55.4, 52.3, 44.6, 43.6, 33.6, 21.6.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_3S[M+H]^+$, 459.1737, found 459.1739.



2h

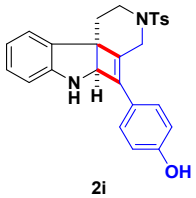
5-(p-tolyl)-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta[1,2-*b*]indole (2h)

The reaction was performed at 25 ℃ for 8 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 8: 1). The title compound was obtained as a light-yellow solid (50.2 mg of **2h** was obtained from 53.7 mg starting material, 94%yield), m.p.: 88~92 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 7.71 – 7.67 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.20 (s, 4H), 7.08 (dd, J = 7.5, 1.3 Hz, 1H), 7.03 (td, J = 7.6, 1.3 Hz, 1H), 6.68 (td, J = 7.4, 1.0 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 4.59 (d, J = 13.8 Hz, 1H), 4.53 (d, J = 1.2 Hz, 1H), 3.87 (dt, J = 13.2, 4.5 Hz, 1H), 3.73 (d, J = 13.8 Hz, 1H), 3.27 (ddd, J = 12.9, 11.2, 3.5 Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H), 2.27 (dt, J = 13.6, 3.8 Hz, 1H), 2.17 (ddd, J = 13.6, 11.2, 4.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 152.6, 143.5, 138.3, 138.2, 137.7, 134.8, 132.4, 129.7, 129.6, 129.5, 128.2, 127.6, 126.5, 123.5, 118.9, 112.0, 66.0, 52.3, 44.6, 43.6, 33.6, 21.6, 21.4.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_2S[M+H]^+$, 443.1788, found 443.1793.



2i

4-(3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta[1,2-*b*]indol-5-yl) phenol (2i)

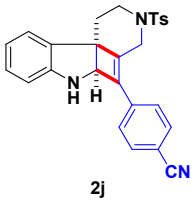
The reaction was performed at 25 ℃ for 6 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 4: 1). The title compound was obtained as a white solid (48.6 mg of **2i** was obtained from 51.6 mg starting material, 94% yield), m.p.: 167~171 ℃.

^{1}H NMR (500 MHz, DMSO-d_6) δ_H 9.68 (s, 1H), 7.66 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.25 – 7.20 (m, 2H), 6.96 (d, J = 7.3 Hz, 1H), 6.88 (td, J = 7.7, 1.3 Hz, 1H), 6.83 – 6.79 (m, 2H), 6.44 (td, J = 7.4, 1.1 Hz, 1H), 6.39 (d, J = 7.7 Hz, 1H), 6.11

(d, J = 3.1 Hz, 1H), 4.45 (d, J = 14.1 Hz, 1H), 4.43 (d, J = 3.2 Hz, 1H), 3.76 (dt, J = 13.4, 4.2 Hz, 1H), 3.53 (d, J = 13.9 Hz, 1H), 3.16 (ddd, J = 13.1, 10.9, 4.2 Hz, 1H), 2.40 (s, 3H), 2.10 – 1.95 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ_C 157.8, 153.8, 143.9, 137.7, 135.3, 134.8, 132.2, 130.2, 128.6, 128.2, 127.8, 124.3, 123.6, 117.2, 115.9, 110.5, 66.2, 51.8, 44.8, 43.8, 34.0, 21.5.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{24}N_2O_3S[M+H]^+$, 445.1580, found 445.1588.



2j

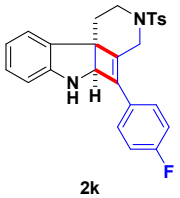
4-(3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta[1,2-*b*]indol-5-yl) benzonitrile (2j)

The reaction was performed at 25 ℃ for 7 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 4: 1). The title compound was obtained as a yellow solid (38.6 mg of **2j** was obtained from 64.1 mg starting material, 60% yield), m.p.: 96~100 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.70 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.10 – 7.04 (m, 2H), 6.72 (t, J = 7.5 Hz, 1H), 6.64 (d, J = 7.9 Hz, 1H), 4.64 (s, 1H), 4.59 (d, J = 13.7 Hz, 1H), 3.89 (dt, J = 13.4, 4.4 Hz, 1H), 3.69 (d, J = 13.8 Hz, 1H), 3.27 – 3.16 (m, 1H), 2.46 (s, 3H), 2.33 (dt, J = 13.7, 3.7 Hz, 1H), 2.25 (ddd, J = 13.6, 11.1, 4.8 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 152.5, 144.3, 143.9, 136.6, 136.0, 134.2, 132.6, 131.8, 129.9, 128.6, 127.6, 127.0, 123.6, 119.6, 118.7, 112.6, 111.1, 66.5, 53.7, 44.5, 43.6, 33.9, 21.6.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{23}N_3O_2S[M+H]^+$, 454.1584, found 454.1587.



2k

5-(4-fluorophenyl)-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta[1,2-*b*]indole (2k)

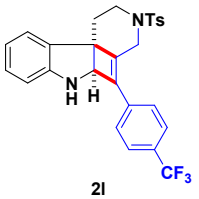
The reaction was performed at 25 ℃ for 1 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 8: 1). The title compound was obtained as a yellow solid (40.1 mg of **2k** was obtained from 49.3 mg starting material, 81% yield), m.p.: 88~92 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.70 (d, *J* = 8.3 Hz, 2H), 7.29 (ddd, *J* = 8.4, 5.0, 1.9 Hz, 5H), 7.09 (d, *J* = 8.6 Hz, 3H), 7.07 – 7.02 (m, 1H), 6.71 (td, *J* = 7.5, 1.1 Hz, 1H), 6.62 (dd, *J* = 7.9, 0.9 Hz, 1H), 4.63 – 4.52 (m, 2H), 3.95 – 3.85 (m, 1H), 3.68 (dd, *J* = 13.9, 1.2 Hz, 1H), 3.24 (ddd, *J* = 13.1, 11.2, 3.7 Hz, 1H), 2.46 (s, 3H), 2.29 (dt, *J* = 13.6, 3.8 Hz, 1H), 2.20 (ddd, *J* = 13.7, 11.2, 4.8 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 162.4 (d, *J* = 248.7 Hz), 152.6, 143.7, 139.0 (d, *J* = 2.1 Hz), 136.7, 134.5, 132.3, 129.8, 128.7 (d, *J* = 3.2 Hz), 128.4, 128.3, 127.6, 123.5, 119.2, 115.9 (d, *J* = 21.7 Hz), 112.3, 66.4, 52.7, 44.6, 43.5, 33.7, 21.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ_F -112.2.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{23}FN_2O_2S[M+H]^+$, 447.1537, found 447.1546.



2l

3-Tosyl-5-(4-(trifluoromethyl)phenyl)-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3] cyclobuta[1,2-*b*]indole (2l)

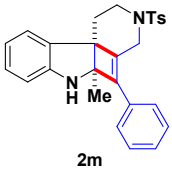
The reaction was performed at 50 ℃ for 2 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 10: 1). The title compound was obtained as a white solid (32.2 mg of **2l** was obtained from 47.7 mg starting material, 68% yield), m.p.: 166~167 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.73 – 7.67 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.06 (td, *J* = 7.7, 1.3 Hz, 1H), 6.72 (td, *J* = 7.5, 1.1 Hz, 1H), 6.67 – 6.58 (m, 1H), 4.63 – 4.62 (m, 1H), 4.60 (d, *J* = 13.8 Hz, 1H), 3.91 (dq, *J* = 13.2, 4.6 Hz, 1H), 3.73 (d, *J* = 13.8 Hz, 1H), 3.26 (ddd, *J* = 13.1, 11.2, 3.6 Hz, 1H), 2.45 (s, 3H), 2.32 (dt, *J* = 13.8, 3.7 Hz, 1H), 2.24 (ddd, *J* = 13.7, 11.2, 4.8 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 152.5, 143.8, 142.7, 136.4, 135.7, 134.4, 132.0, 129.8, 128.5, 127.6, 126.7, 125.7 (q, J = 3.8 Hz), 123.6, 119.4, 112.5, 66.4, 53.3, 44.5, 43.5, 33.8, 21.6.

^{19}F NMR (471 MHz, Chloroform-*d*) δ_F -62.6.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{23}F_3N_2O_2S[M+H]^+$, 497.1505, found 497.1511.



2m

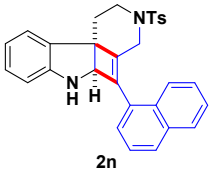
5a-methyl-5-phenyl-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta[1,2-*b*]indole (2m)

The reaction was performed at 25 ℃ for 2 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 7: 1). The title compound was obtained as a white solid (17.9 mg of **2m** was obtained from 55.3 mg starting material, 32% yield), m.p.: 41~43 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 7.73 – 7.69 (m, 2H), 7.37 (td, J = 7.5, 1.4 Hz, 2H), 7.34 – 7.31 (m, 2H), 7.32 – 7.26 (m, 1H), 7.27 – 7.24 (m, 2H), 7.13 (dd, J = 7.6, 1.3 Hz, 1H), 7.04 (td, J = 7.7, 1.3 Hz, 1H), 6.69 (td, J = 7.5, 1.1 Hz, 1H), 6.61 (dd, J = 7.9, 1.0 Hz, 1H), 4.61 (dd, J = 14.1, 1.1 Hz, 1H), 3.87 (dtd, J = 13.3, 4.7, 1.1 Hz, 1H), 3.81 (d, J = 14.1 Hz, 1H), 3.41 (ddd, J = 13.2, 10.8, 3.7 Hz, 1H), 2.43 (s, 3H), 2.15 (ddd, J = 13.7, 10.8, 4.9 Hz, 1H), 2.02 (dt, J = 13.8, 4.0 Hz, 1H), 1.46 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 150.9, 143.5, 139.5, 138.1, 135.2, 132.9, 132.5, 129.8, 128.7, 128.1, 127.9, 127.6, 126.8, 123.8, 118.8, 111.6, 71.0, 55.4, 44.4, 43.5, 29.8, 21.5, 19.4.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_2S[M+H]^+$, 443.1788, found 443.1794.



2n

5-(naphthalen-1-yl)-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta[1,2-*b*]indole (2n)

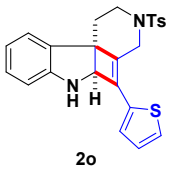
The reaction was performed at 25 ℃ for 8 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate: dichloromethane = 7: 1: 1).

The title compound was obtained as a white solid (39.0 mg of **2n** was obtained from 62.1 mg starting material, 62% yield), m.p.: 83~88 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 7.99 – 7.94 (m, 1H), 7.92 – 7.88 (m, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.52 (ddd, *J* = 7.2, 4.4, 1.7 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.1 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.74 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 4.83 (s, 1H), 4.40 (d, *J* = 13.7 Hz, 1H), 3.98 (dt, *J* = 13.2, 4.3 Hz, 1H), 3.76 (d, *J* = 13.7 Hz, 1H), 3.34 – 3.26 (m, 1H), 2.43 (s, 3H), 2.36 (dt, *J* = 13.7, 3.7 Hz, 1H), 2.30 (ddd, *J* = 13.6, 11.3, 4.6 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 152.5, 143.5, 142.0, 137.3, 134.7, 133.9, 132.5, 131.1, 129.9, 129.8, 128.7, 128.7, 128.4, 127.5, 126.6, 126.1, 126.0, 125.2, 124.9, 123.5, 118.9, 112.0, 68.5, 52.8, 44.7, 44.1, 33.8, 21.5.

HR-ESI-MS(*m/z*): calcd. for $C_{30}H_{26}N_2O_2S[M+H]^+$, 479.1788, found 479.1792.



2o

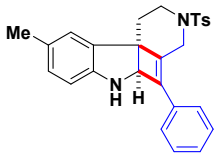
5-(thiophen-2-yl)-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta[1,2-*b*]indole (2o)

The reaction was performed at 25 ℃ for 2 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 7: 1). The title compound was obtained as a white solid (34.3 mg of **2o** was obtained from 42. 8 mg starting material, 80% yield), m.p.: 100~103 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.73 – 7.68 (m, 2H), 7.32 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.10 – 7.03 (m, 4H), 6.72 (td, *J* = 7.5, 1.1 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 4.55 – 4.51 (m, 2H), 3.95 – 3.86 (m, 1H), 3.62 (dd, *J* = 14.0, 1.2 Hz, 1H), 3.24 (ddd, *J* = 13.2, 11.3, 3.5 Hz, 1H), 2.45 (s, 3H), 2.27 (dt, *J* = 13.7, 3.7 Hz, 1H), 2.19 (ddd, *J* = 13.7, 11.3, 4.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 152.5, 143.6, 137.2, 135.3, 134.7, 132.1, 131.6, 129.7, 128.4, 127.6, 127.5, 126.0, 125.3, 123.4, 119.1, 112.1, 67.4, 53.4, 44.5, 43.3, 33.6, 21.6.

HR-ESI-MS(*m/z*): calcd. for $C_{24}H_{22}N_2O_2S[M+H]^+$, 435.1195, found 435.1203.



2p

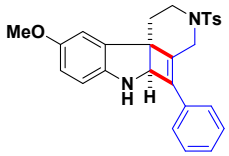
9-methyl-5-phenyl-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta[1,2-*b*]indole (2p)

The reaction was performed at 25 ℃ for 4 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1). The title compound was obtained as a yellow solid (110.1 mg of **2p** was obtained from 144.9 mg starting material,76% yield), m.p.: 157 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.70 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.34 – 7.29 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 1.7 Hz, 1H), 6.87 (ddd, *J* = 8.0, 1.8, 0.8 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 4.61 (d, *J* = 14.0 Hz, 1H), 4.54 (d, *J* = 1.2 Hz, 1H), 3.90 – 3.79 (m, 2H), 3.36 (ddd, *J* = 13.3, 10.9, 3.7 Hz, 1H), 2.44 (s, 3H), 2.30 – 2.23 (m, 4H), 2.17 (ddd, *J* = 13.7, 10.9, 4.7 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 150.3, 143.5, 139.6, 137.8, 134.9, 132.9, 132.4, 129.7, 128.8, 128.7, 128.7, 128.1, 127.6, 126.5, 124.3, 112.4, 66.5, 52.7, 44.5, 43.6, 33.4, 21.6, 20.9.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_2S[M+H]^+$, 443.1788, found 443.1792.



2q

9-methoxy-5-phenyl-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta [1,2-*b*]indole (2q)

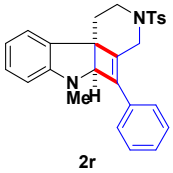
The reaction was performed at 25 ℃ for 4 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1). The title compound was obtained as a chocolate solid (75.4 mg of **2q** was obtained from 115.0 mg starting material, 66% yield), m.p.: 100~112 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 7.69 (d, *J* = 7.9 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 3H), 7.26 (d, *J* = 7.9 Hz, 2H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.64 – 6.58 (m, 2H), 4.62 (d, *J* = 13.8 Hz, 1H), 4.58 (s, 1H), 3.86 (dt, *J* = 13.3, 4.5 Hz, 1H),

3.72 (d, J = 16.4 Hz, 4H), 3.27 – 3.20 (m, 1H), 2.44 (s, 3H), 2.28 (dt, J = 13.7, 3.8 Hz, 1H), 2.19 (td, J = 13.9, 12.6, 4.8 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 153.8, 146.2, 143.7, 139.5, 138.0, 134.7, 134.5, 132.3, 129.8, 128.8, 128.2, 127.5, 126.6, 113.5, 112.5, 110.9, 67.1, 55.9, 53.1, 44.5, 43.7, 33.3, 21.6.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}N_2O_3S[M+H]^+$, 459.1737, found 459.1737.



2r

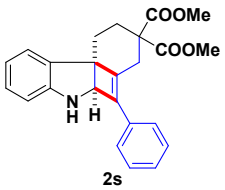
6-methyl-5-phenyl-3-tosyl-1,2,3,4,5a,6-hexahydropyrido[4',3':2,3]cyclobuta[1,2-*b*]indole (2r)

The reaction was performed at 25 ℃ for 0.5 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 15: 1). The title compound was obtained as a green-yellow solid (77.6 mg of **2r** was obtained from 85.5 mg starting material, 91% yield), m.p.: 145~147 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.68 (d, J = 8.2 Hz, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.25 (d, J = 8.0 Hz, 2H), 7.10 (td, J = 7.7, 1.3 Hz, 1H), 7.05 (dd, J = 7.5, 1.3 Hz, 1H), 6.59 (td, J = 7.5, 1.0 Hz, 1H), 6.39 (d, J = 7.9 Hz, 1H), 4.60 (d, J = 13.8 Hz, 1H), 4.46 (s, 1H), 3.90 (dt, J = 13.2, 4.4 Hz, 1H), 3.76 (d, J = 13.7 Hz, 1H), 3.27 (ddd, J = 13.1, 11.3, 3.5 Hz, 1H), 2.94 (s, 3H), 2.45 (s, 3H), 2.27 (dt, J = 13.6, 3.8 Hz, 1H), 2.18 (ddd, J = 13.6, 11.3, 4.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 153.2, 143.6, 139.7, 137.9, 134.7, 133.2, 131.7, 129.7, 128.7, 128.6, 128.1, 127.5, 126.7, 123.1, 116.6, 107.8, 72.3, 50.7, 44.6, 43.2, 34.7, 34.0, 21.6.

HR-ESI-MS(*m/z*): calcd. for $C_{27}H_{26}O_2S[M+H]+$, 443.1788, found 443.1792.



2s

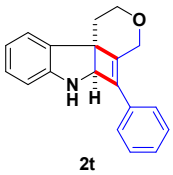
dimethyl-5-phenyl-1,2,5a,6-tetrahydrobenzo[2,3]cyclobuta[1,2-*b*]indole-3,3(4*H*)-dicarboxylate (2s)

The reaction was performed at 25 ℃ for 1 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 10: 1). The title compound was obtained as a yellow solid (43.2 mg of **2s** was obtained from 47.3 mg starting material, 91% yield), m.p.: 55~56 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.46 – 7.41 (m, 2H), 7.36 – 7.30 (m, 3H), 7.25 – 7.19 (m, 1H), 7.04 (td, *J* = 7.7, 1.3 Hz, 1H), 6.75 (td, *J* = 7.4, 1.1 Hz, 1H), 6.62 (dd, *J* = 7.9, 1.0 Hz, 1H), 4.58 (s, 1H), 3.79 (s, 3H), 3.56 (s, 3H), 3.52 (dd, *J* = 13.8, 1.7 Hz, 1H), 2.76 (dd, *J* = 13.8, 1.5 Hz, 1H), 2.66 – 2.57 (m, 1H), 2.44 – 2.31 (m, 2H), 2.08 (td, *J* = 14.2, 4.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 172.0, 170.3, 152.8, 144.2, 136.9, 133.5, 132.8, 128.5, 128.1, 127.5, 126.2, 123.3, 119.1, 112.0, 66.3, 56.2, 53.7, 53.0, 52.5, 31.3, 30.4, 30.1.

HR-ESI-MS(*m/z*): calcd. for $C_{24}H_{23}NO_4[M+H]^+$, 390.1700, found 390.1709.



2t

5-phenyl-1,2,5a,6-tetrahydro-4*H*-pyrano[4',3':2,3]cyclobuta[1,2-*b*]indole (2t)

The reaction was performed at 25 ℃ for 1 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 15: 1). The title compound was obtained as a light-yellow solid (59.2 mg of **2t** was obtained from 63.4 mg starting material, 93% yield), m.p.: 50~54 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.42 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.40 – 7.32 (m, 4H), 7.34 – 7.24 (m, 1H), 7.10 (td, *J* = 7.7, 1.3 Hz, 1H), 6.82 (td, *J* = 7.5, 1.1 Hz, 1H), 6.70 – 6.66 (m, 1H), 4.82 (d, *J* = 0.9 Hz, 1H), 4.66 (dd, *J* = 13.3, 0.8 Hz, 1H), 4.39 (dd, *J* = 13.3, 1.0 Hz, 1H), 4.09 (d, *J* = 3.3 Hz, 1H), 4.07 (t, *J* = 3.3 Hz, 1H), 2.42 (ddd, *J* = 13.6, 9.4, 6.6 Hz, 1H), 2.32 (dtd, *J* = 13.6, 3.2, 0.9 Hz, 1H).

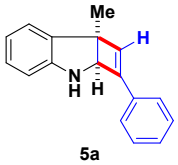
^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 152.5, 143.6, 136.2, 133.1, 132.9, 128.7, 128.2, 127.9, 126.5, 123.7, 119.3, 112.2, 66.8, 65.7, 63.2, 52.2, 36.3.

HR-ESI-MS(*m/z*): calcd. for $C_{19}H_{17}NO[M+H]^+$, 276.1383, found 276.1389.

5. General procedure for the synthesis of compounds 5a-5p, 6a, 6p, 6k

A Schlenk flask equipped with a magnetic stirring bar was charged with **3** (0.5 mmol,

1 eq.), $Fe(NO_3)_3 \cdot 9H_2O$ (0.025 mmol, 5 mol%) and aryl alkynes **4** (0.75 mmol, 1.5 eq.) in TFE (2.5 mL). Then a solution of HNO_3 (0.5 mmol, 1.0 eq.) in TFE (2.5 mL, 0.2 M) was added *via* syringe. The reaction was performed at 25 ℃. Upon the completion as indicated by TLC, the reaction was quenched by the addition of Et_3N. Then the mixture was filtered through the silica gel. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography to give compound **5** and/or the compound **6**.



5a

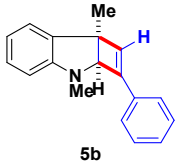
7b-methyl-2-phenyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indole (5a)

The reaction was performed at 25 ℃ for 2 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 20: 1). The title compound was obtained as a yellow film (71.5 mg of **5a** and **6a** was obtained from 130.2 mg starting material, 31% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ_H 7.47 (d, J = 7.6 Hz, 2H), 7.36 (dd, J = 7.5 Hz, 2H), 7.28 (dd, J = 7.4 Hz, 1H), 7.07 (d, J = 7.3 Hz, 1H), 6.91 (dd, J = 7.6 Hz, 1H), 6.61 (d, J = 2.1 Hz, 1H), 6.53 (dd, J = 7.4 Hz, 1H), 6.42 (d, J = 7.8 Hz, 1H), 6.27 (s, 1H), 4.56 (d, J = 2.2 Hz, 1H), 1.51 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ_C 152.5, 142.8, 135.7, 133.3, 133.2, 128.9, 128.3, 128.0, 125.7, 123.2, 116.9, 109.8, 66.3, 54.0, 21.2.

HR-ESI-MS(*m/z*): calcd. for $C_{17}H_{15}N[M+H]^+$, 234.1277, found 234.1280.



5b

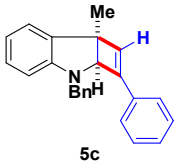
3,7b-dimethyl-2-phenyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indole (5b)

The reaction was performed at 25 ℃ for 5 h. The crude product was purified by flash column chromatography (petroleum ether). The title compound was obtained as a yellow solid (40.8 mg of **5b** and **6b** was obtained from 140.9 mg starting material, 17% yield), m.p.: 44~46 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.45 (d, *J* = 8.3 Hz, 2H), 7.35 (dd, *J* = 7.5 Hz, 2H), 7.28 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.12 (dd, *J* = 7.9 Hz, 2H), 6.67 (dd, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 1.7 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 1H), 4.54 (d, *J* = 2.0 Hz, 1H), 3.03 (s, 2H), 1.62 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 152.1, 142.8, 135.7, 133.8, 133.4, 128.4, 128.1, 127.8, 125.4, 122.5, 116.4, 107.1, 72.8, 52.7, 34.7, 20.9.

HR-ESI-MS(*m/z*): calcd. for $C_{18}H_{17}N[M+H]^+$, 248.1434, found 248.1438.



5c

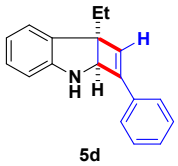
3-benzyl-7b-methyl-2-phenyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indole (5c)

The reaction was performed at 25 ℃ for 2 h. The crude product was purified by flash column chromatography (petroleum ether). The title compound was obtained as a yellow solid (94.7 mg of **5c** and **6c** was obtained from 225.5 mg starting material, 29% yield), m.p.: 64~66 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.33 – 7.22 (m, 10H), 7.20 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.10 (td, *J* = 7.7, 1.4 Hz, 1H), 6.74 (td, *J* = 7.4, 1.0 Hz, 1H), 6.62 (d, *J* = 2.1 Hz, 1H), 6.46 (d, *J* = 7.9 Hz, 1H), 4.66 – 4.52 (m, 3H), 1.64 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 152.2, 143.6, 138.7, 135.7, 133.5, 133.4, 128.5, 128.3, 128.1, 127.8, 127.3, 127.0, 125.5, 122.7, 117.1, 108.0, 71.7, 53.2, 52.4, 21.2.

HR-ESI-MS(*m/z*): calcd. for $C_{24}H_{21}N$ $[M+H]^+$, 324.1747 ,found 324.1754.



5d

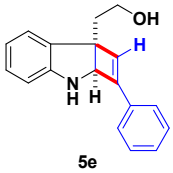
7b-ethyl-2-phenyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indole (5d)

The reaction was performed at 25 ℃ for 1 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 50: 1). The title compound was obtained as a yellow solid (42.5 mg of **5d** and **6d** was obtained from 189.4 mg starting material, 13% yield), m.p.: 60~61 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.49 – 7.43 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.25 (m, 1H), 7.17 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.08 (td, *J* = 7.6, 1.4 Hz, 1H), 6.82 – 6.75 (m, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 1.9 Hz, 1H), 4.77 (d, *J* = 2.0 Hz, 1H), 2.01 (ddt, *J* = 23.4, 14.2, 7.2 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 151.9, 142.9, 134.9, 132.8, 132.7, 128.6, 128.0, 127.9, 125.2, 123.3, 118.9, 111.5, 63.3, 59.2, 26.7, 10.3.

HR-ESI-MS(*m/z*): calcd. for $C_{19}H_{19}N[M+H]^+$, 248.1434, found 248.1441.



5e

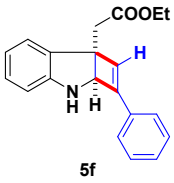
2-(2-phenyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl)ethan-1-ol (5e)

The reaction was performed at 25 ℃ for 4 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 3: 1). The title compound was obtained as an orange solid (46.2 mg of **5e** and **6e** was obtained from 79.3 mg starting material, 36% yield), m.p.: 150~152 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.45 – 7.41 (m, 2H), 7.39 – 7.34 (m, 2H), 7.32 – 7.27 (m, 1H), 7.16 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.07 (td, *J* = 7.6, 1.3 Hz, 1H), 6.78 (td, *J* = 7.4, 1.0 Hz, 1H), 6.64 (dt, *J* = 7.9, 0.7 Hz, 1H), 6.62 (d, *J* = 1.8 Hz, 1H), 4.90 (d, *J* = 1.8 Hz, 1H), 3.81 (ddd, *J* = 7.1, 5.9, 1.1 Hz, 2H), 2.33 – 2.19 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 151.6, 143.0, 134.5, 132.6, 132.0, 128.6, 128.2, 128.1, 125.3, 123.4, 119.0, 111.7, 64.4, 60.6, 56.6, 36.3.

HR-ESI-MS(*m/z*): calcd. for $C_{18}H_{17}NO[M+H]^+$, 264.1383 ,found 264.1389.



5f

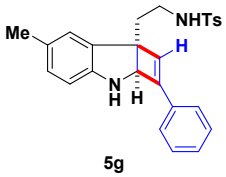
ethyl 2-(2-phenyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl)acetate (5f)

The reaction was performed at 25 ℃ for 4 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate =7: 1). The title compound was obtained as a yellow film (93.6 mg of **5f** and **6f** was obtained from 162.7 mg starting material, 38% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.37 – 7.33 (m, 2H), 7.29 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 7.11 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.98 (td, *J* = 7.6, 1.3 Hz, 1H), 6.68 (td, *J* = 7.4, 1.0 Hz, 1H), 6.57 (d, *J* = 1.8 Hz, 1H), 6.56 – 6.54 (m, 1H), 4.90 (d, *J* = 1.8 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.01 – 2.72 (m, 2H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 171.4, 151.9, 143.6, 133.5, 132.5, 131.5, 128.6, 128.4, 128.3, 125.4, 123.4, 119.0, 111.9, 65.2, 60.5, 55.2, 39.9, 14.2.

HR-ESI-MS(*m/z*): calcd. for $C_{18}H_{17}NO[M+H]^+$, 264.1383 ,found 264.1389.



5g

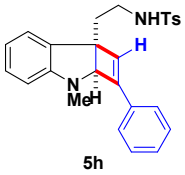
4-methyl-*N*-(2-(6-methyl-2-phenyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl)ethyl)benzenesulfonamide (5g)

The reaction was performed at 25 ℃ for 6 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1). The title compound was obtained as a yellow solid (86.1 mg of **5g** and **6g** was obtained from 125.1 mg starting material, 54% yield), m.p.: 55~61 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.66 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.31 – 7.22 (m, 3H), 6.87 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.83 (d, *J* = 1.8 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 6.52 (d, *J* = 1.8 Hz, 1H), 4.83 (t, *J* = 6.2 Hz, 1H), 4.77 (d, *J* = 1.8 Hz, 1H), 3.10 (dtd, *J* = 12.5, 7.3, 5.2 Hz, 1H), 2.95 (dtd, *J* = 12.8, 7.7, 5.3 Hz, 1H), 2.42 (s, 3H), 2.25 (s, 3H), 2.21 – 2.11 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 148.9, 143.3, 143.1, 136.7, 134.3, 132.4, 131.4, 129.7, 129.7, 128.8, 128.6, 128.3, 127.1, 127.0, 125.3, 123.9, 112.1, 64.4, 56.6, 40.7, 33.4, 21.5, 20.9.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{26}N_2O_2S[M+H]^+$, 431.1788 ,found 431.1792.



5h

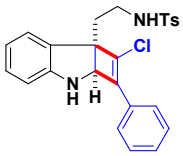
2-methyl-*N*-(2-(3-methyl-2-phenyl-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl) ethyl)benzenesulfonamide (5h)

The reaction was performed at 25 ℃ for 4 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 8: 1). The title compound was obtained as a yellow solid (41.2 mg of **5h** and **6h** was obtained from 98.1 mg starting material, 32% yield), m.p.: 56~58 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.64 (t, *J* = 8.4 Hz, 3H), 7.46 (d, *J* = 7.1 Hz, 2H), 7.36 (dd, *J* = 8.0, 6.2 Hz, 4H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.02 – 6.93 (m, 2H), 6.59 (d, *J* = 1.9 Hz, 1H), 6.54 (t, *J* = 7.3 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 4.62 (d, *J* = 1.9 Hz, 1H), 2.89 (s, 3H), 2.84 – 2.62 (m, 2H), 2.36 (s, 3H), 1.97 (dddd, *J* = 23.7, 13.9, 9.8, 5.9 Hz, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ_C 152.7, 143.3, 143.1, 137.9, 135.0, 133.5, 131.8, 130.1, 129.0, 128.5, 127.0, 125.9, 123.0, 116.7, 107.9, 70.3, 55.1, 35.0, 33.8, 21.4.

HR-ESI-MS(*m/z*): calcd for $C_{26}H_{26}N_2O_2S[M+H]^+$, 431.1788 ,found 431.1792.



5i

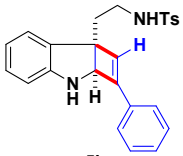
_N_-(2-(1-chloro-2-phenyl-2a,3-dihydro-7b_H_-cyclobuta[_b_]indol-7b-yl)ethyl)-4-methylbenzenesulfonamide (5i)

The reaction was performed at 25 ℃ for 6 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1). The title compound was obtained as a yellow solid (33.62 mg of **5i** and **6i** was obtained from 110.8 mg starting material, 21% yield), m.p.: 57~62 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 7.68 – 7.63 (m, 2H), 7.61 – 7.57 (m, 2H), 7.41 – 7.37 (m, 2H), 7.35 – 7.31 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.10 (td, J = 7.7, 1.3 Hz, 1H), 7.07 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.77 (td, *J* = 7.4, 1.0 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 4.86 (s, 1H), 4.66 – 4.60 (m, 1H), 3.12 (dtd, *J* = 12.5, 7.4, 5.0 Hz, 1H), 3.01 – 2.93 (m, 1H), 2.41 (s, 3H), 2.28 (ddd, *J* = 14.5, 7.2, 5.0 Hz, 1H), 2.19 (dt, *J* = 14.5, 7.8 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 151.3, 143.5, 137.6, 136.5, 130.7, 129.7, 129.0, 128.7, 128.7, 128.6, 127.9, 127.0, 126.5, 123.7, 119.4, 112.2, 62.8, 62.6, 40.1, 31.1, 21.5.

HR-ESI-MS(*m/z*): calcd. for $C_{25}H_{23}ClN_2O_2S[M+H]^+$, 451.1242, found 451.1246.



5j

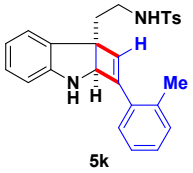
4-methyl-_N_-(2-(2-phenyl-2a,3-dihydro-7b_H_-cyclobuta[_b_]indol-7b-yl)ethyl) benzenesulfonamide (5j)

The reaction was performed at 25 ℃ for 7 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1). The title compound was obtained as a yellow solid (123.2 mg of **5j** and **6j** was obtained from 138.9 mg starting material, 67% yield), m.p.: 60~63 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*) δ_H 7.67 – 7.63 (m, 2H), 7.40 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.06 (td, *J* = 7.7, 1.3 Hz, 1H), 7.02 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.73 (td, *J* = 7.4, 1.0 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.53 (d, *J* = 1.7 Hz, 1H), 4.79 (d, *J* = 1.7 Hz, 1H), 4.65 (t, *J* = 6.3 Hz, 1H), 3.11 (dtd, *J* = 12.7, 7.3, 5.3 Hz, 1H), 2.98 (dtd, *J* = 13.0, 7.6, 5.5 Hz, 1H), 2.42 (s, 3H), 2.25 – 2.11 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ_C 151.3, 143.3, 143.1, 136.7, 134.1, 132.3, 131.0, 129.7, 128.6, 128.4, 128.3, 127.0, 125.3, 123.3, 119.2, 111.9, 64.0, 56.5, 40.7, 33.5, 21.5.

HR-ESI-MS(*m/z*): calcd for $C_{25}H_{24}N_2O_2S[M+H]^+$, 417.1631 ,found 417.1638.



5k

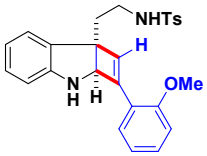
4-methyl-*N*-(2-(2-(*o*-tolyl)-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl)ethyl) benzenesulfonamide (5k)

The reaction was performed at 25 ℃ for 6 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1). The title compound was obtained as a yellow solid (53.6 mg of **5k** and **6k** was obtained from 84.9 mg starting material, 46% yield), m.p.: 44~49 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.69 – 7.62 (m, 2H), 7.58 (t, *J* = 5.6 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.15 (m, 3H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.90 (td, *J* = 7.6, 1.6 Hz, 1H), 6.52 (dd, *J* = 7.4 Hz, 1H), 6.44 – 6.39 (m, 1H), 6.39 (d, *J* = 1.8 Hz, 1H), 6.20 (d, *J* = 2.8 Hz, 1H), 4.74 – 4.69 (m, 1H), 2.91 – 2.66 (m, 2H), 2.35 (s, 3H), 2.26 (s, 3H), 2.12 – 1.92 (m, 2H).

^{13}C NMR (101 MHz, DMSO) δ_C 152.3, 143.1, 142.5, 137.4, 137.1, 136.8, 131.0, 130.9, 130.6, 129.5, 127.7, 127.6, 127.4, 126.4, 125.6, 122.8, 116.5, 109.6, 65.1, 56.1, 39.9, 33.6, 21.4, 20.9.

HR-ESI-MS(m/z): calcd. for $C_{26}H_{26}N_2O_2S[M+H]^+$, 431.1788, found 431.1794.



5l

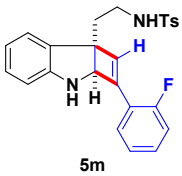
***N*-(2-(2-(2-methoxyphenyl)-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl)ethyl)-4-methylbenzenesulfonamide (5l)**

The reaction was performed at 25 ℃ for 3 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1). The title compound was obtained as a yellow solid (64.7 mg of **5l** and **6l** was obtained from 147.5 mg starting material, 31% yield), m.p.: 63~66 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.63 (d, *J* = 8.2 Hz, 2H), 7.33 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.04 (td, *J* = 7.6, 1.3 Hz, 1H), 6.99 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 1.7 Hz, 1H), 4.72 (d, *J* = 1.7 Hz, 1H), 4.68 (dd, *J* = 7.4, 5.2 Hz, 1H), 3.88 (s, 3H), 3.11 (ddd, *J* = 13.2, 7.2, 5.7 Hz, 1H), 2.97 (dtd, *J* = 12.8, 7.6, 5.1 Hz, 1H), 2.41 (s, 3H), 2.17 (dd, *J* = 7.5, 5.3 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 158.1, 151.2, 143.2, 139.8, 136.8, 131.4, 129.7, 129.4, 128.2, 127.2, 127.0, 123.1, 121.2, 120.5, 118.7, 111.4, 111.0, 65.4, 56.7, 55.3, 40.8, 33.4, 21.5.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{26}N_2O_3S[M+H]^+$, 447.1737, found 447.1741.



5m

***N*-(2-(2-(2-fluorophenyl)-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl)ethyl)-4-methylbenzenesulfonamide (5m)**

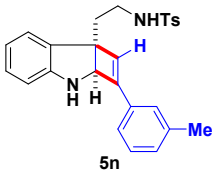
The reaction was performed at 25 ℃ for 6 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1). The title compound was obtained as a yellow solid (69.8 mg of **5m** and **6m** was obtained from 129.2 mg starting material, 40% yield), m.p.: 59~61 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.69 – 7.61 (m, 2H), 7.37 (td, *J* = 7.5, 1.8 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 3H), 7.11 (td, *J* = 7.5, 1.1 Hz, 1H), 7.08 – 7.03 (m, 2H), 7.01 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.65 – 6.58 (m, 2H), 4.80 – 4.73 (m, 2H), 3.10 (dtd, *J* = 12.8, 7.3, 5.5 Hz, 1H), 2.98 (dtd, *J* = 13.0, 7.6, 5.4 Hz, 1H), 2.41 (s, 3H), 2.23 – 2.11 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 161.12 (d, *J* = 250.7 Hz), 151.1, 143.3, 138.1 (d, *J* = 5.0 Hz), 137.7, 136.7, 130.8, 129.7, 129.6 (d, *J* = 8.2 Hz), 128.4, 127.5 (d, *J* = 4.3 Hz), 127.0, 124.2 (d, *J* = 3.4 Hz), 123.2, 120.5 (d, *J* = 14.0 Hz), 118.8, 116.0 (d, *J* = 21.3 Hz), 111.4, 65.3, 57.6, 40.7, 33.4, 21.5.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -114.6.

HR-ESI-MS(*m/z*): calcd. for $C_{25}H_{23}FN_2O_2S[M+H]^+$, 435.1537, found 435.1540.



5n

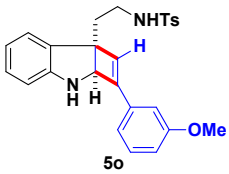
4-methyl-*N*-(2-(2-(*m*-tolyl)-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl)ethyl) benzenesulfonamide (5n)

The reaction was performed at 25 ℃ for 6 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1). The title compound was obtained as a yellow solid (63.7 mg of **5n** and **6n** was obtained from 91.8 mg starting material, 51% yield), m.p.: 51~57 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.66 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.18 (m, 5H), 7.11 (d, *J* = 7.4 Hz, 1H), 7.07 (ddd, *J* = 7.7, 1.3 Hz, 1H), 7.03 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.75 (dd, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 1.7 Hz, 1H), 4.84 – 4.74 (m, 2H), 3.18 – 3.04 (m, 1H), 2.96 (dtd, *J* = 12.8, 7.5, 5.3 Hz, 1H), 2.41 (s, 3H), 2.36 (s, 3H), 2.26 – 2.11 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 150.9, 143.4, 143.1, 138.4, 136.8, 134.2, 132.2, 131.4, 129.8, 129.3, 128.7, 128.4, 127.1, 126.1, 123.4, 122.6, 119.6, 112.3, 63.9, 56.5, 40.8, 33.6, 21.6, 21.5.

HR-ESI-MS(*m/z*): calcd for $C_{26}H_{26}N_2O_2S[M+H]^+$, 431.1788 ,found 431.1792.



5o

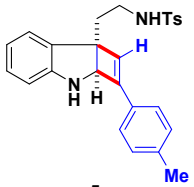
***N*-(2-(2-(3-methoxyphenyl)-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl)ethyl)-4-methylbenzenesulfonamide (5o)**

The reaction was performed at 25 ℃ for 6 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1). The title compound was obtained as a yellow solid (82.4 mg of **5o** and **6o** was obtained from 97.0 mg starting material, 60% yield), m.p.: 44~48 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.66 (d, *J* = 8.0 Hz, 2H), 7.25 (dd, *J* = 8.1, 3.4 Hz, 3H), 7.05 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 2.0 Hz, 1H), 6.84 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.51 (d, *J* = 1.7 Hz, 1H), 4.82 (t, *J* = 6.2 Hz, 1H), 4.74 (d, *J* = 1.7 Hz, 1H), 3.82 (s, 3H), 3.13 – 3.02 (m, 1H), 2.97 (tdd, *J* = 13.0, 8.5, 4.6 Hz, 1H), 2.41 (s, 3H), 2.27 – 2.10 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 159.8, 151.5, 143.3, 143.0, 136.7, 134.4, 133.7, 130.9, 129.7, 129.7, 128.3, 127.0, 123.2, 118.9, 117.9, 114.1, 111.7, 110.6, 64.0, 56.4, 55.3, 40.7, 33.5, 21.5.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{26}N_2O_3S[M+H]^+$, 447.1737, found 447.1742.



5p

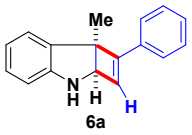
4-methyl-*N*-(2-(2-(p-tolyl)-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl)ethyl) benzenesulfonamide (5p)

The reaction was performed at 25 ℃ for 6 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 5: 1). The title compound was obtained as a yellow solid (65 mg of **5p** and **6p** was obtained from 89.1 mg starting material, 53% yield), m.p.: 50~53 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.66 – 7.60 (m, 2H), 7.31 – 7.22 (m, 4H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.05 (ddd, *J* = 7.7, 1.3 Hz, 1H), 7.01 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.71 (ddd, *J* = 7.4, 1.0 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 1.7 Hz, 1H), 4.75 (d, *J* = 1.7 Hz, 1H), 4.52 (s, 1H), 3.11 (dtd, *J* = 12.8, 6.6 Hz, 1H), 2.97 (dtd, *J* = 12.8, 7.4 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H), 2.22 – 2.12 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 151.4, 143.3, 143.0, 138.4, 136.7, 132.9, 130.9, 129.7, 129.6, 129.3, 128.3, 127.0, 125.3, 123.2, 118.9, 111.6, 64.0, 56.3, 40.8, 33.5, 21.5, 21.4.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{26}N_2O_2S[M+H]^+$, 431.1788, found 431.1790.



6a

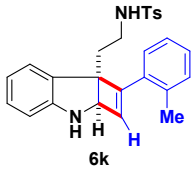
7b-methyl-1-phenyl-2a,7b-dihydro-3*H*-cyclobuta[*b*]indole (6a)

White solid, m.p.: 82~87 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.85 – 7.79 (m, 1H), 7.62 – 7.54 (m, 3H), 7.42 (td, *J* = 7.6, 1.5 Hz, 1H), 7.39 – 7.30 (m, 4H), 6.97 (d, *J* = 1.4 Hz, 1H), 5.61 (d, *J* = 1.4 Hz, 1H), 1.64 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ_C 143.0, 141.1, 140.0, 136.8, 131.6, 129.3, 129.3, 129.0, 127.7, 125.6, 125.1, 113.3, 65.2, 52.5, 19.9.

HR-ESI-MS(*m/z*): calcd. for $C_{17}H_{15}FN[M+H]^+$, 234.1277, found 234.1274.



6k

4-methyl-*N*-(2-(1-(*o*-tolyl)-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl)ethyl) benzenesulfonamide (6k)

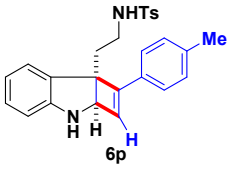
Light yellow solid, m.p.: 55~57 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.78 (d, *J* = 7.9 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.51 (t, *J* = 5.7 Hz, 1H), 7.48 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.41 (ddd, *J* = 7.7, 1.4 Hz, 1H), 7.36 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.20 (m, 2H), 7.20 – 7.16 (m,

1H), 6.71 (d, J = 1.4 Hz, 1H), 5.90 (d, J = 1.4 Hz, 1H), 2.79 – 2.70 (m, 2H), 2.35 (s, 3H), 2.25 (s, 3H), 2.21 – 2.10 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 142.9, 142.6, 141.7, 141.1, 137.0, 136.9, 134.7, 130.6, 129.8, 129.6, 128.9, 128.6, 127.1, 126.5, 125.8, 124.6, 113.3, 64.0, 54.8, 39.5, 31.7, 21.5, 20.9.

HR-ESI-MS(m/z): calcd. for $C_{26}H_{26}N_2O_2S[M+H]^+$, 431.1788, found 431.1773.



6p

4-methyl-*N*-(2-(1-(*p*-tolyl)-2a,3-dihydro-7b*H*-cyclobuta[*b*]indol-7b-yl)ethyl) benzenesulfonamide (6p)

Yellow solid, m.p.: 61~68 ℃.

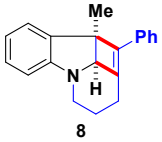
^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.83 – 7.78 (m, 1H), 7.70 – 7.65 (m, 2H), 7.43 – 7.39 (m, 2H), 7.41 – 7.23 (m, 5H), 7.13 (d, J = 7.9 Hz, 2H), 6.59 (d, J = 1.3 Hz, 1H), 5.63 (d, J = 1.3 Hz, 1H), 4.89 (t, J = 6.1 Hz, 1H), 2.98 (q, J = 7.0 Hz, 2H), 2.41 (s, 3H), 2.34 (s, 3H), 2.30 – 2.19 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 144.4, 143.7, 141.6, 139.3, 136.4, 134.6, 134.1, 129.9, 129.2, 129.1, 128.1, 127.1, 127.1, 125.5, 124.1, 113.8, 62.8, 54.4, 40.2, 33.4, 21.6, 21.4.

HR-ESI-MS(*m/z*): calcd. for $C_{26}H_{26}N_2O_2S[M+H]^+$, 431.1788, found 431.1760.

6. General procedure for the synthesis of compounds 8 and 10

A Schlenk flask equipped with a magnetic stirring bar was charged with the substrate (0.2 mmol, 1 eq.), $Fe(NO_3)_3 \cdot 9H_2O$ (0.02 mmol, 10 mmol%) and TsOH (0.2 mmol, 1.0 eq.) under air. Then TFE (2 mL) was added *via* syringe. The reaction was performed at 50 ℃. Upon completion as indicated by TLC, the reaction was quenched by the addition of Et_3N. Then the mixture was filtered through the silica gel. After the solvent was removed under reduced pressure, the residue was purified by column chromatography to give the title compound.



8

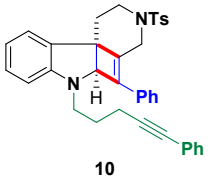
9b-methyl-1-phenyl-1a[1],3,4,9b-tetrahydro-2*H*-benzo[*b*]cyclobuta[*hi*]indolizine (8)

The reaction was performed for 10 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 50: 1). The title compound was obtained as a yellow solid (20.3 mg of **8** was obtained from 34.7 mg starting material, 58% yield), m.p.: 146~151 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ_H 7.46 – 7.42 (m, 2H), 7.40 – 7.29 (m, 3H), 7.24 – 7.17 (m, 1H), 7.10 (td, *J* = 7.7, 1.3 Hz, 1H), 6.74 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 4.17 (s, 1H), 3.59 (dt, *J* = 14.5, 3.3 Hz, 1H), 3.43 (ddd, *J* = 14.7, 12.5, 2.7 Hz, 1H), 2.74 (ddd, *J* = 13.1, 5.0, 2.3 Hz, 1H), 2.54 – 2.42 (m, 1H), 2.02 – 1.95 (m, 1H), 1.73 (d, *J* = 1.1 Hz, 3H), 1.69 (ddt, *J* = 13.0, 5.1, 2.6 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ_C 152.0, 145.1, 139.0, 137.7, 134.0, 128.5, 127.9, 127.0, 126.3, 124.7, 118.2, 112.0, 67.7, 54.8, 45.9, 27.8, 26.2, 18.3.

HR-ESI-MS(*m/z*): calcd. for $C_{20}H_{19}N[M+H]^+$, 274.1590, found 274.1601.



10

5-phenyl-6-(5-phenylpent-4-yn-1-yl)-3-tosyl-1,2,3,4,5a,6-hexahydropyrido [4',3':2,3]cyclobuta[1,2-*b*]indole (10)

The reaction was performed for 1 h. The crude product was purified by flash column chromatography (petroleum ether: ethyl acetate = 10: 1). The title compound was obtained as a yellow solid (87.0 mg of **10** was obtained from 137.5 mg starting material, 63% yield), m.p.: 125~129 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*) δ_H 7.69 – 7.66 (m, 2H), 7.45 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.36 – 7.32 (m, 5H), 7.31 – 7.28 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.04 (m, 2H), 6.60 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 4.61 – 4.51 (m, 2H), 3.89 (dt, *J* = 13.2, 4.4 Hz, 1H), 3.76 (d, *J* = 13.7 Hz, 1H), 3.52 (dt, *J* = 14.8, 7.4 Hz, 1H), 3.41

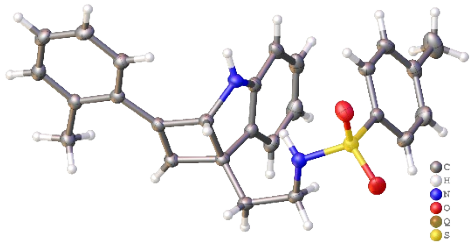
(ddd, J = 14.3, 8.1, 5.4 Hz, 1H), 3.28 (ddd, J = 13.1, 11.2, 3.5 Hz, 1H), 2.43 (d, J = 7.9 Hz, 5H), 2.29 (dt, J = 13.6, 3.7 Hz, 1H), 2.18 (ddd, J = 13.6, 11.2, 4.7 Hz, 1H), 1.94 – 1.85 (m, 1H), 1.76 (dq, J = 12.9, 6.4 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ_C 152.8, 143.5, 139.6, 138.8, 134.7, 133.0, 131.5, 131.3, 129.7, 128.7, 128.6, 128.3, 128.1, 127.8, 127.5, 126.7, 123.8, 123.3, 116.6, 107.9, 89.3, 81.4, 71.5, 51.0, 46.9, 44.6, 43.1, 34.2, 27.0, 21.6, 16.8.

HR-ESI-MS(*m/z*): calcd. for $C_{37}H_{34}N_2O_2S[M+H]^+$, 571.2414, found 571.2418.

Crystallographic Date

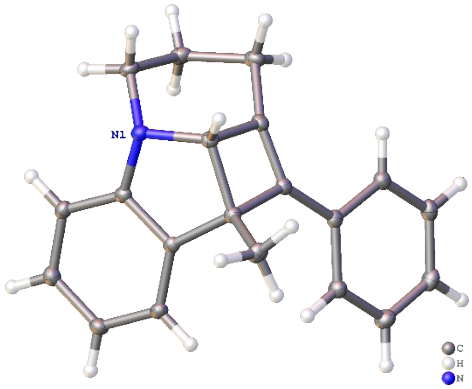
X-ray crystallographic data for 5k (CDCC number: 2173560)



Crystal data and structure refinement for **5k**.

Empirical formula	$C_{26}H_{26}N_2O_2S$
Formula weight	430.55
Temperature/K	200.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.55350(10)
b/Å	11.41710(10)
c/Å	18.3424(2)
α/°	90
β/°	92.7640(10)
γ/°	90
Volume/Å^3	2207.51(4)
Z	4
ρ_{calc}g/cm^3	1.295
μ/mm^{-1}	1.500
F(000)	912.0
Crystal size/mm^3	0.15 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.388 to 143.152
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 13$, $-22 \le l \le 22$
Reflections collected	11203
Independent reflections	4219 [R_{int} = 0.0141, R_{sigma} = 0.0155]
Data/restraints/parameters	4219/0/291
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0335, wR_2 = 0.0917
Final R indexes [all data]	R_1 = 0.0345, wR_2 = 0.0924
Largest diff. peak/hole / e Å^{-3}	0.29/-0.33

X-ray crystallographic data for compound 8 (CDCC number: 2173559)



Crystal data and structure refinement for **8**

Empirical formula	$C_{20}H_{19}N$
Formula weight	273.36
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.71530(10)
b/Å	9.2902(2)
c/Å	9.50980(10)
α/°	107.989(2)
β/°	94.9730(10)
γ/°	92.730(2)
Volume/Å^3	727.33(2)
Z	2
ρ_{calc}g/cm^3	1.248
μ/mm^{-1}	0.545
F(000)	292.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.836 to 143.996
Index ranges	$-10 \le h \le 10$, $-11 \le k \le 7$, $-11 \le l \le 11$
Reflections collected	6281
Independent reflections	2750 [R_{int} = 0.0122, R_{sigma} = 0.0115]
Data/restraints/parameters	2750/0/192
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0375, wR_2 = 0.0953
Final R indexes [all data]	R_1 = 0.0392, wR_2 = 0.0964
Largest diff. peak/hole / e Å^{-3}	0.26/-0.16

Figure S1. The ^{1}H-NMR spectra copy of compound 2a.

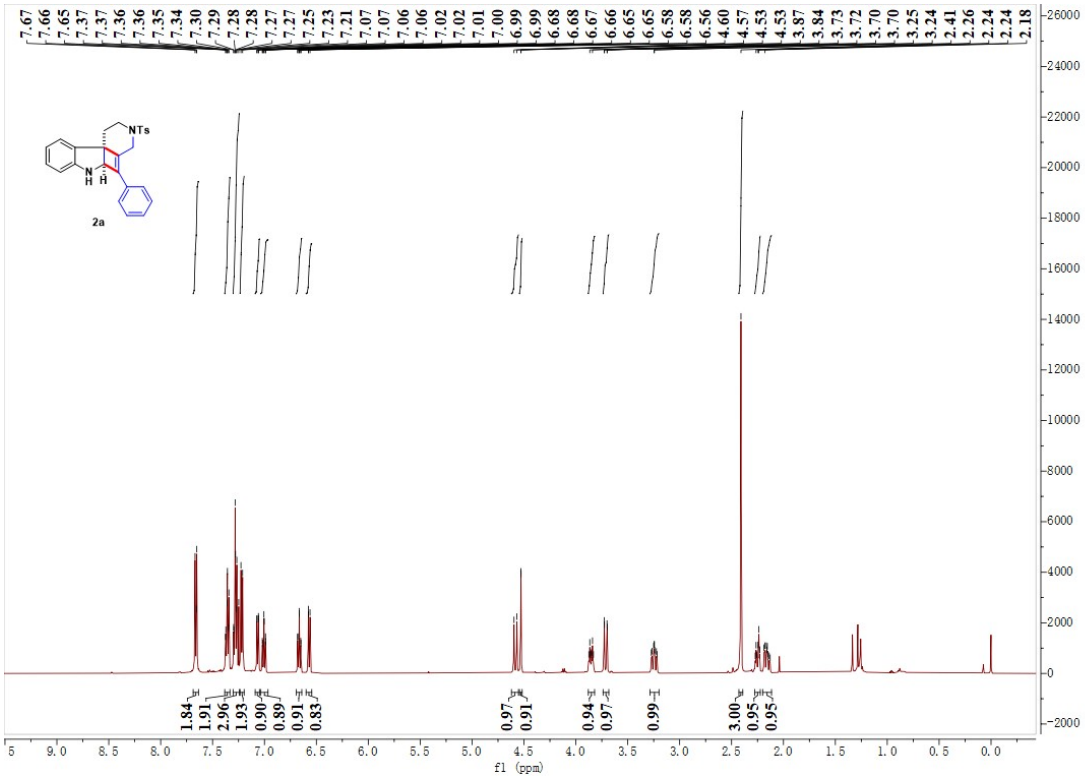


Figure S2. The ^{13}C-NMR spectra copy of compound 2a.

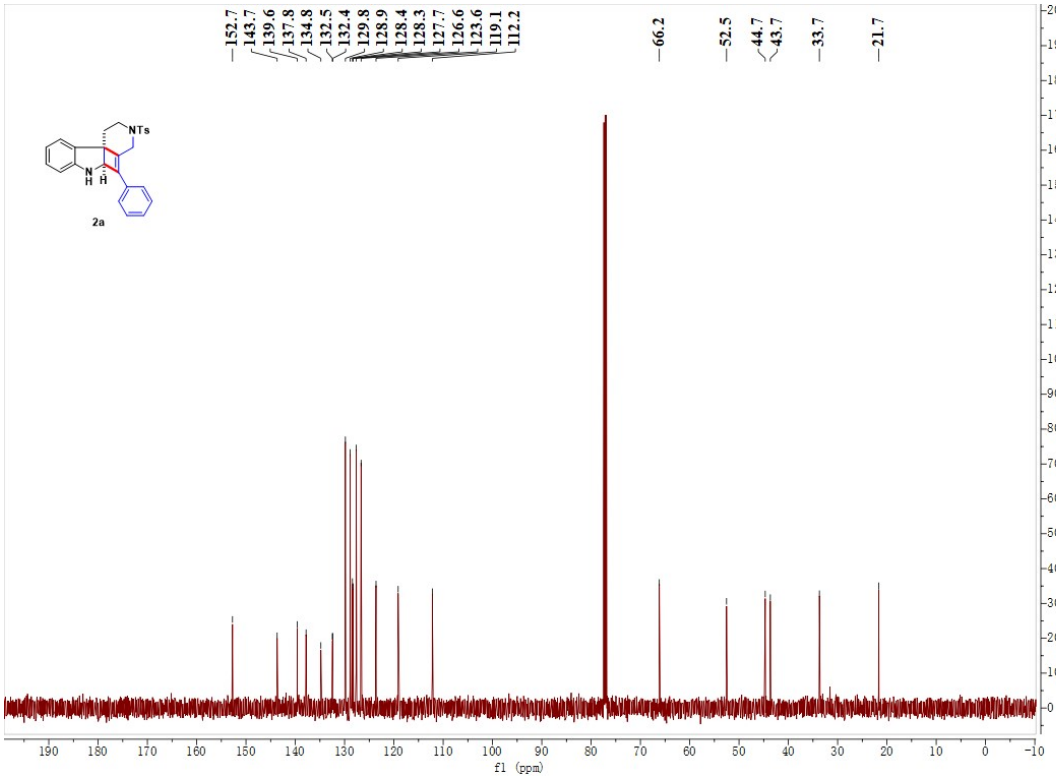


Figure S3. The ^{1}H-NMR spectra copy of compound 2b.

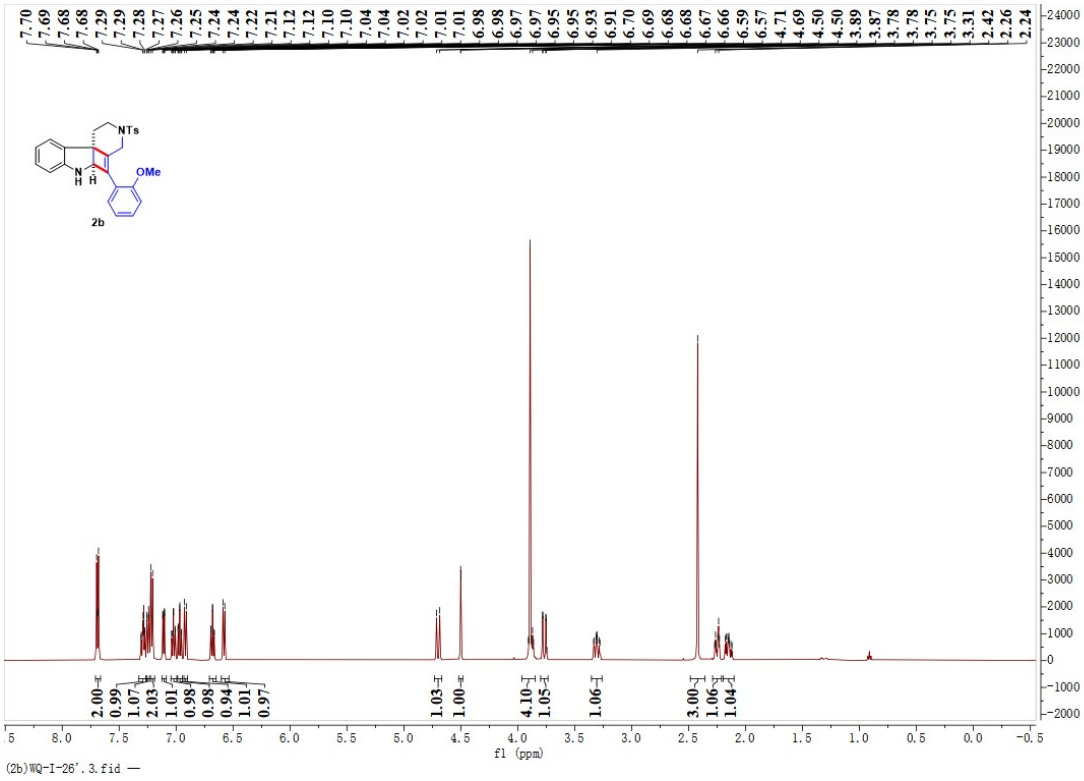


Figure S4. The ^{13}C-NMR spectra copy of compound 2b.

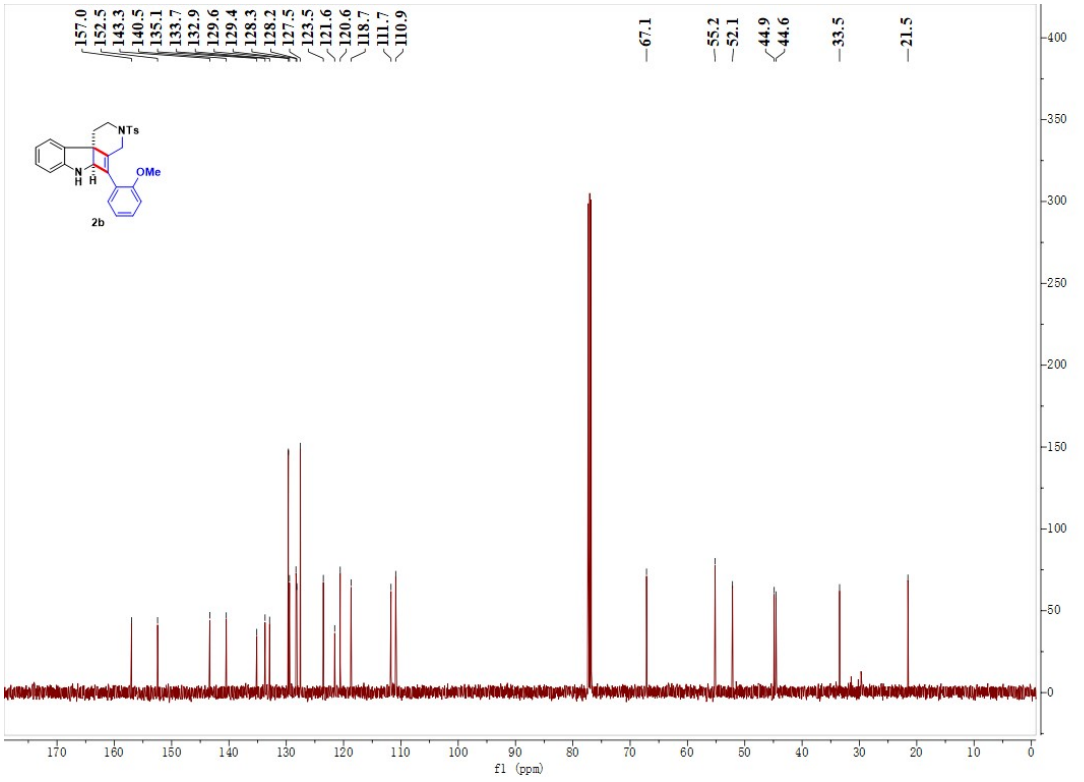


Figure S5. The ^{1}H-NMR spectra copy of compound 2c.

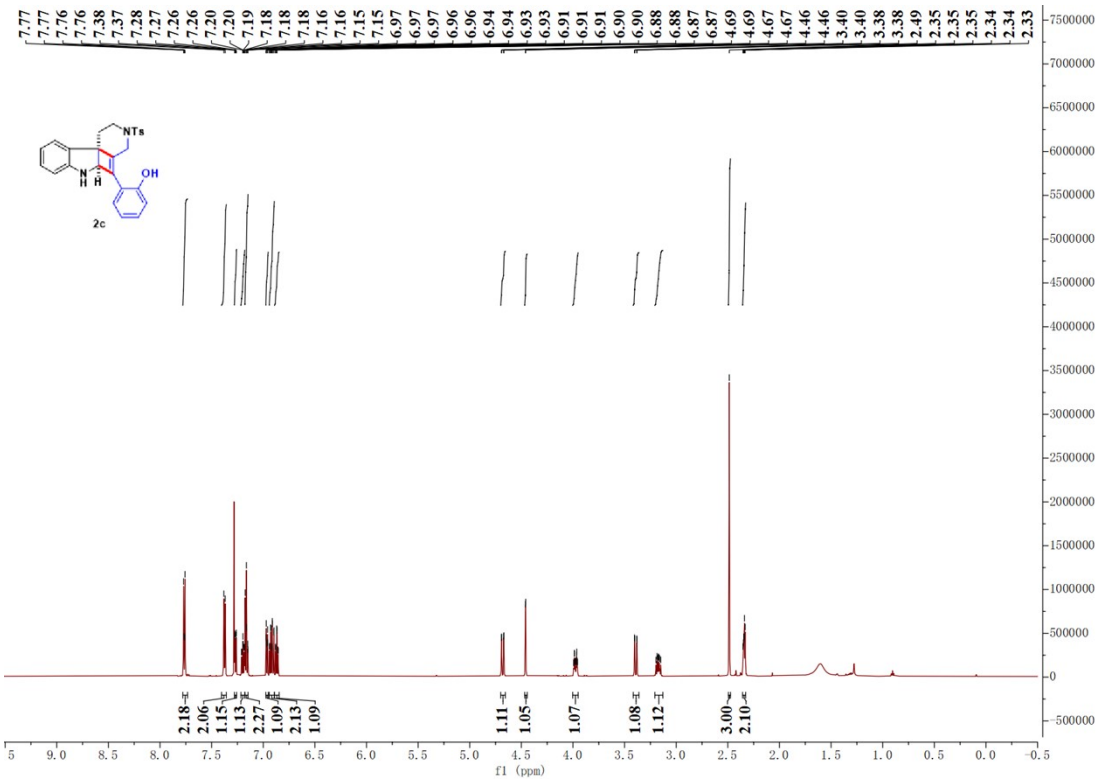


Figure S6. The ^{13}C-NMR spectra copy of compound 2c.

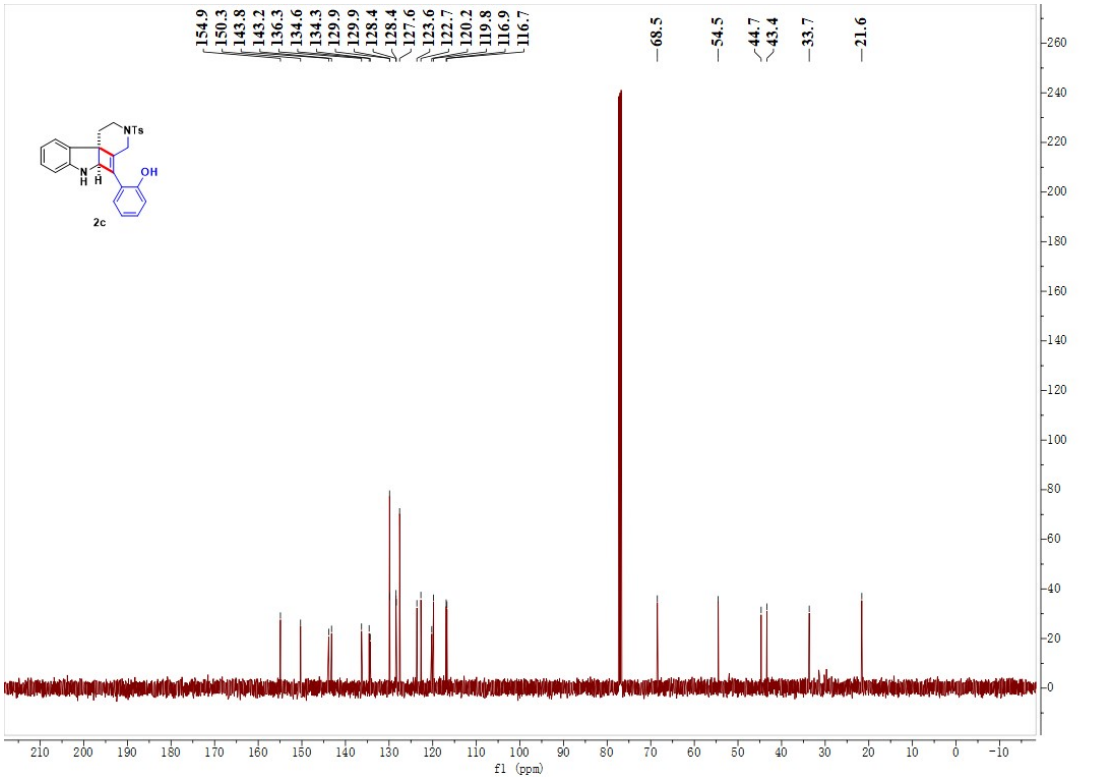


Figure S7. The ^{1}H-NMR spectra copy of compound 2d.

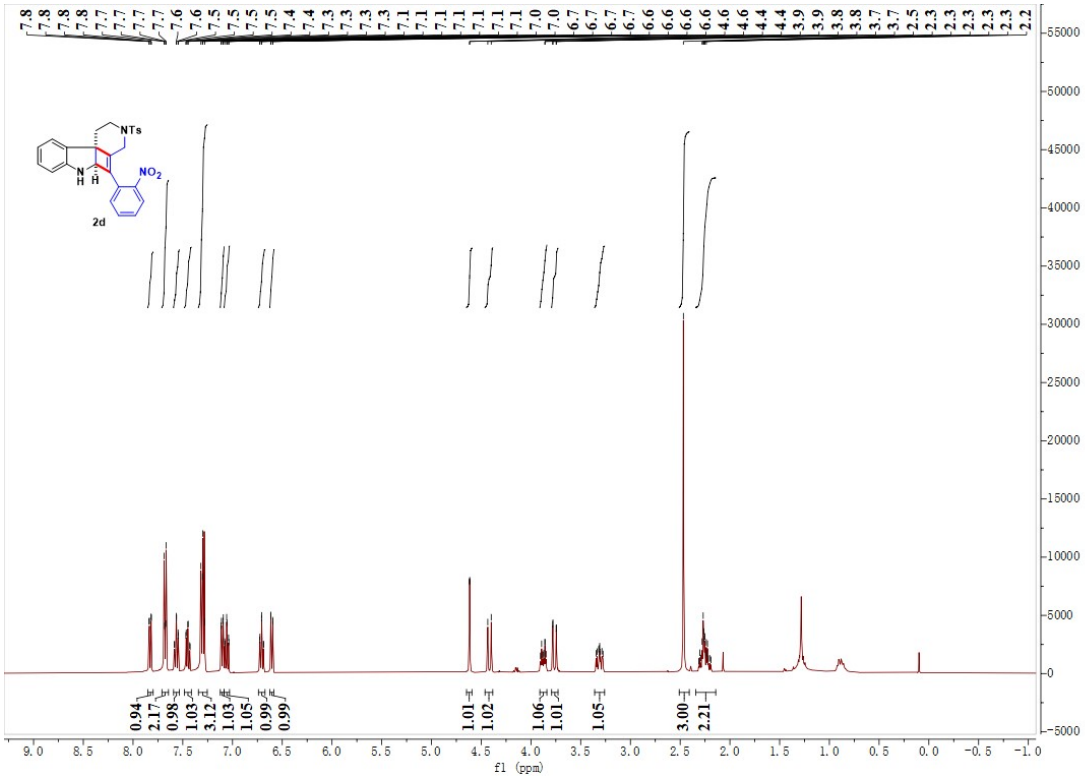


Figure S8. The ^{13}C-NMR spectra copy of compound 2d.

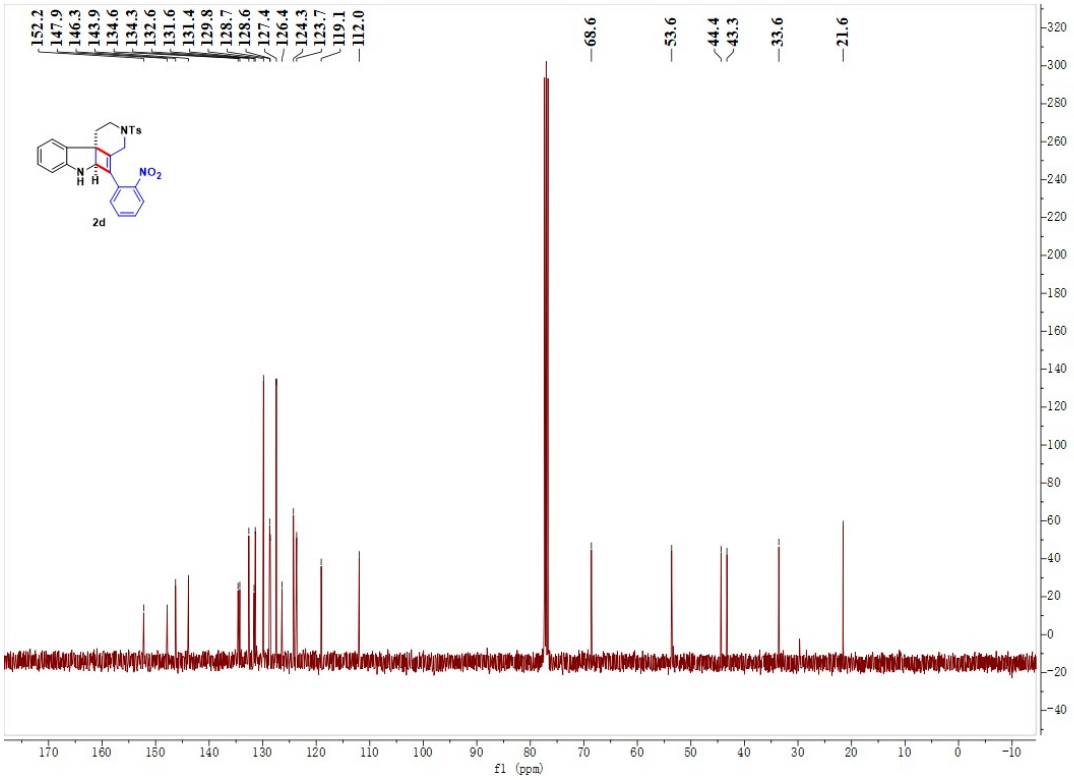


Figure S9. The ^{1}H-NMR spectra copy of compound 2e.

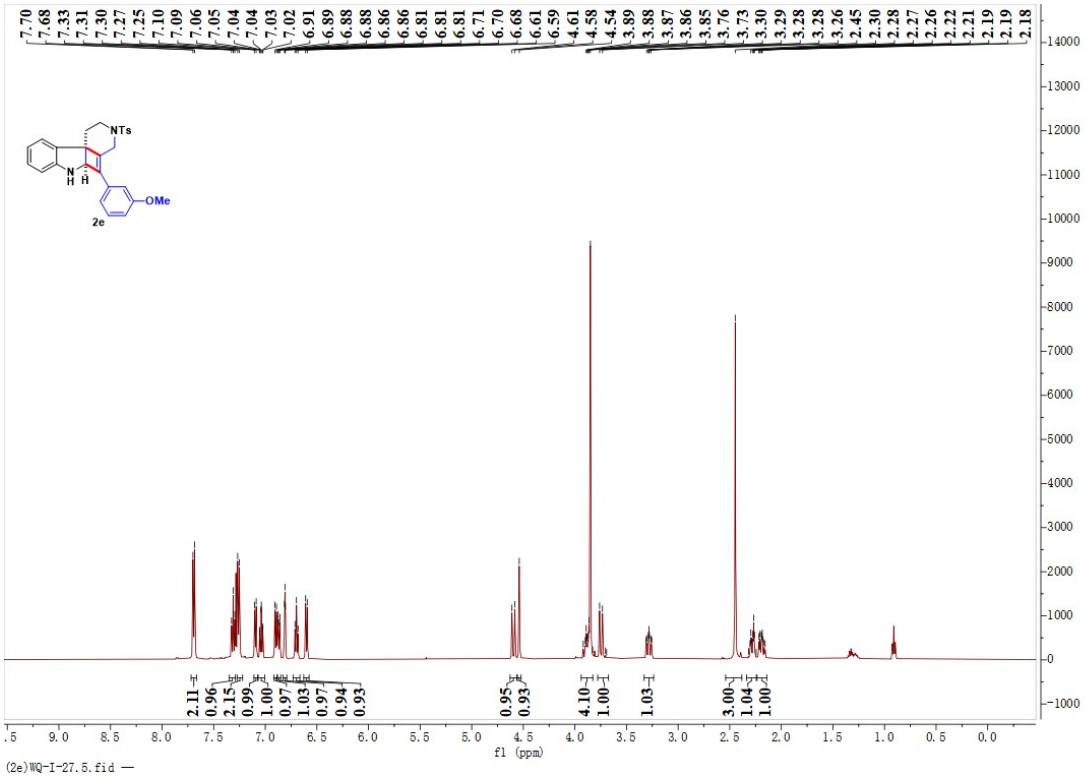


Figure S10. The ^{13}C-NMR spectra copy of compound 2e.

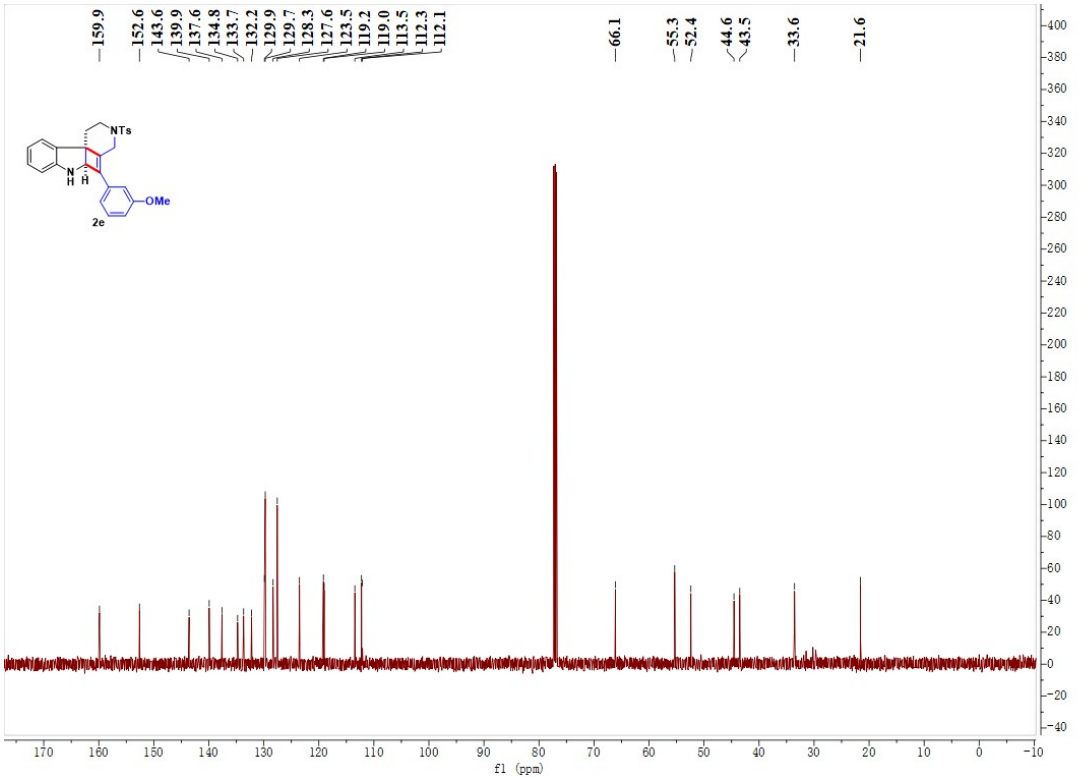


Figure S11. The ^{1}H-NMR spectra copy of compound 2f.

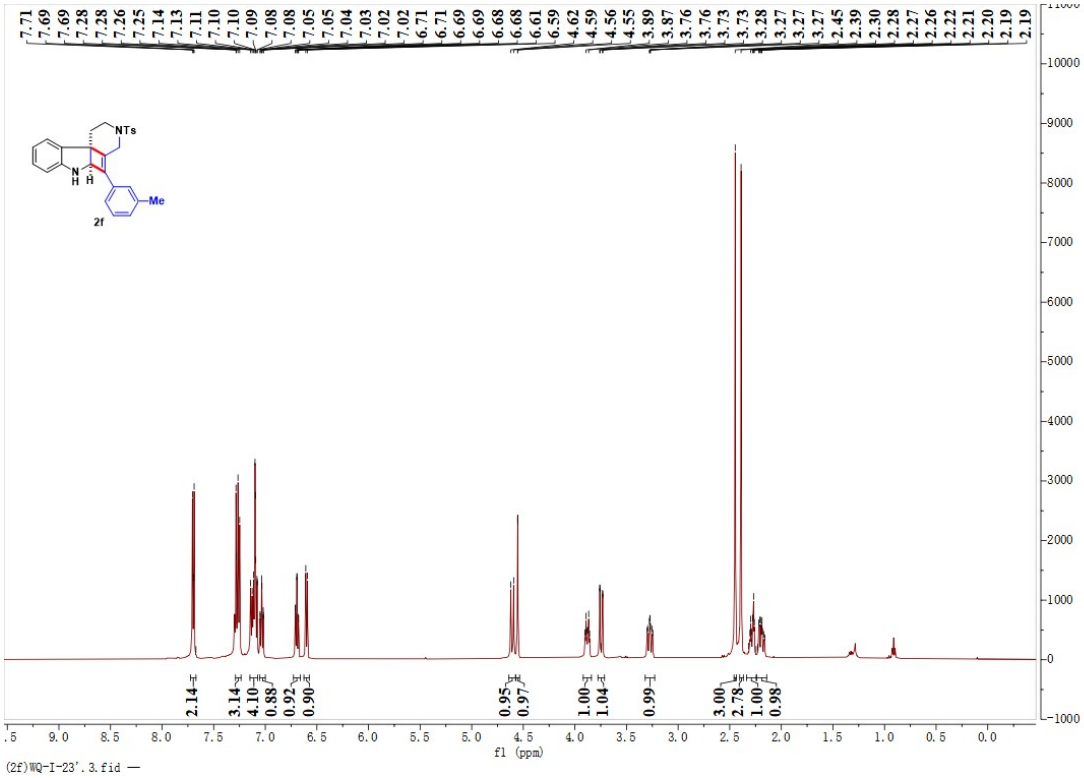


Figure S12. The ^{13}C-NMR spectra copy of compound 2f.

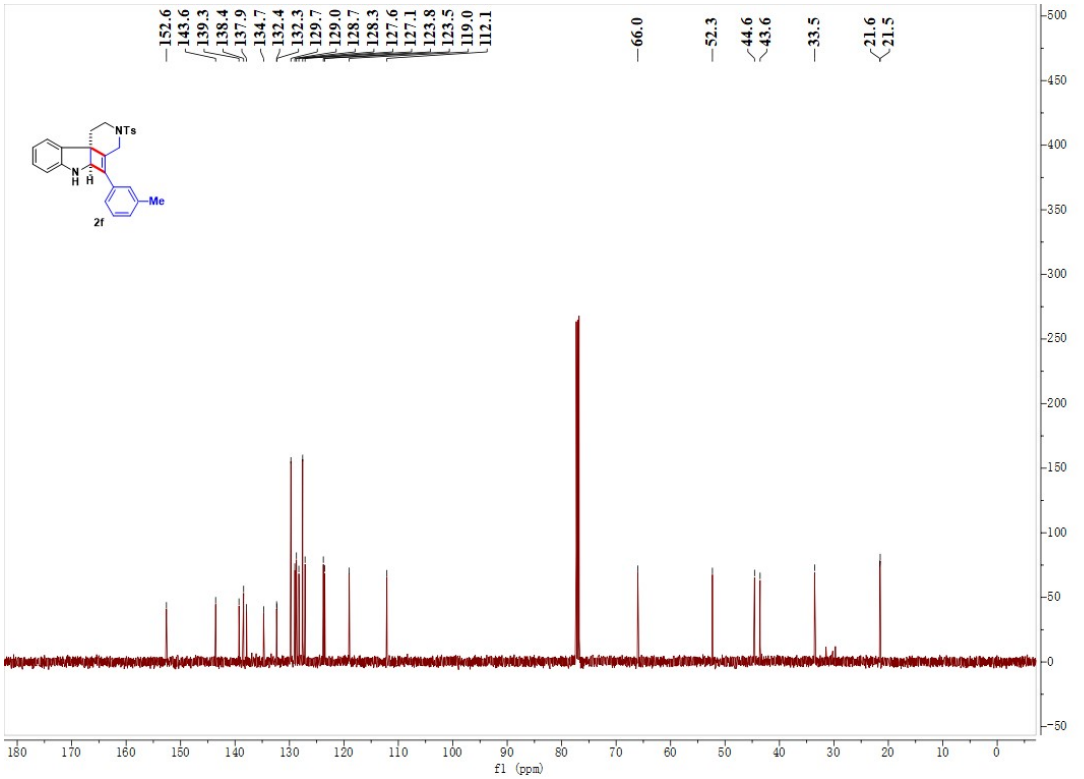


Figure S13. The ^{1}H-NMR spectra copy of compound 2g.

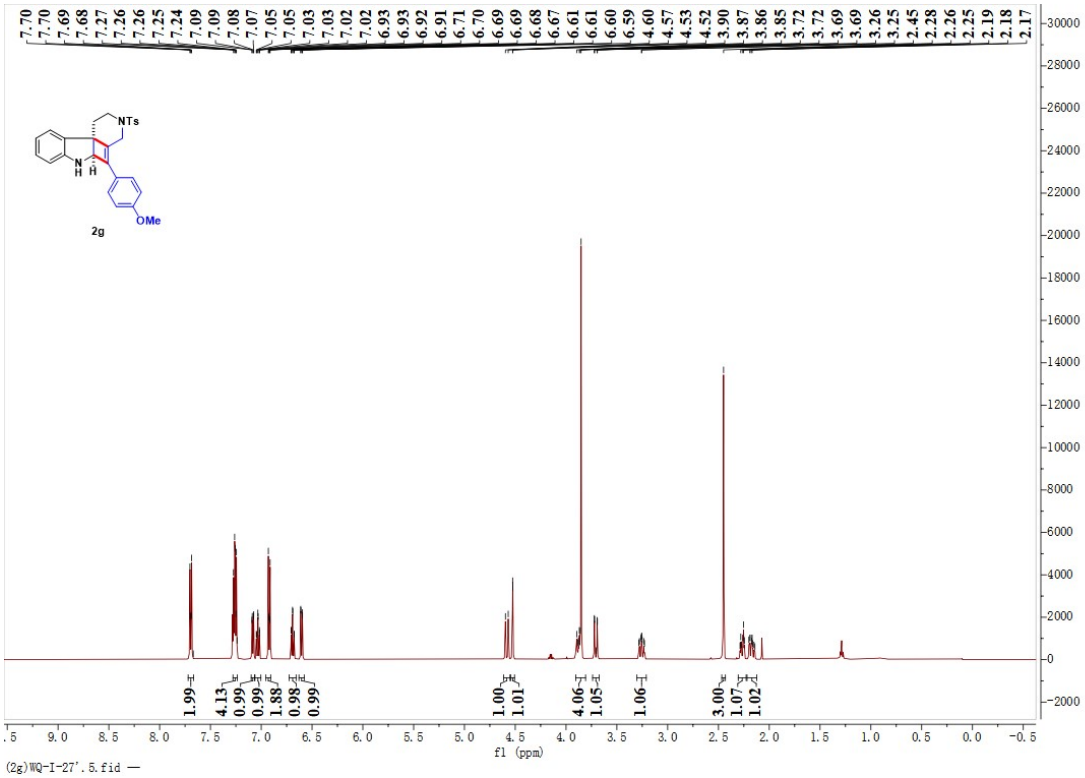


Figure S14. The ^{13}C-NMR spectra copy of compound 2g.

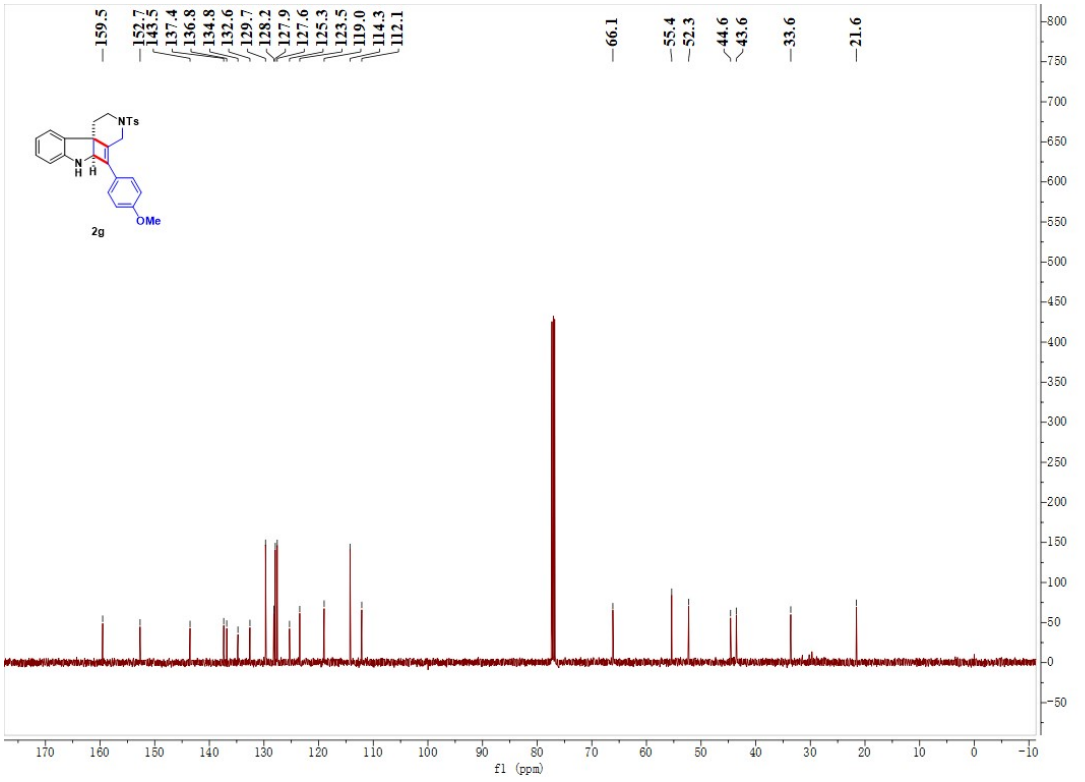


Figure S15. The ^{1}H-NMR spectra copy of compound 2h.

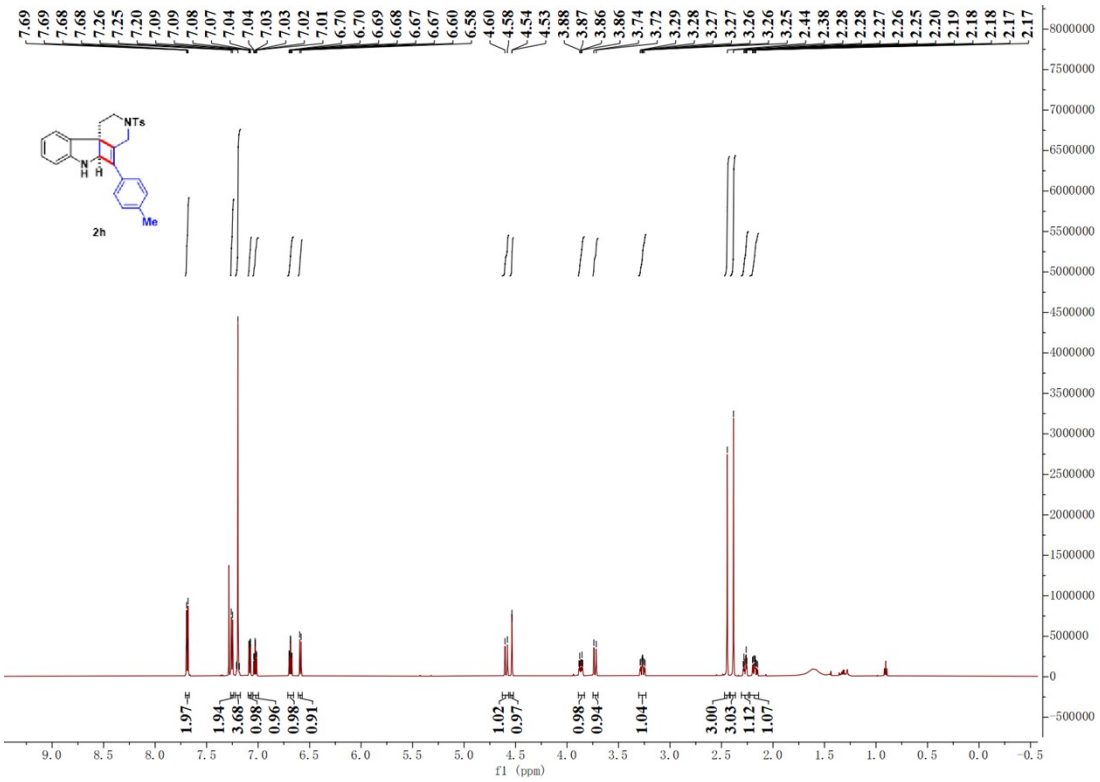


Figure S16. The ^{13}C-NMR spectra copy of compound 2h.

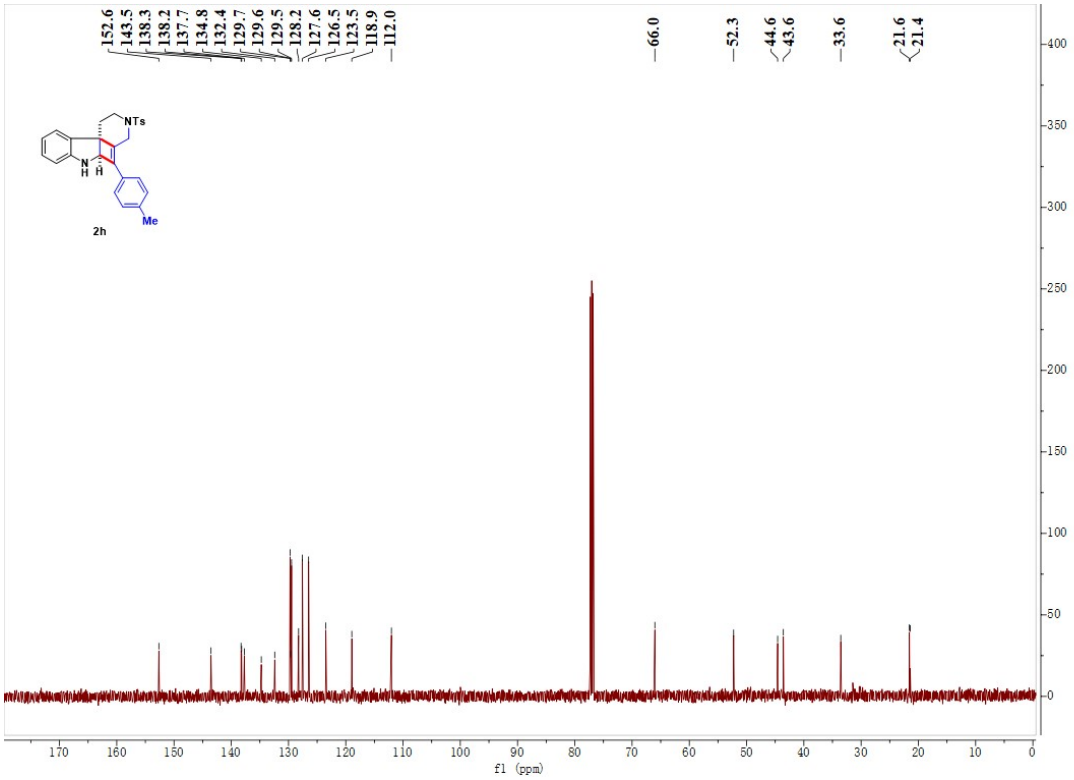


Figure S17. The ^{1}H-NMR spectra copy of compound 2i.

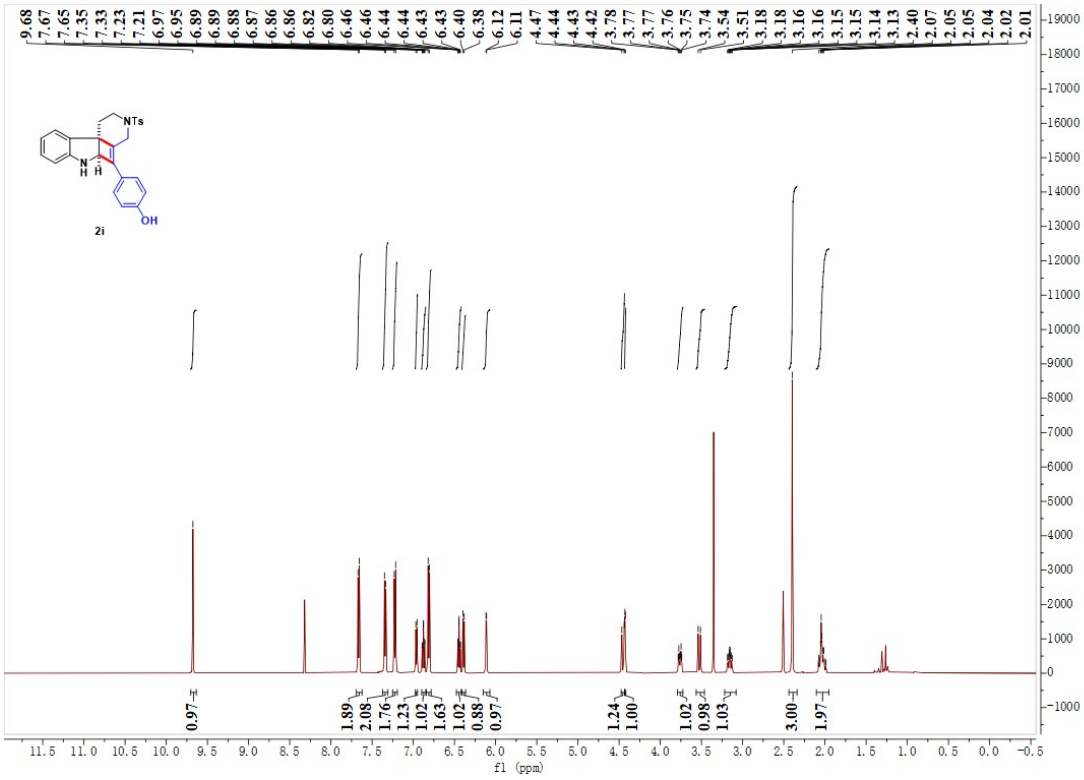


Figure S18. The ^{13}C-NMR spectra copy of compound 2i.

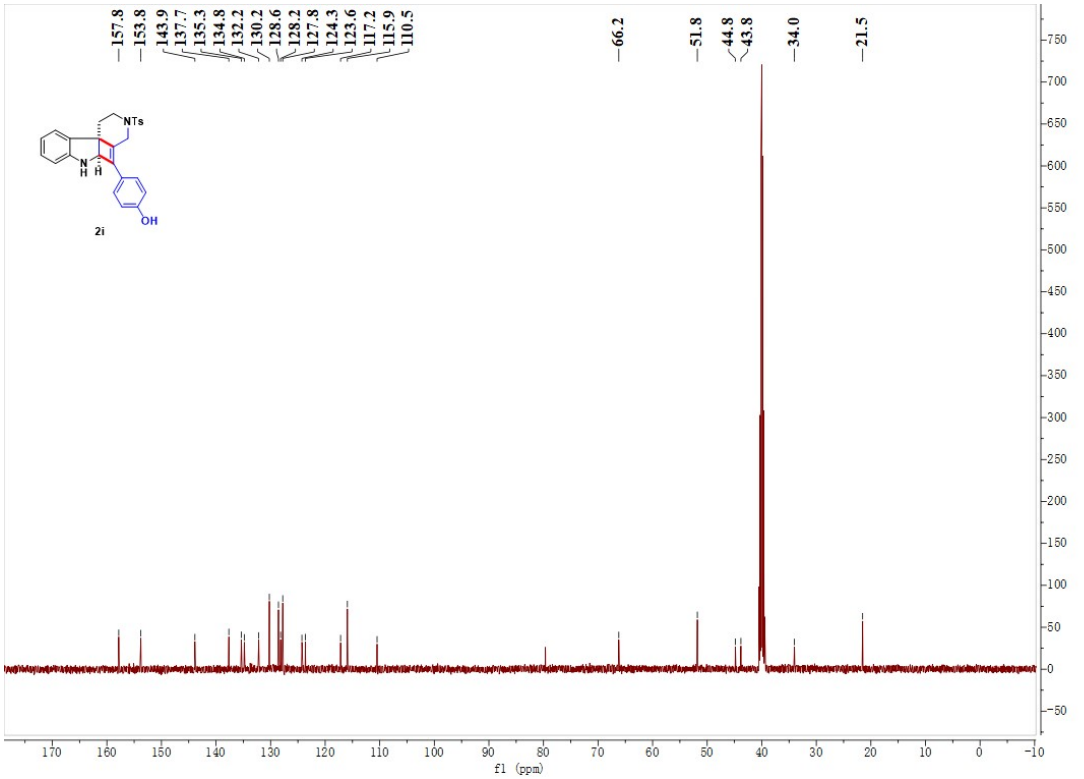


Figure S19. The ^{1}H-NMR spectra copy of compound 2j.

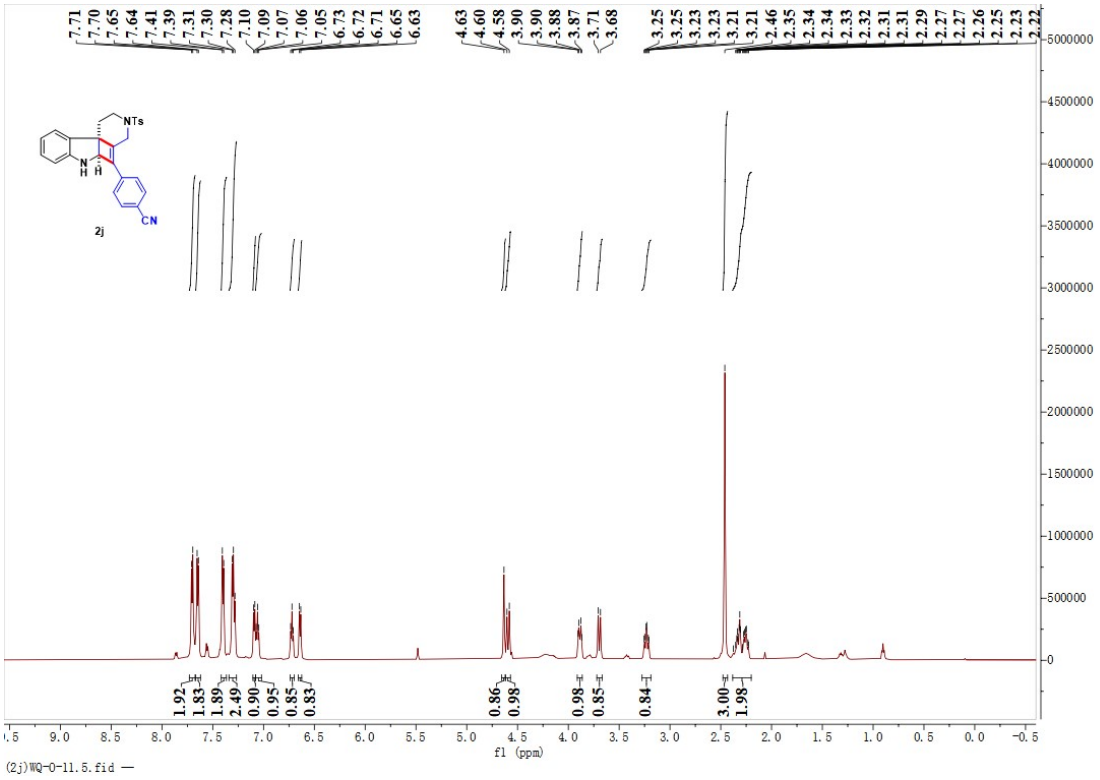


Figure S20. The ^{13}C-NMR spectra copy of compound 2j.

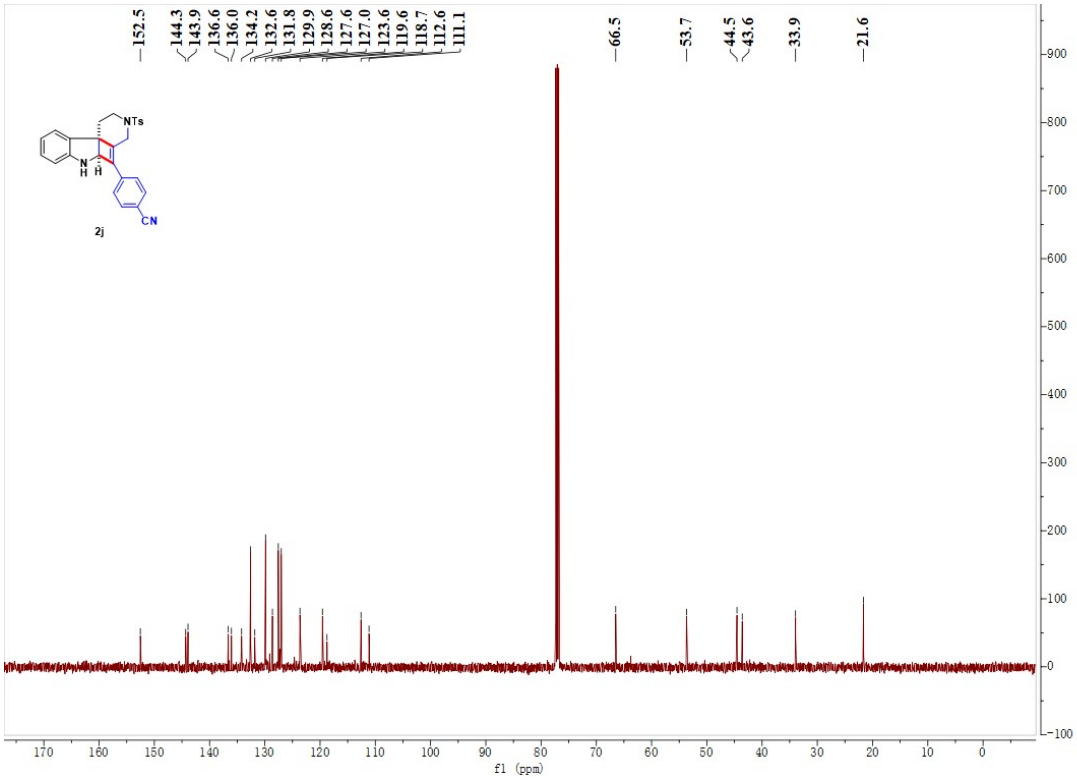


Figure S21. The ^{1}H-NMR spectra copy of compound 2k.

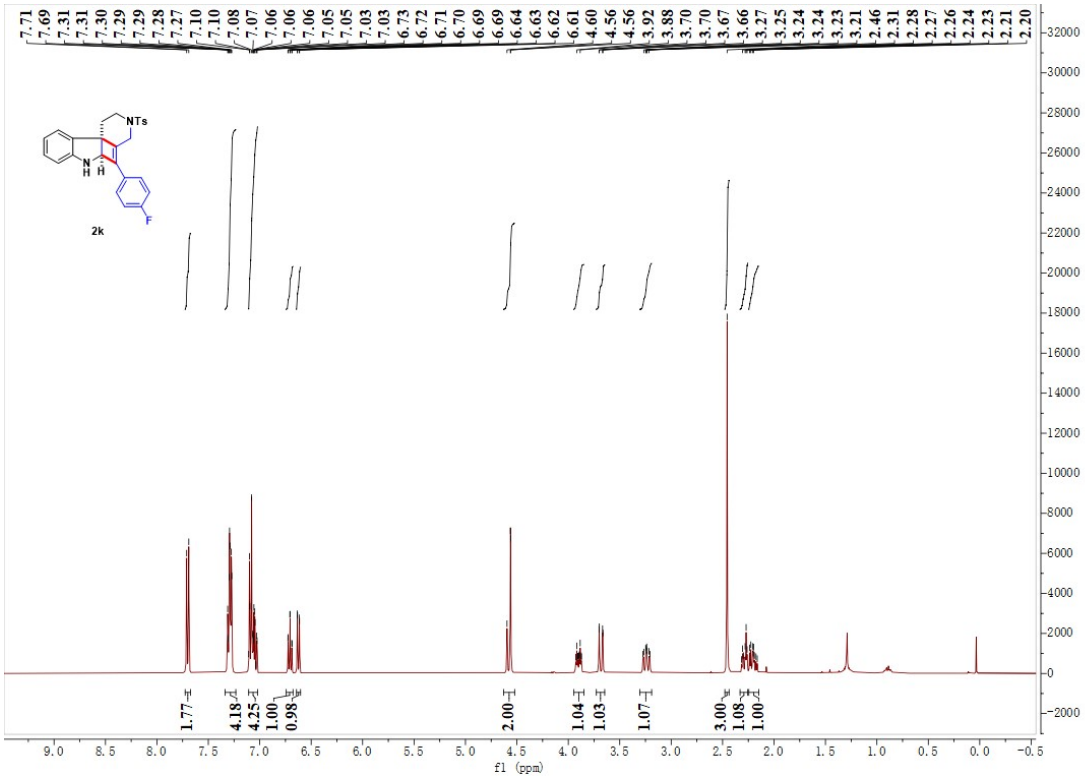


Figure S22. The ^{13}C-NMR spectra copy of compound 2k.

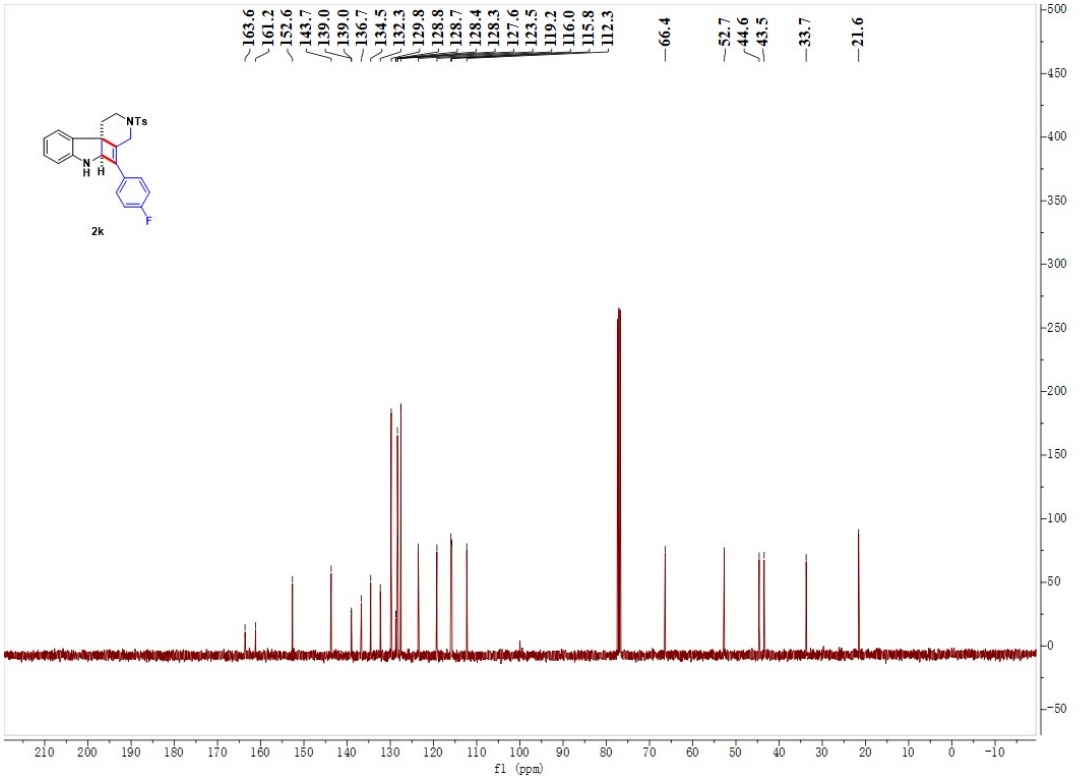


Figure S23. The^{19}F-NMR spectra copy of compound 2k

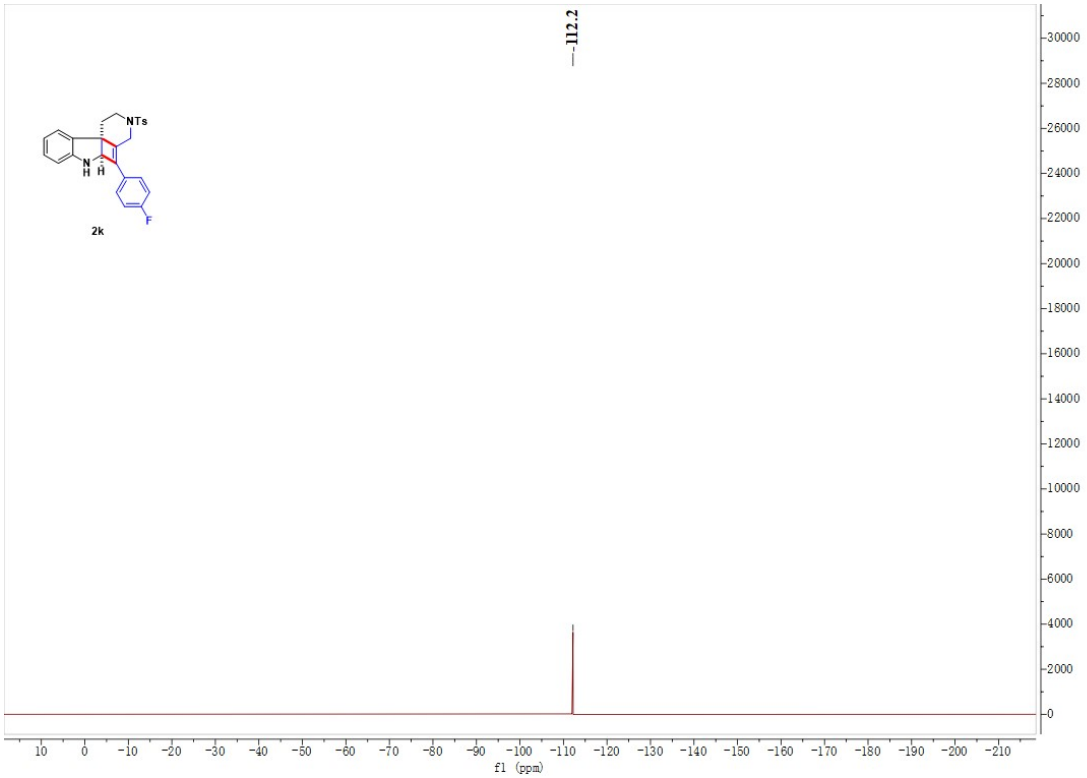


Figure S24. The ^{1}H-NMR spectra copy of compound 2l.

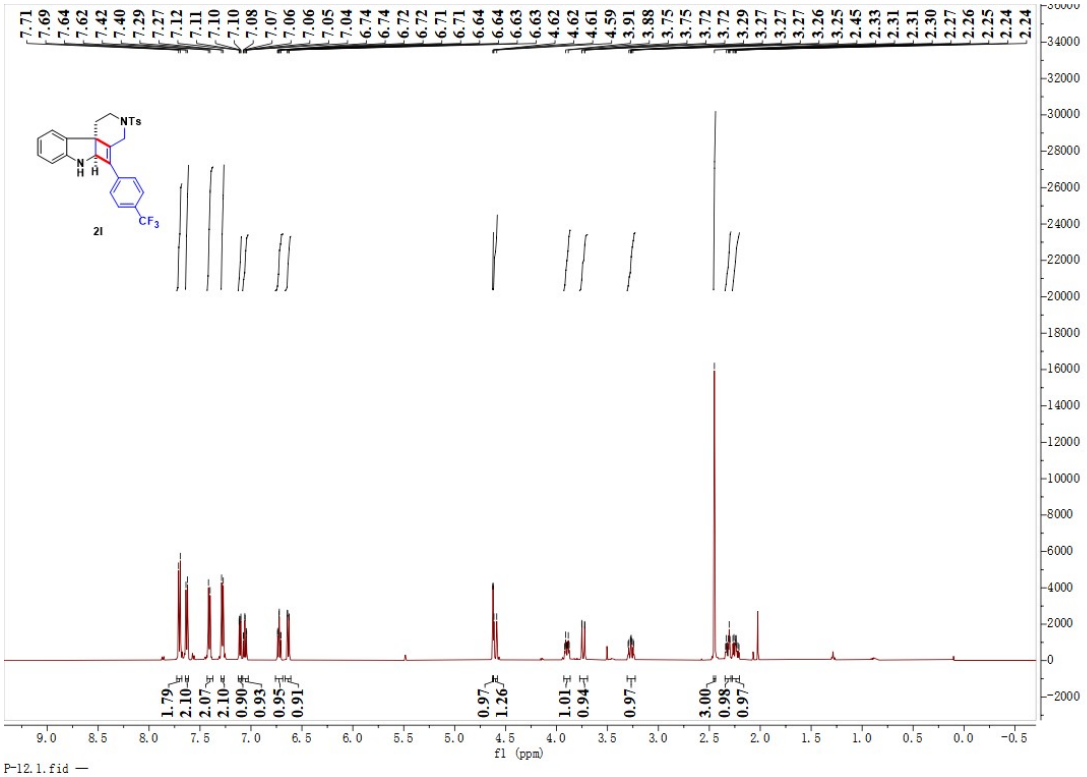


Figure S25. The ^{13}C-NMR spectra copy of compound 2l.

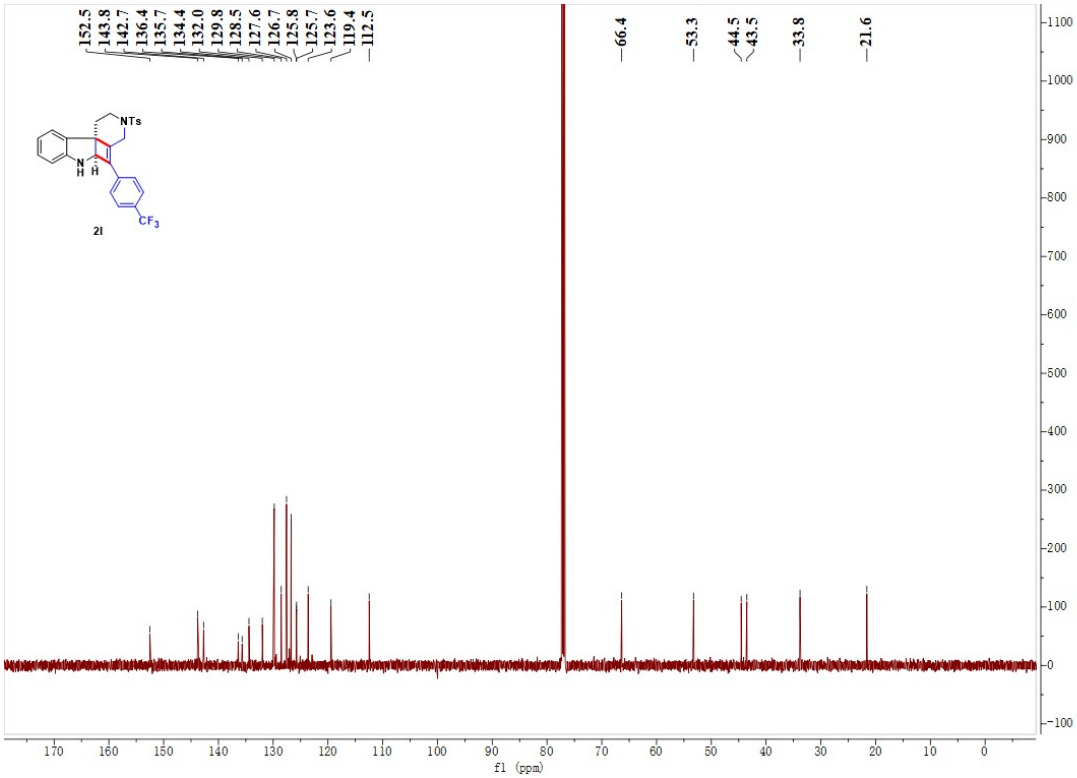


Figure S26. The ^{19}F-NMR spectra copy of compound 2l.

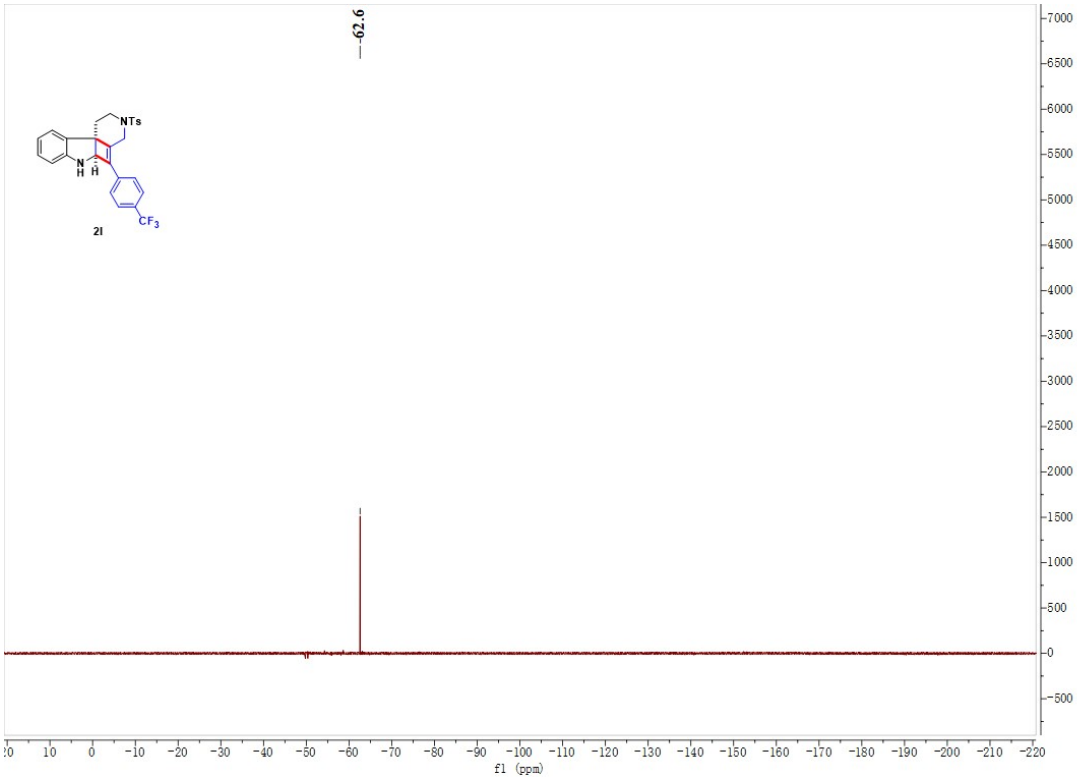


Figure S27. The ^{1}H-NMR spectra copy of compound 2m.

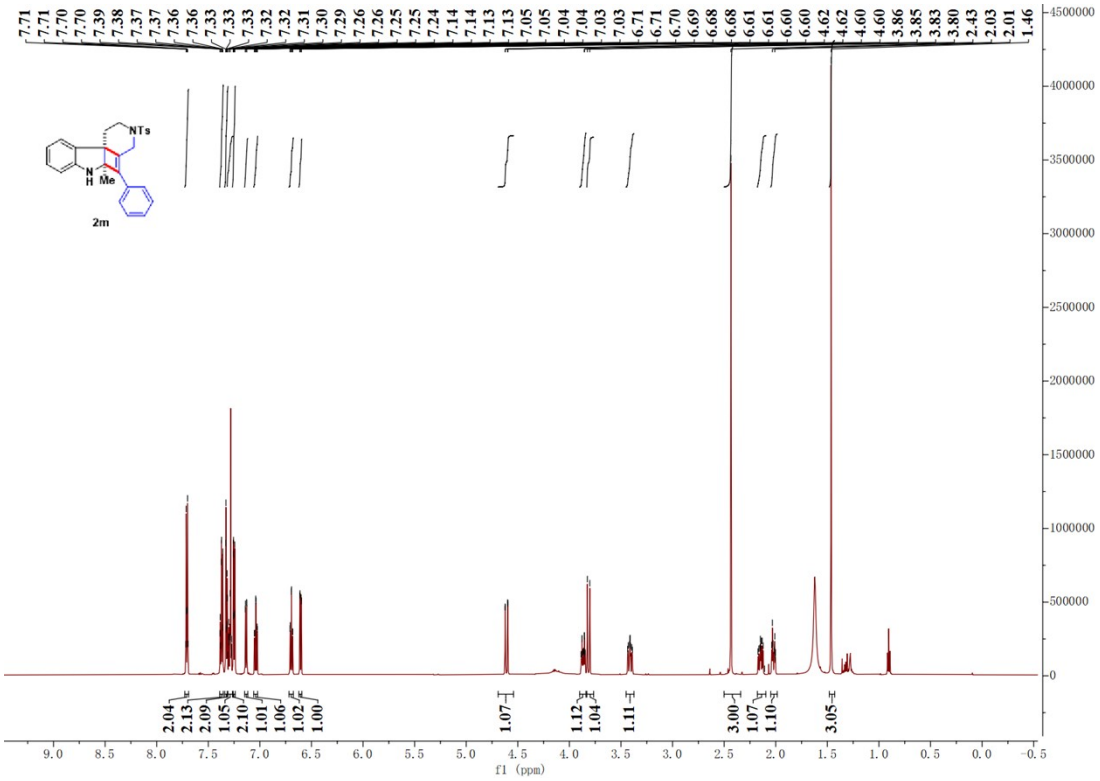


Figure S28. The ^{13}C-NMR spectra copy of compound 2m.

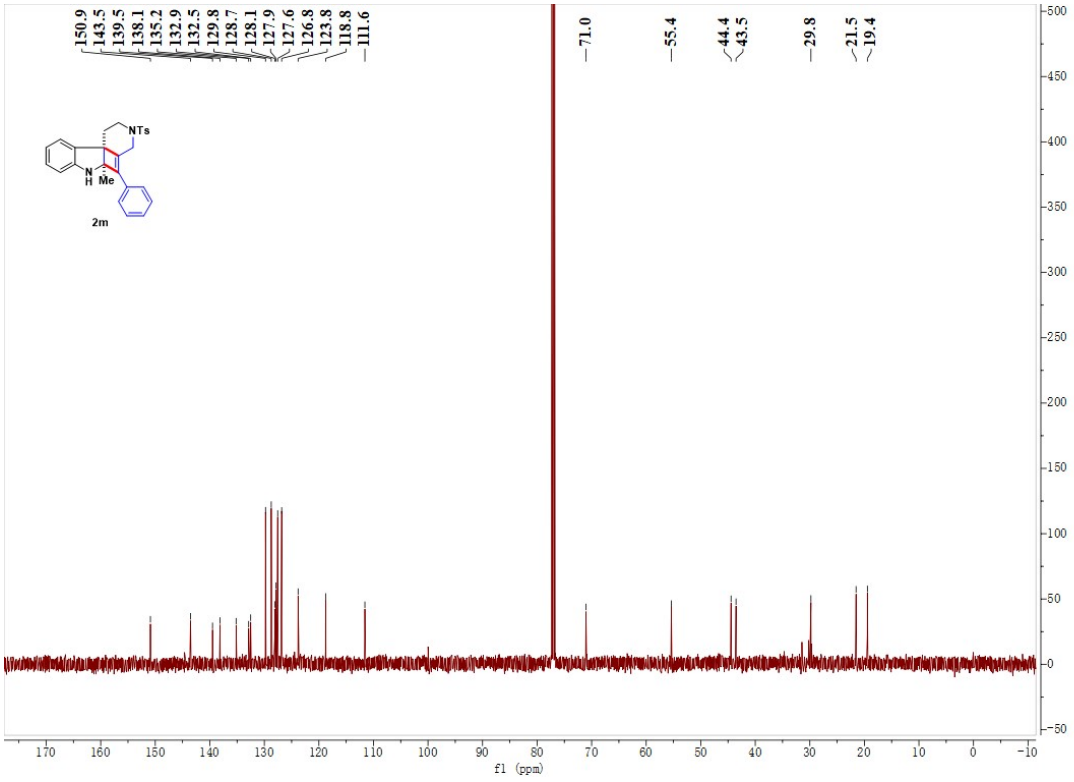


Figure S29. The ^{1}H-NMR spectra copy of compound 2n.

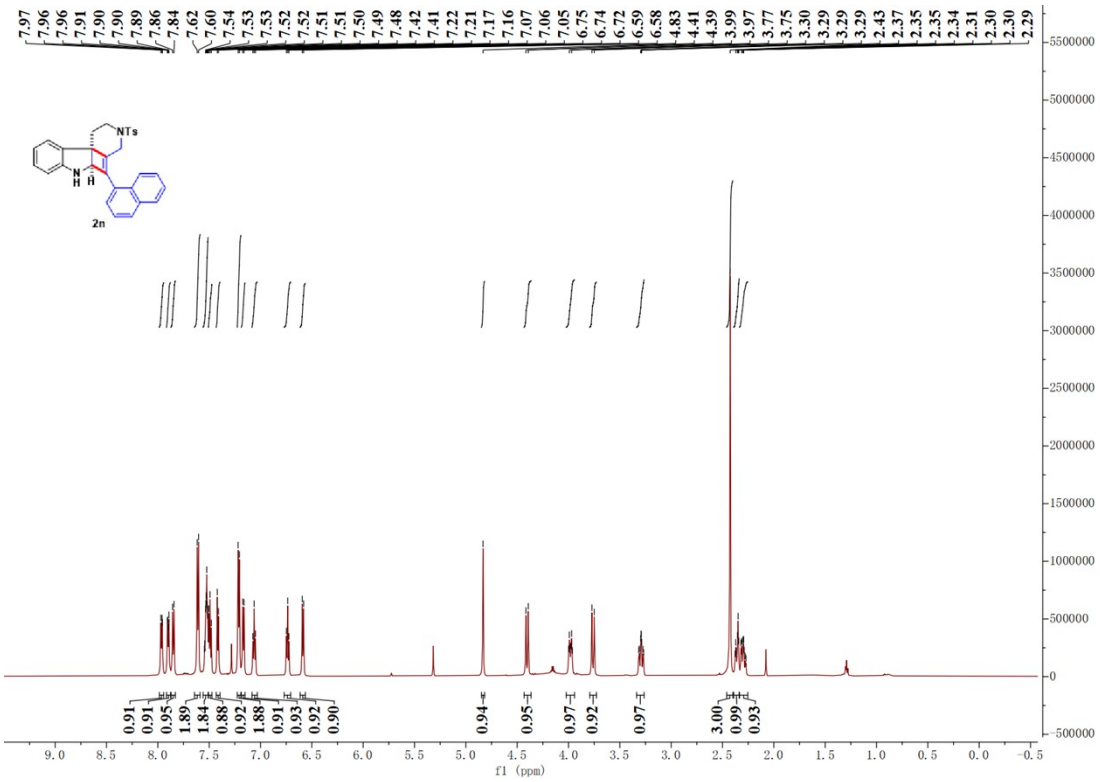


Figure S30. The ^{13}C-NMR spectra copy of compound 2n.

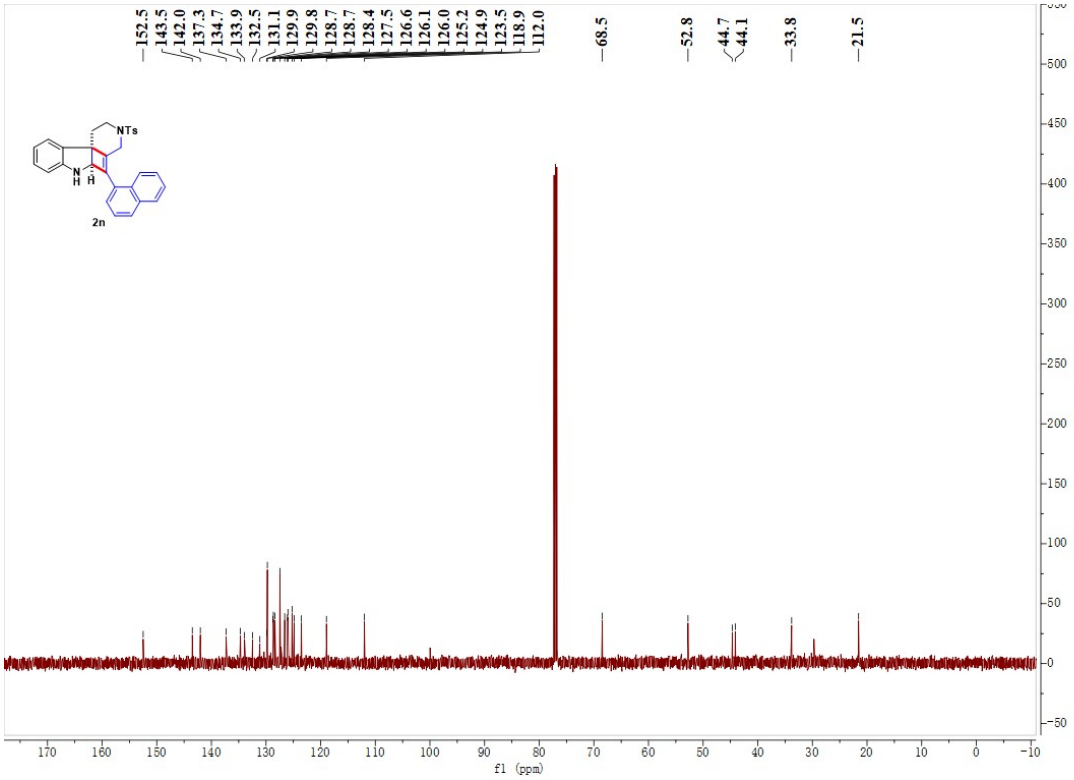


Figure S31. The ^{1}H-NMR spectra copy of compound 2o.

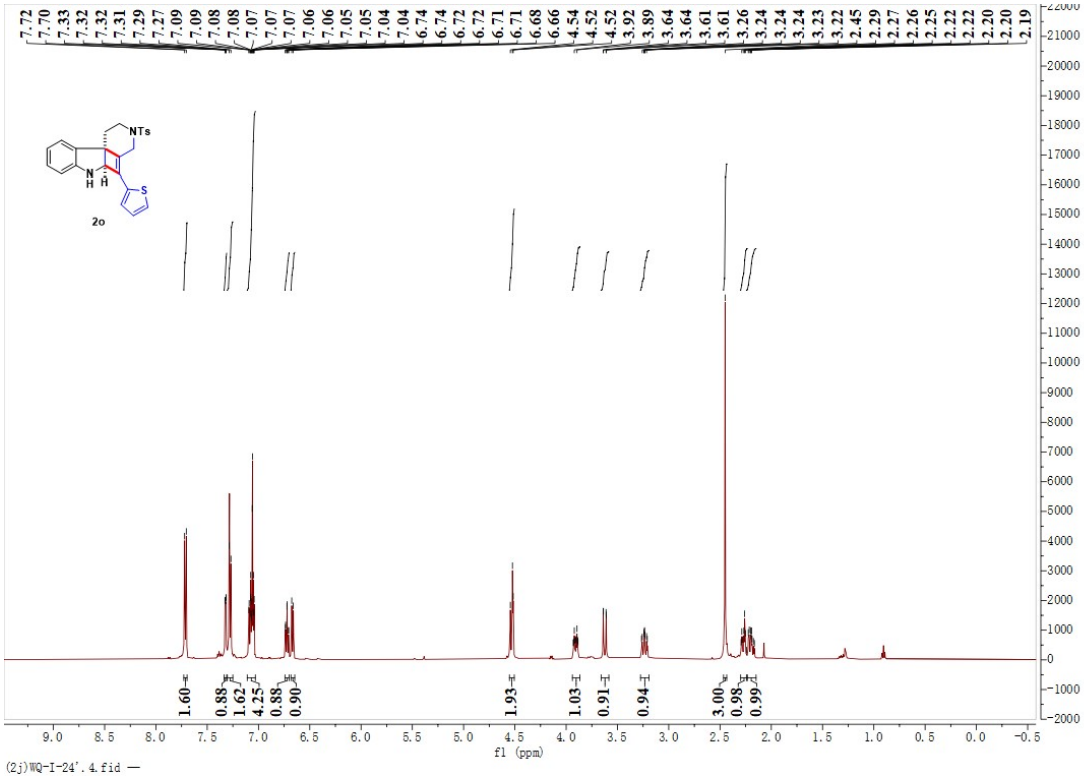


Figure S32. The ^{13}C-NMR spectra copy of compound 2o.

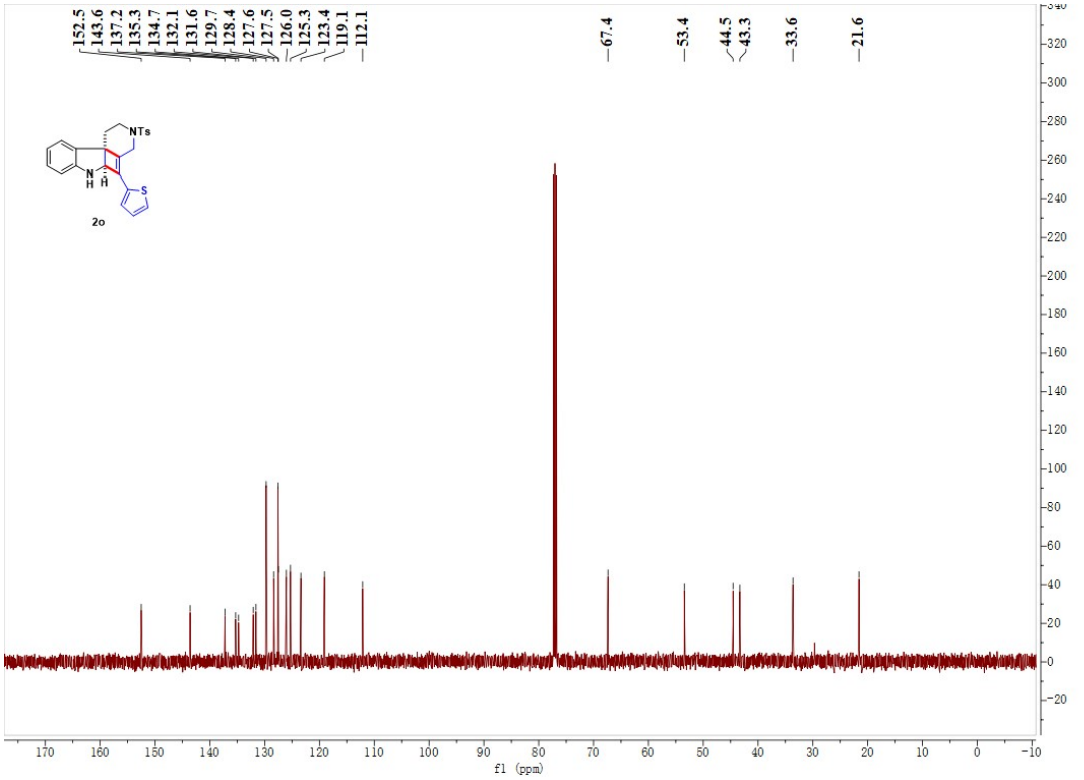


Figure S33. The ^{1}H-NMR spectra copy of compound 2p.

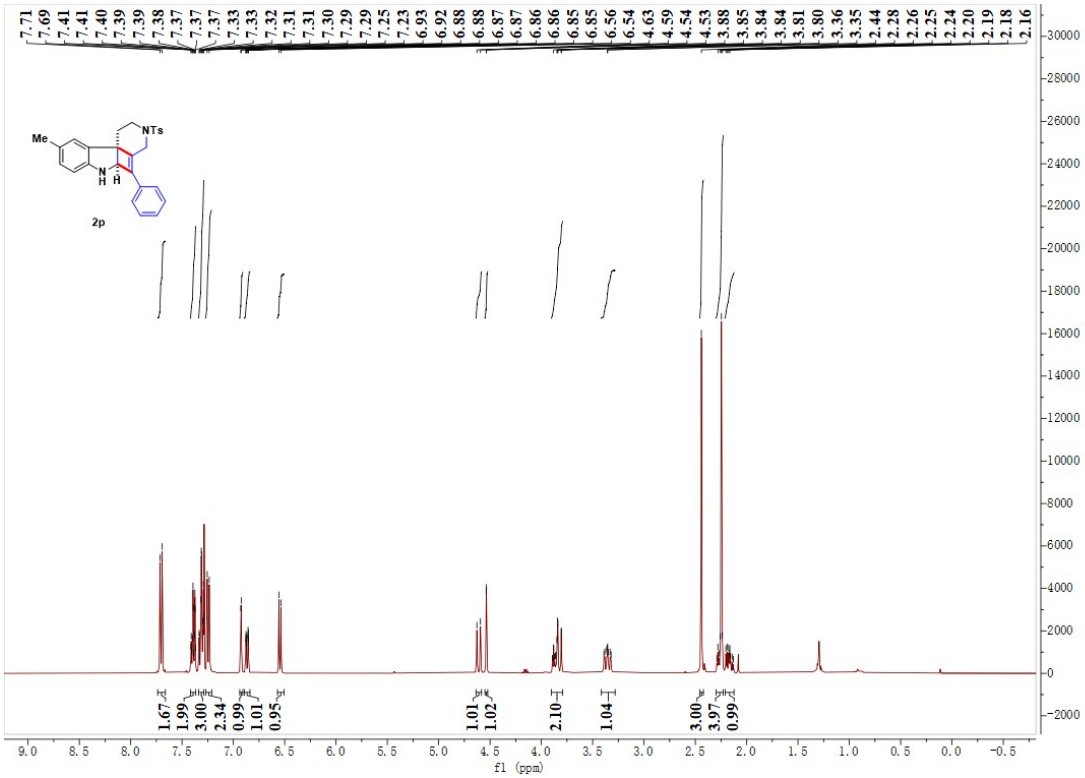


Figure S34. The ^{13}C-NMR spectra copy of compound 2p.

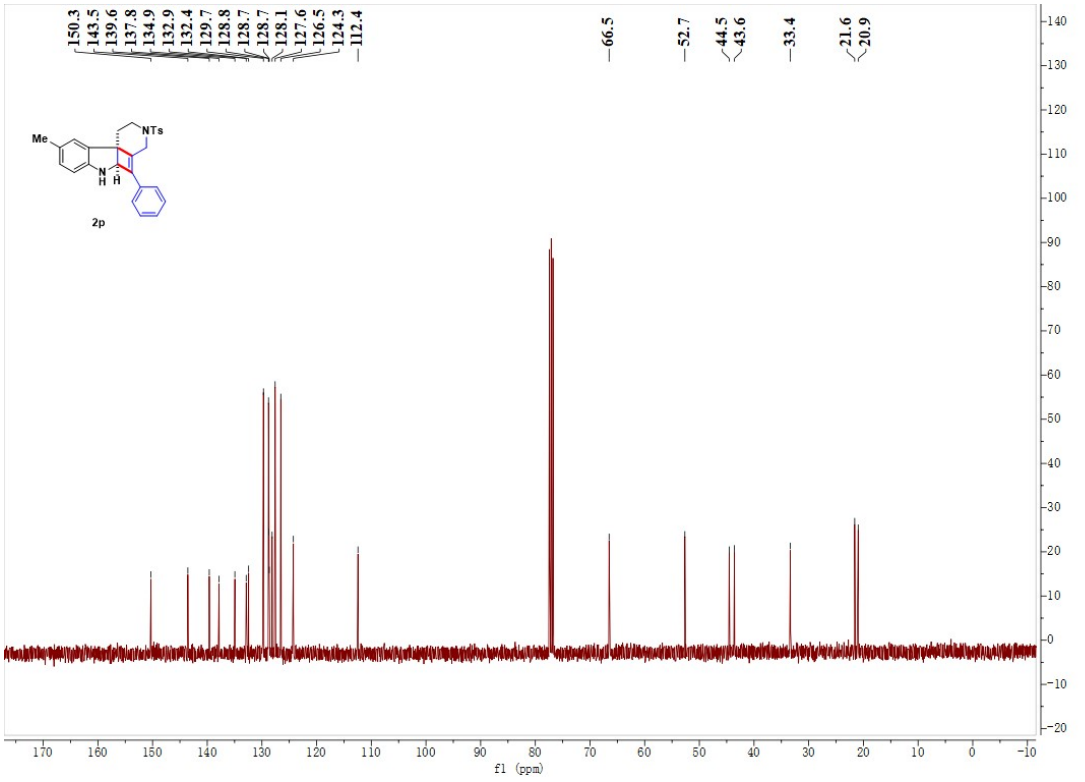


Figure S35. The ^{1}H-NMR spectra copy of compound 2q.

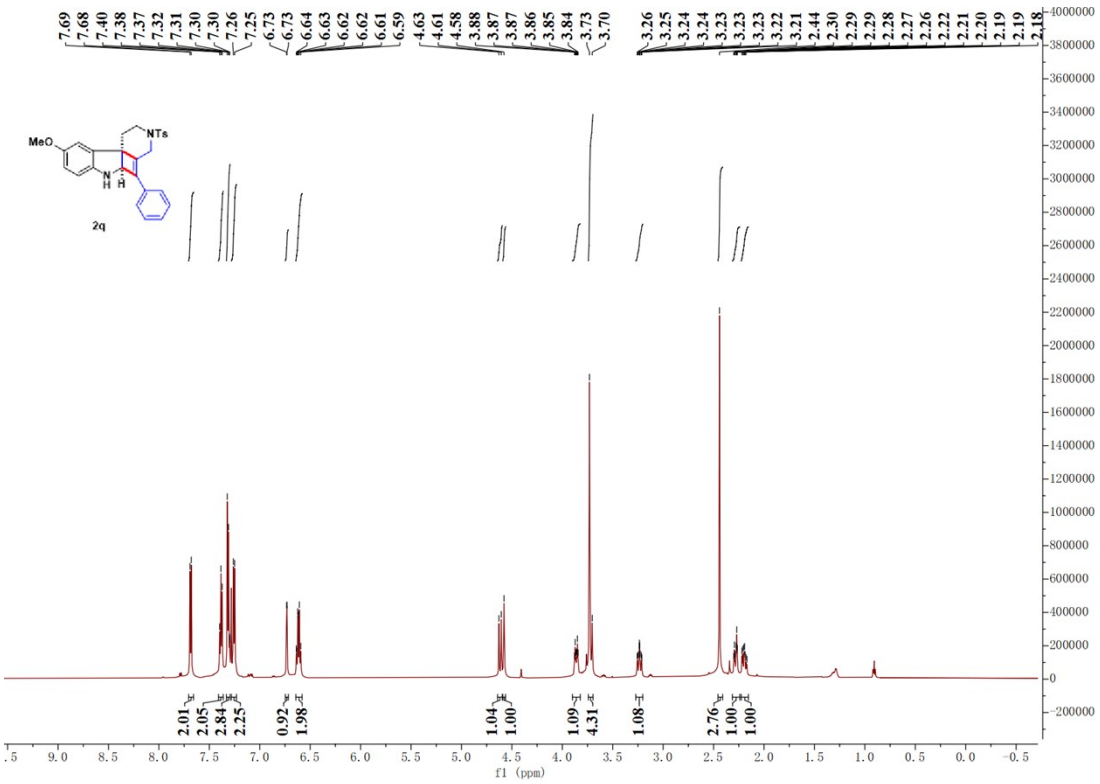


Figure S36. The ^{13}C-NMR spectra copy of compound 2q.

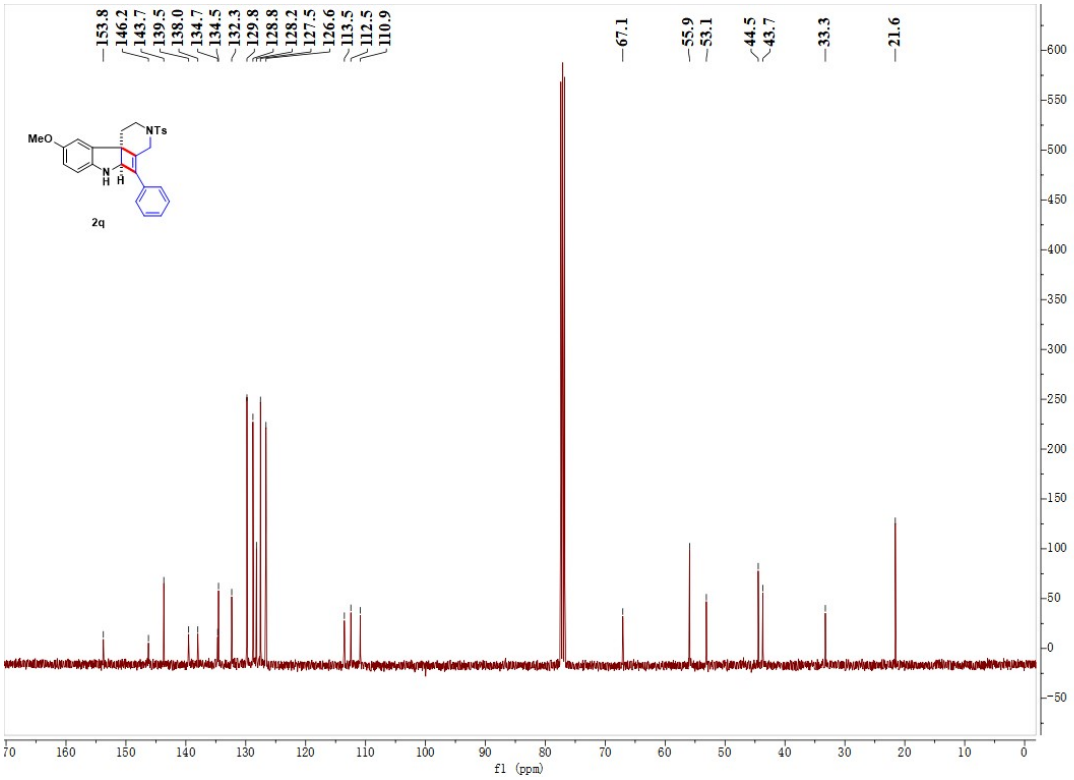


Figure S37. The ^{1}H-NMR spectra copy of compound 2r.

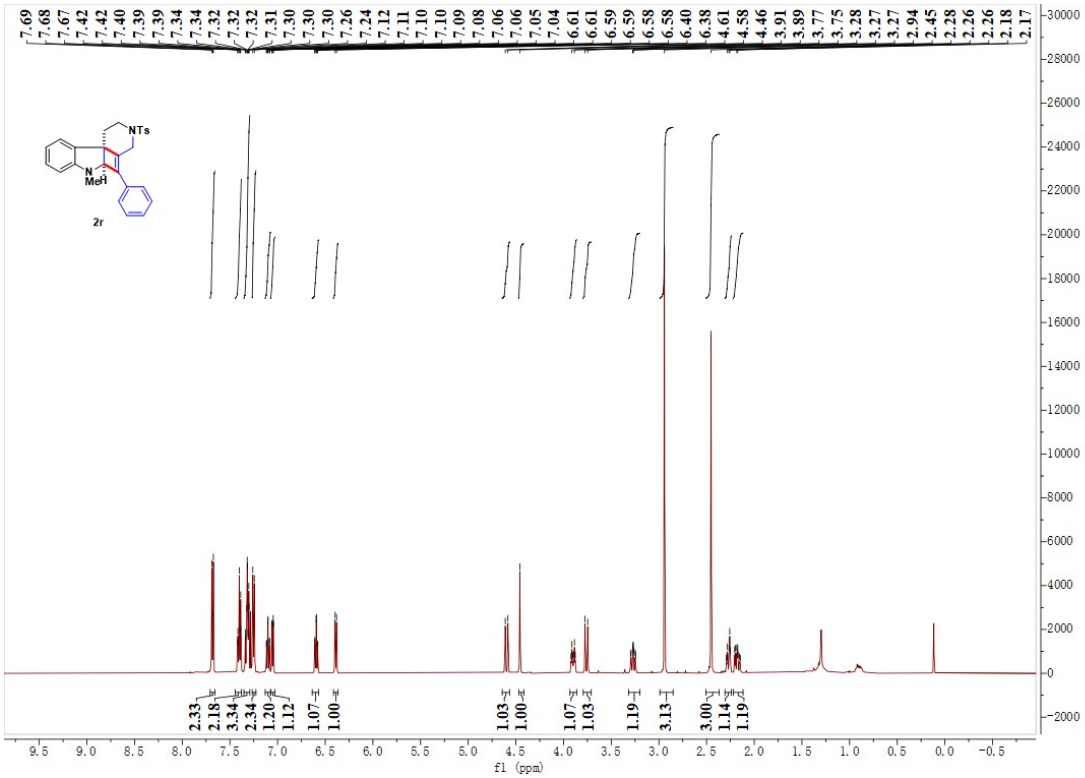


Figure S38. The ^{13}C-NMR spectra copy of compound 2r.

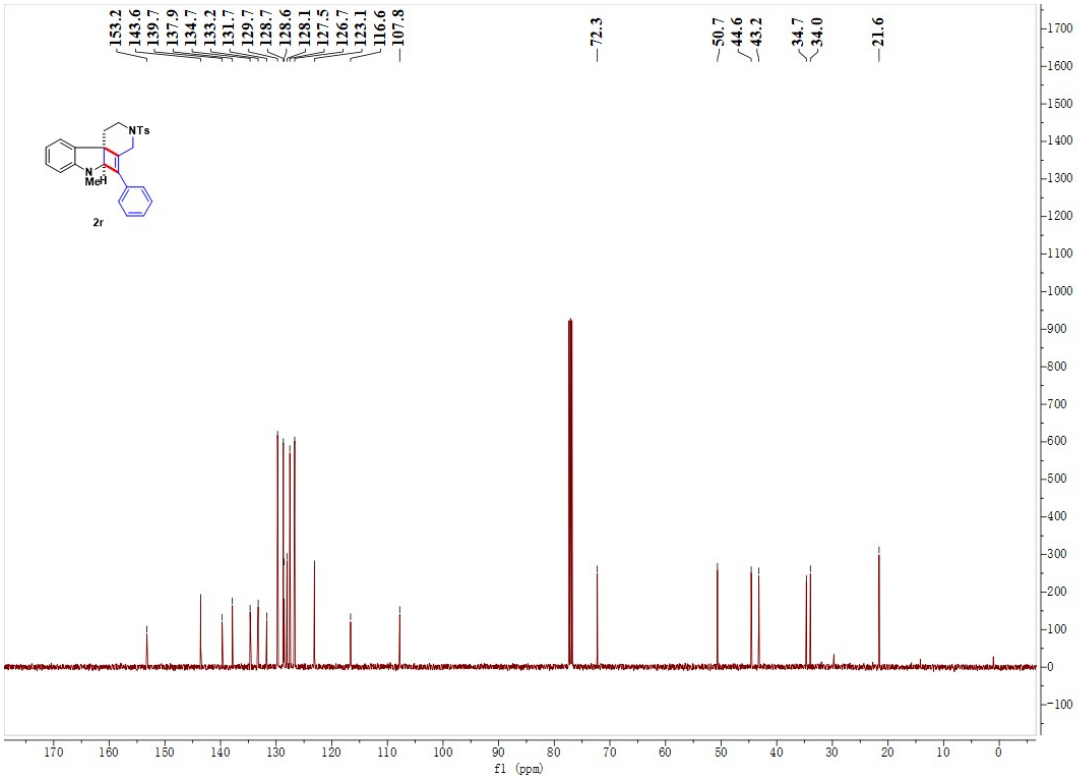


Figure S39. The ^{1}H-NMR spectra copy of compound 2s.

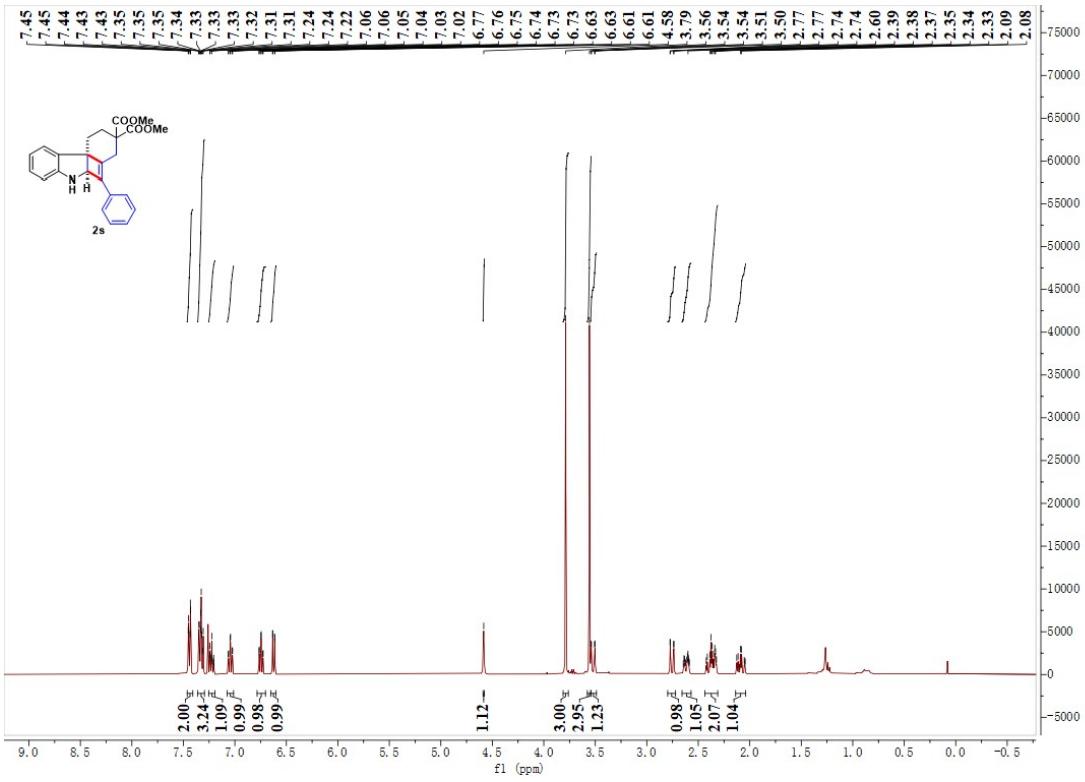


Figure S40. The ^{13}C-NMR spectra copy of compound 2s.

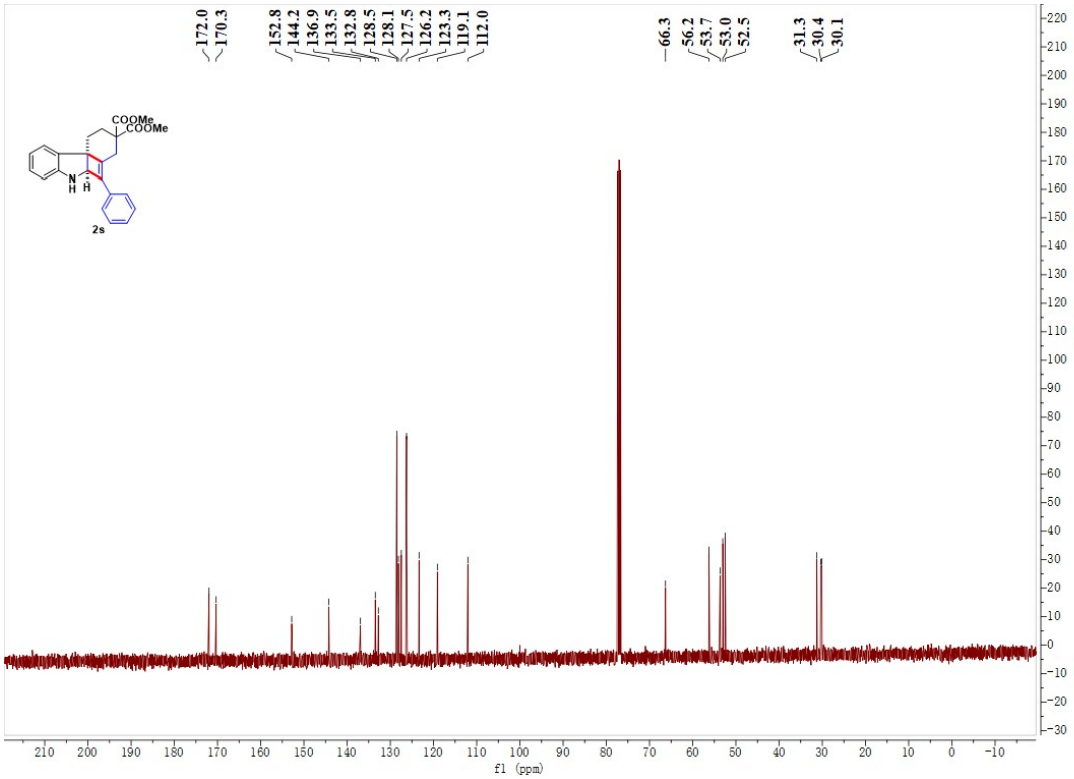


Figure S41. The ^{1}H-NMR spectra copy of compound 2t

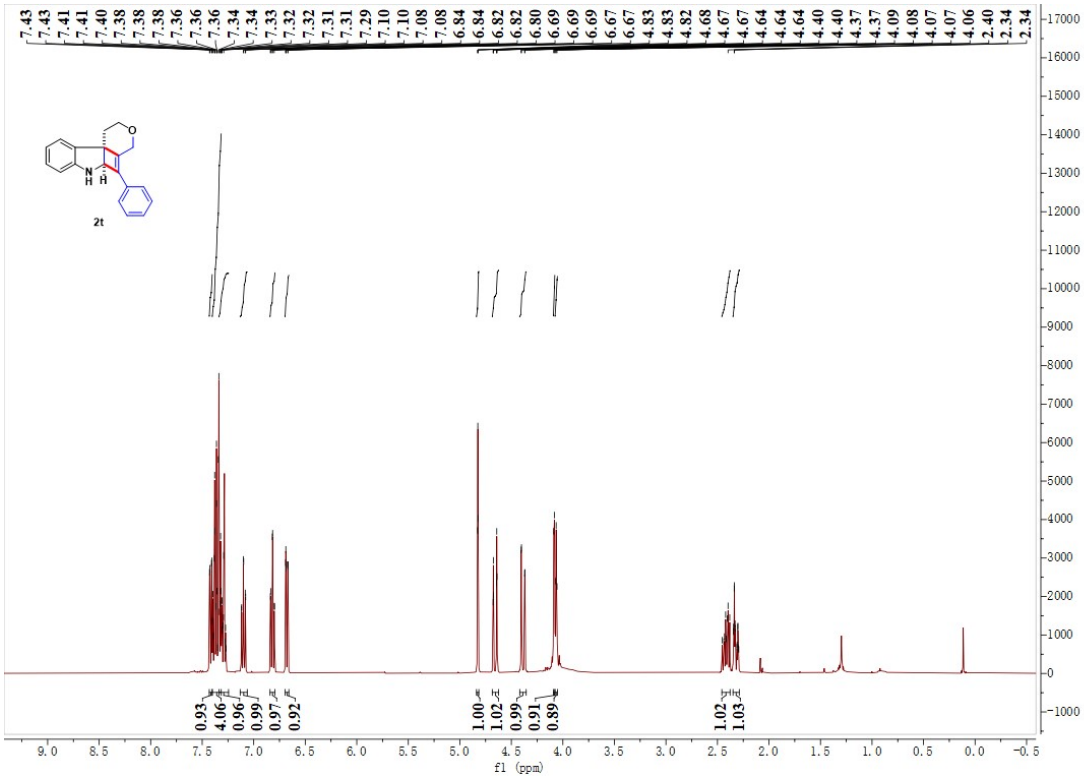


Figure S42. The ^{13}C-NMR spectra copy of compound 2t.

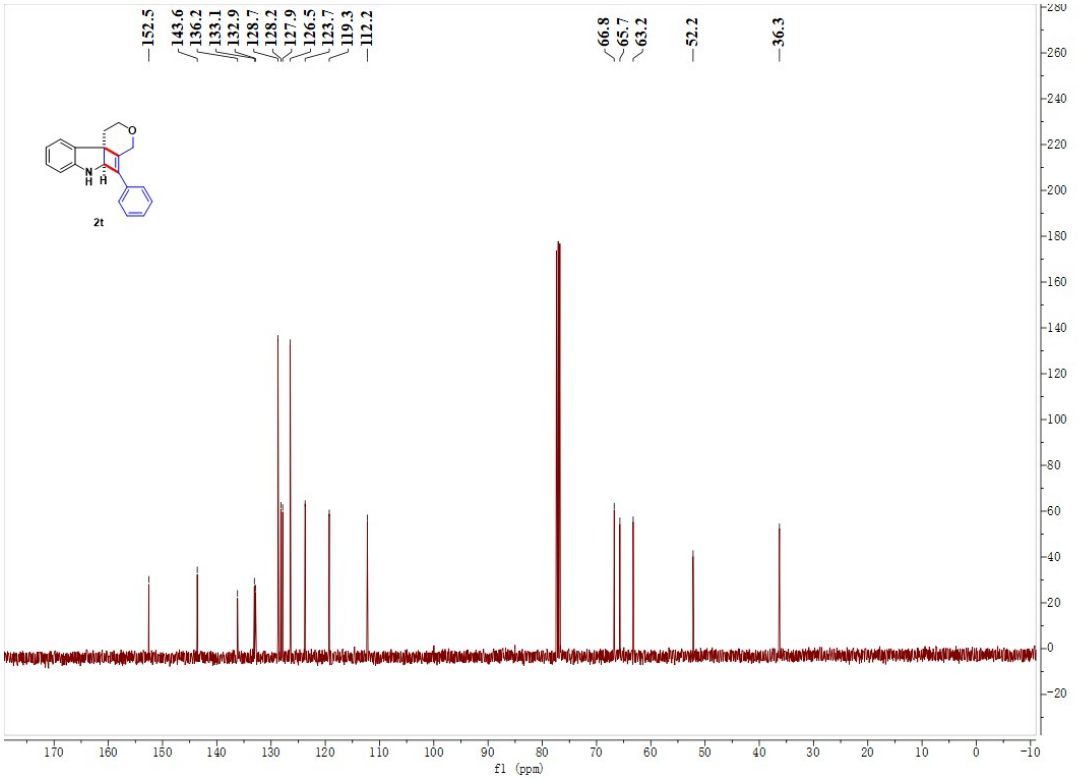


Figure S43. The ^{1}H-NMR spectra copy of compound5a.

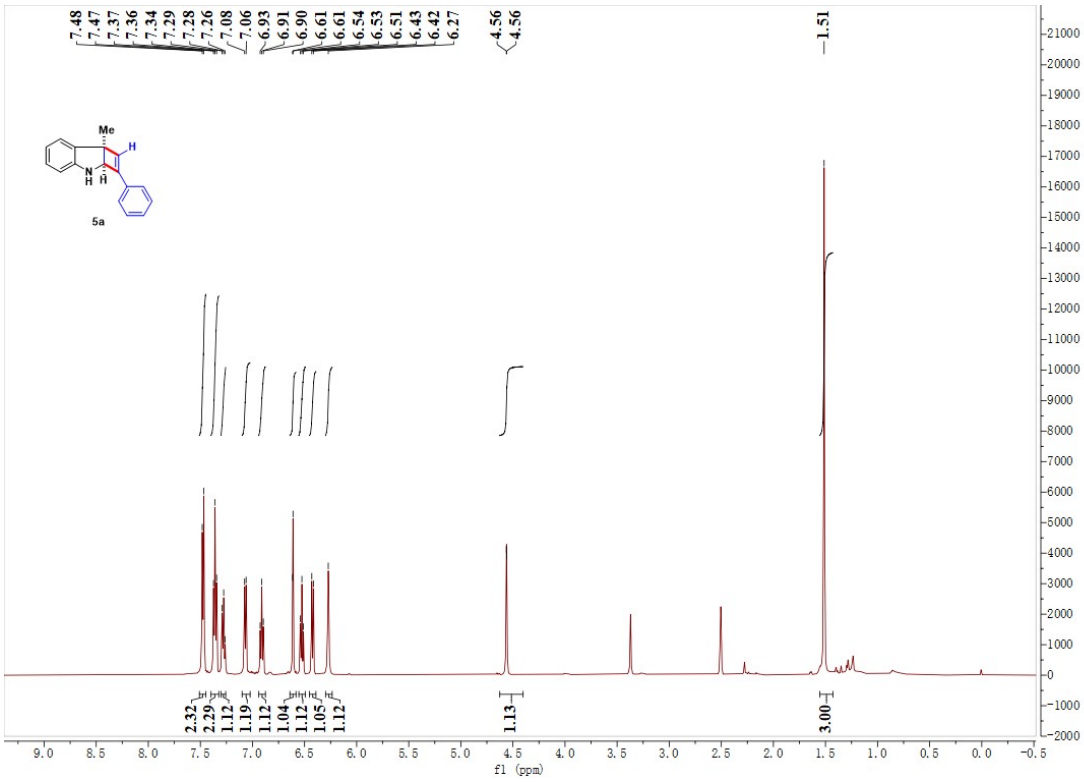


Figure S44. The ^{13}C-NMR spectra copy of compound 5a.

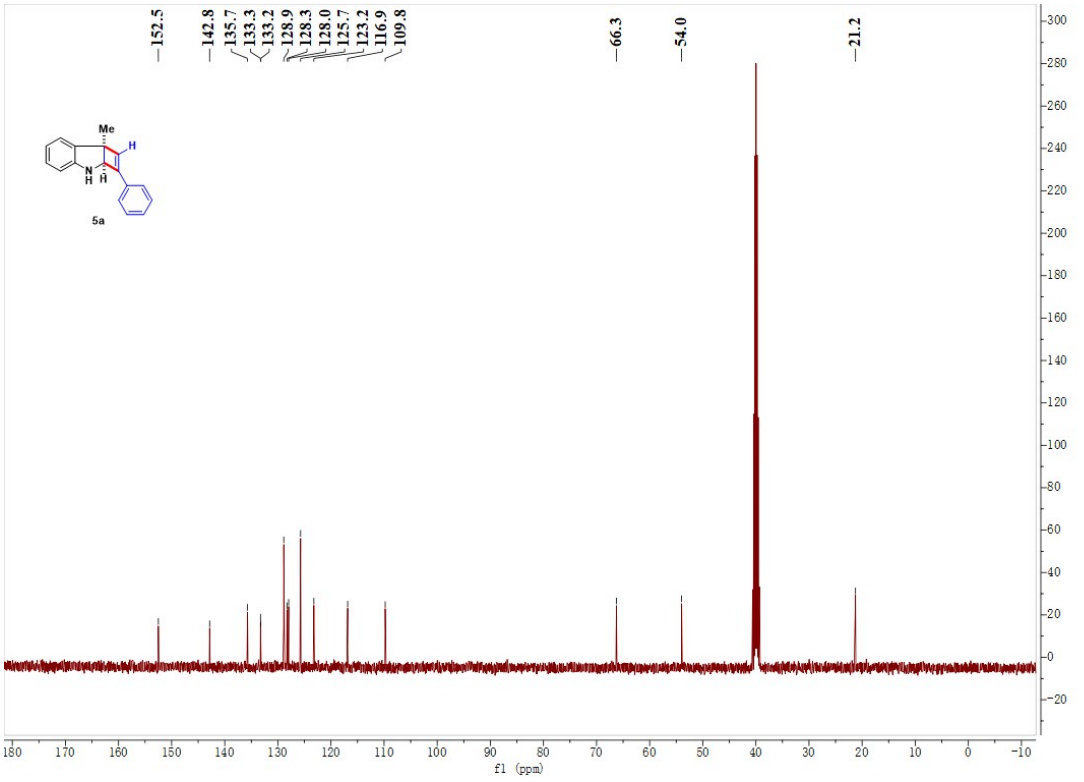


Figure S45. The H/H-COSY spectra copy of compound 5a.

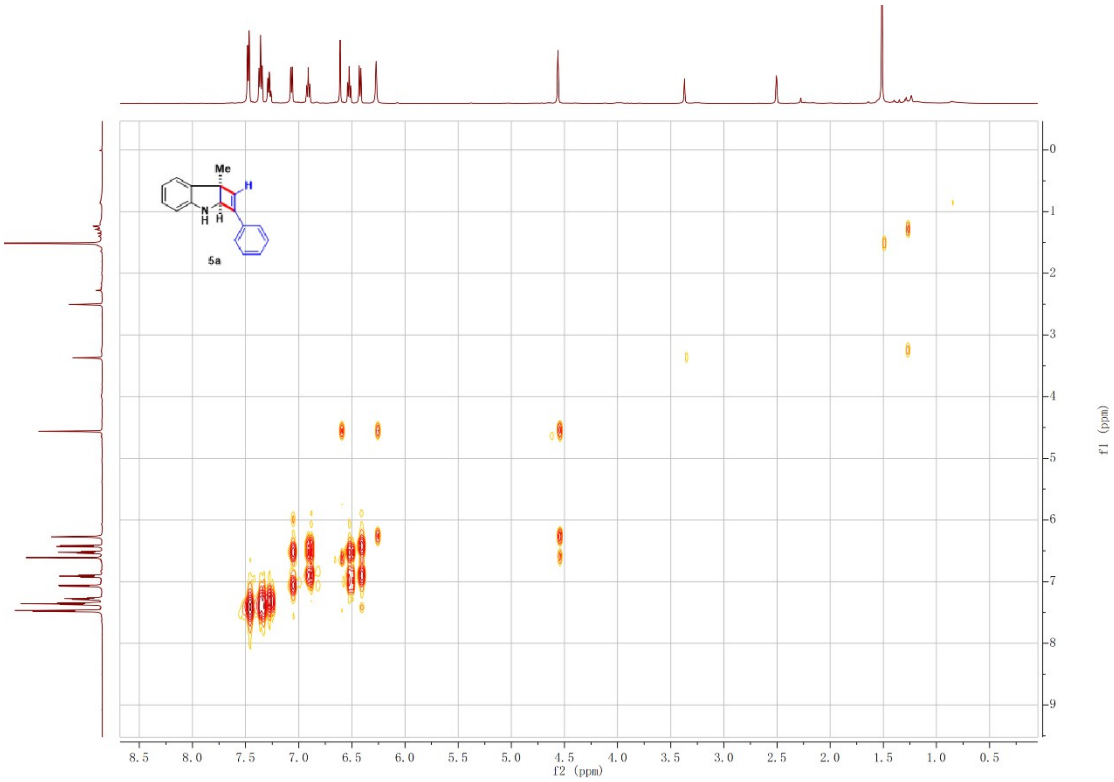


Figure S46. The HSQC spectra copy of compound 5a.

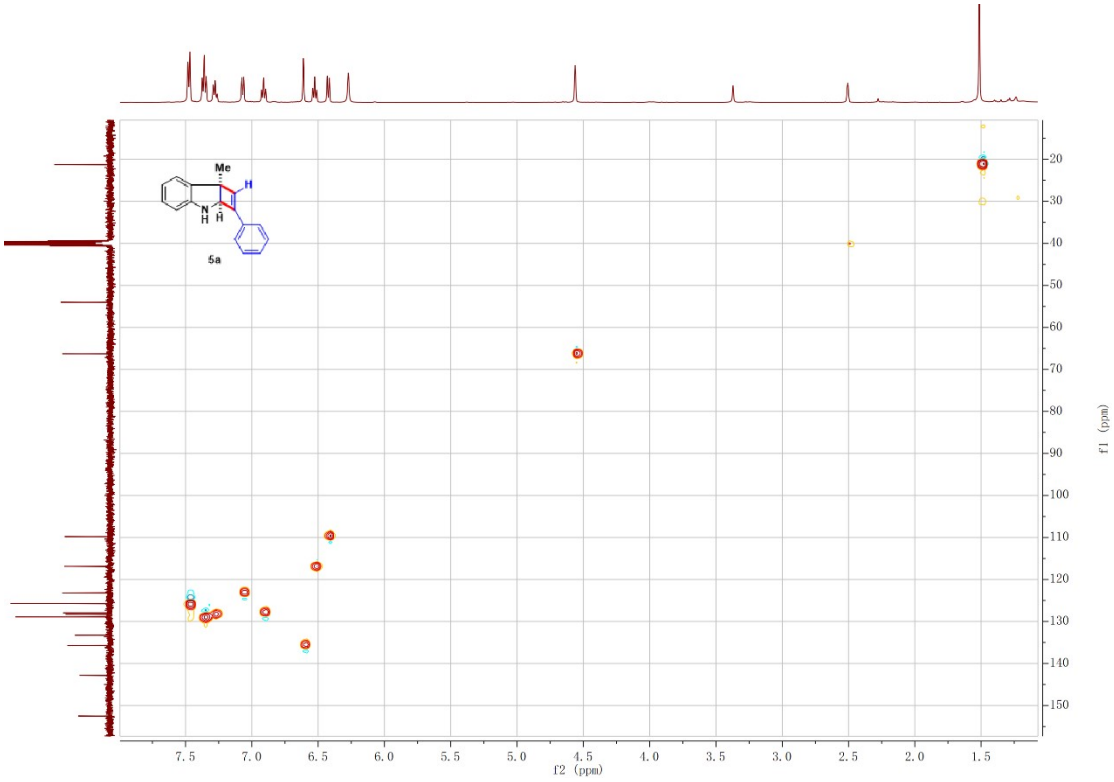


Figure S47. The HMBC spectra copy of compound 5a.

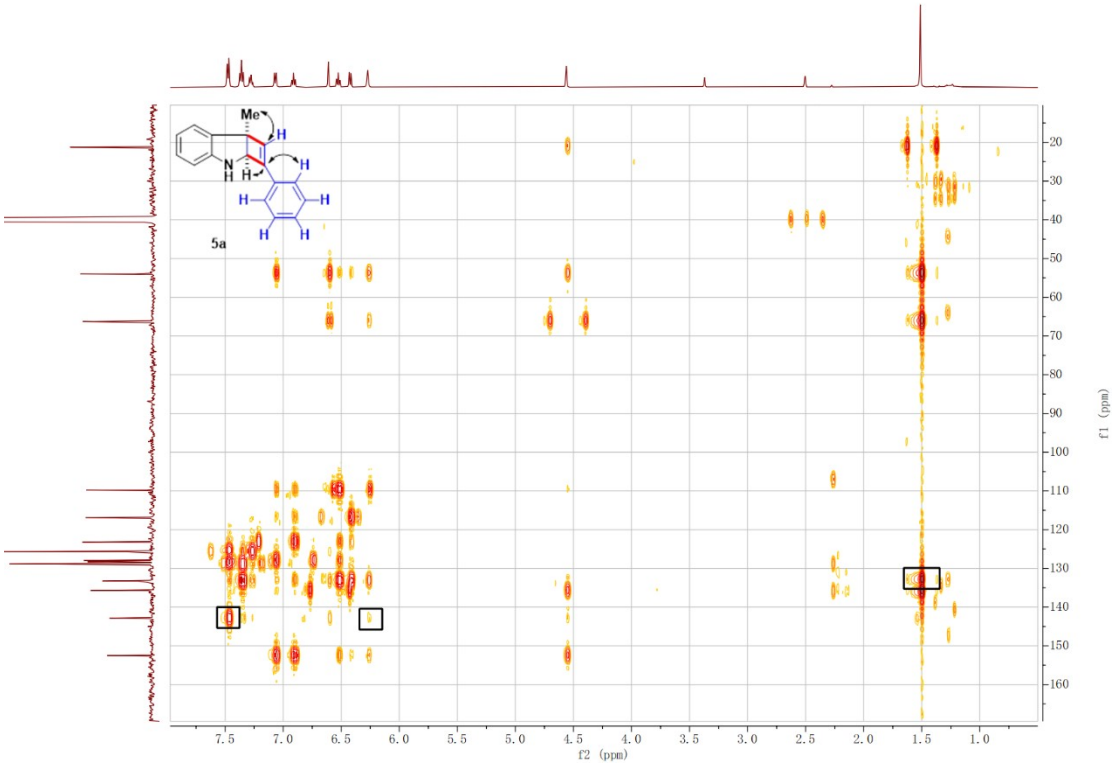


Figure S48. The NOESY spectra copy of compound 5a.

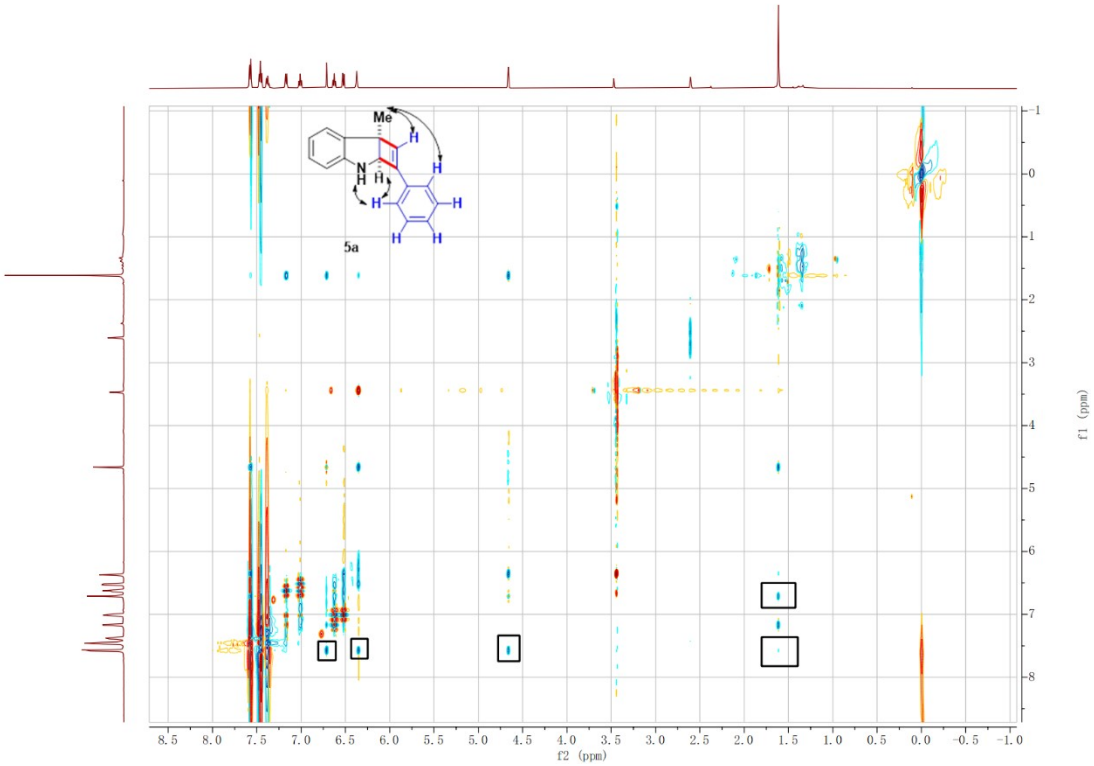


Figure S49. The DEPT-135 spectra copy of compound 5a.

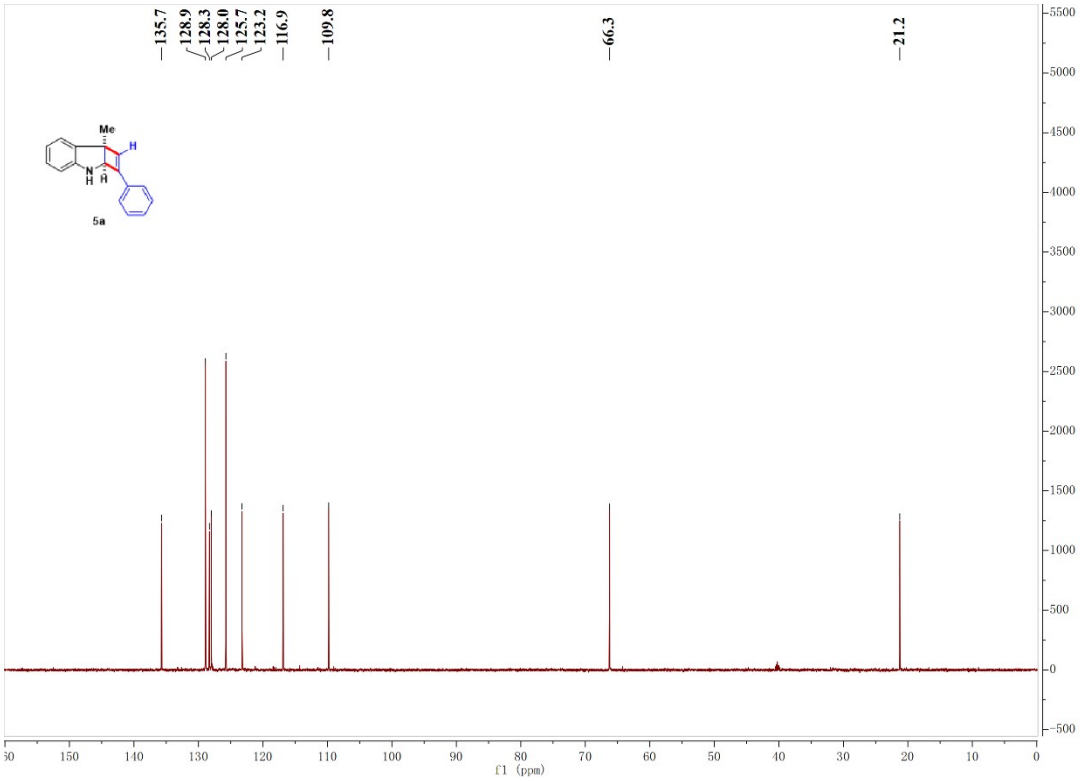


Figure S50. The ^{1}H-NMR spectra copy of compound 5b.

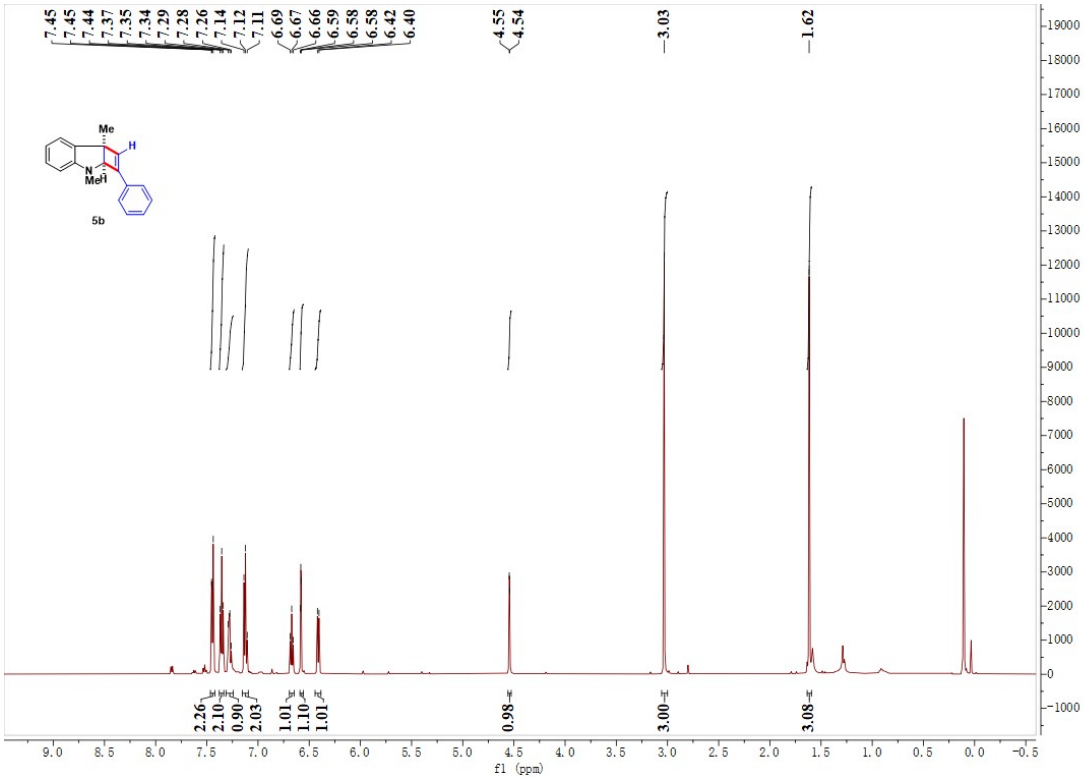


Figure S51. The ^{13}C-NMR spectra copy of compound 5b.

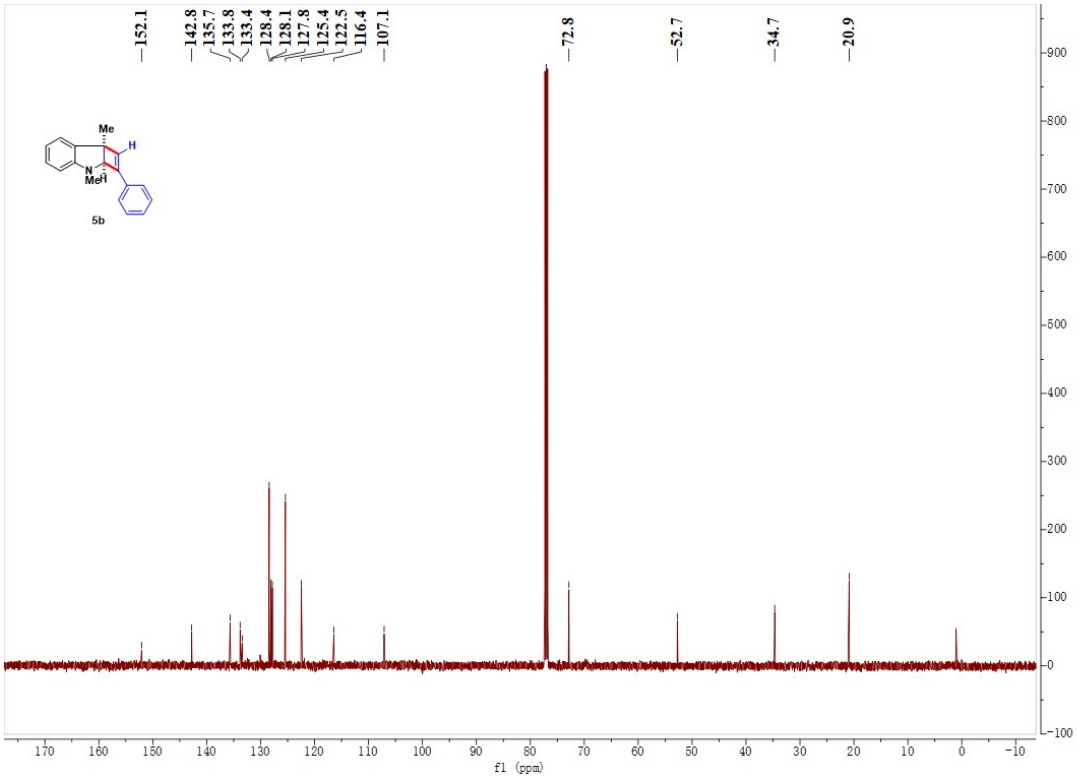


Figure S52. The ^{1}H-NMR spectra copy of compound 5c.

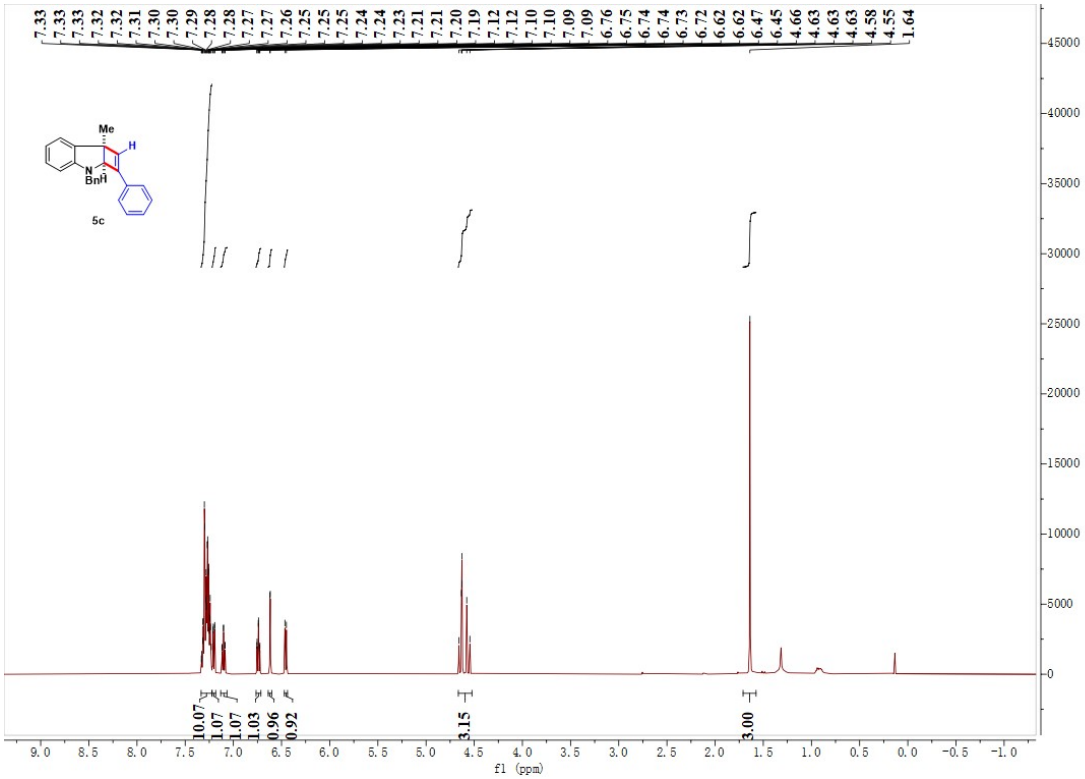


Figure S53. The ^{13}C-NMR spectra copy of compound 5c.

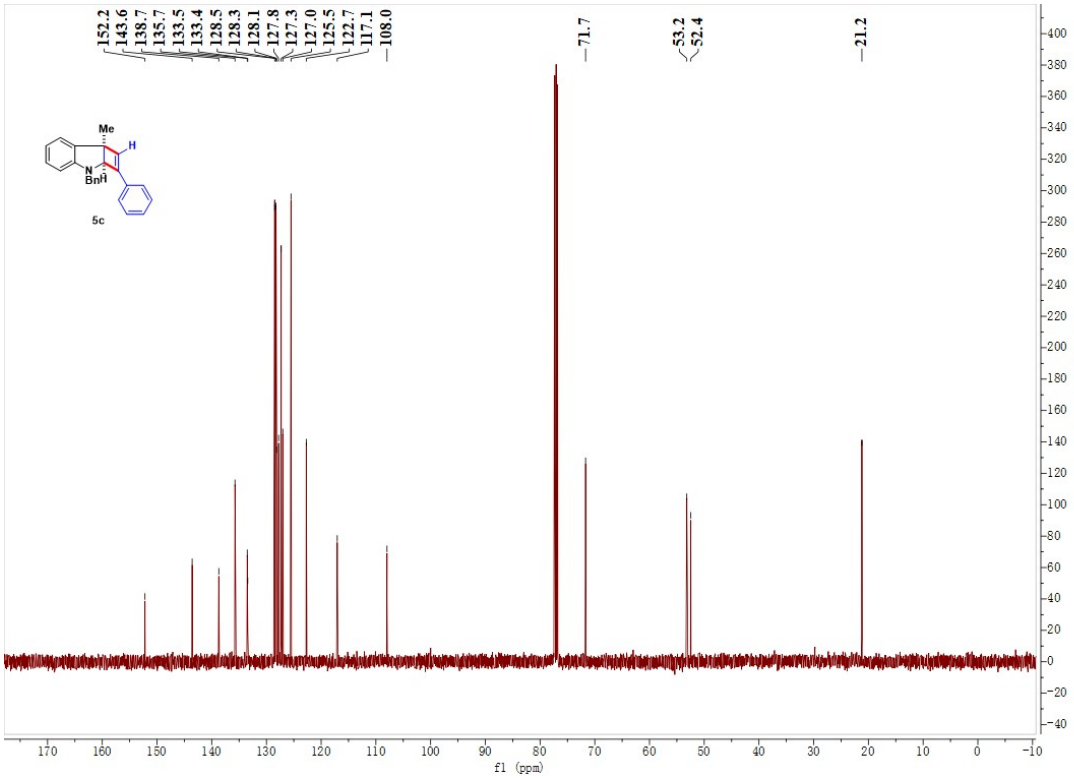


Figure S54. The ^{1}H-NMR spectra copy of compound 5d.

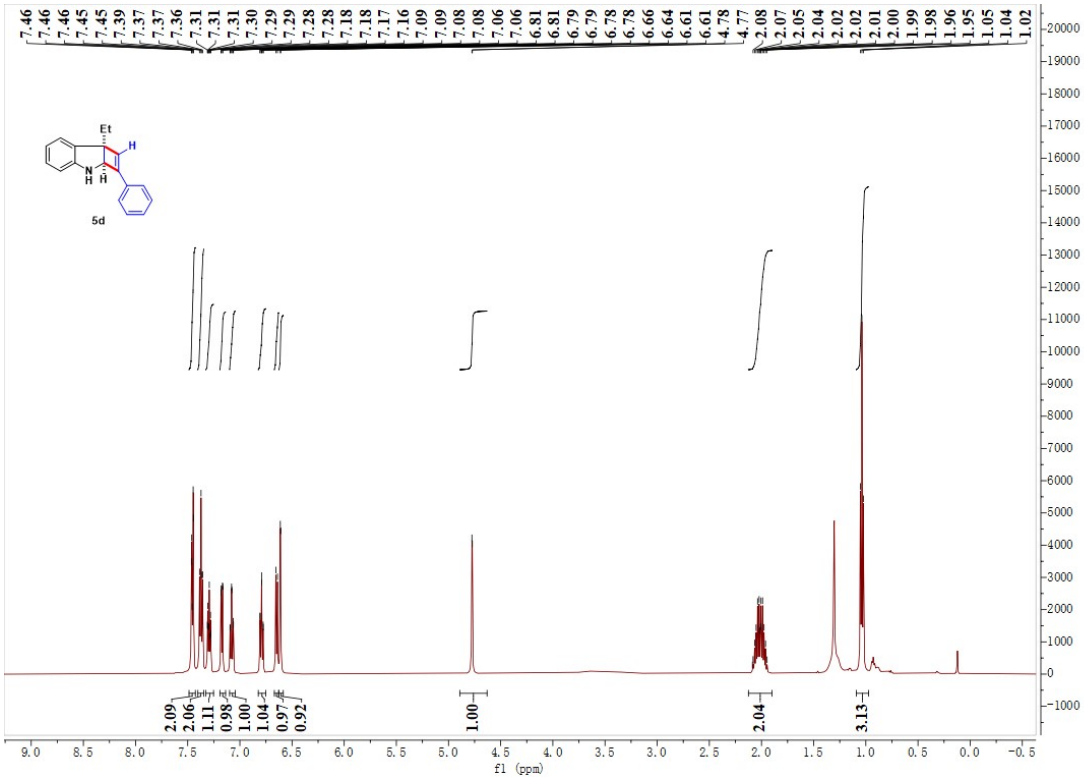


Figure S55. The ^{13}C-NMR spectra copy of compound 5d.

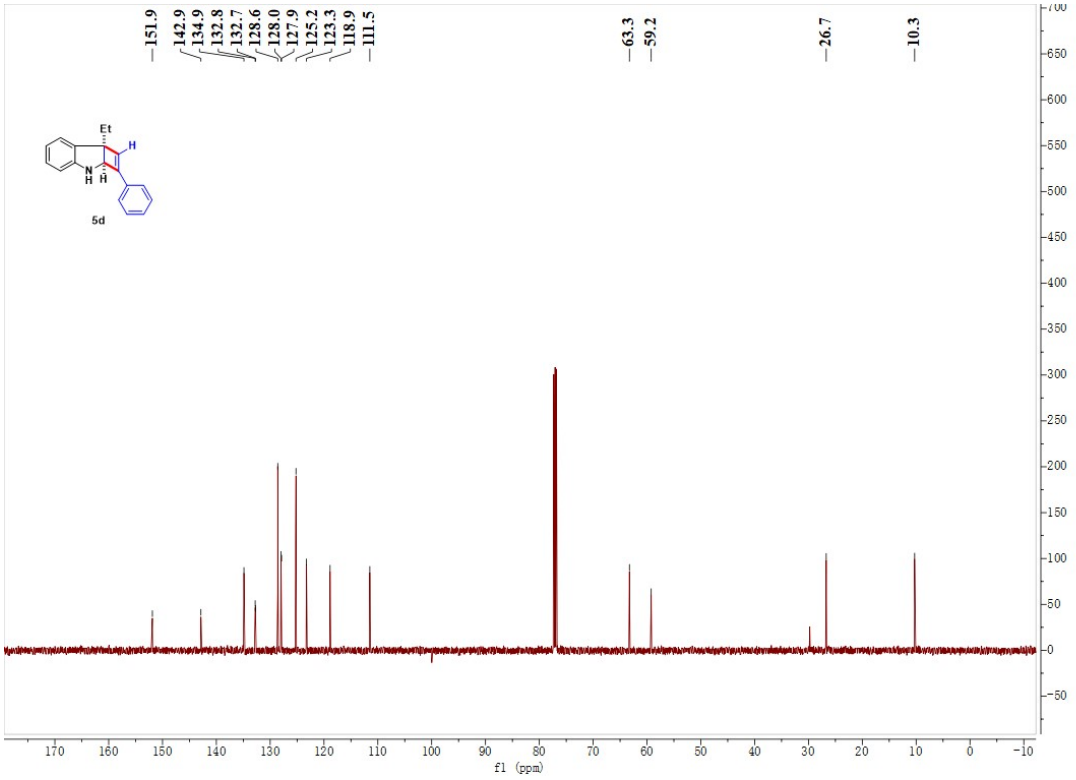


Figure S56. The ^{1}H-NMR spectra copy of compound 5e.

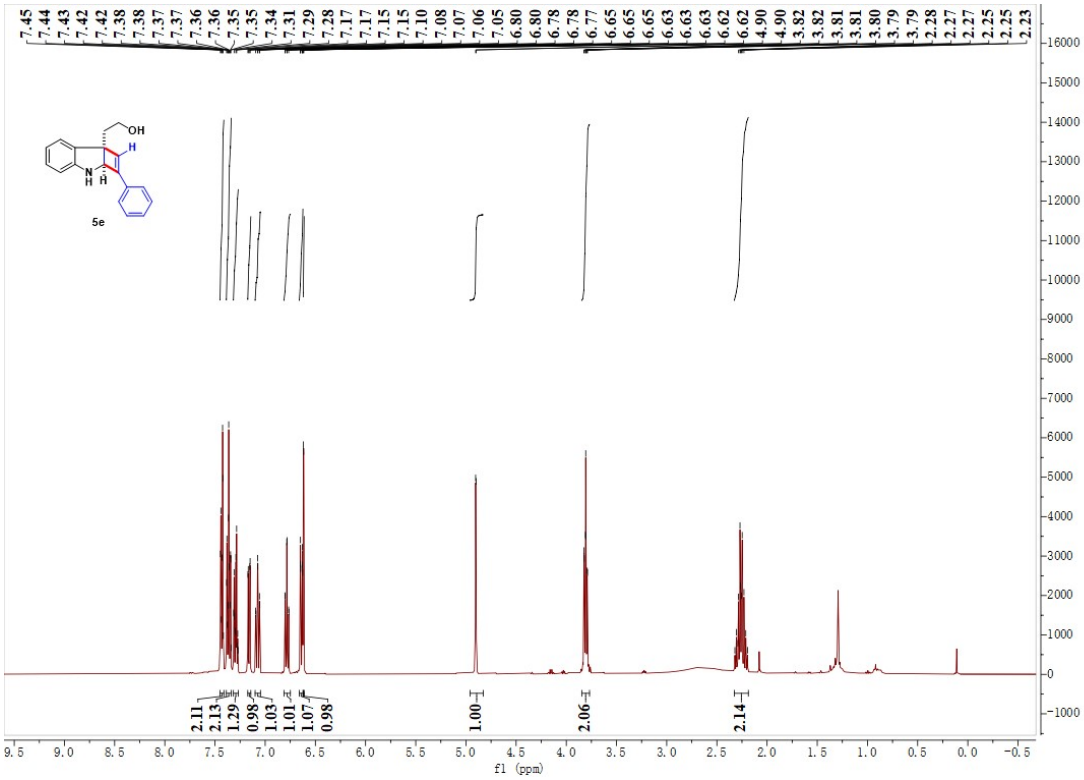


Figure S57. The ^{13}C-NMR spectra copy of compound 5e.

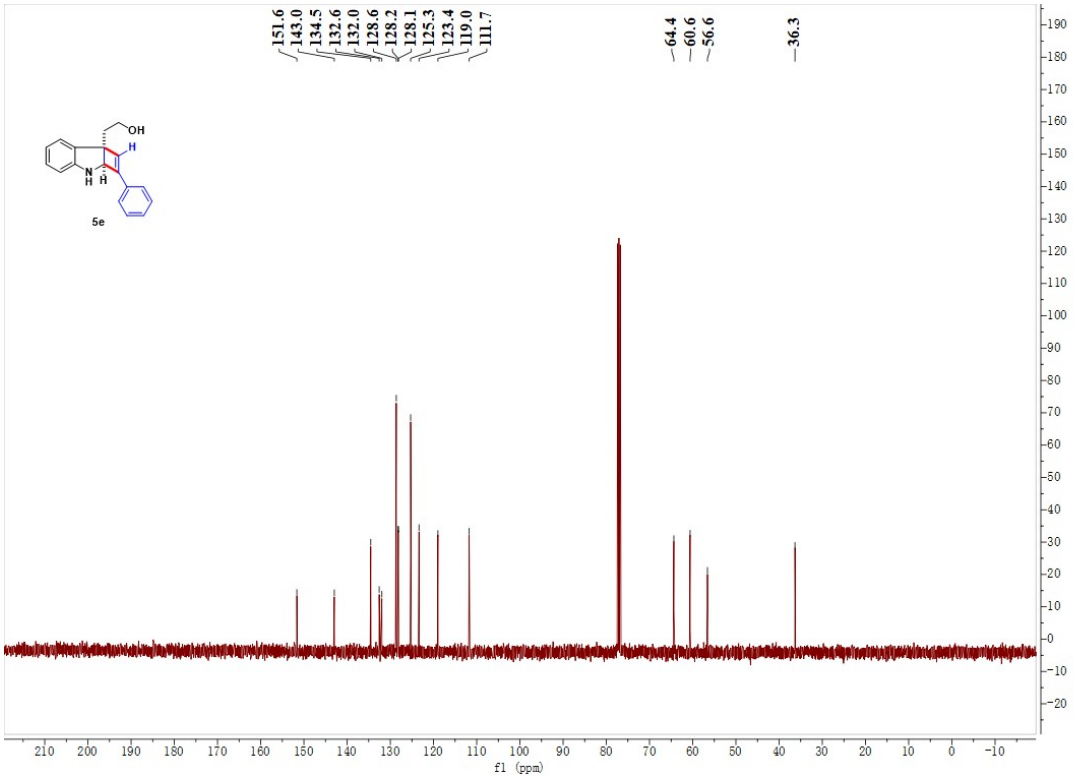


Figure S58. The ^{1}H-NMR spectra copy of compound 5f.

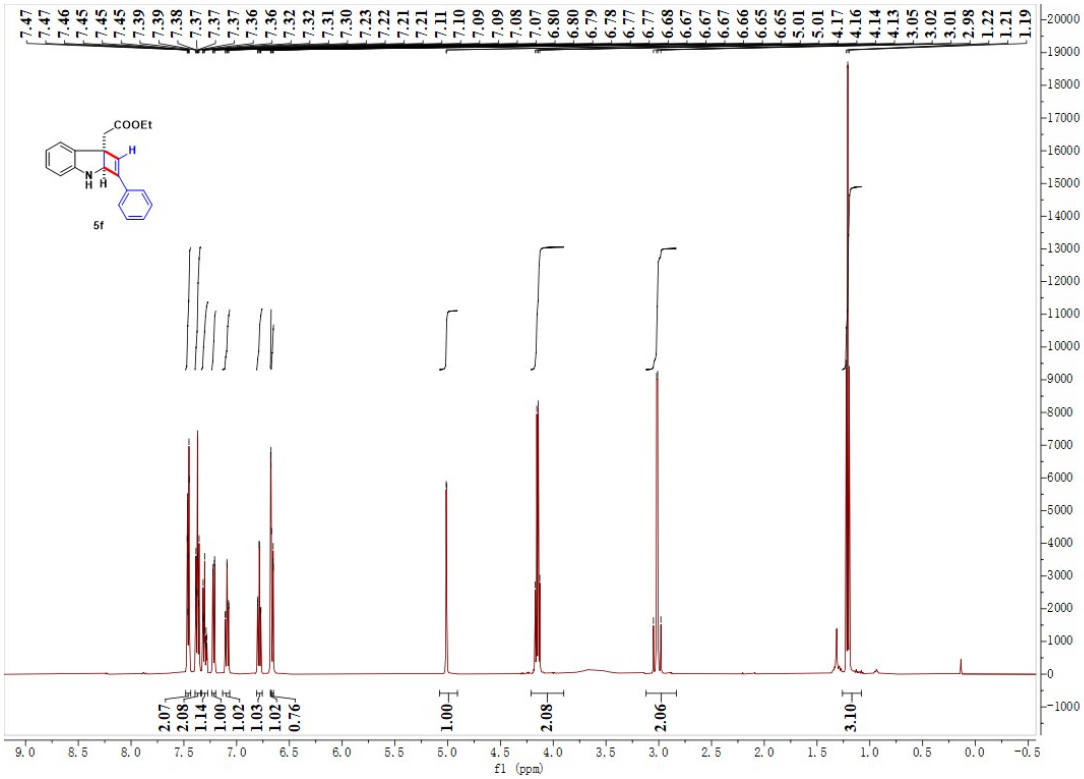


Figure S59. The ^{13}C-NMR spectra copy of compound 5f.

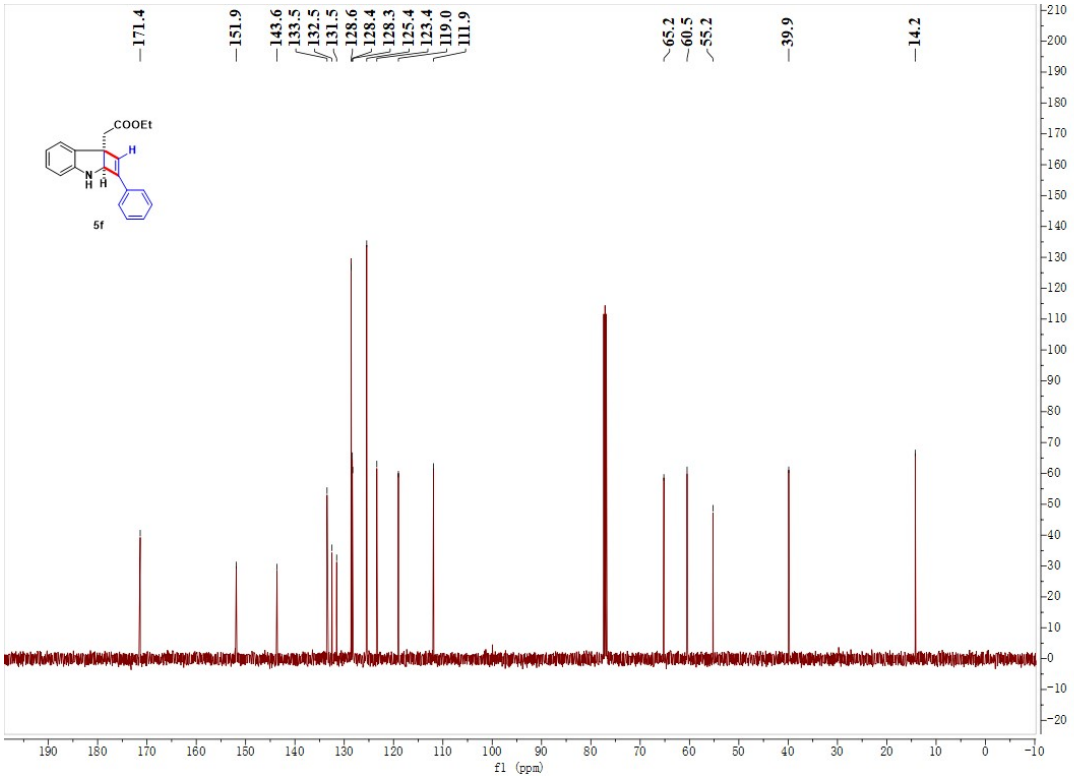


Figure S60. The ^{1}H-NMR spectra copy of compound 5g.

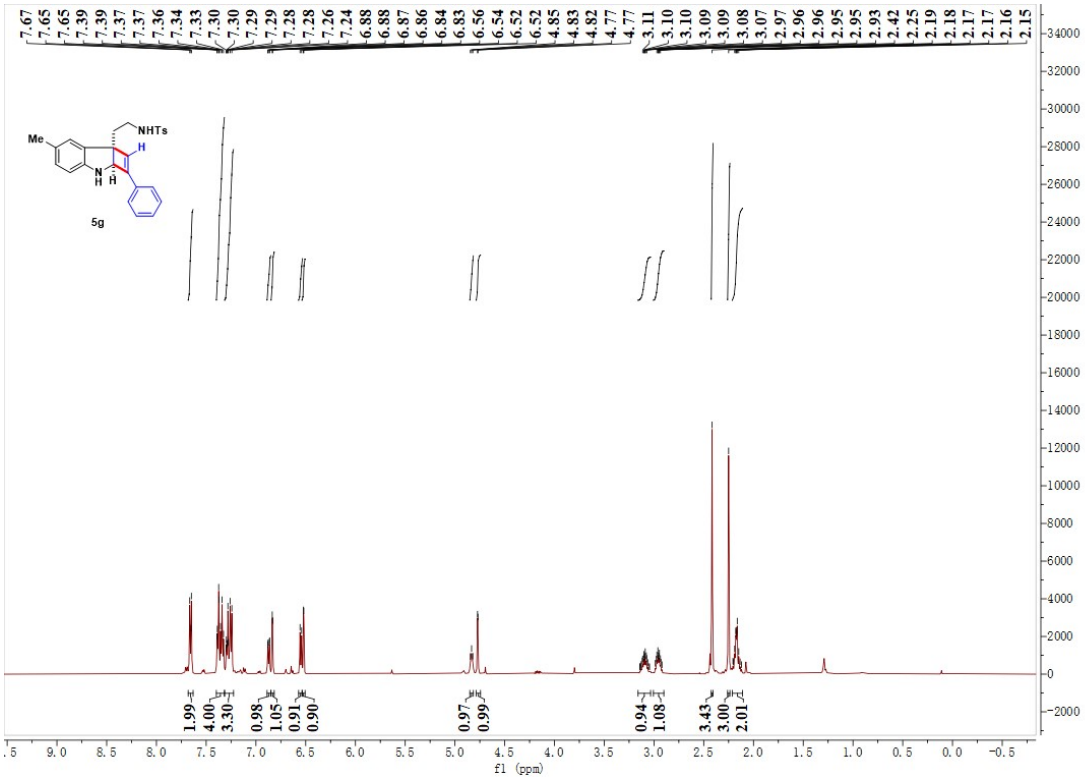


Figure S61. The ^{13}C-NMR spectra copy of compound 5g.

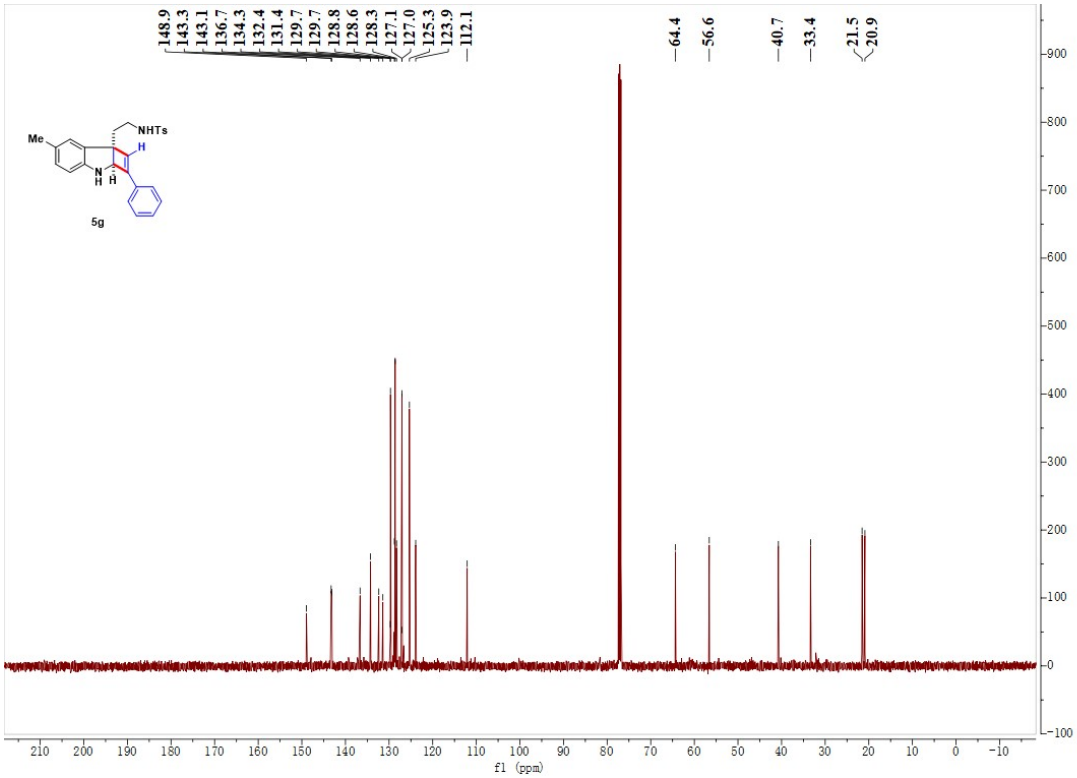


Figure S62. The ^{1}H-NMR spectra copy of compound 5h.

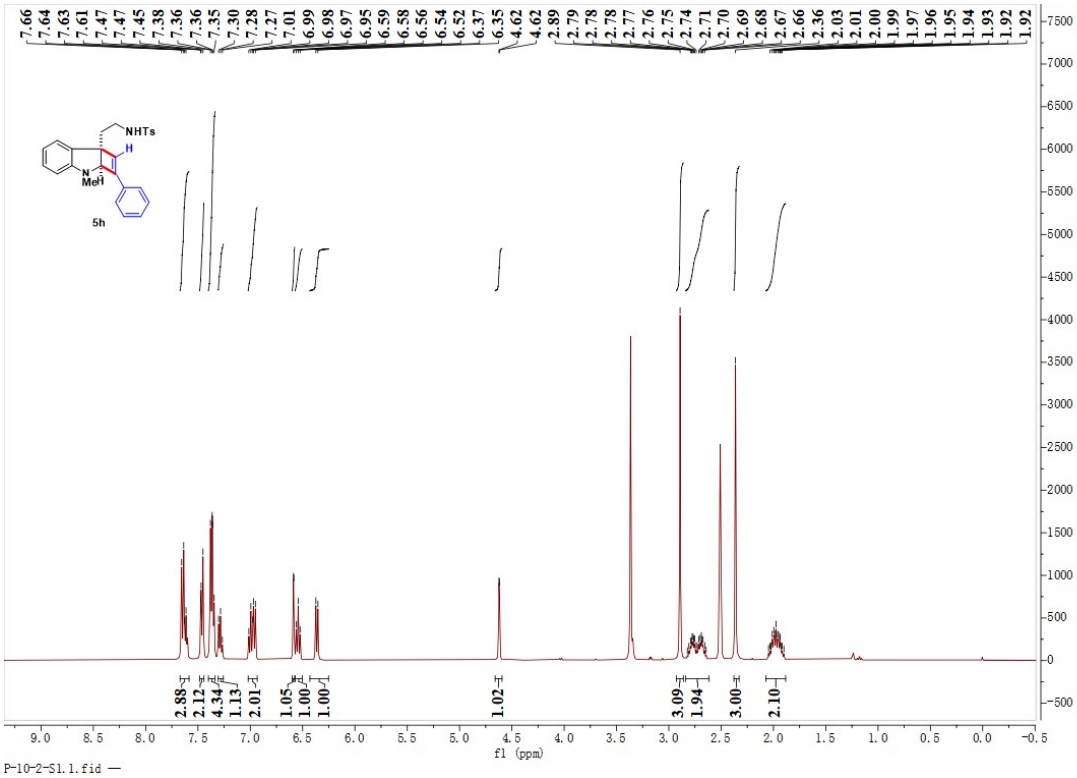


Figure S63. The ^{13}C-NMR spectra copy of compound 5h.

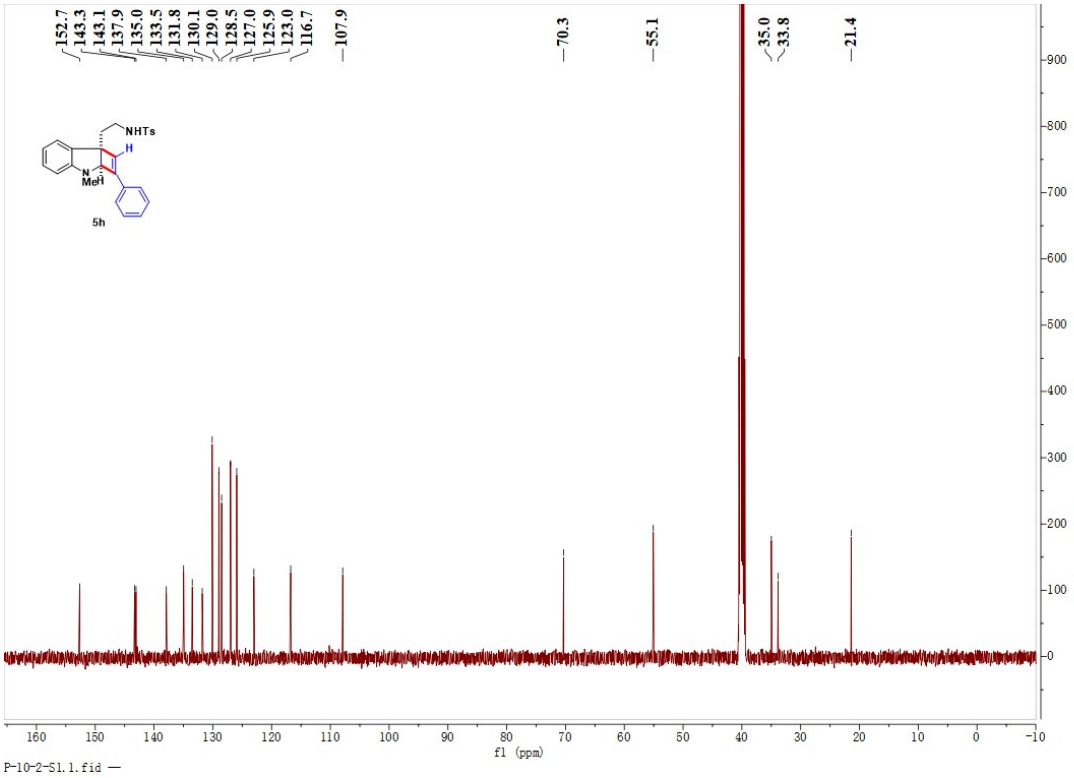


Figure S64. The ^{1}H-NMR spectra copy of compound 5i.

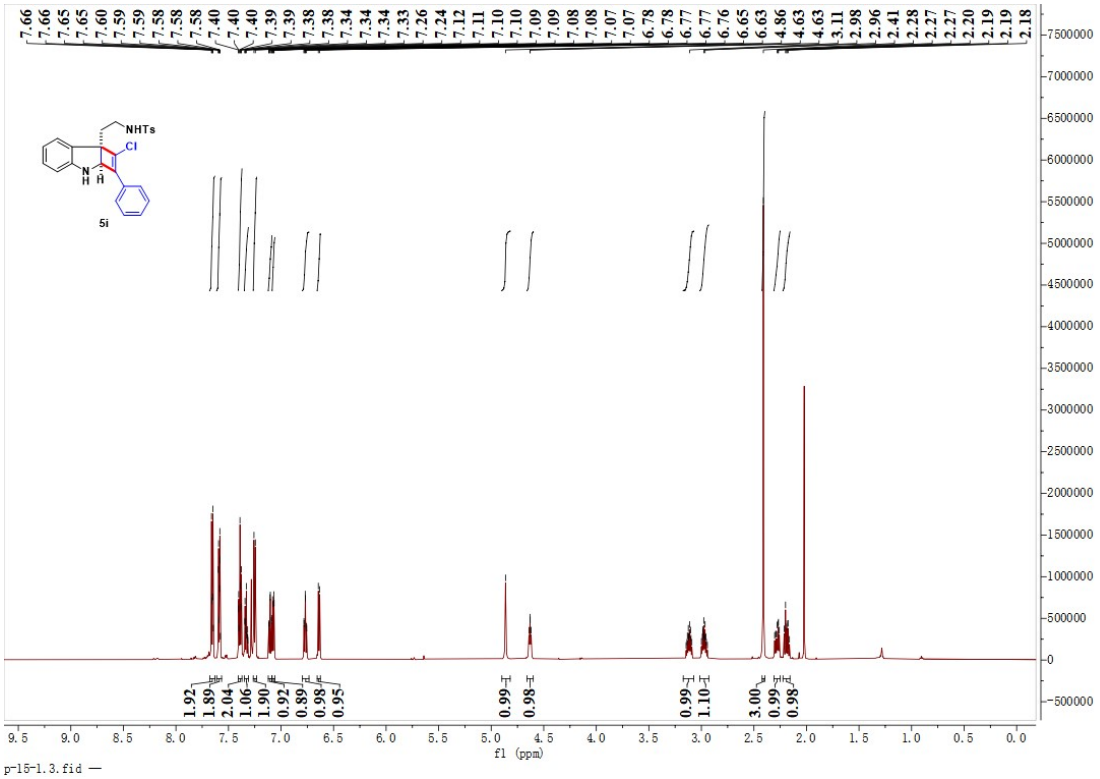


Figure S65. The ^{13}C-NMR spectra copy of compound 5i.

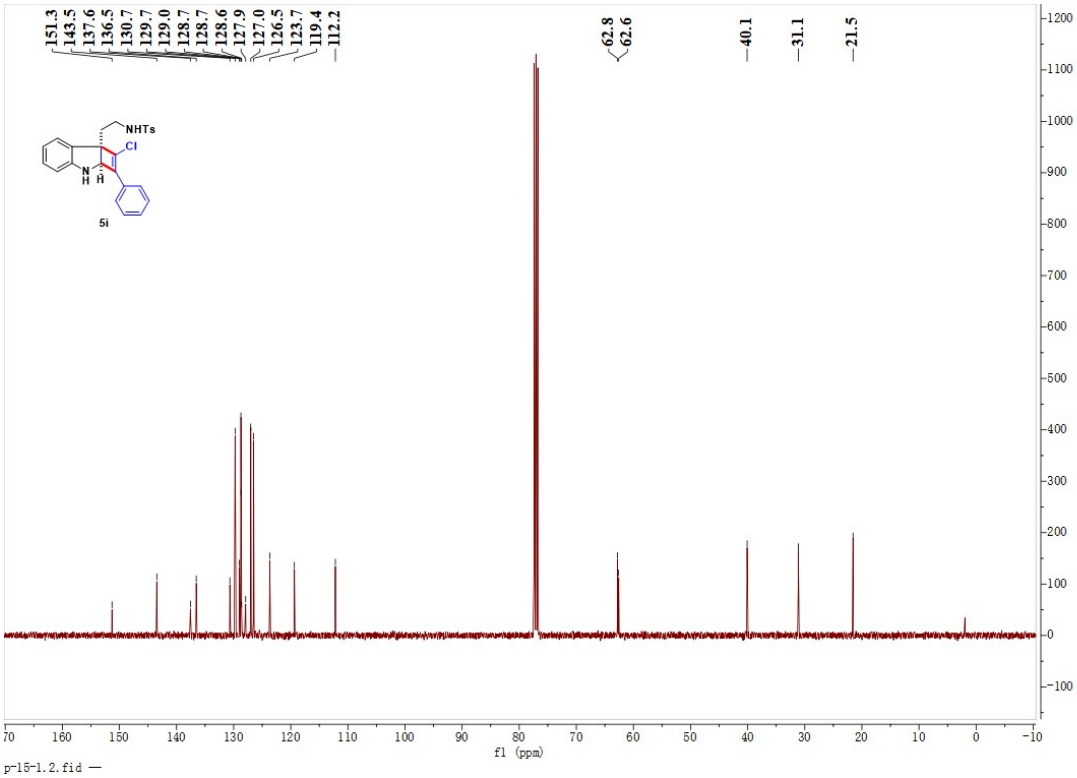


Figure S66. The ^{1}H-NMR spectra copy of compound 5j.

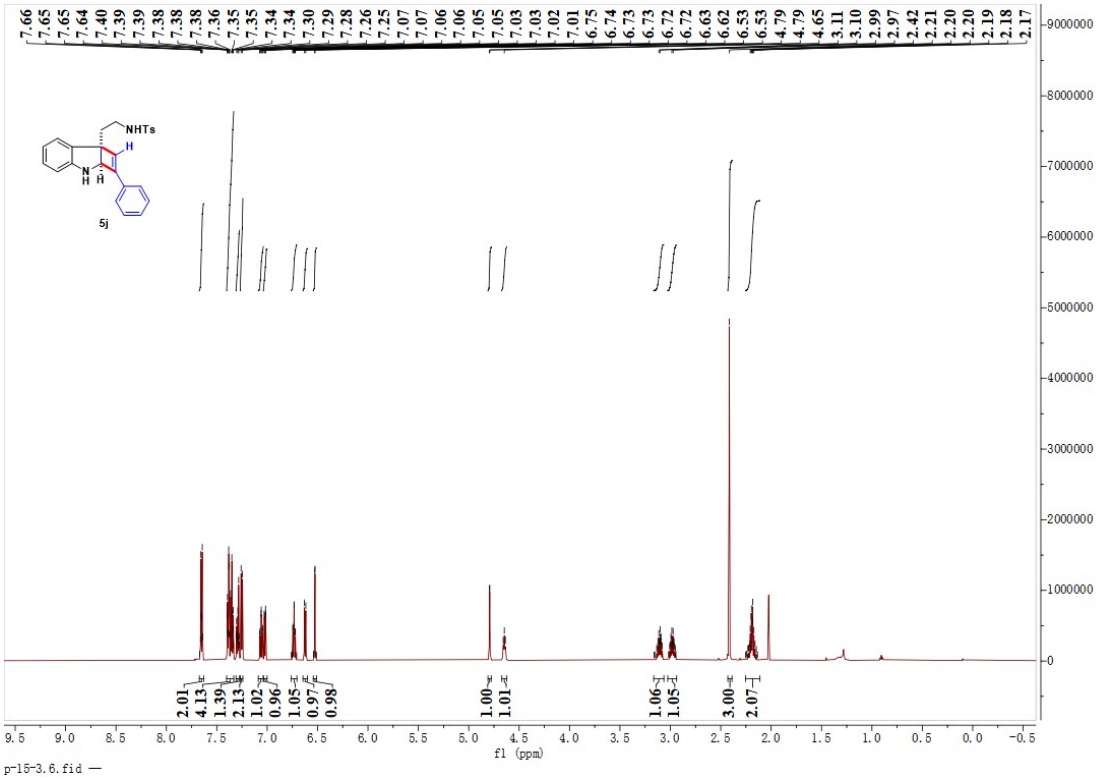


Figure S67. The ^{13}C-NMR spectra copy of compound 5j.

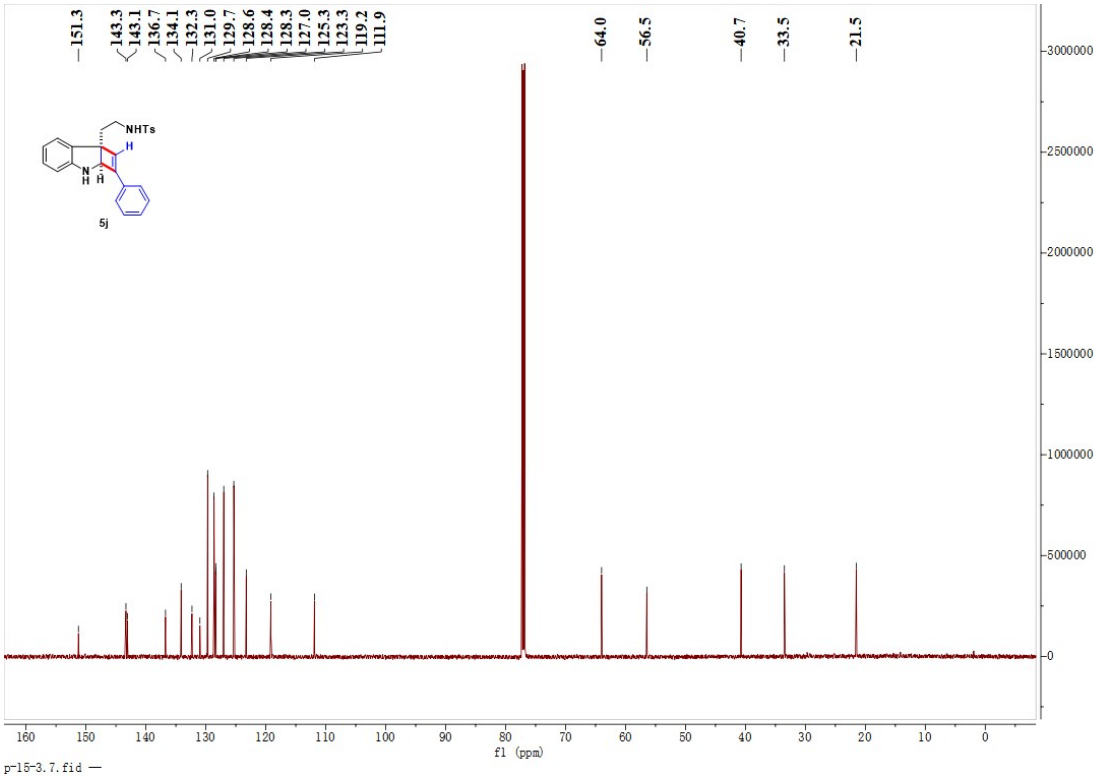


Figure S68. The ^{1}H-NMR spectra copy of compound 5k.

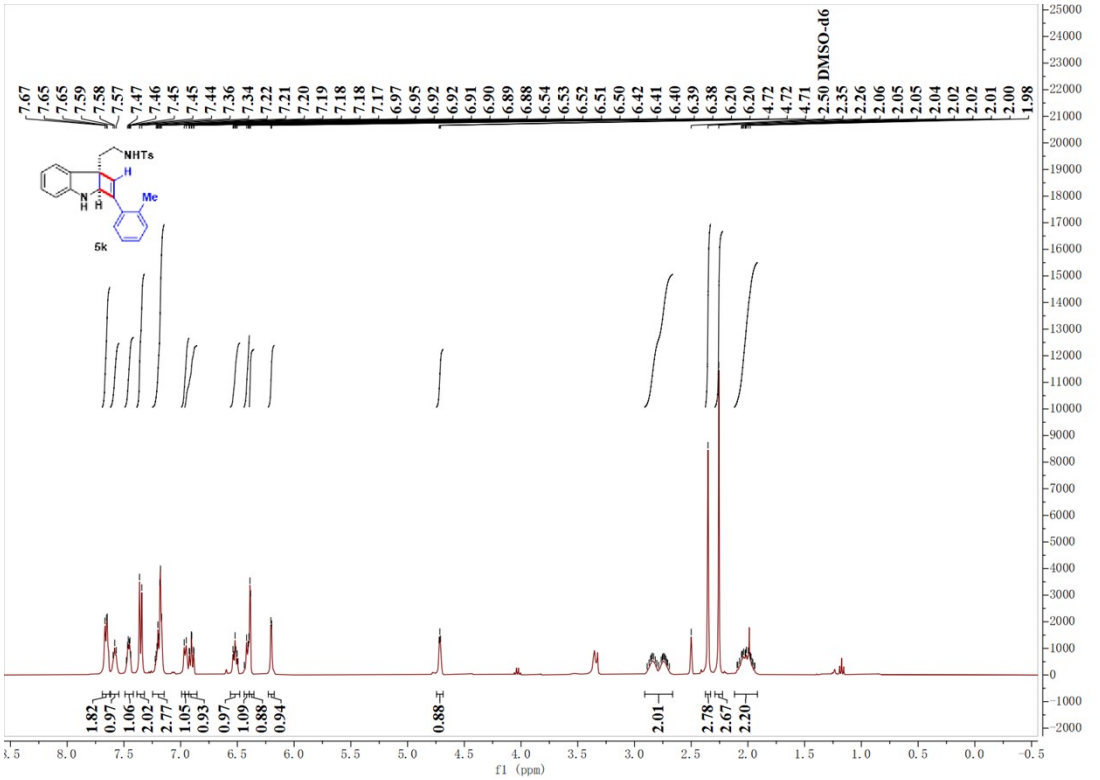


Figure S69. The ^{13}C-NMR spectra copy of compound 5k.

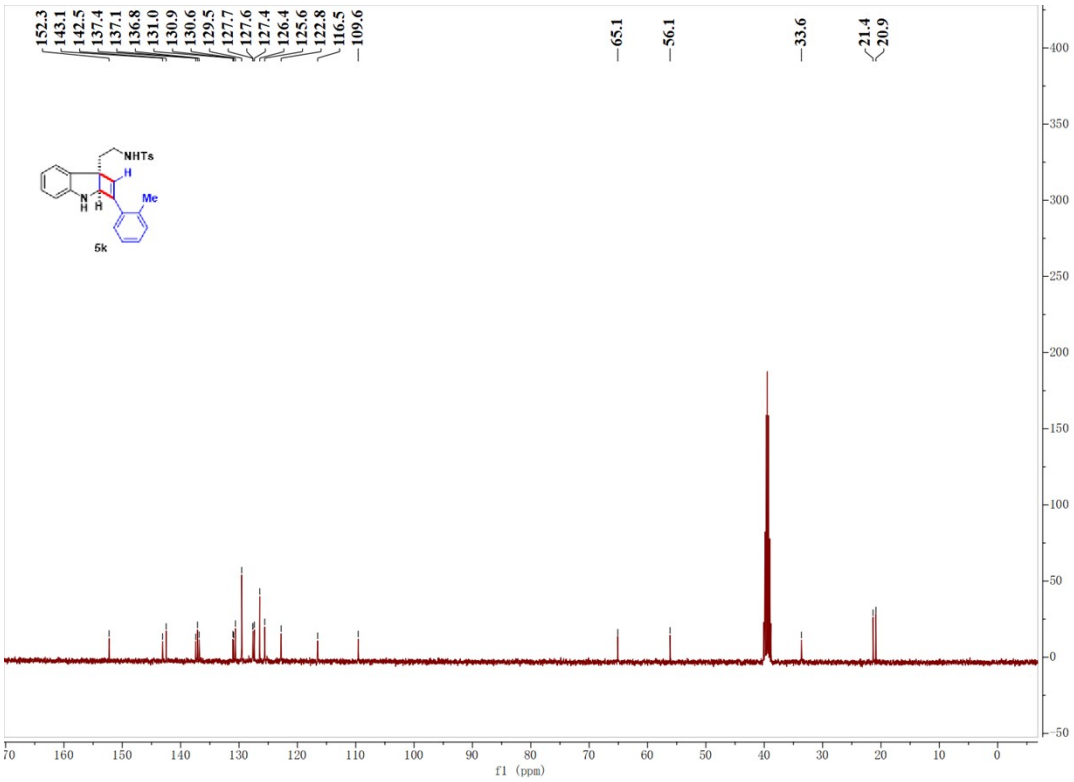


Figure S70. The DEPT-135 spectra copy of compound 5k.

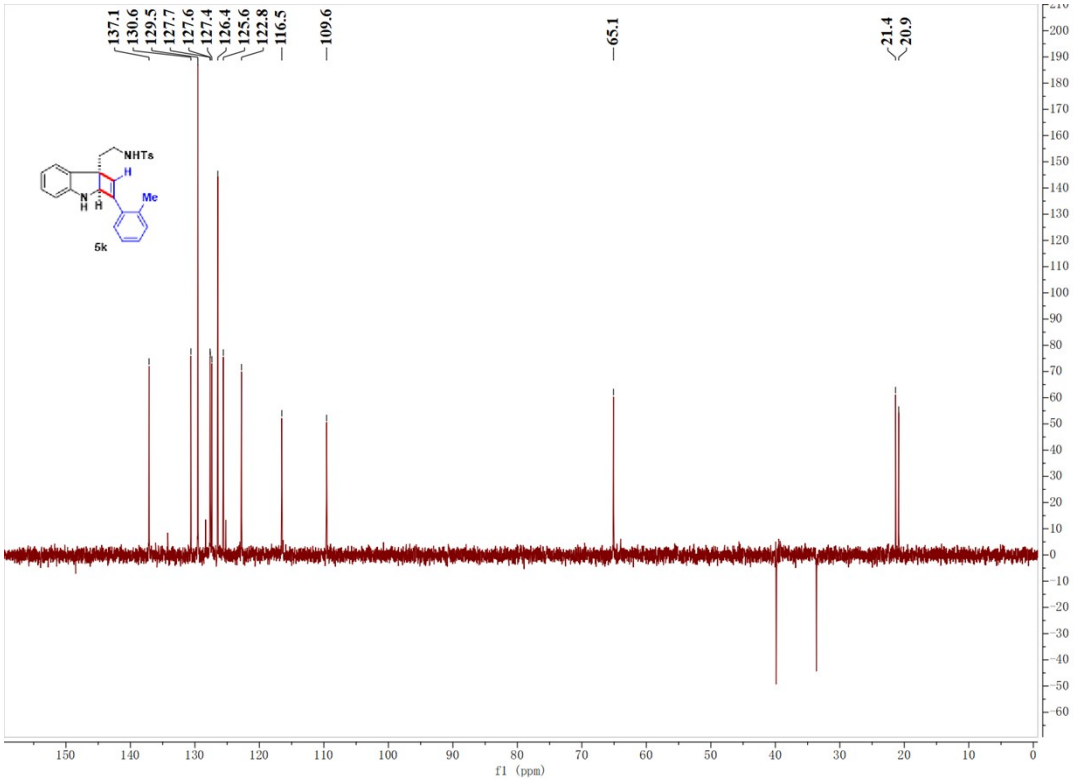


Figure S71. The H/H-COSY spectra copy of compound 5k.

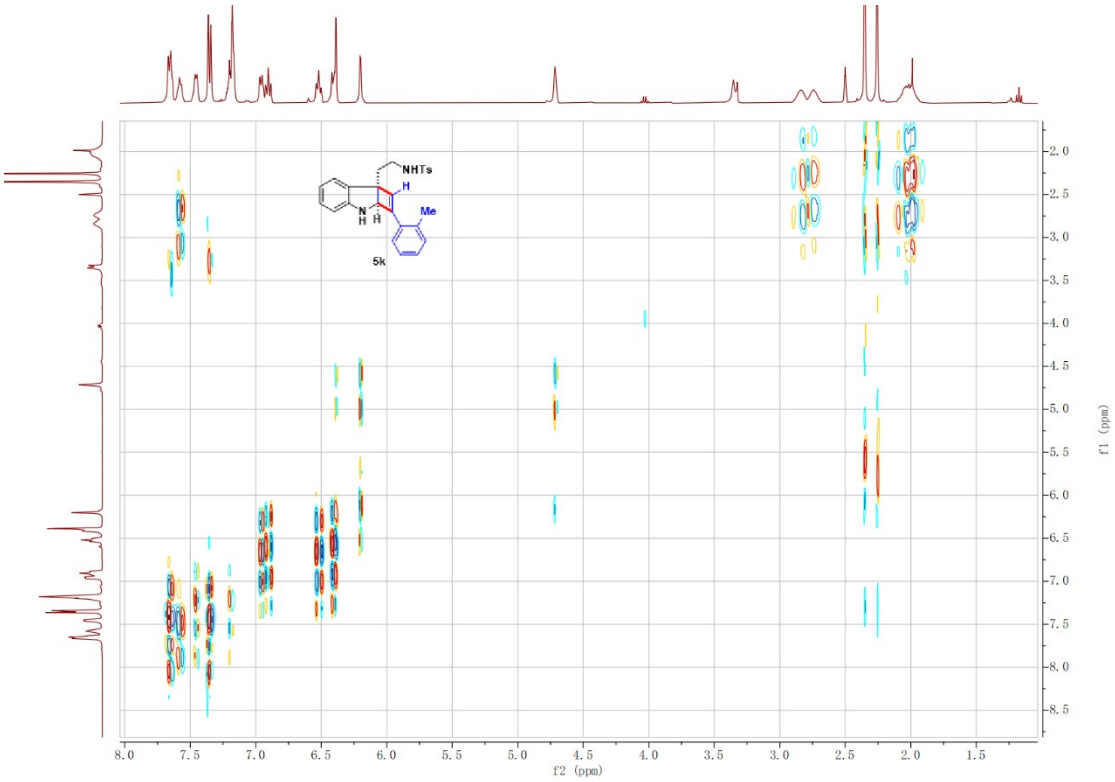


Figure S72. The HSQC spectra copy of compound 5k.

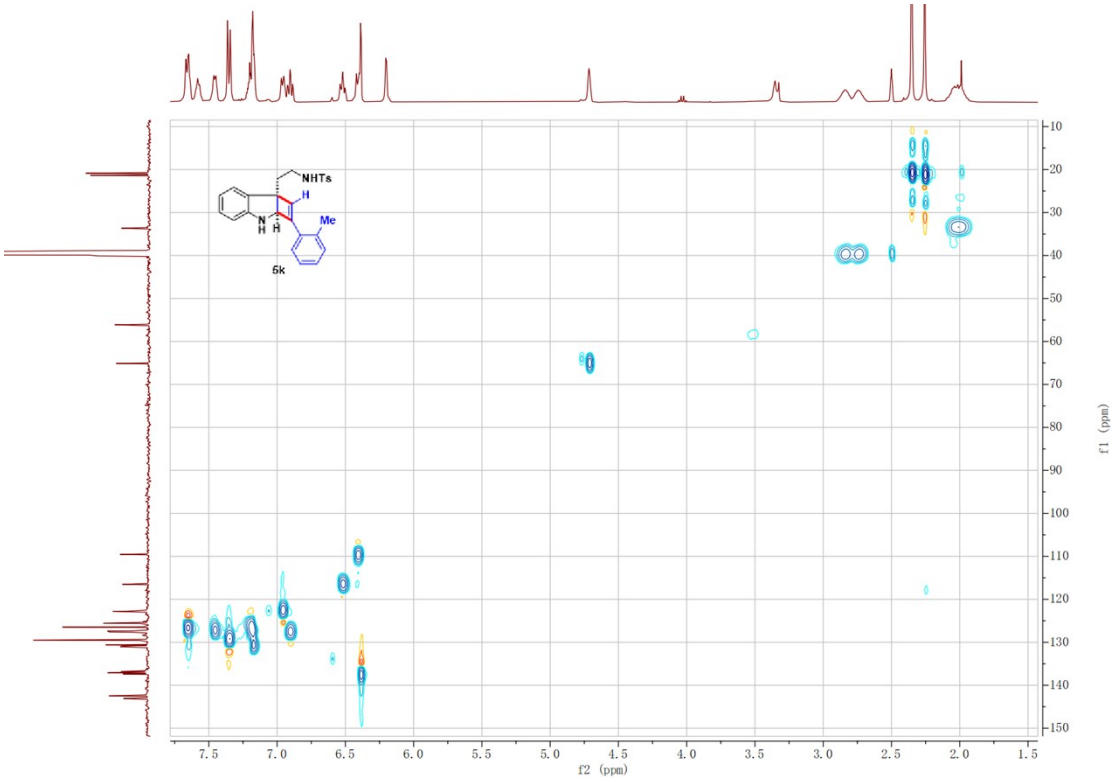


Figure S73. The HMBC spectra copy of compound 5k.

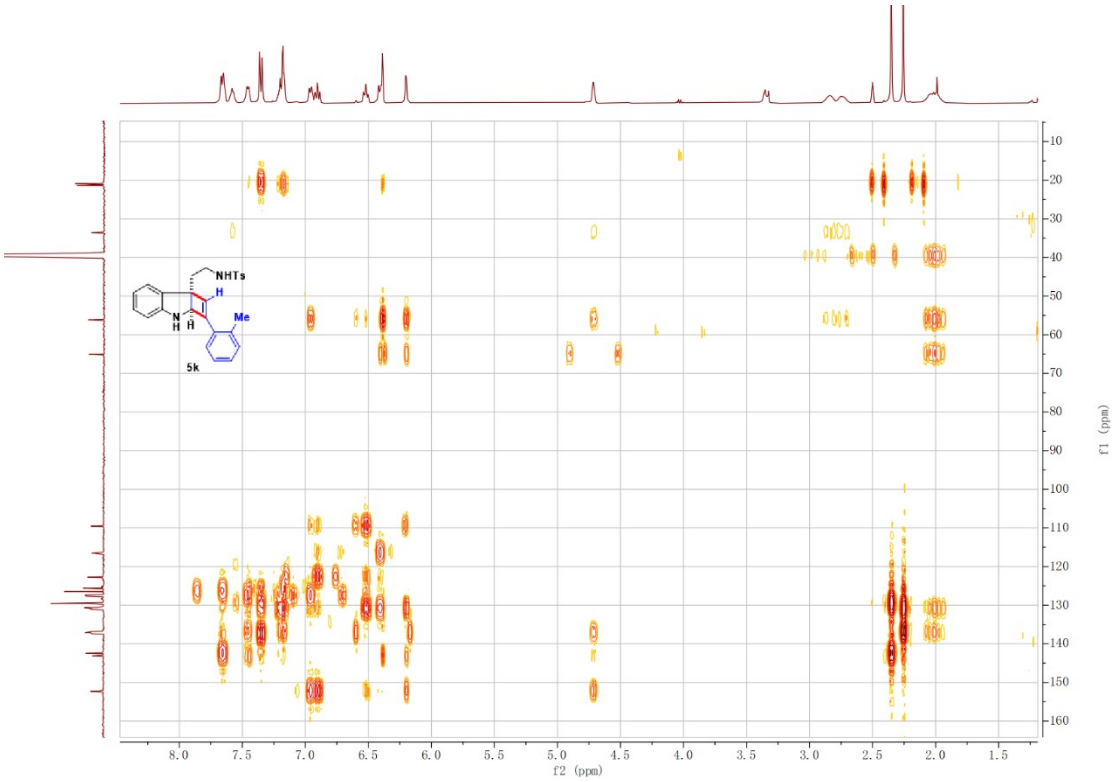


Figure S74. The NOESY spectra copy of compound 5k.

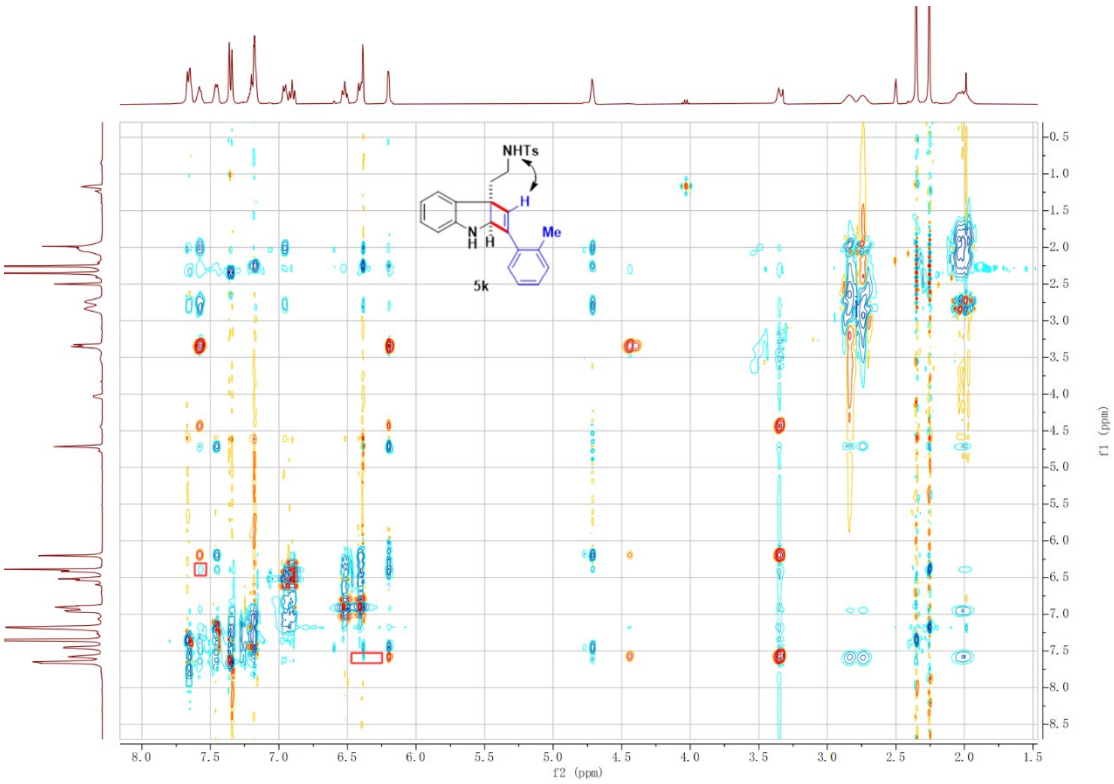


Figure S75. The ^{1}H-NMR spectra copy of compound 5l.

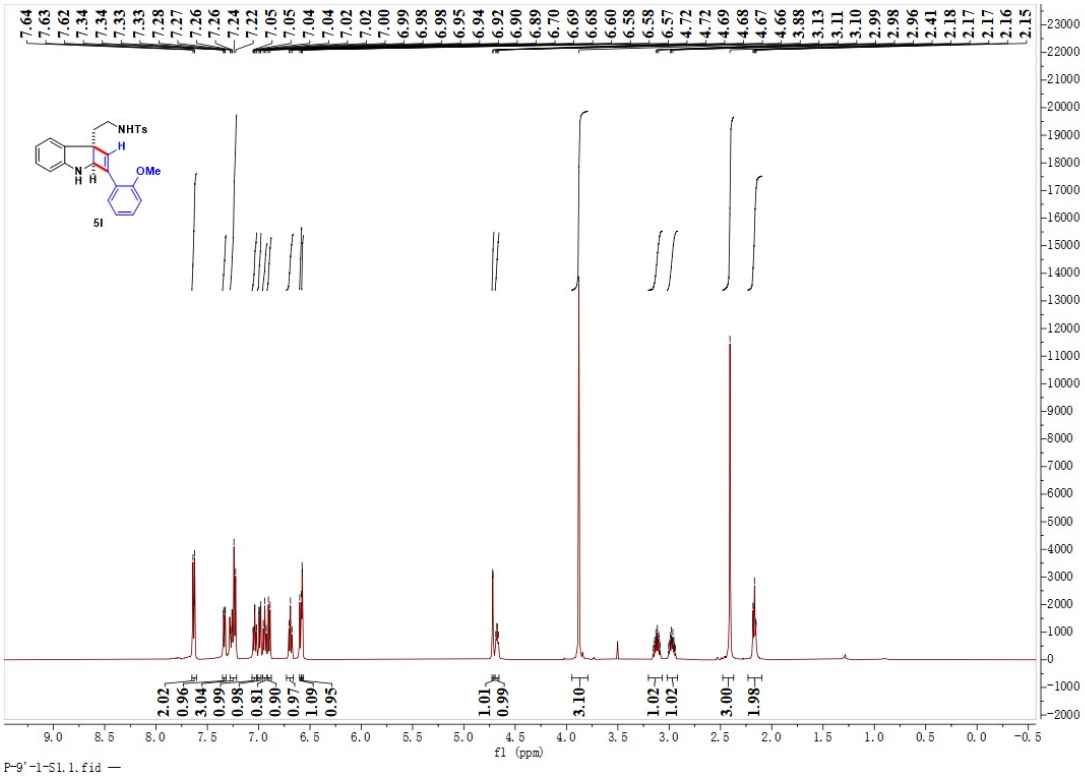


Figure S76. The ^{13}C-NMR spectra copy of compound 5l.

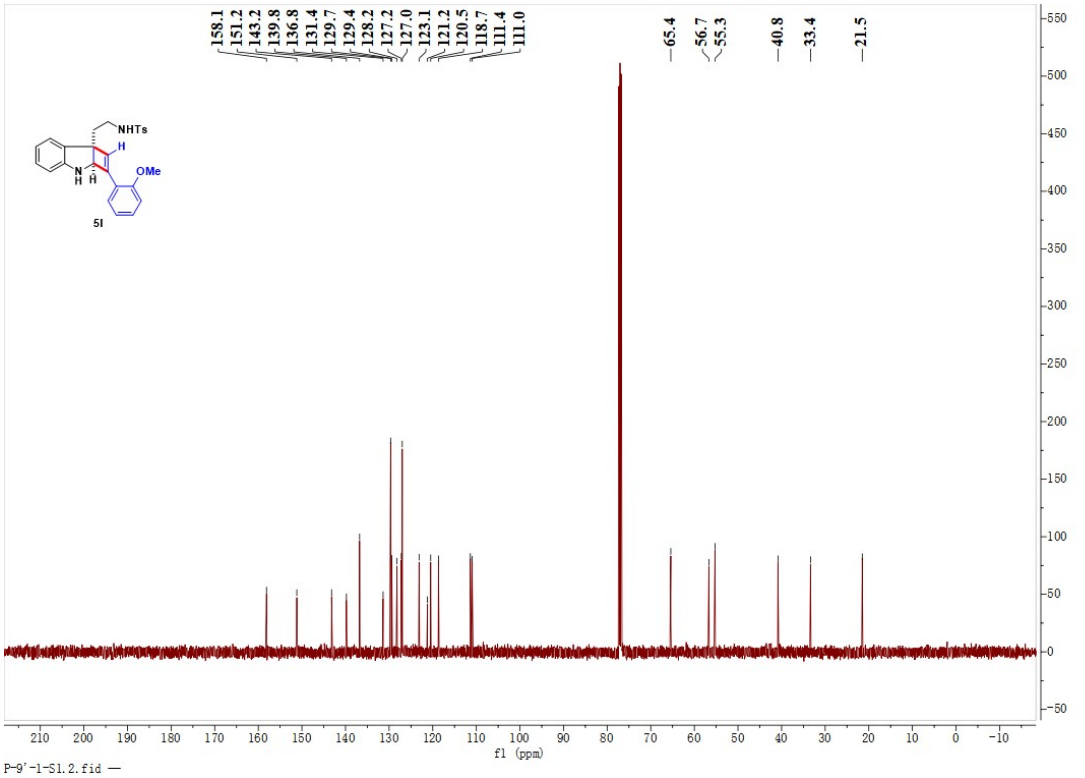


Figure S77. The ^{1}H-NMR spectra copy of compound 5m.

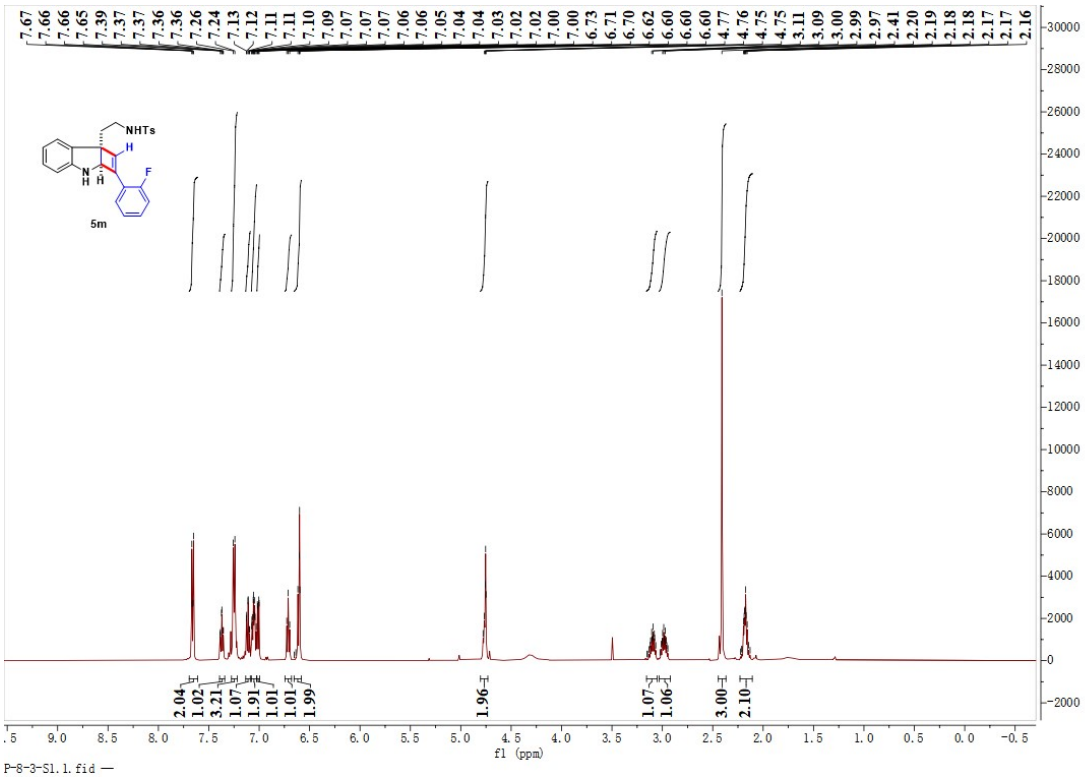


Figure S78. The ^{13}C-NMR spectra copy of compound 5m.

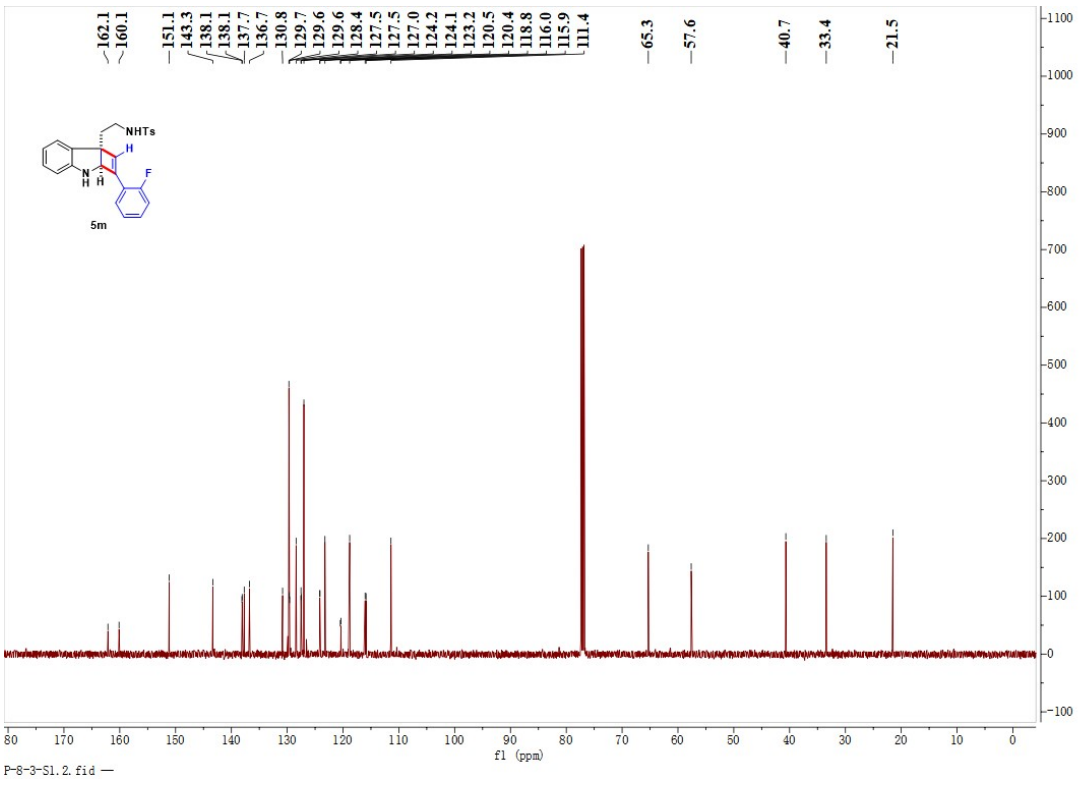


Figure S79. The ^{19}F-NMR spectra copy of compound 5m.

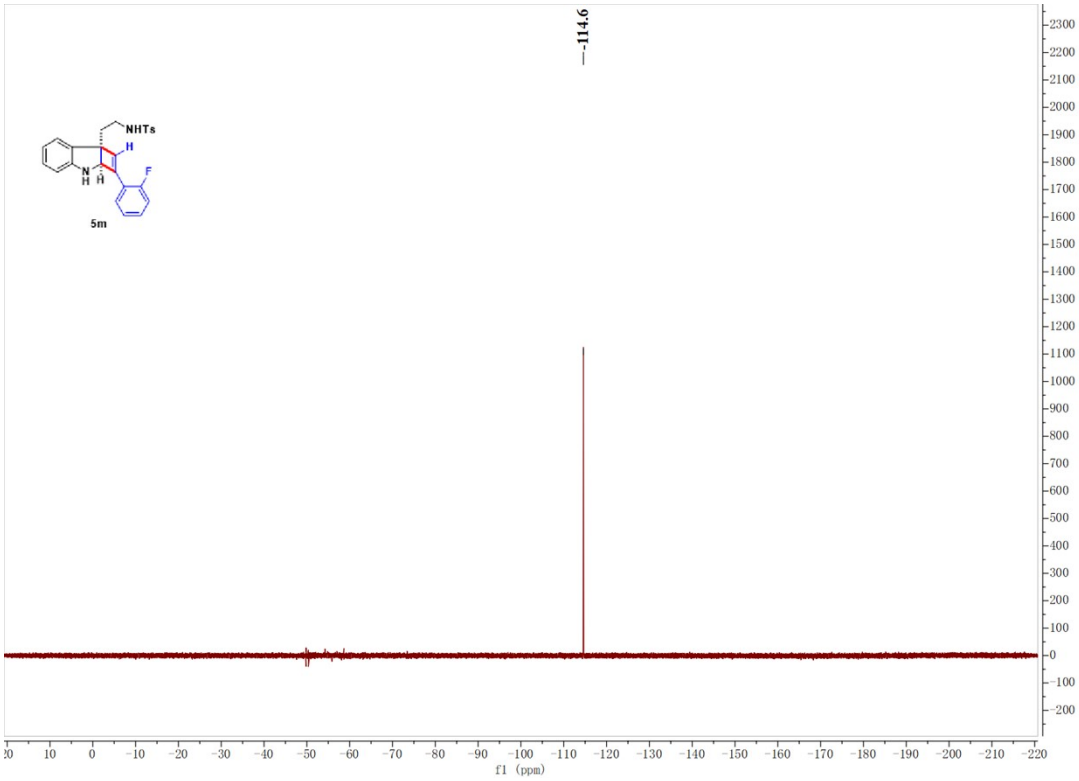


Figure S80. The ^{1}H-NMR spectra copy of compound 5n.

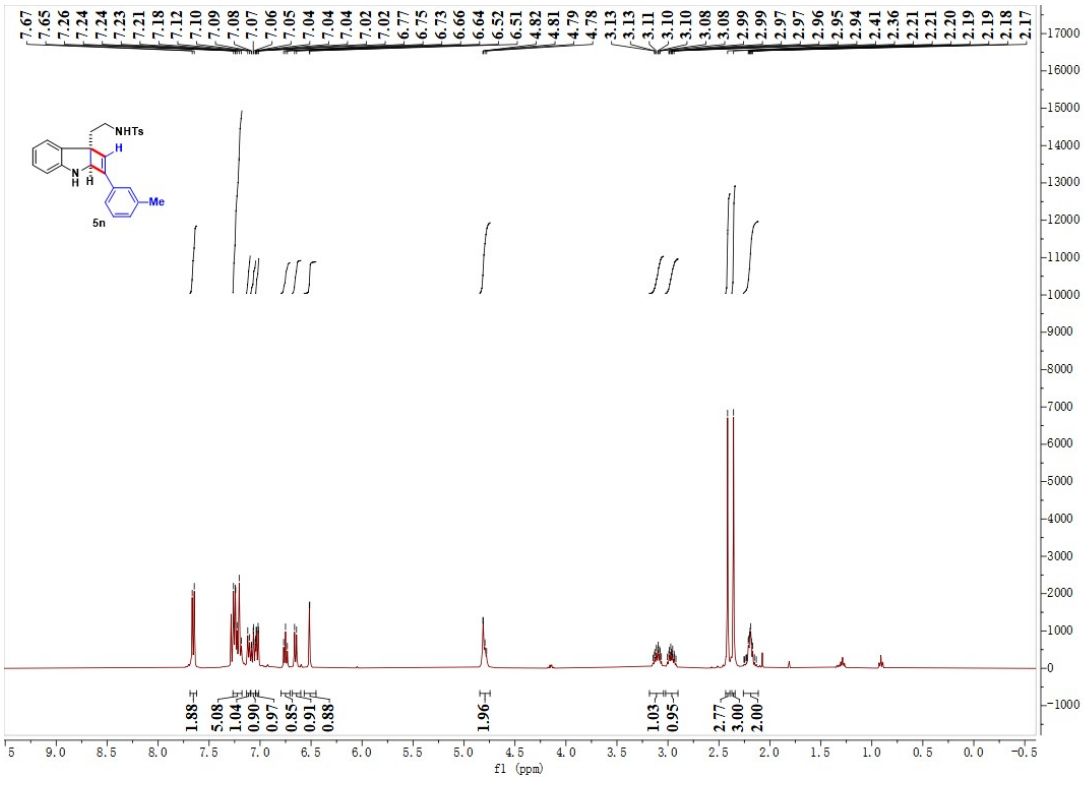


Figure S81. The ^{13}C-NMR spectra copy of compound 5n.

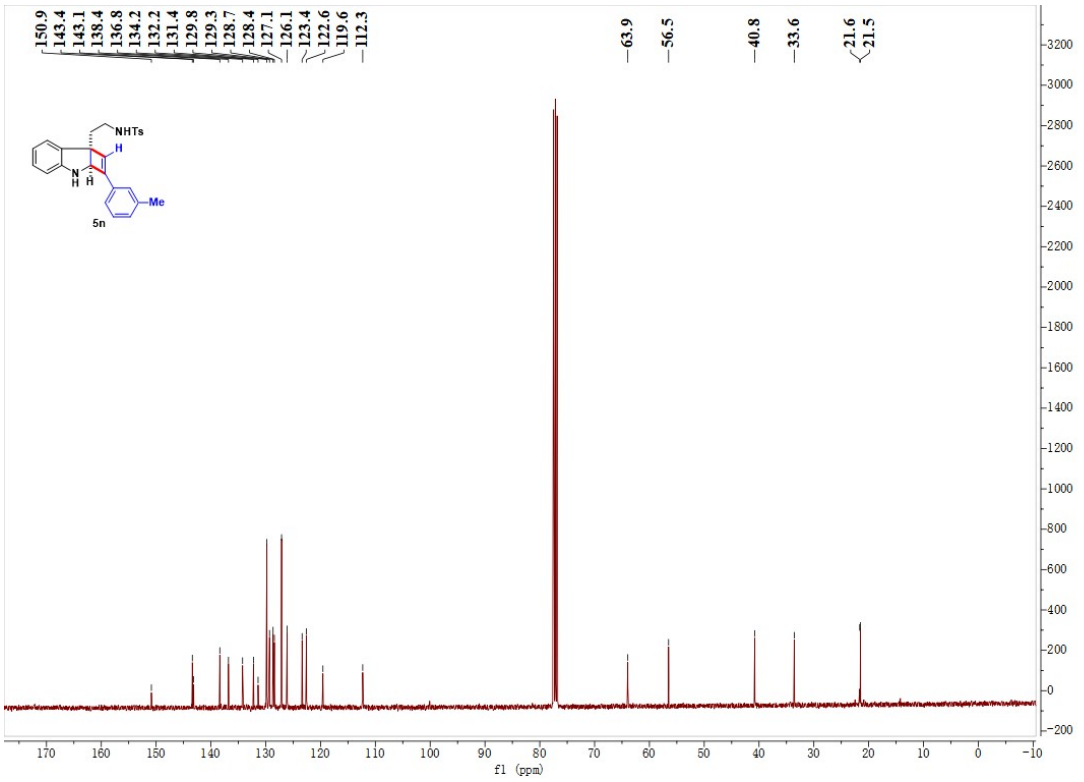


Figure S82. The ^{1}H-NMR spectra copy of compound 5o.

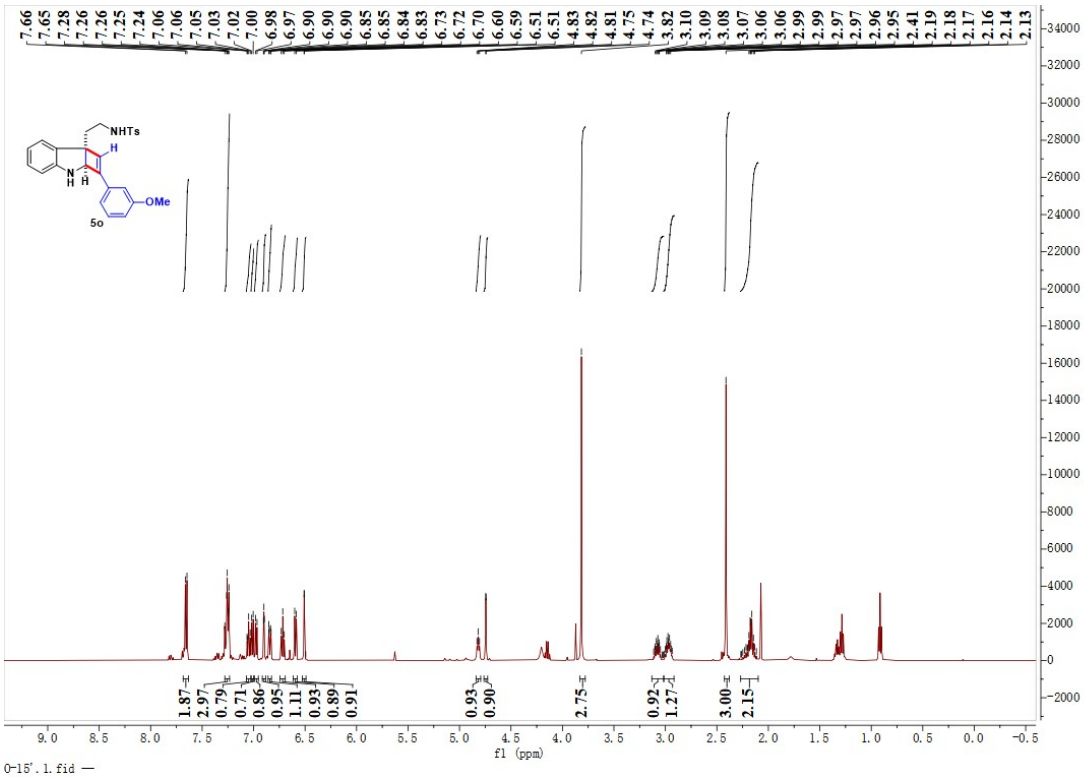


Figure S83. The ^{13}C-NMR spectra copy of compound 5o.

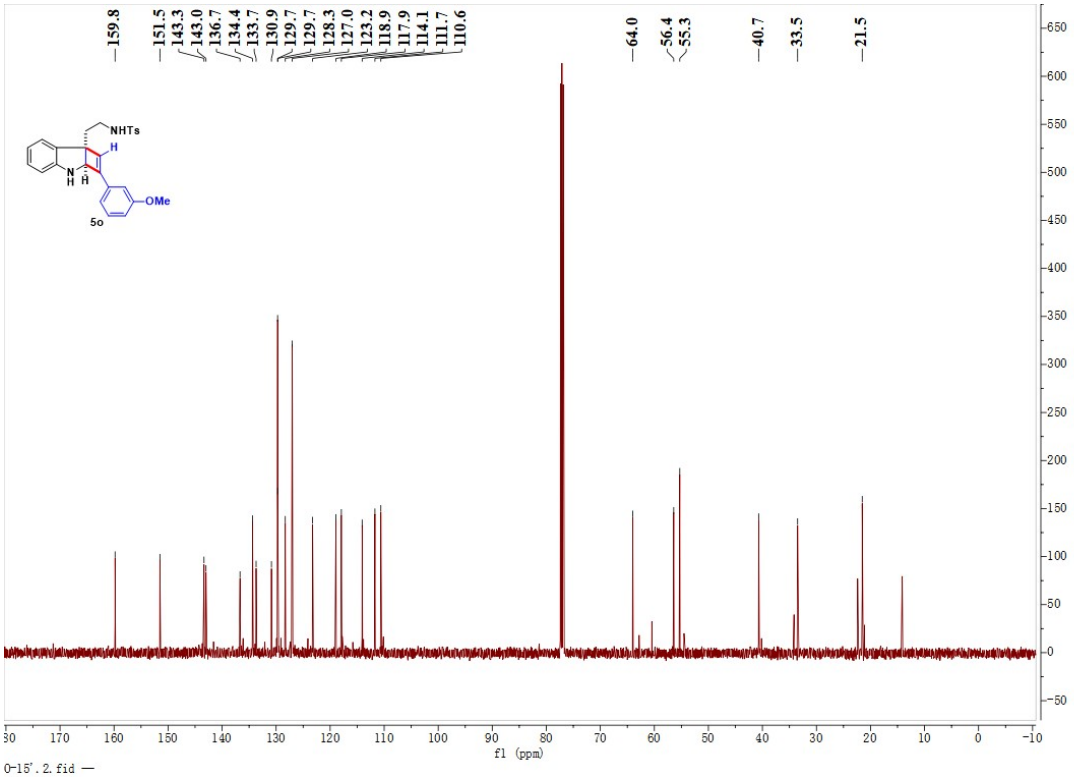


Figure S84. The ^{1}H-NMR spectra copy of compound 5p.

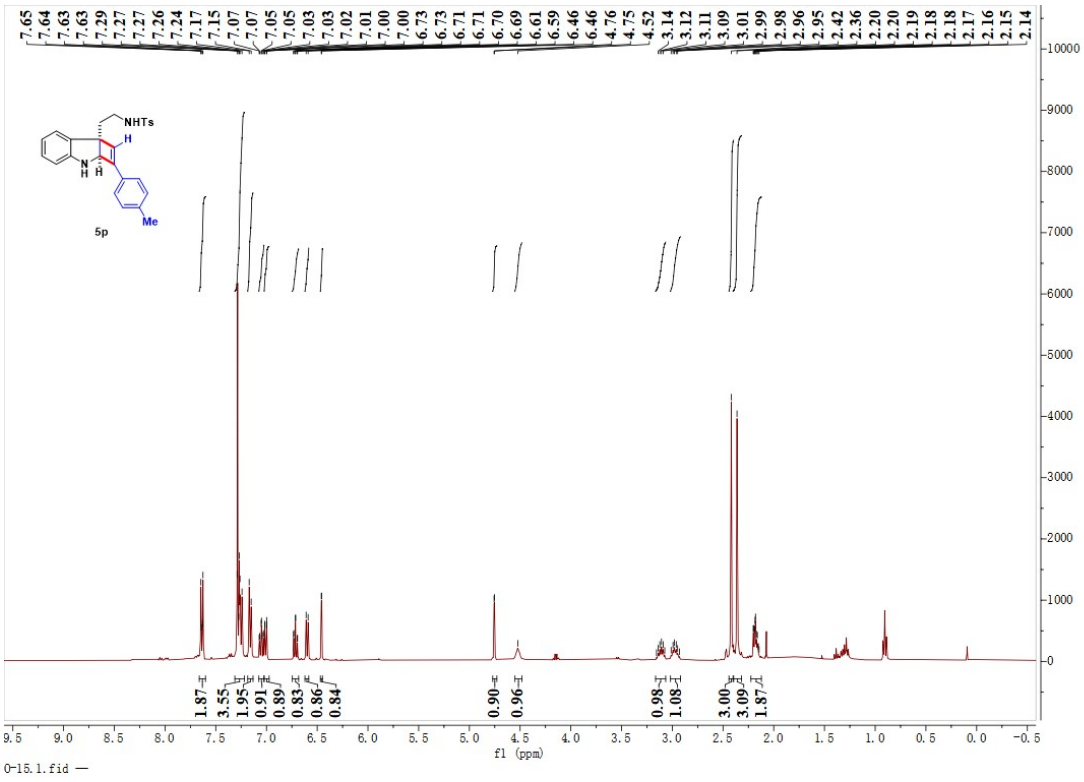


Figure S85. The ^{13}C-NMR spectra copy of compound 5p.

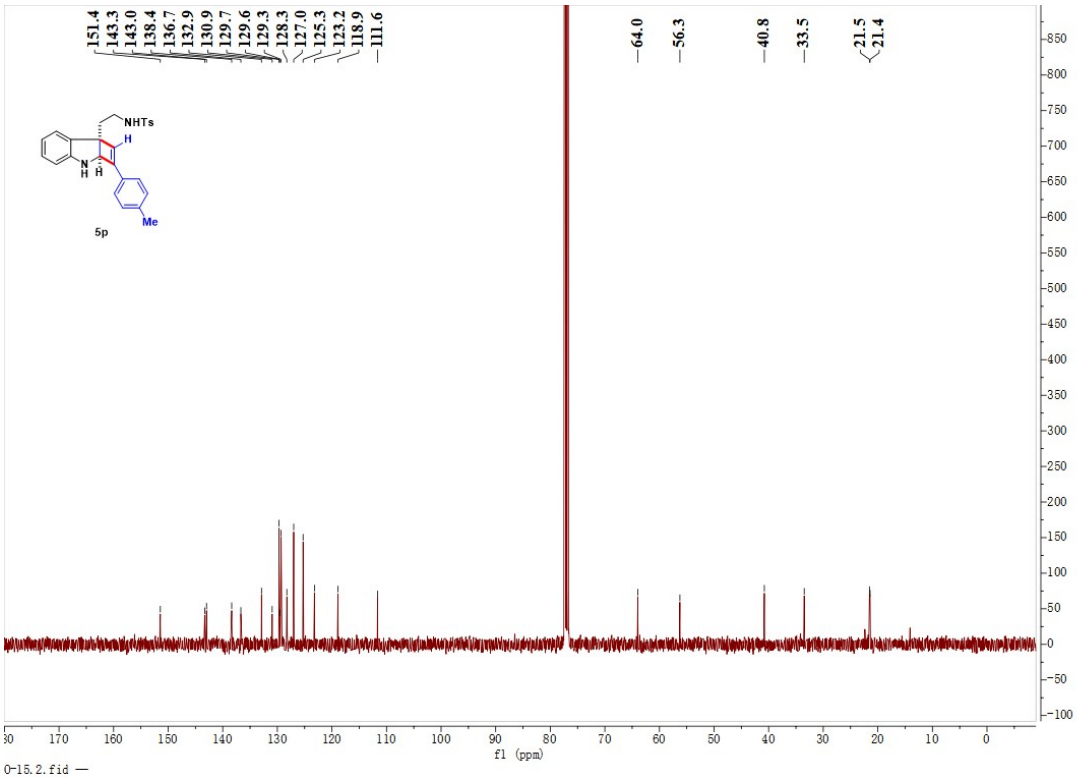


Figure S86. The ^{1}H-NMR spectra copy of compound 6a.

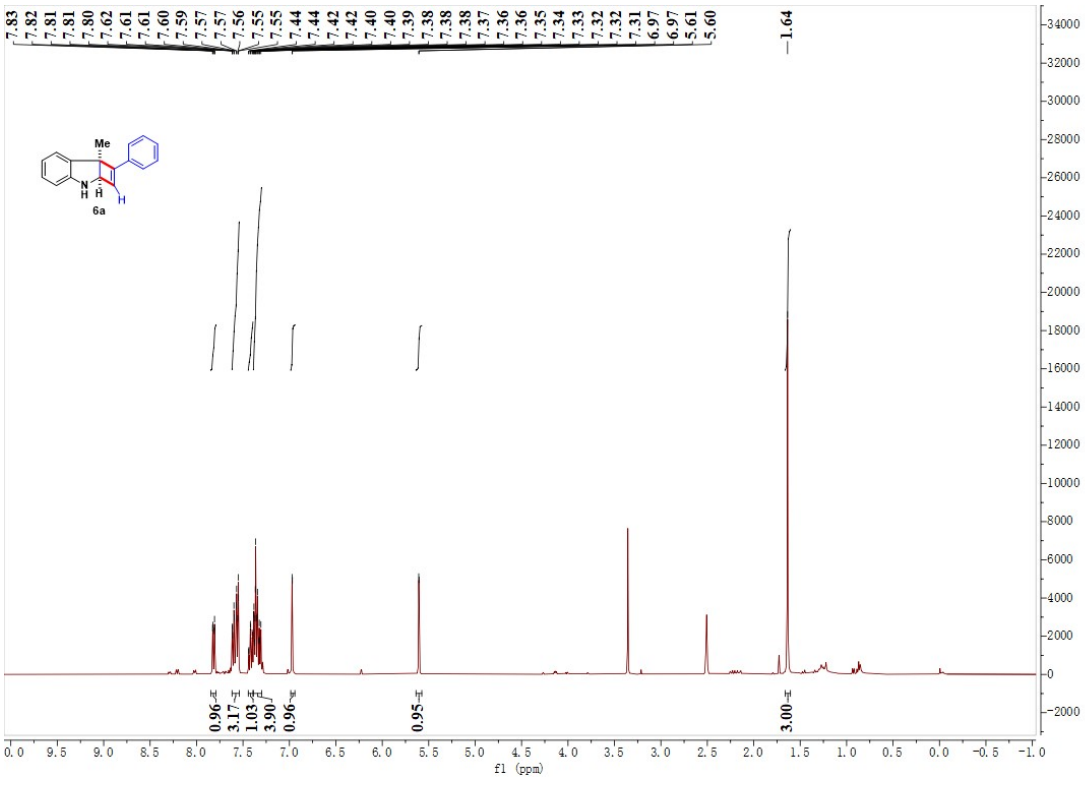


Figure S87. The ^{13}C-NMR spectra copy of compound 6a.

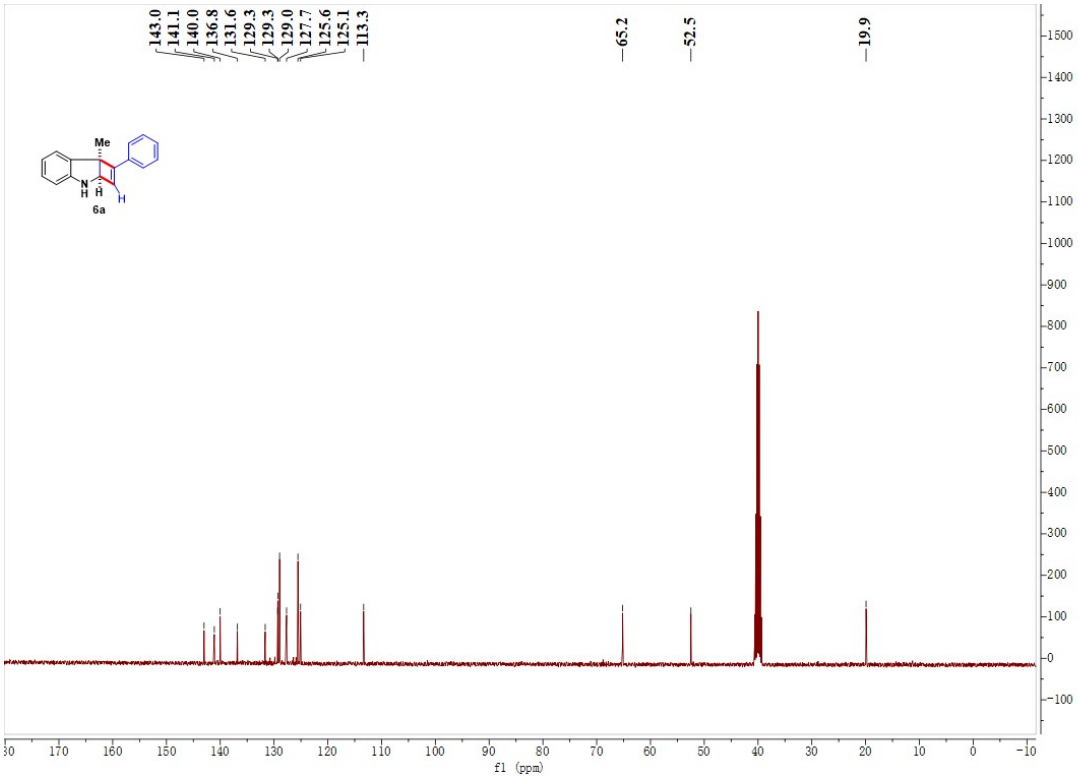


Figure S88. The H/H-COSY spectra copy of compound 6a.

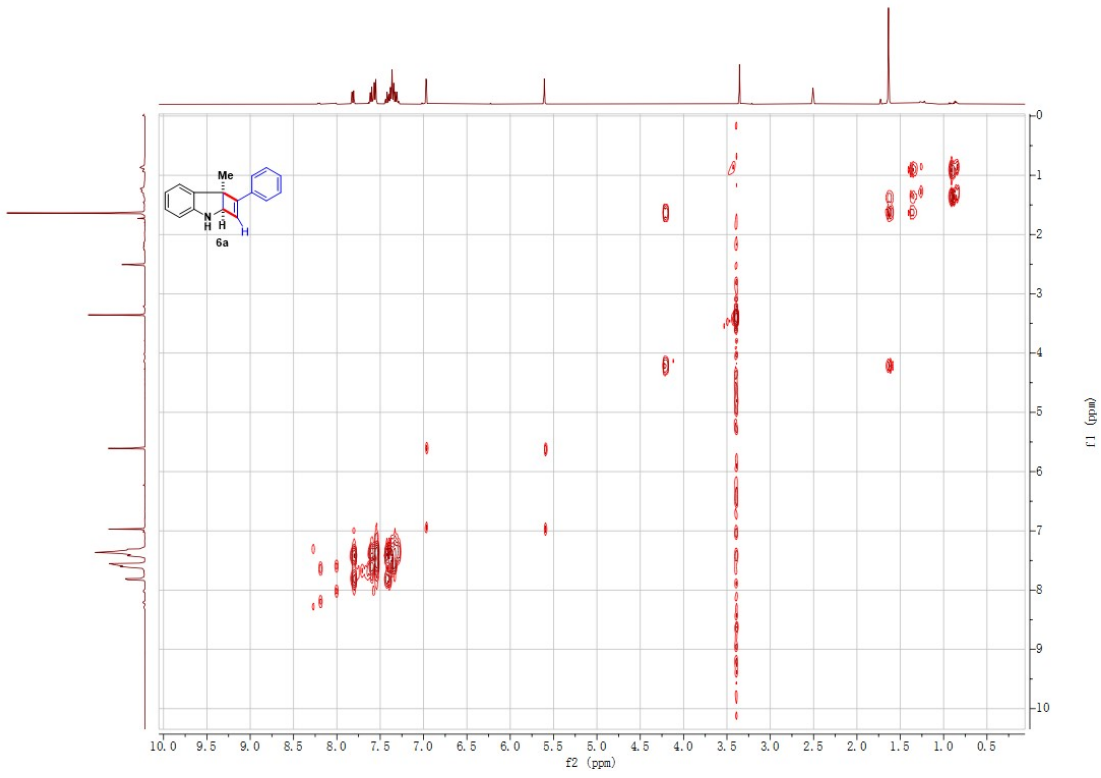


Figure S89. The HSQC spectra copy of compound 6a.

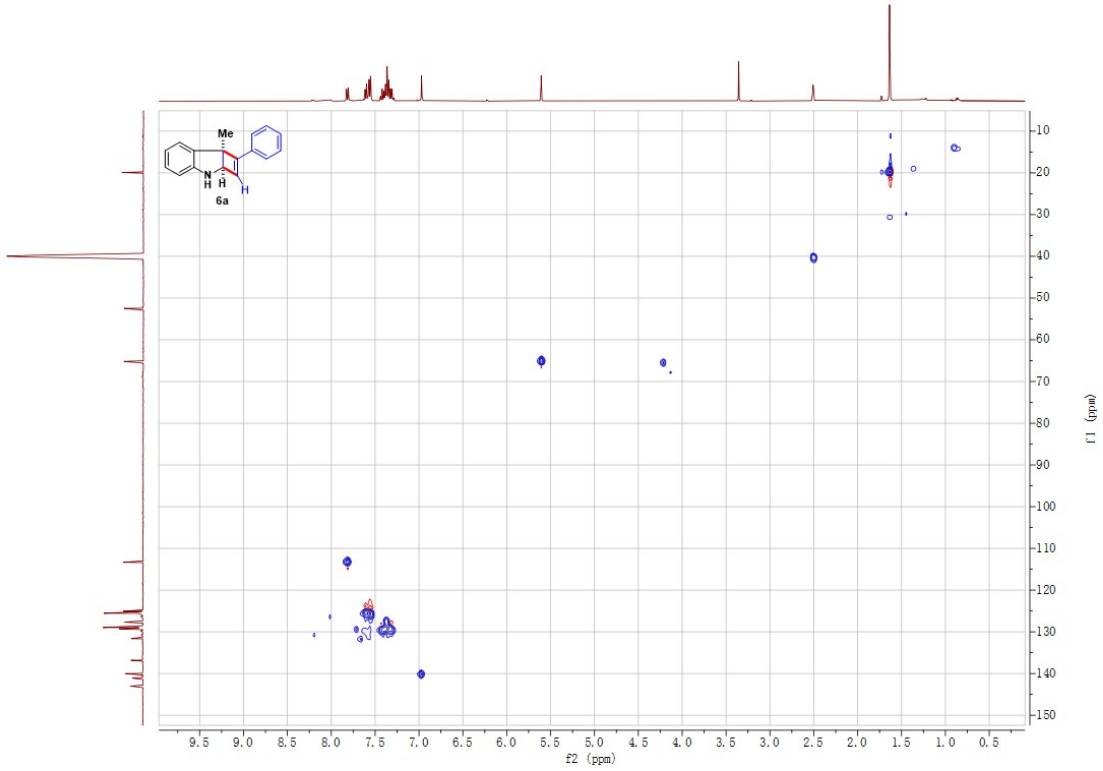


Figure S90. The HMBC spectra copy of compound 6a.

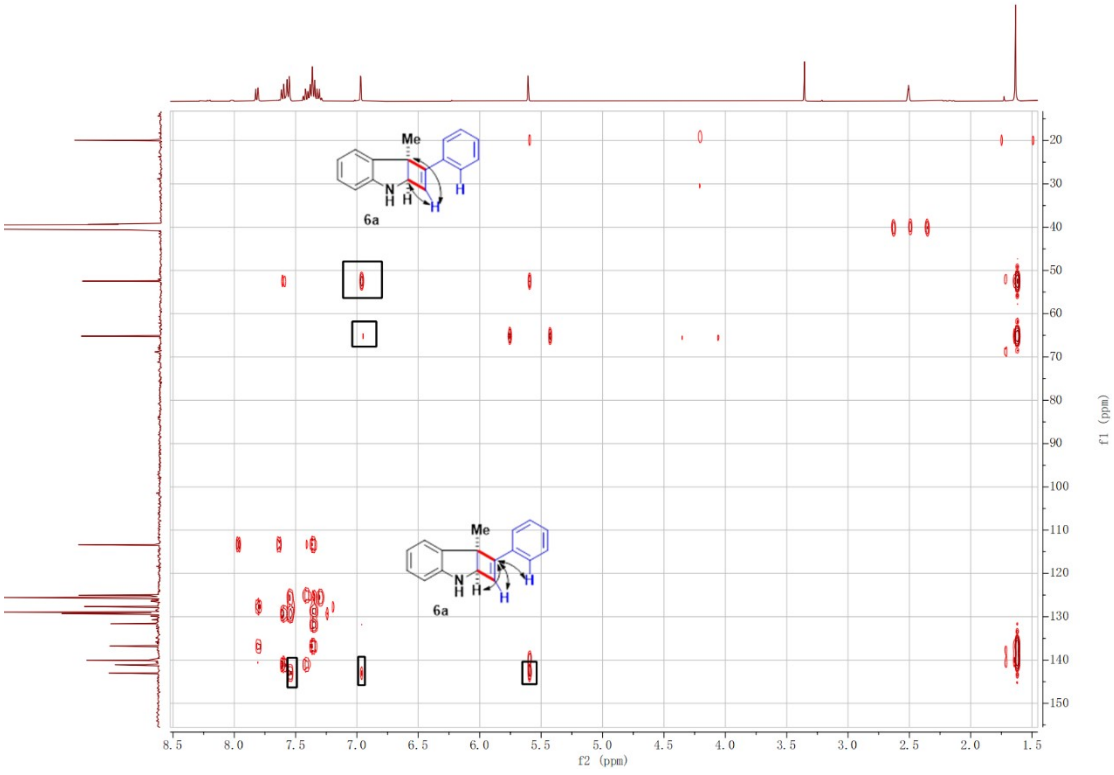


Figure S91. The DEPT-135 spectra copy of compound 6a.

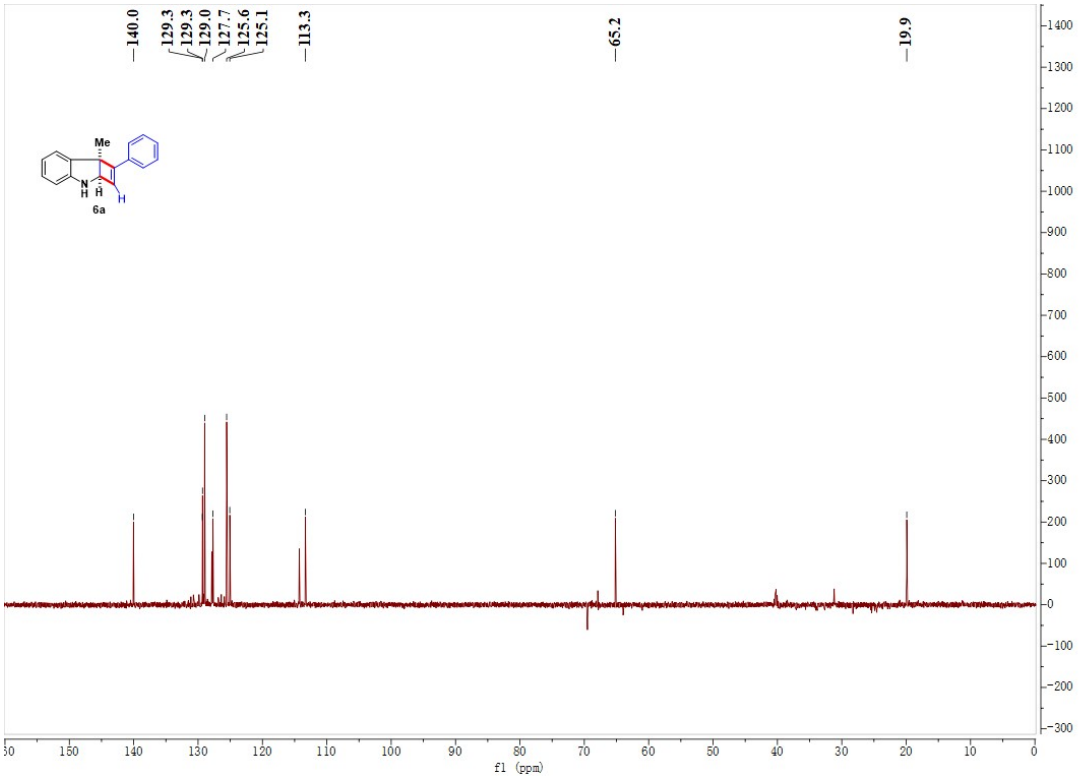


Figure S92. The NOESY spectra copy of compound 6a.

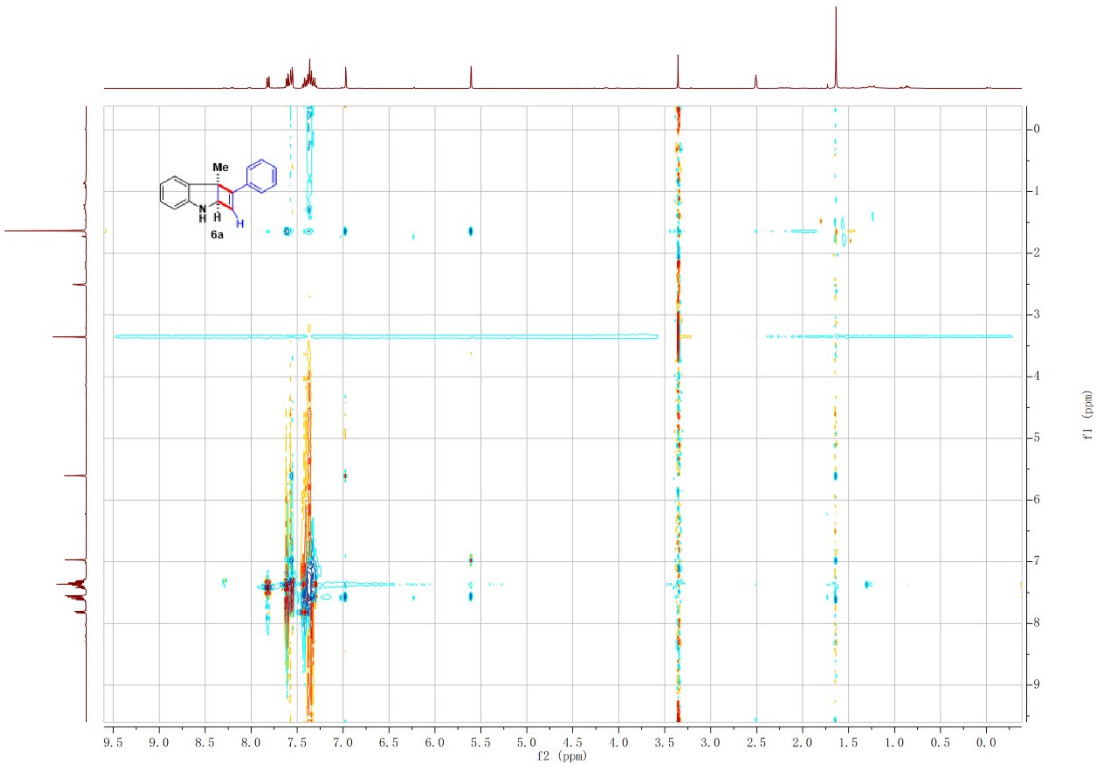


Figure S93. The ^{1}H-NMR spectra copy of compound 6k.

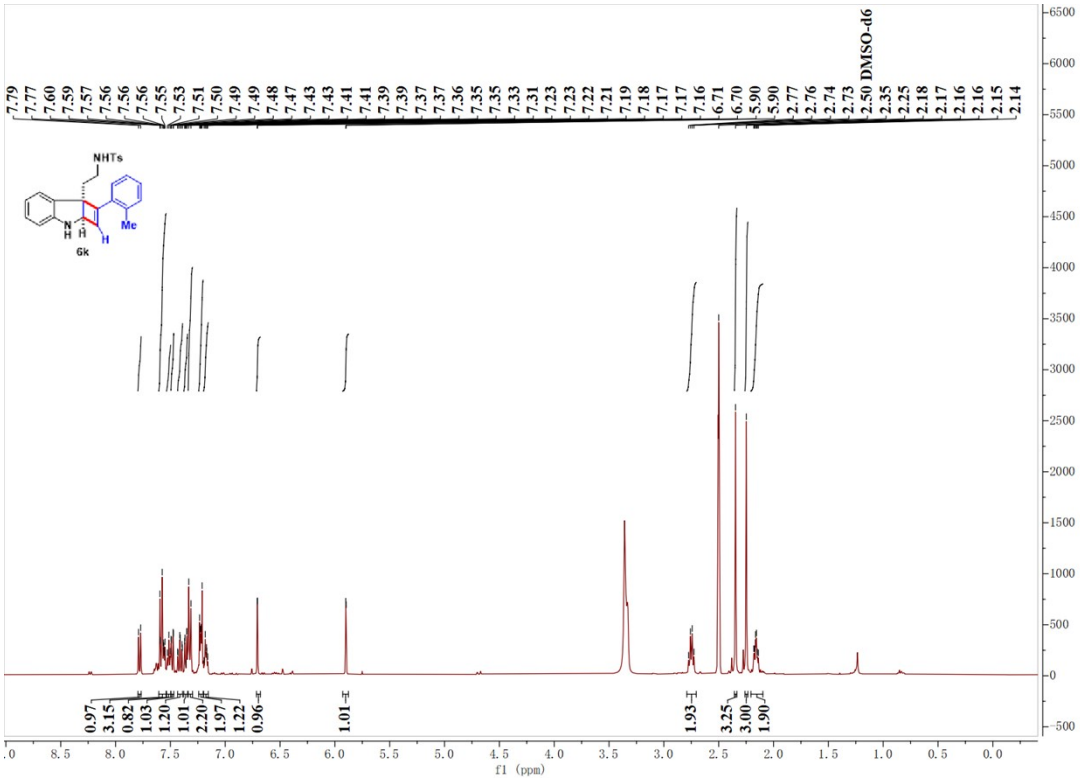


Figure S94. The ^{13}C-NMR spectra copy of compound 6k.

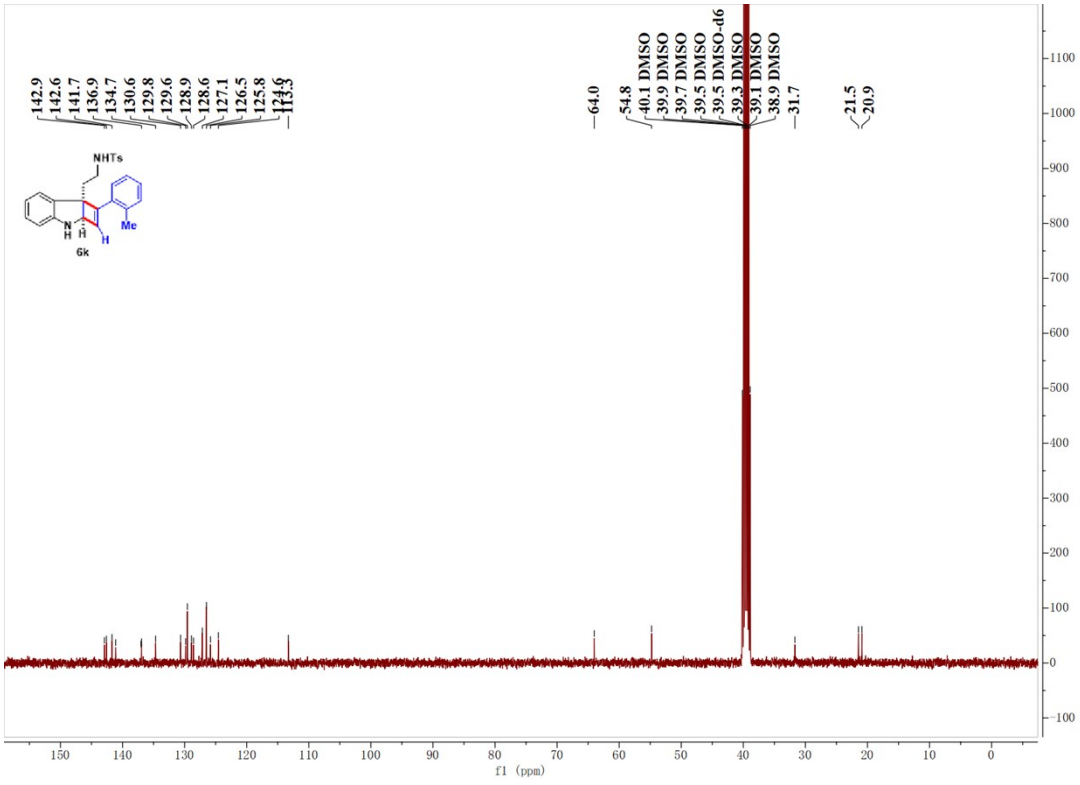


Figure S95. The DEPT-135 spectra copy of compound 6k.

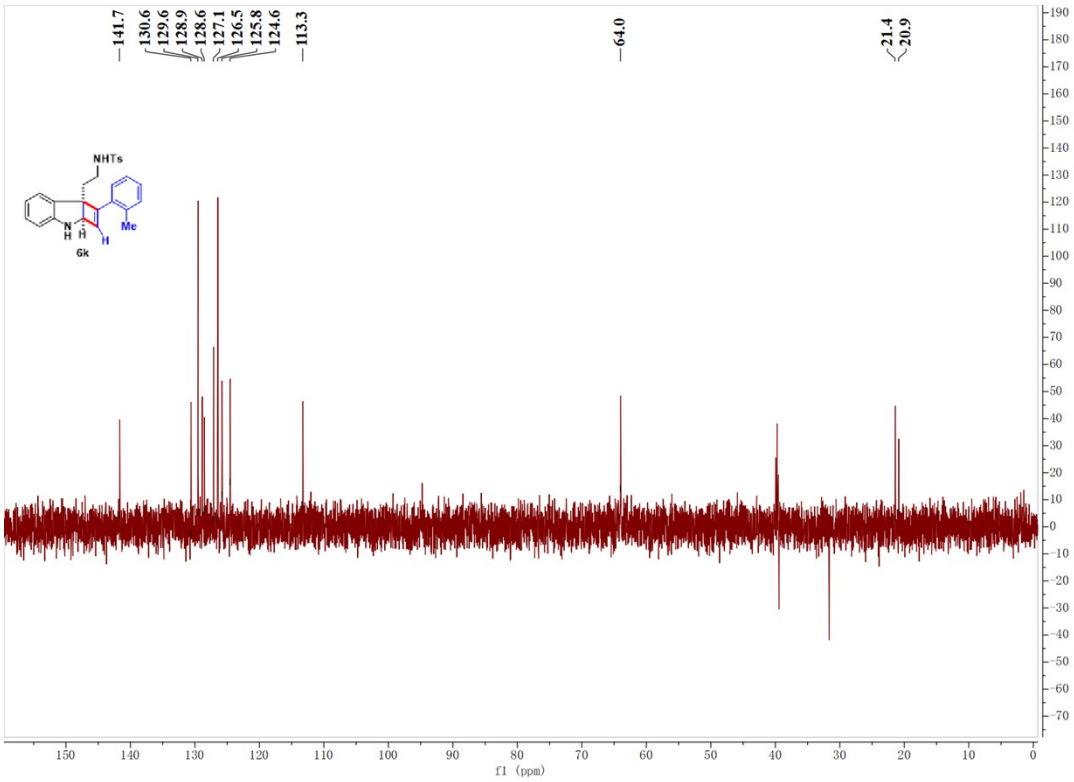


Figure S96. The H/H-COSY spectra copy of compound 6k.

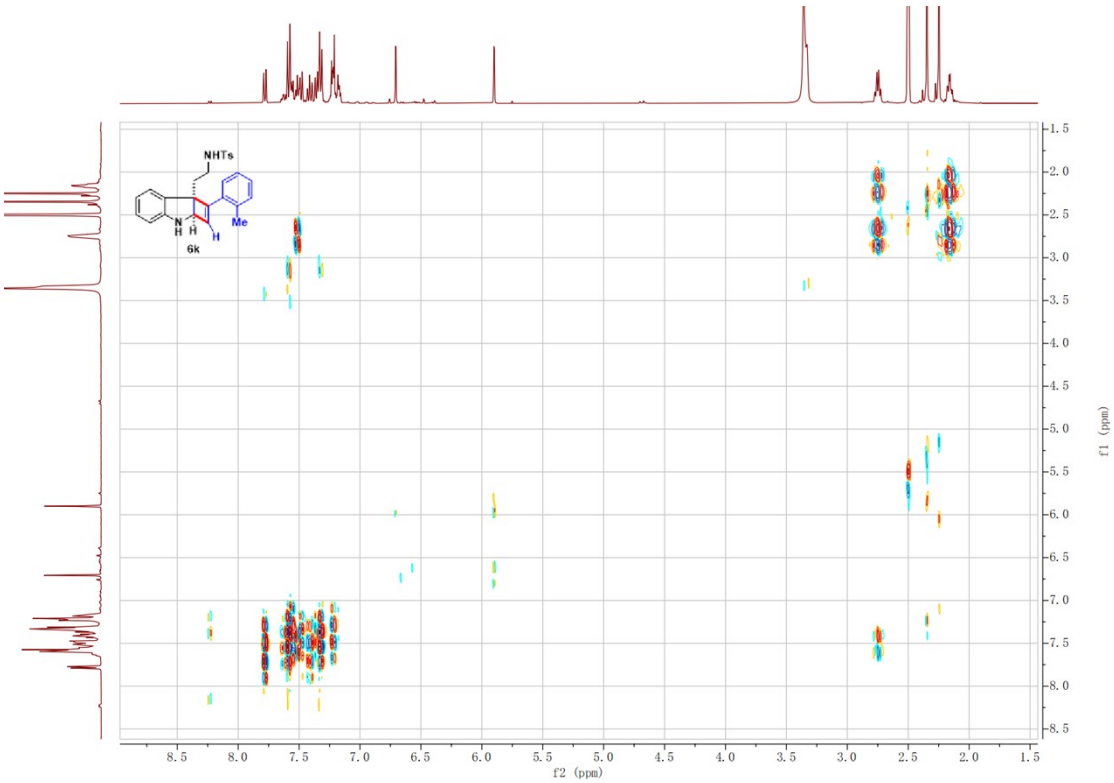


Figure S97. The HSQC spectra copy of compound 6k.

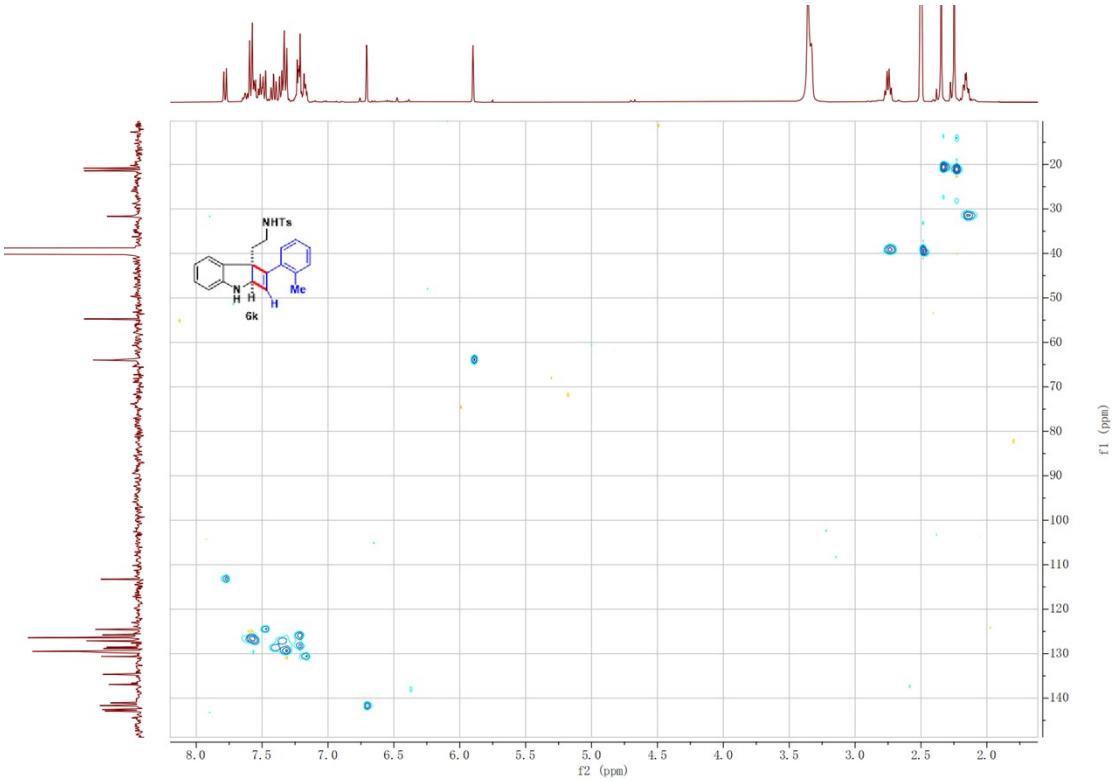


Figure S98. The HMBC spectra copy of compound 6k.

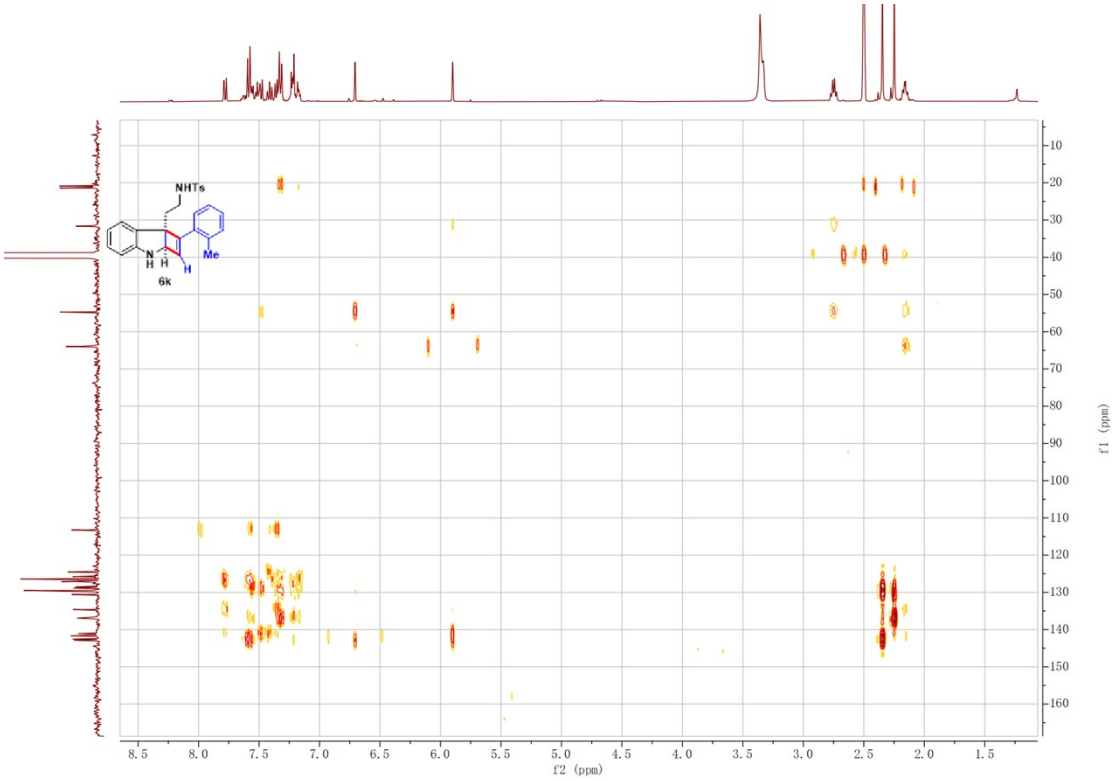


Figure S99. The NOESY spectra copy of compound 6k.

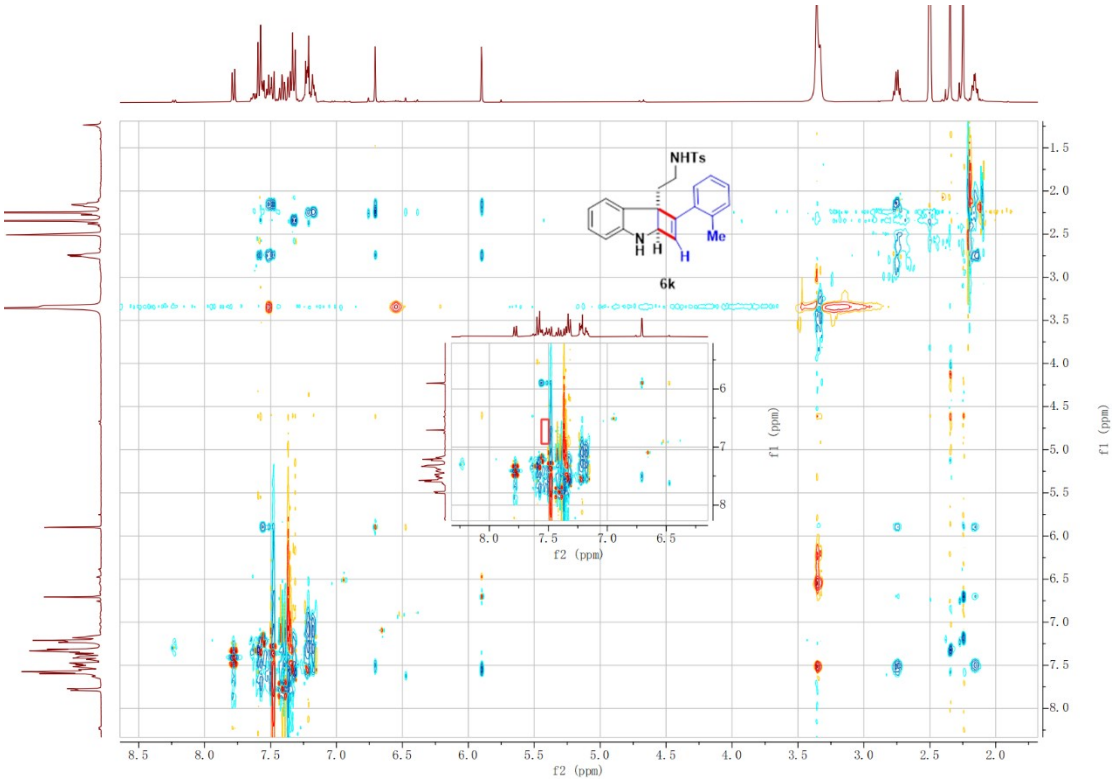


Figure S100. The ^{1}H-NMR spectra copy of compound 6p.

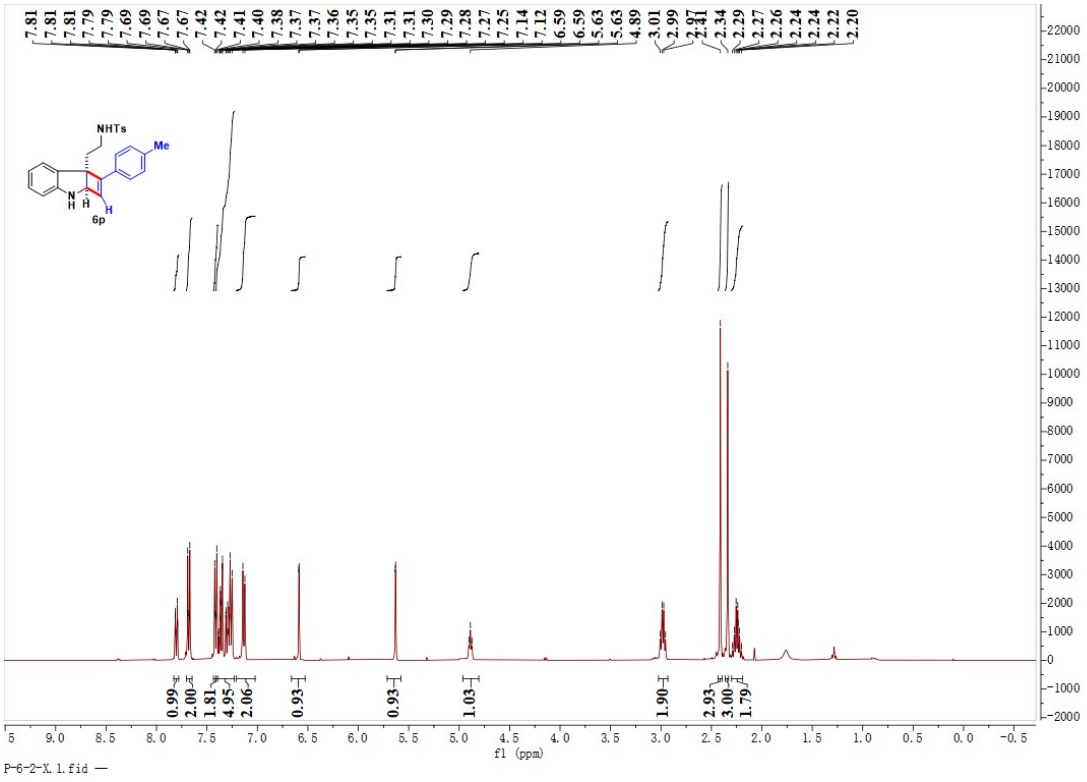


Figure S101. The ^{13}C-NMR spectra copy of compound 6p.

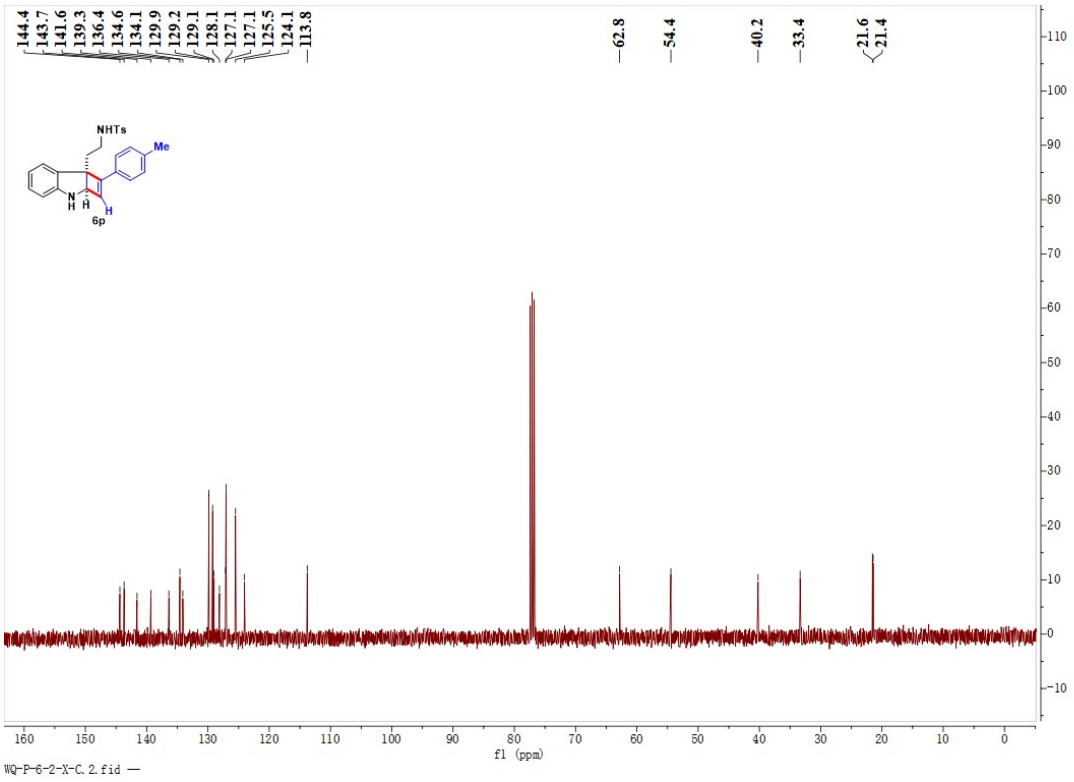


Figure S102. The ^{1}H-NMR spectra copy of compound 8.

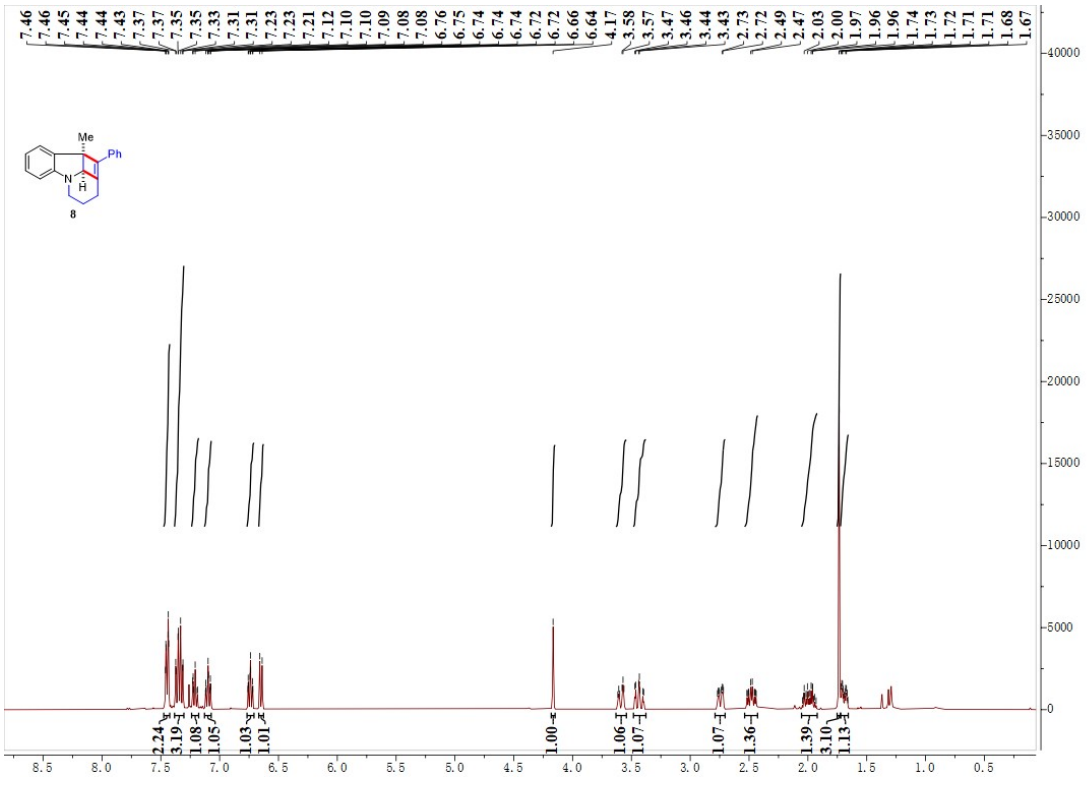


Figure S103. The ^{13}C-NMR spectra copy of compound 8.

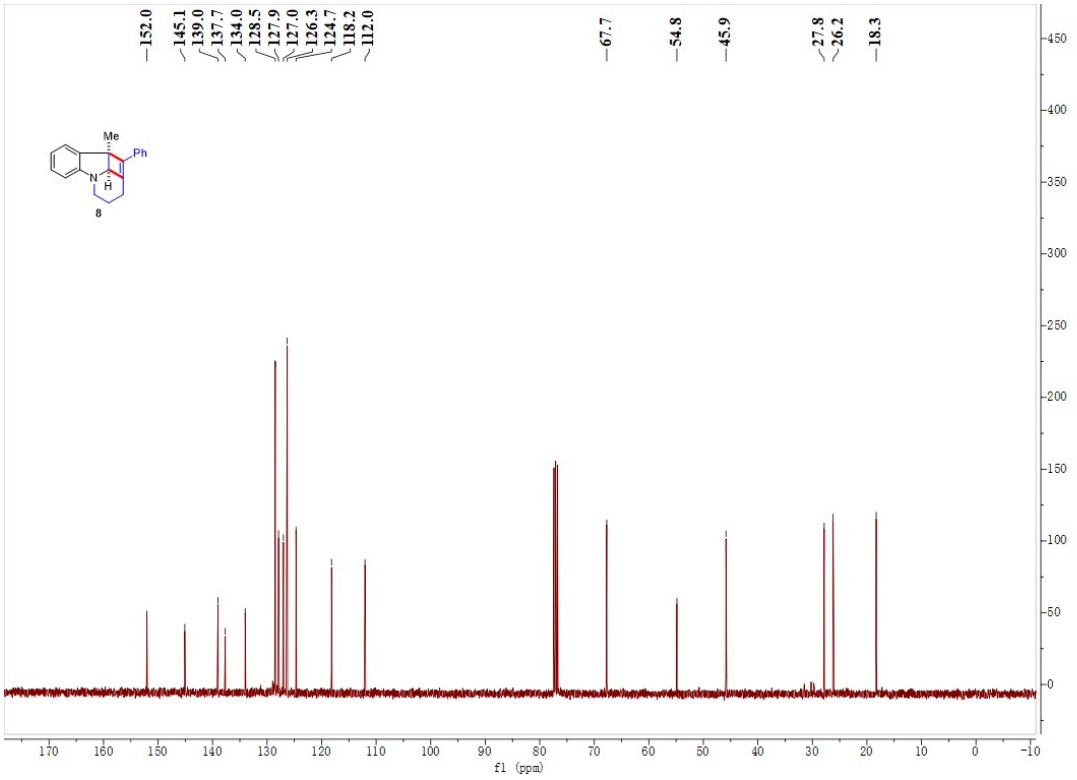


Figure S104. The ^{1}H-NMR spectra copy of compound 10.

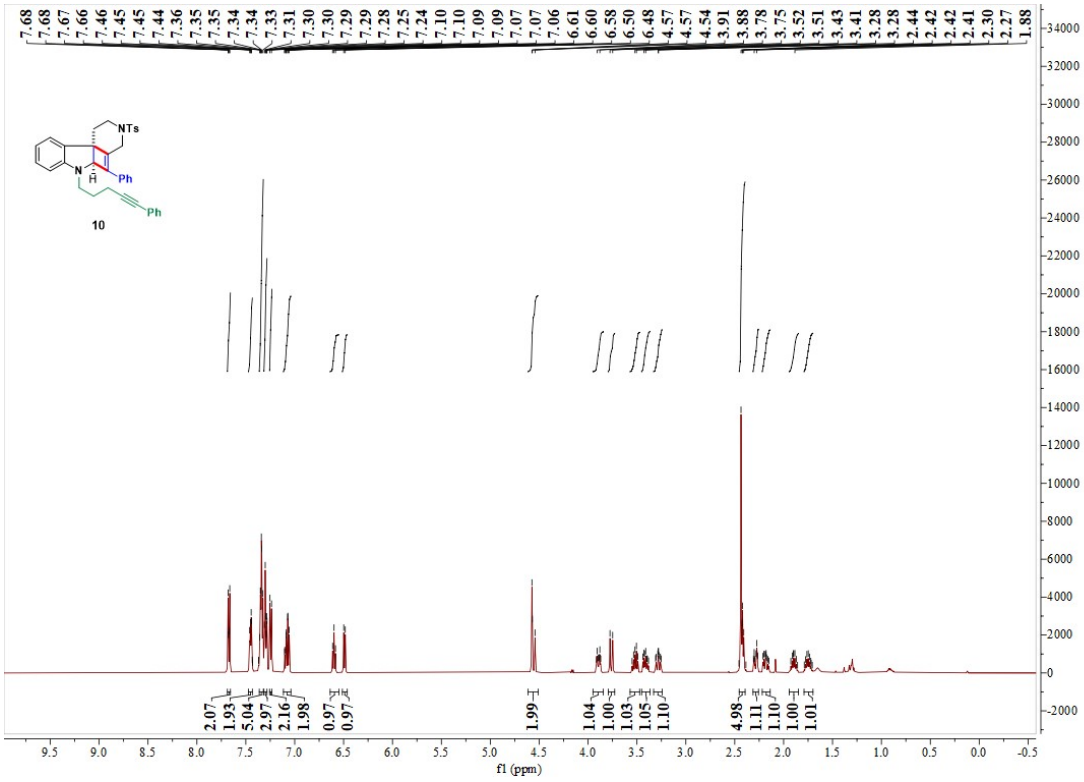


Figure S105. The ^{13}C-NMR spectra copy of compound 10.

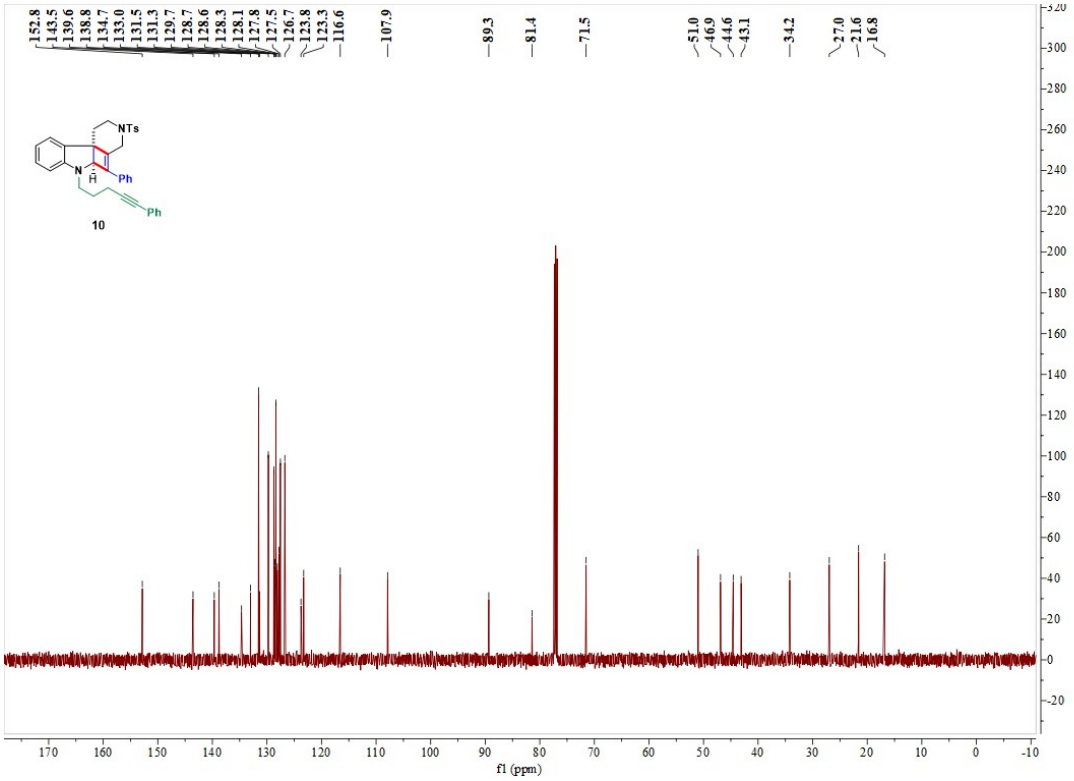


Figure S106. The ^{1}H-NMR spectra copy of compound 1a.

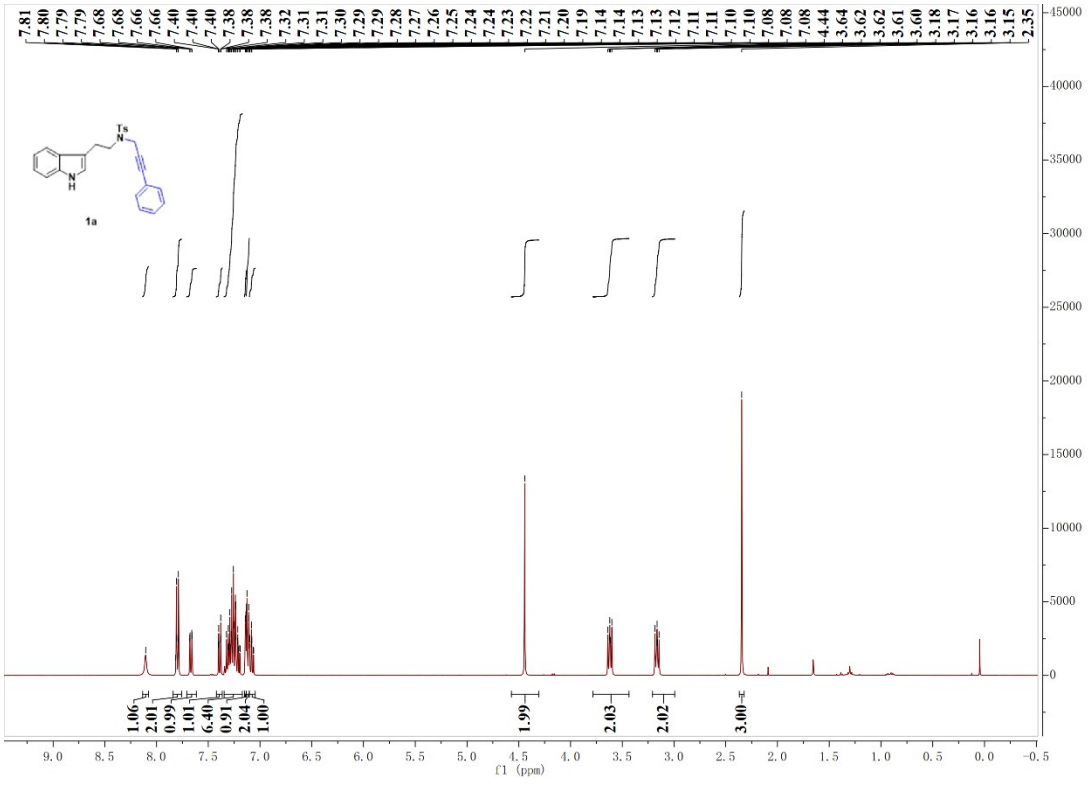


Figure S107. The ^{13}C-NMR spectra copy of compound 1a.

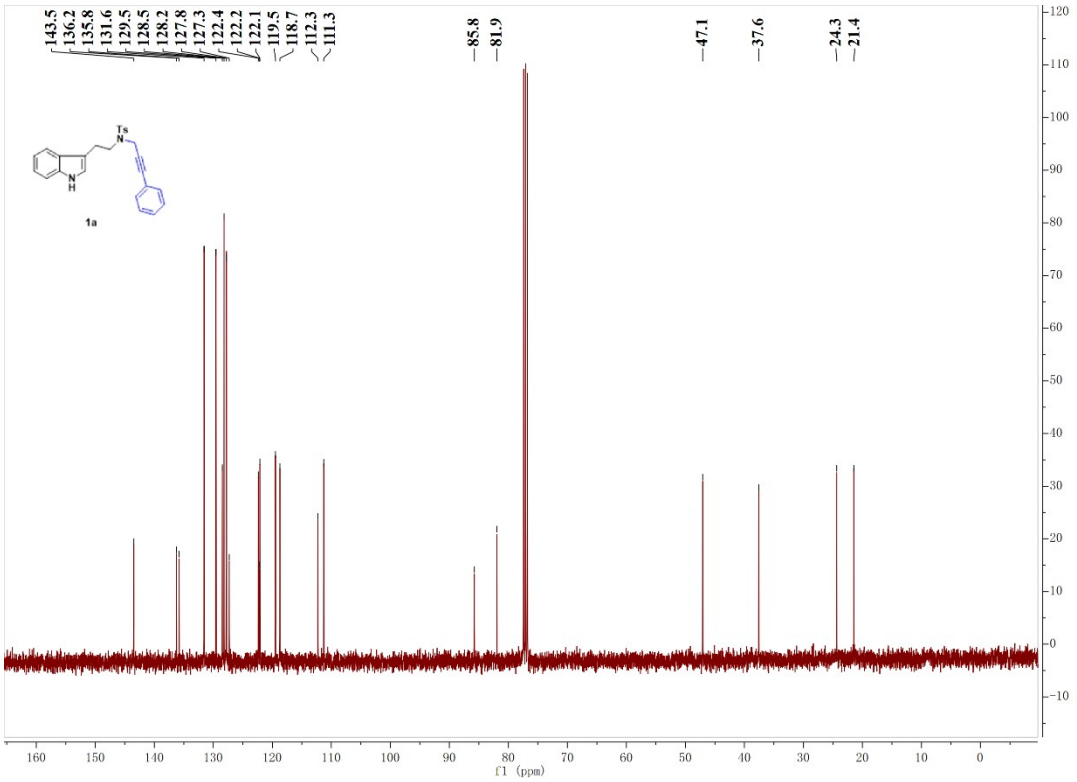


Figure S108. The ^{1}H-NMR spectra copy of compound 1b.

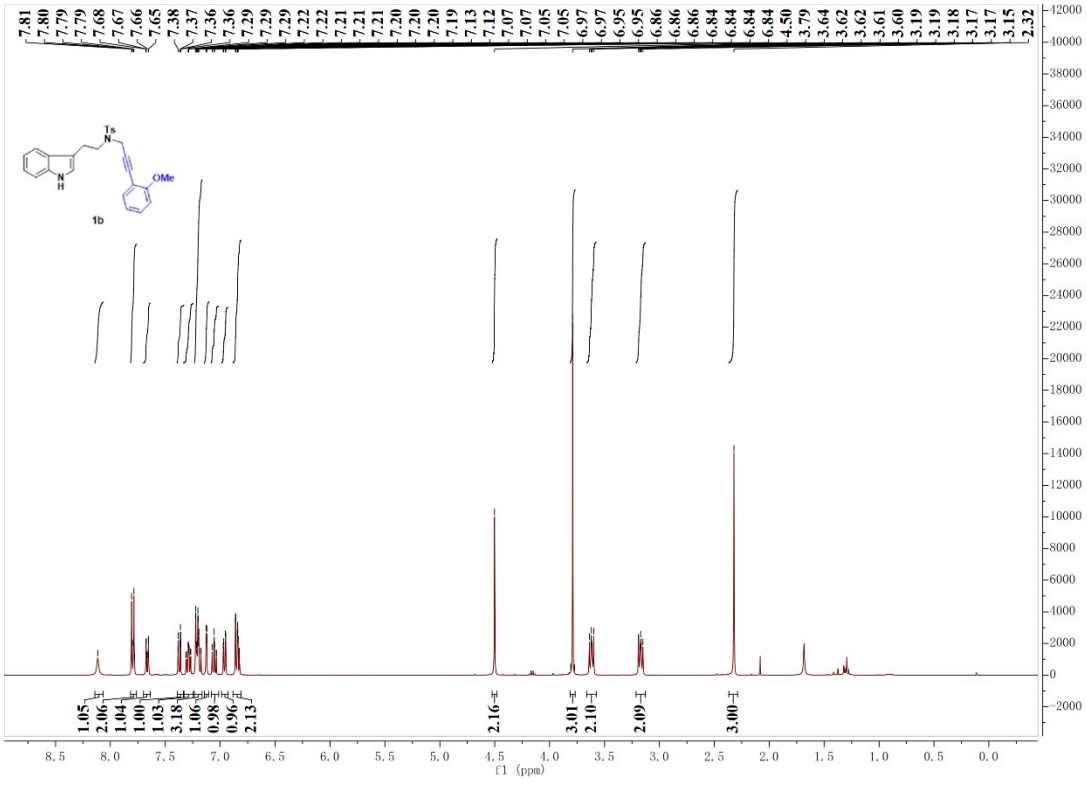


Figure S109. The ^{13}C-NMR spectra copy of compound 1b.

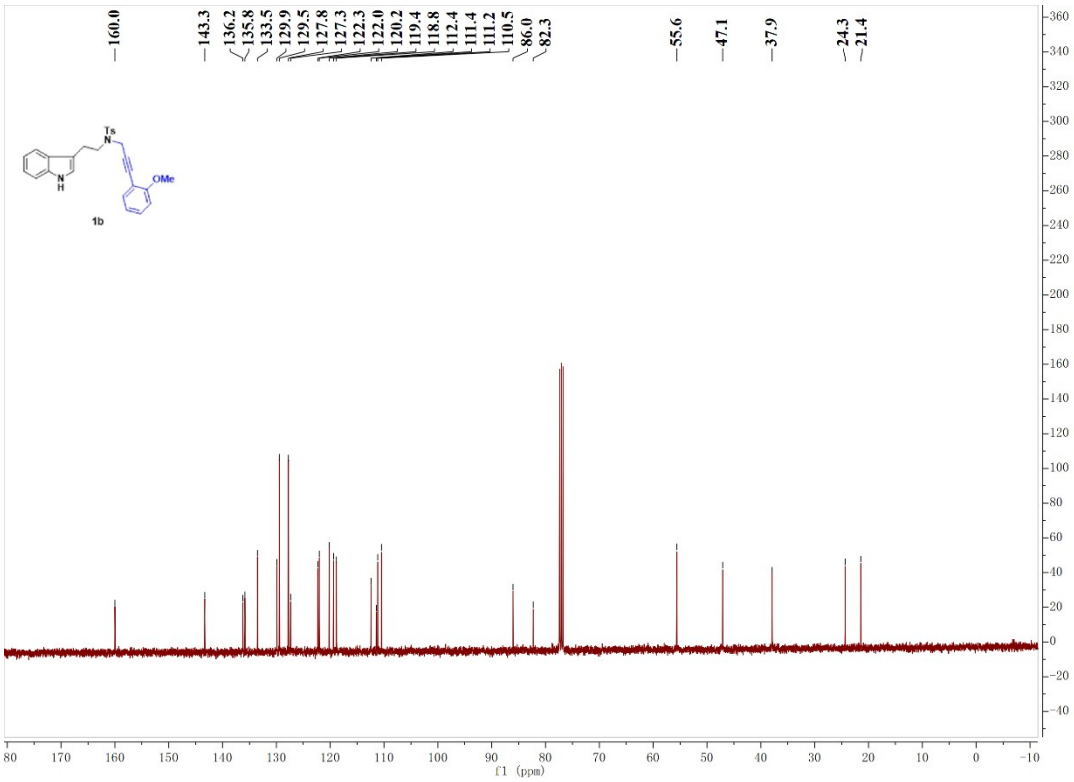


Figure S110. The ^{1}H-NMR spectra copy of compound 1c.

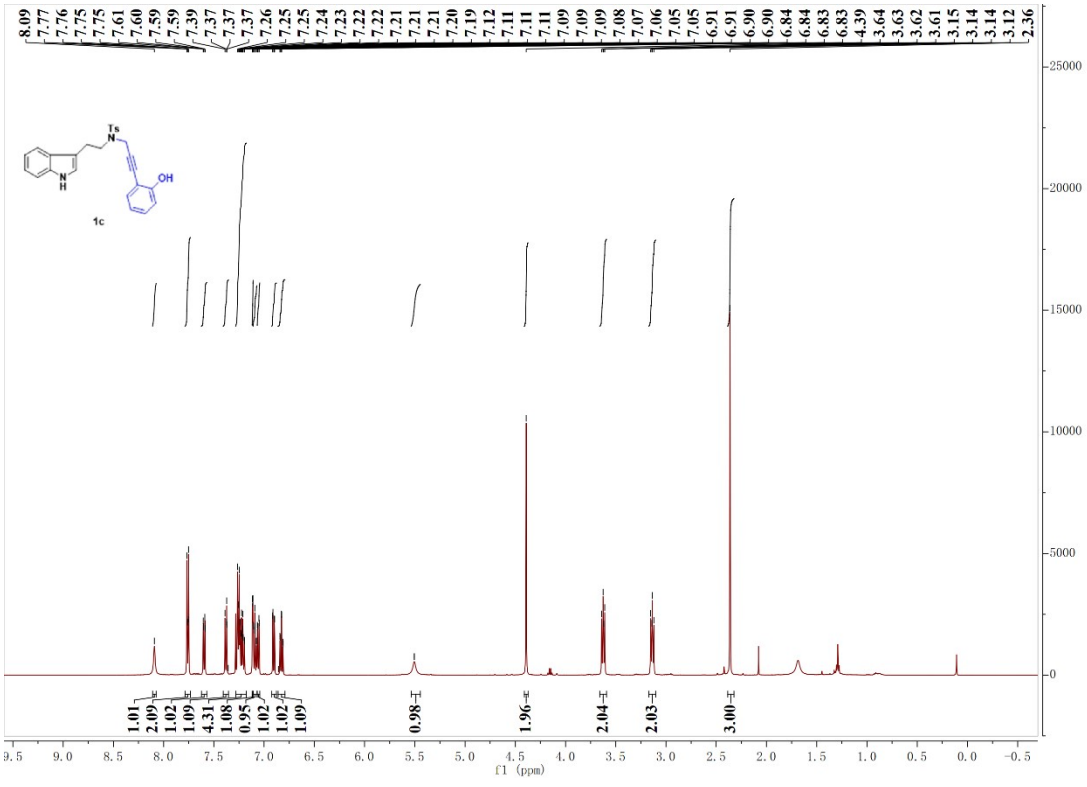


Figure S111. The ^{13}C-NMR spectra copy of compound 1c.

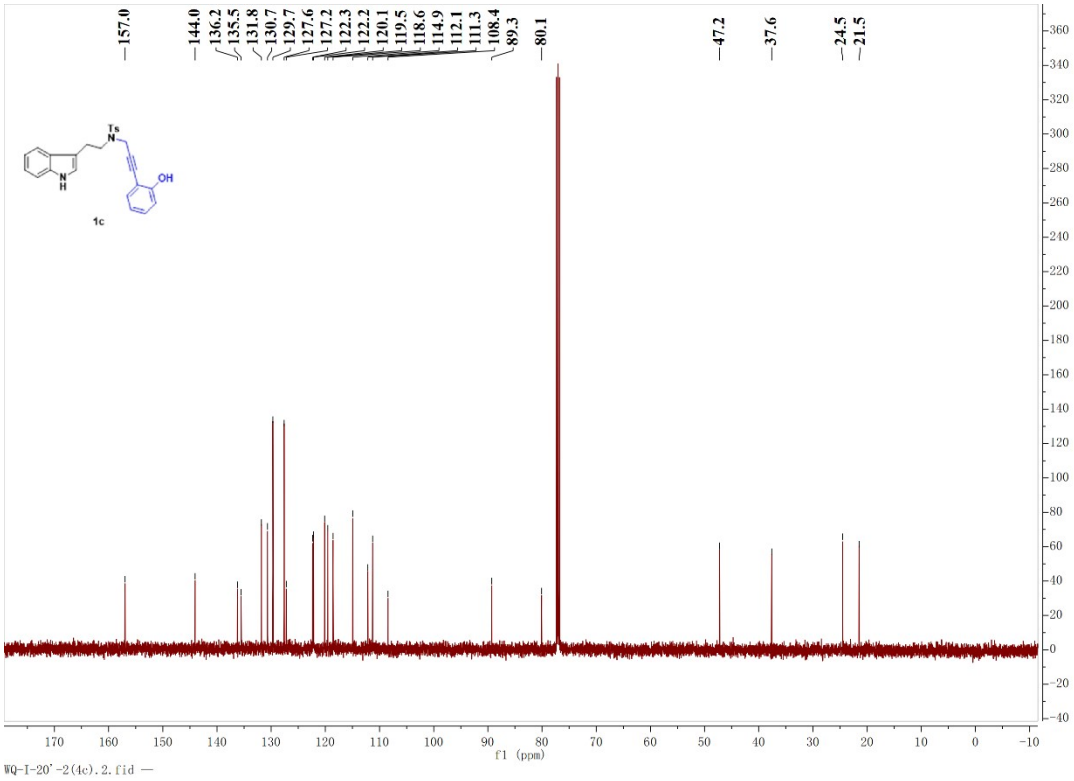


Figure S112. The ^{1}H-NMR spectra copy of compound 1d.

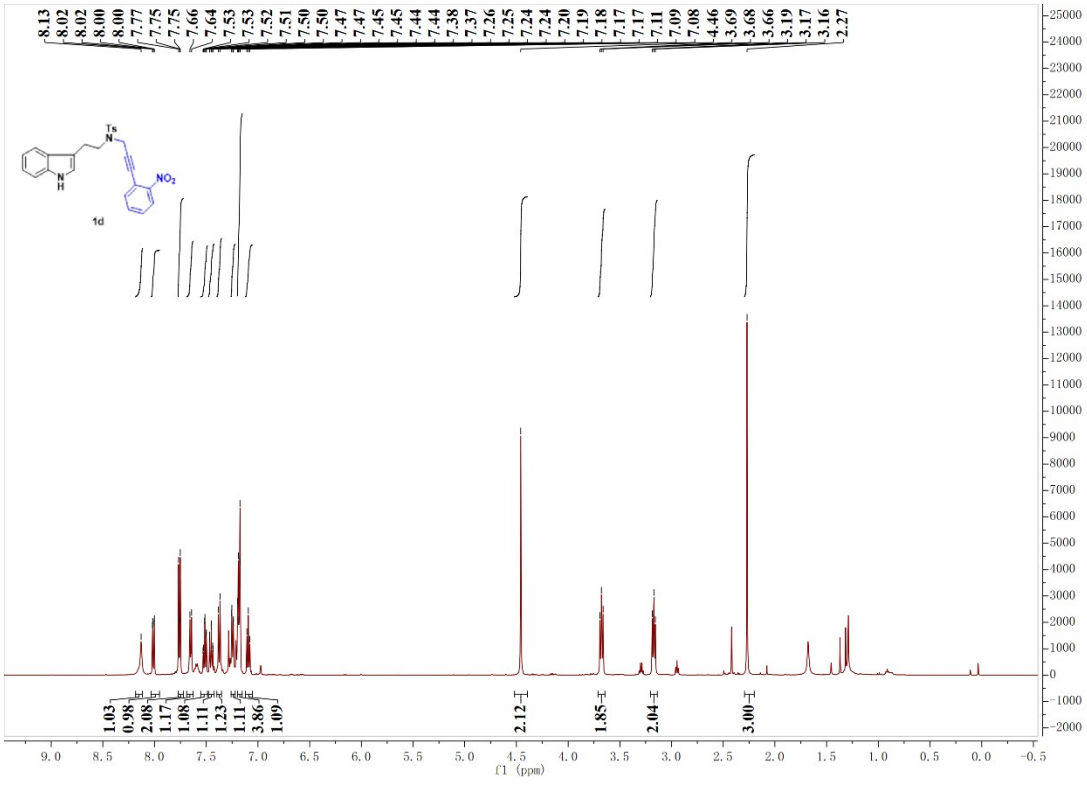


Figure S113. The ^{13}C-NMR spectra copy of compound 1d.

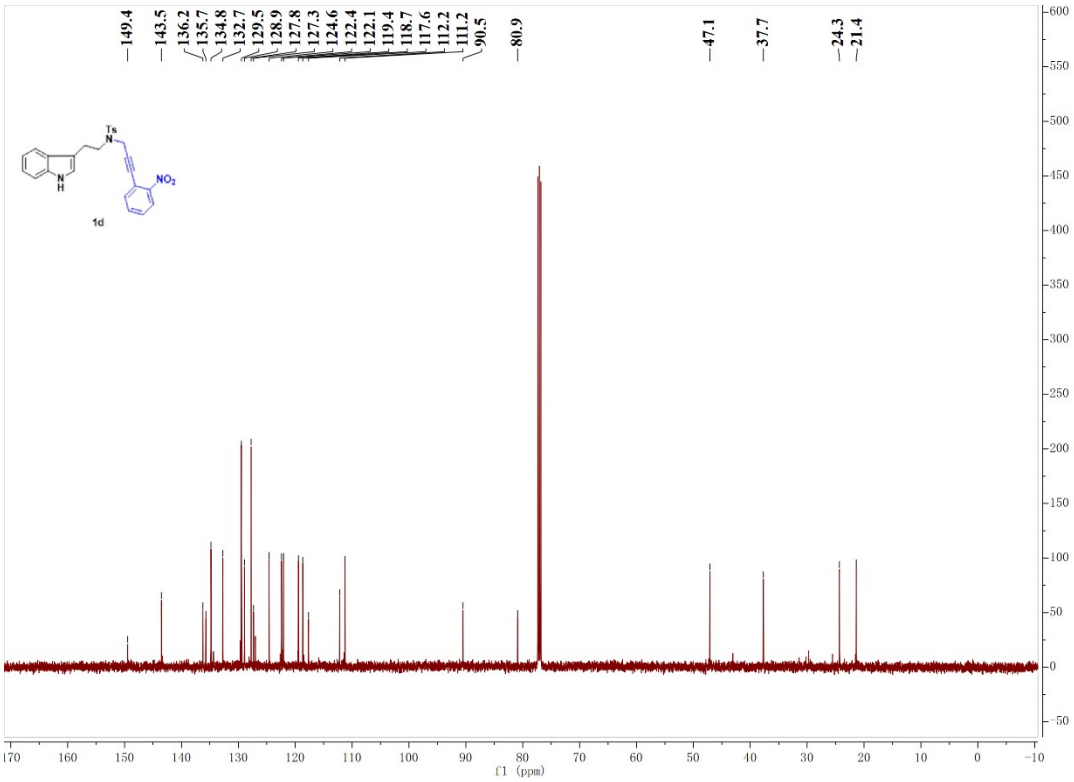


Figure S114. The ^{1}H-NMR spectra copy of compound 1e.

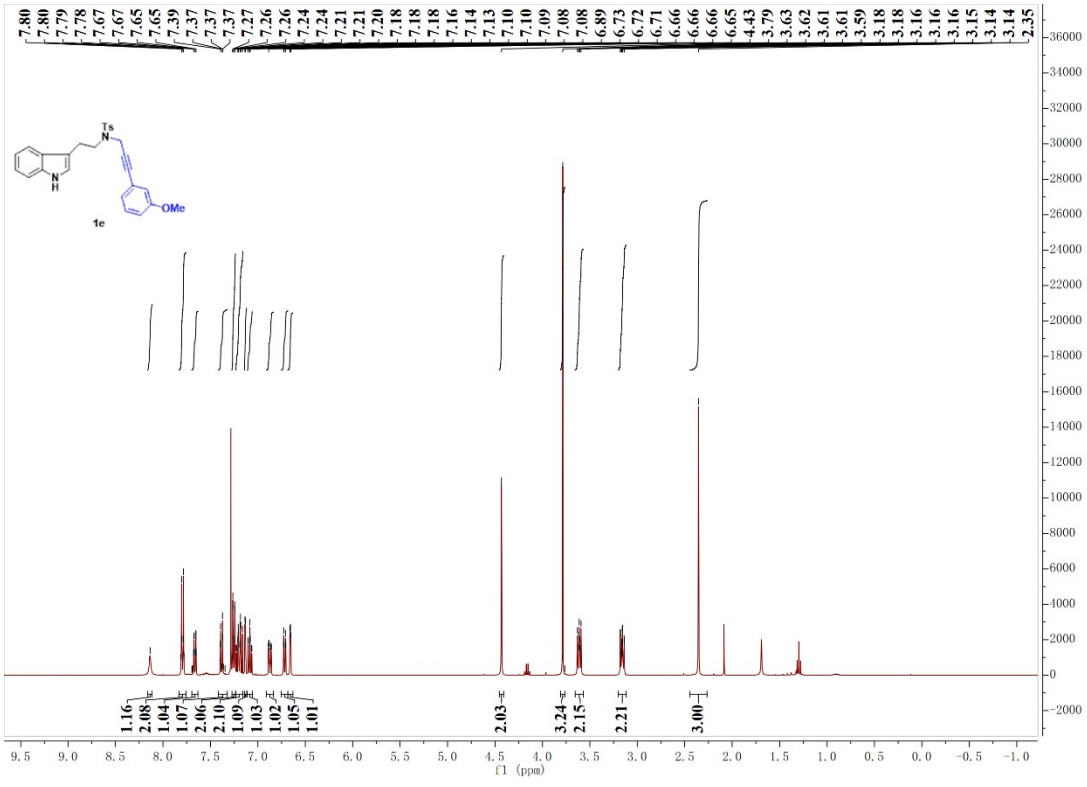


Figure S115. The ^{13}C-NMR spectra copy of compound 1e.

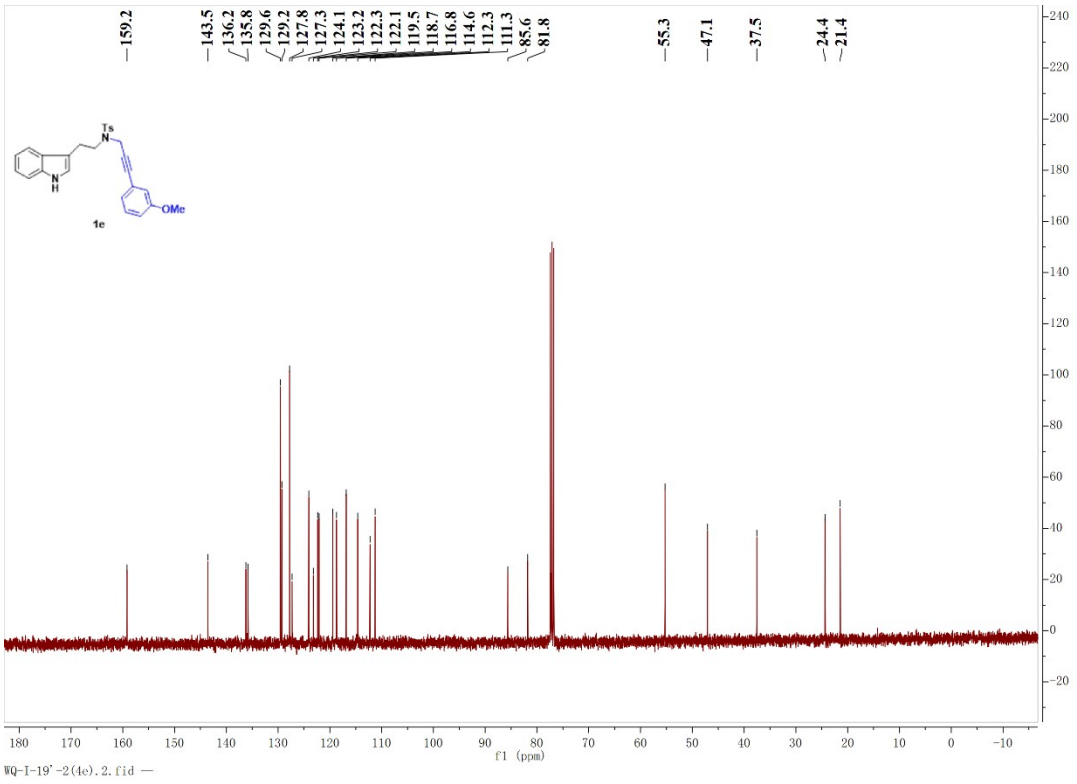


Figure S116. The ^{1}H-NMR spectra copy of compound 1f.

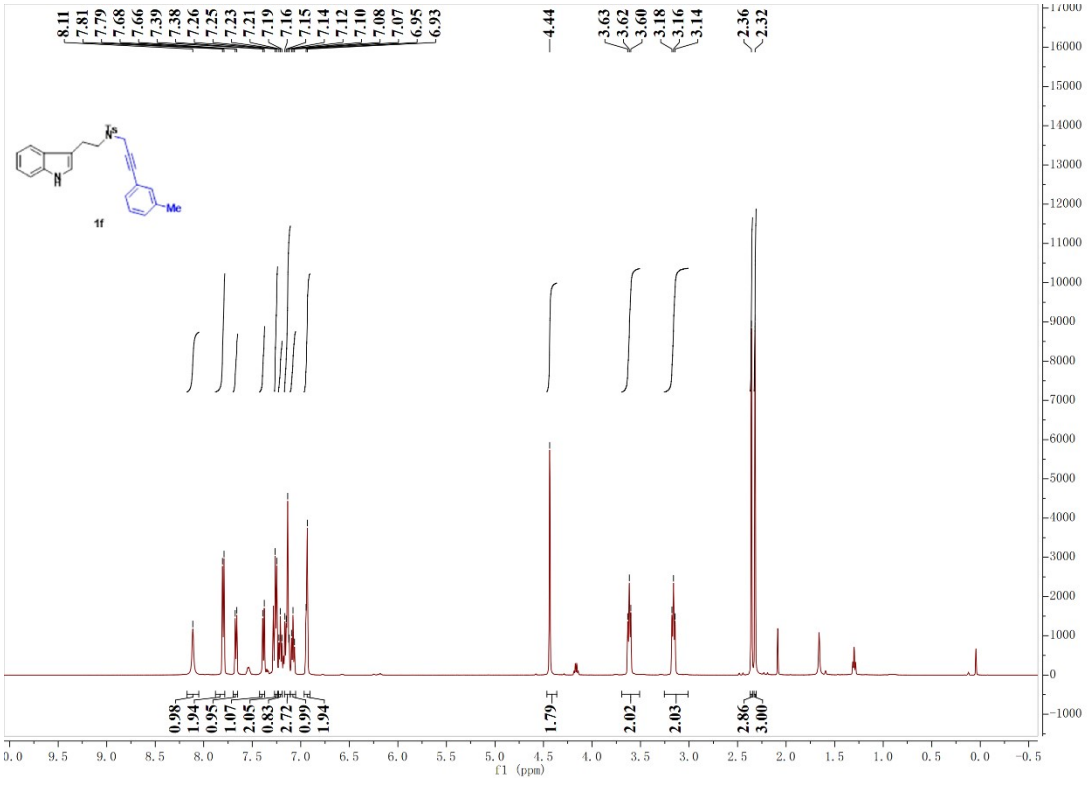


Figure S117. The ^{13}C-NMR spectra copy of compound 1f.

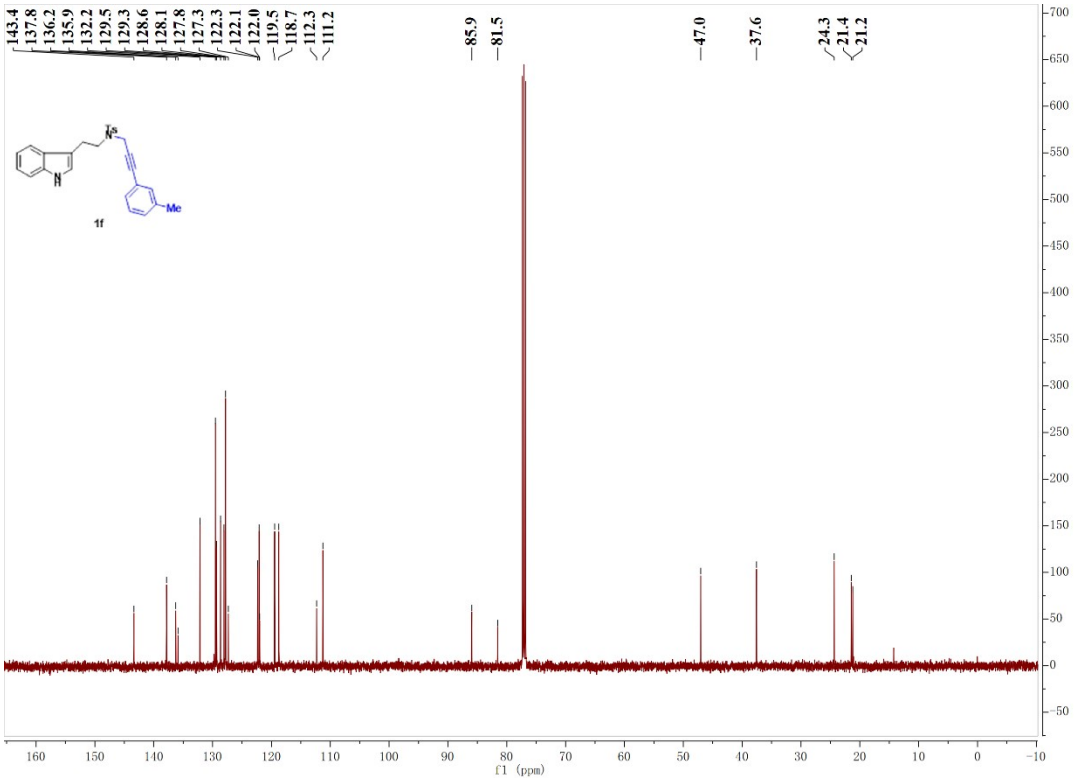


Figure S118. The ^{1}H-NMR spectra copy of compound 1g.

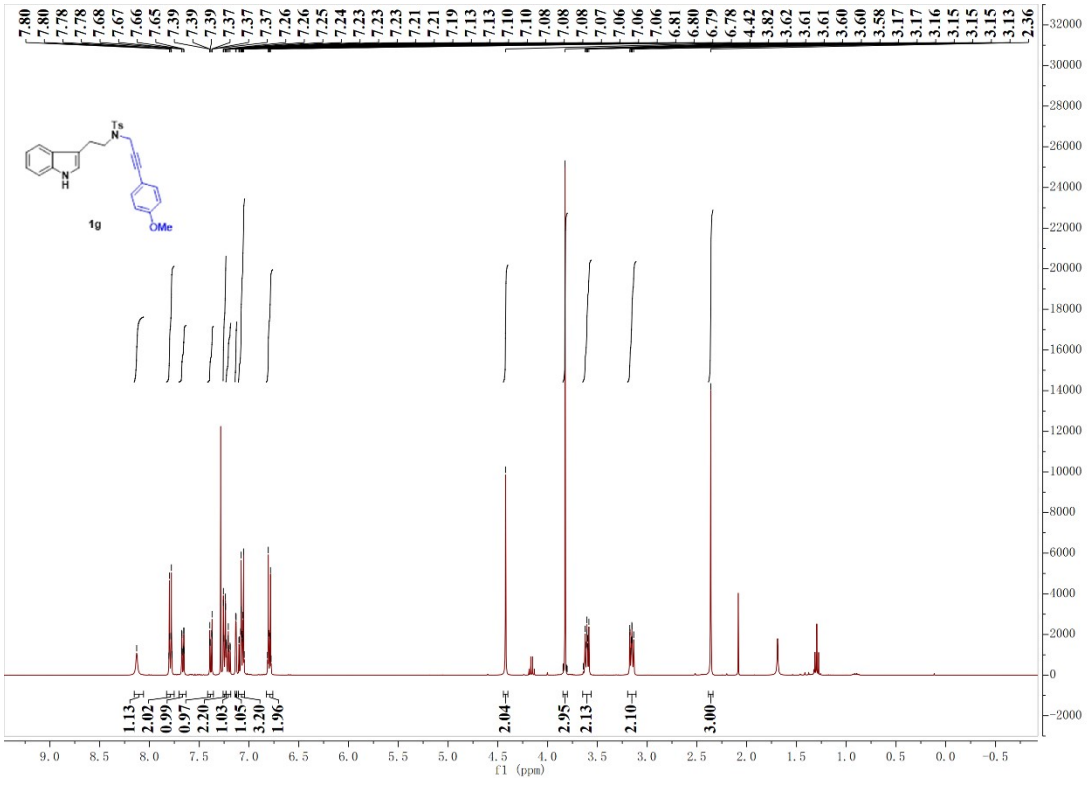


Figure S119. The ^{13}C-NMR spectra copy of compound 1g.

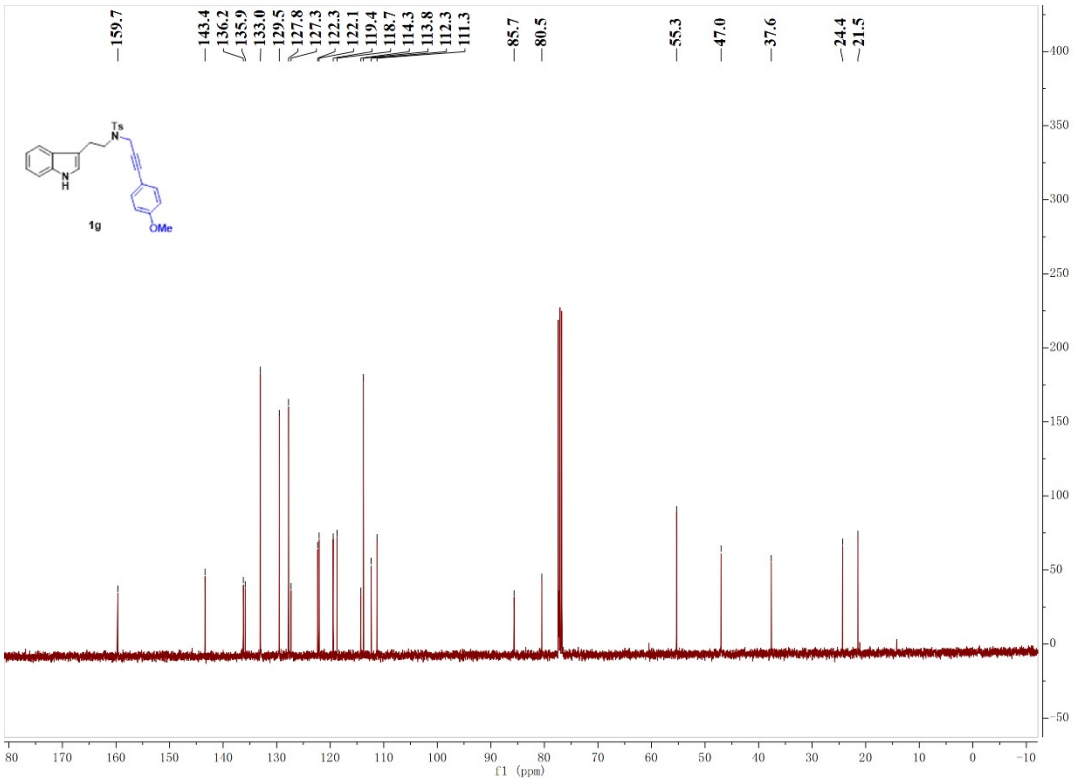


Figure S120. The ^{1}H-NMR spectra copy of compound 1h.

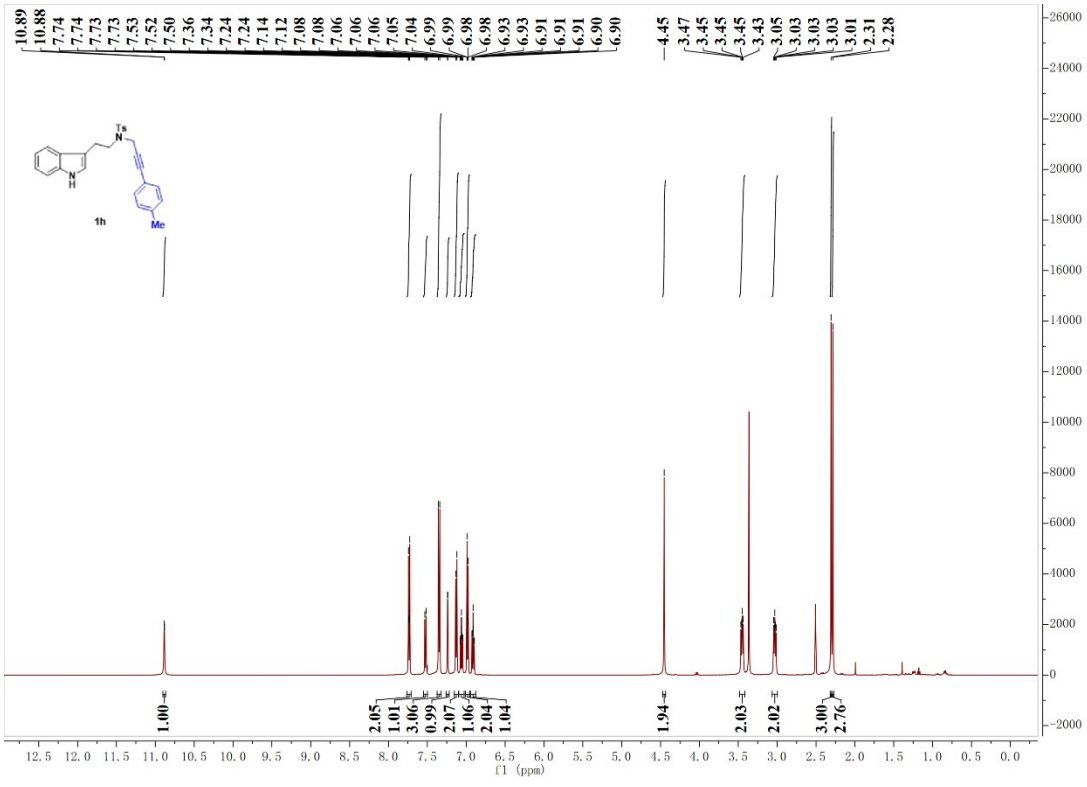


Figure S121. The ^{13}C-NMR spectra copy of compound 1h.

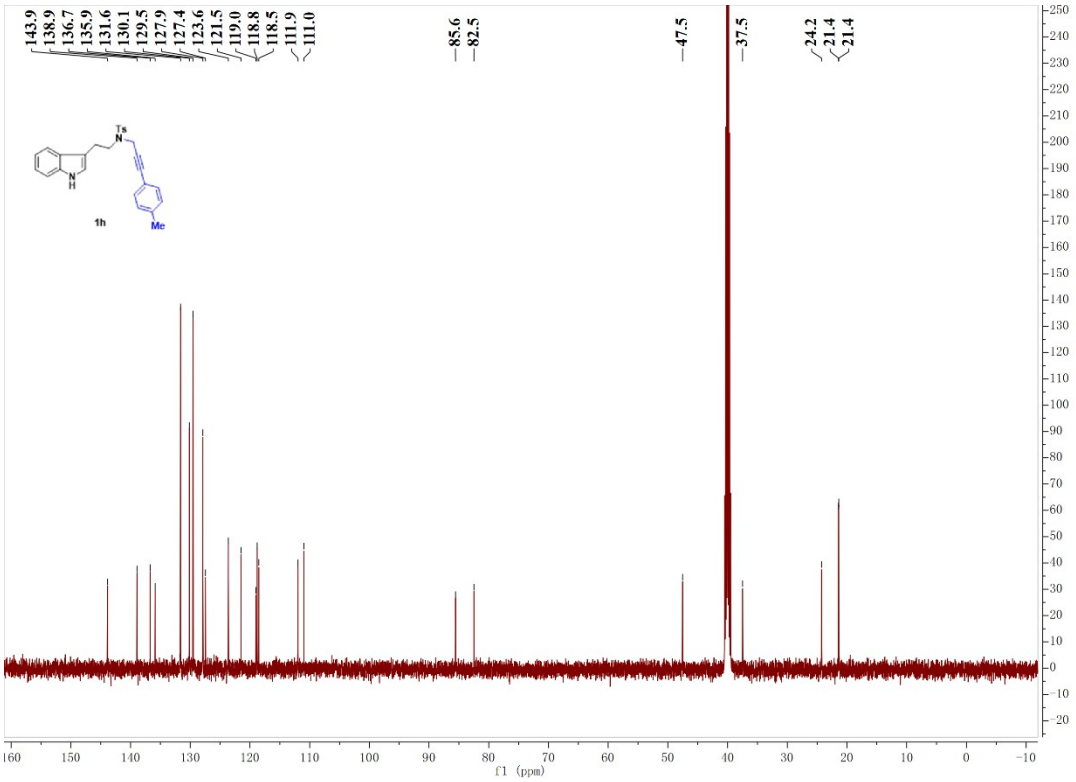


Figure S122. The ^{1}H-NMR spectra copy of compound 1i.

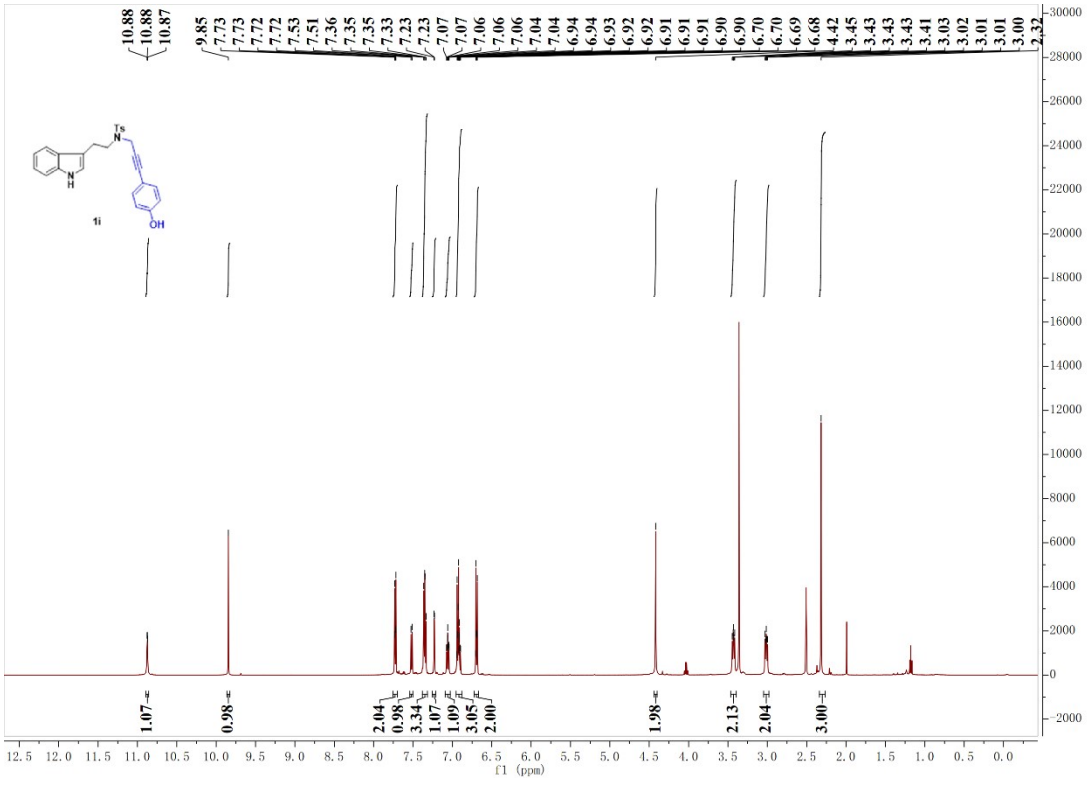


Figure S123. The ^{13}C-NMR spectra copy of compound 1i.

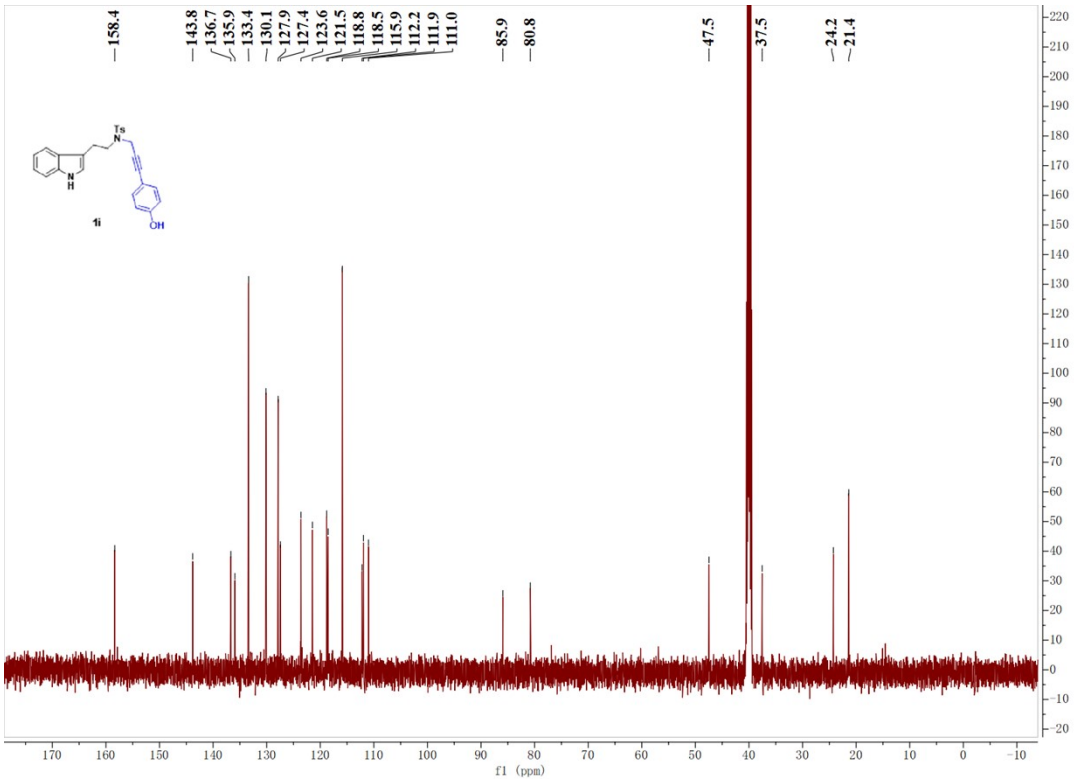


Figure S124. The ^{1}H-NMR spectra copy of compound 1j.

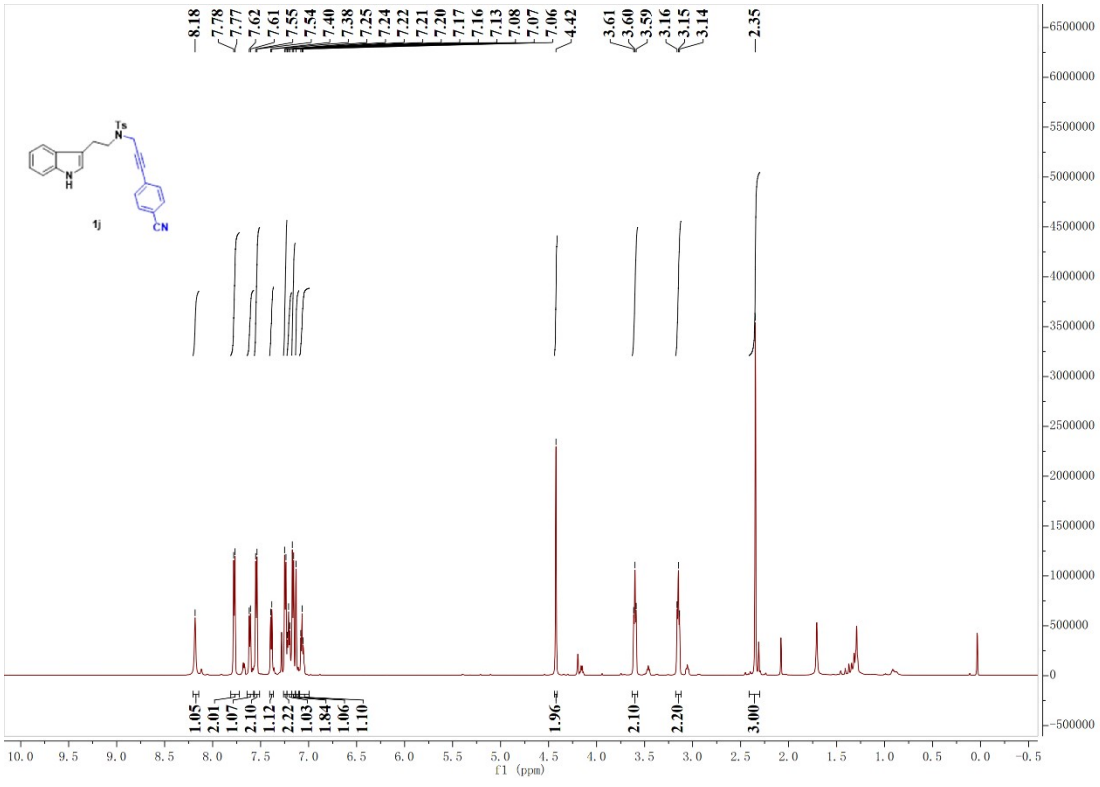


Figure S125. The ^{13}C-NMR spectra copy of compound 1j.

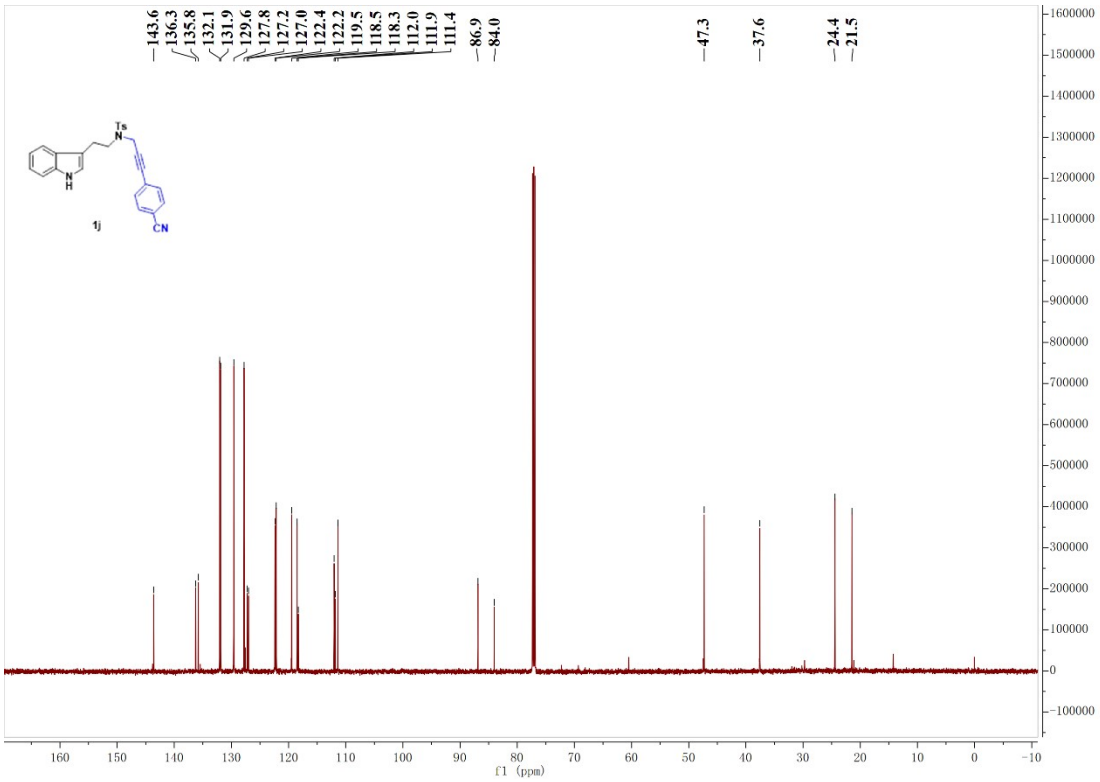


Figure S126. The ^{1}H-NMR spectra copy of compound 1k.

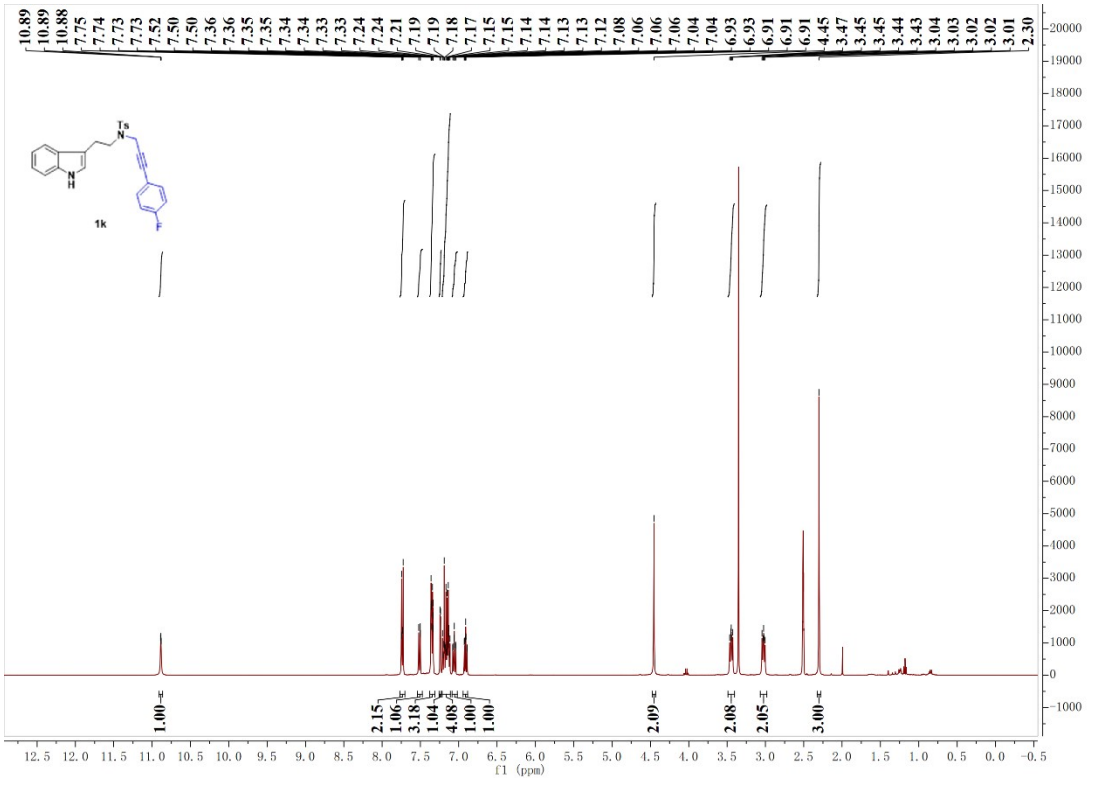


Figure S127. The ^{13}C-NMR spectra copy of compound 1k.

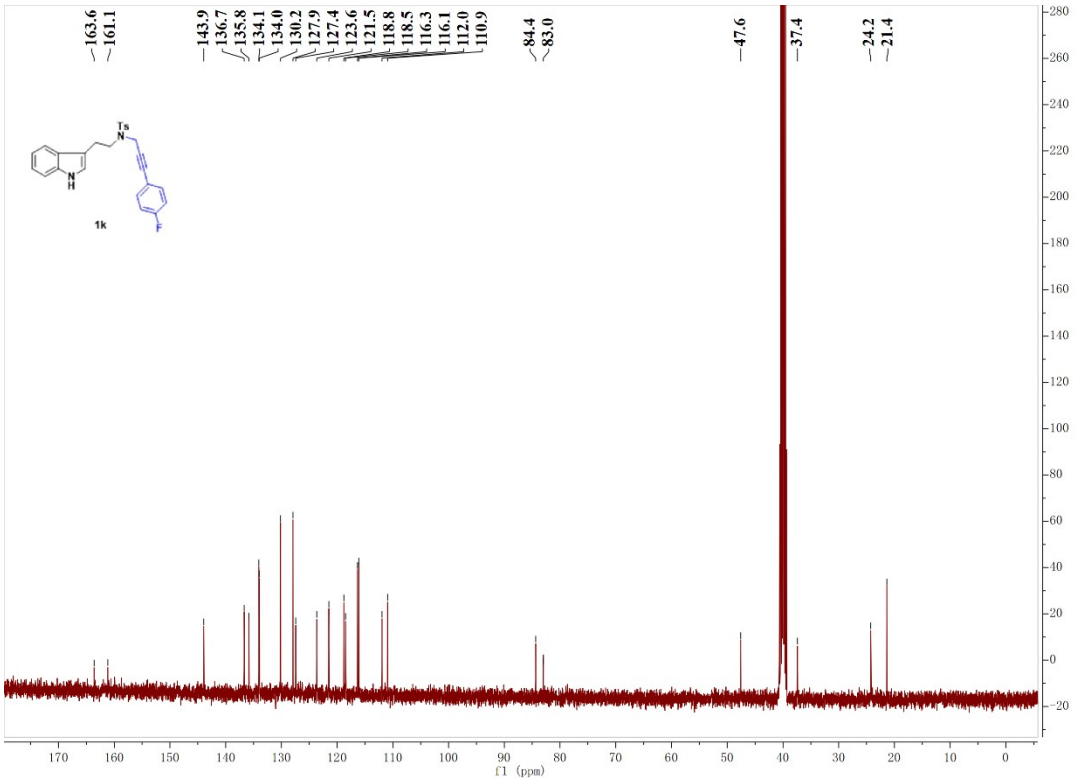


Figure S128. The ^{19}F-NMR spectra copy of compound 1k.

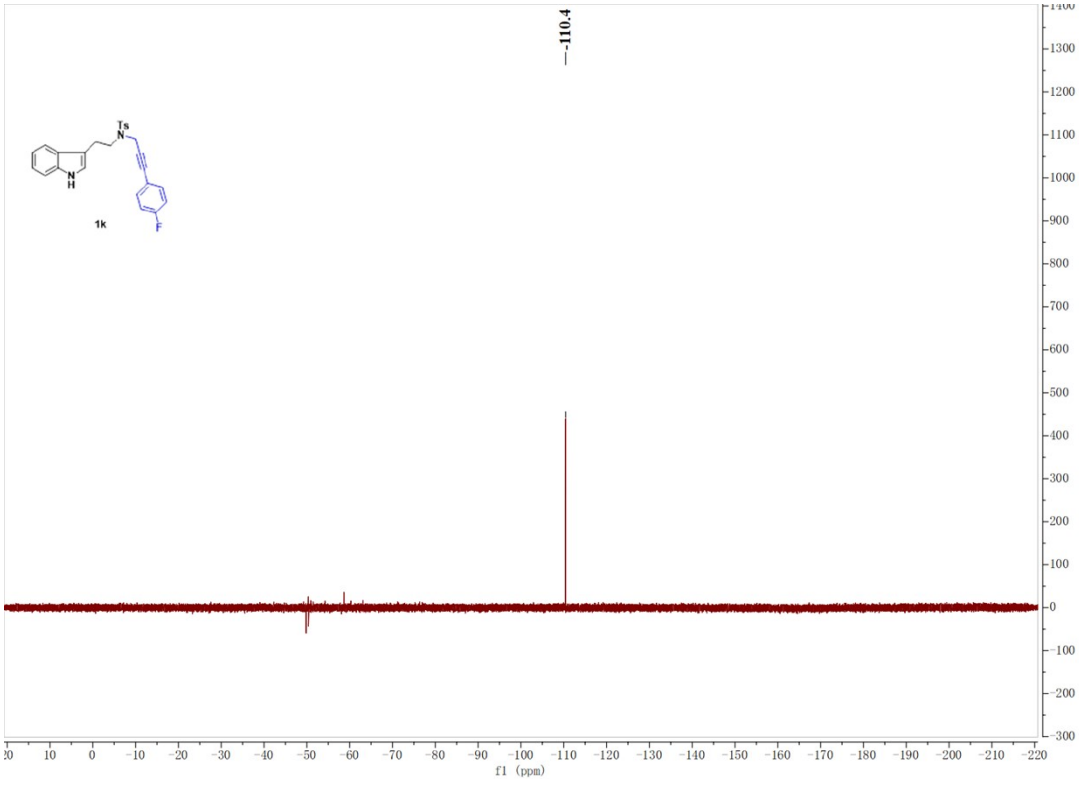


Figure S129. The ^{1}H-NMR spectra copy of compound 1l.

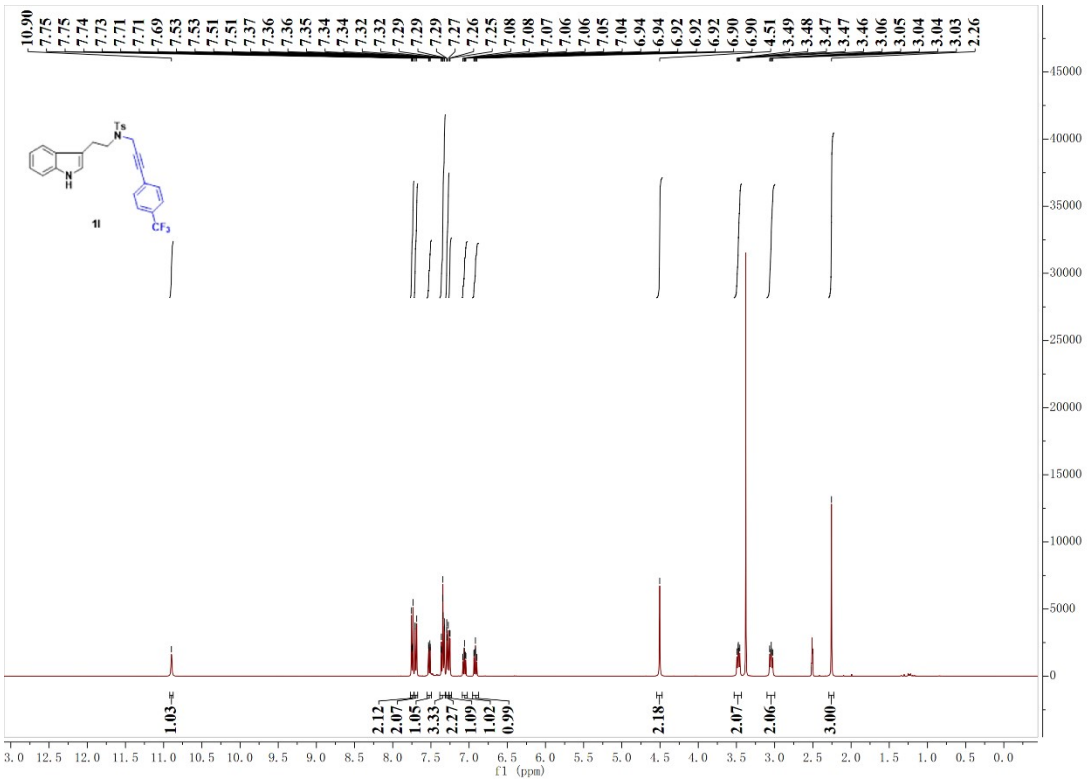


Figure S130. The ^{13}C-NMR spectra copy of compound 1l.

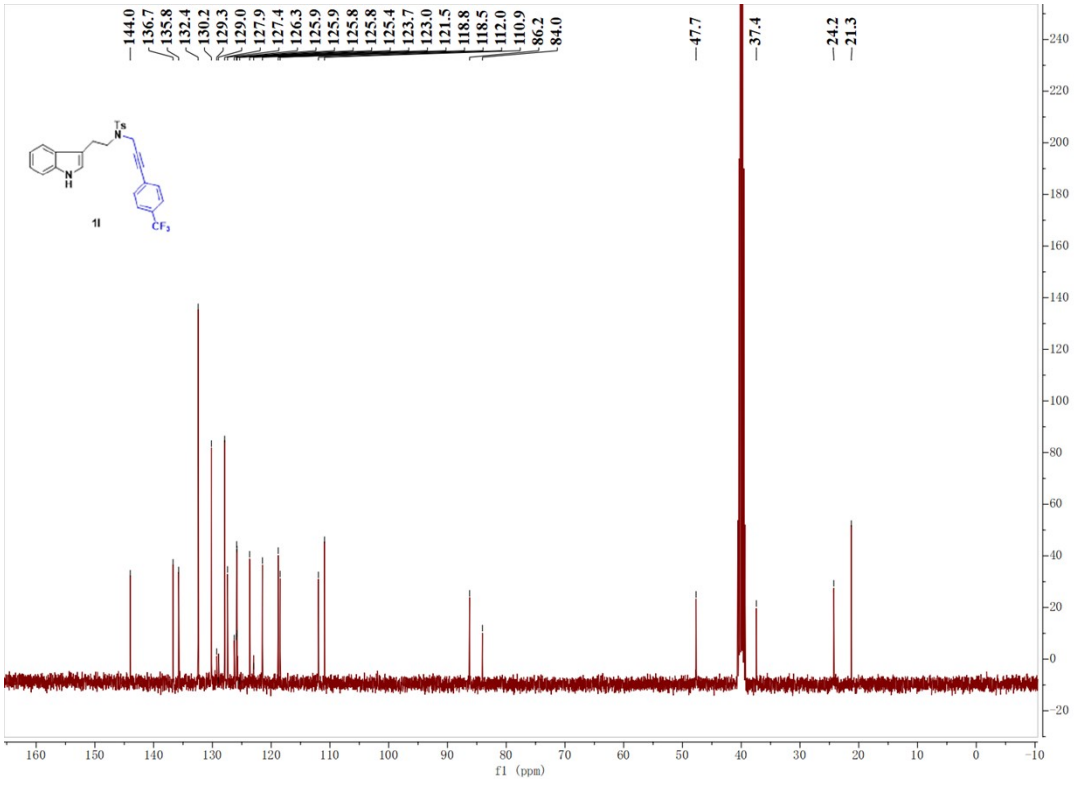


Figure S131. The ^{19}F-NMR spectra copy of compound 1l.

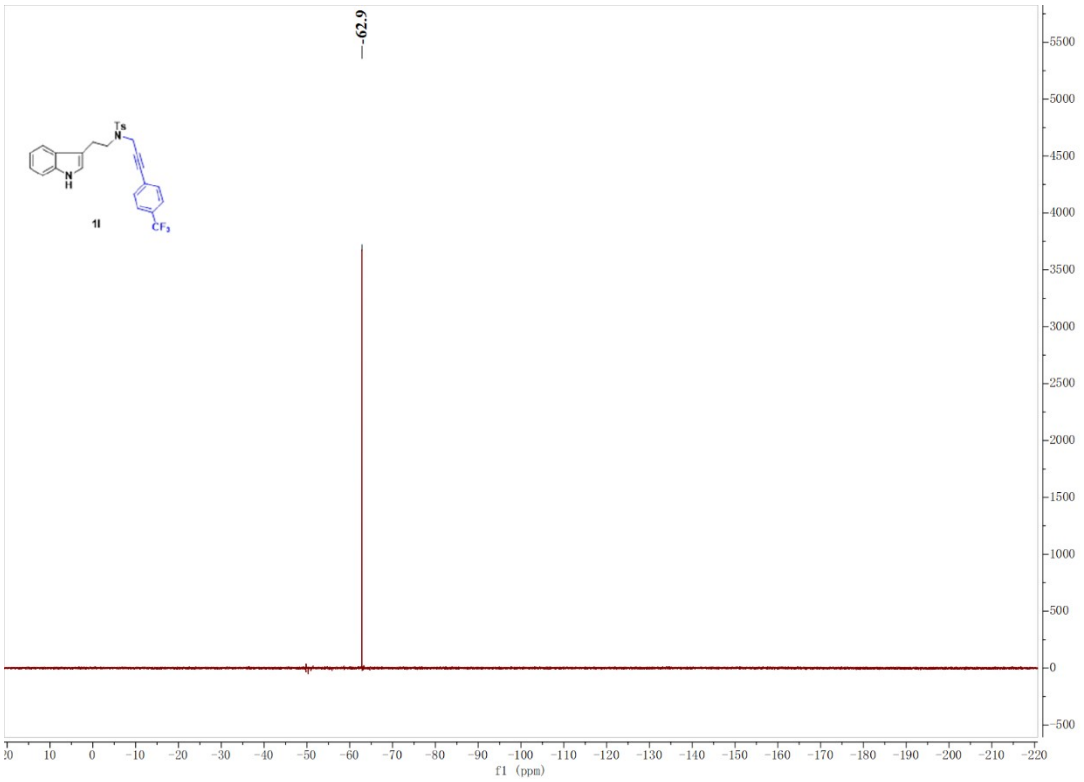


Figure S132. The ^{1}H-NMR spectra copy of compound 1m.

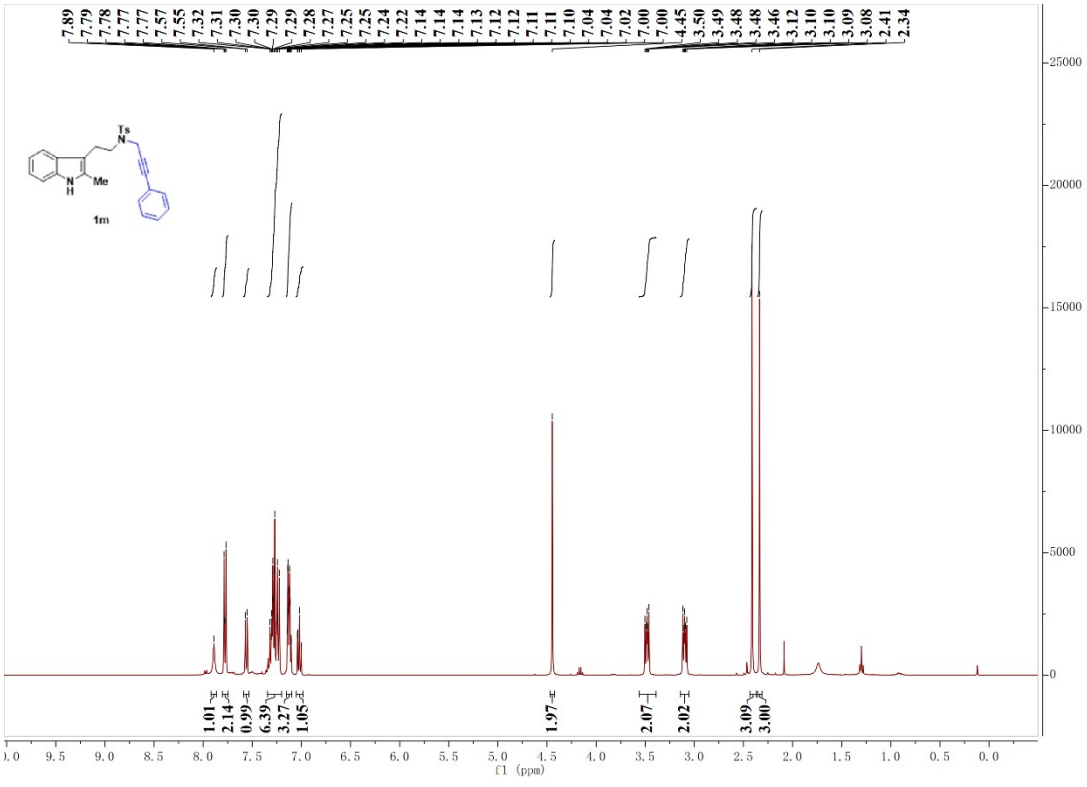


Figure S133. The ^{13}C-NMR spectra copy of compound 1m.

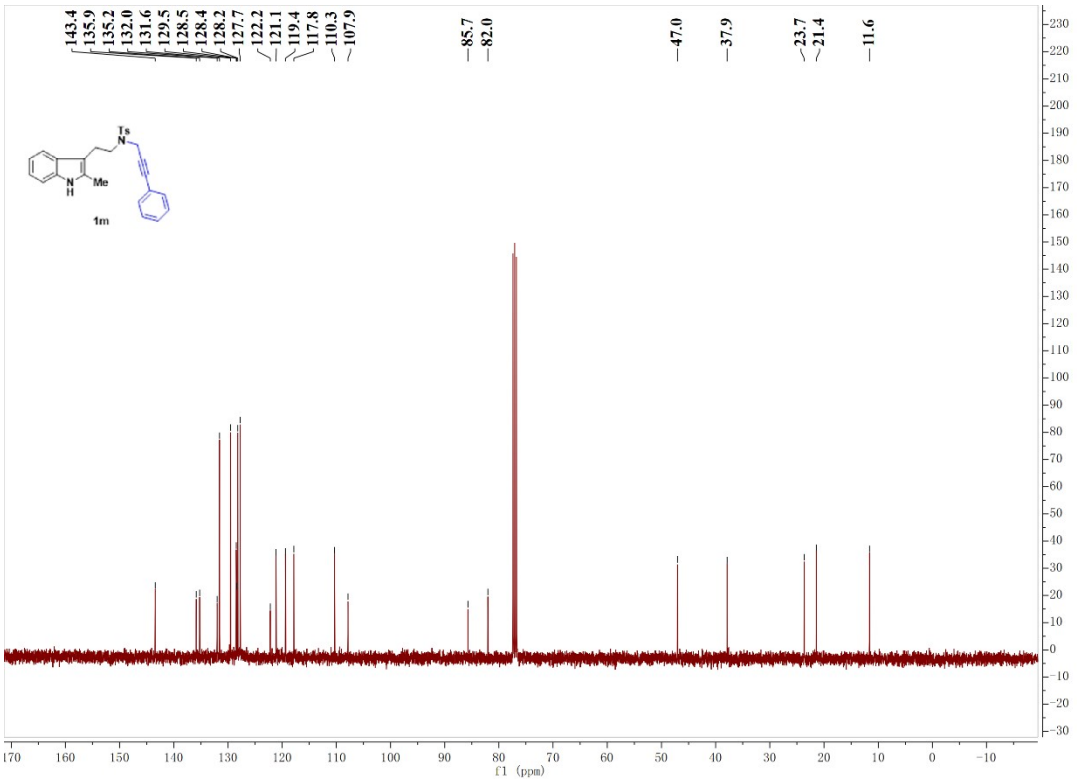


Figure S134. The ^{1}H-NMR spectra copy of compound 1n.

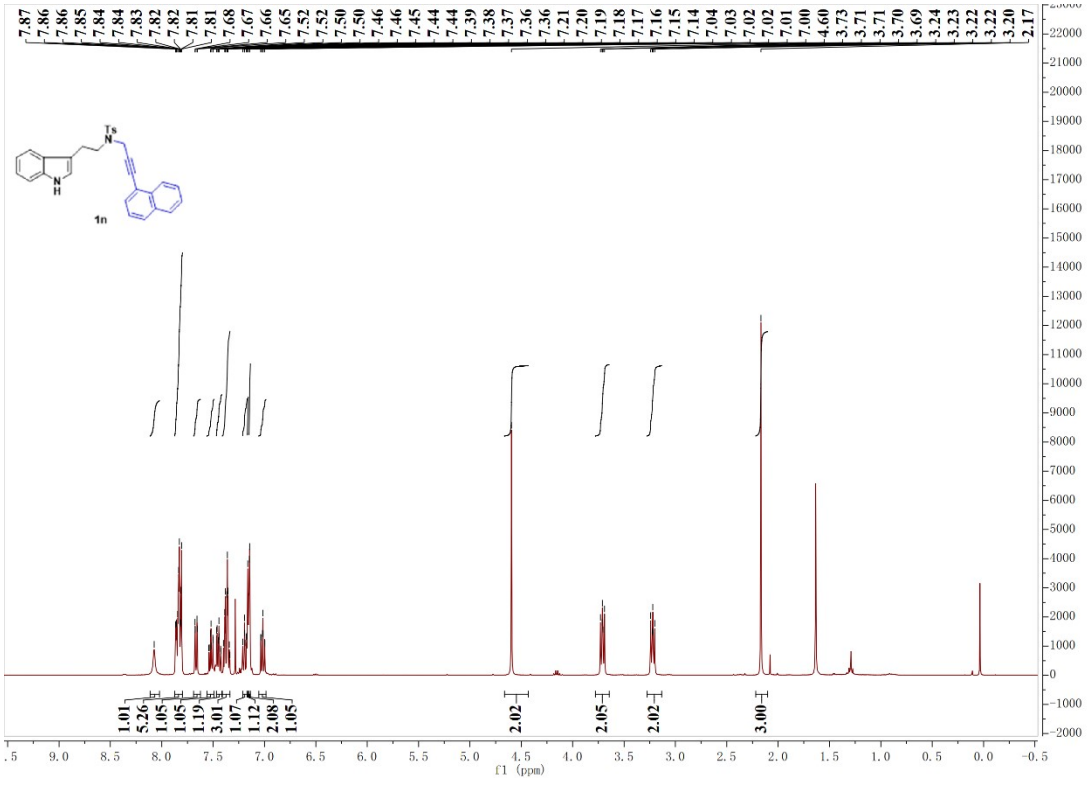


Figure S135. The ^{13}C-NMR spectra copy of compound 1n.

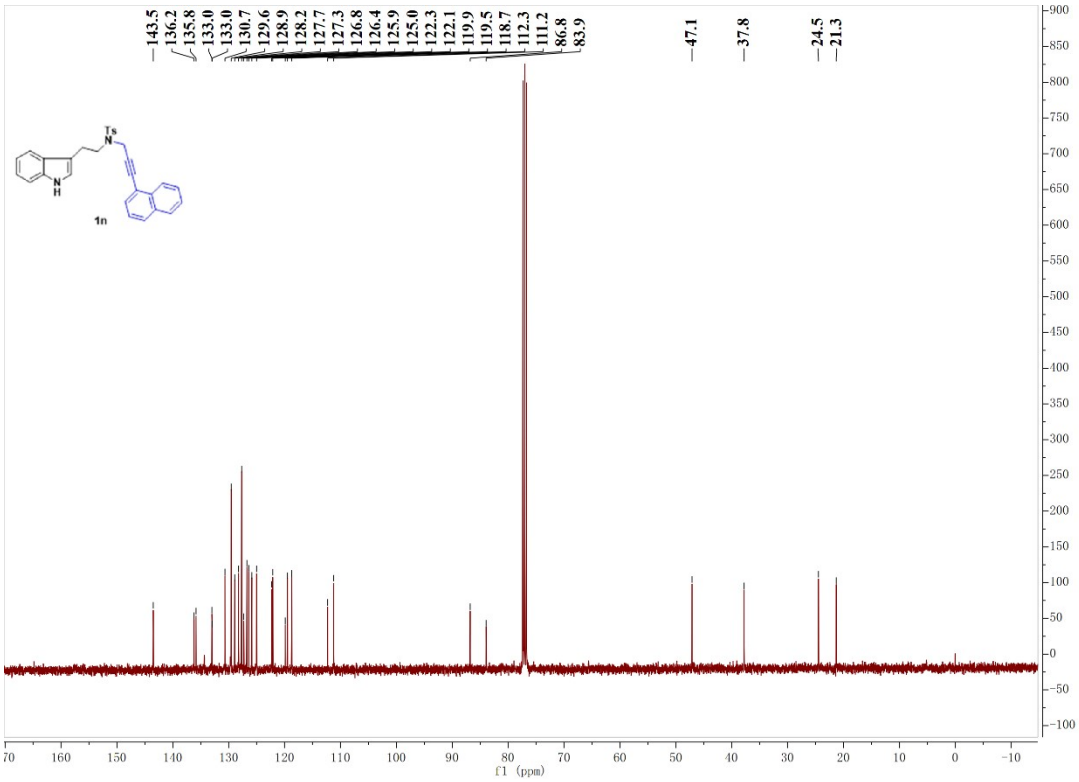


Figure S136. The ^{1}H-NMR spectra copy of compound 1o.

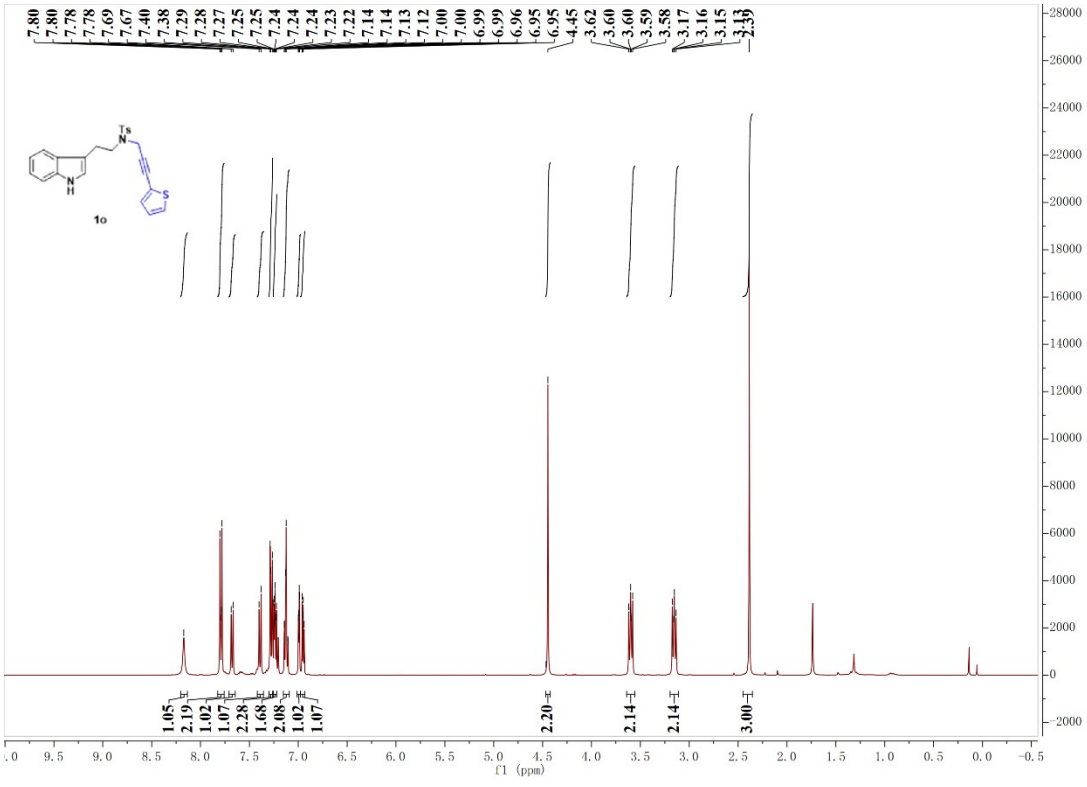


Figure S137. The ^{13}C-NMR spectra copy of compound 1o.

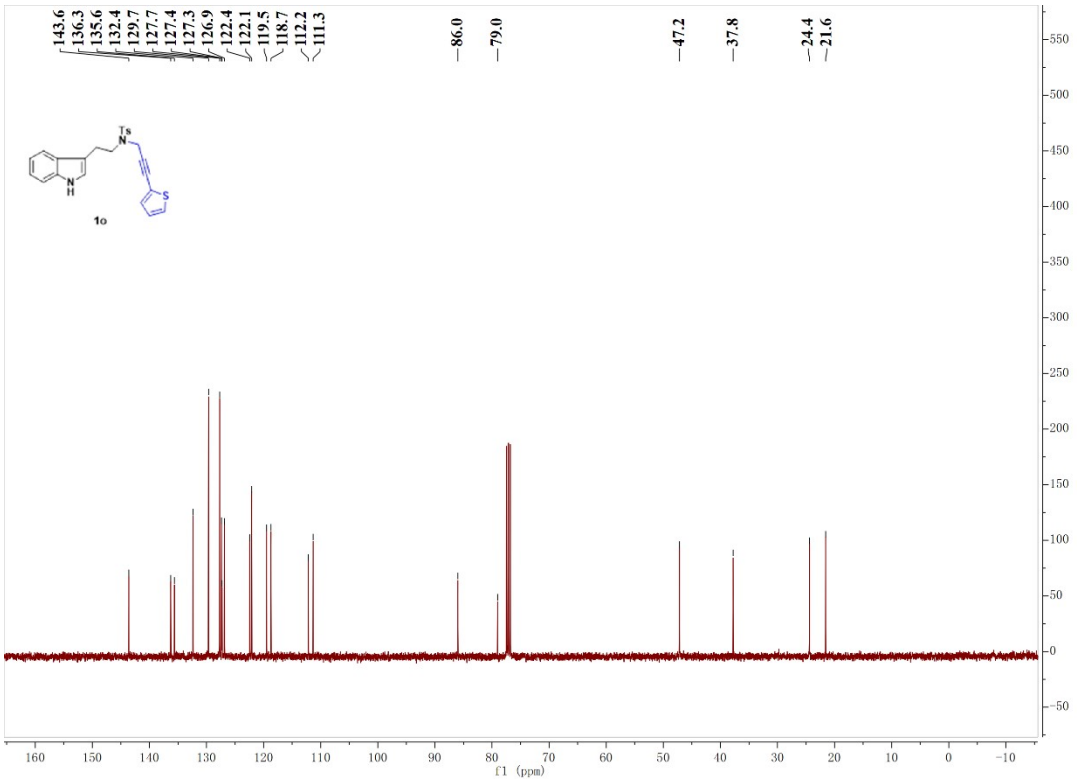


Figure S138. The ^{1}H-NMR spectra copy of compound 1p.

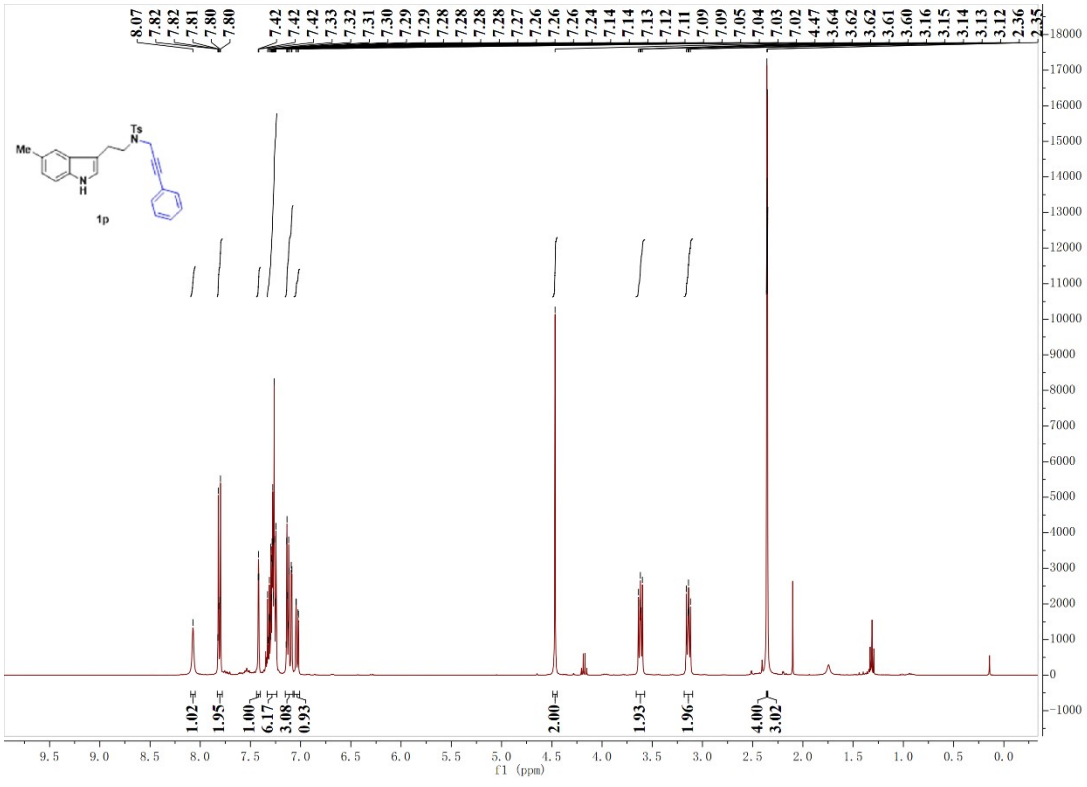


Figure S139. The ^{13}C-NMR spectra copy of compound 1p.

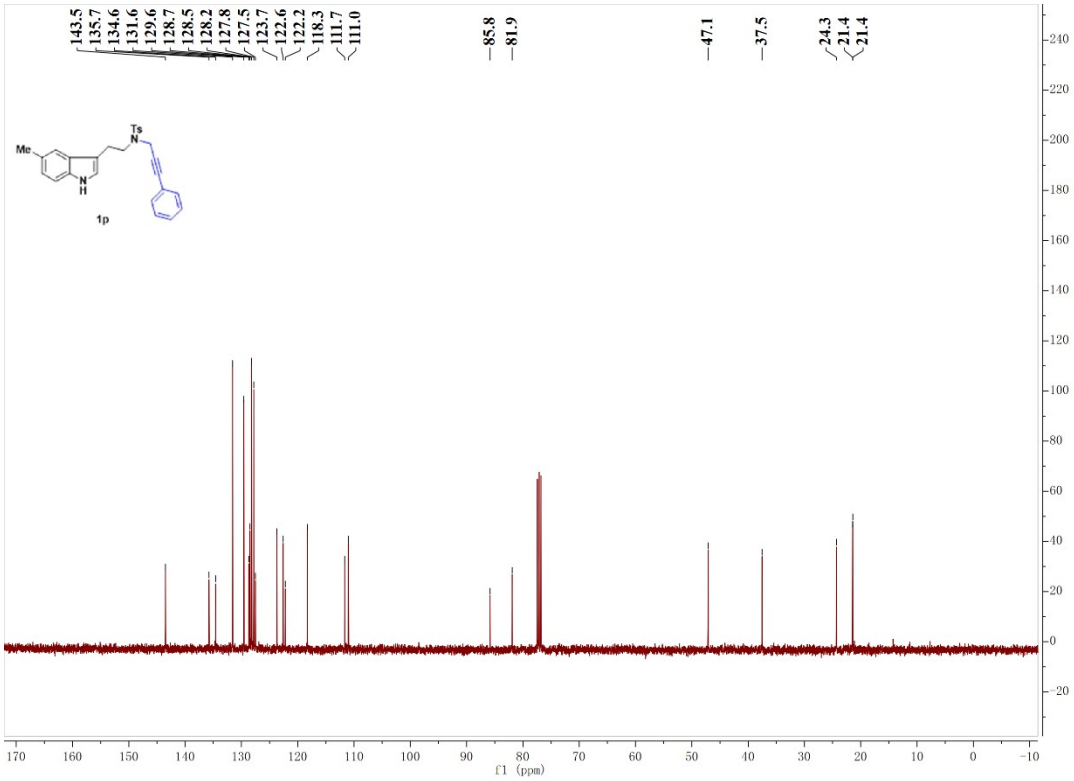


Figure S140. The ^{1}H-NMR spectra copy of compound 1q.

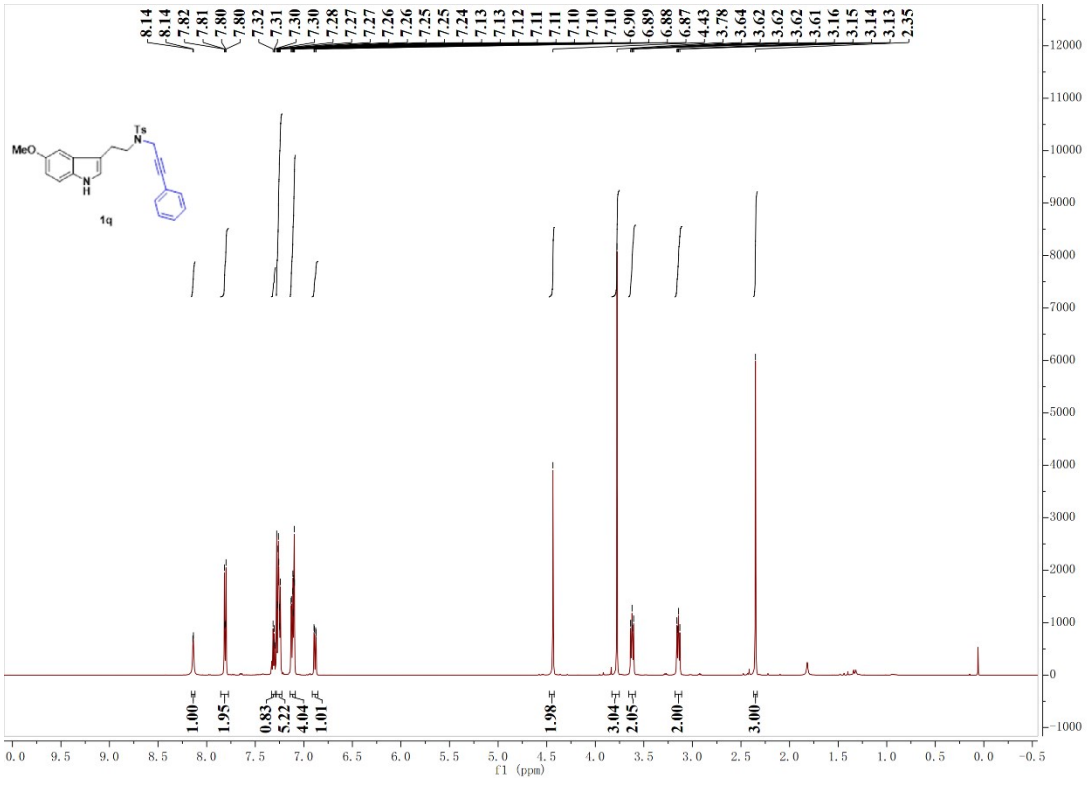


Figure S141. The ^{13}C-NMR spectra copy of compound 1q.

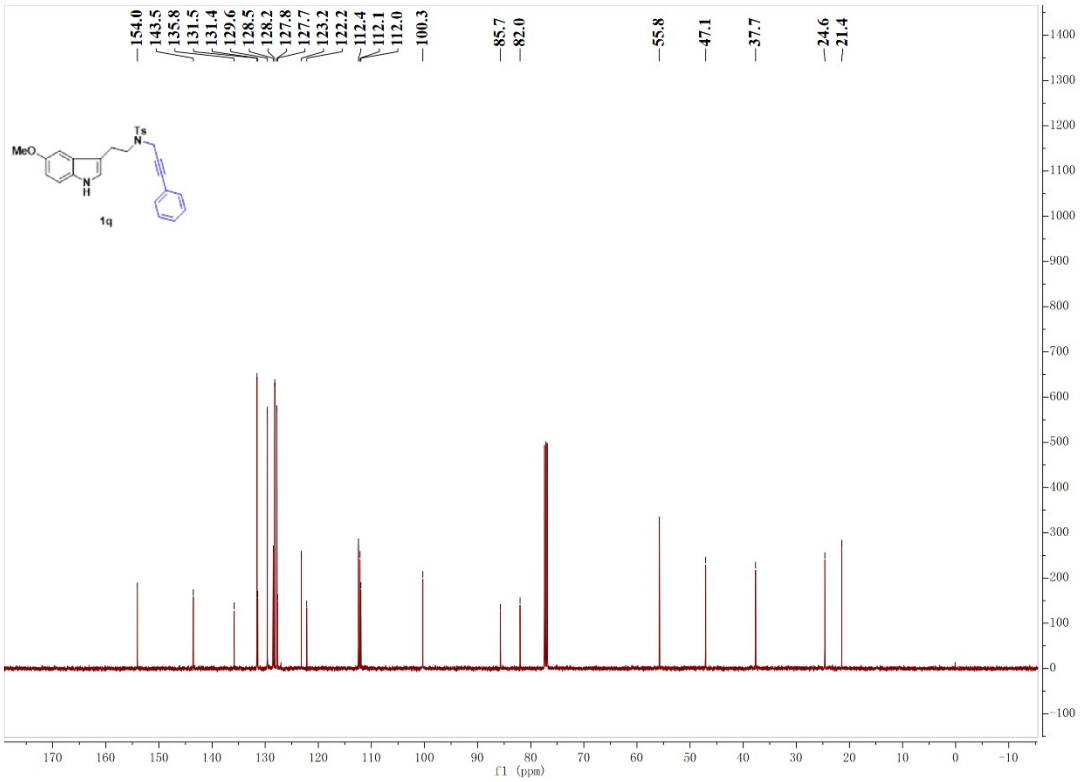


Figure S142. The ^{1}H-NMR spectra copy of compound 1r.

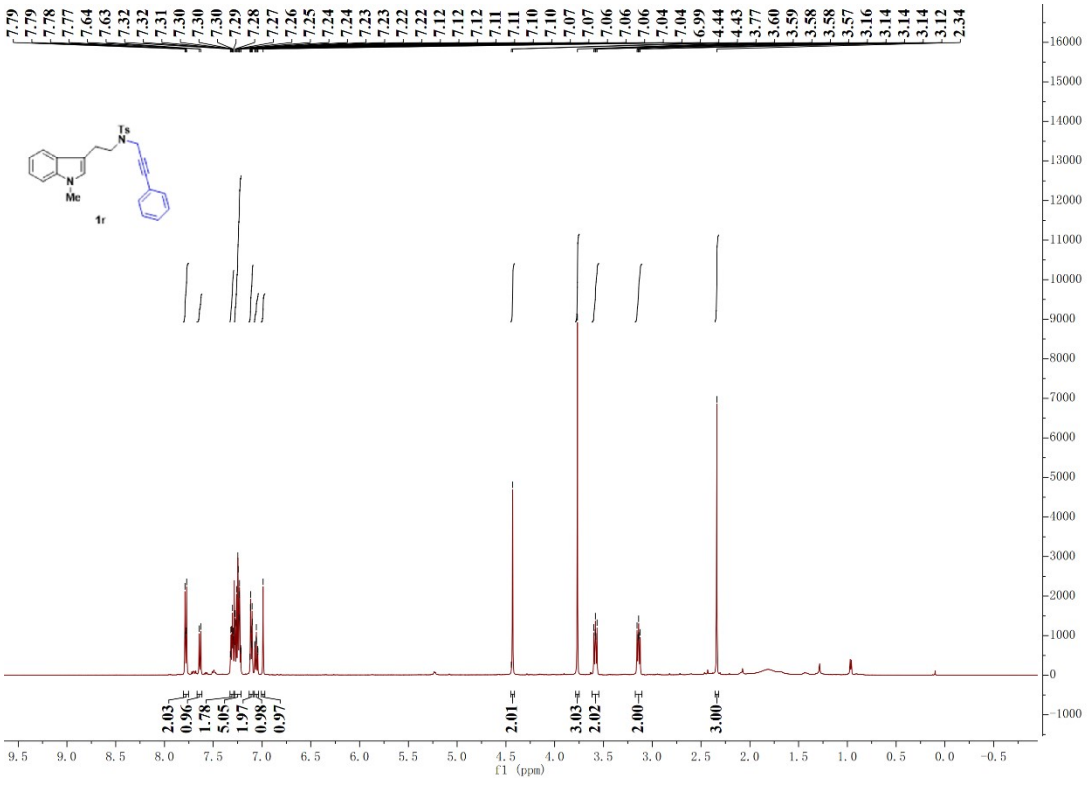


Figure S143. The ^{13}C-NMR spectra copy of compound 1r.

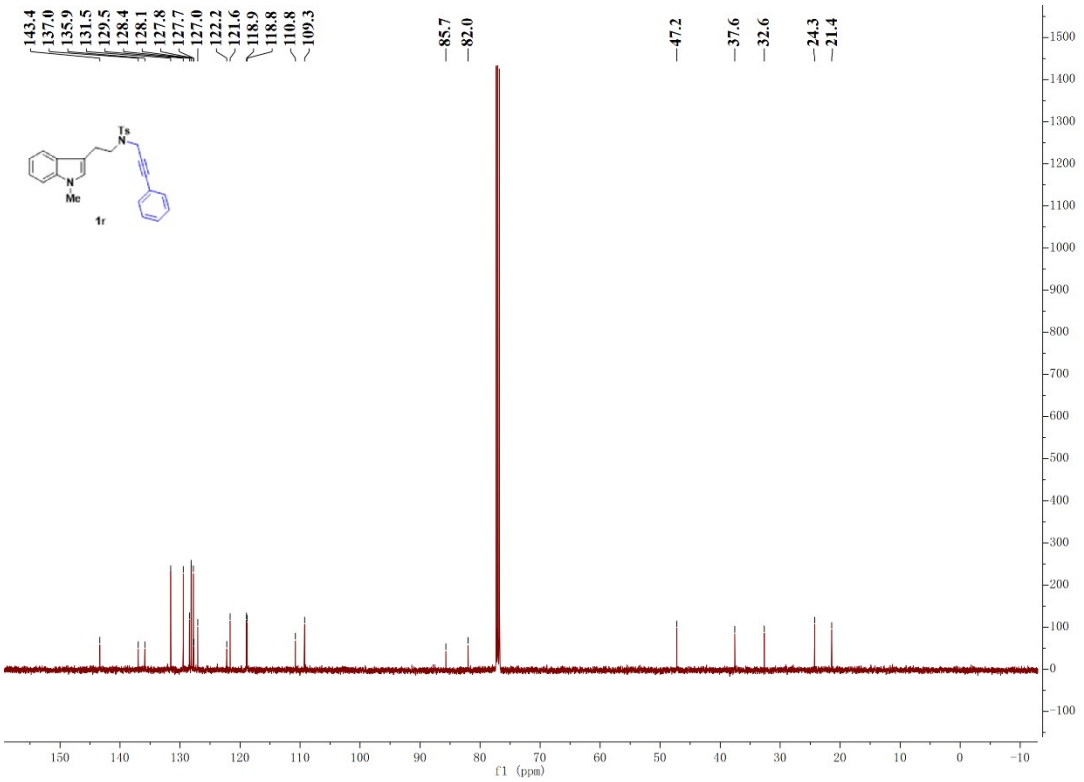


Figure S144. The ^{1}H-NMR spectra copy of compound 1s.

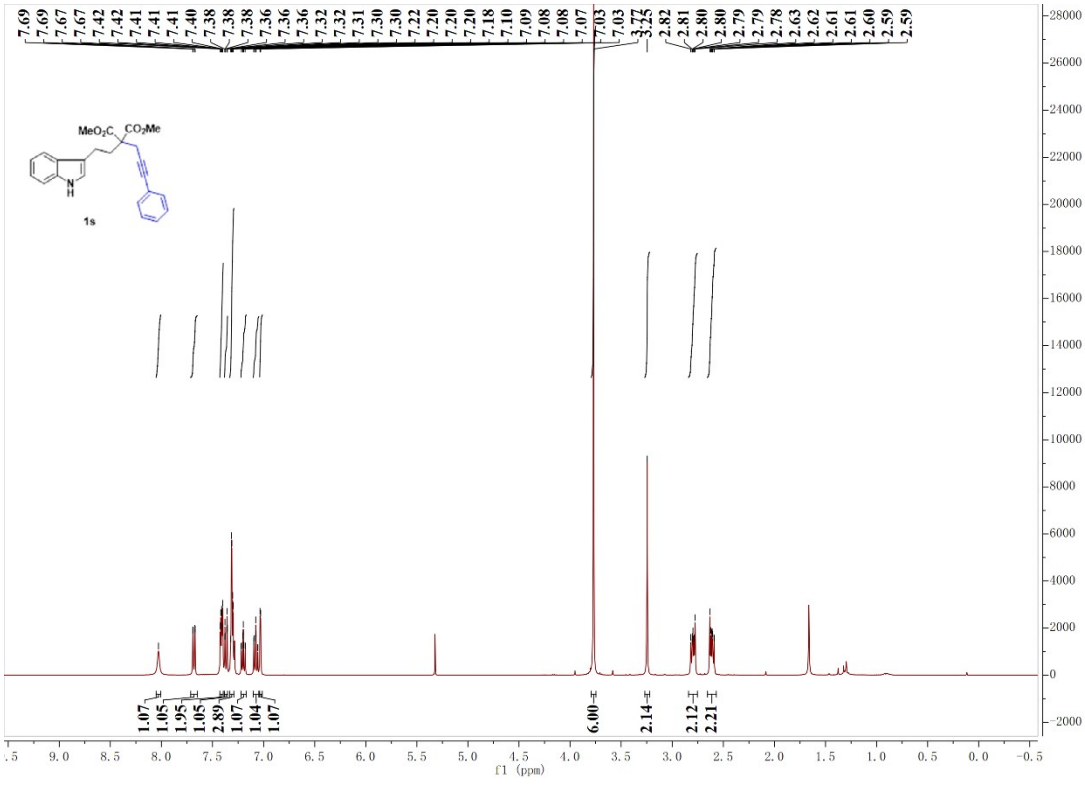


Figure S145. The ^{13}C-NMR spectra copy of compound 1s.

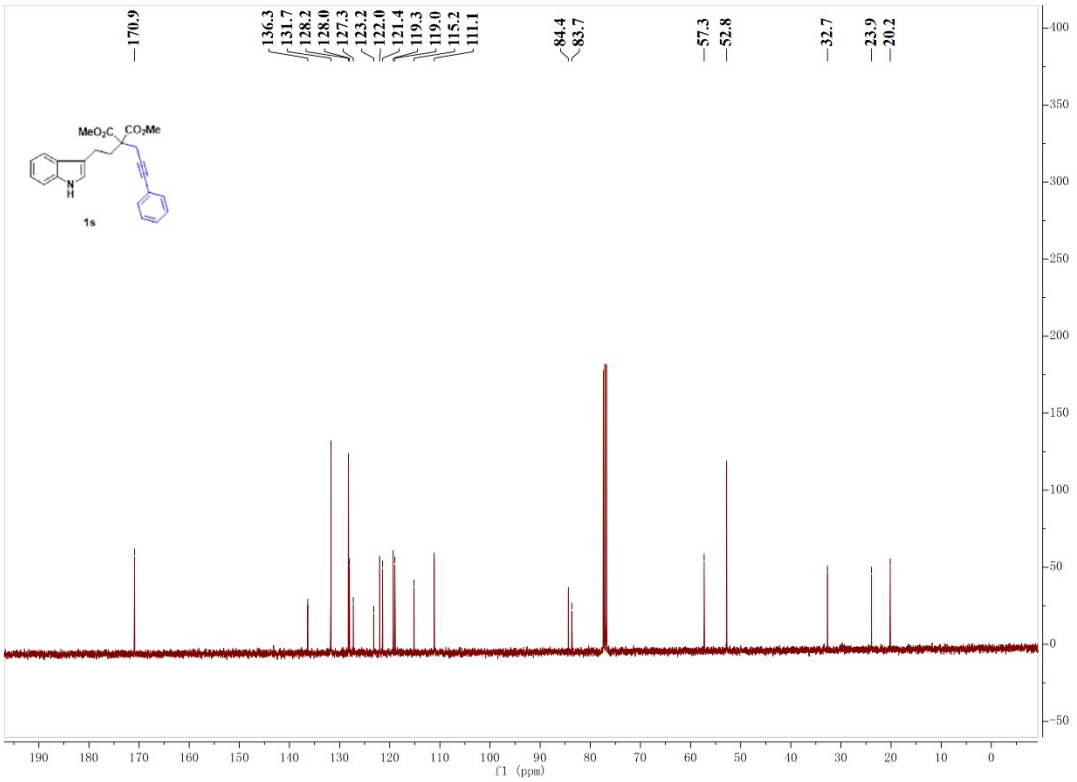


Figure S146. The ^{1}H-NMR spectra copy of compound 1t.

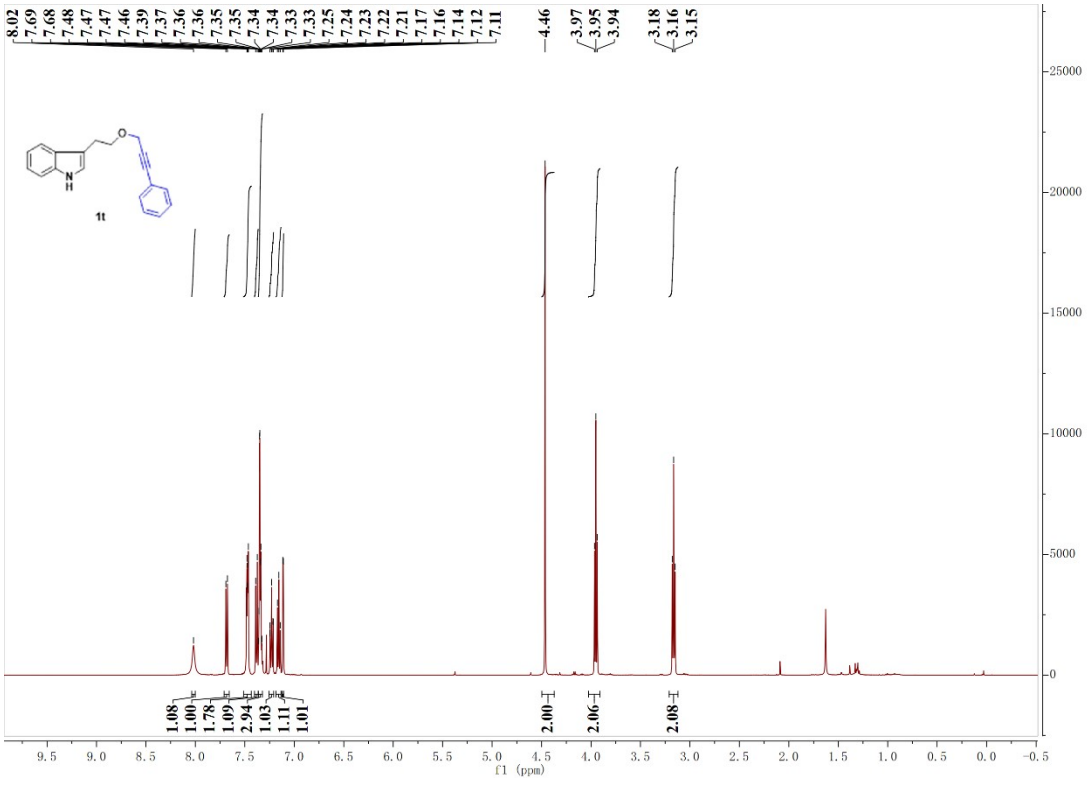


Figure S147. The ^{13}C-NMR spectra copy of compound 1t.

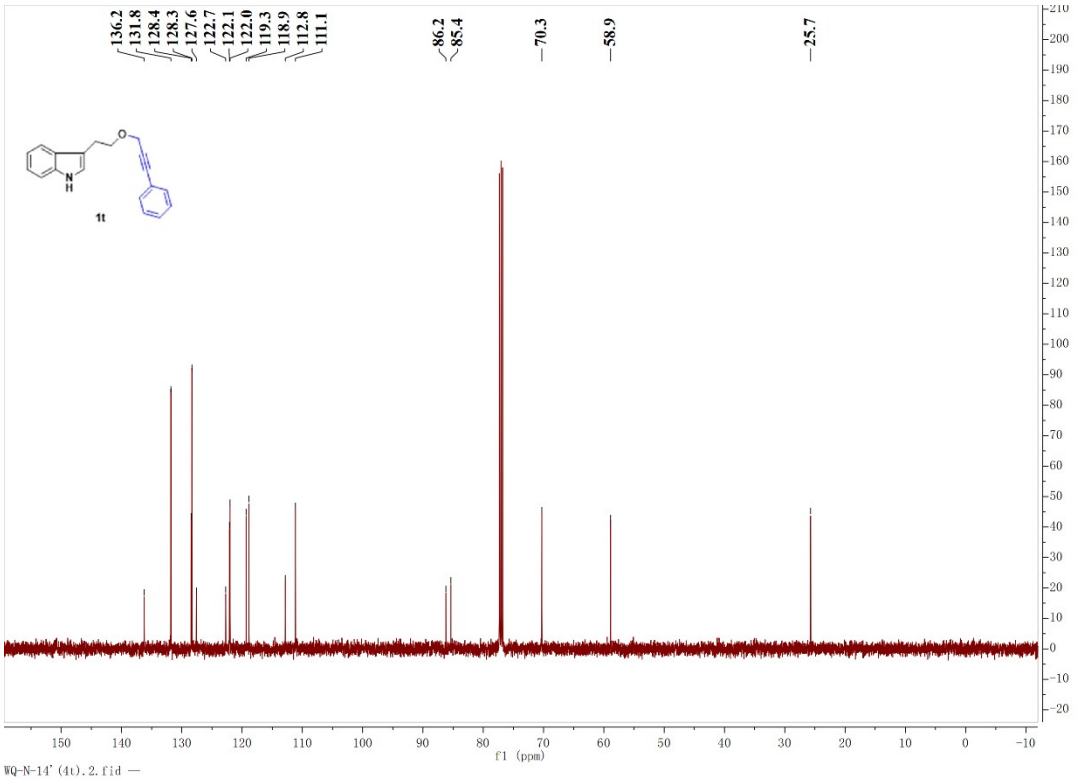


Figure S148. The ^{1}H-NMR spectra copy of compound 7.

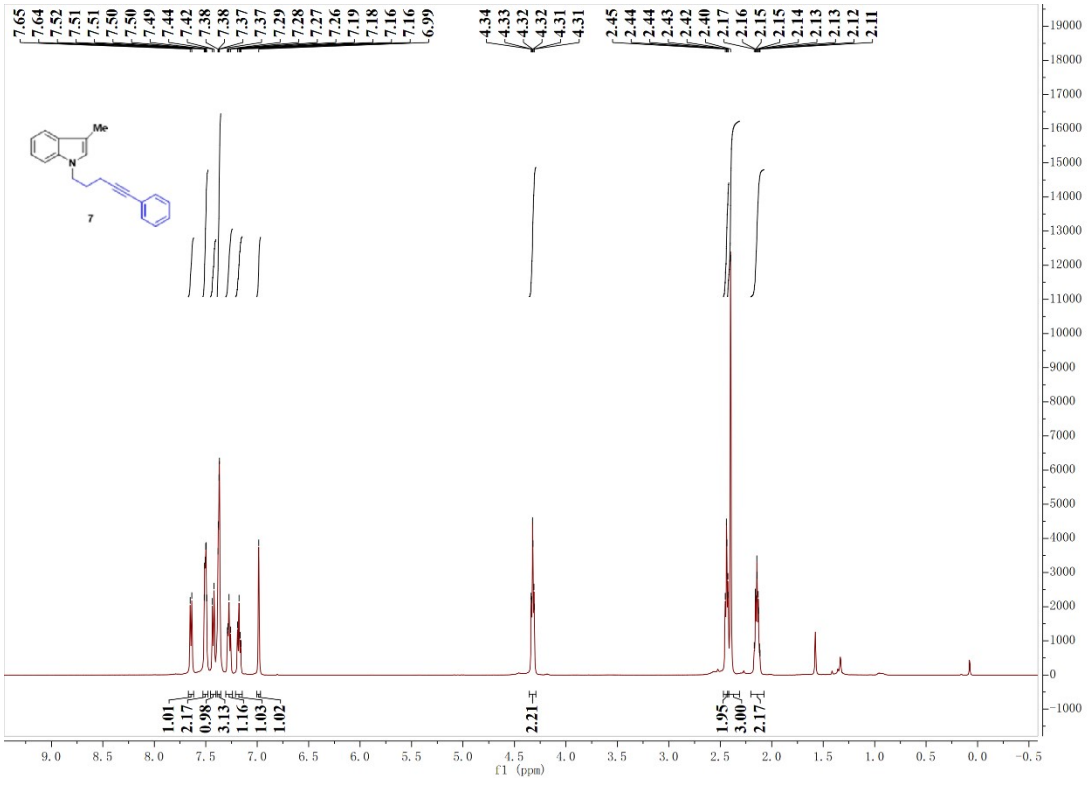


Figure S149. The ^{13}C-NMR spectra copy of compound 7.

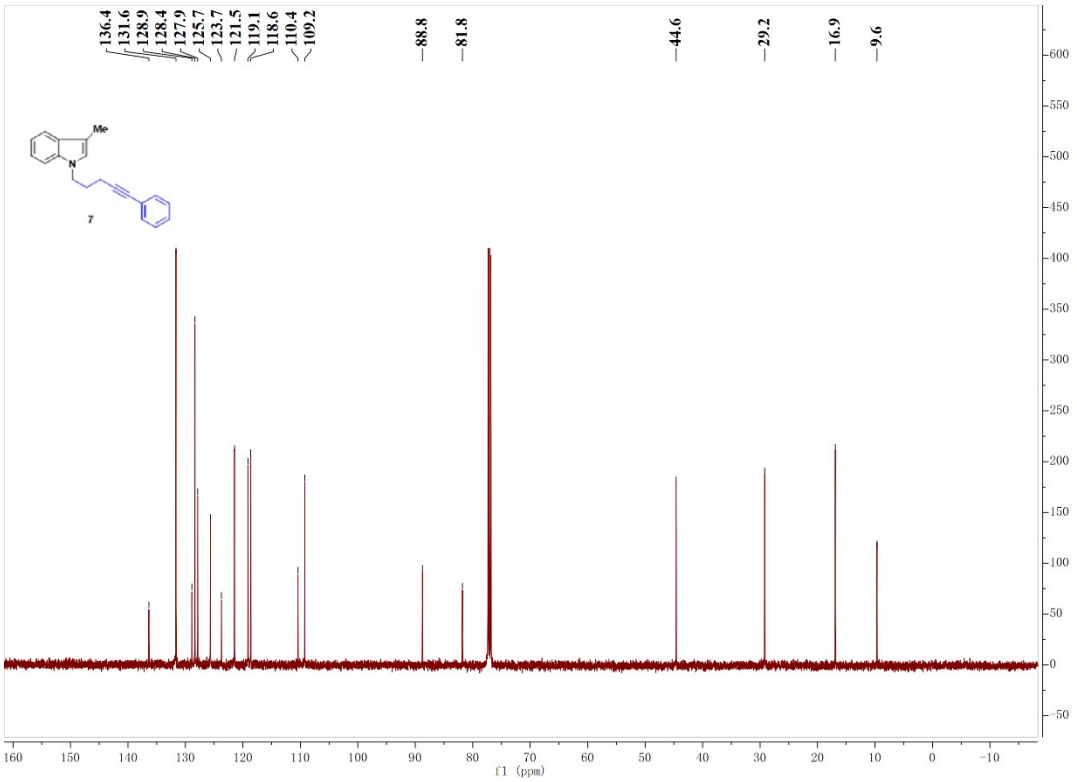


Figure S150. The ^{1}H-NMR spectra copy of compound 9.

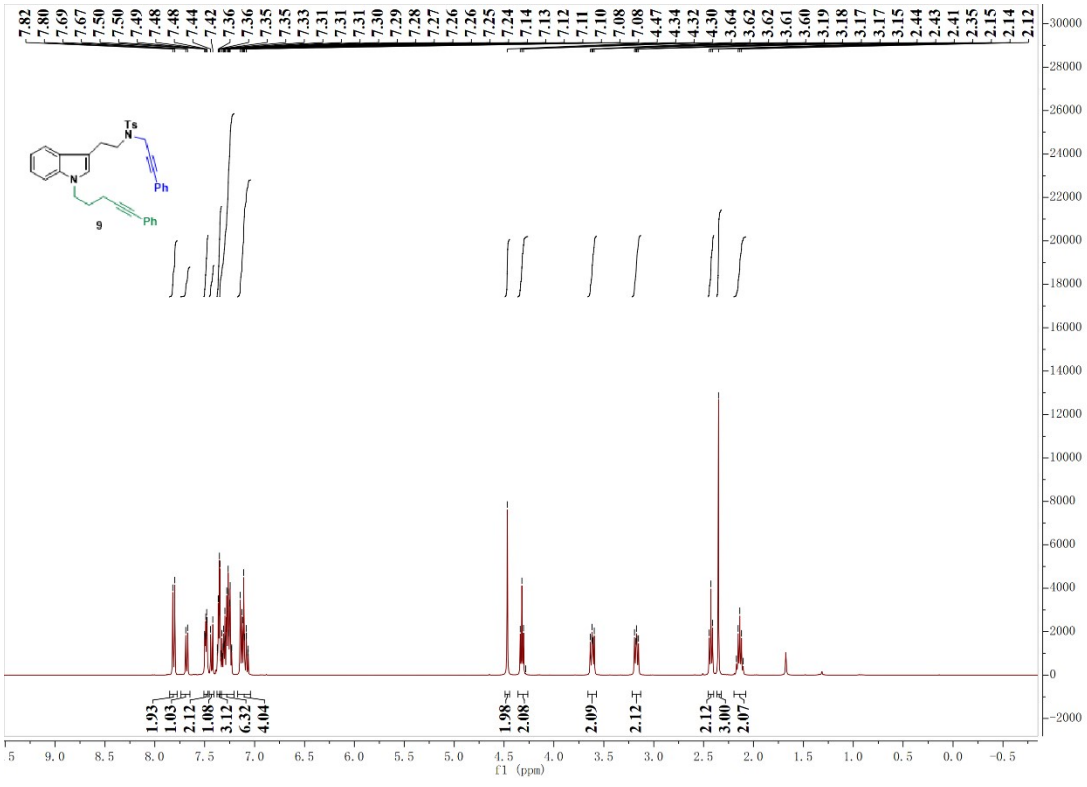


Figure S151. The ^{13}C-NMR spectra copy of compound 9.