Electronic Supplementary Information

Lewis Acid-Catalyzed Intramolecular Cyclization of 7-Alkynylcycloheptatrienes with Carbonyls: Access to 3,4-Disubstituted 2,5-Dihydropyrroles

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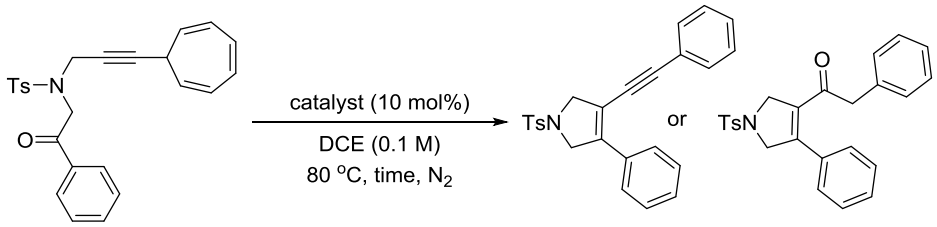
CONTENTS

1. General information

Unless otherwise stated, all reactions were performed in sealed tube (capacity 15 mL). Commercially available reagents were used without further purification. NMR spectra were recorded on Bruker Avance NEO 500 or Bruker Avance III 600 instruments and calibrated using residual solvent peaks as internal reference. Chemical shifts (δ) were expressed in ppm with reference to the solvent signals. Coupling constants *J* are given in Hz. High-resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) [quantitative time-of-flight (Q-TOF)] ionization sources on an Agilent 6200 Q-TOF MS. Melting points were determined on a SGW X-4A melting point apparatus. X-ray diffraction was obtained by Bruker D8 QUEST. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel GF254. Silica gel (Huanghai 300-400 mesh) was used for flash column chromatography.

2. Screening of reaction conditions.

Table S1 Optimization of the catalyst.

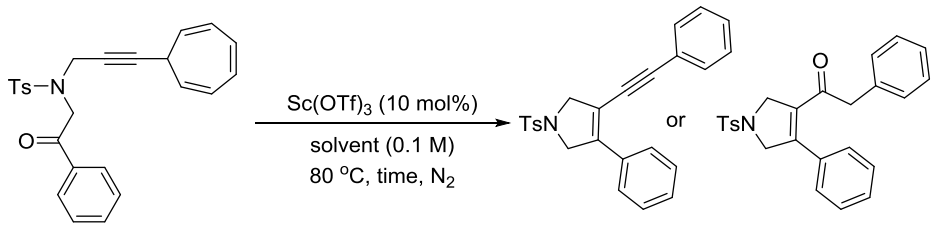


1a **2a** **3a**

Entry[a]	Catalyst	Solvent	Time	Conversion (%)	yield of **2a/3a** (%)[b]
1	AgOTf	DCE	14 h	94	40 / <5
2	$AgNTf_2$	DCE	14 h	95	21 / trace
3	CuOTf	DCE	14 h	95	45 / <5
4	$Cu(OTf)_2$	DCE	14 h	>95	57 / <5
5	$Fe(OTf)_2$	DCE	14 h	0	NR
6	***$Sc(OTf)_3$***	***DCE***	***10 h***	***>95***	***70 / <5***
7	$B(C_6F_5)_3$	DCE	14 h	<10	trace / trace
8	$Hg(OTf)_2$	DCE	14 h	>95	13 / <5
9	$Sn(OTf)_2$	DCE	14 h	>95	54 / <5
10	$Zn(OTf)_2$	DCE	14 h	0	NR
11	$Ni(OTf)_2$	DCE	14 h	0	NR
12	$In(OTf)_3$	DCE	14 h	90	40 / <5
13	HOTf	DCE	14 h	73	52 / trace
14	$HNTf_2$	DCE	14 h	>95	43 / <5
15	TMSOTf	DCE	14 h	82	45 / trace
16	$Yb(OTf)_3$	DCE	10 h	63	42 / trace
17	$BF_3•Et_2O$	DCE	10 h	>95	42 / 28
18	$Y(OTf)_3$	DCE	10 h	60	37 / trace
19	$La(OTf)_3$	DCE	10 h	30	13 / trace
20	$Er(OTf)_3$	DCE	10 h	73	39 / trace
21	TsOH	DCE	14 h	46	trace / ND
22	$TsOH•H_2O$	DCE	14 h	47	trace / ND
23	$Fe(OTf)_3$	DCE	10 h	>95	54 / <5
24	$CuCl_2$	DCE	14 h	<10	ND / ND
25[c]	$CuCl_2$ / $NaBAr_F$	DCE	14 h	>95	11 / 15
26	$Cu(MeCN)_4PF_6$	DCE	14 h	52	11 / trace
27	$Sc(OTf)_3$	TFE	10 h	>95	trace / 60
28	$Yb(OTf)_3$	TFE	10 h	>95	trace / 51
29	$BF_3•Et_2O$	TFE	10 h	>99	trace / 51
30	$Y(OTf)_3$	TFE	10 h	>99	14 / 50
31	$La(OTf)_3$	TFE	10 h	>99	18 / 37
32	$Er(OTf)_3$	TFE	10 h	>99	<10 / 47
33	$Fe(OTf)_3$	TFE	10 h	>99	11 / 57
34		DCE	10 h	0	NR
35		TFE	10 h	0	NR

[a] Reaction conditions: **1a** (0.1 mmol), catalyst (10 mol%), additive (1.0 equiv), dry solvent (1.0 mL), at 80 °C, N_2.
[b] Isolated yields. [c] $CuCl_2$ (10 mol%) / $NaBAr_F$ (20 mol%) was used. NR = no reaction. ND = not dectected.

Table S2 Optimization of the solvent.

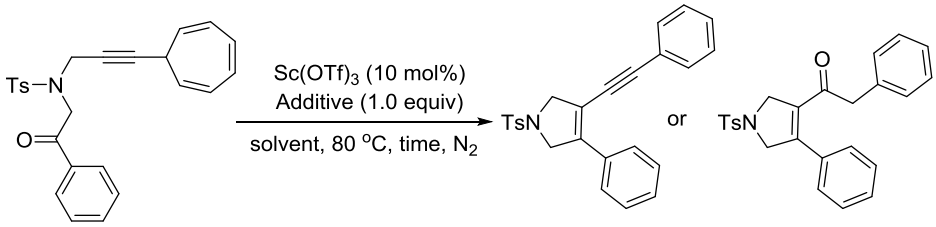


1a **2a** **3a**

Entry[a]	Catalyst	Solvent	Time	Conversion (%)	yield of **2a/3a** (%)[b]
1	$Sc(OTf)_3$	toluene	10 h	>95	45 / <10
2	$Sc(OTf)_3$	THF	10 h	45	13 / <10
3	$Sc(OTf)_3$	DMF	10 h	0	NR
4	$Sc(OTf)_3$	DMSO	10 h	0	NR
5	$Sc(OTf)_3$	acetone[c]	10 h	30	trace / 14
6	$Sc(OTf)_3$	MeCN	10 h	66	10 / 22
7	$Sc(OTf)_3$	MeOH	10 h	<10	trace / trace
8	$Sc(OTf)_3$	DCM	10 h	>95	38 / <5
9	$Sc(OTf)_3$	$CHCl_3$[c]	10 h	>95	43 / 22
10	$Sc(OTf)_3$	PhCl	10 h	>95	41 / <5
11	$Sc(OTf)_3$	CCl_4[c]	10 h	91	31 / 13
12	$Sc(OTf)_3$	HFIP[c]	10 h	>95	trace / trace
13	$Sc(OTf)_3$	TFE[c]	10 h	>95	trace / 60

[a] Reaction conditions: **1a** (0.1 mmol), catalyst (10 mol%), additive (1.0 equiv), dry solvent (1.0 mL), at 80 °C, N_2. [b] Isolated yields. [c] The solvent was not dry. NR = no reaction. ND = not dectected.

Table S3 Optimization of the additive.



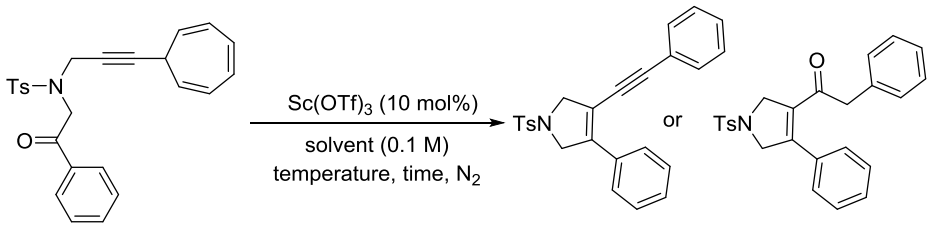
1a **2a** **3a**

Entry[a]	Catalyst	Additive	Solvent	Time	Conversion (%)[b]	yield of **2a/3a** (%)[b]
1	$Sc(OTf)_3$	K_2CO_3	DCE	10 h	>95	39 / trace
2	$Sc(OTf)_3$	K_2CO_3	TFE	10 h	>95	Messy
3[c]	$Sc(OTf)_3$	K_2CO_3	DCE	10 h	<10	ND / ND
4[c]	$Sc(OTf)_3$	K_2CO_3	TFE	10 h	<10	ND / ND
5[d]	$Sc(OTf)_3$	K_2CO_3	DCE	10 h	<10	trace / ND
6[d]	$Sc(OTf)_3$	K_2CO_3	TFE	10 h	<10	ND / ND
7[c]	$Sc(OTf)_3$	NaOAc	DCE	10 h	<5	ND / ND
8[c]	$Sc(OTf)_3$	NaOAc	TFE	10 h	<5	ND / ND
9[c]	$Sc(OTf)_3$	DIPEA	DCE	10 h	<5	ND / ND
10[c]	$Sc(OTf)_3$	DIPEA	TFE	10 h	>95	<5 / <5
11[c]	$Sc(OTf)_3$	DBU	DCE	10 h	<10	ND / ND
12[c]	$Sc(OTf)_3$	DBU	TFE	10 h	<5	ND / ND
13[c]	$Sc(OTf)_3$	Et_3N	DCE	10 h	<10	trace / trace
14[c]	$Sc(OTf)_3$	Et_3N	TFE	10 h	<5	ND / ND
15[c]	$Sc(OTf)_3$	KOMe	DCE	10 h	<10	ND / ND
16[c]	$Sc(OTf)_3$	KOMe	TFE	10 h	<10	ND / ND
17[c]	$Sc(OTf)_3$	HOAc	DCE	10 h	<10	<5 / trace
18[c]	$Sc(OTf)_3$	HOAc	TFE	10 h	>95	<5 / 43
19	$Sc(OTf)_3$	3 Å MS	DCE	10 h	>95	56 / <5
20	$Sc(OTf)_3$	3 Å MS	TFE	10 h	>99	8 / 21
21	$Sc(OTf)_3$	4 Å MS	DCE	10 h	>95	51 / <5

22	$Sc(OTf)_3$	4 Å MS	TFE	10 h	>99	<10 / 51
23	$Sc(OTf)_3$	Na_2SO_4	DCE	10 h	>90	51 / <5
24	$Sc(OTf)_3$	Na_2SO_4	TFE	10 h	>99	<10 / 50
25	$Sc(OTf)_3$	$MgSO_4$	DCE	10 h	>90	46 / <5
26	$Sc(OTf)_3$	$MgSO_4$	TFE	10 h	>99	5 / 47
27	$Sc(OTf)_3$	H_2O	TFE	10 h	>99	<10 / 50

[a] Reaction conditions: **1a** (0.1 mmol), catalyst (10 mol%), additive (1.0 equiv), dry solvent (1.0 mL), at 80 °C, N_2. [b] Isolated yields. [c] At room temperature. [d] At 50 °C. ND = not dectected.

Table S4 Optimization of the temperature.

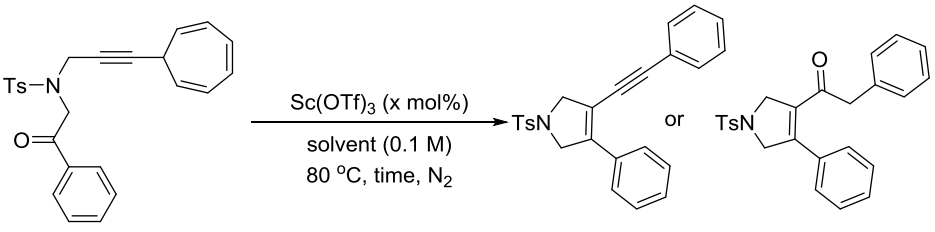


1a **2a** **3a**

Entry[a]	Catalyst	Solvent	Temp. (°C)	Time	Conversion (%)[b]	yield of **2a/3a** (%)[b]
1	$Sc(OTf)_3$	DCE	60	10 h	>95	37 / <5
2	$Sc(OTf)_3$	TFE	60	10 h	>95	<5 / 37
3	$Sc(OTf)_3$	DCE	100	10 h	>95	49 / trace
4	$Sc(OTf)_3$	TFE	100	10 h	>95	trace / 52
5	$Sc(OTf)_3$	DCE	90	10 h	>95	51 / trace
6	$Sc(OTf)_3$	TFE	90	10 h	>95	ND / 54
7	$Sc(OTf)_3$	DCE	85	10 h	>95	63 / trace
8	$Sc(OTf)_3$	TFE	85	10 h	>95	trace / 55

[a] Reaction conditions: **1a** (0.1 mmol), catalyst (10 mol%), additive (1.0 equiv), dry solvent (1.0 mL), at temperature, N_2. [b] Isolated yields. ND = not dectected.

Table S5 Optimization of the equivalent of catalyst.

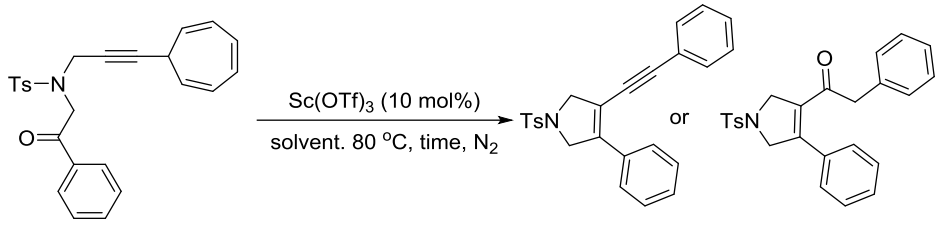


1a **2a** **3a**

Entry[a]	Catalyst (x mol%)	Solvent	Time	Conversion (%)[b]	yield of **2a/3a** (%)[b]
1	$Sc(OTf)_3$ (5)	DCE	10 h	>95	63 / 13
2	$Sc(OTf)_3$ (5)	TFE	10 h	>99	9 / 59
3	$Sc(OTf)_3$ (20)	DCE	10 h	>95	49 / 18
4	$Sc(OTf)_3$ (20)	TFE	10 h	>99	7 / 50
5	HOTf (20)	DCE	14 h	>99	46 / <5

[a] Reaction conditions: **1a** (0.1 mmol), catalyst (x mol%), additive (1.0 equiv), dry solvent (1.0 mL), at 80 °C, N_2. [b] Isolated yields.

Table S6 Optimization of the concentration.



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

Entry[a]	Catalyst	Solvent (y mL)	Time	Conversion (%)[b]	yield of **2a/3a** (%)[b]
1	$Sc(OTf)_3$	DCE (0.5)	10 h	>95	54 / 15
2	$Sc(OTf)_3$	TFE (0.5)	10 h	>99	9 / 48
3	$Sc(OTf)_3$	DCE (2.0)	10 h	>95	63 / <5
4	***$Sc(OTf)_3$***	***TFE (2.0)***	***10 h***	***>99***	***9 / 70***
5	$Sc(OTf)_3$	DCE (4.0)	10 h	>95	62 / <5
6	$Sc(OTf)_3$	TFE (4.0)	10 h	>99	7 / 68

[a] Reaction conditions: **1a** (0.1 mmol), catalyst (10 mol%), additive (1.0 equiv), dry solvent (y mL), at 80 °C, N_2. [b] Isolated yields.

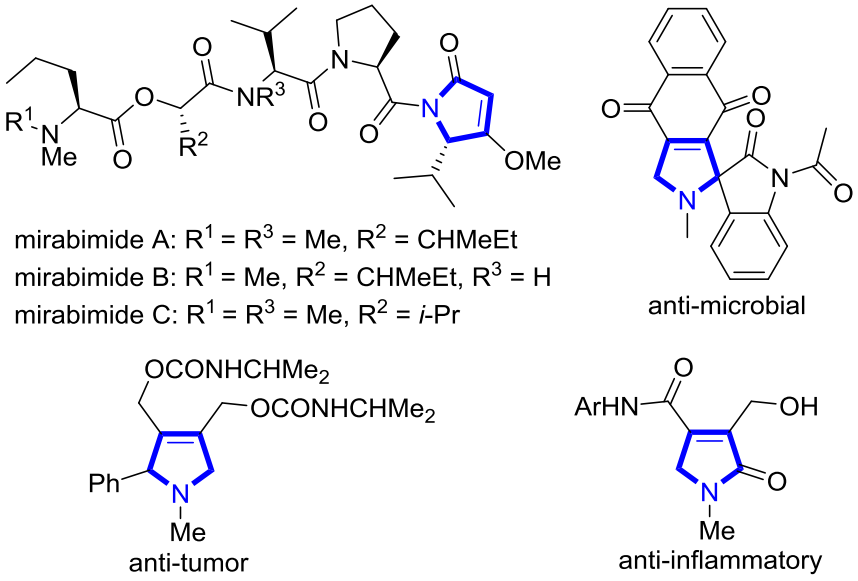
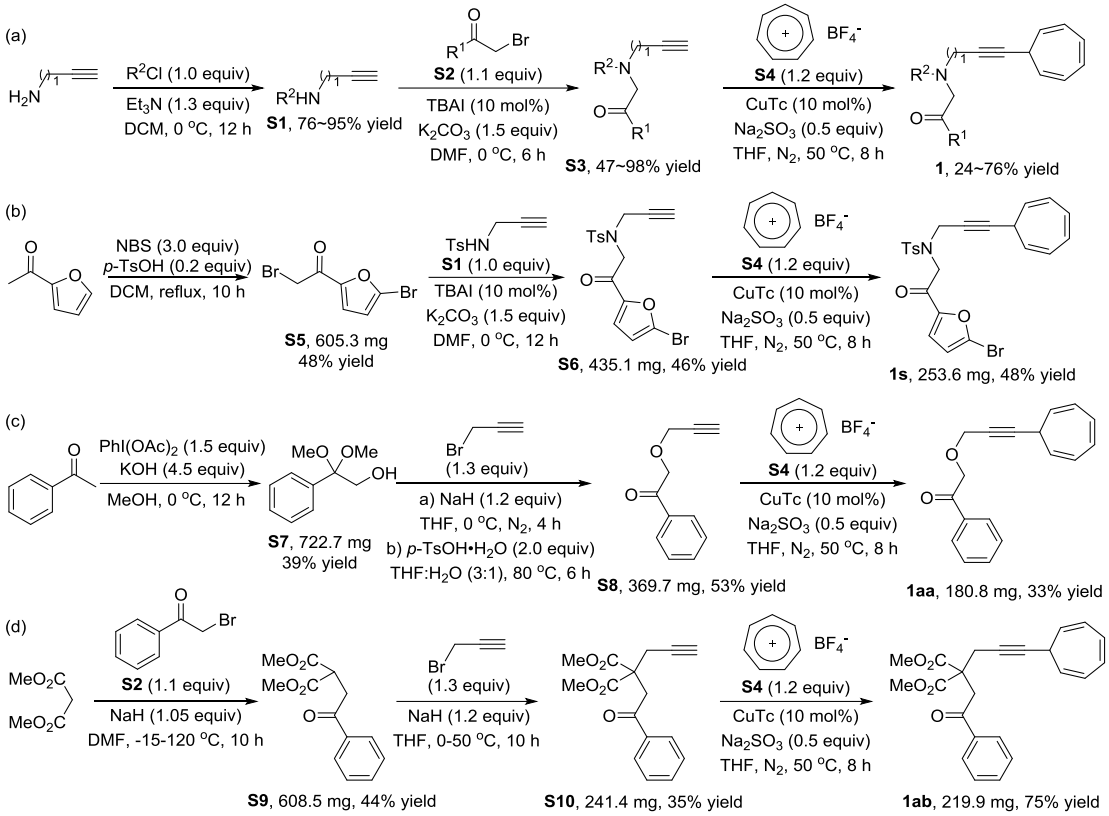


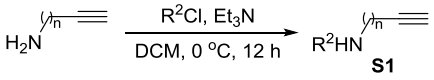
Figure S1 Natural alkaloids and bioactive compounds containing a 2,5-dihydropyrrole core.

3. Experimental procedures and characterization data for substrates.

3.1. General procedure for the synthesis of 1a-1ab



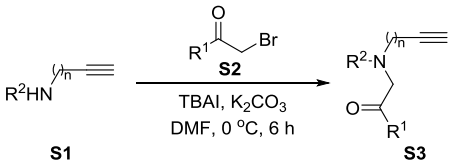
Except for **1s**, **1aa** and **1ab**, all other substrates were obtained following general procedure (a). Substrate **1s** was obtained following general procedure (b). Substrate **1aa** was obtained following general procedure (c). Substrate **1ab** was obtained following general procedure (d). Unless otherwise stated, all yields reported only refer to the final step.



R^2 = Ts, n = 1, **S1a**, 1.988 g, 95% yield; R^2 = $PhSO_2$, n = 1, **S1d**, 0.734 g, 76% yield;
R^2 = Bs, n = 1, **S1b**, 1.260 g, 92% yield; R^2 = *m*-$(Me)C_6H_4SO_2$, n = 1, **S1e**, 0.938 g, 90% yield;
R^2 = Ns, n = 1, **S1c**, 1.031 g, 86% yield; R^2 = Ts, n = 2, **S1f**, 0.983 g, 88% yield;

Preparation for **S1**[1]: After prop-2-yn-1-amine in DCM (0.3 M) and triethylamine (1.3 equiv) was added to a round-bottomed flask (100 mL) equipped with a stir bar, the reaction mixture was cooled down to 0 °C, followed by the addition of sulfonyl chlorides (1.0 equiv) in DCM (1.0 M). The reaction mixture was stirred at 0 °C

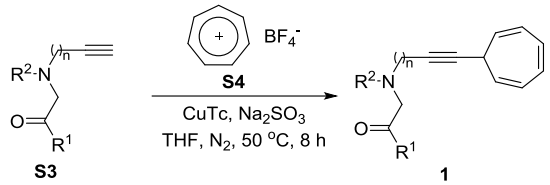
overnight. After consumption of sulfonyl chloride indicated by TLC, the reaction was quenched with water, and extracted with DCM. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 4/1) to give the corresponding product **S1** (76~95% yield) as yellow solids.



S1 **S3**

R^1 = Ph, R^2 = Ts, n = 1, **S3a**, 1.337 g, 82% yield;
R^1 = *p*-(Me)C_6H_4, R^2 = Ts, n = 1, **S3b**, 1.233 g, 72% yield;
R^1 = *p*-(OMe)C_6H_4, R^2 = Ts, n = 1, **S3c**, 1.182 g, 67% yield;
R^1 = *p*-(F)C_6H_4, R^2 = Ts, n = 1, **S3d**, 401.2 mg, 58% yield;
R^1 = *p*-(Cl)C_6H_4, R^2 = Ts, n = 1, **S3e**, 1.780 g, 98% yield;
R^1 = *p*-(Br)C_6H_4, R^2 = Ts, n = 1, **S3f**, 1.791 g, 80% yield;
R^1 = *p*-(I)C_6H_4, R^2 = Ts, n = 1, **S3g**, 473.1 mg, 52% yield;
R^1 = *p*-(CF_3)C_6H_4, R^2 = Ts, n = 1, **S3h**, 567.2 mg, 72% yield;
R^1 = *p*-(CN)C_6H_4, R^2 = Ts, n = 1, **S3i**, 647.7 mg, 61% yield;
R^1 = *p*-(Ph)C_6H_4, R^2 = Ts, n = 1, **S3j**, 589.8 mg, 73% yield;
R^1 = *m*-(Me)C_6H_4, R^2 = Ts, n = 1, **S3k**, 730.7 mg, 47% yield;
R^1 = *m*-(OMe)C_6H_4, R^2 = Ts, n = 1, **S3l**, 643.9 mg, 90% yield;
R^1 = *m*-(Cl)C_6H_4, R^2 = Ts, n = 1, **S3m**, 546.2 mg, 75% yield;
R^1 = *m*-(Br)C_6H_4, R^2 = Ts, n = 1, **S3n**, 469.4 mg, 58% yield;
R^1 = *o*-(Me)C_6H_4, R^2 = Ts, n = 1, **S3o**, 1.237 g, 72% yield;
R^1 = *o*-(Cl)C_6H_4, R^2 = Ts, n = 1, **S3p**, 589.3 mg, 81% yield;
R^1 = *β*-naphthyl, R^2 = Ts, n = 1, **S3q**, 691.0 mg, 91% yield;
R^1 = 2-thienyl, R^2 = Ts, n = 1, **S3r**, 534.8 mg, 80% yield;
R^1 = Ph, R^2 = Bs, n = 1, **S3t**, 750.1 mg, 96% yield;
R^1 = *p*-(Br)C_6H_4, R^2 = Bs, n = 1, **S3u**, 850.2 mg, 82% yield;
R^1 = Ph, R^2 = Ns, n = 1, **S3v**, 426.0 mg, 59% yield;
R^1 = Ph, R^2 = $PhSO_2$, n = 1, **S3w**, 561.3 mg, 90% yield;
R^1 = Ph, R^2 = *m*-(Me)$C_6H_4SO_2$, n = 1, **S3x**, 551.5 mg, 77% yield;
R^1 = cyclopropyl, R^2 = Ts, n = 1, **S3y**, 407.1 mg, 70% yield;
R^1 = Ph, R^2 = Ts, n = 2, **S3z**, 631.7 mg, 91% yield;

Preparation for **S3**[1]: The above crude product **S1** was dissolved in DMF (0.5 M) in a 100 mL round-bottomed flask, and then 2-bromo-1-ones (**S2**, 1.1 equiv) and TBAI (10 mmol%) were added to the solution. The reaction mixture was cooled down to 0 °C and then K_2CO_3 (1.5 equiv) was added and stirred at 0 °C for 6 hours. After reaction completed, reaction mixture was poured into ice-cold water and extracted into ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 4/1) to give the corresponding product **S3** (47~98% yield) as yellow solids.



S3 1

R^1 = Ph, R^2 = Ts, n = 1, **1a**, 634.1 mg, 76% yield;
R^1 = *p*-(Me)C_6H_4, R^2 = Ts, n = 1, **1b**, 466.7 mg, 54% yield;
R^1 = *p*-(OMe)C_6H_4, R^2 = Ts, n = 1, **1c**, 365.2 g, 41% yield;
R^1 = *p*-(F)C_6H_4, R^2 = Ts, n = 1, **1d**, 239.6 mg, 63% yield;
R^1 = *p*-(Cl)C_6H_4, R^2 = Ts, n = 1, **1e**, 285.0 mg, 63% yield;
R^1 = *p*-(Br)C_6H_4, R^2 = Ts, n = 1, **1f**, 242.6 mg, 49% yield;
R^1 = *p*-(I)C_6H_4, R^2 = Ts, n = 1, **1g**, 224.0 mg, 41% yield;
R^1 = *p*-(CF_3)C_6H_4, R^2 = Ts, n = 1, **1h**, 465.3 mg, 48% yield;
R^1 = *p*-(CN)C_6H_4, R^2 = Ts, n = 1, **1i**, 411.1 mg, 57% yield;
R^1 = *p*-(Ph)C_6H_4, R^2 = Ts, n = 1, **1j**, 164.9 mg, 33% yield;
R^1 = *m*-(Me)C_6H_4, R^2 = Ts, n = 1, **1k**, 216.4 mg, 50% yield;
R^1 = *m*-(OMe)C_6H_4, R^2 = Ts, n = 1, **1l**, 272.4 mg, 48% yield;
R^1 = *m*-(Cl)C_6H_4, R^2 = Ts, n = 1, **1m**, 189.3 mg, 42% yield;
R^1 = *m*-(Br)C_6H_4, R^2 = Ts, n = 1, **1n**, 231.0 mg, 41% yield;
R^1 = *o*-(Me)C_6H_4, R^2 = Ts, n = 1, **1o**, 655.1 mg, 76% yield;
R^1 = *o*-(Cl)C_6H_4, R^2 = Ts, n = 1, **1p**, 281.4 mg, 49% yield;
R^1 = *β*-naphthyl, R^2 = Ts, n = 1, **1q**, 538.4 mg, 63% yield;
R^1 = 2-thienyl, R^2 = Ts, n = 1, **1r**, 210.0 mg, 50% yield;
R^1 = Ph, R^2 = Bs, n = 1, **1t**, 315.4 mg, 36% yield;
R^1 = *p*-(Br)C_6H_4, R^2 = Bs, n = 1, **1u**, 215.0 mg, 38% yield;
R^1 = Ph, R^2 = Ns, n = 1, **1v**, 251.0 mg, 56% yield;
R^1 = Ph, R^2 = $PhSO_2$, n = 1, **1w**, 221.8 mg, 55% yield;
R^1 = Ph, R^2 = *m*-(Me)$C_6H_4SO_2$, n = 1, **1x**, 306.8 mg, 48% yield;
R^1 = cyclopropyl, R^2 = Ts, n = 1, **1y**, 127.2 mg, 24% yield;
R^1 = Ph, R^2 = Ts, n = 2, **1z**, 494.1 mg, 62% yield;

Preparation for **1** [2]: A 25 mL round-bottomed flask was charged with a mixture of **S3**, **S4** (1.2 equiv), CuTc (10 mmol%) and Na_2SO_3 (0.5 equiv). After three cycles of nitrogen replacement, THF (0.2 M) was added to the mixture, and the resulting solution was stirred at 50 °C in an oil bath for 8 hours, then cooled to room temperature, filtered through celite, and washed with ethyl acetate. The mixture was concentrated and purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 8/1) to give the corresponding product **1** (24~76% yield) as yellow solids or yellow oils.

Preparation for **S5**[3]: After *N*-bromosuccinimide (2.672 g, 15 mmol) and 4-methyl-benzenesulfonic acid (179.9 mg, 1 mmol) dissolved in DCM (12 mL) and added to a round-bottomed flask (100 mL) equipped with a stir bar, the reaction mixture was cooled down to 0 °C, followed by the addition of 1-(furan-2-yl)ethan-1-one (0.5 mL, 5 mmol) in DCM (3 mL). Then, the resulting solution was stirred at 80 °C in an oil bath for 10 hours. After reaction completed, the reaction mixture was quenched with water, and extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 11/1) to give the corresponding product **S5** (605.3 mg, 48% yield) as a yellow solid.

Preparation for **S6**[1]: **S1** (418.7 mg, 2.0 mmol) was dissolved in DMF (6 mL) in a 100

mL round-bottomed flask, and then **S5** (605.3 mg, 2.4 mmol) and TBAI (74.1 mg, 0.2 mmol) were added to the solution. The reaction mixture was cooled down to 0 °C and then K_2CO_3 (415.1 mg, 3.0 mmol) was added and stirred at 0 °C for 10 hours. After reaction completed, reaction mixture was poured into ice-cold water and extracted into ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6/1) to give the corresponding product **S6** (435.1 mg, 46% yield) as a yellow oil.

Preparation for **1s**[2]: A 50 mL round-bottomed flask was charged with a mixture of **S4** (293.0 mg, 1.63 mmol), CuTc (17.9 mg, 0.14 mmol) and Na_2SO_3 (130.4 mg, 0.68 mmol). After three cycles of nitrogen replacement, **S6** (430.1 mg, 1.09 mmol) in THF (5 mL) was added to the mixture, and the resulting solution was stirred at 50 °C in an oil bath for 8 hours, then cooled to room temperature, filtered through celite, and washed with ethyl acetate. The mixture was concentrated and purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 8/1) to give the corresponding product **1s** (253.6 mg, 48% yield) as a yellow solid.

Preparation for **S7**[4]: A 50 mL round-bottomed flask was charged with a mixture of $PhI(OAc)_2$ (4.841 g, 15 mmol) and KOH (2.522 g, 45 mmol). After three cycles of nitrogen replacement, the reaction mixture was cooled down to 0 °C and then acetophenone (1.17 mL, 10 mmol) in MeOH (15 mL) was added and stirred at 0 °C for 12 hours. After reaction completed, reaction mixture was poured into ice-cold water and extracted into ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6/1) to give the corresponding product **S7** (722.7 mg, 39% yield) as a yellow oil.

Preparation for **S8**[4]: Step 1: A 50 mL round-bottomed flask was charged with a mixture

of **S7** (722.7 mg, 4 mmol) and NaH (201.7 mg, 5 mmol, 60% in mineral oil). After three cycles of nitrogen replacement, THF (8 mL) was added and the reaction mixture was cooled down to 0 °C. 3-bromoprop-1-yne (0.43 mL, 5 mmol) was added dropwise after above mixture was stirred at 0 °C for 1 hour and stirred at 0 °C for another 4 hours. After reaction completed, reaction mixture was poured into ice-cold water and extracted into ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was used for the next step without further purification.

Step 2: The above crude product was dissolved in THF/H_2O (3:1, 8 mL) in a 25 mL round-bottomed flask, and then *p*-TsOH•H_2O (1.522 g, 8 mmol) was added to the solution. The resulting solution was stirred at 50 °C in an oil bath for 6 hours. After reaction completed, reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted into ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 8/1) to give the corresponding product **S8** (369.7 mg, 53% yield) as a yellow oil.

Preparation for **1aa**[2]: A 50 mL round-bottomed flask was charged with a mixture of **S4** (443.2 mg, 2.47 mmol), CuTc (28.4 mg, 0.21 mmol) and Na_2SO_3 (200.6 mg, 1.03 mmol). After three cycles of nitrogen replacement, **S8** (359.3 mg, 2.06 mmol) in THF (10 mL) was added to the mixture, and the resulting solution was stirred at 50 °C in an oil bath for 8 hours, then cooled to room temperature, filtered through celite, and washed with ethyl acetate. The mixture was concentrated and purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 8/1) to give the corresponding product **1aa** (180.8 mg, 33% yield) as a yellow oil.

Preparation for **S9**[5]: A 50 mL round-bottomed flask was charged with a mixture of NaH (203.7 mg, 5.1 mmol, 60% in mineral oil) and DMF (10 mL), the reaction mixture was cooled down to -15 °C and then dimethyl malonate (0.57 mL, 5 mmol) was added

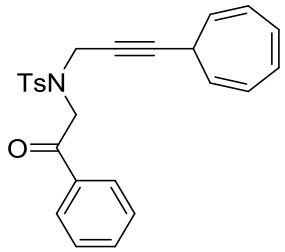
dropwise and stirred at -15 ºC for 2 hours. After that, **S2** (1.083 g, 5.5 mmol) was added to above mixture and the resulting solution was stirred at 120 ºC in an oil bath for 10 hours. After reaction completed, reaction mixture was poured into ice-cold water and extracted into ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 8/1) to give the corresponding product **S9** (608.5 mg, 44% yield) as a yellow oil.

Preparation for **S10**[5]: A 50 mL round-bottomed flask was charged with a mixture of **S9** (608.5 mg, 2.4 mmol), NaH (129.1 mg, 3.6 mmol, 60% in mineral oil) and THF (24 mL), the reaction mixture stirred at room temperature for 45 mins. After that, 3-bromoprop-1-yne (0.32 mL, 3.7 mmol) was added to above mixture and the resulting solution was stirred at 50 ºC in an oil bath for 10 hours. After reaction completed, reaction mixture was poured into ice-cold water and extracted into ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 8/1) to give the corresponding product **S10** (241.4 mg, 35% yield) as a yellow oil.

Preparation for **1ab**[2]: A 50 mL round-bottomed flask was charged with a mixture of **S4** (171.8 mg, 0.94 mmol), CuTc (10.2 mg, 0.08 mmol) and Na_2SO_3 (74.6 mg, 0.39 mmol). After three cycles of nitrogen replacement, **S10** (224.8 mg, 0.78 mmol) in THF (5 mL) was added to the mixture, and the resulting solution was stirred at 50 ºC in an oil bath for 8 hours, then cooled to room temperature, filtered through celite, and washed with ethyl acetate. The mixture was concentrated and purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 8/1) to give the corresponding product **1ab** (219.9 mg, 75% yield) as a yellow oil.

3.2. Characterization of 1a-1ab

***N*-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methyl-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide (1a)**

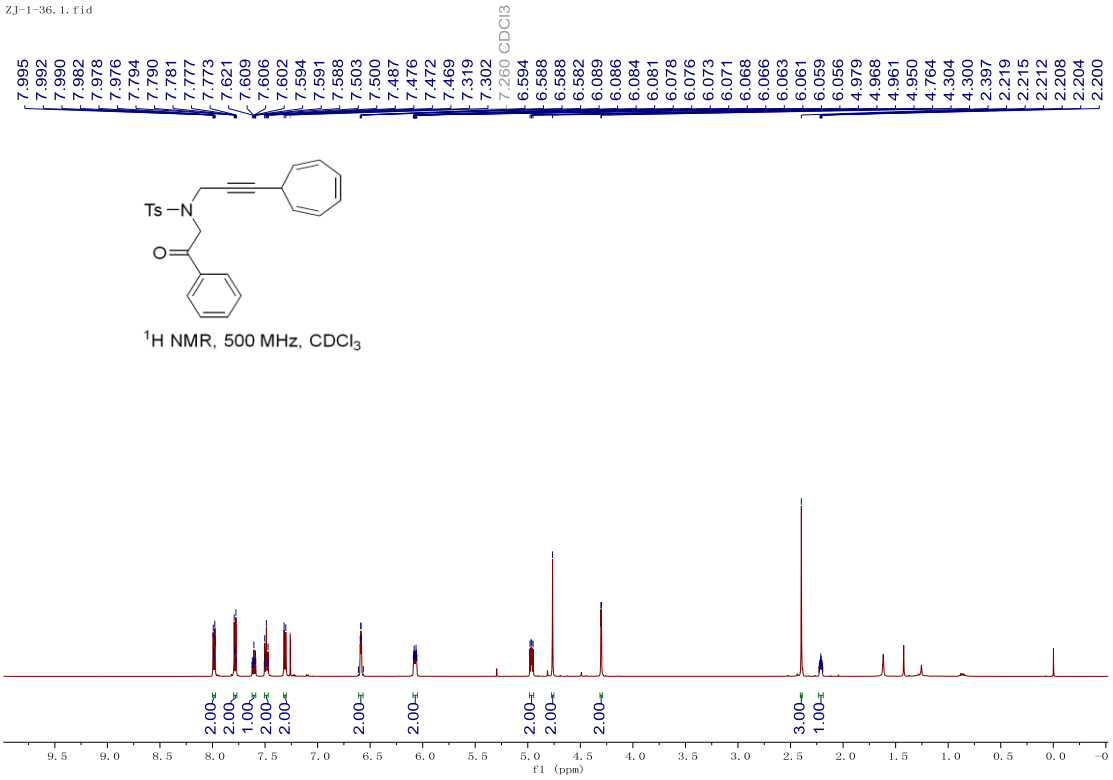


Compound **1a**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.25. 634.1 mg, 76% yield. m.p. 50-54 °C.

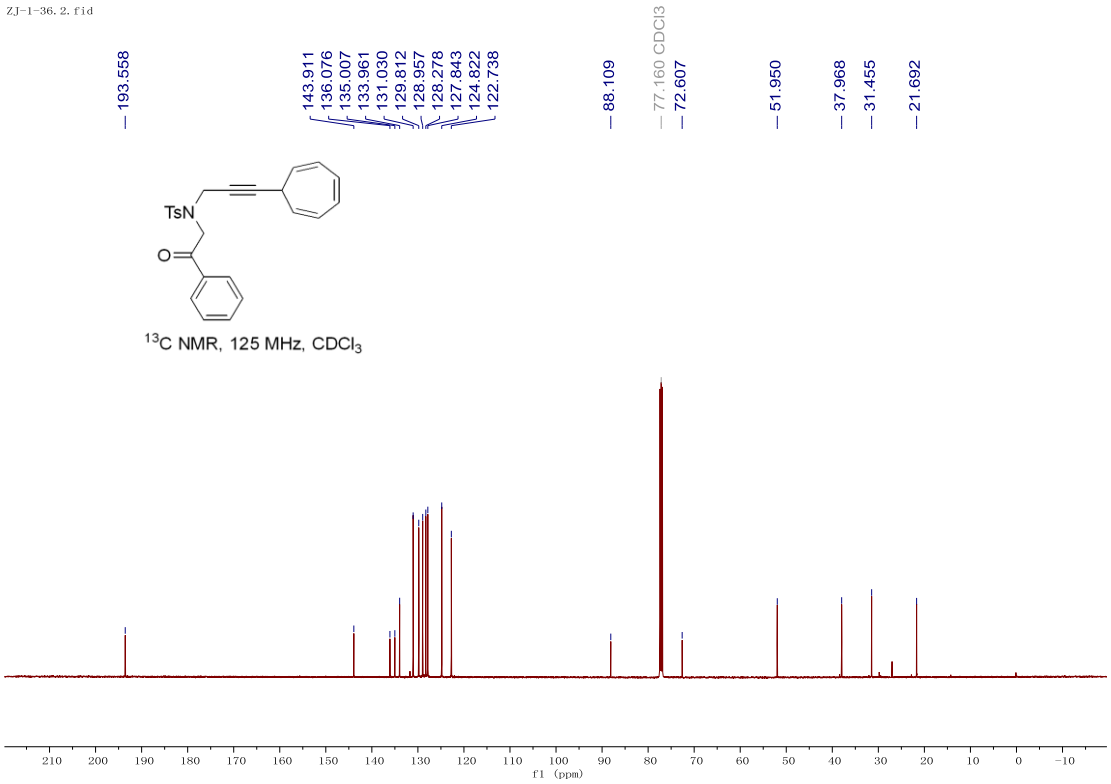
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00-7.98 (m, 2H), 7.80-7.77 (m, 2H), 7.61 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.51-7.47 (m, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 6.61-6.57 (m, 2H), 6.09-6.06 (m, 2H), 4.97 (dd, *J* = 9.0, 5.5 Hz, 2H), 4.76 (s, 2H), 4.30 (d, *J* = 2.0 Hz, 2H), 2.40 (s, 3H), 2.23-2.20 (m, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.6, 143.9, 136.1, 135.0, 134.0, 131.0, 129.8, 129.0, 128.3, 127.8, 124.8, 122.7, 88.1, 72.6, 52.0, 38.0, 31.5, 21.7.

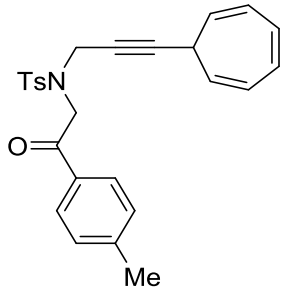
HRMS (ESI) m/z: calcd for $[C_{25}H_{23}NO_3S+H]^+$ requires: 418.1471, found: 418.1473.



^{1}H NMR, 500 MHz, $CDCl_3$



_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methyl-_N_-(2-oxo-2-(p-tolyl)ethyl)benzenesulfonamide (1b)

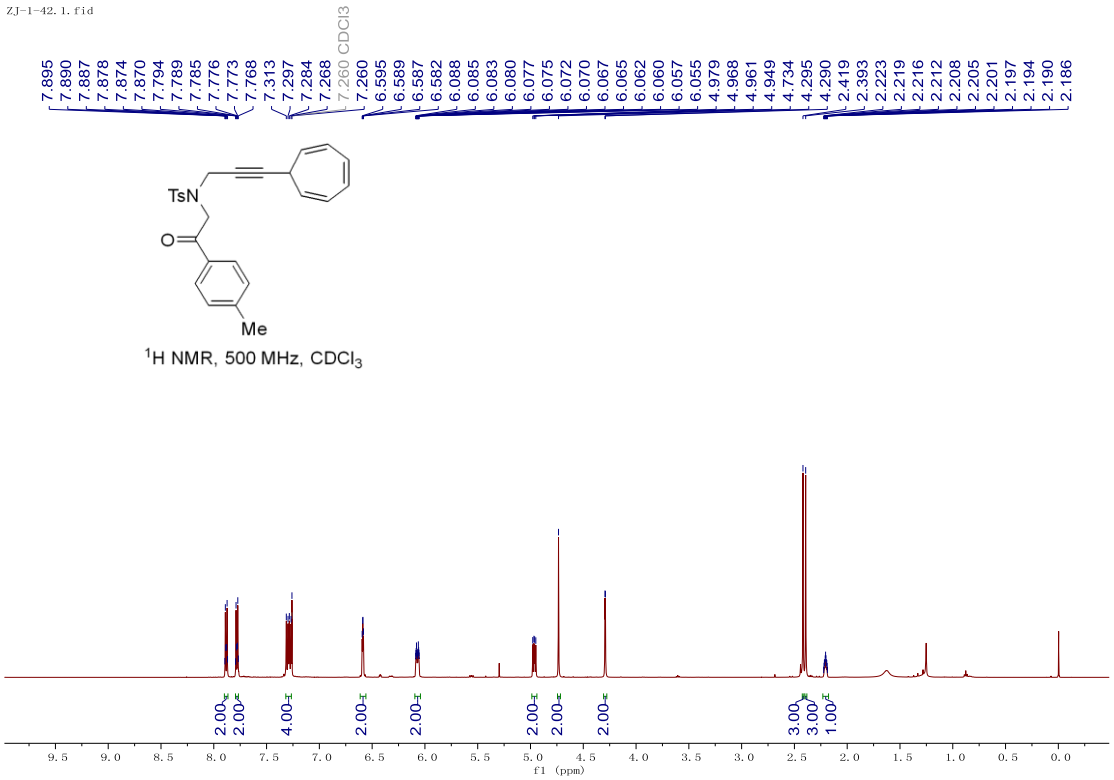


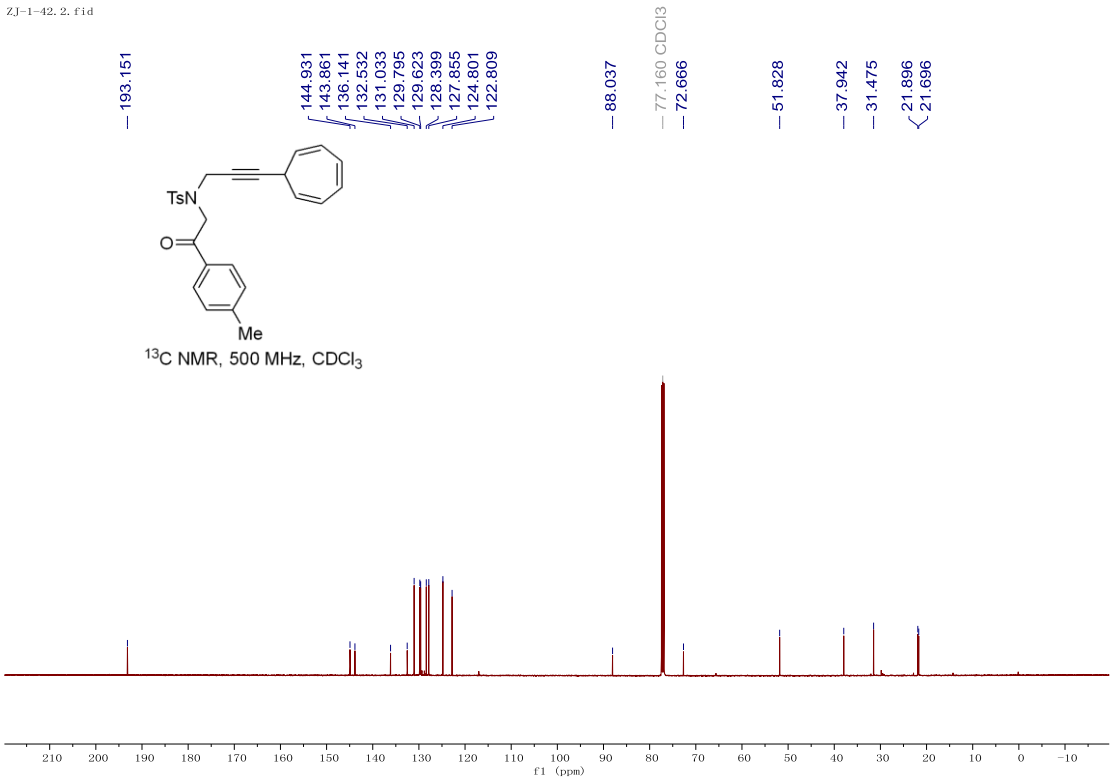
Compound **1b**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.32. 446.7 mg, 54% yield. m.p. 86-89 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90-7.87 (m, 2H), 7.79-7.77 (m, 2H), 7.31-7.27 (m, 4H), 6.61-6.57 (m, 2H), 6.09-6.06 (m, 2H), 4.96 (dd, J = 9.0, 5.5 Hz, 2H), 4.73 (s, 2H), 4.29 (d, J = 2.5 Hz, 2H), 2.42 (s, 3H), 2.39 (s, 3H), 2.22-2.19 (m, 1H).

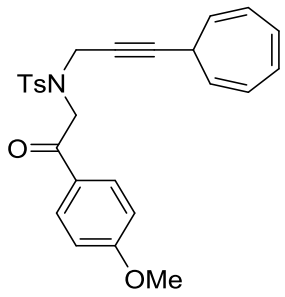
^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.2, 144.9, 143.9, 136.1, 132.5, 131.0, 129.8, 129.6, 128.4, 127.9, 124.8, 122.8, 88.0, 72.7, 51.8, 37.9, 31.5, 21.9, 21.7.

HRMS (ESI) m/z: calcd for $[C_{26}H_{25}NO_3S+H]^+$ requires: 432.1628, found: 432.1630.





_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-_N_-(2-(4-methoxyphenyl)-2-oxoethyl)-4-methylbenzenesulfonamide (1c)

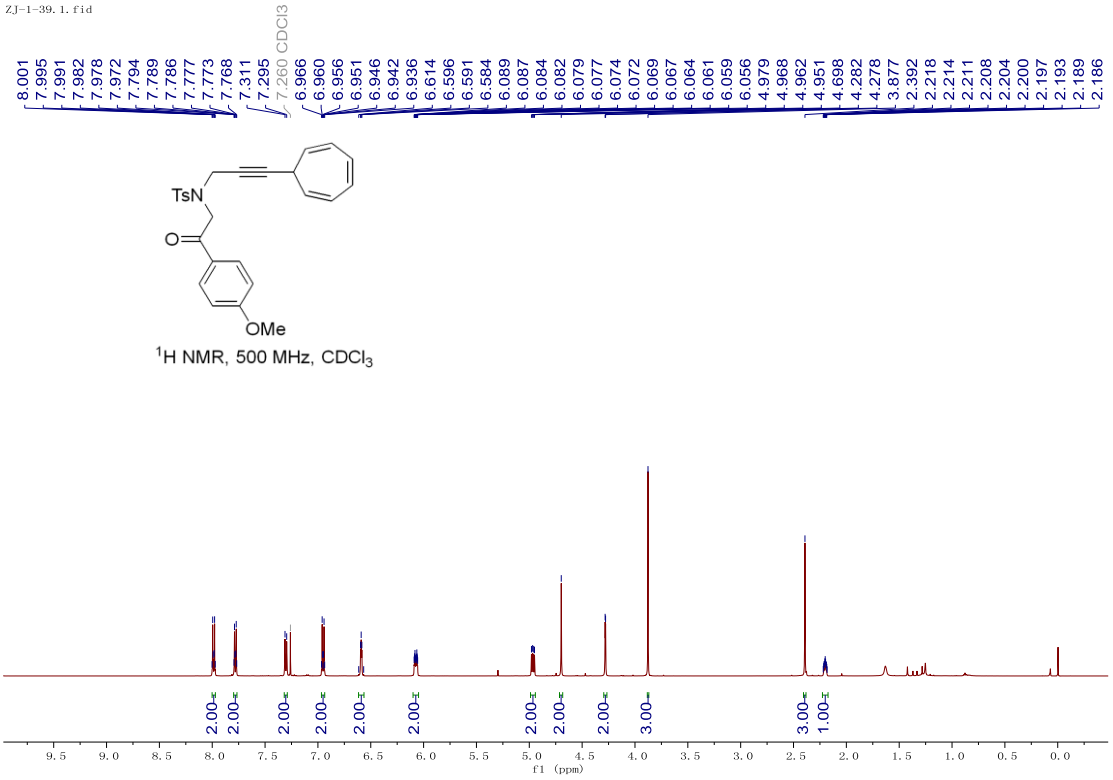


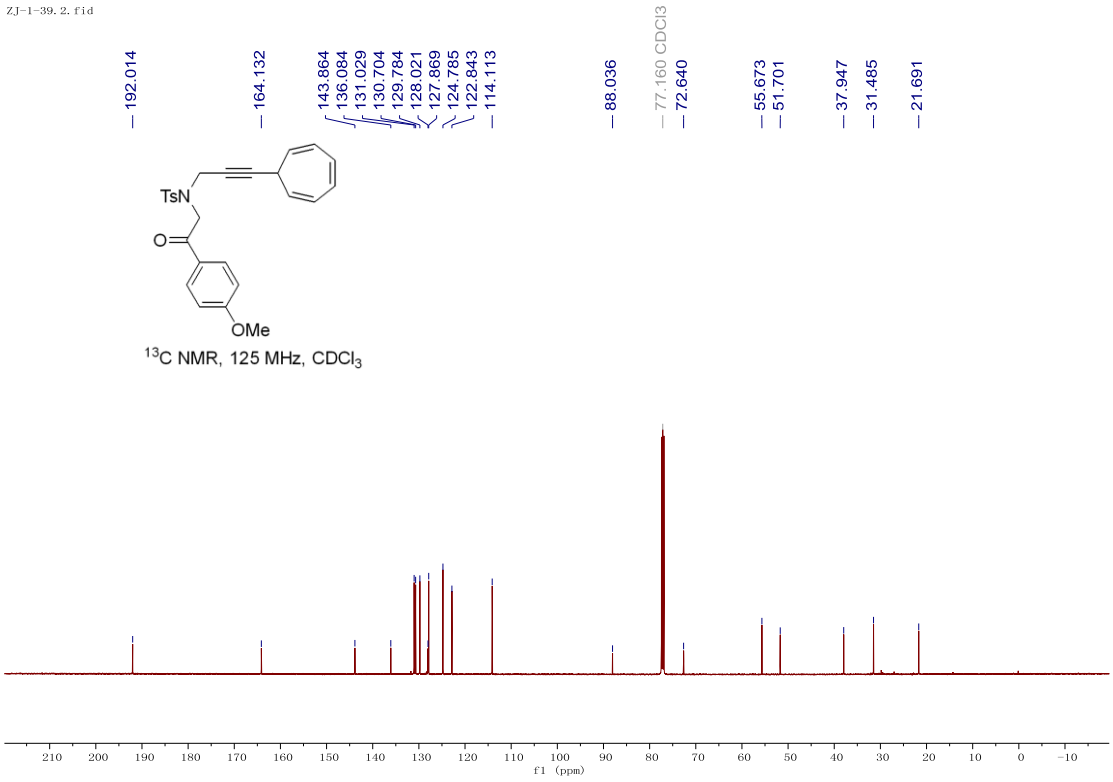
Compound **1c**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.20. 365.2 mg, 41% yield. m.p. 64-68 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00-7.97 (m, 2H), 7.79-7.77 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.97-6.94 (m, 2H), 6.61-6.57 (m, 2H), 6.09-6.06 (m, 2H), 4.97 (dd, J = 8.5, 5.5 Hz, 2H), 4.70 (s, 2H), 4.28 (d, J = 2.0 Hz, 2H), 3.88 (s, 3H), 2.39 (s, 3H), 2.22-2.18 (m, 1H).

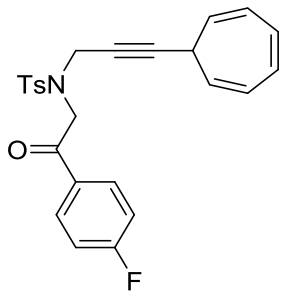
^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.0, 164.1, 143.9, 136.1, 131.0, 130.7, 129.8, 128.0, 127.9, 124.8, 122.8, 114.1, 88.0, 72.6, 55.7, 51.7, 37.9, 31.5, 21.7.

HRMS (ESI) m/z: calcd for $[C_{26}H_{25}NO_4S+H]^+$ requires: 448.1577, found: 448.1578.





_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-_N_-(2-(4-fluorophenyl)-2-oxoethyl)-4-methylbenzenesulfonamide (1d)



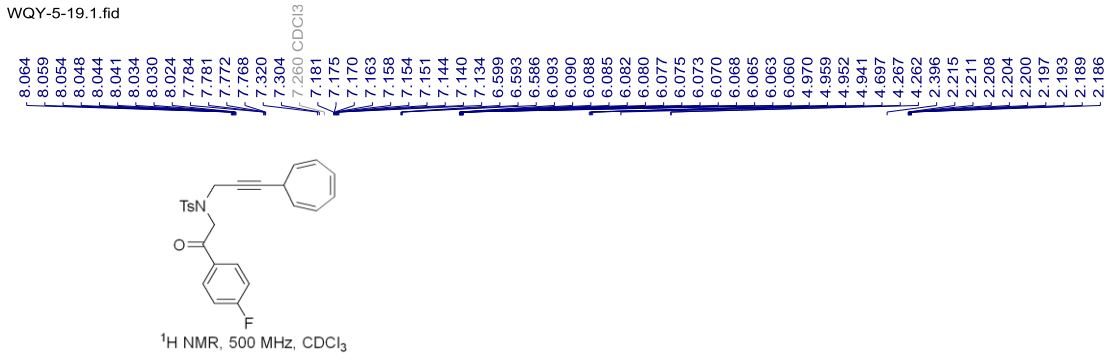
Compound **1d**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.34. 239.6 mg, 55% yield. m.p. 79-84 °C.

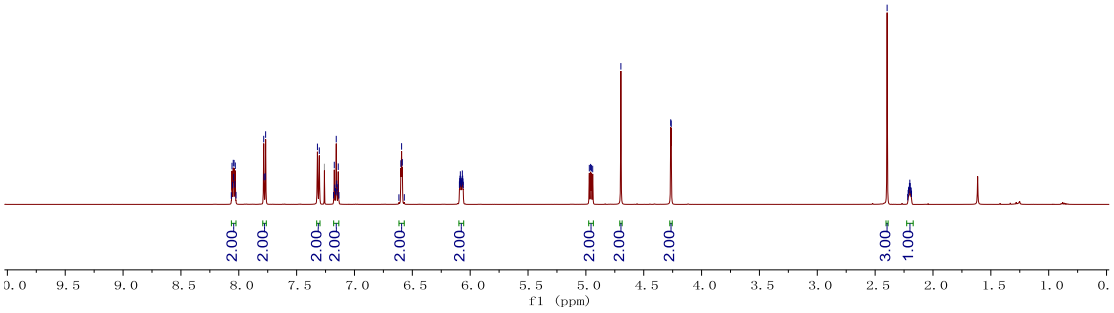
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06-8.02 (m, 2H), 7.78-7.76 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.18-7.13 (m, 2H), 6.62-6.57 (m, 2H), 6.09-6.06 (m, 2H), 4.96 (dd, *J* = 9.0, 5.5 Hz, 2H), 4.70 (s, 2H), 4.26 (d, *J* = 2.5 Hz, 2H), 2.40 (s, 3H), 2.22-2.19 (m, 1H).

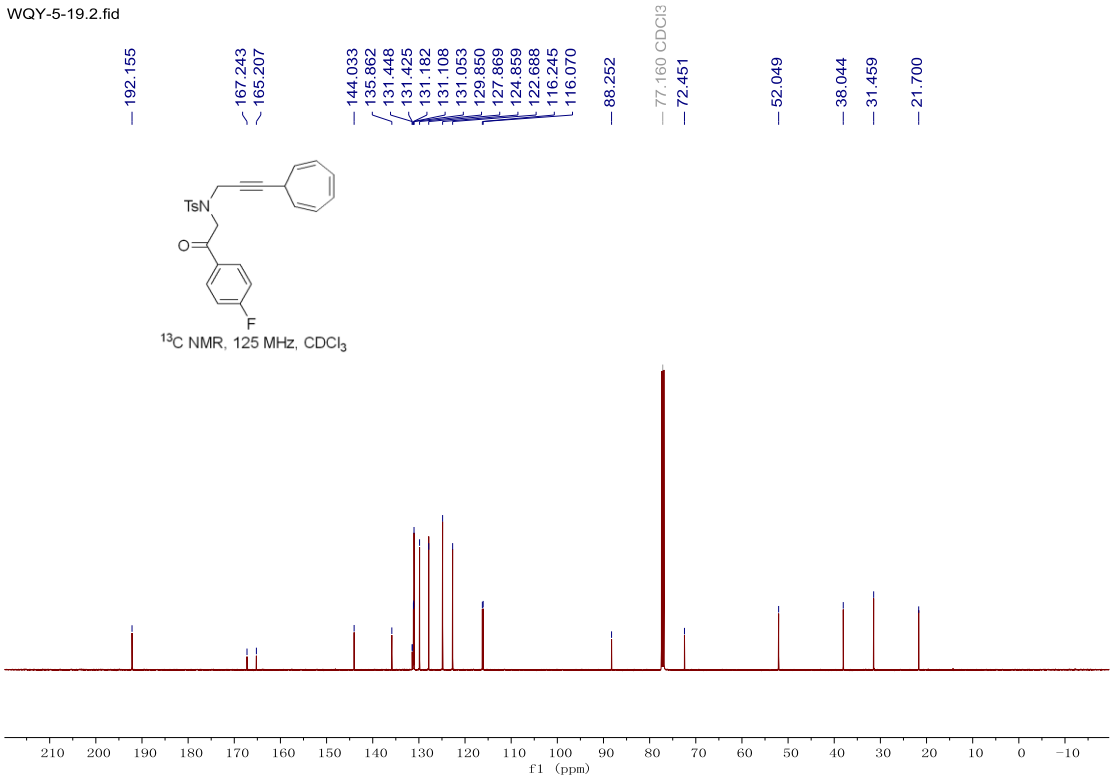
^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.2, 166.2 (d, *J* = 254.5 Hz), 144.0, 135.9, 131.4 (d, *J* = 2.9 Hz), 131.15 (d, *J* = 9.3 Hz), 131.05, 129.9, 127.9, 124.9, 122.7, 116.2 (d, *J* = 21.9 Hz), 88.3, 72.5, 52.0, 38.0, 31.5, 21.7.

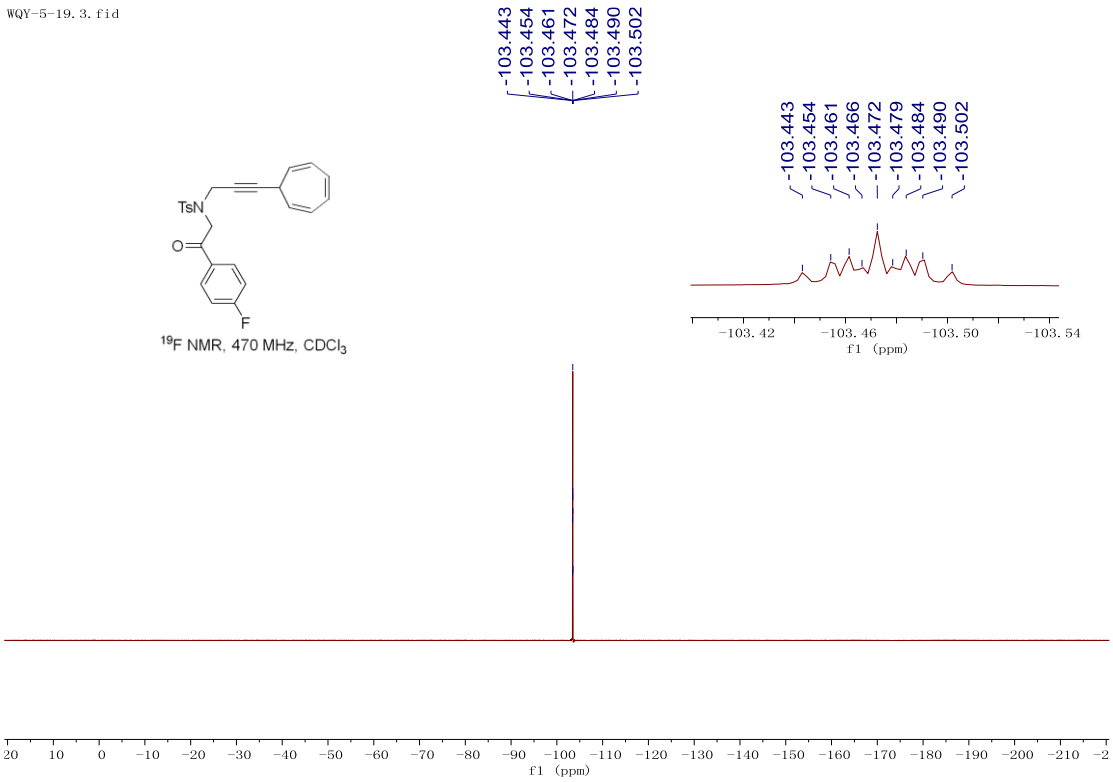
^{19}F NMR (470 MHz, Chloroform-*d*) δ (m) (-103.44)-(-103.50).

HRMS (ESI) m/z: calcd for $[C_{25}H_{22}FNO_3S+H]^+$ requires: 436.1377, found: 436.1380.

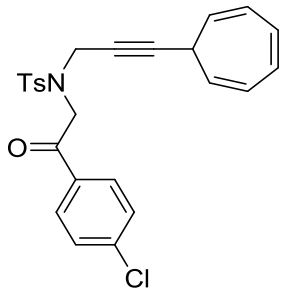








_N_-(2-(4-chlorophenyl)-2-oxoethyl)-_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1e)

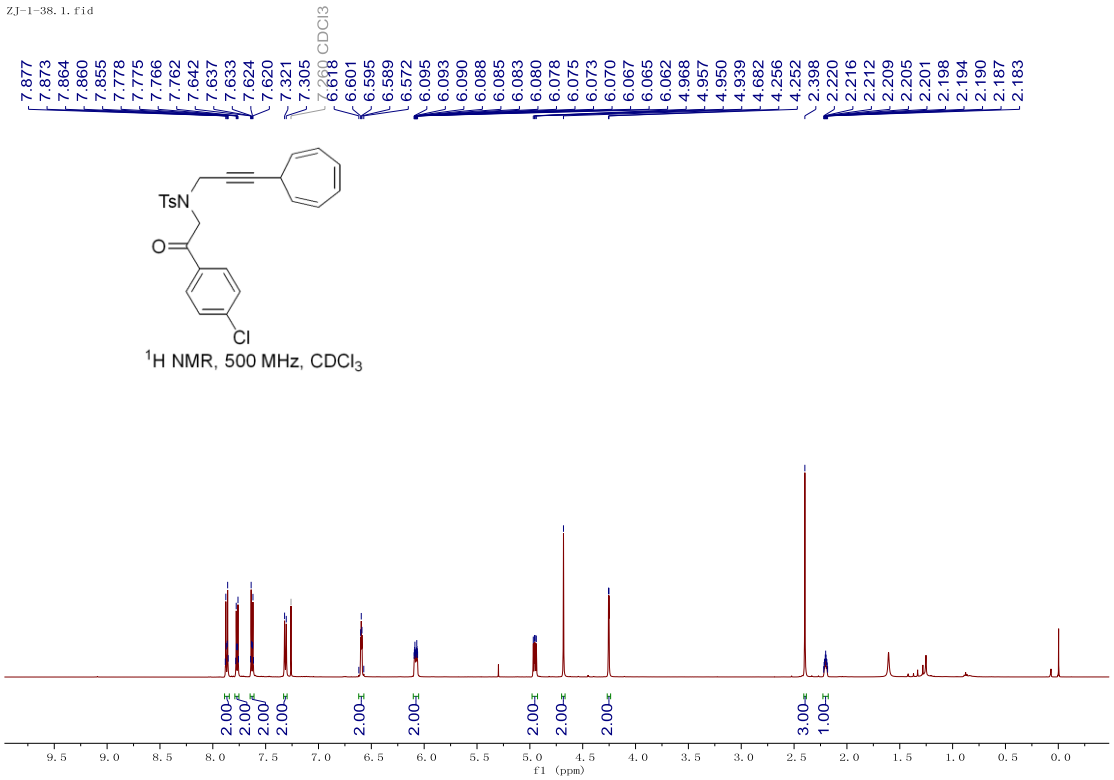


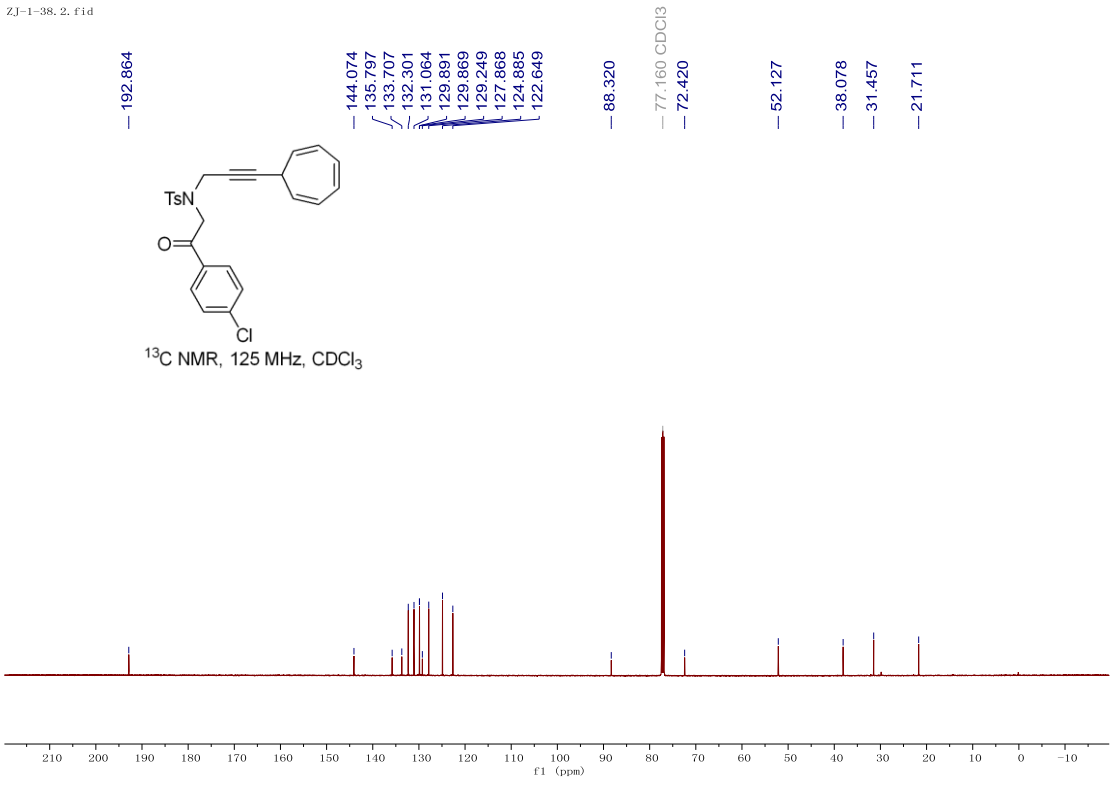
Compound **1e**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.35. 285.0 mg, 63% yield. m.p. 110-114 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88-7.86 (m, 2H), 7.78-7.76 (m, 2H), 7.64-7.62 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.62-6.57 (m, 2H), 6.10-6.06 (m, 2H), 4.95 (dd, *J* = 9.0, 5.5 Hz, 2H), 4.68 (s, 2H), 4.25 (d, *J* = 2.0 Hz, 2H), 2.40 (s, 3H), 2.22-2.18 (m, 1H).

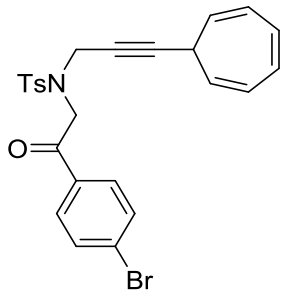
^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.9, 144.1, 135.8, 133.7, 132.3, 131.1, 129.89, 129.87, 129.2, 127.9, 124.9, 122.6, 88.3, 72.4, 52.1, 38.1, 31.5, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{22}ClNO_3S+H]^+$ requires: 452.1082, found: 452.1084.





_N_-(2-(4-bromophenyl)-2-oxoethyl)-_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1f)

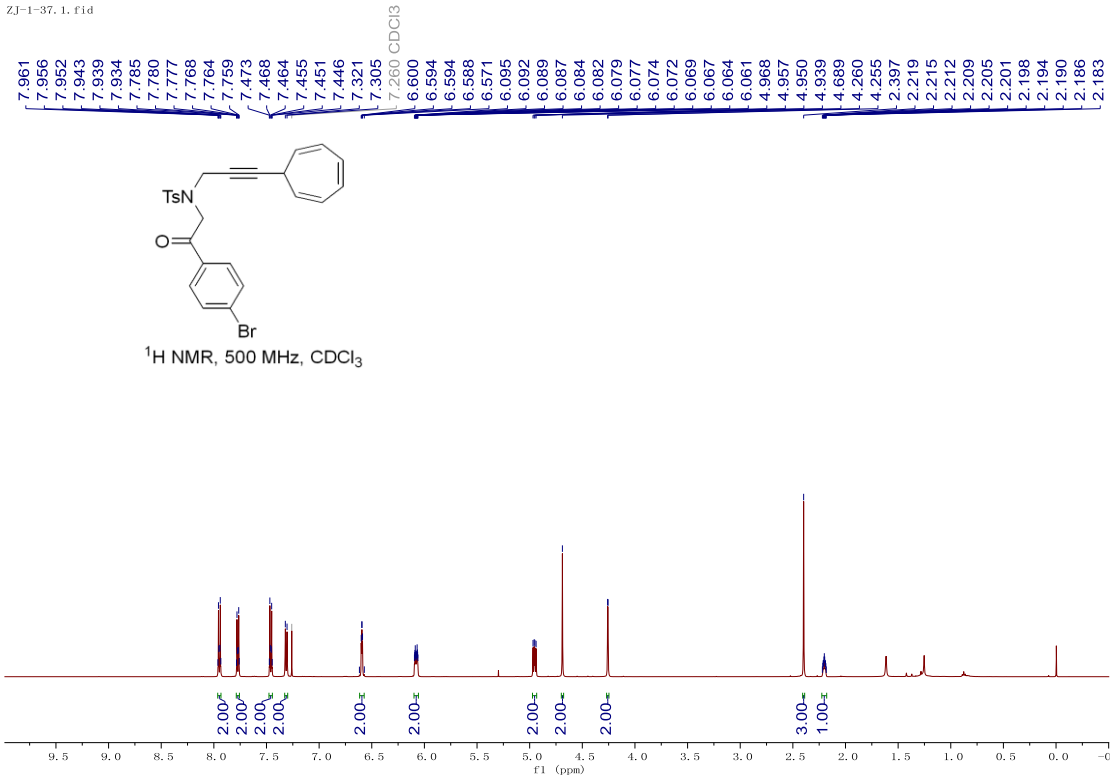


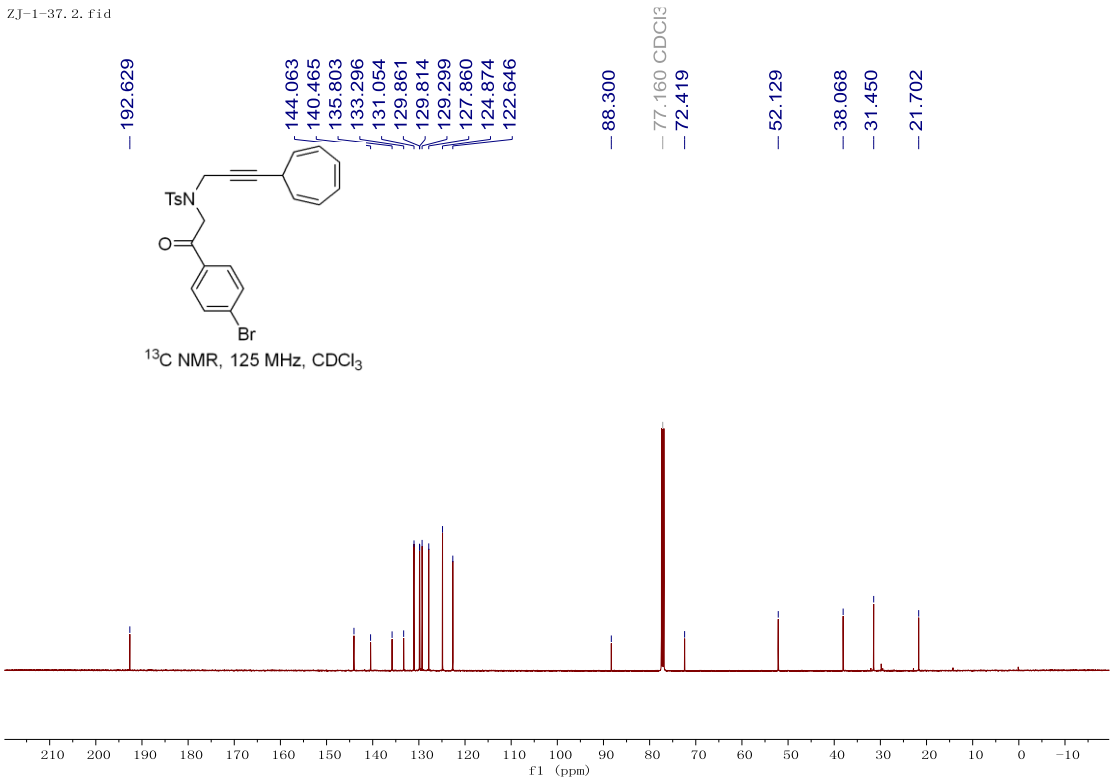
Compound **1f**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0. 41. 242.6 mg, 49% yield. m.p. 94-98 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96-7.93 (m, 2H), 7.79-7.76 (m, 2H), 7.47-7.45 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.62-6.57 (m, 2H), 6.10-6.06 (m, 2H), 4.95 (dd, J = 9.0, 5.5 Hz, 2H), 4.69 (s, 2H), 4.26 (d, J = 2.5 Hz, 2H), 2.40 (s, 3H), 2.22-2.18 (m, 1H).

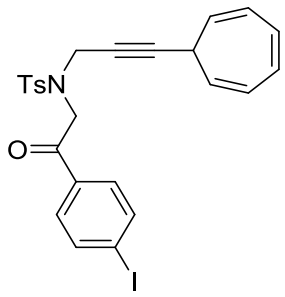
^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.6, 144.1, 140.5, 135.8, 133.3, 131.1, 129.9, 129.8, 129.3, 127.9, 124.9, 122.6, 88.3, 72.4, 52.1, 38.1, 31.5, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{22}BrNO_3S+H]^+$ requires: 496.0577, found: 496.0579.





***N*-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-*N*-(2-(4-iodophenyl)-2-oxoethyl)-4-methylbenzenesulfonamide (1g)**

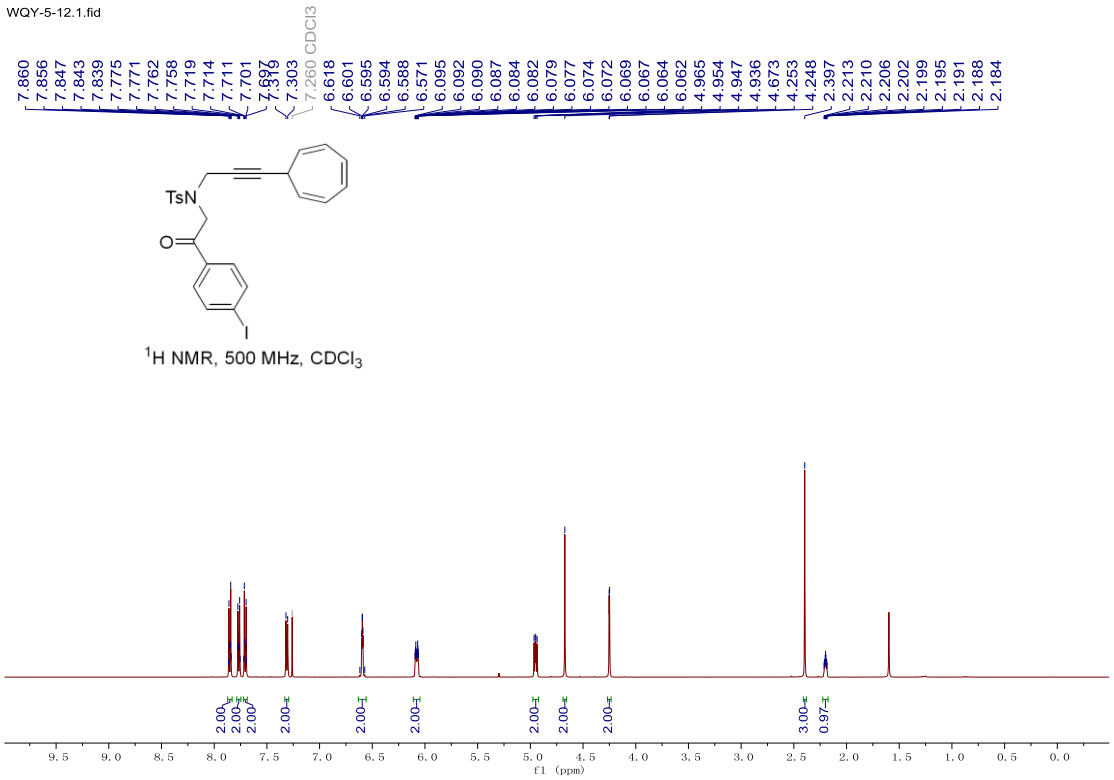


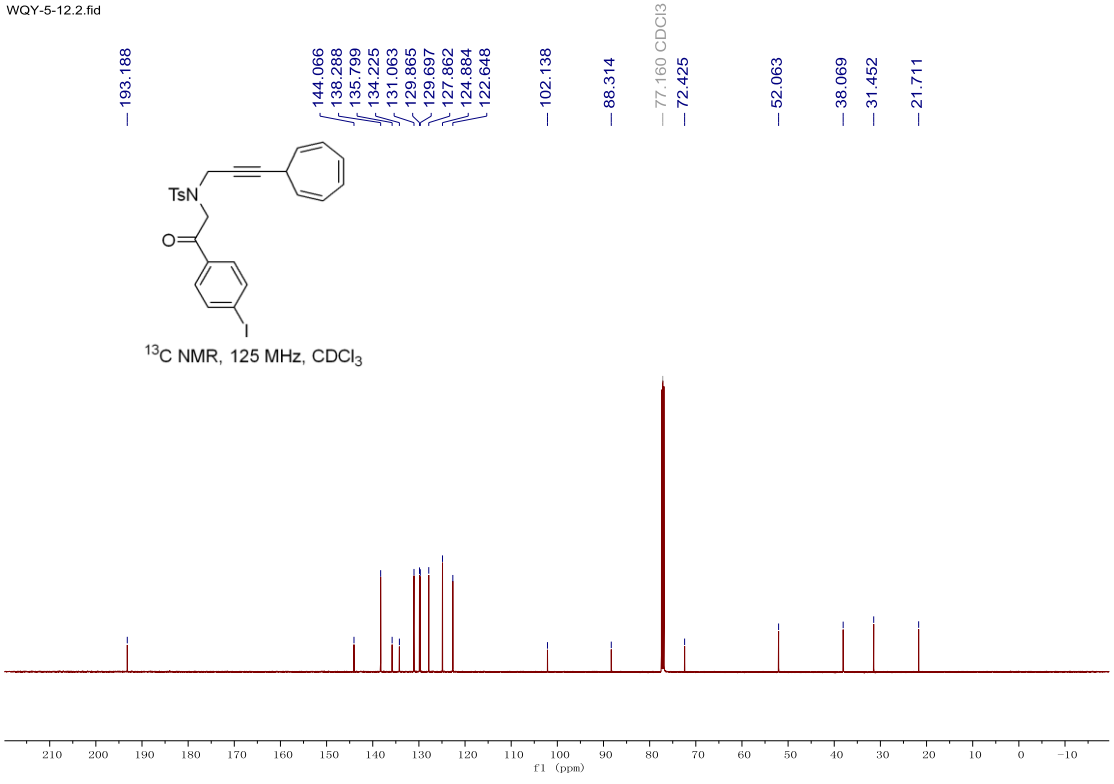
Compound **1g**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.28. 224.0 mg, 41% yield. m.p. 130-133 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87-7.84 (m, 2H), 7.78-7.75 (m, 2H), 7.72-7.69 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.62-6.57 (m, 2H), 6.10-6.06 (m, 2H), 4.95 (dd, J = 9.0, 5.5 Hz, 2H), 4.67 (s, 2H), 4.25 (d, J = 2.5 Hz, 2H), 2.40 (s, 3H), 2.21-2.18 (m, 1H).

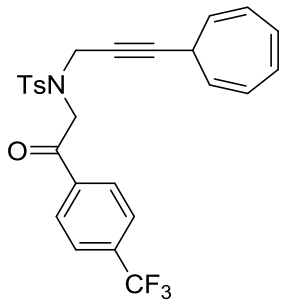
^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.2, 144.1, 138.3, 135.8, 134.2, 131.1, 129.9, 129.7, 127.9, 124.9, 122.6, 102.1, 88.3, 72.4, 52.1, 38.1, 31.5, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{22}INO_3S+H]^+$ requires: 544.0438, found: 544.0442.





_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methyl-_N_-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)benzenesulfonamide (1h)



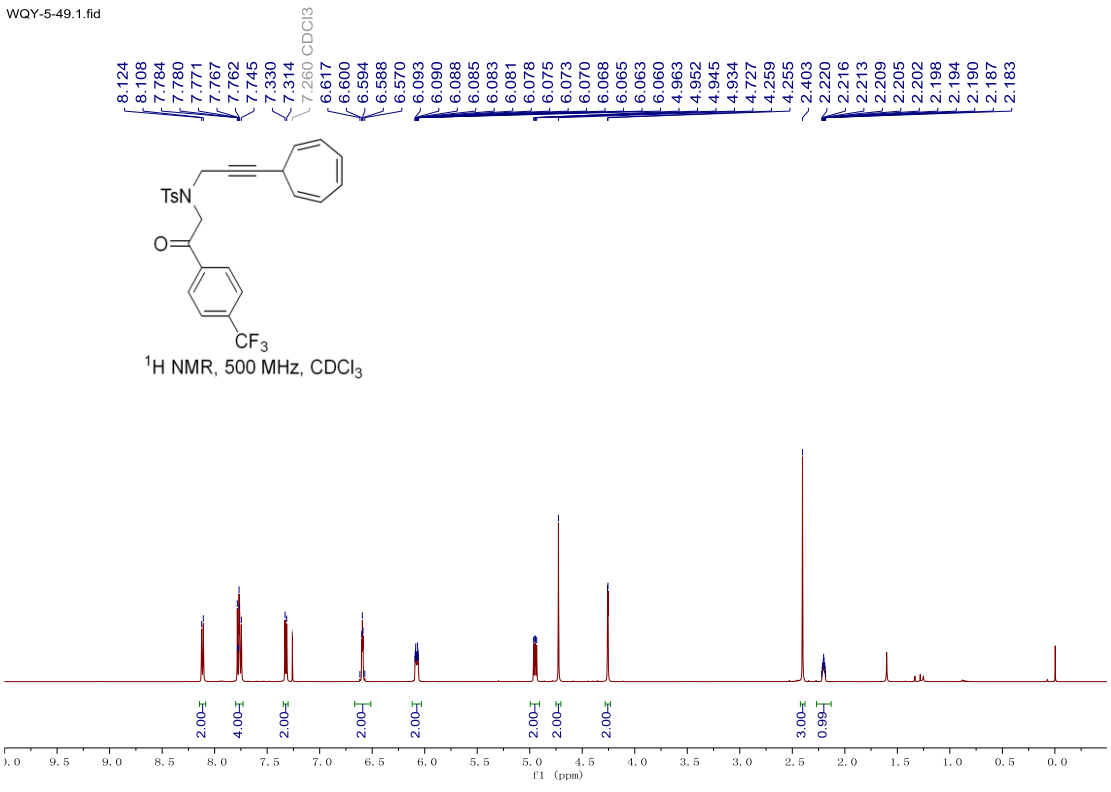
Compound **1h**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.48. 465.3 mg, 48% yield. m.p. 96-100 ºC.

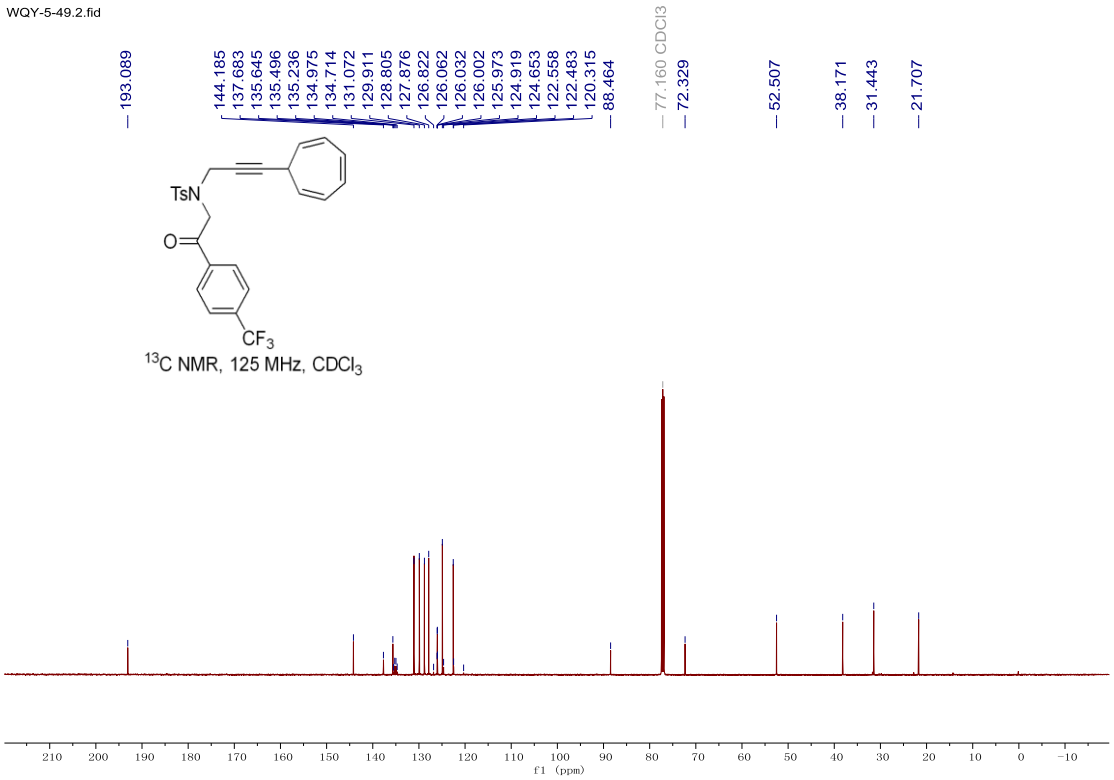
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (d, J = 8.0 Hz, 2H), 7.78-7.75 (m, 4H), 7.32 (d, J = 8.0 Hz, 2H), 6.62-6.57 (m, 2H), 6.09-6.06 (m, 2H), 4.95 (dd, J = 9.0, 5.5 Hz, 2H), 4.73 (s, 2H), 4.26 (d, J = 2.0 Hz, 2H), 2.40 (s, 3H), 2.22-2.18 (m, 1H).

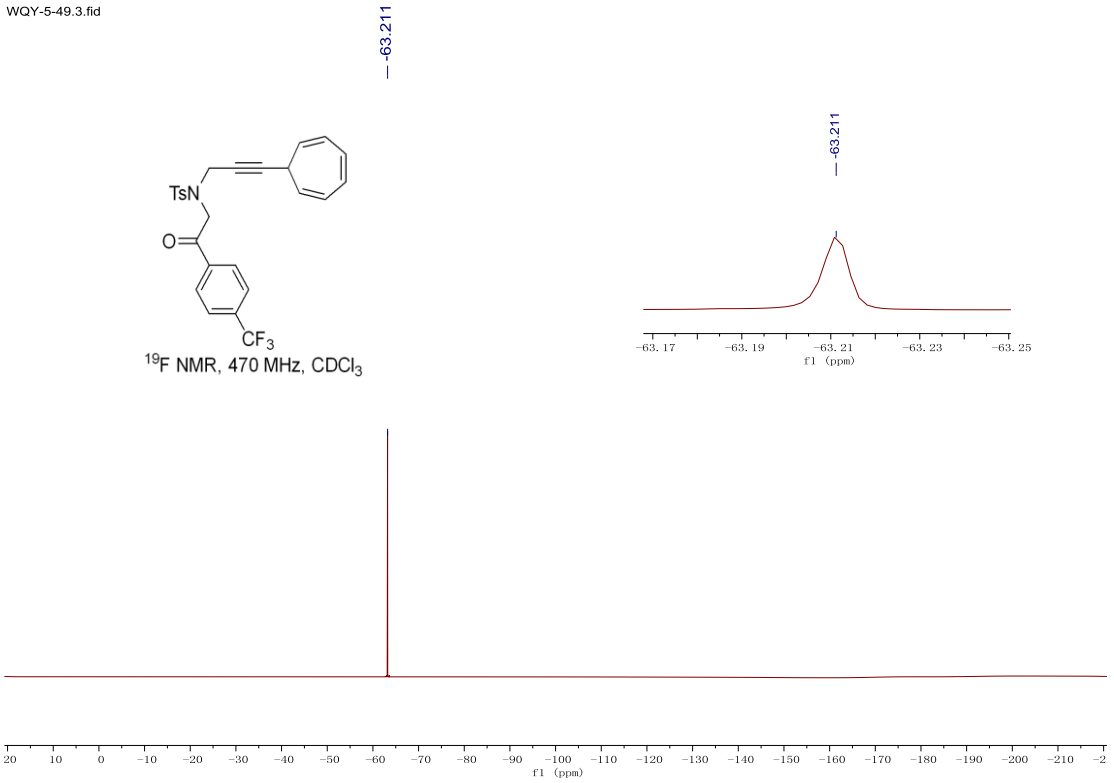
^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.1, 144.2, 137.7, 135.6, 135.1 (q, J = 32.5 Hz), 131.1, 129.9, 128.8, 127.9, 126.0 (q, J = 3.8 Hz), 124.9, 123.6 (q, J = 271.1 Hz), 122.6, 88.5, 72.3, 52.5, 38.2, 31.4, 21.7.

^{19}F NMR (470 MHz, $CDCl_3$) δ (s) (-63.21).

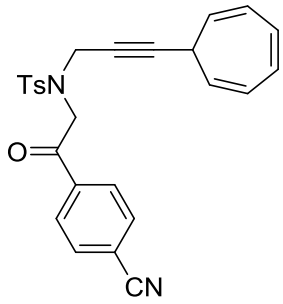
HRMS (ESI) m/z: calcd for $[C_{26}H_{22}F_3NO_3S+H]^+$ requires: 486.1345, found: 486.1346.







_N_-(2-(4-cyanophenyl)-2-oxoethyl)-_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1i)

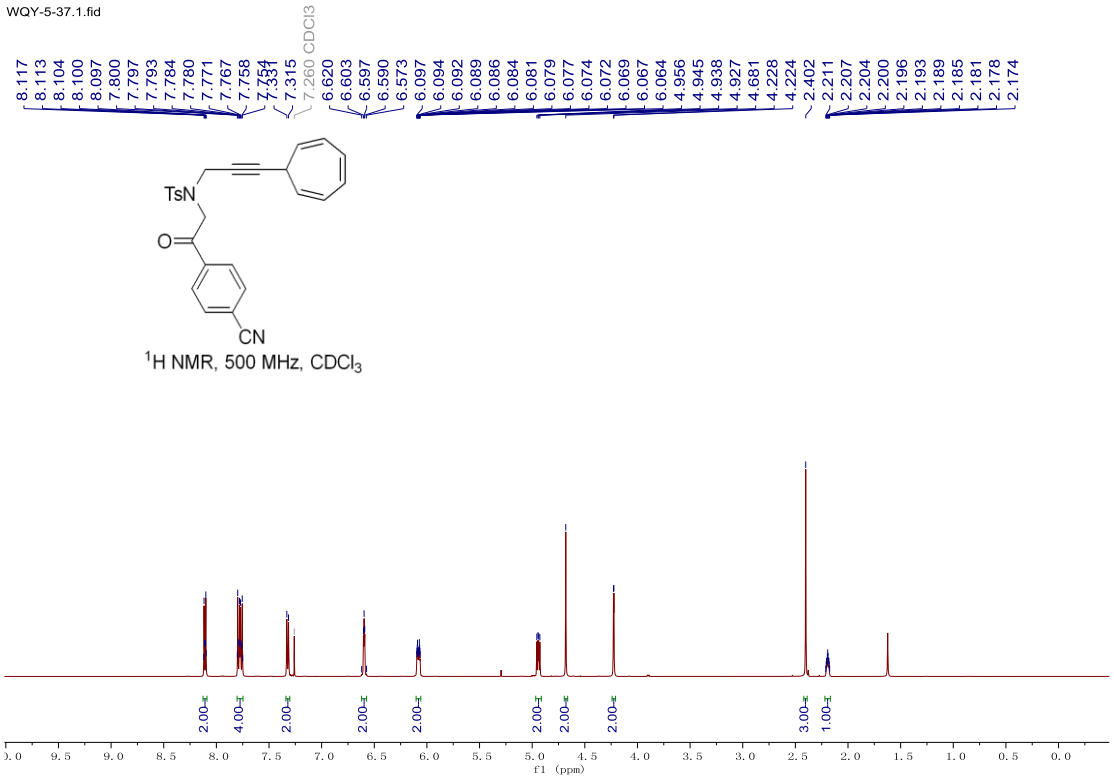


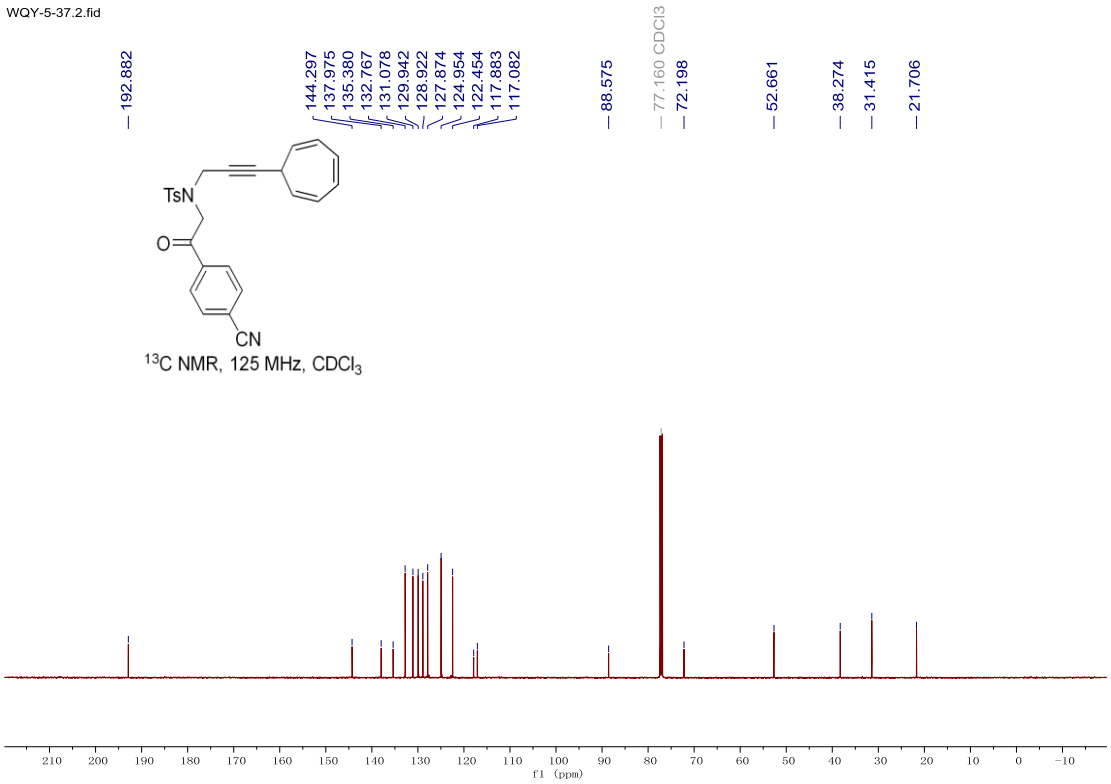
Compound **1i**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.24. 411.1 mg, 57% yield. m.p. 118-122 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12-8.10 (m, 2H), 7.80-7.75 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.62-6.57 (m, 2H), 6.10-6.06 (m, 2H), 4.94 (dd, *J* = 9.0, 5.5 Hz, 2H), 4.68 (s, 2H), 4.23 (d, *J* = 2.0 Hz, 2H), 2.40 (s, 3H), 2.21-2.17 (m, 1H).

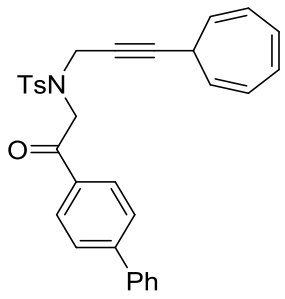
^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.9, 144.3, 138.0, 135.4, 132.8, 131.1, 129.9, 128.9, 127.9, 125.0, 122.5, 117.9, 117.1, 88.6, 72.2, 52.7, 38.3, 31.4, 21.7.

HRMS (ESI) m/z: calcd for $[C_{26}H_{22}N_2O_3S+H]^+$ requires: 443.1424, found: 443.1425.





_N_-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1j)

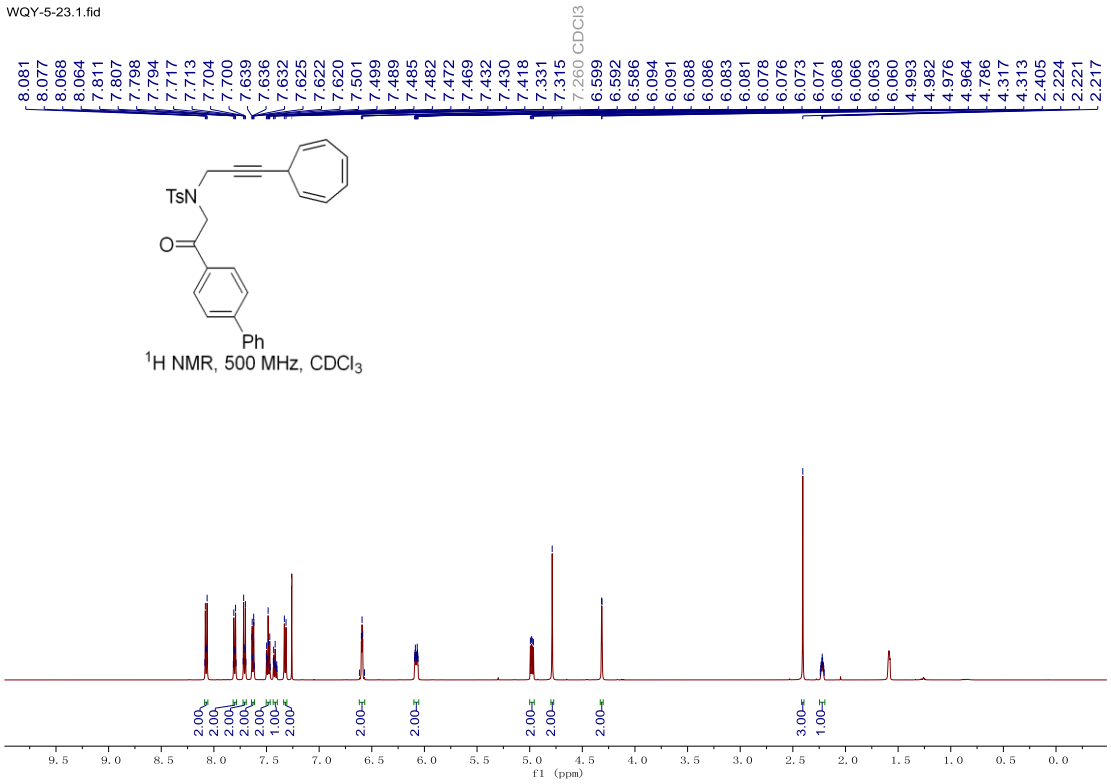


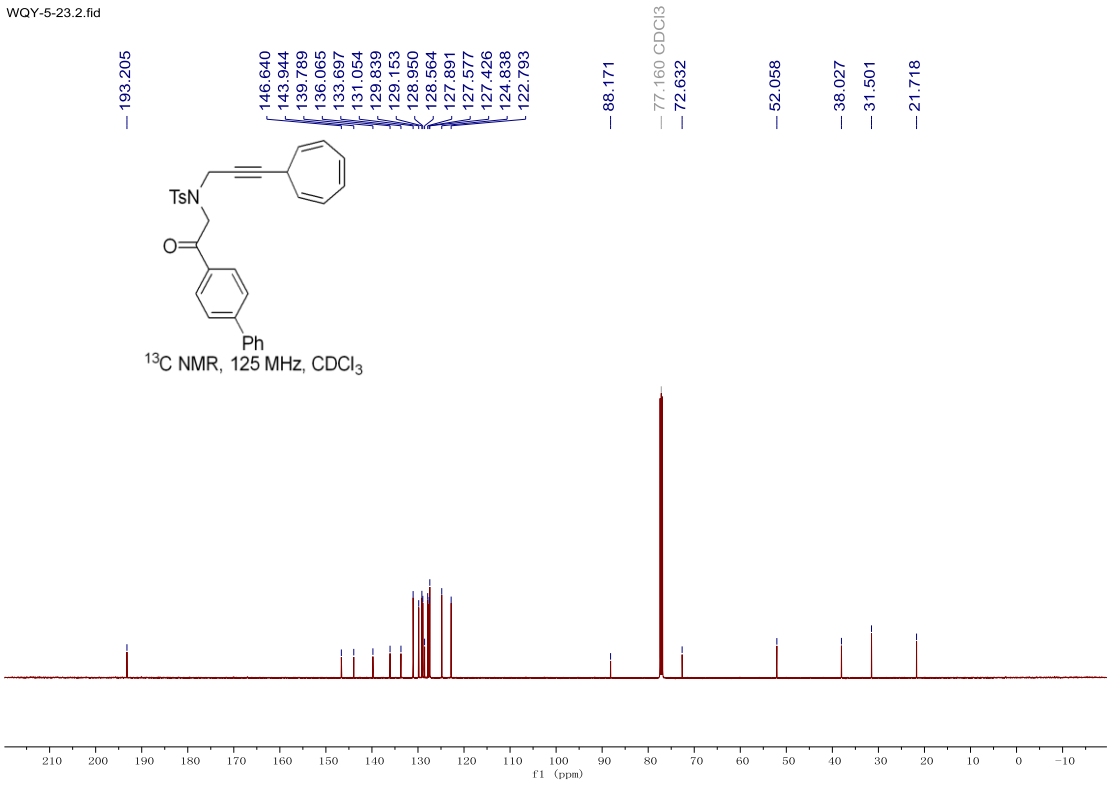
Compound **1j**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.30. 164.9 mg, 33% yield. m.p. 153-155 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.09-8.06 (m, 2H), 7.82-7.79 (m, 2H), 7.71 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.64-7.62 (m, 2H), 7.50-7.47 (m, 2H), 7.44-7.40 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.62-6.57 (m, 2H), 6.09-6.06 (m, 2H), 4.98 (dd, *J* = 9.0, 5.5 Hz, 2H), 4.79 (s, 2H), 4.31 (d, *J* = 2.0 Hz, 2H), 2.41 (s, 3H), 2.24-2.20 (m, 1H).

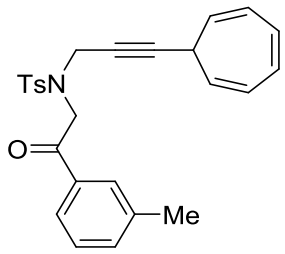
^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.2, 146.6, 143.9, 139.8, 136.1, 133.7, 131.1, 129.8, 129.2, 129.0, 128.6, 127.9, 127.6, 127.4, 124.8, 122.8, 88.2, 72.6, 52.1, 38.0, 31.5, 21.7.

HRMS (ESI) m/z: calcd for $[C_{31}H_{27}NO_3S+H]^+$ requires: 494.1784, found: 494.1787.





N-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methyl-*N*-(2-oxo-2-(m-tolyl)ethyl)benzenesulfonamide (1k)

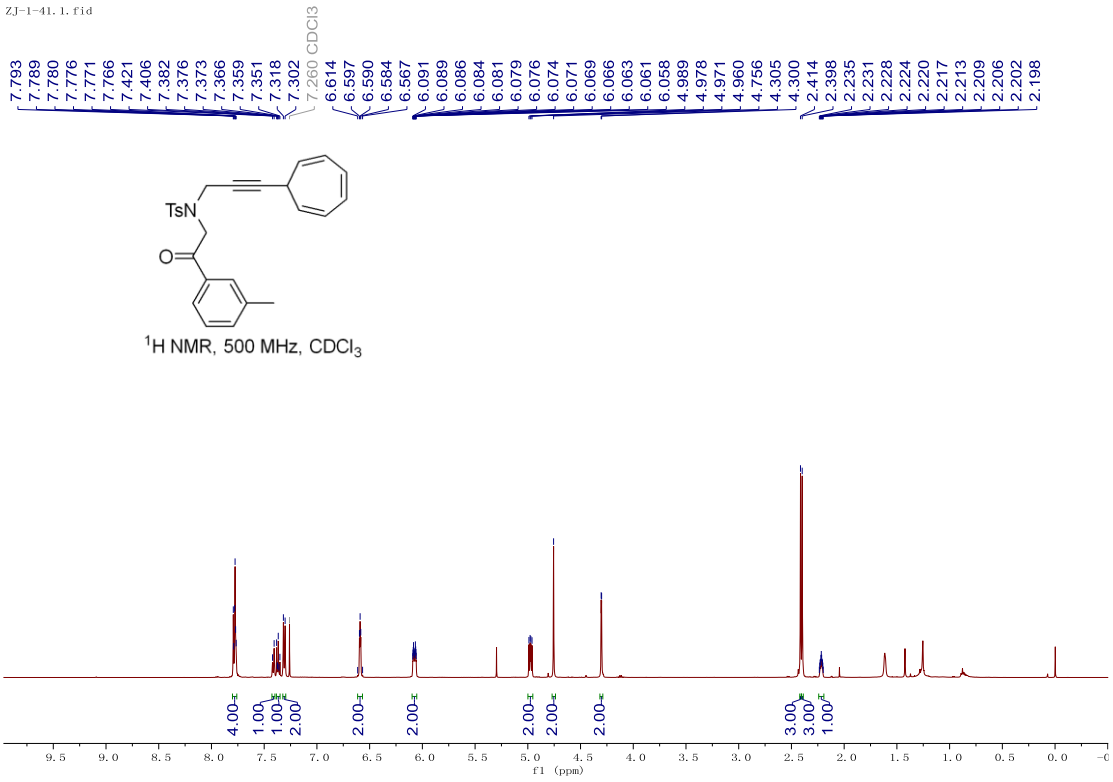


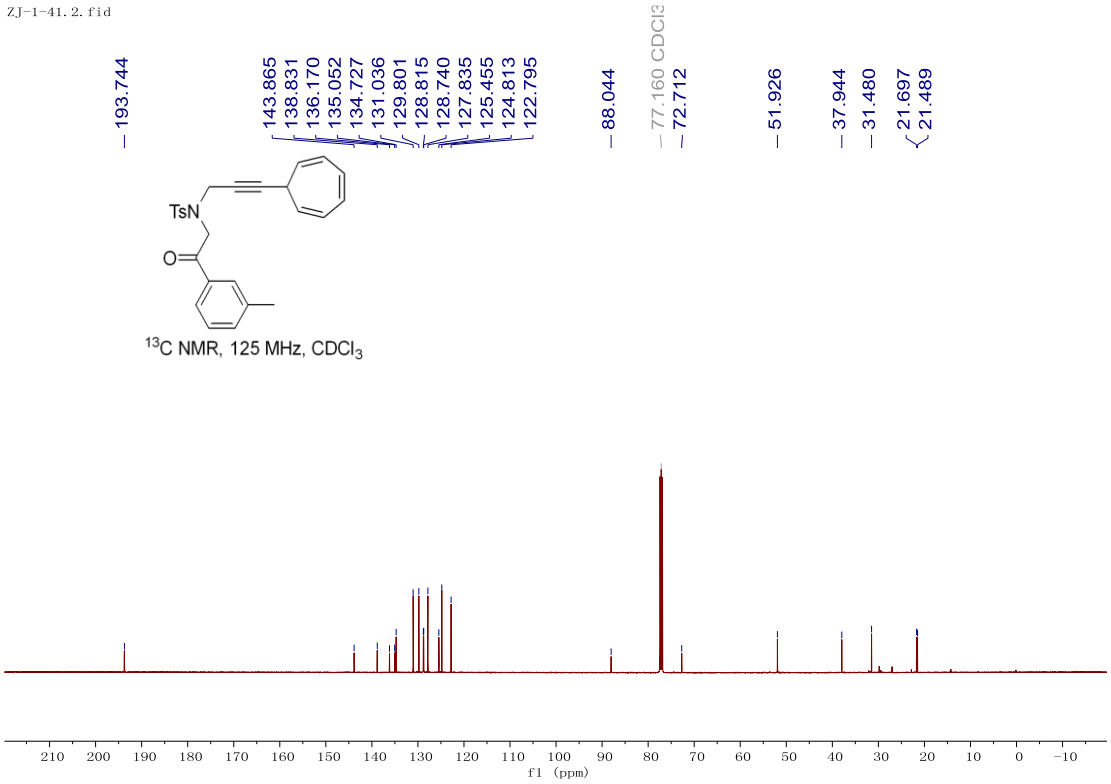
Compound **1k**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.26. 216.4 mg, 50% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79-7.77 (m, 4H), 7.41 (d, J = 7.5 Hz, 1H), 7.38-7.35 (m, 1H), 7.31 (d, J = 8.0 Hz, 2H), 6.61-6.57 (m, 2H), 6.09-6.06 (m, 2H), 4.97 (dd, J = 9.0, 5.5 Hz, 2H), 4.76 (s, 2H), 4.30 (d, J = 2.5 Hz, 2H), 2.41 (s, 3H), 2.40 (s, 3H), 2.24-2.20 (m, 1H).

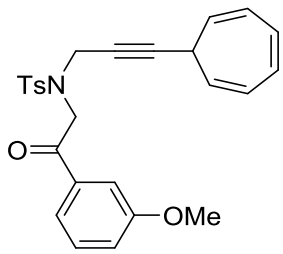
^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.7, 143.9, 138.8, 136.2, 135.1, 134.7, 131.0, 129.8, 128.8, 128.7, 127.8, 125.5, 124.8, 122.8, 88.0, 72.7, 51.9, 37.9, 31.5, 21.7, 21.5.

HRMS (ESI) m/z: calcd for $[C_{26}H_{25}NO_3S+H]^+$ requires: 432.1628, found: 432.1630.





***N*-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-*N*-(2-(3-methoxyphenyl)-2-oxoethyl)-4-methylbenzenesulfonamide (1l)**

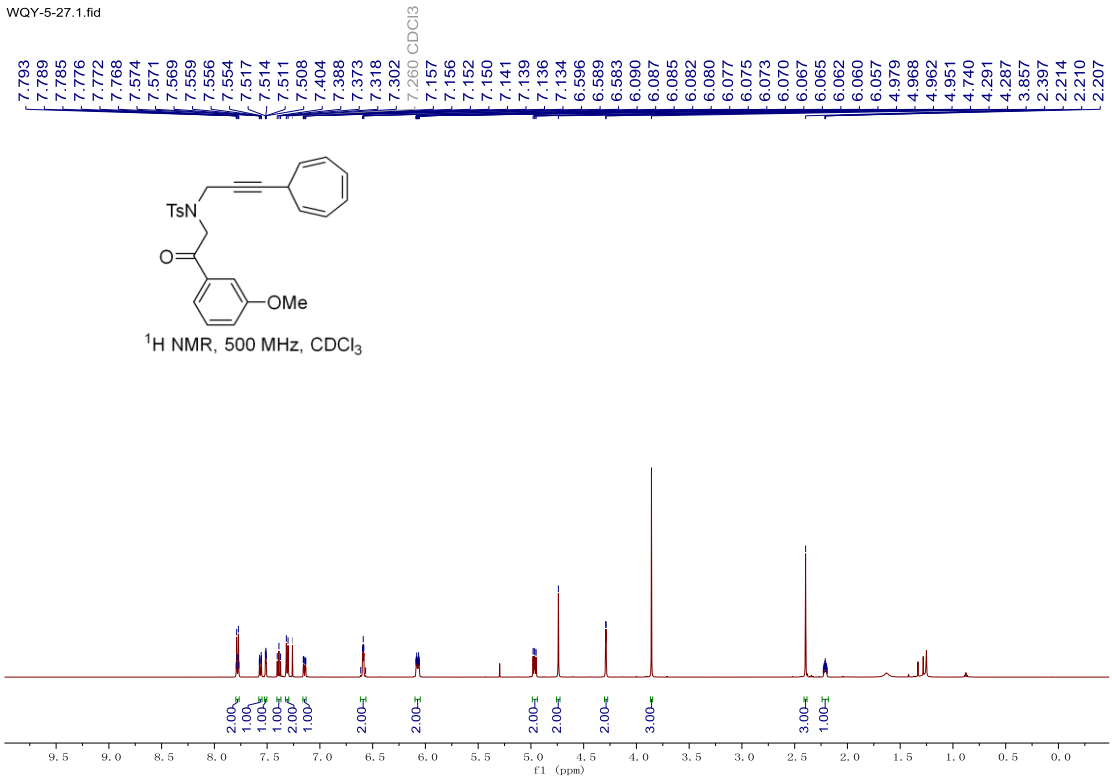


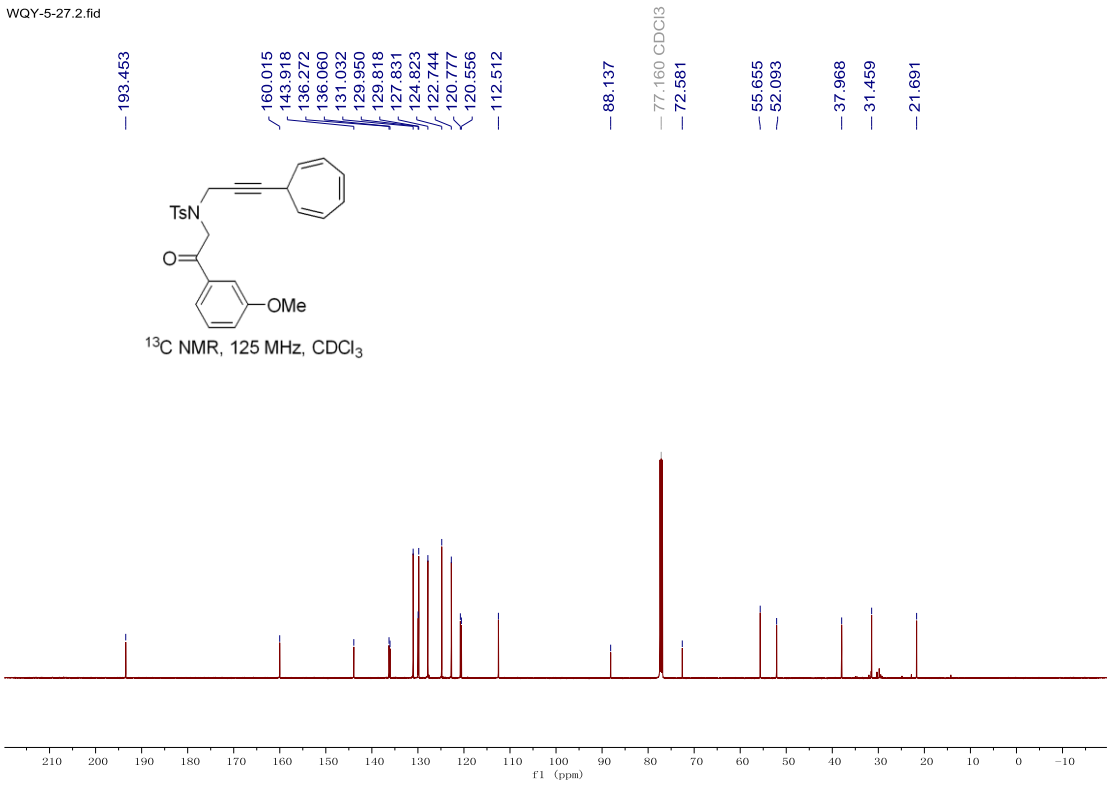
Compound **1l**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.18. 272.4 mg, 48% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79-7.77 (m, 2H), 7.57-7.55 (m, 1H), 7.52-7.51 (m, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.15 (ddd, *J* = 8.0, 2.5, 1.0 Hz, 1H), 6.61-6.57 (m, 2H), 6.09-6.06 (m, 2H), 4.97 (dd, *J* = 8.5, 5.5 Hz, 2H), 4.74 (s, 2H), 4.29 (d, *J* = 2.0 Hz, 2H), 3.86 (s, 3H), 2.40 (s, 3H), 2.23-2.19 (m, 1H).

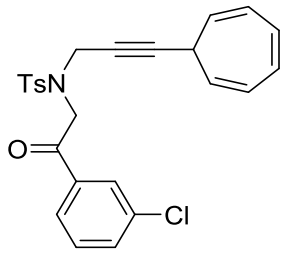
^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.5, 160.0, 143.9, 136.3, 136.1, 131.0, 130.0, 129.8, 127.8, 124.8, 122.7, 120.8, 120.6, 112.5, 88.1, 72.6, 55.7, 52.1, 38.0, 31.5, 21.7.

HRMS (ESI) m/z: calcd for $[C_{26}H_{25}NO_4S+H]^+$ requires: 448.1577, found: 448.1578.





_N_-(2-(3-chlorophenyl)-2-oxoethyl)-_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1m)

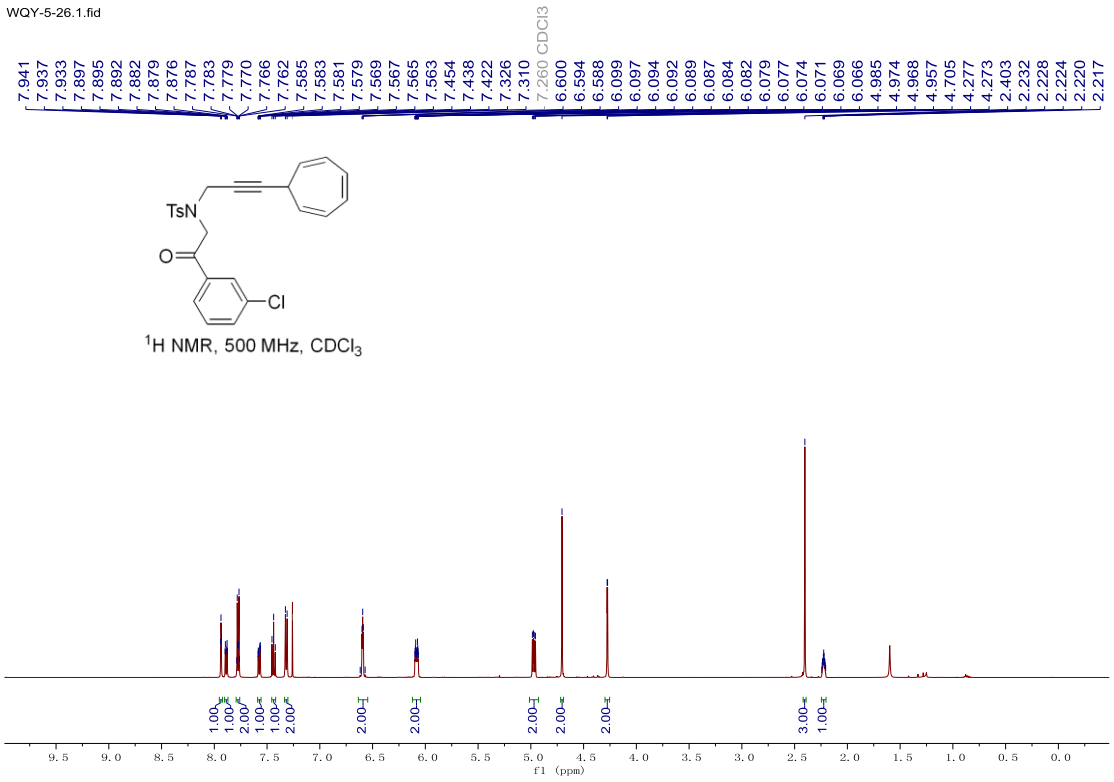


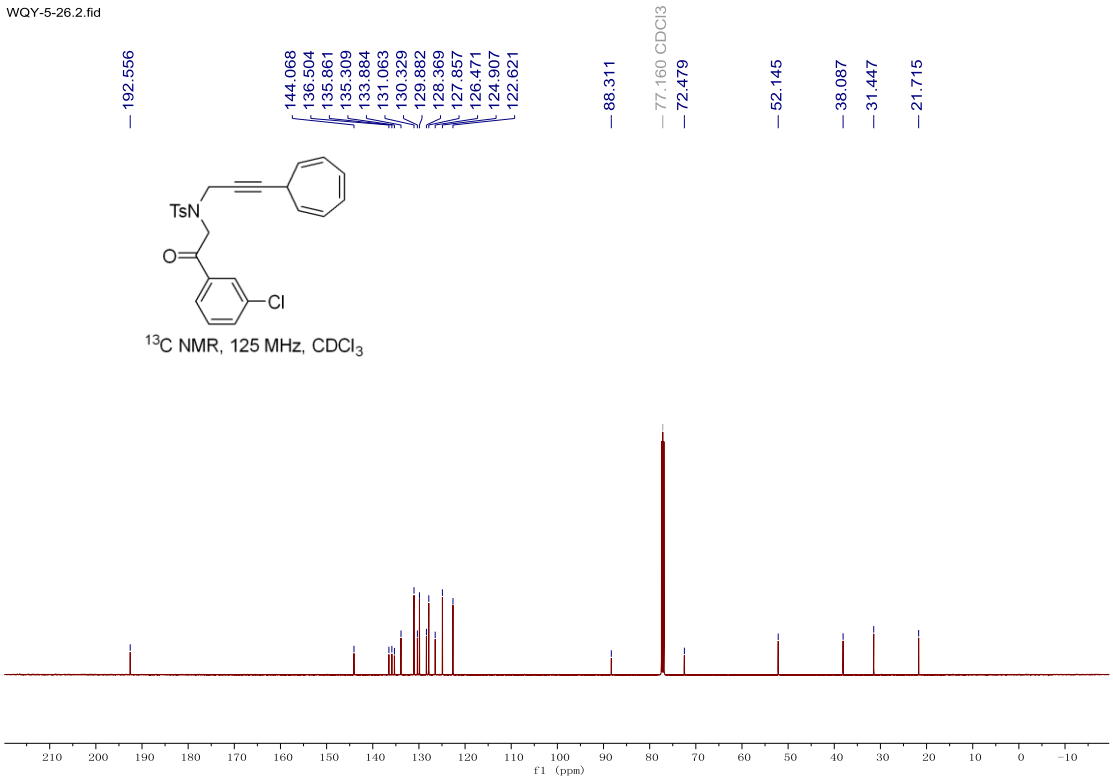
Compound **1m**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.33. 189.3 mg, 42% yield. m.p. 88-94 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (t, *J* = 2.0 Hz, 1H), 7.89 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.79-7.76 (m, 2H), 7.57 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.62-6.57 (m, 2H), 6.10-6.07 (m, 2H), 4.97 (dd, *J* = 8.5, 5.5 Hz, 2H), 4.71 (s, 2H), 4.27 (d, *J* = 2.0 Hz, 2H), 2.40 (s, 3H), 2.24-2.21 (m, 1H).

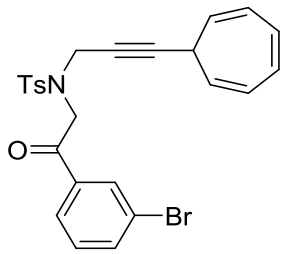
^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.6, 144.1, 136.5, 135.9, 135.3, 133.9, 131.1, 130.3, 129.9, 128.4, 127.9, 126.5, 124.9, 122.6, 88.3, 72.5, 52.1, 38.1, 31.4, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{22}ClNO_3S+H]^+$ requires: 452.1082, found: 452.1084.





***N*-(2-(3-bromophenyl)-2-oxoethyl)-*N*-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1n)**

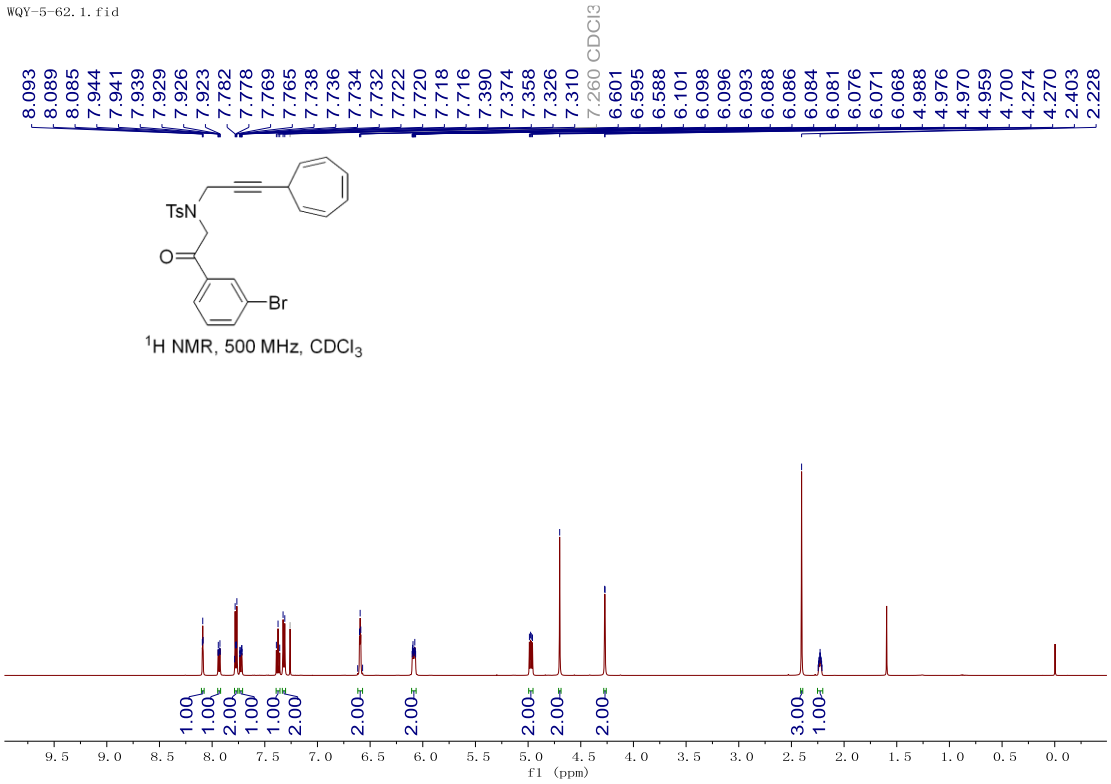


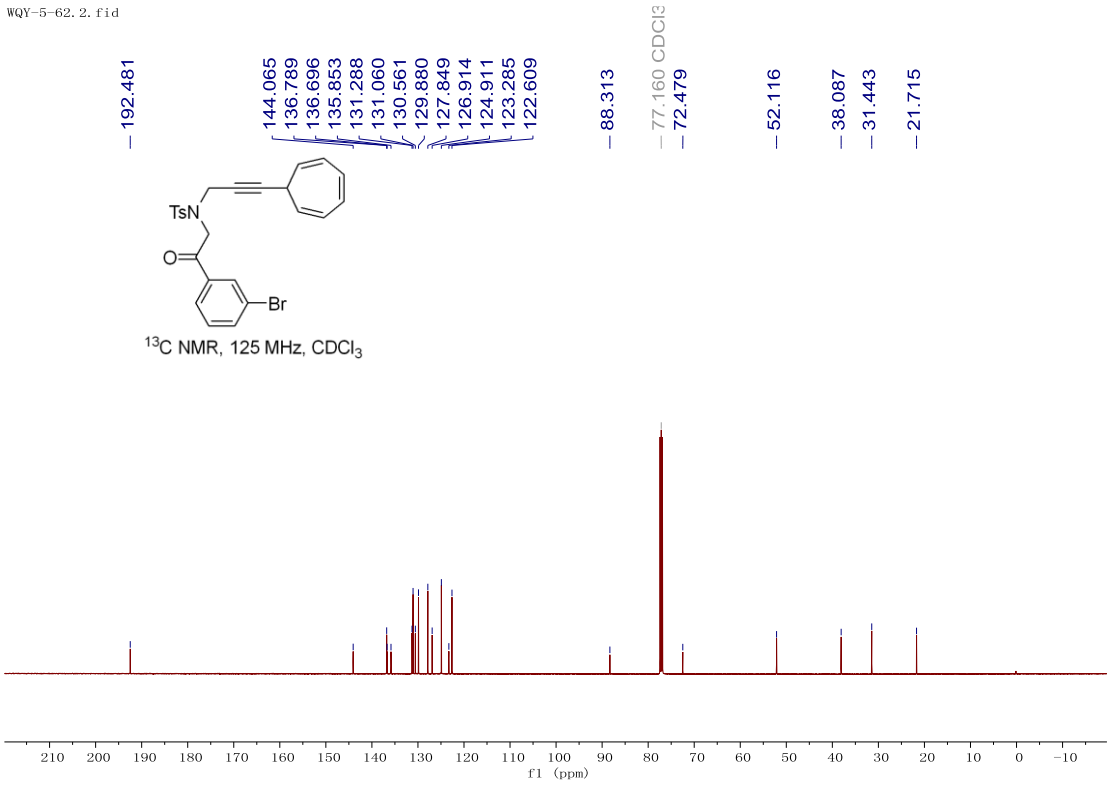
Compound **1n**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.26. 231.0 mg, 41% yield. m.p. 110-113 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.09 (t, *J* = 2.0 Hz, 1H), 7.93 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.79-7.77 (m, 2H), 7.73 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.62-6.57 (m, 2H), 6.10-6.07 (m, 2H), 4.97 (dd, *J* = 9.0, 5.5 Hz, 2H), 4.70 (s, 2H), 4.27 (d, *J* = 2.0 Hz, 2H), 2.40 (s, 3H), 2.25-2.21 (m, 1H).

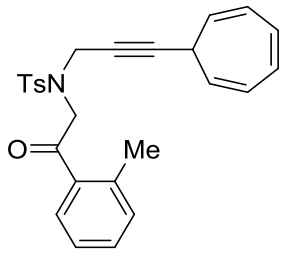
^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.5, 144.1, 136.8, 136.7, 135.9, 131.3, 131.1, 130.6, 129.9, 127.8, 126.9, 124.9, 123.3, 122.6, 88.3, 72.5, 52.1, 38.1, 31.4, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{22}BrNO_3S+H]^+$ requires: 496.0577, found: 496.0579.





_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methyl-_N_-(2-oxo-2-(o-tolyl)ethyl)benzenesulfonamide (1o)

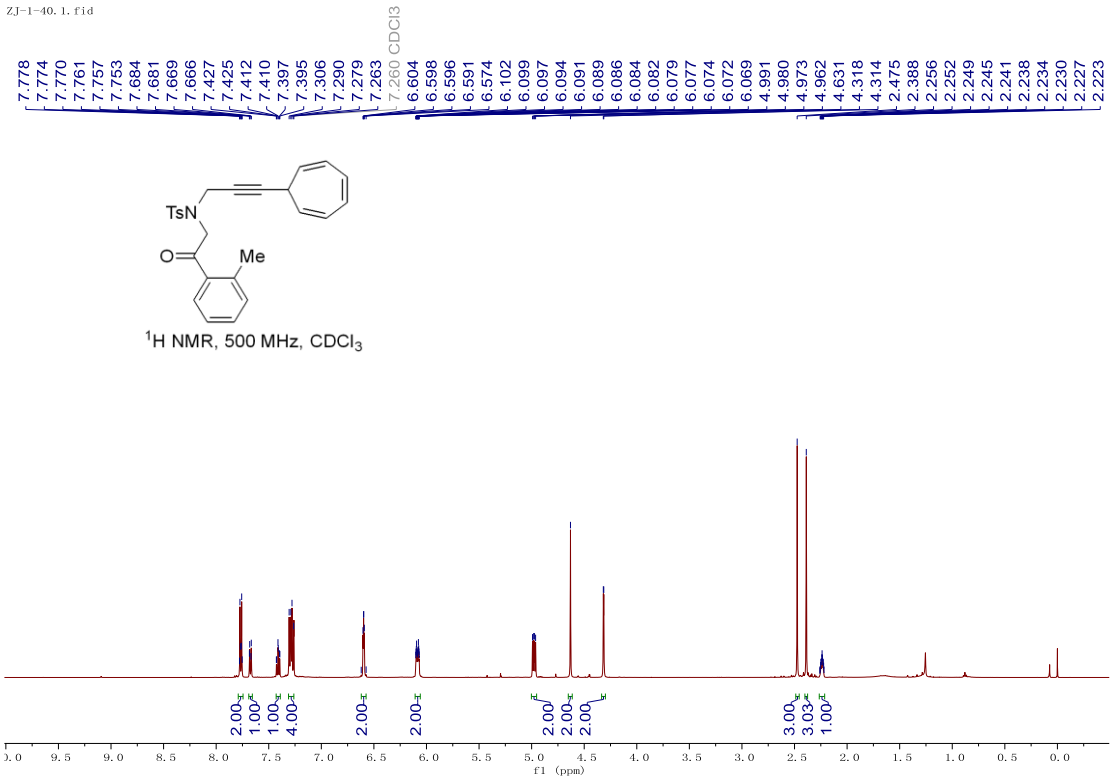


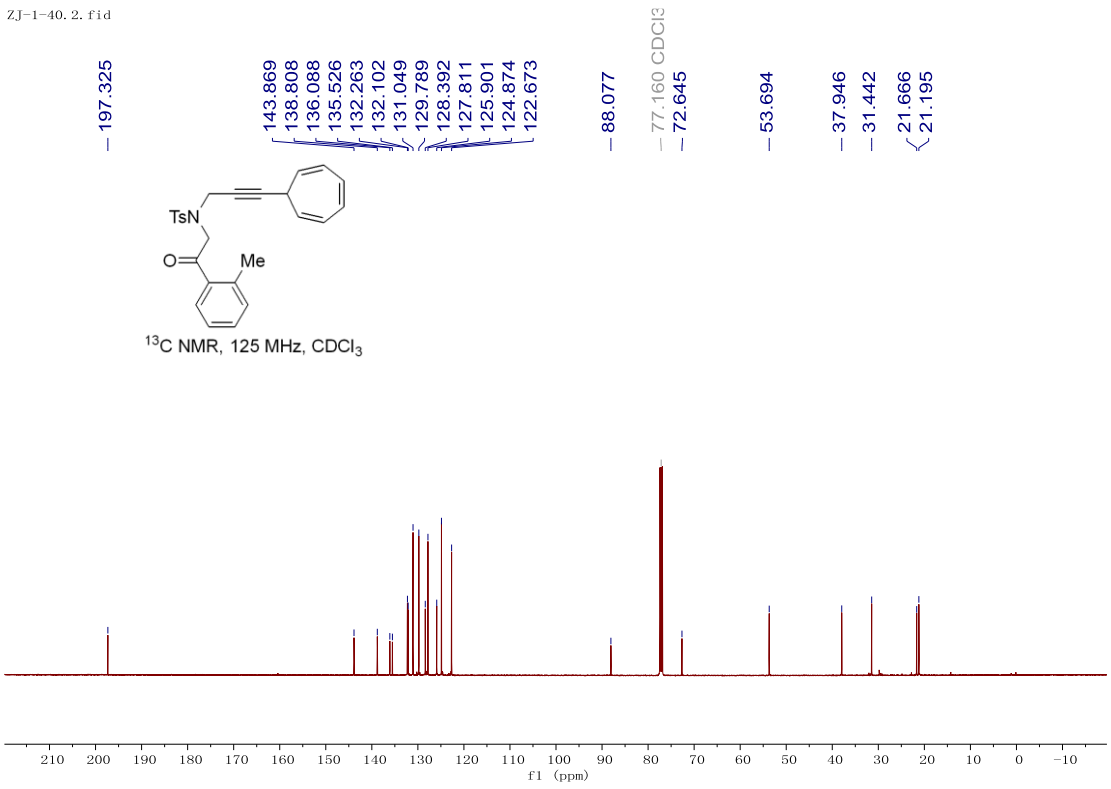
Compound **1o**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.26. 655.1 mg, 76% yield. m.p. 74-78 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78-7.75 (m, 2H), 7.68-7.67 (m, 1H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H), 7.31-7.26 (m, 4H), 6.62-6.57 (m, 2H), 6.10-6.07 (m, 2H), 4.98 (dd, *J* = 9.0, 5.5 Hz, 2H), 4.63 (s, 2H), 4.32 (d, *J* = 2.0 Hz, 2H), 2.48 (s, 3H), 2.39 (s, 3H), 2.26-2.22 (m, 1H).

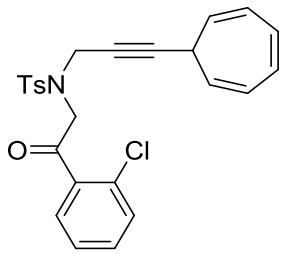
^{13}C NMR (125 MHz, Chloroform-*d*) δ 197.3, 143.9, 138.8, 136.1, 135.5, 132.3, 132.1, 131.0, 129.8, 128.4, 127.8, 125.9, 124.9, 122.7, 88.1, 72.6, 53.7, 37.9, 31.4, 21.7, 21.2.

HRMS (ESI) m/z: calcd for $[C_{26}H_{25}NO_3S+H]^+$ requires: 432.1628, found: 432.1630.





***N*-(2-(2-chlorophenyl)-2-oxoethyl)-*N*-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1p)**

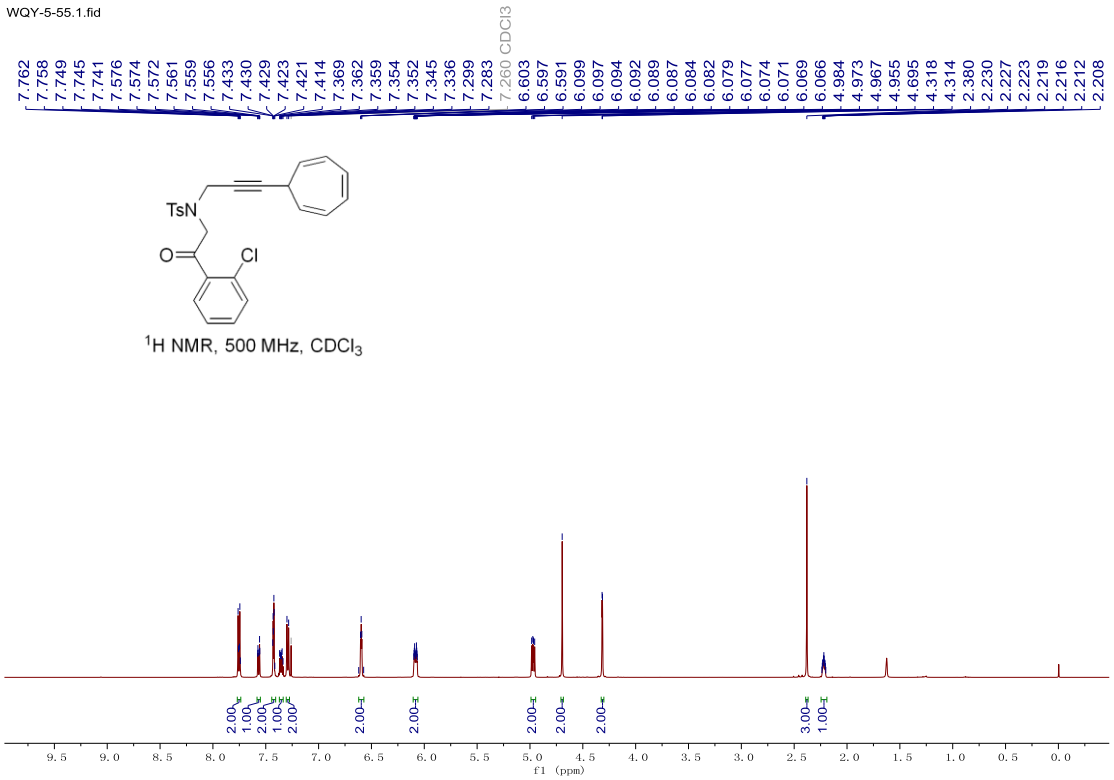


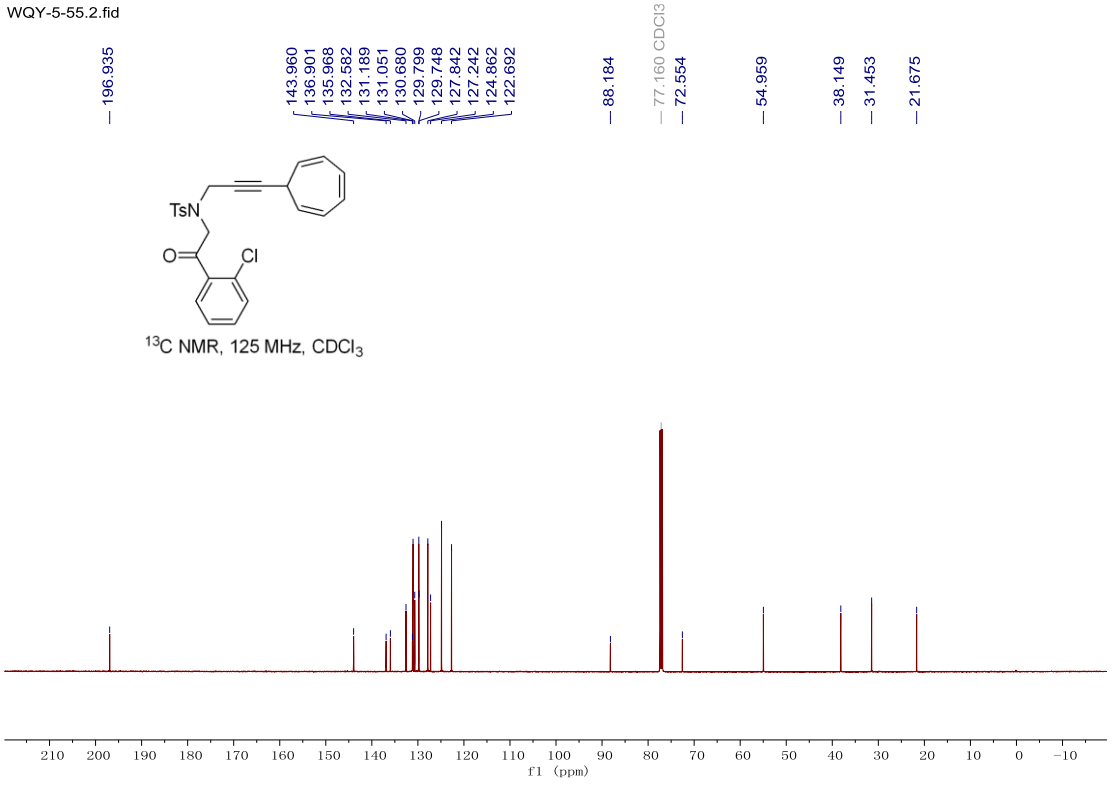
Compound **1p**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.25. 281.4 mg, 49% yield. m.p. 138-143 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76-7.74 (m, 2H), 7.58-7.56 (m, 1H), 7.43-7.41 (m, 2H), 7.37-7.34 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.62-6.57 (m, 2H), 6.10-6.07 (m, 2H), 4.97 (dd, *J* = 8.5, 5.5 Hz, 2H), 4.70 (s, 2H), 4.32 (d, *J* = 2.0 Hz, 2H), 2.38 (s, 3H), 2.24-2.20 (m, 1H).

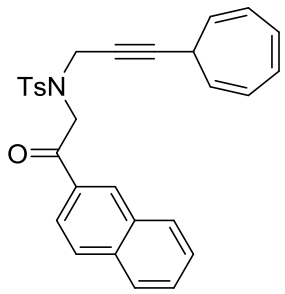
^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.9, 144.0, 136.9, 136.0, 132.6, 131.2, 131.1, 130.7, 129.8, 129.7, 127.8, 127.2, 124.9, 122.7, 88.2, 72.6, 55.0, 38.1, 31.5, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{22}ClNO_3S+H]^+$ requires: 452.1082, found: 452.1083.





_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methyl-_N_-(2-(naphthalen-2-yl)-2-oxoethyl)benzenesulfonamide (1q)

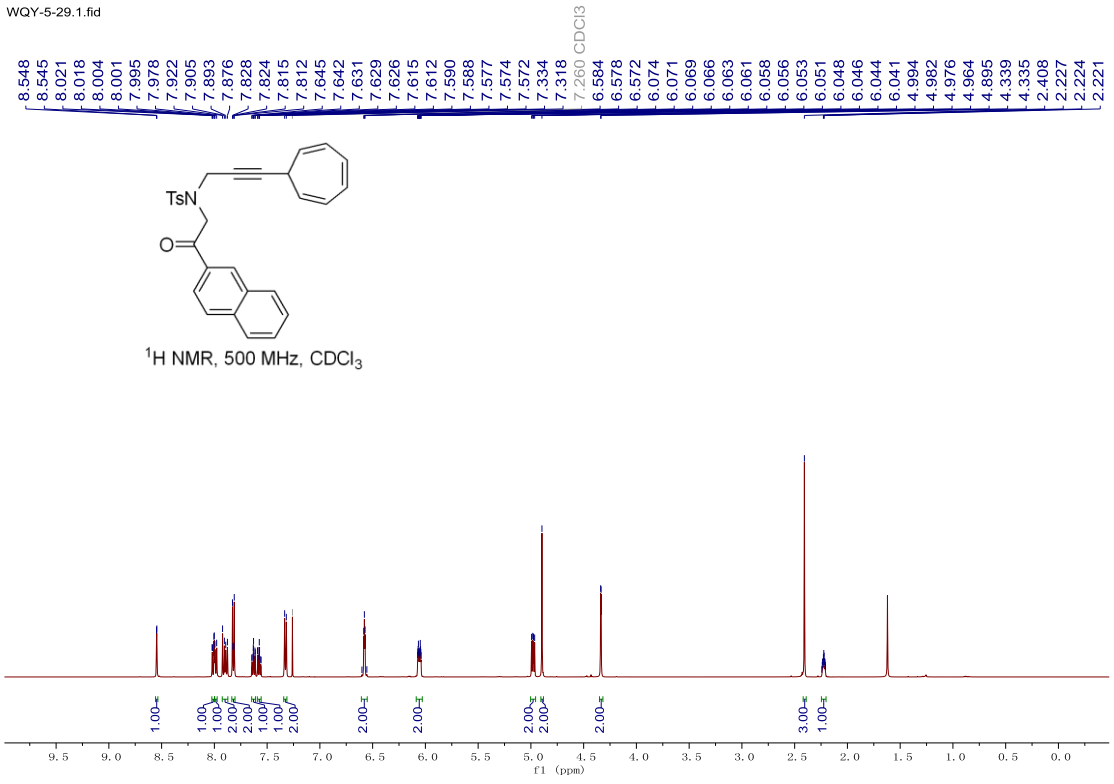


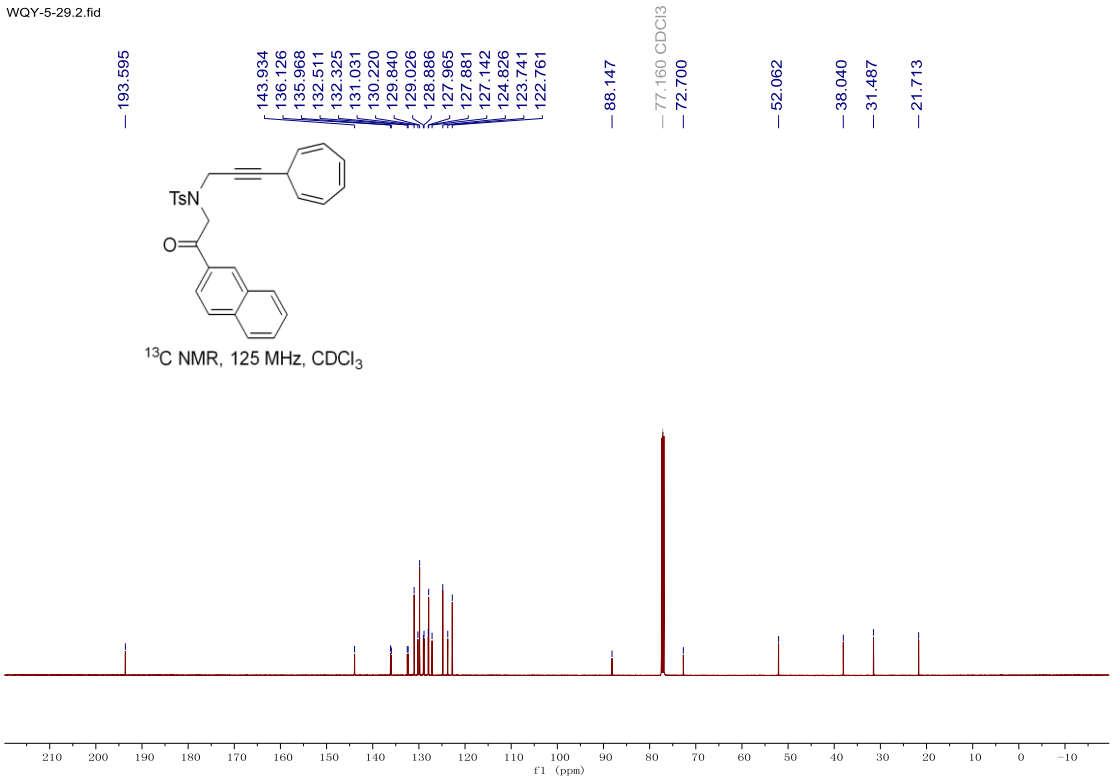
Compound **1q**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.30. 538.4 mg, 63% yield. m.p. 92-97 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 1.5 Hz, 1H), 8.01 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.92-7.88 (m, 2H), 7.83-7.81 (m, 2H), 7.65-7.61 (m, 1H), 7.59-7.56 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.60-6.56 (m, 2H), 6.07-6.04 (m, 2H), 4.98 (dd, *J* = 9.0, 6.0 Hz, 2H), 4.90 (s, 2H), 4.34 (d, *J* = 2.0 Hz, 2H), 2.41 (s, 3H), 2.24-2.21 (m, 1H).

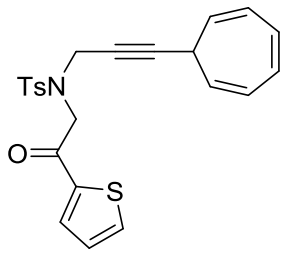
^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.6, 143.9, 136.1, 136.0, 132.5, 132.3, 131.0, 130.2, 129.8, 129.0, 128.9, 128.0, 127.9, 127.1, 124.8, 123.7, 122.8, 88.1, 72.7, 52.1, 38.0, 31.5, 21.7.

HRMS (ESI) m/z: calcd for $[C_{29}H_{25}NO_3S+H]^+$ requires: 468.1628, found: 468.1631.





***N*-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methyl-*N*-(2-oxo-2-(thiophen-2-yl)ethyl)benzenesulfonamide (1r)**

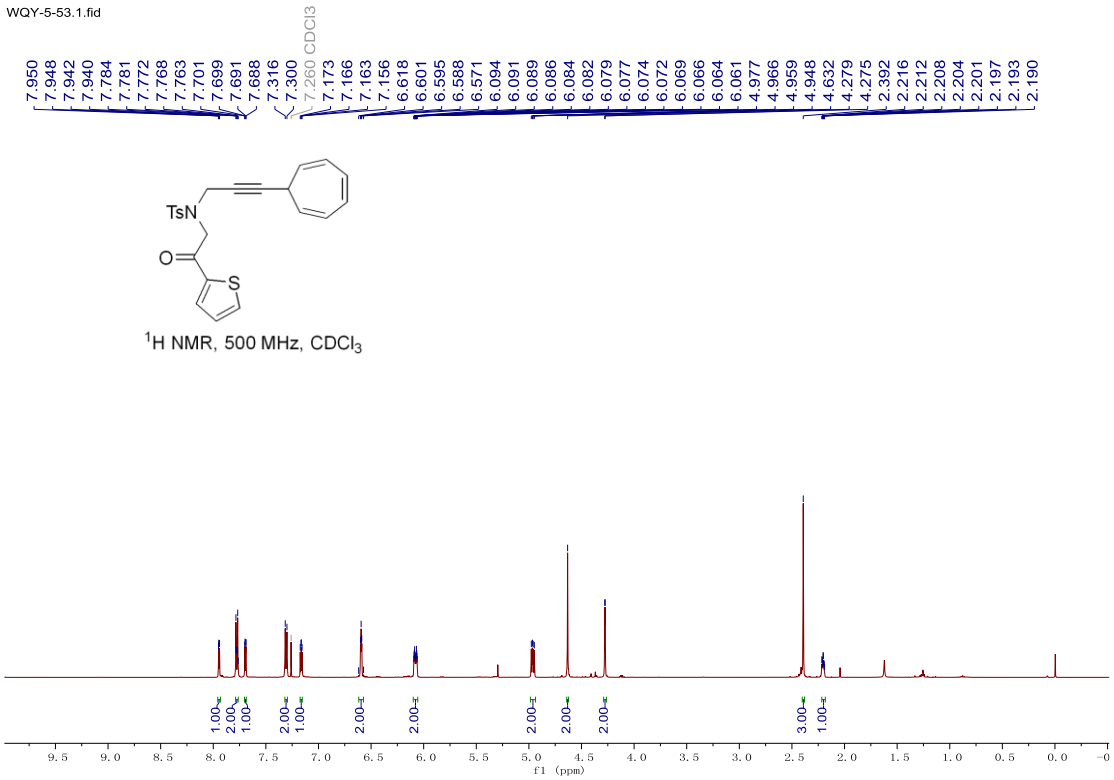


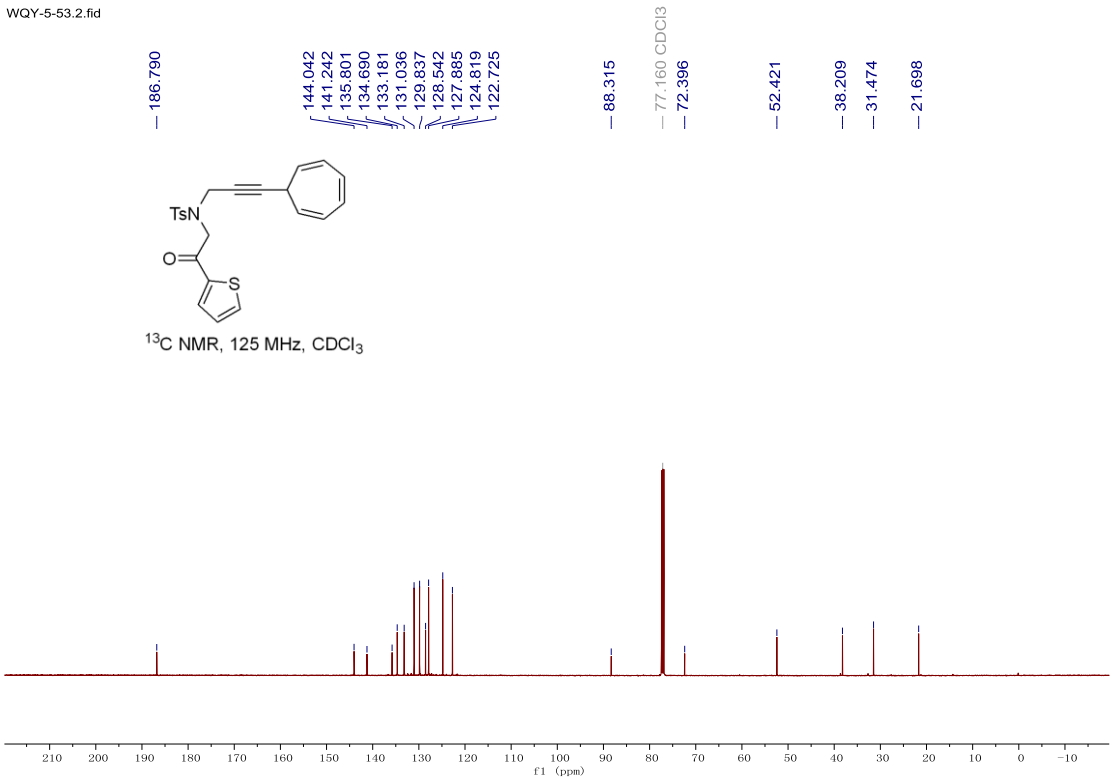
Compound **1r**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.16. 210.0 mg, 50% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 4.0, 1.0 Hz, 1H), 7.78-7.76 (m, 2H), 7.69 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.16 (dd, *J* = 5.0, 1.5 Hz, 1H), 6.62-6.57 (m, 2H), 6.09-6.06 (m, 2H), 4.96 (dd, *J* = 9.0, 5.5 Hz, 2H), 4.63 (s, 2H), 4.28 (d, *J* = 2.0 Hz, 2H), 2.39 (s, 3H), 2.22-2.19 (m, 1H).

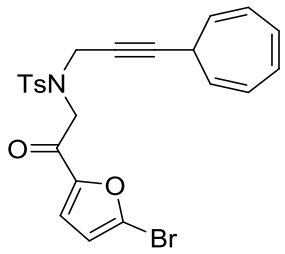
^{13}C NMR (125 MHz, Chloroform-*d*) δ 186.8, 144.0, 141.2, 135.8, 134.7, 133.2, 131.0, 129.8, 128.5, 127.9, 124.8, 122.7, 88.3, 72.4, 52.4, 38.2, 31.5, 21.7.

HRMS (ESI) m/z: calcd for $[C_{23}H_{21}NO_3S_2+H]^+$ requires: 424.1036, found: 424.1037.





_N_-(2-(5-bromofuran-2-yl)-2-oxoethyl)-_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1s)

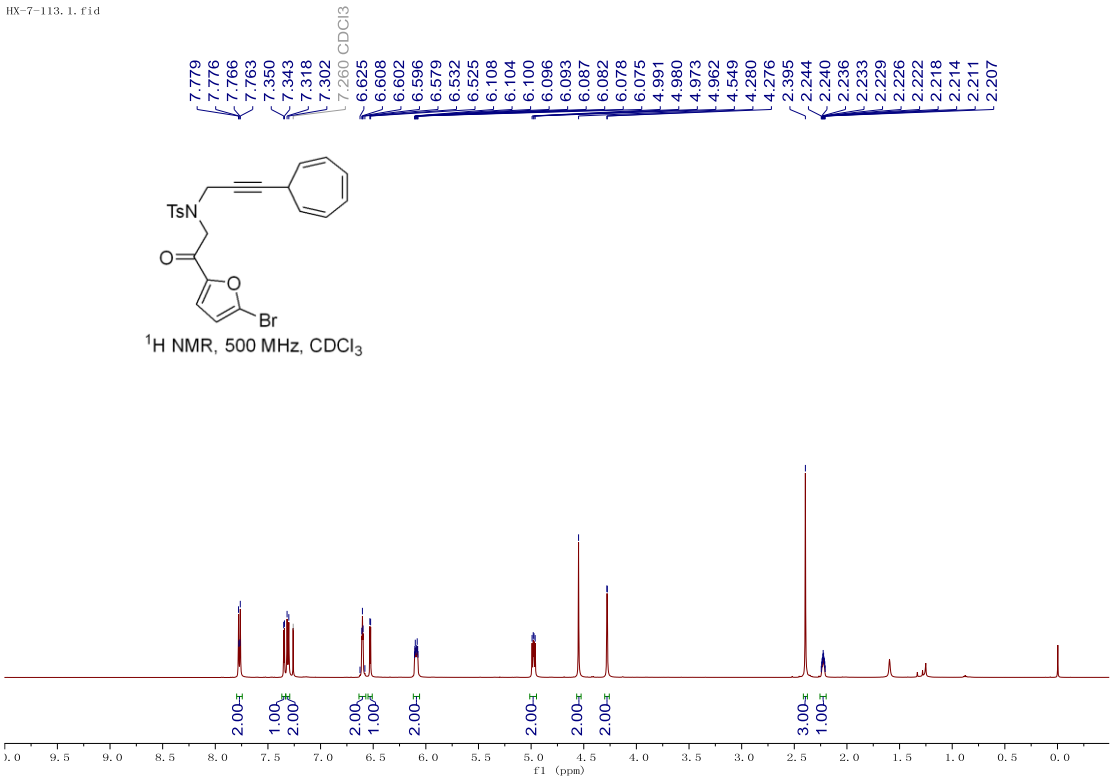


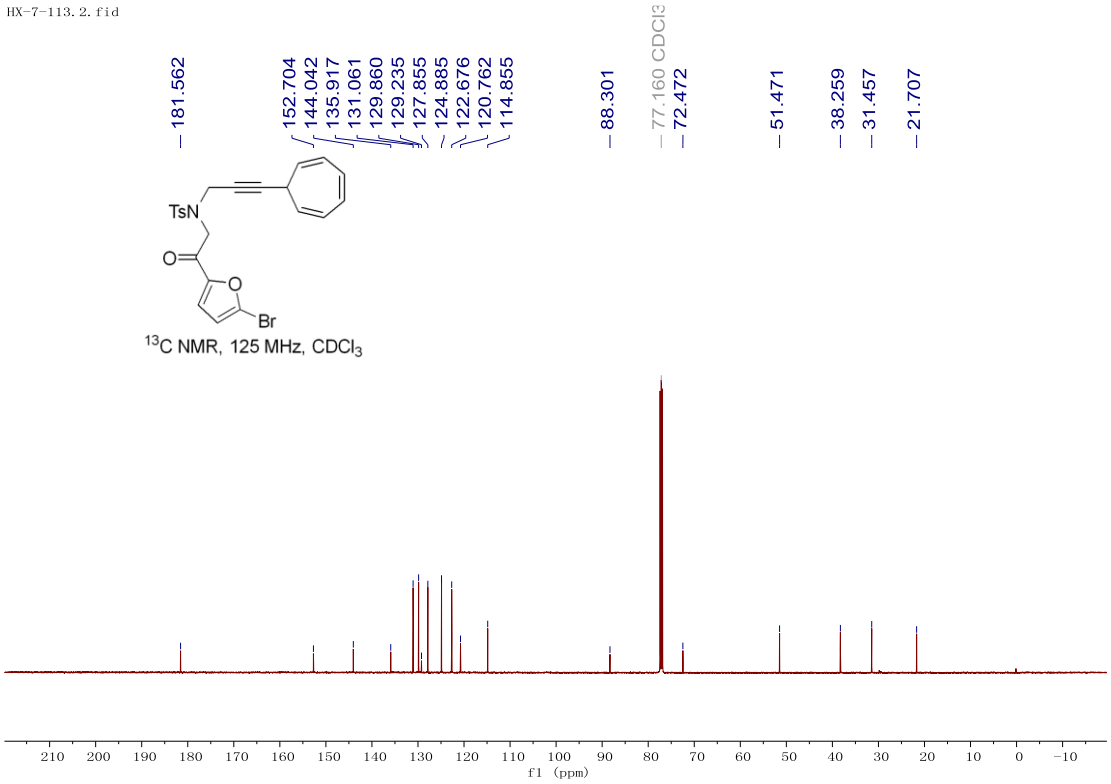
Compound **1s**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.23. 253.6 mg, 48% yield. m.p. 95-99 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78-7.76 (m, 2H), 7.35 (d, *J* = 3.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.63-6.58 (m, 2H), 6.53 (d, *J* = 3.5 Hz, 1H), 6.11-6.08 (m, 2H), 4.98 (dd, *J* = 9.0, 5.5 Hz, 2H), 4.55 (s, 2H), 4.28 (d, *J* = 2.0 Hz, 2H), 2.40 (s, 3H), 2.24-2.21 (m, 1H).

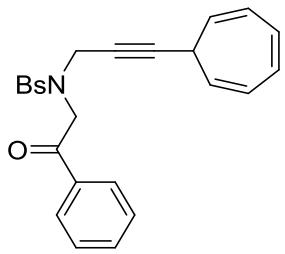
^{13}C NMR (125 MHz, Chloroform-*d*) δ 181.6, 152.7, 144.0, 135.9, 131.1, 129.9, 129.2, 127.9, 124.9, 122.7, 120.8, 114.9, 88.3, 72.5, 51.5, 38.3, 31.5, 21.7.

HRMS (ESI) m/z: calcd for $[C_{23}H_{20}BrNO_4S+H]^+$ requires: 486.0369, found: 486.0371.





4-bromo-*N*-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-*N*-(2-oxo-2-phenylethyl)benzenesulfonamide (1t)

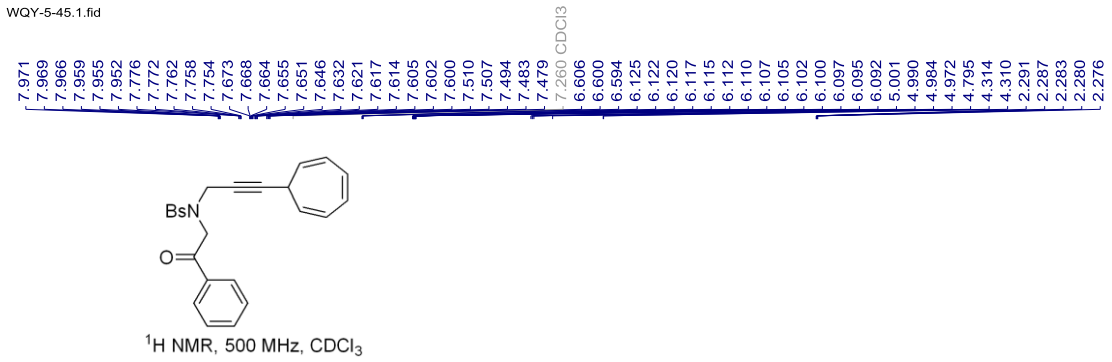


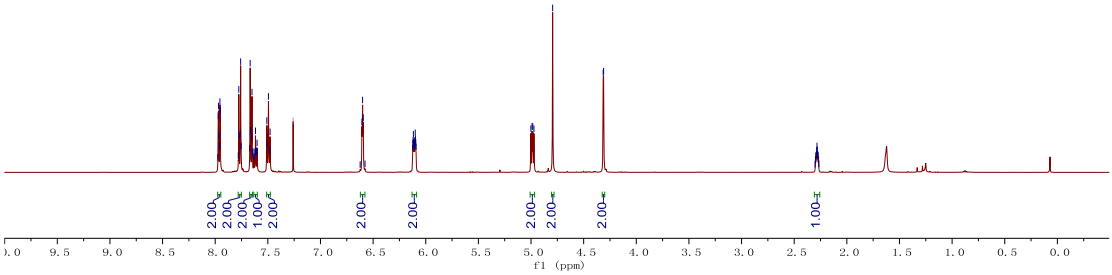
Compound **1t**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.39. 315.4 mg, 36% yield. m.p. 77-81 °C.

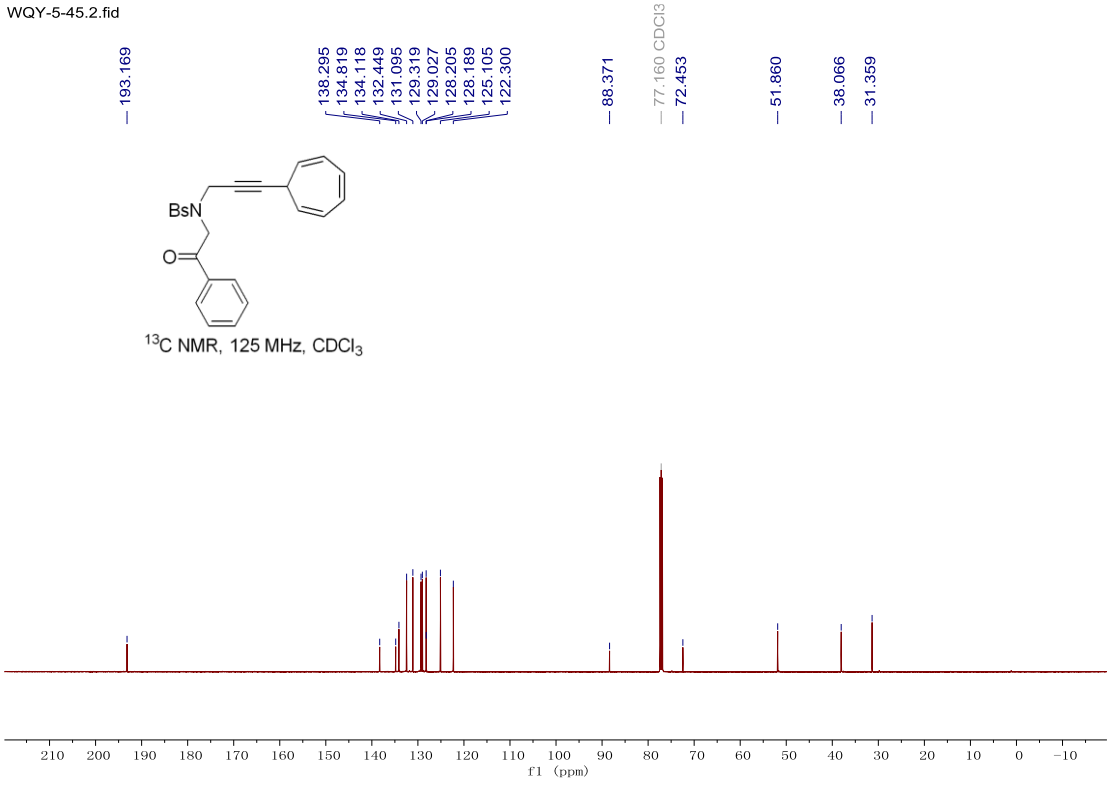
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98-7.95 (m, 2H), 7.78-7.75 (m, 2H), 7.67-7.65 (m, 2H), 7.64-7.60 (m, 1H), 7.51-7.48 (m, 2H), 6.62-6.58 (m, 2H), 6.13-6.09 (m, 2H), 4.99 (dd, J = 9.0, 5.5 Hz, 2H), 4.80 (s, 2H), 4.31 (d, J = 2.0 Hz, 2H), 2.30-2.27 (m, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.2, 138.3, 134.8, 134.1, 132.4, 131.1, 129.3, 129.0, 128.21, 128.19, 125.1, 122.3, 88.4, 72.5, 51.9, 38.1, 31.4.

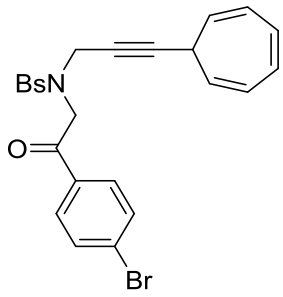
HRMS (ESI) m/z: calcd for $[C_{24}H_{20}BrNO_3S+H]^+$ requires: 482.0420, found: 482.0423.







4-bromo-*N*-(2-(4-bromophenyl)-2-oxoethyl)-*N*-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)benzenesulfonamide (1u)

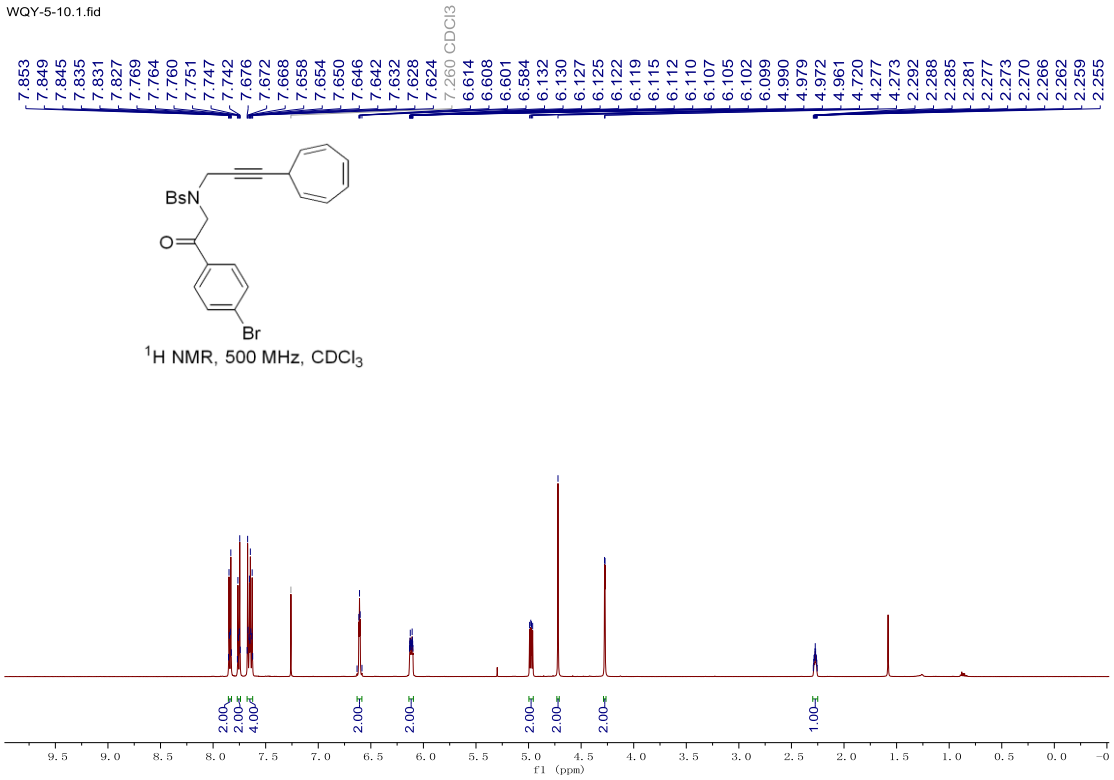


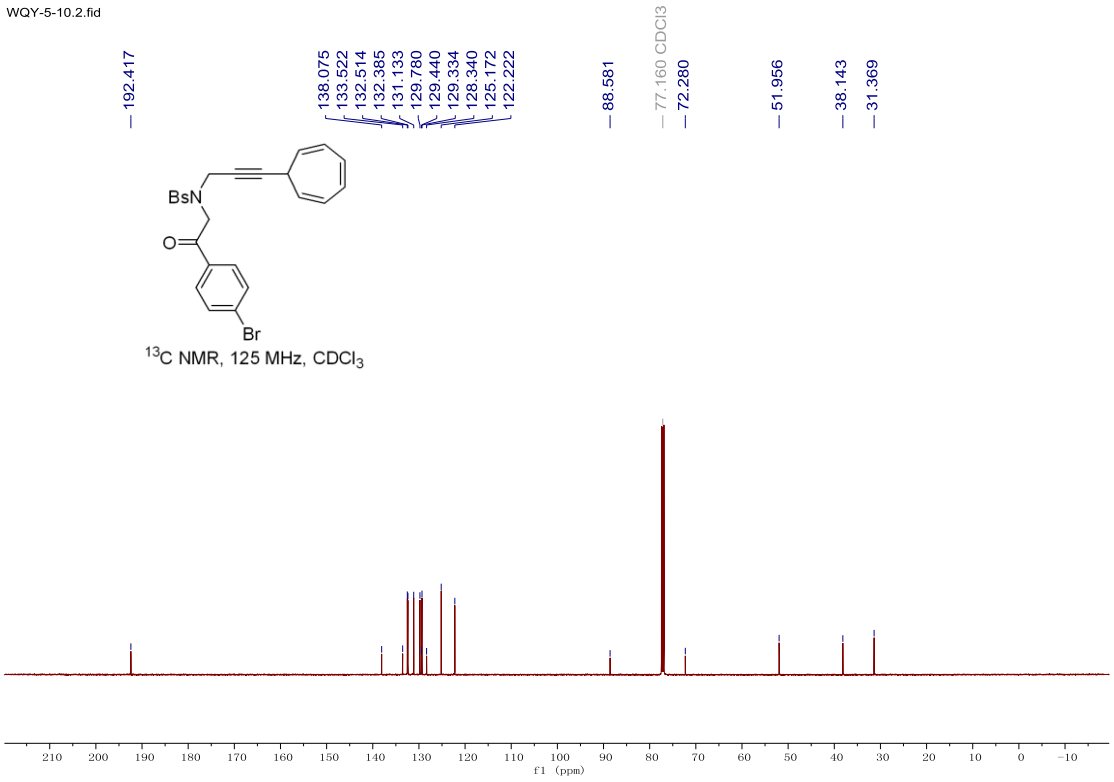
Compound **1u**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.43. 215.0 mg, 38% yield. m.p. 138-142 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85-7.83 (m, 2H), 7.77-7.74 (m, 2H), 7.68-7.62 (m, 4H), 6.63-6.58 (m, 2H), 6.13-6.10 (m, 2H), 4.98 (dd, J = 9.0, 5.5 Hz, 2H), 4.72 (s, 2H), 4.28 (d, J = 2.0 Hz, 2H), 2.29-2.26 (m, 1H).

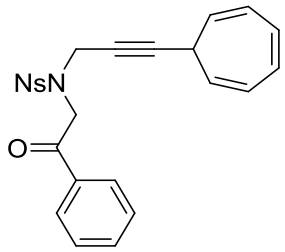
^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.4, 138.1, 133.5, 132.5, 132.4, 131.1, 129.8, 129.4, 129.3, 128.3, 125.2, 122.2, 88.6, 72.3, 52.0, 38.1, 31.4.

HRMS (ESI) m/z: calcd for $[C_{24}H_{19}Br_2NO_3S+H]^+$ requires: 559.9525, found: 559.9532.





_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-4-nitro-_N_-(2-oxo-2-phenylethyl)benzenesulfonamide (1v)

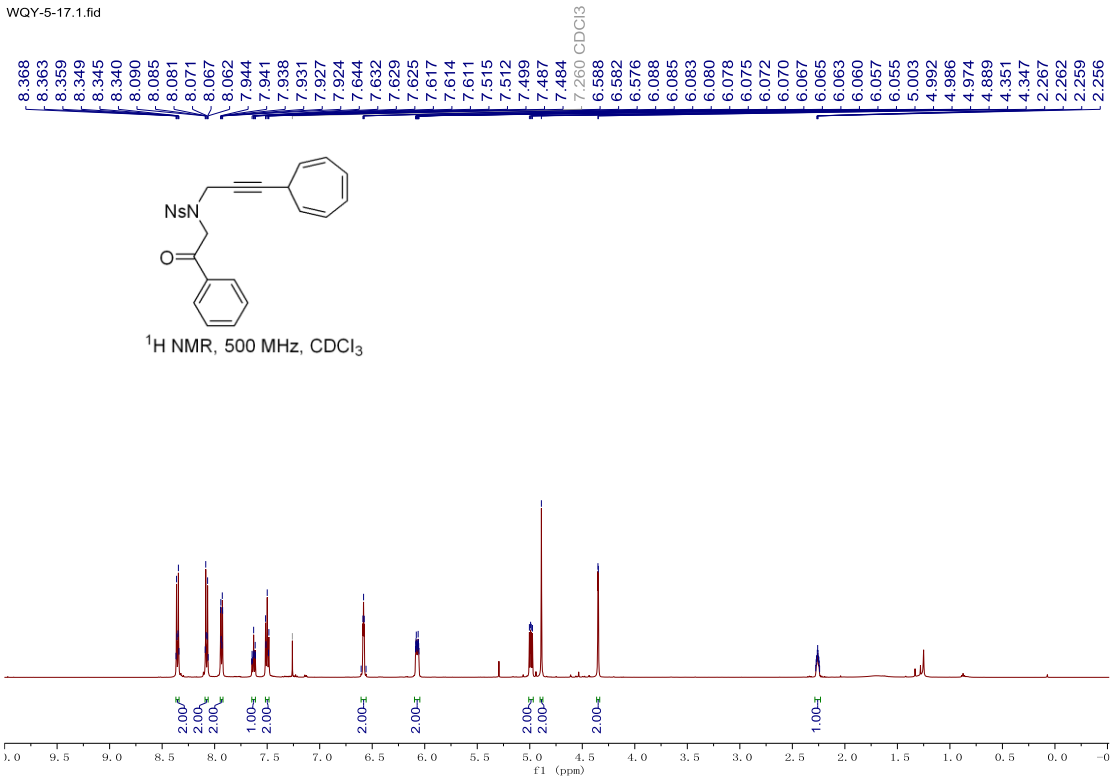


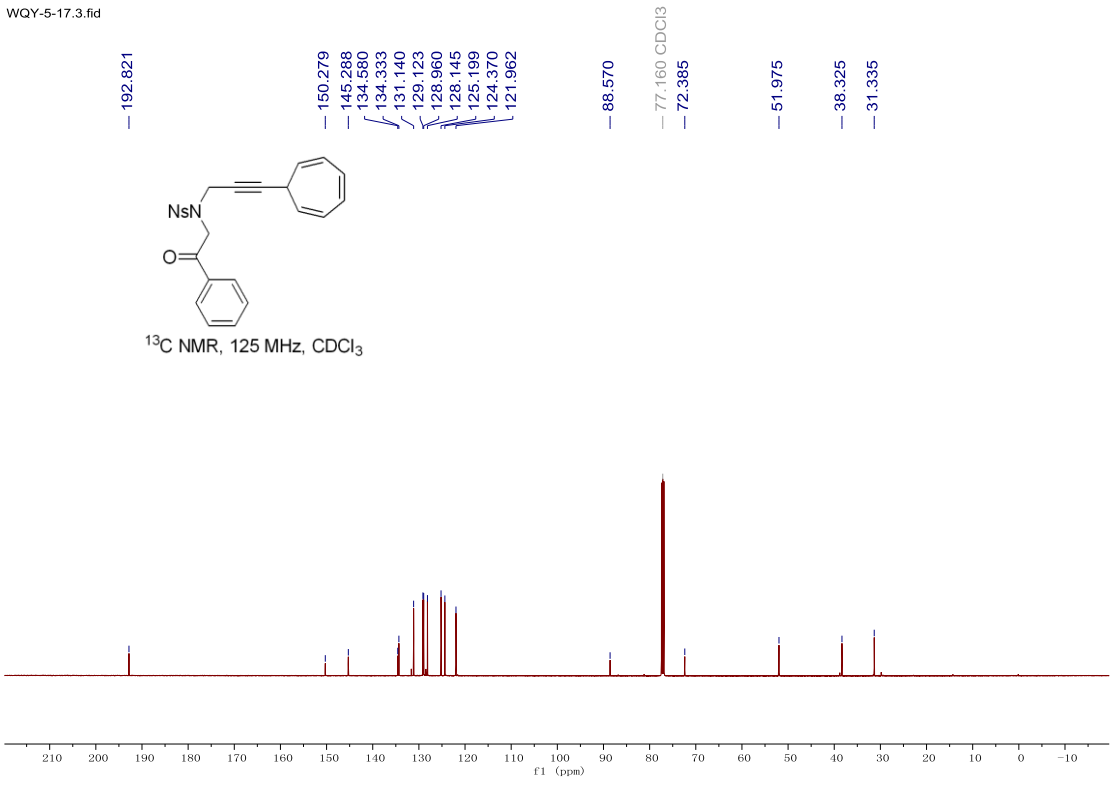
Compound **1v**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.19. 251.0 mg, 56% yield. m.p. 110-114 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.37-8.34 (m, 2H), 8.09-8.06 (m, 2H), 7.94-7.92 (m, 2H), 7.63 (tt, *J* = 7.0, 1.0 Hz, 1H), 7.52-7.48 (m, 2H), 6.61-6.56 (m, 2H), 6.09-6.06 (m, 2H), 4.99 (dd, *J* = 8.5, 5.5 Hz, 2H), 4.89 (s, 2H), 4.35 (d, *J* = 2.0 Hz, 2H), 2.28-2.24 (m, 1H).

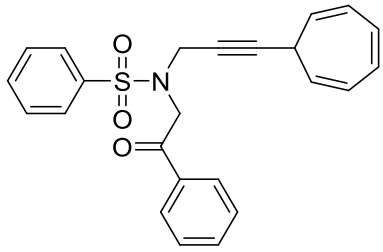
^{13}C NMR (125 MHz, Chloroform-*d*) δ 192.8, 150.3, 145.3, 134.6, 134.3, 131.1, 129.1, 129.0, 128.1, 125.2, 124.4, 122.0, 88.6, 72.4, 52.0, 38.3, 31.3.

HRMS (ESI) m/z: calcd for $[C_{24}H_{20}N_2O_5S+H]^+$ requires: 449.1166, found: 449.1166.





_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-_N_-(2-oxo-2-phenylethyl)benzeneesulfonamide (1w)

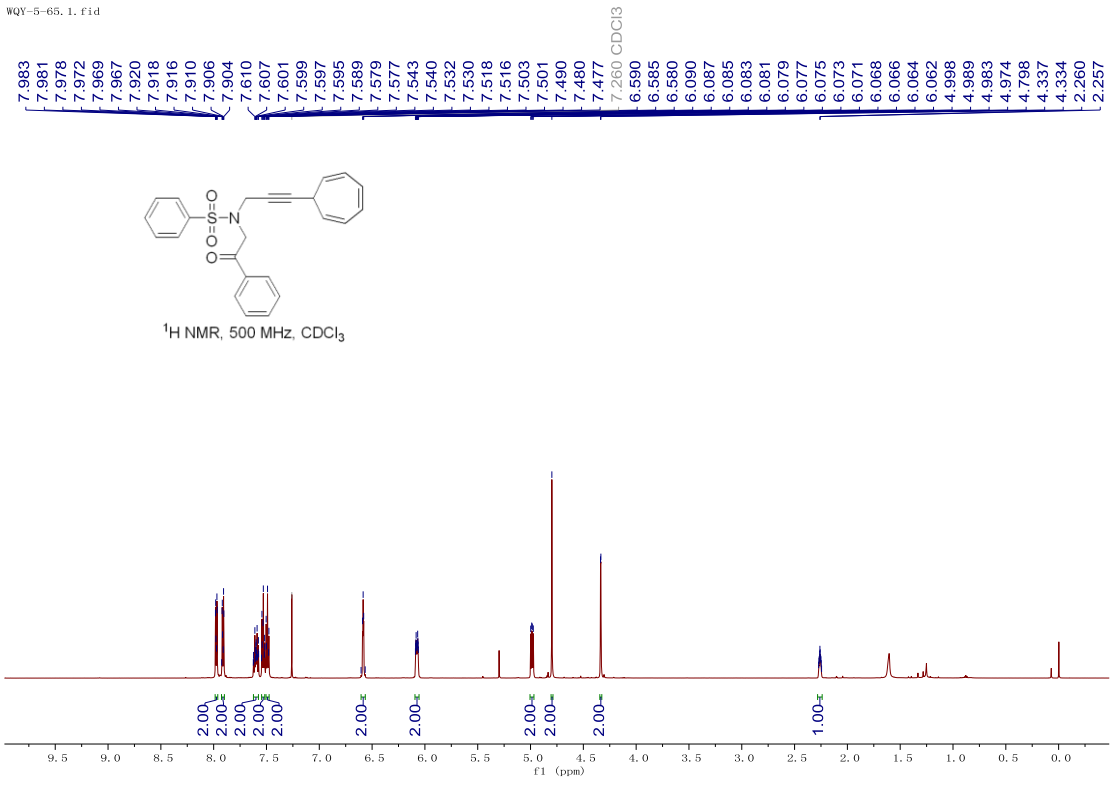


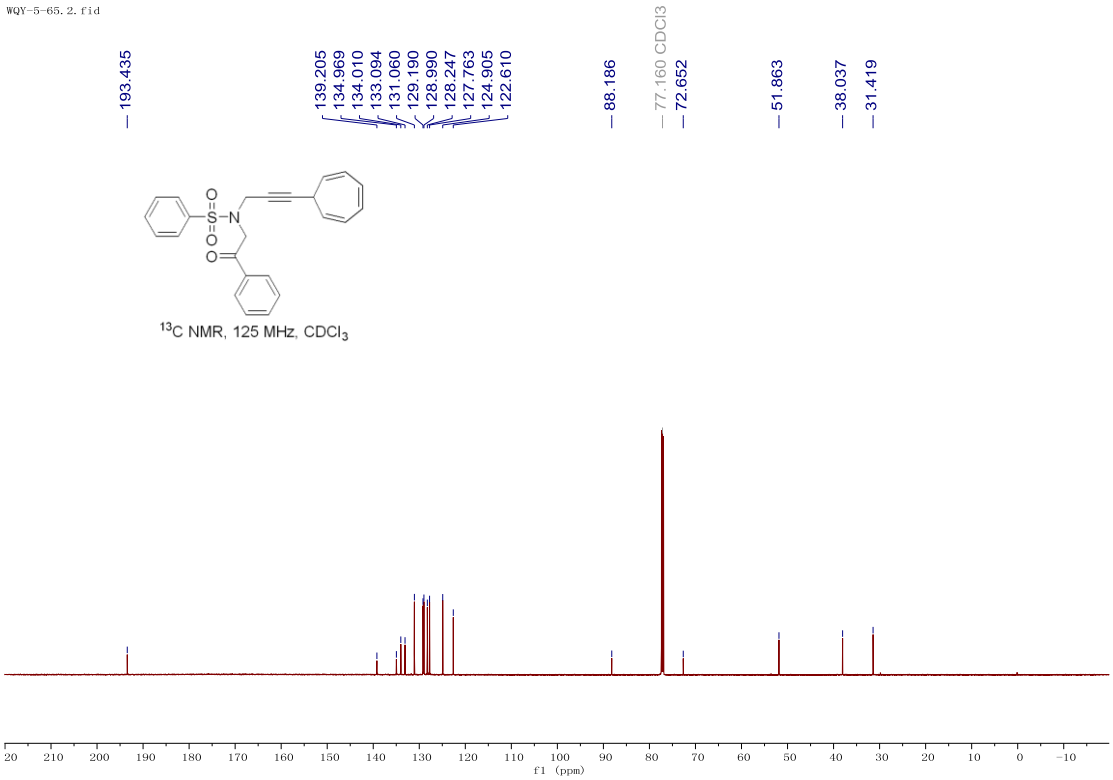
Compound **1w**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.23. 221.8 mg, 55% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98-7.97 (m, 2H), 7.92-7.90 (m, 2H), 7.62-7.57 (m, 2H), 7.55-7.52 (m, 2H), 7.50-7.48 (m, 2H), 6.60-6.57 (m, 2H), 6.09-6.06 (m, 2H), 4.99 (dd, *J* = 7.5, 4.5 Hz, 2H), 4.80 (s, 2H), 4.34 (d, *J* = 1.5 Hz, 2H), 2.27-2.24 (m, 1H).

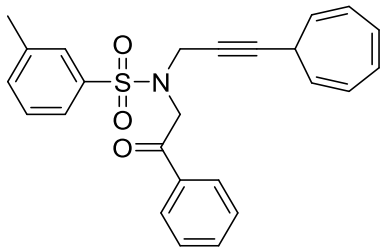
^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.4, 139.2, 135.0, 134.0, 133.1, 131.1, 129.2, 129.0, 128.2, 127.8, 124.9, 122.6, 88.2, 72.7, 51.9, 38.0, 31.4.

HRMS (ESI) m/z: calcd for $[C_{24}H_{21}NO_3S+H]^+$ requires: 404.1315, found: 404.1317.





_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-3-methyl-_N_-(2-oxo-2-phenylethyl)benzenesulfonamide (1x)

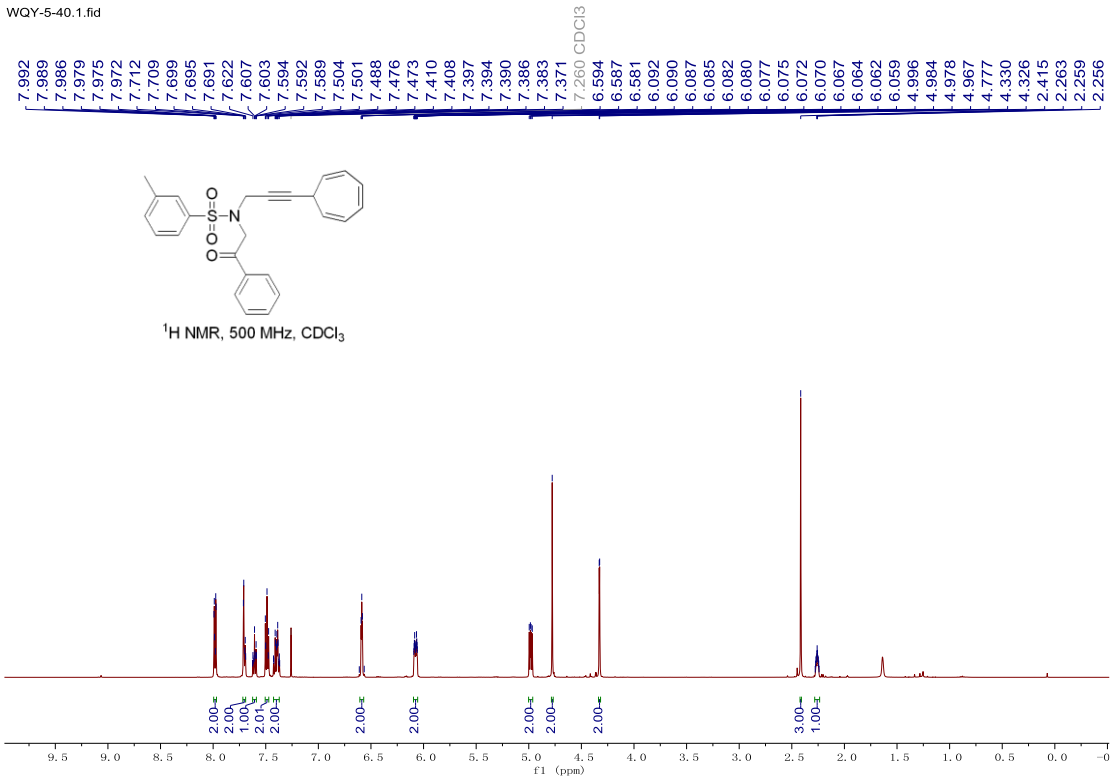


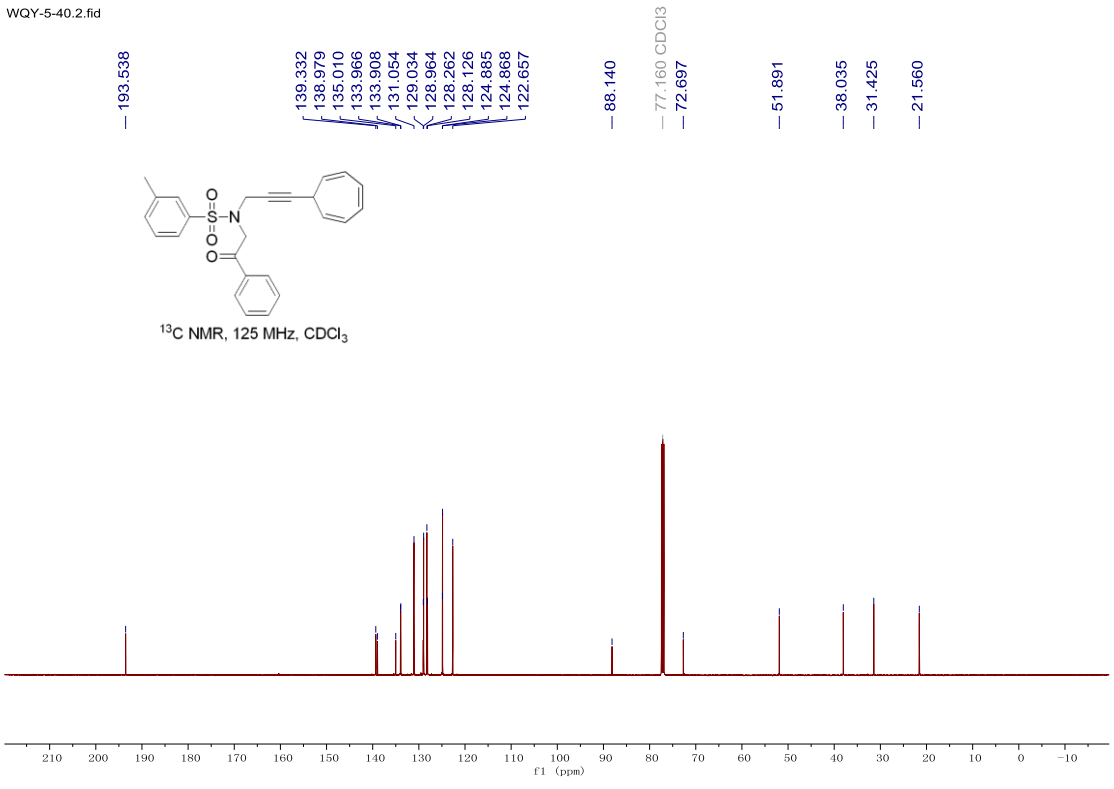
Compound **1x**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.25. 306.8 mg, 48% yield. m.p. 79-84 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99-7.97 (m, 2H), 7.71-7.69 (m, 2H), 7.62-7.59 (m, 1H), 7.50-7.47 (m, 2H), 7.43-7.37 (m, 2H), 6.61-6.56 (m, 2H), 6.09-6.06 (m, 2H), 4.98 (dd, *J* = 9.0, 6.0 Hz, 2H), 4.78 (s, 2H), 4.33 (d, *J* = 2.0 Hz, 2H), 2.42 (s, 3H), 2.28-2.24 (m, 1H).

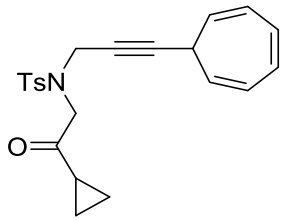
^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.5, 139.3, 139.0, 135.0, 134.0, 133.9, 131.1, 129.03, 128.96, 128.3, 128.1, 124.89, 124.87, 122.7, 88.1, 72.7, 51.9, 38.0, 31.4, 21.6.

HRMS (ESI) m/z: calcd for $[C_{25}H_{23}NO_3S+H]^+$ requires: 418.1471, found: 418.1473.





_N_-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-_N_-(2-cyclopropyl-2-oxoethyl)-4-methylbenzenesulfonamide (1y)

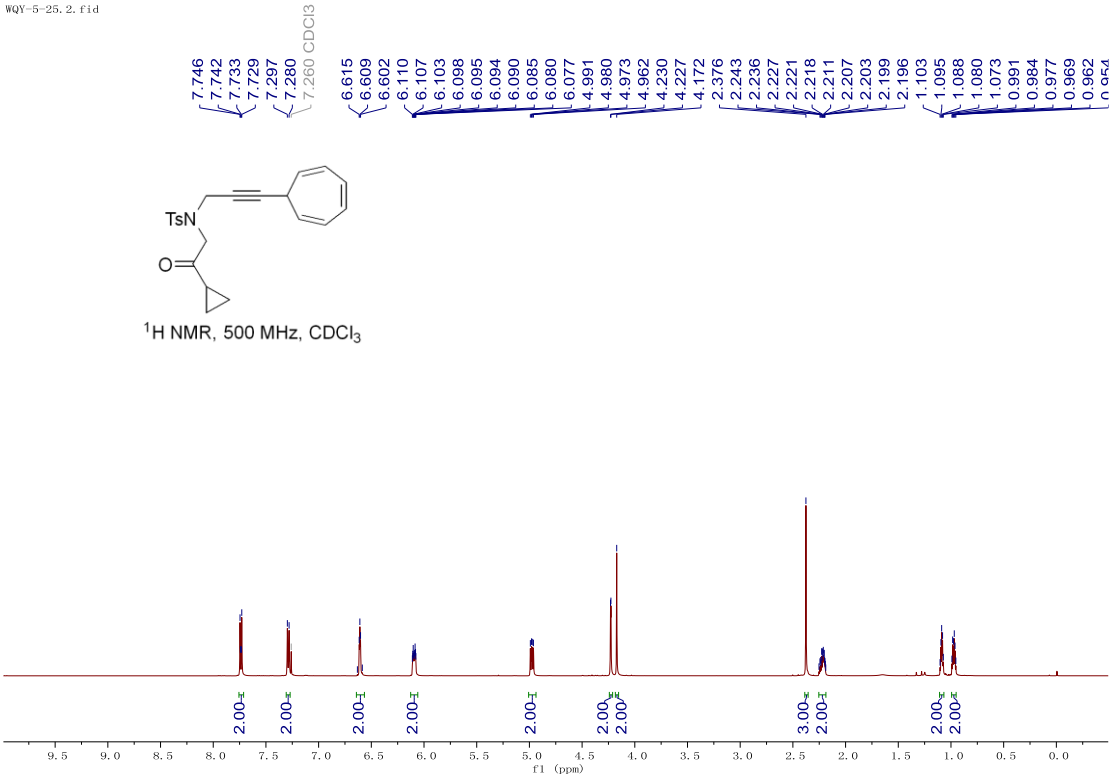


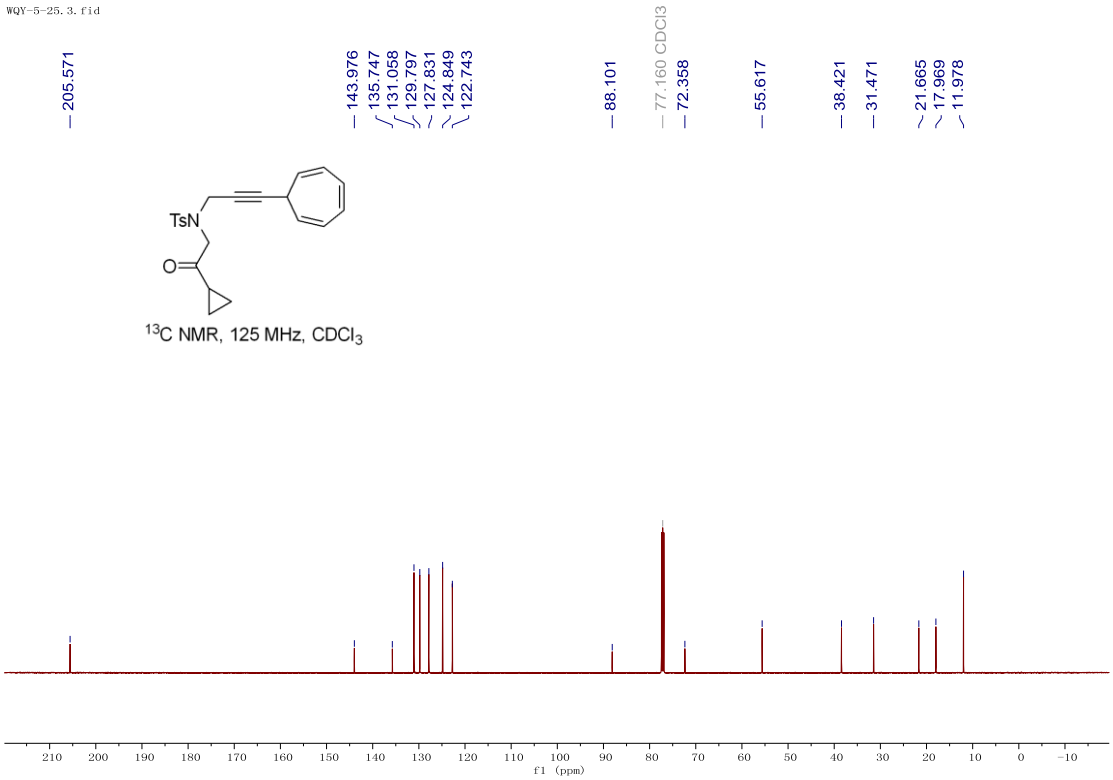
Compound **1y**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.31. 127.2 mg, 24% yield. m.p. 84-88 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75-7.73 (m, 2H), 7.29 (d, J = 8.5 Hz, 2H), 6.63-6.59 (m, 2H), 6.11-6.08 (m, 2H), 4.98 (dd, J = 9.0, 5.5 Hz, 2H), 4.23 (d, J = 1.5 Hz, 2H), 4.17 (s, 2H), 2.38 (s, 3H), 2.25-2.19 (m, 2H), 1.10-1.07 (m, 2H), 0.99-0.95 (m, 2H).

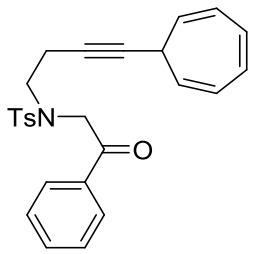
^{13}C NMR (125 MHz, Chloroform-*d*) δ 205.6, 144.0, 135.7, 131.1, 129.8, 127.8, 124.8, 122.7, 88.1, 72.4, 55.6, 38.4, 31.5, 21.7, 18.0, 12.0.

HRMS (ESI) m/z: calcd for $[C_{22}H_{23}NO_3S+H]^+$ requires: 382.1471, found: 382.1472.





_N_-(4-(cyclohepta-2,4,6-trien-1-yl)but-3-yn-1-yl)-4-methyl-_N_-(2-oxo-2-phenylethyl)benzenesulfonamide (1z)

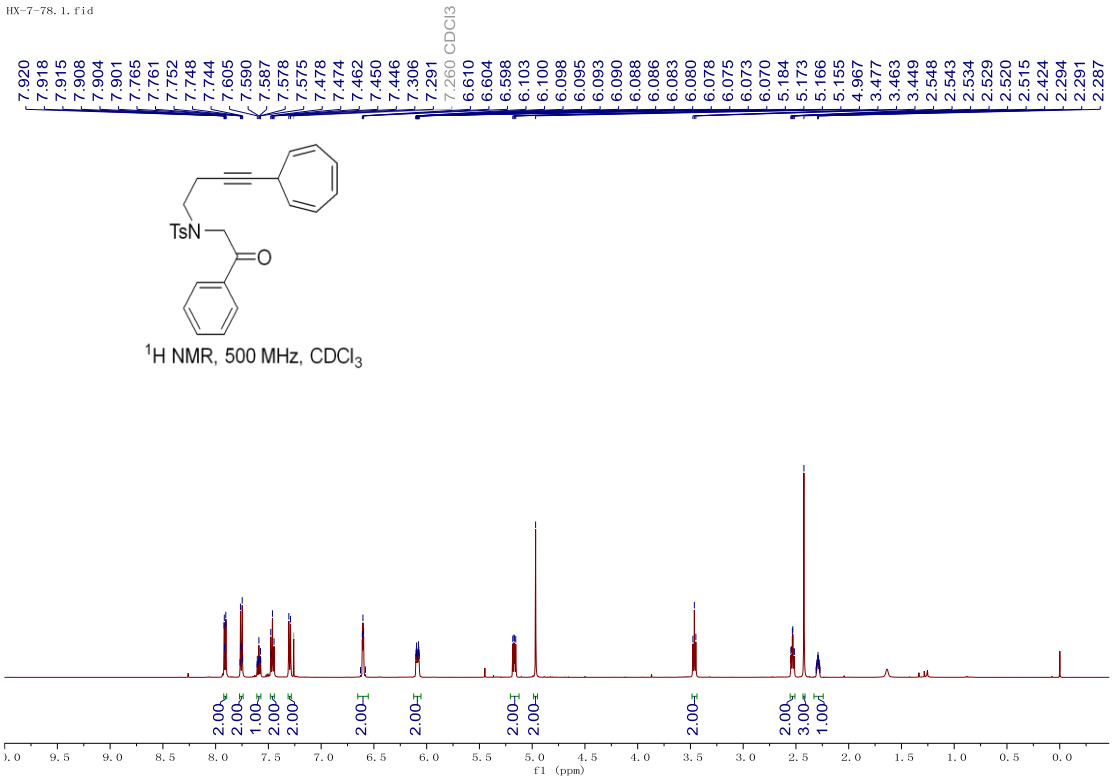


Compound **1z**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.24. 494.1 mg, 62% yield. m.p. 57-61 °C.

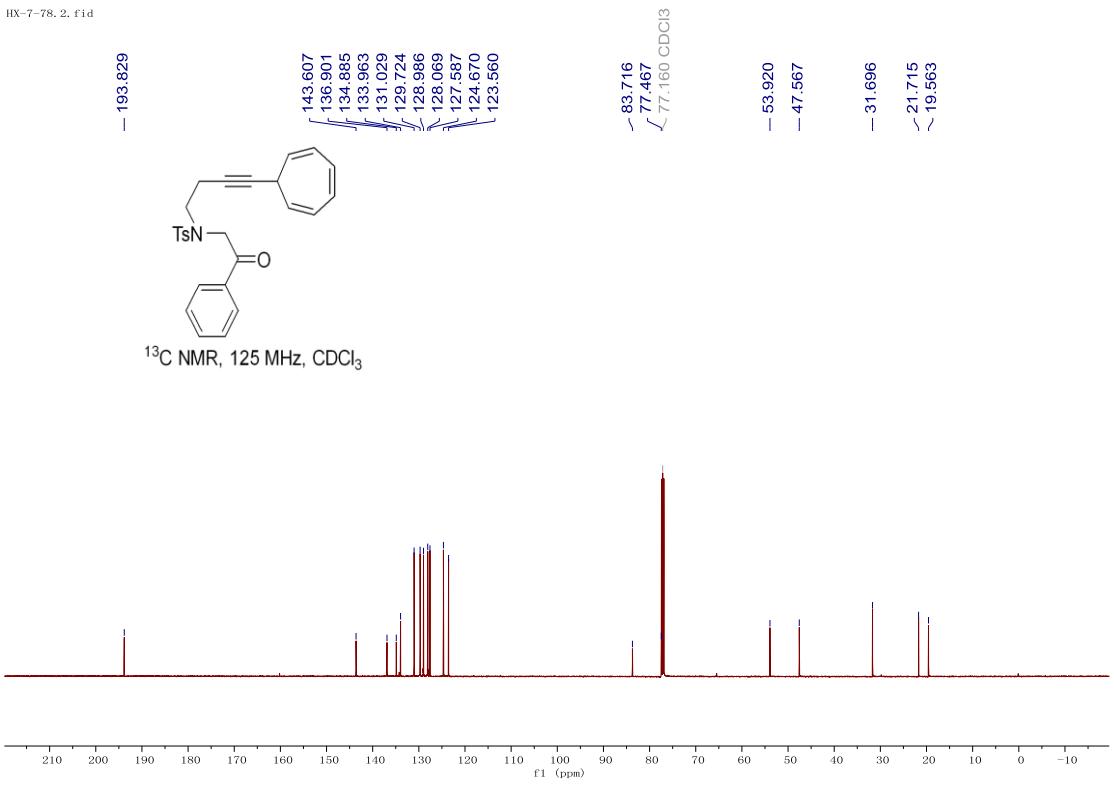
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92-7.90 (m, 2H), 7.77-7.74 (m, 2H), 7.59 (tt, *J* = 7.0, 1.5 Hz, 1H), 7.48-7.45 (m, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 6.63-6.58 (m, 2H), 6.10-6.07 (m, 2H), 5.17 (dd, *J* = 9.0, 5.5 Hz, 2H), 4.97 (s, 2H), 3.46 (t, *J* = 7.0 Hz, 2H), 2.53 (td, *J* = 7.0, 2.5 Hz, 2H), 2.42 (s, 3H), 2.31-2.27 (m, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.8, 143.6, 136.9, 134.9, 134.0, 131.0, 129.7, 129.0, 128.1, 127.6, 124.7, 123.6, 83.7, 77.5, 53.9, 47.6, 31.7, 21.7, 19.6.

HRMS (ESI) m/z: calcd for $[C_{26}H_{25}NO_3S+H]^+$ requires: 432.1628, found: 432.1630.

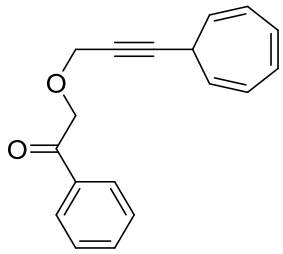


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

2-((3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)oxy)-1-phenylethan-1-one (1aa)

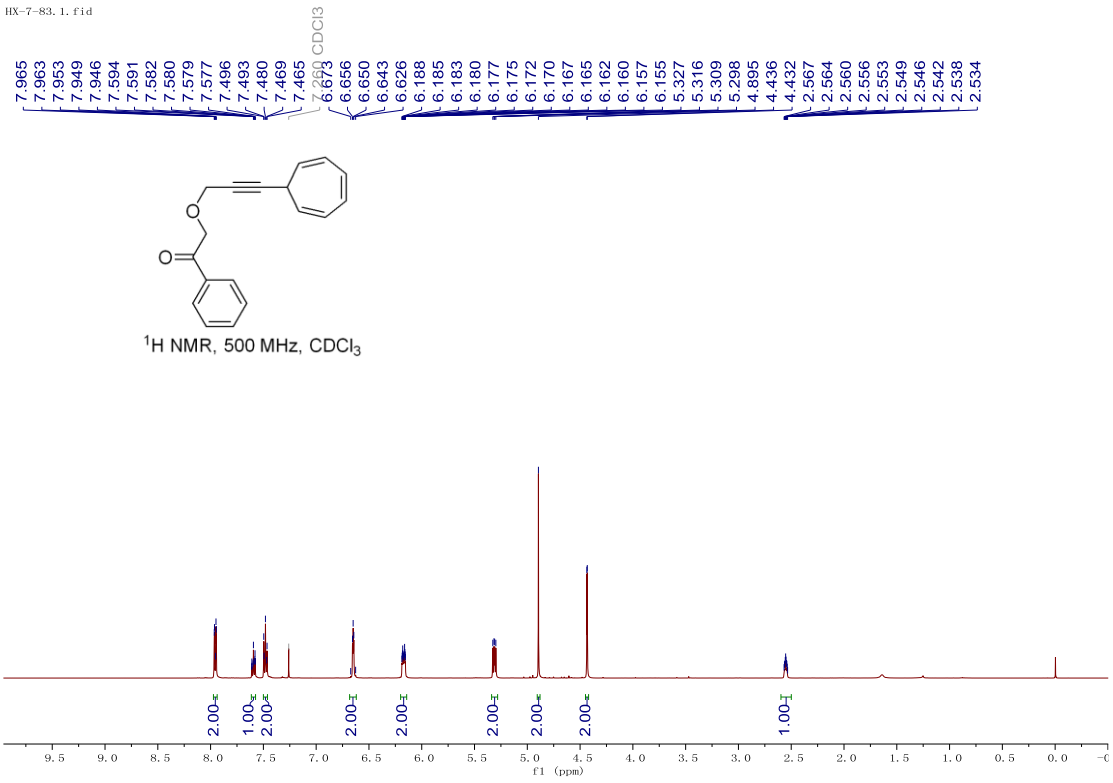


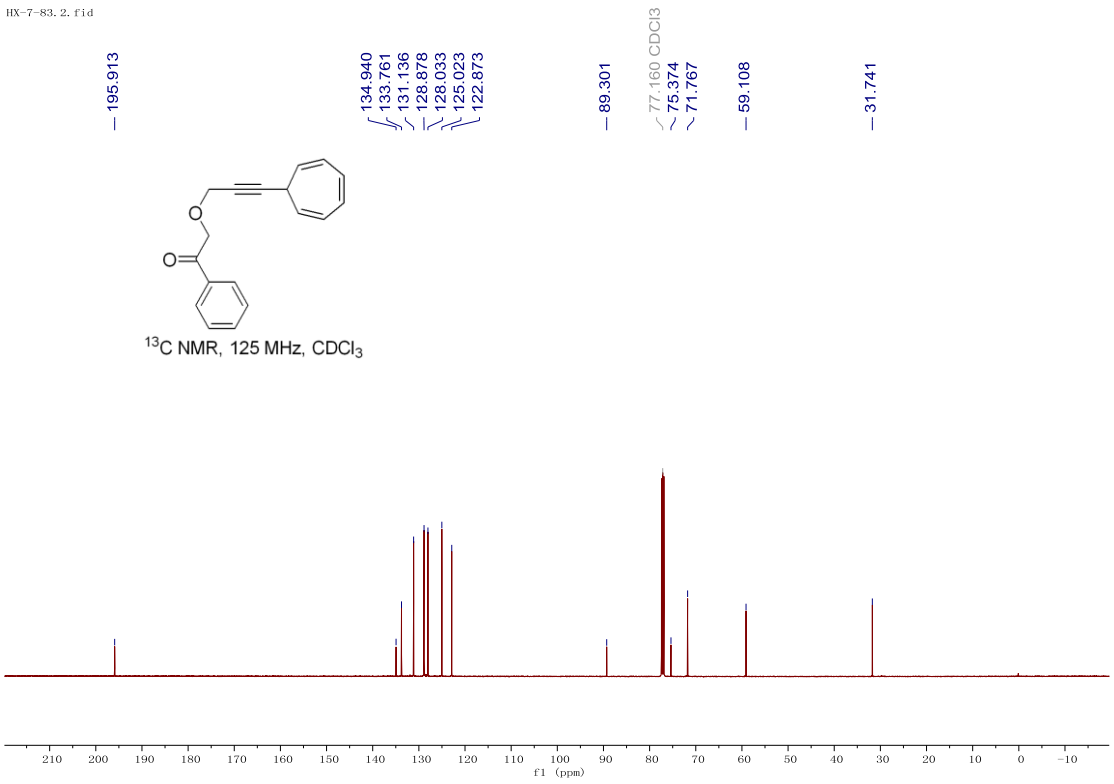
Compound **1aa**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.50. 180.8 mg, 33% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97-7.95 (m, 2H), 7.61-7.58 (m, 1H), 7.50-7.47 (m, 2H), 6.67-6.63 (m, 2H), 6.19-6.16 (m, 2H), 5.31 (dd, J = 9.0, 5.5 Hz, 2H), 4.90 (s, 2H), 4.43 (d, J = 2.0 Hz, 2H), 2.57-2.53 (m, 1H).

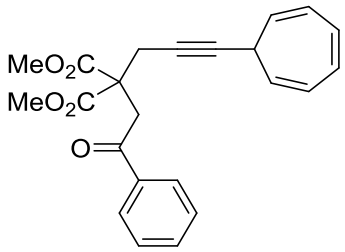
^{13}C NMR (125 MHz, Chloroform-*d*) δ 195.9, 134.9, 133.8, 131.1, 128.9, 128.0, 125.0, 122.9, 89.3, 75.4, 71.8, 59.1, 31.7.

HRMS (ESI) m/z: calcd for $[C_{18}H_{16}O_2+H]^+$ requires: 265.1223, found: 265.1224.





Dimethyl 2-(3-(cyclohepta-2,4,6-trien-1-yl)prop-2-yn-1-yl)-2-(2-oxo-2-phenylethyl)malonate (1ab)

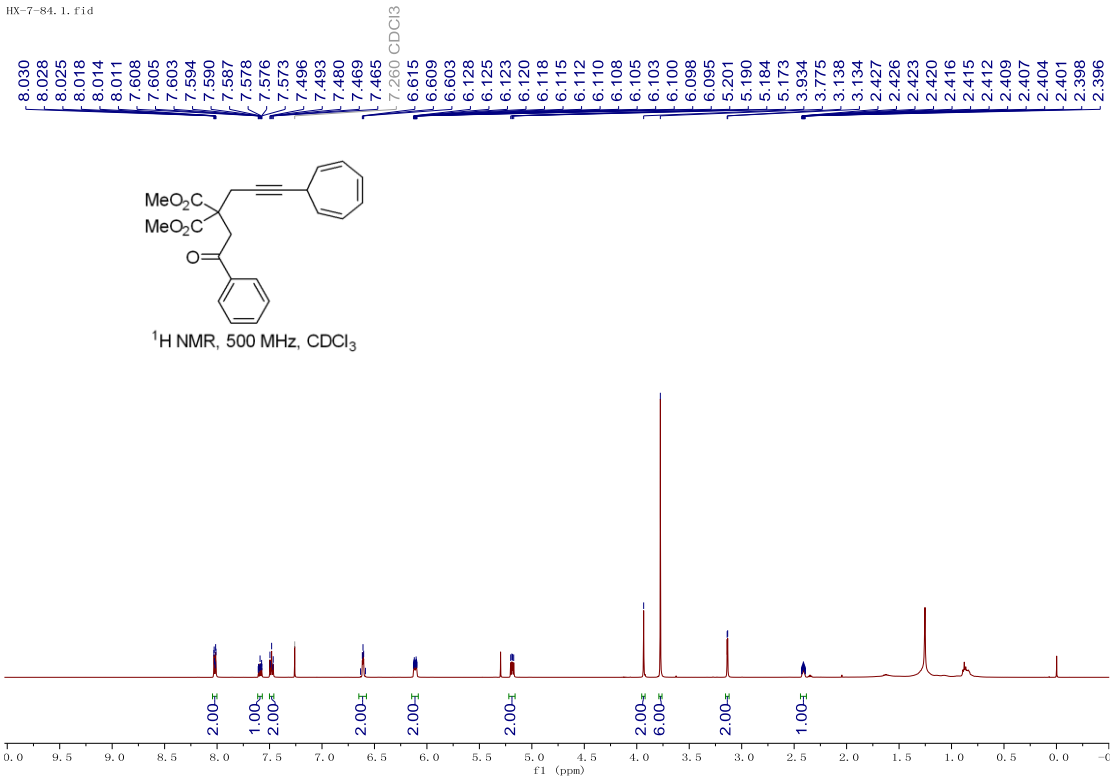


Compound **1ab**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.30. 219.9 mg, 75% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.03-8.01 (m, 2H), 7.59 (tt, J = 7.5, 1.5 Hz, 1H), 7.50-7.47 (m, 2H), 6.63-6.59 (m, 2H), 6.13-6.10 (m, 2H), 5.19 (dd, J = 8.5, 5.5 Hz, 2H), 3.93 (s, 2H), 3.78 (s, 6H), 3.14 (d, J = 2.0 Hz, 2H), 2.43-2.39 (m, 1H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 197.0, 170.1, 136.5, 133.7, 131.1, 128.8, 128.3, 124.8, 123.6, 85.4, 75.3, 55.1, 53.3, 41.2, 31.7, 23.8.

HRMS (ESI) m/z: calcd for $[C_{23}H_{22}O_5+H]^+$ requires: 379.1540, found: 379.1541.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8.025
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8.011
7.608
7.605
7.603
7.594
7.590
7.587
7.578
7.576
7.573
7.496
7.493
7.480
7.469
7.465
7.260 CDCl3
6.615
6.609
6.603
6.128
6.125
6.123
6.120
6.118
6.115
6.112
6.110
6.108
6.105
6.103
6.100
6.098
6.095
5.201
5.190
5.184
5.173
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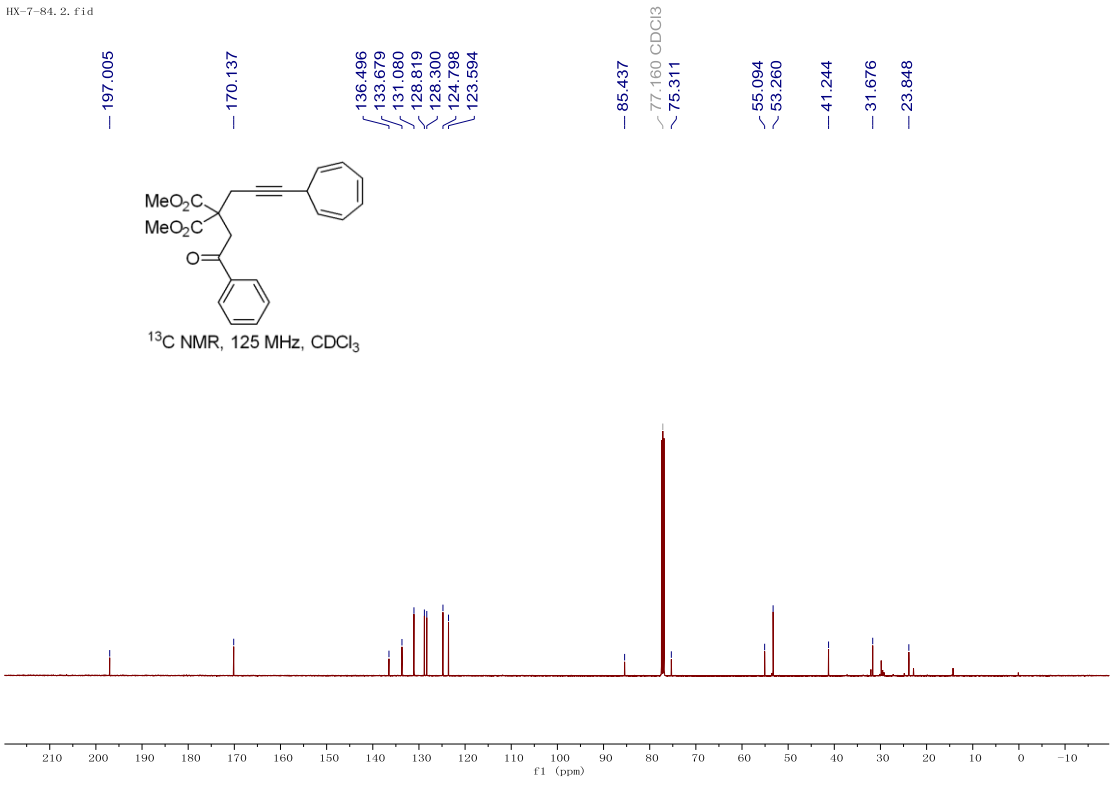
2.427
2.426
2.423
2.420
2.416
2.415
2.412
2.409
2.407
2.404
2.401
2.398
2.396
MeO2C
MeO2C
O
1H NMR, 500 MHz, CDCl3
2.00
1.00
2.00
2.00
2.00
2.00
2.00
6.00
2.00
1.00
f1 (ppm)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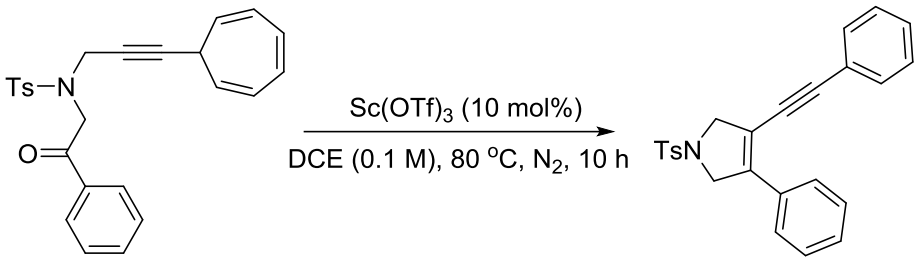
85.437
77.160 CDCl3
75.311
55.094
53.260
41.244
31.676
23.848
MeO2C
MeO2C
O
13C NMR, 125 MHz, CDCl3
f1 (ppm)

4. Experimental procedure and characterization data for products 2a-2y, 5 and 6

4.1 General procedure B for products 2a-2y, 5 and 6.

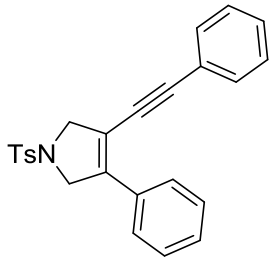


1a **2a**

Under N_2 atmosphere, 1,2-Dichloroethane (DCE) (1.0 mL, 1.0 M) was added to a mixture of **1a** (41.8 mg, 0.1 mmol), $Sc(OTf)_3$ (4.9 mg, 0.01 mmol). The reaction system was stirred at 80 °C in a parallel reactor for 10 hours. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate, 8/1) to give the product **2a** (28.0 mg, 70% yield) as a yellow solid

4.2. Characterization date of products 2a-2y, 5 and 6.

3-phenyl-4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2a)

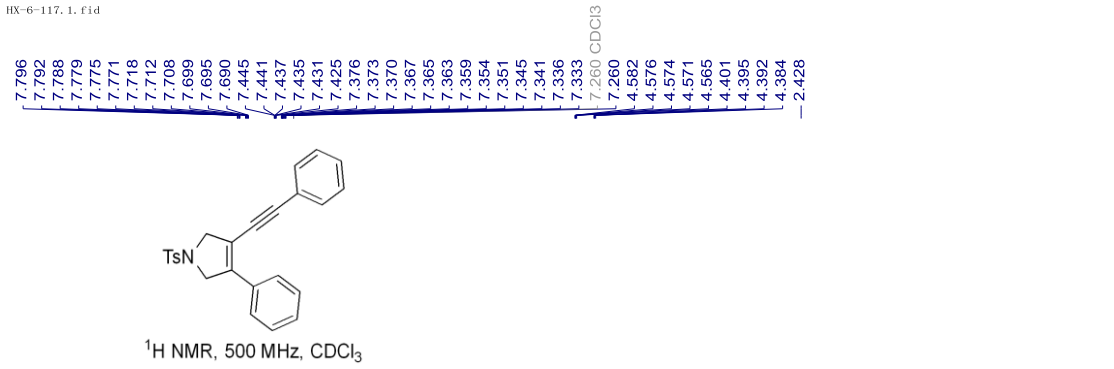


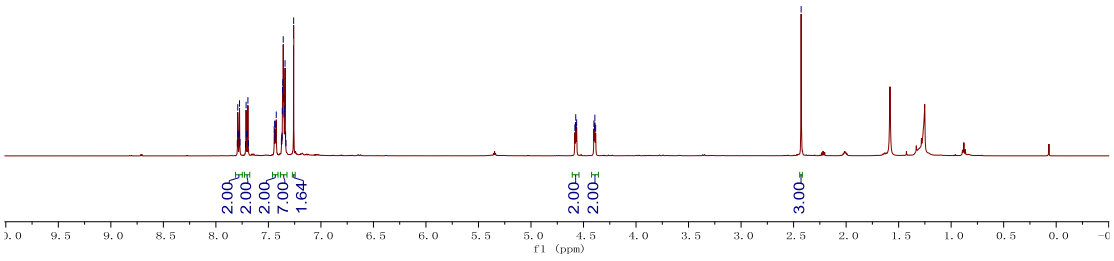
Compound **2a**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.33. 28.0 mg, 70% yield. m.p. 144-149 °C.

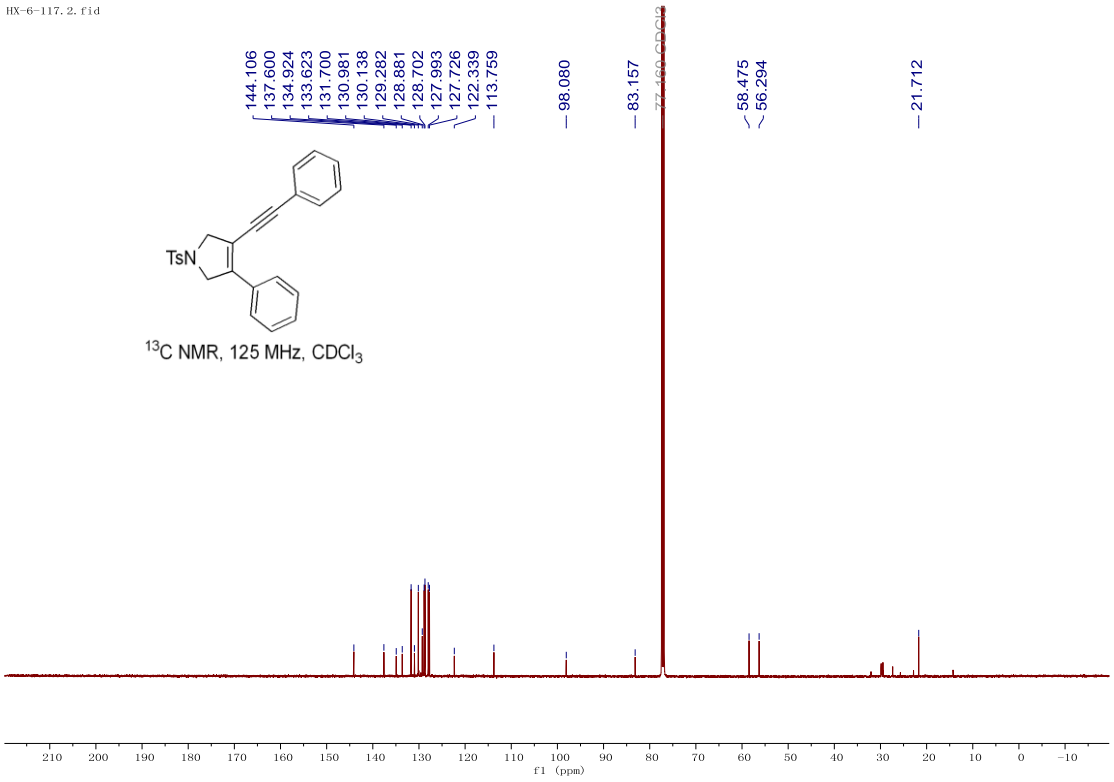
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (dt, J = 8.5, 2.0 Hz, 2H), 7.70 (dt, J = 9.0, 2.0 Hz, 2H), 7.45-7.43 (m, 2H), 7.38-7.33 (m, 7H), 7.26 (s, 1H), 4.58-4.57 (m, 2H), 4.40-4.38 (m, 2H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.1, 137.6, 134.9, 133.6, 131.7, 131.0, 130.1, 129.3, 128.9, 128.7, 128.0, 127.7, 122.3, 113.8, 98.1, 83.2, 58.5, 56.3, 21.7.

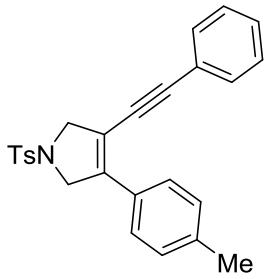
HRMS (ESI) m/z: calcd for $[C_{25}H_{21}NO_2S+H]^+$ requires: 400.1366, found: 400.1368.







3-(phenylethynyl)-4-(*p*-tolyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2b)

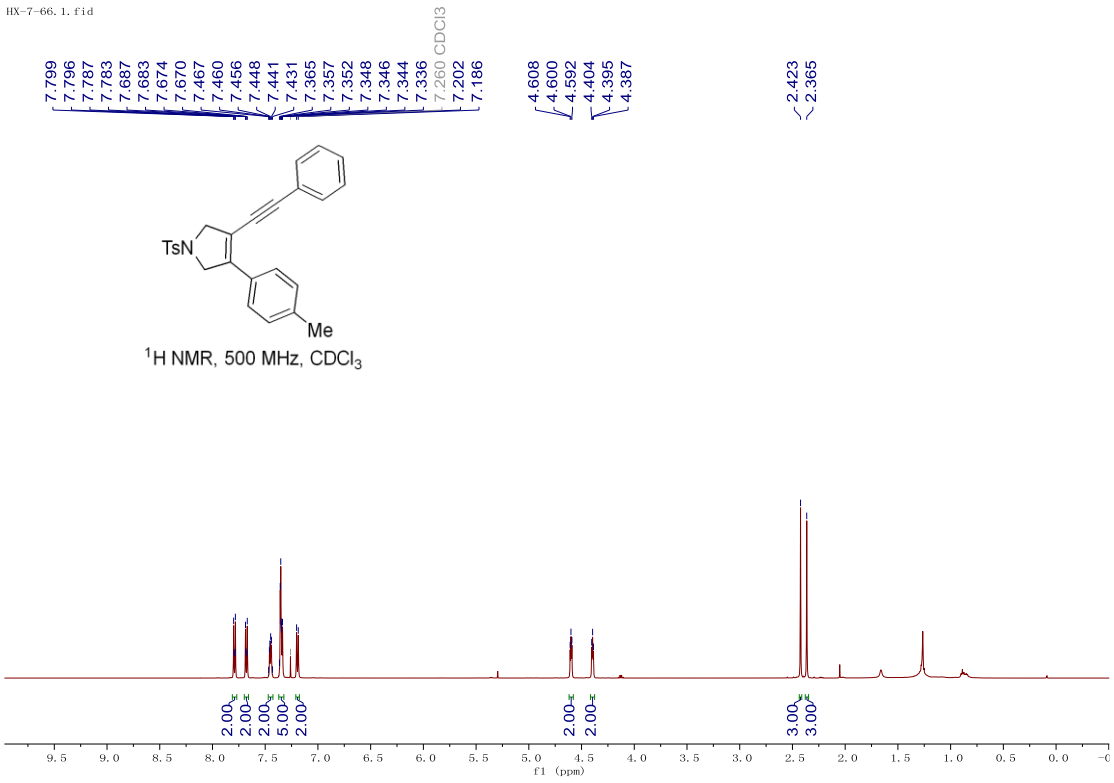


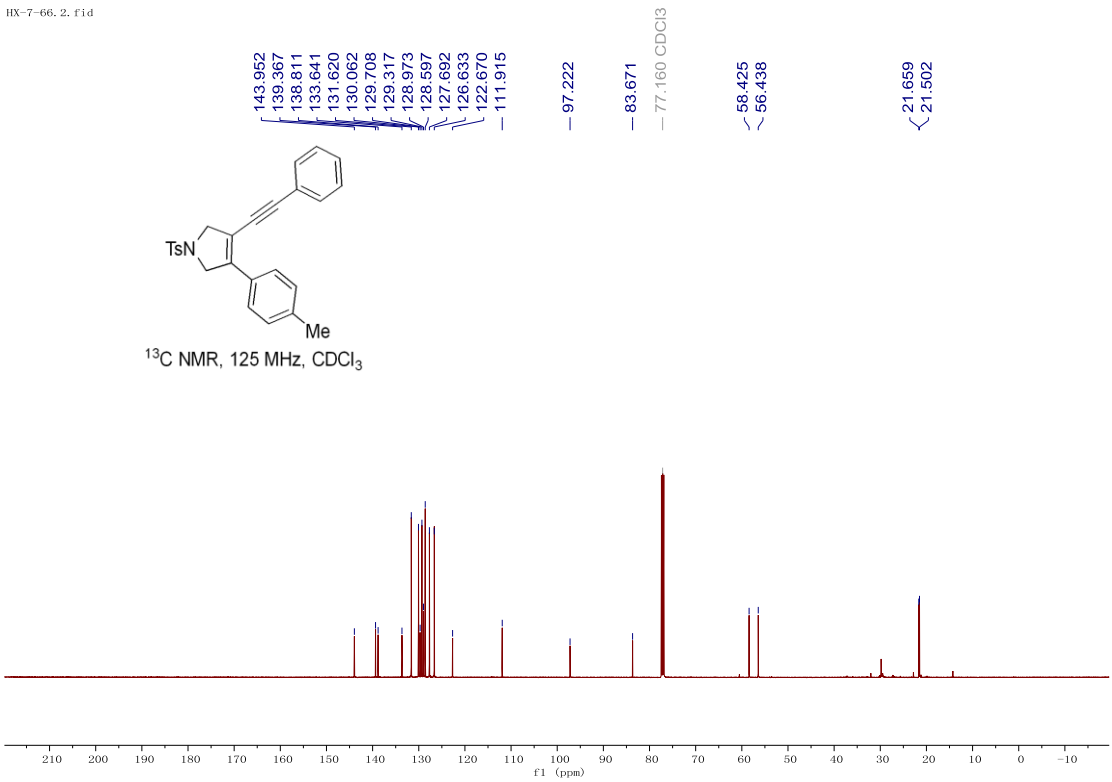
Compound **2b**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.41. 28.4 mg, 66% yield. m.p. 132-136 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80-7.78 (m, 2H), 7.69-7.67 (m, 2H), 7.47-7.43 (m, 2H), 7.37-7.34 (m, 5H), 7.19 (d, J = 8.0 Hz, 2H), 4.60 (t, J = 4.0 Hz, 2H), 4.40 (t, J = 4.0 Hz, 2H), 2.42 (s, 3H), 2.37 (s, 3H).

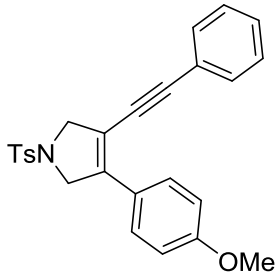
^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.0, 139.4, 138.8, 133.6, 131.6, 130.1, 129.7, 129.3, 129.0, 128.6, 127.7, 126.6, 122.7, 111.9, 97.2, 83.7, 58.4, 56.4, 21.7, 21.5.

HRMS (ESI) m/z: calcd for $[C_{26}H_{23}NO_2S+H]^+$ requires: 414.1522, found: 414.1524.





3-(4-methoxyphenyl)-4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2c)

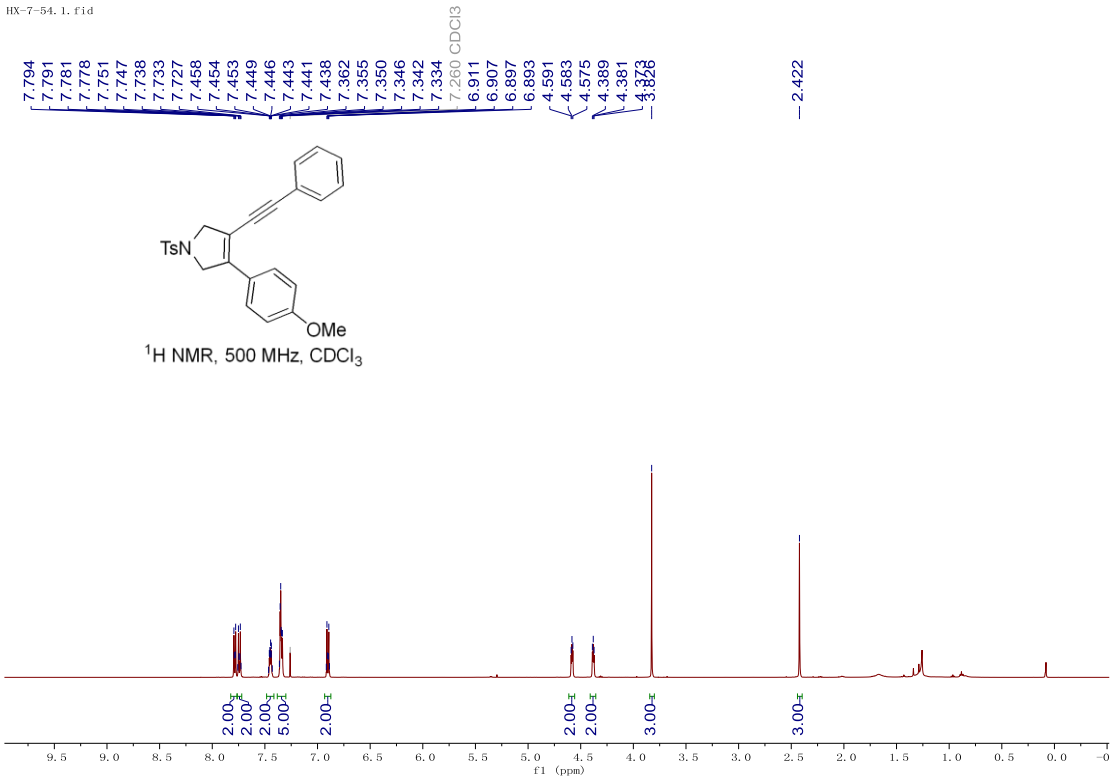


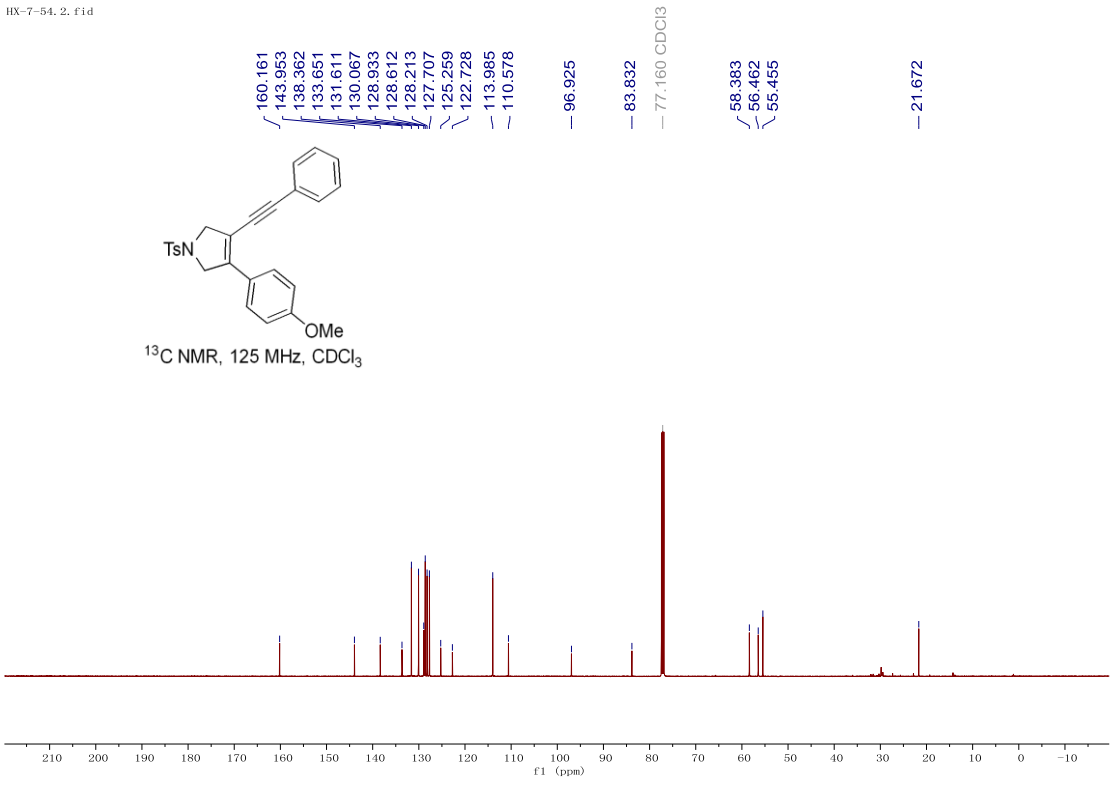
Compound **2c**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.31. 20.1 mg, 45% yield. m.p. 114-118 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79-7.78 (m, 2H), 7.74 (dt, J = 9.0, 2.5 Hz, 2H), 7.47-7.43 (m, 2H), 7.36-7.33 (m, 5H), 6.92-6.89 (m, 2H), 4.58 (t, J = 4.0 Hz, 2H), 4.38 (t, J = 4.0 Hz, 2H), 3.83 (s, 3H), 2.42 (s, 3H).

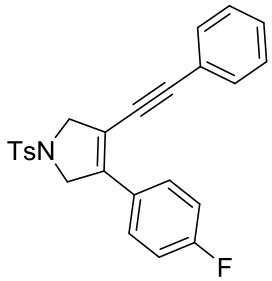
^{13}C NMR (125 MHz, Chloroform-*d*) δ 160.2, 144.0, 138.4, 133.7, 131.6, 130.1, 128.9, 128.6, 128.2, 127.7, 125.3, 122.7, 114.0, 110.6, 96.9, 83.8, 58.4, 56.5, 55.5, 21.7.

HRMS (ESI) m/z: calcd for $[C_{26}H_{23}NO_3S+H]^+$ requires: 430.1471, found: 430.1473.





3-(4-fluorophenyl)-4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2d)



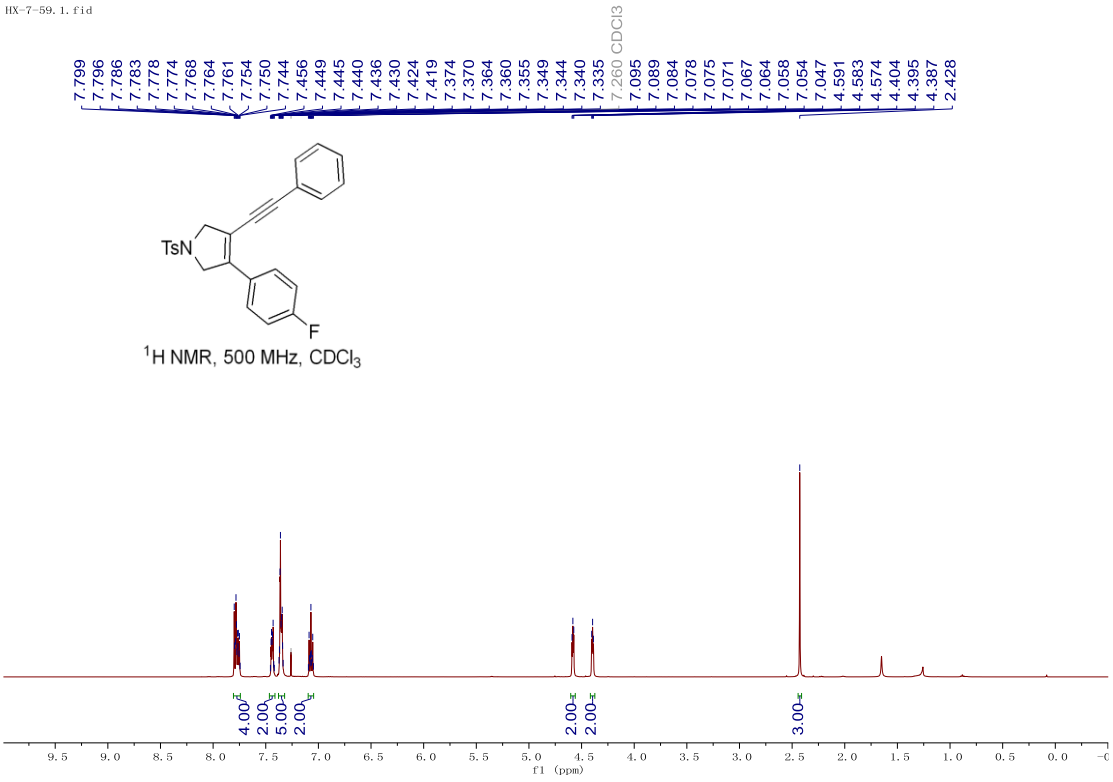
Compound **2d**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.36. 31.0 mg, 71% yield. m.p. 158-162 ºC.

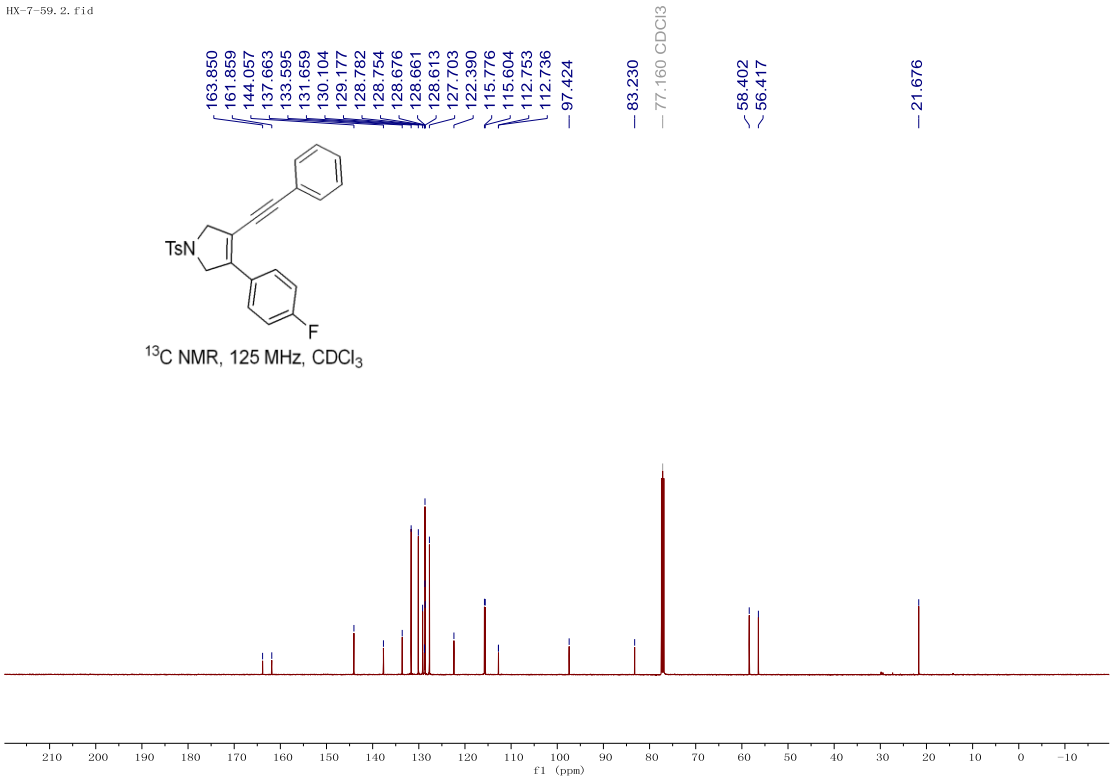
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80-7.74 (m, 4H), 7.46-7.42 (m, 2H), 7.37-7.34 (m, 5H), 7.10-7.05 (m, 2H), 4.58 (t, *J* = 4.0 Hz, 2H), 4.40 (t, *J* = 4.0 Hz, 2H), 2.43 (s, 3H).

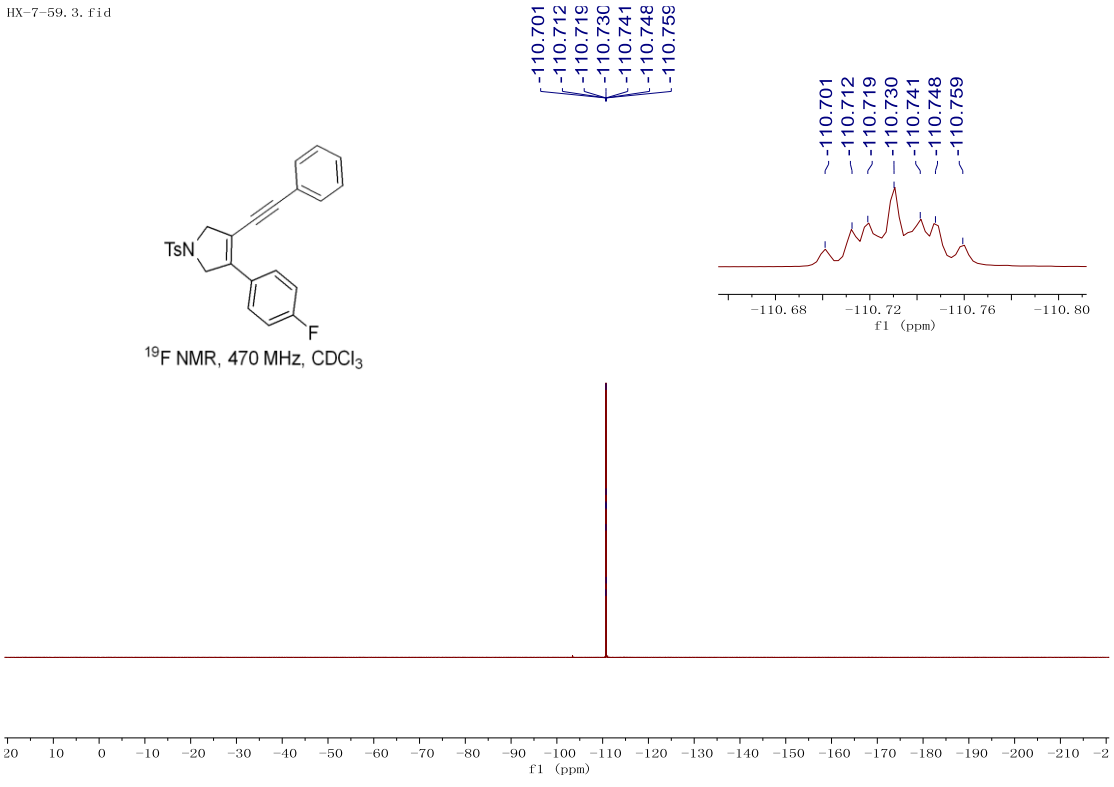
^{13}C NMR (125 MHz, Chloroform-*d*) δ 162.9 (d, *J* = 248.9 Hz), 144.1, 137.7, 133.6, 131.7, 130.1, 129.2, 128.8 (d, *J* = 3.5 Hz), 128.7, 128.6 (d, *J* = 7.9 Hz), 127.7, 122.4, 115.7 (d, *J* = 21.5 Hz), 112.7 (d, *J* = 2.1 Hz), 97.4, 83.2, 58.4, 56.4, 21.7.

^{19}F NMR (470 MHz, $CDCl_3$) δ (m) (-110.70)-(-110.76).

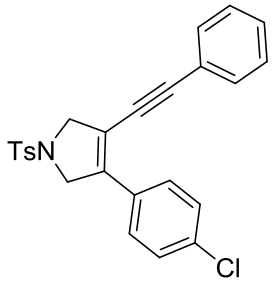
HRMS (ESI) m/z: calcd for $[C_{25}H_{20}FNO_2S+H]^+$ requires: 418.1272, found: 418.1272.







3-(4-chlorophenyl)-4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2e)

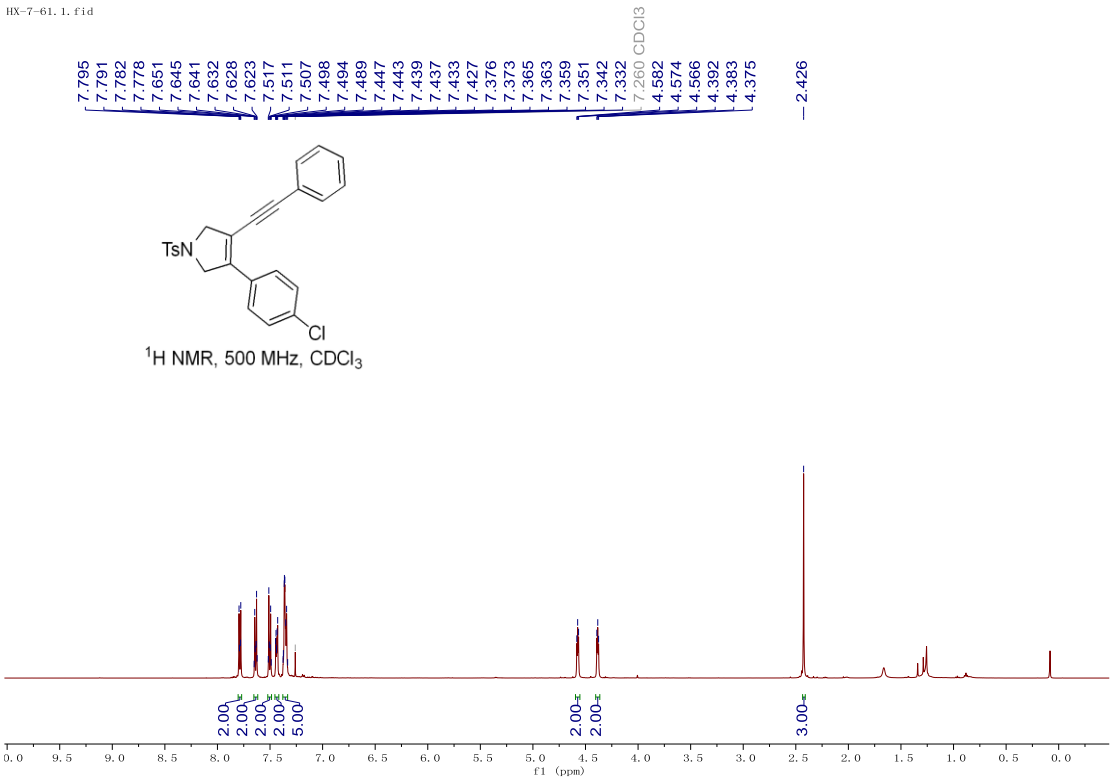


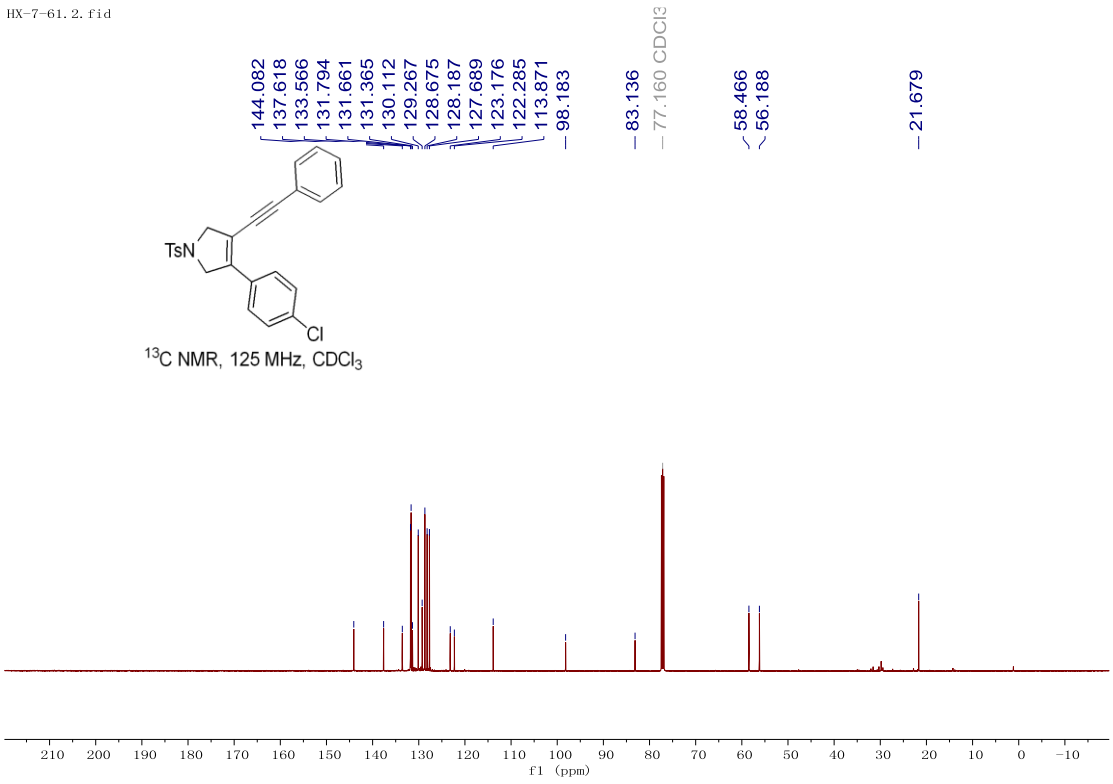
Compound **2e**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.39. 37.2 mg, 82% yield. m.p. 145-149 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80-7.78 (m, 2H), 7.64 (dt, J = 9.5, 2.0 Hz, 2H), 7.50 (dt, J = 9.5, 2.0 Hz, 2H), 7.45-7.43 (m, 2H), 7.38-7.33 (m, 5H), 4.57 (t, J = 4.0 Hz, 2H), 4.38 (t, J = 4.0 Hz, 2H), 2.43 (s, 3H).

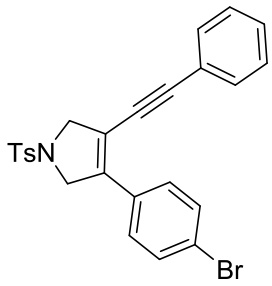
^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.1, 137.6, 133.6, 131.8, 131.7, 131.4, 130.1, 129.3, 128.7, 128.2, 127.7, 123.2, 122.3, 113.9, 98.2, 83.1, 58.5, 56.2, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{20}ClNO_2S+H]^+$ requires: 434.0976, found: 434.0978.





3-(4-bromophenyl)-4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2f)

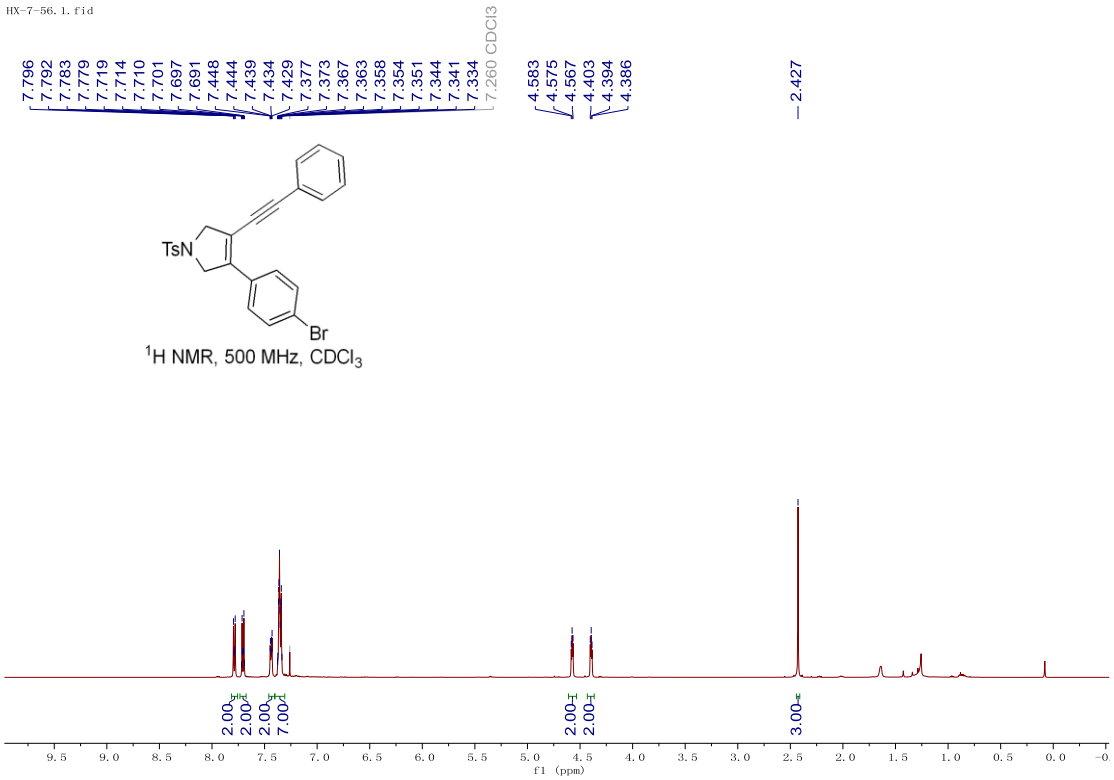


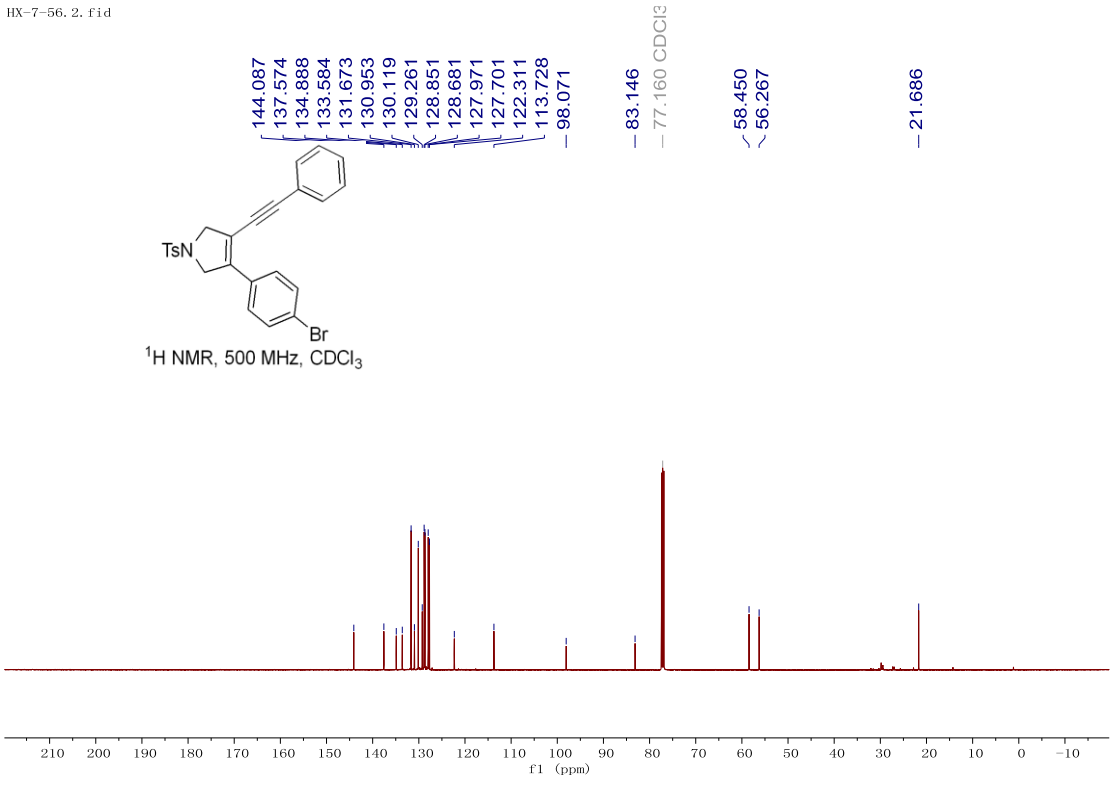
Compound **2f**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.44. 32.4 mg, 65% yield. m.p. 151-155 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80-7.78 (m, 2H), 7.71 (dt, J = 9.0, 2.0 Hz, 2H), 7.45-7.43 (m, 2H), 7.38-7.33 (m, 7H), 4.58 (t, J = 4.0 Hz, 2H), 4.39 (t, J = 4.0 Hz, 2H), 2.43 (s, 3H).

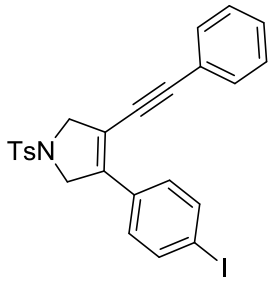
^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.1, 137.6, 134.9, 133.6, 131.7, 131.0, 130.1, 129.3, 128.9, 128.7, 128.0, 127.7, 122.3, 113.7, 98.1, 83.1, 58.5, 56.3, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{20}BrNO_2S+H]^+$ requires: 478.0471, found: 478.0457.





3-(4-iodophenyl)-4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2g)

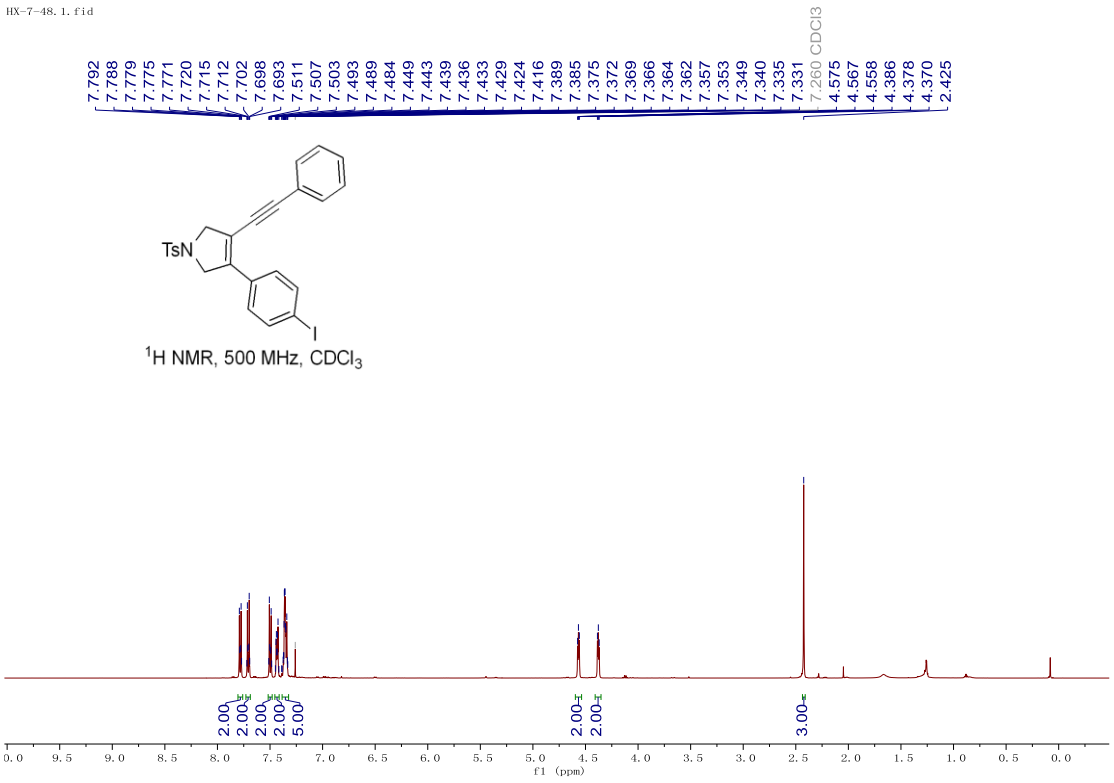


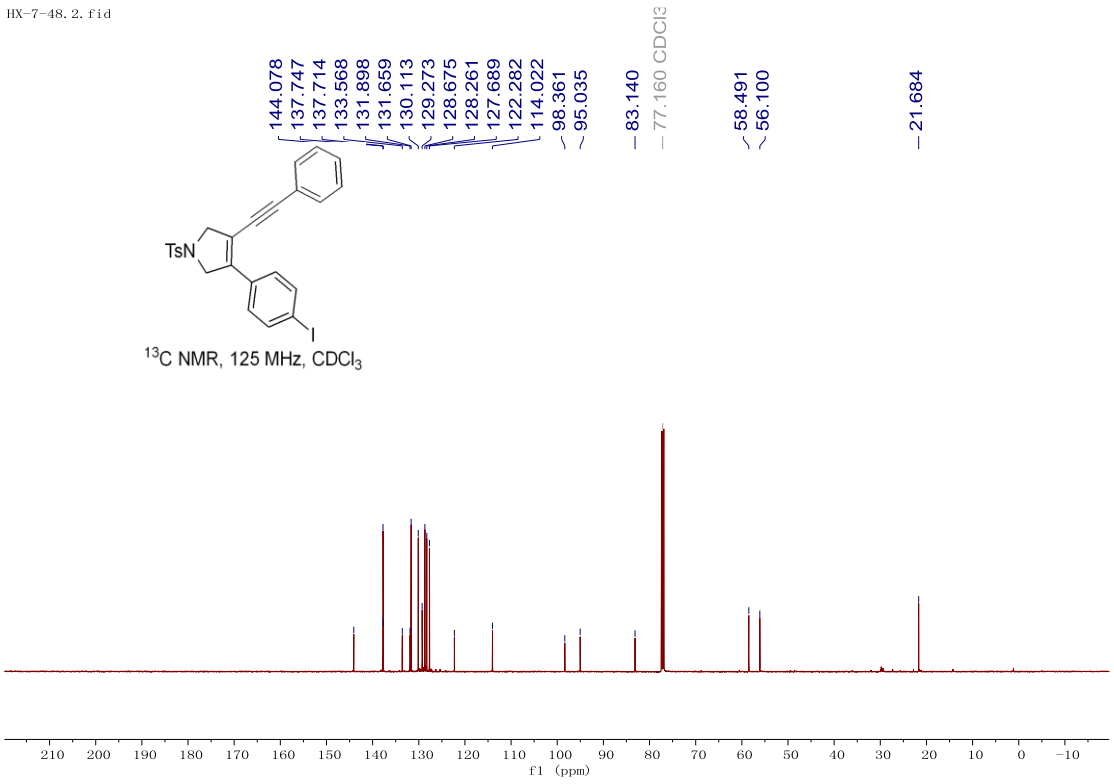
Compound **2g**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.32. 32.0 mg, 59% yield. m.p. 178-182 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79-7.77 (m, 2H), 7.71 (dt, J = 9.0, 2.0 Hz, 2H), 7.50 (dt, J = 9.0, 2.0 Hz, 2H), 7.45-7.42 (m, 2H), 7.39-7.33 (m, 5H), 4.57 (t, J = 4.0 Hz, 2H), 4.38 (t, J = 4.0 Hz, 2H), 2.43 (s, 3H).

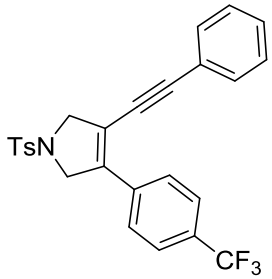
^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.1, 137.75, 137.71, 133.6, 131.9, 131.7, 130.1, 129.3, 128.7, 128.3, 127.7, 122.3, 114.0, 98.4, 95.0, 83.1, 58.5, 56.1, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{20}INO_2S+H]^+$ requires: 526.0332, found: 526.0336.





3-(phenylethynyl)-1-tosyl-4-(4-(trifluoromethyl)phenyl)-2,5-dihydro-1*H*-pyrrole (2h)



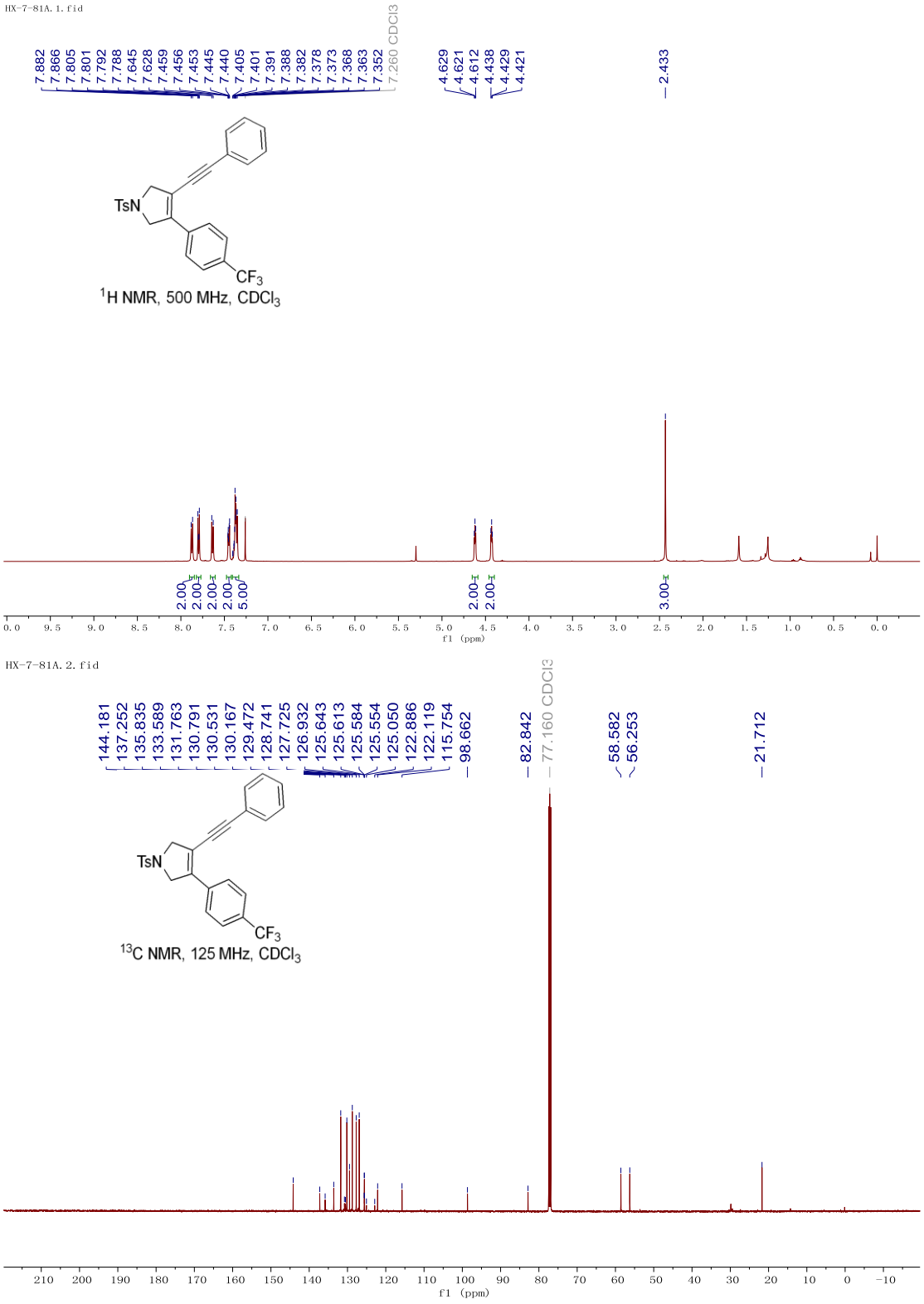
Compound **2h**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.51. 15.0 mg, 31% yield. m.p. 173-178 ºC.

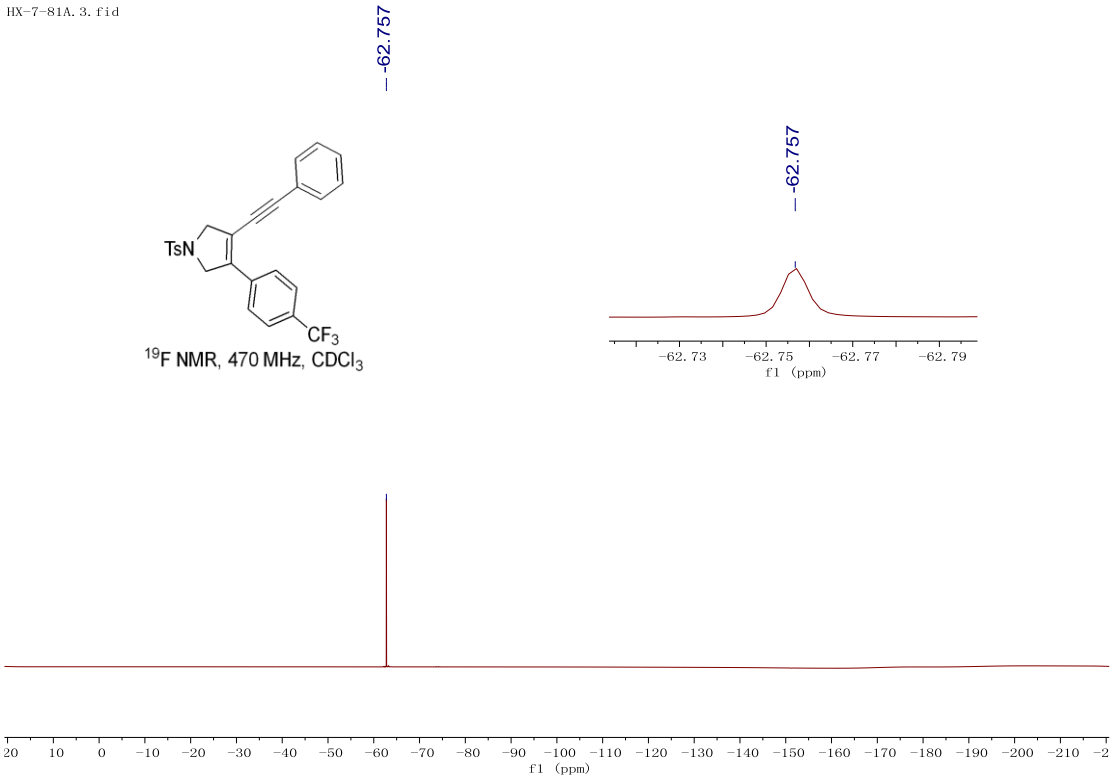
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (d, J = 8.0 Hz, 2H), 7.81-7.79 (m, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.46-7.44 (m, 2H), 7.41-7.35 (m, 5H), 4.62 (t, J = 4.0 Hz, 2H), 4.43 (t, J = 4.0 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.2, 137.3, 135.8, 133.6, 131.8, 130.7 (q, J = 32.3 Hz), 130.2, 129.5, 128.7, 127.7, 126.9, 125.6 (q, J = 3.8 Hz), 124.0 (q, J = 270.5 Hz), 122.1, 115.8, 98.7, 82.8, 58.6, 56.3, 21.7.

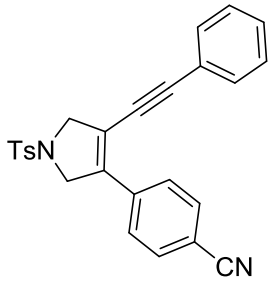
^{19}F NMR (470 MHz, $CDCl_3$) δ (s) (-62.76).

HRMS (ESI) m/z: calcd for $[C_{26}H_{20}F_3NO_2S+H]^+$ requires: 468.1240, found: 468.1242.





4-(4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)benzonitrile (2i)

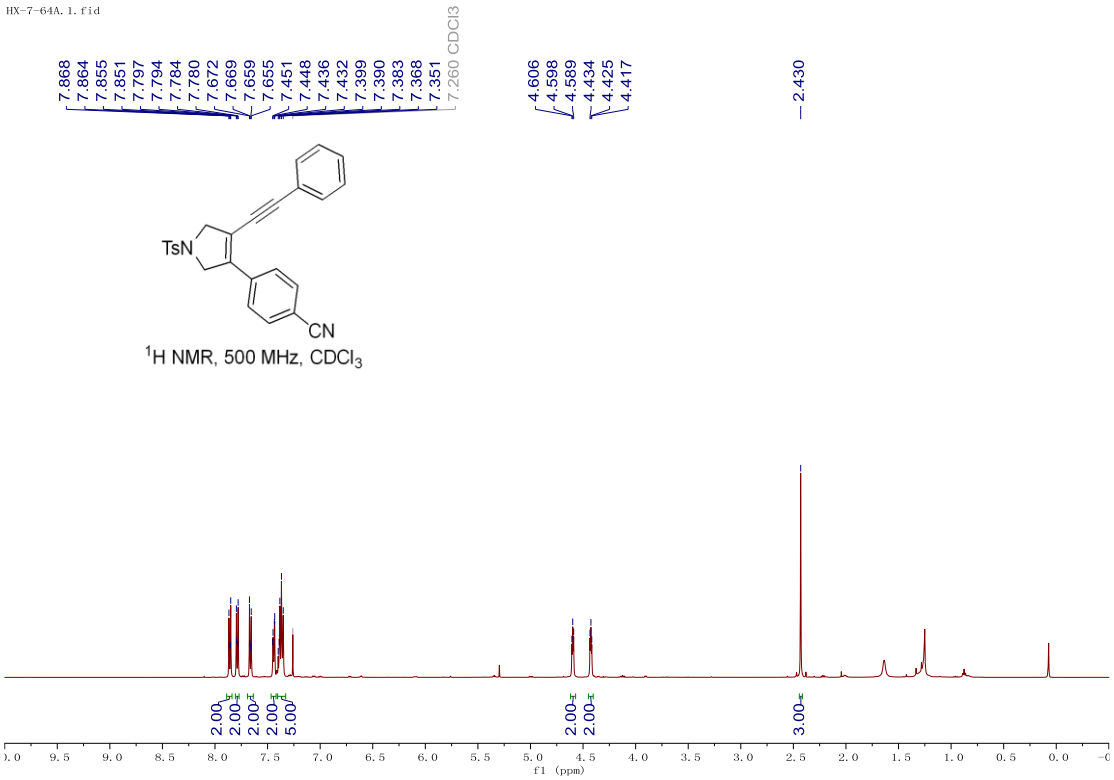


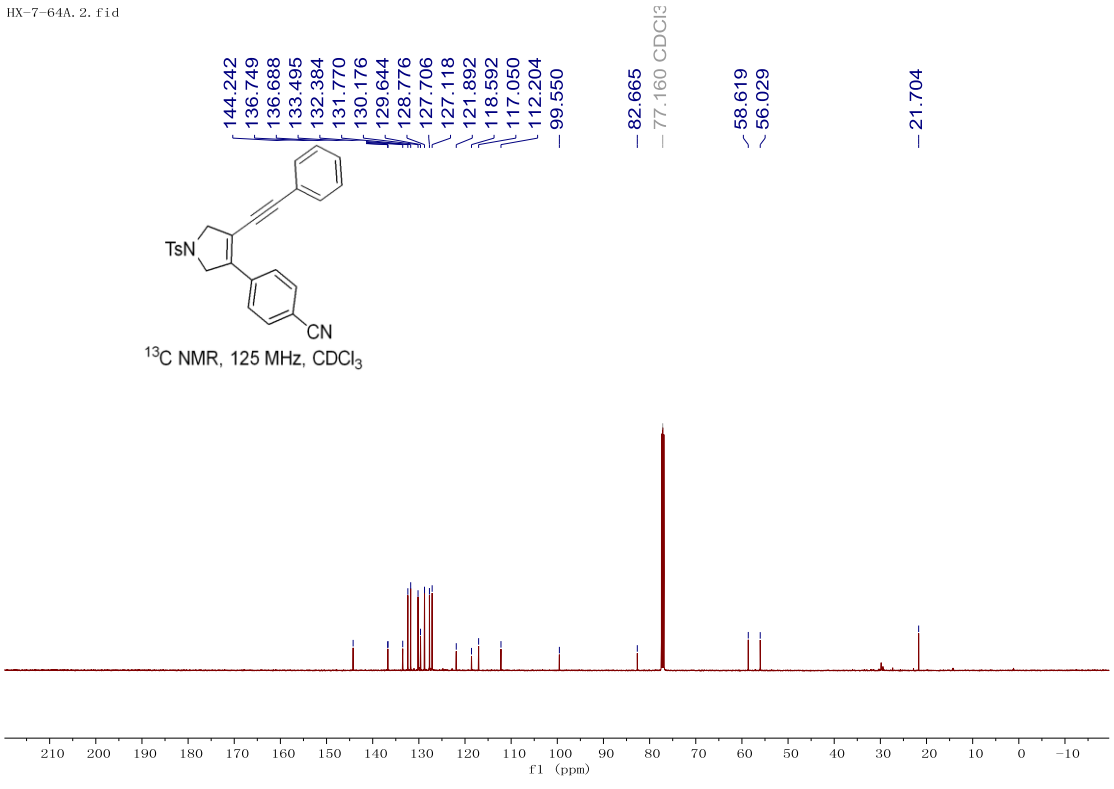
Compound **2i**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.26. 6.7 mg, 15% yield. m.p. 162-166 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87-7.85 (m, 2H), 7.80-7.78 (m, 2H), 7.67-7.66 (m, 2H), 7.45-7.43 (m, 2H), 7.40-7.35 (m, 5H), 4.60 (t, J = 4.0 Hz, 2H), 4.43 (t, J = 4.0 Hz, 2H), 2.43 (s, 3H).

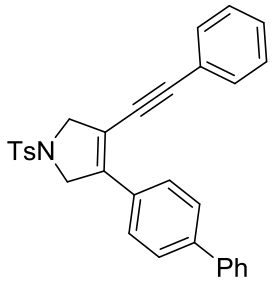
^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.2, 136.75, 136.69, 133.5, 132.4, 131.8, 130.2, 129.6, 128.8, 127.7, 127.1, 121.9, 118.6, 117.1, 112.2, 99.6, 82.7, 58.6, 56.0, 21.7.

HRMS (ESI) m/z: calcd for $[C_{26}H_{20}N_2O_2S+H]^+$ requires: 425.1318, found: 425.1318.





3-([1,1'-biphenyl]-4-yl)-4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2j)

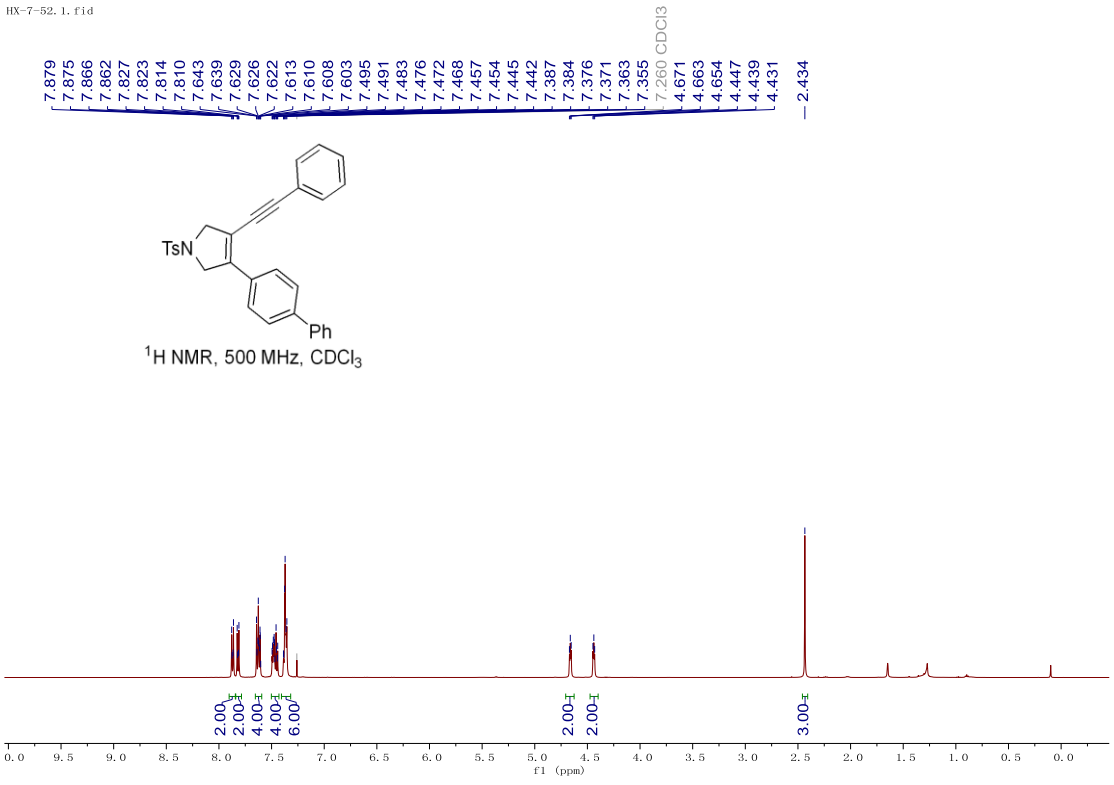


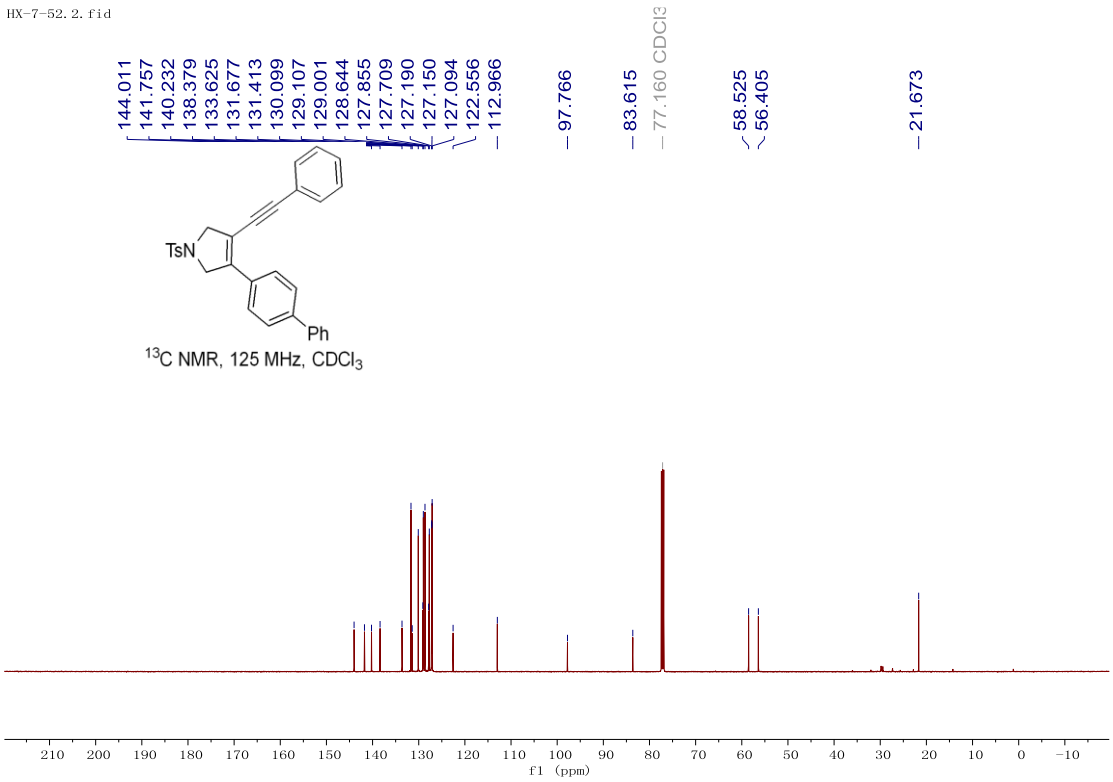
Compound **2j**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.36. 29.3 mg, 59% yield. m.p. 181-185 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88-7.86 (m, 2H), 7.83-7.81 (m, 2H), 7.64-7.60 (m, 4H), 7.50-7.44 (m, 4H), 7.39-7.36 (m, 6H), 4.66 (t, J = 4.0 Hz, 2H), 4.44 (t, J = 4.0 Hz, 2H), 2.43 (s, 3H).

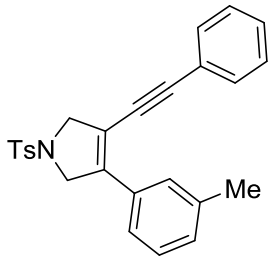
^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.0, 141.8, 140.2, 138.4, 133.6, 131.7, 131.4, 130.1, 129.1, 129.0, 128.6, 127.9, 127.7, 127.19, 127.15, 127.1, 122.6, 113.0, 97.8, 83.6, 58.5, 56.4, 21.7.

HRMS (ESI) m/z: calcd for $[C_{31}H_{25}NO_2S+H]^+$ requires: 476.1679, found: 476.1681.





3-(phenylethynyl)-4-(m-tolyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2k)

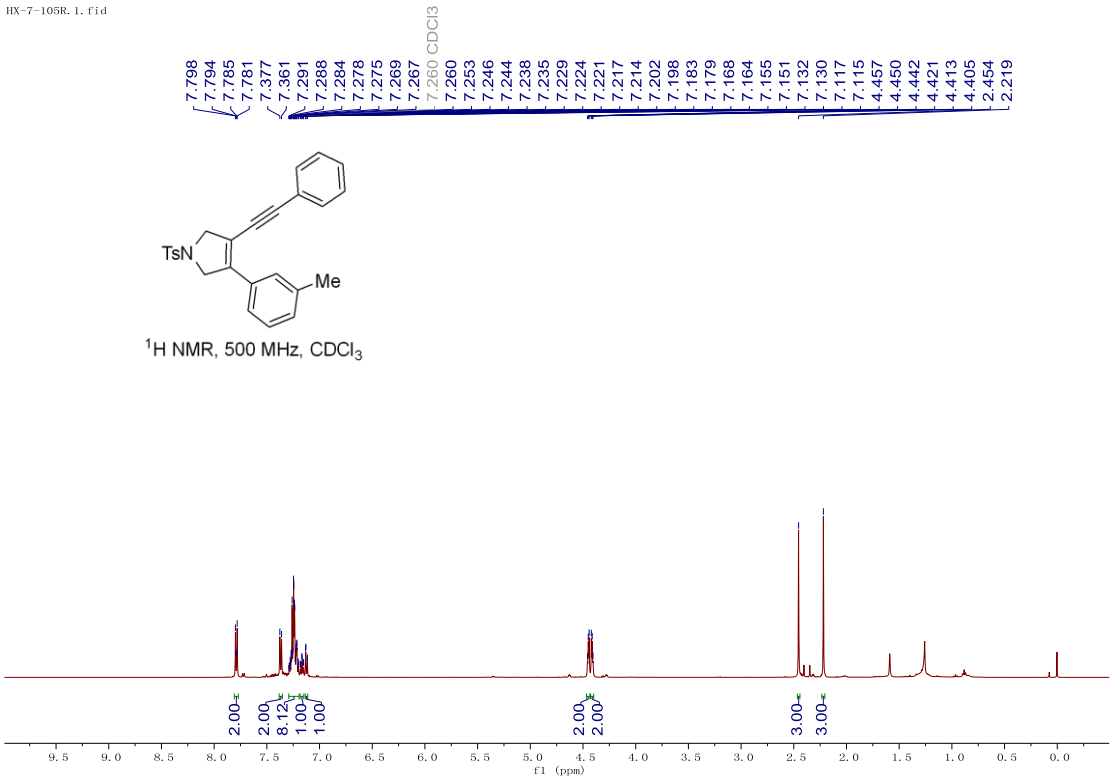


Compound **2k**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.30. 21.7 mg, 51% yield.

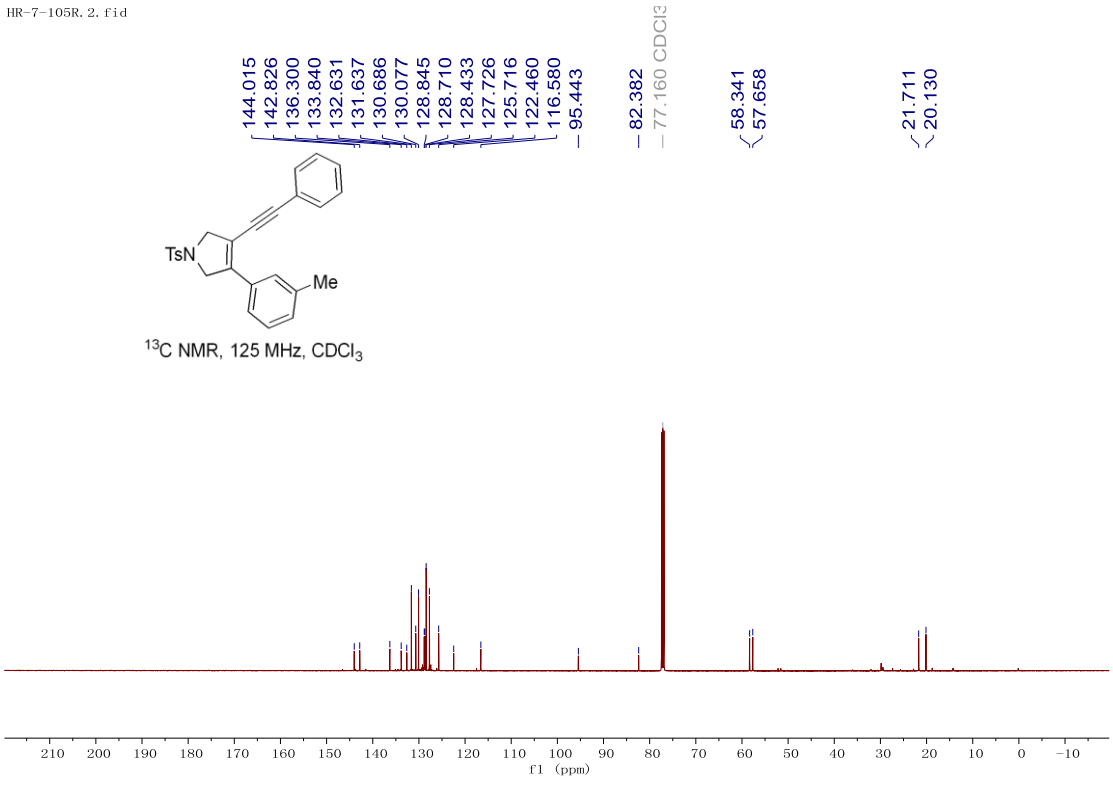
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80-7.78 (m, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.29-7.20 (m, 7H), 7.17 (td, J = 7.5, 2.0 Hz, 1H), 7.12 (dd, J = 7.5, 1.0 Hz, 1H), 4.45 (t, J = 4.0 Hz, 2H), 4.41 (t, J = 4.0 Hz, 2H), 2.45 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.0, 142.8, 136.3, 133.8, 132.6, 131.6, 130.7, 130.1, 128.8, 128.7, 128.4, 127.7, 125.7, 122.5, 116.6, 95.4, 82.4, 58.3, 57.7, 21.7, 20.1.

HRMS (ESI) m/z: calcd for $[C_{26}H_{23}NO_2S+H]^+$ requires: 414.1522, found: 414.1523.

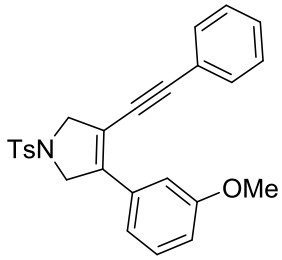


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

3-(3-methoxyphenyl)-4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2l)

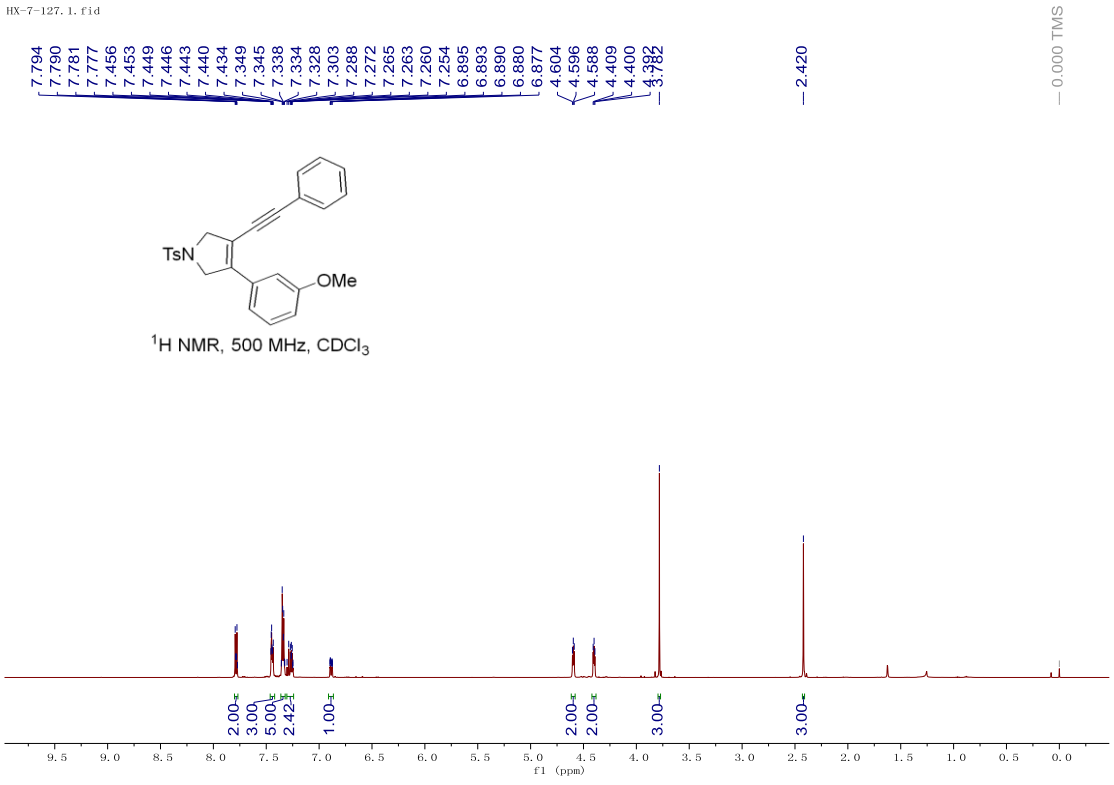


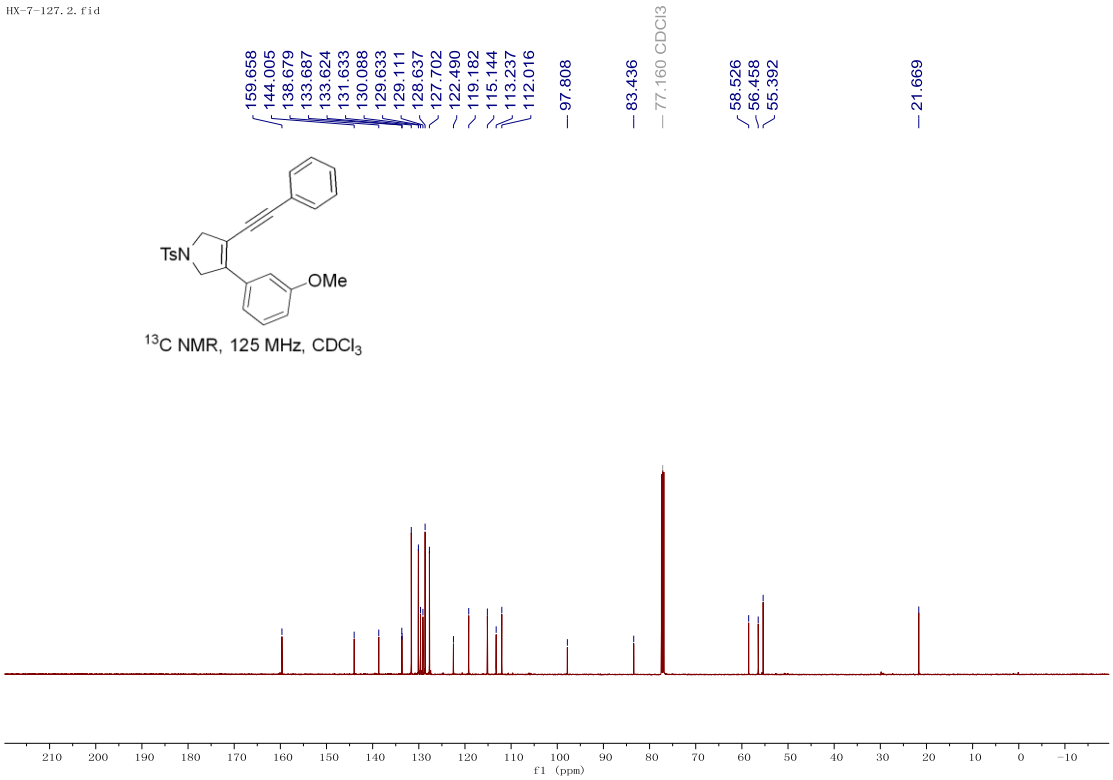
Compound **2l**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.23. 25.5 mg, 57% yield. m.p. 136-140 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*, TMS) δ 7.79-7.77 (m, 2H), 7.46-7.43 (m, 3H), 7.36-7.33 (m, 5H), 7.30-7.25 (m, 2H), 6.89 (ddd, J = 8.0, 2.5, 1.5 Hz, 1H), 4.60 (t, J = 4.0 Hz, 2H), 4.40 (t, J = 4.0 Hz, 2H), 3.78 (s, 3H), 2.42 (s, 3H).

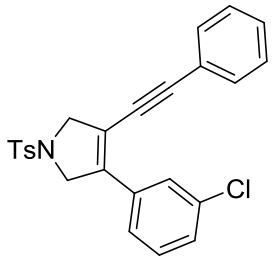
^{13}C NMR (125 MHz, Chloroform-*d*) δ 159.7, 144.0, 138.7, 133.7, 133.6, 131.6, 130.1, 129.6, 129.1, 128.6, 127.7, 122.5, 119.2, 115.1, 113.2, 112.0, 97.8, 83.4, 58.5, 56.5, 55.4, 21.7.

HRMS (ESI) m/z: calcd for $[C_{26}H_{23}NO_3S+H]^+$ requires: 430.1471, found: 430.1471.





3-(3-chlorophenyl)-4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2m)

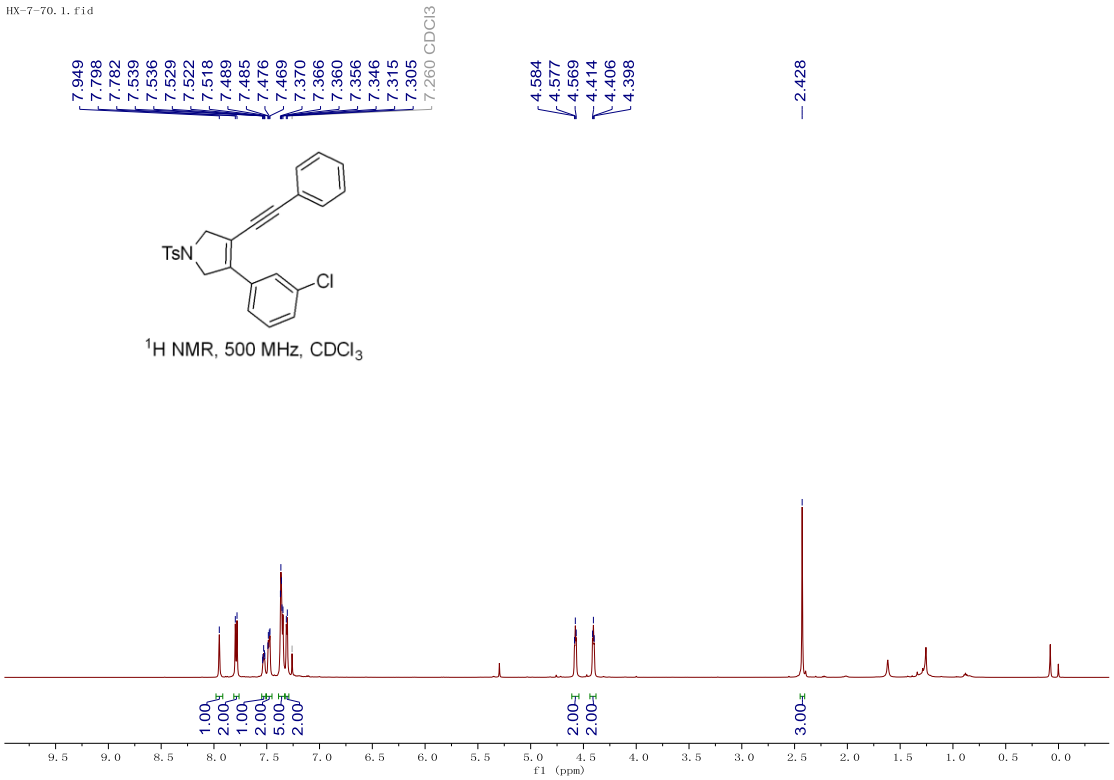


Compound **2m**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.37. 23.8 mg, 53% yield. m.p. 150-154 ºC.

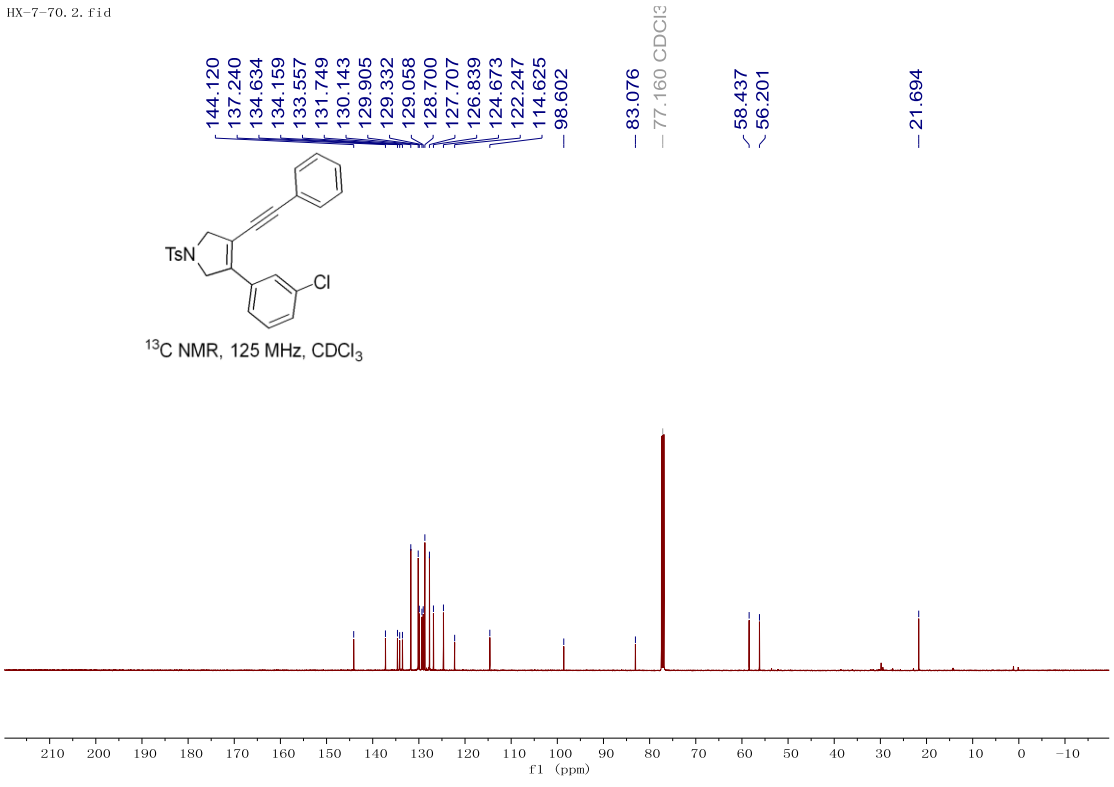
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.54-7.52 (m, 1H), 7.49-7.47 (m, 2H), 7.37-7.35 (m, 5H), 7.32-7.31 (m, 2H), 4.58 (t, J = 4.0 Hz, 2H), 4.41 (t, J = 4.0 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.1, 137.2, 134.6, 134.2, 133.6, 131.7, 130.1, 129.9, 129.3, 129.1, 128.7, 127.7, 126.8, 124.7, 122.2, 114.6, 98.6, 83.1, 58.4, 56.2, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{20}ClNO_2S+H]^+$ requires: 434.0976, found: 434.0978.

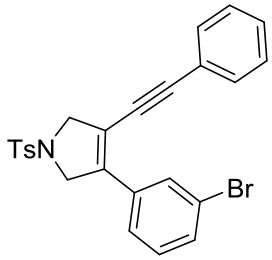


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

3-(3-bromophenyl)-4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2n)

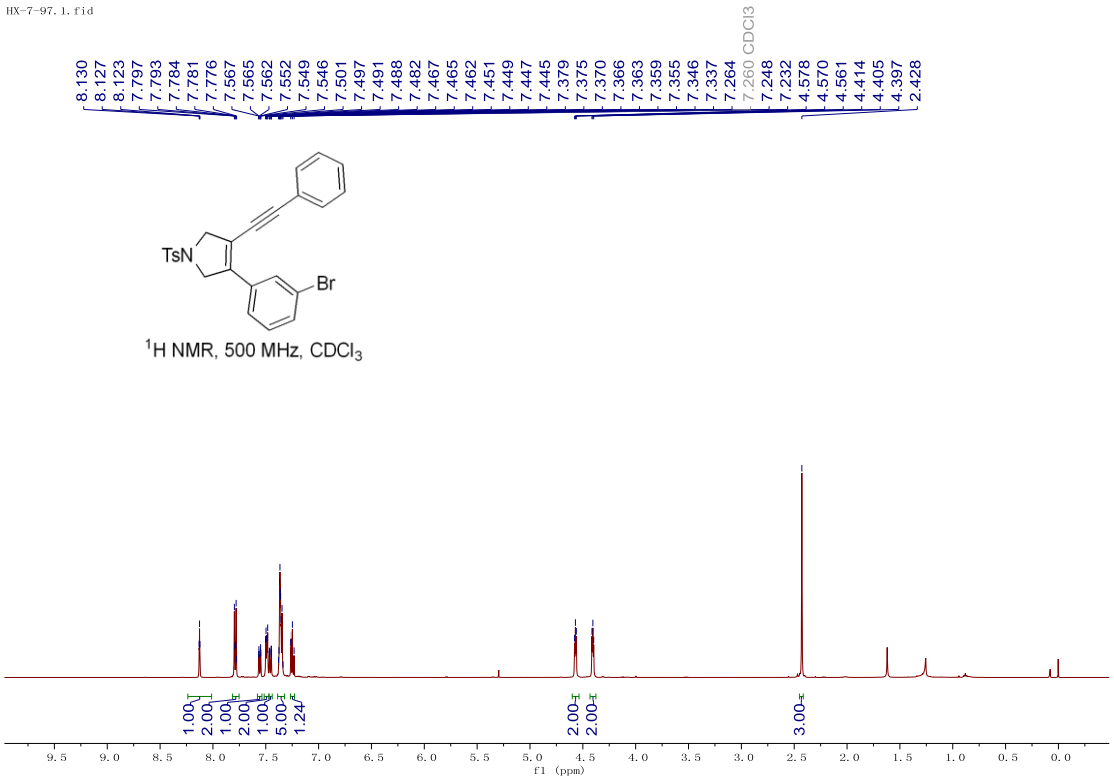


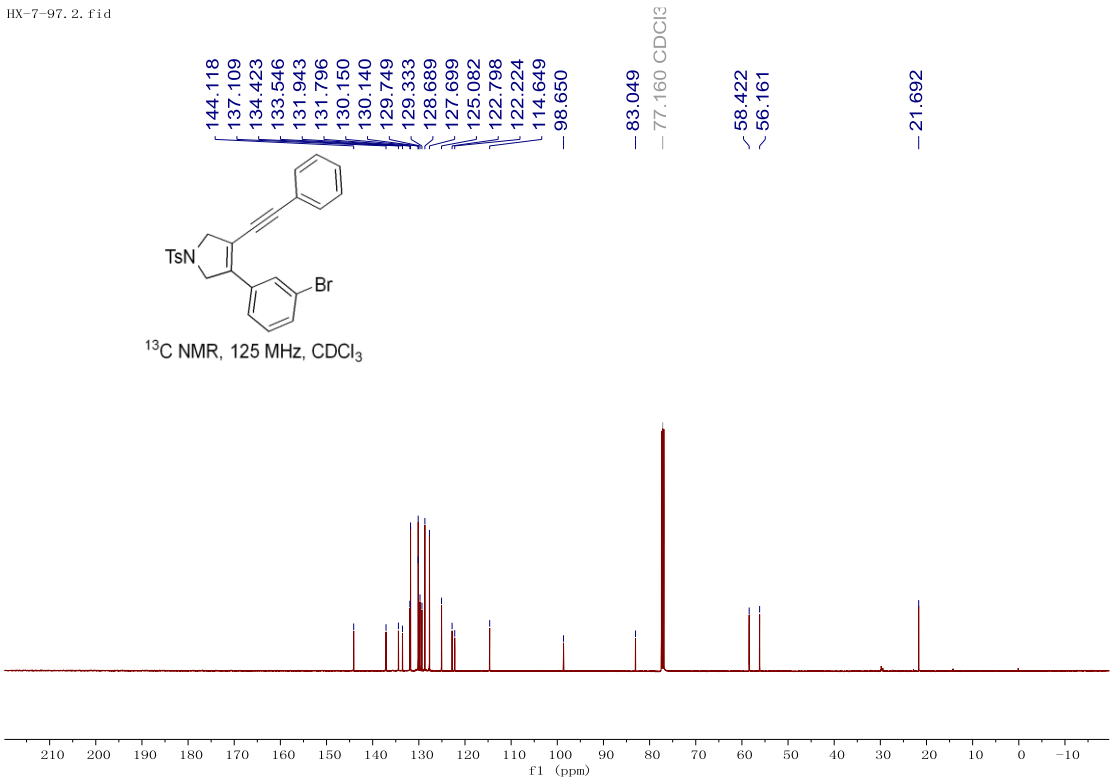
Compound **2n**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.29. 26.7 mg, 54% yield. m.p. 164-167 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.13 (t, J = 2.0 Hz, 1H), 7.80-7.78 (m, 2H), 7.56 (dt, J = 8.0, 1.5 Hz, 1H), 7.50-7.48 (m, 2H), 7.47-7.45 (m, 1H), 7.38-7.34 (m, 5H), 7.25 (t, J = 8.0 Hz, 1H), 4.57 (t, J = 4.0 Hz, 2H), 4.41 (t, J = 4.0 Hz, 2H), 2.43 (s, 3H).

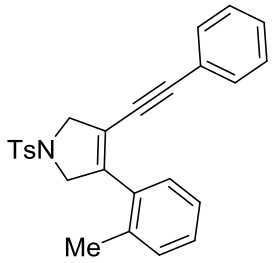
^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.1, 137.1, 134.4, 133.5, 131.9, 131.8, 130.2, 130.1, 129.7, 129.3, 128.7, 127.7, 125.1, 122.8, 122.2, 114.6, 98.7, 83.0, 58.4, 56.2, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{20}BrNO_2S+H]^+$ requires: 478.0471, found: 478.0472.





3-(phenylethynyl)-4-(*o*-tolyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2o)

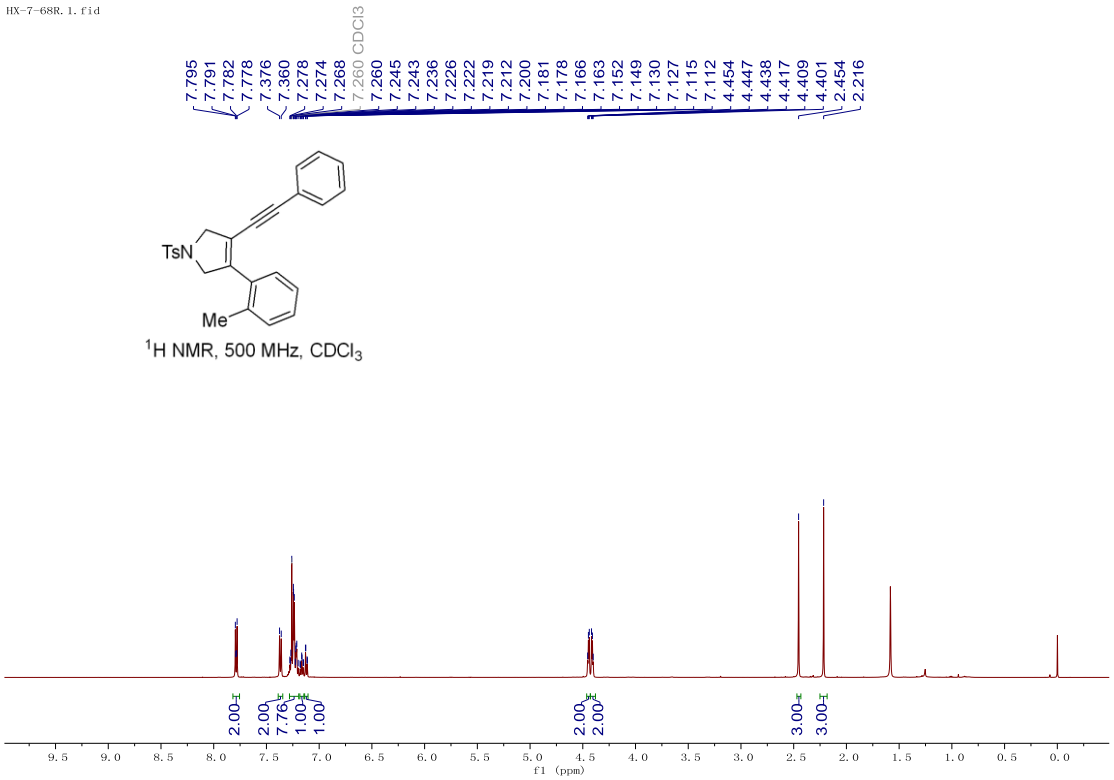


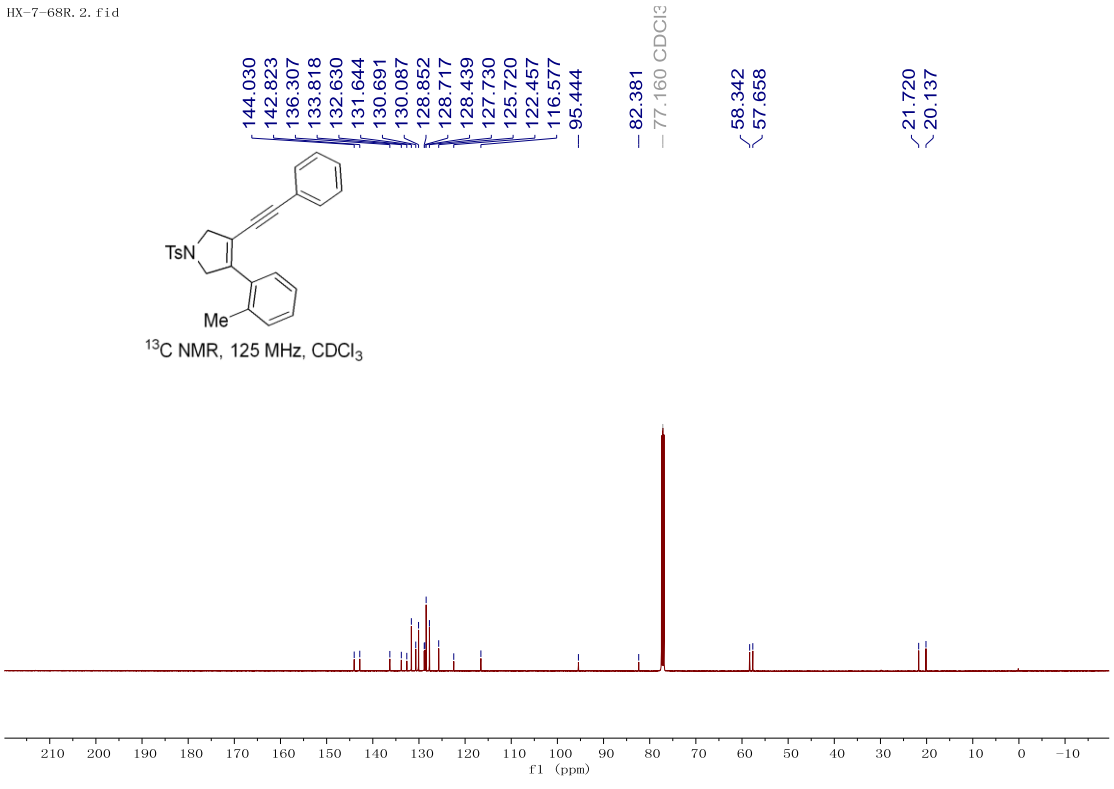
Compound **2o**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.33. 15.4 mg, 36% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80-7.78 (m, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.28-7.20 (m, 7H), 7.17 (td, J = 7.5, 1.5 Hz, 1H), 7.12 (dd, J = 7.5, 1.5 Hz, 1H), 4.45 (t, J = 4.0 Hz, 2H), 4.41 (t, J = 4.0 Hz, 2H), 2.45 (s, 3H), 2.22 (s, 3H).

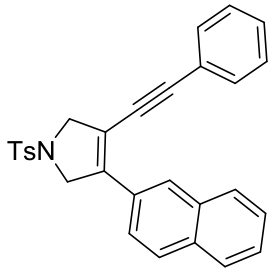
^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.0, 142.8, 136.3, 133.8, 132.6, 131.6, 130.7, 130.1, 128.9, 128.7, 128.4, 127.7, 125.7, 122.5, 116.6, 95.4, 82.4, 58.3, 57.7, 21.7, 20.1.

HRMS (ESI) m/z: calcd for $[C_{26}H_{23}NO_2S+H]^+$ requires: 414.1522, found: 414.1523.





3-(naphthalen-2-yl)-4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2q)

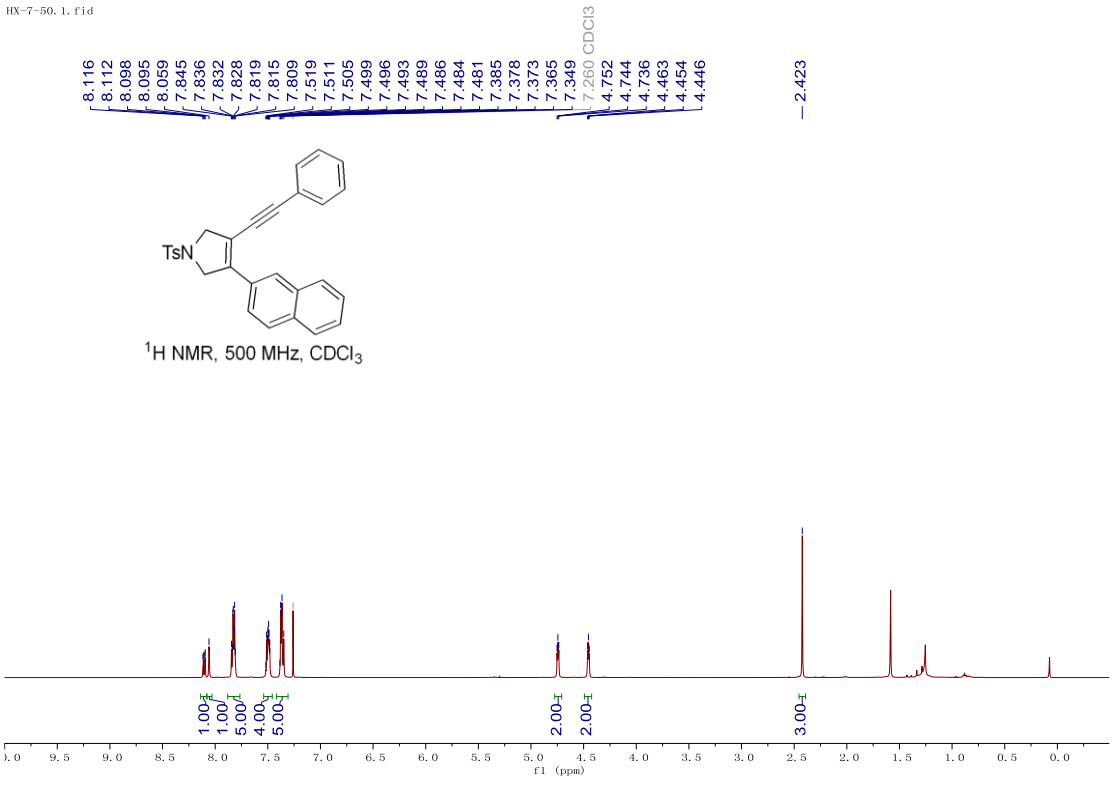


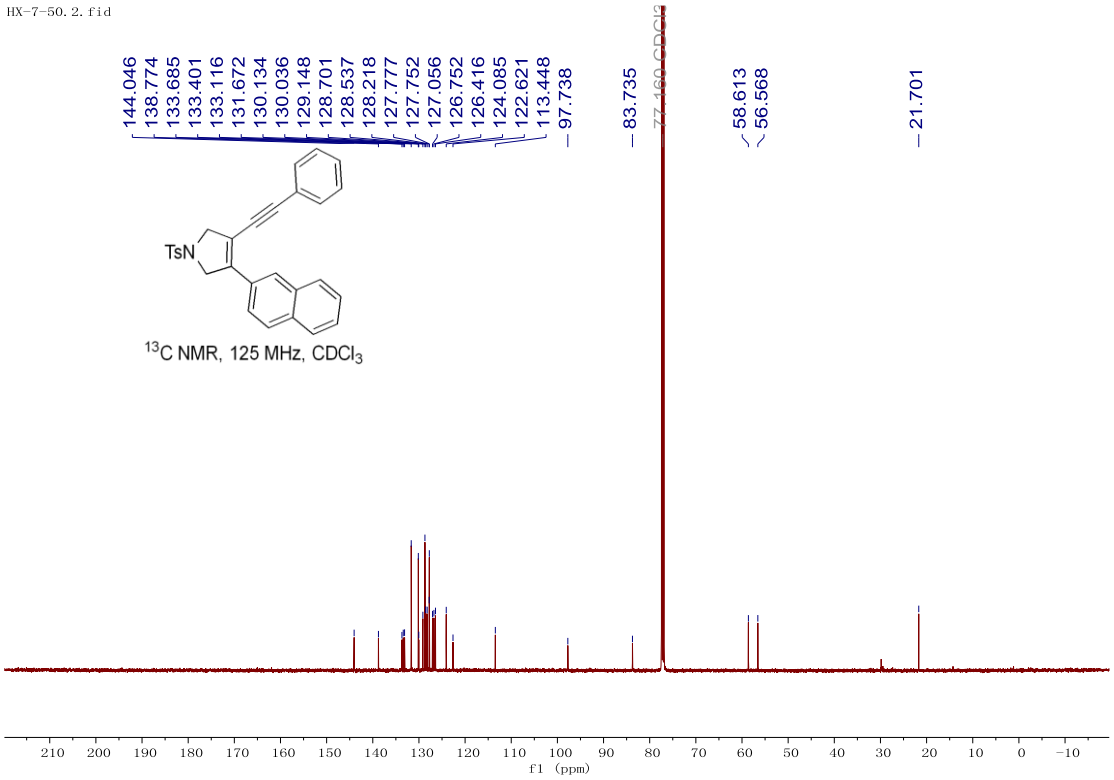
Compound **2q**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.36. 24.1 mg, 52% yield. m.p. 203-207 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (dd, J = 9.0, 2.0 Hz, 1H), 8.06 (s, 1H), 7.85-7.81 (m, 5H), 7.52-7.48 (m, 4H), 7.39-7.35 (m, 5H), 4.74 (t, J = 4.0 Hz, 2H), 4.45 (t, J = 4.0 Hz, 2H), 2.42 (s, 3H).

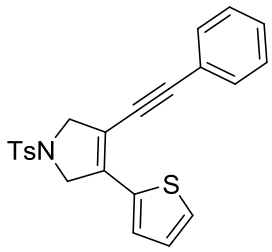
^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.0, 138.8, 133.7, 133.4, 133.1, 131.7, 130.1, 130.0, 129.1, 128.7, 128.5, 128.2, 127.78, 127.75, 127.1, 126.8, 126.4, 124.1, 122.6, 113.4, 97.7, 83.7, 58.6, 56.6, 21.7.

HRMS (ESI) m/z: calcd for $[C_{29}H_{23}NO_2S+H]^+$ requires: 450.1522, found: 450.1524.





3-(phenylethynyl)-4-(thiophen-2-yl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2r)

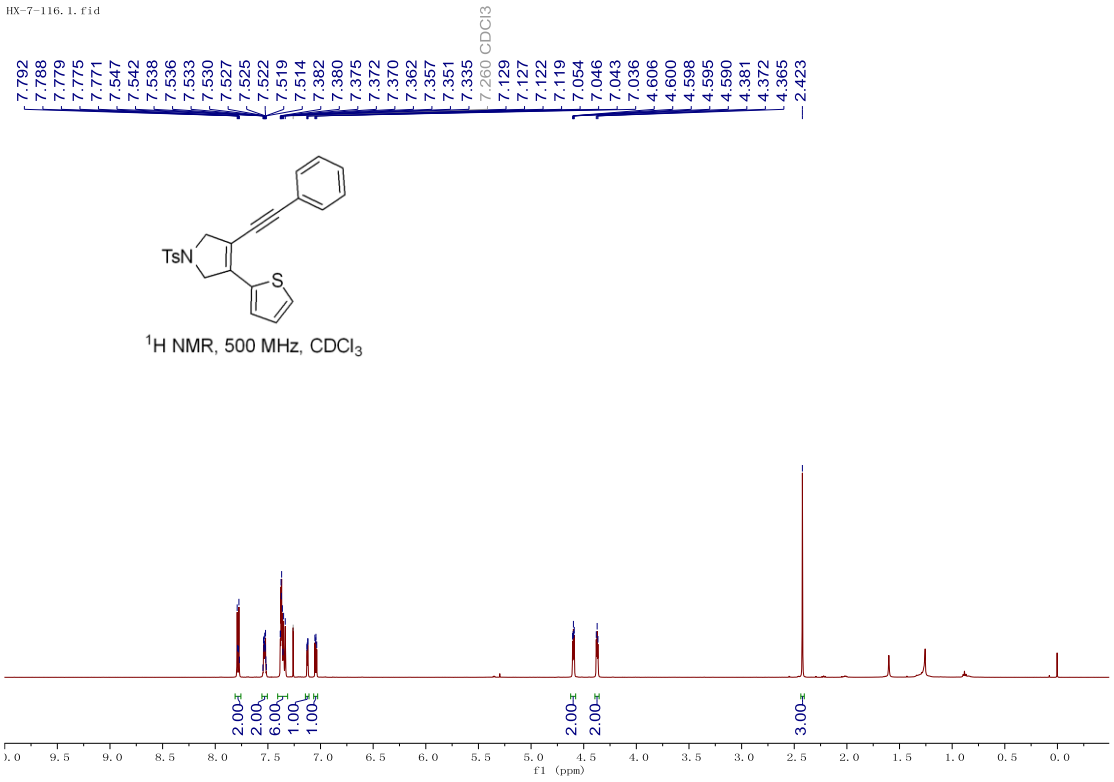


Compound **2r**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.24. 26.0 mg, 62% yield. m.p. 165-168 ºC.

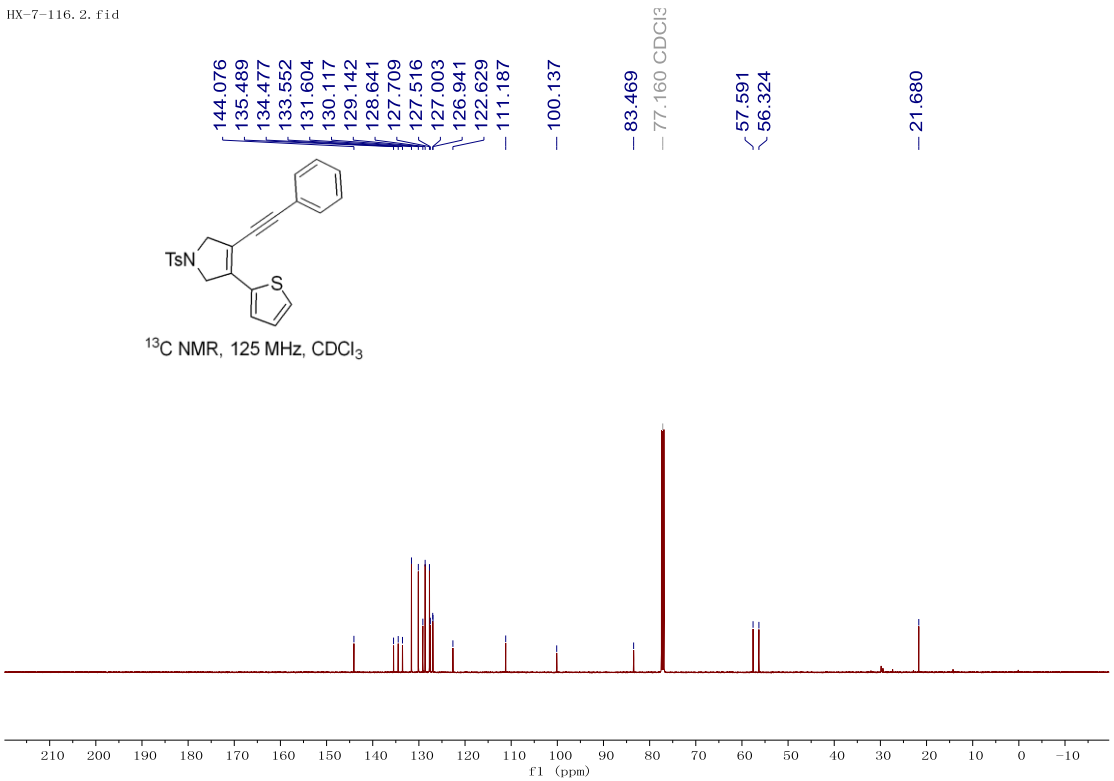
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79-7.77 (m, 2H), 7.55-7.51 (m, 2H), 7.38-7.34 (m, 6H), 7.12 (dd, *J* = 4.0, 1.0 Hz, 1H), 7.05 (dd, *J* = 5.0, 4.0 Hz, 1H), 4.61-4.59 (m, 2H), 4.37 (t, *J* = 4.0 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.1, 135.5, 134.5, 133.6, 131.6, 130.1, 129.1, 128.6, 127.7, 127.5, 127.0, 126.9, 122.6, 111.2, 100.1, 83.5, 57.6, 56.3, 21.7.

HRMS (ESI) m/z: calcd for $[C_{23}H_{19}NO_2S_2+H]^+$ requires: 406.0930, found: 406.0930.

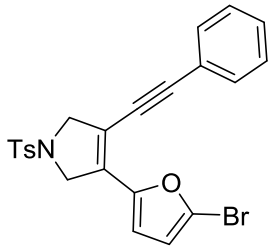


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

3-(5-bromofuran-2-yl)-4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2s)

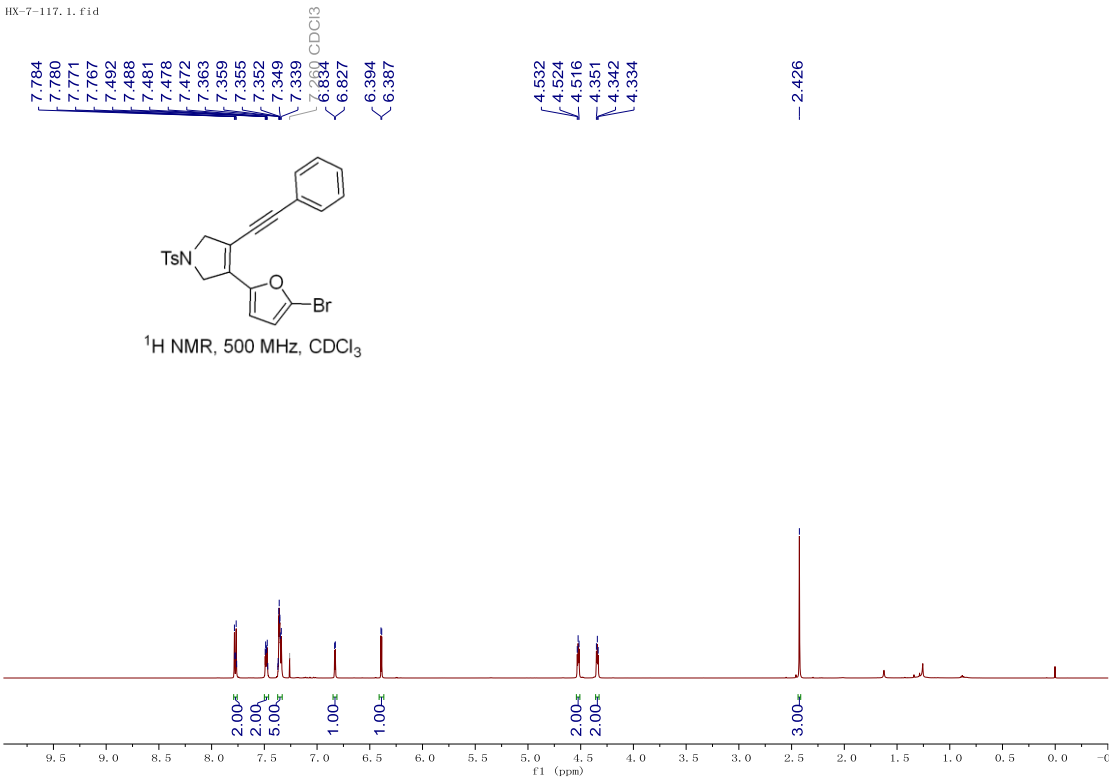


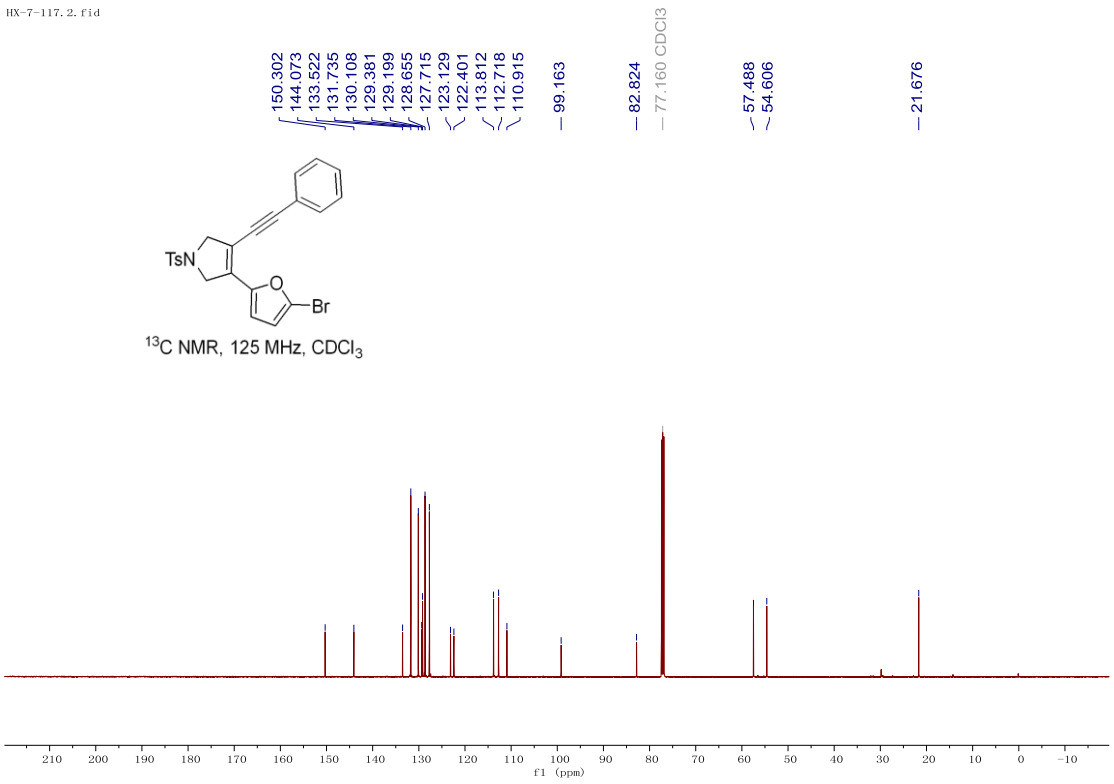
Compound **2s**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.28. 34.6 mg, 71% yield. m.p. 152-156 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78-7.76 (m, 2H), 7.49-7.47 (m, 2H), 7.37-7.34 (m, 5H), 6.83 (d, J = 3.5 Hz, 1H), 6.39 (d, J = 3.5 Hz, 1H), 4.52 (t, J = 4.0 Hz, 2H), 4.34 (t, J = 4.0 Hz, 2H), 2.43 (s, 3H).

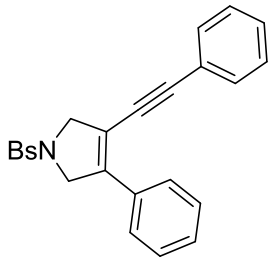
^{13}C NMR (125 MHz, Chloroform-*d*) δ 150.3, 144.1, 133.5, 131.7, 130.1, 129.4, 129.2, 128.7, 127.7, 123.1, 122.4, 113.8, 112.7, 110.9, 99.2, 82.8, 57.5, 54.6, 21.7.

HRMS (ESI) m/z: calcd for $[C_{23}H_{18}BrNO_3S+H]^+$ requires: 468.0264, found: 468.0264.





1-((4-bromophenyl)sulfonyl)-3-phenyl-4-(phenylethynyl)-2,5-dihydro-1*H*-pyrrole (2t)

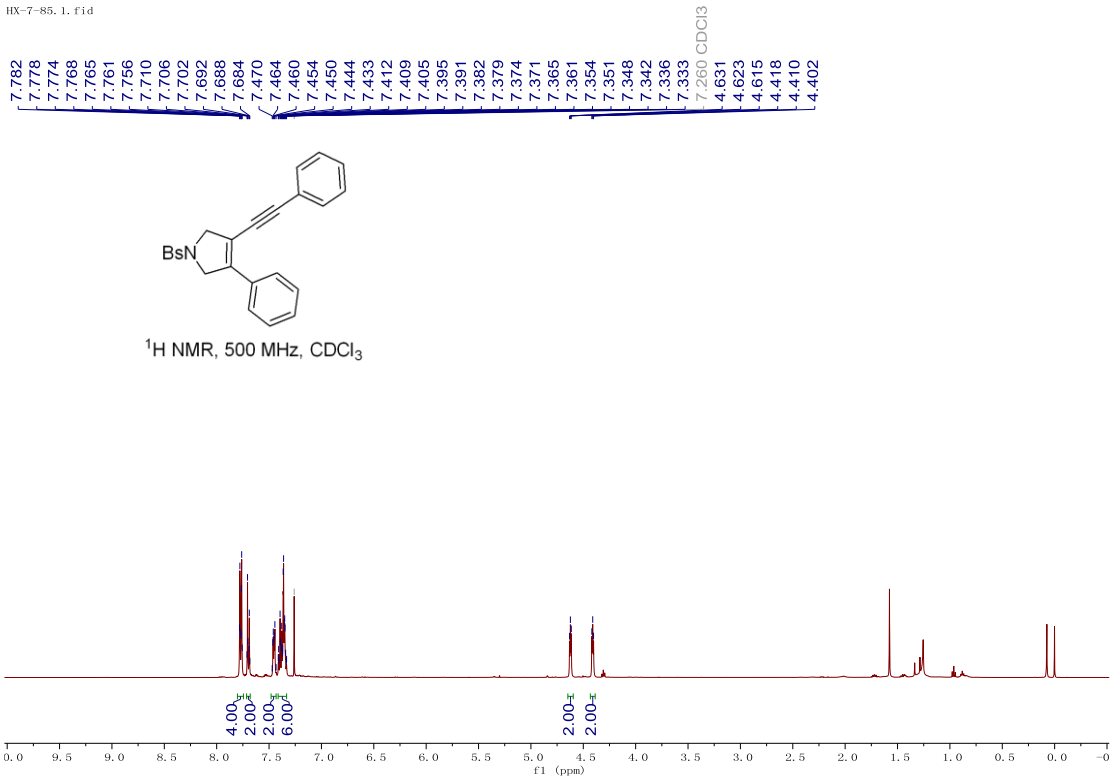


Compound **2t**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.56. 25.5 mg, 53% yield. m.p. 191-196 ºC.

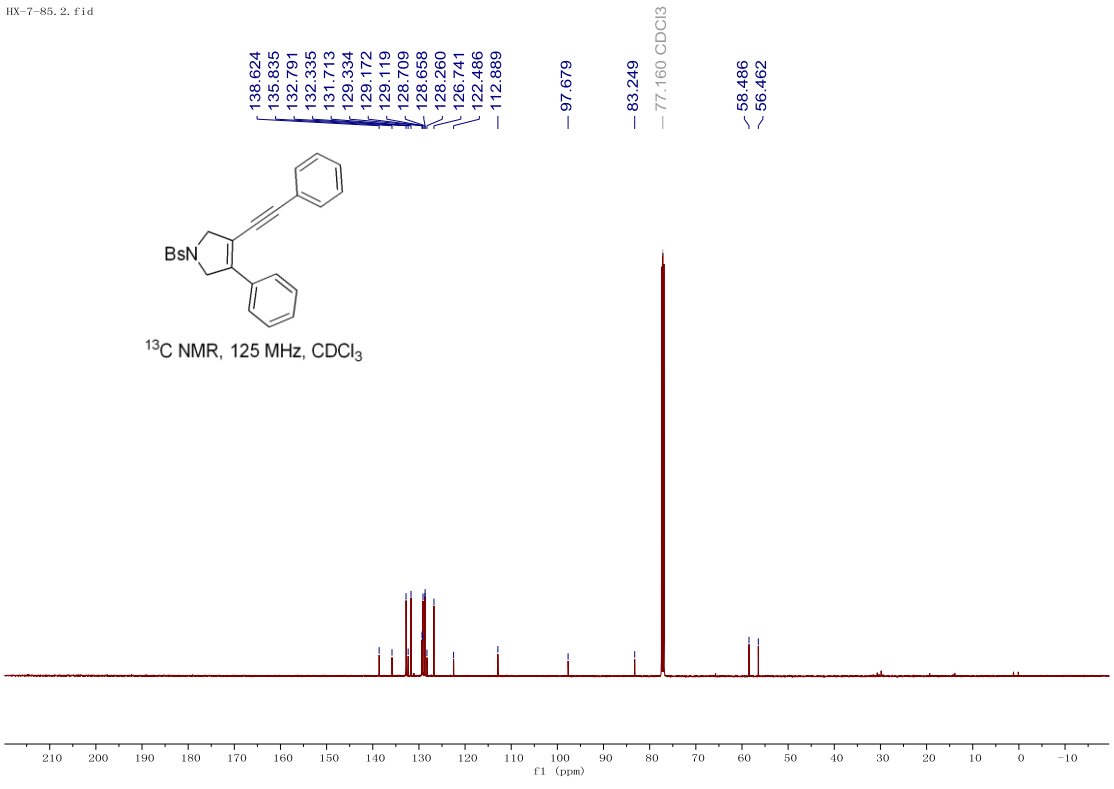
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78-7.76 (m, 4H), 7.70 (dt, J = 9.0, 2.0 Hz, 2H), 7.47-7.43 (m, 2H), 7.41-7.33 (m, 6H), 4.62 (t, J = 4.0 Hz, 2H), 4.41 (t, J = 4.0 Hz, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 138.6, 135.8, 132.8, 132.3, 131.7, 129.3, 129.2, 129.1, 128.71, 128.66, 128.3, 126.7, 122.5, 112.9, 97.7, 83.2, 58.5, 56.5.

HRMS (ESI) m/z: calcd for $[C_{24}H_{18}BrNO_2S+H]^+$ requires: 464.0314, found: 464.0315.

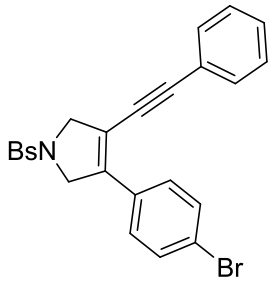


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

3-(4-bromophenyl)-1-((4-bromophenyl)sulfonyl)-4-(phenylethynyl)-2,5-dihydro-1*H*-pyrrole (2u)

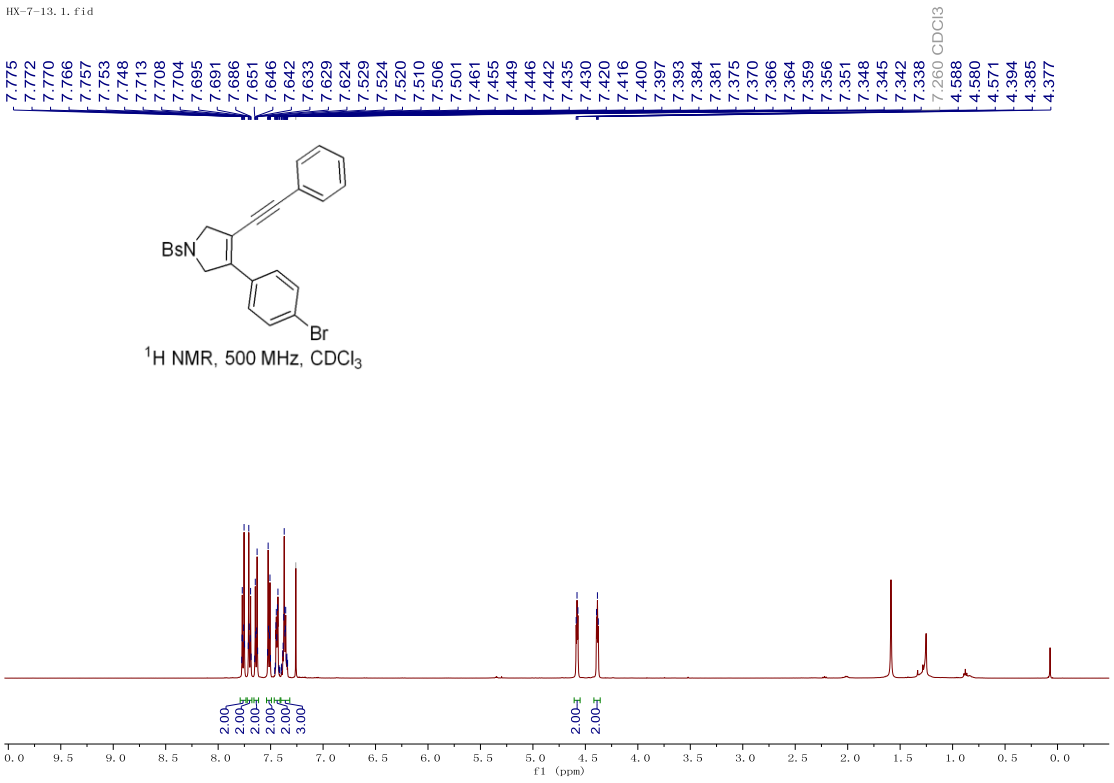


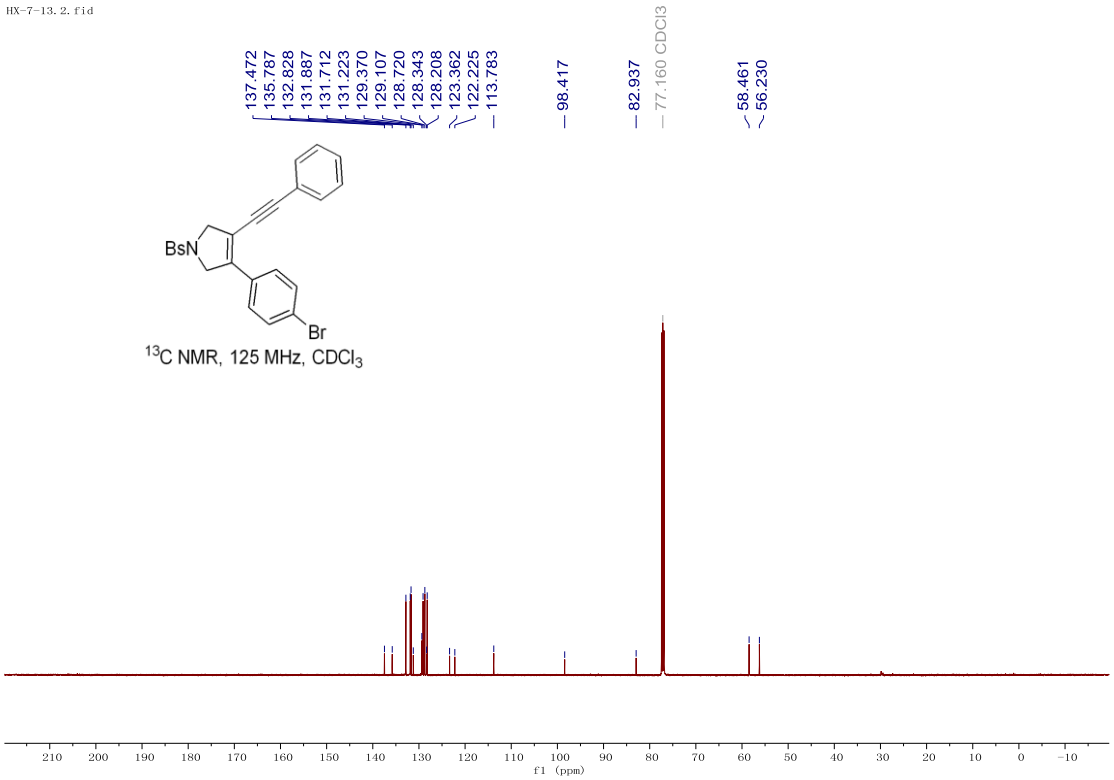
Compound **2u**: a white solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.54. 30.2 mg, 55% yield. m.p. 154-159 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.70 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.64 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.52 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.46-7.42 (m, 2H), 7.40-7.34 (m, 3H), 4.58 (t, *J* = 4.0 Hz, 2H), 4.39 (t, *J* = 4.0 Hz, 2H).

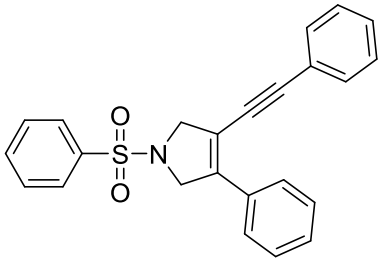
^{13}C NMR (125 MHz, Chloroform-*d*) δ 137.5, 135.8, 132.8, 131.9, 131.7, 131.2, 129.4, 129.1, 128.7, 128.3, 128.2, 123.4, 122.2, 113.8, 98.4, 82.9, 58.5, 56.2.

HRMS (ESI) m/z: calcd for $[C_{24}H_{17}Br_2NO_2S+H]^+$ requires: 541.9420, found: 541.9426.





3-phenyl-4-(phenylethynyl)-1-(phenylsulfonyl)-2,5-dihydro-1*H*-pyrrole (2w)

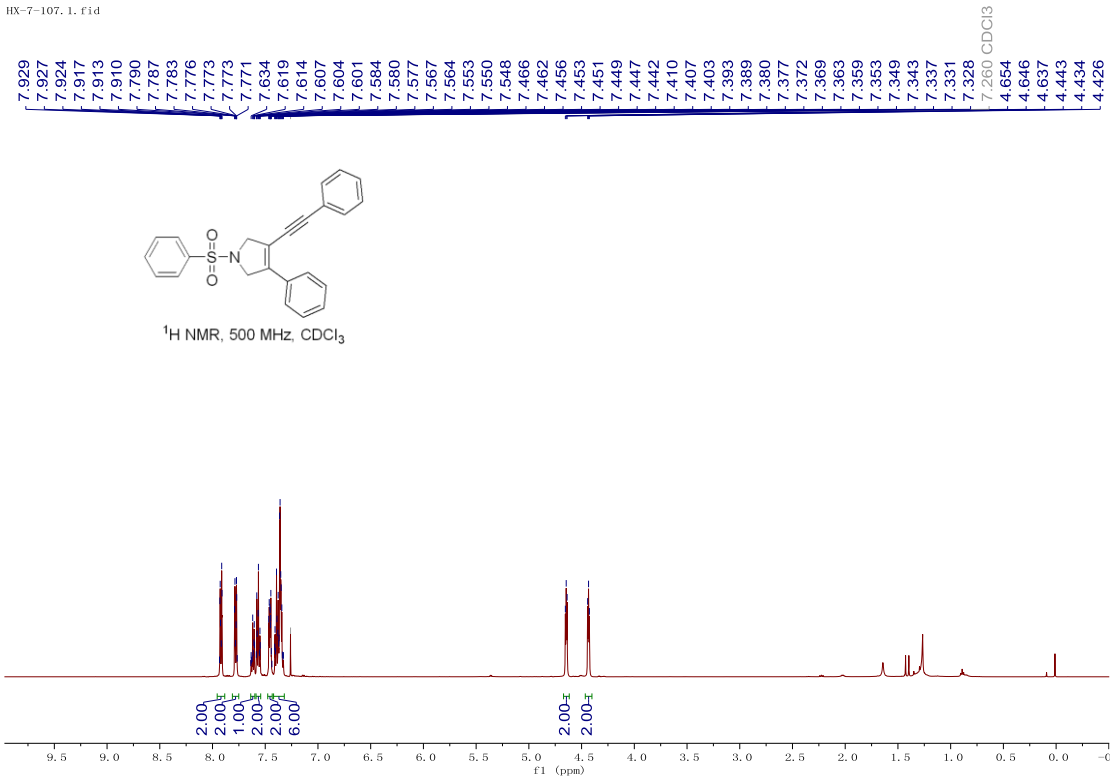


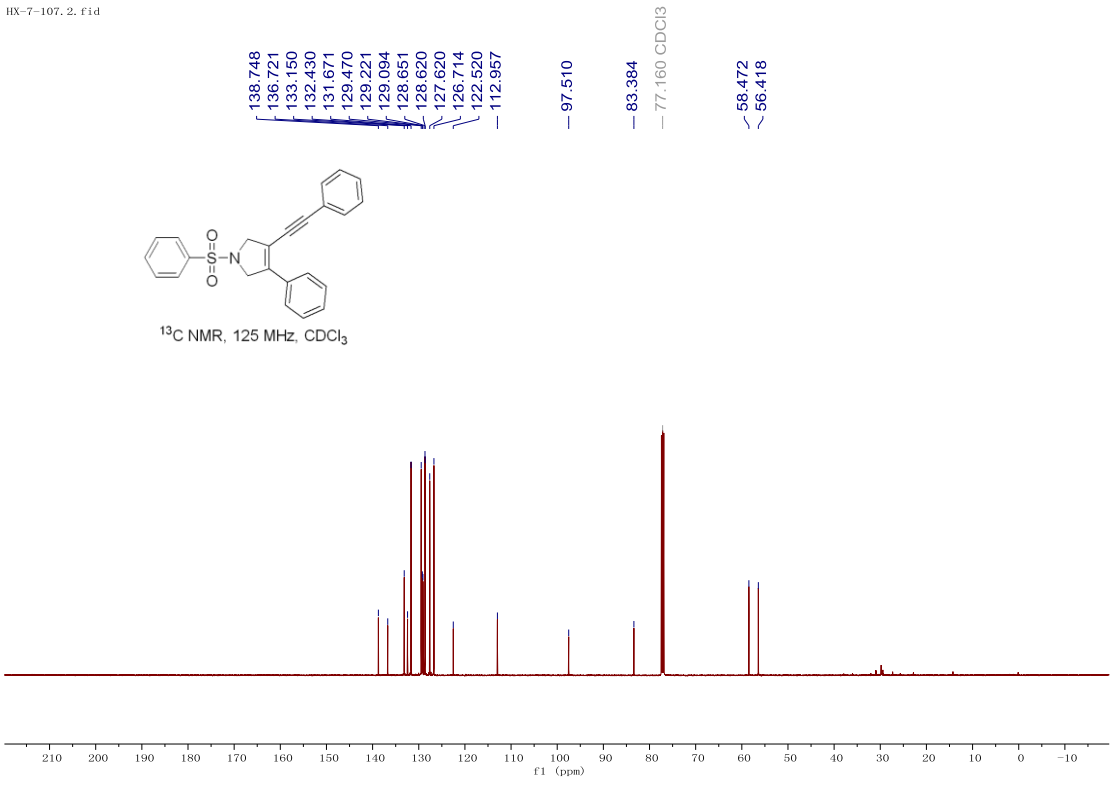
Compound **2w**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.28. 27.7 mg, 69% yield. m.p. 133-137 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93-7.91 (m, 2H), 7.79-7.77 (m, 2H), 7.64-7.60 (m, 1H), 7.58-7.55 (m, 2H), 7.47-7.44 (m, 2H), 7.41-7.33 (m, 6H), 4.65 (t, J = 4.0 Hz, 2H), 4.43 (t, J = 4.0 Hz, 2H).

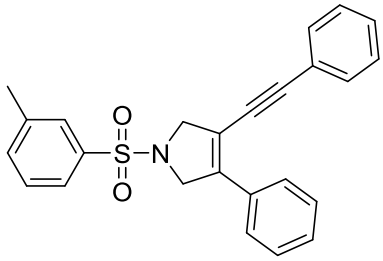
^{13}C NMR (125 MHz, Chloroform-*d*) δ 138.7, 136.7, 133.2, 132.4, 131.7, 129.5, 129.2, 129.1, 128.7, 128.6, 127.6, 126.7, 122.5, 113.0, 97.5, 83.4, 58.5, 56.4.

HRMS (ESI) m/z: calcd for $[C_{24}H_{19}NO_2S+H]^+$ requires: 386.1209, found: 386.1207.





3-phenyl-4-(phenylethynyl)-1-(m-tolylsulfonyl)-2,5-dihydro-1*H*-pyrrole (2x)

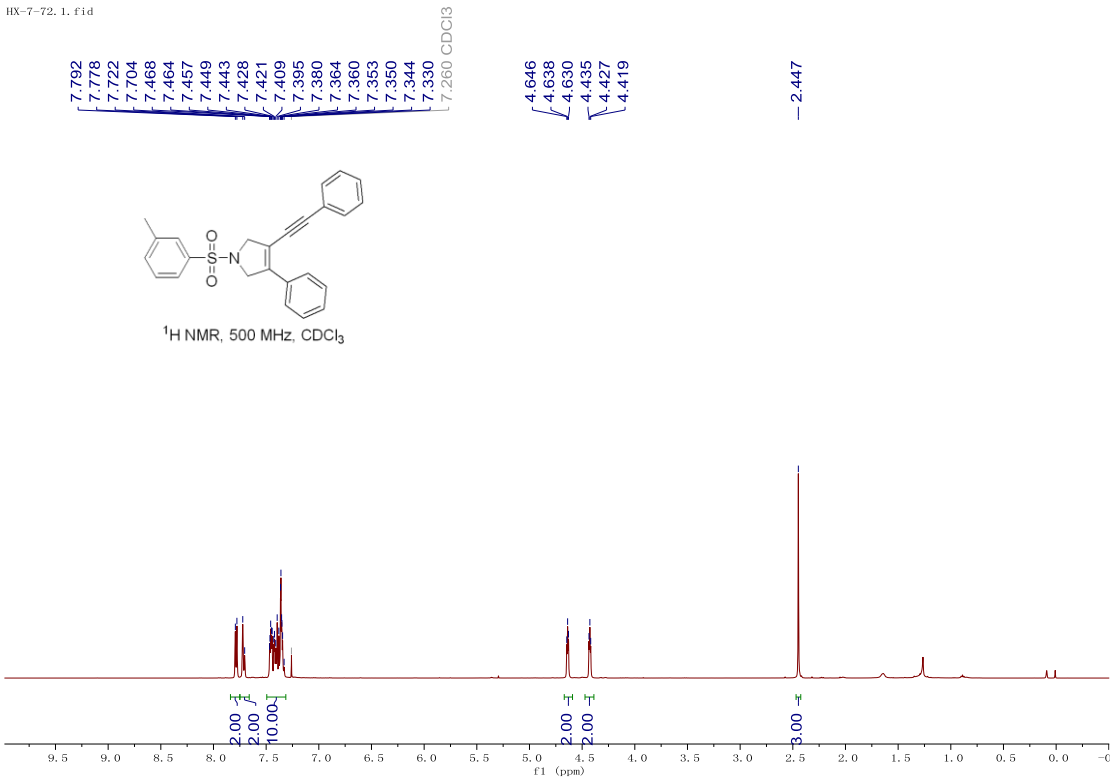


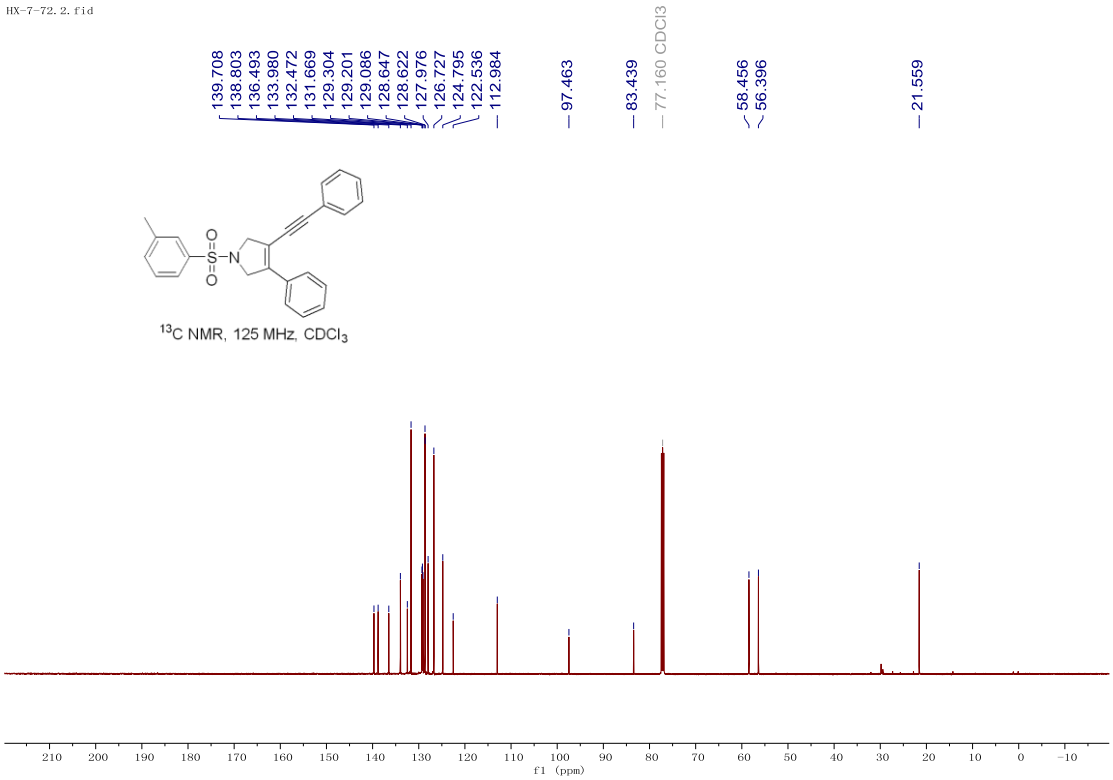
Compound **2x**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.33. 25.4 mg, 61% yield. m.p. 112-116 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (d, J = 7.0 Hz, 2H), 7.71 (d, J = 9.0 Hz, 2H), 7.47-7.33 (m, 10H), 4.64 (t, J = 4.0 Hz, 2H), 4.43 (t, J = 4.0 Hz, 2H), 2.45 (s, 3H).

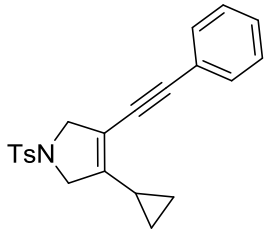
^{13}C NMR (125 MHz, Chloroform-*d*) δ 139.7, 138.8, 136.5, 134.0, 132.5, 131.7, 129.3, 129.2, 129.1, 128.65, 128.62, 128.0, 126.7, 124.8, 122.5, 113.0, 97.5, 83.4, 58.5, 56.4, 21.6.

HRMS (ESI) m/z: calcd for $[C_{25}H_{21}NO_2S+H]^+$ requires: 400.1366, found: 400.1365.





3-cyclopropyl-4-(phenylethynyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (2y)

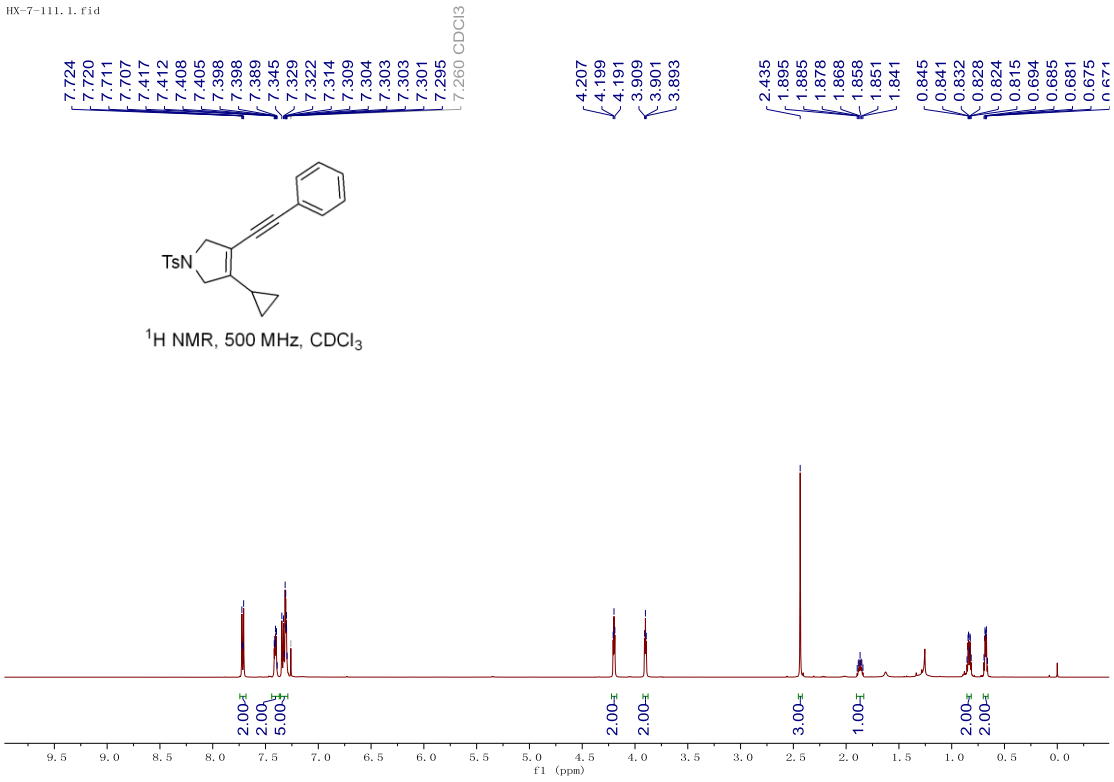


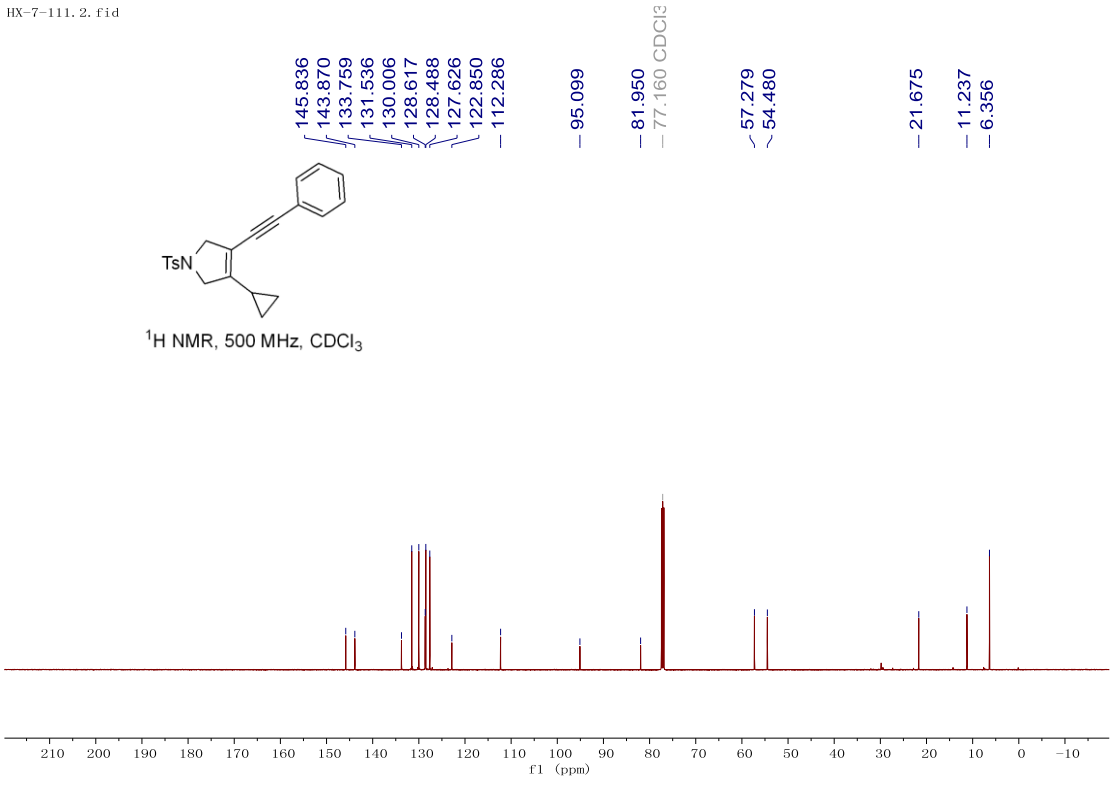
Compound **2y**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.45. 24.8 mg, 65% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72-7.71 (m, 2H), 7.42-7.39 (m, 2H), 7.35-7.30 (m, 5H), 4.20 (t, J = 4.0 Hz, 2H), 3.90 (t, J = 4.0 Hz, 2H), 2.44 (s, 3H), 1.90-1.84 (m, 1H), 0.86-0.82 (m, 2H), 0.69-0.66 (m, 2H).

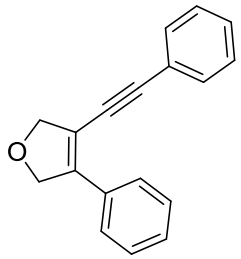
^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.8, 143.9, 133.8, 131.5, 130.0, 128.6, 128.5, 127.6, 122.9, 112.3, 95.1, 82.0, 57.3, 54.5, 21.7, 11.2, 6.4.

HRMS (ESI) m/z: calcd for $[C_{22}H_{21}NO_2S+H]^+$ requires: 364.1366, found: 364.1364.





3-phenyl-4-(phenylethynyl)-2,5-dihydrofuran (5)

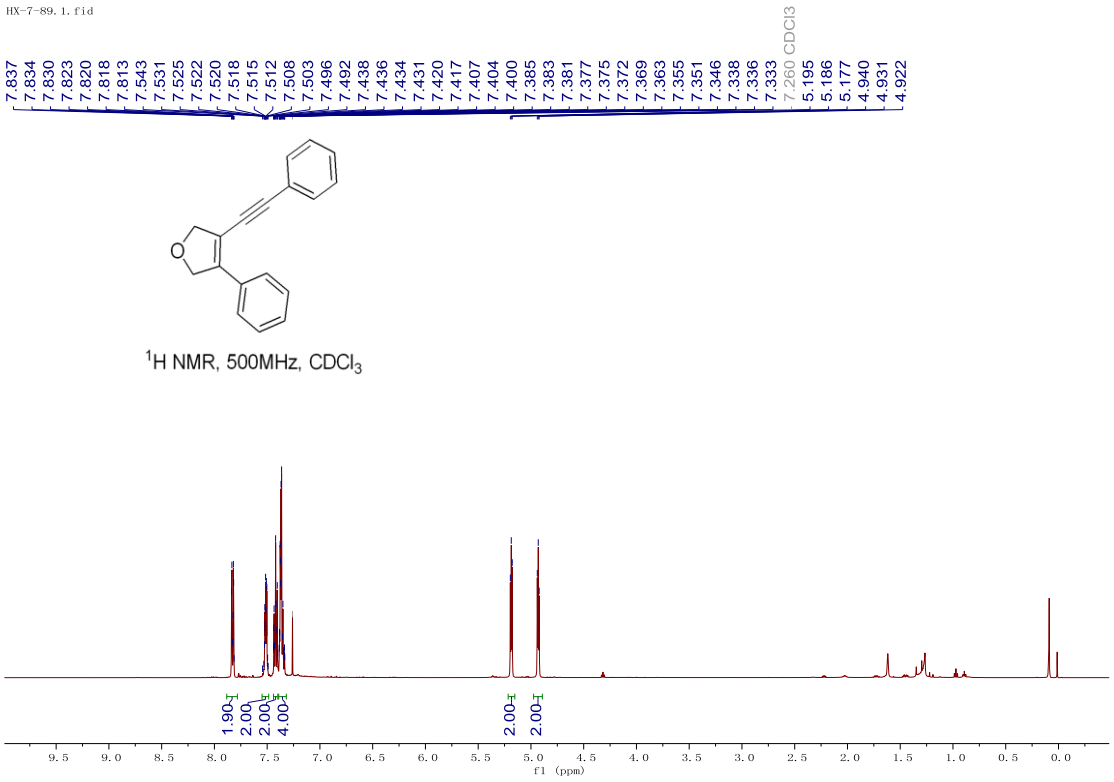


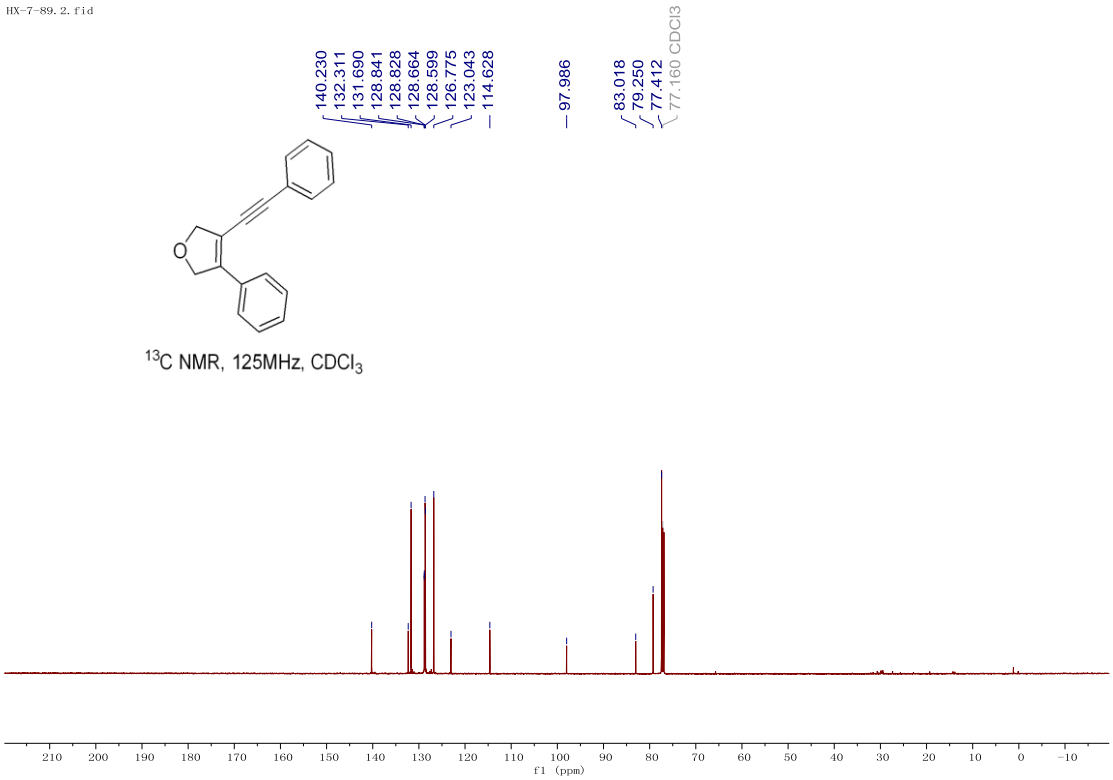
Compound **5**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.64. 18.3 mg, 68% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84-7.81 (m, 2H), 7.54-7.49 (m, 2H), 7.44-7.40 (m, 2H), 7.39-7.33 (m, 4H), 5.19 (t, J = 4.5 Hz, 2H), 4.93 (t, J = 4.5 Hz, 2H).

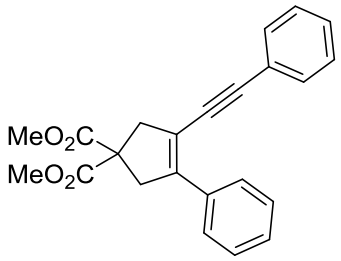
^{13}C NMR (125 MHz, Chloroform-*d*) δ 140.2, 132.3, 131.7, 128.84, 128.83, 128.7, 128.6, 126.8, 123.0, 114.6, 98.0, 83.0, 79.3, 77.4.

HRMS (ESI) m/z: calcd for $[C_{18}H_{14}O+H]^+$ requires:247.1117, found: 247.1118.





dimethyl 3-phenyl-4-(phenylethynyl)cyclopent-3-ene-1,1-dicarboxylate (6)



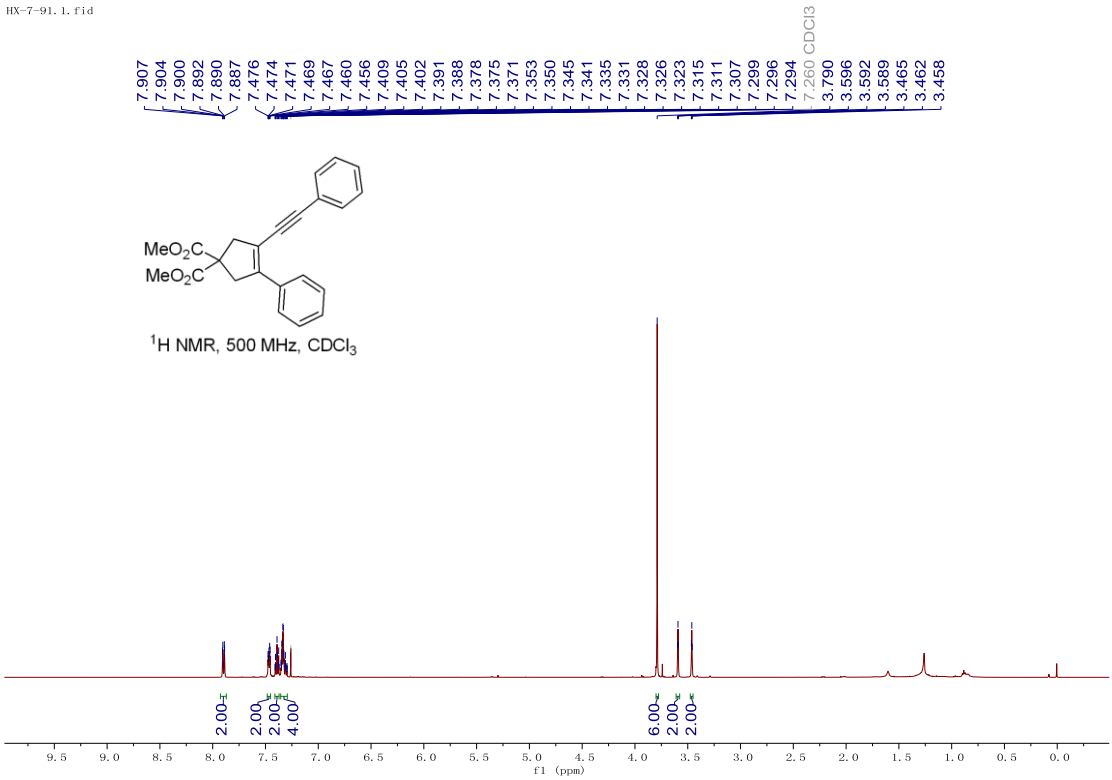
Compound **6**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.37. 16.3 mg, 43% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91-7.89 (m, 2H), 7.48-7.46 (m, 2H), 7.41-7.37 (m, 2H), 7.35-7.29 (m, 4H), 3.79 (s, 6H), 3.59 (t, J = 2.0 Hz, 2H), 3.46 (t, J = 2.0 Hz, 2H).

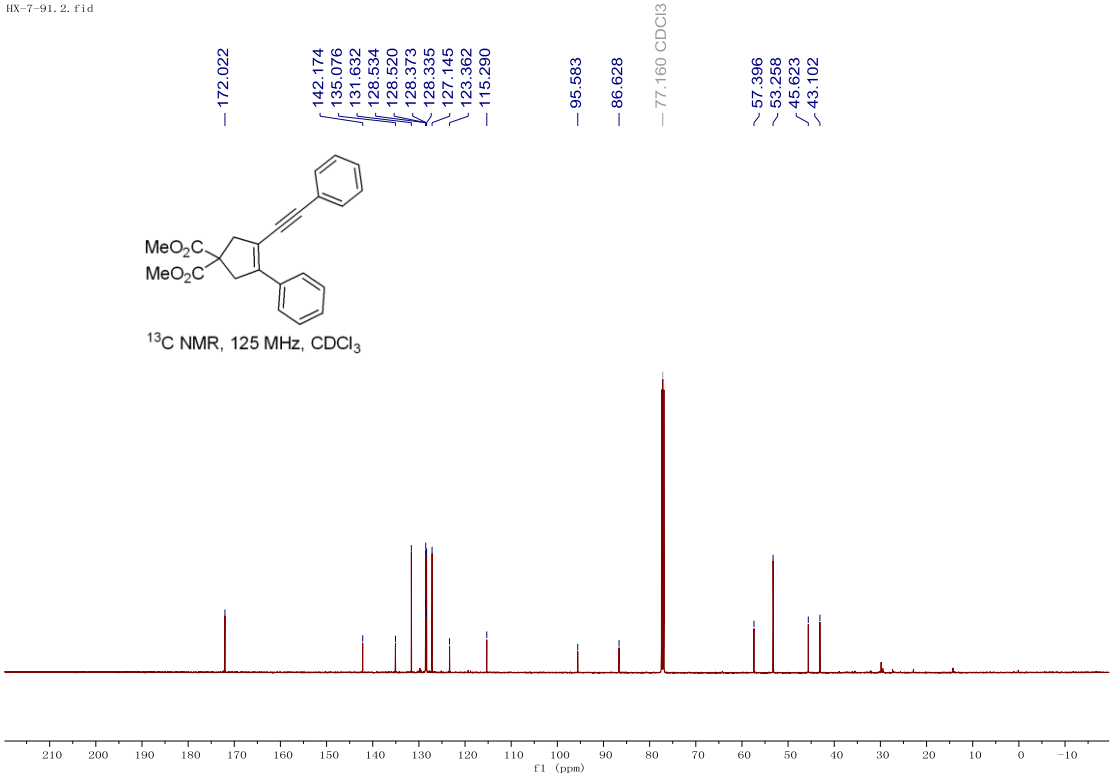
^{13}C NMR (125 MHz, Chloroform-*d*) δ 172.0, 142.2, 135.1, 131.6, 128.53, 128.52, 128.4, 128.3, 127.1, 123.4, 115.3, 95.6, 86.6, 57.4, 53.3, 45.6, 43.1.

HRMS (ESI) m/z: calcd for $[C_{23}H_{20}O_4+H]^+$ requires:361.1434, found: 361.1433.

HX-7-91.1.fid

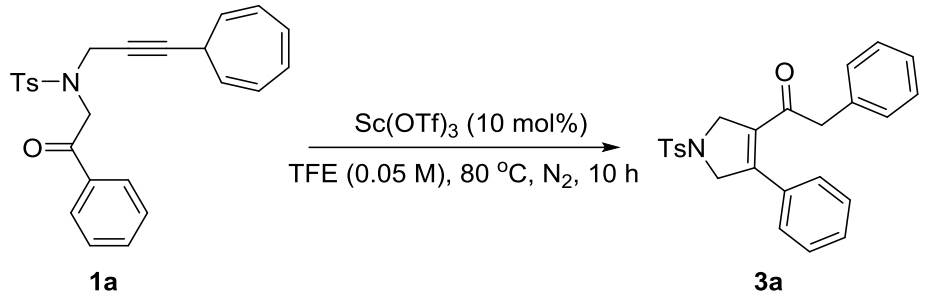


HX-7-91.2.fid



5. Experimental procedure and characterization data for products 3a-3y, 8 and 9

5.1 General procedure C for products 3a-3y, 8 and 9.

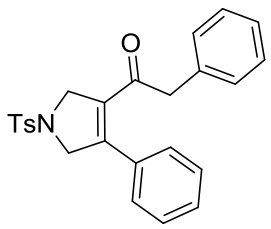


1a **3a**

Under N_2 atmosphere, 2,2,2-Trifluoroethanol (TFE) (2.0 mL, 0.05 M) was added to a mixture of **1a** (41.8 mg, 0.1 mmol), $Sc(OTf)_3$ (4.9 mg, 0.01 mmol). The reaction system was stirred at 80 °C in a parallel reactor for 10 hours until **1a** was completely consumed by TLC monitoring. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate, 8/1) to give the product **3a** (29.4 mg, 70% yield) as a yellow solid.

5.2. Characterization date of products 3a-3y, 8 and 9.

2-phenyl-1-(4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)ethan-1-one (3a)



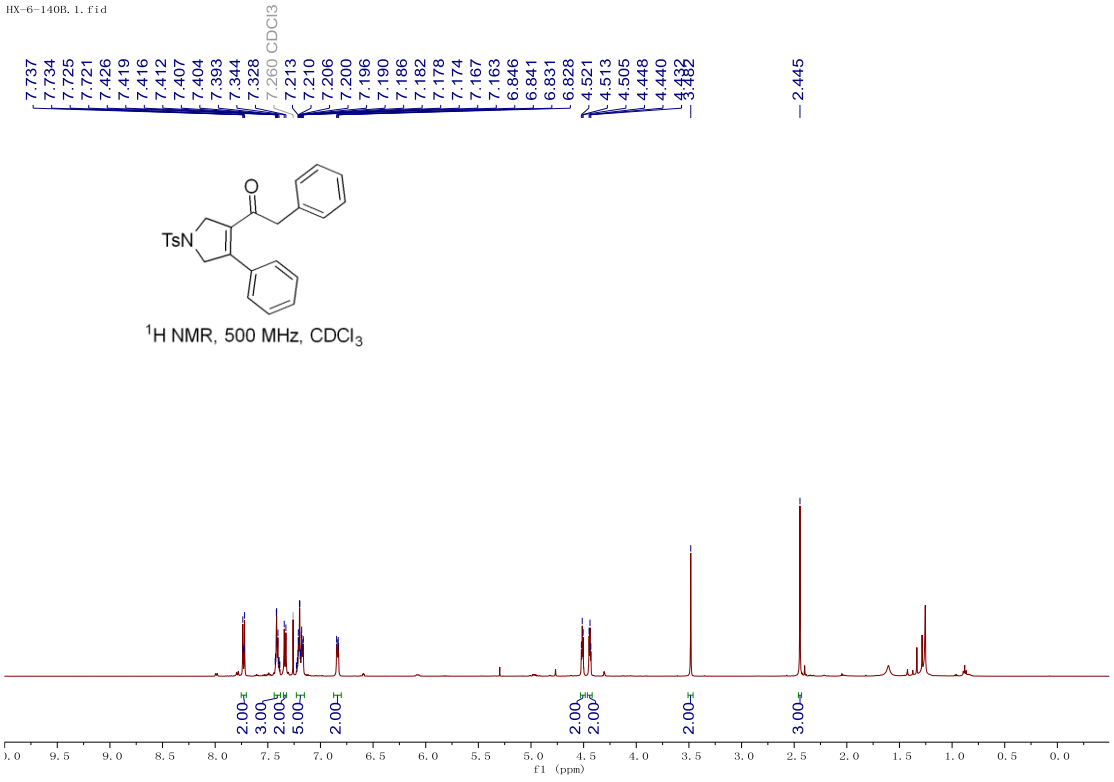
Compound **3a**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.18. 29.4 mg, 70% yield. m.p. 106-110 °C.

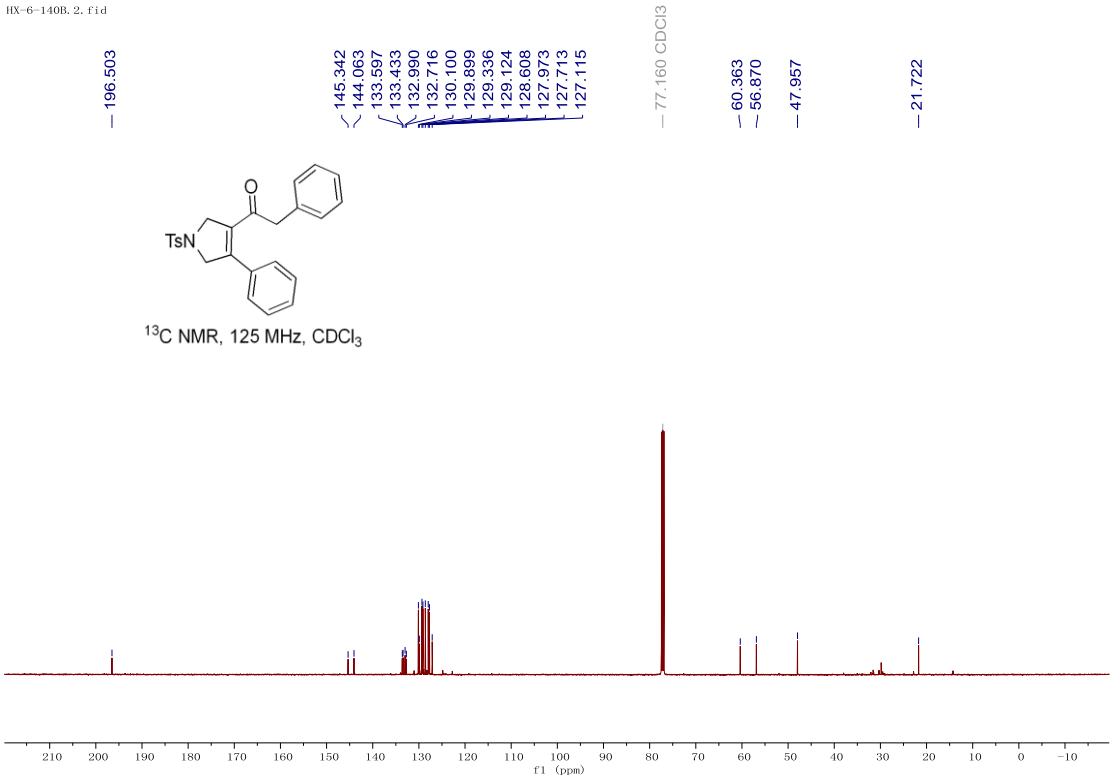
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74-7.72 (m, 2H), 7.43-7.39 (m, 3H), 7.34 (d, J = 8.0 Hz, 2H), 7.23-7.16 (m, 5H), 6.85-6.83 (m, 2H), 4.51 (t, J = 4.0 Hz, 2H), 4.44 (t, J = 4.0 Hz, 2H), 3.48 (s, 2H), 2.45 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.5, 145.3, 144.1, 133.6, 133.4, 133.0, 132.7,

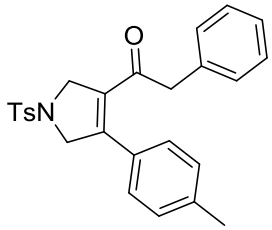
130.1, 129.9, 129.3, 129.1, 128.6, 128.0, 127.7, 127.1, 60.4, 56.9, 48.0, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{23}NO_3S+H]^+$ requires: 418.1471, found: 418.1485.





2-phenyl-1-(4-(*p*-tolyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)ethan-1-one (3b)

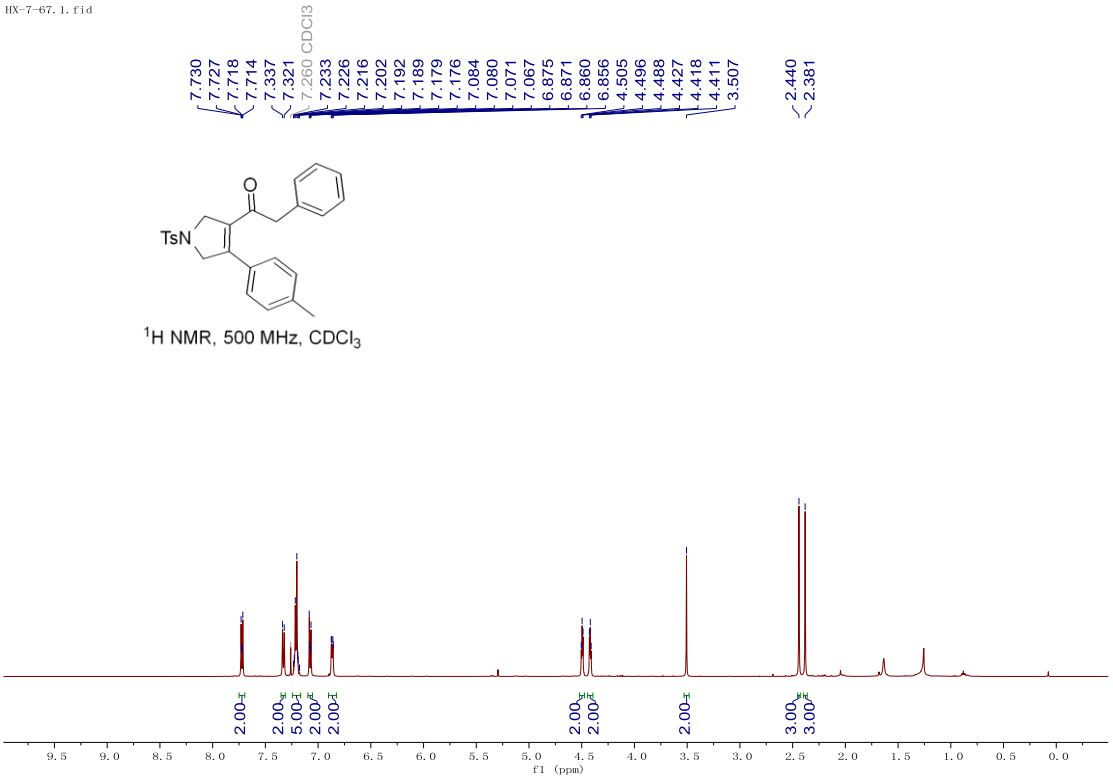


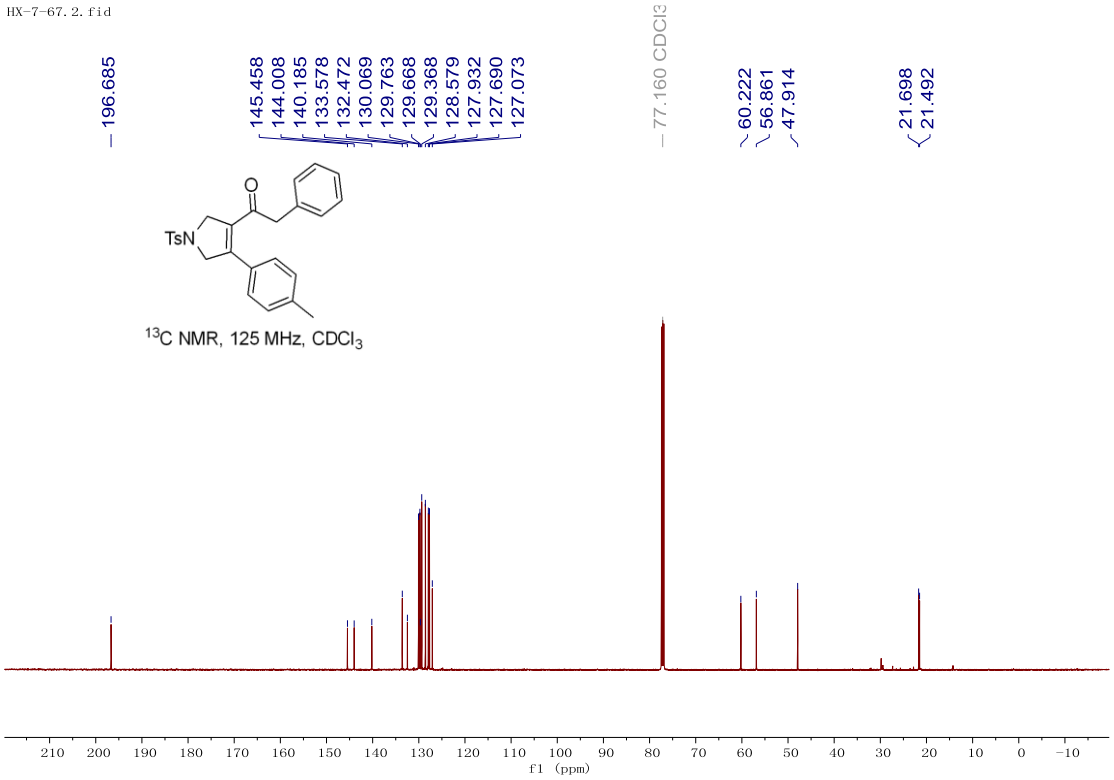
Compound **3b**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.26. 24.9 mg, 58% yield. m.p. 137-141 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73-7.71 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.23-7.18 (m, 5H), 7.08-7.07 (m, 2H), 6.87 (dd, J = 7.5, 2.0 Hz, 2H), 4.50 (t, J = 4.0 Hz, 2H), 4.42 (t, J = 4.0 Hz, 2H), 3.51 (s, 2H), 2.44 (s, 3H), 2.38 (s, 3H).

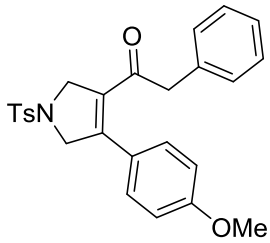
^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.7, 145.5, 144.0, 140.2, 133.6, 132.5, 130.1, 129.8, 129.7, 129.4, 128.6, 127.9, 127.7, 127.1, 60.2, 56.9, 47.9, 21.7, 21.5.

HRMS (ESI) m/z: calcd for $[C_{26}H_{25}NO_3S+H]^+$ requires: 432.1628, found: 432.1633.





1-(4-(4-methoxyphenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3c)

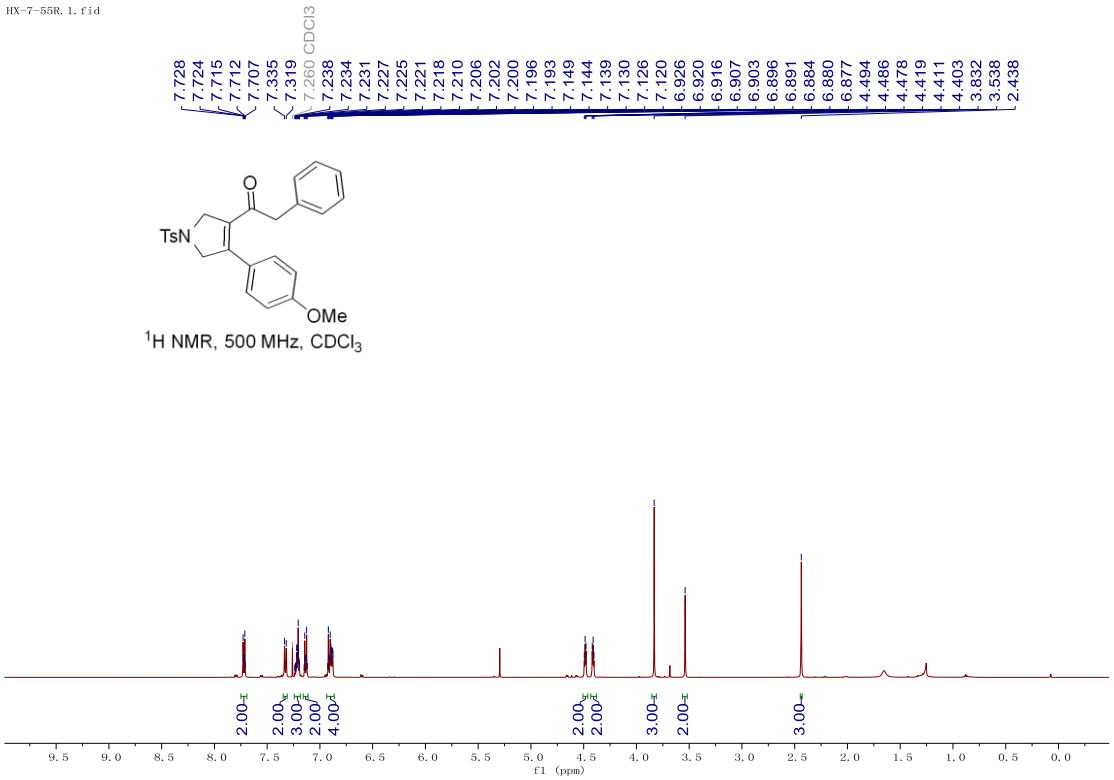


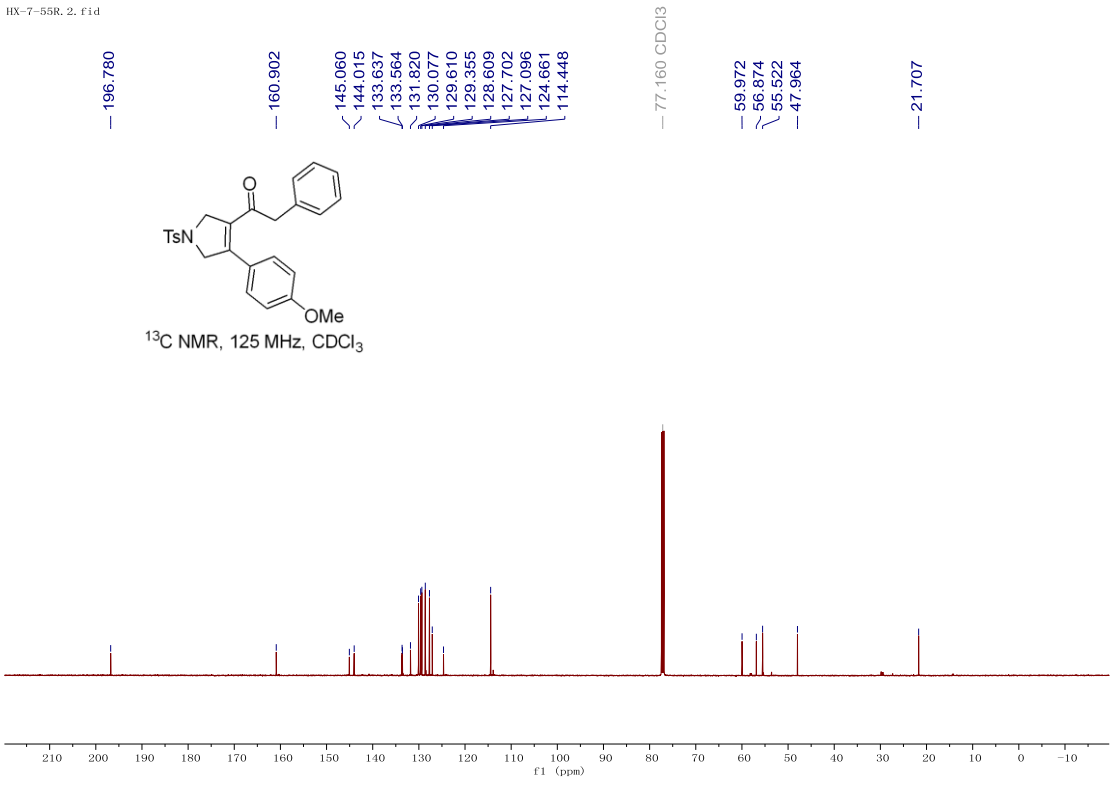
Compound **3c**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.18. 20.2 mg, 45% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73-7.71 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.24-7.19 (m, 3H), 7.14 (dt, J = 9.5, 2.5 Hz, 2H), 6.93-6.88 (m, 4H), 4.49 (t, J = 4.0 Hz, 2H), 4.41 (t, J = 4.0 Hz, 2H), 3.83 (s, 3H), 3.54 (s, 2H), 2.44 (s, 3H).

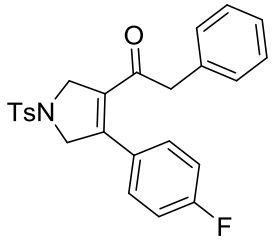
^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.8, 160.9, 145.1, 144.0, 133.64, 133.56, 131.8, 130.1, 129.6, 129.4, 128.6, 127.7, 127.1, 124.7, 114.4, 60.0, 56.9, 55.5, 48.0, 21.7.

HRMS (ESI) m/z: calcd for $[C_{26}H_{25}NO_4S+H]^+$ requires: 448.1577, found: 448.1582.





1-(4-(4-fluorophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3d)



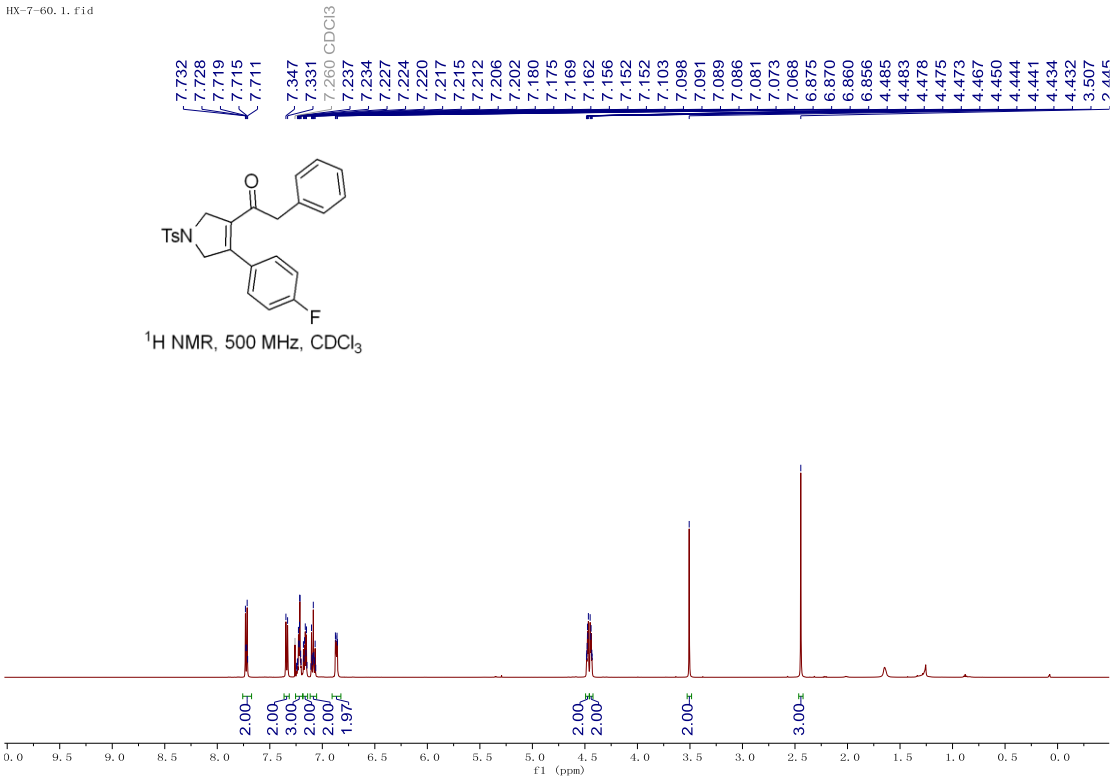
Compound **3d**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.20. 23.4 mg, 54% yield. m.p. 93-96 ºC.

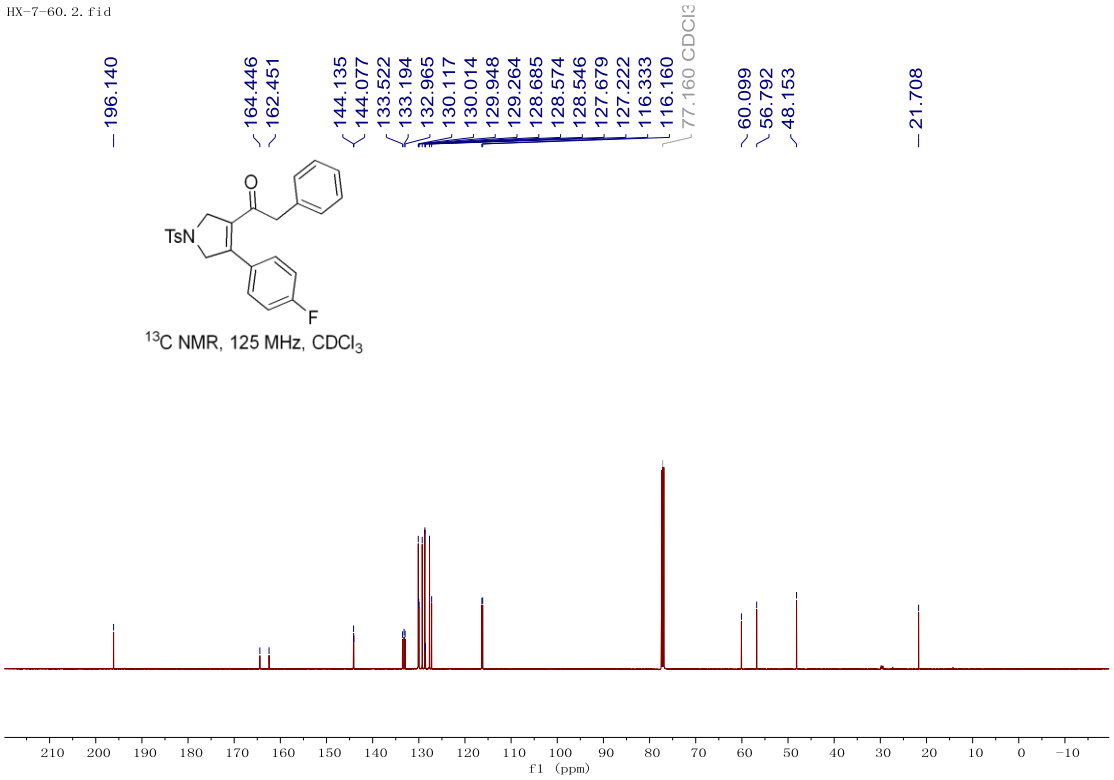
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73-7.71 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.25-7.20 (m, 3H), 7.18-7.15 (m, 2H), 7.11-7.06 (m, 2H), 6.87 (dd, J = 7.5, 2.0 Hz, 2H), 4.49-4.47 (m, 2H), 4.45-4.43 (m, 2H), 3.51 (s, 2H), 2.45 (s, 3H).

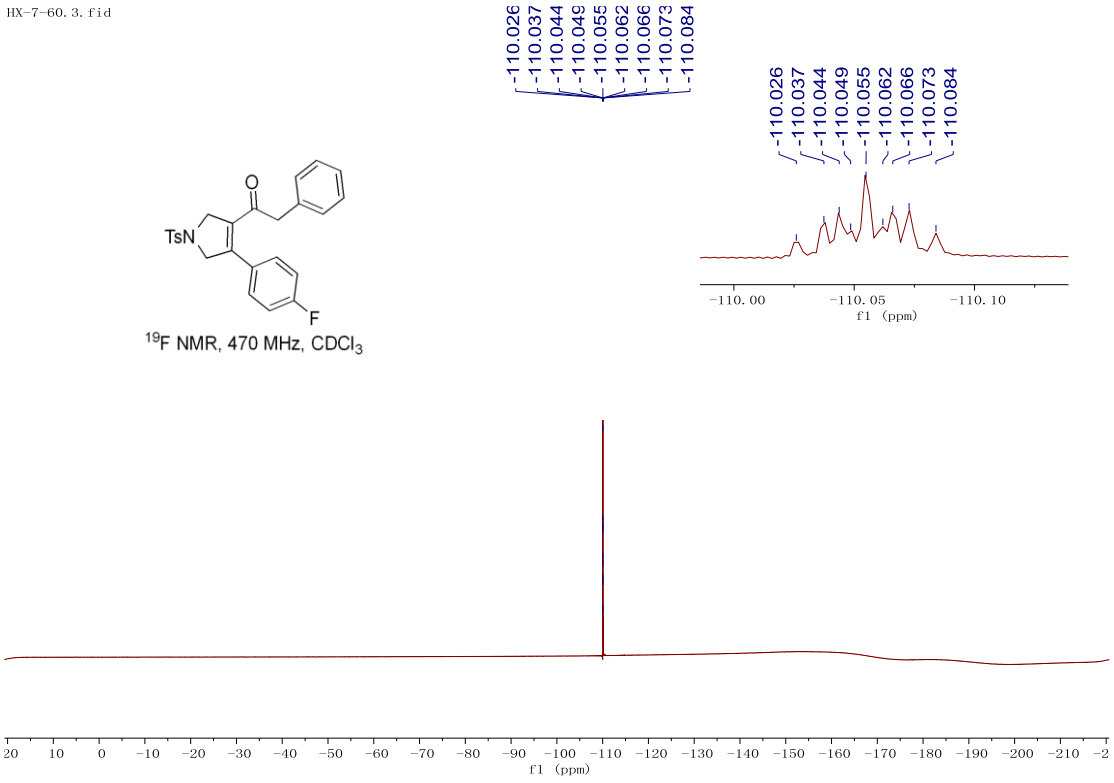
^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.1, 163.4 (d, J = 249.4 Hz), 144.14, 144.08, 133.5, 133.2, 133.0, 130.1, 130.0 (d, J = 8.3 Hz), 129.3, 128.7, 128.6 (d, J = 3.5 Hz), 127.7, 127.2, 116.2 (d, J = 21.6 Hz), 60.1, 56.8, 48.2, 21.7.

^{19}F NMR (470 MHz, $CDCl_3$) δ (m) (-110.03)-(-110.08).

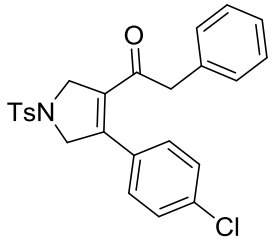
HRMS (ESI) m/z: calcd for $[C_{25}H_{22}FNO_3S+H]^+$ requires: 436.1377, found: 436.1380.







1-(4-(4-chlorophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3e)

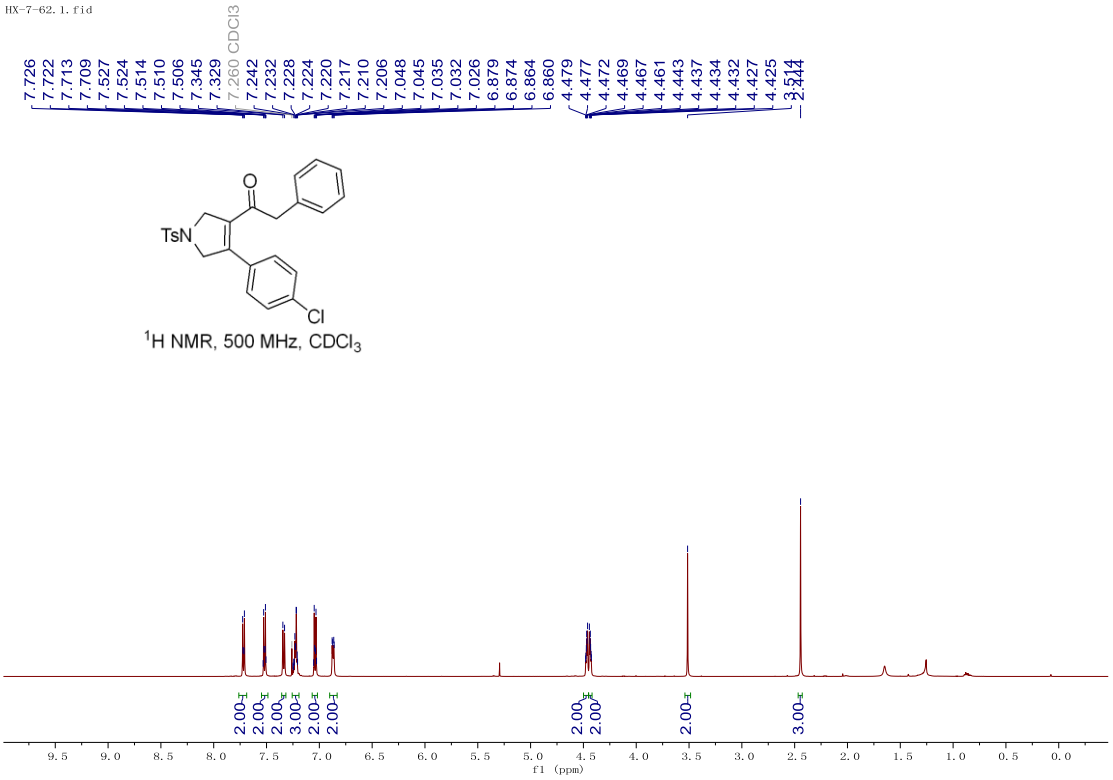


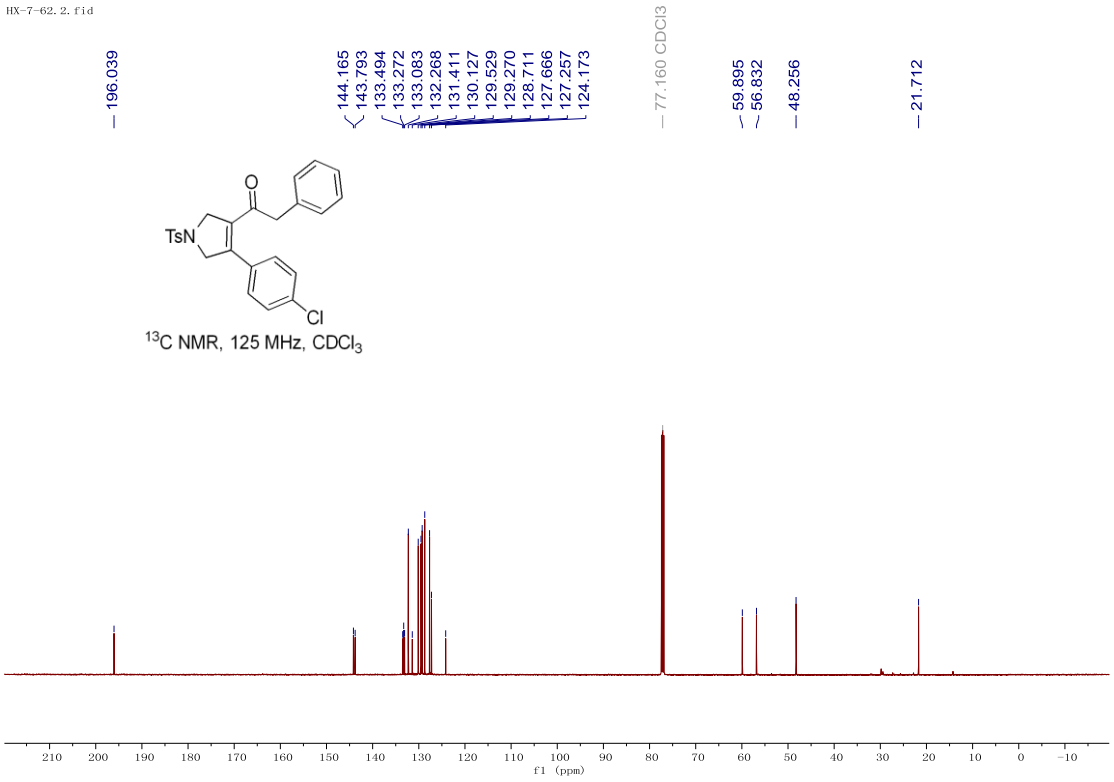
Compound **3e**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.29. 30.8 mg, 68% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73-7.71 (m, 2H), 7.52 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.25-7.21 (m, 3H), 7.04 (dt, *J* = 8.0, 2.5 Hz, 2H), 6.87 (dd, *J* = 7.5, 2.0 Hz, 2H), 4.48-4.46 (m, 2H), 4.44-4.43 (m, 2H), 3.51 (s, 2H), 2.44 (s, 3H).

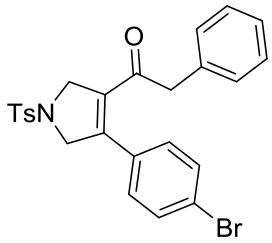
^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.0, 144.2, 143.8, 133.5, 133.3, 133.1, 132.3, 131.4, 130.1, 129.5, 129.3, 128.7, 127.7, 127.3, 124.2, 59.9, 56.8, 48.3, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{22}ClNO_3S+H]^+$ requires: 452.1082, found: 452.1081.





1-(4-(4-bromophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3f)

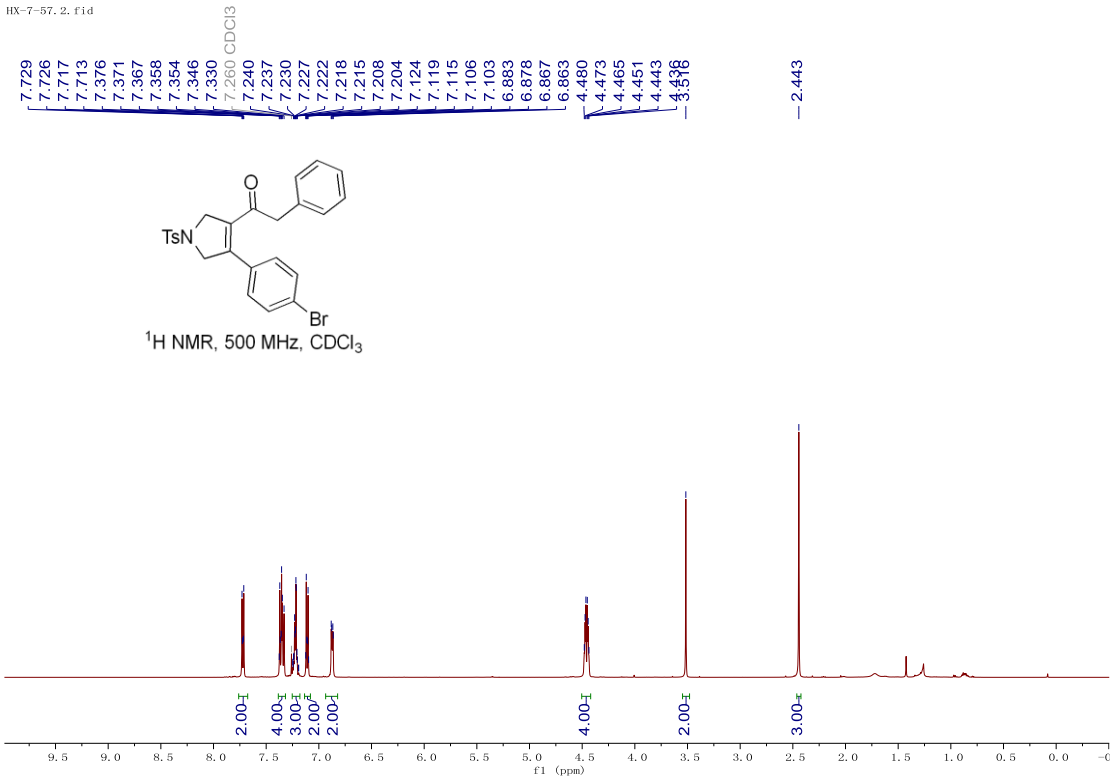


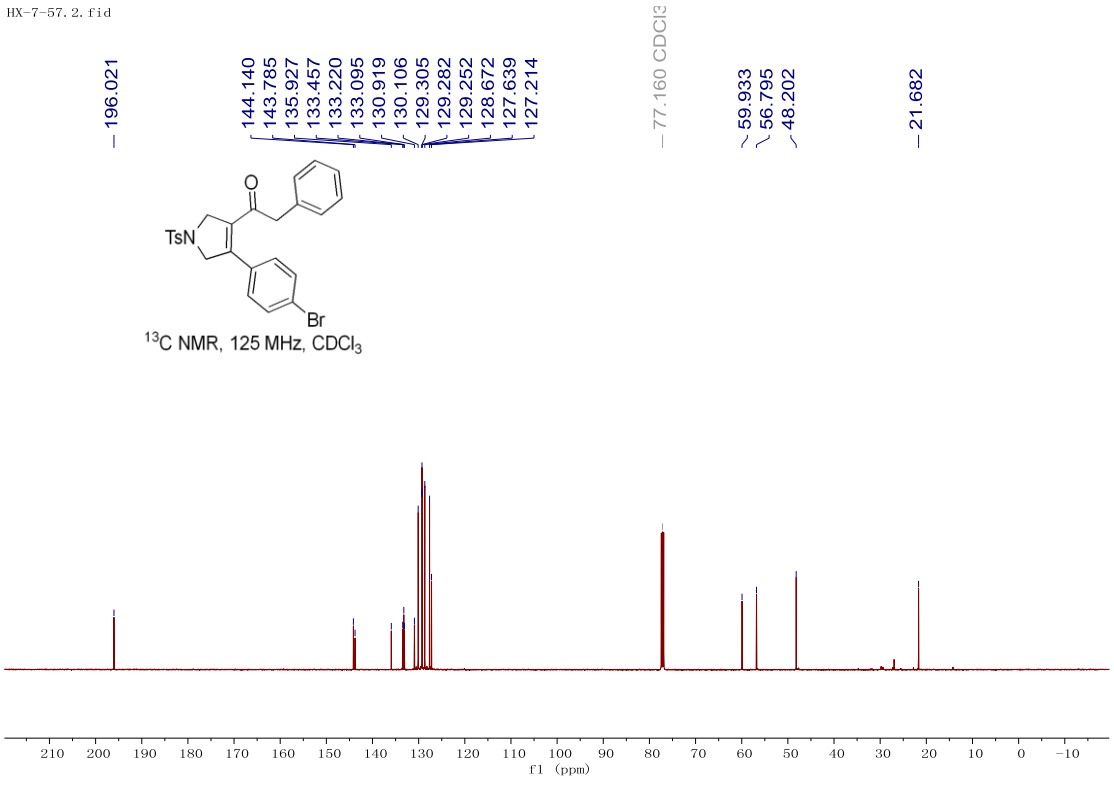
Compound **3f**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.22. 34.2 mg, 69% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73-7.71 (m, 2H), 7.38-7.33 (m, 4H), 7.25-7.19 (m, 3H), 7.11 (dt, *J* = 8.0, 2.0 Hz, 2H), 6.87 (dd, *J* = 7.5, 2.0 Hz, 2H), 4.48-4.44 (m, 4H), 3.52 (s, 2H), 2.44 (s, 3H).

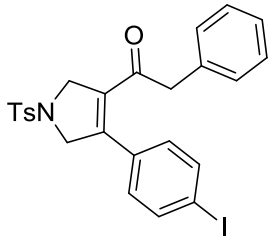
^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.0, 144.1, 143.8, 135.9, 133.5, 133.2, 133.1, 130.9, 130.1, 129.31, 129.28, 129.25, 128.7, 127.6, 127.2, 59.9, 56.8, 48.2, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{22}BrNO_3S+H]^+$ requires: 496.0577, found: 496.0580.





1-(4-(4-iodophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3g)

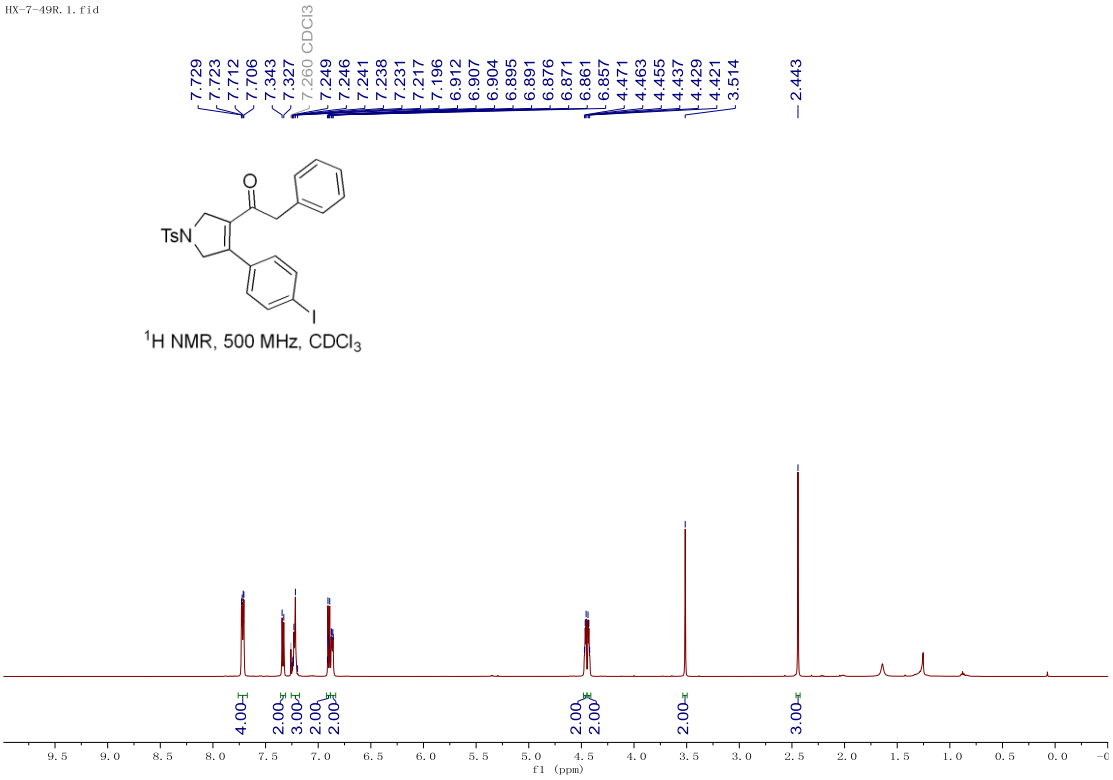


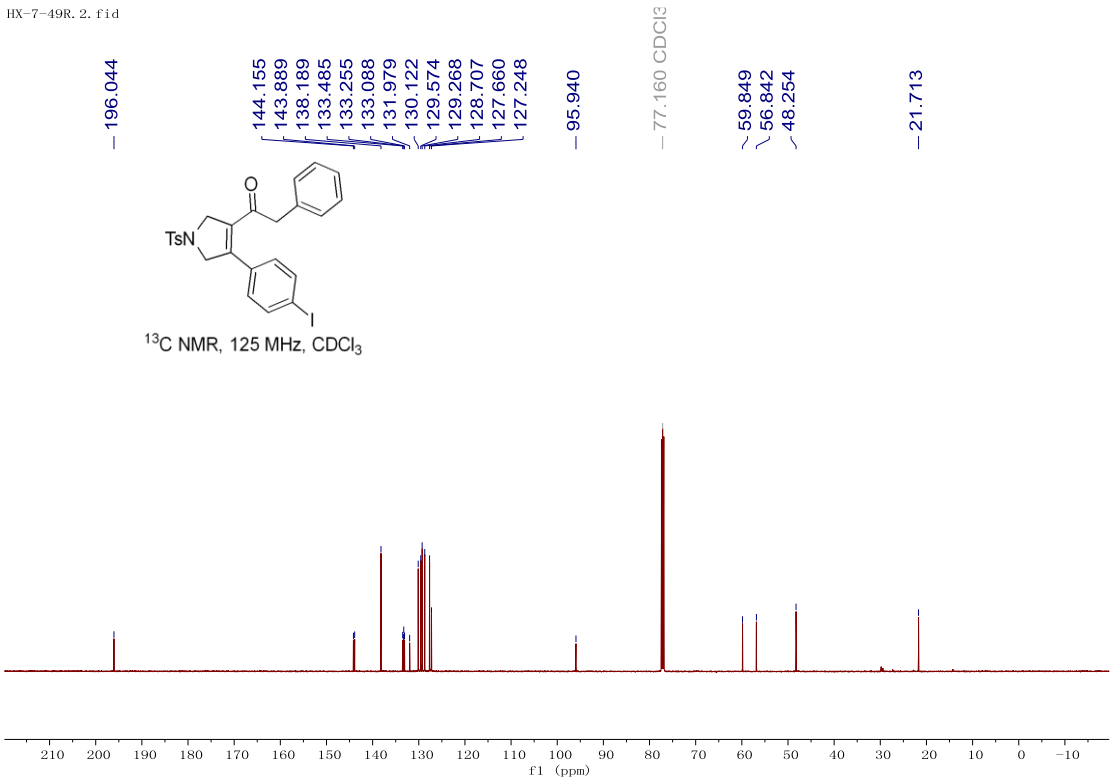
Compound **3g**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.19. 37.5 mg, 69% yield. m.p. 99-103 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, J = 3.0 Hz, 2H), 7.71 (d, J = 3.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.25-7.20 (m, 3H), 6.91-6.89 (m, 2H), 6.87 (dd, J = 7.5, 2.5 Hz, 2H), 4.46 (t, J = 4.0 Hz, 2H), 4.43 (t, J = 4.0 Hz, 2H), 3.51 (s, 2H), 2.44 (s, 3H).

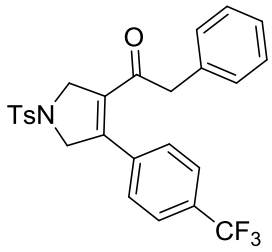
^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.0, 144.2, 143.9, 138.2, 133.5, 133.3, 133.1, 132.0, 130.1, 129.6, 129.3, 128.7, 127.7, 127.2, 95.9, 59.8, 56.8, 48.3, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{22}INO_3S\text{-}H]^-$ requires: 542.0292, found: 542.0315.





2-phenyl-1-(1-tosyl-4-(4-(trifluoromethyl)phenyl)-2,5-dihydro-1*H*-pyrrol-3-yl)ethan-1-one (3h)



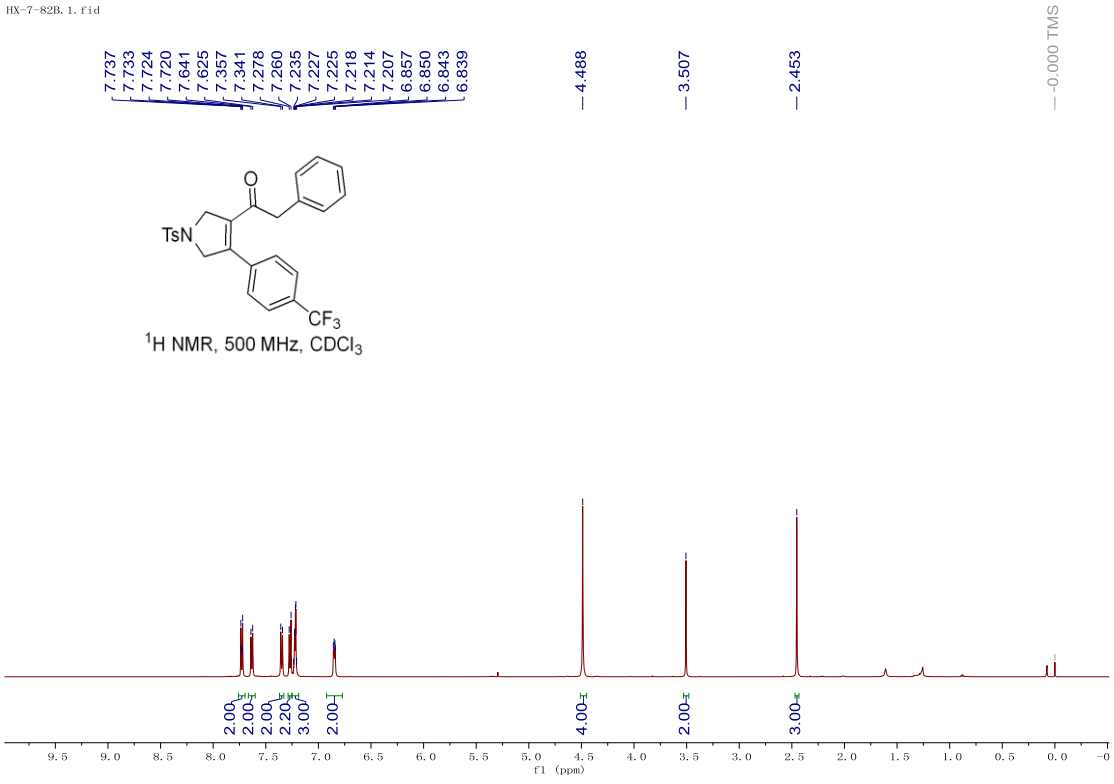
Compound **3h**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.36. 30.2 mg, 62% yield. m.p. 107-112 °C.

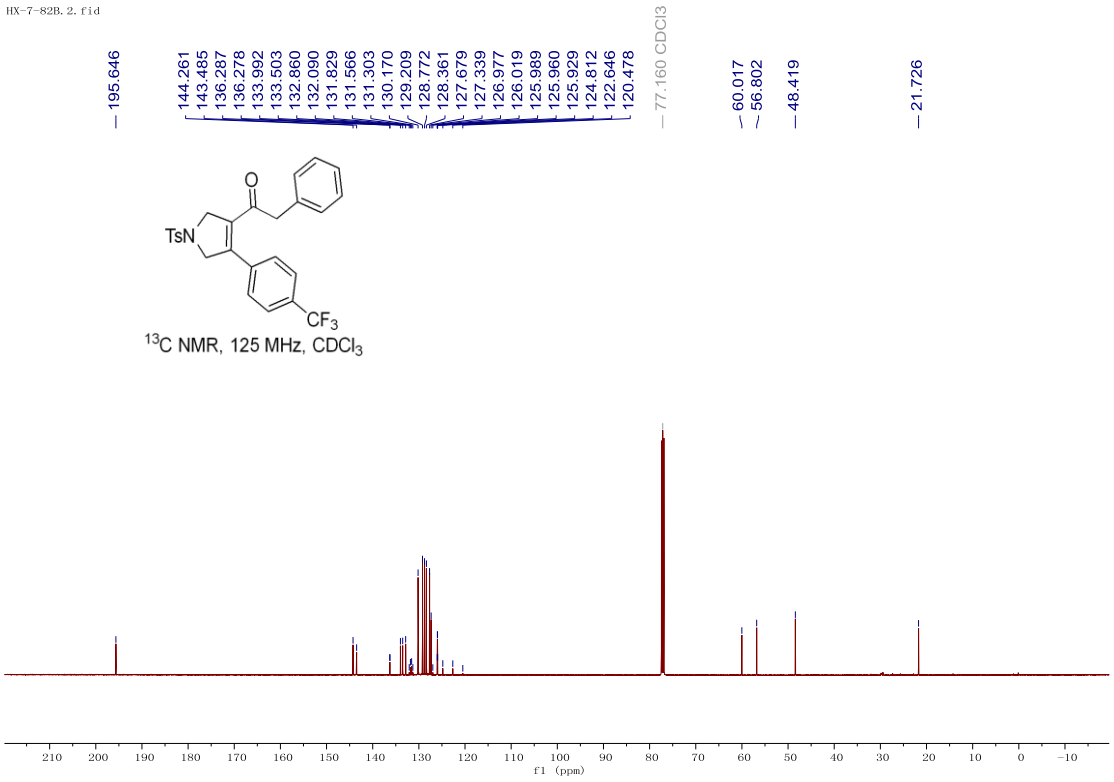
^{1}H NMR (500 MHz, Chloroform-*d*, TMS) δ 7.74-7.72 (m, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 9.0 Hz, 2H), 7.24-7.21 (m, 3H), 6.86-6.84 (m, 2H), 4.49 (s, 4H), 3.51 (s, 2H), 2.45 (s, 3H).

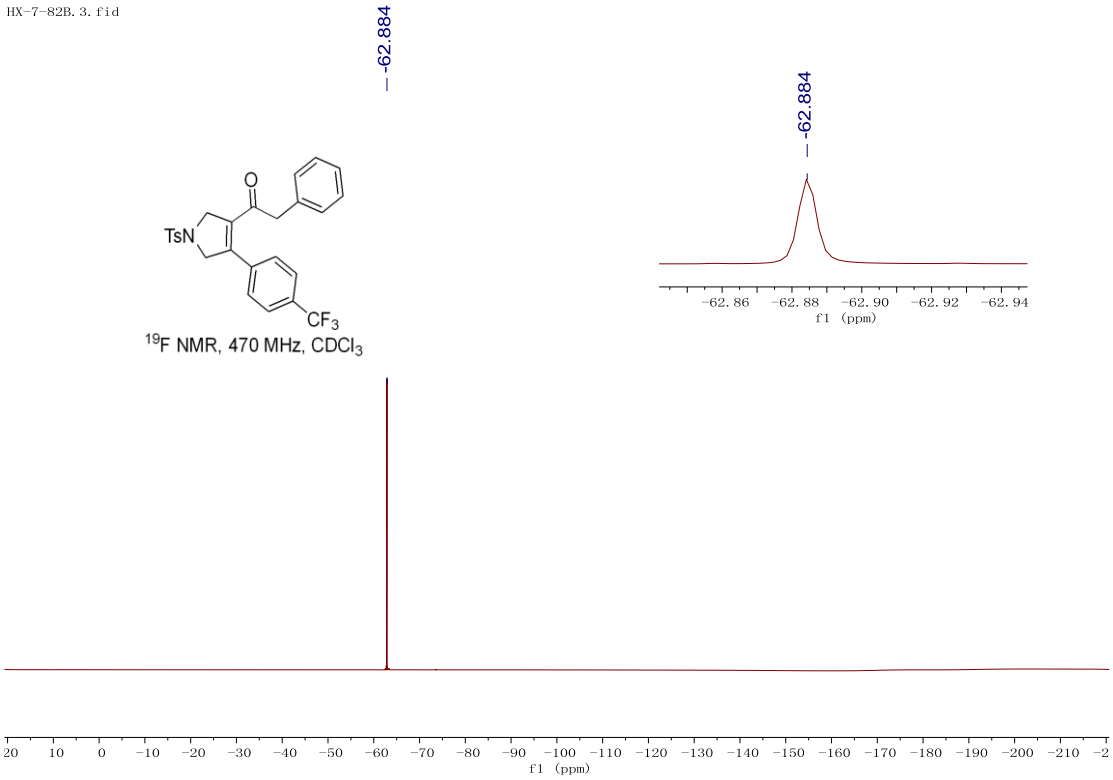
^{13}C NMR (125 MHz, Chloroform-*d*) δ 195.6, 144.3, 143.5, 136.3 (q, J = 1.1 Hz), 134.0, 133.5, 132.9, 131.7 (q, J = 32.6 Hz), 130.2, 129.2, 128.8, 128.4, 127.7, 127.3, 126.0 (q, J = 3.8 Hz), 123.7 (q, J = 270.8 Hz), 60.0, 56.8, 48.4, 21.7.

^{19}F NMR (470 MHz, $CDCl_3$) δ (s) (-62.88)

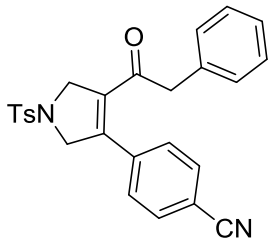
HRMS (ESI) m/z: calcd for $[C_{26}H_{22}F_3NO_3S+H]^+$ requires: 486.1345, found: 486.1346.







4-(4-(2-phenylacetyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)benzonitrile (3i)

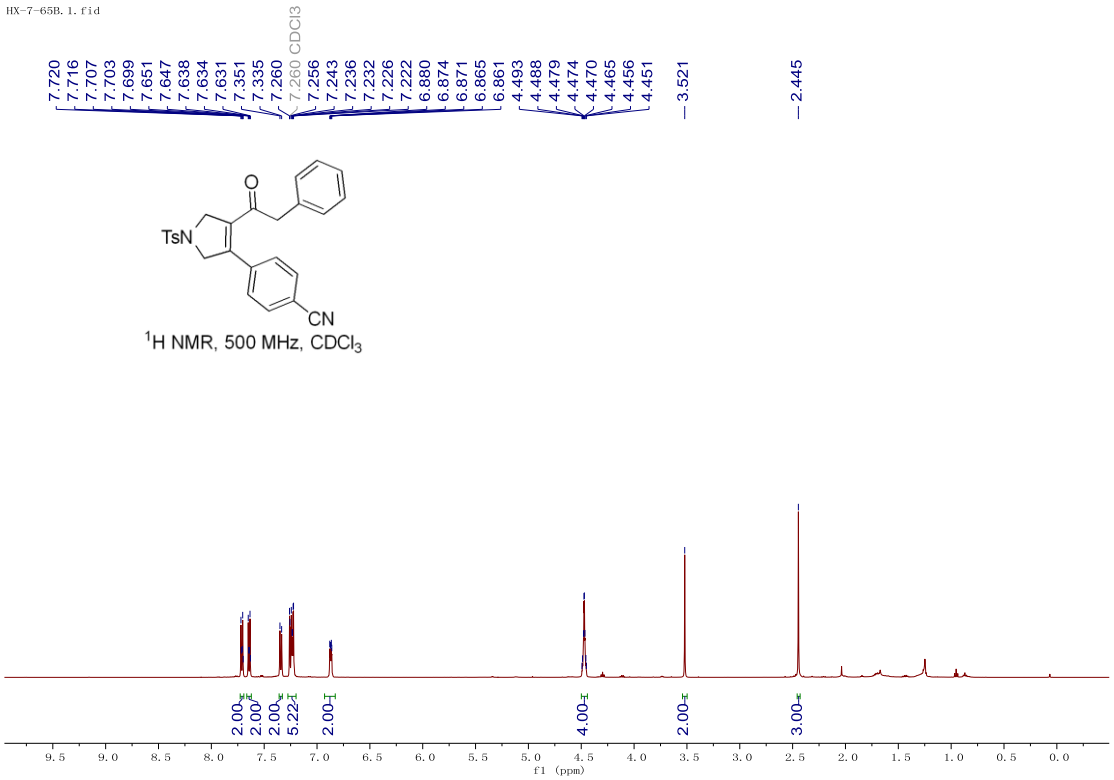


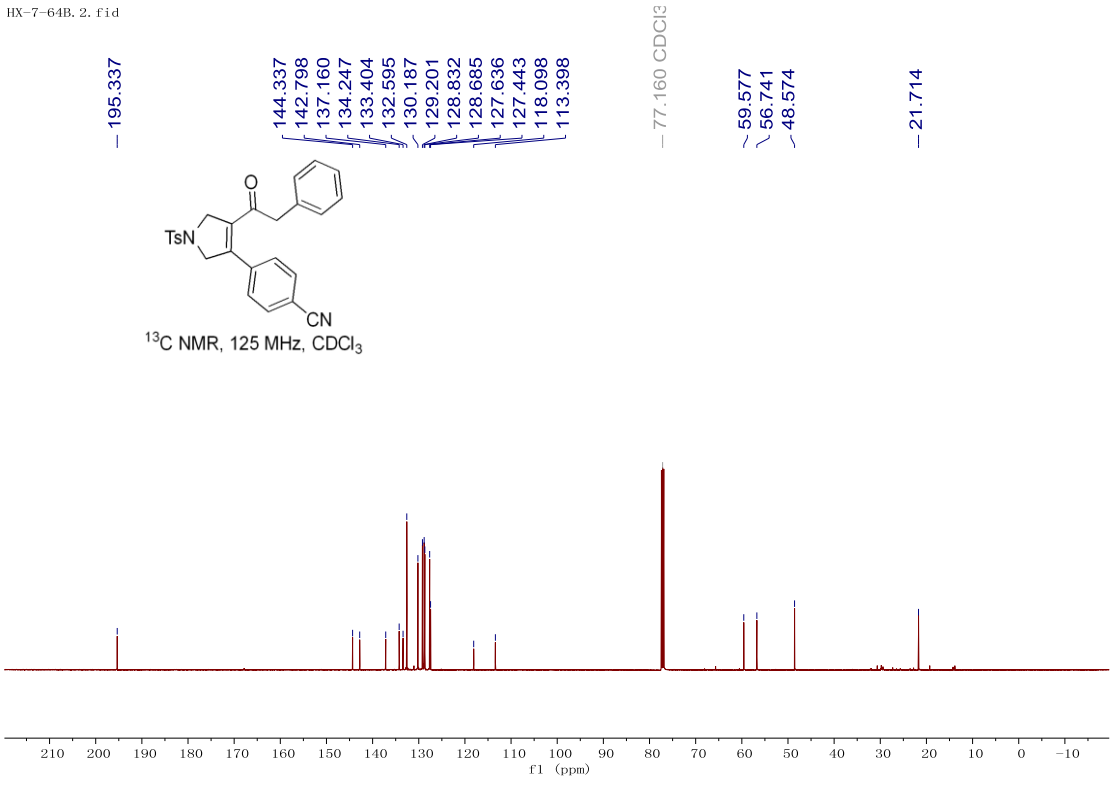
Compound **3i**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.10. 26.1 mg, 59% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72-7.70 (m, 2H), 7.65-7.63 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.26-7.22 (m, 5H), 6.88-6.86 (m, 2H), 4.49-4.45 (m, 4H), 3.52 (s, 2H), 2.45 (s, 3H).

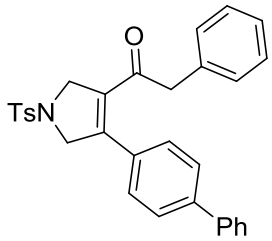
^{13}C NMR (125 MHz, Chloroform-*d*) δ 195.3, 144.3, 142.8, 137.2, 134.2, 133.4, 132.6, 130.2, 129.2, 128.8, 128.7, 127.6, 127.4, 118.1, 113.4, 59.6, 56.7, 48.6, 21.7.

HRMS (ESI) m/z: calcd for $[C_{26}H_{22}N_2O_3S+H]^+$ requires: 443.1424, found: 443.1426.





1-(4-([1,1'-biphenyl]-4-yl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3j)

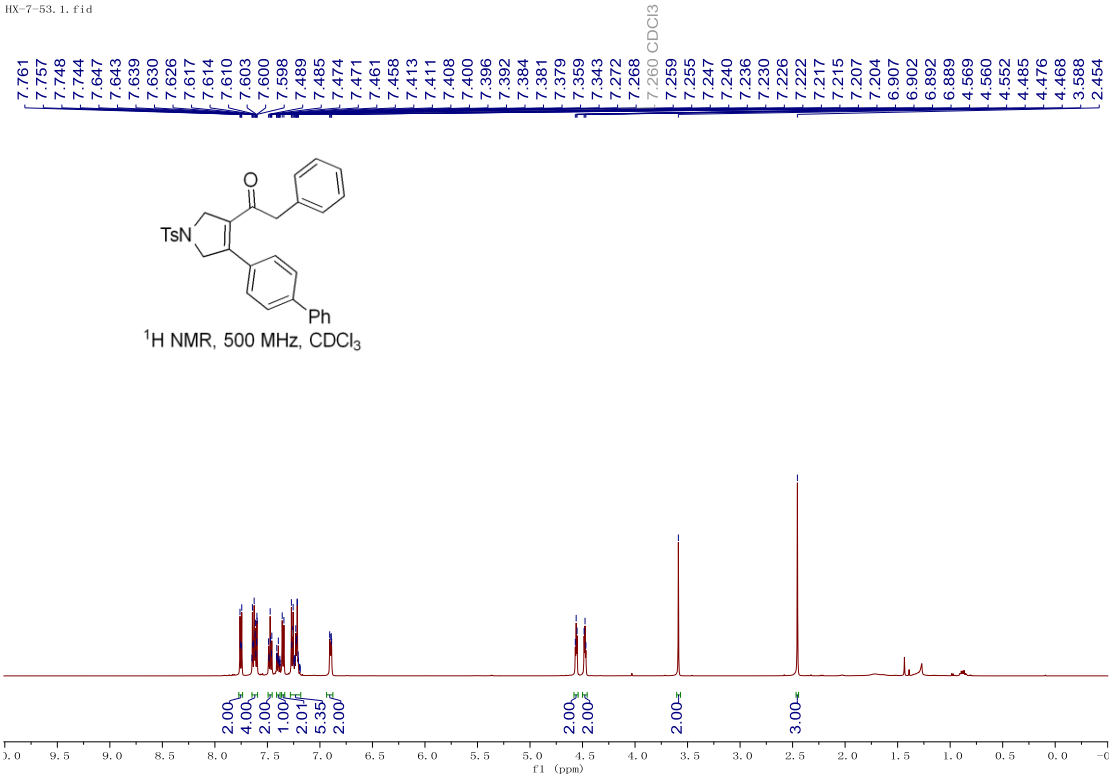


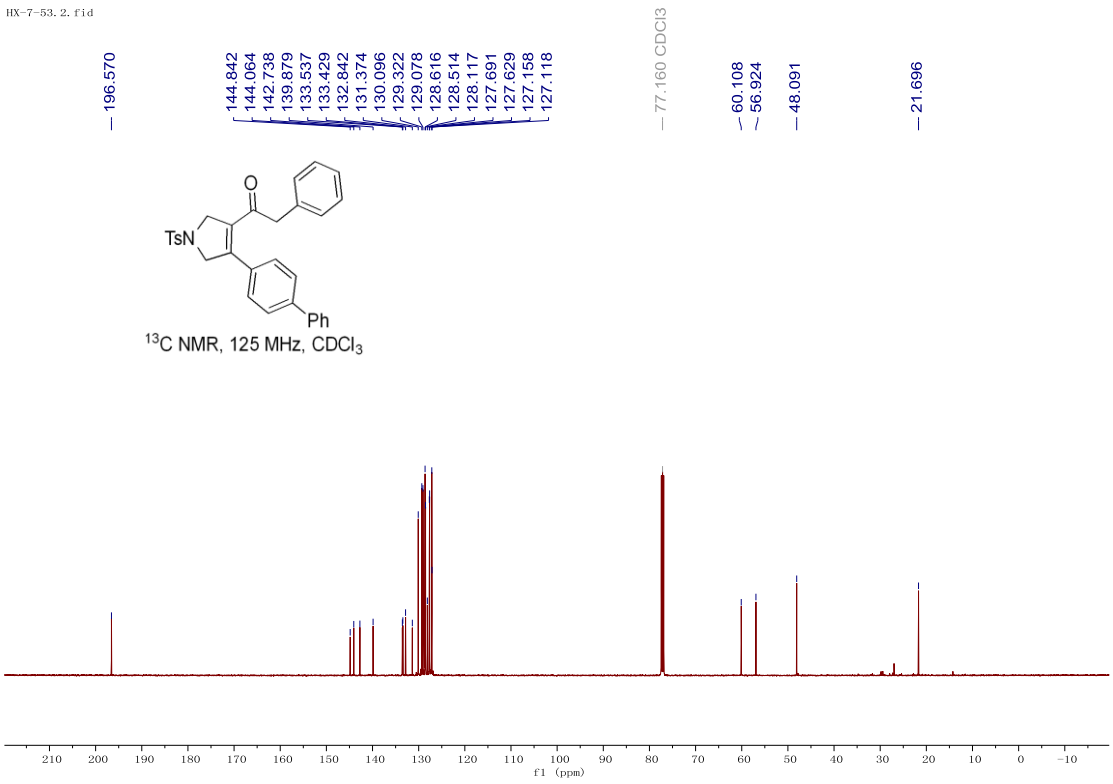
Compound **3j**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.23. 28.9 mg, 59% yield. m.p. 110-114 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76-7.74 (m, 2H), 7.65-7.60 (m, 4H), 7.49-7.46 (m, 2H), 7.41-7.38 (m, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.27-7.19 (m, 5H), 6.91-6.89 (m, 2H), 4.56 (t, J = 4.0 Hz, 2H), 4.48 (t, J = 4.0 Hz, 2H), 3.59 (s, 2H), 2.45 (s, 3H).

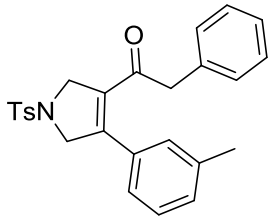
^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.6, 144.8, 144.1, 142.7, 139.9, 133.5, 133.4, 132.8, 131.4, 130.1, 129.3, 129.1, 128.6, 128.5, 128.1, 127.7, 127.6, 127.2, 127.1, 60.1, 56.9, 48.1, 21.7.

HRMS (ESI) m/z: calcd for $[C_{31}H_{27}NO_3S+H]^+$ requires: 494.1784, found: 494.1790.





2-phenyl-1-(4-(*m*-tolyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)ethan-1-one (3k)

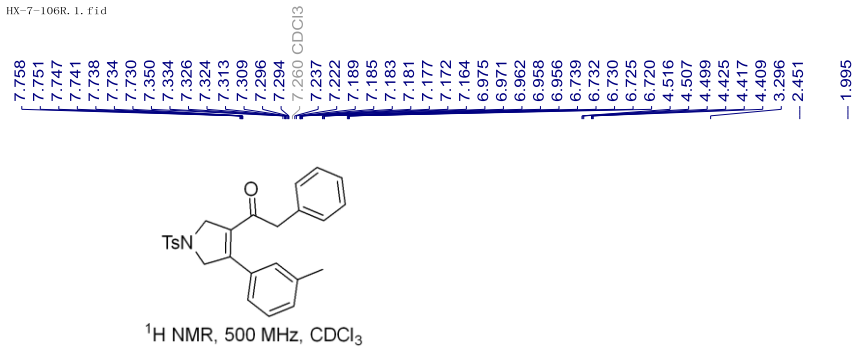


Compound **3k**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.22. 8.9 mg, 21% yield. m.p. 111-115 °C.

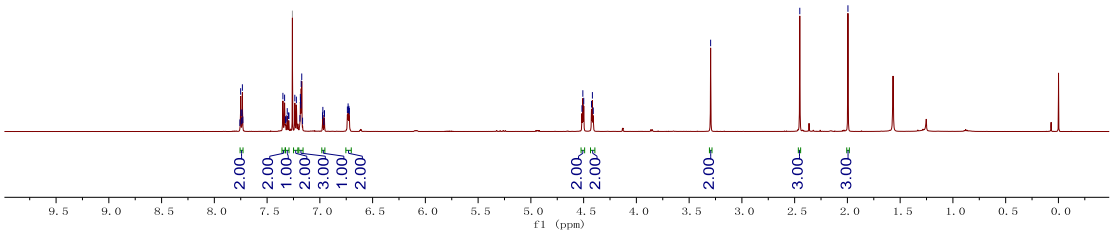
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76-7.73 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.33-7.29 (m, 1H), 7.23 (d, J = 7.5 Hz, 2H), 7.19-7.16 (m, 3H),6.98-6.96 (m, 1H), 6.74-6.72 (m, 2H), 4.51 (t, J = 4.0 Hz, 2H), 4.42 (t, J = 4.0 Hz, 2H), 3.30 (s, 2H), 2.45 (s, 3H), 2.00 (s, 3H).

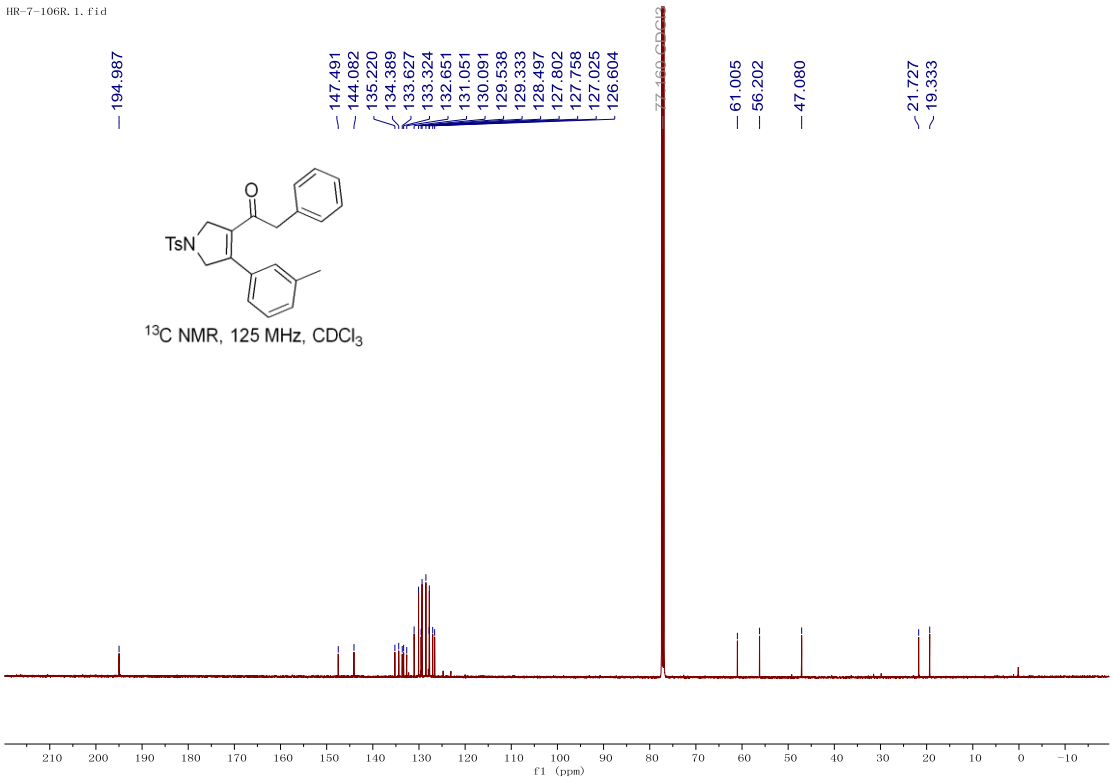
^{13}C NMR (125 MHz, Chloroform-*d*) δ 195.0, 147.5, 144.1, 135.2, 134.4, 133.6, 133.3, 132.7, 131.1, 130.1, 129.5, 129.3, 128.5, 127.80, 127.76, 127.0, 126.6, 61.0, 56.2, 47.1, 21.7, 19.3.

HRMS (ESI) m/z: calcd for $[C_{26}H_{25}NO_3S+H]^+$ requires: 432.1628, found: 432.1629.



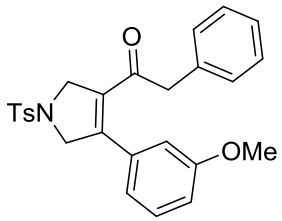
^{1}H NMR, 500 MHz, $CDCl_3$





^{13}C NMR, 125 MHz, $CDCl_3$

1-(4-(3-methoxyphenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3l)

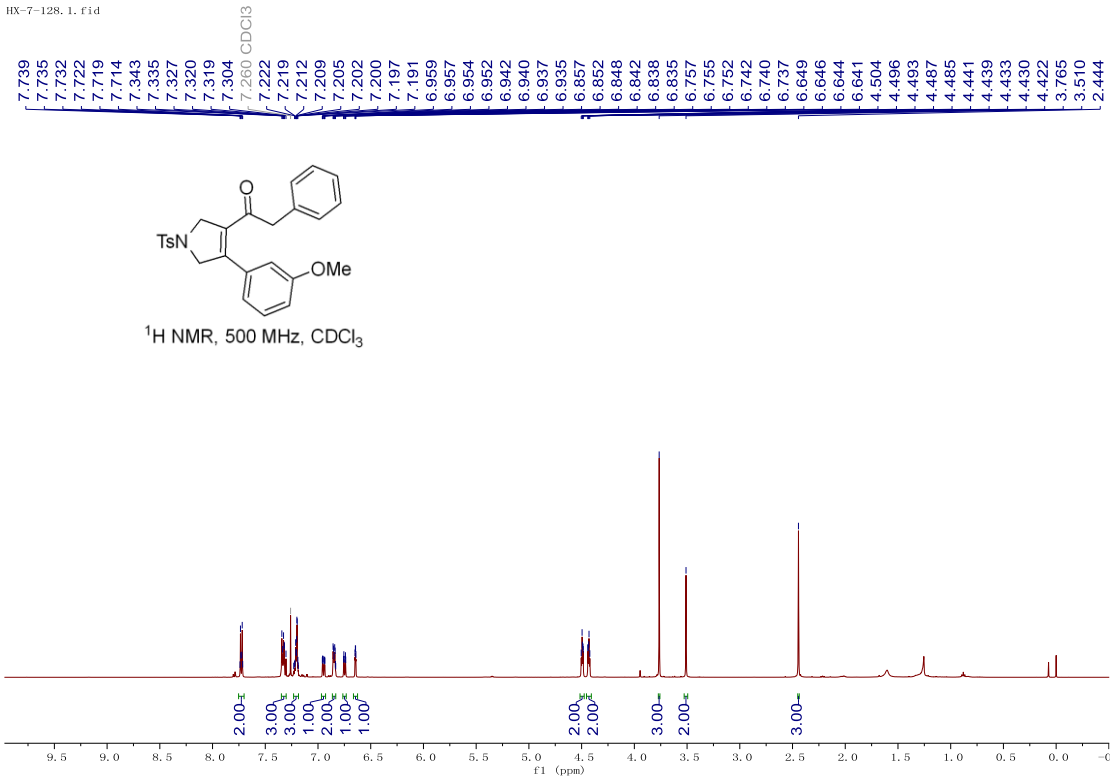


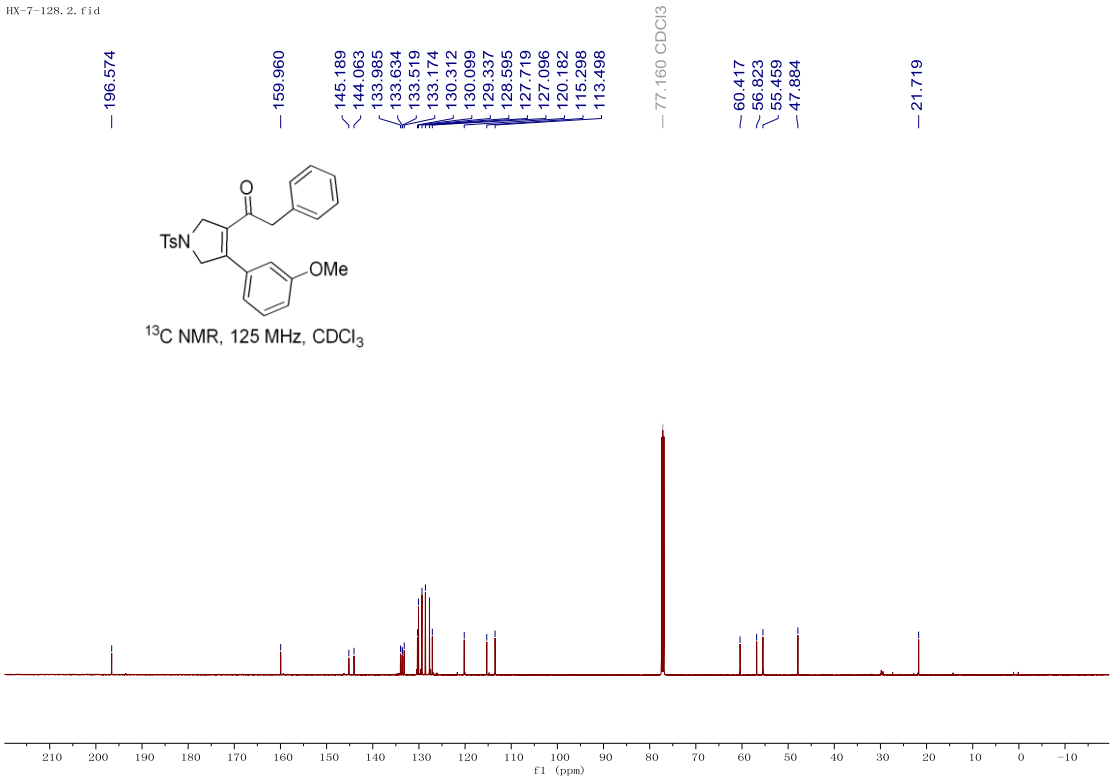
Compound **3l**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.13. 11.3 mg, 25% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74-7.71 (m, 2H), 7.34-7.30 (m, 3H), 7.23-7.19 (m, 3H), 6.95 (ddd, *J* = 8.5, 2.5, 1.0 Hz, 1H), 6.86-6.83 (m, 2H), 6.75 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.64 (dd, *J* = 2.5, 1.5 Hz, 1H), 4.50-4.49 (m, 2H), 4.44-4.42 (m, 2H), 3.77 (s, 3H), 3.51 (s, 2H), 2.44 (s, 3H).

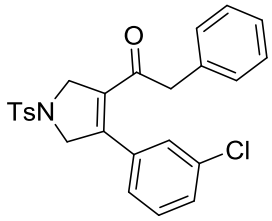
^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.6, 160.0, 145.2, 144.1, 134.0, 133.6, 133.5, 133.2, 130.3, 130.1, 129.3, 128.6, 127.7, 127.1, 120.2, 115.3, 113.5, 60.4, 56.8, 55.5, 47.9, 21.7.

HRMS (ESI) m/z: calcd for $[C_{26}H_{25}NO_4S+H]^+$ requires: 448.1577, found: 448.1575.





1-(4-(3-chlorophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3m)

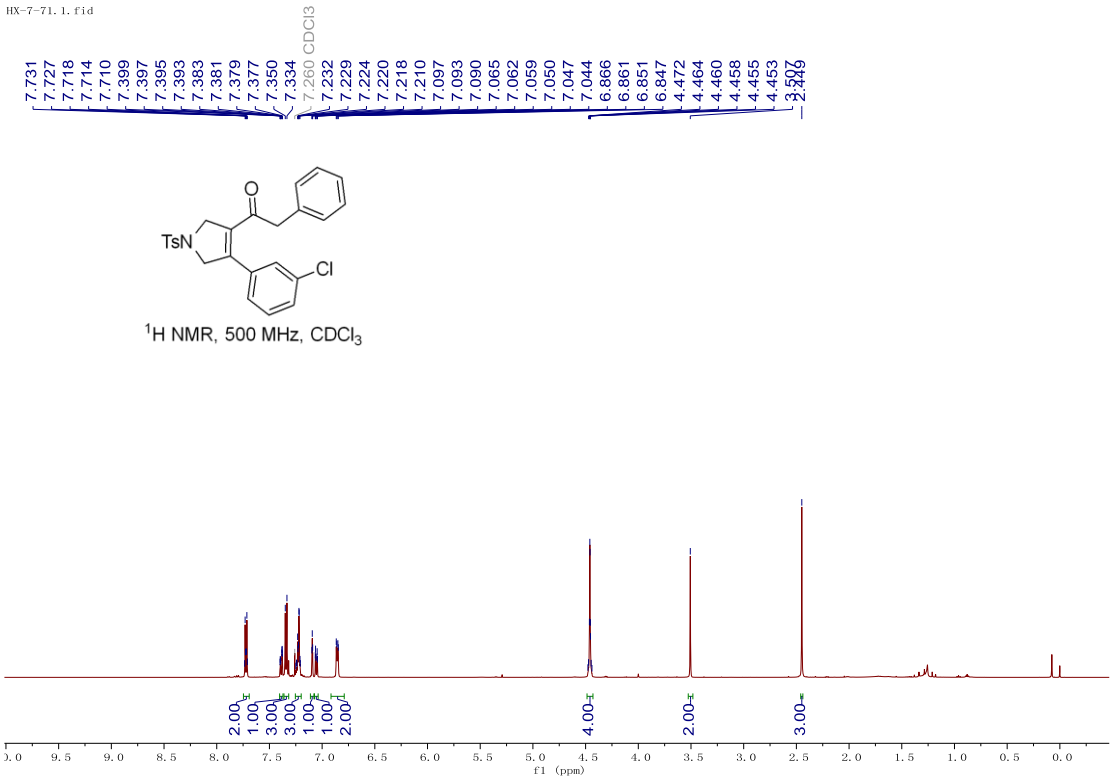


Compound **3m**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.28. 28.3 mg, 63% yield.

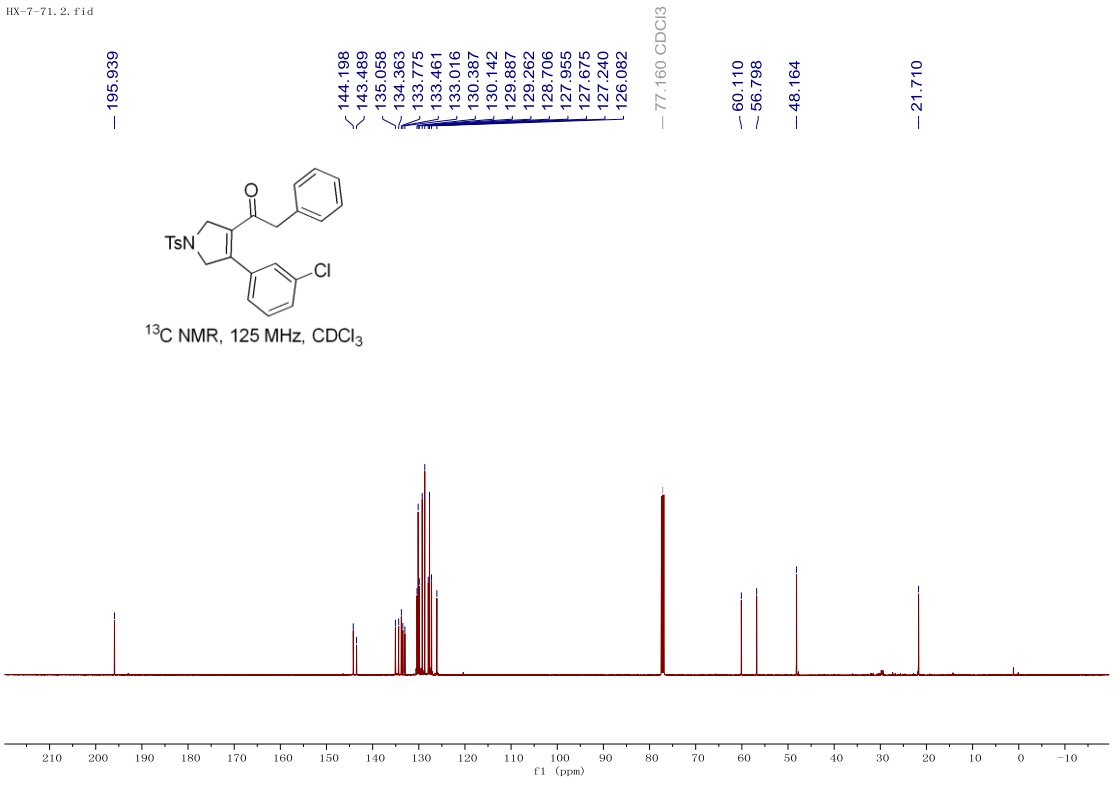
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (dt, J = 9.5, 2.0 Hz, 2H), 7.39 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H), 7.35-7.32 (m, 3H), 7.25-7.21 (m, 3H), 7.09 (t, J = 2.0 Hz, 1H), 7.05 (dt, J = 7.5, 1.5 Hz, 1H), 6.86 (dd, J = 7.5, 2.5 Hz, 2H), 4.48-4.44 (m, 4H), 3.51 (s, 2H), 2.45 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 195.9, 144.2, 143.5, 135.1, 134.4, 133.8, 133.5, 133.0, 130.4, 130.1, 129.9, 129.3, 128.7, 128.0, 127.7, 127.2, 126.1, 60.1, 56.8, 48.2, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{22}ClNO_3S+H]^+$ requires: 452.1082, found: 452.1088.

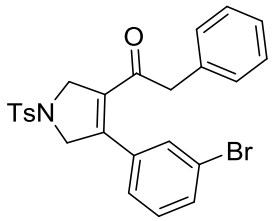


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

1-(4-(3-bromophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3n)

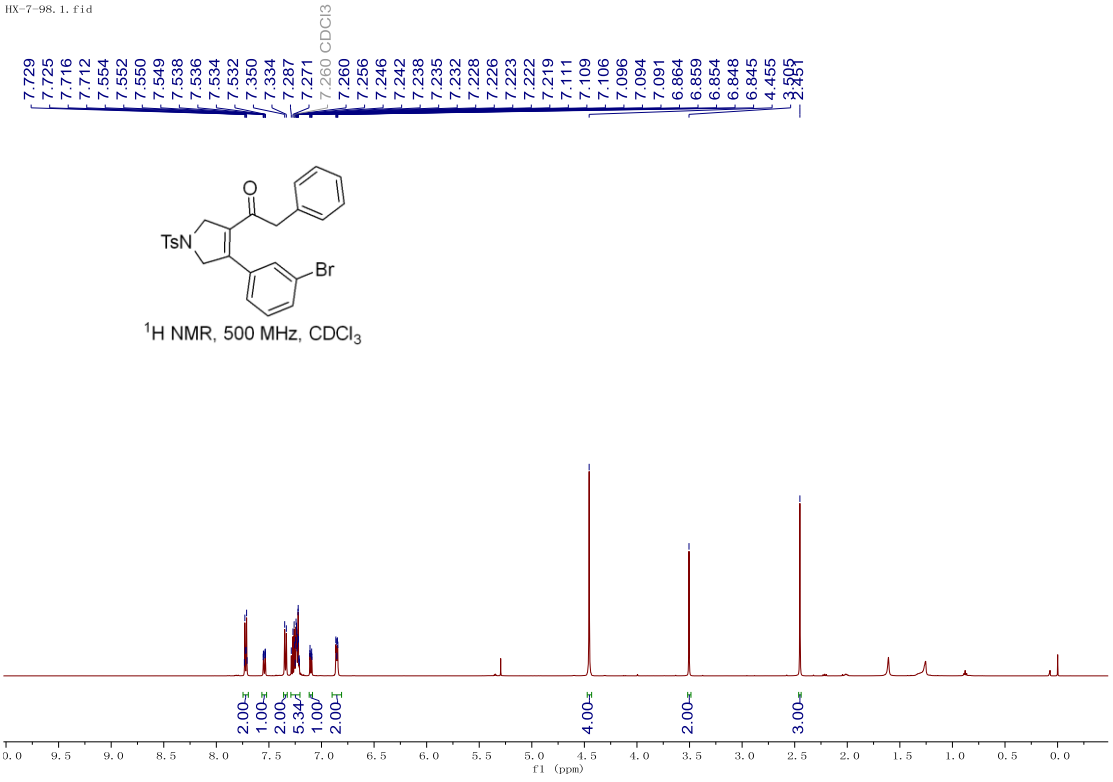


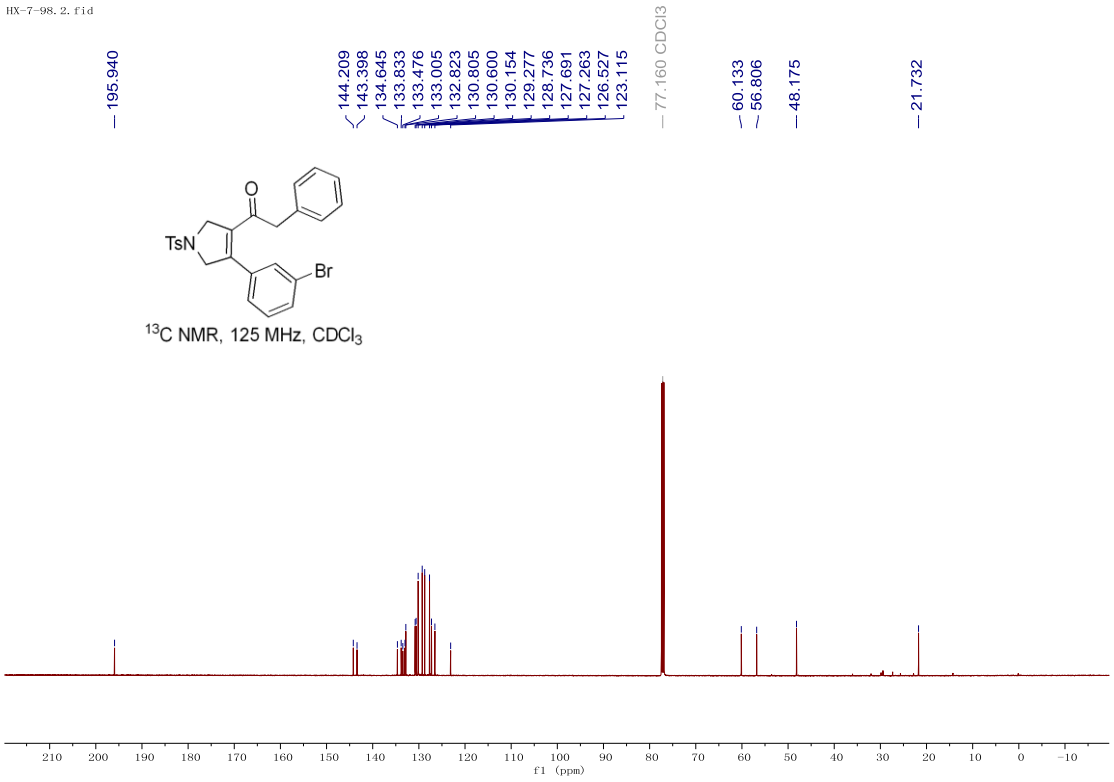
Compound **3n**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.18. 17.0 mg, 35% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (dt, J = 7.5, 2.0 Hz, 2H), 7.54 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.29-7.21 (m, 5H), 7.10 (dt, J = 7.5, 1.0 Hz, 1H), 6.86-6.85 (m, 2H), 4.46 (s, 4H), 3.51 (s, 2H), 2.45 (s, 3H).

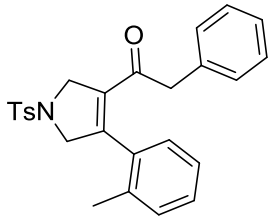
^{13}C NMR (125 MHz, Chloroform-*d*) δ 195.9, 144.2, 143.4, 134.6, 133.8, 133.5, 133.0, 132.8, 130.8, 130.6, 130.2, 129.3, 128.7, 127.7, 127.3, 126.5, 123.1, 60.1, 56.8, 48.2, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{22}BrNO_3S+H]^+$ requires: 496.0577, found: 496.0577.





2-phenyl-1-(4-(*o*-tolyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)ethan-1-one (3o)

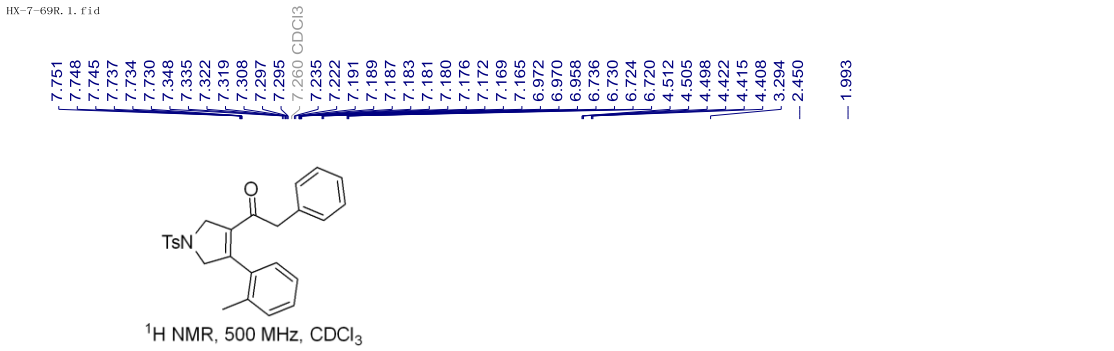


Compound **3o**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.12. 8.1 mg, 20% yield.

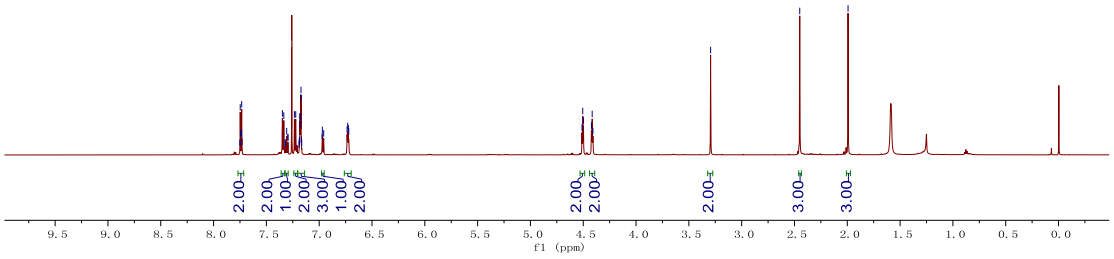
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (dt, J = 7.5, 1.5 Hz, 2H), 7.34 (d, J = 6.5 Hz, 2H), 7.32-7.30 (m, 1H), 7.23 (d, J = 6.5 Hz, 2H), 7.19-7.17 (m, 3H), 6.97-6.96 (m, 1H), 6.74-6.72 (m, 2H), 4.51 (t, J = 3.5 Hz, 2H), 4.42 (t, J = 3.5 Hz, 2H), 3.29 (s, 2H), 2.45 (s, 3H), 1.99 (s, 3H).

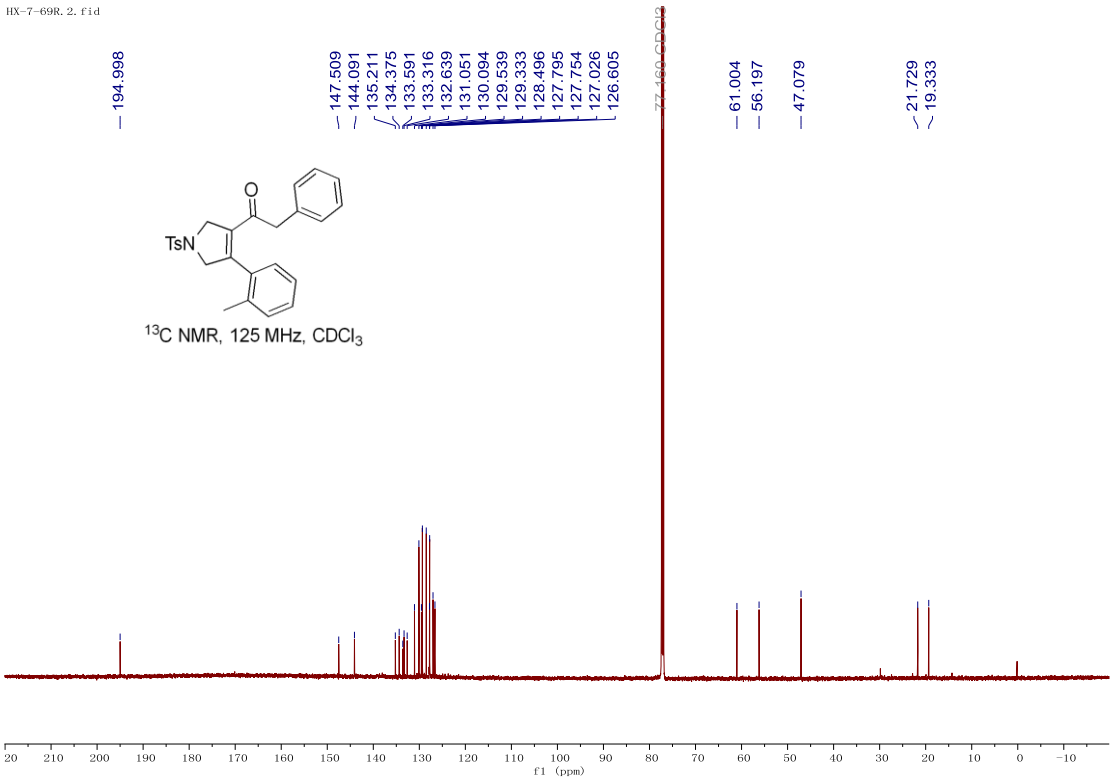
^{13}C NMR (125 MHz, Chloroform-*d*) δ 195.0, 147.5, 144.1, 135.2, 134.4, 133.6, 133.3, 132.6, 131.1, 130.1, 129.5, 129.3, 128.5, 127.80, 127.75, 127.0, 126.6, 61.0, 56.2, 47.1, 21.7, 19.3.

HRMS (ESI) m/z: calcd for $[C_{26}H_{25}NO_3S+H]^+$ requires: 432.1628, found: 432.1628.



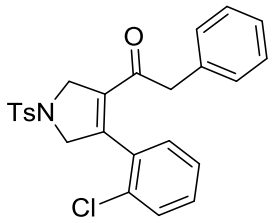
^{1}H NMR, 500 MHz, $CDCl_3$





^{13}C NMR, 125 MHz, $CDCl_3$

1-(4-(2-chlorophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3p)

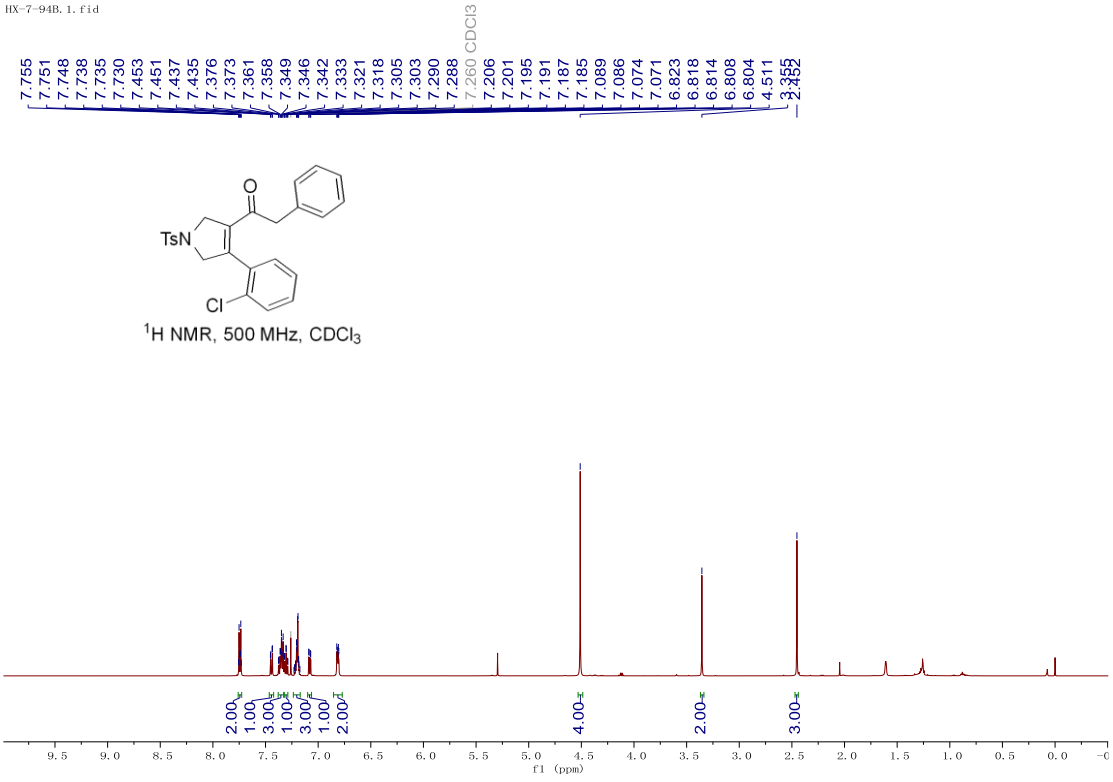


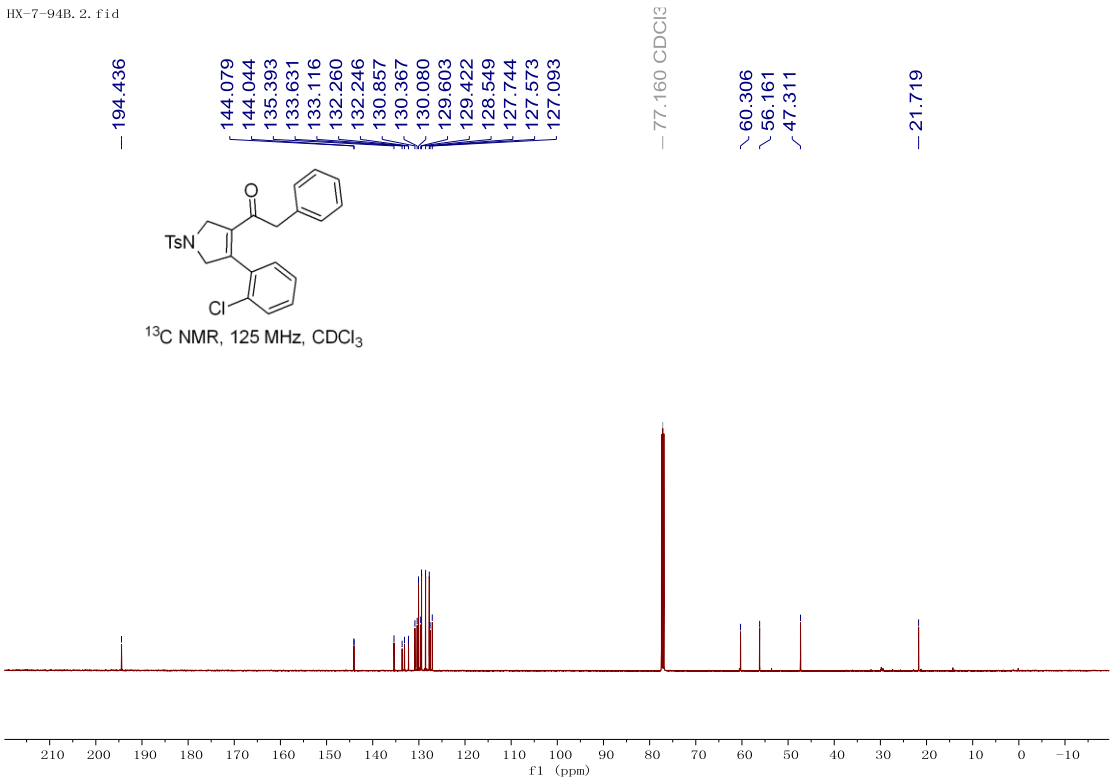
Compound **3p**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.18. 20.6 mg, 46% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.44 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.38-7.33 (m, 3H), 7.30 (td, *J* = 8.0, 1.0 Hz, 1H), 7.23-7.17 (m, 3H), 7.08 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.82-6.80 (m, 2H), 4.51 (s, 4H), 3.36 (s, 2H), 2.45 (s, 3H).

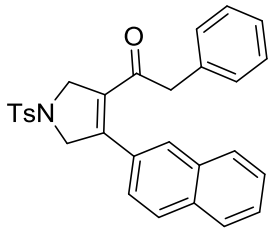
^{13}C NMR (125 MHz, Chloroform-*d*) δ 194.4, 144.1, 144.0, 135.4, 133.6, 133.1, 132.3, 132.2, 130.9, 130.4, 130.1, 129.6, 129.4, 128.5, 127.7, 127.6, 127.1, 60.3, 56.2, 47.3, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{22}ClNO_3S+H]^+$ requires: 452.1082, found: 452.1080.





1-(4-(naphthalen-2-yl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3q)

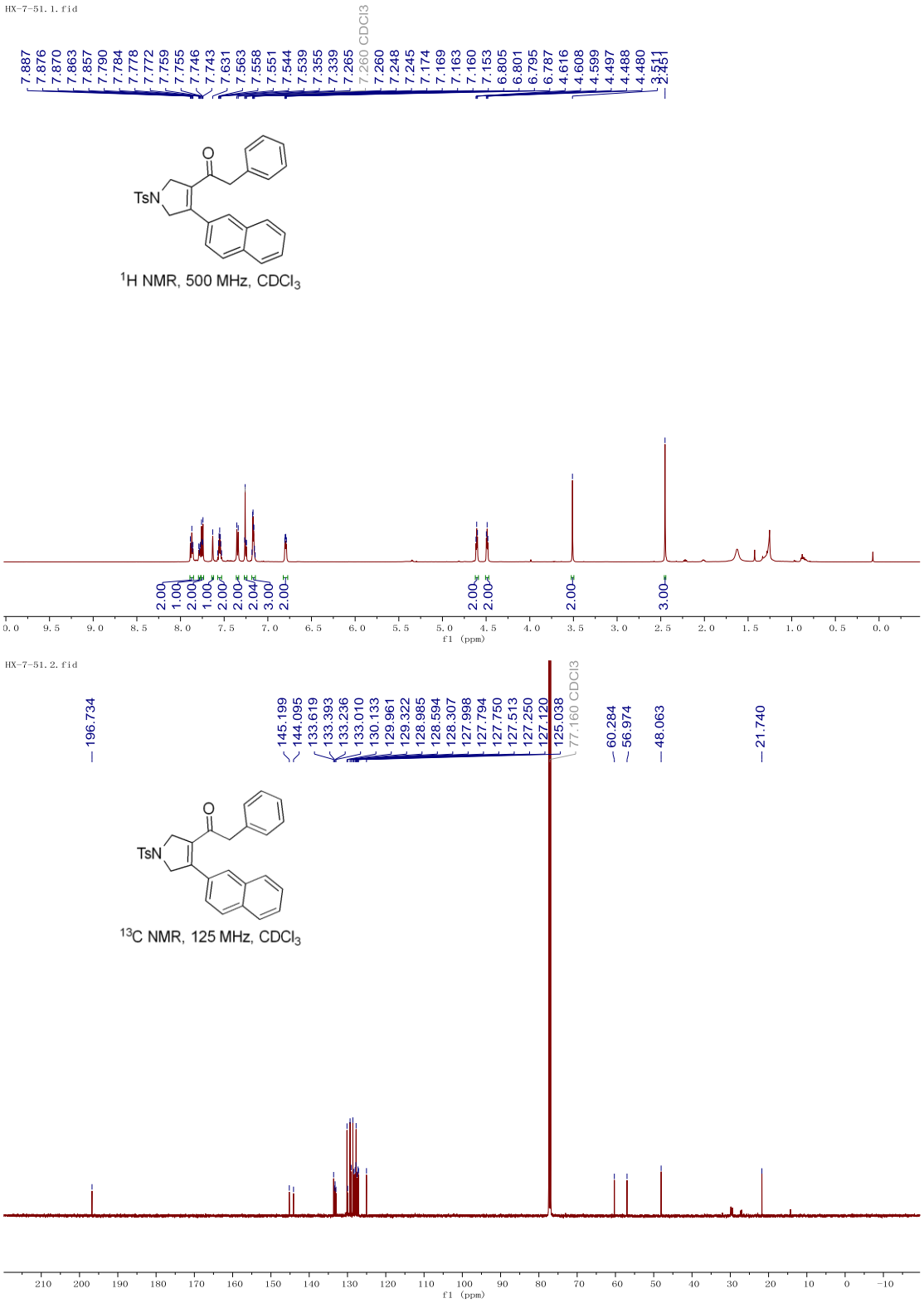


Compound **3q**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.22. 7.8 mg, 17% yield. m.p. 54-58 ºC.

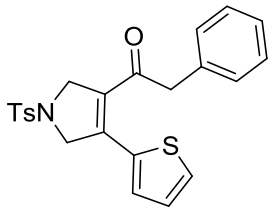
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89-7.86 (m, 2H), 7.79-7.77 (m, 1H), 7.76-7.74 (m, 2H), 7.63 (s, 1H), 7.58-7.53 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.27-7.25 (m, 1H), 7.18-7.15 (m, 3H), 6.81-6.79 (m, 2H), 4.61 (t, J = 4.0 Hz, 2H), 4.49 (t, J = 4.0 Hz, 2H), 3.51 (s, 2H), 2.45 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.7, 145.2, 144.1, 133.6, 133.4, 133.2, 133.0, 130.1, 130.0, 129.3, 129.0, 128.6, 128.3, 128.0, 127.79, 127.75, 127.5, 127.3, 127.1, 125.0, 60.3, 57.0, 48.1, 21.7.

HRMS (ESI) m/z: calcd for $[C_{29}H_{25}NO_3S+H]^+$ requires: 468.1628, found: 468.1642.



2-phenyl-1-(4-(thiophen-2-yl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)ethan-1-one (3r)

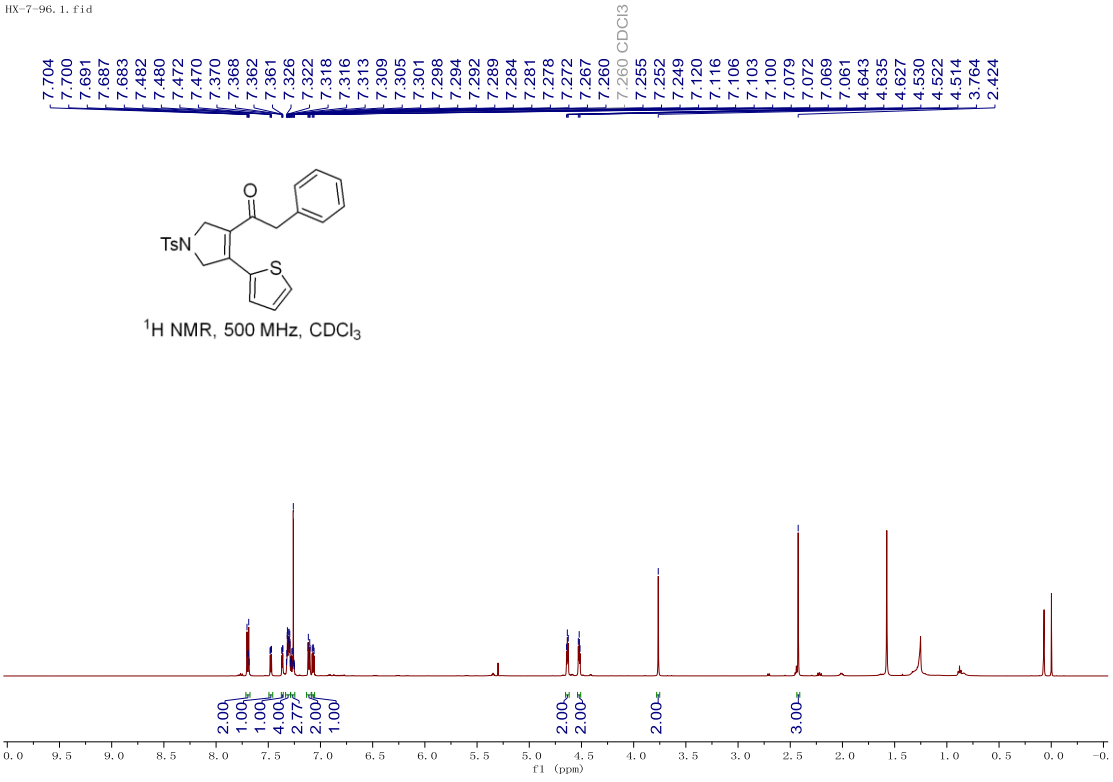


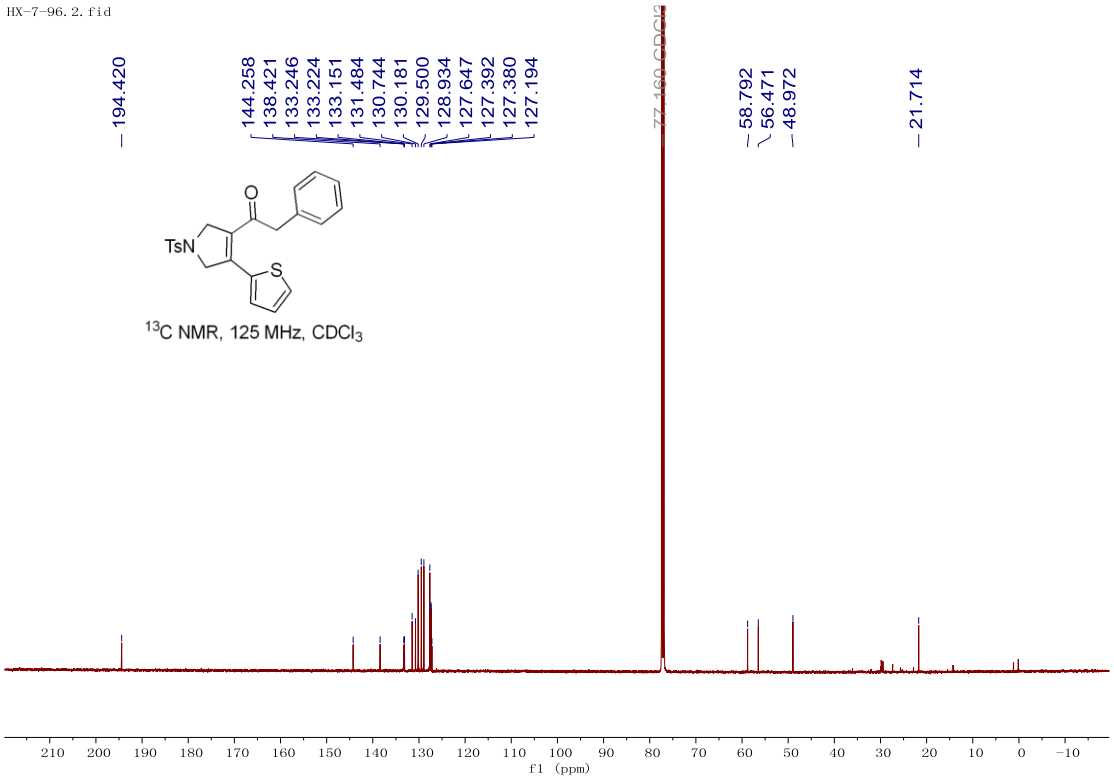
Compound **3r**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.17. 5.4 mg, 13% yield. m.p. 133-136 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70-7.68 (m, 2H), 7.48 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.37 (dd, *J* = 4.0, 1.0 Hz, 1H), 7.33-7.29 (m, 4H), 7.28-7.25 (m, 1H), 7.12-7.10 (m, 2H), 7.07 (dd, *J* = 5.0, 4.0 Hz, 1H), 4.64 (t, *J* = 4.0 Hz, 2H), 4.52 (t, *J* = 4.0 Hz, 2H), 3.76 (s, 2H), 2.42 (s, 3H).

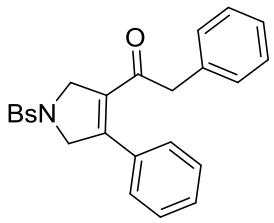
^{13}C NMR (125 MHz, Chloroform-*d*) δ 194.4, 144.3, 138.4, 133.25, 133.22, 133.15, 131.5, 130.7, 130.2, 129.5, 128.9, 127.6, 127.39, 127.38, 127.2, 58.8, 56.5, 49.0, 21.7.

HRMS (ESI) m/z: calcd for $[C_{23}H_{21}NO_3S_2+H]^+$ requires: 424.1036, found: 424.1036.





1-(1-((4-bromophenyl)sulfonyl)-4-phenyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3t)

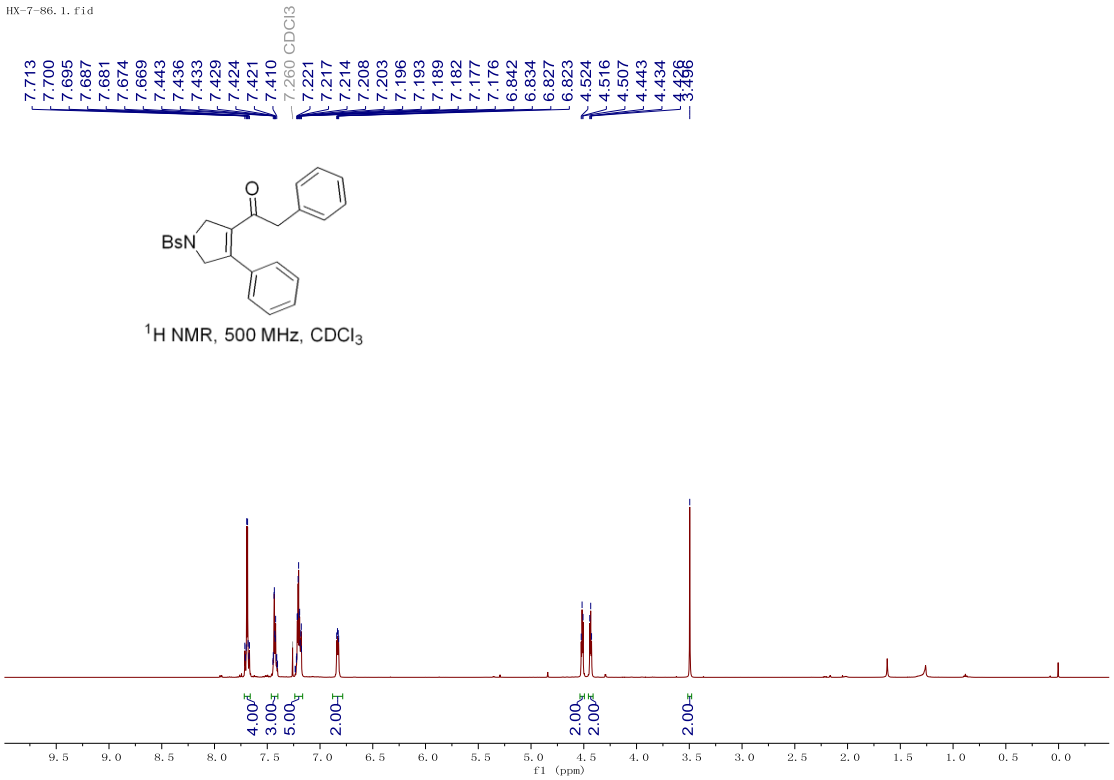


Compound **3t**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.33. 30.6 mg, 63% yield. m.p. 133-137 ºC.

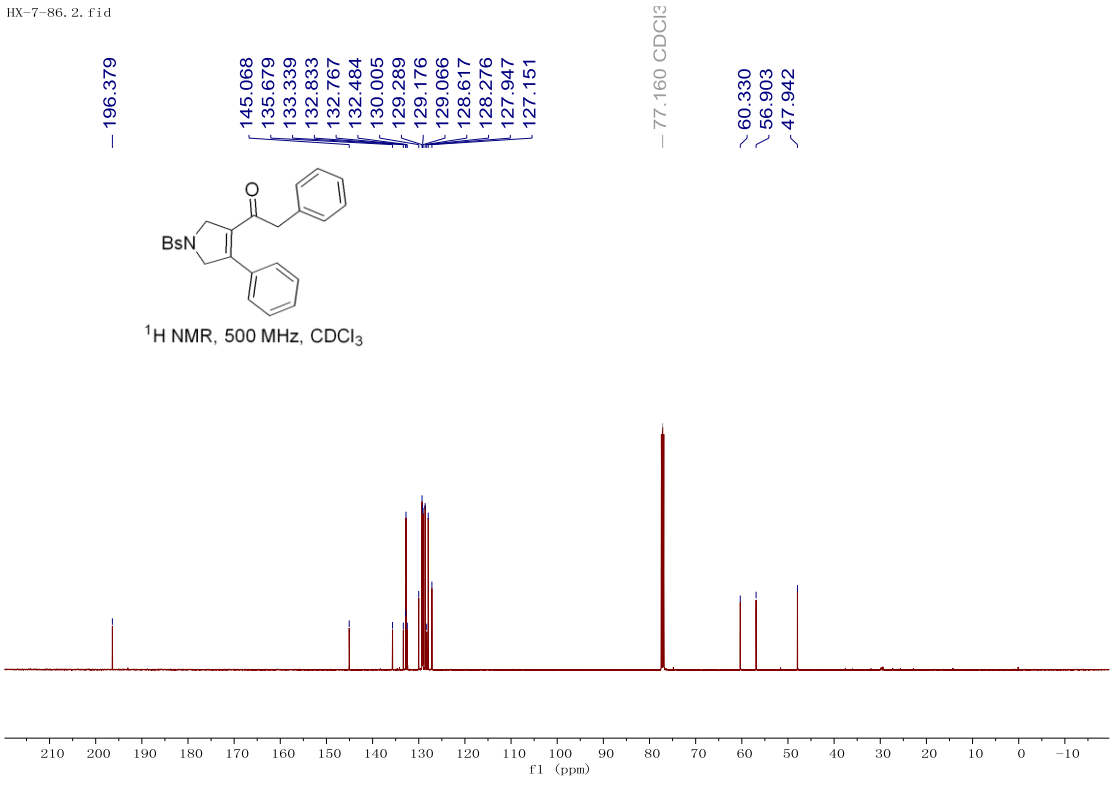
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71-7.67 (m, 4H), 7.45-7.40 (m, 3H), 7.24-7.18 (m, 5H), 6.84-6.82 (m, 2H), 4.52 (t, *J* = 4.0 Hz, 2H), 4.43 (t, *J* = 4.0 Hz, 2H), 3.50 (s, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.4, 145.1, 135.7, 133.3, 132.83, 132.77, 132.5, 130.0, 129.3, 129.2, 129.1, 128.6, 128.3, 127.9, 127.2, 60.3, 56.9, 47.9.

HRMS (ESI) m/z: calcd for $[C_{24}H_{20}BrNO_3S+H]^+$ requires: 482.0420, found: 482.0421.

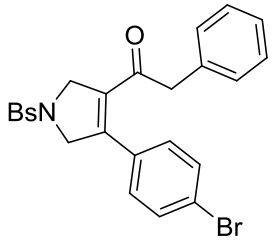


^{1}H NMR, 500 MHz, $CDCl_3$



^{1}H NMR, 500 MHz, $CDCl_3$

1-(4-(4-bromophenyl)-1-((4-bromophenyl)sulfonyl)-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3u)

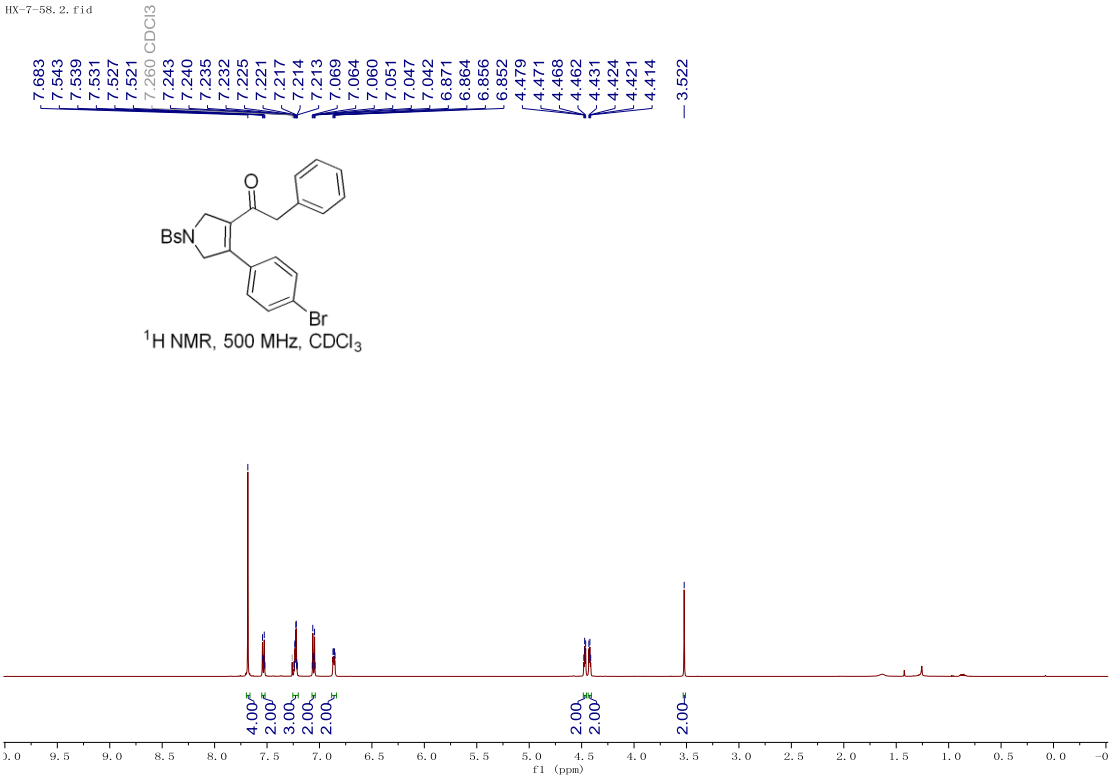


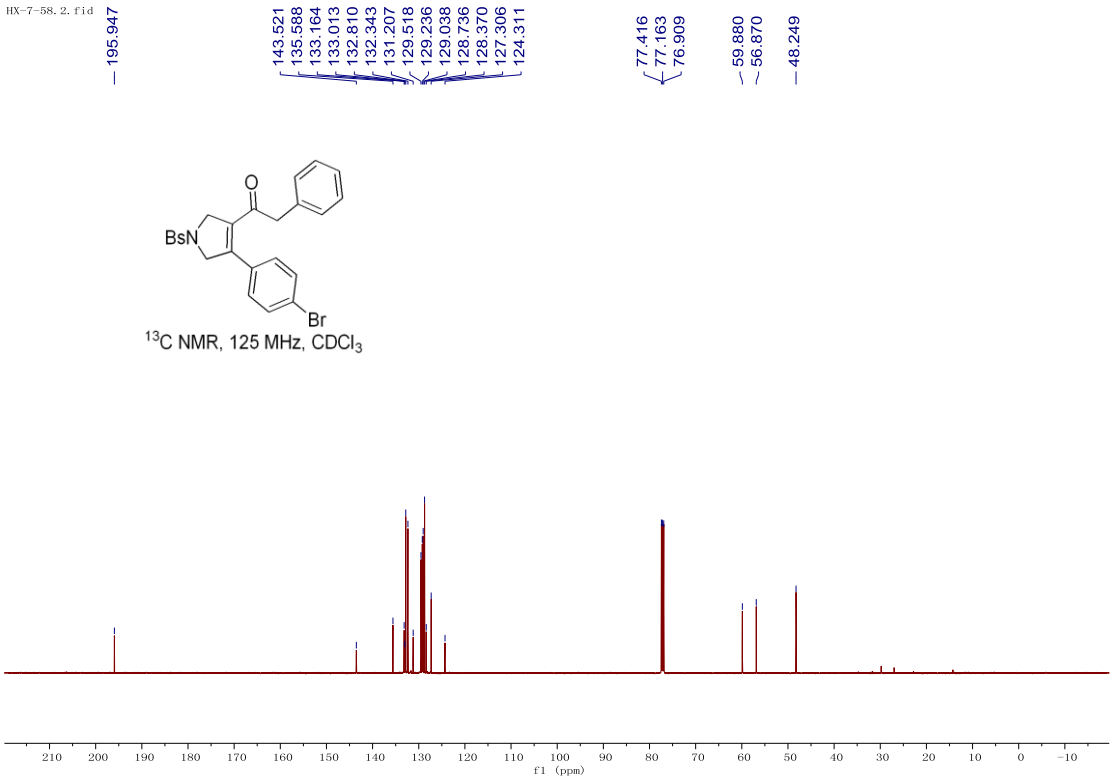
Compound **3u**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.32. 40.7 mg, 73% yield. m.p. 112-116 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (s, 4H), 7.54-7.52 (m, 2H), 7.24-7.21 (m, 3H), 7.06 (dt, J = 9.0, 2.0 Hz, 2H), 6.87-6.85 (m, 2H), 4.48-4.46 (m, 2H), 4.43-4.41 (m, 2H), 3.52 (s, 2H).

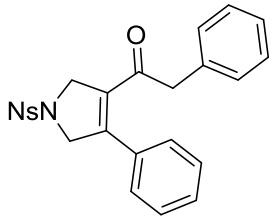
^{13}C NMR (125 MHz, Chloroform-*d*) δ 195.9, 143.5, 135.6, 133.2, 133.0, 132.8, 132.3, 131.2, 129.5, 129.2, 129.0, 128.7, 128.4, 127.3, 124.3, 59.9, 56.9, 48.2.

HRMS (ESI) m/z: calcd for $[C_{24}H_{19}Br_2NO_3S+H]^+$ requires: 559.9525, found: 559.9547.





1-(1-((4-nitrophenyl)sulfonyl)-4-phenyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3v)

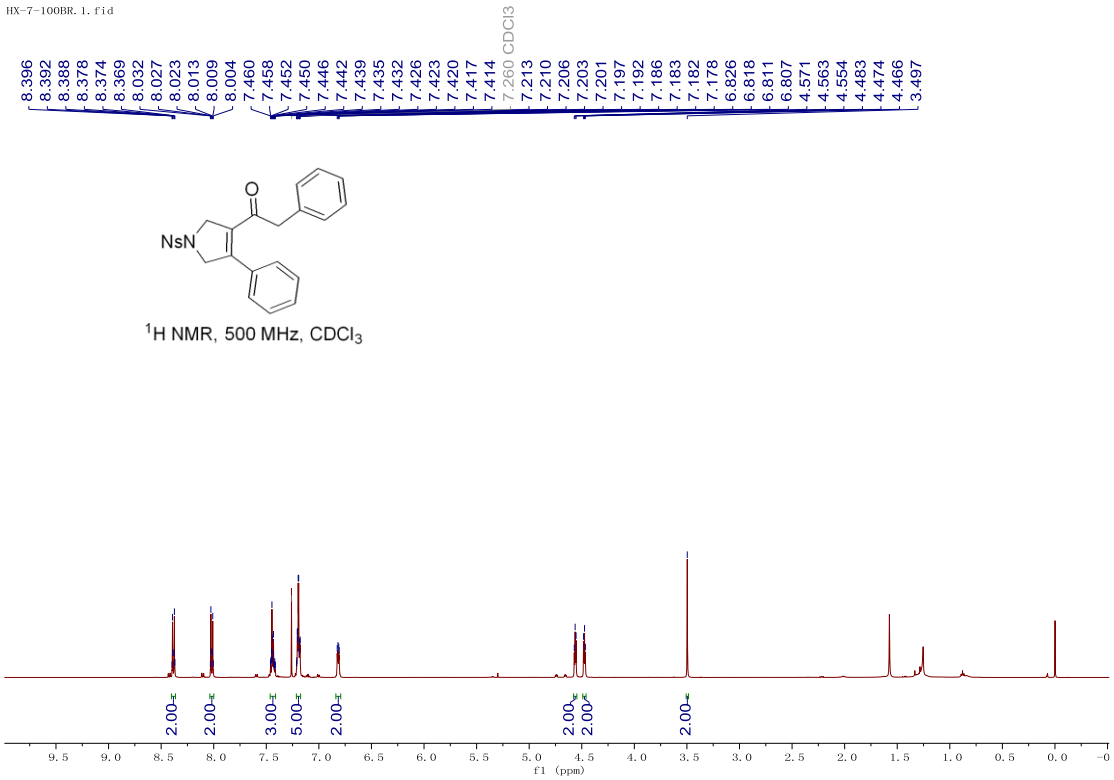


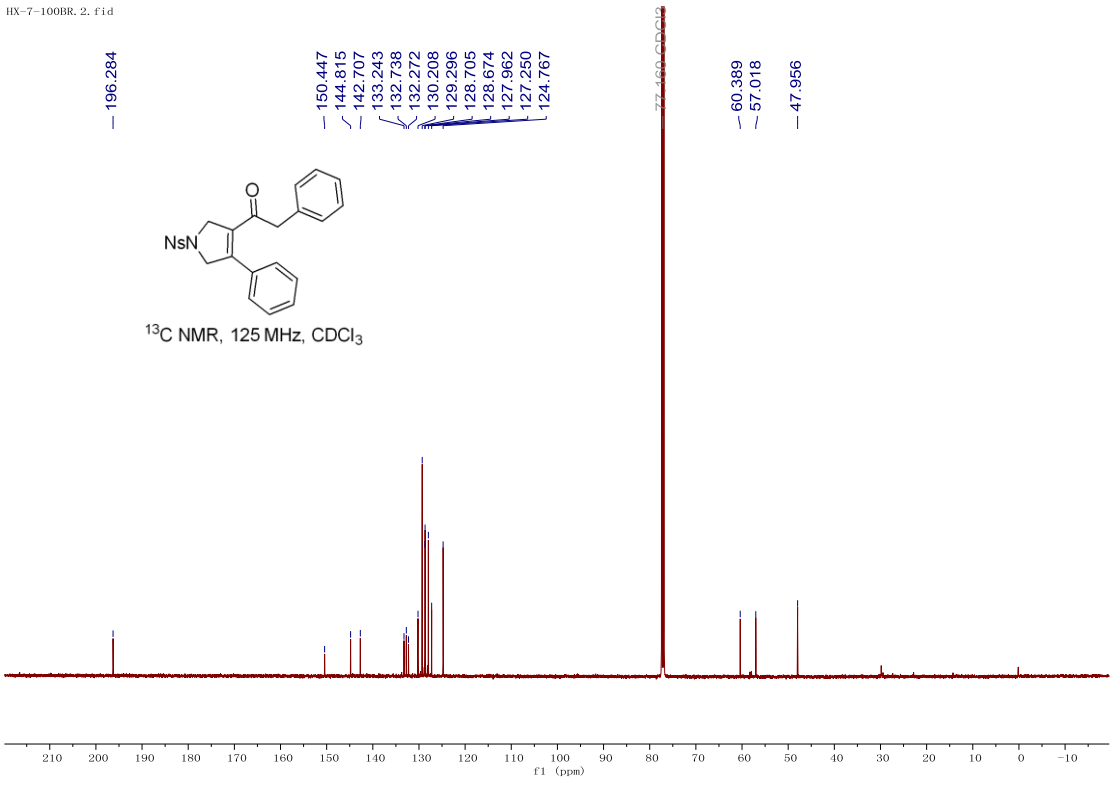
Compound **3v**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.17. 32.7 mg, 73% yield. m.p. 137-140 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.38 (dt, J = 9.0, 2.0 Hz, 2H), 8.02 (dt, J = 9.0, 2.0 Hz, 2H), 7.46-7.41 (m, 3H), 7.21-7.18 (m, 5H), 6.83-6.81 (m, 2H), 4.56 (t, J = 4.0 Hz, 2H), 4.47 (t, J = 4.0 Hz, 2H), 3.50 (s, 2H).

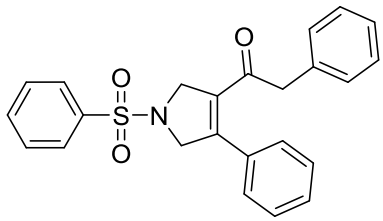
^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.3, 150.4, 144.8, 142.7, 133.2, 132.7, 132.3, 130.2, 129.3, 128.71, 128.67, 128.0, 127.3, 124.8, 60.4, 57.0, 48.0.

HRMS (ESI) m/z: calcd for $[C_{24}H_{20}N_2O_5S+H]^+$ requires: 449.1166, found: 449.1168.





2-phenyl-1-(4-phenyl-1-(phenylsulfonyl)-2,5-dihydro-1*H*-pyrrol-3-yl)ethan-1-one (3w)

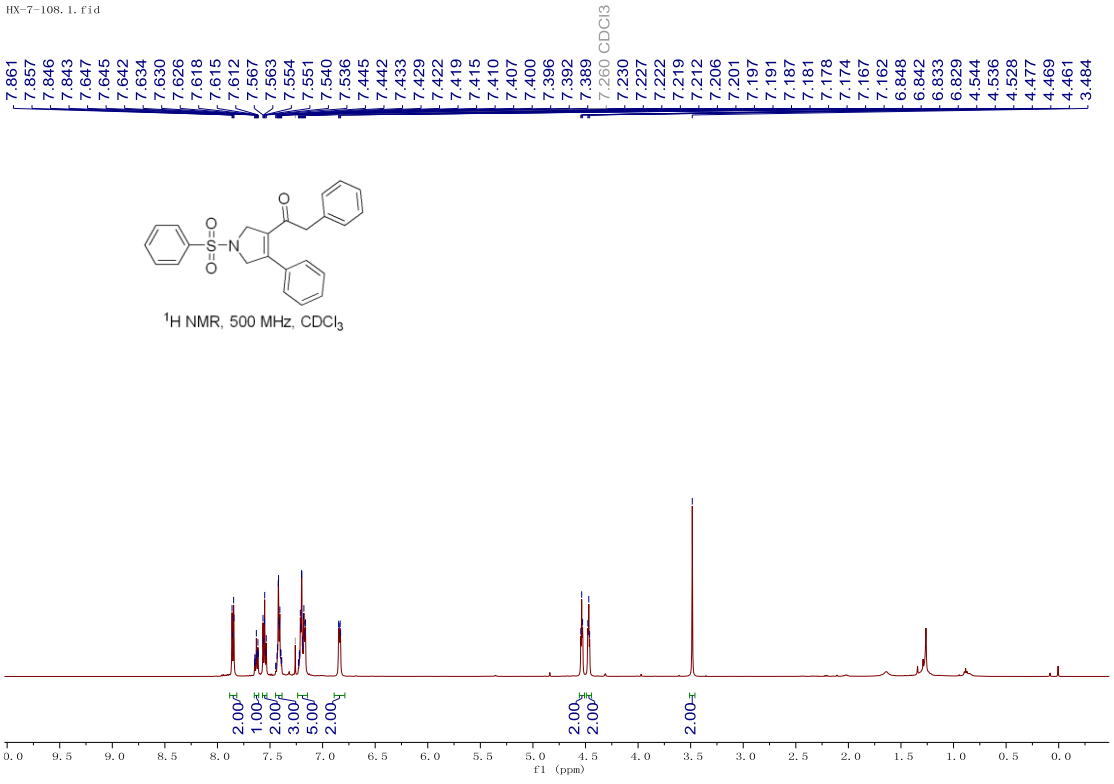


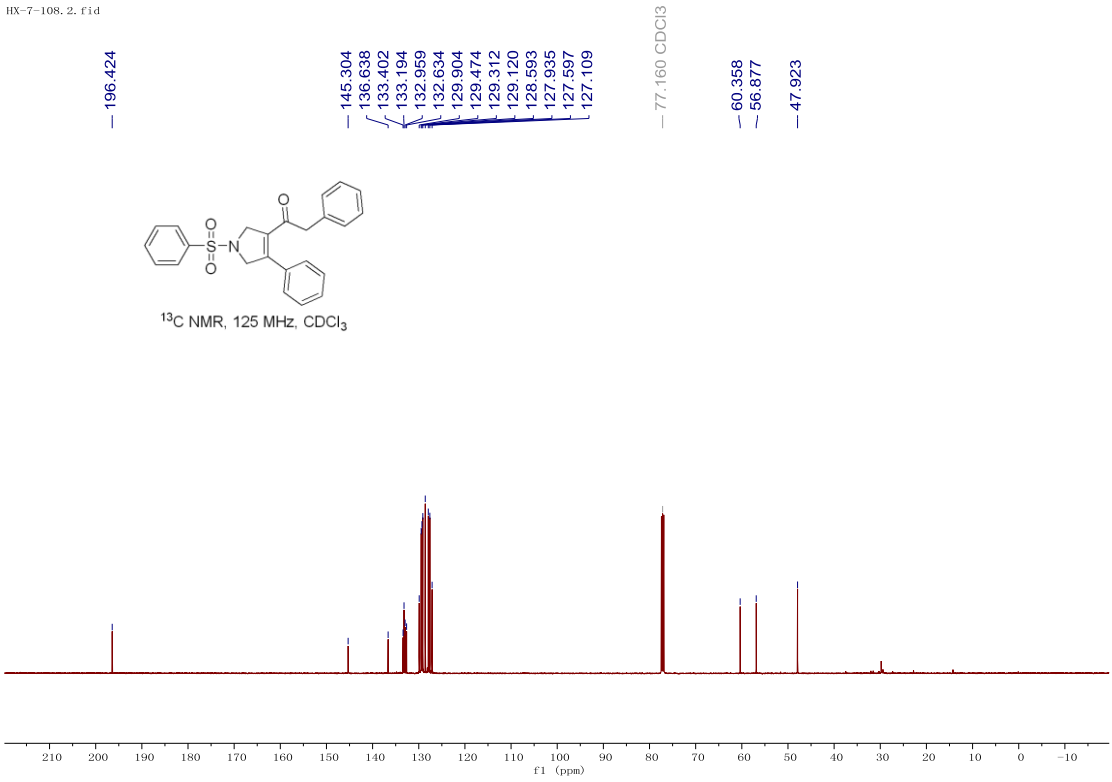
Compound **3w**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.18. 27.8 mg, 69% yield. m.p. 112-116 ºC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86-7.84 (m, 2H), 7.63 (tt, J = 7.5, 2.0 Hz, 1H), 7.57-7.54 (m, 2H), 7.45-7.39 (m, 3H), 7.23-7.16 (m, 5H), 6.84 (dd, J = 6.5, 2.0 Hz, 2H), 4.54 (t, J = 4.0 Hz, 2H), 4.47 (t, J = 4.0 Hz, 2H), 3.48 (s, 2H).

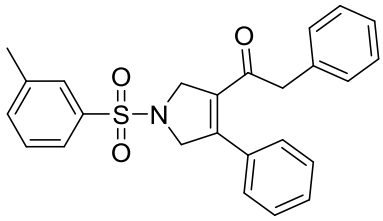
^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.4, 145.3, 136.6, 133.4, 133.2, 133.0, 132.6, 129.9, 129.5, 129.3, 129.1, 128.6, 127.9, 127.6, 127.1, 60.4, 56.9, 47.9.

HRMS (ESI) m/z: calcd for $[C_{24}H_{21}NO_3S+H]^+$ requires: 404.1315, found: 404.1313.





2-phenyl-1-(4-phenyl-1-(*m*-tolylsulfonyl)-2,5-dihydro-1*H*-pyrrol-3-yl)ethan-1-one (3x)

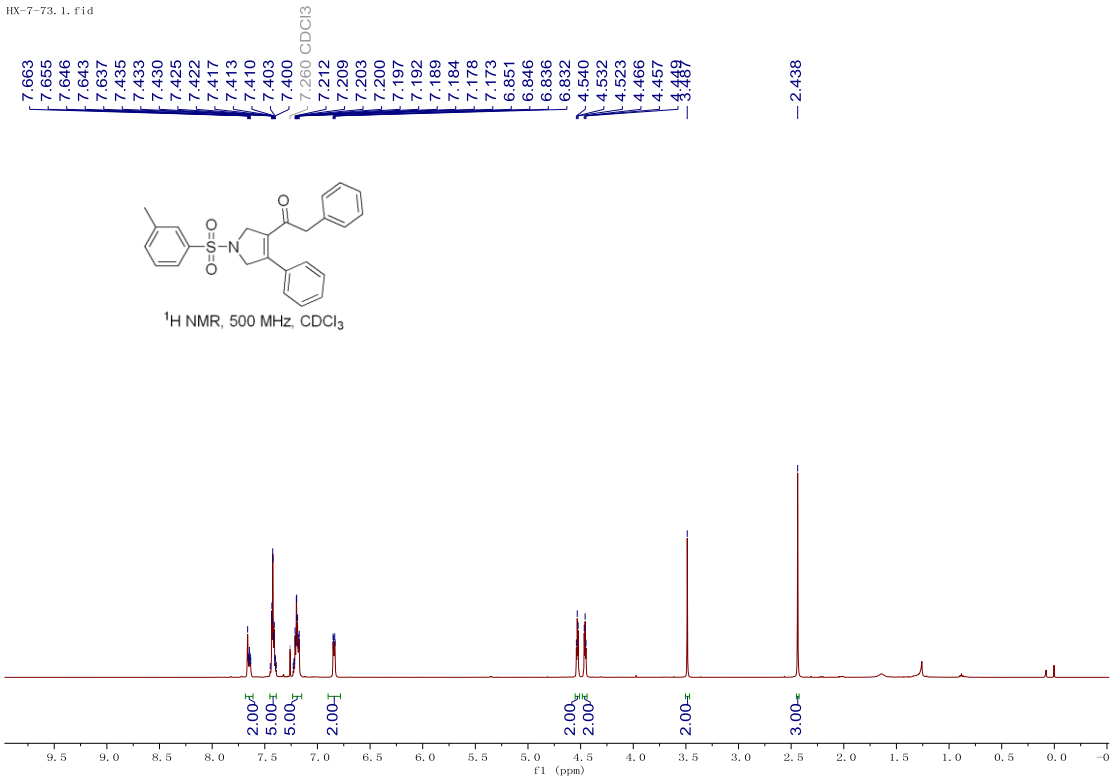


Compound **3x**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.21. 23.7 mg, 57% yield. m.p. 119-122 °C.

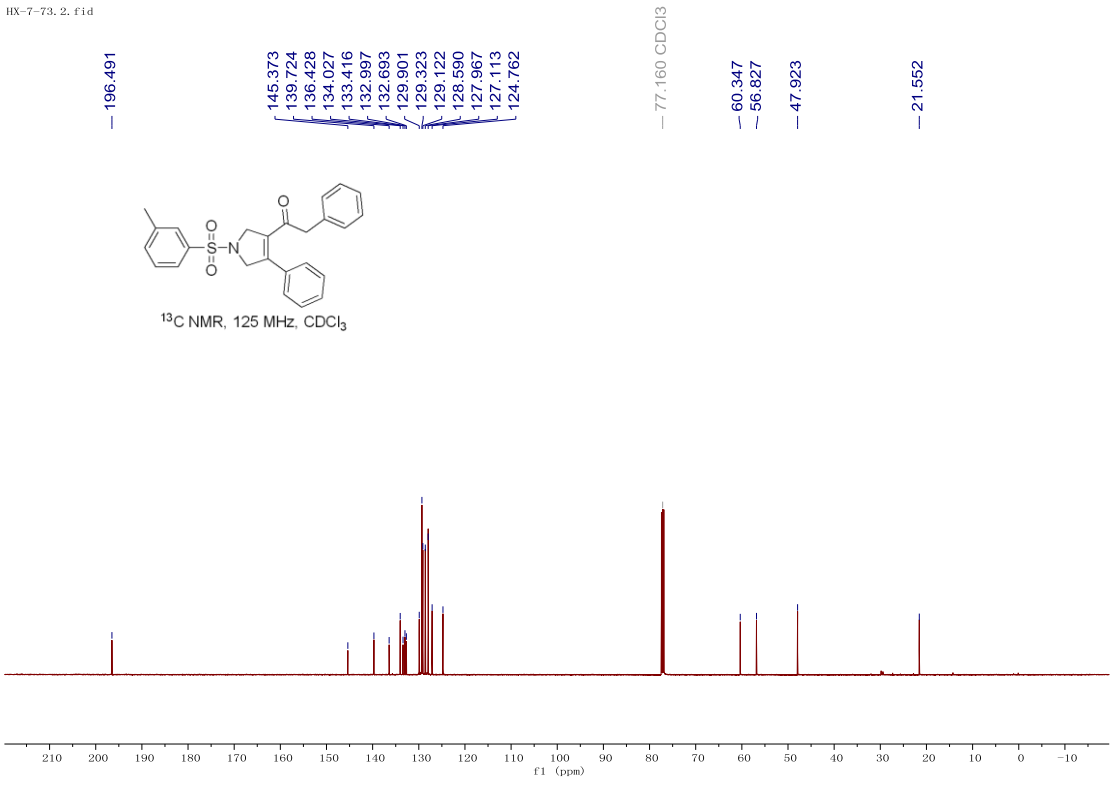
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66-7.63 (m, 2H), 7.45-7.39 (m, 5H), 7.23-7.17 (m, 5H), 6.84 (dd, *J* = 7.5, 2.0 Hz, 2H), 4.53 (t, *J* = 4.0 Hz, 2H), 4.46 (t, *J* = 4.0 Hz, 2H), 3.49 (s, 2H), 2.44 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.5, 145.4, 139.7, 136.4, 134.0, 133.4, 133.0, 132.7, 129.9, 129.3, 129.1, 128.6, 128.0, 127.1, 124.8, 60.3, 56.8, 47.9, 21.6.

HRMS (ESI) m/z: calcd for $[C_{25}H_{23}NO_3S+H]^+$ requires: 418.1471, found: 418.1476.

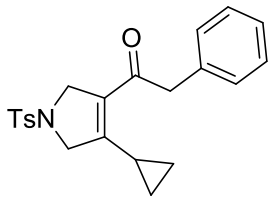


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

1-(4-cyclopropyl-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-2-phenylethan-1-one (3y)

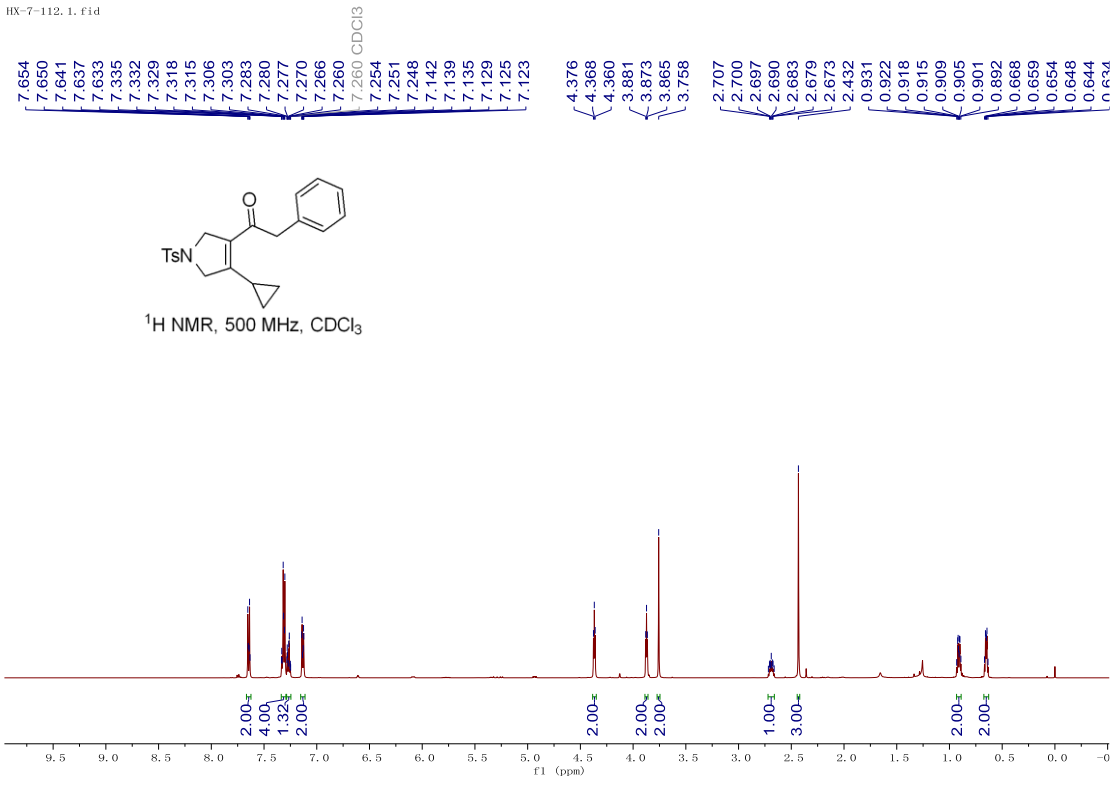


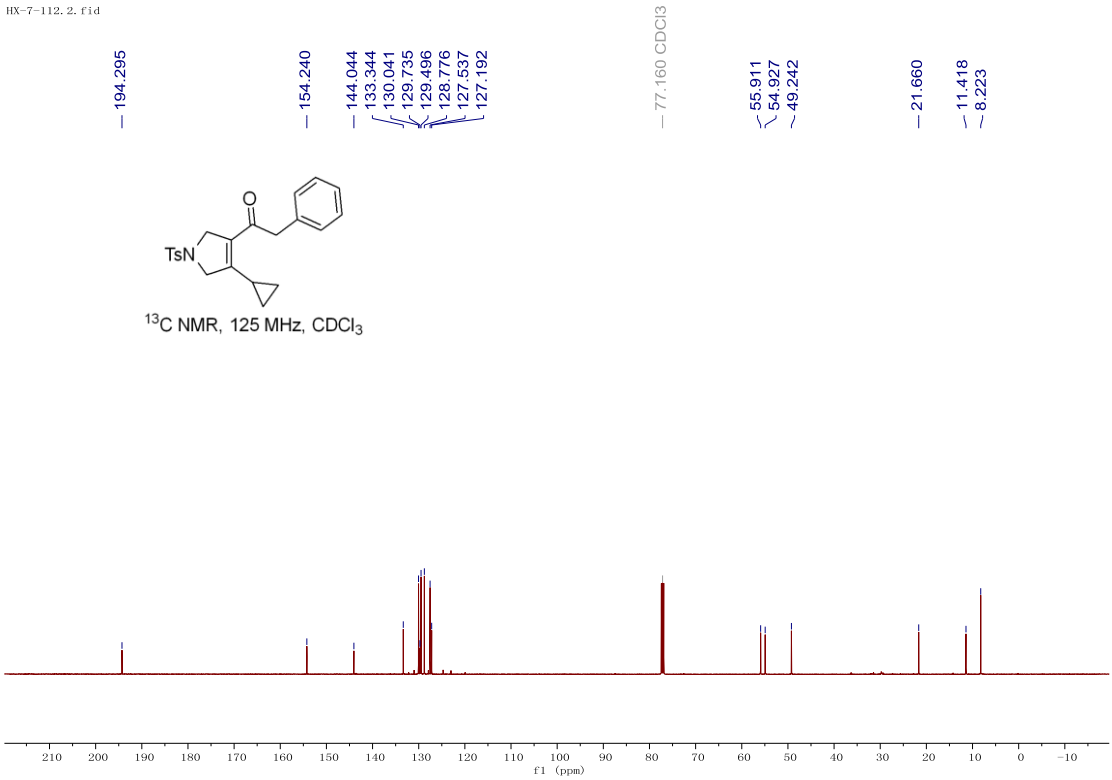
Compound **3y**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.27. 31.5 mg, 83% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65-7.63 (m, 2H), 7.34-7.30 (m, 4H), 7.28-7.25 (m, 1H), 7.14-7.12 (m, 2H), 4.37 (t, J = 4.0 Hz, 2H), 3.87 (t, J = 4.0 Hz, 2H), 3.76 (s, 2H), 2.72-2.66 (m, 1H), 2.43 (s, 3H), 0.93-0.89 (m, 2H), 0.67-0.63 (m, 2H).

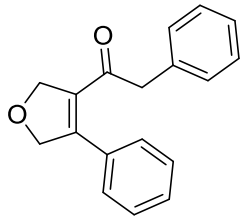
^{13}C NMR (125 MHz, Chloroform-*d*) δ 194.3, 154.2, 144.0, 133.3, 130.0, 129.7, 129.5, 128.8, 127.5, 127.2, 55.9, 54.9, 49.2, 21.7, 11.4, 8.2.

HRMS (ESI) m/z: calcd for $[C_{22}H_{23}NO_3S+H]^+$ requires: 382.1471, found: 382.1471.





2-phenyl-1-(4-phenyl-2,5-dihydrofuran-3-yl)ethan-1-one (8)

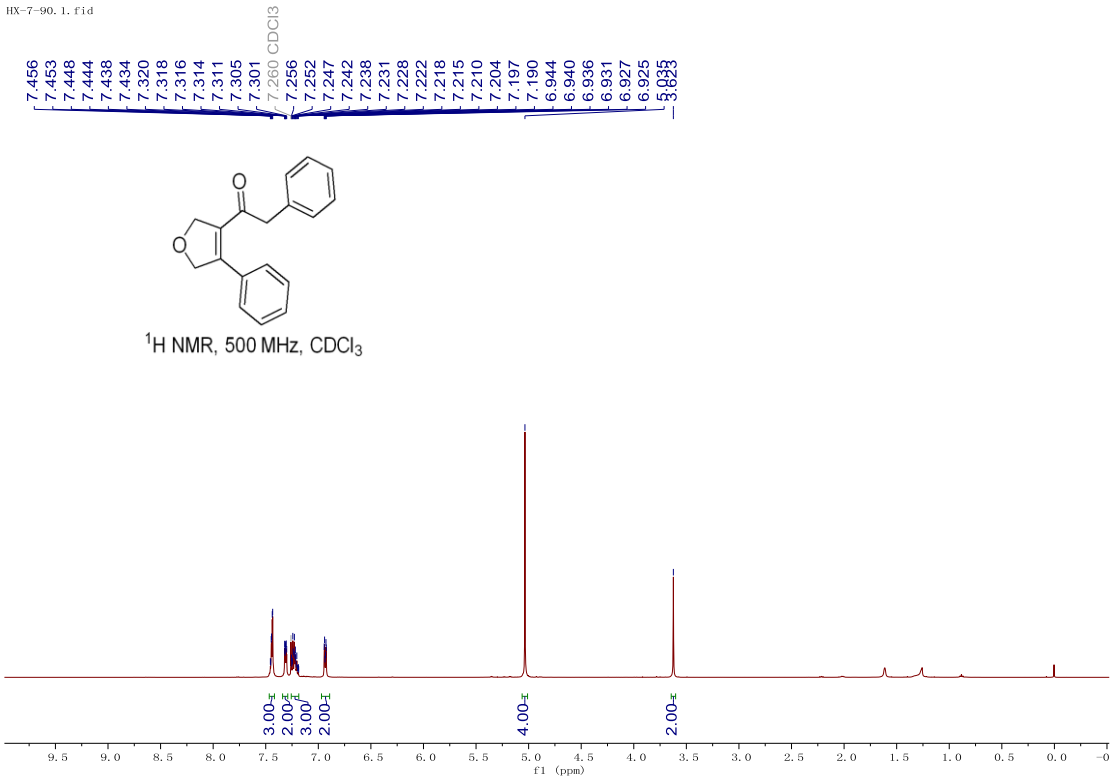


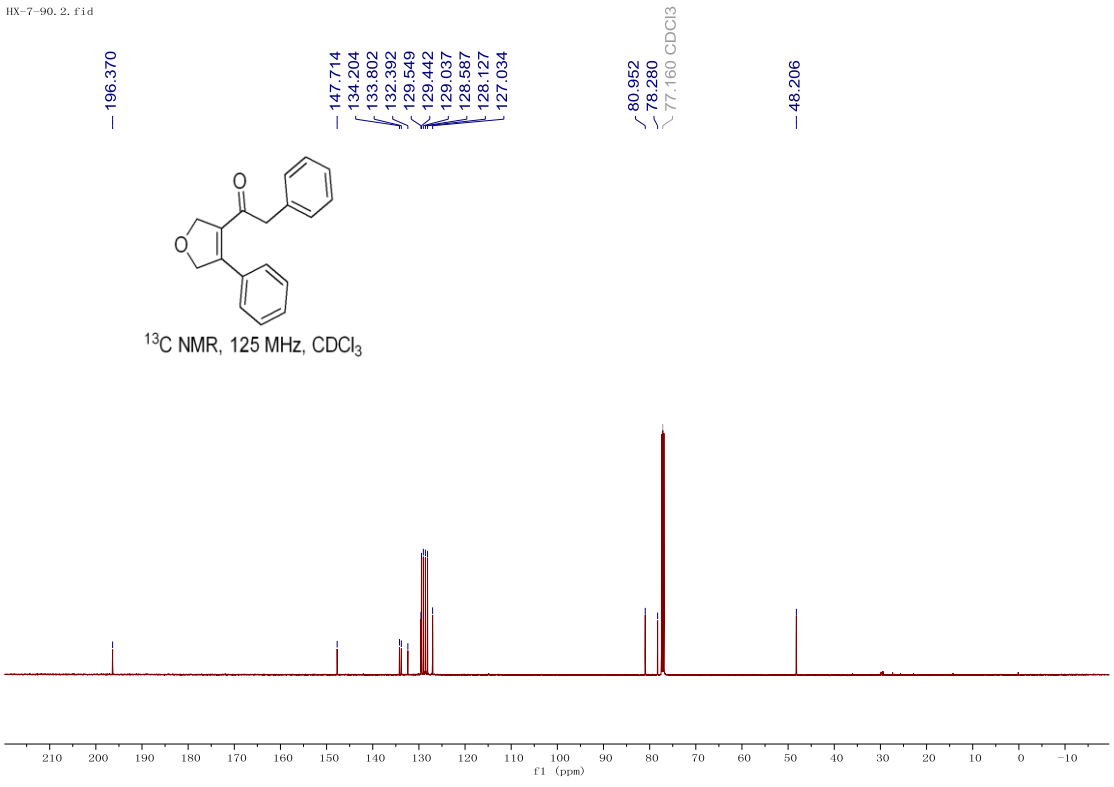
Compound **8**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.41. 12.4 mg, 47% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46-7.43 (m, 3H), 7.32-7.30 (m, 2H), 7.26-7.19 (m, 3H), 6.94-6.93 (m, 2H), 5.04 (s, 4H), 3.62 (s, 2H).

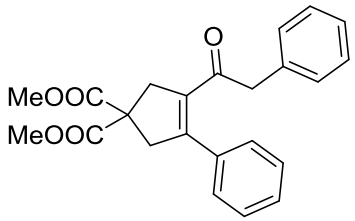
^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.4, 147.7, 134.2, 133.8, 132.4, 129.5, 129.4, 129.0, 128.6, 128.1, 127.0, 81.0, 78.3, 48.2.

HRMS (ESI) m/z: calcd for $[C_{18}H_{16}O_2+H]^+$ requires: 265.1223, found: 265.1224.





dimethyl 3-phenyl-4-(2-phenylacetyl)cyclopent-3-ene-1,1-dicarboxylate (9)

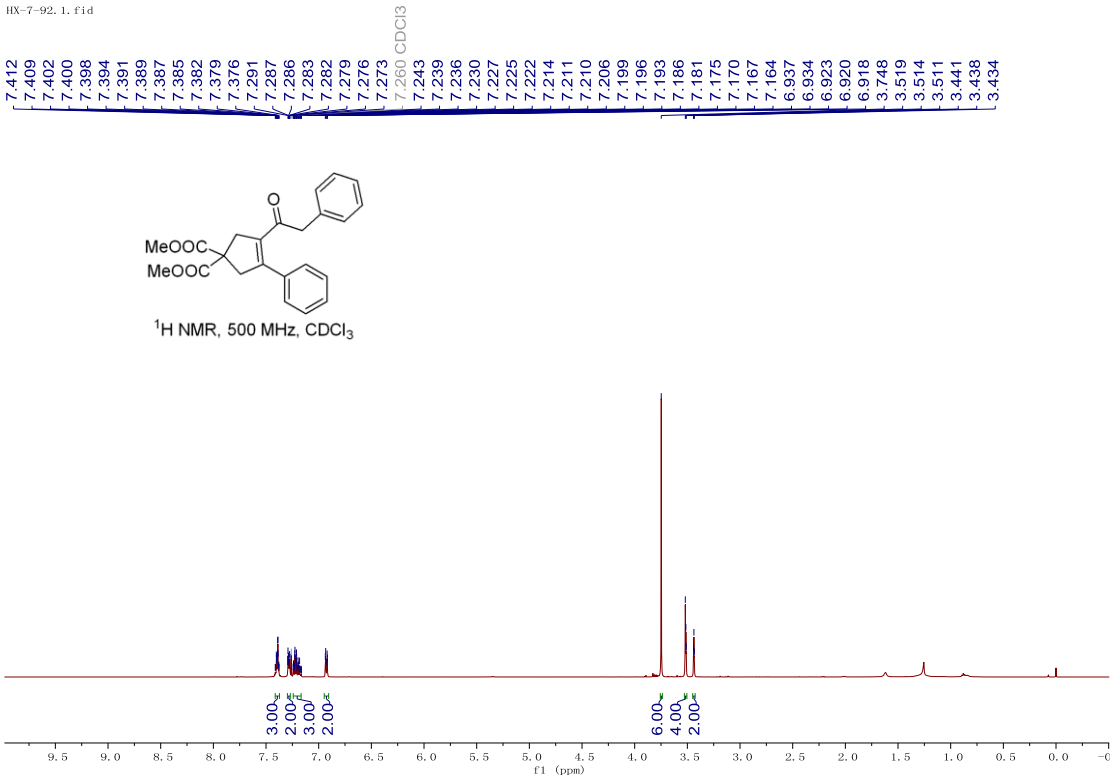


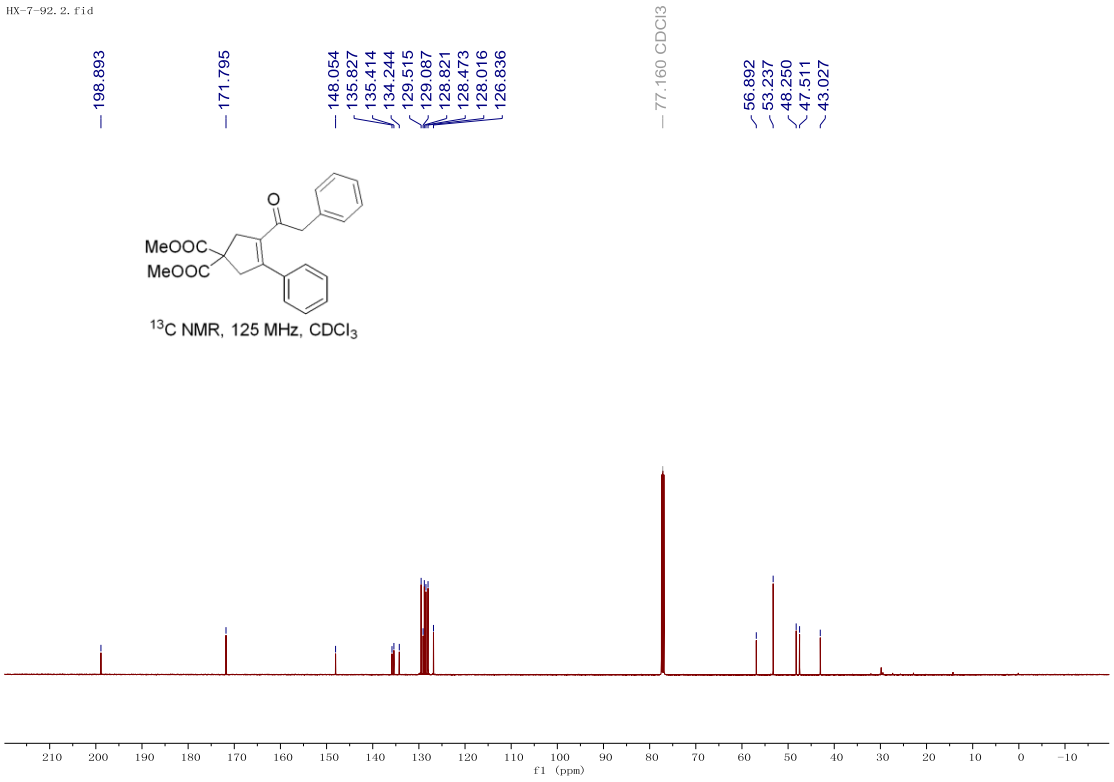
Compound **9**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.27. 15.5 mg, 41% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41-7.38 (m, 3H), 7.29-7.27 (m, 2H), 7.24-7.16 (m, 3H), 6.94-6.92 (m, 2H), 3.75 (s, 6H), 3.52-3.51 (m, 4H), 3.44 (t, J = 2.0 Hz, 2H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 198.9, 171.8, 148.1, 135.8, 135.4, 134.2, 129.5, 129.1, 128.8, 128.5, 128.0, 126.8, 56.9, 53.2, 48.3, 47.5, 43.0.

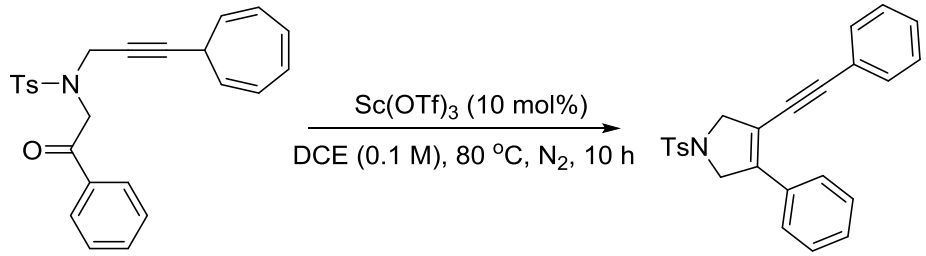
HRMS (ESI) m/z: calcd for $[C_{23}H_{22}O_5+H]^+$ requires: 379.1540, found: 379.1541.




HX-7-92.2.fid
198.893
171.795
148.054
135.827
135.414
134.244
129.515
129.087
128.821
128.473
128.016
126.836
77.160 CDCl3
56.892
53.237
48.250
47.511
43.027
O
MeOOC
MeOOC
13C NMR, 125 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

6. Gram scale experiment of 2a and 3a

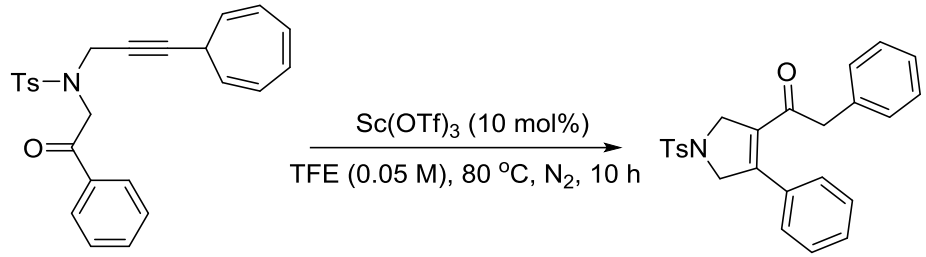
6.1 Gram scale experiment of 2a



1a, 1.044 g **2a,** 0.5572 g, 56% yield

Under N_2 atmosphere, dry 1,2-dichloroethane (DCE) (25 mL, 0.1 M) was added to a mixture of **1a** (1.044 g, 2.5 mmol), $Sc(OTf)_3$ (123.2 mg, 0.25 mmol). The reaction system was stirred at 80 °C for 10 hours in oil bath until **1a** was completely consumed by TLC monitoring. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate, 8/1) to give the product **2a** (0.5572 g, 56% yield) as a yellow solid.

6.2 Gram scale experiment of 3a

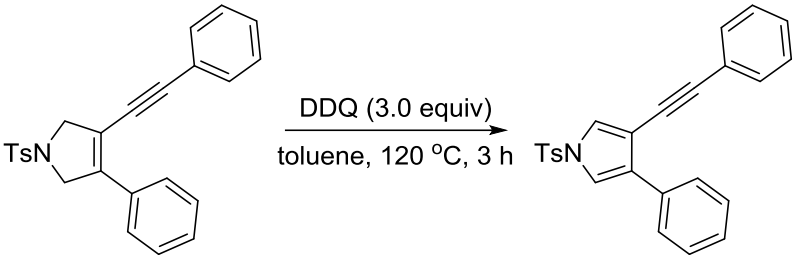


1a, 1.047 g **3a,** 0.6316 g, 60% yield

Under N_2 atmosphere, 2,2,2-Trifluoroethanol (TFE) (50 mL, 0.05 M) was added to a mixture of **1a** (1.047 g, 2.5 mmol), $Sc(OTf)_3$ (123.4 mg, 0.25 mmol). The reaction system was stirred at 80 °C for 10 hours in oil bath until **1a** was completely consumed by TLC monitoring. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate, 8/1) to give the product **3a** (0.6316 g, 60% yield) as a yellow solid.

7. Product transformations

3-phenyl-4-(phenylethynyl)-1-tosyl-1*H*-pyrrole (10)



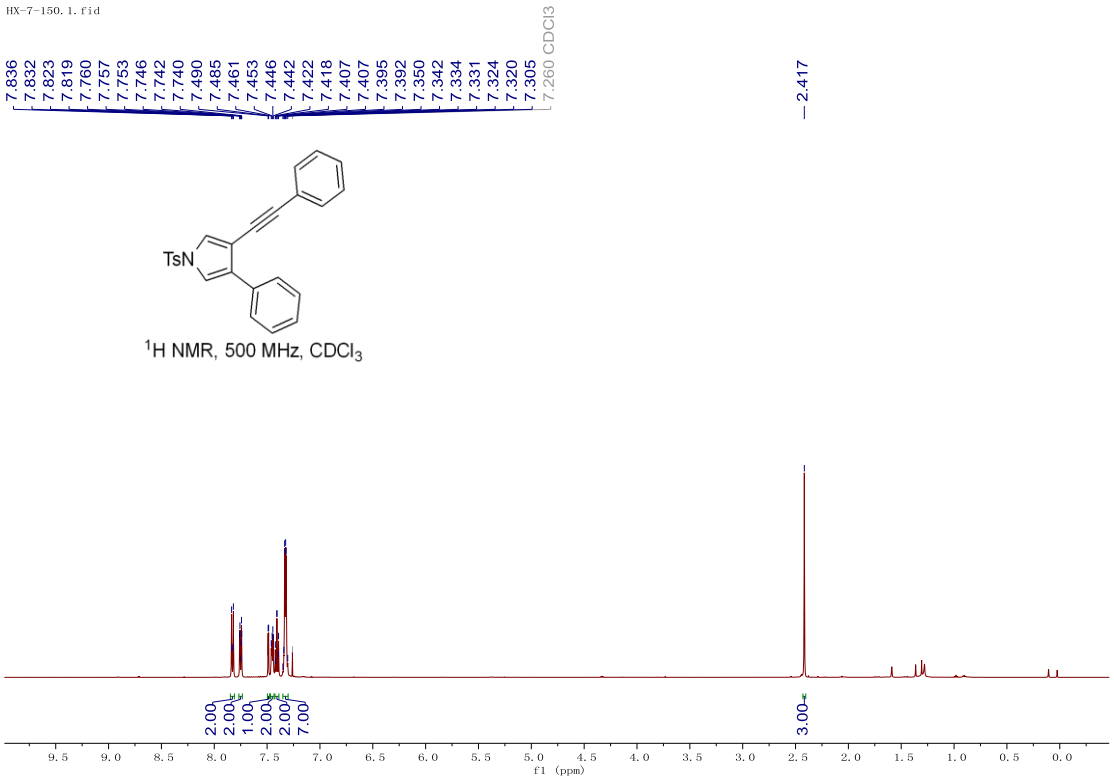
2a, 40.1 mg, 0.1 mmol **10,** 33.4 mg, 84% yield

Under air atmosphere, toluene (2 mL, 0.05 M) was added to a mixture of **2a** (40.1 mg, 0.1 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 68.3 mg, 0.3 mmol) in a dried reaction tube. The reaction system was stirred at 120 °C for 3 hours in parallel reactor until **2a** was completely consumed by TLC monitoring. Then the system was filtered through celite, and washed with ethyl acetate. The mixture was concentrated and purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 8/1) to give the product **10** (33.4 mg, 84% yield) as a yellow solid. Compound **10**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.40. 33.4 mg, 84% yield. m.p. 107-111 °C.

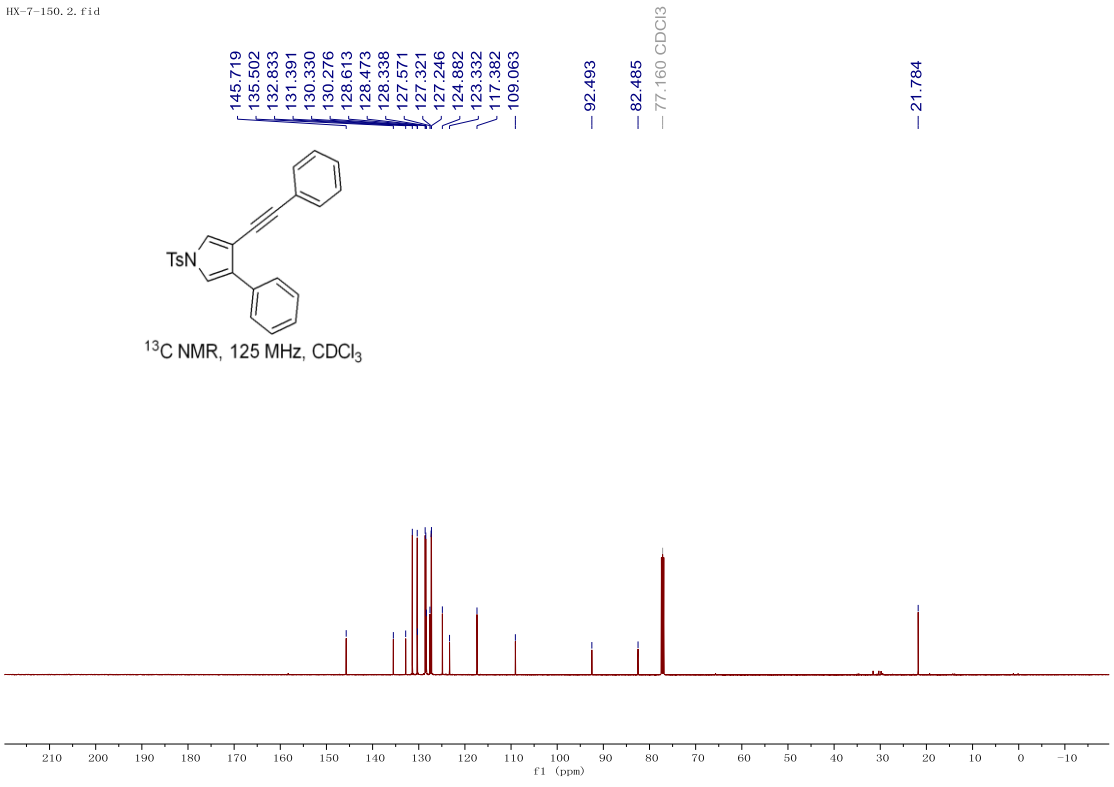
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84-7.82 (m, 2H), 7.76-7.74 (m, 2H), 7.49 (d, *J* = 2.5 Hz, 1H), 7.46-7.44 (m, 2H), 7.42-7.39 (m, 2H), 7.35-7.31 (m, 7H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 145.7, 135.5, 132.8, 131.4, 130.33, 130.28, 128.6, 128.5, 128.3, 127.6, 127.3, 127.2, 124.9, 123.3, 117.4, 109.1, 92.5, 82.5, 21.8.

HRMS (ESI) m/z: calcd for $[C_{25}H_{19}NO_2S+H]^+$ requires: 398.1209, found: 398.1212.

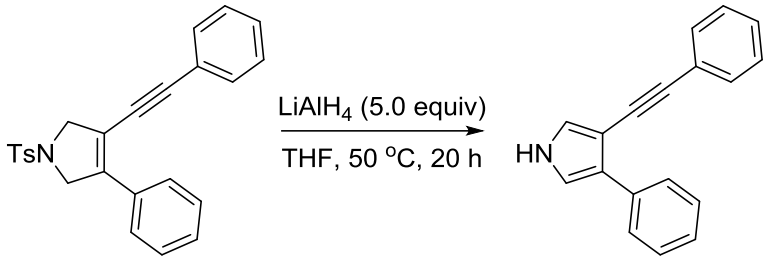


^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

3-phenyl-4-(phenylethynyl)-1*H*-pyrrole (11)



2a, 40.0 mg, 0.1 mmol

11, 5.2 mg, 21% yield

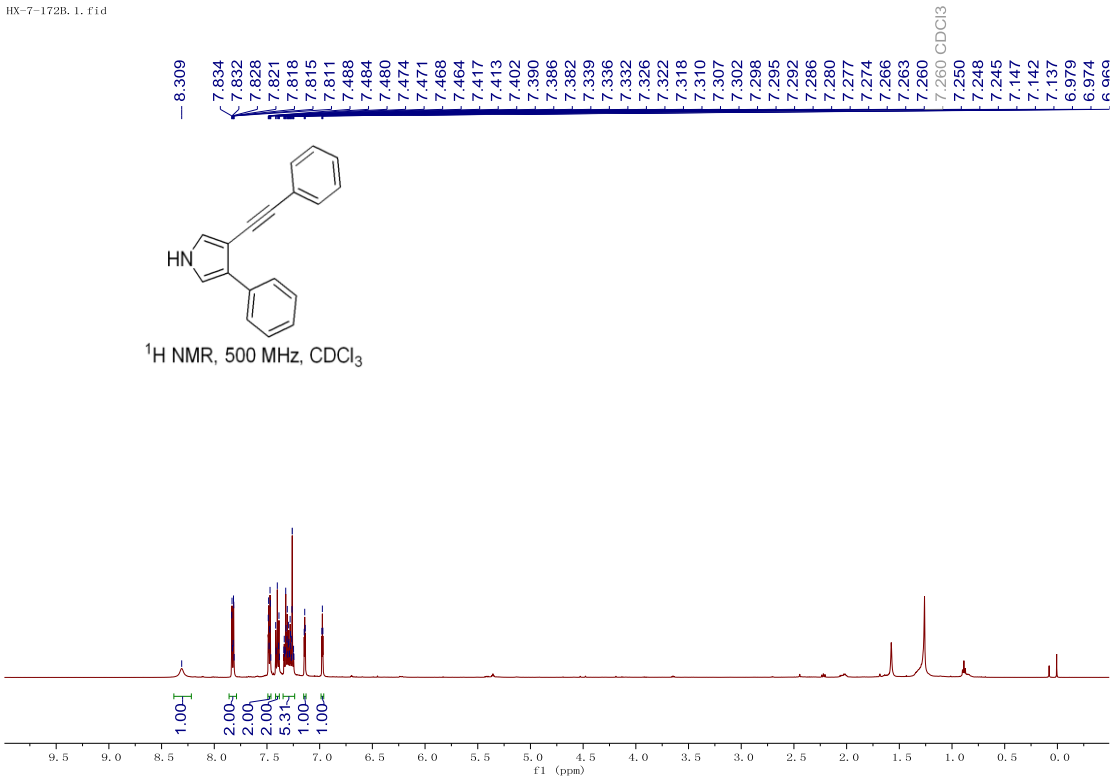
$LiAlH_4$ (20.1 mg, 0.5 mmol) was added to a solution of **2a** (40.0 mg, 0.1 mmol) dissolved in THF (2 mL) in a dried reaction tube. The reaction system was stirred at 50 °C for 20 hours in parallel reactor until **2a** was completely consumed by TLC monitoring. Then the mixture was extracted with ethyl acetate and water. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent under vacuum and was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 8/1) to give the product **11** (5.2 mg, 21% yield) as a yellow oil.

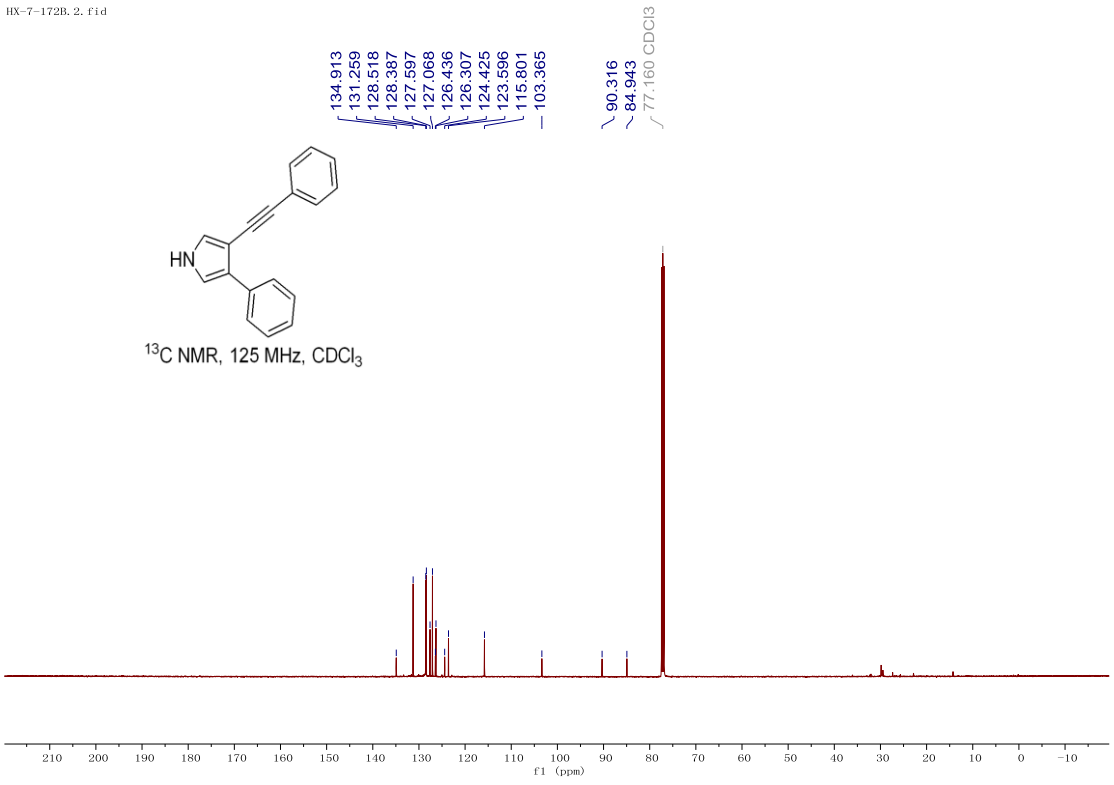
Compound **11**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.23. 5.2 mg, 21% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.31 (broad, 1H), 7.83-7.81 (m, 2H), 7.49-7.46 (m, 2H), 7.42-7.38 (m, 2H), 7.34-7.25 (m, 4H), 7.14 (t, J = 2.5 Hz, 1H), 6.97 (t, J = 2.5 Hz, 1H).

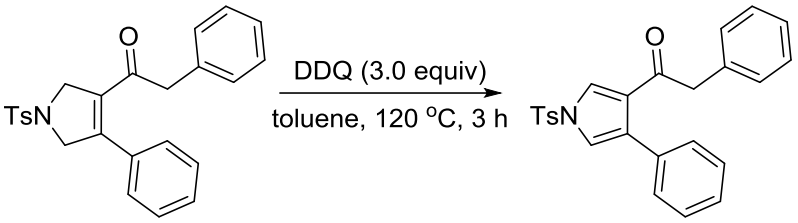
^{13}C NMR (125 MHz, Chloroform-*d*) δ 134.9, 131.3, 128.5, 128.4, 127.6, 127.1, 126.4, 126.3, 124.4, 123.6, 115.8, 103.4, 90.3, 84.9.

HRMS (ESI) m/z: calcd for $[C_{18}H_{13}N+H]^+$ requires: 244.1121, found: 244.1122.





2-phenyl-1-(4-phenyl-1-tosyl-1*H*-pyrrol-3-yl)ethan-1-one (12)



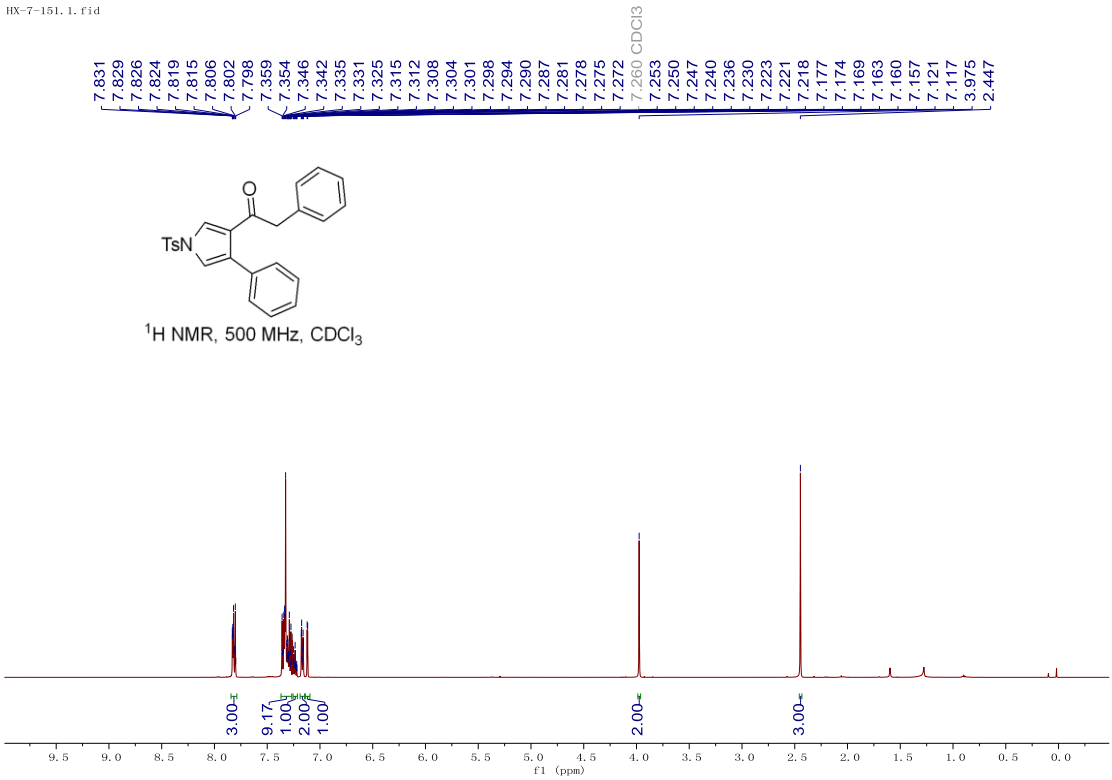
3a, 41.9 mg, 0.1 mmol **12**, 26.8 mg, 64% yield

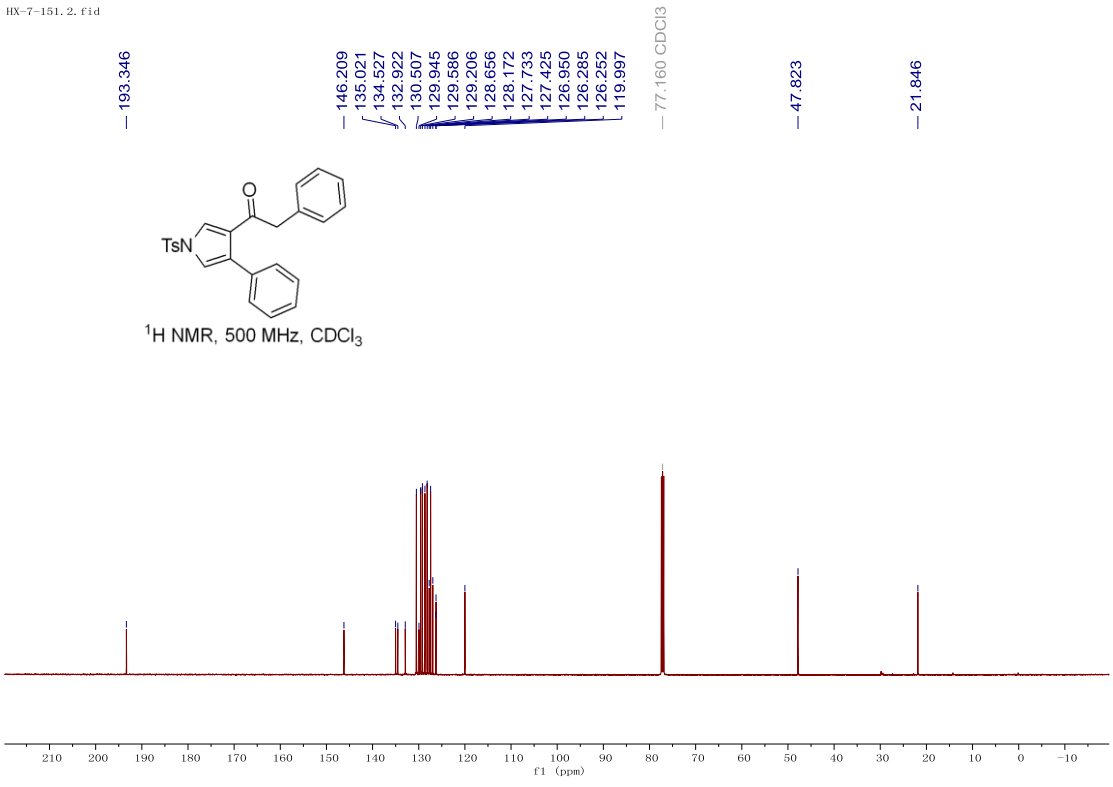
Under air atmosphere, toluene (2 mL, 0.05 M) was added to a mixture of **3a** (41.9 mg, 0.1 mmol) and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 68.3 mg, 0.3 mmol) in a dried reaction tube. The reaction system was stirred at 120 °C for 3 hours in parallel reactor until **3a** was completely consumed by TLC monitoring. Then the system was filtered through celite, and washed with ethyl acetate. The mixture was concentrated and purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 8/1) to give the product **12** (26.8 mg, 64% yield) as a yellow solid. Compound **12**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 8/1, R_f = 0.27. 26.8 mg, 64% yield. m.p. 115-119 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83-7.80 (m, 3H), 7.36-7.27 (m, 9H), 7.25-7.22 (m, 1H), 7.18-7.16 (m, 2H), 7.12 (d, J = 2.0 Hz, 1H), 3.98 (s, 2H), 2.45 (s, 3H).

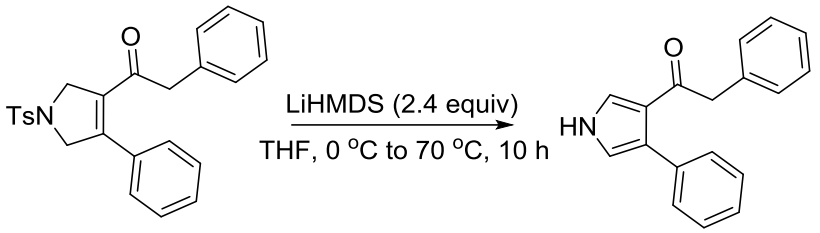
^{13}C NMR (125 MHz, Chloroform-*d*) δ 193.3, 146.2, 135.0, 134.5, 132.9, 130.5, 129.9, 129.6, 129.2, 128.7, 128.2, 127.7, 127.4, 127.0, 126.29, 126.25, 120.0, 47.8, 21.8.

HRMS (ESI) m/z: calcd for $[C_{25}H_{21}NO_3S+H]^+$ requires: 416.1315, found: 416.1313.





2-phenyl-1-(4-phenyl-1H-pyrrol-3-yl)ethan-1-one (13)



3a, 41.8 mg, 0.1 mmol **13**, 12.8 mg, 49% yield

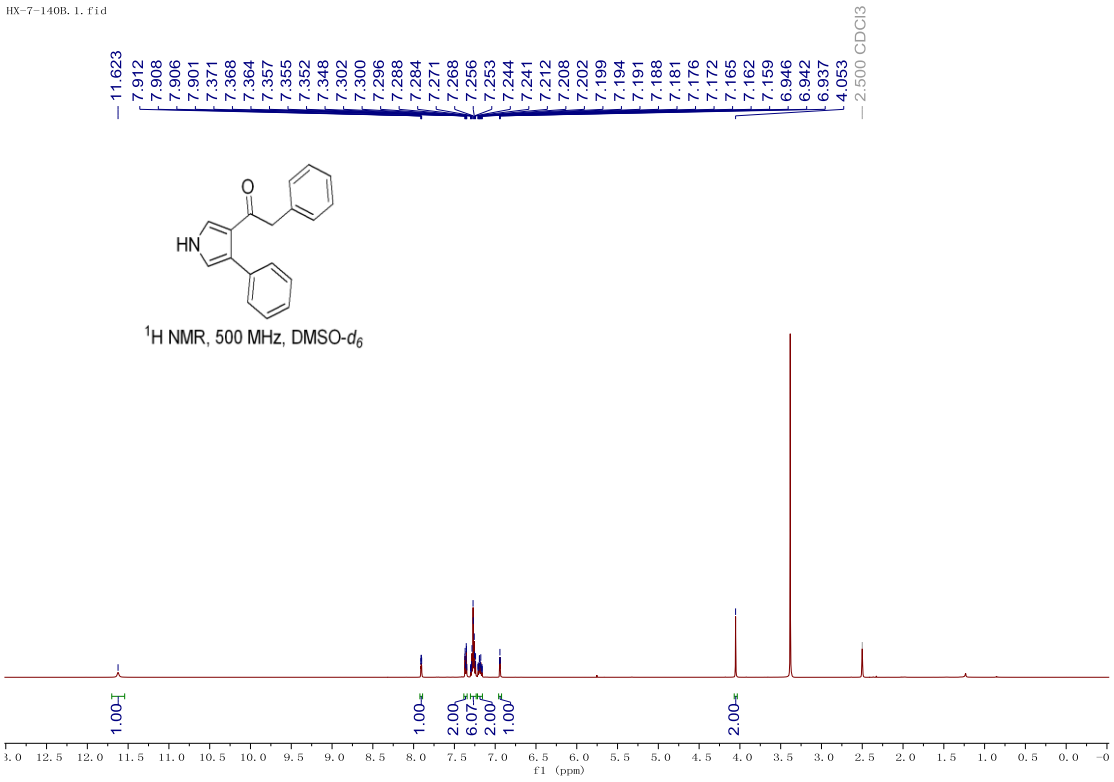
Under N_2 atmosphere, Lithium bis(trimethylsilyl)amide (LiHMDS) (0.24 mL, 1.0 M in THF, 0.24 mmol) was added dropwise to a mixture of **3a** (41.8 mg, 0.1 mmol) dissolved in THF (1 mL) in a 0 °C ice bath. Then, the ice bath was removed and the reaction system was stirred at 70 °C for 10 hours in parallel reactor until **3a** was completely consumed by TLC monitoring. After that, the mixture was extracted with ethyl acetate and water. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent under vacuum and was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 4/1) to give the product **13** (12.8 mg, 49% yield) as a yellow powder.

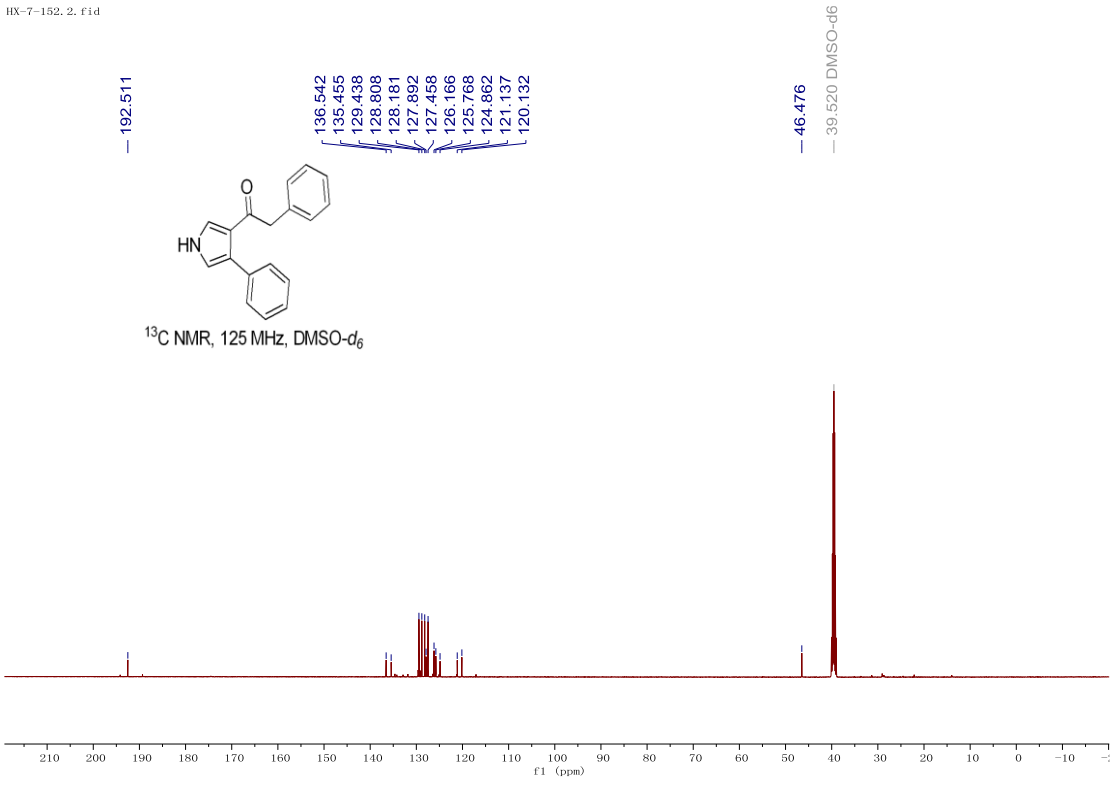
Compound **13**: a yellow powder. Column chromatography, eluent: petroleum ether/ethyl acetate, 4/1, R_f = 0.16. 12.8 mg, 49% yield. m.p. 198-202 °C.

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.62 (broad, 1H), 7.91 (dd, J = 3.0, 2.0 Hz, 1H), 7.37-7.35 (m, 2H), 7.30-7.24 (m, 6H), 7.21-7.16 (m, 2H), 6.94 (t, J = 2.0 Hz, 1H), 4.05 (s, 2H).

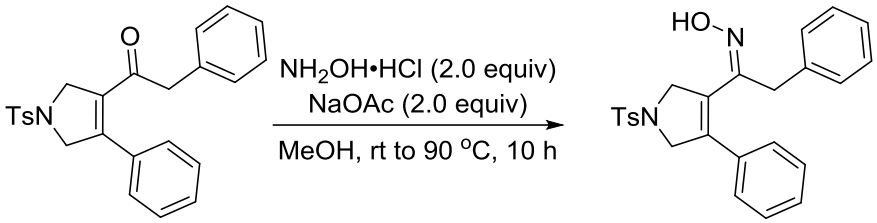
^{13}C NMR (125 MHz, DMSO-d_6) δ 192.5, 136.5, 135.5, 129.4, 128.8, 128.2, 127.9, 127.5, 126.2, 125.8, 124.9, 121.1, 120.1, 46.5.

HRMS (ESI) m/z: calcd for $[C_{18}H_{15}NO+H]^+$ requires: 262.1226, found: 262.1226.





2-phenyl-1-(4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)ethan-1-one oxime (14)



3a, 41.8 mg, 0.1 mmol

14, 31.1 mg, 72 % yield, *E*/*Z*=1:3

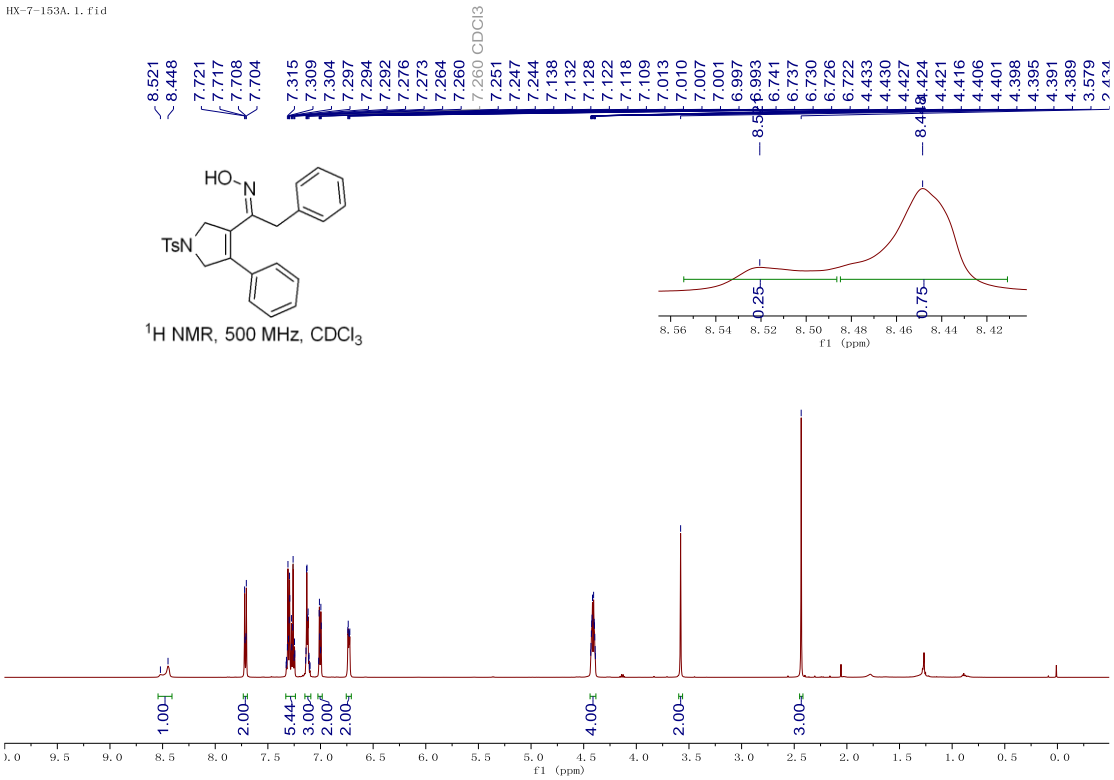
To a magnetically stirred solution of **3a** (41.8 mg, 0.1 mmol) in methanol (1 mL) was added hydroxylamine hydrochloride (13.8 mg, 0.2 mmol), and NaOAc (16.8 mg, 0.2 mmol) at room temperature. The reaction mixture stirred at 90 °C for 10 hours in parallel reactor. After reaction was monitored by TLC, the solvent was evaporated upon completion, quenched with water, extracted with ethyl acetate and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure and purification of the crude by a flash column chromatography (eluent: petroleum ether/ethyl acetate = 4/1) to give the inseparable mixture of diastereomers (*E*/*Z*=1:3) **14** (31.1 mg, 72%)

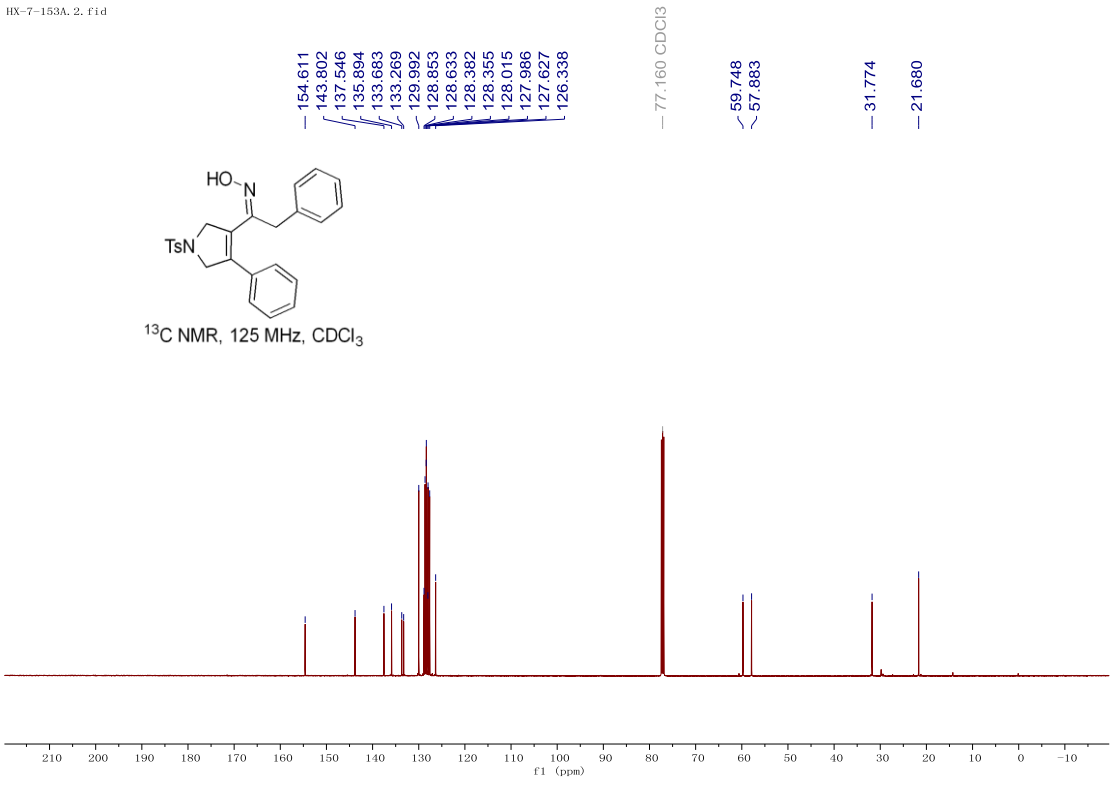
Compound **14**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 4/1, R_f = 0.25. 31.1 mg, 72% yield. m.p. 116-119 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.52 (s, 0.25H), 8.45 (s, 0.75H), 7.72-7.70 (m, 2H), 7.33-7.24 (m, 5H), 7.14-7.10 (m, 3H), 7.02-6.99 (m, 2H), 6.74-6.72 (m, 2H), 4.43-4.39 (m, 4H), 3.58 (s, 2H), 2.43 (s, 3H).

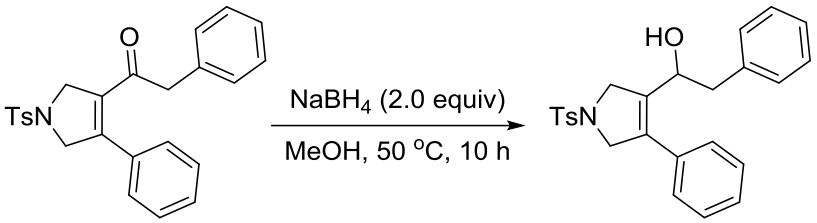
^{13}C NMR (125 MHz, Chloroform-*d*) δ 154.6, 143.8, 137.5, 135.9, 133.7, 133.3, 130.0, 128.9, 128.6, 128.38, 128.36, 128.02, 127.99, 127.6, 126.3, 59.7, 57.9, 31.8, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{24}N_2O_3S+H]^+$ requires: 433.1580, found: 433.1574.





2-phenyl-1-(4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)ethan-1-ol (15)



3a, 42.3 mg, 0.1 mmol **15**, 42.8 mg, equivalent yield

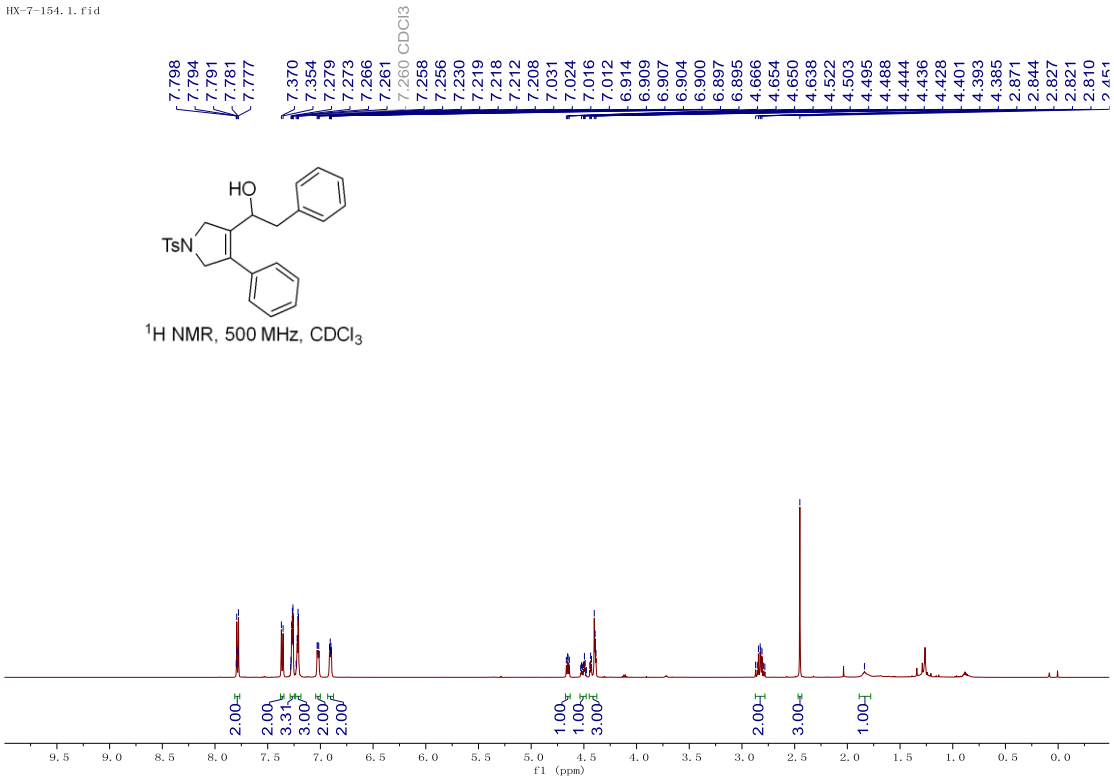
To a solution of the **3a** (42.3 mg, 0.1 mmol) in dry MeOH (1 mL) was added $NaBH_4$ (8.0 mg, 0.2 mmol) and the reaction mixture stirred at 50 °C for 10 hours in parallel reactor. After reaction was monitored by TLC, the solvent was evaporated upon completion, quenched with water, extracted with ethyl acetate and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure and purification of the crude by a flash column chromatography (eluent: petroleum ether/ethyl acetate = 4/1) to give the product **15** (42.8 mg, equivalent yield).

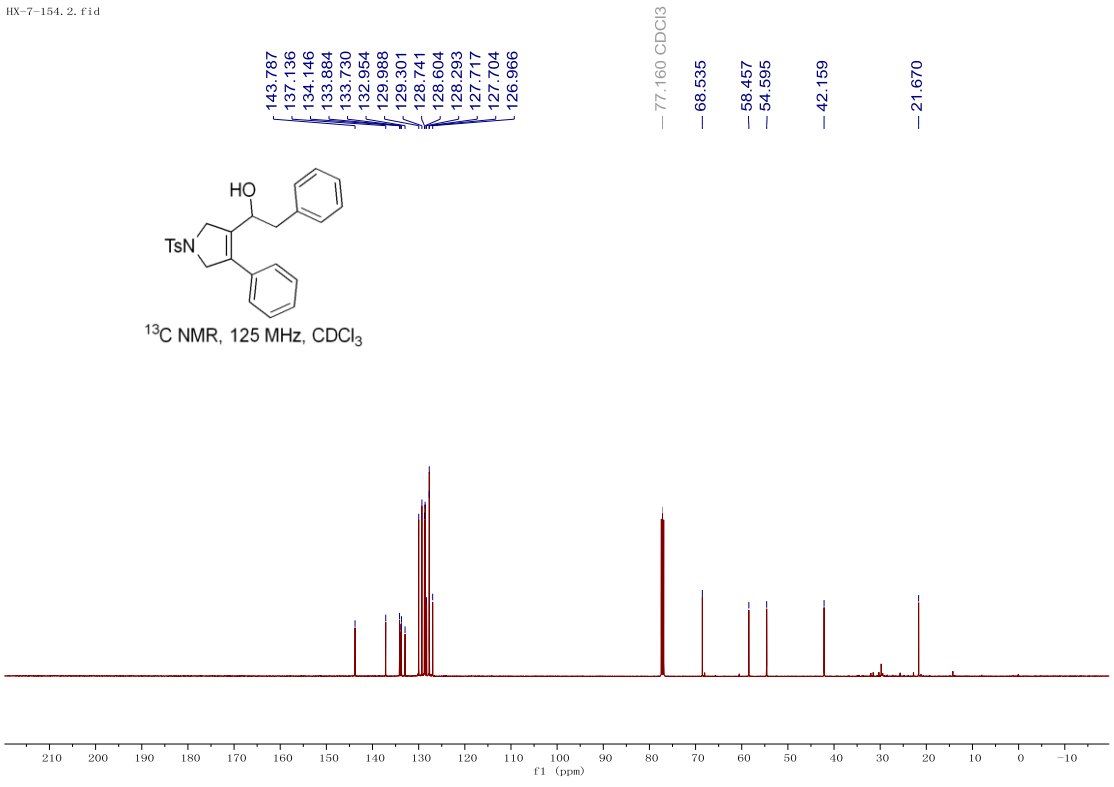
Compound **15**: a yellow oil. Column chromatography, eluent: petroleum ether/ethyl acetate, 4/1, R_f = 0.18. 42.8 mg, equivalent yield.

^{1}H NMR (500 MHz, Chloroform-*d*, TMS) δ 7.80-7.78 (m, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.28-7.26 (m, 3H), 7.23-7.21 (m, 3H), 7.03-7.01 (m, 2H), 6.91-6.90 (m, 2H), 4.65 (dd, J = 8.0, 6.0 Hz, 1H), 4.53-4.48 (m, 1H), 4.44-4.39 (m, 3H), 2.87-2.78 (m, 2H), 2.45 (s, 3H), 1.84 (broad, 1H).

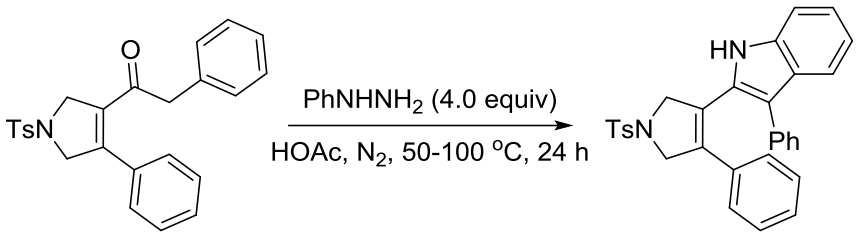
^{13}C NMR (125 MHz, Chloroform-*d*) δ 143.8, 137.1, 134.1, 133.9, 133.7, 133.0, 130.0, 129.3, 128.7, 128.6, 128.3, 127.72, 127.70, 127.0, 68.5, 58.5, 54.6, 42.2, 21.7.

HRMS (ESI) m/z: calcd for $[C_{25}H_{25}NO_3S+H]^+$ requires: 420.1628, found: 420.1623.





3-phenyl-2-(4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-1*H*-indole (16)



3a, 41.6 mg, 0.1 mmol

16, 29.4 mg, 60% yield

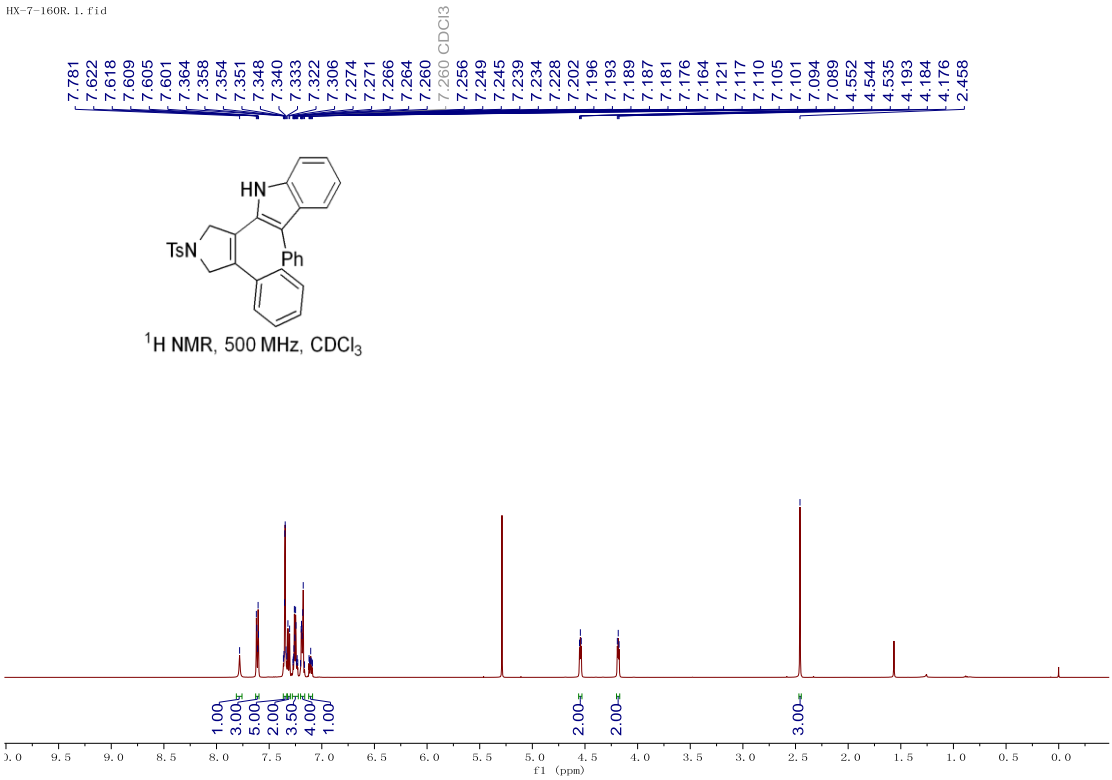
Under nitrogen atmosphere, a flame-dried 15 mL vial charged with a stir bar was subsequently added phenylhydrazine (43.8 mg, 0.4 mmol) and acetic acid (1 mL). The mixture was heated to 50 °C before **3a** (41.6 mg, 0.1 mmol) was added in one portion. Then the reaction was stirred at 100 °C for 24 hours in parallel reactor. Upon completion, the reaction mixture was quenched with $NaHCO_3$ and extracted with ethyl acetate and water. The combined organic layers were washed with saturated aqueous NaCl solution, dried over Na_2SO_4, and concentrated under vacuum. The residue was then purified by a flash column chromatography (eluent: petroleum ether/ethyl acetate = 5/1) to give the product **16** (29.4 mg, 60% yield).

Compound **16**: a yellow solid. Column chromatography, eluent: petroleum ether/ethyl acetate, 5/1, R_f = 0.27. 29.4 mg, 60% yield. m.p. 150-154 °C.

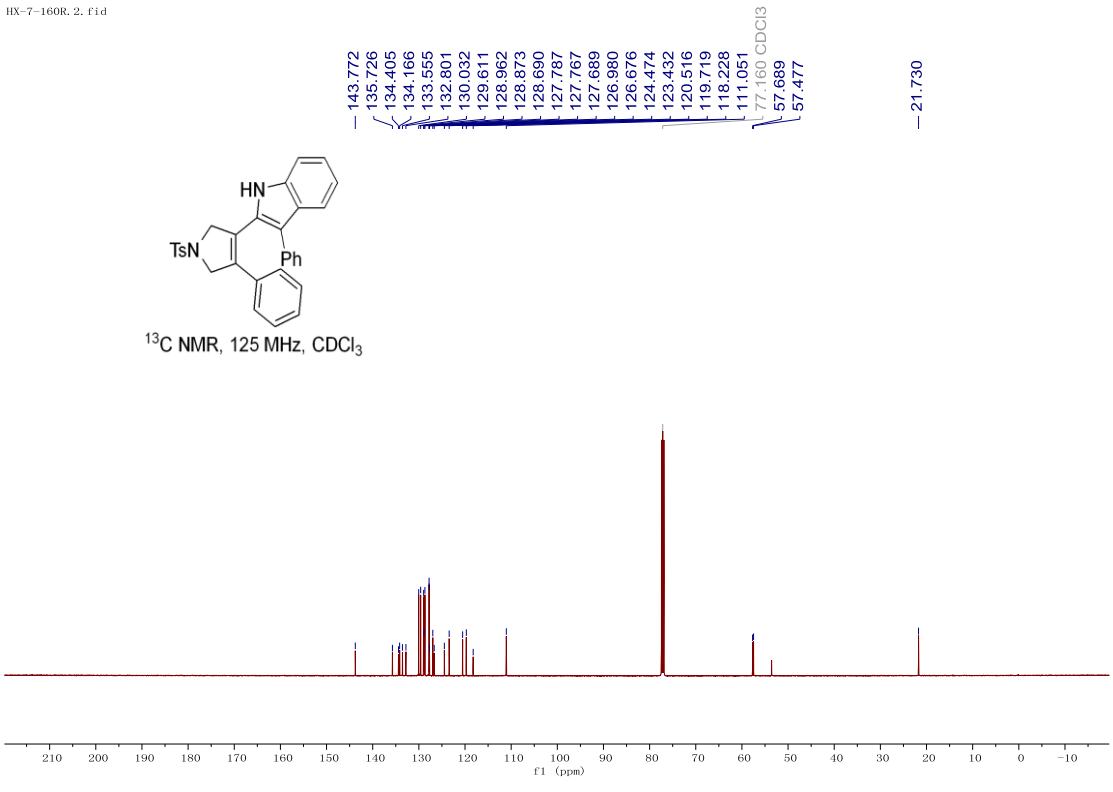
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.62-7.60 (m, 3H), 7.36-7.33 (m, 5H), 7.31 (d, J = 8.0 Hz, 2H), 7.27-7.23 (m, 3H), 7.20-7.16 (m, 4H), 7.12-7.09 (m, 1H), 4.54 (t, J = 4.0 Hz, 2H), 4.18 (t, J = 4.0 Hz, 2H), 2.46 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 143.8, 135.7, 134.4, 134.2, 133.6, 132.8, 130.0, 129.6, 129.0, 128.9, 128.7, 127.79, 127.77, 127.69, 127.0, 126.7, 124.5, 123.4, 120.5, 119.7, 118.2, 111.1, 57.7, 57.5, 21.7.

HRMS (ESI) m/z: calcd for $[C_{31}H_{26}N_2O_2S+H]^+$ requires: 491.1788, found: 491.1787.



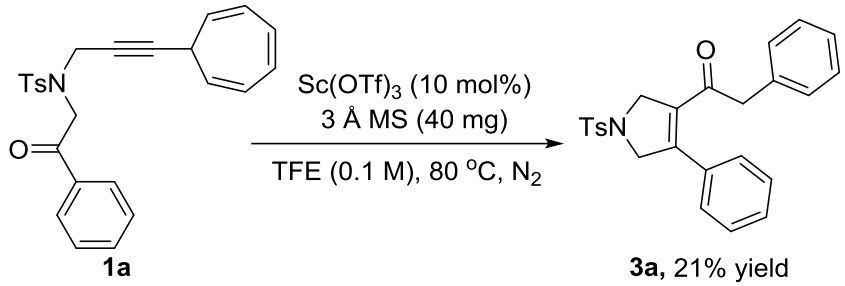
^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$

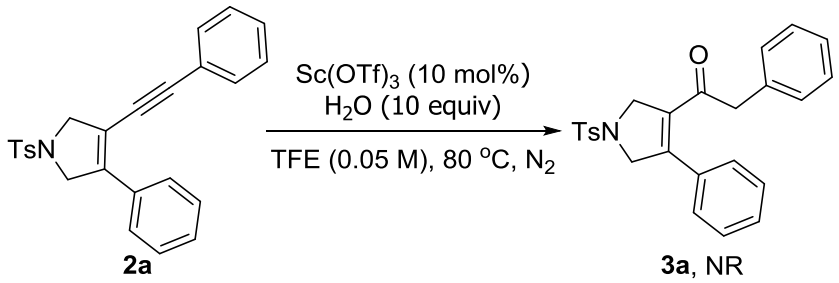
8. Control experiments and isotopic labeling experiments

8.1 Control experiments



1a **3a,** 21% yield

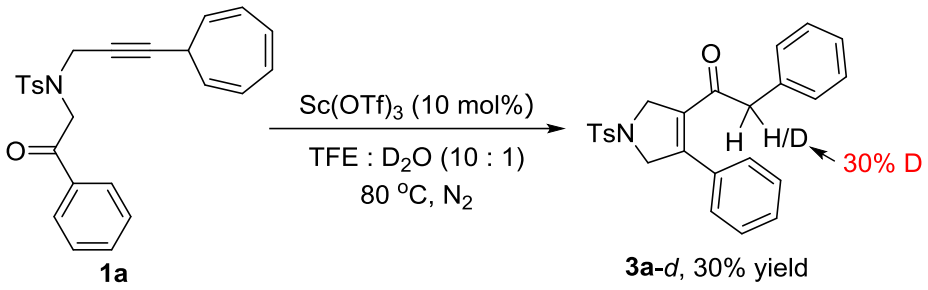
Under N_2 atmosphere, 2,2,2-Trifluoroethanol (TFE) (1 mL, 0.1 M) was added to a mixture of **1a** (41.9 mg, 0.1 mmol), $Sc(OTf)_3$ (4.8 mg, 0.01 mmol) and 3 Å MS (40 mg). The reaction system was stirred at 80 °C for 10 hours in oil bath and monitored by TLC. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate, 8/1) to give the product **3a** (8.8 mg, 21% yield) as a yellow solid.



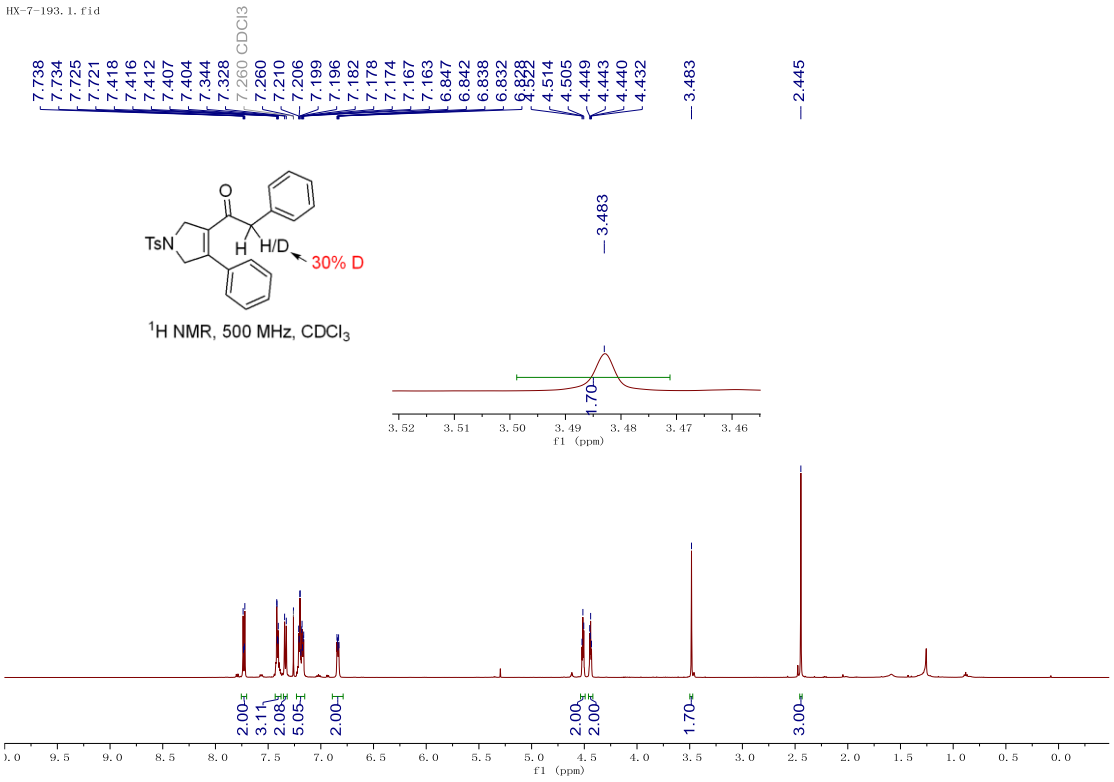
2a **3a**, NR

Under N_2 atmosphere, 2,2,2-Trifluoroethanol (TFE) (2 mL, 0.05 M) was added to a mixture of **2a** (39.9 mg, 0.1 mmol), $Sc(OTf)_3$ (5.0 mg, 0.01 mmol) and H_2O (18 μL, 1.0 mmol). The reaction system was stirred at 80 °C for 10 hours in oil bath and monitored by TLC. Unfortunately, we found that no reaction occurred.

8.2 Isotopic labeling experiments

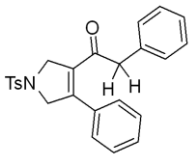


Procedure for 3a-*d*: Under N_2 atmosphere, 2,2,2-Trifluoroethanol (TFE) (1 mL, 0.1 M) and D_2O (0.1 mL) was added to a mixture of **1a** (41.9 mg, 0.1 mmol), $Sc(OTf)_3$ (5.0 mg, 0.01 mmol). The reaction system was stirred at 80 °C for 20 hours in oil bath and monitored by TLC. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate, 8/1) to give the product **3a-*d*** (12.4 mg, 30% yield) as a yellow solid. The percentage of deuterium incorporation was measured by ^1H NMR.

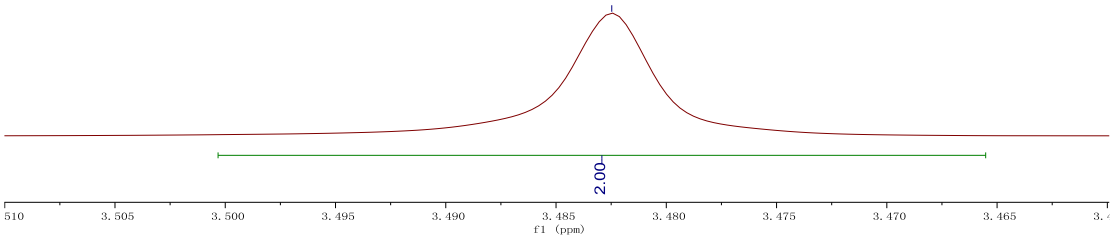


HX-6-140B.1.fid

3.482



^{1}H NMR, 500 MHz, $CDCl_3$



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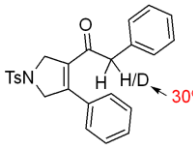
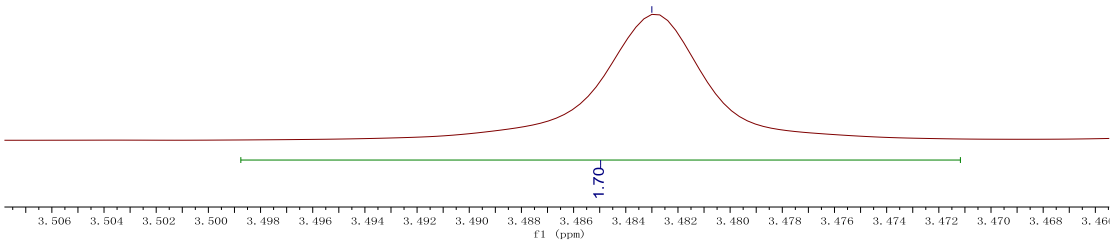
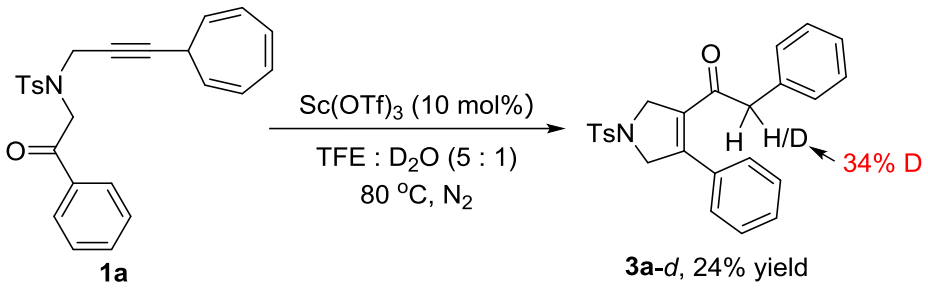
3.483

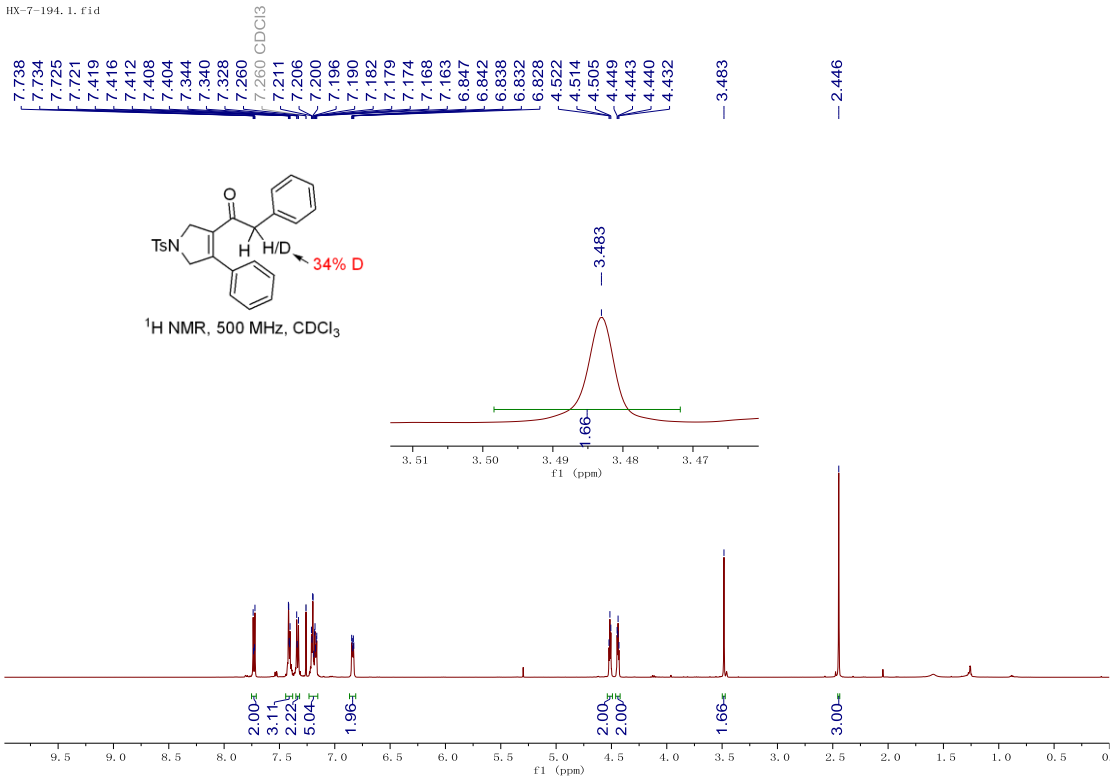


^{1}H NMR, 500 MHz, $CDCl_3$





Procedure for 3a-*d*: Under N_2 atmosphere, 2,2,2-Trifluoroethanol (TFE) (1 mL, 0.1 M) and D_2O (0.2 mL) was added to a mixture of **1a** (41.8 mg, 0.1 mmol), $Sc(OTf)_3$ (5.1 mg, 0.01 mmol). The reaction system was stirred at 80 °C for 20 hours in oil bath and monitored by TLC. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate, 8/1) to give the product **3a-*d*** (9.8 mg, 24% yield) as a yellow solid. The percentage of deuterium incorporation was measured by ^1H NMR.



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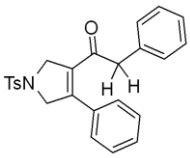
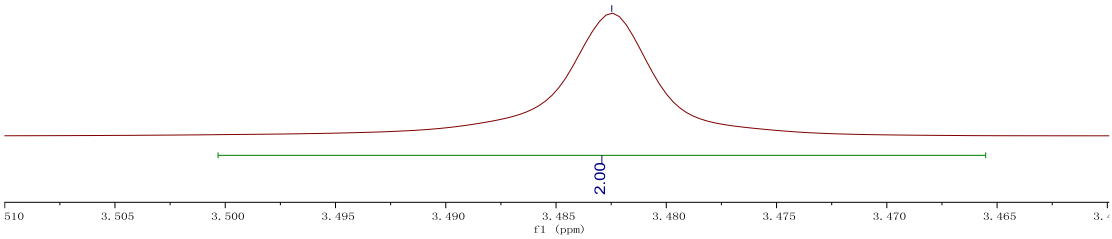
3.482



^{1}H NMR, 500 MHz, $CDCl_3$



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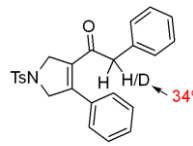
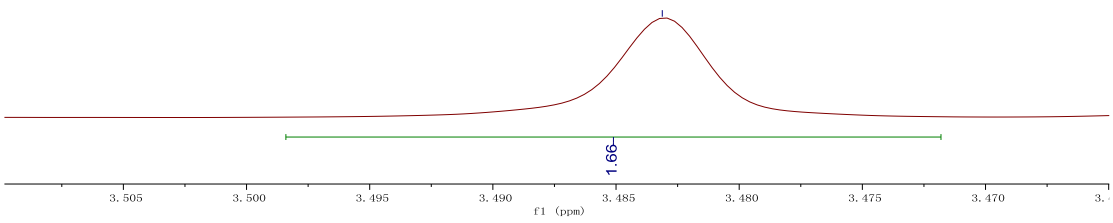
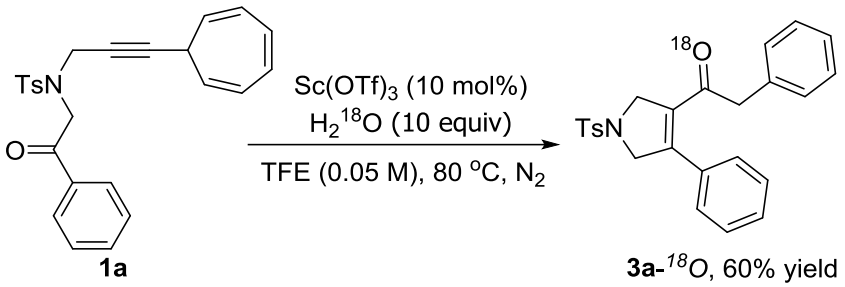
3.483

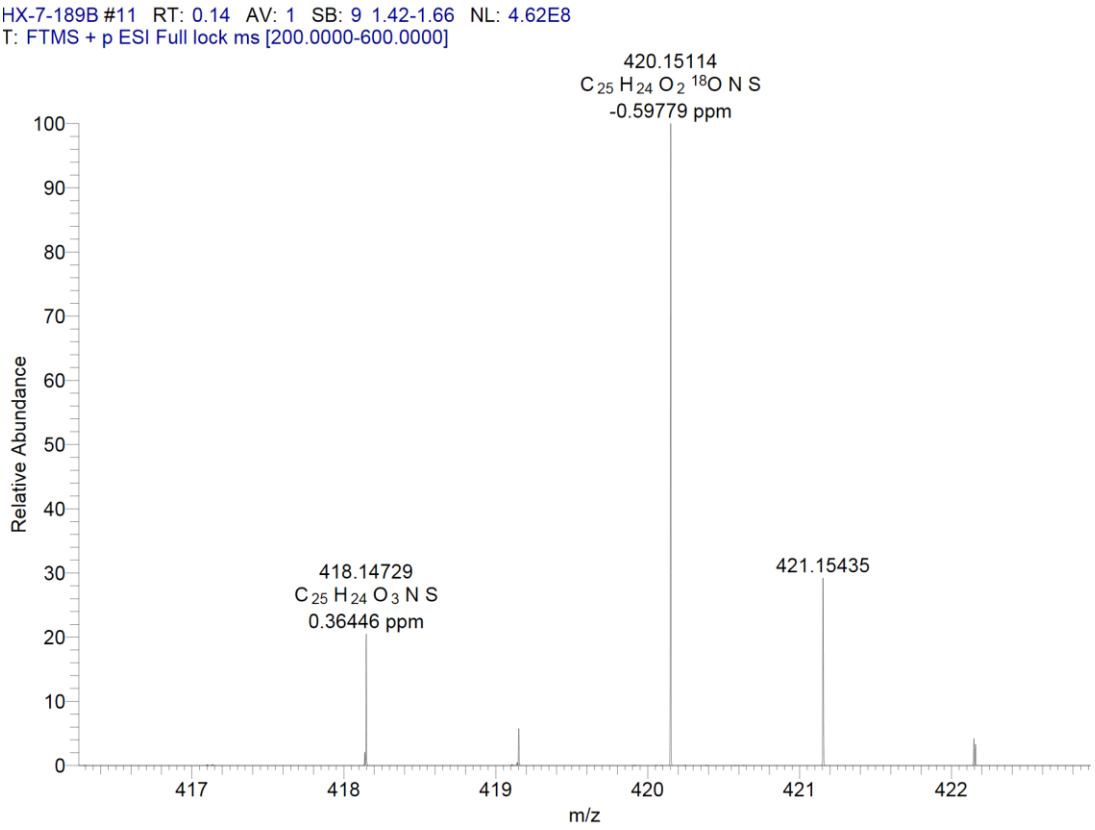


^{1}H NMR, 500 MHz, $CDCl_3$





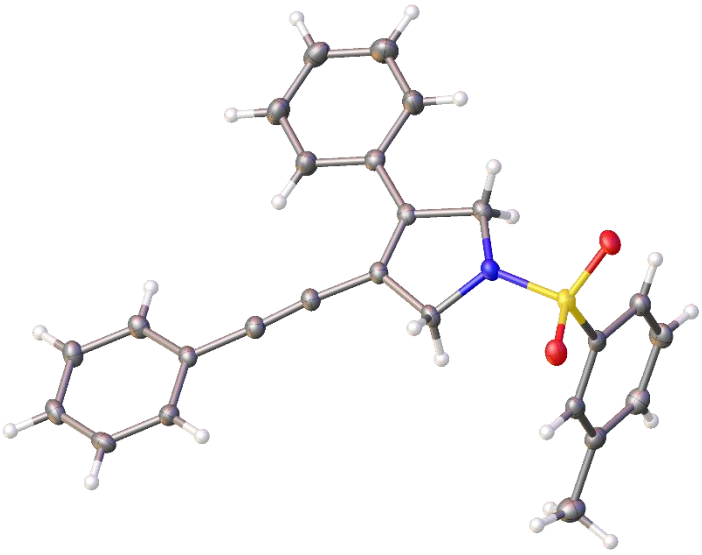
Procedure for 3a-^{18}O: Under N_2 atmosphere, 2,2,2-Trifluoroethanol (TFE) (2 mL, 0.1 M) was added to a mixture of **1a** (41.8 mg, 0.1 mmol), $Sc(OTf)_3$ (5.1 mg, 0.01 mmol) and $H_2{}^{18}O$ (20 μL, 1.0 mmol). The reaction system was stirred at 80 °C for 10 hours in oil bath and monitored by TLC. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate, 8/1) to give the product **3a** (25.0 mg, 60% yield) as a yellow solid, in which the ^{18}O content was *ca.* 83% (detected by HRMS; calcd for $[C_{25}H_{23}O_2{}^{18}ONS+H]^+$ requires: 420.1514, found: 420.1511).



9. X-ray crystal data of compound 2x

Crystal Growth Process: The compound **2x** was synthesized according to **General Procedure B** and then dissolved in dichloromethane to obtain a homogeneous solution. An appropriate amount of petroleum ether was added, and the solvent evaporation method was utilized to allow crystal growth at room temperature.

A suitable crystal was selected and put on a Super Nova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 170.00(10) K during data collection.



View of a molecule of 7_72 with 50% probability thermal ellipsoids.

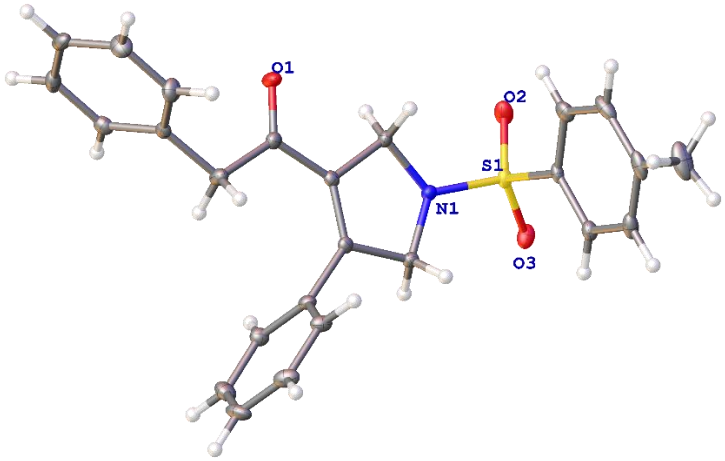
CCDC Number	2414218
Identification code	7_72
Empirical formula	$C_{25}H_{21}NO_2S$
Formula weight	399.49
Temperature/K	170.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.18890(10)
b/Å	17.9266(5)
c/Å	21.5874(6)
α/°	90

β/°	90
γ/°	90
Volume/Å^3	2008.05(9)
Z	4
ρ_{calc}g/cm^3	1.321
μ/mm^{-1}	1.596
F(000)	840.0
Crystal size/mm^3	0.16 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.408 to 147.172
Index ranges	-2 ≤ h ≤ 6, -22 ≤ k ≤ 21, -22 ≤ l ≤ 26
Reflections collected	7771
Independent reflections	3959 [R_{int} = 0.0371, R_{sigma} = 0.0541]
Data/restraints/parameters	3959/0/263
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0457, wR_2 = 0.1135
Final R indexes [all data]	R_1 = 0.0508, wR_2 = 0.1194
Largest diff. peak/hole / e Å^{-3}	0.24/-0.31
Flack parameter	0.003(16)

10. X-ray crystal data of compound 3a

Crystal Growth Process: The compound **3a** was synthesized according to **General Procedure C** and then dissolved in dichloromethane to obtain a homogeneous solution. An appropriate amount of petroleum ether was added, and the solvent evaporation method was utilized to allow crystal growth at room temperature.

A suitable crystal was selected and put on a diffractometer. The crystal was kept at 100.00 K during data collection.



View of a molecule of 6_148 with 50% probability thermal ellipsoids.

CCDC number	2414219
Identification code	6_148
Empirical formula	$C_{25}H_{23}NO_3S$
Formula weight	417.50
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.6274(4)
b/Å	13.9439(4)
c/Å	22.4596(7)
α/°	90
β/°	99.9330(10)
γ/°	90
Volume/Å^3	4203.8(2)
Z	8
ρ_{calc}g/cm^3	1.319
μ/mm^{-1}	1.583
F(000)	1760.0
Crystal size/mm^3	0.16 × 0.14 × 0.12

Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.584 to 136.512
Index ranges	-16 ≤ h ≤ 15, -16 ≤ k ≤ 16, -27 ≤ l ≤ 27
Reflections collected	62383
Independent reflections	7655 [R_{int} = 0.0448, R_{sigma} = 0.0268]
Data/restraints/parameters	7655/0/543
Goodness-of-fit on F^2	1.171
Final R indexes [I>=2σ (I)]	R_1 = 0.0506, wR_2 = 0.1311
Final R indexes [all data]	R_1 = 0.0556, wR_2 = 0.1334
Largest diff. peak/hole / e $Å^{-3}$	0.44/-0.55

11. References

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