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Supporting Information

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Supporting Information

Pd-Catalyzed Double Carbopalladation/*syn*-Insertion Cascades toward Pragmatic Synthesis of Aminated Polyheterocyclic 1,2-benzothiazepine 1-oxides

Zhigang Huang,[a] Longji Dai,[a] and Zhiyuan Chen*[,a,b]

[a] College of Chemistry & Chemical Engineering, Jiangxi Normal University, 99 Ziyang Road, Nanchang, Jiangxi 330022, China.

[b] School of Medicine, Zhejiang University City College, Hangzhou 310015, China.

E-mail: chenzy@zucc.edu.cn

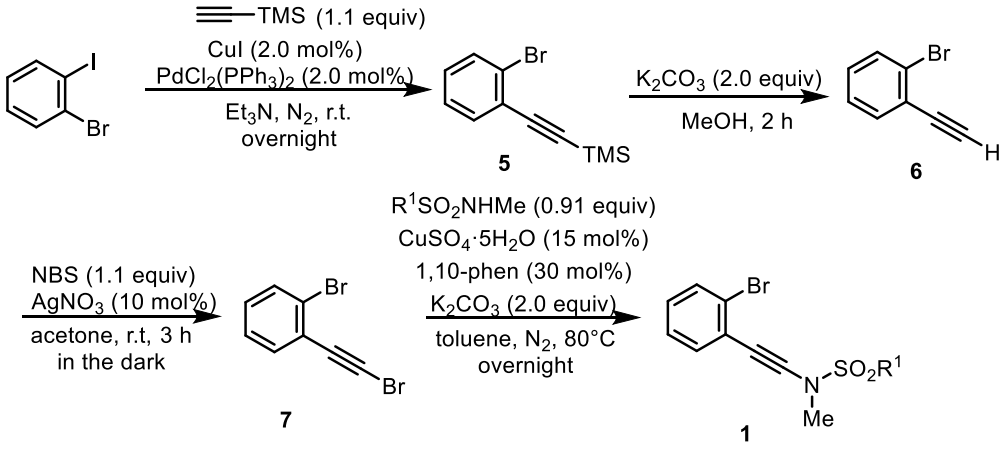
Contents:

1. General remarks.

Unless otherwise noted, commercial reagents were purchased from commercial suppliers and were used as received. All solvents were dried and distilled according to standard procedures before use. The Flash column chromatography was performed using silica gel (60 Å pore size, 32-63 μm, standard grade). Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25-35 °C. Nuclear magnetic resonance (NMR) spectra were recorded in parts per million (ppm) from internal trimethylsilane (TMS) on the δ scale. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. High resolution mass spectrometry (HRMS) spectra analysis was performed by electrospray ionization (ESI-micrOTOF).

2. General procedure for the preparation of starting material 1a-1h.

Preparation of starting material **1a-1c**.[12]



To a solution of Et_3N (40 mL), $PdCl_2(PPh_3)_2$ (2 mol %), CuI (2 mol %) and 20 mmol of 2-bromoiodobenzene was slowly added 22 mmol of ethynyltrimethylsilane and stirring was continued for another 5 min before flushing with nitrogen three times and the flask was then sealed. The reaction mixture was allowed to stir at room temperature overnight and the resulting solution was filtered and washed with saturated aq NaCl solution and extracted with ethyl acetate (2 x 30 mL). The combined organic phases was dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was purified by flash chromatography on silica gel and compound **5** was obtained using hexane as the eluent

To a solution of **5** (2.53 g, 10 mmol) in MeOH (20 mL) were added K_2CO_3 (2.76 g, 20 mmol). The reaction was stirred at room temperature for 2 h then was added water and extracted with ethyl acetate (2 x 15 mL). The organic layer was collected, dried over $MgSO_4$, and filtrated. The solvent was evaporated under vacuum to afford **6** without further purification.

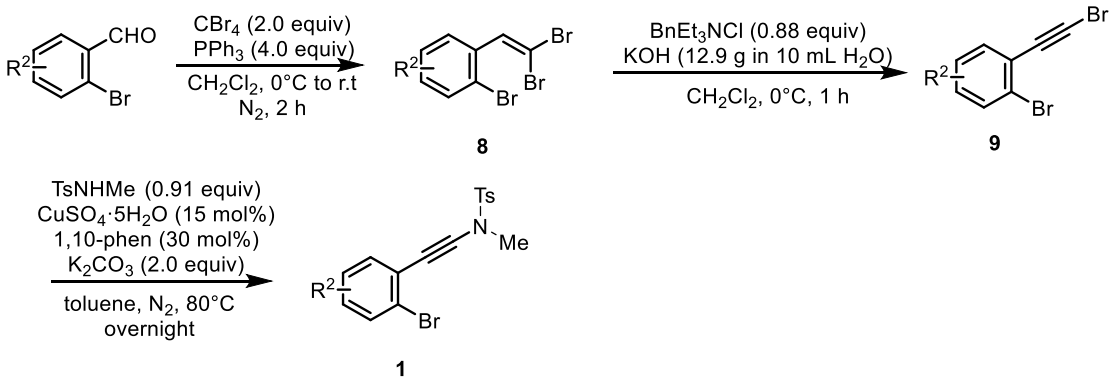
In the dark, to a solution of **6** (996 mg, 5.5 mmol) in 25 mL acetone was added NBS (1077 mg, 6.05 mmol) and $AgNO_3$ (94 mg, 0.55 mmol). The resulting mixture was stirred at room temperature for 3 h, filtered, and the filtrate was evaporated. Then

1. Tian, X.; Song, L.; Rudolph, M.; Wang, Q.; Song, X.; Rominger, F.; Hashmi, A. S. K. *Org. Lett*. **2019**, 21, 1598–1601.
2. Meesin, A.; Pohmakotr, M.; Reutrakul, V.; Soorukram, D.; Leowanawat, P.; Saithong, S.; Kuhakarn, C. *Org. Lett.* **2017** *19*, 6546-6549.

20 mL petroleum ether was added, filtered again and the filtrate was evaporated under vacuum to give the alkynyl bromide **7**.

Following the previous step, compound **7** (5.0 mmol), amide (4.55 mmol), copper sulfate pentahydrate (187.0 mg, 0.75 mmol), 1,10- phenanthroline (270.0 mg, 1.5 mmol) and K_2CO_3 (1.38 g, 10.0 mmol), toluene (25 mL) were added under a nitrogen atmosphere. The reaction flask was evacuated under vacuum and flushed with nitrogen three times, then sealed under nitrogen and heated to 80 ºC. The reaction mixture was stirred overnight, then cooled down to room temperature, filtered through a pad of silica gel, the filtrate was evaporated and purified by flash silica gel column chromatrography to give the desired Compound (**1a-1c)**.

Preparation of starting material **1d-1i.**[3]



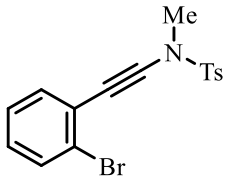
To a cooled (0 °C) orange-colored suspension of tetrabromomethane (3.58 g, 10.8 mmol) and triphenylphosphine (5.67 g, 21.6 mmol) in CH_2Cl_2 (30 mL) was added a CH_2Cl_2 (10 mL) solution of 2-bromobenzaldehyde (1.0 g, 5.4 mmol). After stirring at room temperature for a few minutes, the reaction was quenched with water and extracted with CH_2Cl_2. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated partially. The solution was poured slowly into hexane (100 mL). The resulting suspension was filtrated and the filtrate was concentrated partially. The resulting suspension was filtrated, concentrated, and quickly purified on a silica gel column chromatography (hexane) to furnish compound **8** .

3. Chen, X.; Wang, L.; Frings, M.; Bolm, C. *Org. Lett.* **2014**, *16*, 3796-3799.

To the vigorously stirred solution of the **8** (5 mmol) in CH_2Cl_2 (25 mL) at 0 °C, $BnEt_3NCl$ (1.00 g, 4.4 mmol) was added. Subsequently, a solution of KOH (12.9 g, 230 mmol) in H_2O (10 mL) was added to the reaction mixture. After stirring for 5 h at 0 °C, H_2O (20 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with brine and dried over $MgSO_4$. All volatiles were removed under reduced pressure. The product was purified by SiO_2 column chromatography to give the desired compound **9**.

Compound **9** (5.0 mmol), amide (4.55 mmol), copper sulfate pentahydrate (187.0 mg, 0.75 mmol), 1, 10-phenanthroline (270.0 mg, 1.5 mmol) and K_2CO_3 (1.38 g, 10.0 mmol), toluene (25 mL) were added under a nitrogen atmosphere. The reaction flask was evacuated under vacuum and flushed with nitrogen three times, then sealed under nitrogen and heated to 80 ºC. The reaction mixture was stirred overnight, then cooled down to room temperature, filtered through a pad of silica gel, the filtrate was evaporated and purified by flash silica gel column chromatrography to give the desired Compound **1e-1h** in high yield**.**

3. Spectroscopic data for compounds 1



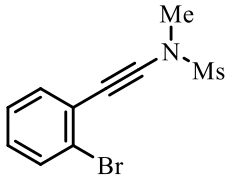
N-((2-Bromophenyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide (**1a**)

Yield: 98%, 1.66 g; white solid; mp: 61-63 ºC.

Eluent: ethyl acetate/petroleum ether =1: 20.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 - 7.74 (m, 2H), 7.39 – 7.29 (m, 1H), 7.25 – 7.11 (m, 3H), 7.10 – 6.98 (m, 1H), 6.95 - 6.90 (m, 1H), 3.04 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 133.2, 132.6, 132.3, 130.0, 128.9, 127.8, 127.2, 125.0, 124.6, 88.7, 77.8, 77.5, 77.2, 68.4, 39.4, 21.6.



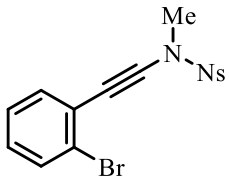
N-((2-Bromophenyl)ethynyl)-*N*-methylmethanesulfonamide (**1b**)

Yield: 90%, 1.18 g; white solid; mp: 50-52 ºC.

Eluent: ethyl acetate/petroleum ether =1: 20.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.42 - 7.40 (m, 1H), 7.28 – 7.21 (m, 1H), 7.15 - 7.12 (m, 1H), 3.33 (s, 3H), 3.19 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 132.3, 129.1, 127.1, 125.1, 124.7, 87.6, 77.5, 77.2, 76.9, 68.9, 39.2, 37.1.



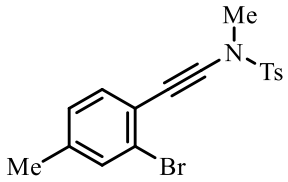
N-((2-Bromophenyl)ethynyl)-*N*-methyl-4-nitrobenzenesulfonamide (**1c**)

Yield: 90%, 1.43 g; yellow solid; mp: 142-144 ºC.

Eluent: ethyl acetate/petroleum ether =1: 20.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 - 8.41 (m, 2H), 8.22 - 8.20 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.27 - 7.24 (m, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 3.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 141.7, 132.9, 132.5, 129.3, 129.1, 127.2, 125.0, 124.5, 124.3, 86.8, 77.4, 77.1, 76.7, 69.0, 39.6.



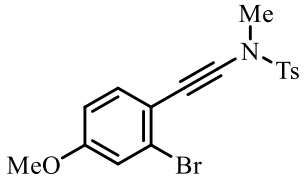
N-((2-Bromo-4-methylphenyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide (**1d**)

Yield: 96%, 1.65 g; white solid; mp: 89-91 ºC.

Eluent: ethyl acetate/petroleum ether =1: 20.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 - 7.90 (m, 2H), 7.39 - 7.37 (m, 3H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 3.20 (s, 3H), 2.47 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 139.5, 133.3, 132.8, 132.5, 129.9, 127.9, 124.8, 121.9, 87.5, 77.4, 77.1, 76.8, 68.2, 39.4, 21.7, 21.1.



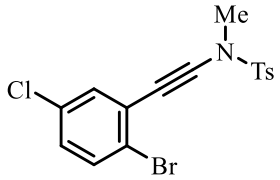
N-((2-Bromo-4-methoxyphenyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide (**1e**)

Yield: 85%, 1.53 g; white solid; mp: 85-87 ºC.

Eluent: ethyl acetate/petroleum ether =1: 20.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.88 (m, 2H), 7.38 - 7.36 (m, 3H), 6.90 (d, *J* = 3.0 Hz, 1H), 6.70 - 6.67 (m, 1H), 3.75 (s, 3H), 3.18 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 145.0, 133.3, 132.9, 129.9, 127.9, 125.6, 117.3, 115.7, 115.4, 88.2, 77.5, 77.2, 76.8, 68.5, 55.6, 39.3, 21.7.



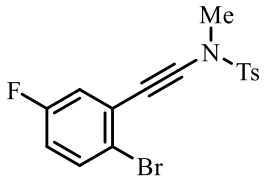
N-((2-Bromo-5-chlorophenyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide (**1f**)

Yield: 85%, 1.54 g; white solid; mp: 122-124 ºC.

Eluent: ethyl acetate/petroleum ether =1: 20.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 - 7.87 (m, 2H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.39 - 7.37 (m, 2H), 7.34 (d, *J* = 2.3 Hz, 1H), 7.09 - 7.06 (m, 1H), 3.19 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 133.3, 133.0, 131.8, 123.0, 128.7, 127.9, 126.7, 122.5, 89.7, 77.4, 77.1, 76.8, 67.8, 39.2, 21.7.



N-((2-Bromo-5-fluorophenyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide (**1g**)

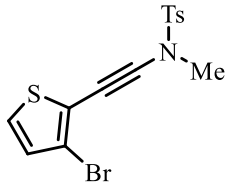
Yield: 80%, 1.39 g; white solid; mp: 83-85 ºC.

Eluent: ethyl acetate/petroleum ether =1: 20.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 - 7.87 (m, 2H), 7.49 - 7.46 (m, 1H), 7.39 - 7.36 (m, 2H), 7.09 - 7.06 (m, 1H), 6.86 - 6.81 (m, 1H), 3.20 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 160.1, 145.2, 133.6, 133.5, 133.3, 130.0, 129.7, 127.9, 127.6, 127.3, 126.8, 126.6, 119.1, 119.0, 119.0, 118.9, 116.3, 116.1, 89.5, 77.4, 77.1, 76.8, 67.9, 39.2, 29.4, 21.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.01 – -115.12.



N-((3-Bromothiophen-2-yl)ethynyl)-*N*,4-dimethylbenzenesulfonamide (**1h**)

Yield: 78%, 1.31 g; white solid; mp: 63-65 ^{o}C.

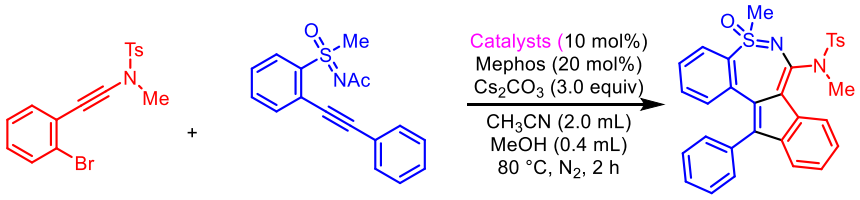
Eluent: ethyl acetate/petroleum ether =1: 40.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 - 7.87 (m, 2H), 7.39 - 7.37 (m, 2H), 7.21 (d, *J* = 5.4 Hz, 1H), 6.94 (d, *J* = 5.4 Hz, 1H), 3.16 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 133.3, 130.0, 130.0, 127.9, 127.6, 120.4, 117.0, 91.2, 77.5, 77.1, 76.8, 61.2, 39.4, 21.7.

4. Optimization of the reaction conditions.

a) Screening of catalysts.

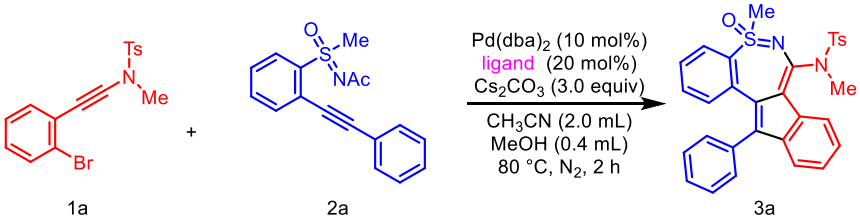


1a 2a 3a

Entry	Catalysts	Yield (%)[a]
1	$Pd(OAc)_2$	28
2	$PdCl_2$	n.r
3	Pd/C	n.r
4	$Pd(PPh_3)_2Cl_2$	n.r
5	$Pd(PPh_3)_4$	11
6	$Pd(CH_3CN)_2Cl_2$	n.r
7	$Pd(OCOCF_3)_2$	n.r
8	$Pd_2(dba)_3$	14
9	**$Pd(dba)_2$**	**40**
10	$Pd(dba)_2$ (2 mol%)	15
11	$Pd(dba)_2$ (5 mol%)	35

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), CH_3CN (2.0 mL), CH_3OH (0.4 mL), Catalysts (10 mol%), Mephos (20 mol%), Cs_2CO_3 (3.0 equiv.), under N_2 atmosphere. Yields are given for isolated products after column chromatography.

b) Screening of ligand.



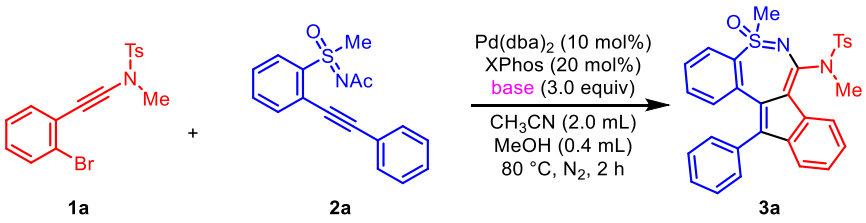
1a 2a 3a

Entry	ligand	Yield (%)[a]
1	PPh_3	n.r
2	PCy_3	35
3	DPPF	n.r
4	S-phos	n.r

5	$P(4\text{-}CF_3C_6H_4)_3$	n.r
6	Mephos	40
7	$P(3\text{-}MeC_6H_4)_3$	n.r
8	Xantphos	n.r
9	*t*BuXphos	n.r
10	DPEPHOS	n.r
11	DPPY-phos	n.r
12	Davephos	20
13	PhDAVE-phos	21
14	Ruphos	53
15	**X-phos**	**62**
16	X-phos (10 mol%)	32
17	X-phos (15 mol%)	54
18	X-phos (25 mol%)	52
19	X-phos (30 mol%)	40

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), CH_3CN (2.0 mL), CH_3OH (0.4 mL), $Pd(dba)_2$ (10 mol%), ligand (20 mol%), Cs_2CO_3 (3.0 equiv.), under N_2 atmosphere. Yields are given for isolated products after column chromatography.

c) Screening of base.

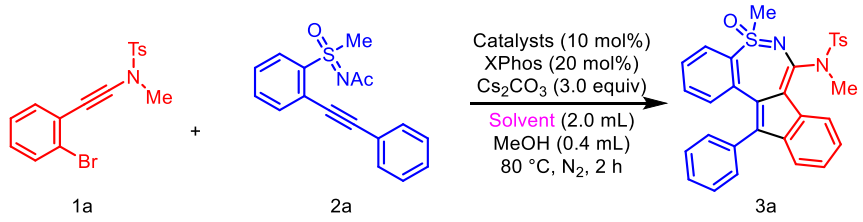


Entry	base	Yield (%)[a]
1	Py	n.r.
2	TEA	n.r.
3	K_2CO_3	trace
4	**Cs_2CO_3**	**60**
5	Li_2CO_3	n.r.
6	Na_2CO_3	n.r.
7	DBU	trace

8	tBuOK	trace
9	NaOH	40
10	LiOH	47
11	NaOAc	n.r.
12	$NaOCH_3$	56
13	$LiOCH_3$	48
14	Cs_2CO_3 (2.5 equiv)	47
15	Cs_2CO_3 (4.0 equiv.)	41

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), CH_3CN (2.0 mL), CH_3OH (0.4 mL), $Pd(dba)_2$ (10 mol%), XPhos (20 mol%), Base (3.0 equiv), under N_2 atmosphere. Yields are given for isolated products after column chromatography.

d) Screening of solvent.



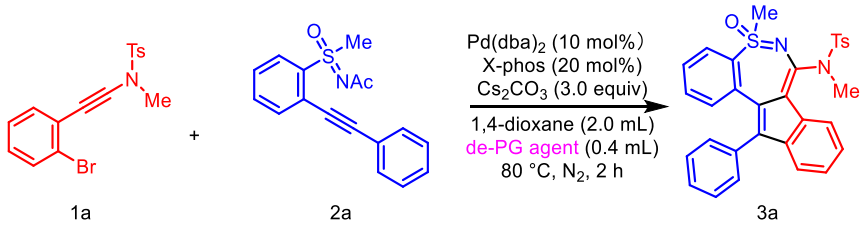
1a 2a 3a

Entry	solvent	Yield(%)[a]
1	**1,4-dioxoane**	**84**
2	toluene	trace
3	DMSO	Trace
4	DMF	77
5	THF	76
6	CH_3CN	63
7	DCE	69
8	DCM	76
9	Et2O	trace
10	acetone	41
11	CH_3OH	trace
12	1,4-dioxane:DCE(9:1)	82
13	1,4-dioxane:DCE(3:1)	80
14	1,4-dioxane:DCE(1:1)	75

15	1,4-dioxane:DCE(1:3)	68
16	1,4-dioxane:CH_3OH(1:1)	74

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), solvent (2.0 mL), CH_3OH (0.4 mL), $Pd(dba)_2$ (10 mol%), X-phos (20 mol%), Cs_2CO_3 (3.0 equiv), under N_2 atmosphere. Yields are given for isolated products after column chromatography.

e) Screening of de-PG agent

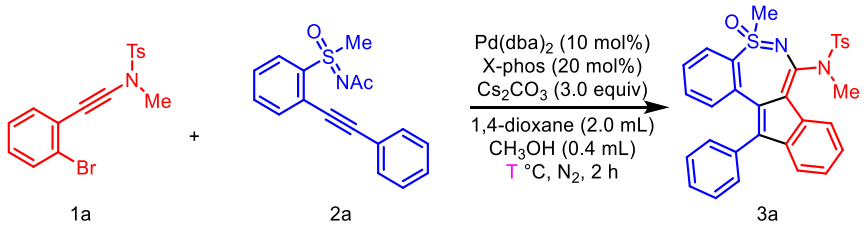


1a 2a 3a

Entry	de-PG agent	Yield(%)[a]
1	**CH_3OH**	**84**
2	EtOH	25
3	PirOH	n.r
4	HFIP	trace
5	phenol	trace
6	H_2O	trace

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), 1, 4-dioxane (2.0 mL), de-PG agent (0.4 mL), $Pd(dba)_2$ (10 mol%), XPhos (20 mol%), Cs_2CO_3 (3.0 equiv.), under N_2 atmosphere. Yields are given for isolated products after column chromatography.

f) Screening of T



1a 2a 3a

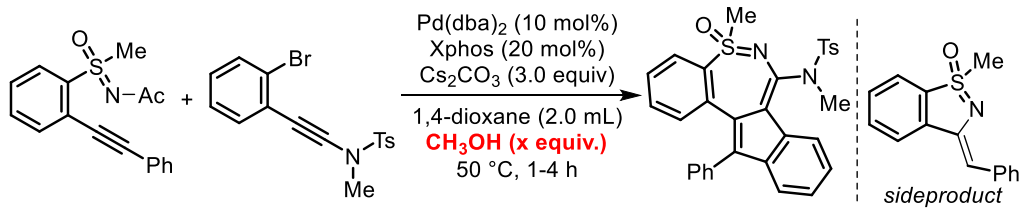
Entry	T/℃	Yield(%)[a]
1	25	Trace
2	**50**	**92**
3	80	85

4	100	81
5	120	40

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), 1, 4-dioxane (2.0 mL), CH_3OH (0.4 mL), $Pd(dba)_2$ (10 mol%), XPhos (20 mol%), Cs_2CO_3 (3.0 equiv.), under N_2 atmosphere. Yields are given for isolated products after column chromatography.

The influence of different amounts of MeOH.

The control parallel experiments to test the amount of MeOH on its influence were conducted. That is, the different equivalents of MeOH were selected as 0 equiv, 5 equiv., 10 equiv., 20 equiv., 40 equiv., 60 equiv., 80 equiv., and 100 equiv. as compared with substrate **1a** (0.2 mmol) and **2a** (0.2 mmol) under the standard conditions. And as a result, the yield of **3a** and **4** were isolated and collected.



1a **2a** **3a** **4**

	x/equiv.	**3a**/%	**4**/%
1	0	0	0
2	5 (40 uL)	23	10
3	10 (80 uL)	39	22
4	20 (0.16 mL)	54	44
5	40 (0.32 mL)	74	25
6	60 (0.48 mL)	73	22
7	80 (0.64 mL)	52	48
8	100 (0.8 mL)	41	55

[a] Reaction conditions: sulfoximine **1a** (0.20 mmol), ynamide **2a** (0.20 mmol), and $Pd(dba)_2$ (10 mol%), XPhos (20 mol%), base (3.0 equiv) in 2.0 mL of solvent (2.0 mL) under N_2.

The figure was depicted in **Figure 2**.

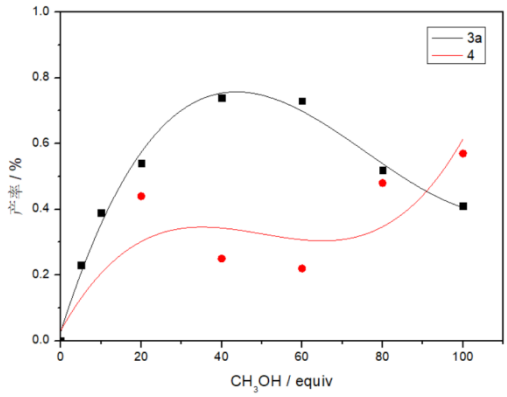
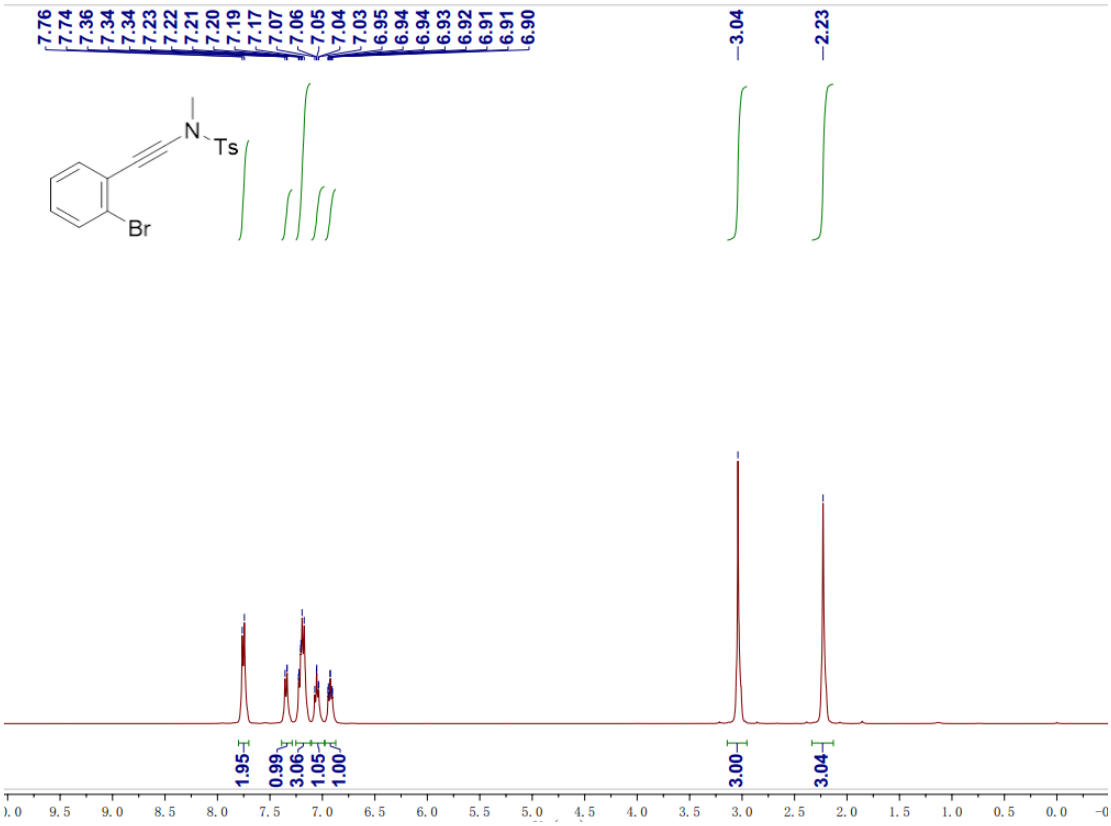


Figure S1. Influence of MeOH on the yields of **3a** and **4**,

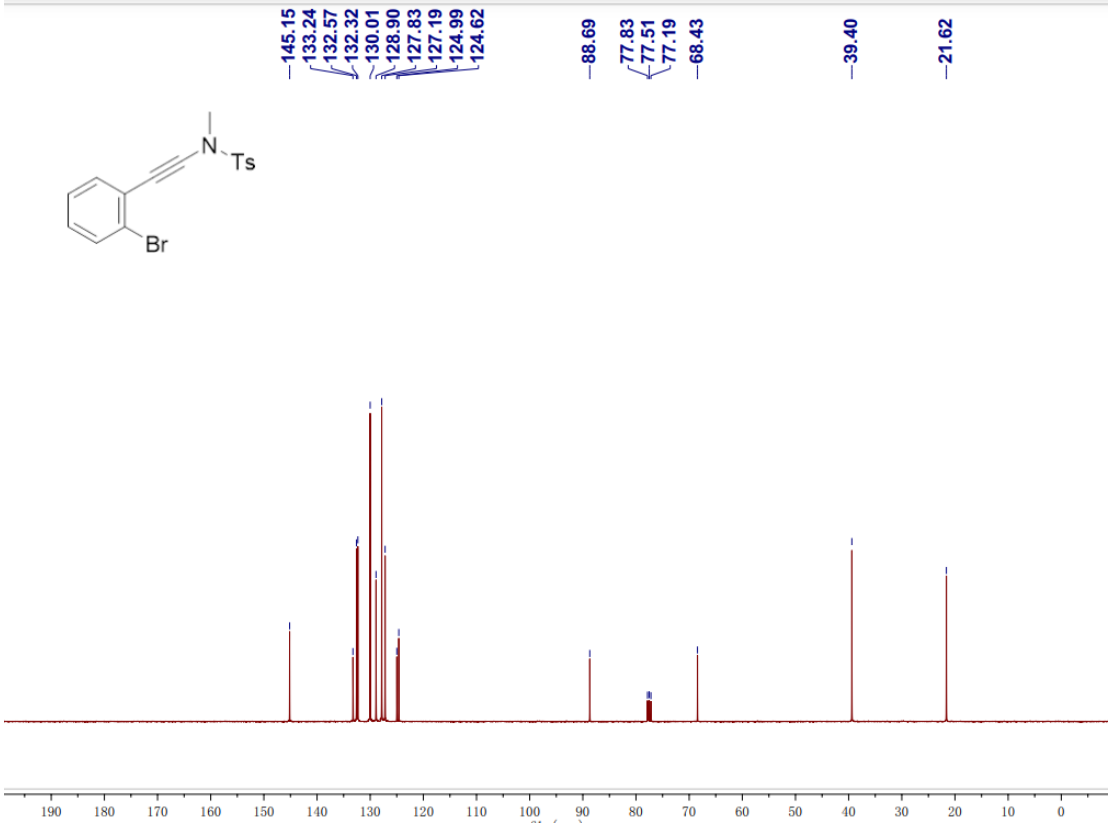
Since it was discovered that the MeOH additive was crucial in this reaction, the influence of MeOH on the yields of **3a** and **4** was studied (Figure 2). As can be seen from Figure 2, with the addition of MeOH increased from 0 to 20 equiv, the yields of both **3a** and **4** increased. A good result was obtained when 0.4 mL of MeOH was added, the yields of **3a** reached tis maximum while the *5-exo-dig* byproduct **4** was suppressed. After this stage, the yield of **3a** was decreasing with the addition of extra MeOH.

5. ^{1}H and ^{13}C NMR Spectra of all new compounds 1.

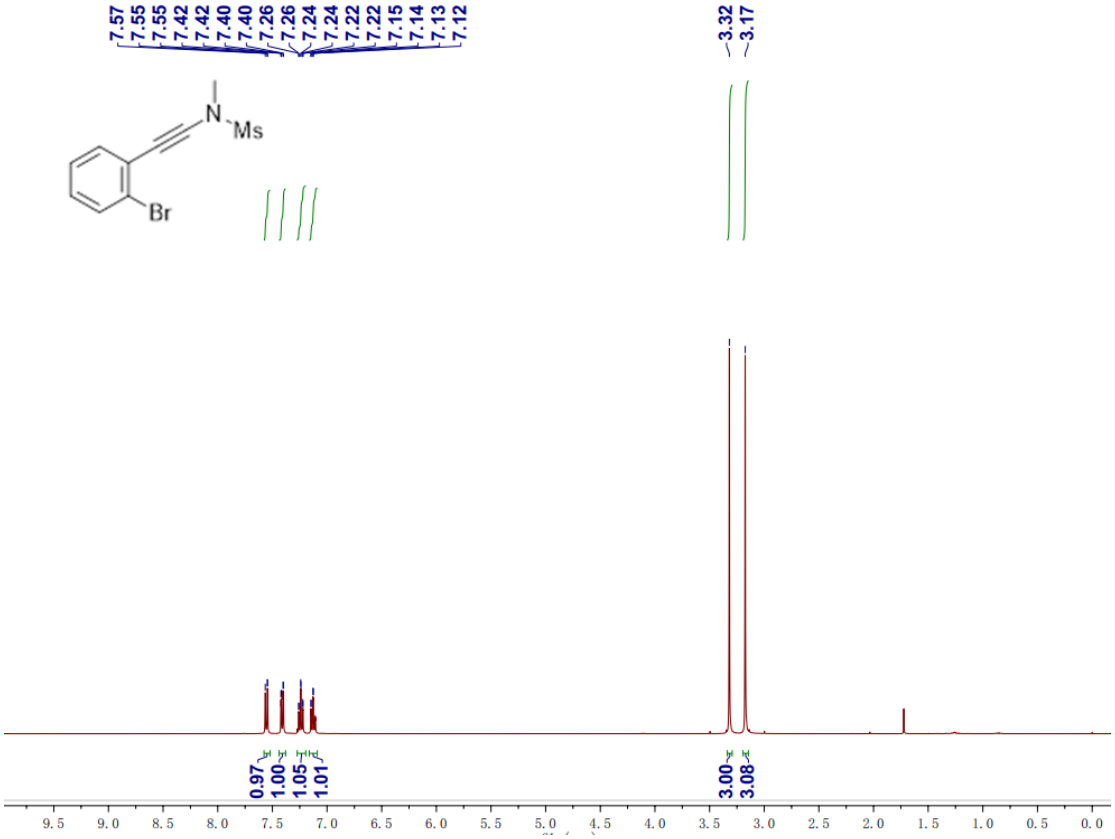
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1a



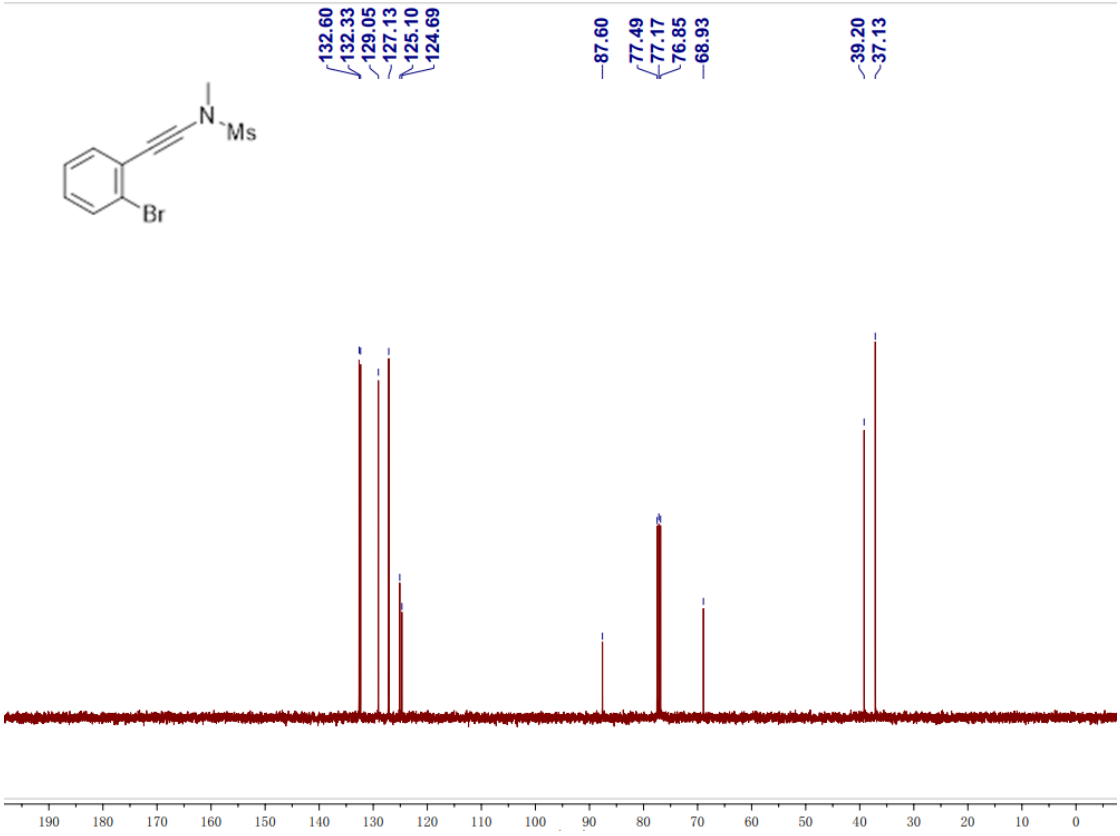
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1a



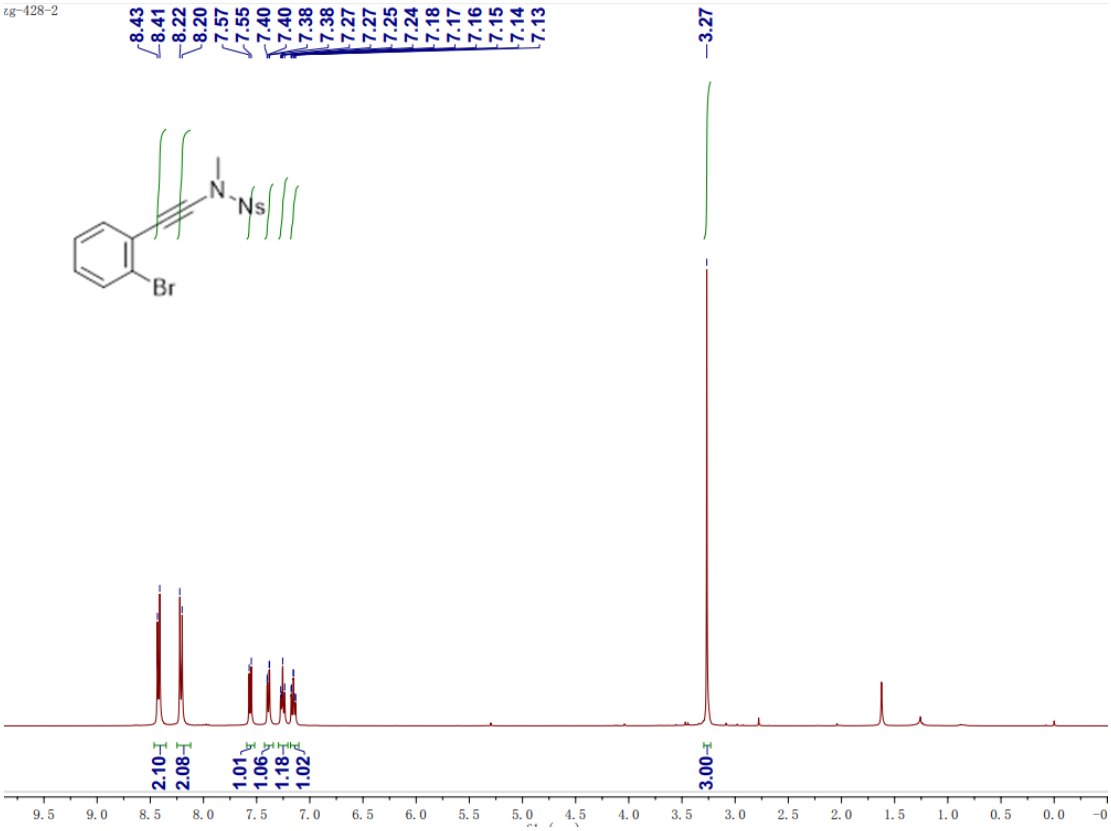
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1b



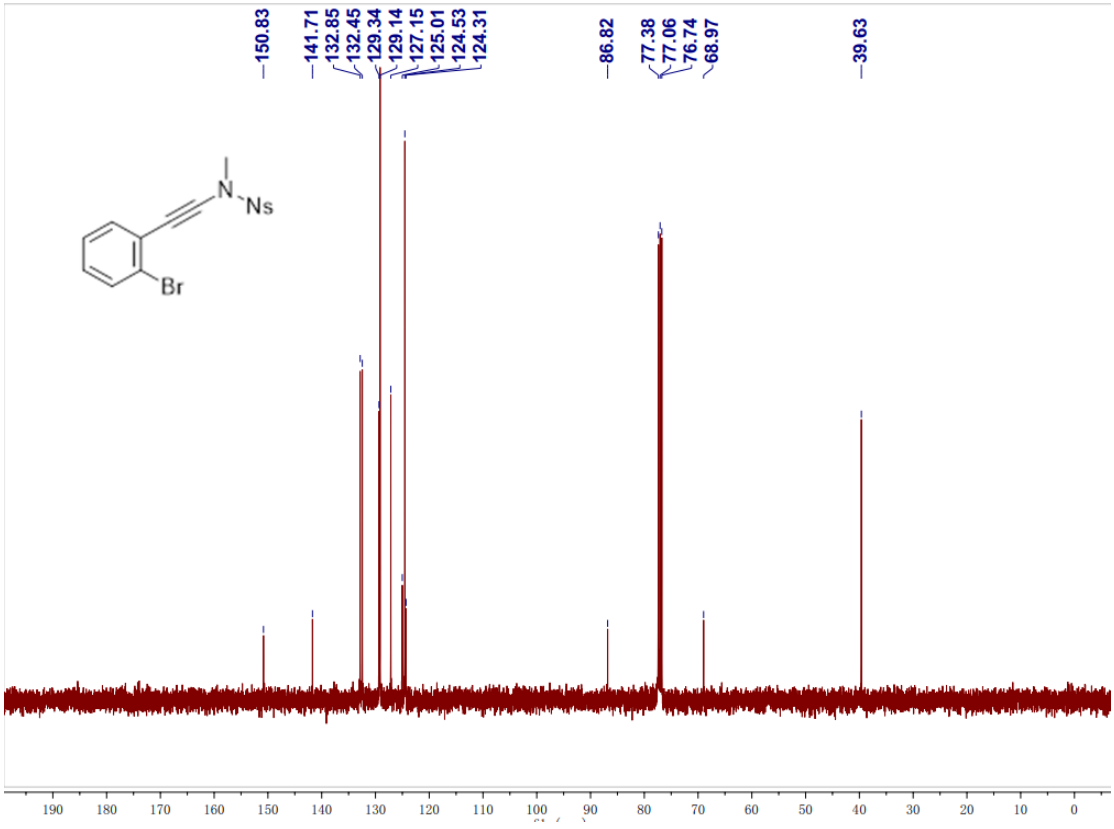
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1b



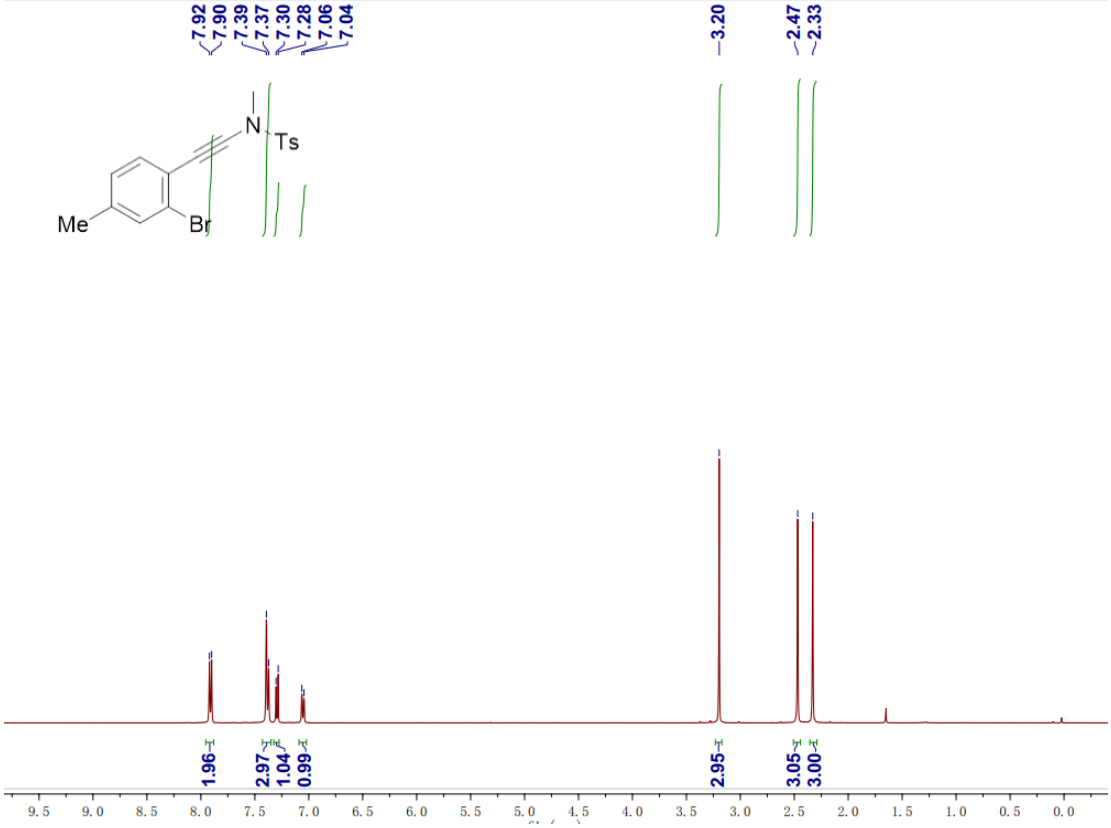
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1c



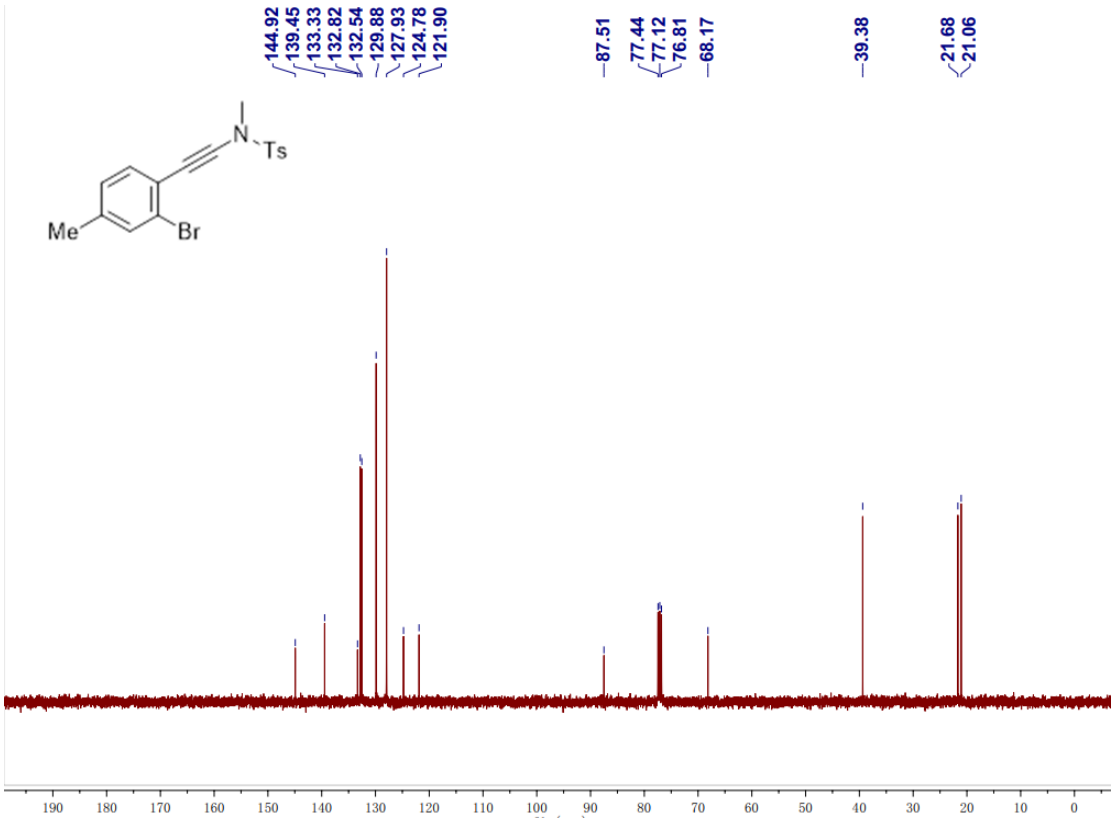
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1c



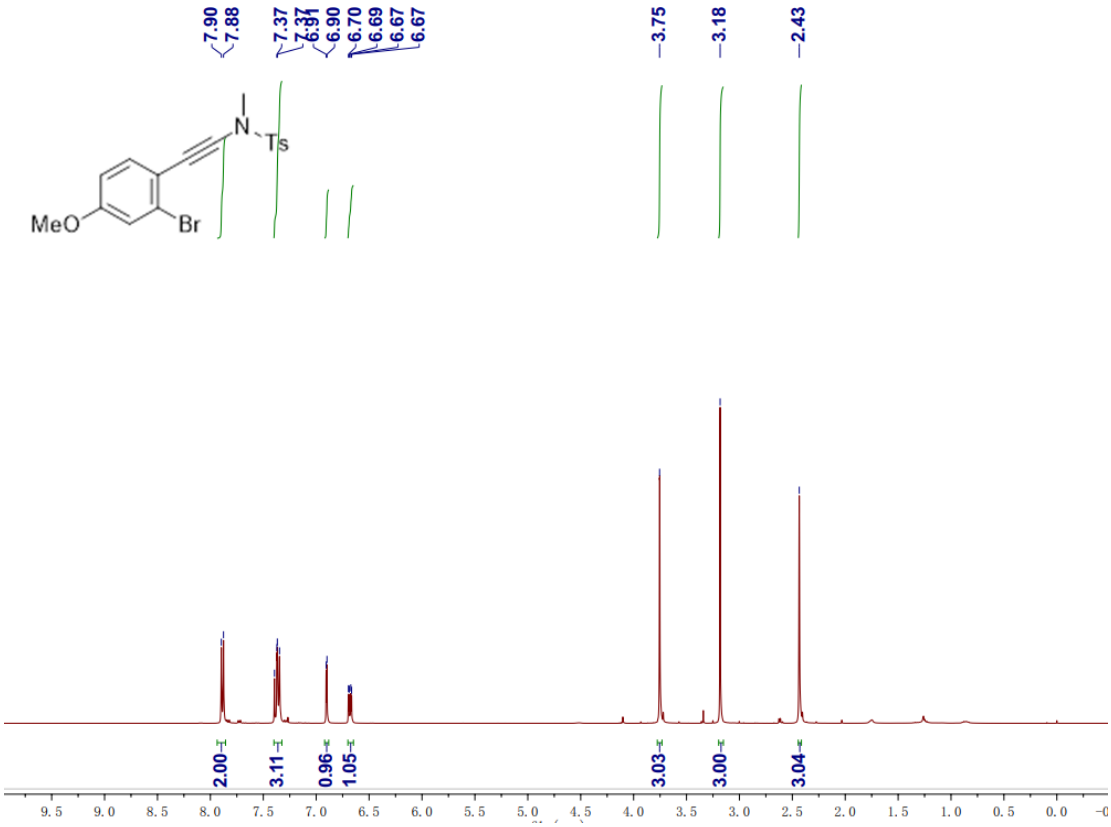
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1d



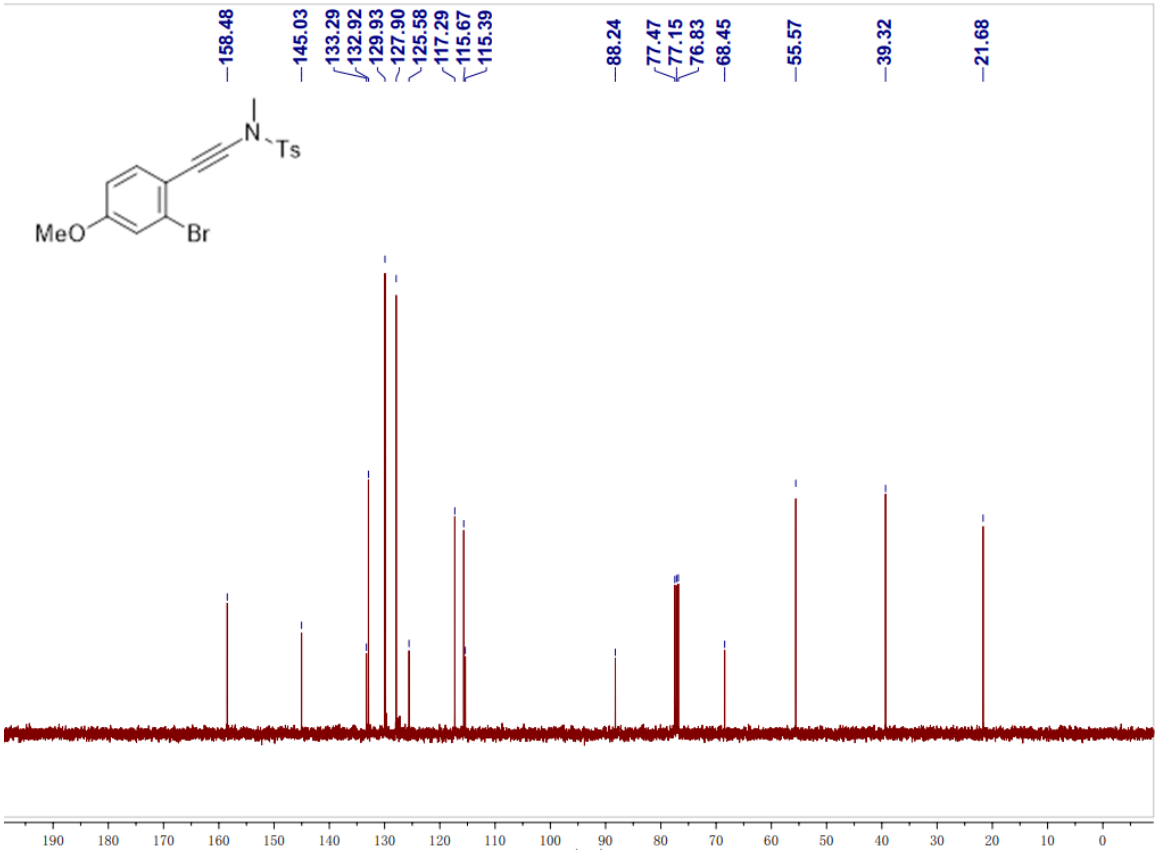
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1d



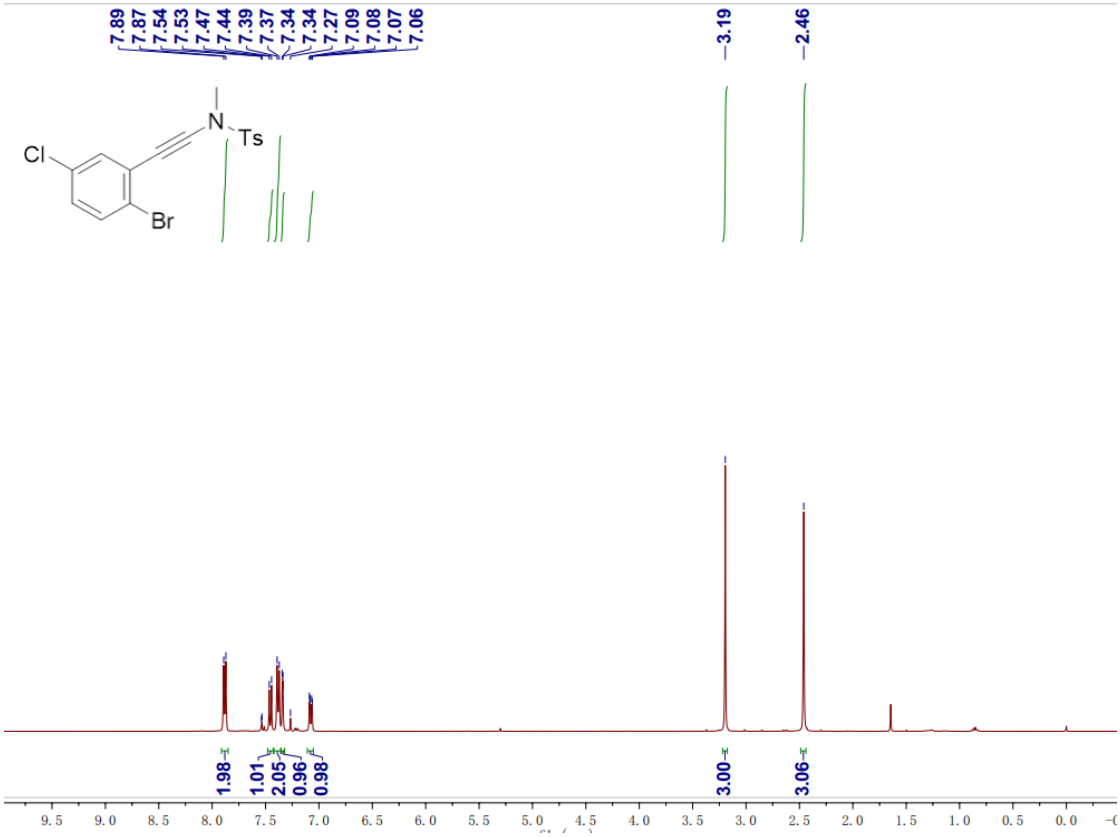
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1e



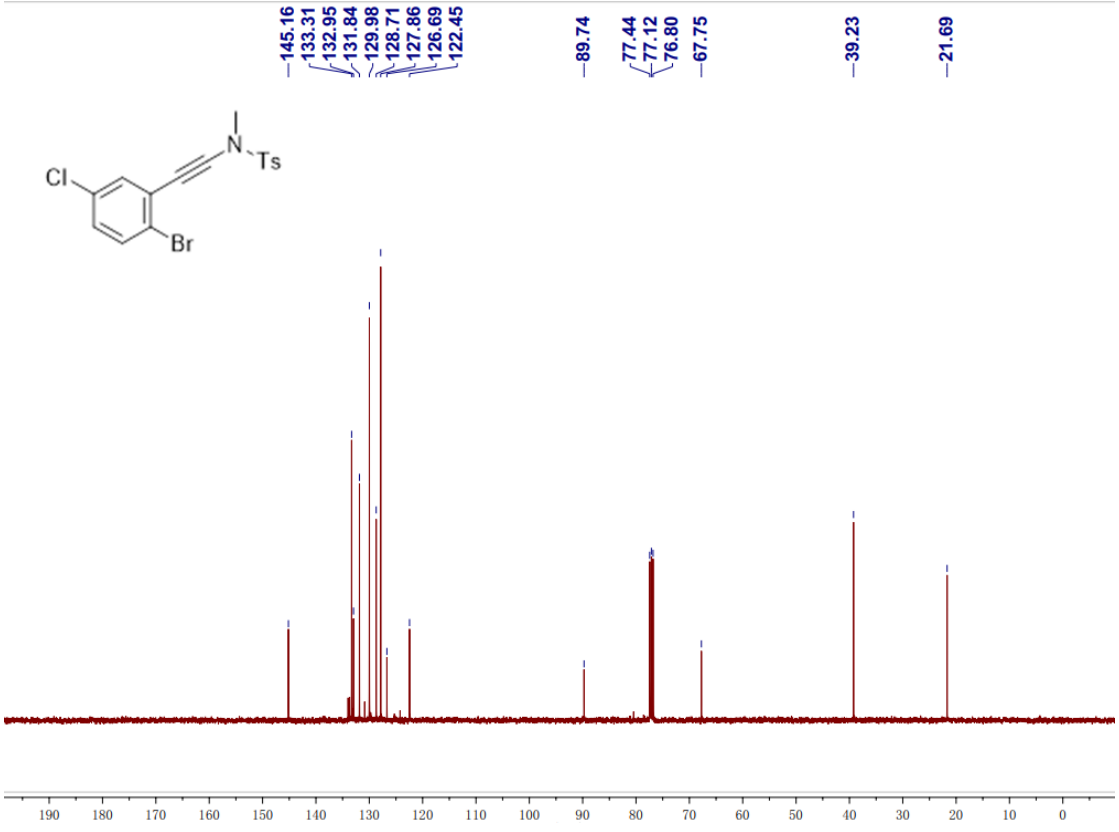
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1e



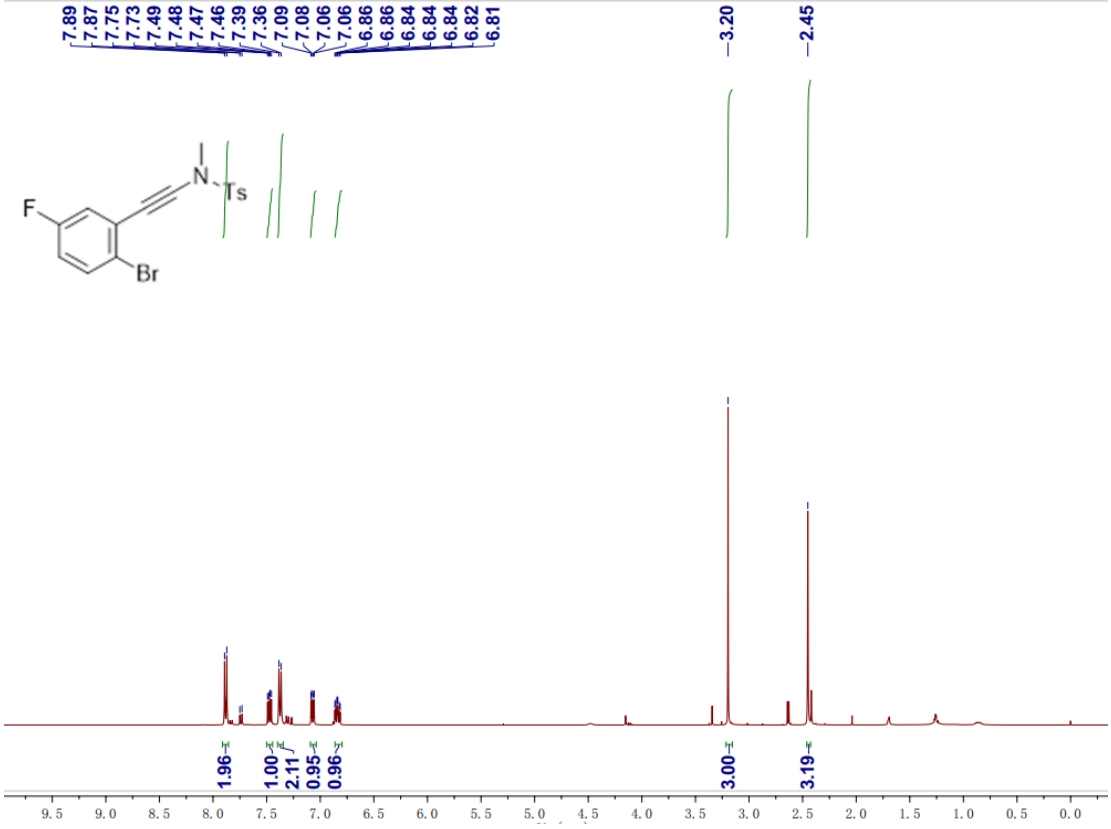
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1f



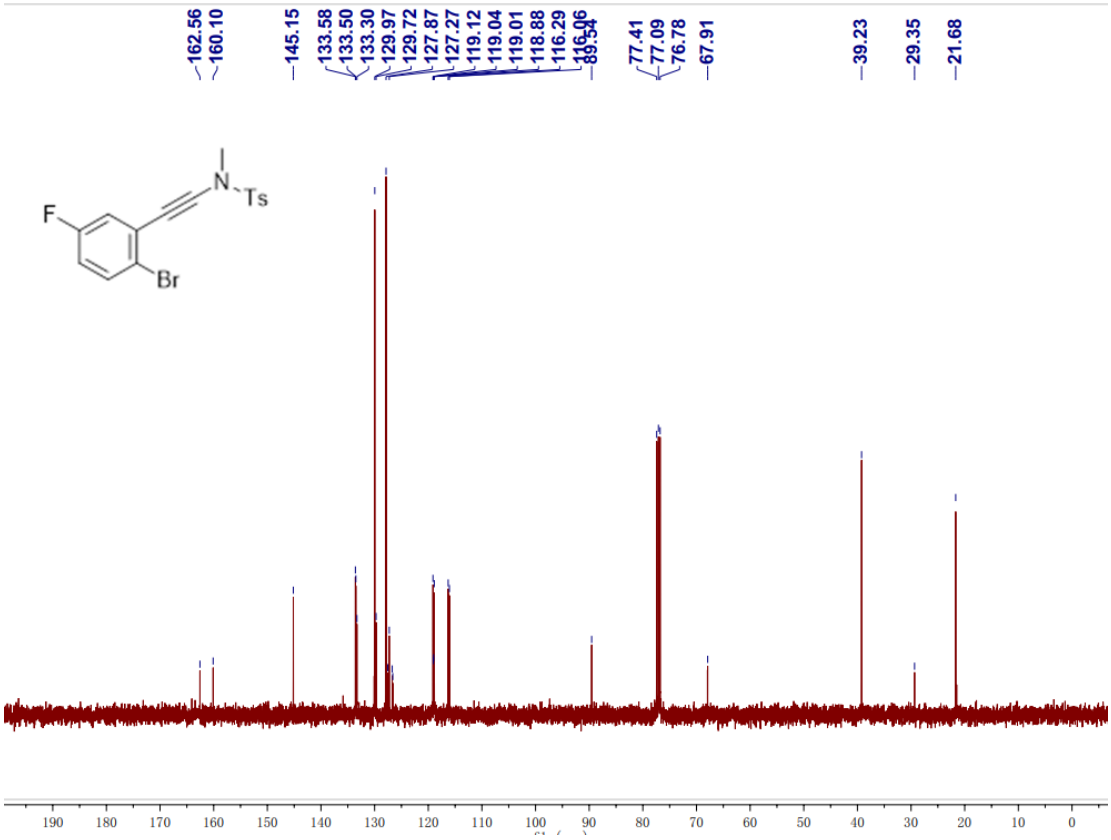
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1f



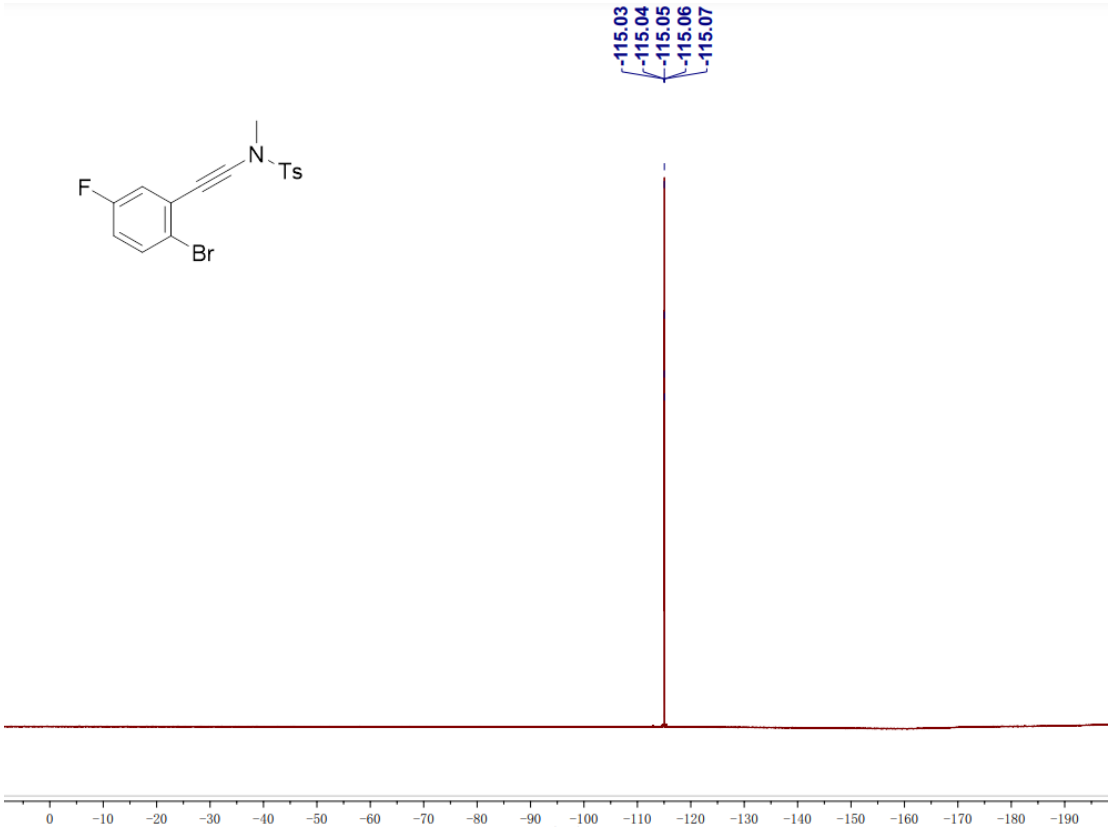
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1g



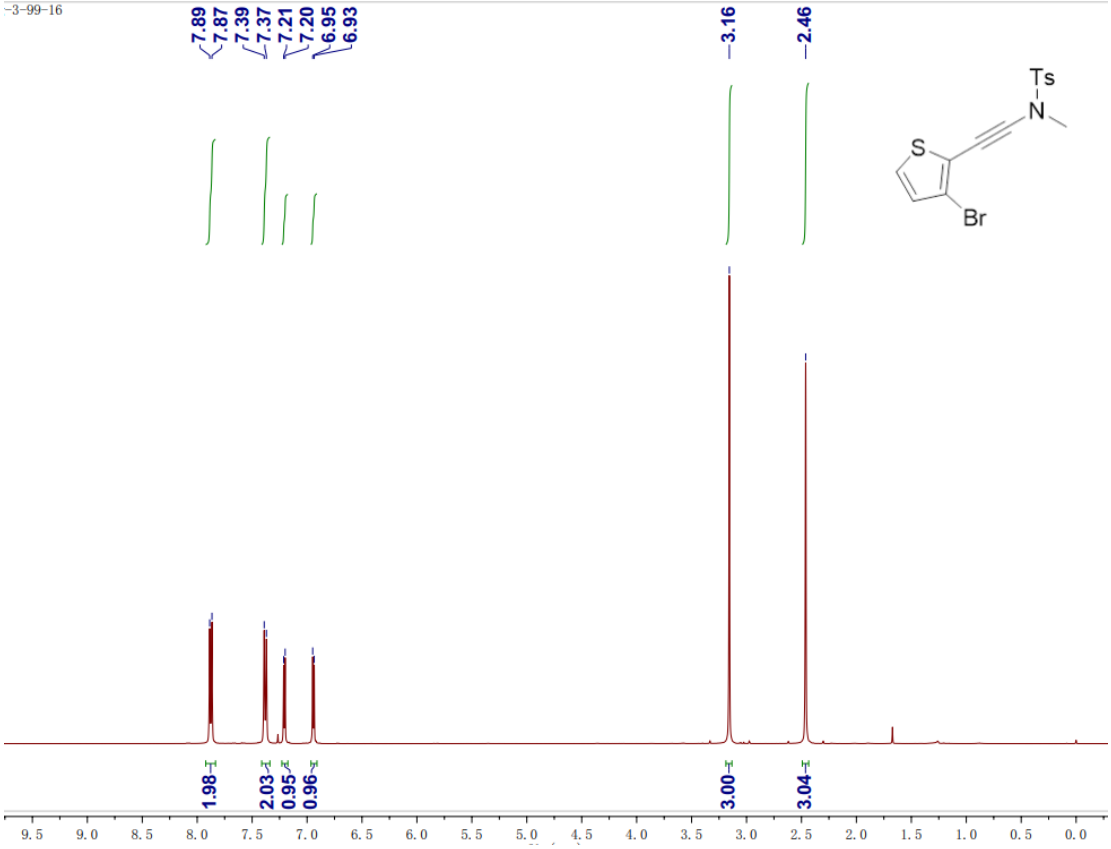
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1g



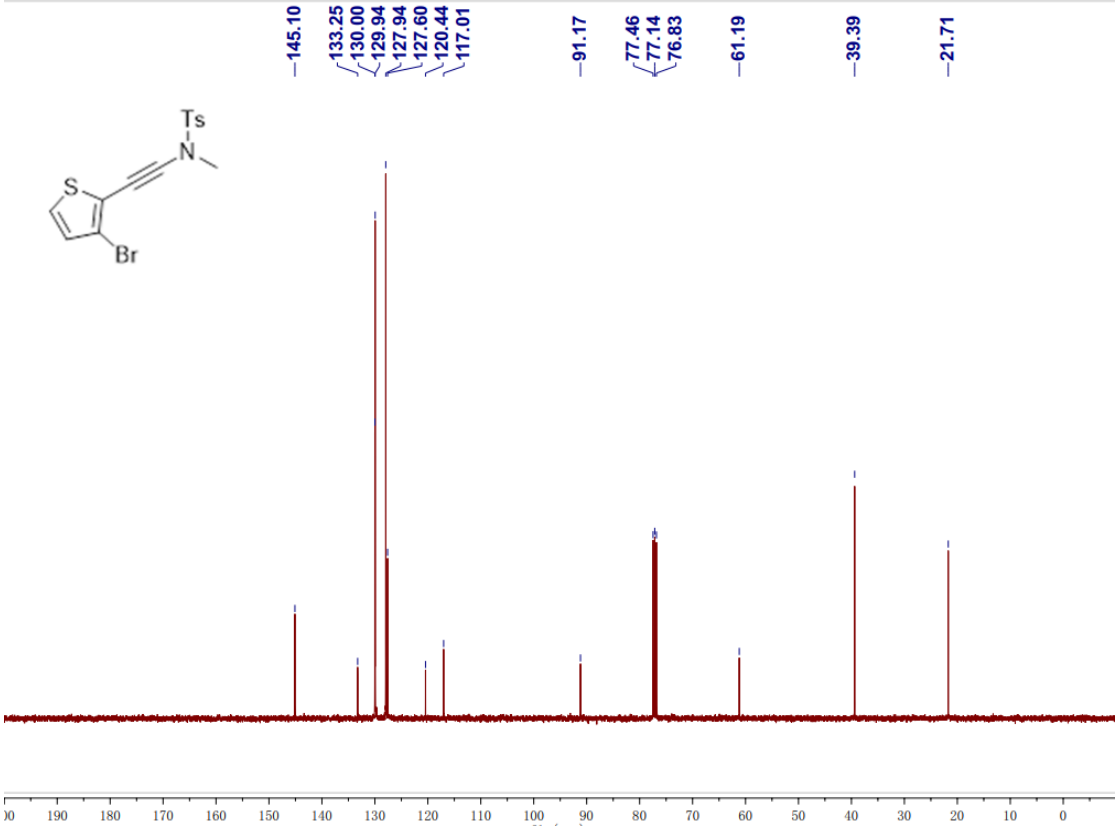
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 1g



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

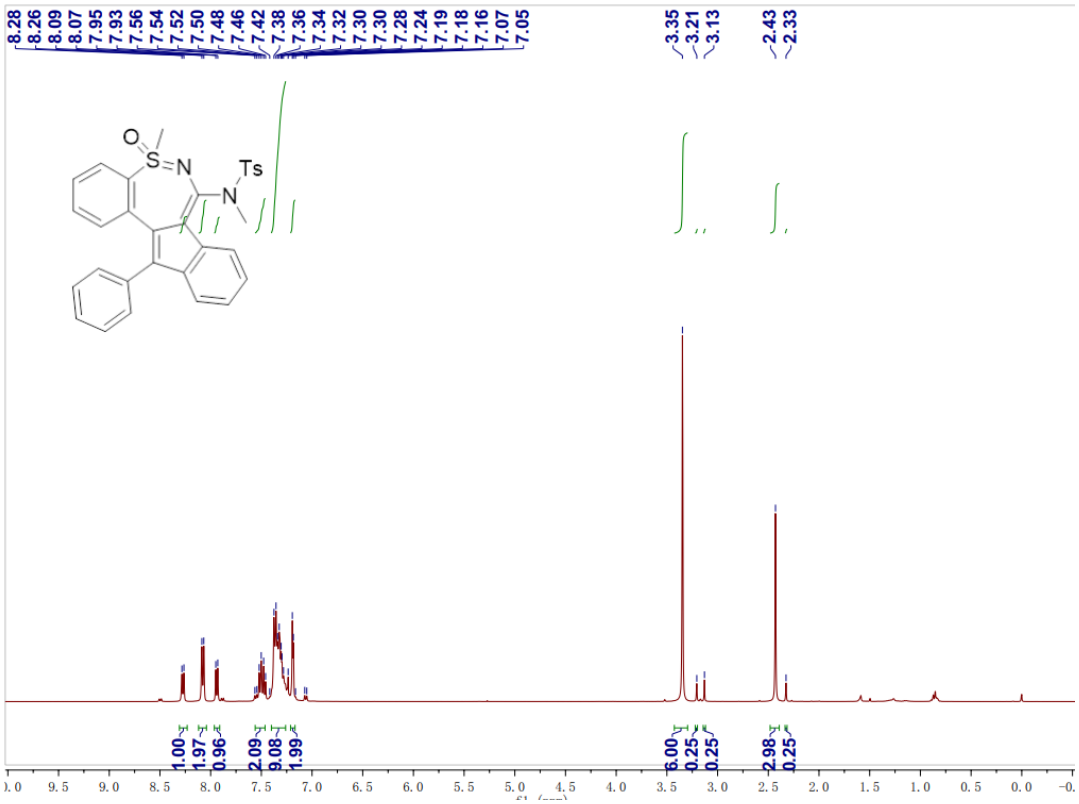


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 1h

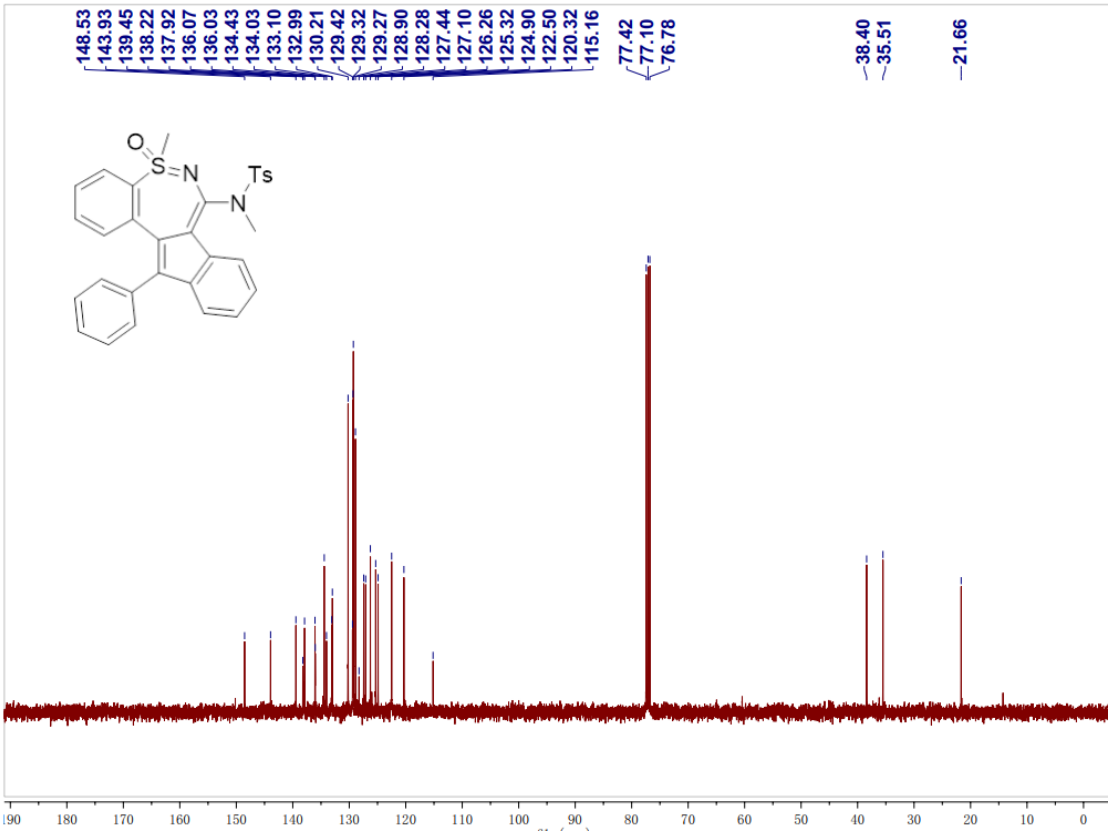


6. ^{1}H and ^{13}C NMR Spectra of all new compounds 3.

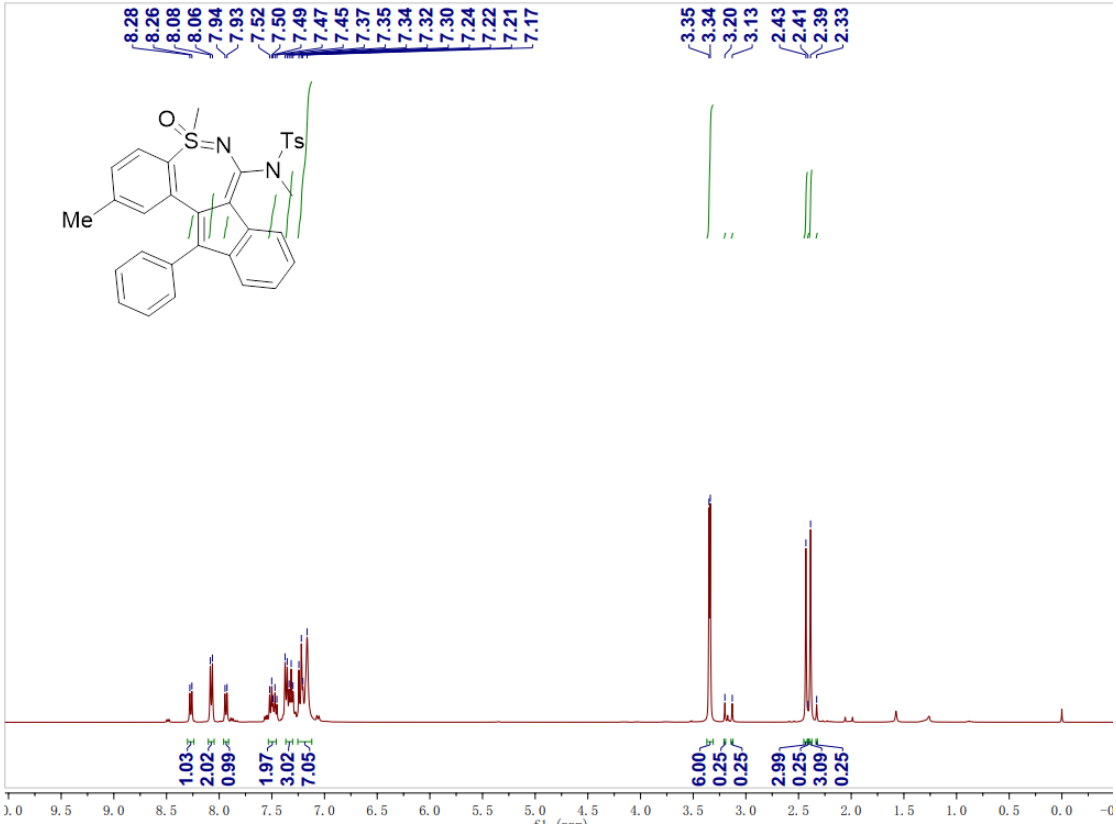
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3a



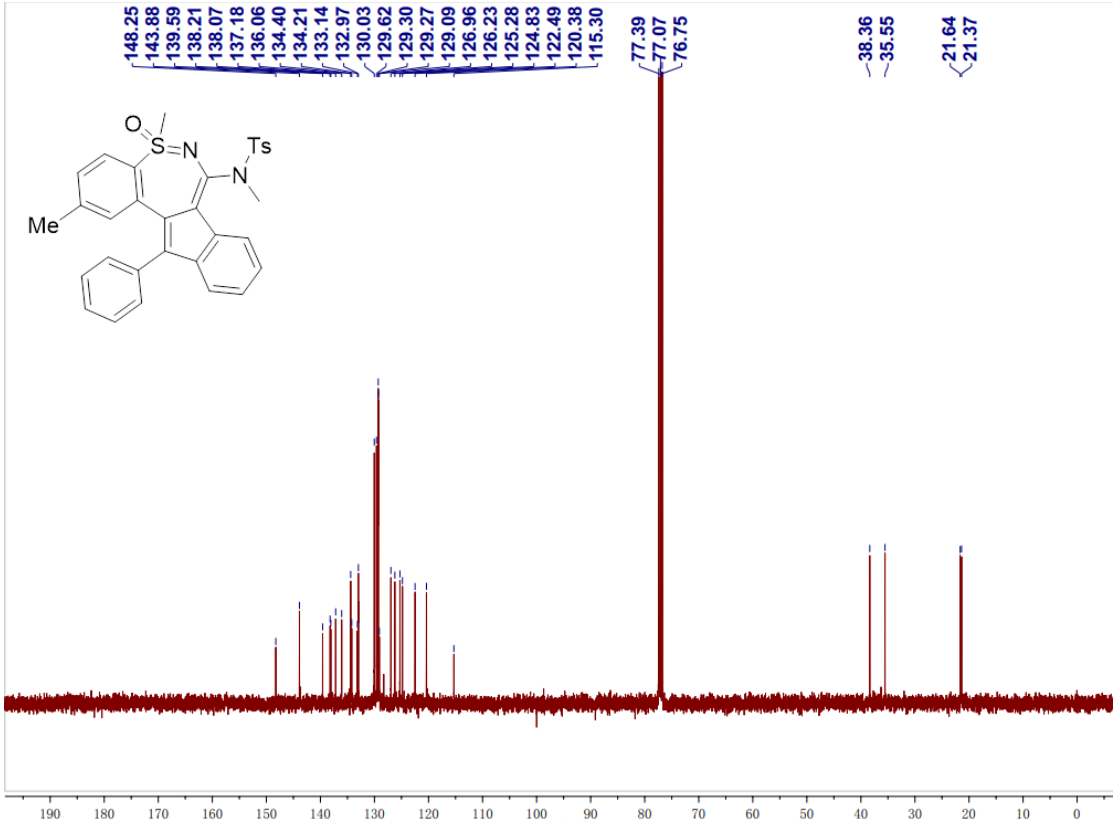
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3a



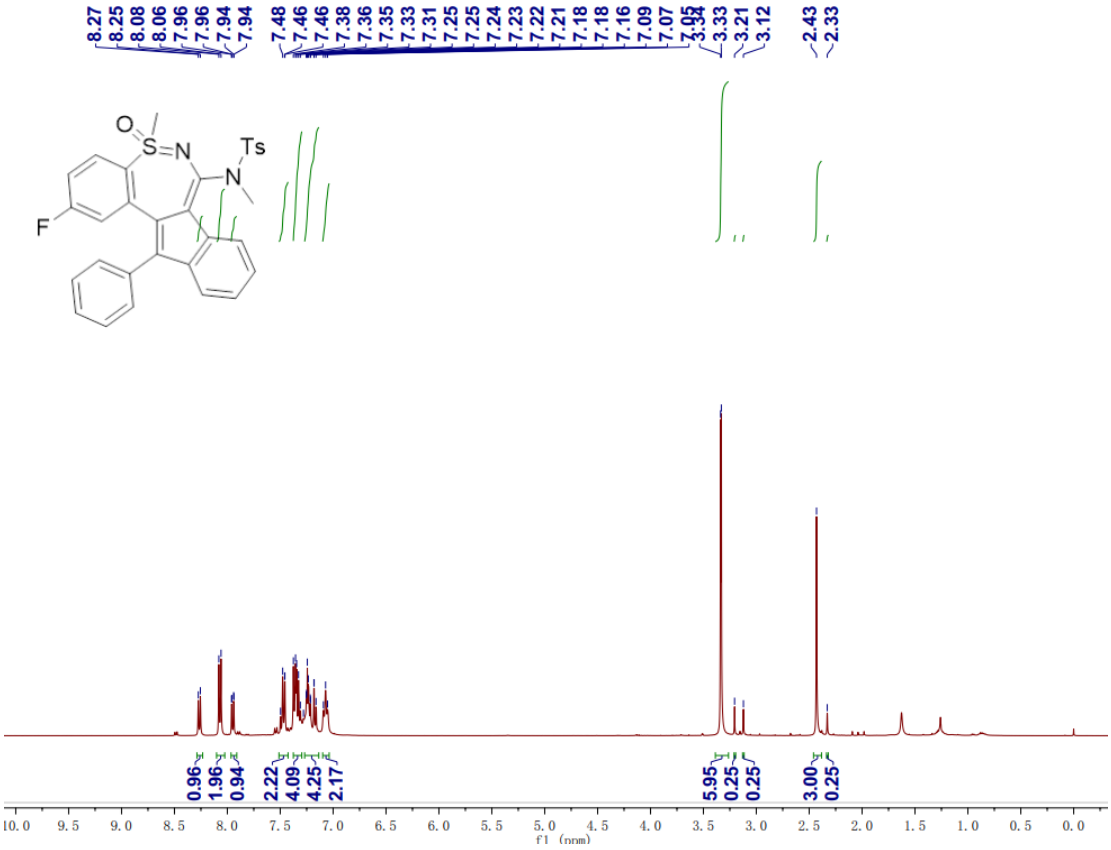
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3b



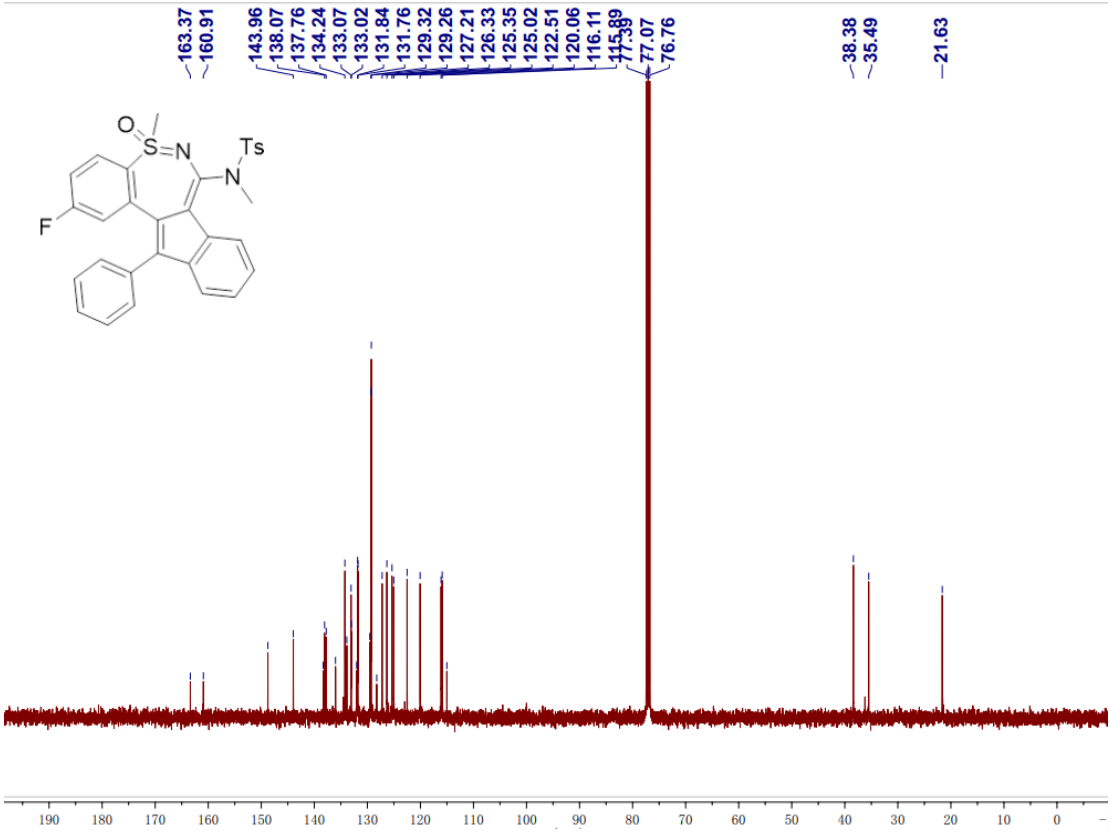
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3b



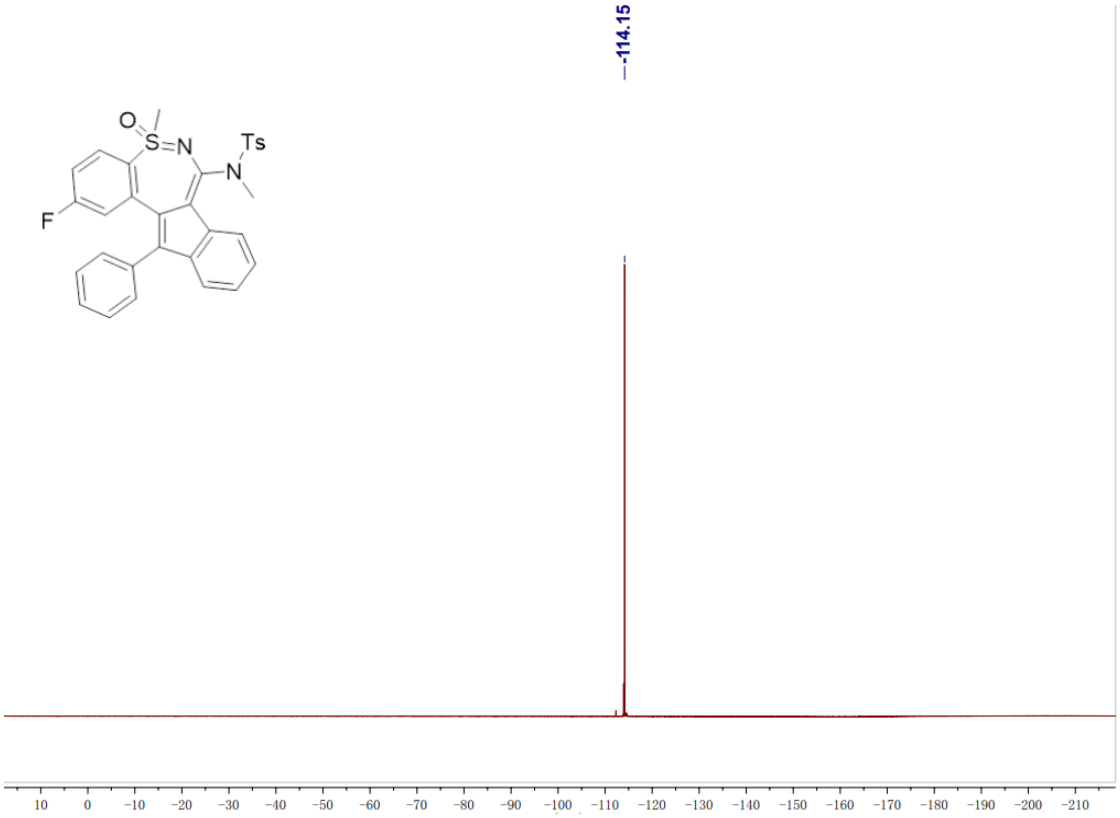
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3c



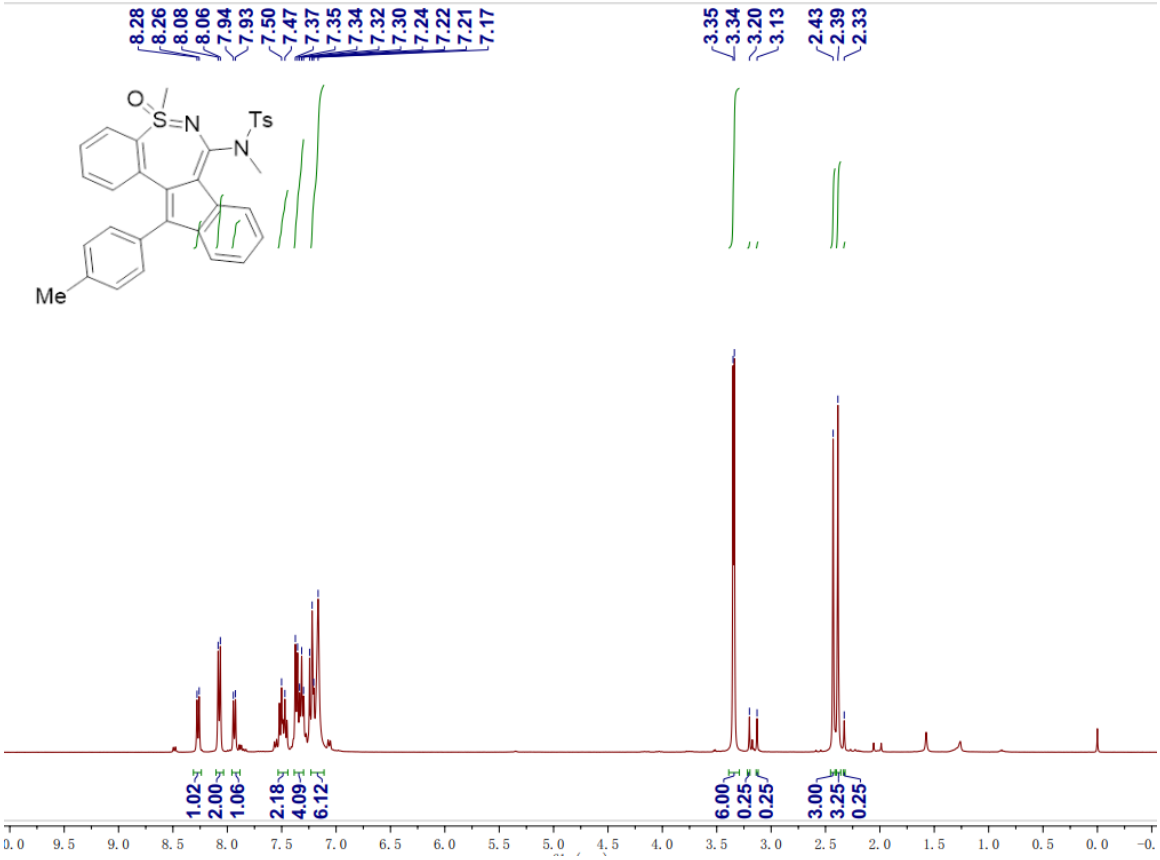
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3c



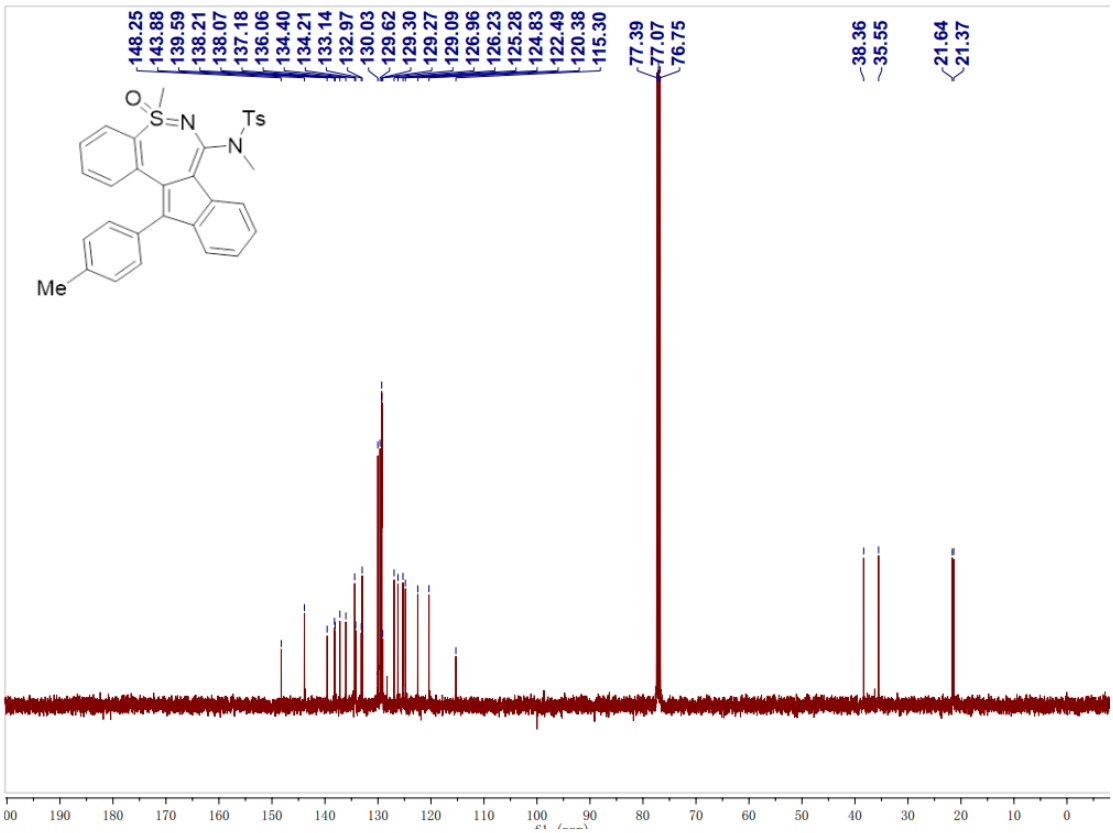
^{19}F NMR spectrum (376 MHz, **$CDCl_3$) of 3c**



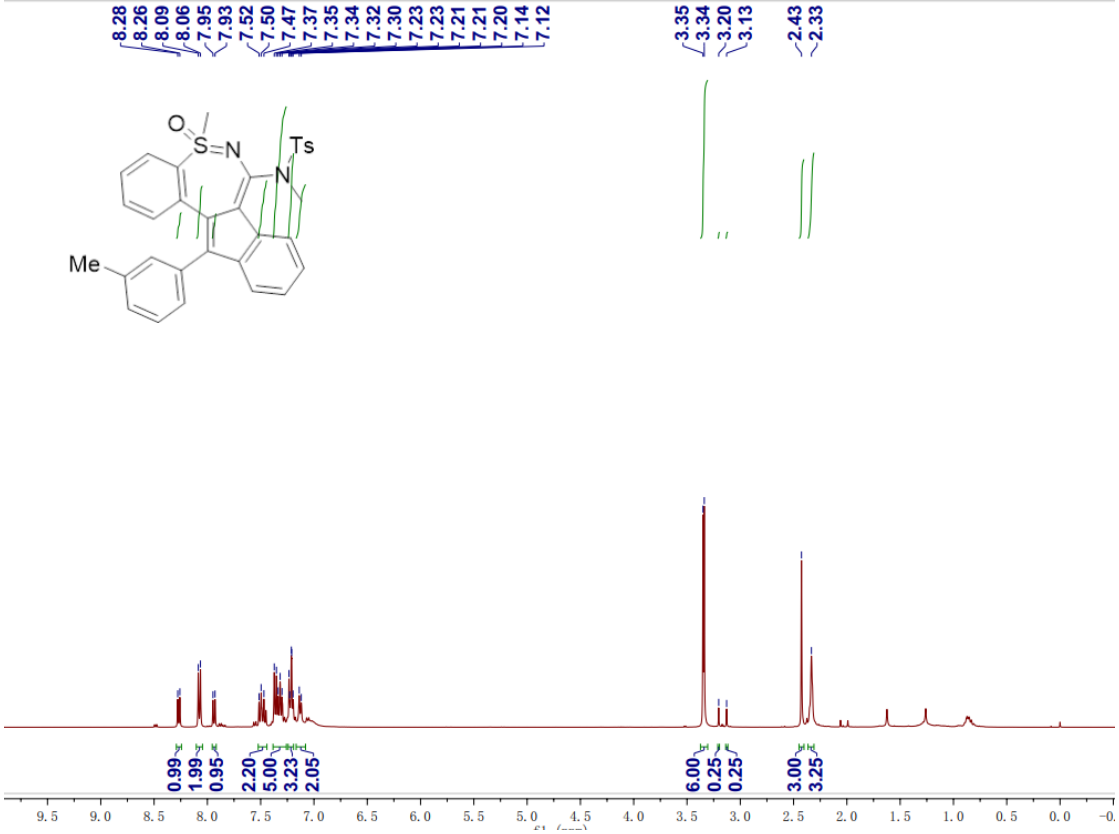
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3d



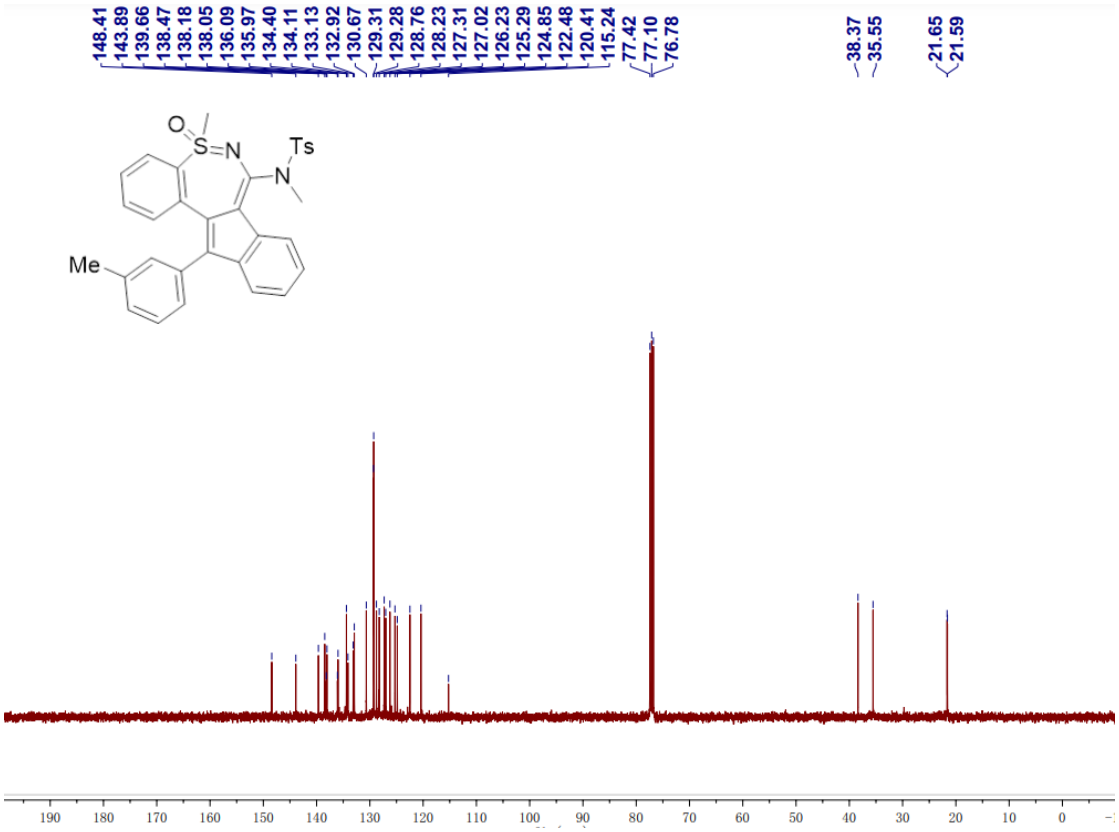
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3d



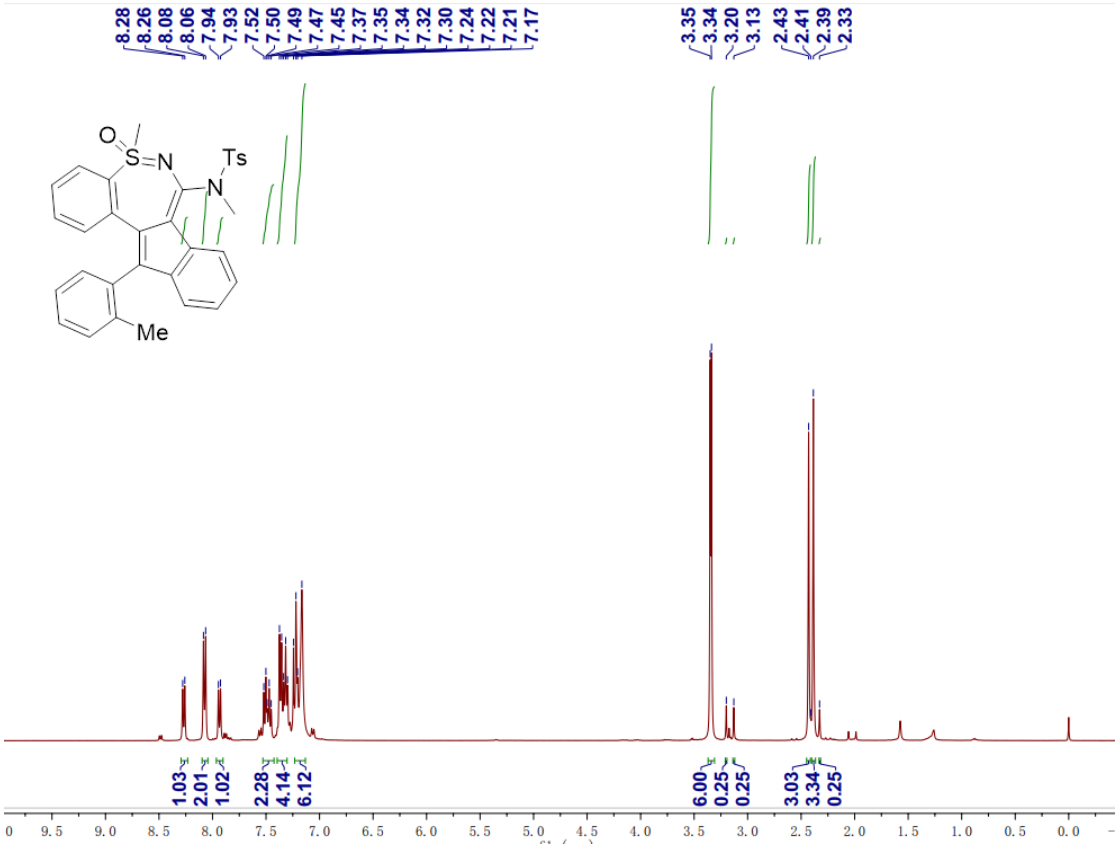
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3e



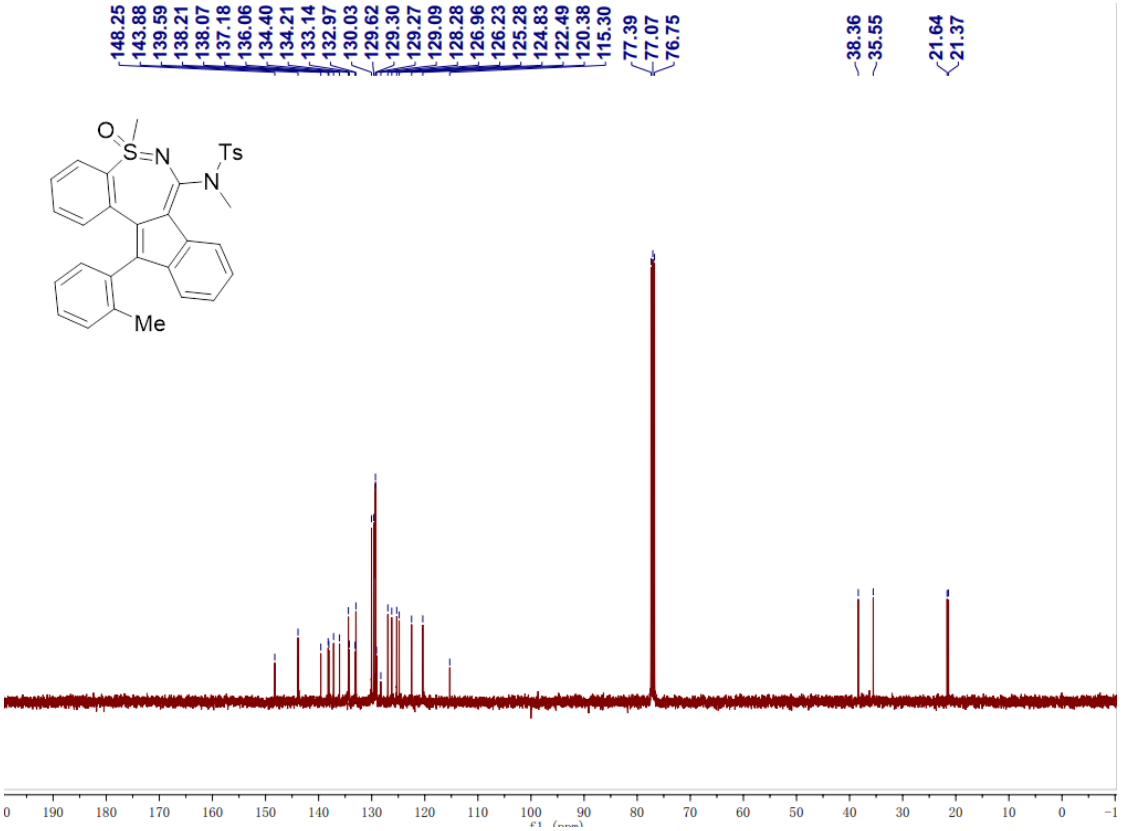
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3e



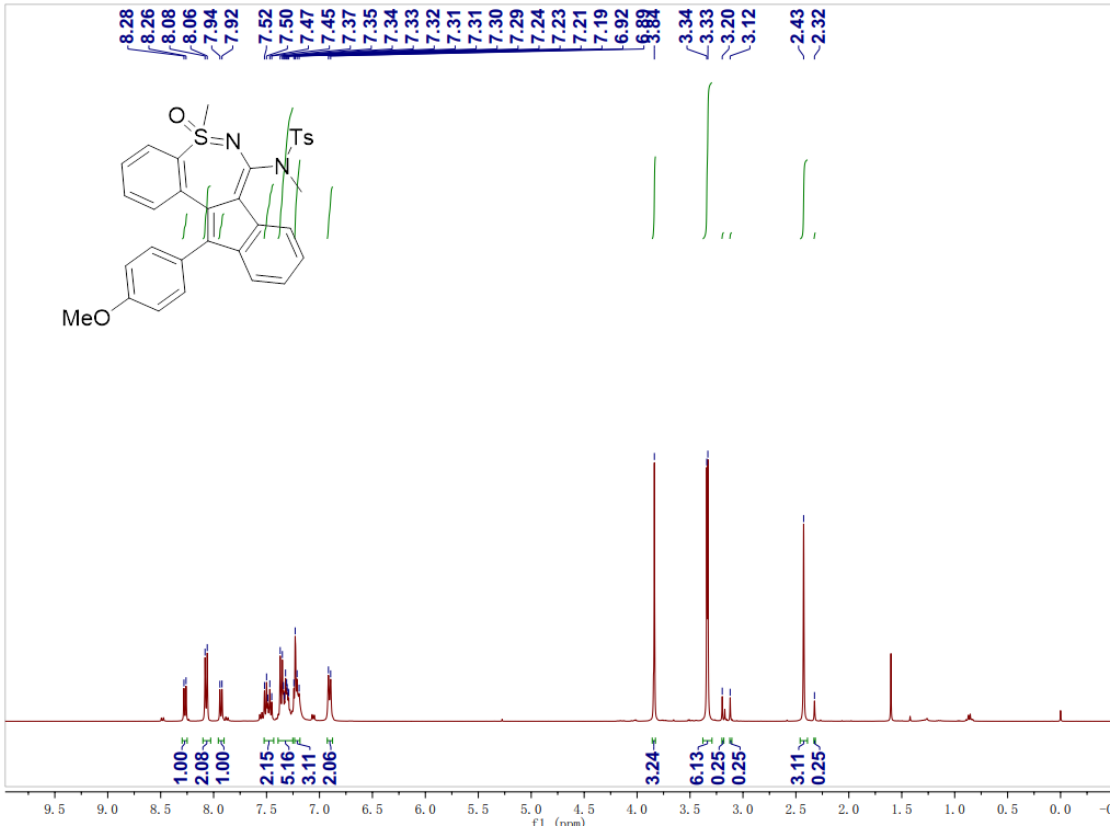
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3f



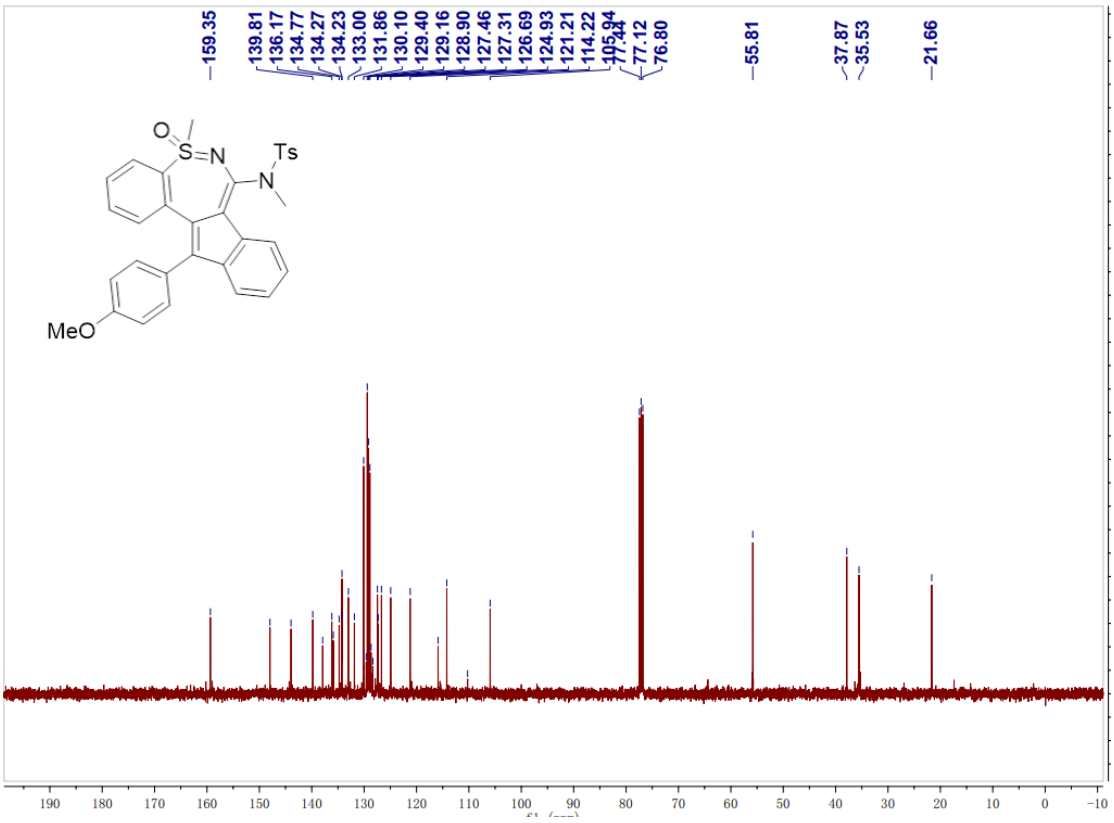
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3f



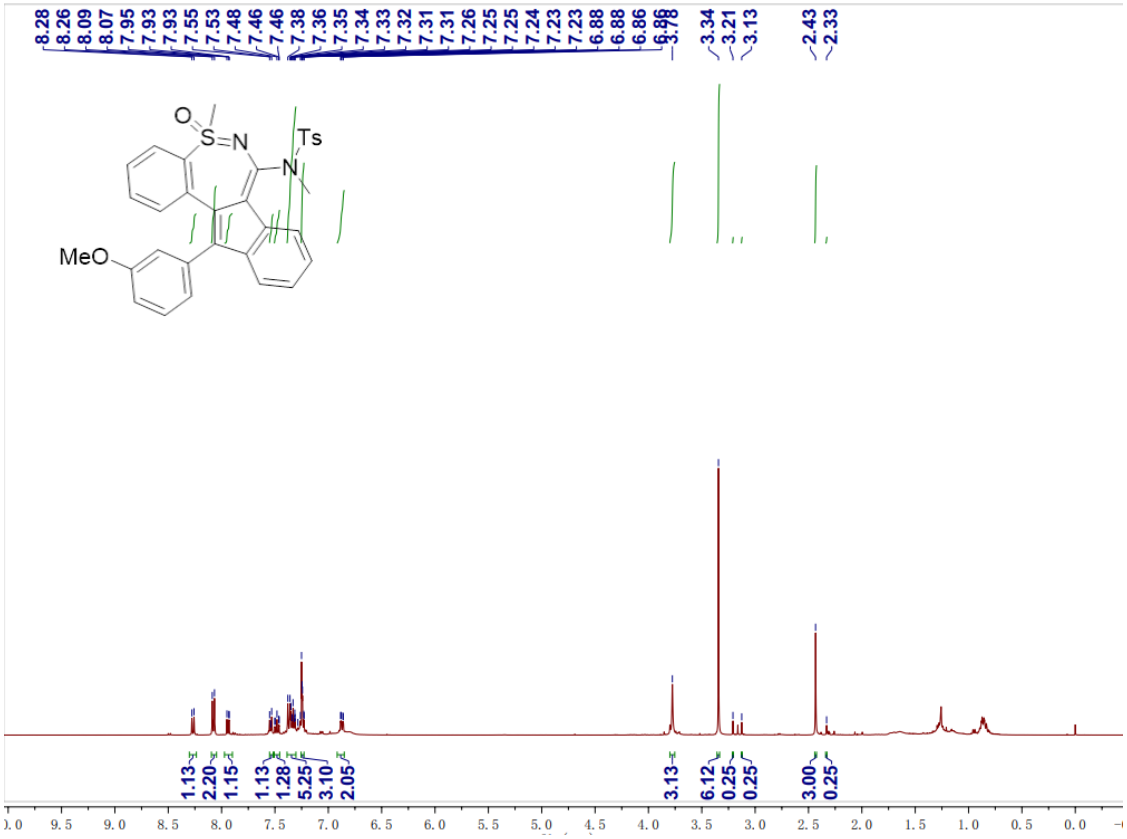
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3g



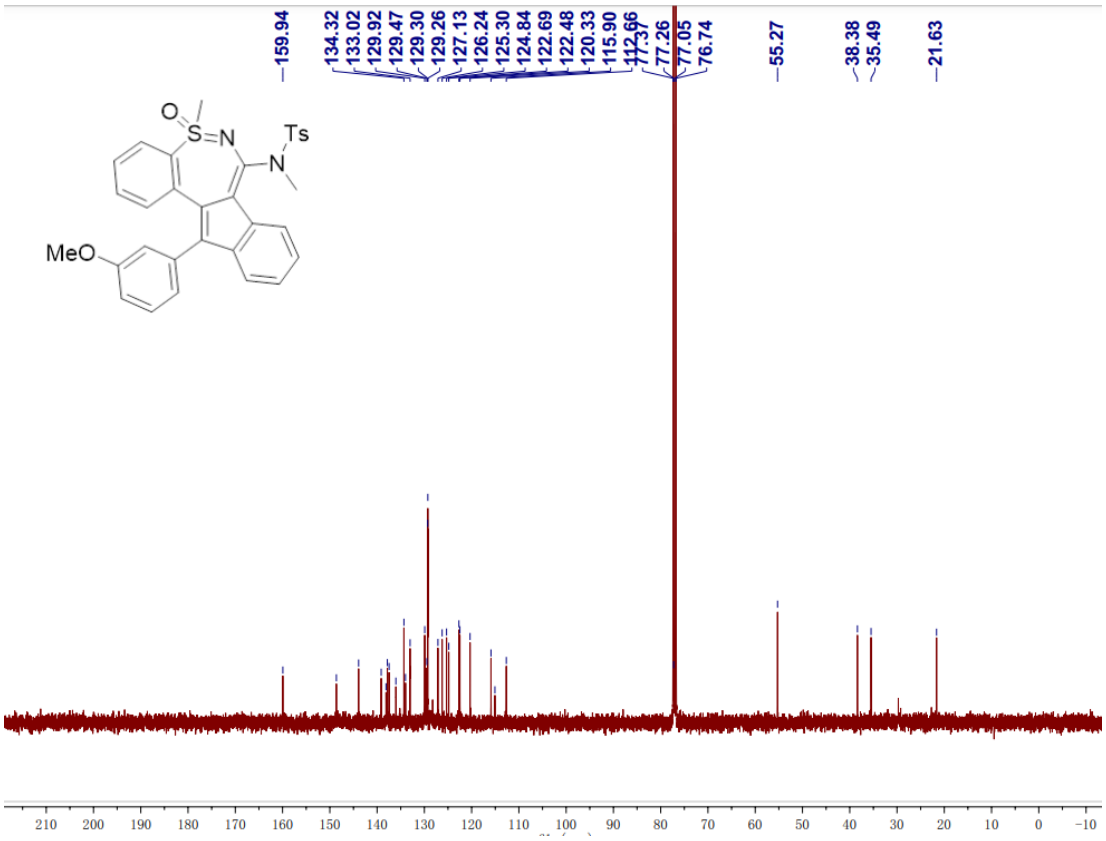
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3g



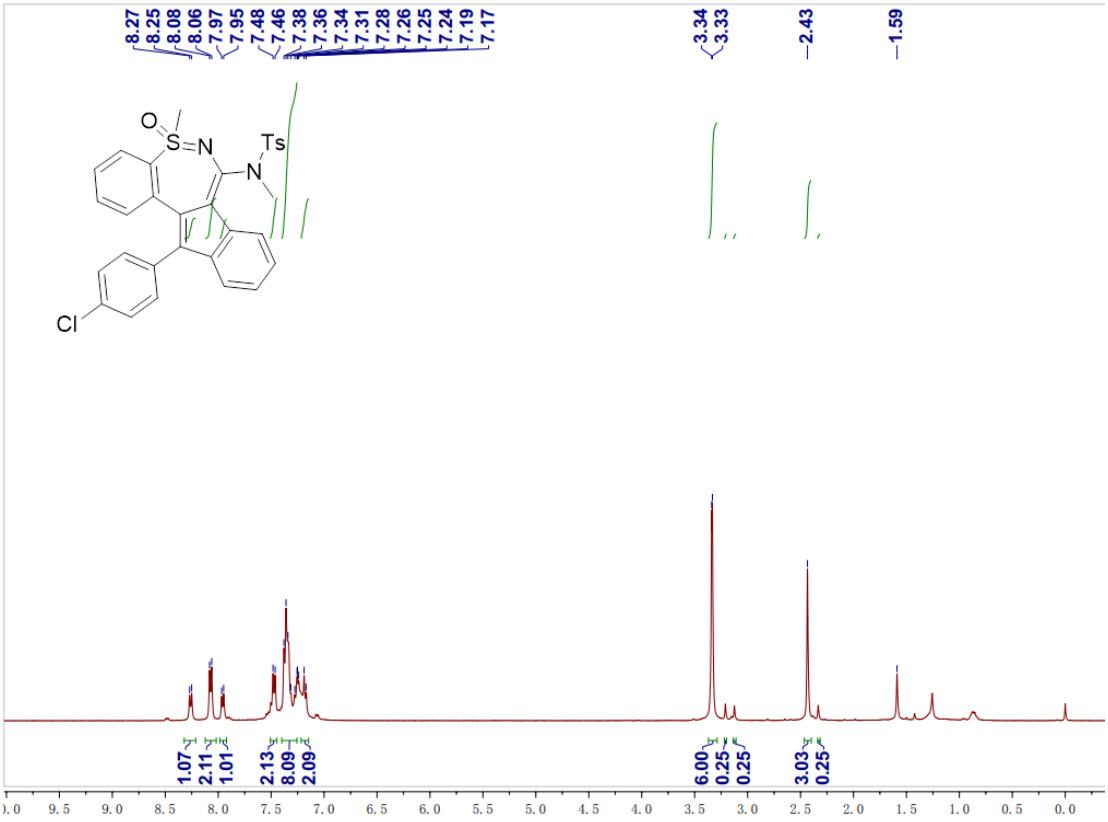
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3h



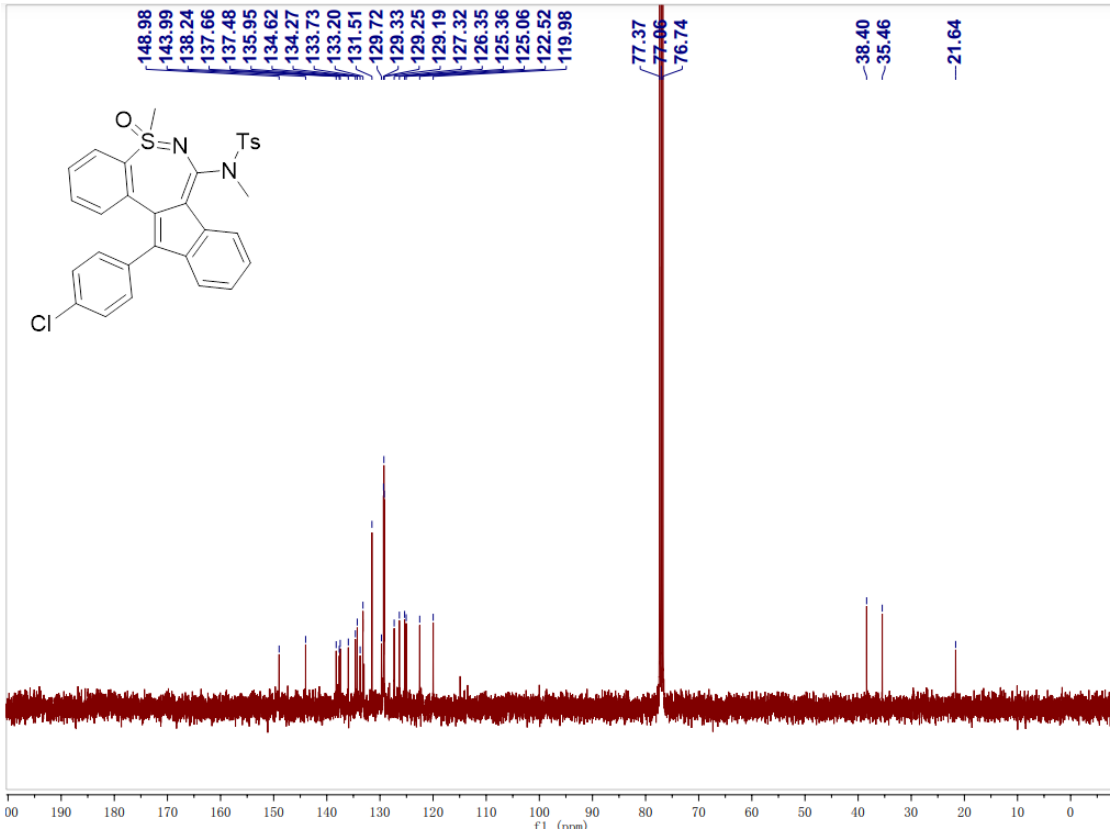
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3h



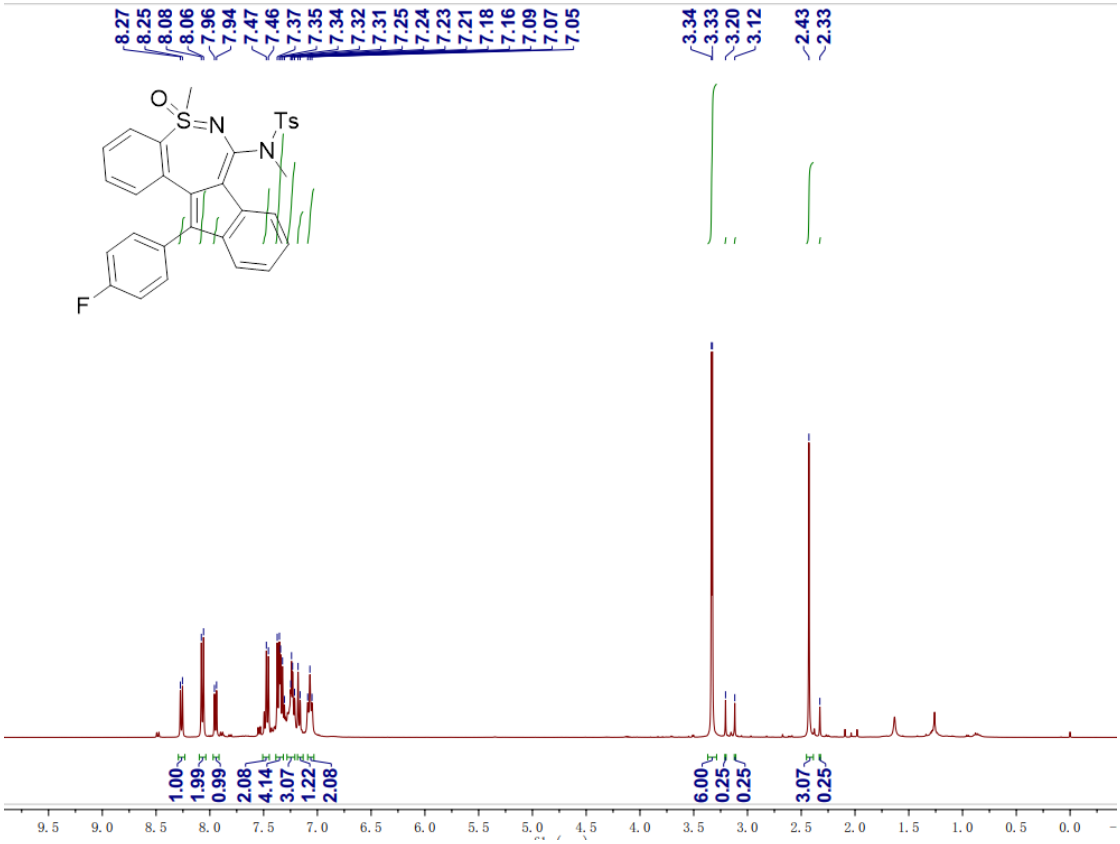
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3i



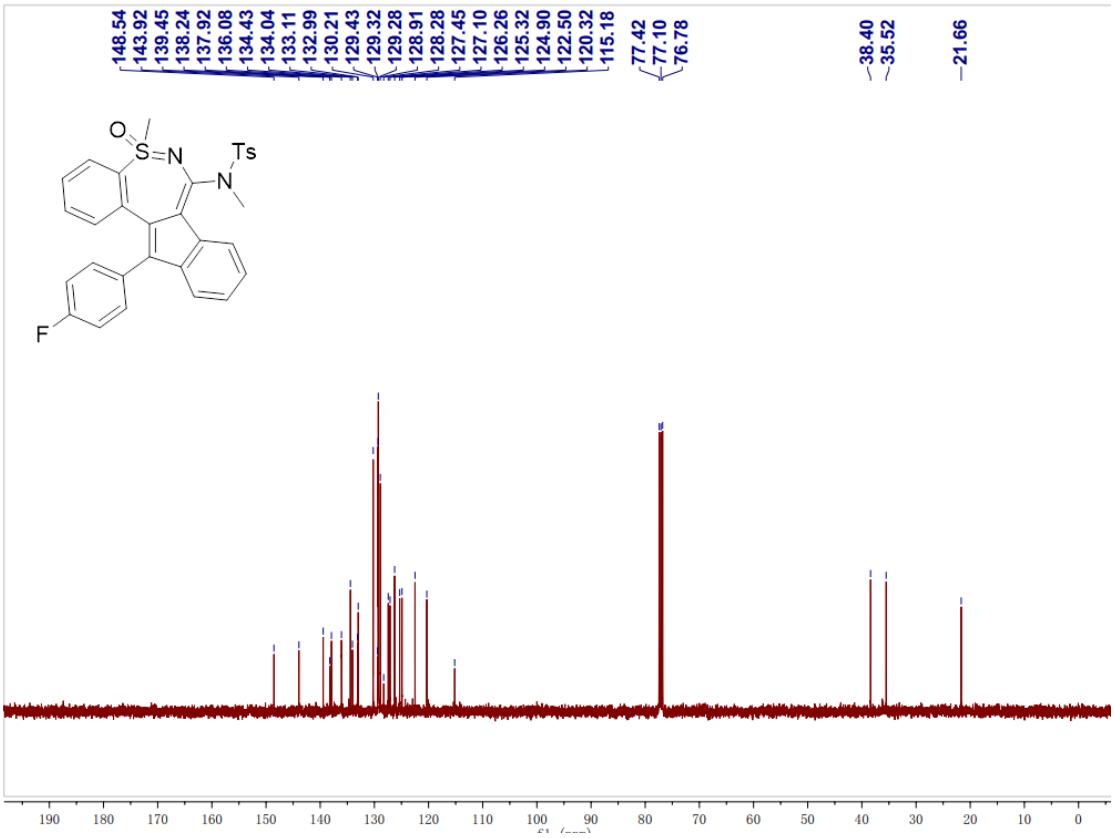
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3i



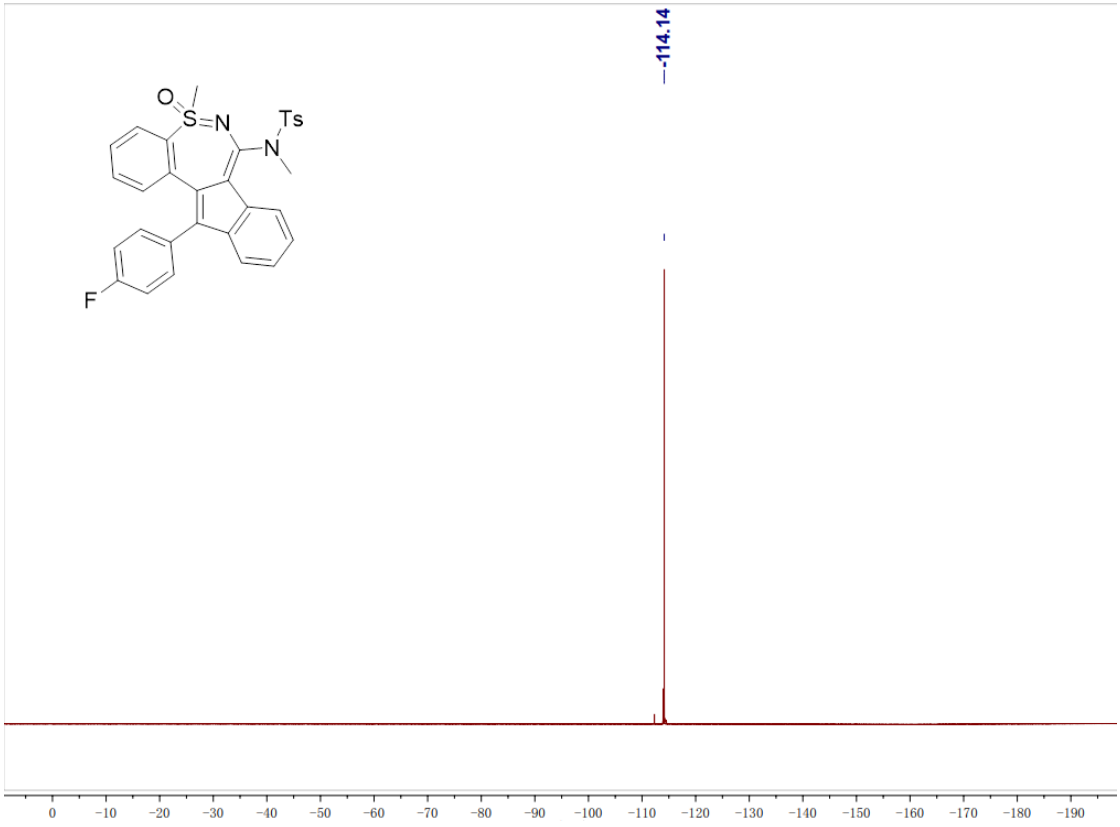
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3j



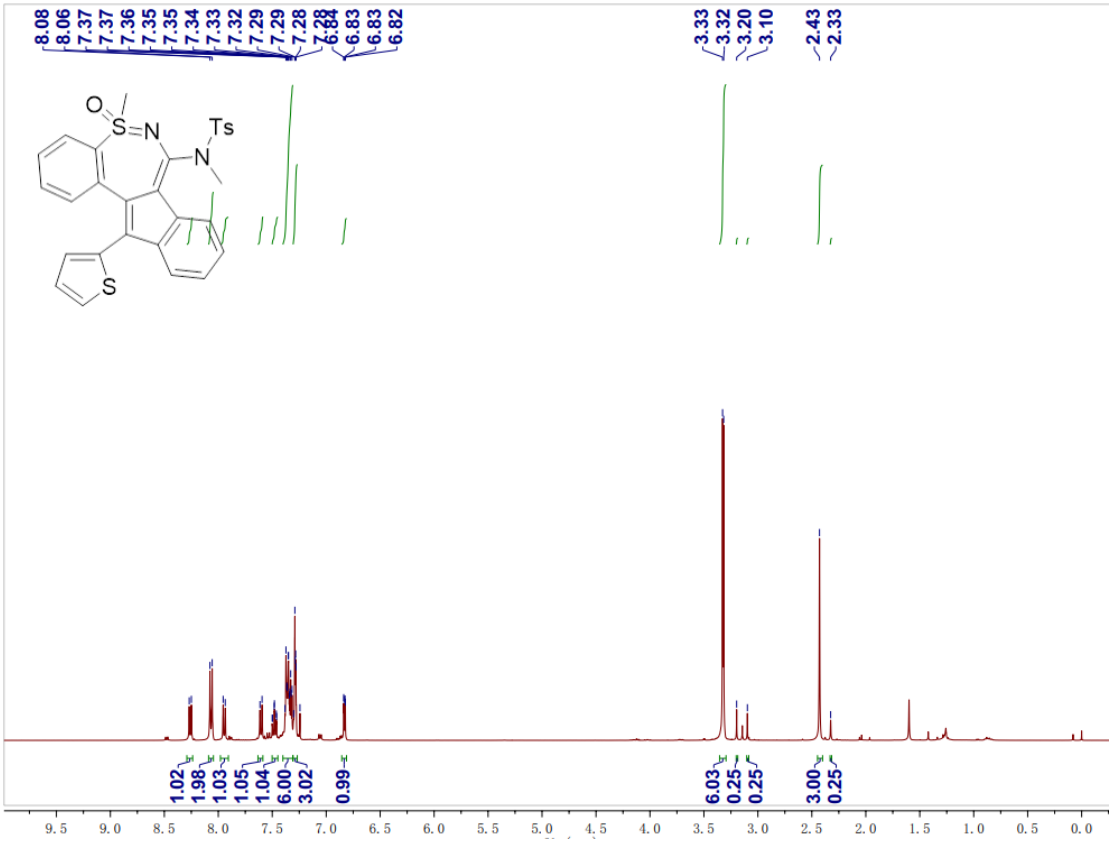
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3j



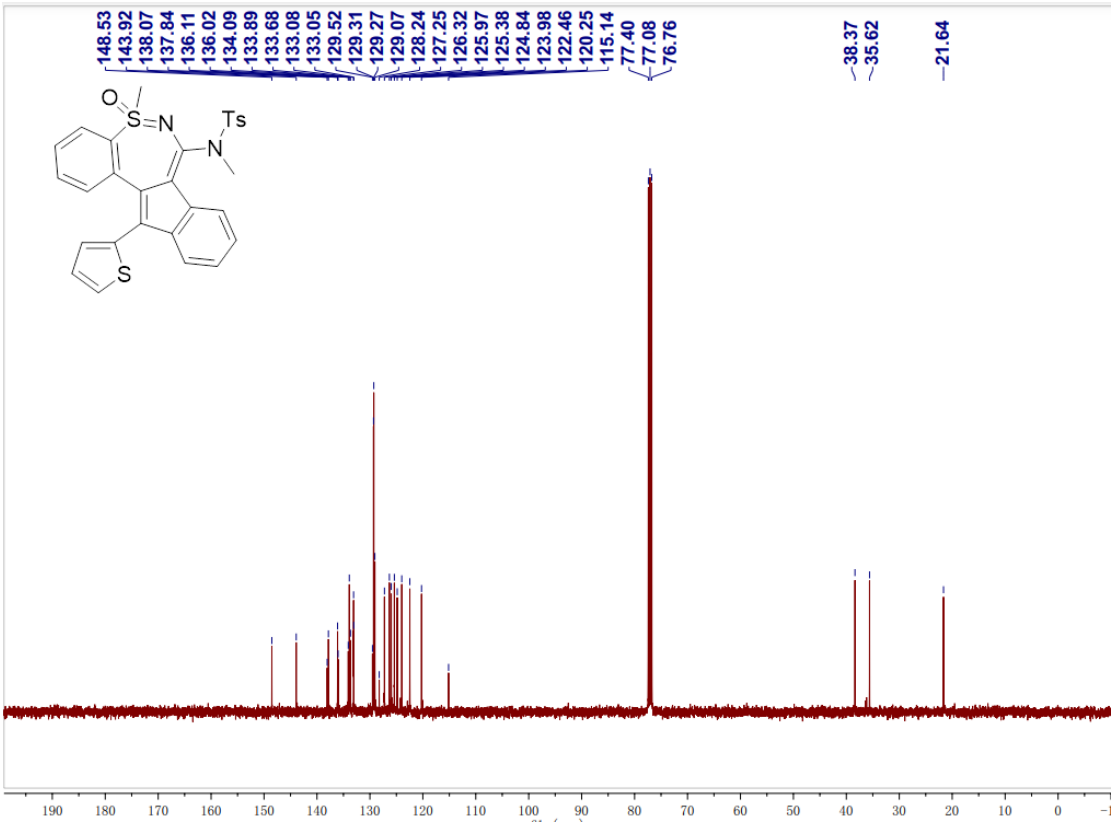
^{19}F NMR spectrum (376 MHz, **$CDCl_3$) of 3j**



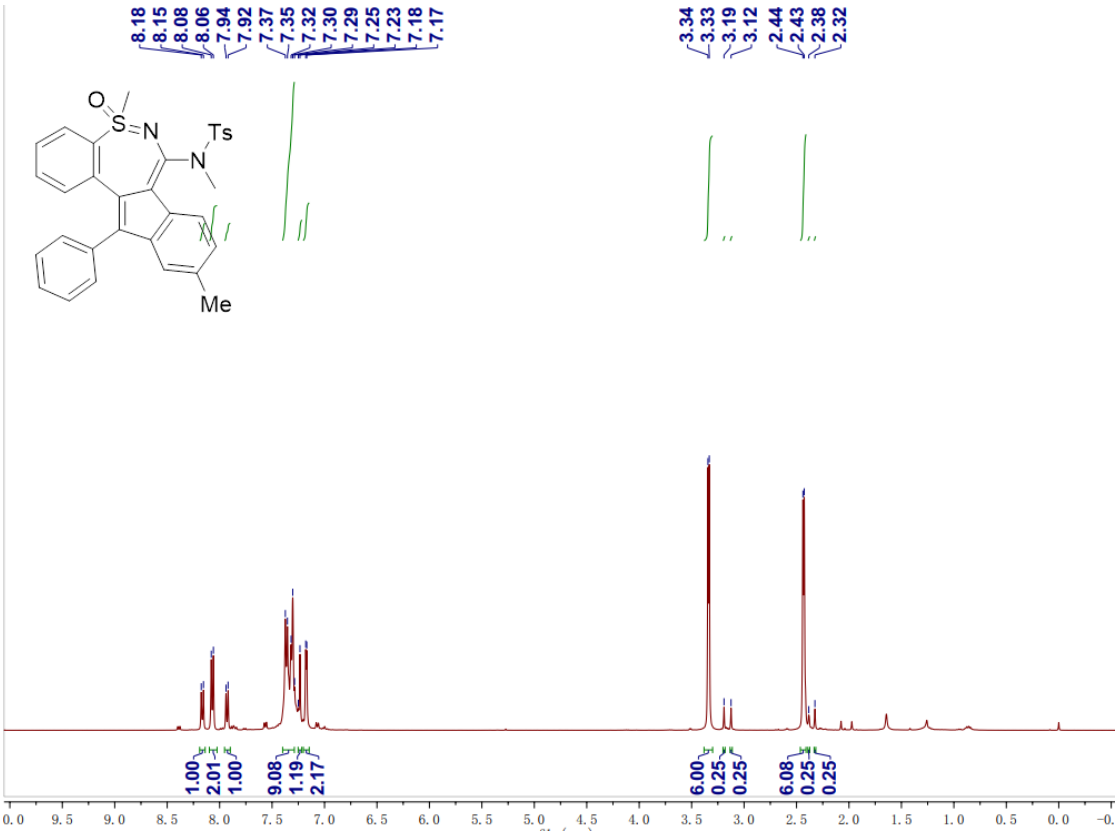
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3k



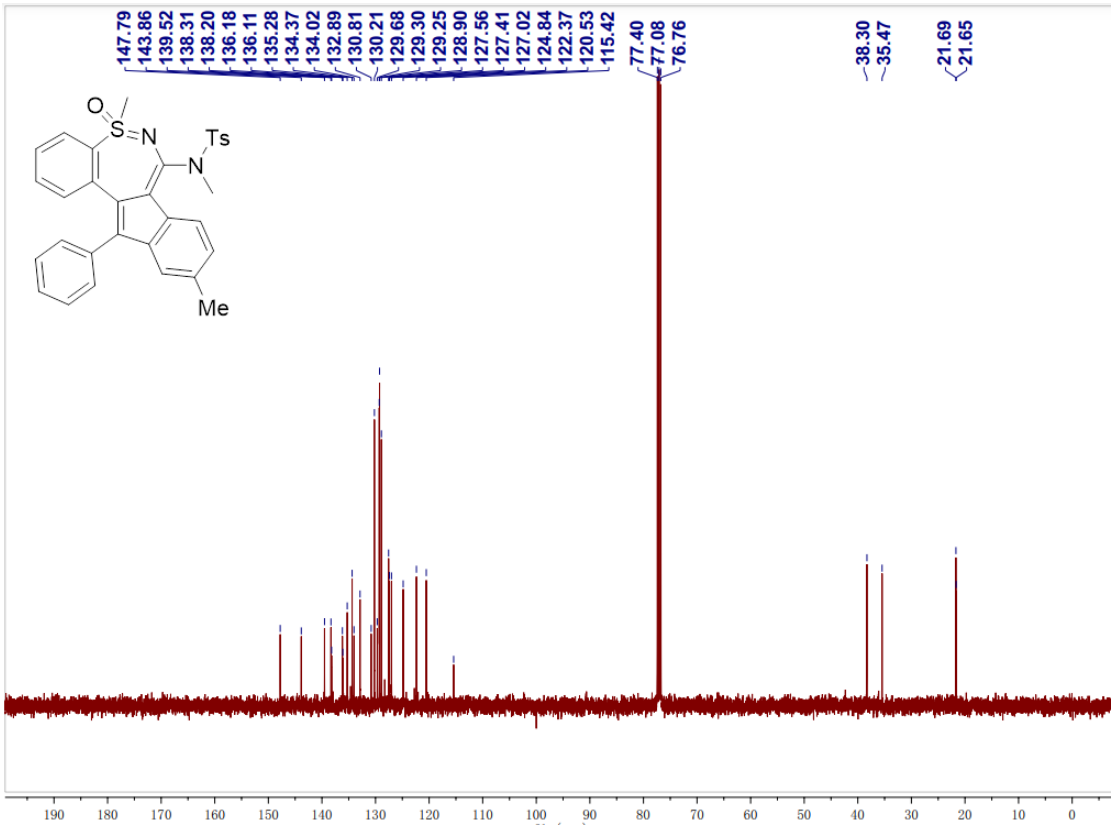
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3k



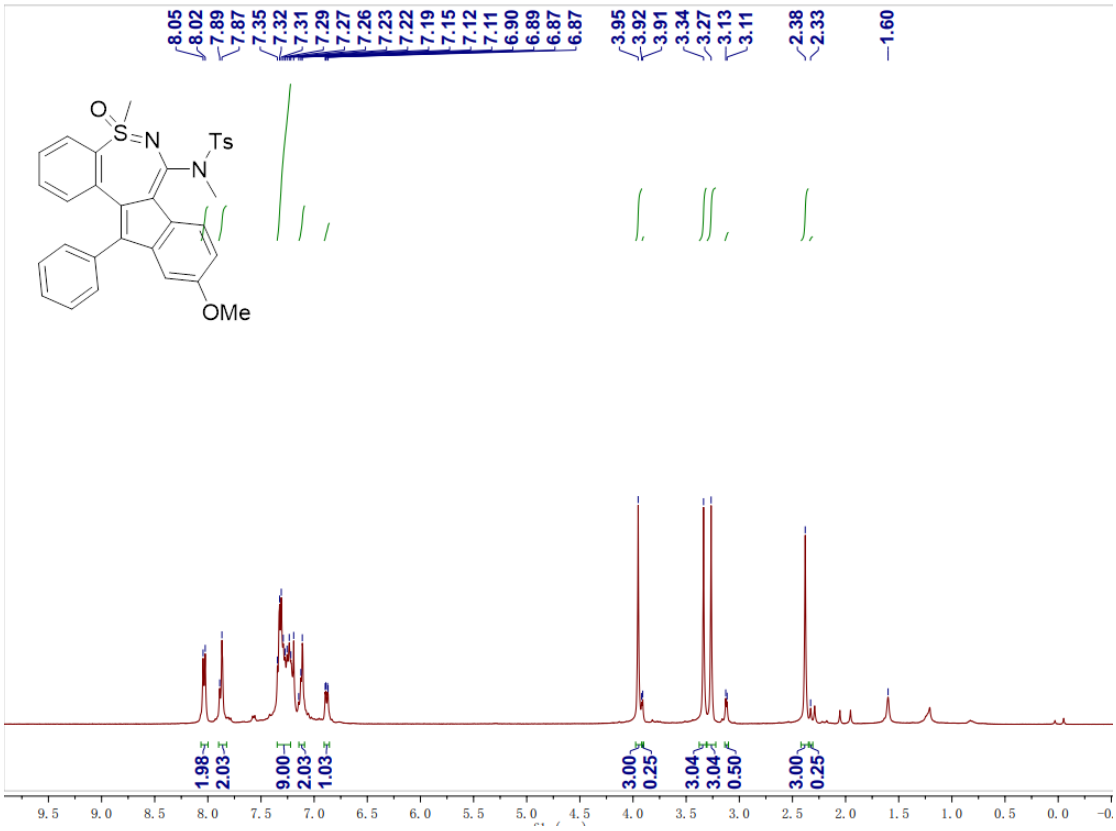
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3l



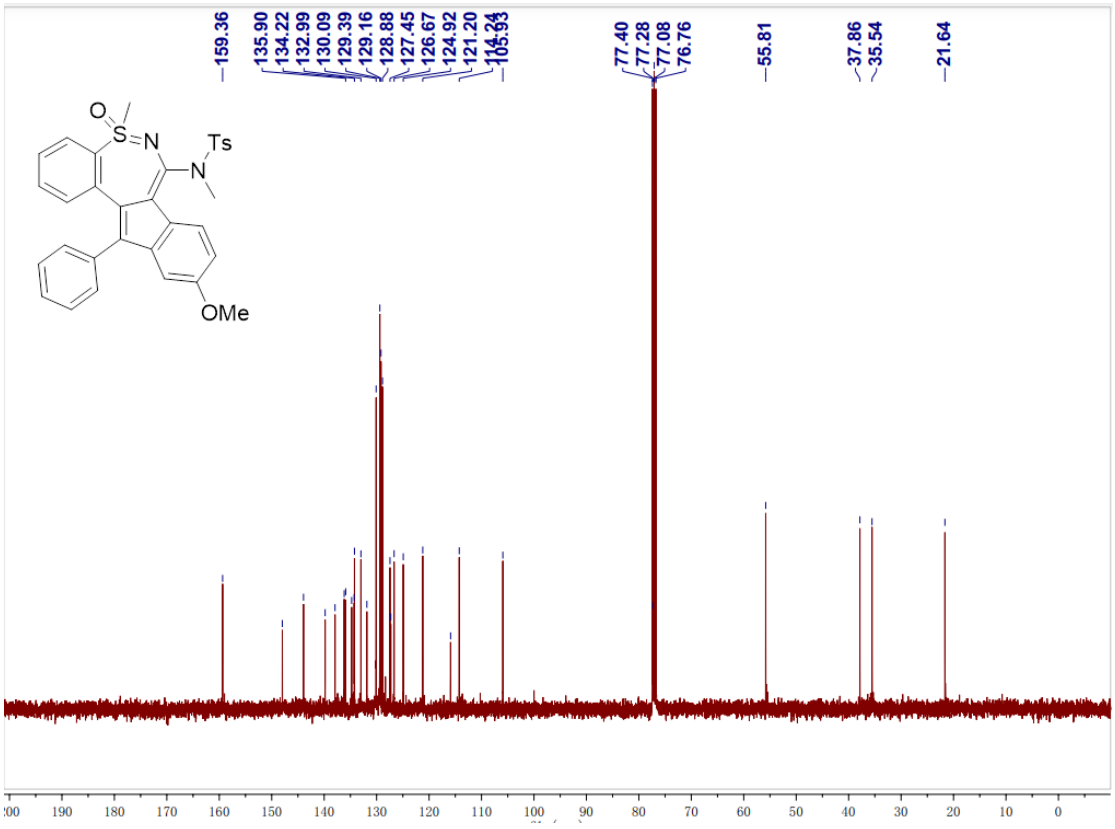
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3l



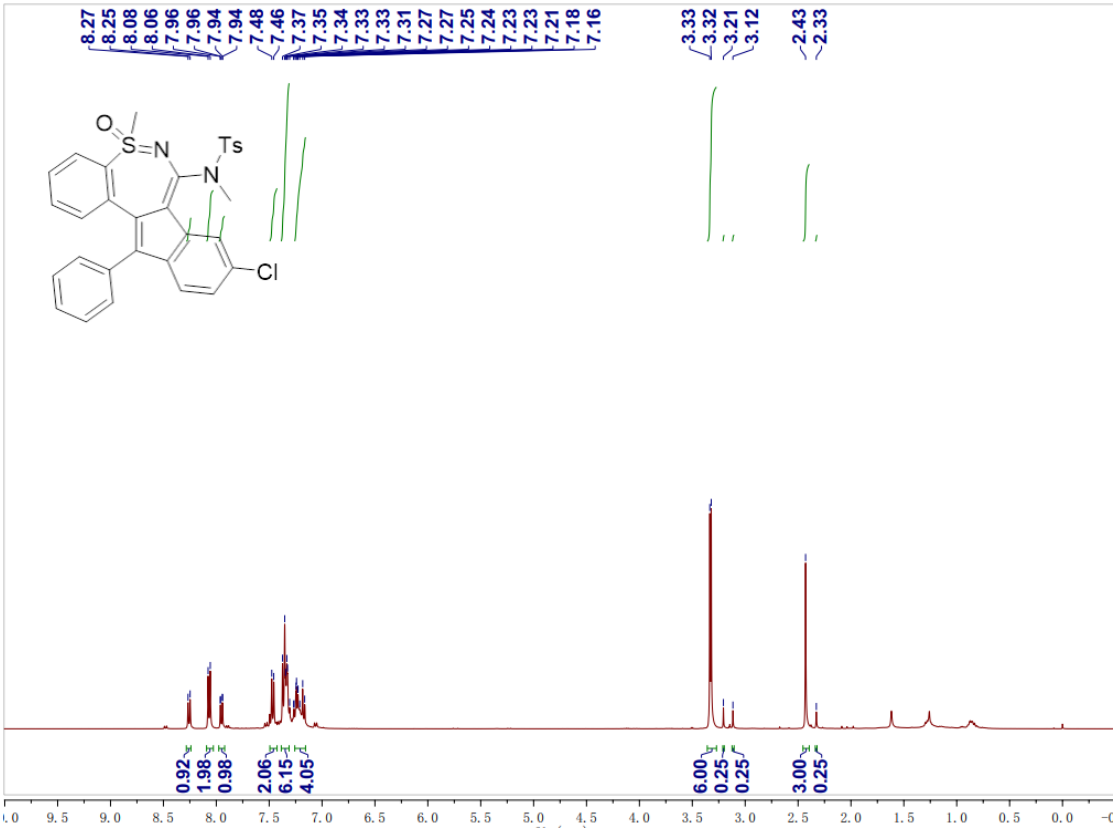
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3m



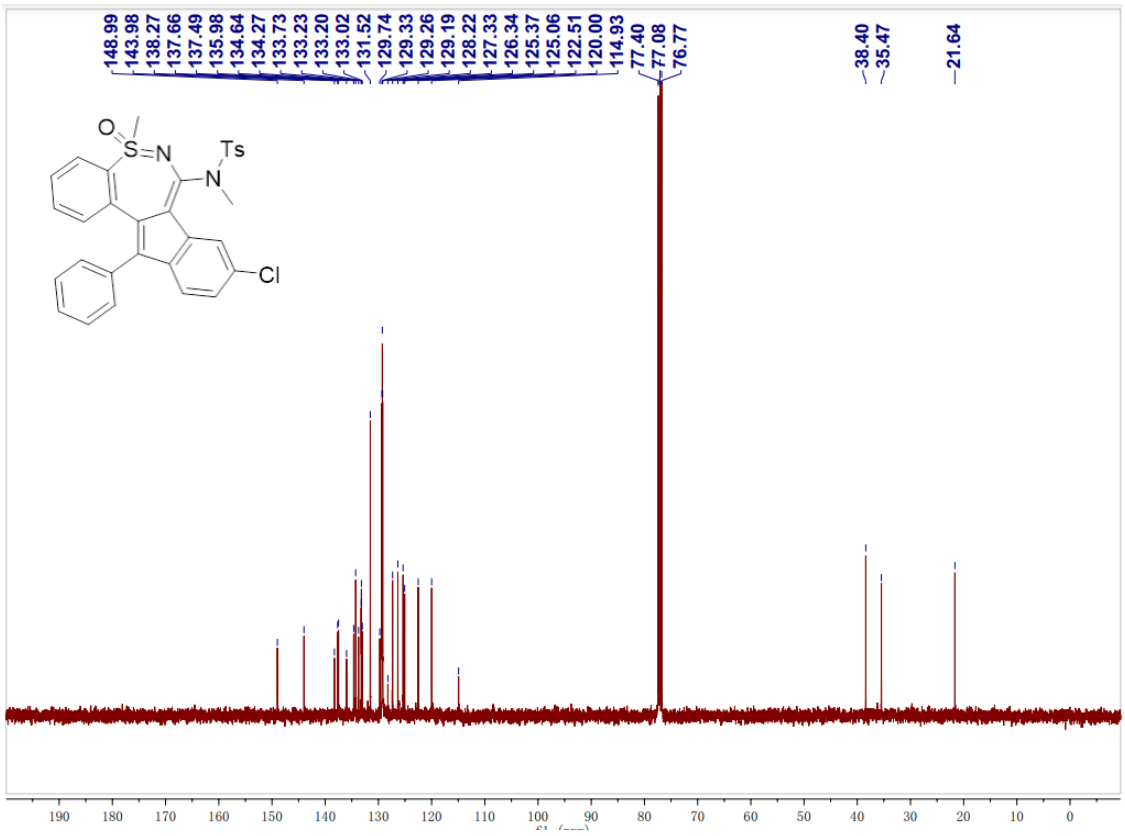
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3m



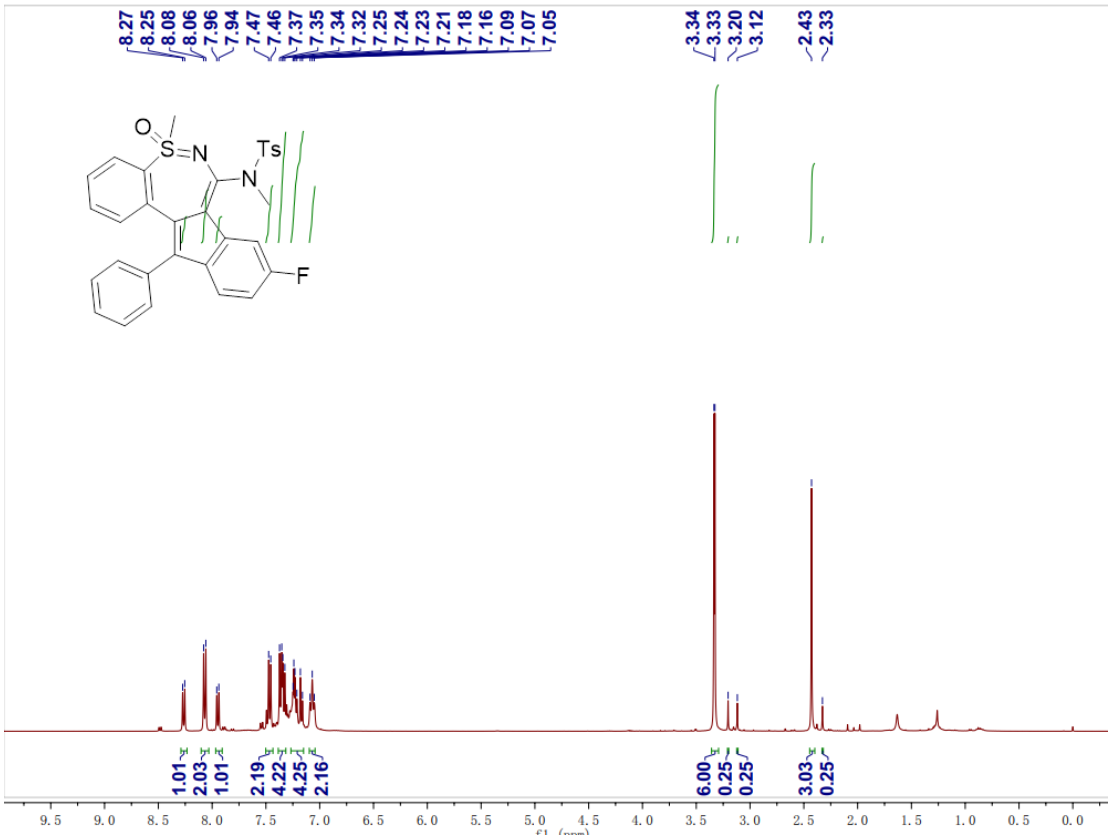
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3n



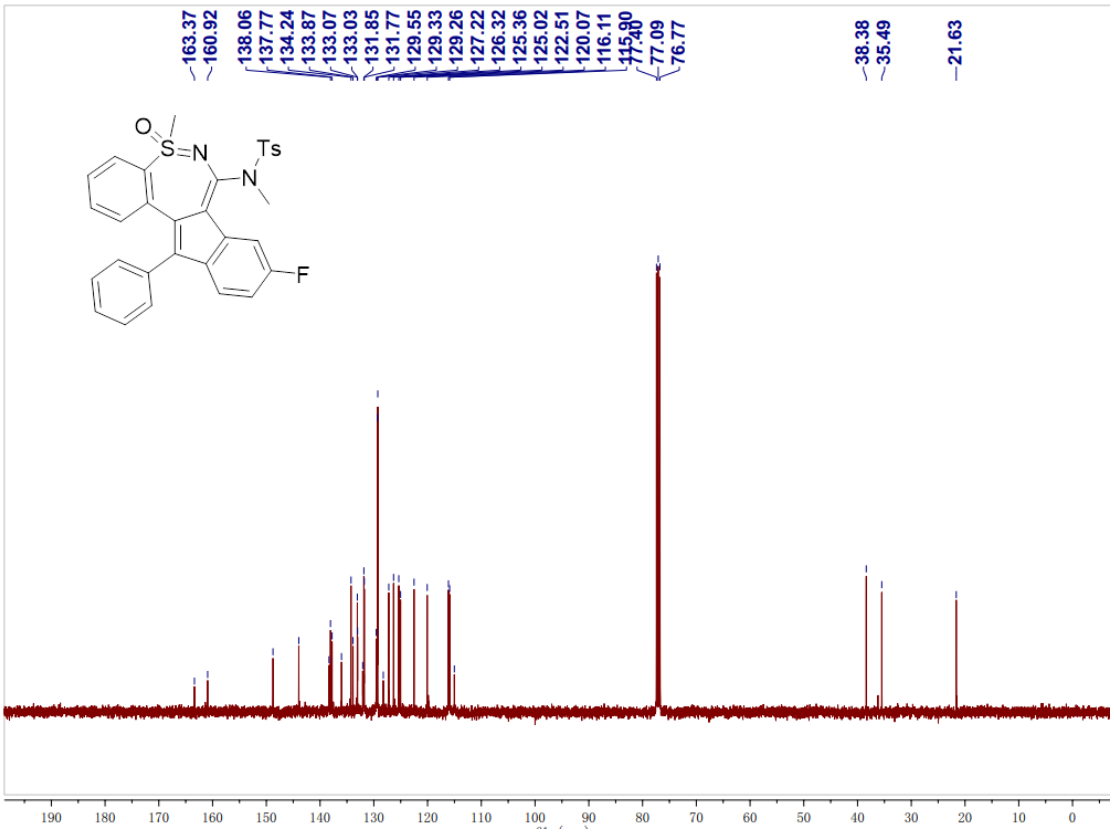
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3n



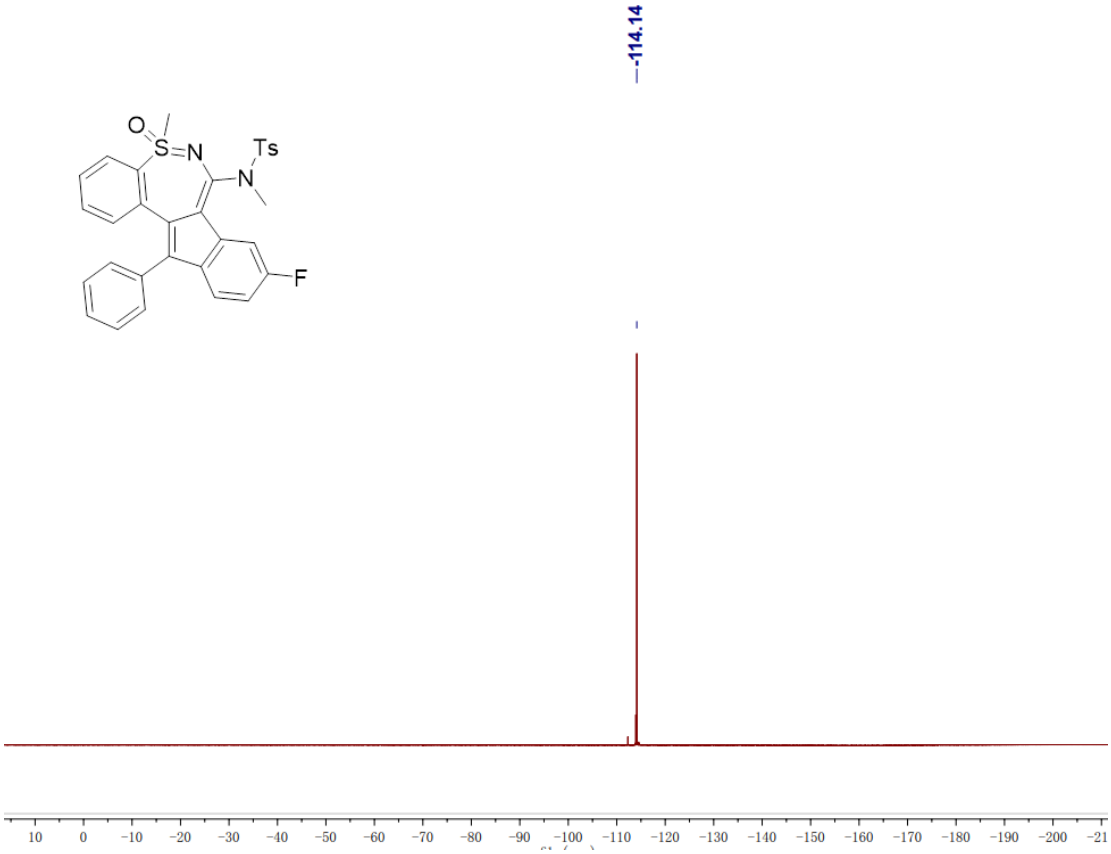
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3o



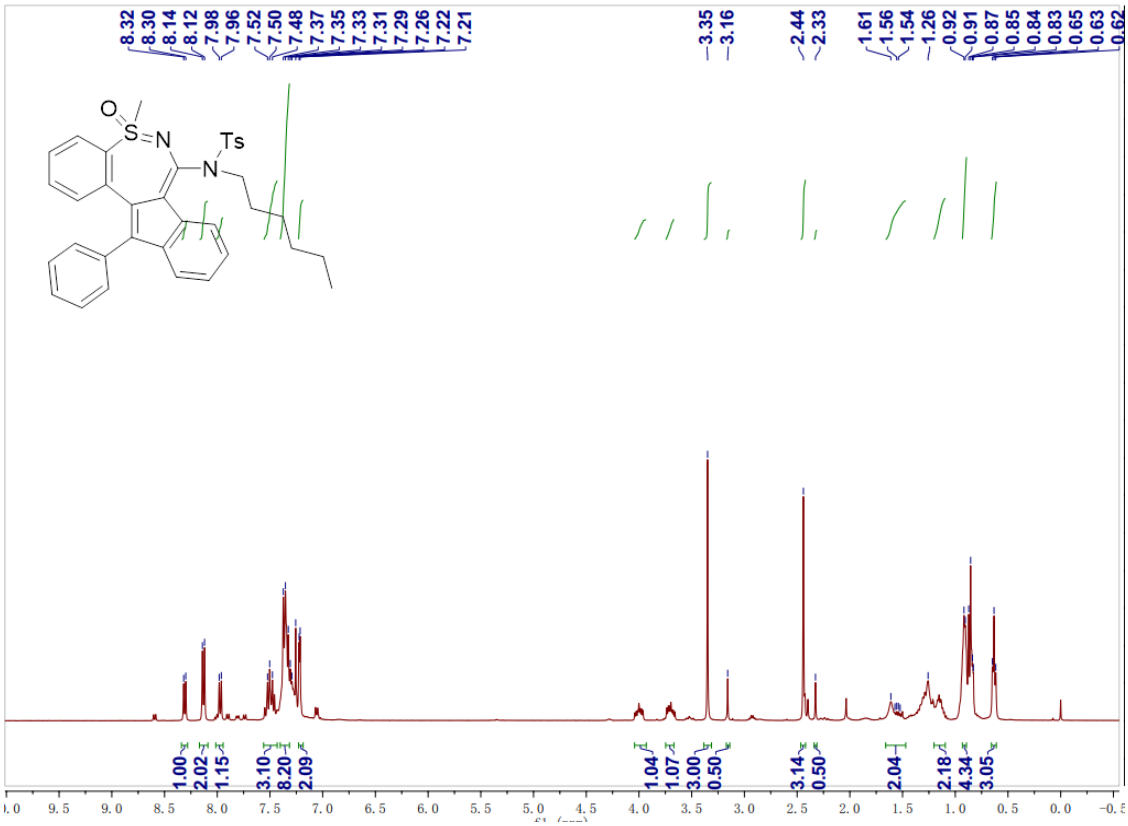
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3o



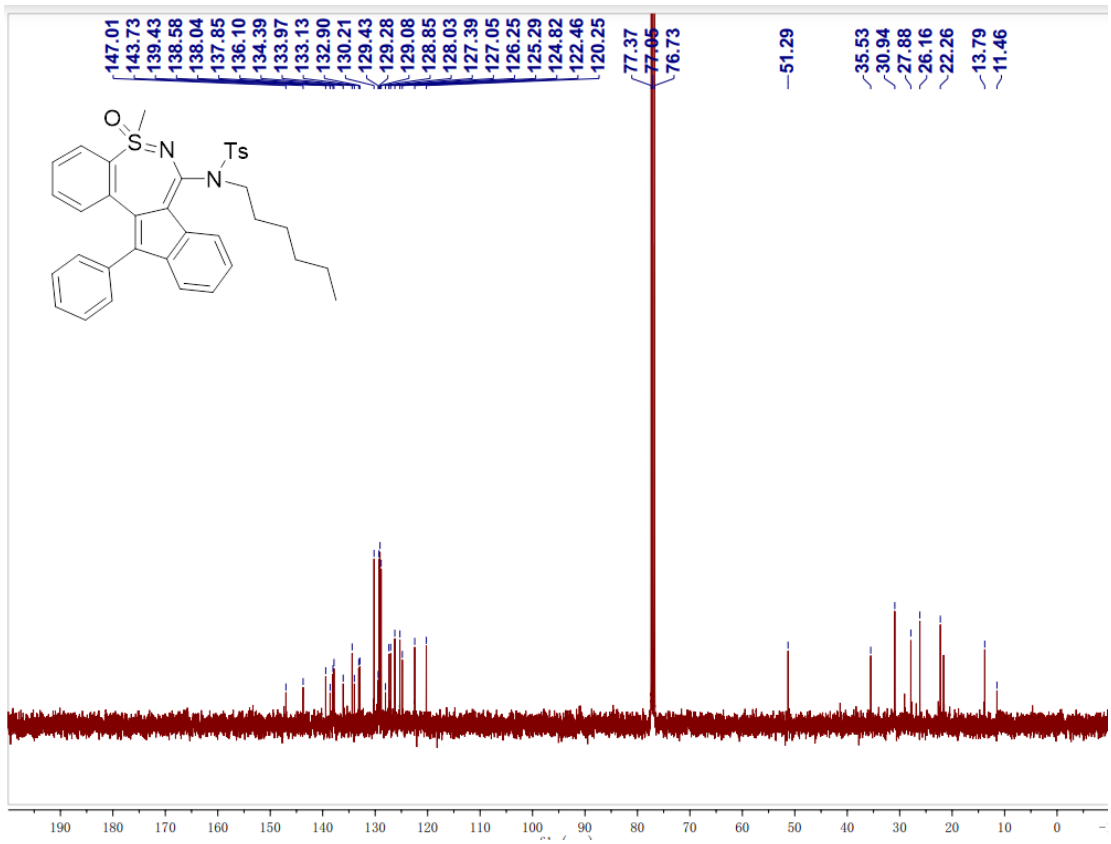
^{19}F NMR spectrum (376 MHz, **$CDCl_3$) of 3o**



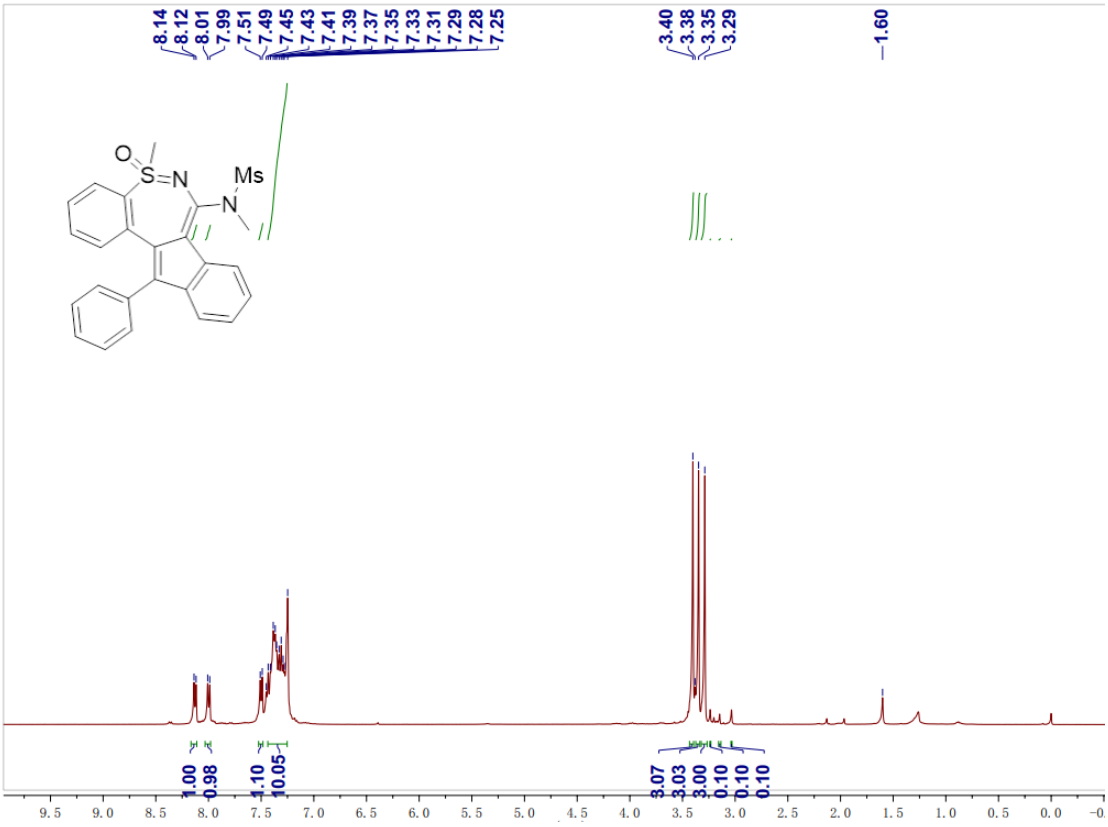
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3p



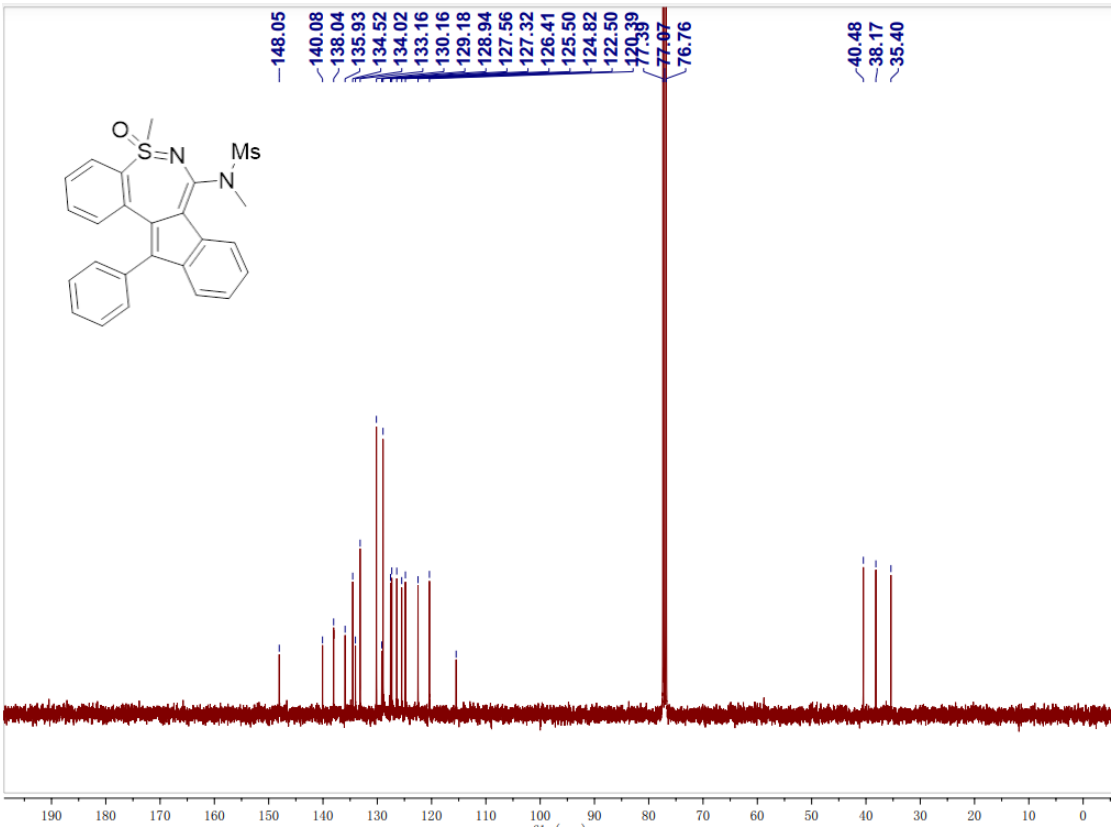
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3p



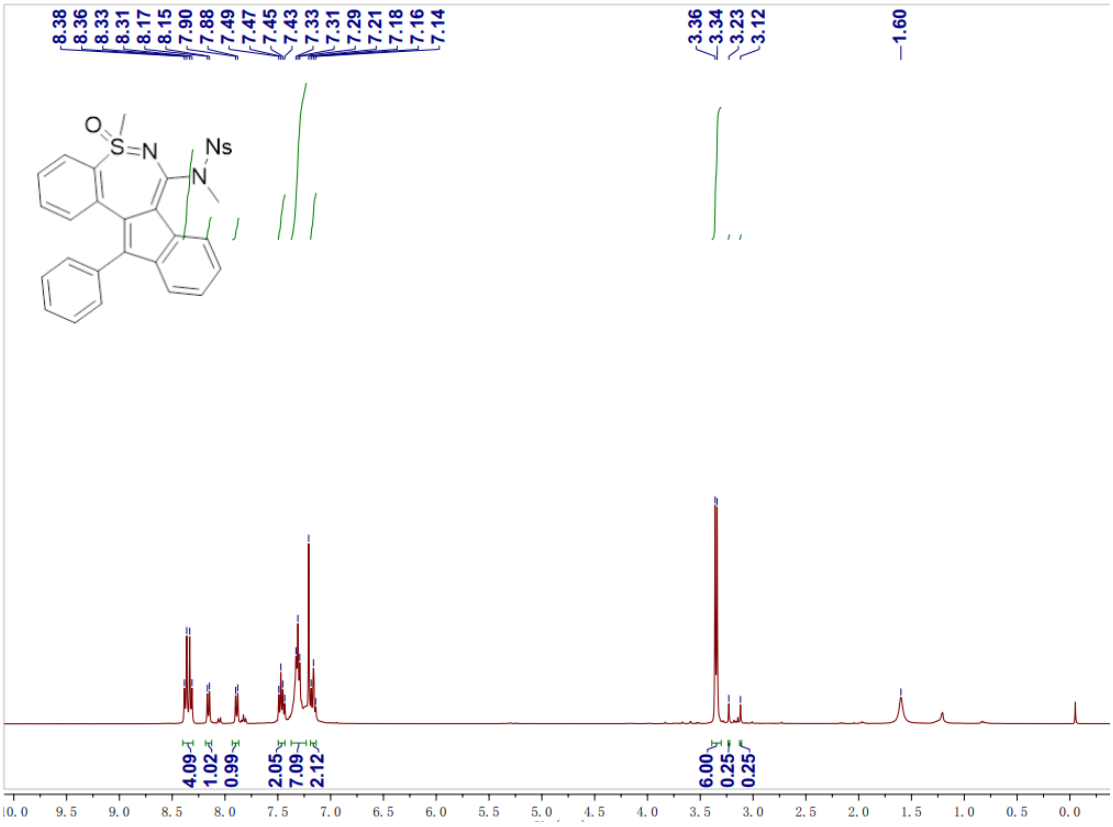
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3q



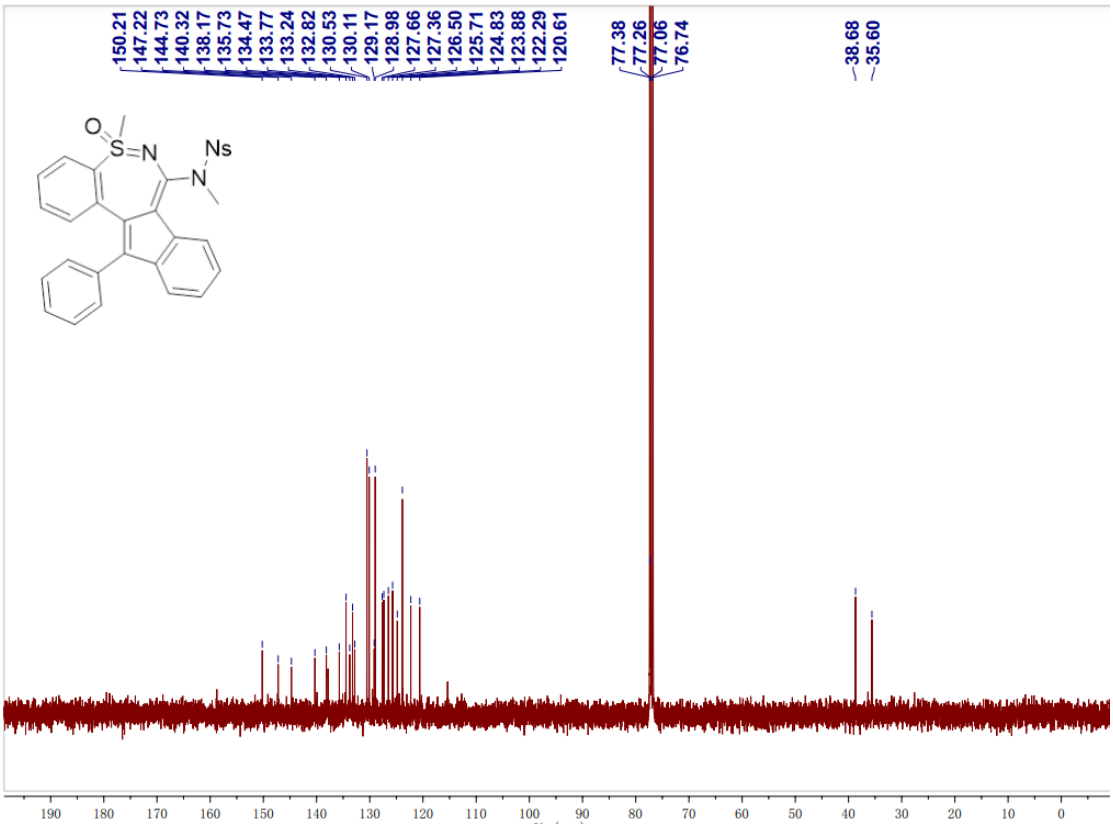
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3q



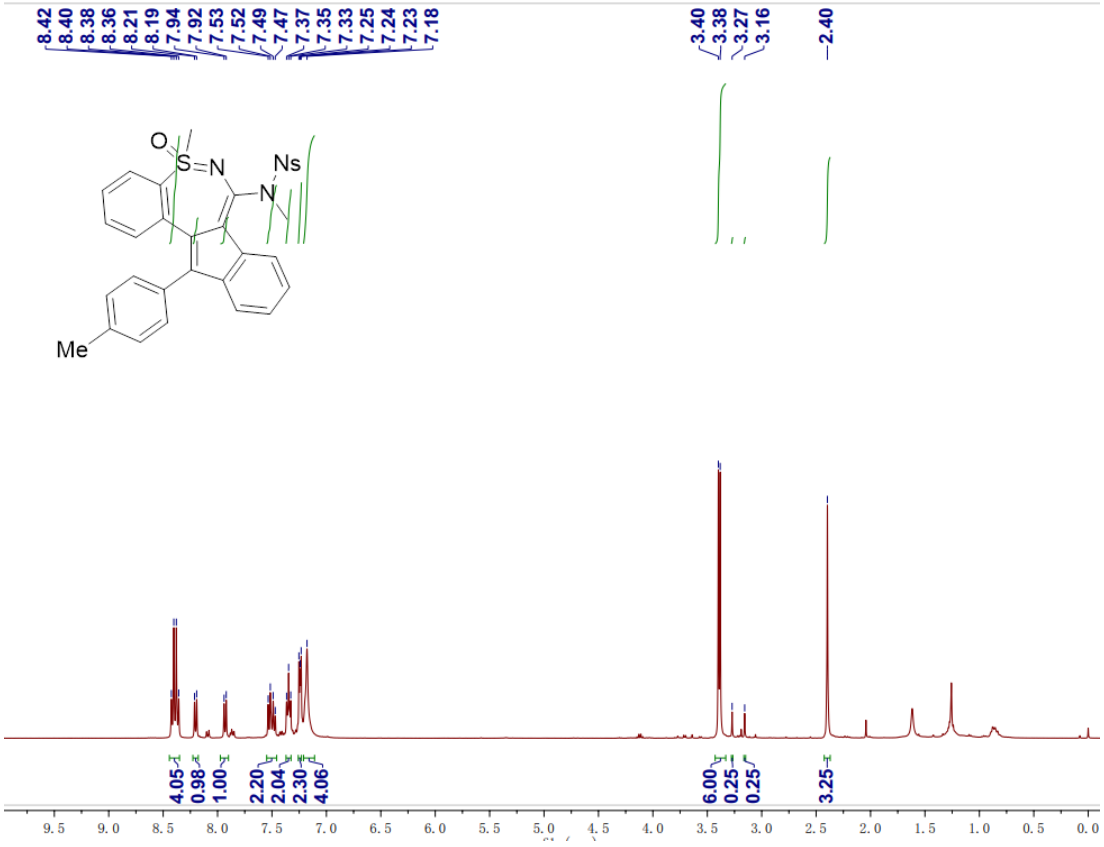
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3r



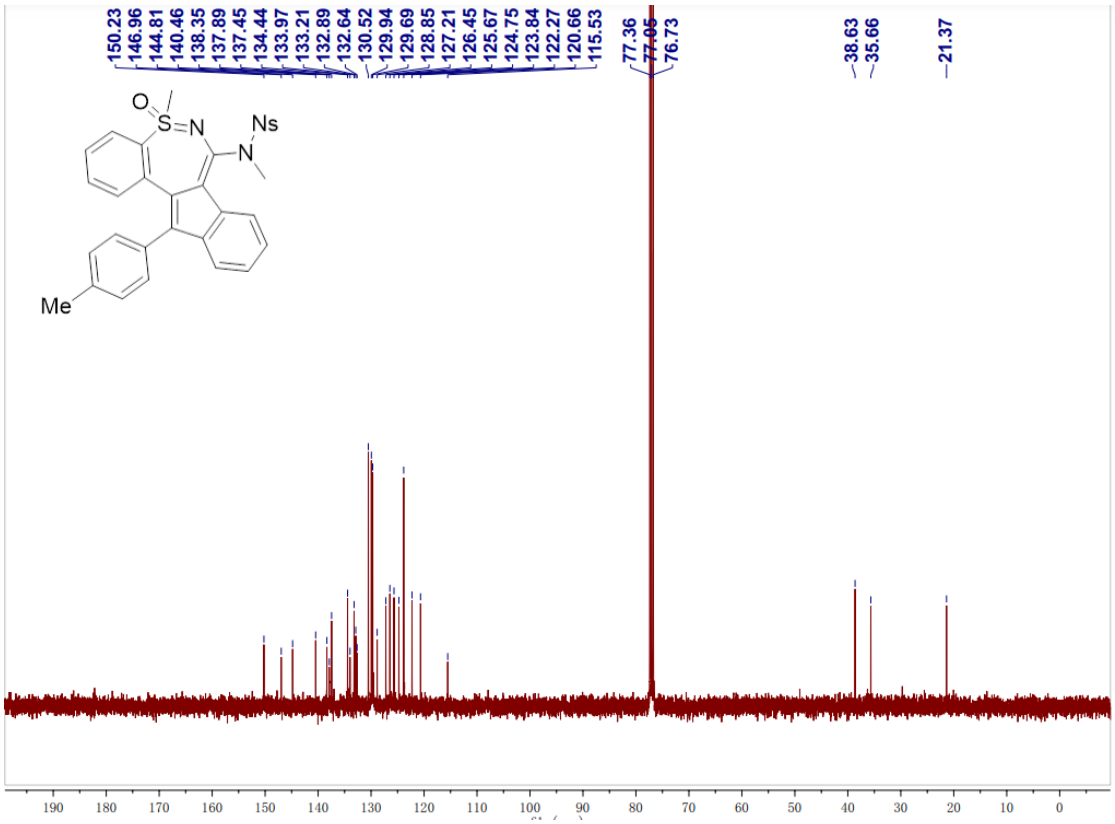
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3r



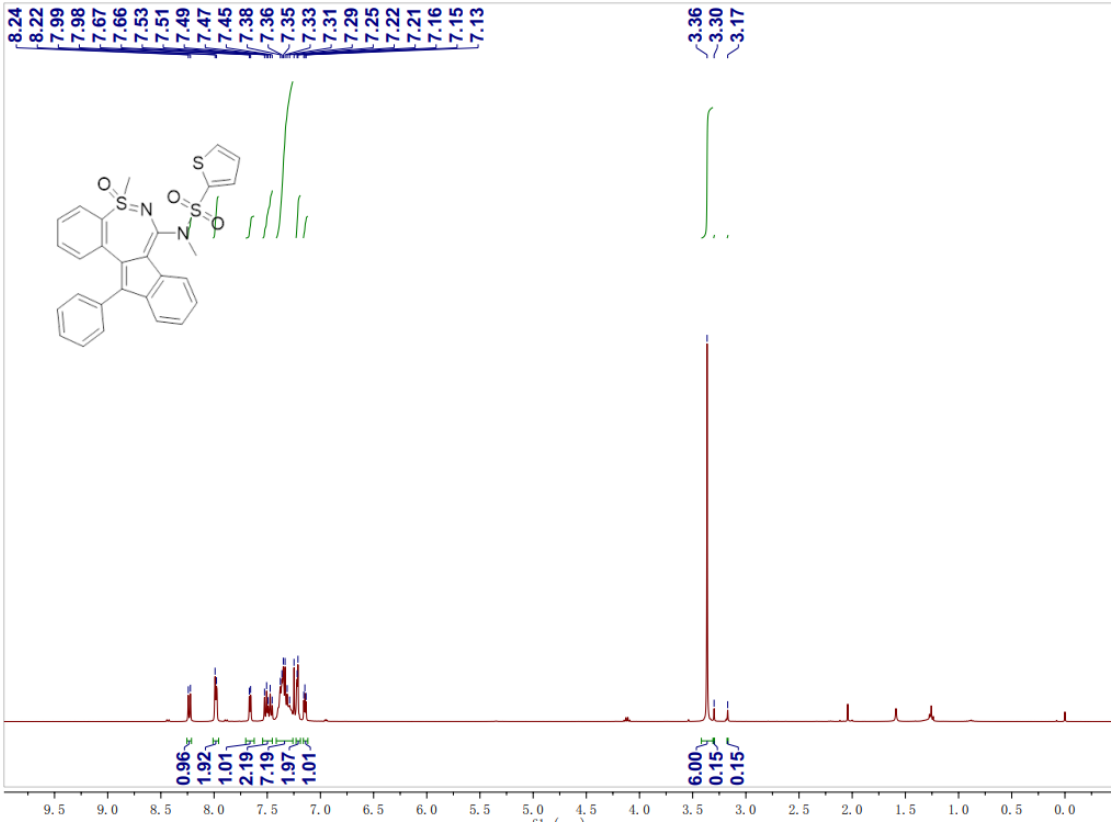
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3s



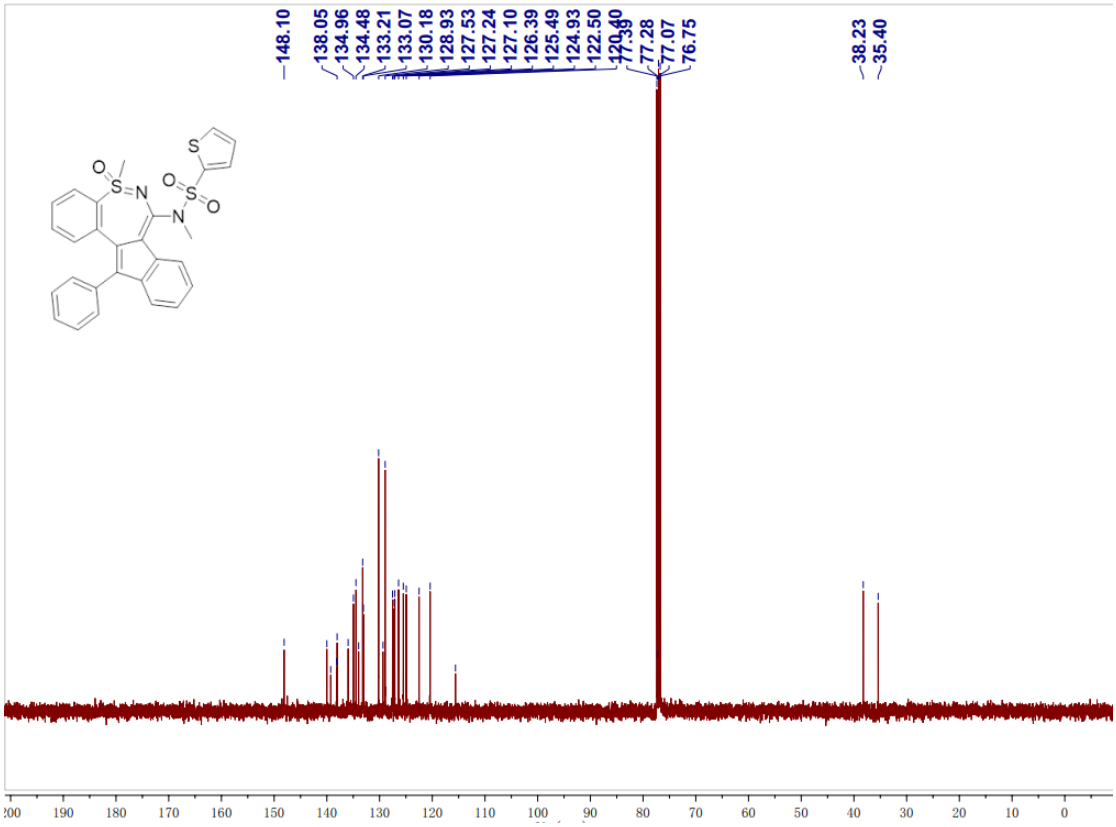
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3s



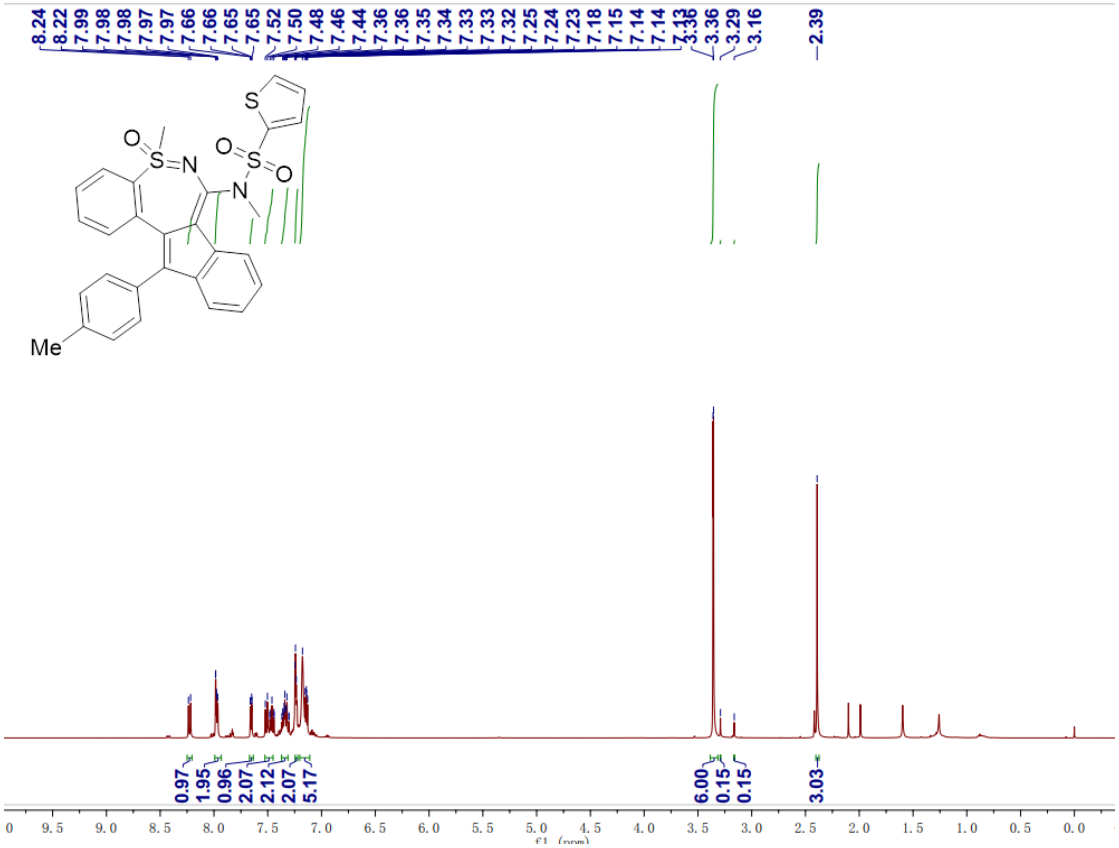
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3t



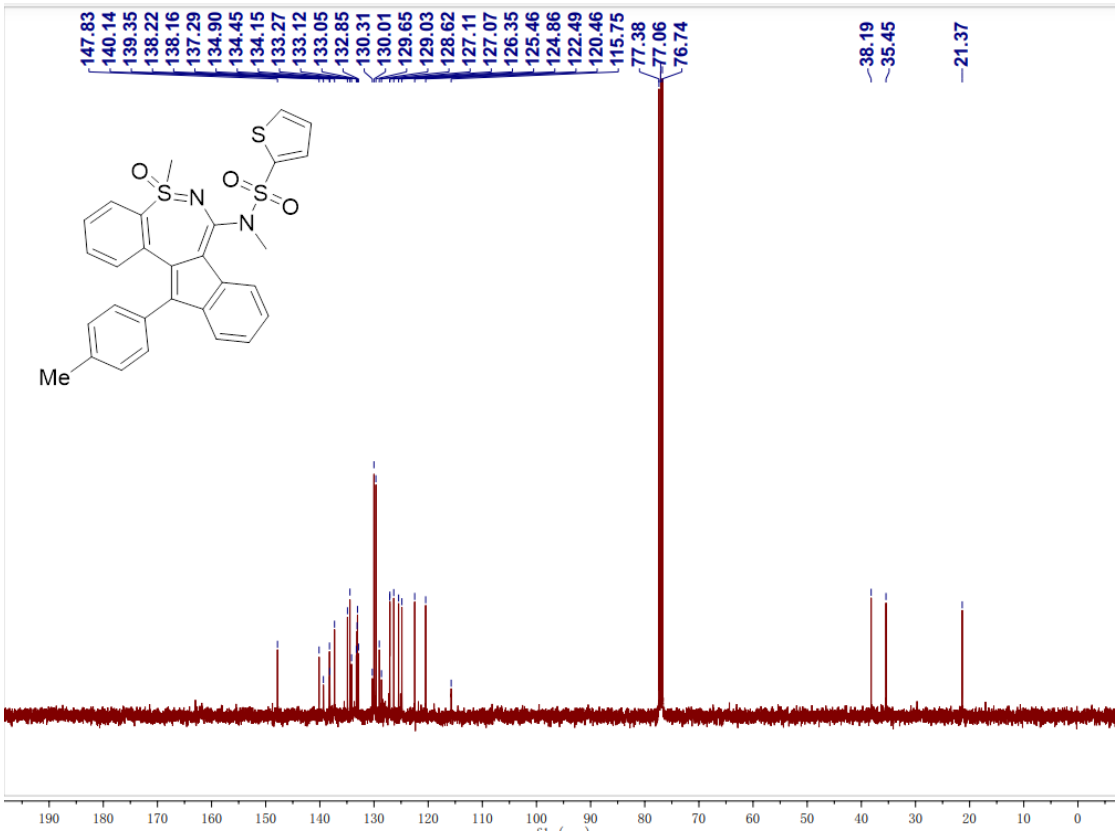
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3t



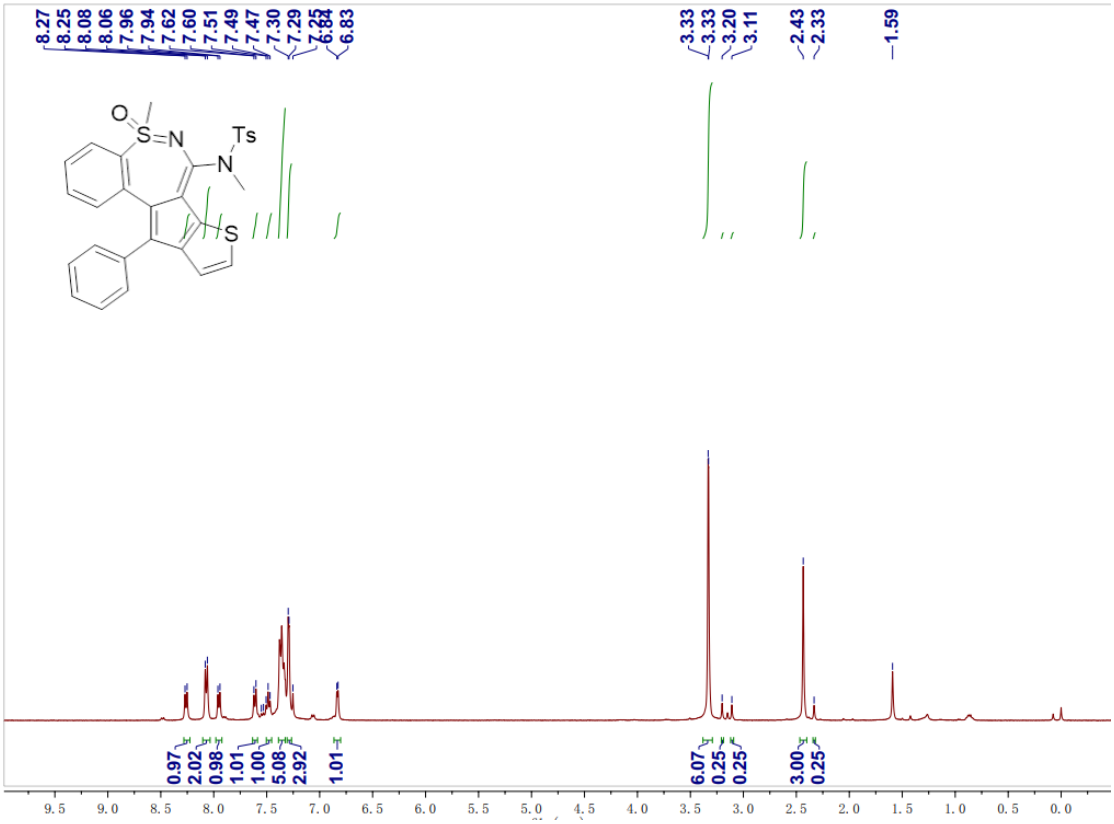
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3u



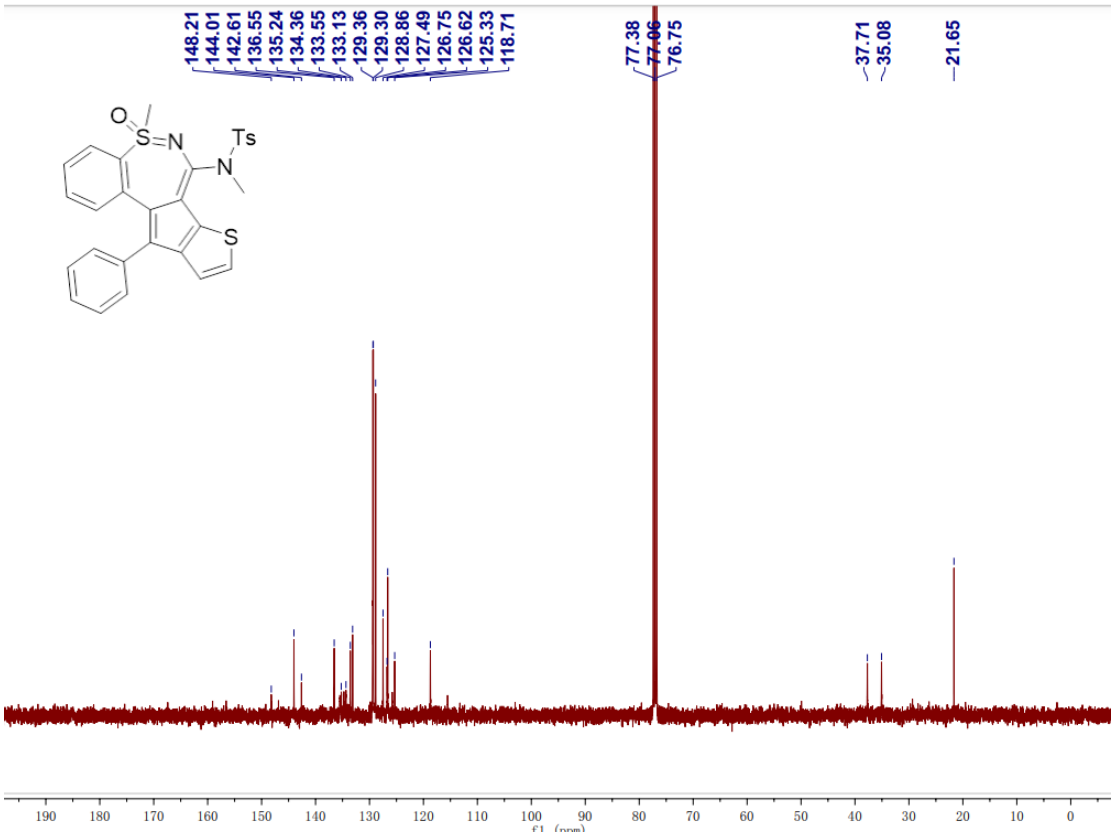
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3u



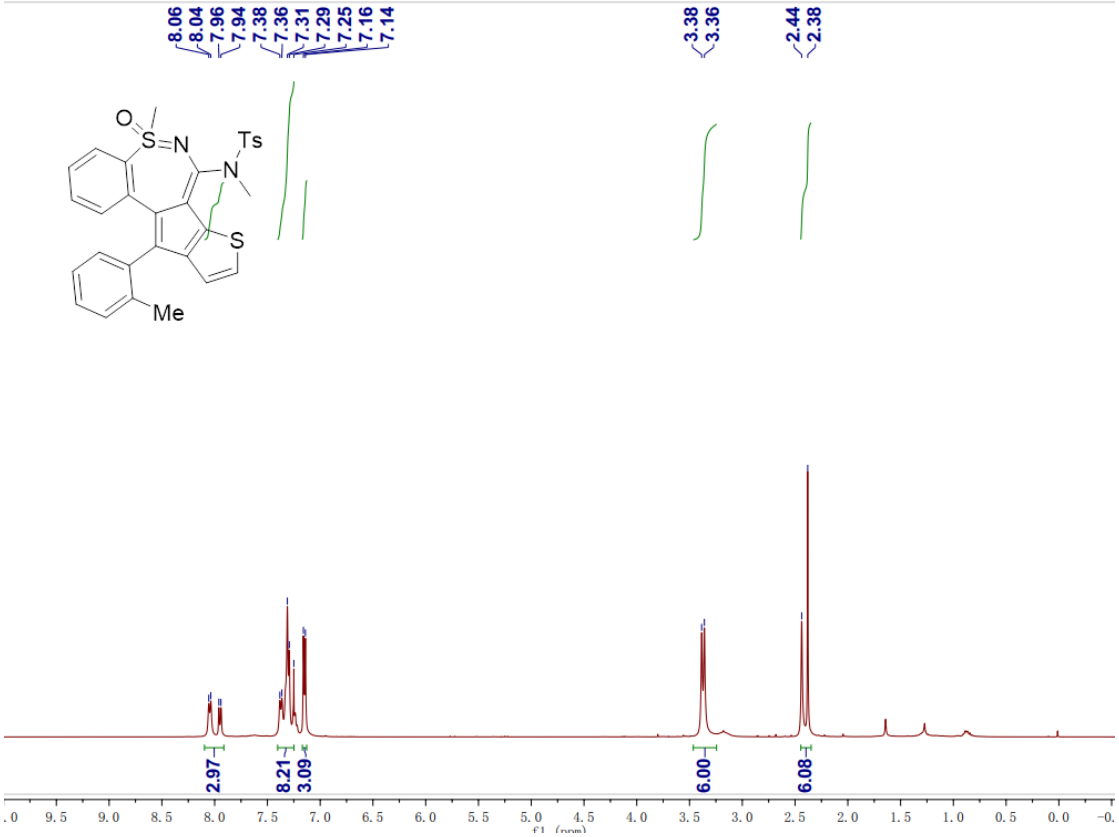
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3v



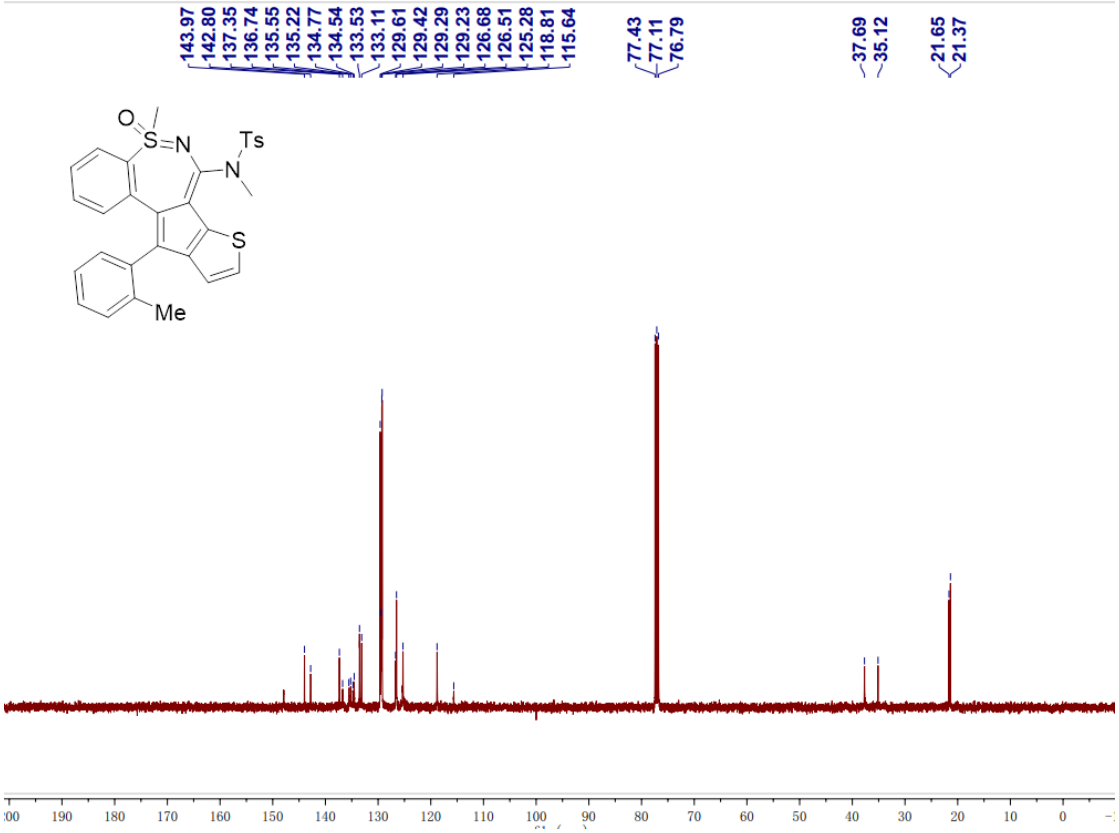
^{13}C NMR spectrum (101MHz, $CDCl_3$) of 3v



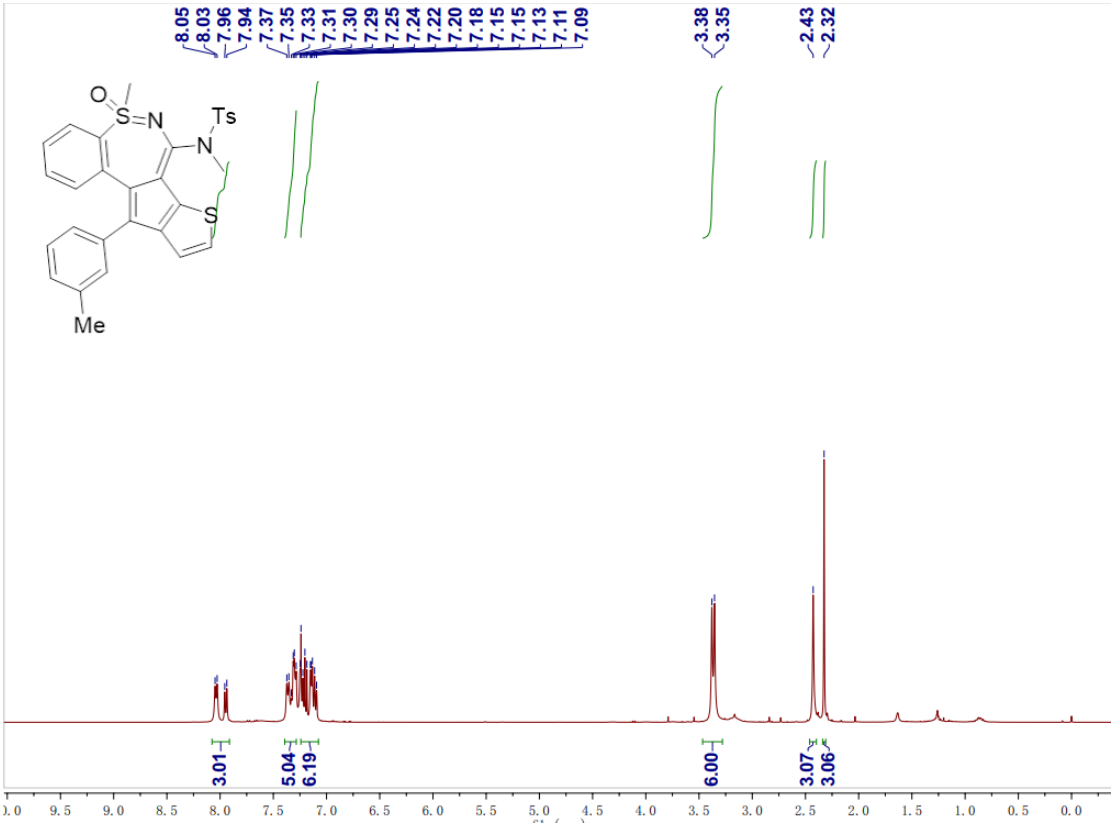
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3w



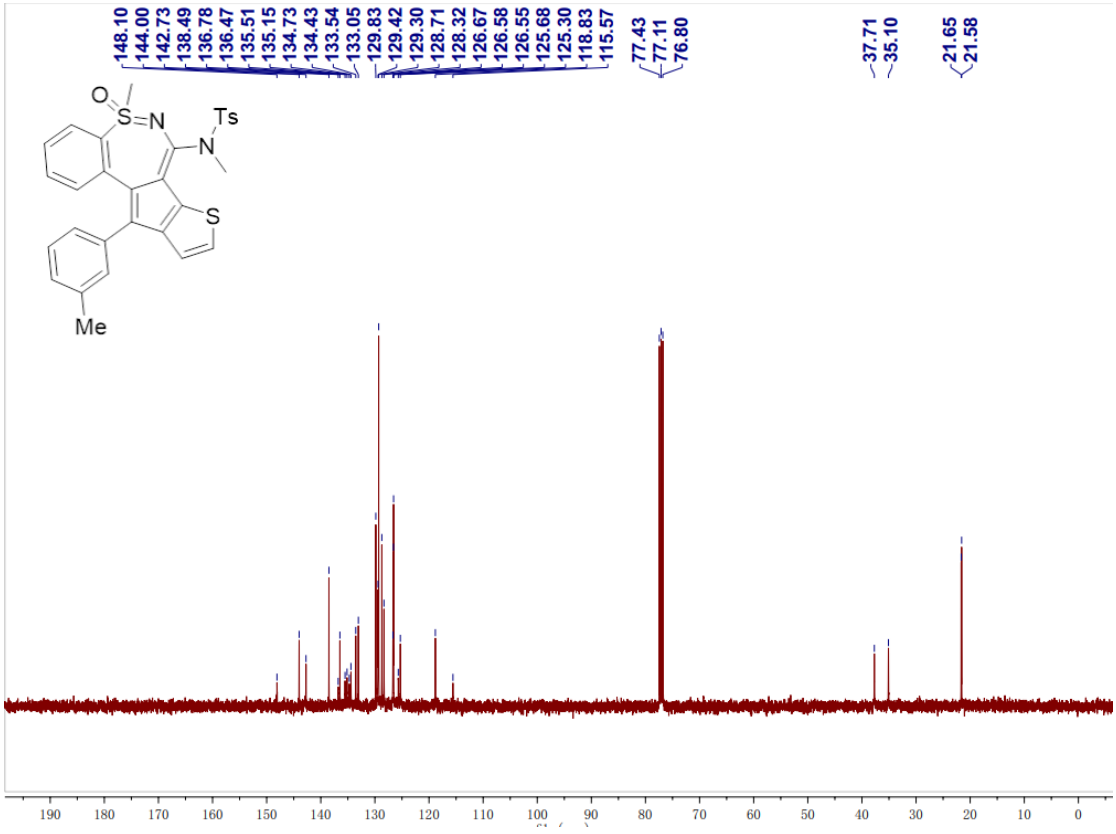
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3w



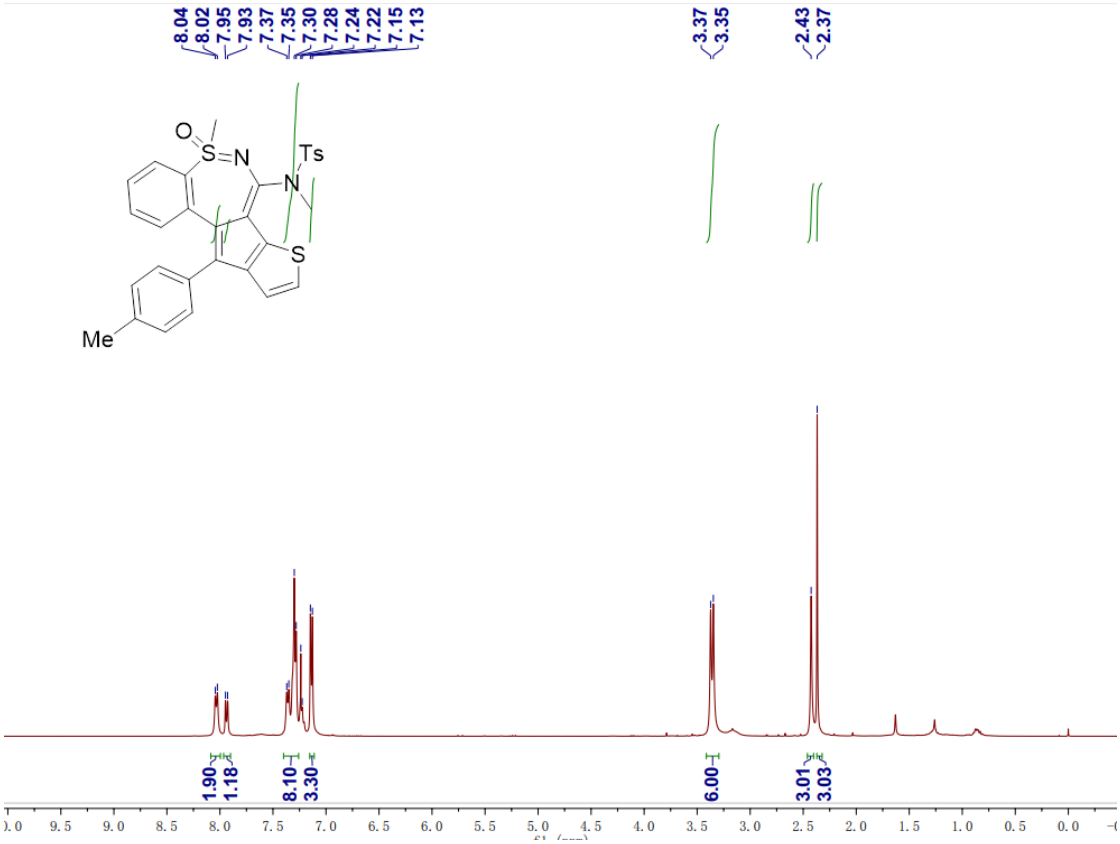
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3x



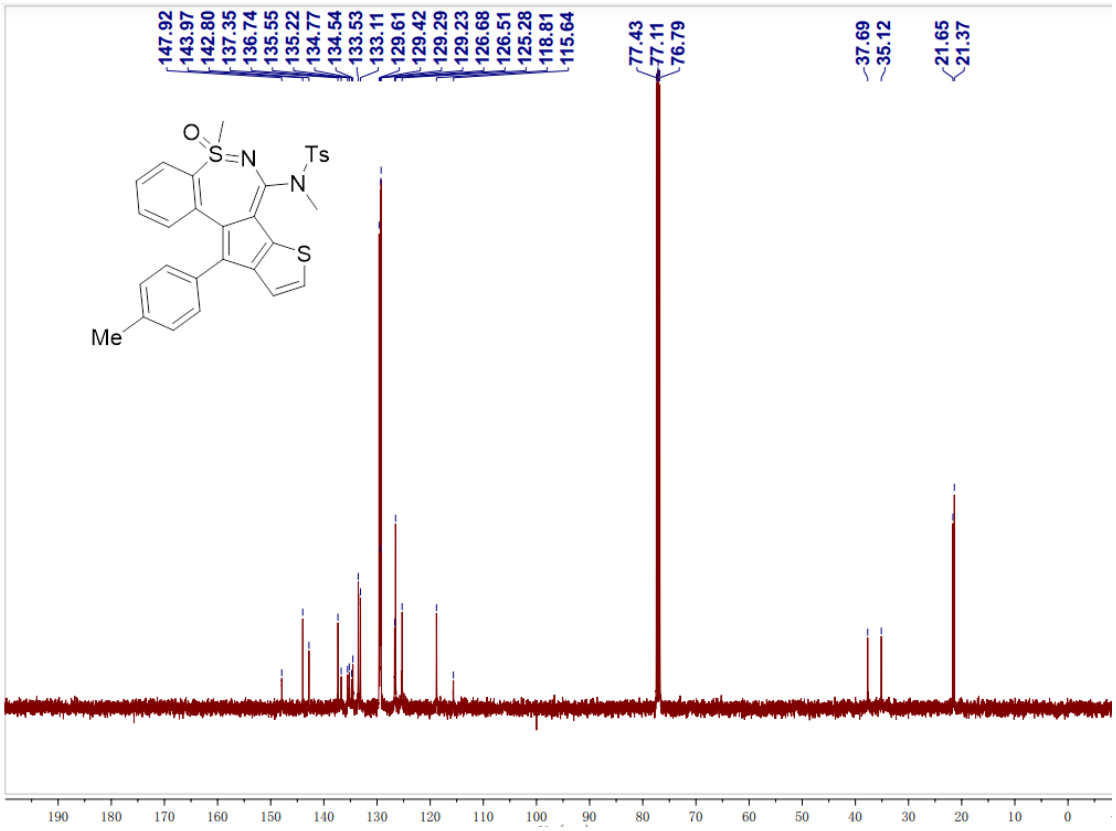
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3x



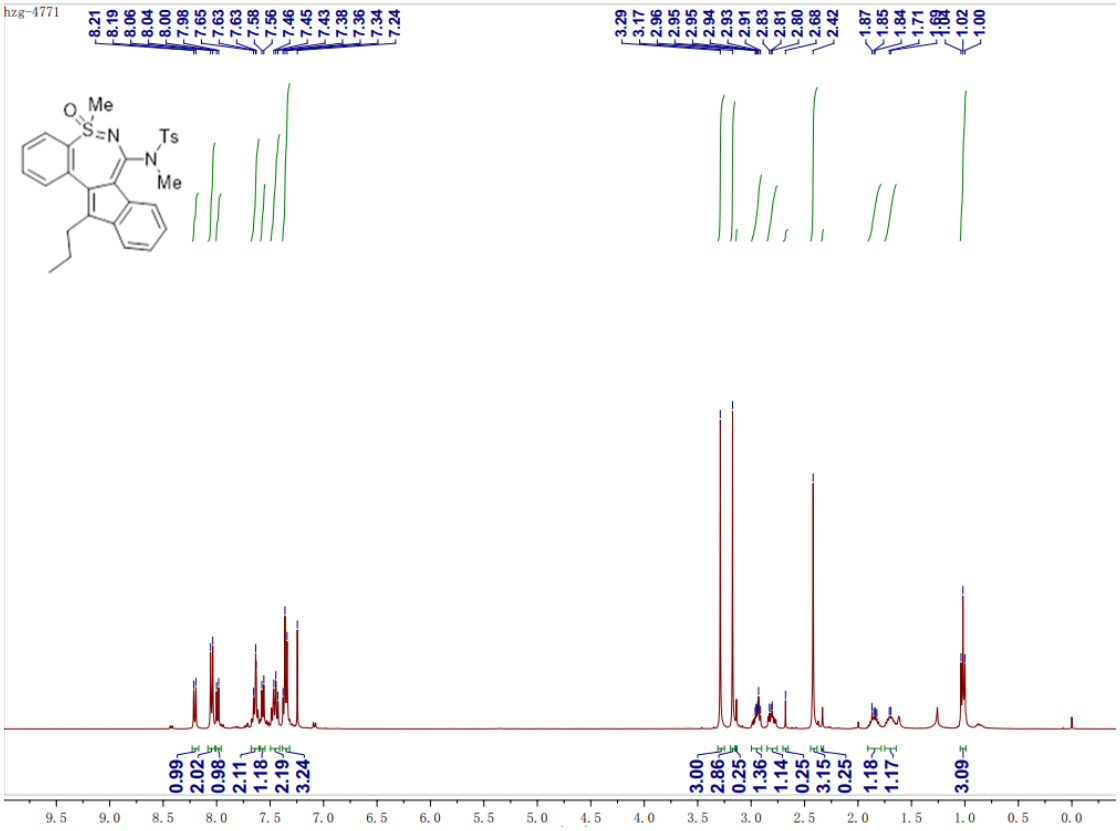
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3y



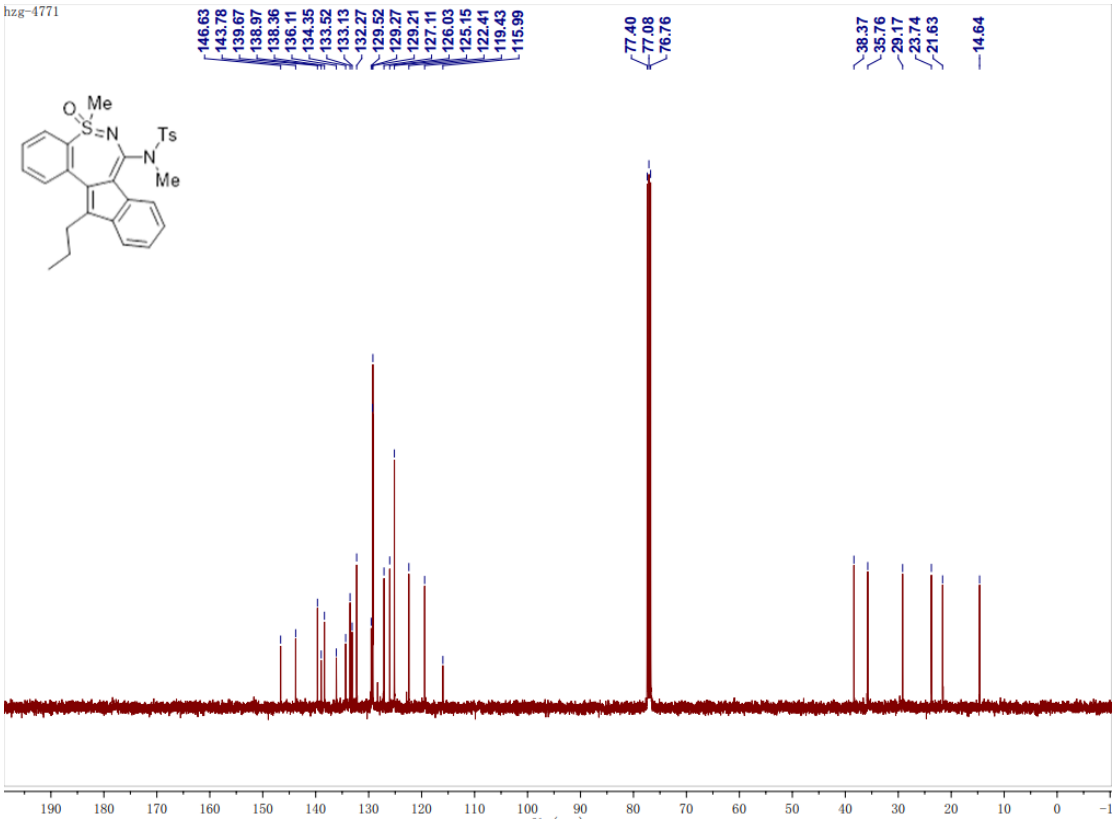
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3y



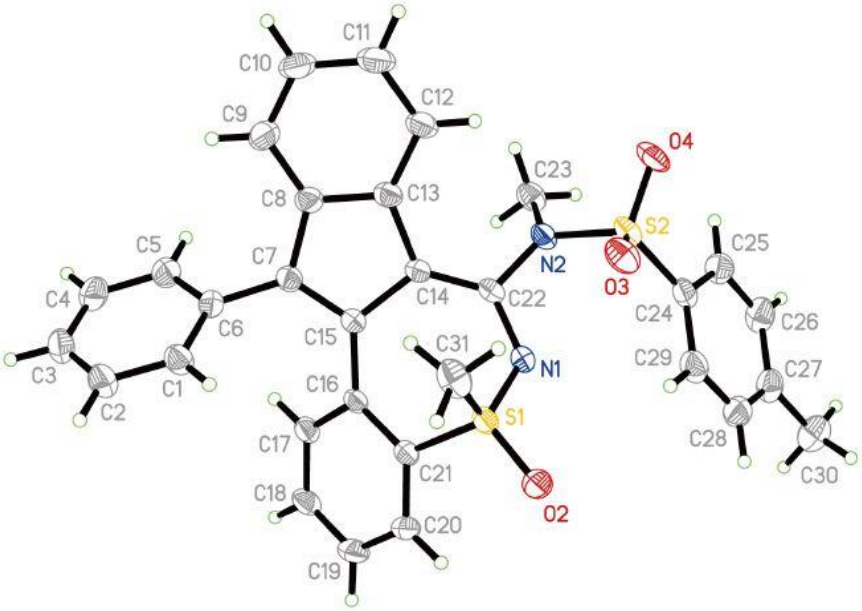
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3z

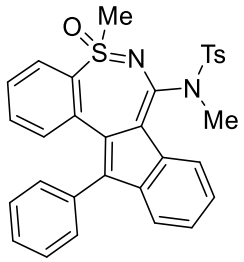


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 3z



7. X-ray ORTEP illustration of compound 3a.





3a

Table 1. Crystal data and structure refinement for 2.

Identification code	2	
Empirical formula	C31 H26 N2 O3 S2	
Formula weight	538.66	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.553(6) Å	α= 90°.
	b = 12.155(5) Å	β= 100.612(7)°.
	c = 16.702(7) Å	γ = 90°.
Volume	2904(2) $Å^3$	
Z	4	
Density (calculated)	1.232 Mg/m^3	
Absorption coefficient	0.217 mm^{-1}	
F(000)	1128	
Crystal size	0.260 x 0.250 x 0.240 mm^3	
Theta range for data collection	2.481 to 24.994°.	
Index ranges	-17<=h<=9, -13<=k<=14, -19<=l<=19	
Reflections collected	14441	
Independent reflections	5103 [R(int) = 0.0267]	
Completeness to theta = 24.994°	99.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5103 / 1 / 346	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0461, wR2 = 0.1319	
R indices (all data)	R1 = 0.0643, wR2 = 0.1432	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.217 and -0.348 $e.Å^{-3}$	