Supporting Information

Palladium-Catalyzed Cascade Cyclization of Allenamide with 2-Iodoaniline to Access Functionalized Indoloquinolines

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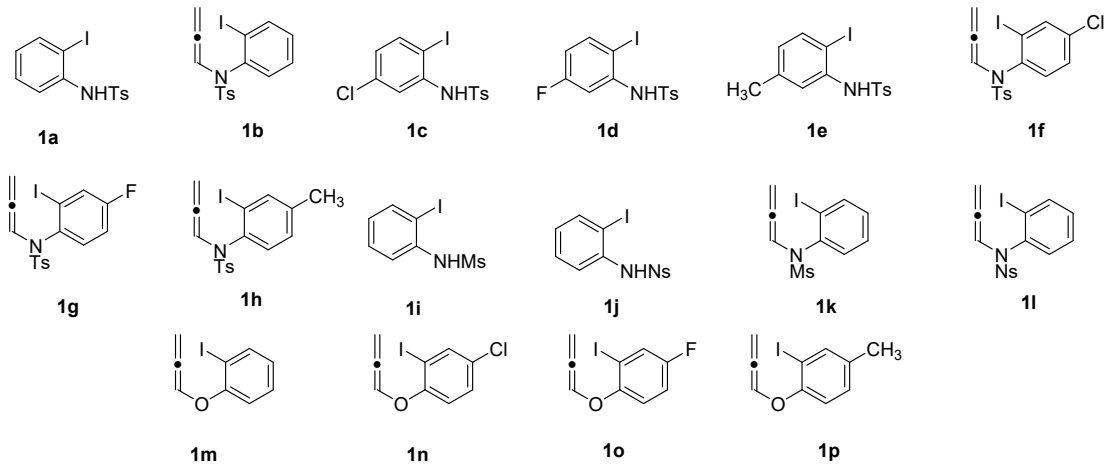
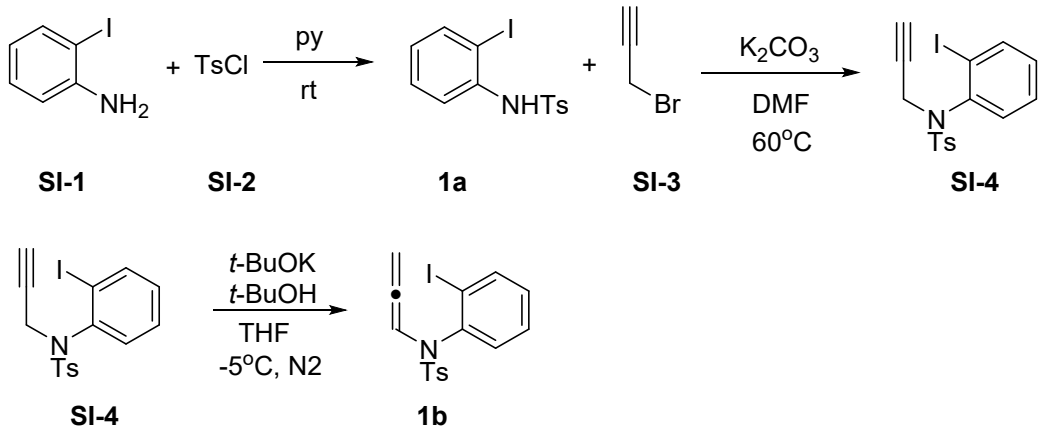
1. General Information

Organic solvents (Aldrich) were used without further purification. Purifications of reactions products were carried out by flash chromatography using Merck silica gel (40-63 μm). ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) were measured on a Brucker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm, δ) downfield fromresidual solvents peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), …. Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Electrospray mass spectra were obtained using an ESI/TOF Mariner Mass Spectrometer. Unless otherwise noted, all other commercially available reagents and solvents were used without further purification.

2. Preparation of Starting Material.



General Procedure I:

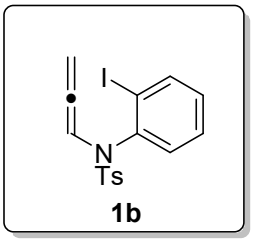


Preparation of alcohol 1a: To a solution of o-iodoaniline (2.2 g, 10.0 mmol, 1.0 equiv) in pyridine (10.0 mL) was added TsCl (2.1 g, 10.5 mmol, 1.05 equiv) at room temperature. The reaction was stirred at room temperature for 8 h before being quenched with H_2O. The quenched mixture was extracted three times with DCM. The combined organic phase was first washed with 1.0 M HCl to remove excess pyridine, and then washed with saturated aqueous $NaHCO_3$, H_2O, brine, and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and crude tosylation product was afforded without further purification.

Preparation of alcohol SI-4: To a solution of the crude tosylation product in DMF (20.0 mL), potassium carbonate (2.1 g, 15.0 mmol, 1.5 equiv) and 3-bromopropyne (1.8 g, 15.0 mmol, 1.5 equiv) was added. The mixture stirred in an oil bath at 60 °C for 8 h. After the reaction was complete, the filtrate was concentrated under reduced pressure and purified by flash column chromatography to give the propargyl amide **SI-4**.

Preparation of alcohol 1b: Dissolve the **SI-4** in t-BuOH, then inject THF (10 mL) into the solution, after that, the solution was added t-BuOK (0.34 g, 3.0 mmol, 0.3 equiv) at 0 °C. The reaction was stirred at -5°C for 1 h before being concentrated under reduced pressure. Subsequently, the residue was suspended in DCM. The filtrate was concentrated under reduced pressure and the crude residue was purified by flash column chromatography to give the allenamide **1b**.

Analytical Data:



1b

***N*-(2-iodophenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide(1b)**

$C_{16}H_{14}INO_2S$

The title compound was prepared according to **general procedure I.**

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.45 (s, 3H), 5.00 (dd, *J* = 18.0, 6.0 Hz, 2H), 6.76 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.02 (td, *J* = 8.0, 1.6 Hz, 1H), 7.09 (t, *J* = 6.4 Hz,1H), 7.22 (td, *J* = 8.0, 1.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 6.4, 1.6 Hz, 2H), 7.89 (dd, *J* =8.0, 1.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 21.9, 87.9, 102.2, 128.2, 128.8, 130.0, 130.4, 130.5,136.3, 140.2, 140.5, 144.4, 201.5.

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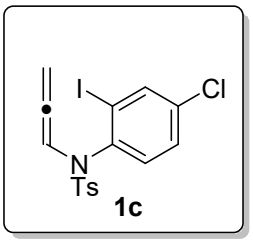

***N*-(4-chloro-2-iodophenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide(1c)**

$C_{16}H_{13}ClINO_2S$

The title compound was prepared according to **general procedure I.**

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.46 (s, 3H), 5.04(dd, *J* = 19.6, 6.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 7.07 (t, *J* = 6.0 Hz, 1H), 7.20 (dd, *J* = 8.4, 2.4 Hz,1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.67 (dd, *J* = 6.4, 2.0 Hz, 2H), 7.88 (d, *J* = 2.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 21.9, 88.3, 102.0, 102.5, 128.2, 129.1, 130.1, 130.9, 135.5, 136.0, 138.9, 140.0, 144.7,201.3.

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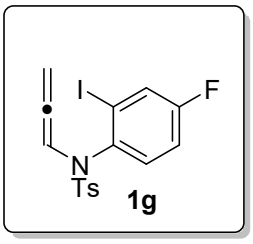

***N*-(4-fluoro-2-iodophenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide(1g)**

$C_{16}H_{13}FINO_2S$

The title compound was prepared according to **general procedure I.**

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):2.17 (s, 3H),2.46 (s, 3H), 5.04(dd, *J* = 19.2, 6.0 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 1H), 7.06 (t, *J* = 6.4 Hz, 1H), 7.34 (m, 3H), 7.66 (dd, *J* =6.8, 1.6 Hz, 2H), 8.03 (d, *J* = 2.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 21.9, 88.4, 102.0, 103.0,123.6, 128.2, 130.1, 131.4, 132.1, 136.0, 139.4, 142.7, 144.7, 201.3.

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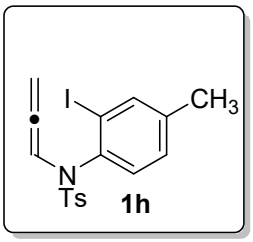


***N*-(2-iodo-4-methylphenyl)-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide(1h)**

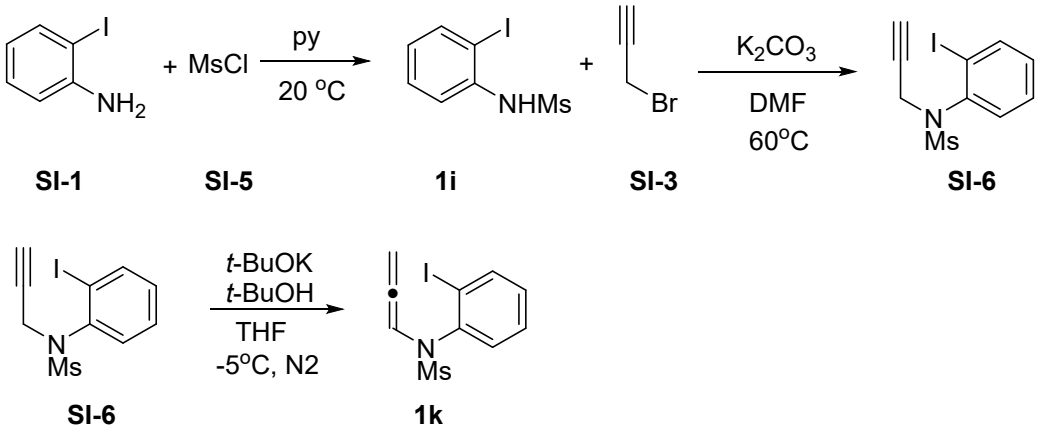
$C_{17}H_{16}INO_2S$

The title compound was prepared according to **general procedure I**.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.46 (s, 3H), 2.49(s,3H),5.04(dd, *J* = 19.2, 6.0 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 1H), 7.06 (t, *J* = 6.4 Hz, 1H), 7.34 (m, 3H), 7.66 (dd, *J* =6.8, 1.6 Hz, 2H), 8.03 (d, *J* = 2.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 21.6, 21.9, 88.4, 102.0, 103.0,123.6, 128.2, 130.1, 131.4, 132.1, 136.0, 139.4, 142.7, 144.7, 201.3.

General Procedure II:



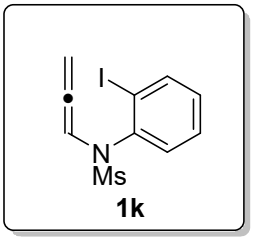
Preparation of alcohol 1i: To a solution of o-iodoaniline (2.2 g, 10.0 mmol, 1.0 equiv) in pyridine (10.0 mL) was added MsCl (1.72 g, 15 mmol, 1.5 equiv) at 20 °C. The reaction was stirred at room temperature for 5h before being quenched with H_2O. The quenched mixture was extracted three times with DCM. The combined organic phase was first washed with 1.0 M HCl to remove excess pyridine, and then washed with saturated aqueous $NaHCO_3$, H_2O, brine, and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and crude tosylation product was afforded without further purification.

Preparation of alcohol SI-4: To a solution of the crude tosylation product in DMF (20.0 mL), potassium carbonate (2.1 g, 15.0 mmol, 1.5 equiv) and 3-bromopropyne (1.8 g, 15.0

mmol, 1.5 equiv) was added. The mixture stirred in an oil bath at 60 °C for 8 h. After the reaction was complete, the filtrate was concentrated under reduced pressure and purified by flash column chromatography to give the propargyl amide **SI-4**.

Preparation of alcohol 1k: Dissolve the **SI-6** in t-BuOH, then inject THF (10 mL) into the solution, after that, the solution was added t-BuOK (0.34 g, 3.0 mmol, 0.3 equiv) at 0 °C. The reaction was stirred at -5°C for 1 h before being concentrated under reduced pressure. Subsequently, the residue was suspended in DCM. The filtrate was concentrated under reduced pressure and the crude residue was purified by flash column chromatography to give the allenamide **1k**.

Analytical Data:



1k

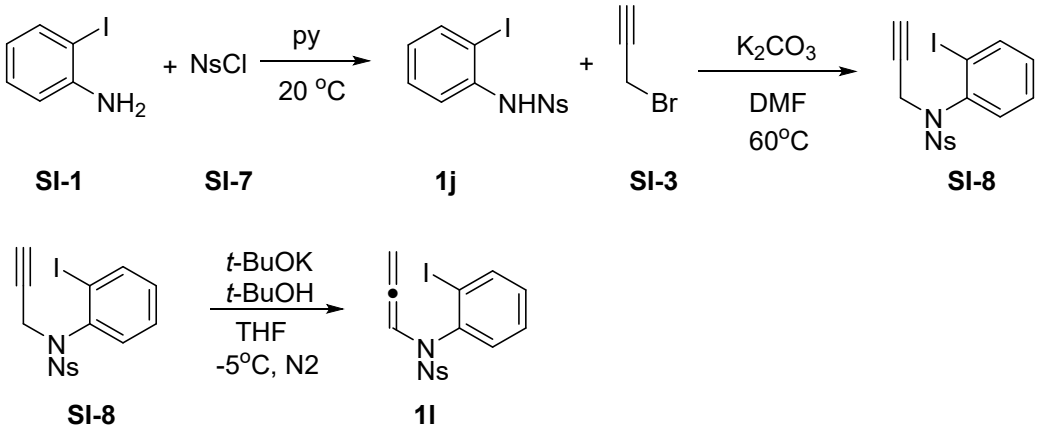
***N*-(2-iodophenyl)-*N*-(propa-1,2-dien-1-yl)methanesulfonamide(1k)**

$C_{10}H_{10}INO_2S$

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.45 (s, 3H), 5.00 (dd, *J* = 18.0, 6.0 Hz, 2H), 7.22 (td, *J* = 8.0, 1.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 6.4, 1.6 Hz, 2H), 7.89 (dd, *J* =8.0, 1.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 21.9, 87.9, 102.2, 128.2, 130.0, 130.5,136.3, 140.2, 144.4, 201.5.

General Procedure III:

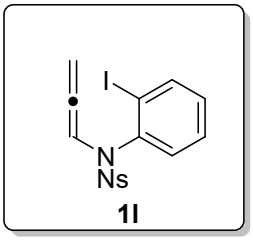


Preparation of alcohol 1j: To a solution of o-iodoaniline (2.2 g, 10.0 mmol, 1.0 equiv) in pyridine (10.0 mL) was added NsCl (2.44 g, 11 mmol, 1.1 equiv) at 20 °C. The reaction was stirred at room temperature for 5h before being quenched with H_2O. The quenched mixture was extracted three times with DCM. The combined organic phase was first washed with 1.0 M HCl to remove excess pyridine, and then washed with saturated aqueous $NaHCO_3$, H_2O, brine, and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and crude tosylation product was afforded without further purification.

Preparation of alcohol SI-8: To a solution of the crude tosylation product in DMF (20.0 mL), potassium carbonate (2.1 g, 15.0 mmol, 1.5 equiv) and 3-bromopropyne (1.8 g, 15.0 mmol, 1.5 equiv) was added. The mixture stirred in an oil bath at 60 °C for 8 h. After the reaction was complete, the filtrate was concentrated under reduced pressure and purified by flash column chromatography to give the propargyl amide **SI-8**.

Preparation of alcohol 1l: Dissolve the **SI-8** in t-BuOH, then inject THF (10 mL) into the solution, after that, the solution was added t-BuOK (0.34 g, 3.0 mmol, 0.3 equiv) at 0 °C. The reaction was stirred at -5°C for 1 h before being concentrated under reduced pressure. Subsequently, the residue was suspended in DCM. The filtrate was concentrated under reduced pressure and the crude residue was purified by flash column chromatography to give the allenamide **1l**.

Analytical Data:



1l

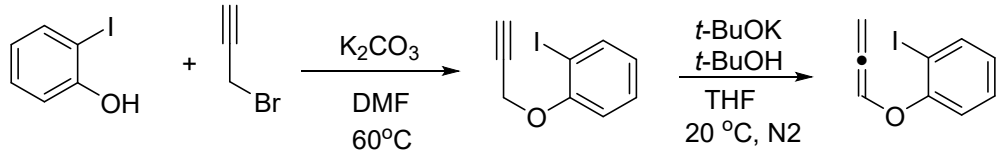
***N*-(2-iodophenyl)-4-nitro-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide(1l)**

$C_{15}H_{11}IN_2O_4S$

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 5.00 (dd, *J* = 18.0, 6.0 Hz, 2H), 6.76 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.02 (td, *J* = 8.0, 1.6 Hz, 1H), 7.09 (t, *J* = 6.4 Hz,1H), 7.22 (td, *J* = 8.0, 1.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 6.4, 1.6 Hz, 2H), 7.89 (dd, *J* =8.0, 1.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 21.9, 87.9, 102.2, 128.2, 128.8, 130.0, 130.4, 130.5, 136.3, 140.2, 140.5, 144.4, 201.5.

General Procedure IV:

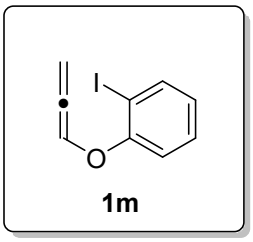


SI-9 **SI-3** **SI-10** **1m**

Preparation of alcohol SI-10: To a solution of the crude tosylation product in DMF (20.0 mL), potassium carbonate (2.1 g, 15.0 mmol, 1.5 equiv) and 3-bromopropyne (1.8 g, 15.0 mmol, 1.5 equiv) was added. The mixture stirred in an oil bath at 60 °C for 8 h. After the reaction was complete, the filtrate was concentrated under reduced pressure and purified by flash column chromatography to give the propargyl amide **SI-10**.

Preparation of alcohol 1m: Dissolve the **SI-10** in t-BuOH, then inject THF (10 mL) into the solution, after that, the solution was added t-BuOK (0.34 g, 3.0 mmol, 0.3 equiv) at 0 °C. The reaction was stirred at 20°C for 12 h before being concentrated under reduced pressure. Subsequently, the residue was suspended in DCM. The filtrate was concentrated under reduced pressure and the crude residue was purified by flash column chromatography to give the allenamide **1m**.

Analytical Data:



1m

1-iodo-2-(propa-1,2-dien-1-yloxy)benzene(1m)

C_9H_7IO

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 5.00 (dd, *J* = 18.0, 6.0 Hz, 2H), 7.22 (td, *J* = 8.0, 1.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 6.4, 1.6 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 87.2, 90,4. 116.8, 118.4, 124.7, 129.3, 139.6, 156.2, 202.4.

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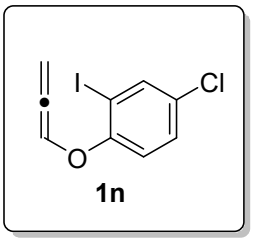

1n

4-chloro-2-iodo-1-(propa-1,2-dien-1-yloxy)benzene(1n)

C_9H_6ClIO

The title compound was prepared according to **general procedure IV.**

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 5.00 (dd, *J* = 18.0, 6.0 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 7.07 (t, *J* = 6.0 Hz, 1H), 7.20 (dd, *J* = 8.4, 2.4 Hz,1H), 7.79 (d, *J* = 8.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 87.2, 90.4, 116.8, 118.4, 124.7, 129.3, 139.6, 156.2, 202.4.

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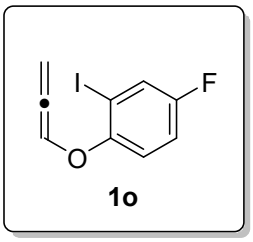

1o

4-fluoro-2-iodo-1-(propa-1,2-dien-1-yloxy)benzene(1o)

C_9H_6FIO

The title compound was prepared according to **general procedure IV.**

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):5.00 (dd, *J* = 18.0, 6.0 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 7.07 (t, *J* = 6.0 Hz, 1H), 7.20 (dd, *J* = 8.4, 2.4 Hz,1H), 7.79 (d, *J* = 8.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 87.2, 90.4, 116.8, 118.4, 124.7, 129.3, 139.6, 156.2, 202.4.

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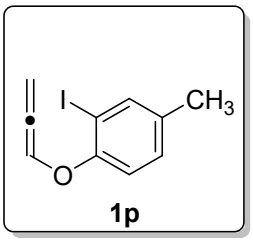


1p

2-iodo-4-methyl-1-(propa-1,2-dien-1-yloxy)benzene(1p)

$C_{10}H_9IO$

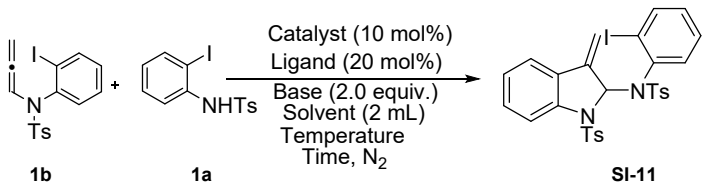
The title compound was prepared according to **general procedure IV.**

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):2.49(s,3H),5.00 (dd, *J* = 18.0, 6.0 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 7.07 (t, *J* = 6.0 Hz, 1H), 7.20 (dd, *J* = 8.4, 2.4 Hz,1H), 7.79 (d, *J* = 8.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 87.2, 90.4, 116.8, 118.4, 124.7, 129.3, 139.6, 156.2, 202.4.

3. Optimization of Reaction Conditions

Table 1.

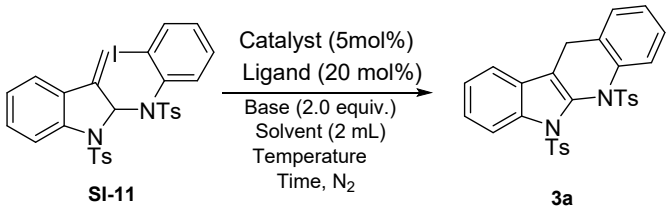


Entry	Catalyst	Ligand	Base	Solvent	Temperature (^{o}C)	Time (h)	Yield (%)
1	$Pd(PPh_3)_4$	-	K_2CO_3	MeCN	80	4	60
2	$Pd(PPh_3)_4$	-	Cs_2CO_3	MeCN	80	4	52
3	$Pd(PPh_3)_4$	-	Na_2CO_3	MeCN	80	4	50
4	$Pd(PPh_3)_4$	-	KF	MeCN	80	4	52
5	$Pd(PPh_3)_4$	-	CsF	MeCN	80	4	56
6	$Pd(dba)_2$	PPh_3	Cs_2CO_3	MeCN	80	4	63
7	$Pd_2(dba)_3$	PPh_3	Cs_2CO_3	MeCN	80	4	62
8	Pd(OAc)2	PPh_3	Cs_2CO_3	MeCN	80	4	-
9	PdCl2(dppe)	-	Cs_2CO_3	MeCN	80	4	-
10	$Pd(dba)_2$	PCy_3	Cs_2CO_3	MeCN	80	4	64
11	$Pd_2(dba)_3$	PCy_3	Cs_2CO_3	MeCN	80	4	60
12	$Pd(PPh_3)_4$	-	Cs_2CO_3	MeCN	100	4	65
13	$Pd(PPh_3)_4$	-	Cs_2CO_3	MeCN	120	4	55
14	$Pd(PPh_3)_4$	-	Cs_2CO_3	toliene	80	4	54
15	$Pd(PPh_3)_4$	-	Cs_2CO_3	DMF	80	4	-
16	$Pd(PPh_3)_4$	-	Cs_2CO_3	dioxane	80	4	55

We embarked on our studies by screening the reaction parameters of the coupling of N-(2-iodophenyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide **1b** with N-(2-iodophenyl)-4-methylbenzenesulfonamide **1a** in the presence of 10 mol% $Pd(PPh_3)_4$ and 2.0 equiv. of K_2CO_3 at 80 ℃ in MeCN under N_2. In this condition, we get intermediate product **SI-11** and product **3a** through the one-pot method. After that, we try to make a complete conversion of product **SI-11** to **3a**. Therefore, we started experimenting with different reaction conditions to improve the reaction efficiency. First of all, it is also critical to increase the yield of intermediate **3a**. Then we used ingredients 1a and 1b in the presence of 10 mol% $Pd(PPh_3)_4$ and 2.0 equiv. of K_2CO_3 at 80 ℃ in MeCN under N_2. In this condition, the intermediate **SI-11** was isolated in 60% yield (entry 1). Base on this, some bases such as Cs_2CO_3, Na_2CO_3, KF and CsF were investigated, which obtained better results (entries 2-5). Then we tried different kinds of catalysts and ligands. Unfortunately,

all of the conditions did not improve the transformation entries (6-11). Furthermore, we tried different reaction temperatures, but increasing the reaction temperature does not increase the efficiency of the reaction (entries 12-13). Different solvents were screened, such as toluene, DMF, and dioxane (entries 14-16), but MeCN still was the best choice. Based on the above results, $Pd(PPh_3)_4$ (10 mol%) and Cs_2CO_3 (2.0 equiv.) in MeCN at 80℃ for 4h were chosen as the optimized conditions. For more reaction conditions, see table 1.

Table 2



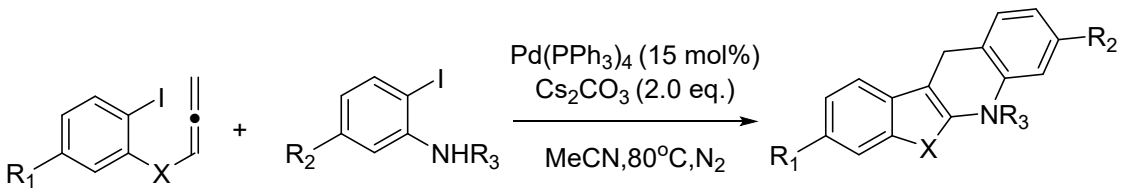
SI-11 **3a**

Entry	Catalyst	Ligand	Base	Solvent	Temperature (^oC)	Time (h)	Yield (%)
1	$Pd(PPh_3)_4$	-	K_2CO_3	MeCN	80	4	82
2	$Pd(PPh_3)_4$	-	Cs_2CO_3	MeCN	80	4	92
3	$Pd(PPh_3)_4$	-	Na_2CO_3	MeCN	80	4	88
4	$Pd(PPh_3)_4$	-	KF	MeCN	80	4	82
5	$Pd(PPh_3)_4$	-	CsF	MeCN	80	4	76
6	$Pd(PPh_3)_4$	-	Et_3N	MeCN	80	4	-
7	$Pd(PPh_3)_4$	-	Cs_2CO_3	MeCN	100	4	83
8	$Pd(PPh_3)_4$	-	Cs_2CO_3	MeCN	120	4	83
9	$Pd(PPh_3)_4$	-	Cs_2CO_3	toluene	100	4	74
10	$Pd(PPh_3)_4$	-	Cs_2CO_3	dioxane	100	4	65
11	$Pd(dba)_2$	PPh_3	Cs_2CO_3	MeCN	80	4	27
12	$Pd_2(dba)_3$	PPh_3	Cs_2CO_3	MeCN	80	4	23
13	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	MeCN	80	4	-
14	$PdCl_2(dppe)$	-	Cs_2CO_3	MeCN	80	4	-
15	$Pd(dba)_2$	PCy_3	Cs_2CO_3	MeCN	80	4	24
16	$Pd_2(dba)_3$	PCy_3	Cs_2CO_3	MeCN	80	4	28

We set out to increase the yield of the final product. Firstly, we also use K_2CO_3 as base, the product **3a** was isolated in 82% yield (entry 1). Refer to the previous reaction results,

and then we use the optimal conditions from the previous step, to our delight, the yield of product **3a** went up to 92% (entry 2). The next, we use different kinds of bases such asNa_2CO_3, KF, CsF and Et_3N, but the structure is not satisfactory to us (entries 3-6). Then we increased the reaction temperature to observe the change of reaction yield, unfortunately, all of the changes did not improve the transformations (entries 7-8). Furthermore, different solvents were screened, such as toluene, and dioxane (entries 9-10), but these two solvents reduce the reaction yield. At last, we screend different kinds of catalysts and ligands, but all the kinds of catalysts and ligands did not work out very well (entries 11-16). Based on the above results, $Pd(PPh_3)_4$ (5 mol%) and Cs_2CO_3 (2.0 equiv.) in MeCN at 80℃ for 4h were chosen as the optimized conditions. All the reaction conditions, see table 2.

4. Typical Procedure and Analytical Data

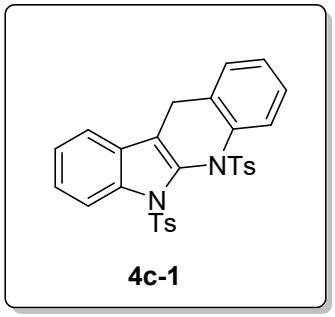


4a **4b** **4c**

Typical Procedure

allenamide derivates **4a** (0.20 mmol, 1.0 equiv), 2-iodide aniline derivates **4b**, (0.20 mmol, 1.0 equiv), Pd (PPh_3)$_3$ (0.03 mmol,0.15 equiv), and Cs_2CO_3 (130.3 mg, 0.40 mmol, 2.0 equiv) were added to a reaction tube and vacuum purged three times, backfilling with N_2. Then the MeCN (3 mL) was added under nitrogen atmosphere. The resulting mixture was stirred at 80 °C for 4 h. After cooling the reaction mixture at rt, it was quenched with H_2O.The aqueous layer was extracted with EA (10 mL ×3). The combined organic phase was sequentially washed with saturated aqueous solution of NaCl and then concentrated in vacuo. The mixture was purified by silica gel column chromatography (PE: EA, 5:1) to give product **4c**.

Analytical Data:



4c-1

5,6-ditosyl-6,11-dihydro-5H-indolo[2,3-b]quinoline

$C_{29}H_{24}N_2O_4S_2$ **MW**: 528.64 g·mol-1

Light yellow solid

Isolated Amount: 97.2 mg **Yield:** 92%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.98 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.2

Hz, 1H), 7.28 (d, *J* = 9.4 Hz, 4H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 4.86 (s, 2H), 2.34 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 129.7, 129.5, 127.9, 127.5, 126.8, 126.6, 126.4, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.6, 21.5.

MS (EI) m/z 528 (M+); **HRMS (ESI)** Calcd for $C_{29}H_{24}N_2O_4S$+H 529.1256, Found 529.1264.

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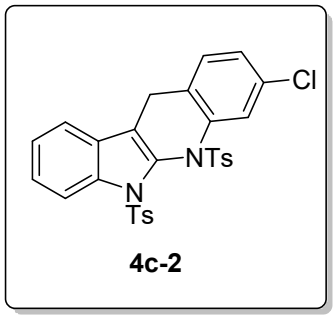

4c-2

3-chloro-5,6-ditosyl-6,11-dihydro-5H-indolo[2,3-b]quinoline

$C_{29}H_{23}ClN_2O_4S_2$ **MW**: 563.08 g·mol-1

Light yellow solid

Isolated Amount: 96.8 mg **Yield**: 86%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.93 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 4H), 7.37 (s, 1H), 7.28 (q, *J* = 8.6, 7.9 Hz, 3H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 7.7 Hz, 2H), 4.80 (s, 2H), 2.35 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 129.7, 129.5, 127.9, 127.5, 126.8, 126.6, 126.4, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.6, 21.5.

MS (EI) m/z 562 (M+); **HRMS (ESI)** Calcd for $C_{29}H_{23}ClN_2O_4S$+H 563.0866, Found 563.0870.

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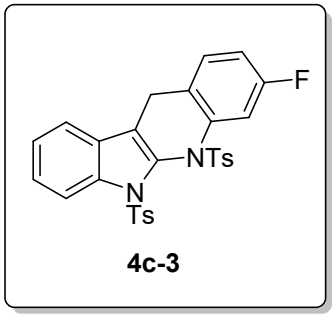

4c-3

3-fluoro-5,6-ditosyl-6,11-dihydro-5H-indolo[2,3-b]quinoline

$C_{29}H_{23}FN_2O_4S_2$ **MW**: 546.11 g·mol^{-1}

Light yellow solid

Isolated Amount: 92.8 mg **Yield:** 85%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.90 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 7.3 Hz, 2H), 7.42 (d, *J* = 6.6 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 3H), 7.22 (dd, *J* = 18.5, 10.2 Hz, 3H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 2H), 4.78 (s, 2H), 2.28 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 162.3, 159.8, 145.0, 144.1, 137.0, 136.1, 135.0, 134.9, 131.6, 131.5, 130.0, 129.8, 129.7, 128.1, 127.1, 126.9, 126.6, 126.2, 125.0, 123.4, 120.3, 116.2, 115.6, 113.5, 45.6, 21.6, 21.6.

MS (EI) m/z 546 (M+); **HRMS (ESI)** Calcd for $C_{29}H_{23}FN_2O_4S_2$+H 547.1162, Found 547.1167.

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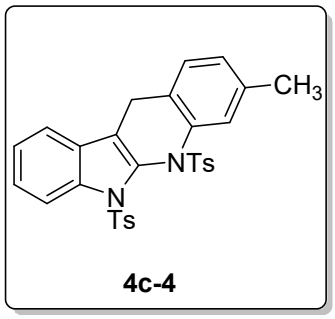

4c-4

3-methyl-5,6-ditosyl-6,11-dihydro-5H-indolo[2,3-b]quinoline

$C_{30}H_{26}N_2O_4S_2$ **MW**: 542.67 g·mol^{-1}

Light yellow solid

Isolated Amount: 91.1 mg **Yield**: 84%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.96 (d, *J* = 7.3 Hz, 1H), 7.57-7.49 (m, 3H), 7.41 (d, *J* = 7.5 Hz, 3H), 7.26 (s, 3H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 2H), 4.83 (s, 2H), 2.38 (s, 3H), 2.35 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 129.7, 129.5, 127.9, 127.5, 126.8, 126.6, 126.4, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.6, 21.5,21.4.

MS (EI) m/z 542 (M+); **HRMS (ESI)** Calcd for $C_{30}H_{26}N_2O_4S_2$+H 543.1412, Found 543.1419.

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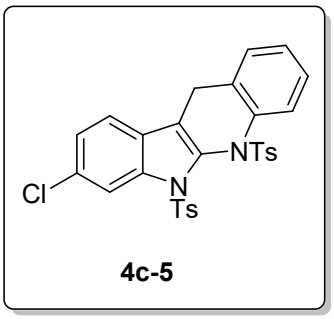

4c-5

8-chloro-5,6-ditosyl-6,11-dihydro-5H-indolo[2,3-b]quinoline

$C_{29}H_{23}ClN_2O_4S_2$ **MW**: 563.08 g·mol^{-1}

Light yellow solid

Isolated Amount: 90.1mg **Yield**: 80%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.93 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 4H), 7.37 (s, 1H), 7.28 (q, *J* = 8.6, 7.9 Hz, 3H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 7.7 Hz, 2H), 4.80 (s, 2H), 2.35 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 129.7, 129.5, 127.9, 127.5, 126.8, 126.6, 126.4, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.6, 21.5.

MS (EI) m/z 562 (M+); **HRMS (ESI)** Calcd for $C_{29}H_{23}ClN_2O_4S_2$+H 563.0866 Found 563.0863.

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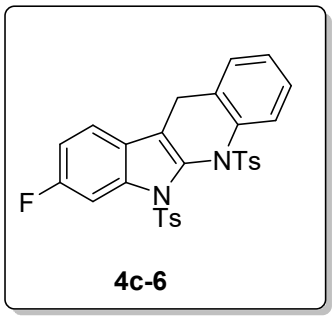

4c-6

8-fluoro-5,6-ditosyl-6,11-dihydro-5H-indolo[2,3-b]quinoline

$C_{29}H_{23}FN_2O_4S_2$ **MW**: 546.11 g·mol^{-1}

Light yellow solid

Isolated Amount: 89.5 mg **Yield**: 82%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.93 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 4H), 7.37 (s, 1H), 7.28 (q, *J* = 8.6, 7.9 Hz, 3H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 7.7 Hz, 2H), 4.80 (s, 2H), 2.35 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 162.3, 159.8, 145.0, 144.1, 137.0, 136.1, 135.0, 134.9, 131.6, 131.5, 130.0, 129.8, 129.7, 128.1, 127.1, 126.9, 126.6, 126.2, 125.0, 123.4, 120.3, 116.2, 115.6, 113.5, 45.6, 21.6, 21.6.

MS (EI) m/z 546 (M+); **HRMS (ESI)** Calcd for $C_{29}H_{23}FN_2O_4S_2$+H 547.1162, Found 547.1165.

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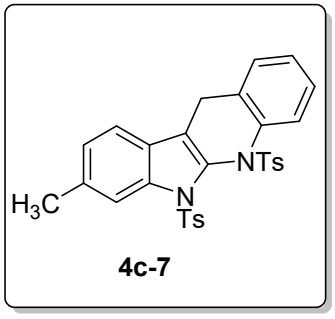

4c-7

8-methyl-5,6-ditosyl-6,11-dihydro-5H-indolo[2,3-b]quinoline

$C_{30}H_{26}N_2O_4S_2$ **MW**: 542.67 g·mol^{-1}

Light yellow solid

Isolated Amount: 89 mg **Yield**: 82%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.96 (d, *J* = 7.3 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.41 (d, *J* = 7.5 Hz, 3H), 7.26 (s, 3H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 2H), 4.83 (s, 2H), 2.38 (s, 3H), 2.35 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 129.7, 129.5, 127.9, 127.5, 126.8, 126.6, 126.4, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.6, 21.5,21.4.

MS (EI) m/z 542 (M+); **HRMS (ESI)** Calcd for $C_{30}H_{26}N_2O_4S_2$+H 543.1412, Found 543.1418.

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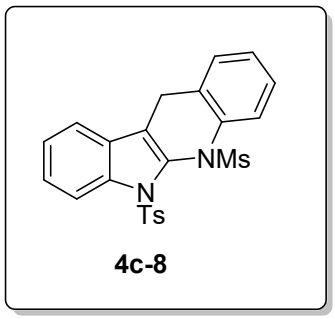

4c-8

5-(methylsulfonyl)-6-tosyl-6,11-dihydro-5H-indolo[2,3-b]quinoline

$C_{23}H_{20}N_2O_4S_2$ **MW**: 452.54 g·mol^{-1}

yellow solid

Isolated Amount: 76 mg **Yield**: 84%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.31 (d, *J* = 8.3 Hz, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.23 – 7.18 (m, 3H), 6.91 (d, *J* = 7.9 Hz, 2H), 4.74 (s, 2H), 2.17 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 127.9, 127.5, 126.6, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.6, 21.5.

MS (EI) m/z 452 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{20}N_2O_4S$+H 453.0943, Found 453.0940.

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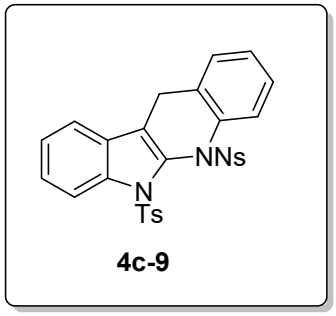

4c-9

5-((4-nitrophenyl)sulfonyl)-6-tosyl-6,11-dihydro-5H-indolo[2,3-b]quinoline

$C_{28}H_{21}N_3O_6S_2$ MW: 559.61 g·mol^{-1}

yellow solid

Isolated Amount: 48.1mg Yield:43%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.98 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 9.4 Hz, 4H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 4.86 (s, 2H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 129.7, 129.5, 127.9, 127.5, 126.8, 126.6, 126.4, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.5.

MS (EI) m/z 559 (M+); **HRMS (ESI)** Calcd for $C_{28}H_{21}N_3O_6S_2$+H 560.0950, Found 560.0957.

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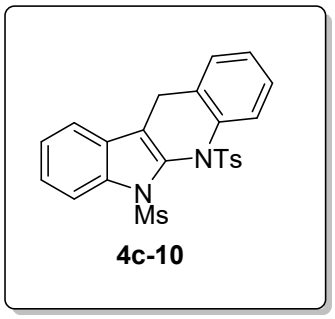

4c-10

5-(methylsulfonyl)-6-tosyl-6,11-dihydro-5H-indolo[2,3-b]quinoline

$C_{23}H_{20}N_2O_4S_2$ **MW**: 452.54 g·mol^{-1}

yellow solid

Isolated Amount: 74.2 mg **Yield**: 82%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.31 (d, *J* = 8.3 Hz, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.23 – 7.18 (m, 3H), 6.91 (d, *J* = 7.9 Hz, 2H), 4.74 (s, 2H), 2.17 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 129.7, 129.5, 127.9, 127.5, 126.6, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.6, 21.5.

MS (EI) m/z 452 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{20}N_2O_4S$+H 453.0943, Found 453.0940.

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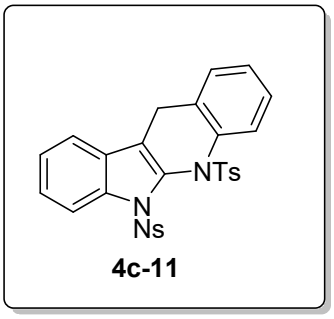

4c-11

6-((4-nitrophenyl)sulfonyl)-5-tosyl-6,11-dihydro-5H-indolo[2,3-b]quinoline

$C_{28}H_{21}N_3O_6S_2$ **MW**: 559.61 g·mol^{-1}

yellow solid

Isolated Amount: 45.8mg **Yield**:41%

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.98 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 9.4 Hz, 4H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 4.86 (s, 2H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 129.7, 129.5, 127.9, 127.5, 126.8, 126.6, 126.4, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.6.

MS (EI) m/z 559 (M+); **HRMS (ESI)** Calcd for $C_{28}H_{21}N_3O_6S_2$+H 560.0950, Found 560.0952.

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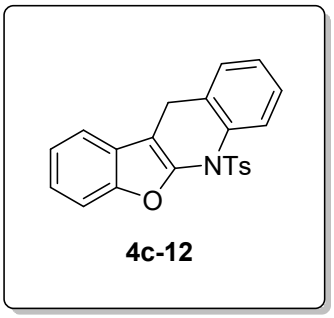

4c-12

6-tosyl-6,11-dihydrobenzofuro[2,3-b]quinoline

$C_{22}H_{17}NO_3S$ **MW**: 375.44 g·mol^{-1}

yellow solid

Isolated Amount: 67.5mg **Yield**: 90%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.83 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 7.0 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.42 – 7.31 (m, 3H), 7.26 (s, 3H), 7.05 (d, *J* = 7.7 Hz, 2H), 6.66 (d, *J* = 7.7 Hz, 2H), 5.10 (s, 2H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 129.7, 129.5, 127.9, 127.5, 126.6, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.5.

MS (EI) m/z 375 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{17}NO_3S$+H 376.1007, Found 376.1010.

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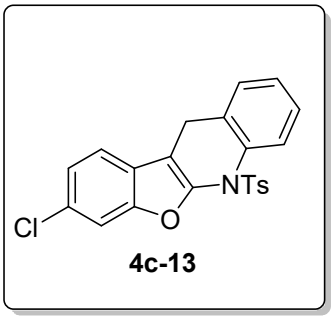

4c-13

3-chloro-6-tosyl-6,11-dihydrobenzofuro[2,3-b]quinoline

$C_{22}H_{16}ClNO_3S$ **MW**: 409.88 g·mol^{-1}

Light yellow solid

Isolated Amount: 72.9 mg **Yield**: 89%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.76 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.34

(t, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 9.7 Hz, 3H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 5.09 (s, 2H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 129.7, 129.5, 127.9, 127.5, 126.6, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.5.

MS (EI) m/z 409 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{16}ClNO_3S$+H 410.0618, Found 410.0622.

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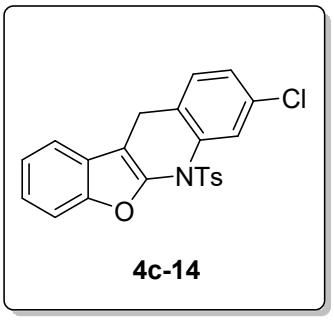
……



4c-14

(8-chloro-6-tosyl-6,11-dihydrobenzofuro[2,3-b]quinoline

$C_{22}H_{16}ClNO_3S$ **MW:** 409.88 g·mol^{-1},

Light Yellow Solid

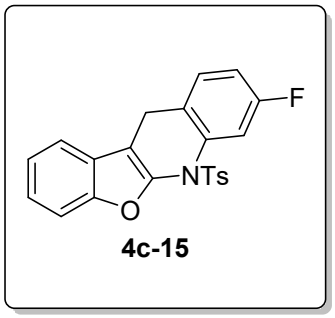
Isolated Amount:72.9 mg **Yield:** 89%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.76 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.34 (t, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 9.7 Hz, 3H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 5.09 (s, 2H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 129.7, 129.5, 127.9, 127.5, 126.6, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.5.

MS (EI) m/z 409 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{16}ClNO_3S$+H 410.0618, Found 410.0615.

……
……



4c-15

8-fluoro-6-tosyl-6,11-dihydrobenzofuro[2,3-b]quinoline

$C_{22}H_{16}FNO_3S$ **MW:** 393.43 g·mol^{-1},

Light Yellow Solid

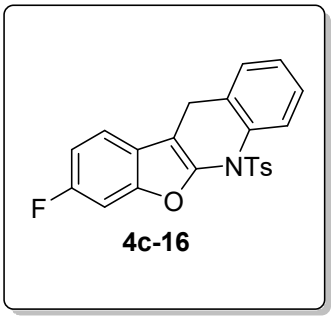
Isolated Amount:71.6 mg **Yield:** 91%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.76 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.34 (t, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 9.7 Hz, 3H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 5.09 (s, 2H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 162.3, 159.8, 145.0, 144.1, 137.0, 136.1, 135.0, 134.9, 131.5, 130.0, 129.8, 129.7, 128.1, 126.9, 126.6, 126.2, 125.0, 123.4, 120.3, 116.2, 115.6, 113.5, 45.6, 21.6, 21.6.

MS (EI) m/z 393 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{16}FNO_3S$+H 394.0913, Found 394.0917.

……
……



4c-16

3-fluoro-6-tosyl-6,11-dihydrobenzofuro[2,3-b]quinoline

$C_{22}H_{16}FNO_3S$ **MW**: 393.43 g·mol^{-1}

Light yellow solid

Isolated Amount: 71.5 mg **Yield**: 91%.

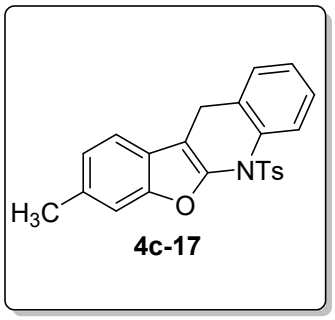
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.76 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.34

(t, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 9.7 Hz, 3H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 5.09 (s, 2H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 162.3, 159.8, 145.0, 144.1, 137.0, 136.1, 135.0, 134.9, 131.6, 130.0, 129.8, 129.7, 128.1, 127.1, 126.6, 126.2, 125.0, 123.4, 120.3, 116.2, 115.6, 113.5, 45.6, 21.6, 21.6.

MS (EI) m/z 393 (M+); **HRMS (ESI)** Calcd for $C_{22}H_{16}FNO_3S$+H 394.0913, Found 394.0920.

……



4c-17

3-methyl-6-tosyl-6,11-dihydrobenzofuro[2,3-b]quinoline

$C_{23}H_{19}NO_3S$ **MW**: 389.47g·mol^{-1}

Light yellow solid

Isolated Amount: 69.3 mg **Yield**: 89%.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.66 (s, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 6.4 Hz, 1H), 7.24 (d, *J* = 2.4 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 2H), 5.06 (s, 2H), 2.46 (s, 3H), 2.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 129.7, 129.5, 127.9, 127.5, 126.6, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.5,19.6.

MS (EI) m/z 389 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{19}NO_3S$+H 390.1164, Found 390.1165.

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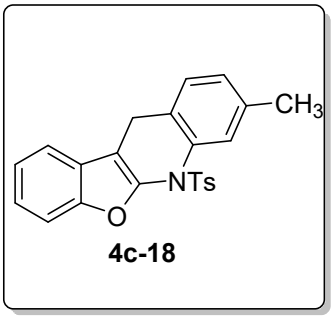


4c-18

8-methyl-6-tosyl-6,11-dihydrobenzofuro[2,3-b]quinoline

$C_{23}H_{19}NO_3S$ **MW**: 389.47g·mol^{-1}

Light yellow solid

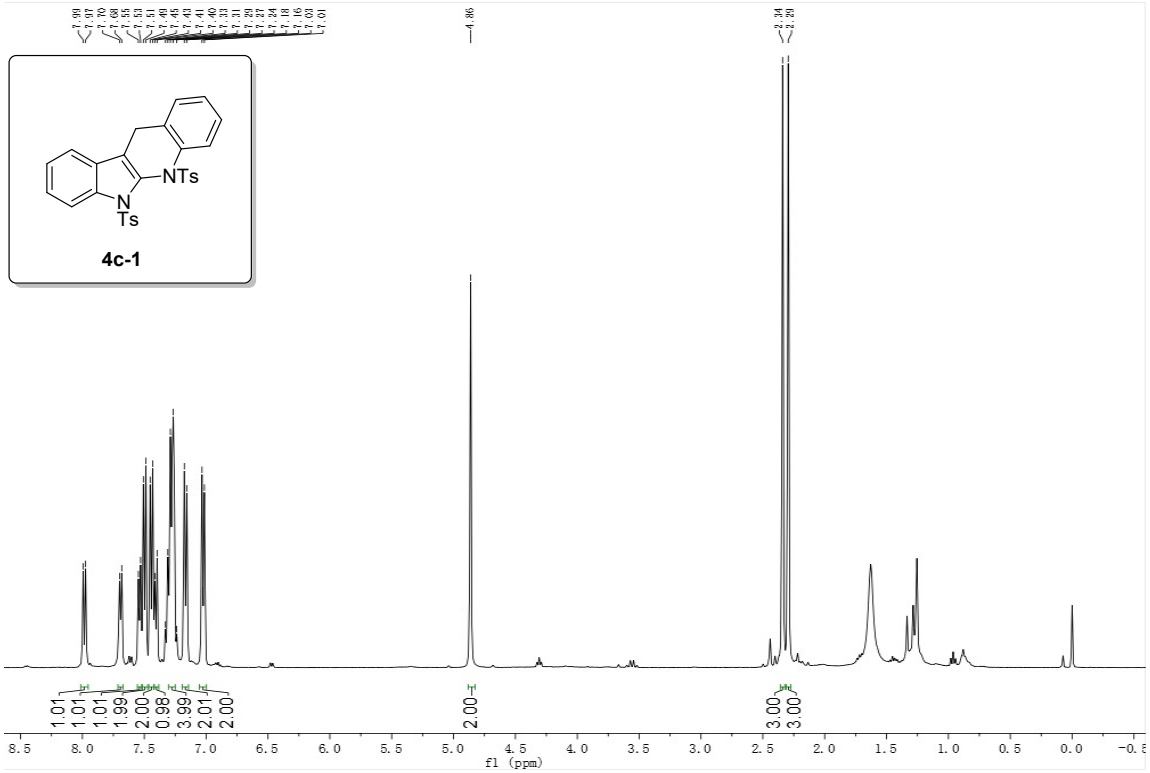
Isolated Amount: 66.9 mg **Yield**: 86%.

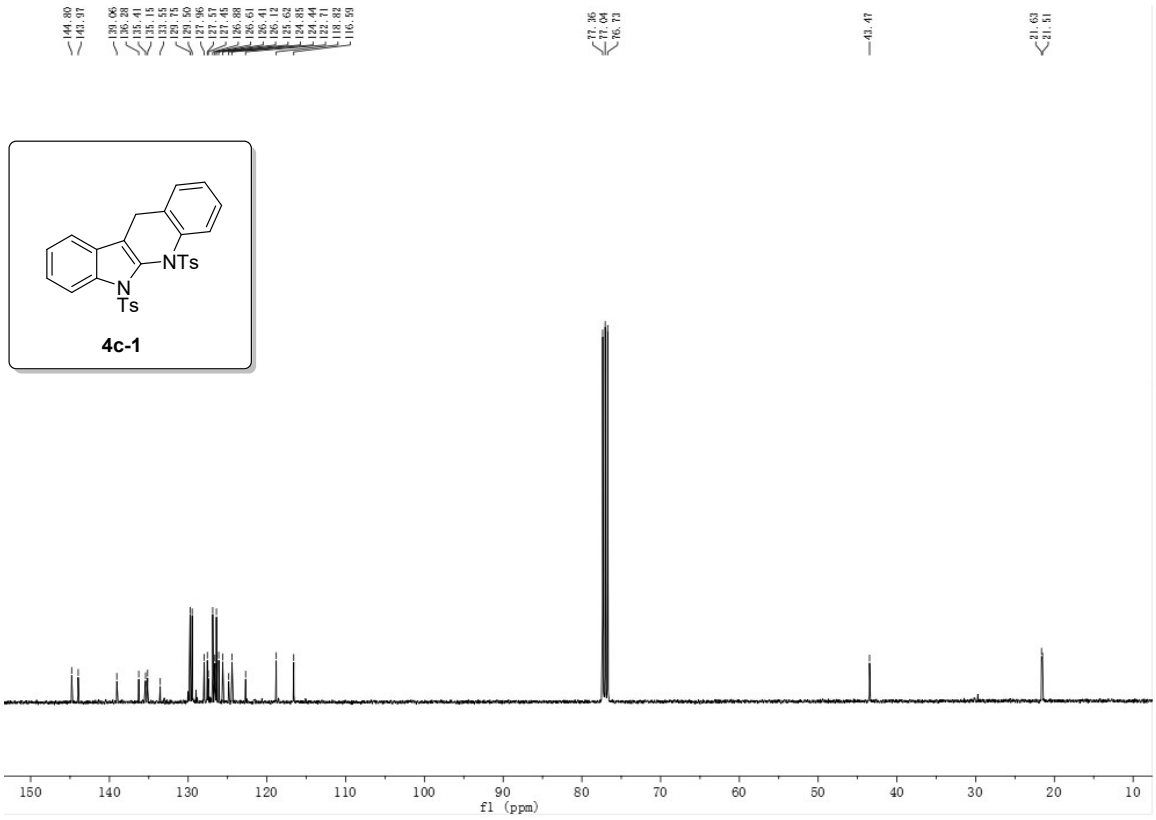
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.66 (s, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 6.4 Hz, 1H), 7.24 (d, *J* = 2.4 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.65 (d, *J* = 7.8 Hz, 2H), 5.06 (s, 2H), 2.46 (s, 3H), 2.05 (s, 3H).

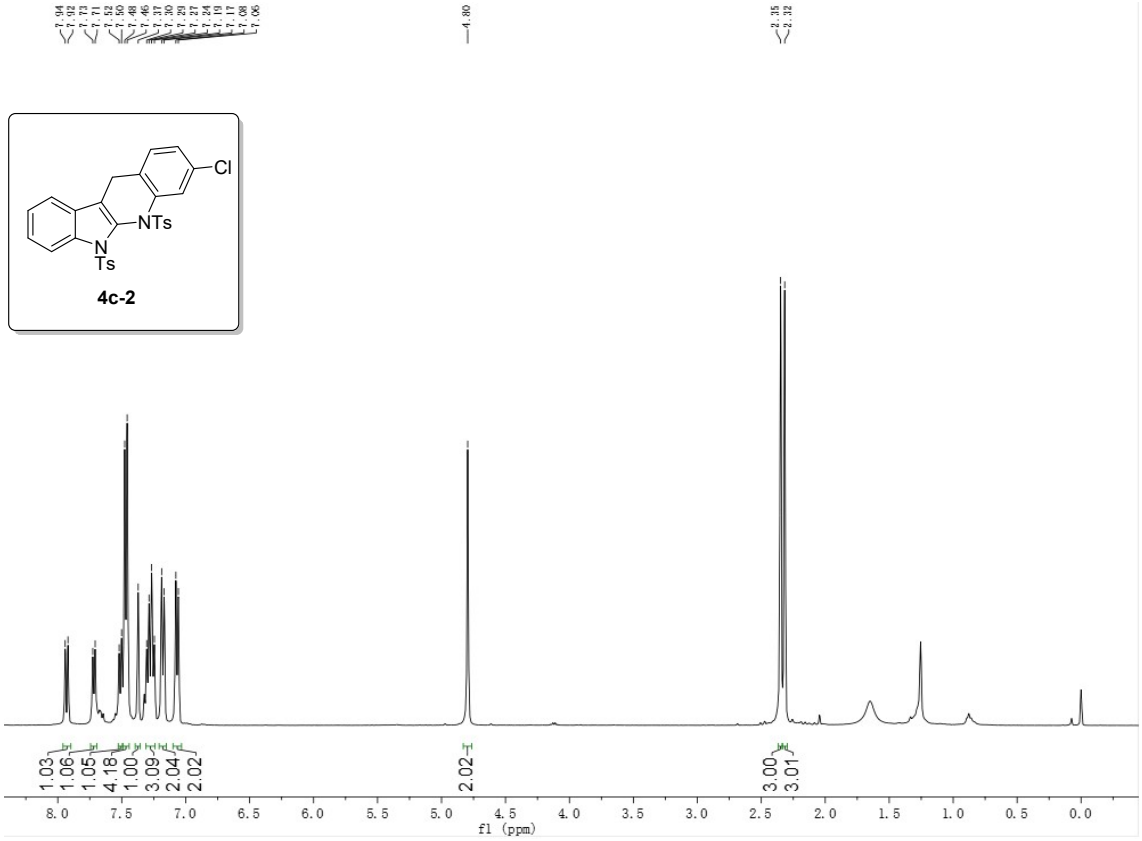
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.8, 143.9, 139.0, 136.2, 135.4, 135.1, 133.5, 129.7, 129.5, 127.9, 127.5, 126.6, 126.1, 125.6, 124.8, 124.4, 122.7, 118.8, 116.5, 43.4, 21.5,19.6.

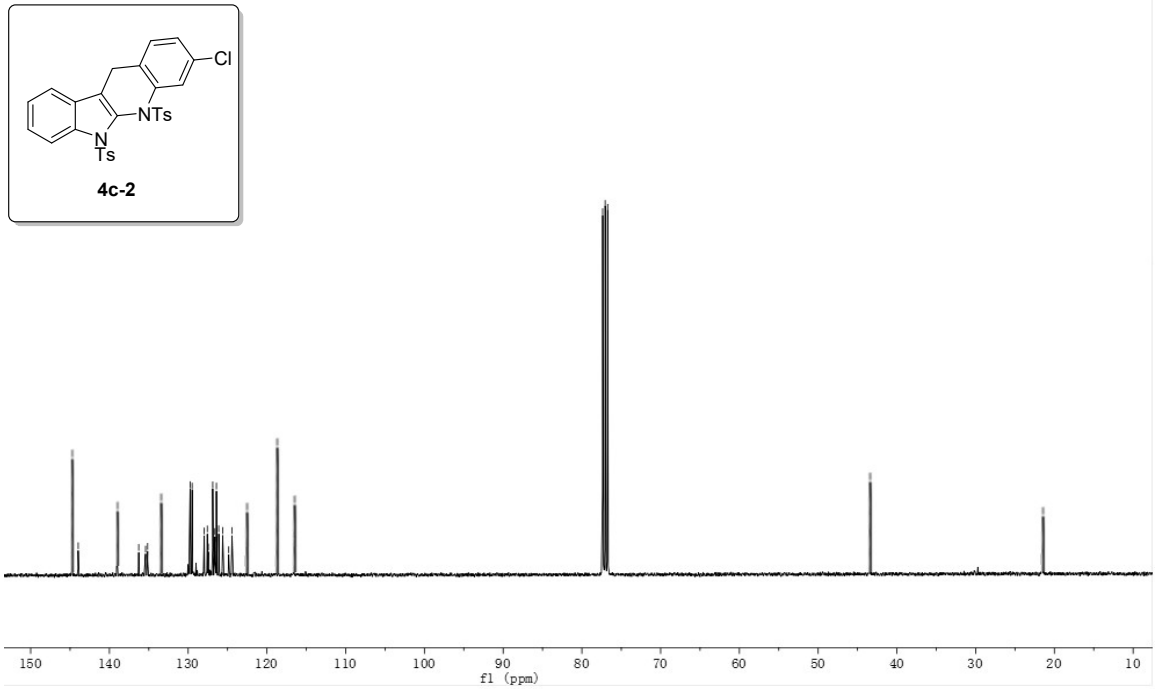
MS (EI) m/z 389 (M+); **HRMS (ESI)** Calcd for $C_{23}H_{19}NO_3S$+H 390.1164, Found 390.1168.

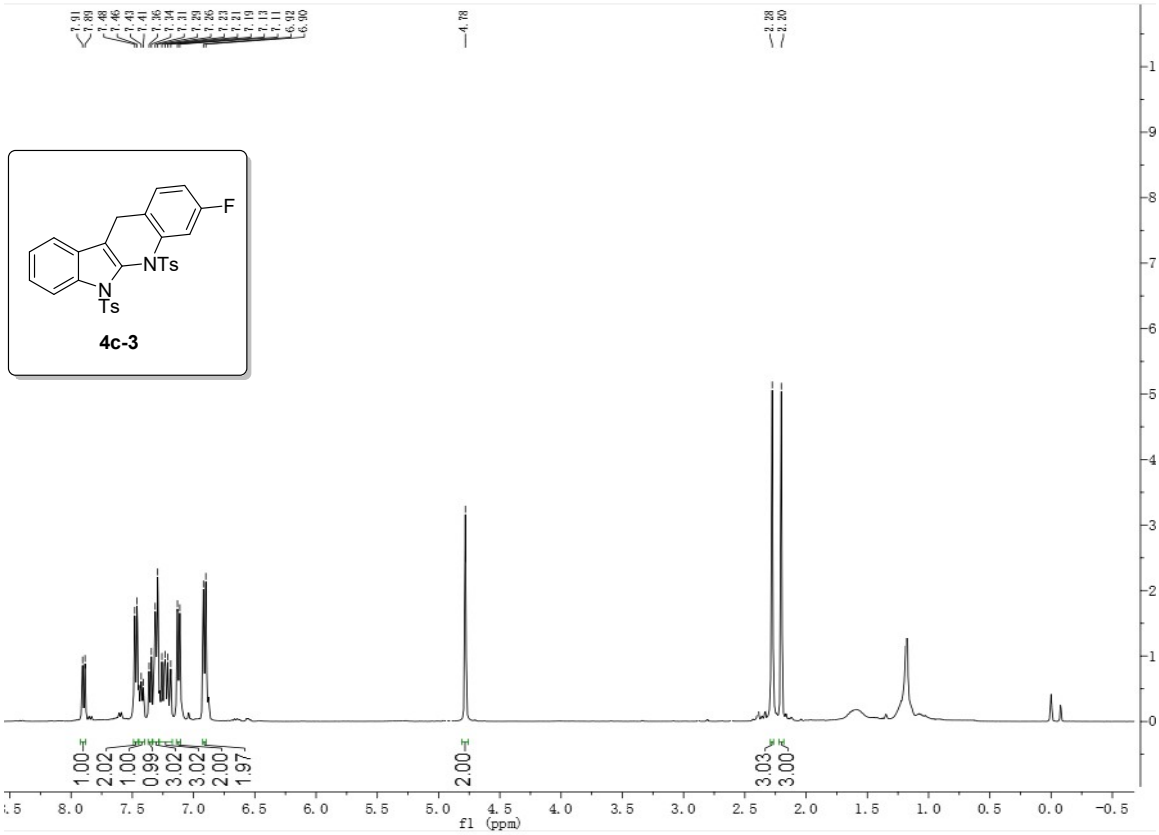
5. Copies of the 1H NMR and 13C NMR for Product

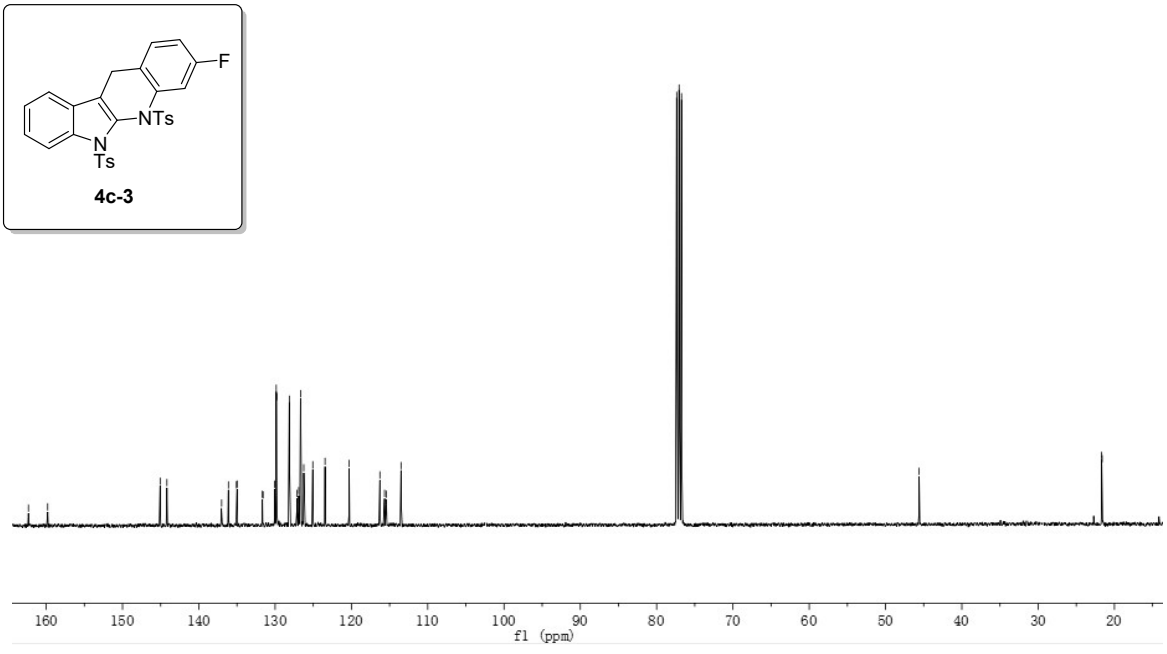


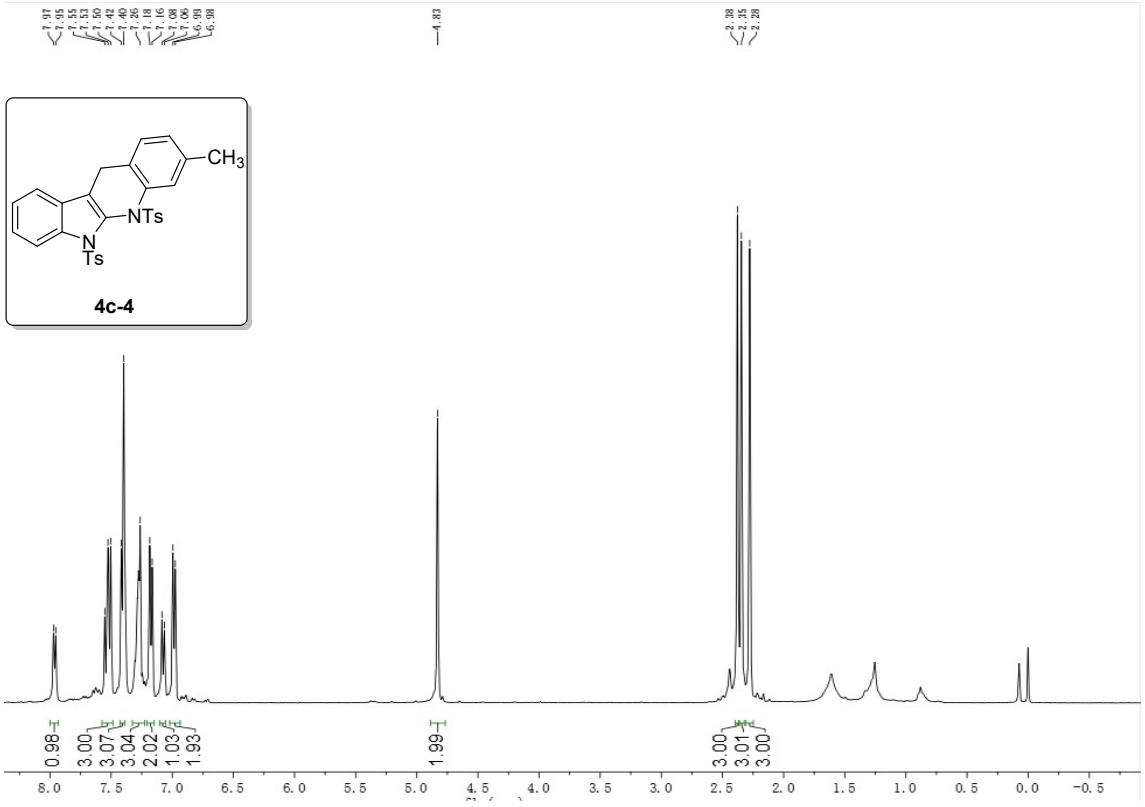


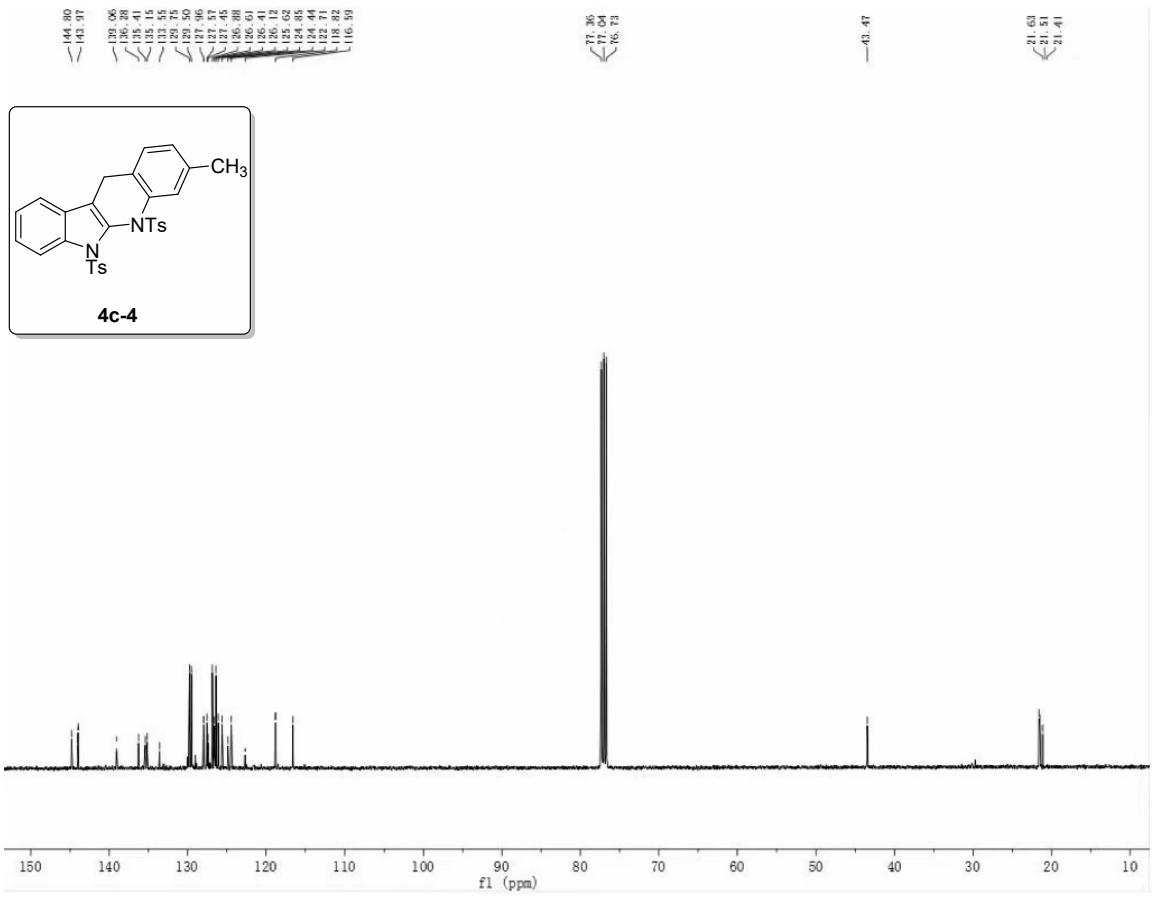

Cl
NTs
N
Ts
4c-2
1.03
1.06
1.05
4.18
1.00
3.09
2.04
2.02
2.02
3.00
3.01
f1 (ppm)

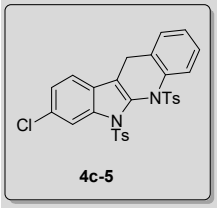

Cl
NTs
N
Ts
4c-2
f1 (ppm)


F
NTs
N
Ts
4c-3
f1 (ppm)

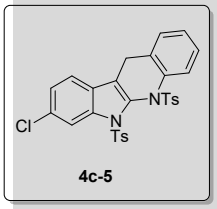

F
NTs
N
Ts
4c-3
f1 (ppm)


CH3
NTs
N
Ts
4c-4

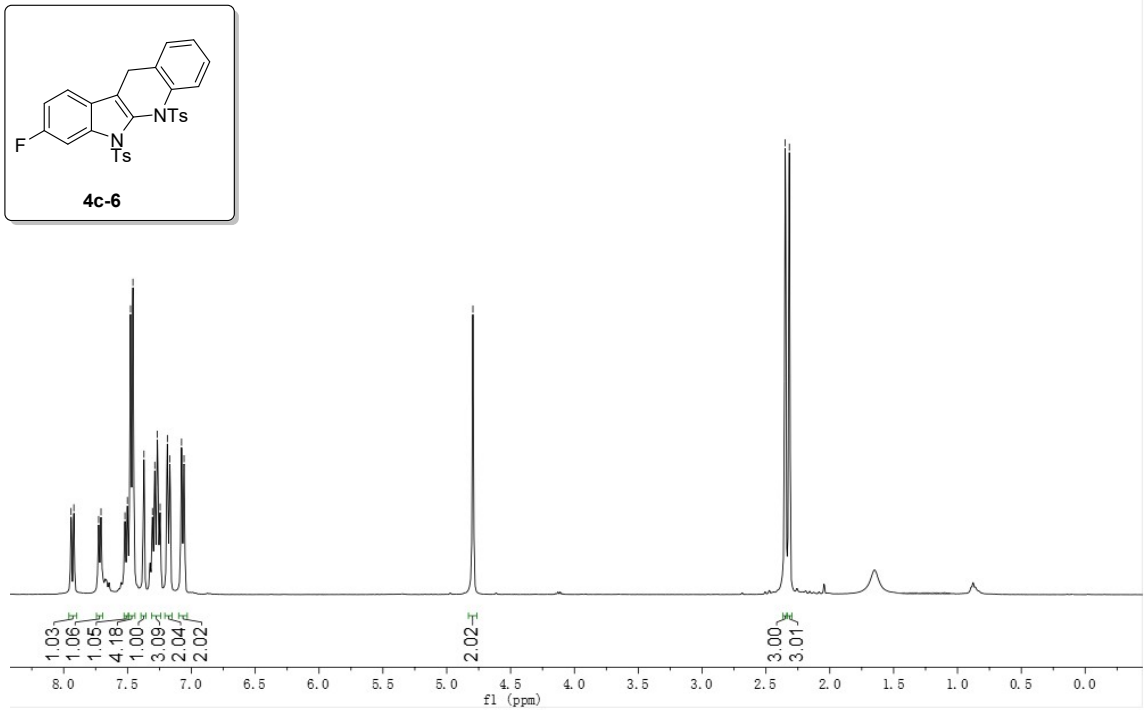

CH3
NTs
N
Ts
4c-4
f1 (ppm)

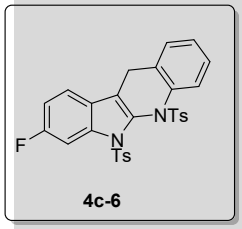


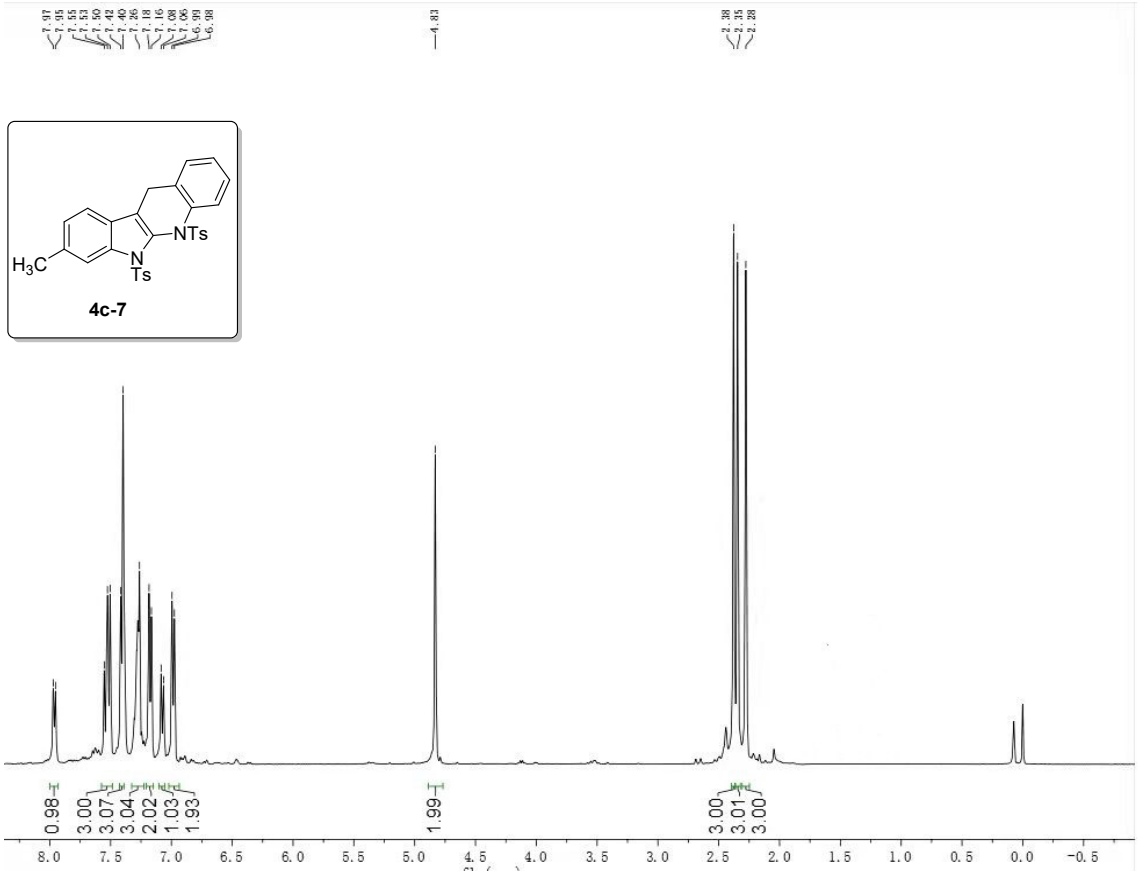
4c-5

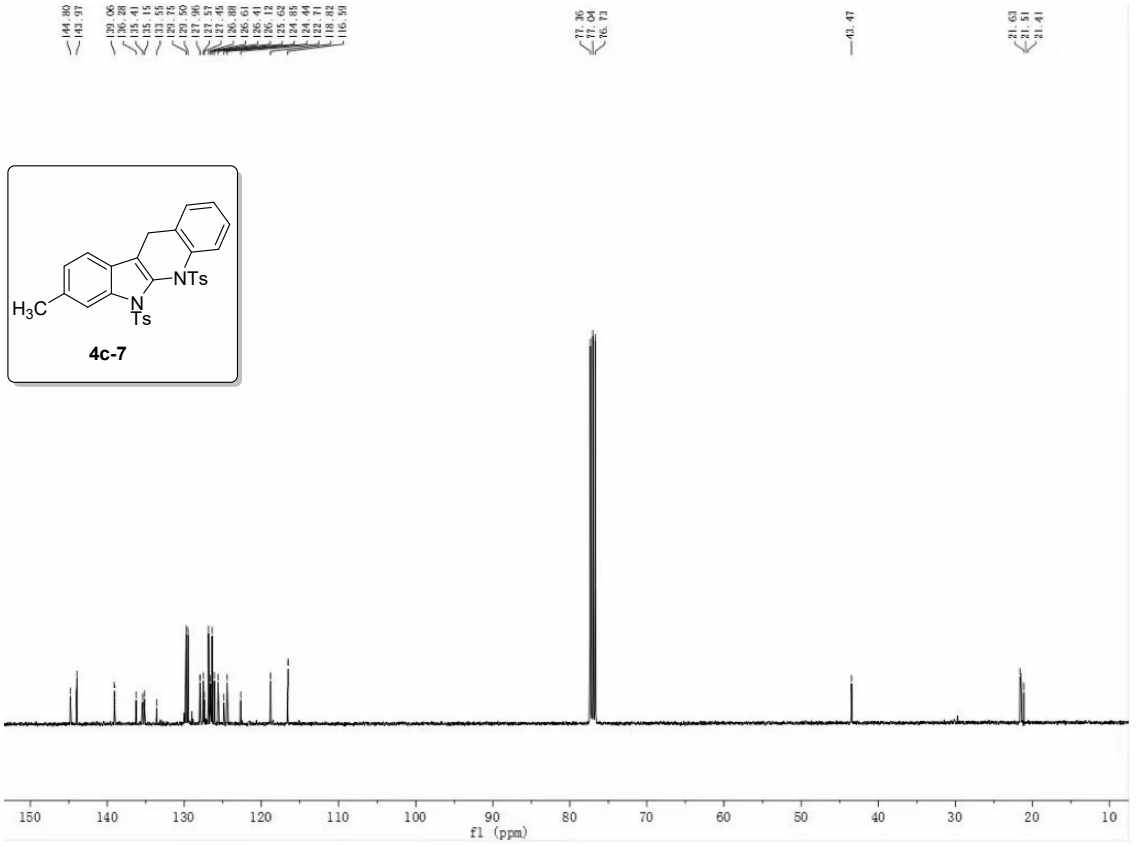


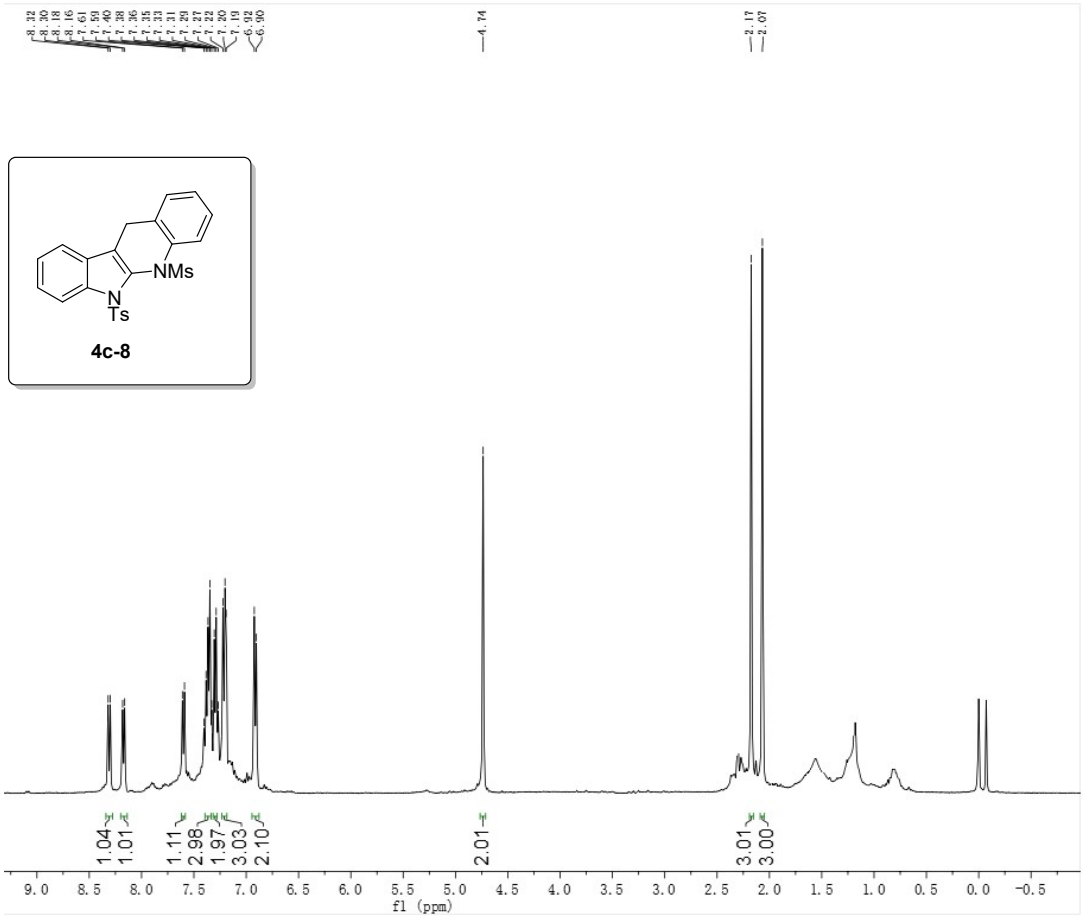
4c-5

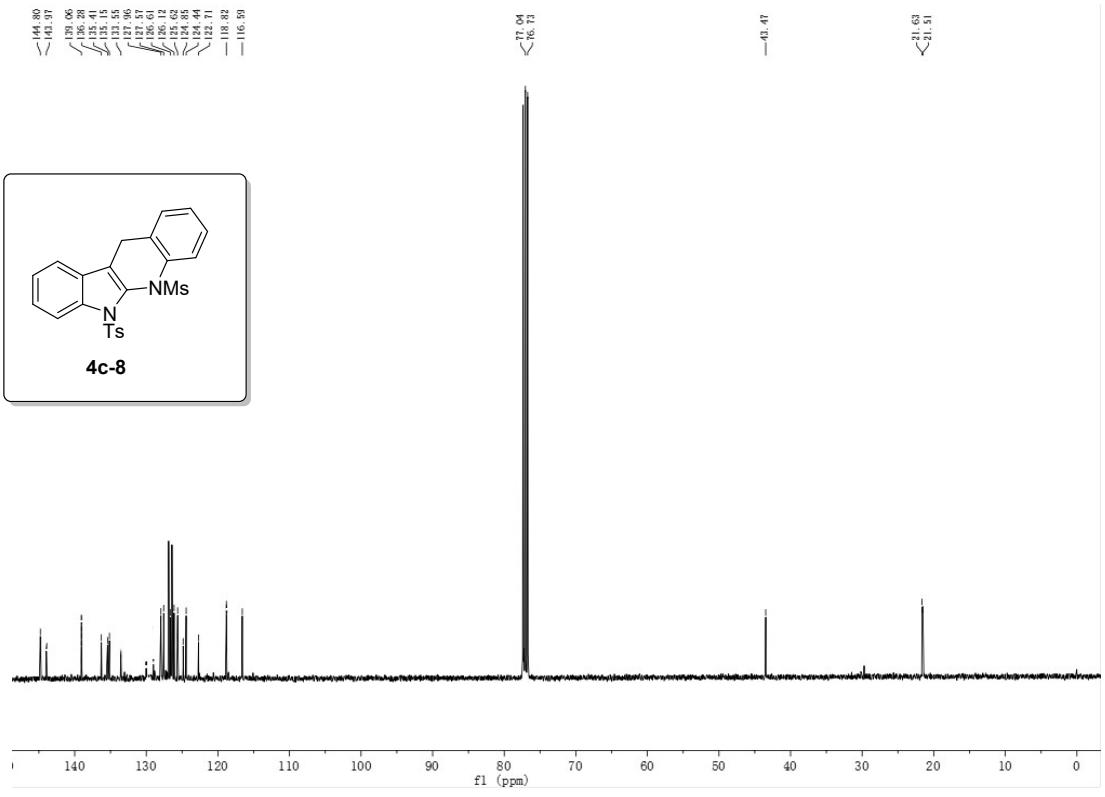

7.94
7.92
7.73
7.71
7.52
7.50
7.48
7.46
7.37
7.30
7.29
7.27
7.24
7.19
7.11
7.08
7.06
4.80
2.35
2.32
NTs
F
N
Ts
4c-6
1.03
1.06
1.05
4.18
1.00
3.09
2.04
2.02
2.02
3.00
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

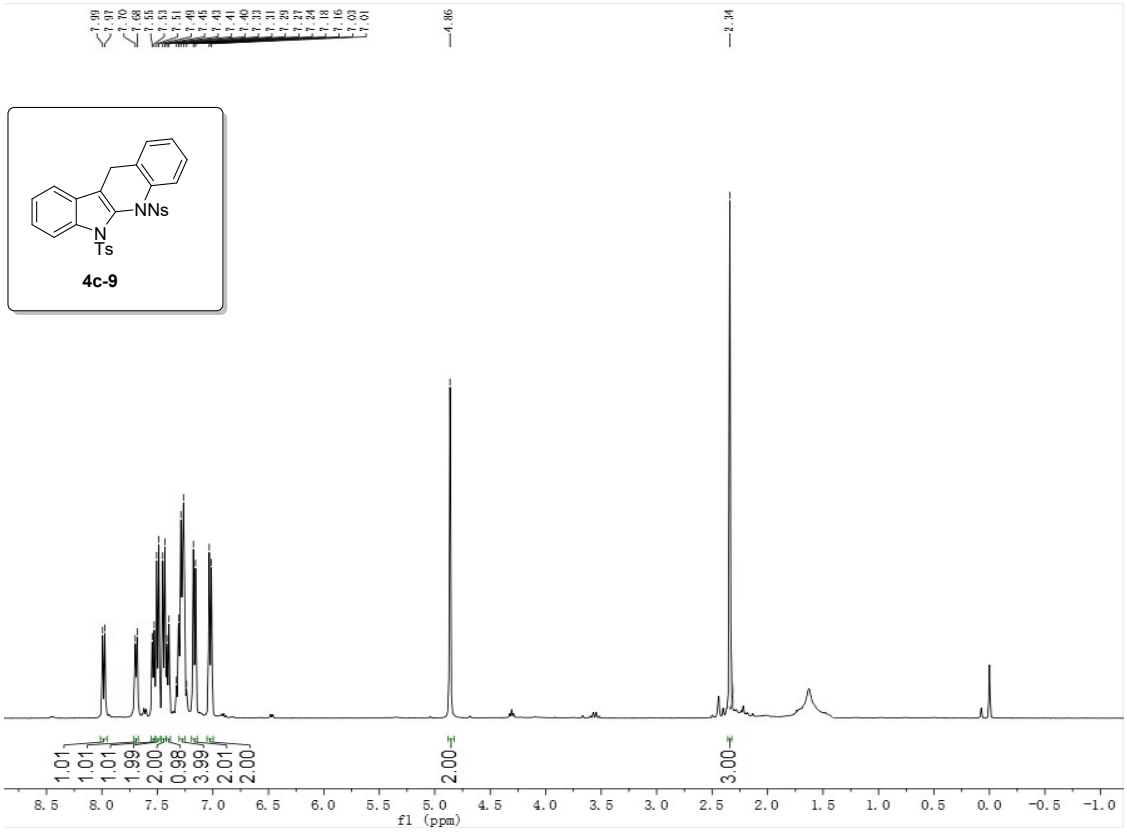

NTs
F
N
Ts
4c-6

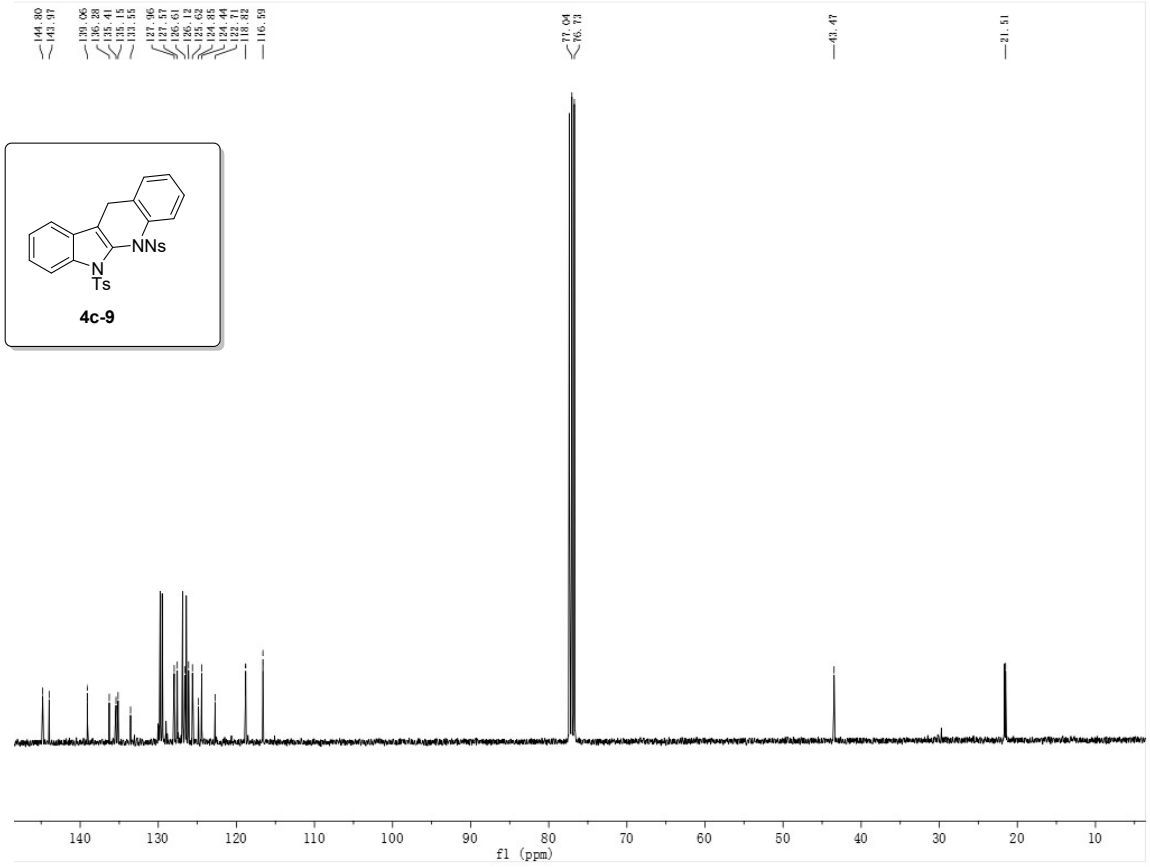

NTs
N
Ts
H3C
4c-7

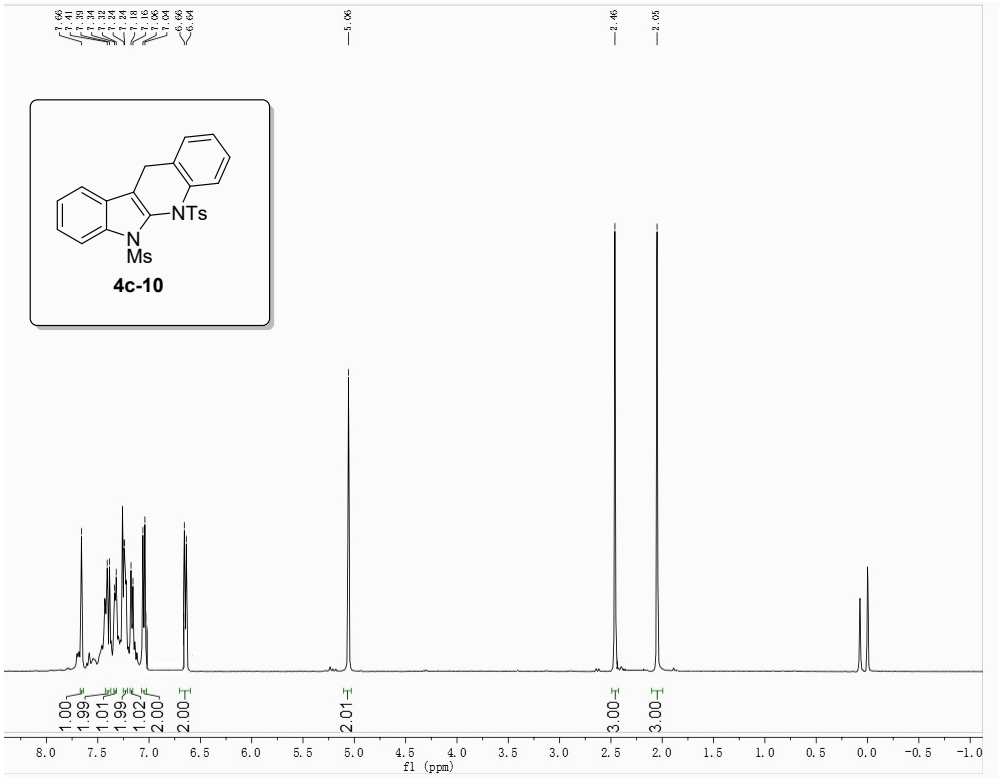

NTs
N
Ts
H3C
4c-7

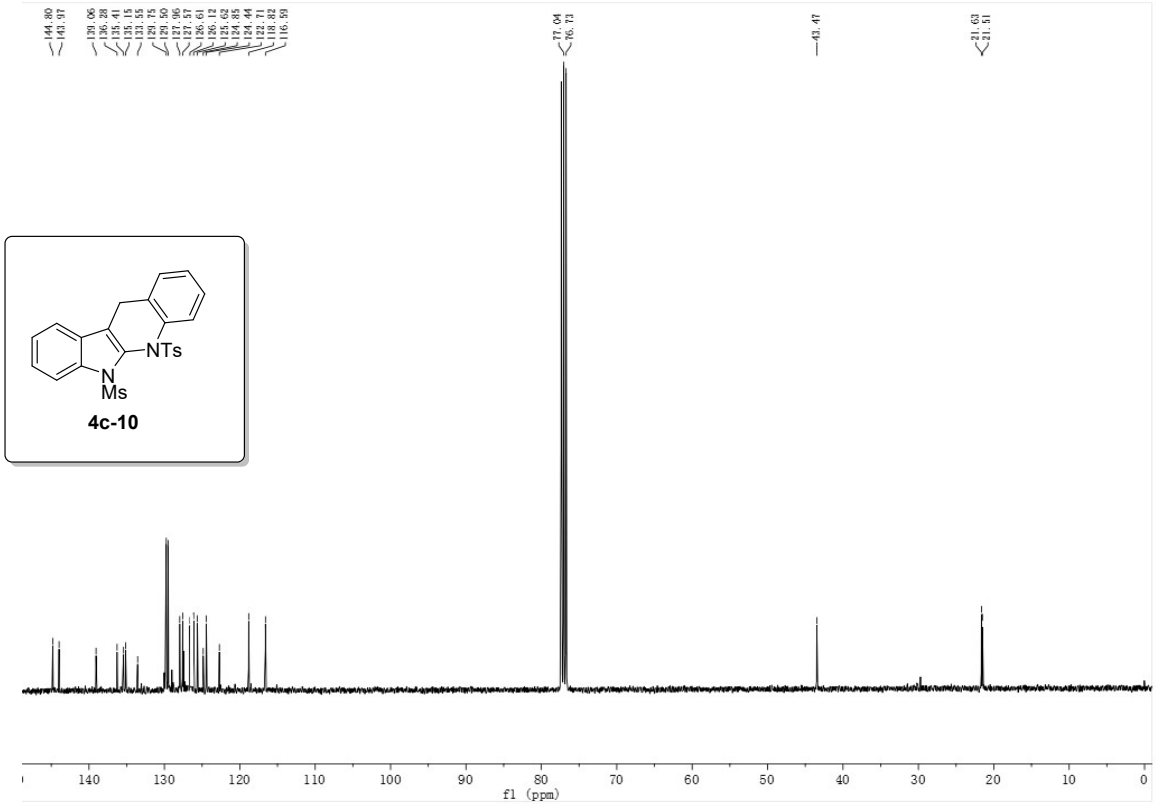

NMs
N
Ts
4c-8
1.04
1.01
1.11
2.98
1.97
3.03
2.10
2.01
3.01
3.00
f1 (ppm)

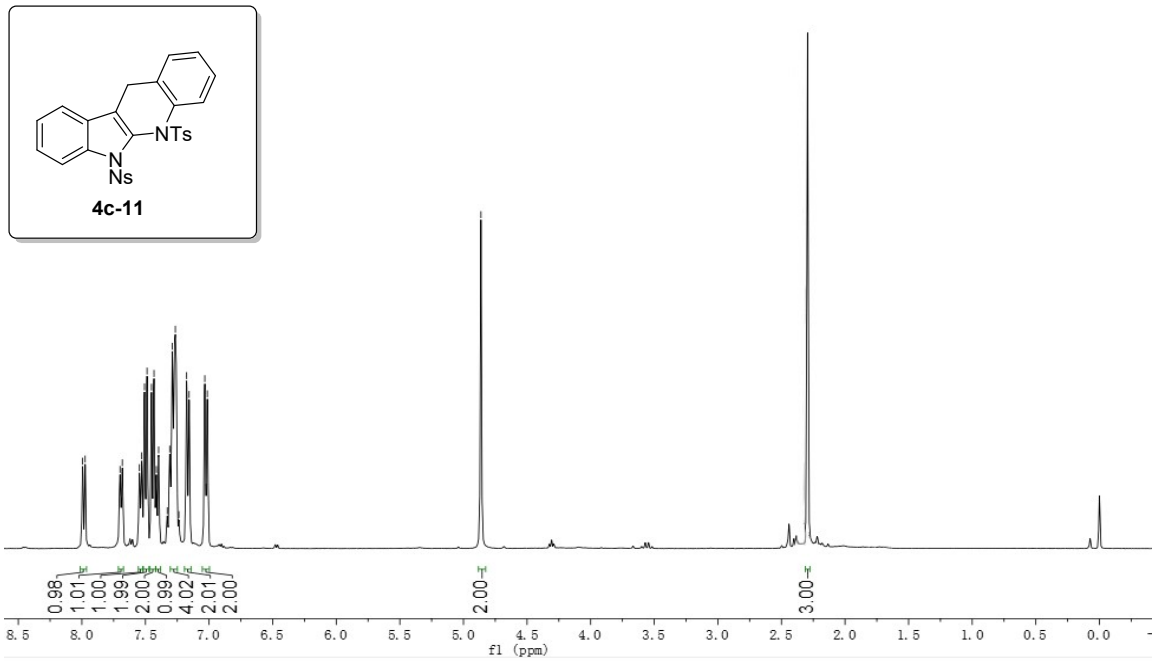

NMs
N
Ts
4c-8
f1 (ppm)

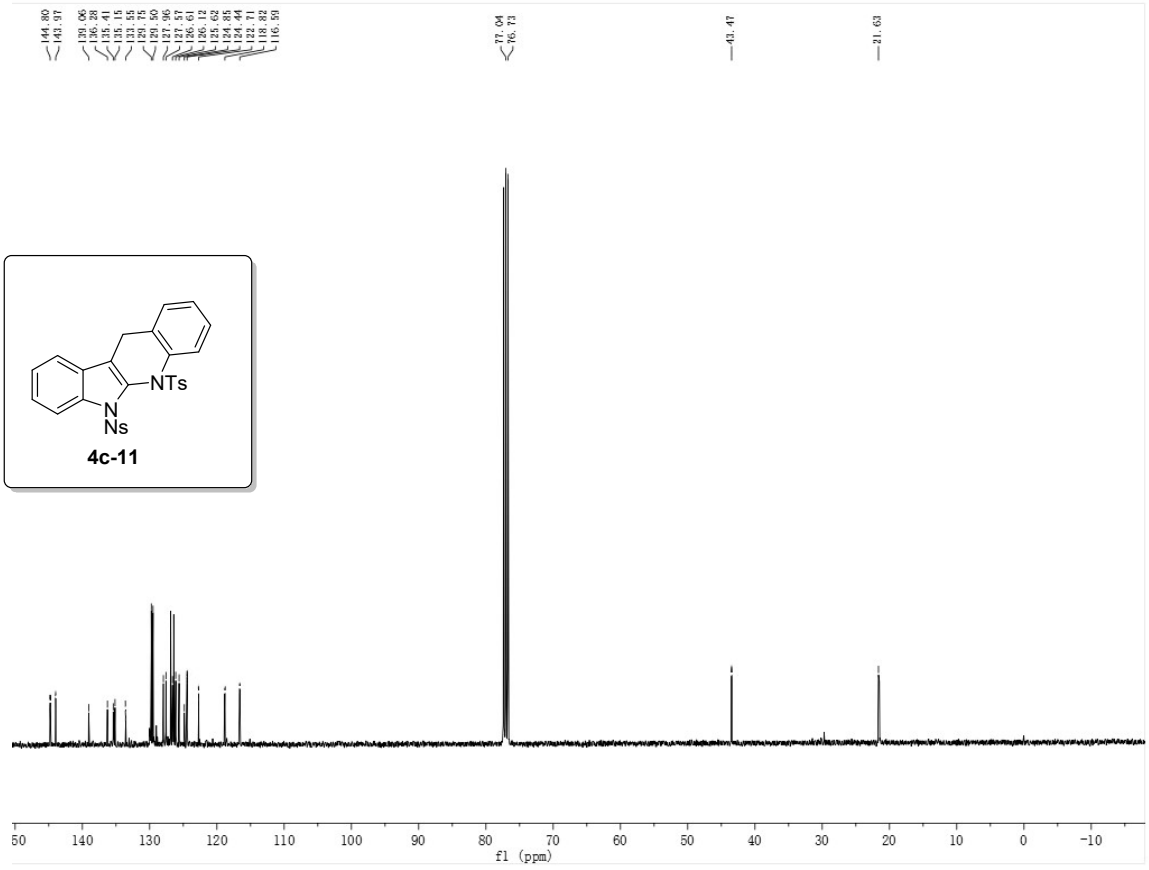

NNs
N
Ts
4c-9
f1 (ppm)

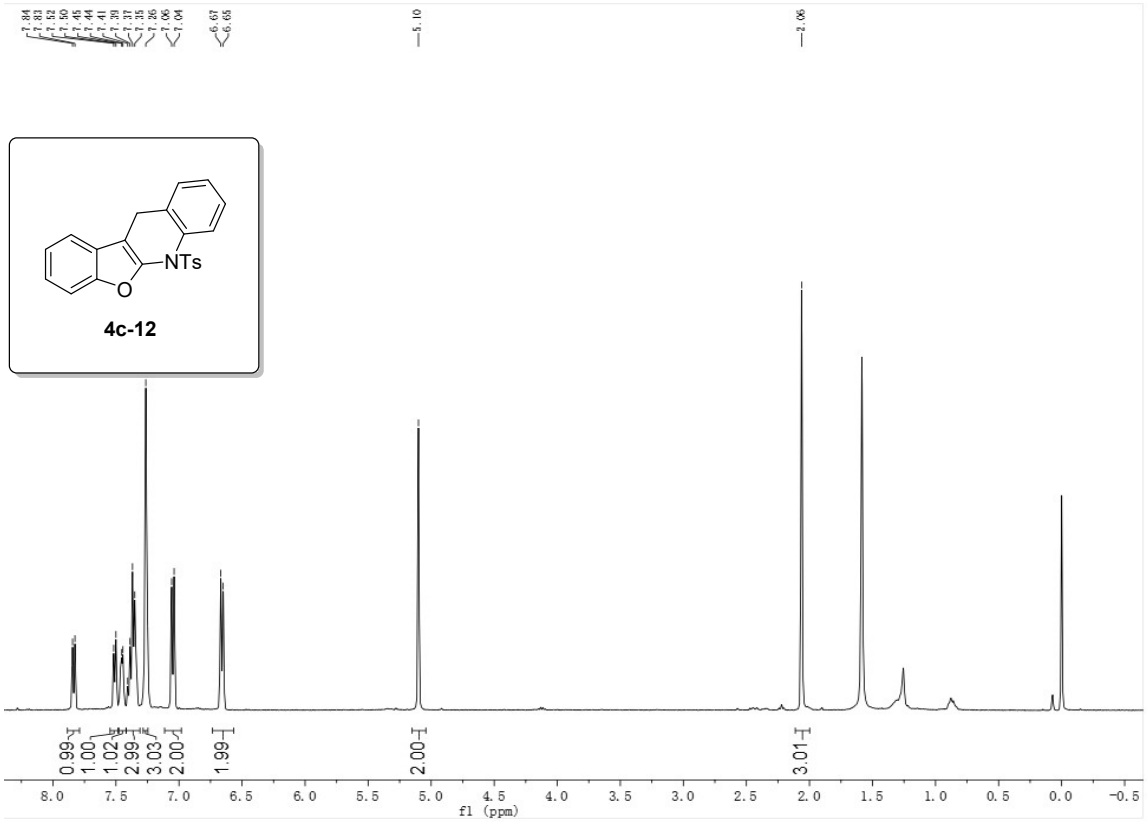

NNs
N
Ts
4c-9
f1 (ppm)

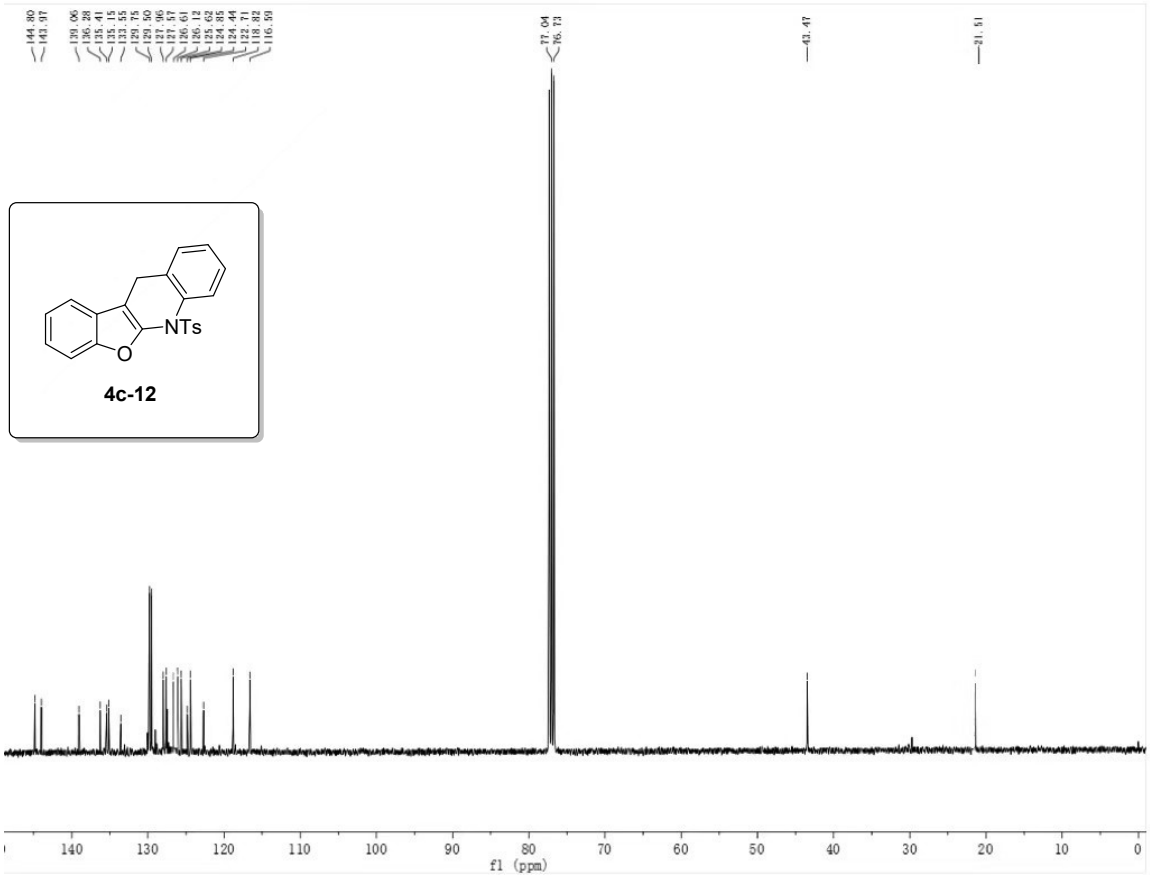

NTs
N
Ms
4c-10
f1 (ppm)

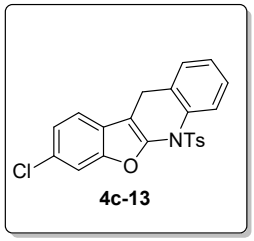

NTs
N
Ms
4c-10
f1 (ppm)


NTs
N
Ns
4c-11
fl (ppm)


NTs
N
Ns
4c-11
fl (ppm)

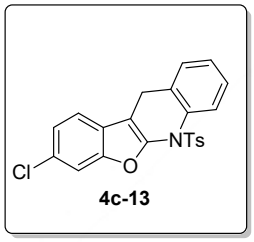

NTs
O
4c-12
fl (ppm)


NTs
O
4c-12
fl (ppm)


NTs
Cl
O

4c-13

7.77
7.75
7.49
7.47
7.46
7.36
7.34
7.32
7.29
7.26
7.09
7.07
6.70
6.68
5.09
2.07
0.98
2.00
2.06
2.97
1.95
1.96
2.01
3.00
f1 (ppm)


NTs
Cl
O

4c-13

144.80
143.97
139.06
136.28
135.41
135.15
133.55
129.75
129.50
127.96
127.57
126.61
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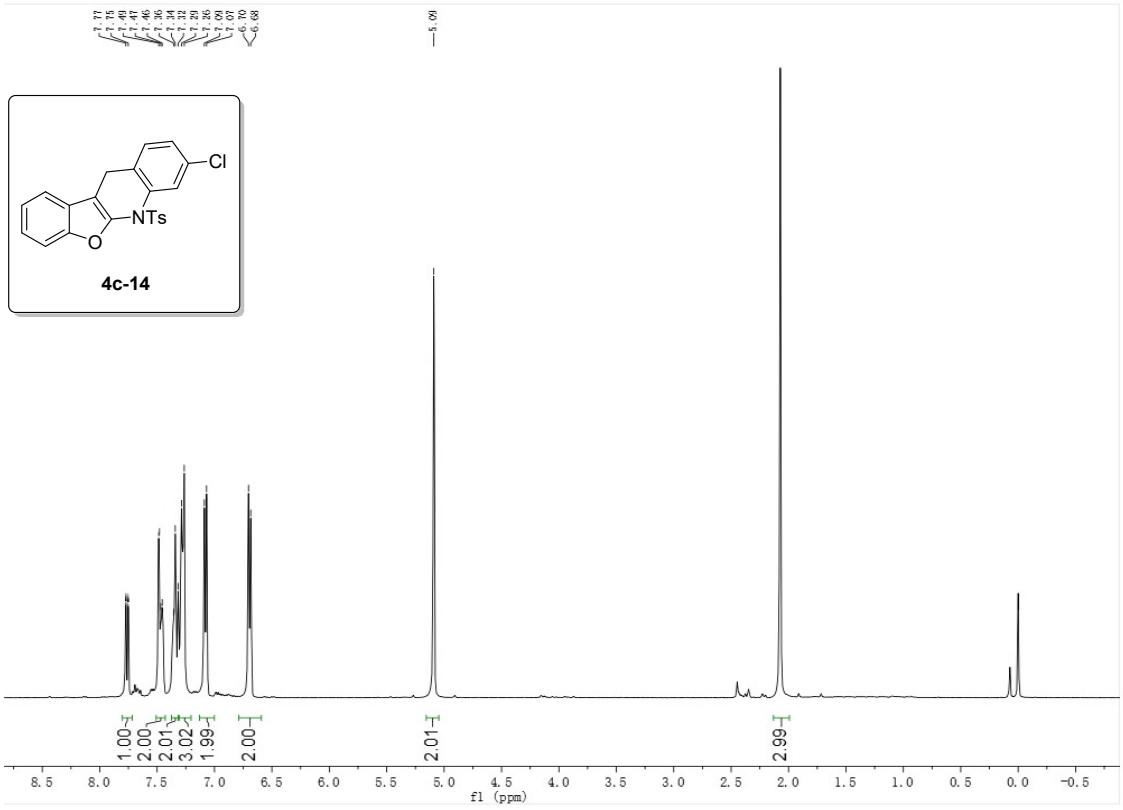
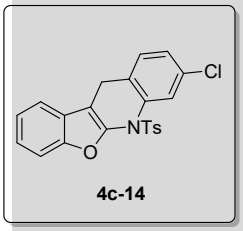
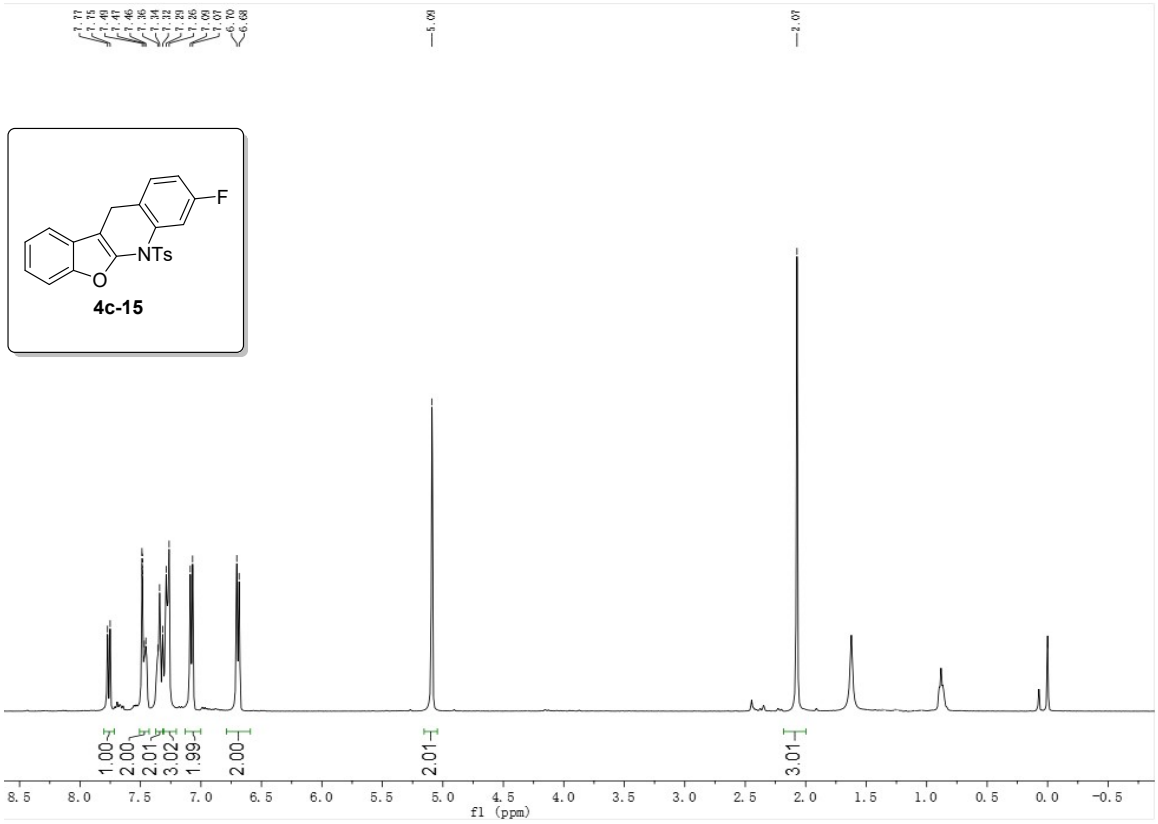
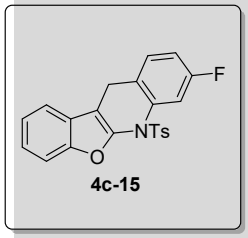
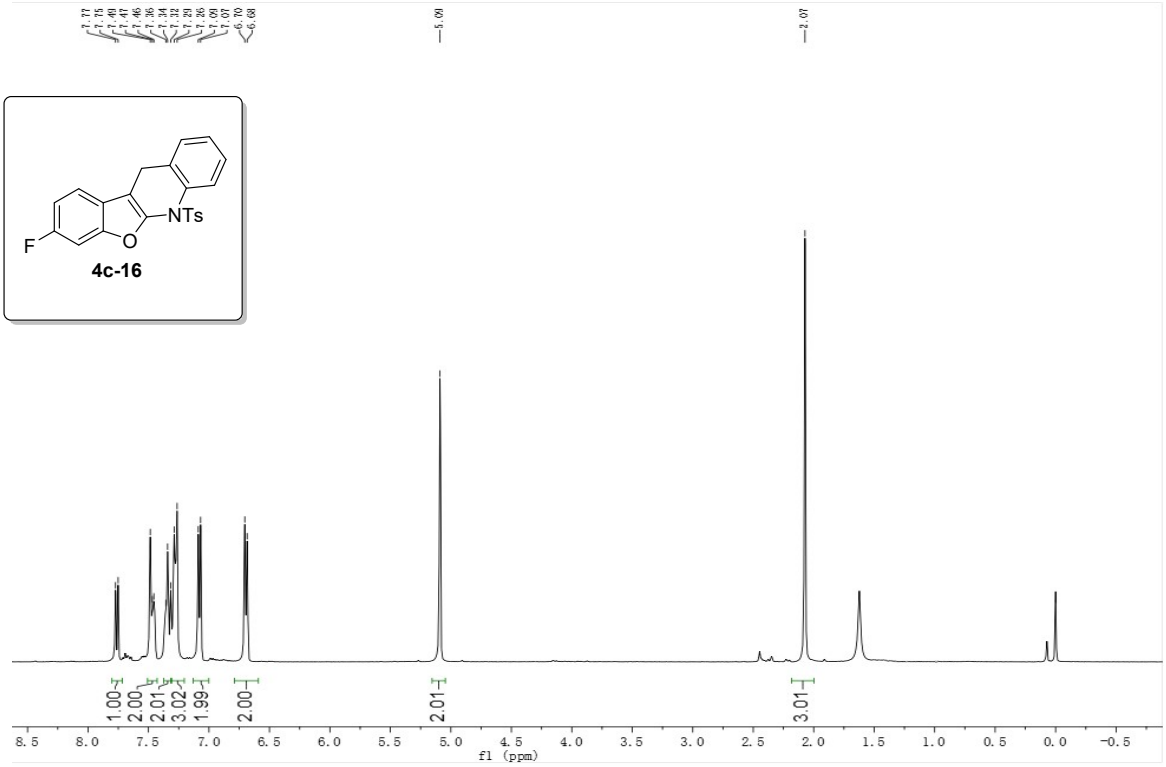
77.04
76.73
43.47
21.51
f1 (ppm)

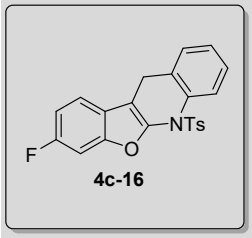

Cl
NTs
O
4c-14
f1 (ppm)

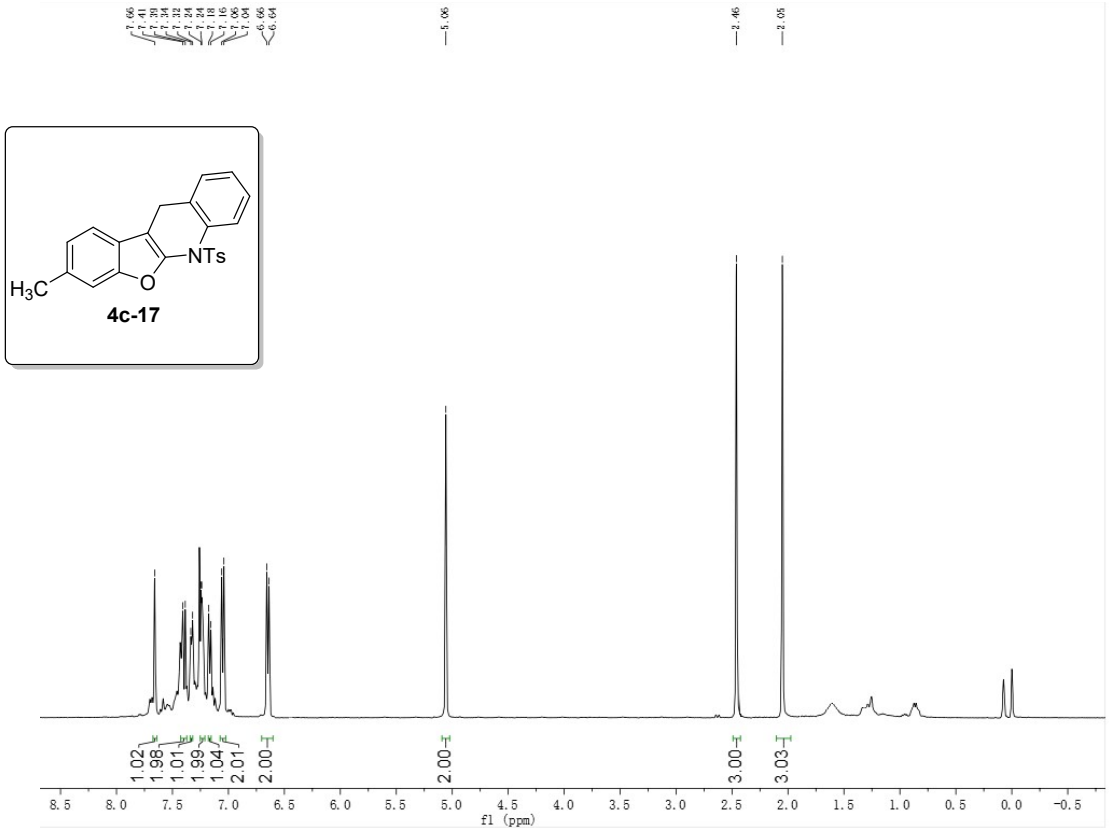

Cl
NTs
O
4c-14

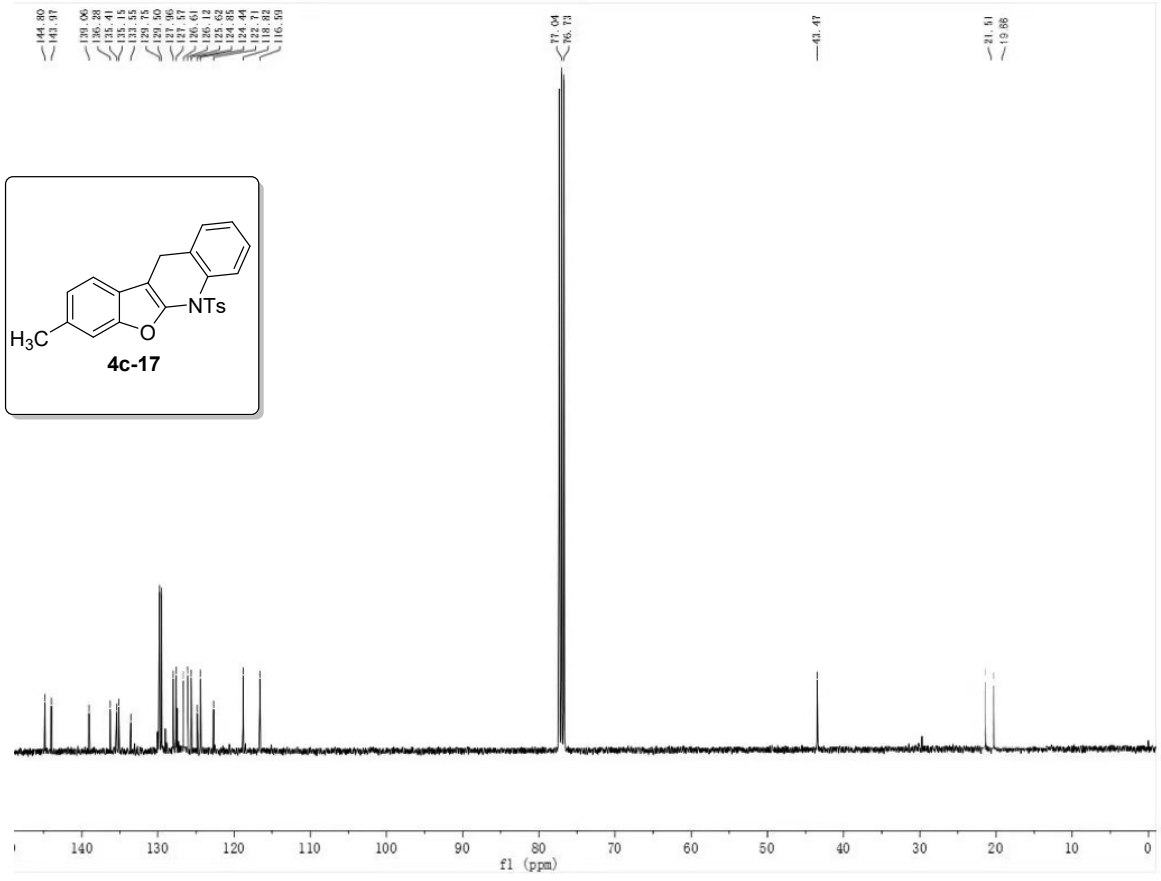

7.77
7.75
7.49
7.47
7.46
7.36
7.34
7.32
7.29
7.26
7.09
7.07
6.70
6.68
5.09
2.07
F
NTs
O
4c-15
1.00
2.00
2.01
3.02
1.99
2.00
2.01
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

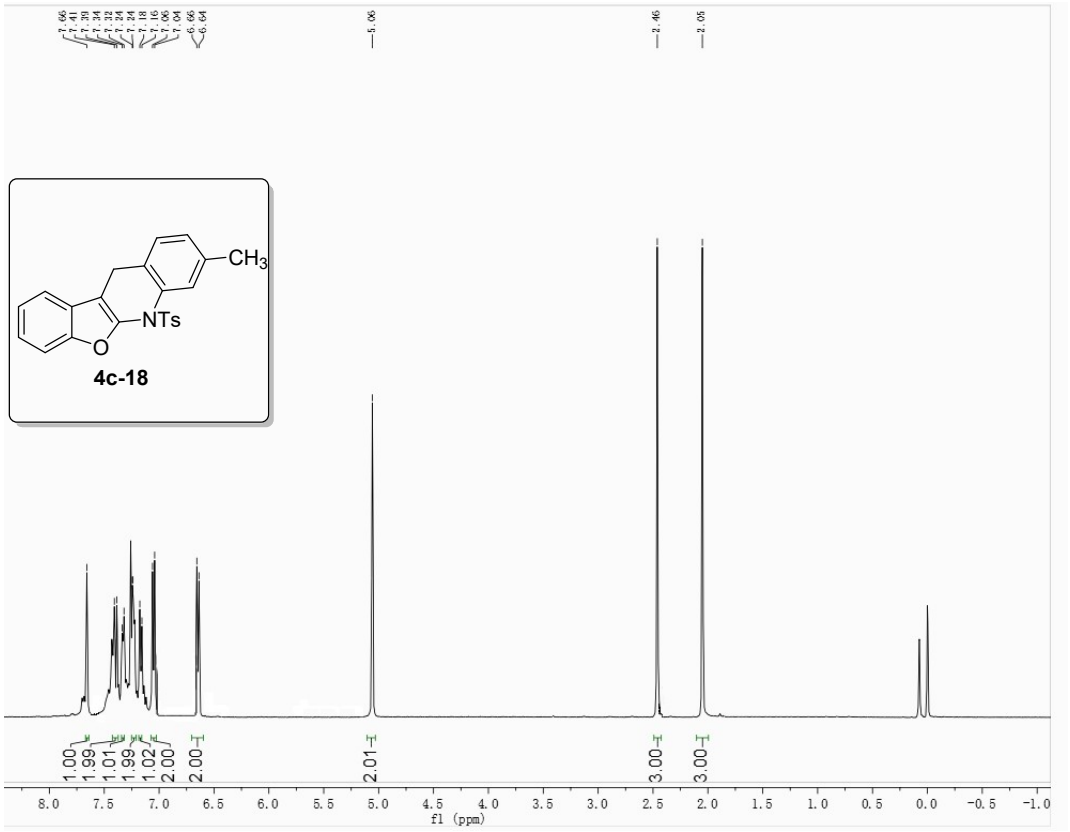

F
NTs
O
4c-15

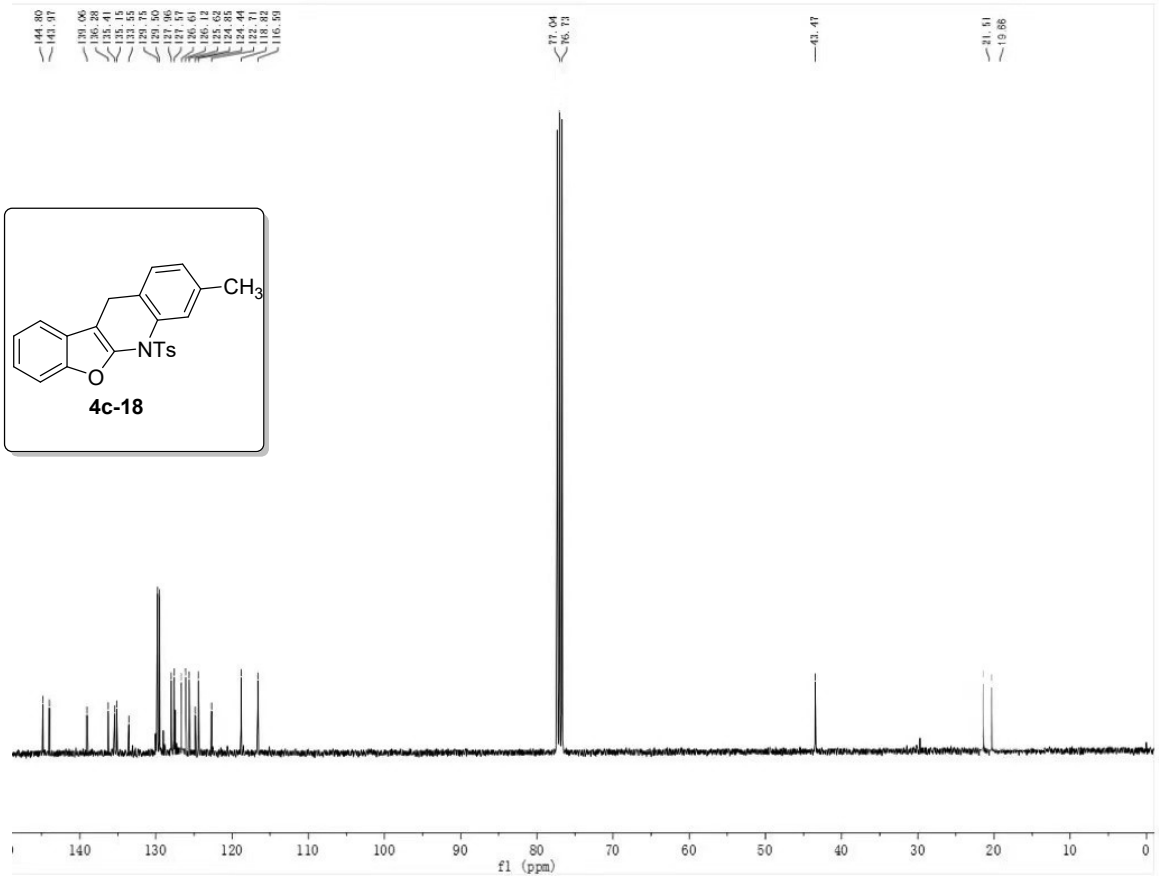

7.77
7.75
7.49
7.47
7.46
7.36
7.34
7.32
7.29
7.26
7.09
7.07
6.70
6.68
5.00
2.07
NTs
F
O
4c-16
1.00
2.00
2.01
3.02
1.99
2.00
2.01
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


NTs
F
O
4c-16


NTs
H3C
O
4c-17
f1 (ppm)


NTs
H3C
O
4c-17
f1 (ppm)


7.66
7.41
7.39
7.34
7.32
7.24
7.24
7.18
7.15
7.06
7.04
6.66
6.64
5.06
2.46
2.05
CH3
NTs
O
4c-18
1.00
1.99
1.01
1.99
1.02
2.00
2.00
2.01
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


144.80
143.97
139.06
136.28
135.41
135.15
133.55
129.75
129.50
127.96
127.57
126.64
126.12
125.62
124.85
124.44
122.71
118.82
116.59
77.04
76.73
43.47
21.51
19.88
CH3
NTs
O
4c-18
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)