Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Palladium-Catalyzed Regiodivergent Arylamination/Aryloxygenation of Allenamide.

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Supporting Information

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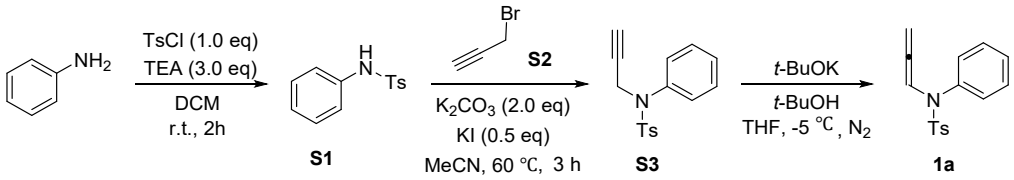
1. Generals information

All starting materials, solvents and ligands were commercially available and were used without further purification unless otherwise noted. All reactions were run under an atmosphere of nitrogen. Anhydrous solvents were transferred via oven-dried syringe. Unless otherwise specified, flash column chromatography was carried out using commercially available 200-300 mesh under pressure. Gradient flash chromatography was conducted eluting with PE/EA, which were listed in volume ratio.

NMR spectra were recorded on an AVANCE III HD 400MHz spectrometer [^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz)]. Chemical shifts are reported in parts per million (ppm, δ) downfield from residual 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.

2. The General Synthetic Procedure



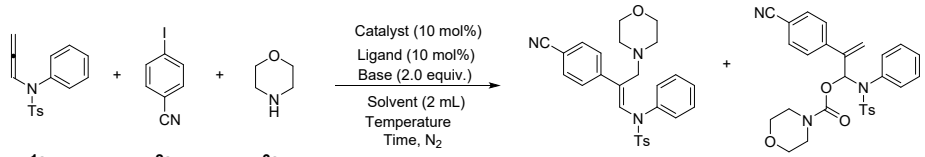
Firstly, prepare 4-methyl-N-phenylbenzenesulfonamide **S1**. In a 100 ml dry eggplant shaped flask, a rotor of appropriate size is prepared. To a solution of aniline (1.4 g, 15 mmol) in DCM (20 mL) was added P-toluenesulfonyl chloride (3.2 g, 16.5 mmol). The resultant solution stirred 2 h at room temperature. Dissolve triethylamine (4.6 mL, 45 mmol) into DCM (10 mL) and slowly drop it into an eggplant shaped flask with a separating funnel. After the reaction, washed the organic phase three times with water and the organic phase was extracted with DCM. Then dried it with anhydrous sodium sulfate. After the reaction system was concentrated in vacuum, the product was separated and purified by recrystallization to give **S1** as white crystal (84% yield).

Synthesis of compound **S3** from propargyl bromide. In a 100 ml dry eggplant shaped flask, a rotor of appropriate size is prepared. To a solution of **S1** (3.0 g, 12 mmol) in DCM (25 mL) was added K_2CO_3 (5.1 g, 24 mmol) and KI (1.0 g, 6 mmol). Measure propargyl bromide and inject it into the eggplant shaped flask slowly and evenly, taking about 10 minutes. Finally, the solution was kept reflux in an oil bath at 60 ℃ for 2 hours. The aqueous layer was extracted three times with EtOAc. The organic phase was combined, dried over Na_2SO_4, evaporated and purified by flash chromatography (PE:EA = 10:1). **SI-3** was afforded as a white solid (73% yield).

Synthesize material **1a** according to the general operation method of preparation of allene. In a 100 ml dry eggplant shaped flask, 1.7 g (1.5 equiv, 15.75 mmol) of potassium tert-butoxide was added under nitrogen atmosphere. Then, 20 ml dry THF was added with stirring at -5 ℃. Next, dissolve **S3** (3 g, 10.5 mmol) into 10 ml of dry THF. The mixed solution was added dropwise with vigorous stirring, keeping the temperature below -5 ℃ over 1 hour. The reaction was followed by TLC. After the reaction, neutral alumina was added to spin dry, and the product was separated and purified by flash chromatography quickly (PE:EA = 10:1). Wash the silica gel three times with 3% triethylamine petroleum ether solution. **1a** was afforded as a white or canary yellow solid (81% yield).

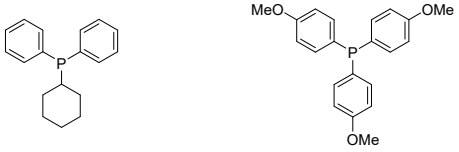
3. General Regiodivergent Arylamination /Aryloxygenation Protocol of Allenamide

3.1 Optimization of Reaction Conditions [a]



1a **2a** **3a** **4a** **5a**

Entry	Catalyst	Ligand	Base	Solvent	Temperature (°C)	Time (h)	Yield[b] (%) of **4a**	Yield[b] (%) of **5a**	4a:5a
1	$Pd_2(dba)_3$	PPh_3	Cy_2NME	dioxane	80	3	54	trace	>99:1
2	$PdCl_2$	PPh_3	Cy_2NME	dioxane	80	3	39	trace	>99:1
3	$Pd(dba)_2$	PPh_3	Cy_2NME	dioxane	80	3	48	trace	>99:1
4	$Pd(OAc)_2$	PPh_3	Cy_2NME	dioxane	80	3	56	trace	>99:1
5	$Pd(PPh_3)_4$	PPh_3	Cy_2NME	dioxane	80	3	74	trace	>99:1
6	$PdCl_2(PPh_3)_2$	-	Cy_2NME	dioxane	80	3	48	trace	>99:1
7	$Pd(PPh_3)_4$	-	Cy_2NME	Toluene	80	3	58	trace	>99:1
8	$Pd(PPh_3)_4$	-	Cy_2NME	MeTHF	80	3	51	trace	>99:1
9	$Pd(PPh_3)_4$	-	Cy_2NME	DMF	80	3	60	trace	>99:1
10	$Pd(PPh_3)_4$	-	Cy_2NME	DCM	80	3	63	trace	>99:1
11	$Pd(PPh_3)_4$	-	Cy_2NME	MeCN	80	3	76	trace	>99:1
12	$Pd(PPh_3)_4$	-	K_2CO_3	MeCN	80	3	49	trace	>99:1
13	$Pd(PPh_3)_4$	-	K_3PO_4	MeCN	80	3	71	trace	>99:1
14	$Pd(PPh_3)_4$	-	Cs_2CO_3	MeCN	80	3	73	trace	>99:1
15	$Pd(PPh_3)_4$	-	TEA	MeCN	80	3	67	trace	>99:1
16	$Pd(PPh_3)_4$	-	DIPEA	MeCN	80	3	63	trace	>99:1
17	$Pd_2(dba)_3$	$PCy_3•HBF_4$	Cy_2NMe	MeCN	80	3	64	trace	>99:1
18	$Pd_2(dba)_3$	L_1	Cy_2NMe	MeCN	80	3	68	trace	>99:1
19	$Pd_2(dba)_3$	dppf	Cy_2NMe	MeCN	80	3	67	trace	>99:1
20	$Pd_2(dba)_3$	dppb	Cy_2NMe	MeCN	80	3	59	trace	>99:1
21	$Pd_2(dba)_3$	L2	Cy_2NMe	MeCN	80	3	65	trace	>99:1
22	$Pd(PPh_3)_4$	-	Cy_2NMe	MeCN	70	1	71	trace	>99:1
23	$Pd(PPh_3)_4$	-	Cy_2NMe	MeCN	100	1	69	trace	>99:1
24	$Pd(PPh_3)_4$	-	Cy_2NMe	MeCN	80	2	74	trace	>99:1
25	***$Pd(PPh_3)_4$***	***-***	***Cy_2NMe***	***MeCN***	***80***	***1***	***80***	***trace***	***>99:1***
26	$Pd(PPh_3)_4$	-	AgF	MeCN	80	2	71	trace	>99:1
27	$Pd(PPh_3)_4$	-	Ag_2SO_4	MeCN	80	2	57	trace	>99:1
28	$Pd(PPh_3)_4$	-	Ag_2O	MeCN	80	2	60	9	87:13
29	$Pd(PPh_3)_4$	-	Ag_2CO_3	MeCN	80	2	40	47	46:54
30	$Pd(PPh_3)_4$	-	Ag_2CO_3	MeCN	60	2	10	43	19:81
31	$Pd(PPh_3)_4$	-	Ag_2CO_3	MeCN	50	2	5	41	11:89
32	$Pd(PPh_3)_4$	-	Ag_2CO_3	DMF	50	2	9	46	17:83
33	$Pd(PPh_3)_4$	-	Ag_2CO_3	DMF	50	4	10	48	17:83
34	$Pd(PPh_3)_4$	-	Ag_2CO_3	DCE	50	2	6	28	18:82
35	$Pd(PPh_3)_4$	-	Ag_2CO_3	DMSO	50	4	9	38	20:80
36	$Pd(PPh_3)_4$	-	Ag_2CO_3	dioxane	50	2	8	33	19:81
37	$Pd_2(dba)_3$	PPh_3	Ag_2CO_3	DMF	50	2	7	32	18:82
38	$Pd(OAc)_2$	PPh_3	Ag_2CO_3	DMF	50	2	11	35	24:76
39	$PdCl_2$(dppf)	-	Ag_2CO_3	DMF	50	2	8	41	17:83
40	$PdCl_2(PCy_3)_2$	-	Ag_2CO_3	DMF	50	2	7	29	20:80
41	$PdCl_2$	PPh_3	Ag_2CO_3	DMF	50	2	21	57	27:73
42	$Pd(PPh_3)_4$	-	Ag_2CO_3	MeCN	50	4	7	53	12:88
43	$Pd(PPh_3)_4$	-	Ag_2CO_3	MeCN	50	5	10	62	13:87
44	$Pd(PPh_3)_4$	-	Ag_2CO_3	MeCN	50	6	11	79	13:87
45	$Pd(PPh_3)_4$	-	Ag_2CO_3	MeCN	50	7	9	69	15:85
46[c]	***$Pd(PPh_3)_4$***	***-***	***Ag_2CO_3***	***MeCN***	***50***	***6***	***11***	***81***	***12:88***



L1 **L2**

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), **3a** (0.24 mmol), Pd (0.02 mmol), Base (0.4 mmol), Solvent (2 mL), N_2 atmosphere.

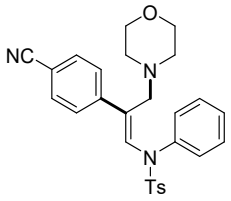
[b] Isolated yields. [c] with Ag_2CO_3 (0.2 mmol) as base.

3.2 The General Synthetic Procedure

Preparation of compound **4a**: In a 20 ml Schlenk tube, $Pd(PPh_3)_4$ (10 mol%, 0.02 mmol), Cy_2NMe (2.0 equiv, 0.4 mmol), morpholine (1.2 equiv, 0.24 mmol) and 4-iodobenzonitrile (1.0 equiv, 0.2 mmol) were added. The allenamide **1** (1.0 equiv, 0.2 mmol) was dissolved in the MeCN (2.0 mL), and the solution was added in the tube. Then the mixture was stirring at 80 ℃ for 1 hour. The consumption of starting material was monitored by TLC and GC-MS analysis. After reaction was finished, the combined organic extracts were evaporated and purified by silica gel column chromatography (PE:EA = 10:1) to afford the desired product **4a**.

Preparation of compound **5a**:In a 20 ml Schlenk tube, $Pd(PPh_3)_4$ (10 mol%, 0.02 mmol), Ag_2CO_3 (1.0 equiv, 0.2 mmol), morpholine (1.2 equiv, 0.24 mmol) and 4-iodobenzonitrile (1.0 equiv, 0.2 mmol) were added. The allenamide **1** (1.0 equiv, 0.2 mmol) was dissolved in the MeCN (2.0 mL), and the solution was added in the tube. Then the mixture was stirring at 50 ℃ for 6 hours. The consumption of starting material was monitored by TLC and GC-MS analysis. After reaction was finished, the combined organic extracts were evaporated and purified by silica gel column chromatography (PE:EA = 5:1) to afford the desired product **4a** and **5a**.

3.3 Analytical Data for product 4a-4r



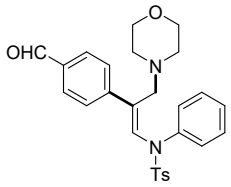
4a

$C_{27}H_{27}N_3O_3S$, MW: 473.18g·mol^{-1}, Light yellow oil (80.5mg), 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.60 (dd, *J* = 23.2 Hz, 8.0 Hz, 4H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.37-7.32 (m, 3H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.77 (s, 1H), 3.49 (s, 4H), 3.23 (s, 2H), 2.45 (s, 3H), 2.20 (s, 4H).

^{13}C NMR (100 MHz, CDCl3, δ ppm): 144.3, 144.1, 140.9, 133.6, 133.3, 131.8, 130.0, 129.5, 129.0, 127.7, 127.6, 127.5, 118.8, 110.8, 66.6, 55.6, 52.8, 21.5.

MS (EI) m/z 473(M+); **HRMS (ESI)** Calcd for $C_{27}H_{27}N_3O_3S$+H 474.1851, Found 474.1856.



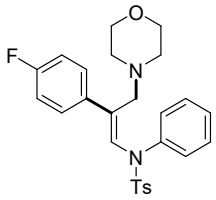
4b

$C_{27}H_{28}N_2O_4S$, MW: 476.18g·mol^{-1}, Light yellow oil (74.2mg), 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 10.03 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.34 (q, *J* = 7.6 Hz, 3H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.79 (s, 1H), 3.50 (s, 4H), 3.27 (s, 2H), 2.45 (s, 3H), 2.21 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 191.7, 145.7, 144.2, 141.0, 135.3, 134.2, 133.7, 129.8, 129.6, 129.5, 129.0, 127.7, 127.6, 127.5, 77.318, 77.0, 76.7, 66.7, 55.8, 52.9, 21.5.

MS (EI) m/z 476(M+); **HRMS (ESI)** Calcd for $C_{27}H_{28}N_2O_4S$+H 477.1848, Found 477.1853.



4c

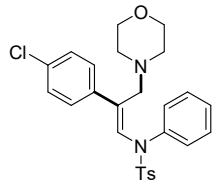
$C_{26}H_{27}N_2O_3S$, MW: 466.17g·mol^{-1}, Light yellow oil (87.7mg), 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.49 – 7.43 (m, 4H), 7.36-7.27 (m, 5H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 8.4 Hz, 2H), 6.53 (s, 1H), 3.52 (s, 4H), 3.31 (s, 2H), 2.45 (s, 3H), 2.23 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 142.81 (d, *J* = 249.7 Hz) , 136.5 , 135.19 (d, *J* = 3.2 Hz), 133.9 , 129.5 , 128.9 , 128.8 , 128.7 , 127.9 , 127.6 , 127.3 , 127.2 , 115.1 , 114.9 , 66.9 , 56.3 , 53.1 , 21.6 .

^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -114.3 (s, 1F).

MS (EI) m/z 466(M+); **HRMS (ESI)** Calcd for $C_{26}H_{27}N_2O_3S$+H 467.1805, Found 467.1809.



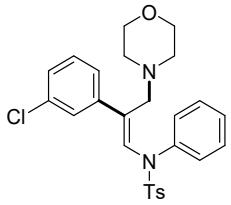
4d

$C_{26}H_{27}ClN_2O_3S$, MW: 482.14g·mol^{-1}, Light yellow oil (78.2mg), 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.48 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.35-7.21 (m, 7H), 7.21 (d, *J* = 7.2 Hz, 2H), 6.61 (s, 1H), 3.52 (s, 4H), 3.31 (s, 2H), 2.45 (s, 3H), 2.23 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.1 , 141.4 , 137.6 , 135.8 , 133.7 , 133.5 , 129.5 , 128.9 , 128.3 , 128.2 , 128.0 , 127.7 , 127.3 , 66.7 , 56.0 , 53.0 , 21.5 .

MS (EI) m/z 482(M+); **HRMS (ESI)** Calcd for $C_{26}H_{27}ClN_2O_3S$ +H 483.1509, Found 483.1517.



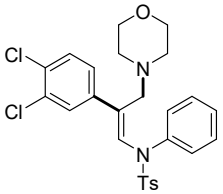
4e

$C_{26}H_{27}ClN_2O_3S$, MW: 482.14g·mol^{-1}, Light yellow oil (72.4mg), 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.47 (t, 7.6 Hz, 3H), 7.36-7.27 (m, 8H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.63 (s, 1H), 3.52 (s, 4H), 3.27 (s, 2H), 2.45 (s, 3H), 2.23 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.1 , 141.3 , 141.2 , 135.3 , 133.8 , 133.7 , 129.5 , 129.3 , 128.9 , 128.6 , 127.8 , 127.6 , 127.4 , 127.3 , 127.1 , 125.3 , 66.8 , 56.0 , 53.0 , 21.5 .

MS (EI) m/z 482(M+); **HRMS (ESI)** Calcd for $C_{26}H_{27}ClN_2O_3S$+H 483.1509, Found 483.1505.



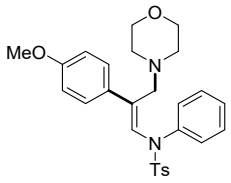
4f

$C_{26}H_{26}Cl_2N_2O_3S$, MW: 516.10g·mol^{-1}, Light yellow oil (66.2mg), 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.55 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.35 – 7.27 (m, 6H), 7.18 (d, *J* = 7.2 Hz, 2H), 6.63 (s, 1H), 3.52 (s, 4H), 3.24 (s, 2H), 2.45 (s, 3H), 2.21 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.3 , 141.2 , 139.4 , 134.3 , 133.8 , 132.1 , 131.6 , 130.0 , 129.6 , 129.1 , 128.89 , 127.8 , 127.5 , 127.5 , 126.45 , 66.8 , 55.9 , 53.0 , 21.6 .

MS (EI) m/z 516(M+); **HRMS (ESI)** Calcd for $C_{26}H_{26}Cl_2N_2O_3S$+H 517.1119, Found 517.1113.



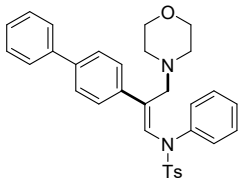
4g

$C_{27}H_{30}N_2O_4S$, MW: 478.19g·mol^{-1}, Light yellow oil (76.6mg), 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.49-7.42 (m, 4H), 7.36 – 7.32 (m, 2H), 7.30 – 7.27 (m, 3H), 7.22 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.51 (s, 1H), 3.85 (s, 3H), 3.53 (s, 4H), 3.36 (s, 2H), 2.45 (s, 3H), 2.25 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.3, 143.9, 141.8, 137.5, 133.9, 131.5, 129.4, 128.9, 128.2, 127.8, 127.1, 127.0, 126.3, 113.5, 66.9, 56.2, 55.2, 53.1, 21.5.

MS (EI) m/z 478(M+); **HRMS (ESI)** Calcd for $C_{27}H_{30}N_2O_4S$+H 479.2005, Found 479.2009.



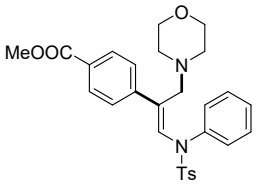
4h

$C_{32}H_{32}N_2O_3S$, MW: 524.21g·mol^{-1}, Light yellow oil (79.7mg), 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.65 (d, *J* = 8.0 Hz, 2H), 7.59 (q, *J* = 8.0 Hz, 4H), 7.52-7.47 (m, 4H), 7.41-7.34 (m, 3H), 7.32-7.24 (m, 5H), 6.69 (s, 1H), 3.55 (s, 4H), 3.37 (s, 2H), 2.45 (s, 3H), 2.29 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 144.0, 141.6, 140.4, 138.2, 136.5, 133.9, 129.4, 128.9, 128.7, 127.8, 127.7, 127.4, 127.3, 127.2, 126.9, 126.8, 66.8, 56.1, 53.1, 21.5.

MS (EI) m/z 524(M+); **HRMS (ESI)** Calcd for $C_{32}H_{32}N_2O_3S$+H 525.2212, Found 525.2218.



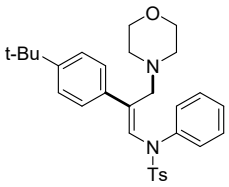
4i

$C_{28}H_{30}N_2O_5S$, MW: 506.19g·mol^{-1}, Light yellow oil (81.1mg), 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.02 (d, *J* = 7.6 Hz, 2H), 7.50 (dd, *J* = 14.4, 8.0 Hz, 4H), 7.37 – 7.27 (m, 5H), 7.21 (d, *J* = 7.6 Hz, 2H), 6.72 (s, 1H), 3.95 (s, 3H), 3.50 (s, 4H), 3.29 (s, 2H), 2.45 (s, 3H), 2.21 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 166.8, 144.2, 141.2, 135.1, 133.8, 129.5, 129.4, 129.2, 129.1, 129.0, 127.8, 127.5, 127.4, 127.0, 66.8, 55.9, 53.0, 52.1, 21.5.

MS (EI) m/z 506(M+); **HRMS (ESI)** Calcd for $C_{28}H_{30}N_2O_5S$+H 507.1954, Found 507.1954.



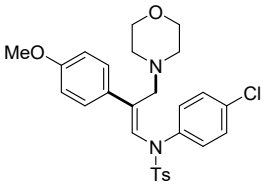
4j

$C_{30}H_{36}N_2O_3S$, MW: 504.24g·mol^{-1}, Light yellow oil (84.7mg), 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.51-7.45 (m, 4H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 3H), 7.22 (d, *J* = 7.6 Hz, 2H), 6.62 (s, 1H), 3.55 (s, 4H), 3.30 (s, 2H), 2.45 (s, 3H), 2.28 (s, 4H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 150.7, 143.9, 141.7, 136.5, 136.4, 133.9, 129.4, 128.8, 127.8, 127.3, 127.0, 126.7, 125.0, 66.9, 56.2, 53.1, 34.5, 31.2, 21.5.

MS (EI) m/z 504(M+); **HRMS (ESI)** Calcd for $C_{30}H_{36}N_2O_3S$+H 505.2525, Found 505.2529.



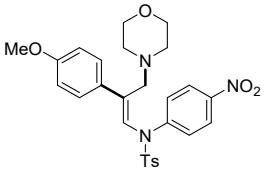
4k

$C_{27}H_{29}ClN_2O_4S$, MW: 512.15g·mol^{-1}, Light yellow oil (85.1mg), 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.48 (d, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 6.8 Hz, 4H), 7.16 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.44 (s, 1H), 3.84 (s, 3H), 3.53 (s, 4H), 3.32 (s, 2H), 2.45 (s, 3H), 2.27 (s, 5H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.4, 144.2, 140.3, 138.0, 133.6, 132.7, 131.2, 129.6, 129.0, 128.2, 127.8, 125.7, 113.5, 66.8, 56.3, 55.2, 53.1, 21.5.

MS (EI) m/z 512(M+); **HRMS (ESI)** Calcd for $C_{27}H_{29}ClN_2O_4S$+H 513.1615, Found 513.1618.



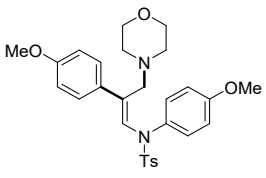
4l

$C_{27}H_{29}N_3O_6S$, MW: 523.18g·mol^{-1}, Light yellow oil (99.4mg), 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.37 (d, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.78-6.72 (m, 4H), 6.36 (s, 1H), 3.72 (s, 6H), 3.43 (s, 4H), 3.25 (s, 2H), 2.33 (s, 3H), 2.17 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.2, 158.5, 143.8, 136.7, 134.3, 133.9, 131.6, 129.4, 128.7, 128.2, 127.9, 126.6, 114.0, 113.4, 56.2, 55.4, 55.2, 53.1, 21.5.

MS (EI) m/z 523(M+); **HRMS (ESI)** Calcd for $C_{27}H_{29}N_3O_6S$+H 524.1855, Found 524.1859.



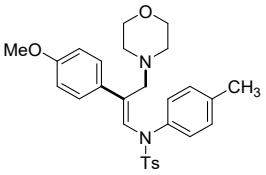
4m

$C_{28}H_{32}N_2O_5S$, MW: 508.20g·mol^{-1}, Light yellow oil (80.3mg), 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.48 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.86 (dd, *J* = 15.5, 8.0 Hz, 4H), 6.47 (s, 1H), 3.84 (s, 6H), 3.55 (s, 4H), 3.37 (s, 2H), 2.45 (s, 3H), 2.29 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.2, 158.4, 143.8, 136.7, 134.3, 133.8, 131.6, 129.4, 128.7, 128.2, 127.9, 126.6, 66.9, 56.1, 55.3, 55.2, 53.1, 21.5.

MS (EI) m/z 508(M+); **HRMS (ESI)** Calcd for $C_{28}H_{32}N_2O_5S$+H 509.2110, Found 509.2105.



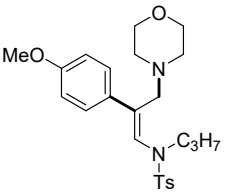
4n

$C_{28}H_{32}N_2O_4S$, MW: 492.21g·mol^{-1}, Light yellow oil (73.9mg), 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.49 (d, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.47 (s, 1H), 3.85 (s, 3H), 3.54 (s, 4H), 3.36 (s, 2H), 2.45 (s, 3H), 2.37 (s, 3H), 2.27 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.3, 143.8, 139.1, 137.2, 137.0, 134.0, 131.6, 129.5, 129.4, 128.2, 127.9, 127.1, 126.5, 113.4, 66.9, 56.2, 55.2, 53.1, 21.5, 21.0.

MS (EI) m/z 492(M+); **HRMS (ESI)** Calcd for $C_{28}H_{32}N_2O_4S$+H 493.2161, Found 493.2167.



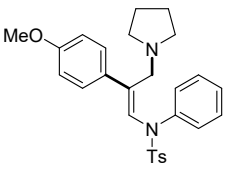
4o

$C_{24}H_{32}N_2O_4S$, MW: 444.21g·mol^{-1}, Light yellow oil (49.8mg), 56% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.65 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.46 (s, 1H), 3.86 (s, 3H), 3.73 (s, 2H), 3.57 (s, 4H), 2.06 (t, *J* = 7.2 Hz, 2H), 2.43 (d, *J* = 11.3 Hz, 7H), 1.57 (p, *J* = 7.2 Hz, 2H), 0.99 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.3, 144.0, 143.5, 134.4, 130.8, 129.6, 128.4, 127.5, 125.2, 113.2, 66.9, 56.7, 55.2, 53.2, 53.1, 21.7, 21.5, 11.5.

MS (EI) m/z 444(M+); **HRMS (ESI)** Calcd for $C_{24}H_{32}N_2O_4S$+H 445.2161, Found 445.2163.



4p

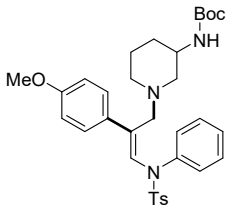
$C_{27}H_{30}N_2O_3S$, MW: 462.20g·mol^{-1}, Light yellow oil (67.5mg), 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.49 (d, *J* = 6.8 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.35-7.26 (m, , 6H), 7.21 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 7.2 Hz, 2H), 6.38 (s, 1H), 3.85 (s, 3H), 3.52 (s, 2H), 2.45 (s, 3H), 2.33 (s, 4H), 1.62 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.3 , 143.8 , 142.0 , 139.6 , 134.0 , 131.5 , 129.4 , 128.9 , 128.2 , 127.9 ,

127.0 , 126.9 , 125.3, 113.6 , 55.2 , 53.7 , 53.3 , 23.5 , 21.5 .

MS (EI) m/z 462(M+); **HRMS (ESI)** Calcd for $C_{27}H_{30}N_2O_3S$+H 463.2055, Found 463.2058.



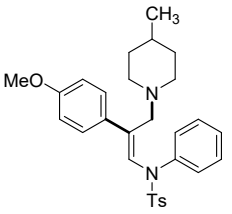
4q

$C_{33}H_{41}N_3O_5S$, MW: 591.28g·mol^{-1}, Light yellow oil (80.4mg), 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.50 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.4 Hz, 4H), 7.29 (t, *J* = 7.6 Hz, 3H), 7.21 (d, *J* = 7.2 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.46 (s, 1H), 4.65 (d, *J* = 7.2 Hz, 1H), 3.85 (s, 3H), 3.56 (s, 1H), 3.41 (s, 2H), 2.45 (s, 3H), 2.17 (s, 1H), 2.01 (s, 1H), 1.43 (s, 9H), 1.33 (d, *J* = 8.0 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.3 , 154.9 , 143.8 , 141.7 , 139.2 , 133.9 , 130.7 , 129.4 , 128.9 , 128.3 , 127.8 , 127.0 , 125.5 , 113.3 , 78.3 , 57.3 , 55.4 , 55.0 , 53.3 , 45.6 , 28.3 , 22.6, 21.5.

MS (EI) m/z 591(M+); **HRMS (ESI)** Calcd for $C_{33}H_{41}N_3O_5S$+H 592.2845, Found 592.2849.



4r

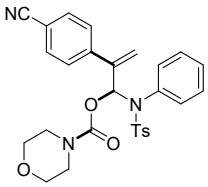
$C_{29}H_{34}N_2O_3S$, MW: 490.23g·mol^{-1}, Light yellow oil (mg), % yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.47 (dd, *J* = 18.8, 7.6 Hz, 4H), 7.35-7.21 (m, 8H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.45 (s, 1H), 3.85 (s, 3H), 3.33 (s, 2H), 2.64 (d, *J* = 10.4 Hz, 2H), 2.45 (s, 3H), 1.78 (t, *J* = 11.2 Hz, 2H), 1.45 (d, *J* = 13.2 Hz, 2H), 1.03 (q, *J* = 11.3 Hz, 2H), 0.85 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.2 , 143.8 , 141.9 , 138.9 , 134.1 , 131.9 , 129.4 , 128.8 , 128.4 , 127.9 , 127.2 , 126.9 , 125.7 , 113.4 , 56.3 , 55.2 , 53.5 , 34.2 , 30.6 , 21.8 , 21.5 .

MS (EI) m/z 490(M+); **HRMS (ESI)** Calcd for $C_{29}H_{34}N_2O_3S$+H 491.2368, Found 491.2367.

3.4 Analytical Data for product **5a-5o**



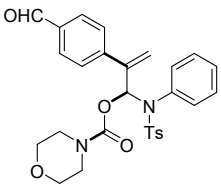
5a

$C_{28}H_{27}N_3O_5S$, MW: 517.16g·mol^{-1}, Light yellow solid (76.7mg), 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.88 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.49 (m, 4H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.25 – 7.20 (m, 4H), 6.75 (d, *J* = 7.2 Hz, 2H), 5.32 (s, 1H), 5.01 (s, 1H), 3.71 (s, 2H), 3.53 (s, 4H), 3.31 (d, *J* = 10.8 Hz, 1H), 3.06 (s, 1H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 153.0 , 144.0 , 141.8 , 141. 6 , 136.5 , 135.0 , 132.2 , 130.9 , 129.3 , 129.0 , 128.5 , 128.0 , 127.3 , 118.6 , 118.6 , 111.9 , 82.2 , 66.3 (d, *J* = 48.5 Hz) , 44.0 (d, *J* = 17.5 Hz) , 21.6.

MS (EI) m/z 517(M+); **HRMS (ESI)** Calcd for $C_{28}H_{27}N_3O_5S$+Na 540.1569, Found 540.1561.



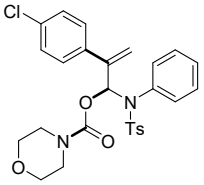
5b

$C_{28}H_{28}N_2O_6S$, MW: 520.17g·mol^{-1}, Light yellow solid (64.8mg), 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 10.05 (s, 1H), 7.94 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.53 (dd, *J* = 16.4, 7.6 Hz, 4H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 8.7 Hz, 4H), 6.75 (d, *J* = 7.6 Hz, 2H), 5.35 (s, 1H), 5.01 (s, 1H), 3.72 – 3.68 (m, 2H), 3.62 – 3.34 (m, 4H), 3.33 (d, *J* = 10.8 Hz, 1H), 3.09 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 191.8, 153.0, 143.9, 143.0, 142.2, 136.6, 135.9, 135.1, 131.0, 129.8, 129.3, 129.0, 128.5, 128.0, 127.3, 118.3, 82.4, 66.4 (d, *J* = 48 Hz) , 43.9 (d, *J* = 18.9 Hz) , 21.6.

MS (EI) m/z 520(M+); **HRMS (ESI)** Calcd for $C_{28}H_{28}N_2O_6S$+Na 543.1566, Found 543.1571.



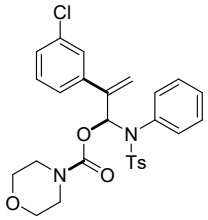
5c

$C_{27}H_{27}ClN_2O_5S$, MW: 526.13g·mol^{-1}, Light yellow solid (73.4mg), 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.86 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.32 (s, 5H), 7.22 (t, *J* = 6.8 Hz, 4H), 6.78 (d, *J* = 7.6 Hz, 2H), 5.20 (s, 1H), 4.88 (s, 1H), 3.71 (s, 2H), 3.62-3.47 (m, 4H), 3.33 (d, *J* = 10.9 Hz, 1H), 3.09 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 153.0, 143.7, 141.9, 136.6, 135.5, 135.1, 134.1, 131.0, 129.2, 128.9, 128.5, 128.4, 128.0, 127.9, 116.4, 82.5, 66.3 (d, *J* = 47.4 Hz), 43.9 (d, *J* = 20.5 Hz), 21.6.

MS (EI) m/z 526(M+); **HRMS (ESI)** Calcd for $C_{27}H_{27}ClN_2O_5S$ +Na 549.1227, Found 549.1233.



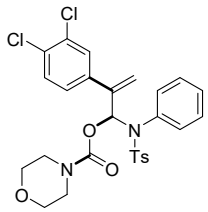
5d

$C_{27}H_{27}ClN_2O_5S$, MW: 526.13g·mol^{-1}, Light yellow solid (72.5mg), 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.84 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.34-7.32 (m, 4H), 7.23 (d, *J* = 8.4 Hz, 5H), 6.81 (d, *J* = 7.6 Hz, 2H), 5.23 (s, 1H), 4.93 (s, 1H), 3.72 – 3.54 (m, 6H), 3.35 (d, *J* = 10.4 Hz, 1H), 3.14 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 153.1 , 143.8 , 142.0 , 138.9 , 136.6 , 135.1 , 134.2 , 131.1 , 129.7 , 129.2 , 128.9 , 128.4 , 128.3 , 128.0 , 126.9 , 124.8 , 117.2 , 82.5 , 66.4 (d, *J* = 44.9 Hz) , 44.0 (d, *J* = 21.6 Hz) , 21.6 .

MS (EI) m/z 526(M+); **HRMS (ESI)** Calcd for $C_{27}H_{27}ClN_2O_5S$ +Na 549.1227, Found 549.1231.



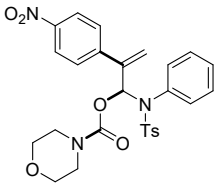
5e

$C_{27}H_{26}Cl_2N_2O_5S$, MW: 560.09g·mol^{-1}, Light yellow solid (72.4mg), 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.78 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.37 – 7.22 (m, 7H), 6.80 (d, *J* = 7.6 Hz, 2H), 5.23 (s, 1H), 4.93 (s, 1H), 3.78 – 3.48 (m, 6H), 3.33 (d, *J* = 10.4 Hz, 1H), 3.11 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 153.0 , 143.9 , 141.1 , 137.1 , 136.5 , 135.0 , 132.5 , 132.2 , 131.0 , 130.4 , 129.3 , 129.0 , 128.7 , 128.5 , 128.0 , 125.9 , 117.5 , 82.3 , 66.3 (d, *J* = 46.1 Hz), 43.9 (d, *J* = 21.1 Hz) , 21.6.

MS (EI) m/z 560(M+); **HRMS (ESI)** Calcd for $C_{27}H_{26}Cl_2N_2O_5S$+ Na 583.0837, Found 583.0828.



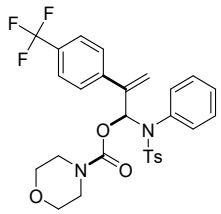
5f

$C_{27}H_{27}N_3O_7S$, MW: 537.16g·mol^{-1}, Light yellow solid (66.2mg), 67% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.21 (d, *J* = 8.0 Hz, 2H), 7.90 (s, 1H), 7.52 (dd, *J* = 15.2, 8.0 Hz, 4H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 8.5 Hz, 4H), 6.76 (d, *J* = 7.6 Hz, 2H), 5.37 (s, 1H), 5.05 (s, 1H), 3.78 – 3.48 (m, 6H), 3.32 (d, *J* = 11.2 Hz, 1H), 3.07 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 153.0, 147.5, 144.0, 143.5, 141.5, 136.5, 135.0, 130.9, 129.3, 129.1, 128.6, 128.0, 127.5, 123.7, 119.2, 82.2, 66.3 (d, *J* = 48.5 Hz), 44.0 (d, *J* = 17.4 Hz), 21.6.

MS (EI) m/z 537(M+); **HRMS (ESI)** Calcd for $C_{27}H_{27}N_3O_7S$+ Na 560.1467, Found 560.1474.



5g

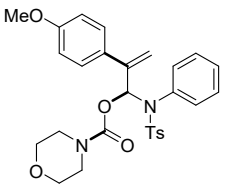
$C_{28}H_{27}F_3N_2O_5S$, MW: 560.16g·mol^{-1}, Light yellow solid (70.3mg), 69% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.91 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 4H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 4H), 6.79 (d, *J* = 7.6 Hz, 2H), 5.29 (s, 1H), 4.98 (s, 1H), 3.79 – 3.50 (m, 6H), 3.34 (d, *J* = 10.8 Hz, 1H), 3.11 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 153.0 , 143.8 , 142.1 , 140.7 , 136.6 , 135.0 , 131.0 , 130.1 (d, *J* = 32.3 Hz)129.9 , 129.2 , 129.0 , 128.5 , 128.0 , 127.0 , 125.3 (q, *J* = 3.8 Hz), 122.6 , 117.9 , 82.4 , 66.3 (d, *J* = 46.8 Hz) , 43.9 (d, *J* = 19.3 Hz) , 21.5 .

^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -62.5 (s, 1F).

MS (EI) m/z 560(M+); **HRMS (ESI)** Calcd for $C_{28}H_{27}F_3N_2O_5S$+ Na 583.1490, Found 583.1485.



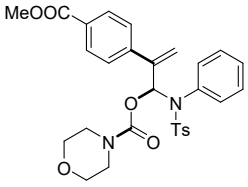
5h

$C_{28}H_{30}N_2O_6S$, MW: 522.18g·mol^{-1}, Light yellow solid (55.5mg), 58% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.89 (s, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.34-7.30 (m, 3H), 7.21 (t, *J* = 8.0 Hz, 4H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.79 (d, *J* = 7.6 Hz, 2H), 5.14 (s, 1H), 4.77 (s, 1H), 3.86 (s, 3H), 3.71-3.51 (m, 6H), 3.34 (d, *J* = 9.6 Hz, 1H), 3.10 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 159.5, 153.1, 143.6 , 142.3 , 136.9, 135.2 , 131.2 , 129.5, 129.1 , 128.8 , 128.3 , 128.0 , 127.9 , 114.3 , 113.7 , 82.8 , 66.4 (d, *J* = 47.4 Hz) , 55.2 , 43.9 (d, *J* = 21.2 Hz) , 21.6 .

MS (EI) m/z 522(M+); **HRMS (ESI)** Calcd for $C_{28}H_{30}N_2O_6S$+ Na 545.1722, Found 545.1726.



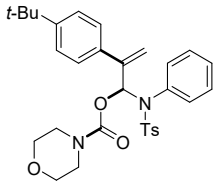
5i

$C_{29}H_{30}N_2O_7S$, MW: 550.18g·mol^{-1}, Light yellow solid (52.7mg), 52% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.02 (d, *J* = 8.0 Hz, 2H), 7.92 (s, 1H), 7.47 (dd, *J* = 28.0, 7.6 Hz, 4H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 4H), 6.76 (d, *J* = 7.6 Hz, 2H), 5.31 (s, 1H), 4.97 (s, 1H), 3.96 (s, 3H), 3.80 – 3.49 (m, 6H), 3.34 (d, *J* = 11.0 Hz, 1H), 3.11 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 166.8, 153.1 , 143.8 , 142.4 , 141.5 , 136.7 , 135.1 , 131.1 , 129.8 , 129.7 , 129.2 , 128.9 , 128.4 , 128.1 , 126.7 , 117.7 , 82.5 , 66.4 (d, *J* = 49.2 Hz), 52.2 , 44.0 (d, *J* = 19.2 Hz) , 21.6 .

MS (EI) m/z 550(M+); **HRMS (ESI)** Calcd for $C_{29}H_{30}N_2O_7S$+ Na 573.1671, Found 573.1676.



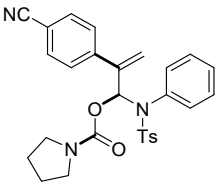
5j

$C_{31}H_{36}N_2O_5S$, MW: 548.23g·mol^{-1}, Light yellow solid (65.6mg), 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.91 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.32 (m, 5H), 7.22 (t, *J* = 7.6 Hz, 4H), 6.81 (d, *J* = 7.6 Hz, 2H), 5.19 (s, 1H), 4.81 (s, 1H), 3.72-3.53 (m, 6H), 3.35 (d, *J* = 10.4 Hz, 1H), 3.12 (s, 1H), 2.45 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 153.1 , 151.2 , 143.5 , 142.8 , 136.9 , 135.3 , 134.2, 131.3 , 129.1 , 128.8 , 128.3 , 128.1 , 126.4 , 125.3 , 115.2 , 82.8 , 66.4 (d, *J* = 44.8 Hz), 43.9 (d, *J* = 21.3 Hz) , 34.6 , 31.3 , 21.6 .

MS (EI) m/z 548(M+); **HRMS (ESI)** Calcd for $C_{31}H_{36}N_2O_5S$+ Na 571.2243, Found 571.2241.



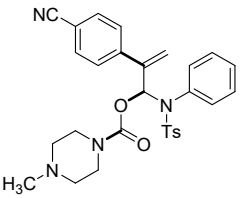
5k

$C_{28}H_{27}N_3O_4S$, MW: 501.17g·mol^{-1}, Light yellow solid (65.0mg), 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.85 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 4H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 4H), 6.84 (d, *J* = 7.6 Hz, 2H), 5.33 (s, 1H), 5.09 (s, 1H), 3.45 – 3.44 (m, 2H), 3.25-3.21 (m, 1H), 2.60 (s, 1H), 2.45 (s, 3H), 1.89-1.80 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 152.4 , 143.6 , 141.8 , 136.7 , 135.3 , 132.1 , 130.8 , 129.1 , 128.8 , 128.4 , 128.0 , 127.3 , 118.8 , 118.7, 111.6, 81.6 , 45.9 (d, *J* = 65.8 Hz) , 25.2 (d, *J* = 72.3 Hz) , 21.5 .

MS (EI) m/z 501(M+); **HRMS (ESI)** Calcd for $C_{28}H_{27}N_3O_4S$+ Na 524.1620, Found 524.1626.



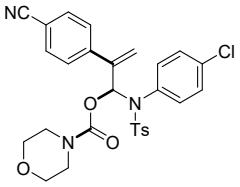
5l

$C_{29}H_{30}N_4O_4S$, MW: 530.20g·mol^{-1}, Light yellow solid (71.1mg), 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.01 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 4H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 4H), 6.88 (d, *J* = 7.6 Hz, 2H), 5.44 (s, 1H), 5.14 (s, 1H), 3.67 (s, 2H), 3.44 (s, 1H), 3.28 (s, 1H), 2.58 (s, 3H), 2.54 (s, 2H), 2.45 (s, 3H), 2.38 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 152.75 , 143.76 , 141.87 , 141.65 , 136.43 , 135.04 , 132.21 , 130.94 , 129.31 , 128.98 , 128.50 , 127.99 , 127.33 , 118.64 , 118.61 , 111.77 , 82.03 , 54.49 , 46.13 , 43.66 , 21.64 .

MS (EI) m/z 530(M+); **HRMS (ESI)** Calcd for $C_{29}H_{30}N_4O_4S$+ Na 553.1885, Found 553.1888.



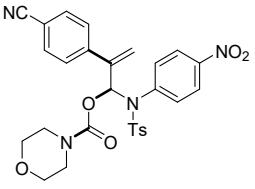
5m

$C_{28}H_{26}ClN_3O_5S$, MW: 551.13g·mol^{-1}, Orange solid (80.3mg), 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.87 (s, 1H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 4H), 7.21 (dd, *J* = 22.4, 7.6 Hz, 4H), 6.66 (d, *J* = 7.6 Hz, 2H), 5.35 (s, 1H), 5.02 (s, 1H), 3.70-3.49 (m, 6H), 3.28 (d, *J* = 8.0 Hz, 1H), 3.02 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 152.8, 144.2, 141.6, 141.3, 136.1, 135.1 , 133.6, 132.3 , 132.0 , 129.4 , 128.8 , 128.0 , 127.2 , 118.8, 118.5, 112.0, 82.0, 66.3 (d, *J* = 50.9 Hz), 44.0 (d, *J* = 12.6 Hz), 21.6.

MS (EI) m/z 551(M+); **HRMS (ESI)** Calcd for $C_{28}H_{26}ClN_3O_5S$+ Na 574.1179, Found 576.1185.



5n

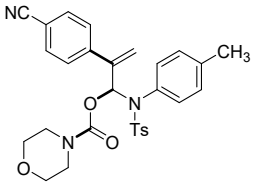
$C_{28}H_{26}N_4O_7S$, MW: 562.15g·mol^{-1}, Light yellow solid (59.1mg), 57% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.07 (d, *J* = 7.6 Hz, 2H), 7.90 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.44 (dd, *J* = 23.2, 8.0 Hz, 4H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 5.35 (s, 1H), 5.05 (s, 1H), 3.70-3.48 (m, 6H), 3.27 (s, 1H), 3.00 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 152.66 , 147.51, 144.72, 141.42, 141.24, 140.87, 135.88, 132.43, 131.46 ,

129.64, 127.90, 127.18, 123.78, 119.04, 118.36, 112.33, 81.96, 66.27 (d, *J* = 53.4 Hz) , 44.05 (d, *J* = 11.4 Hz) , 21.67 .

MS (EI) m/z 562(M+); **HRMS (ESI)** Calcd for $C_{28}H_{26}N_4O_7S$+ Na 585.1420, Found 585.1425.



5o

$C_{29}H_{29}N_3O_7S$, MW: 531.18g·mol^{-1}, Light yellow solid (69.3mg), 71% yield.

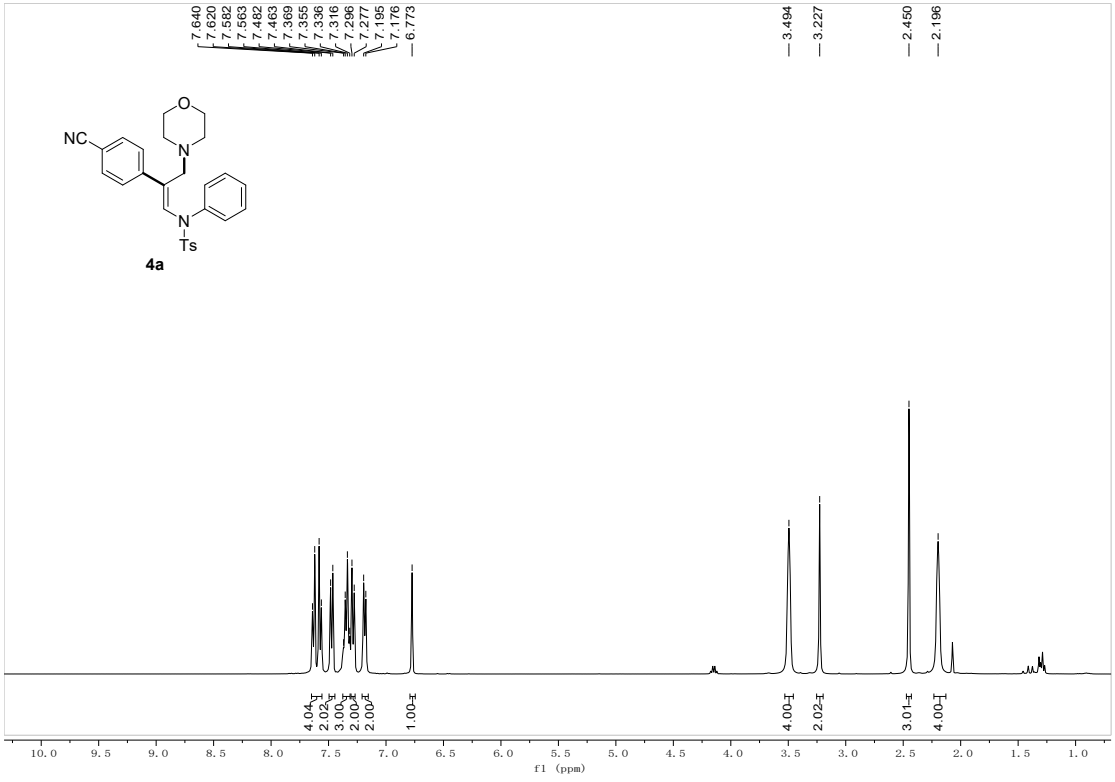
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.85 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 4H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 7.4 Hz, 2H), 6.61 (d, *J* = 7.4 Hz, 2H), 5.32 (s, 1H), 5.00 (s, 1H), 3.70-3.51 (m, 6H), 3.31 – 3.29 (m, 1H), 3.05 (s, 1H), 2.45 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 153.0 , 143.8 , 141.8 , 141.6 , 139.1 , 136.6 , 132.2 , 130.6 , 129.2 , 128.0 , 127.3 , 118.6 , 118.5 , 111.8 , 82.2 , 66.3 (d, *J* = 49.5 Hz) , 43.9 (d, *J* = 16.9 Hz) , 21.6 , 21.1 .

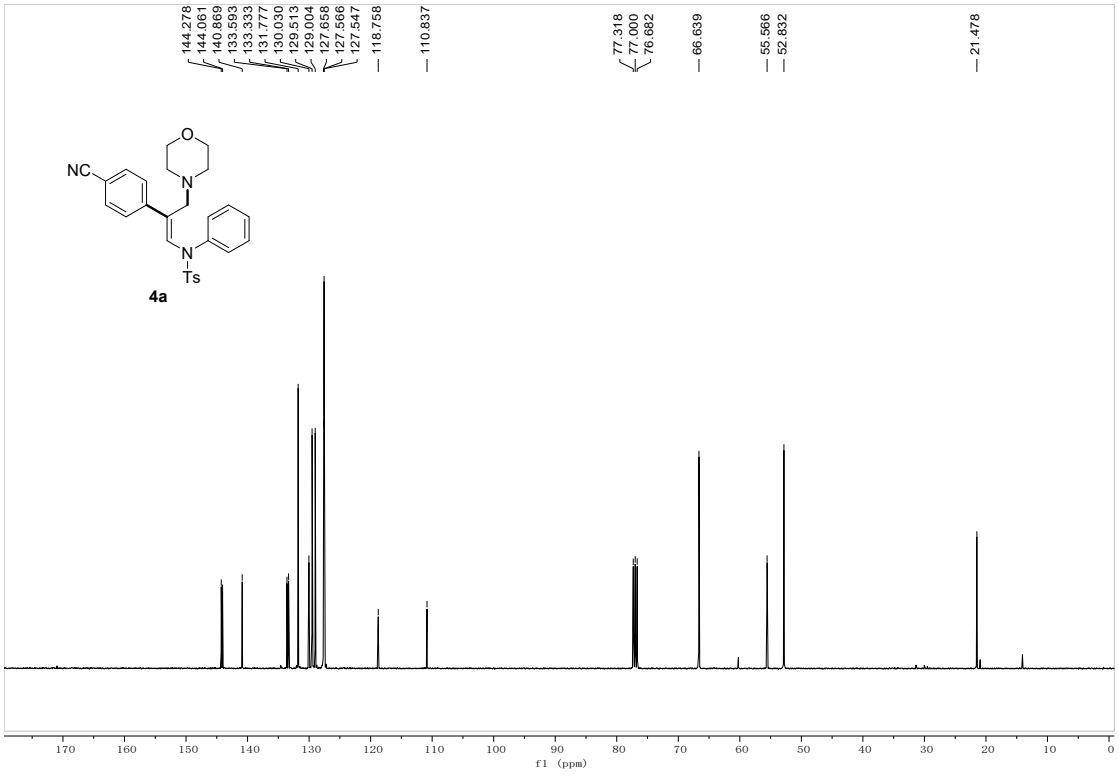
MS (EI) m/z 531(M+); **HRMS (ESI)** Calcd for $C_{29}H_{29}N_3O_7S$+Na 554.1726, Found 554.1722.

4. NMR Spectra

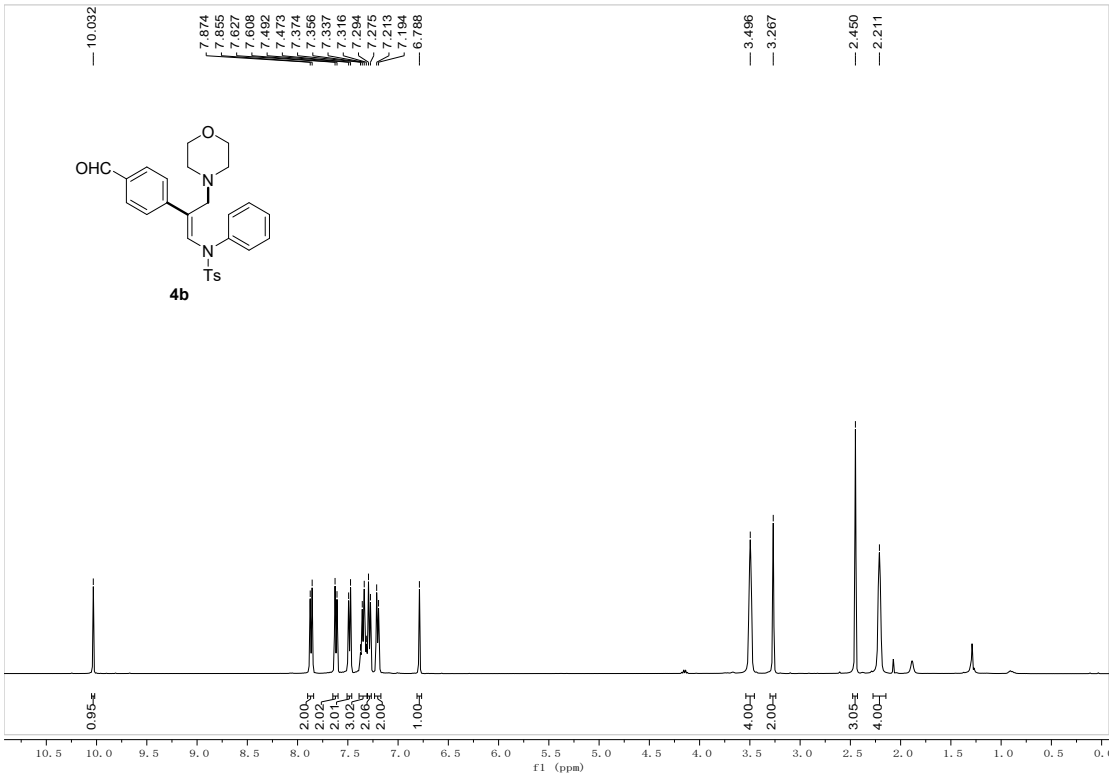
^{1}H NMR (400 MHz, $CDCl_3$)



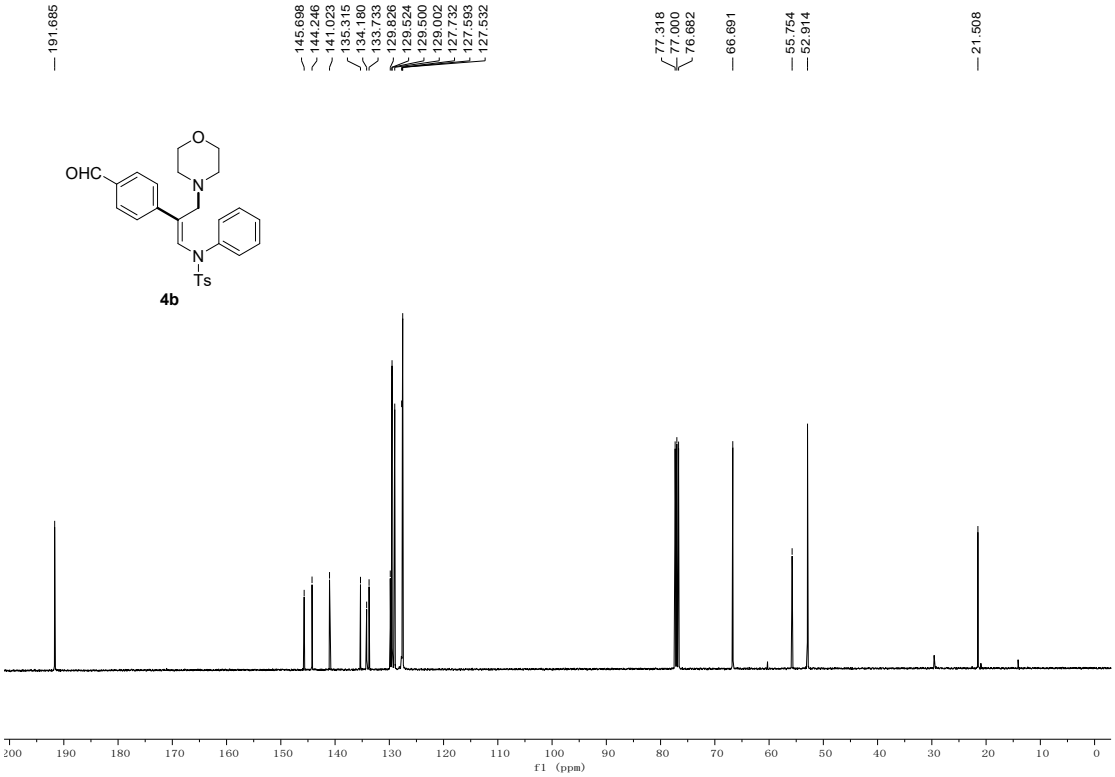
^{13}C NMR (100 MHz, $CDCl_3$)


144.278
144.061
140.869
133.593
133.333
131.777
130.030
129.513
129.004
127.658
127.566
127.547
118.758
110.837
77.318
77.000
76.682
66.639
55.566
52.832
21.478
NC
O
N
N
Ts
4a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

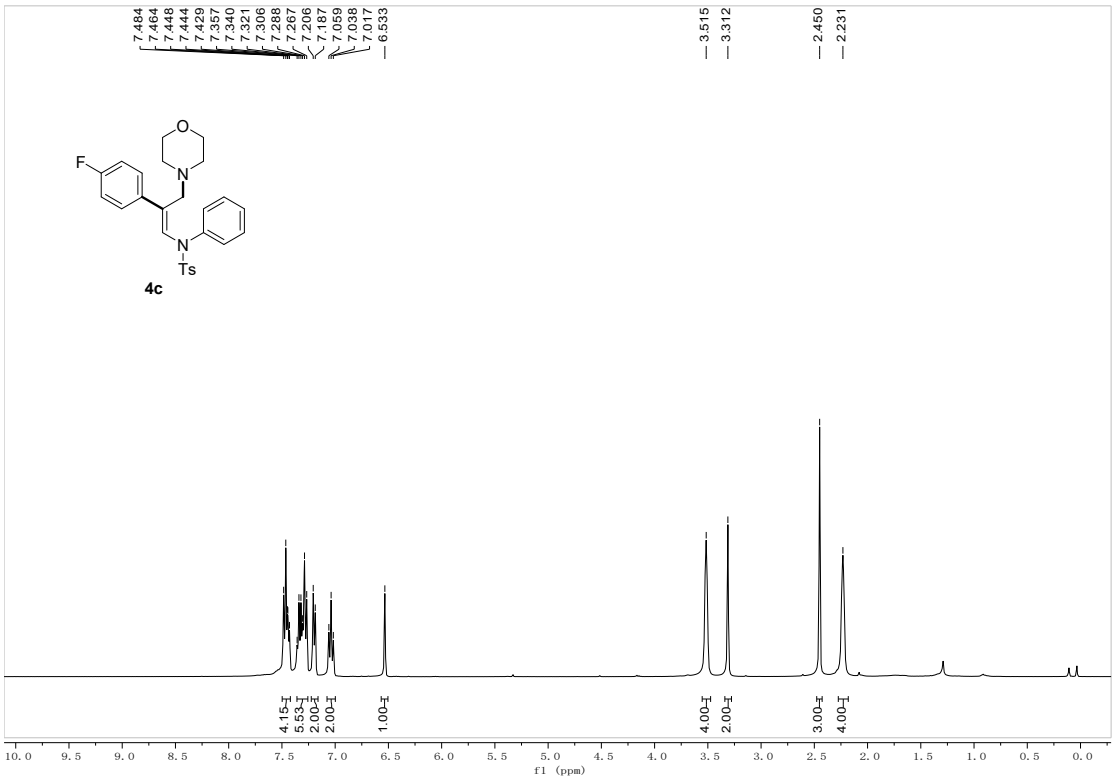
^{1}H NMR (400 MHz, $CDCl_3$)



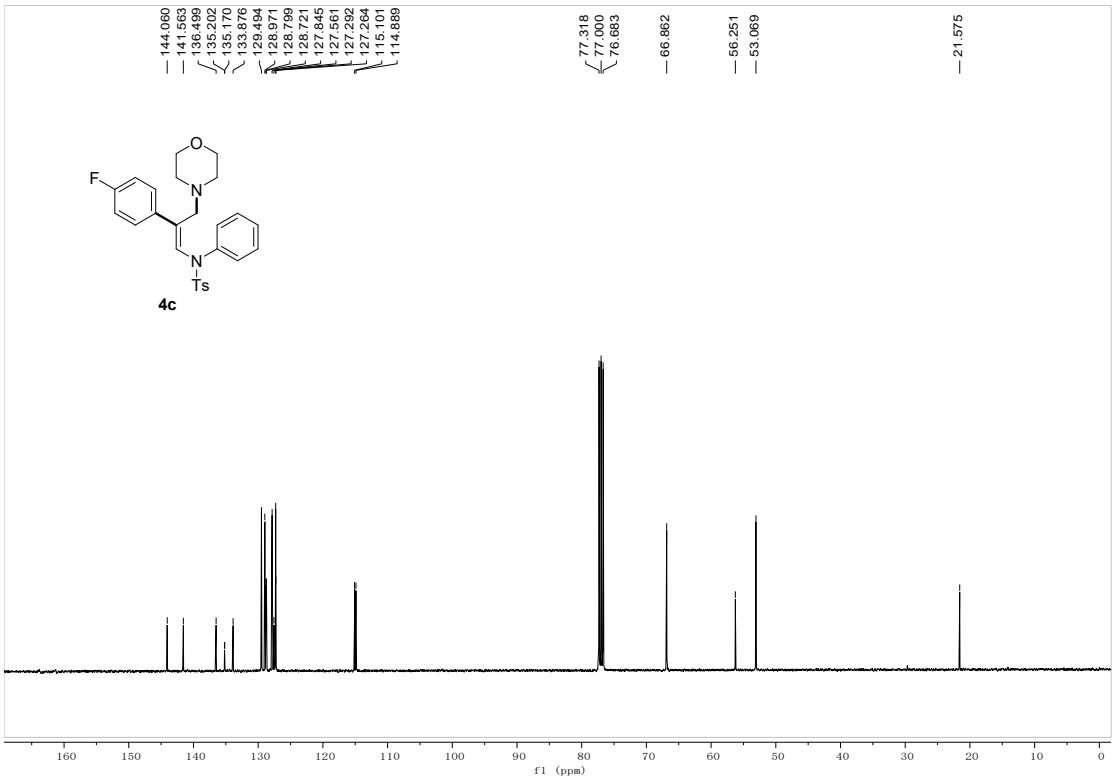
^{13}C NMR (100 MHz, $CDCl_3$)



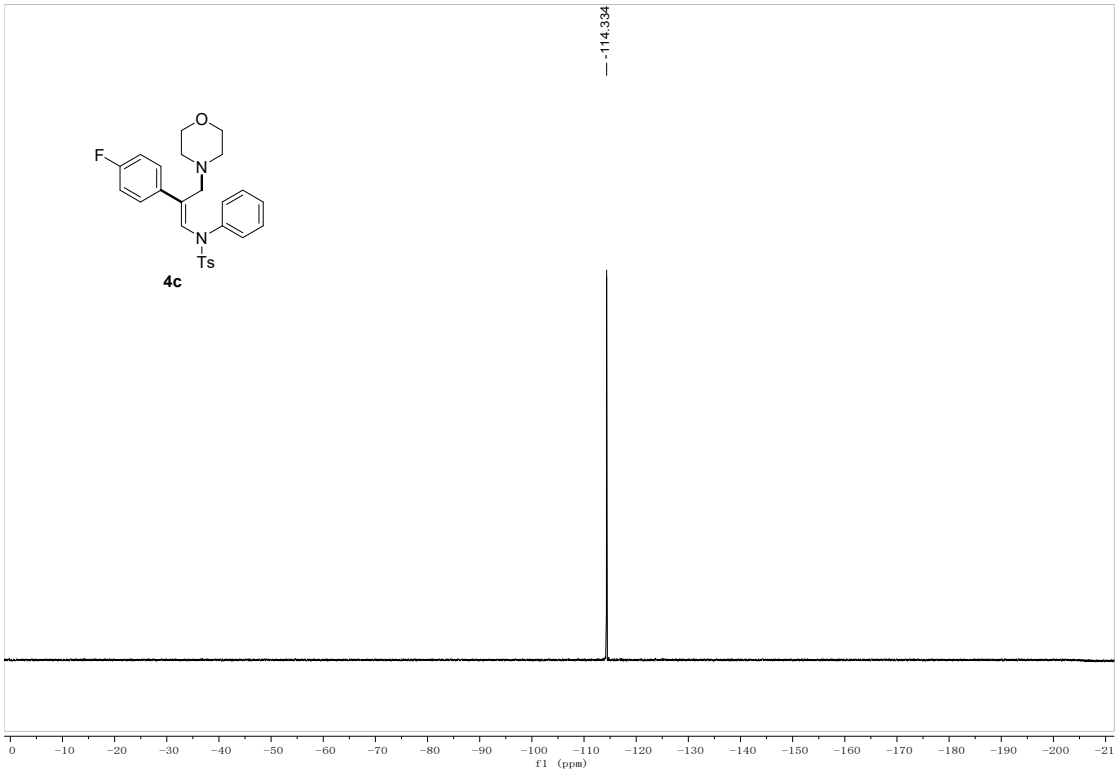
^{1}H NMR (400 MHz, $CDCl_3$)



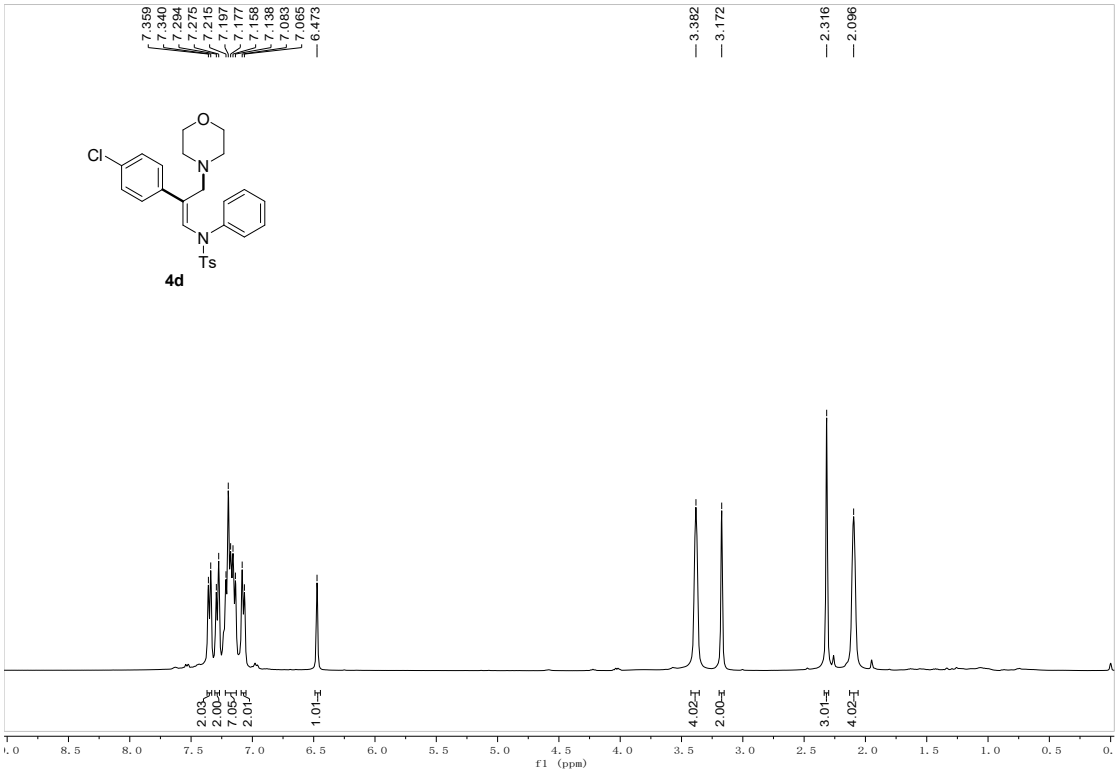
^{13}C NMR (100 MHz, $CDCl_3$)



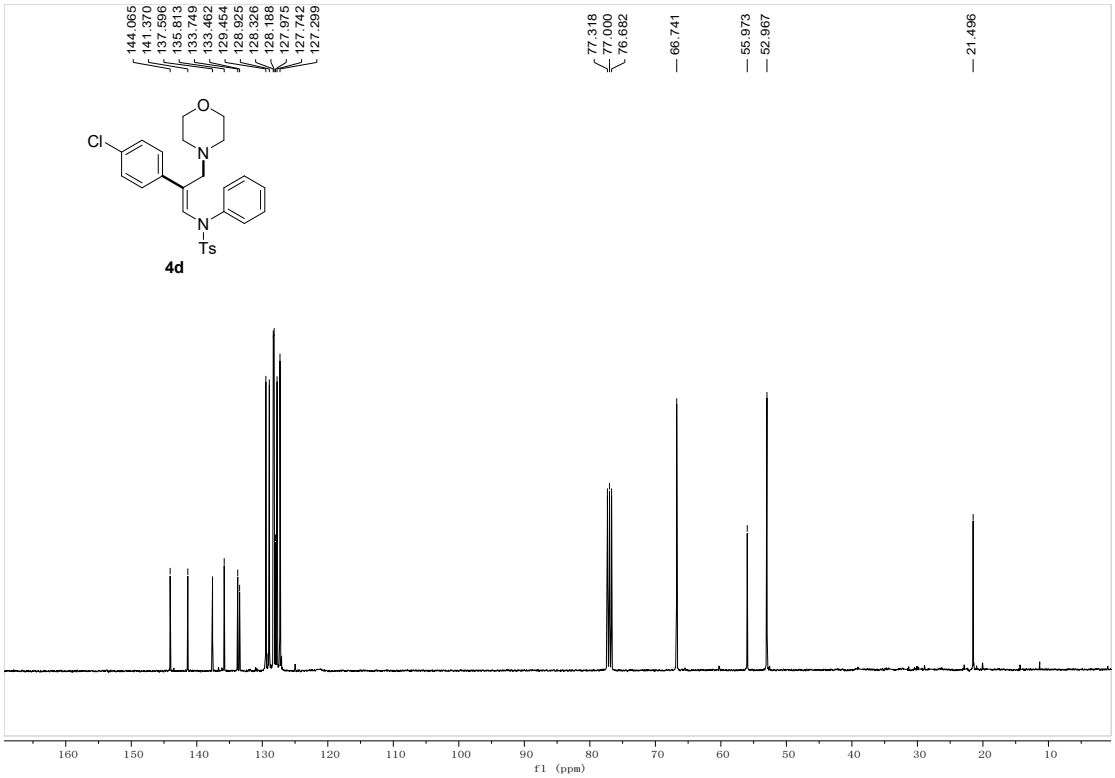
^{19}F NMR (376 MHz, $CDCl_3$)



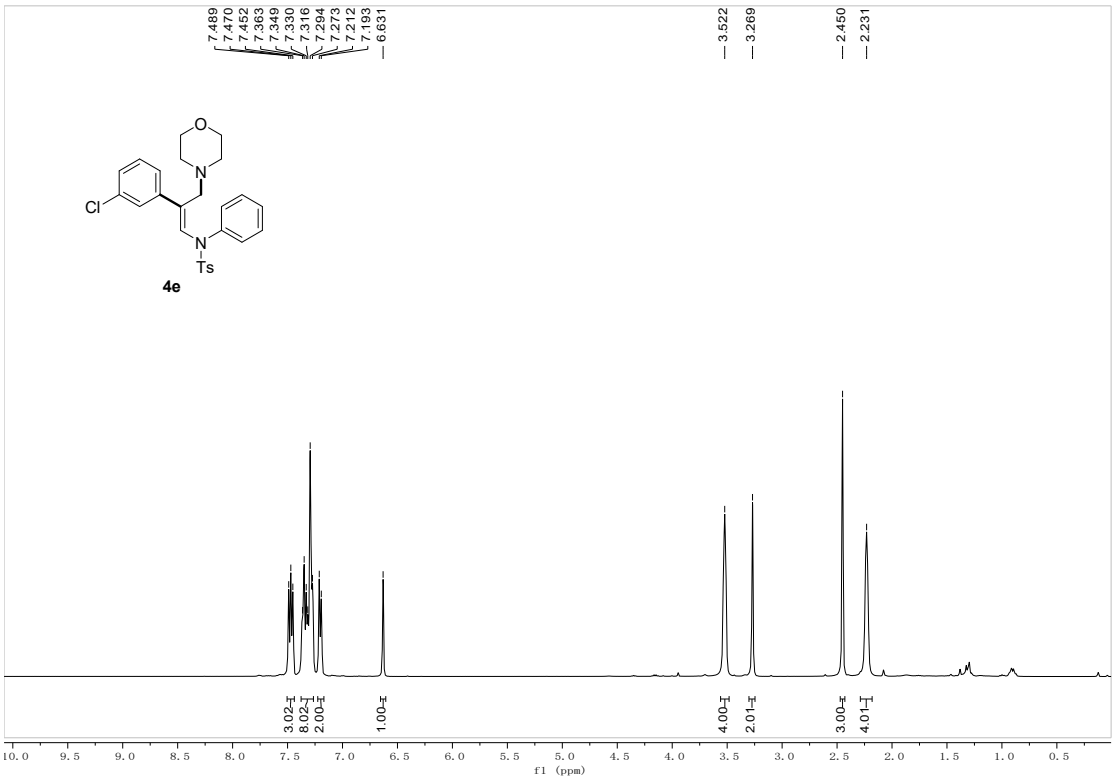
^{1}H NMR (400 MHz, $CDCl_3$)



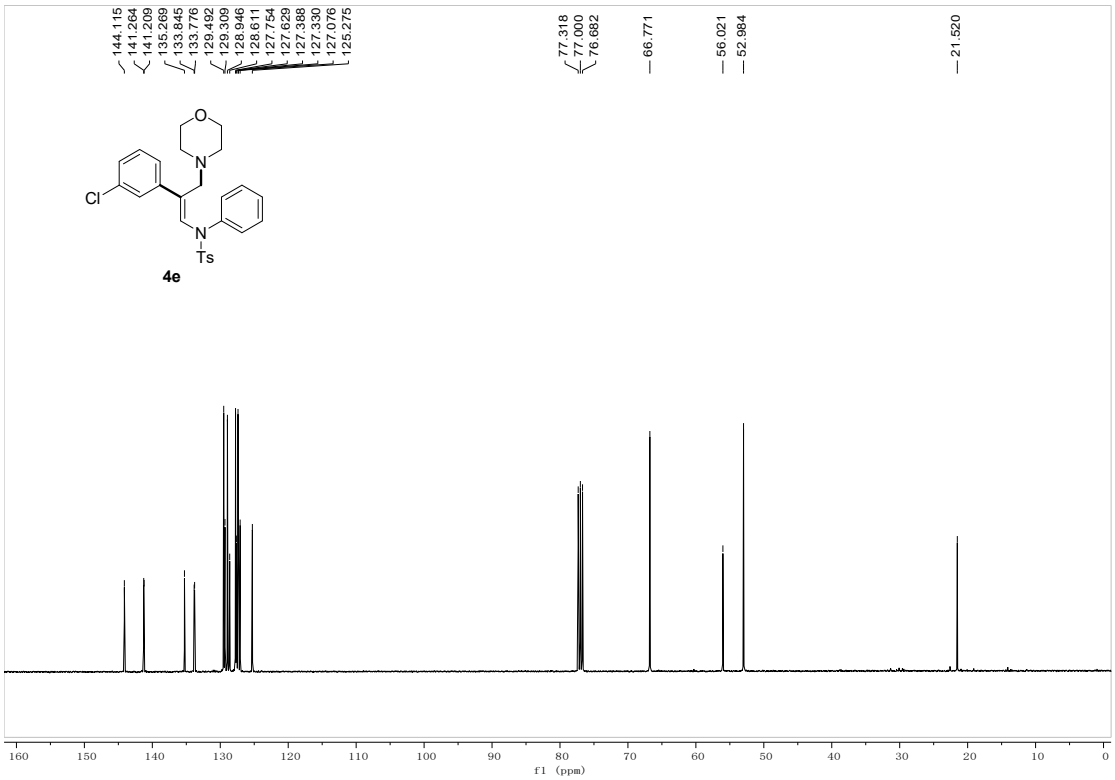
^{13}C NMR (100 MHz, $CDCl_3$)



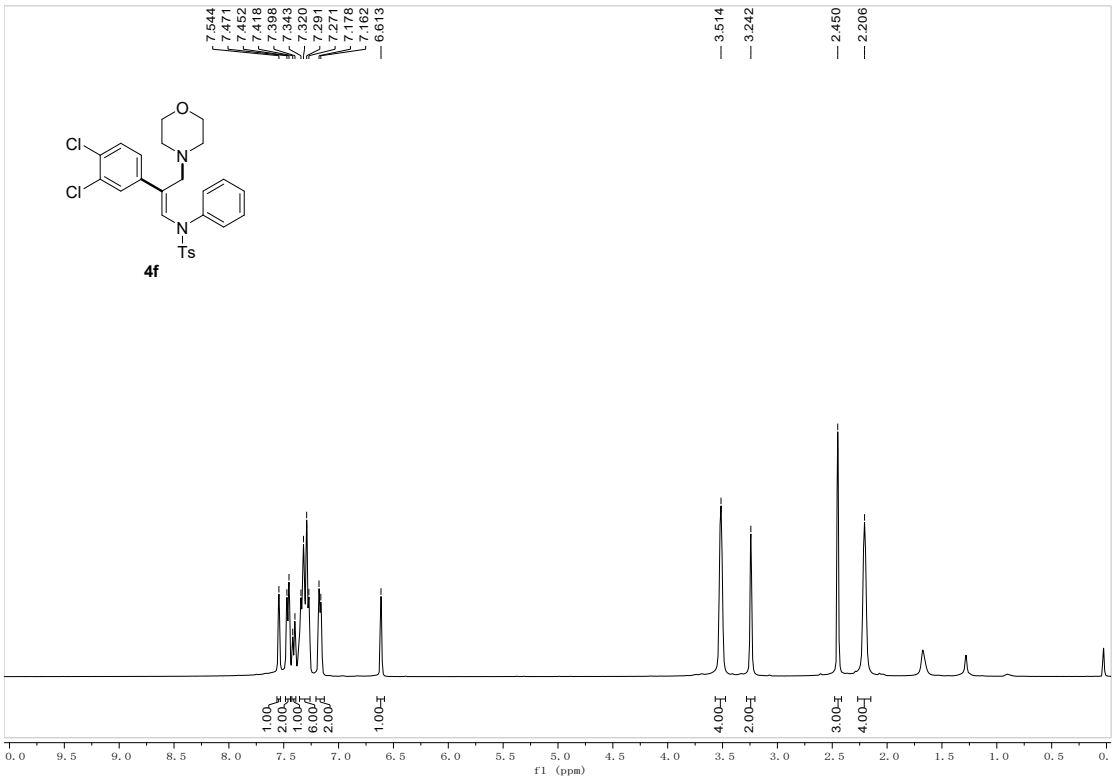
^{1}H NMR (400 MHz, $CDCl_3$)



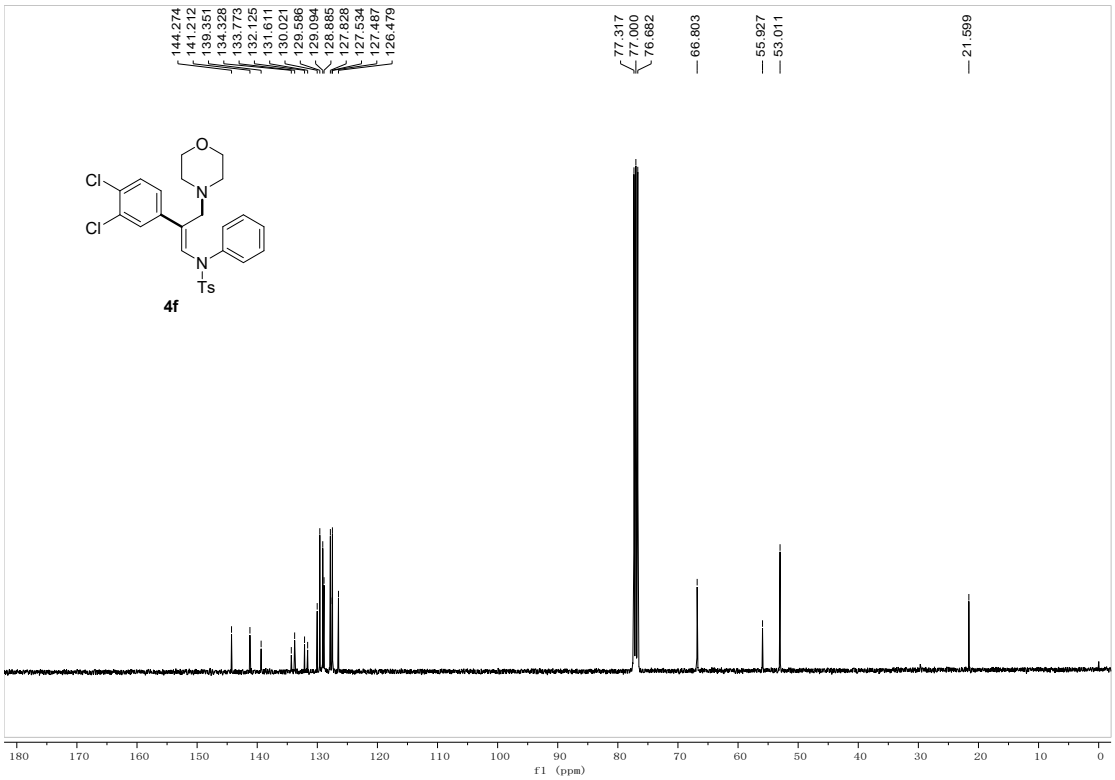
^{13}C NMR (100 MHz, $CDCl_3$)



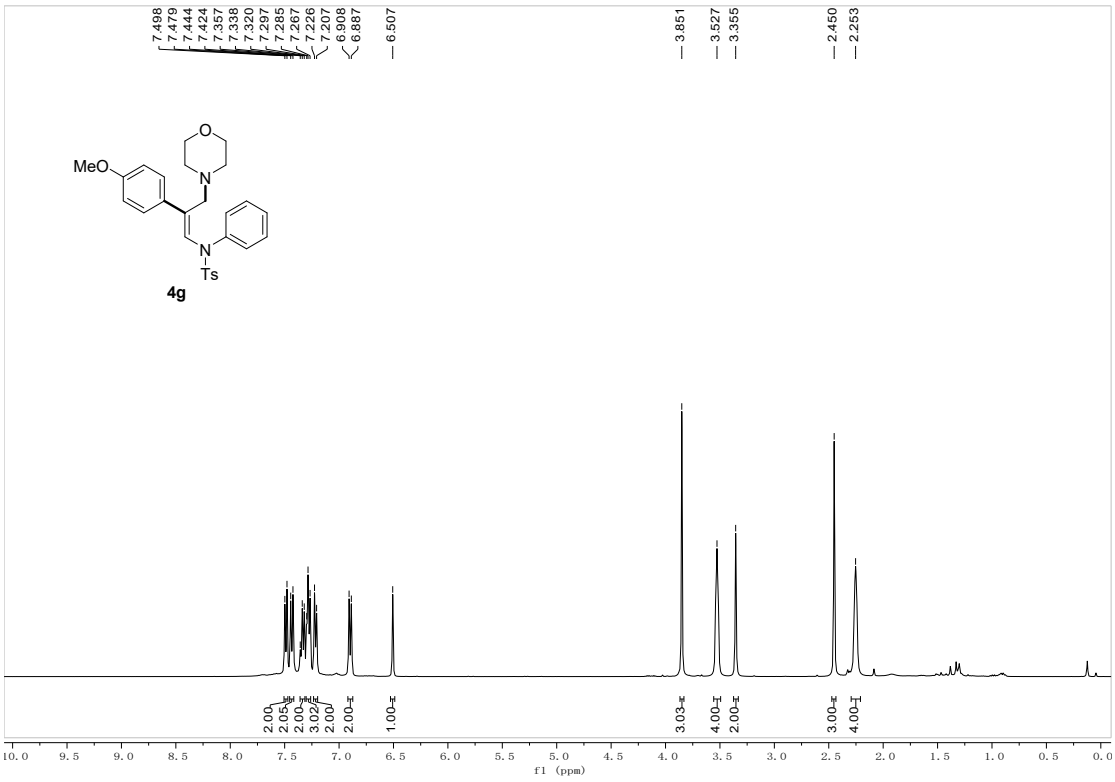
^{1}H NMR (400 MHz, $CDCl_3$)



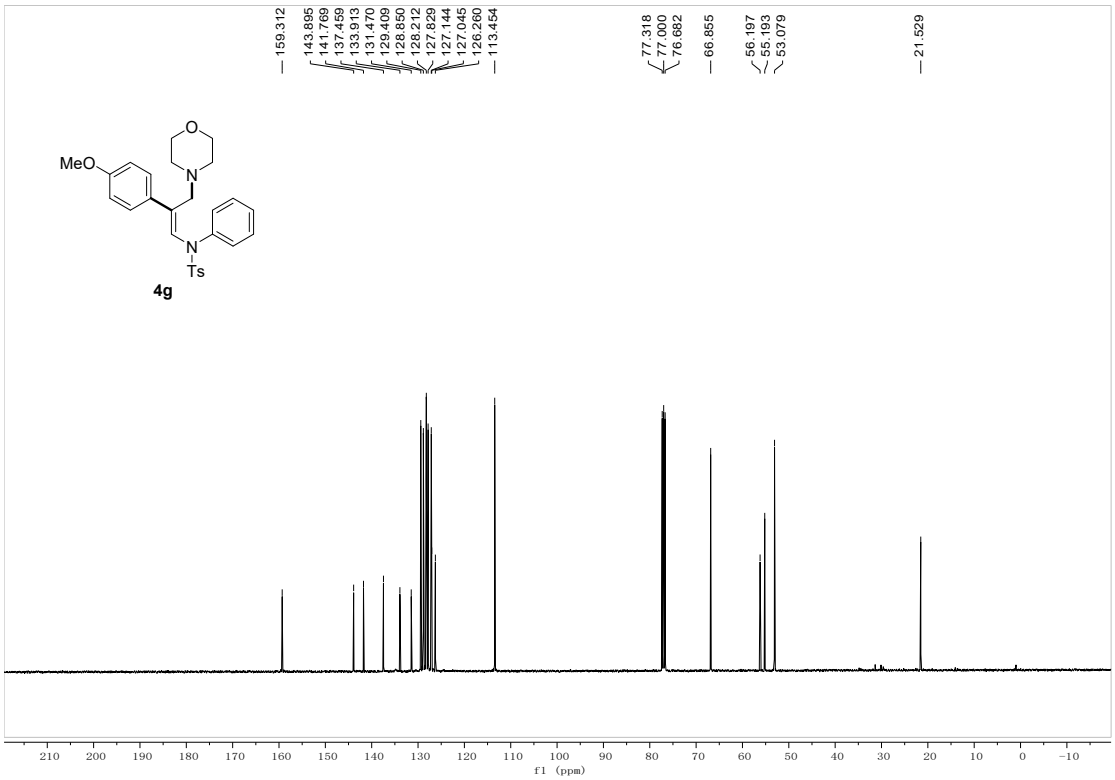
^{13}C NMR (100 MHz, $CDCl_3$)



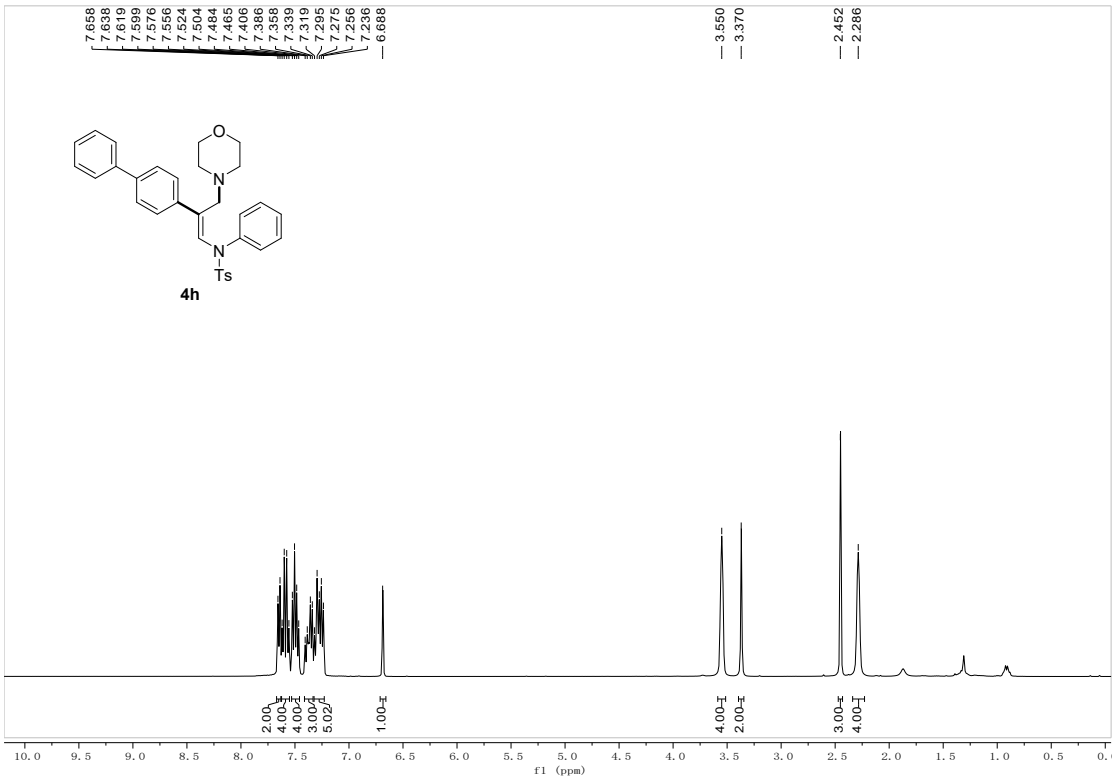
^{1}H NMR (400 MHz, $CDCl_3$)



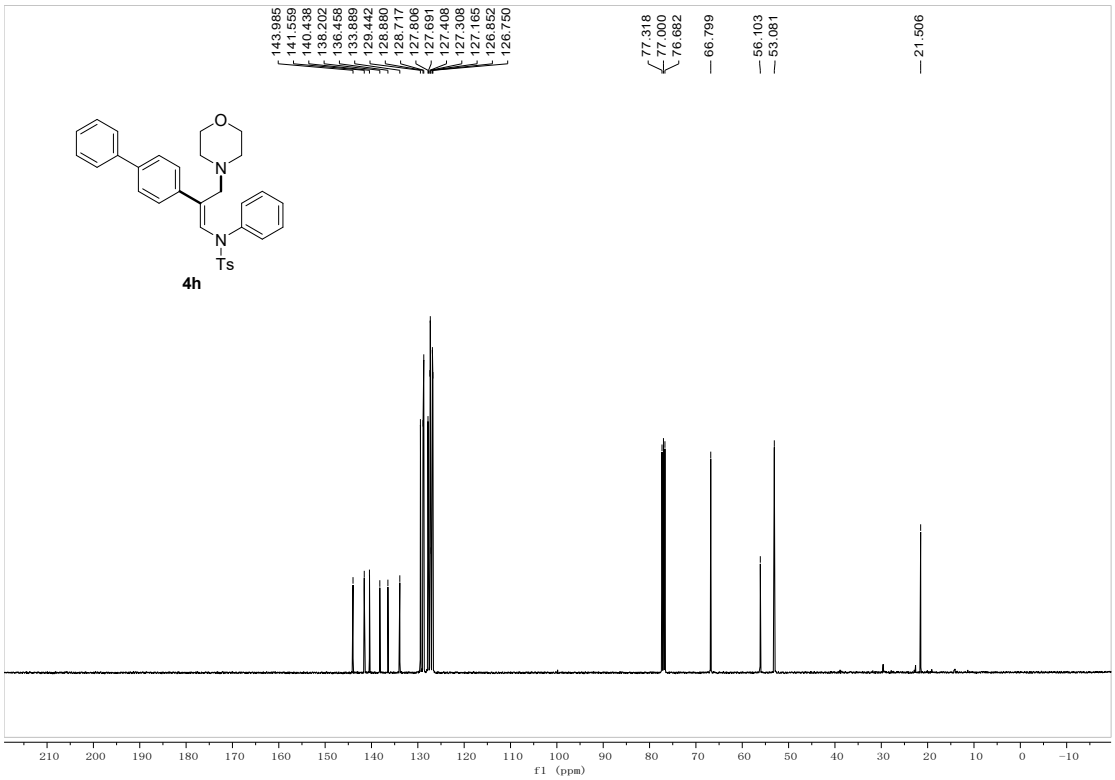
^{13}C NMR (100 MHz, $CDCl_3$)



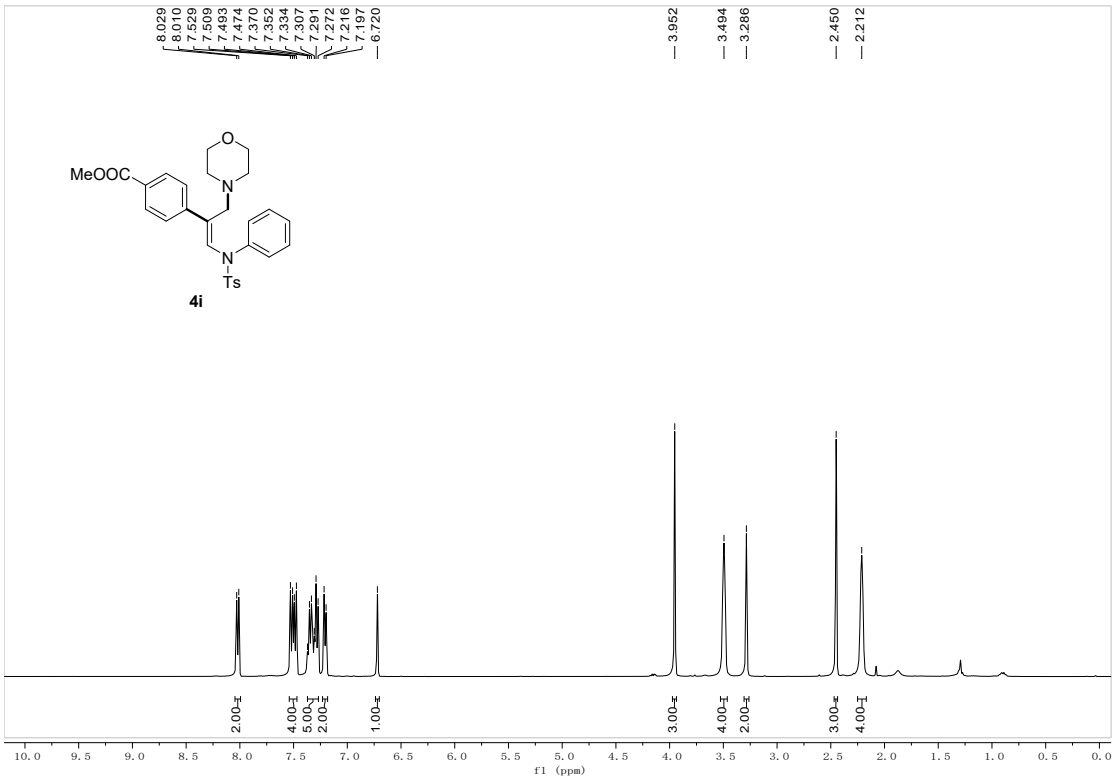
^{1}H NMR (400 MHz, $CDCl_3$)



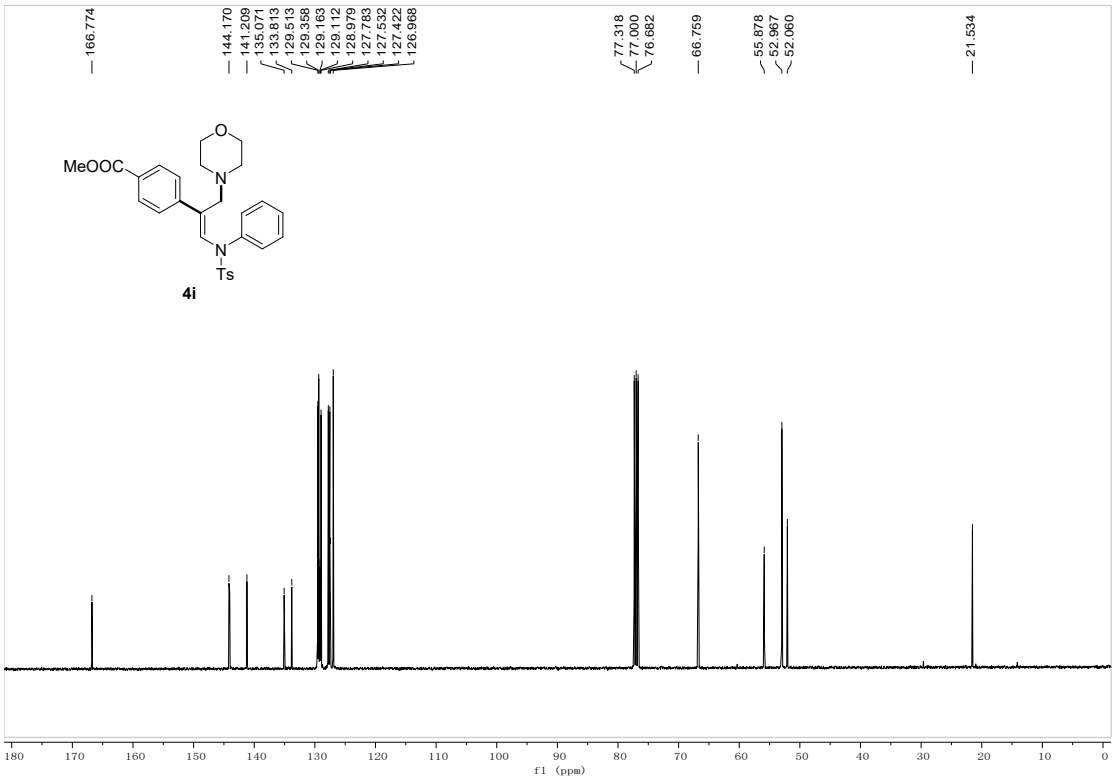
^{13}C NMR (100 MHz, $CDCl_3$)



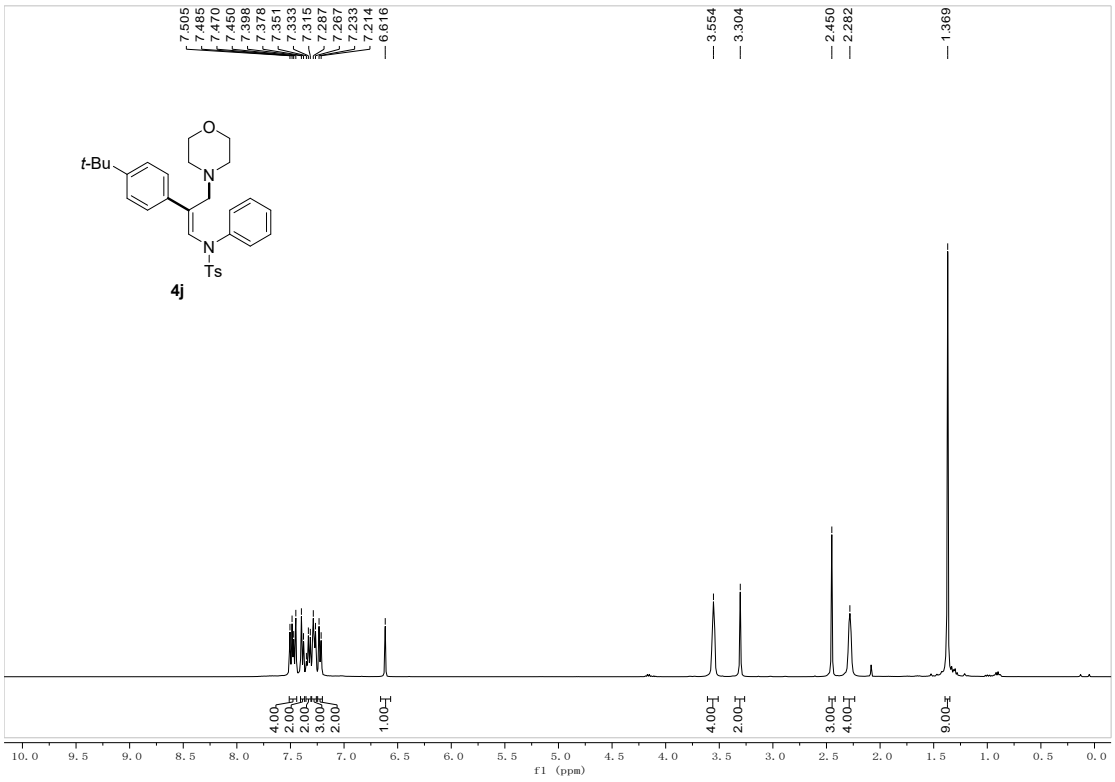
^{1}H NMR (400 MHz, $CDCl_3$)



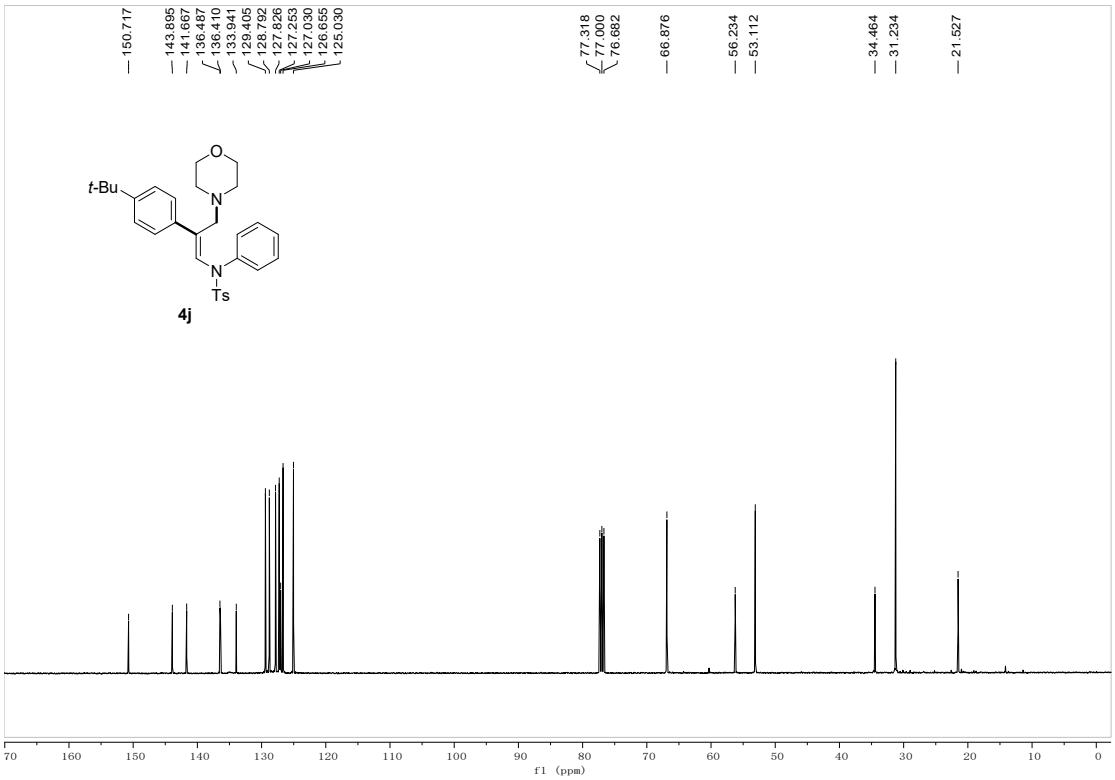
^{13}C NMR (100 MHz, $CDCl_3$)



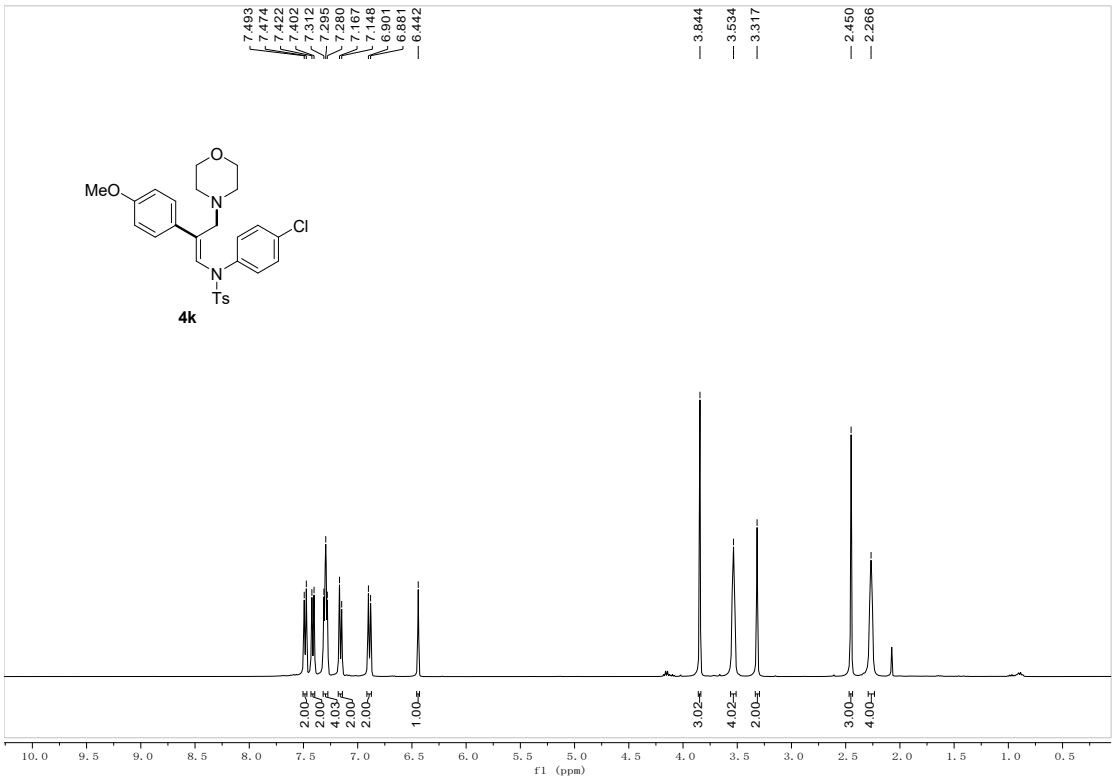
^{1}H NMR (400 MHz, $CDCl_3$)



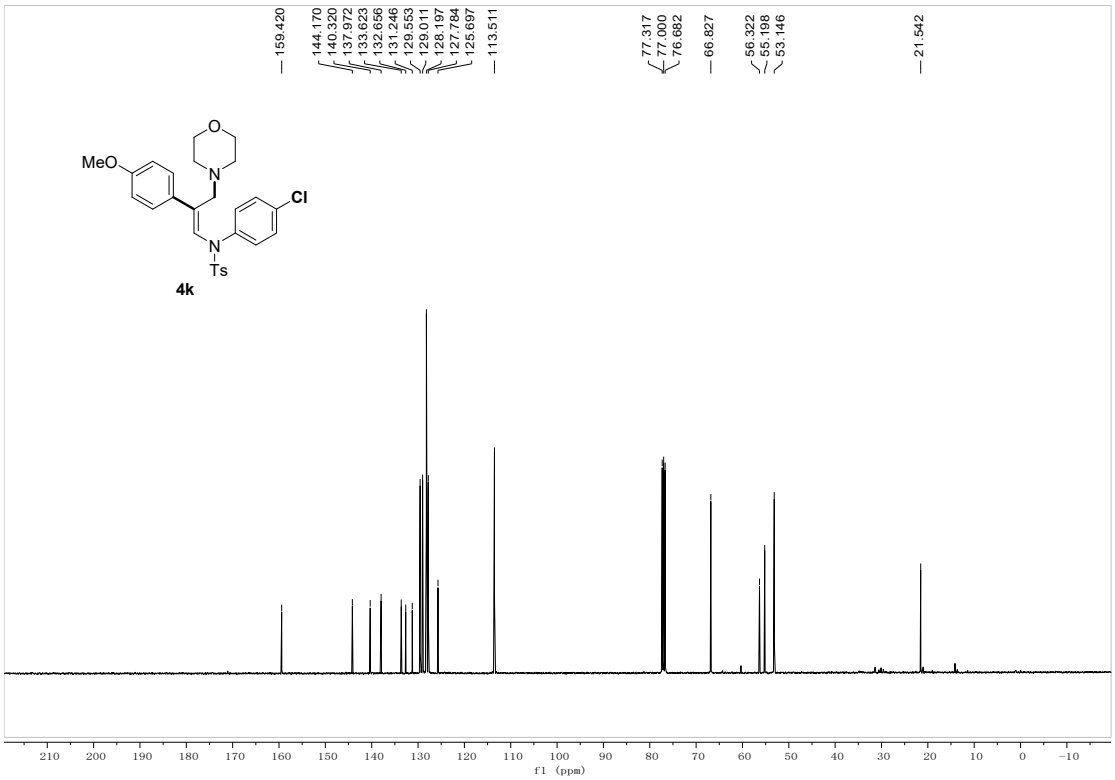
^{13}C NMR (100 MHz, $CDCl_3$)



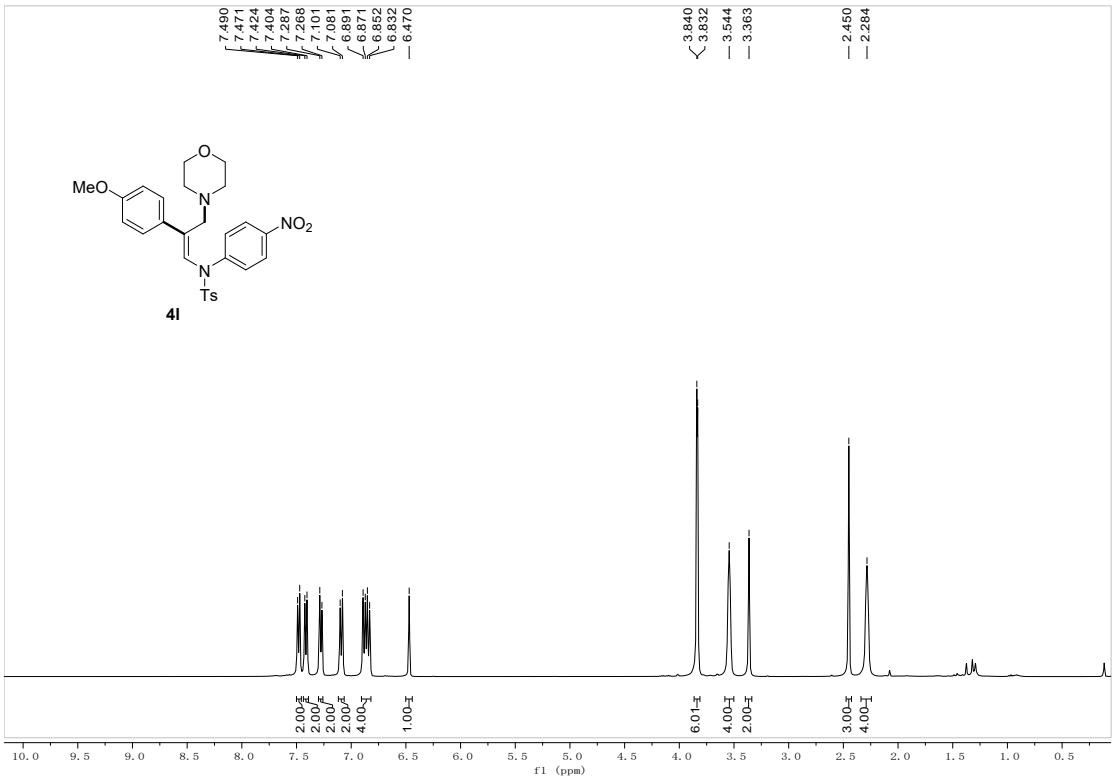
^{1}H NMR (400 MHz, $CDCl_3$)



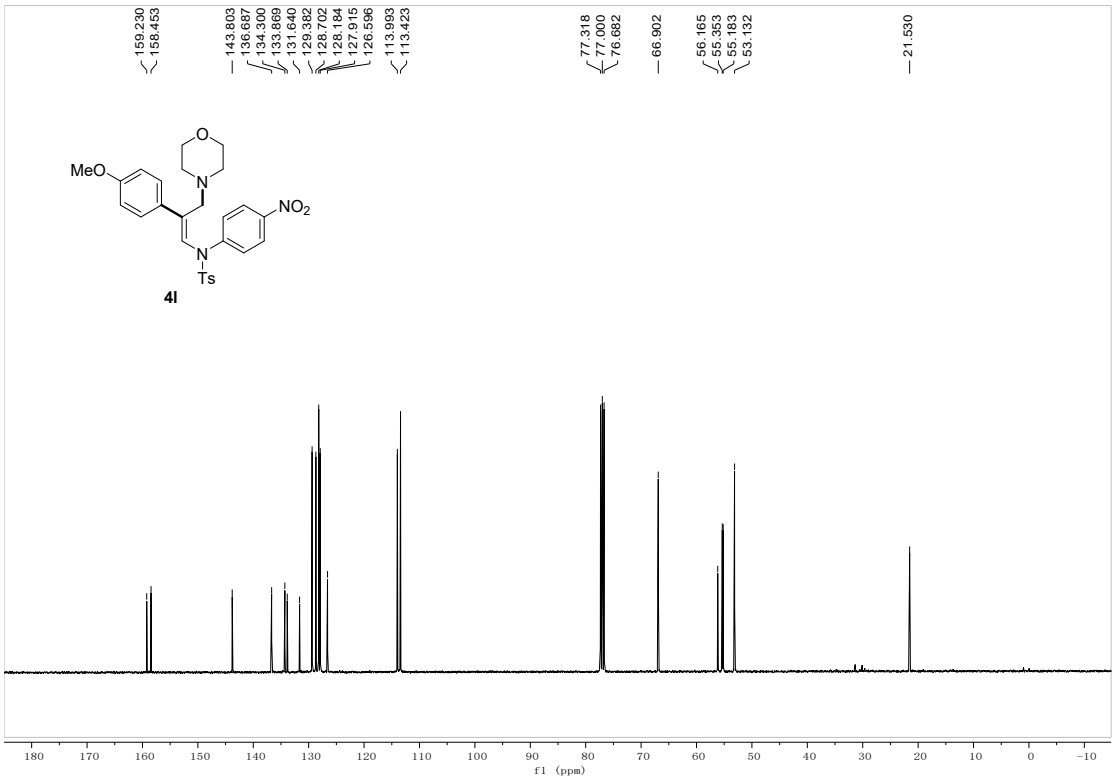
^{13}C NMR (100 MHz, $CDCl_3$)



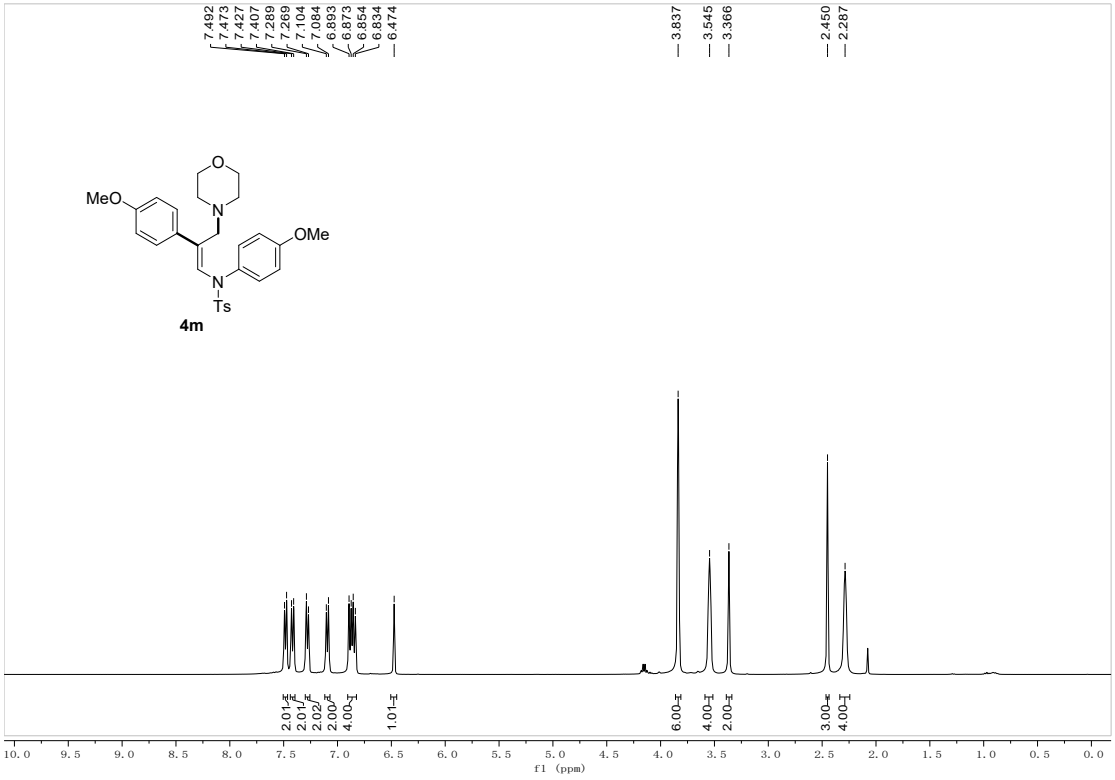
^{1}H NMR (400 MHz, $CDCl_3$)



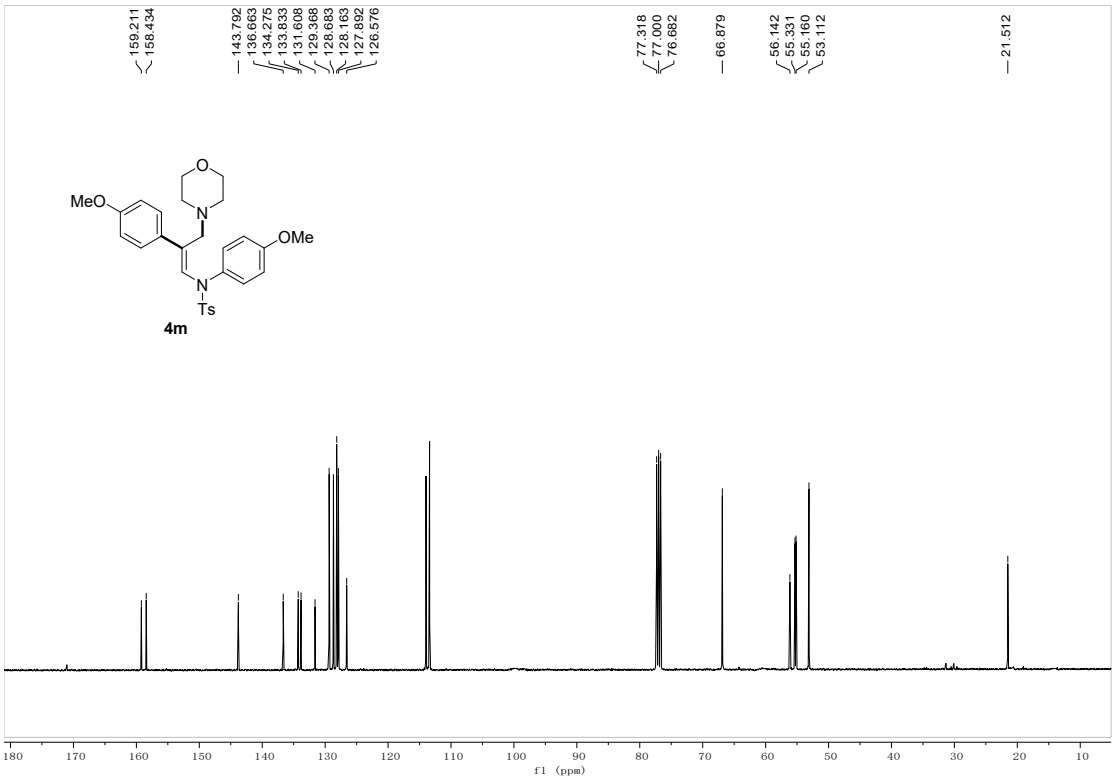
^{13}C NMR (100 MHz, $CDCl_3$)



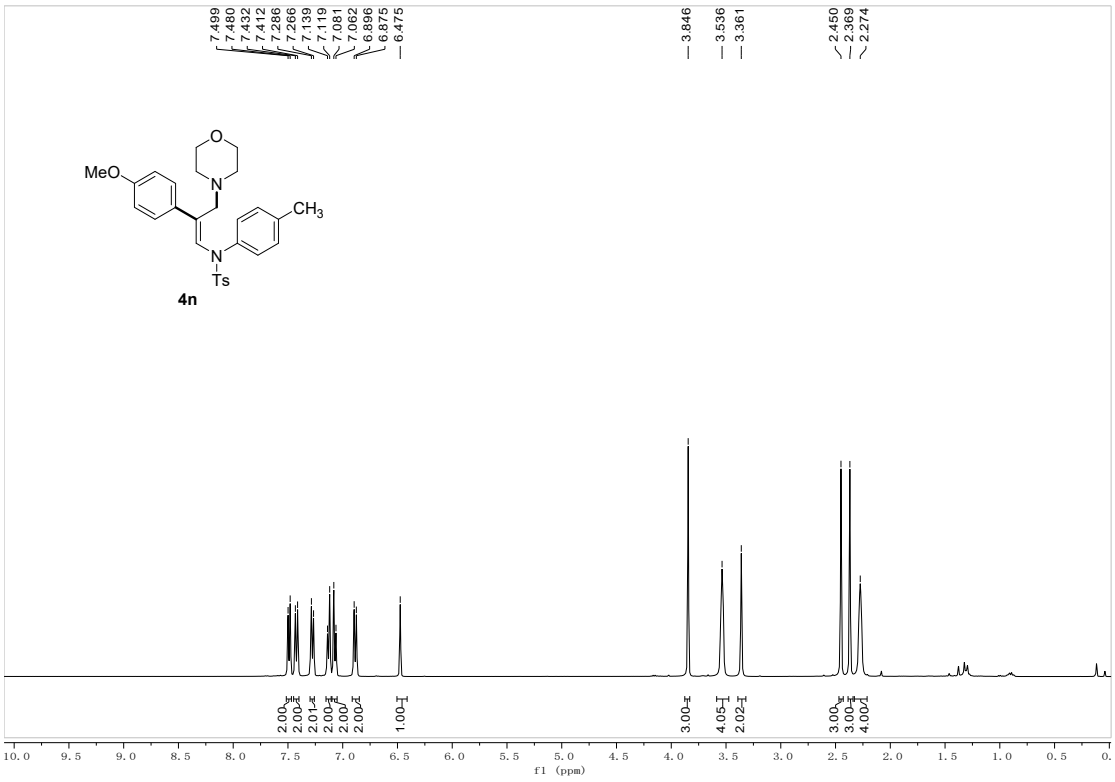
^{1}H NMR (400 MHz, $CDCl_3$)



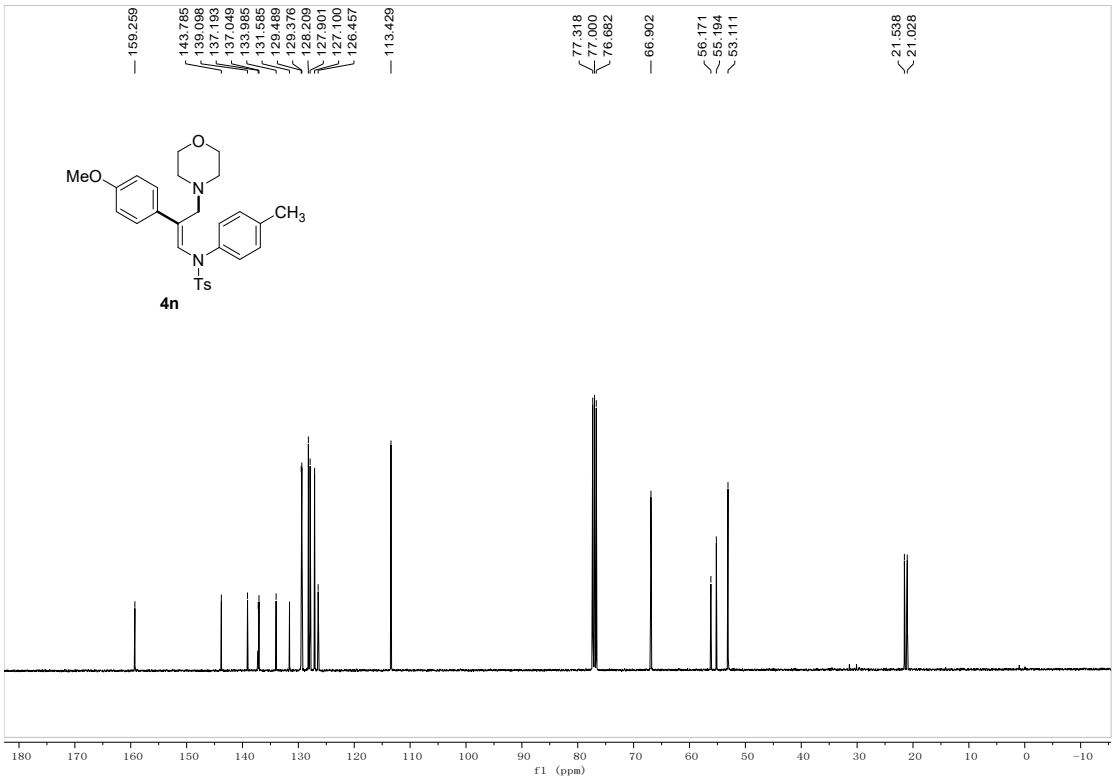
^{13}C NMR (100 MHz, $CDCl_3$)



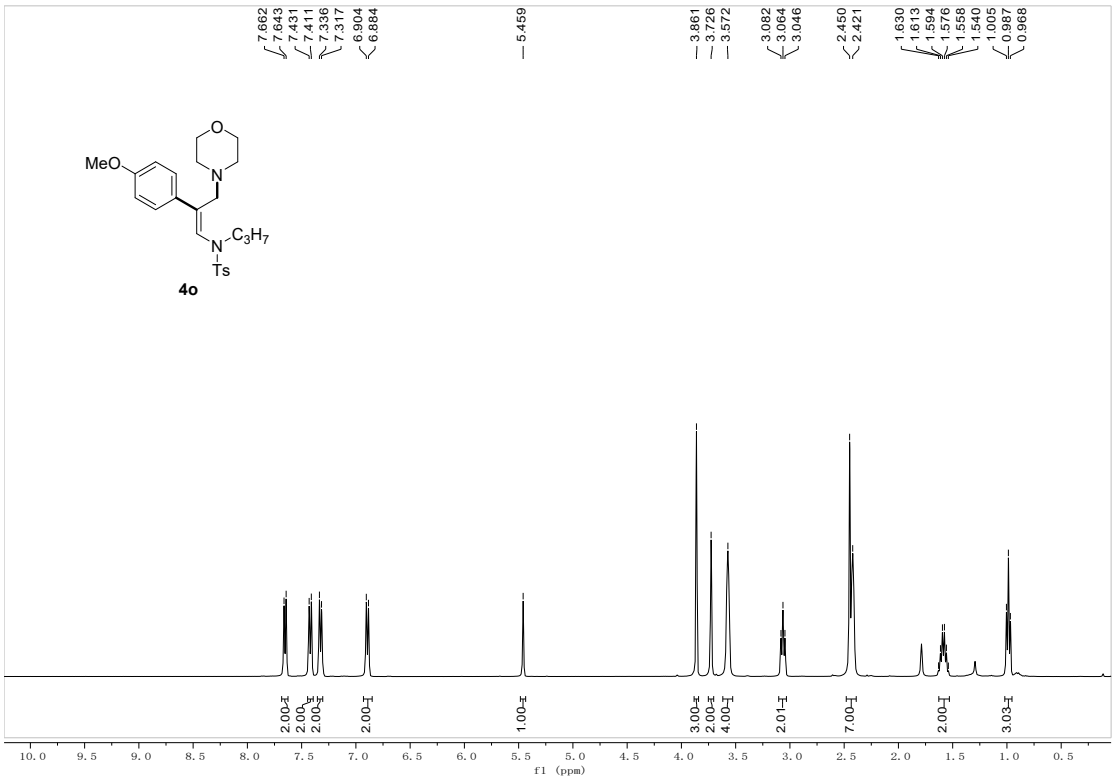
^{1}H NMR (400 MHz, $CDCl_3$)



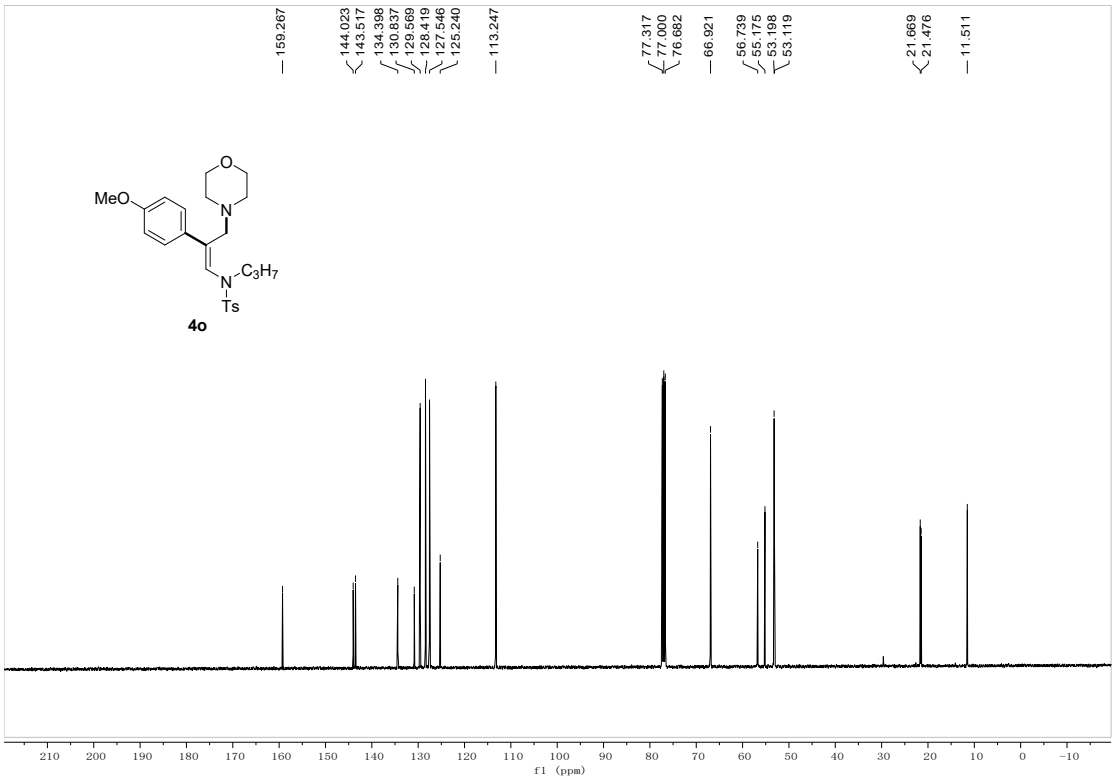
^{13}C NMR (100 MHz, $CDCl_3$)



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



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



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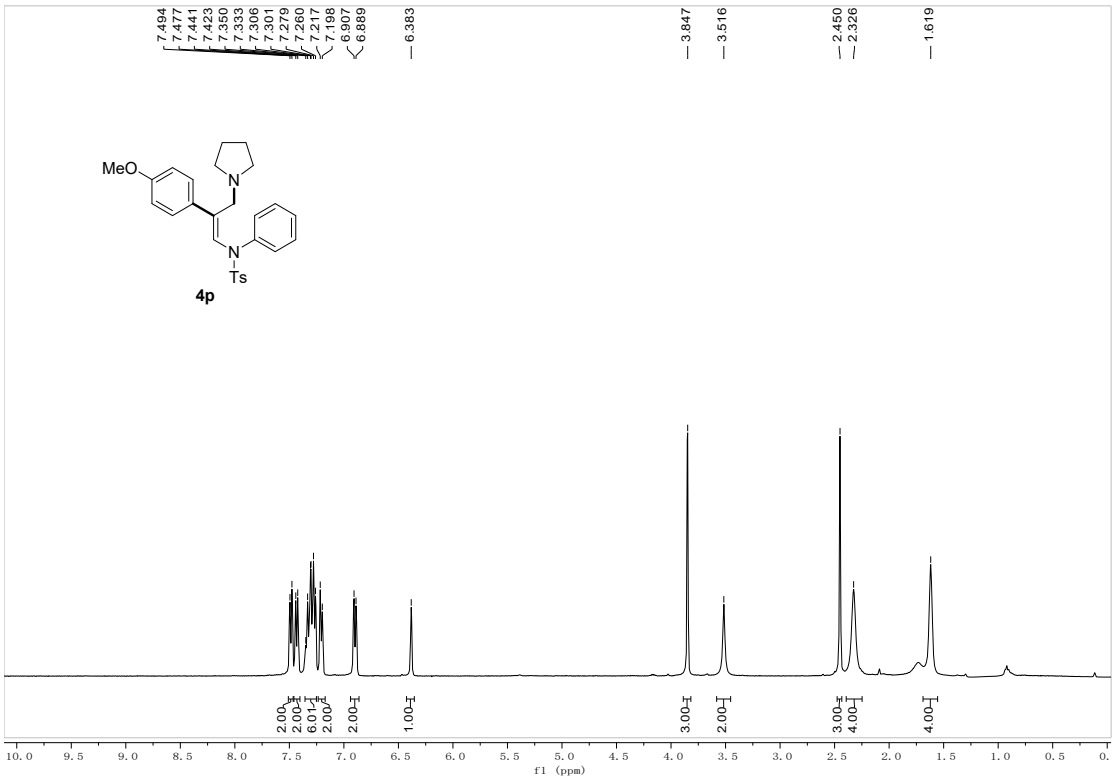
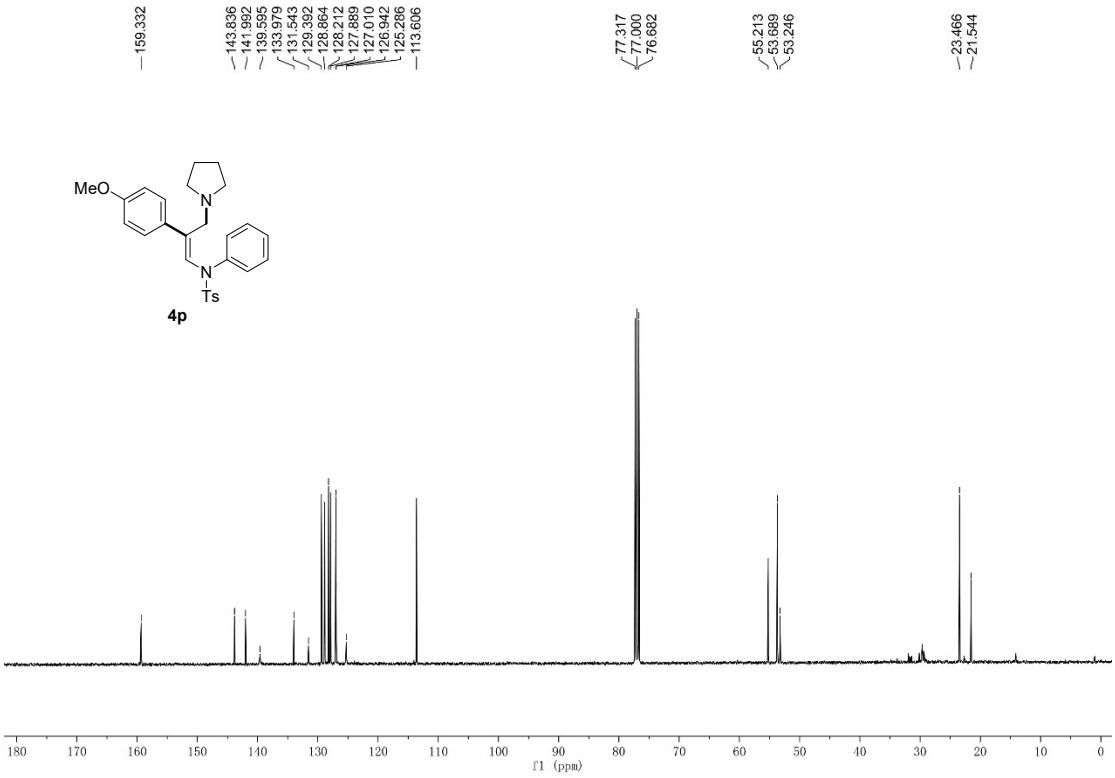
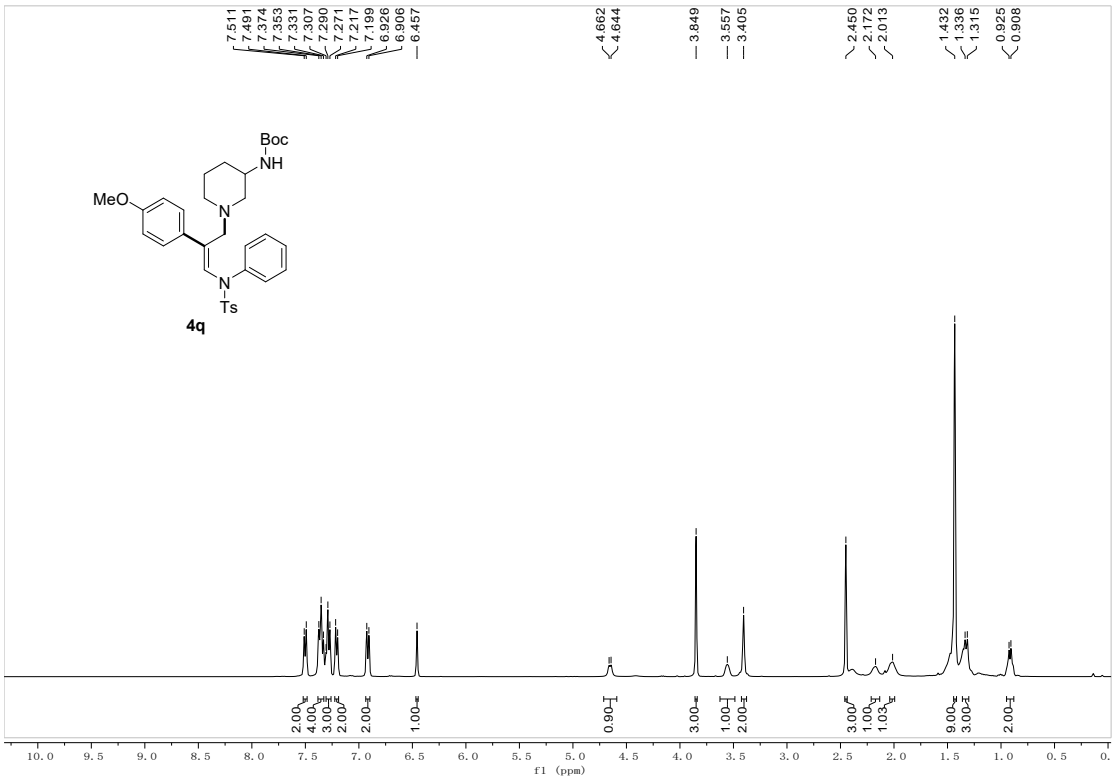


^{13}C NMR (100 MHz, $CDCl_3$)



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



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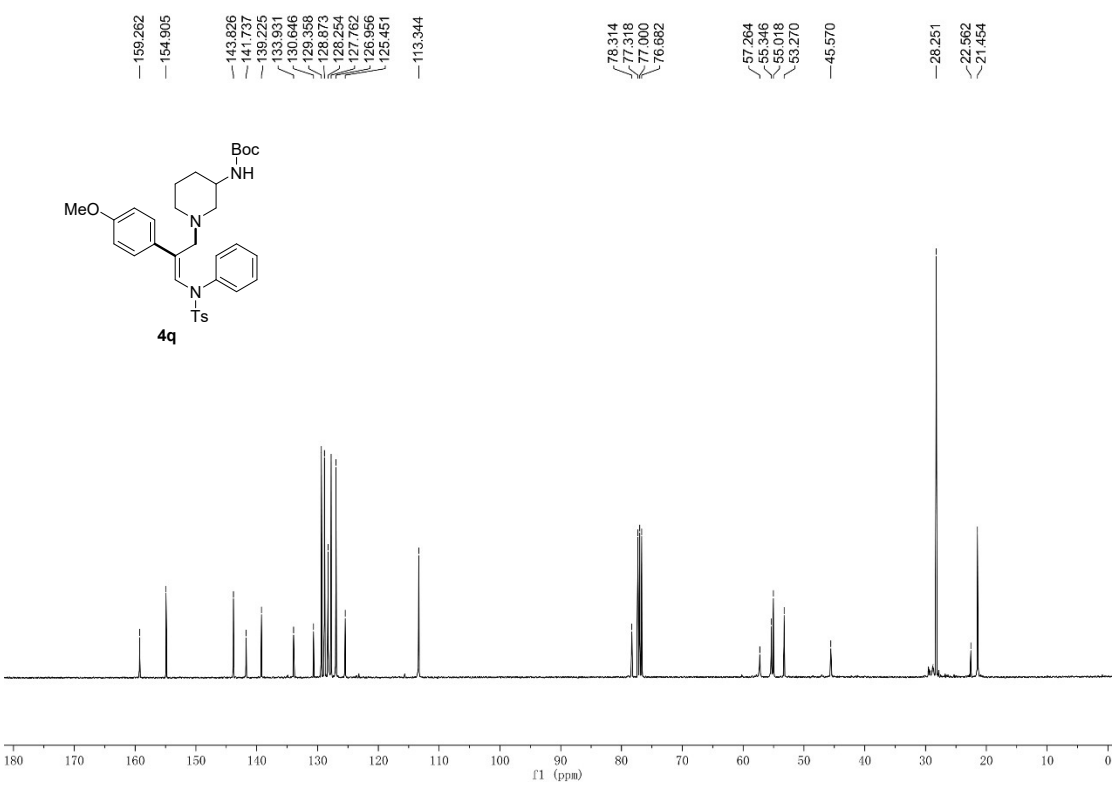
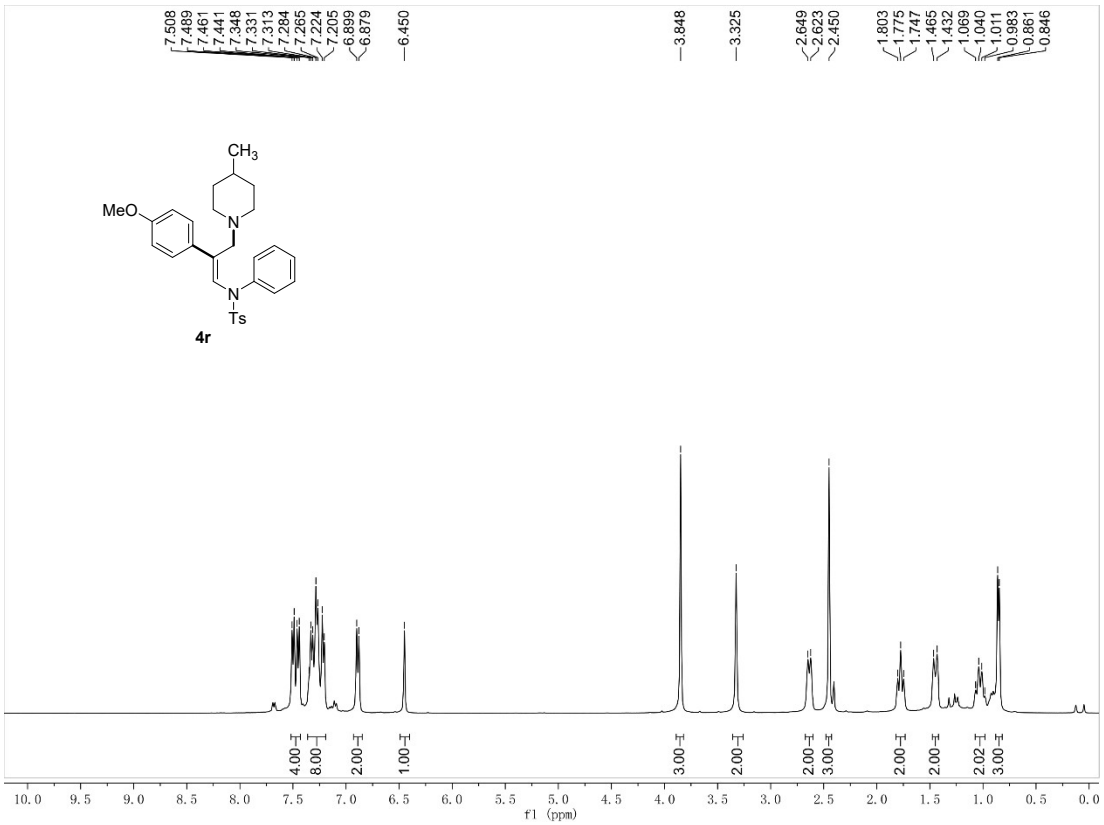
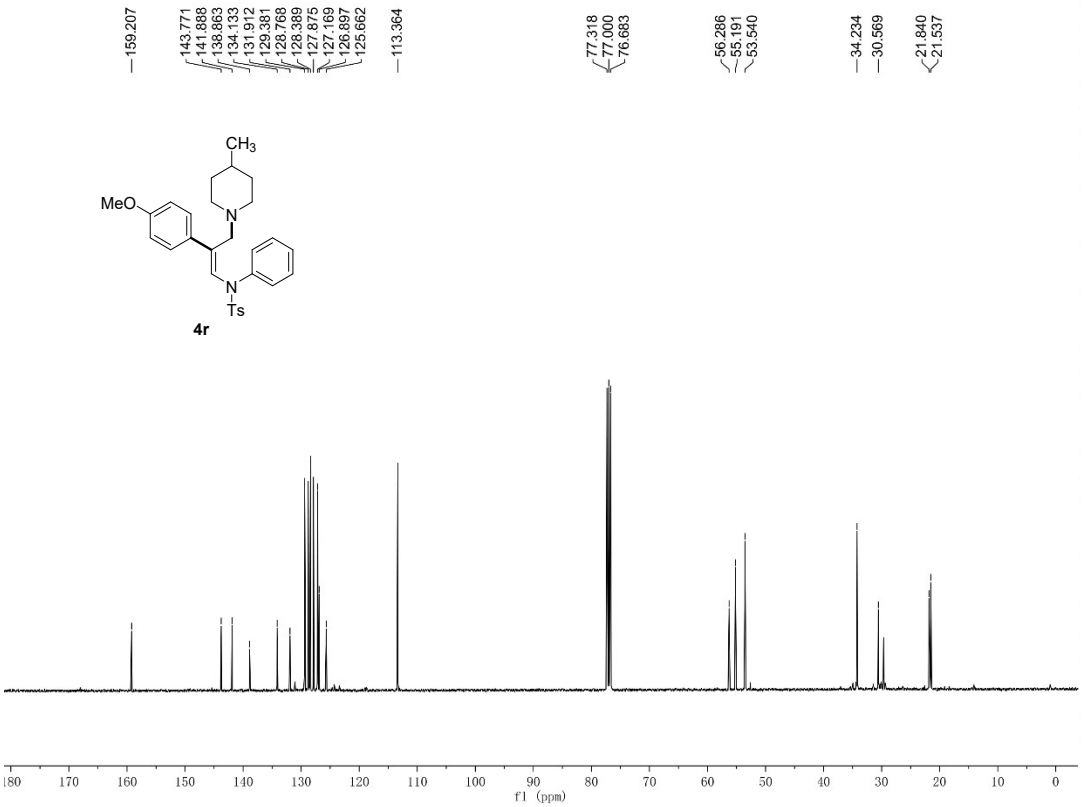


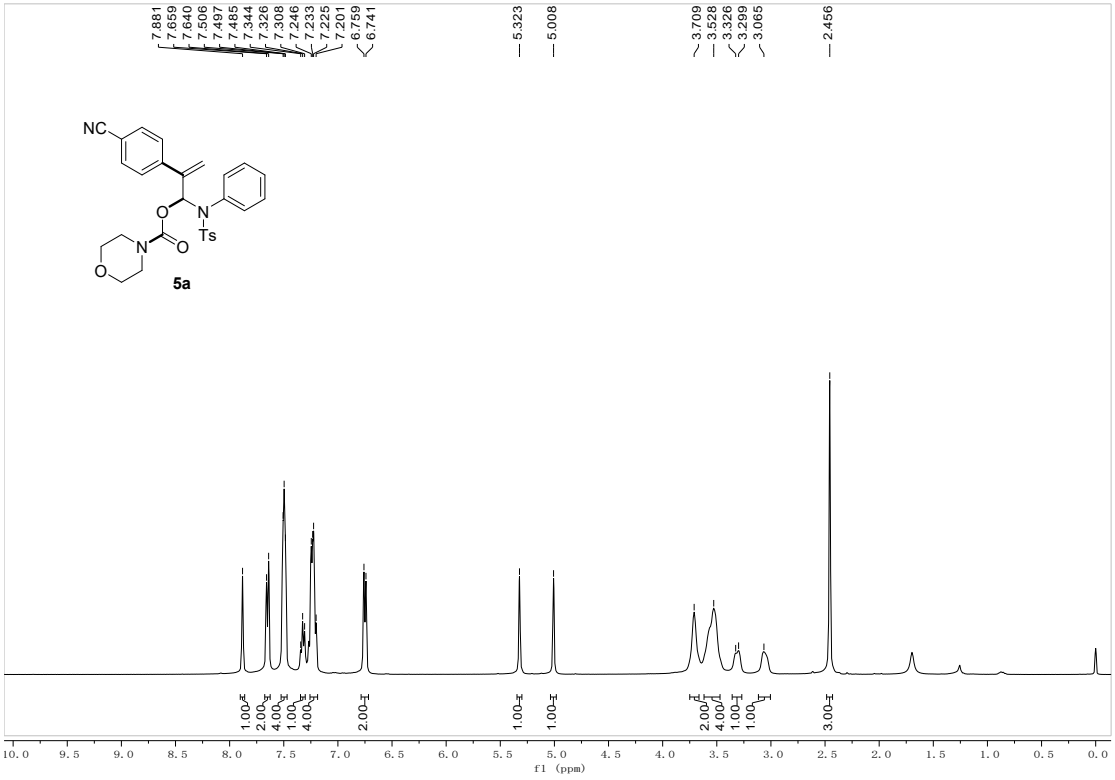
^{1}H NMR (400 MHz, $CDCl_3$)



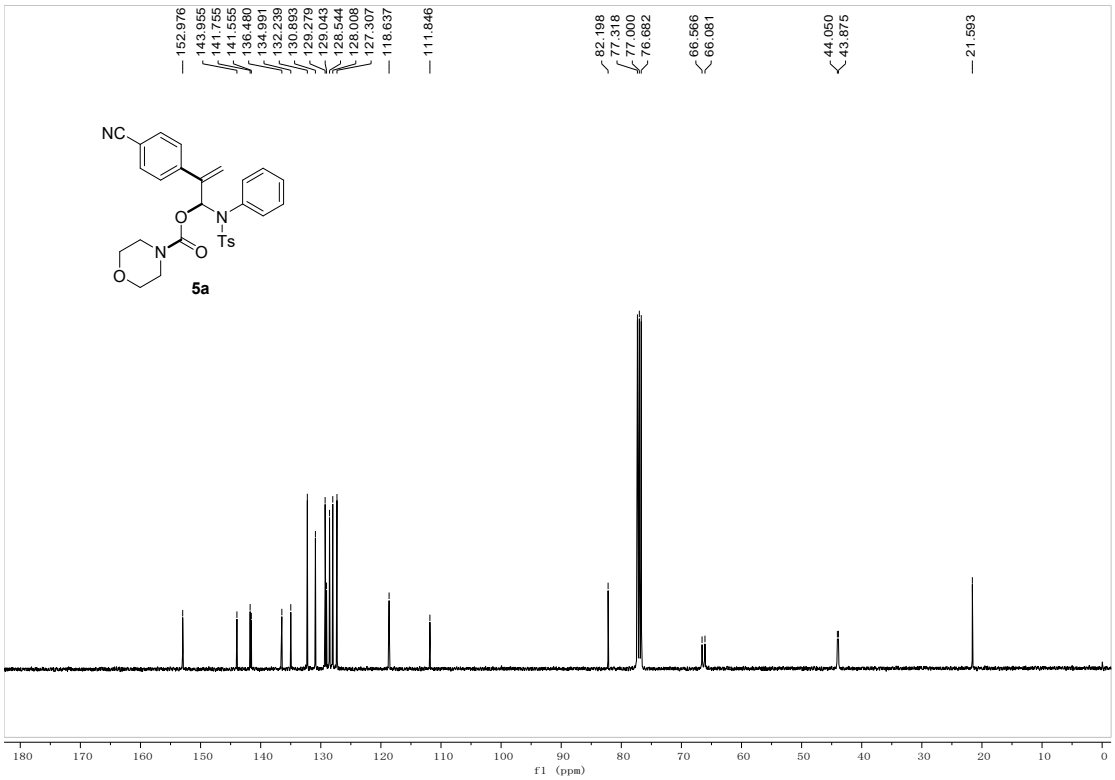
^{13}C NMR (100 MHz, $CDCl_3$)



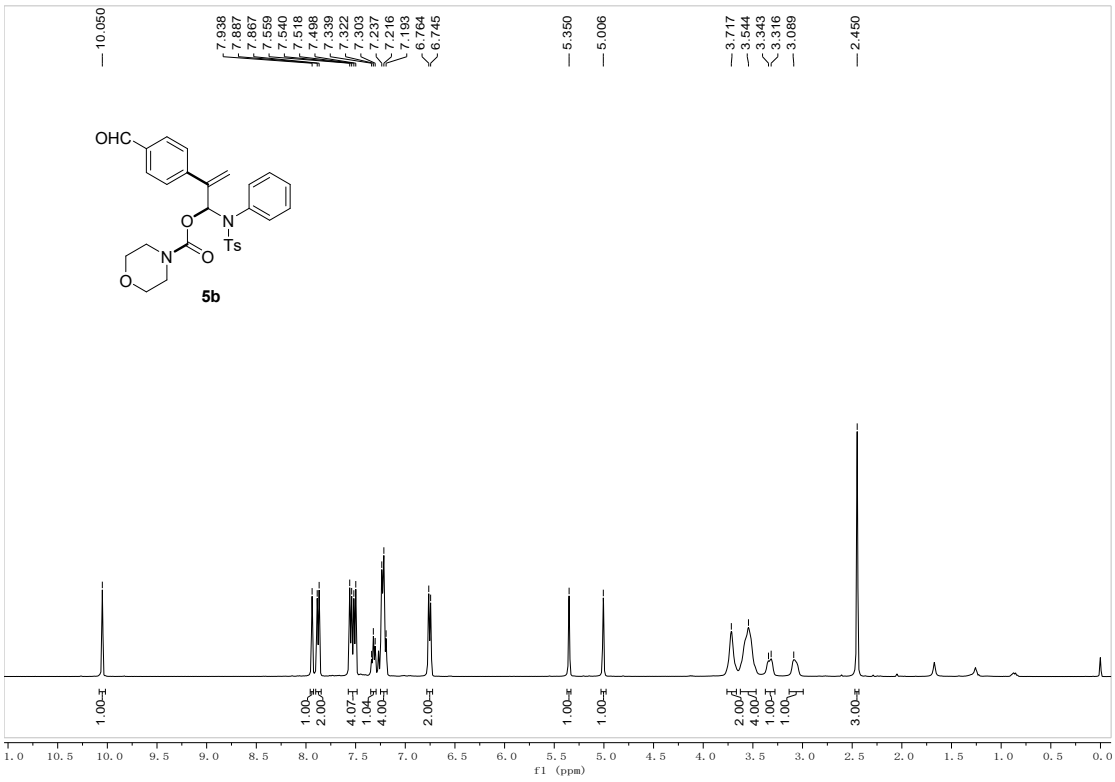
^{1}H NMR (400 MHz, $CDCl_3$)



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



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



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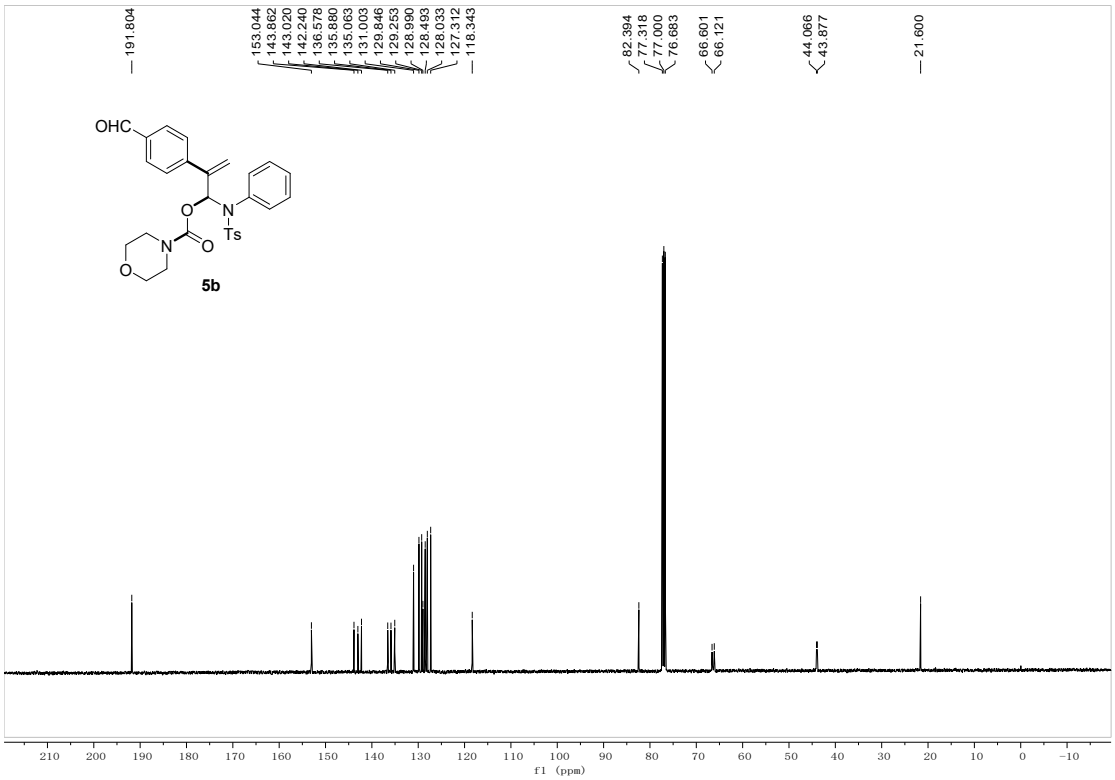

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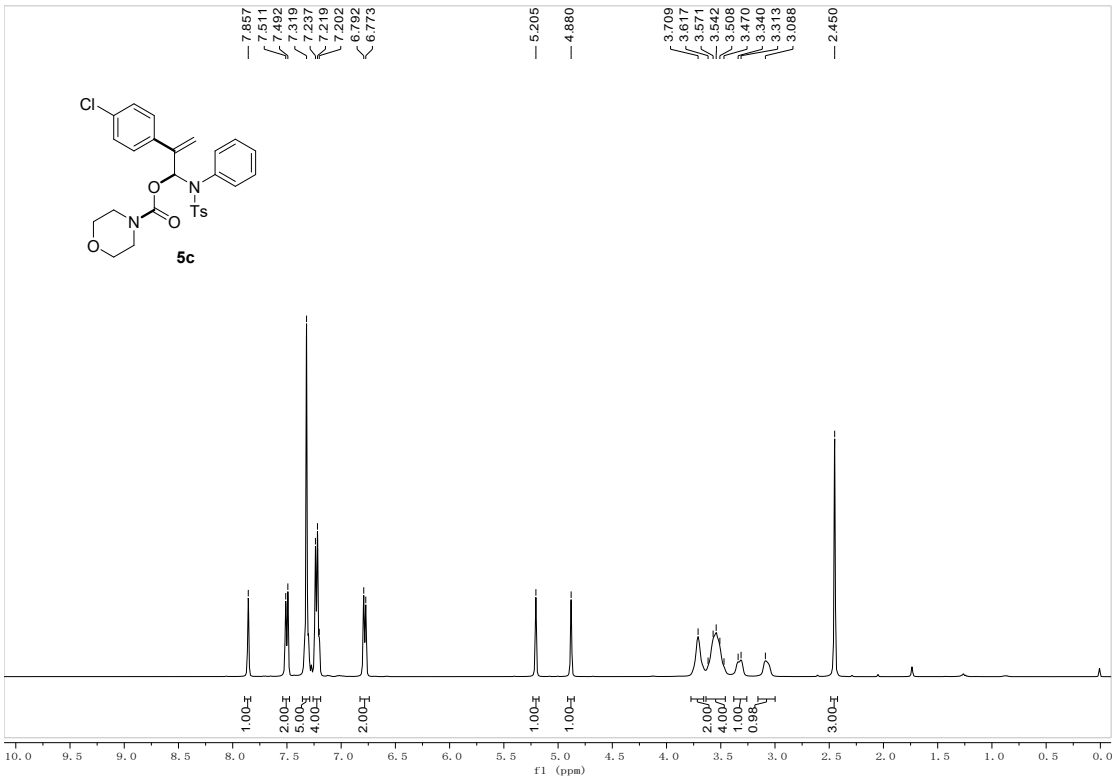

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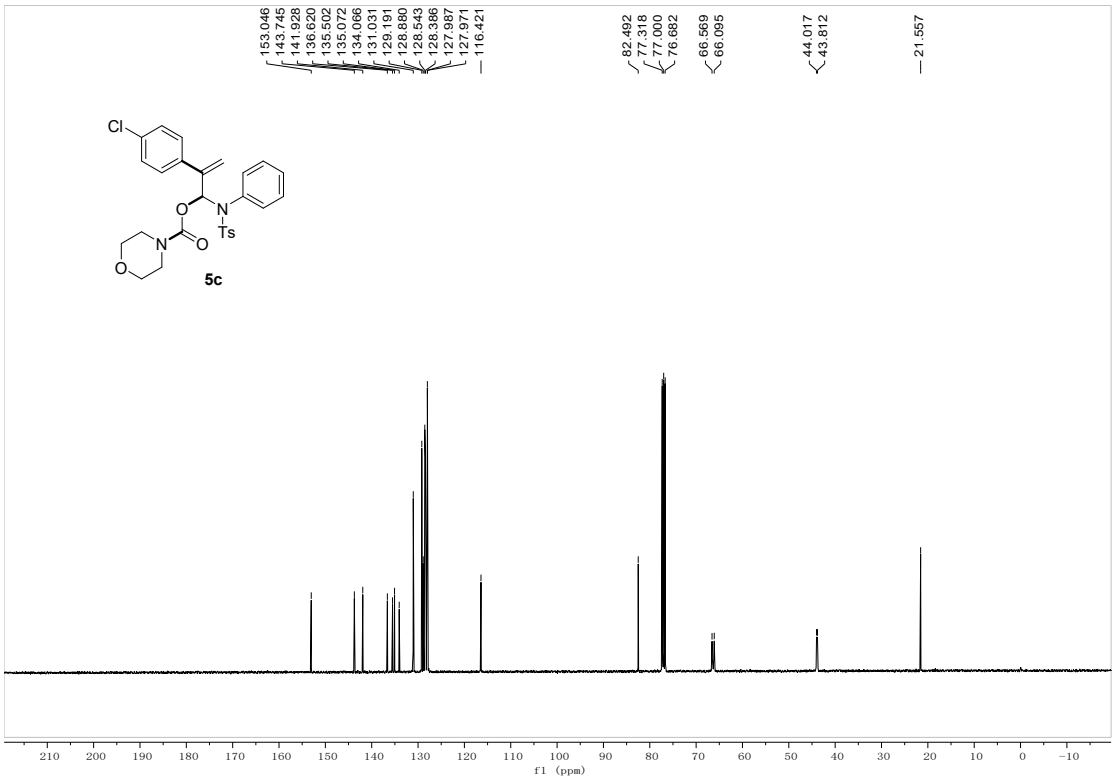
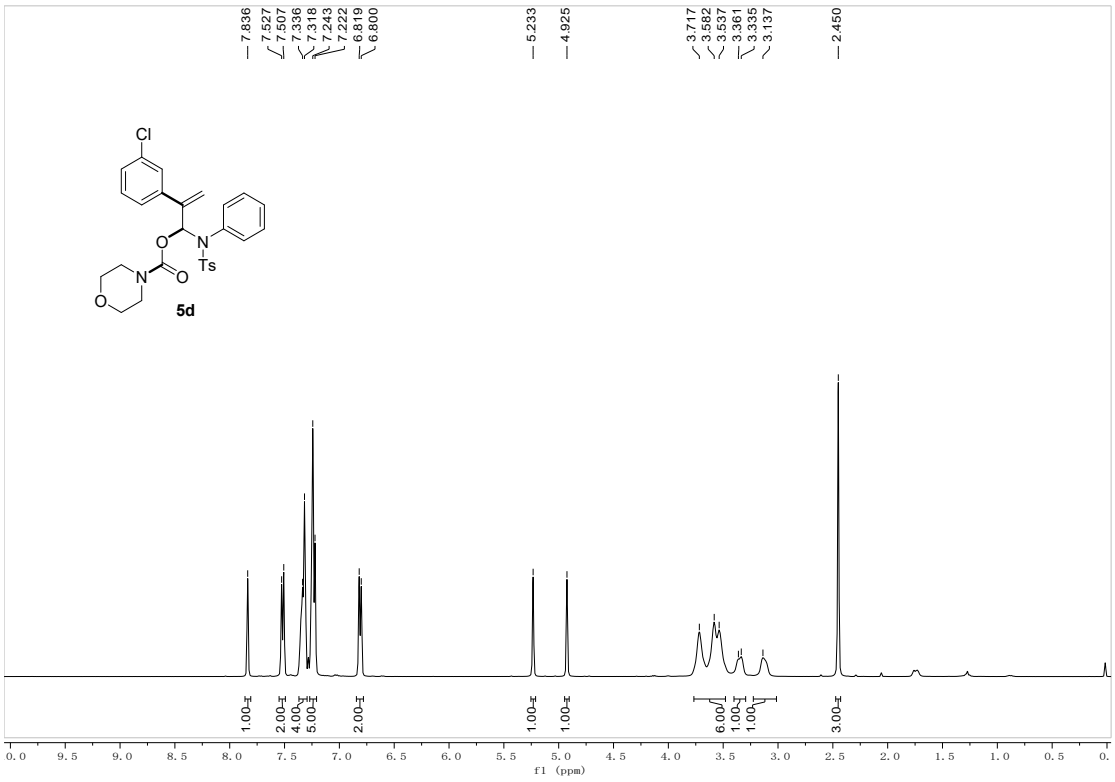
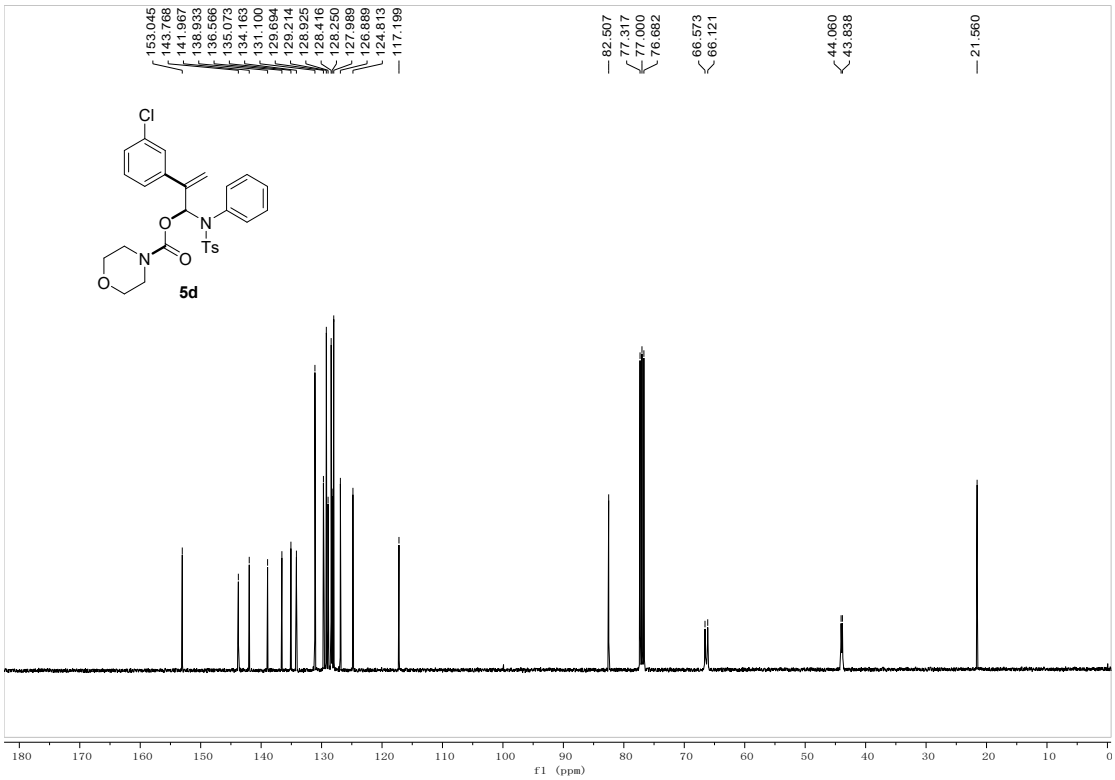


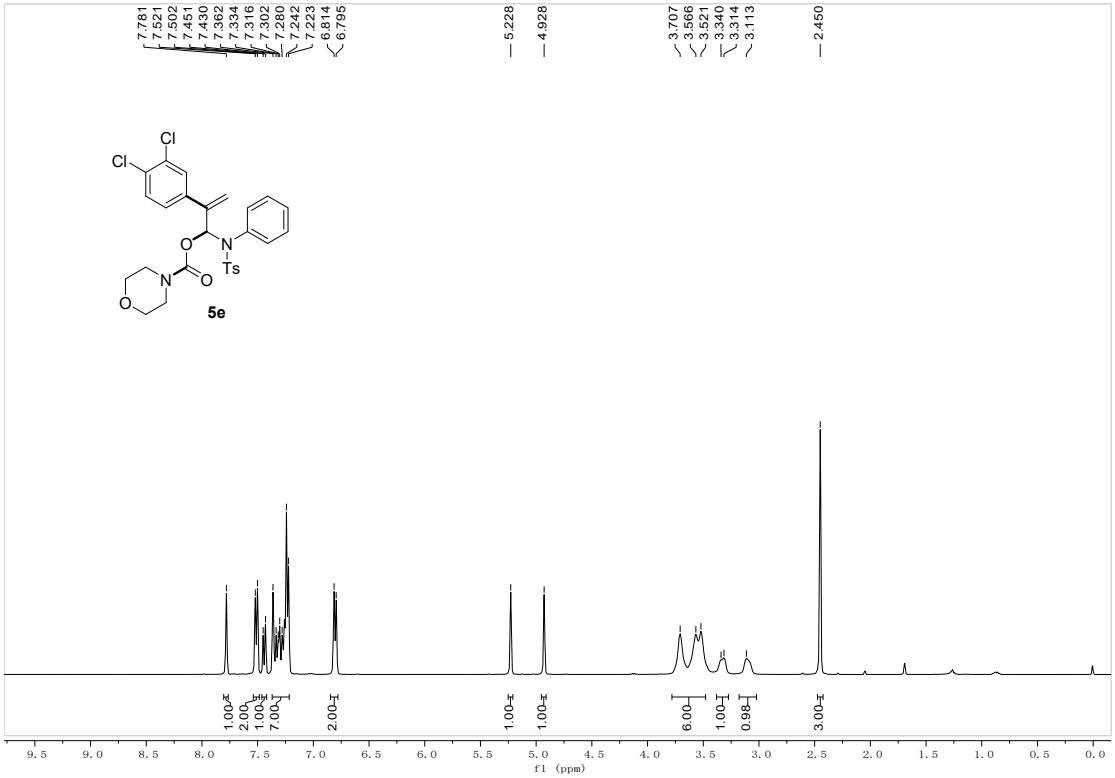
^{1}H NMR (400 MHz, $CDCl_3$)



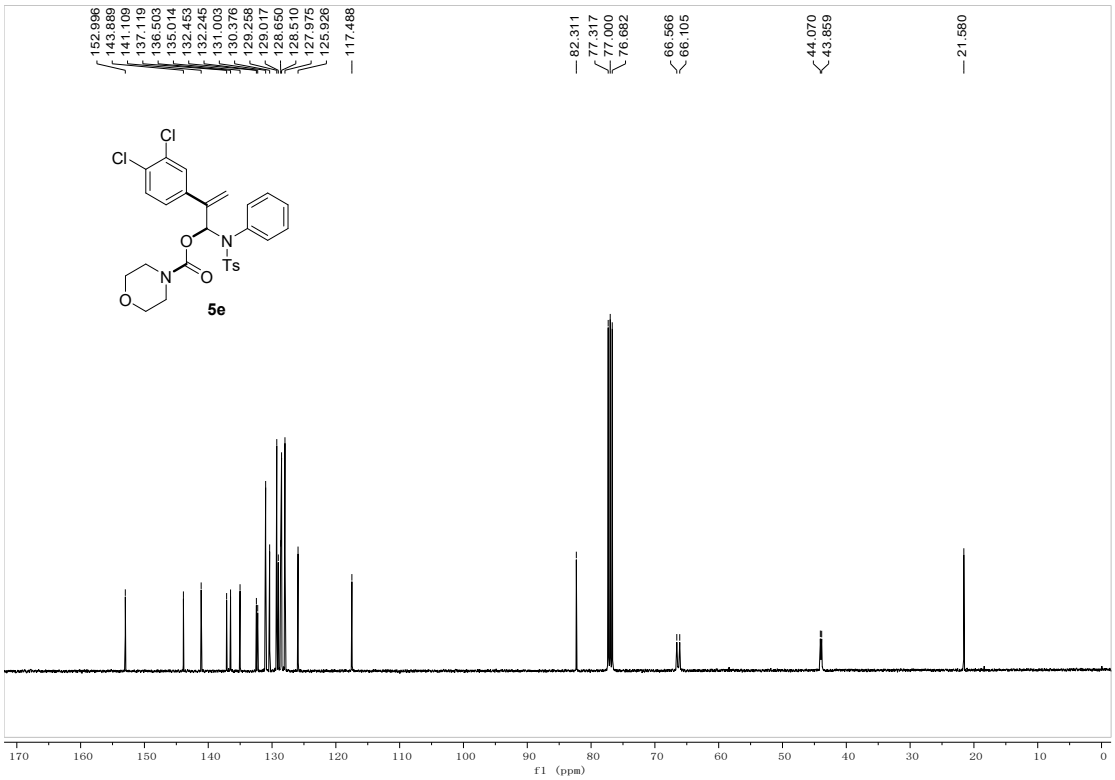
^{13}C NMR (100 MHz, $CDCl_3$)



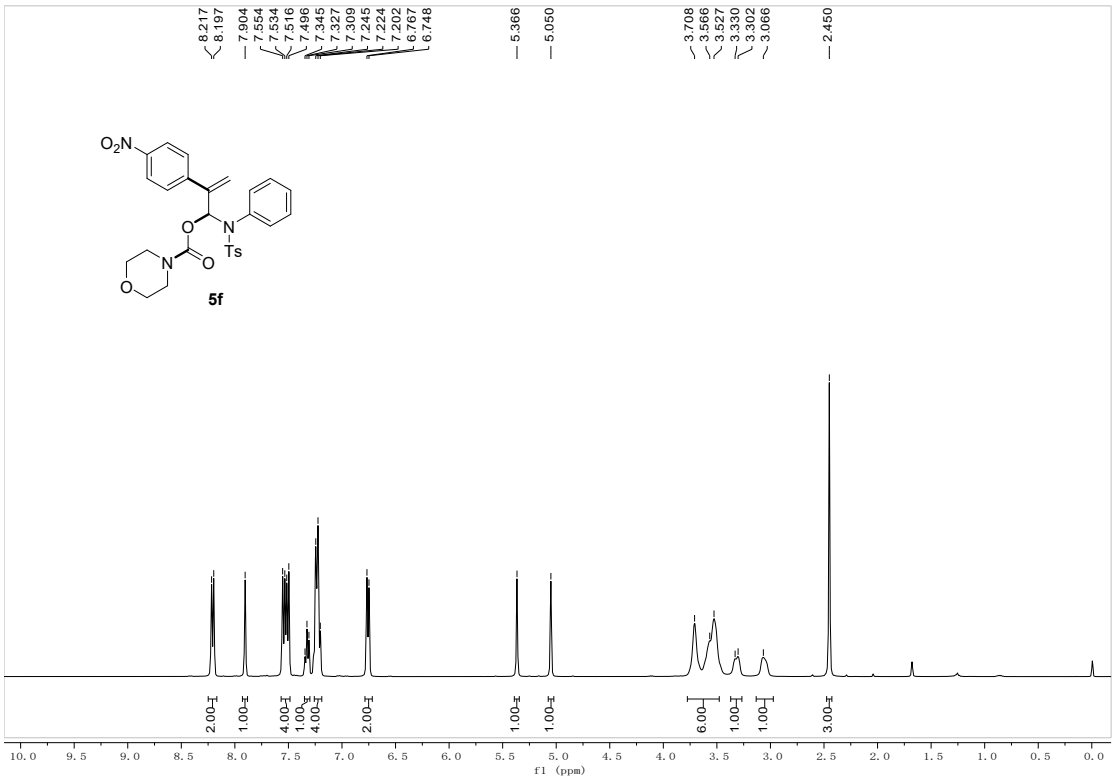
^{1}H NMR (400 MHz, $CDCl_3$)



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



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



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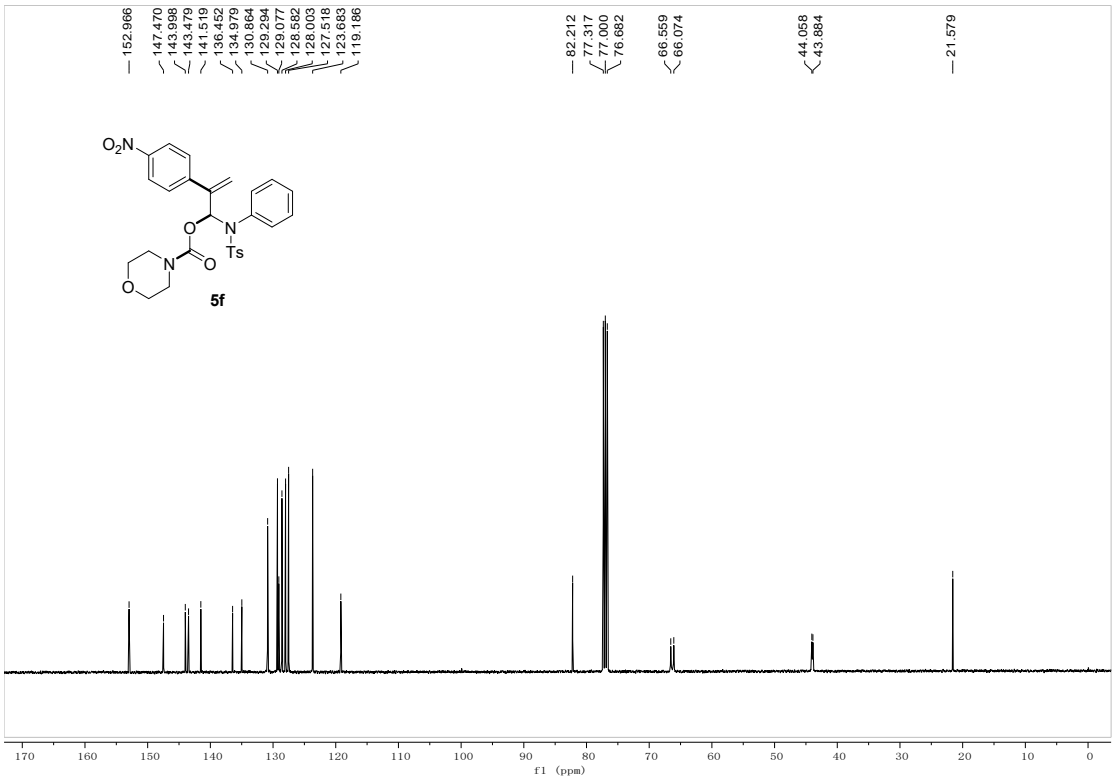
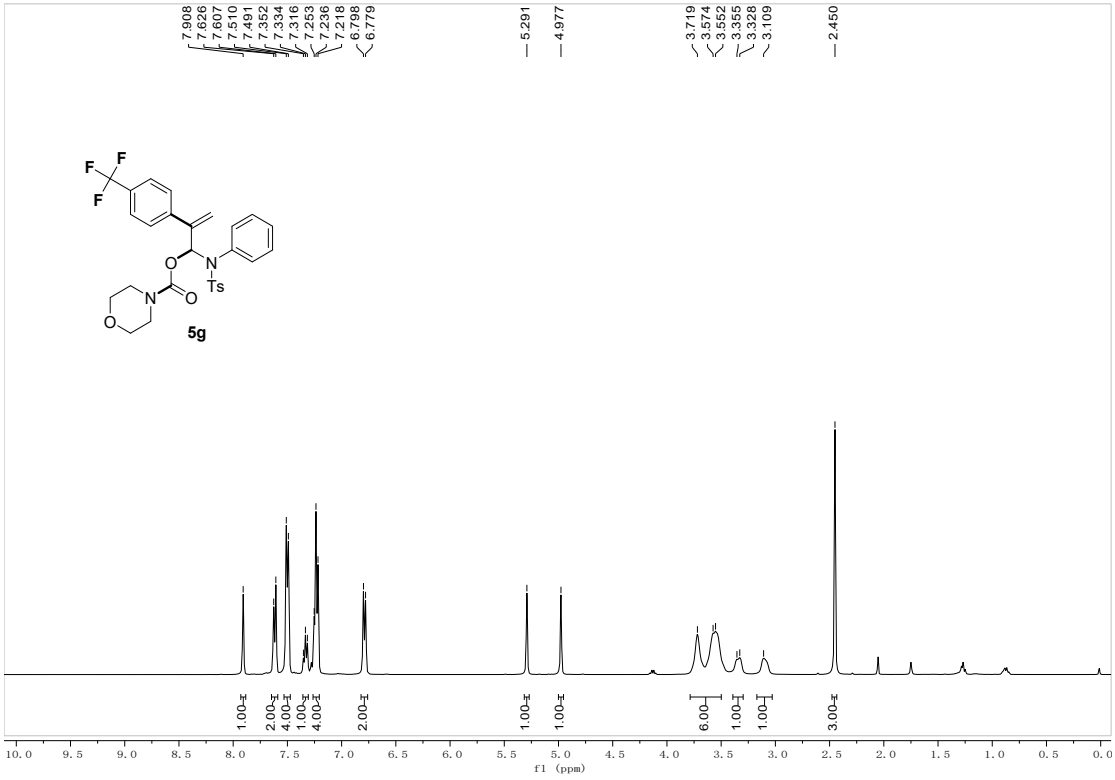
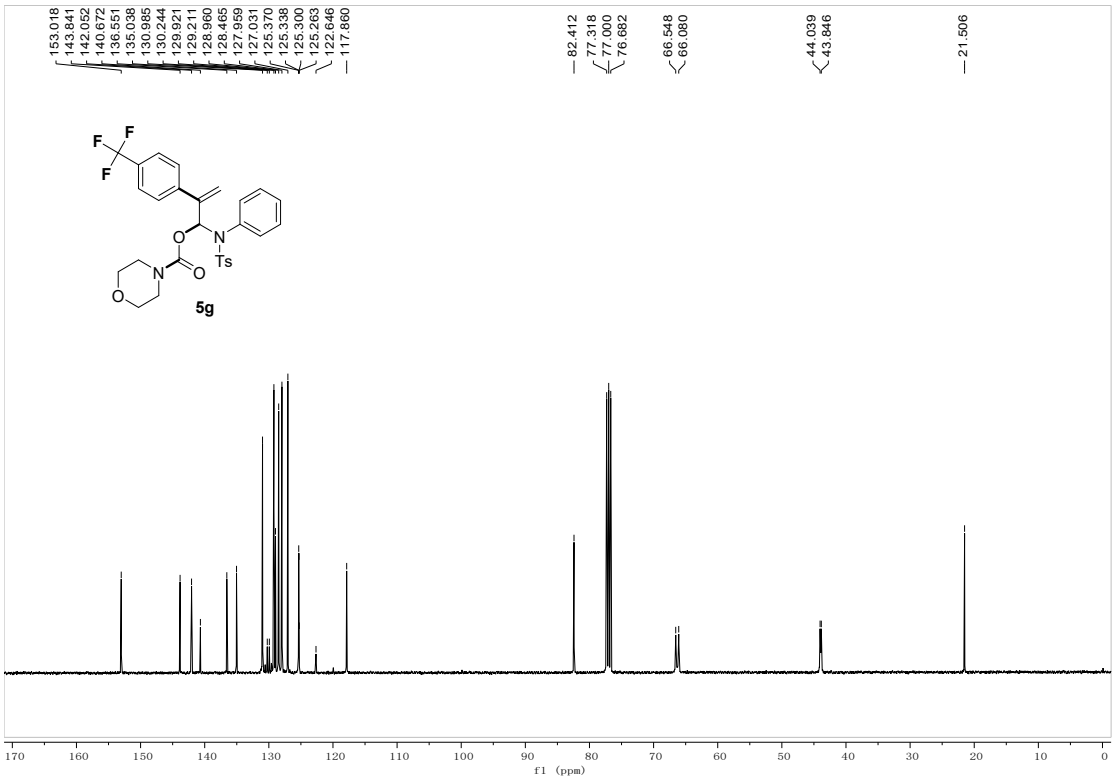


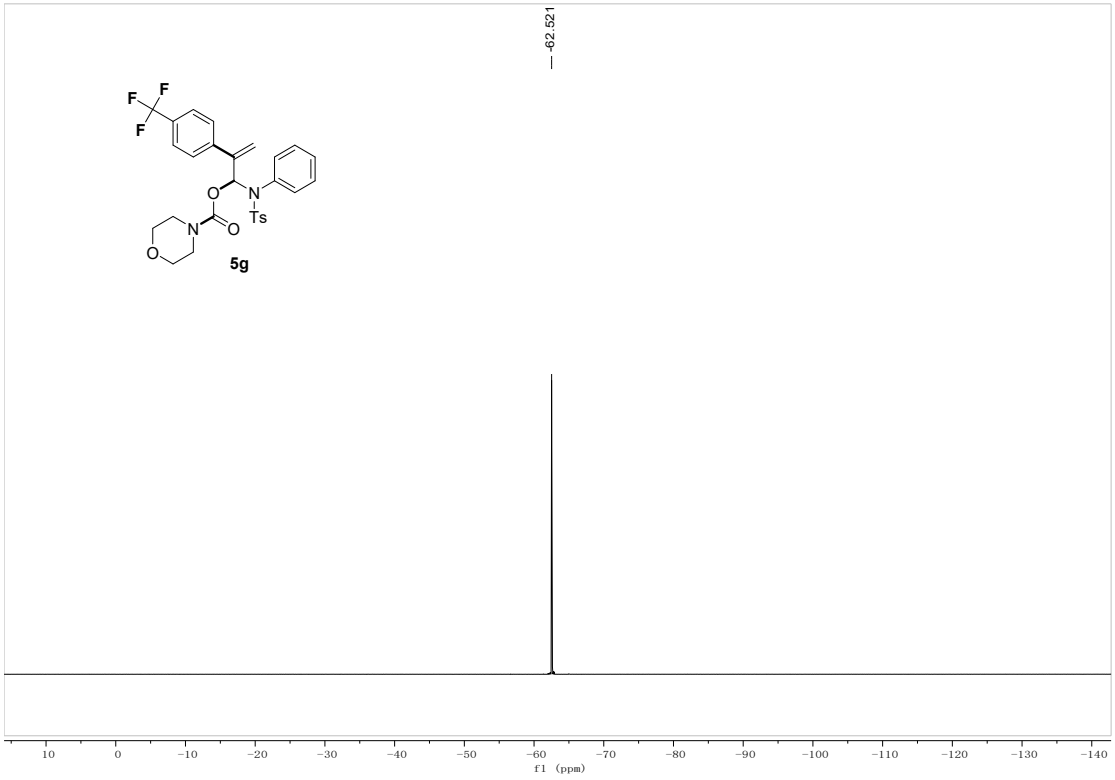
^{1}H NMR (400 MHz, $CDCl_3$)



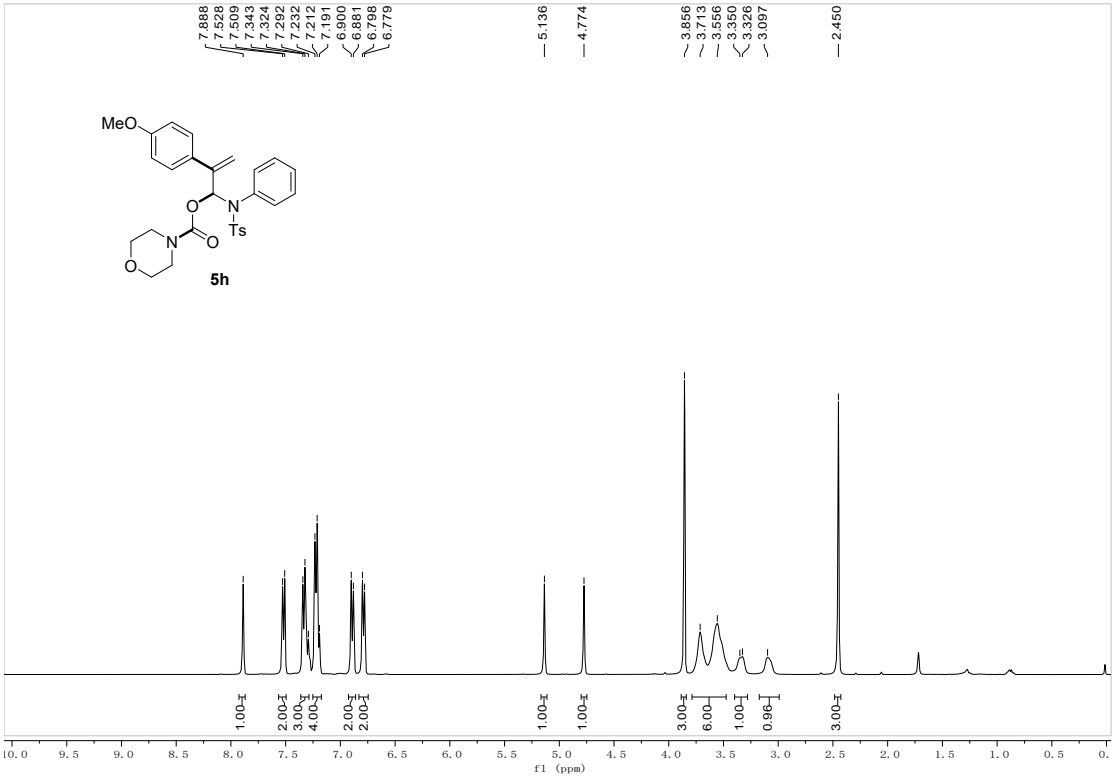
^{13}C NMR (100 MHz, $CDCl_3$)



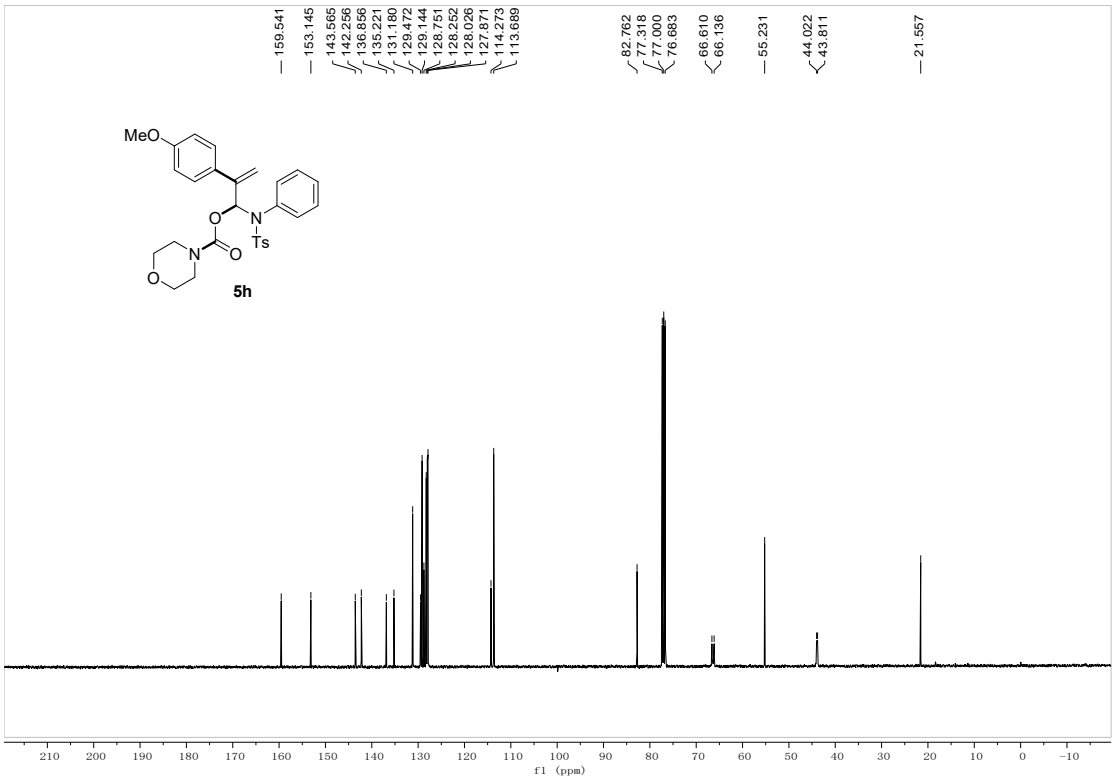
^{19}F NMR (376 MHz, $CDCl_3$)



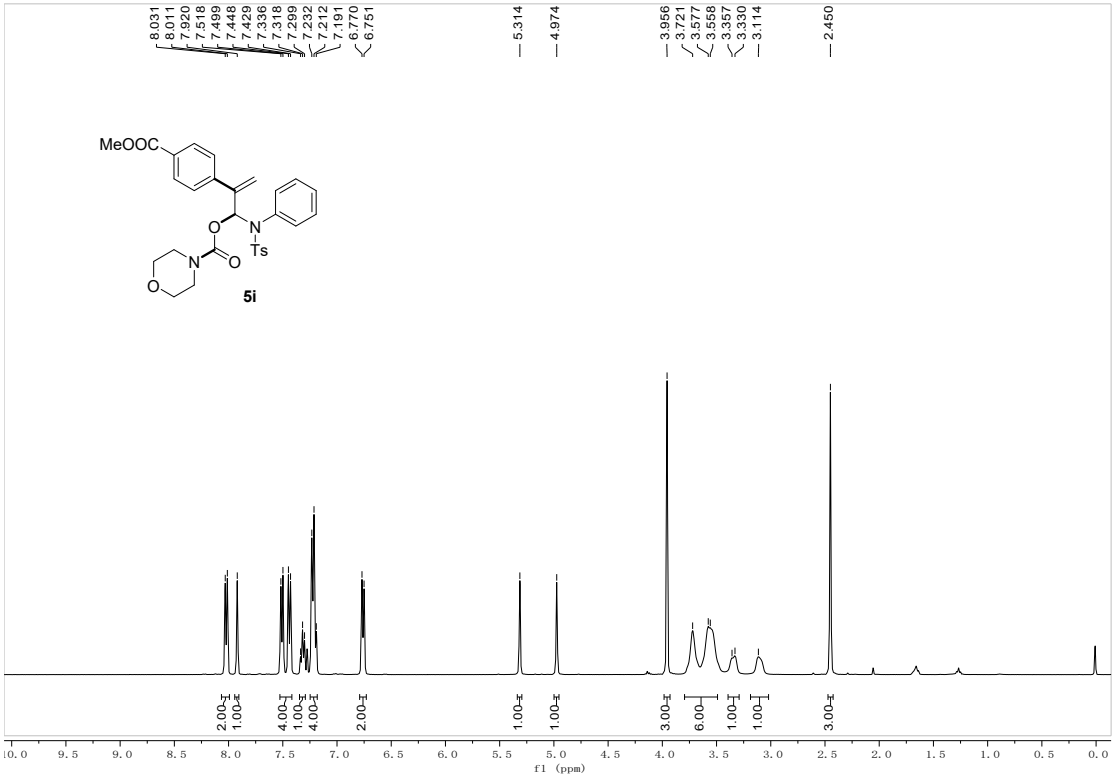
^{1}H NMR (400 MHz, $CDCl_3$)



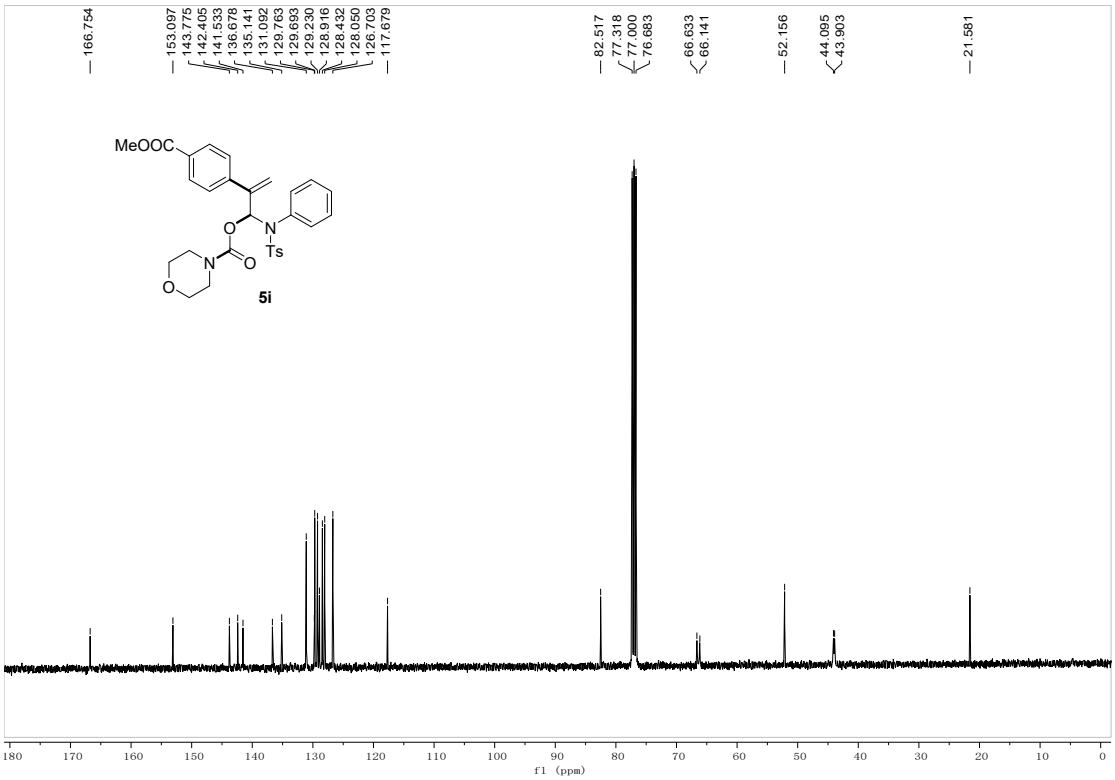
^{13}C NMR (100 MHz, $CDCl_3$)



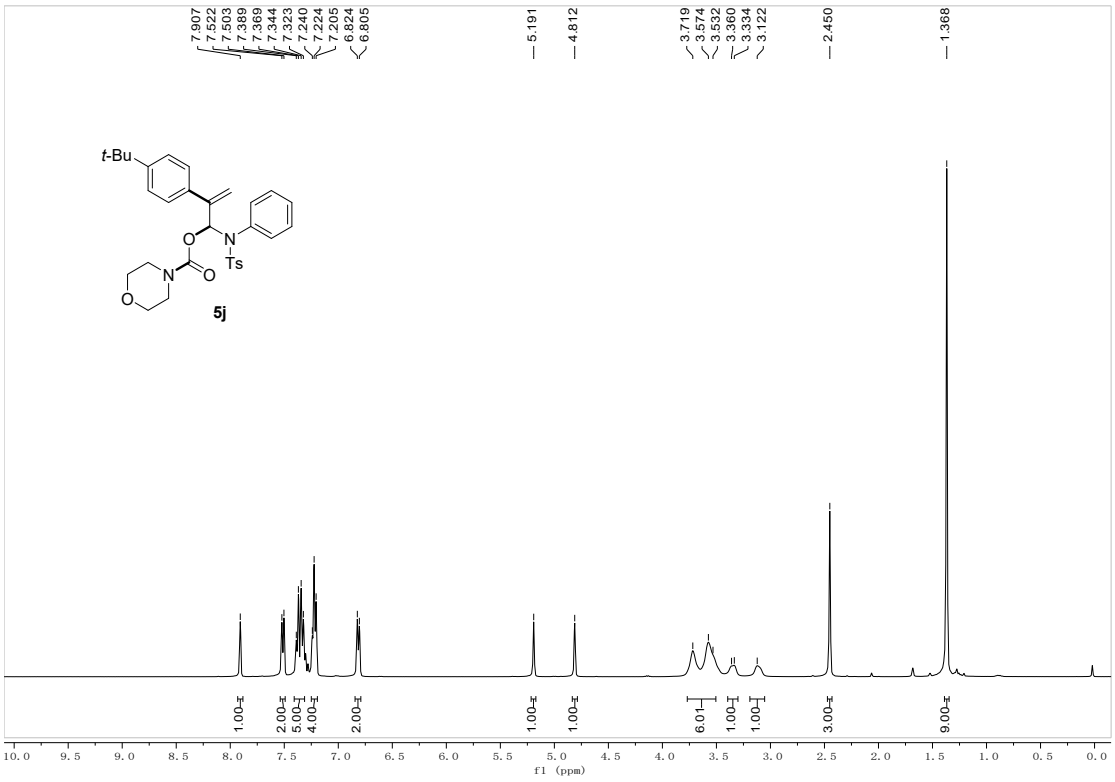
^{1}H NMR (400 MHz, $CDCl_3$)



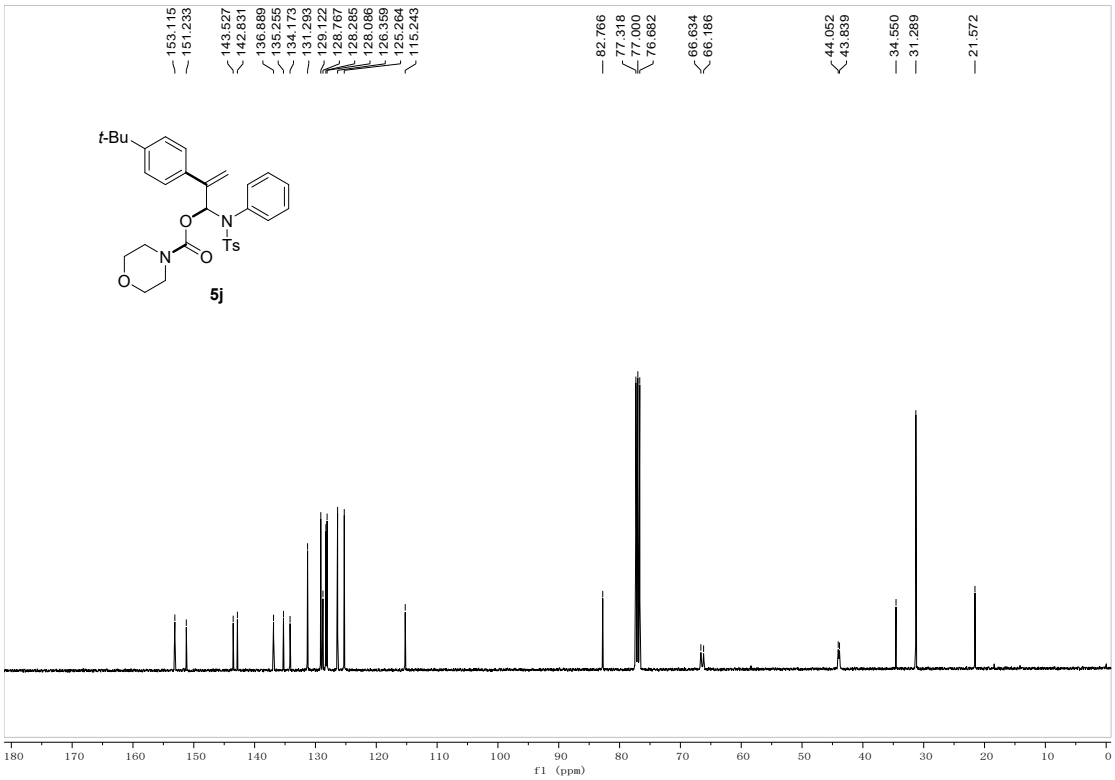
^{13}C NMR (100 MHz, $CDCl_3$)



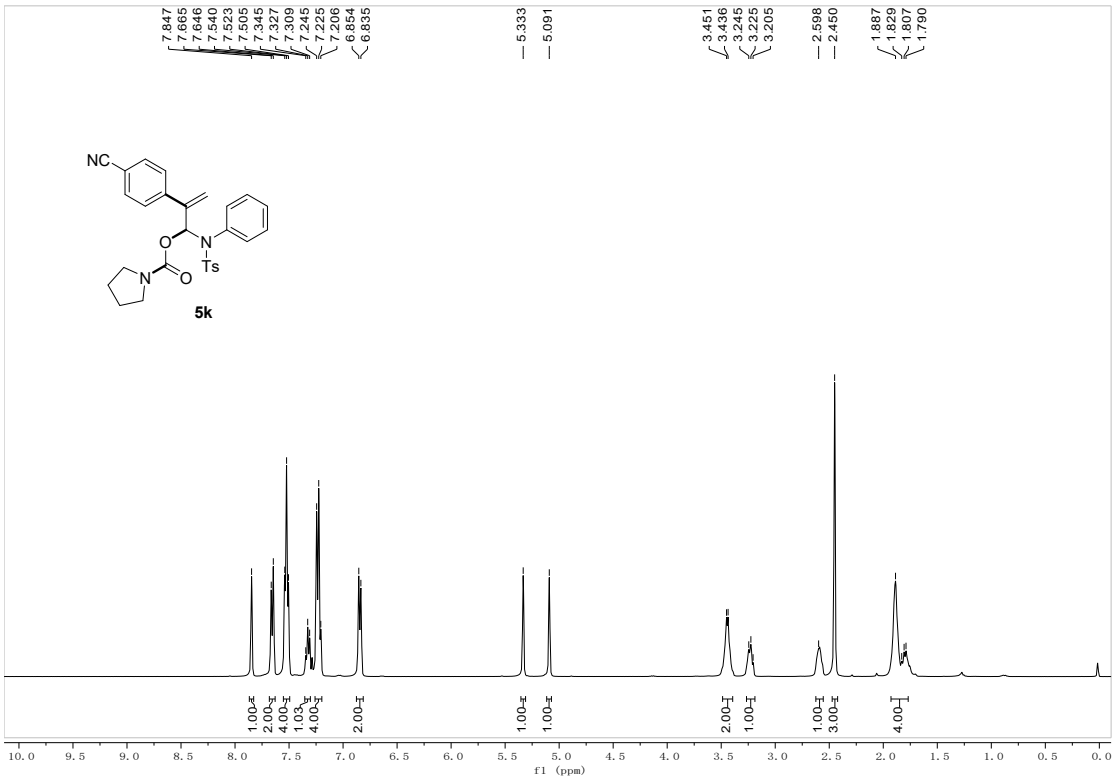
^{1}H NMR (400 MHz, $CDCl_3$)



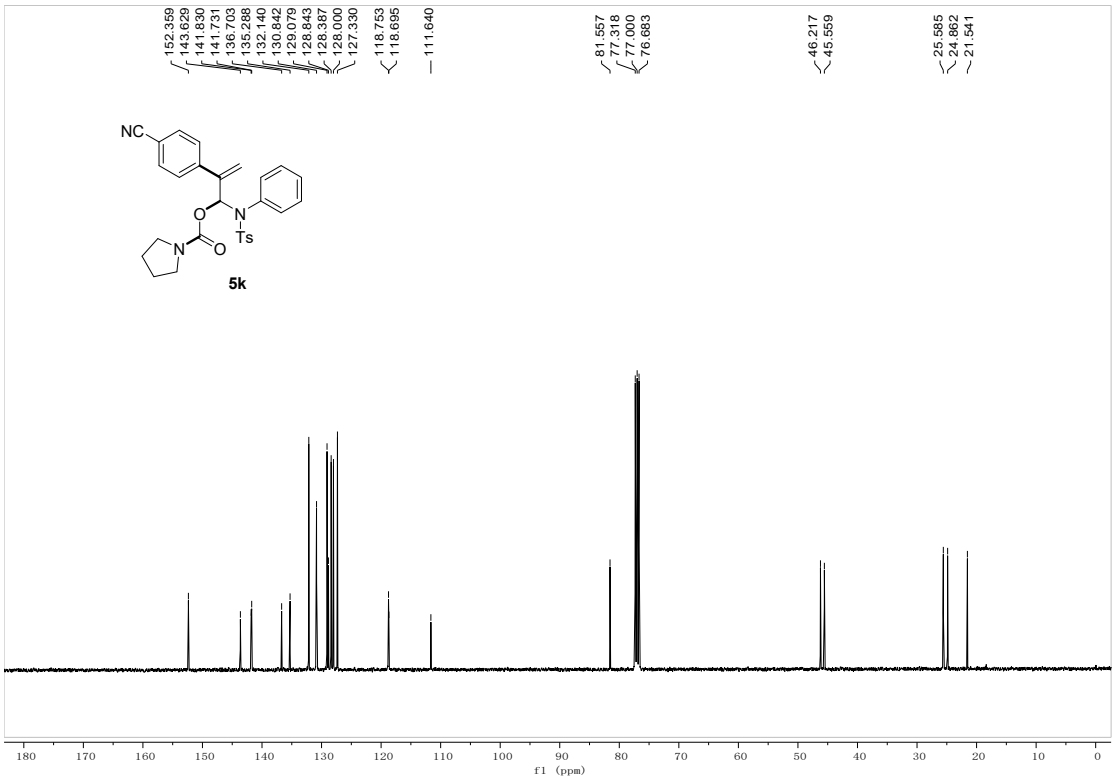
^{13}C NMR (100 MHz, $CDCl_3$)



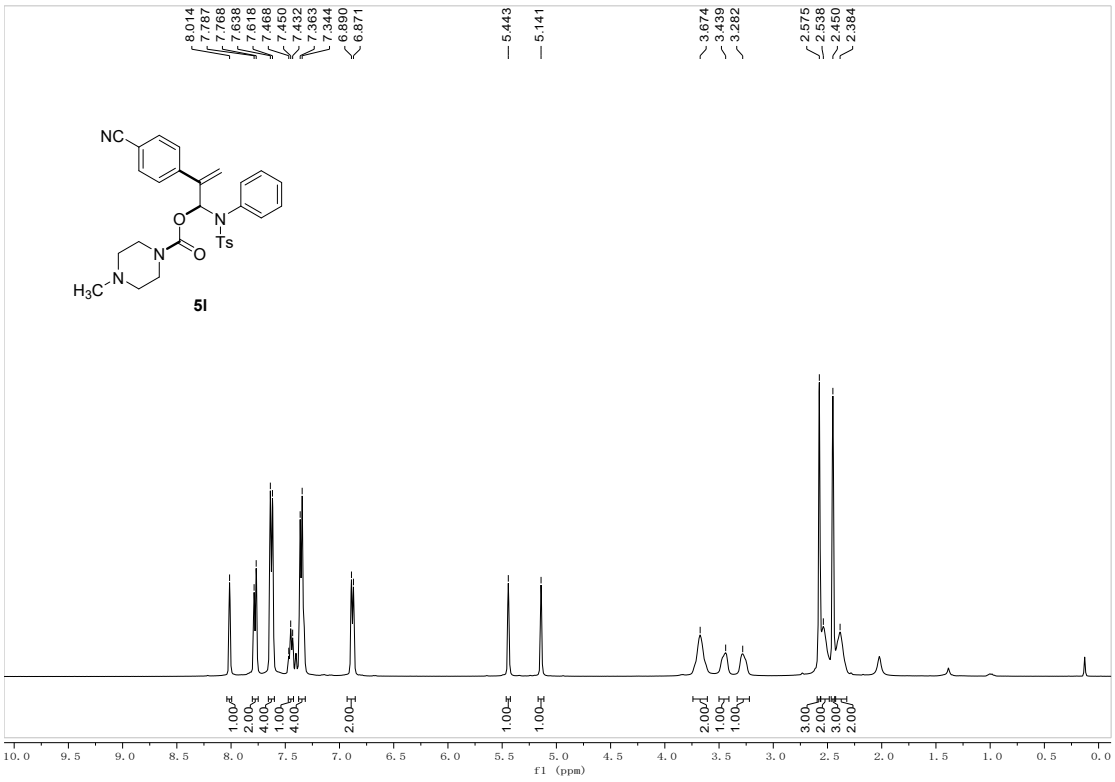
^{1}H NMR (400 MHz, $CDCl_3$)



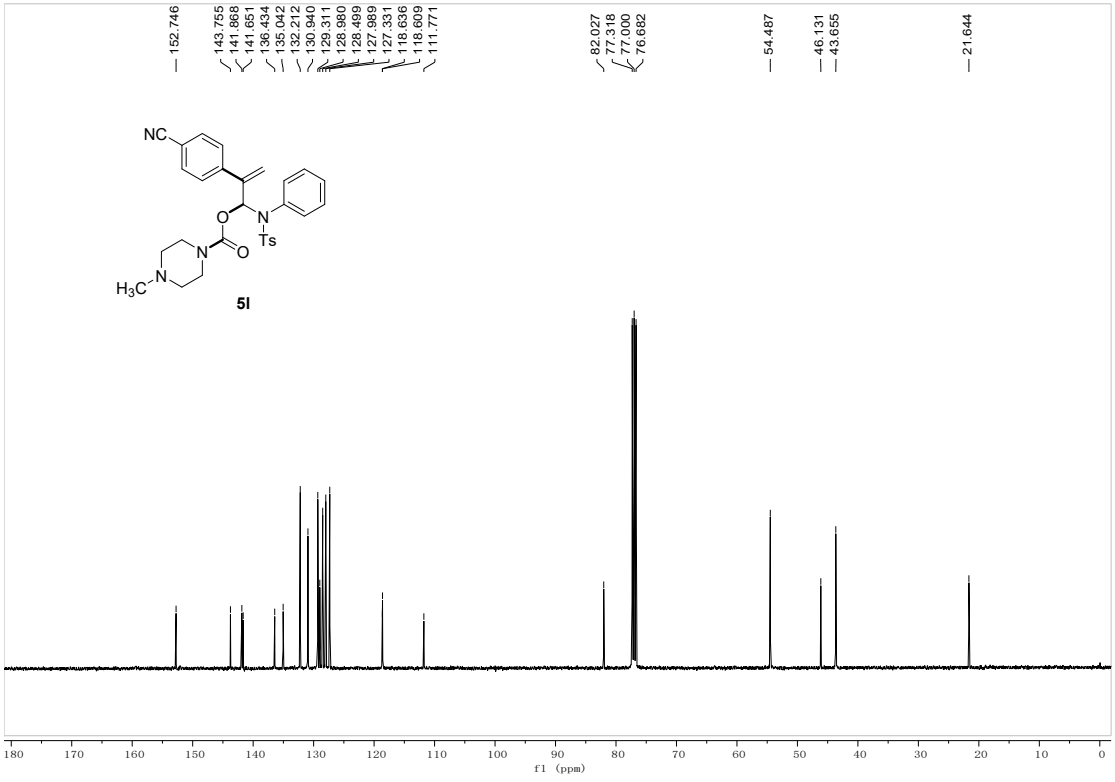
^{13}C NMR (100 MHz, $CDCl_3$)



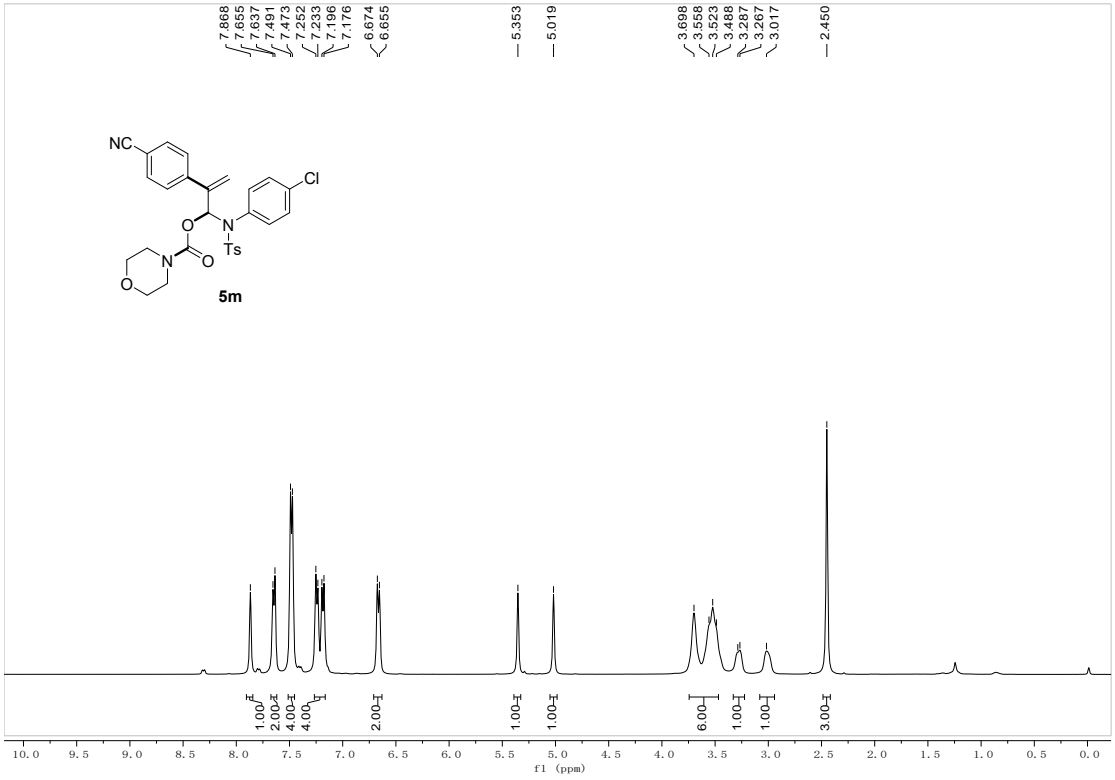
^{1}H NMR (400 MHz, $CDCl_3$)



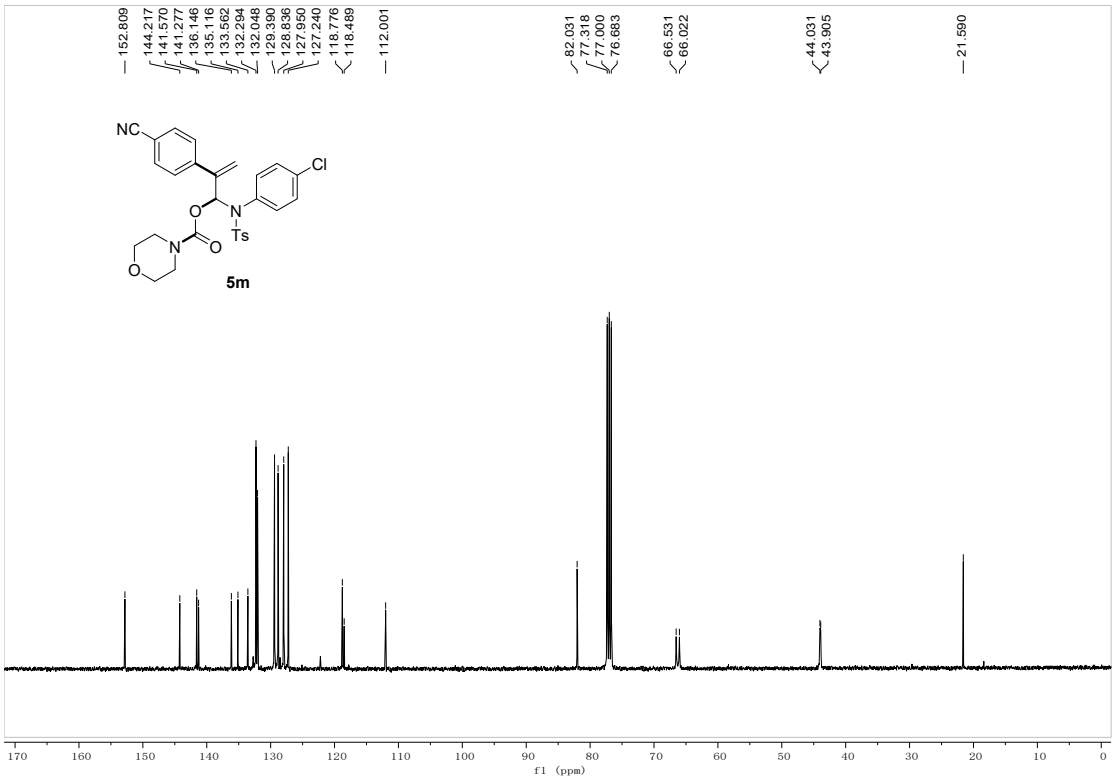
^{13}C NMR (100 MHz, $CDCl_3$)



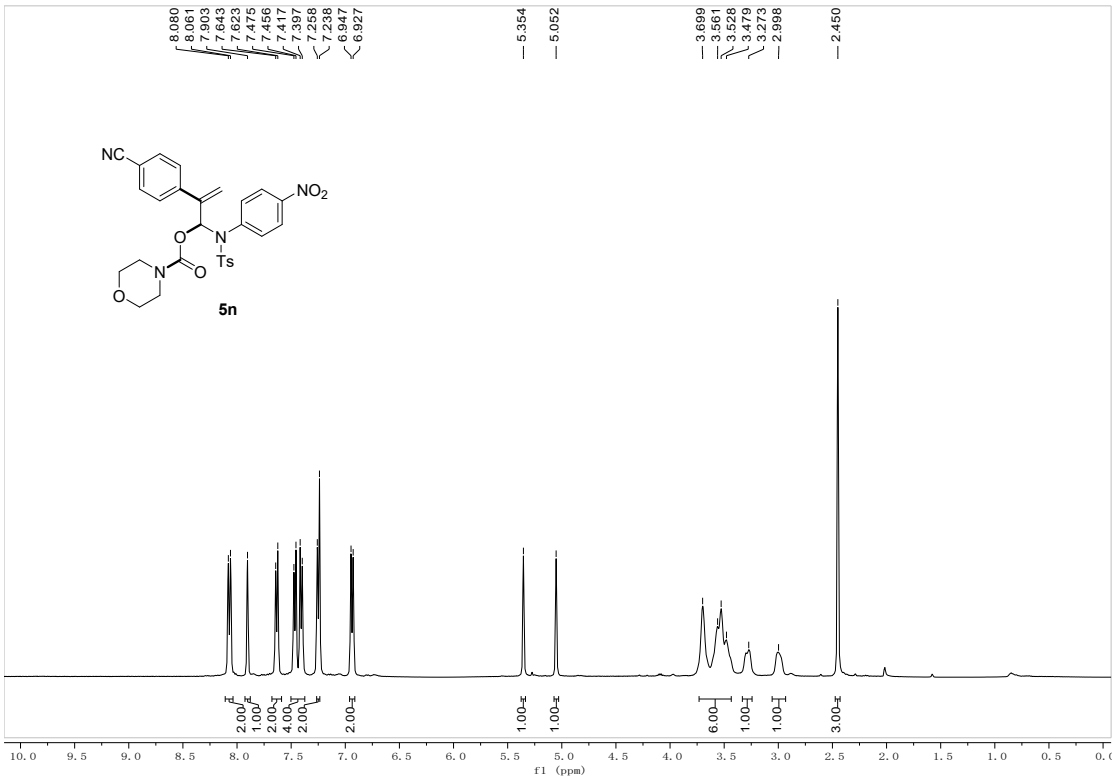
^{1}H NMR (400 MHz, $CDCl_3$)



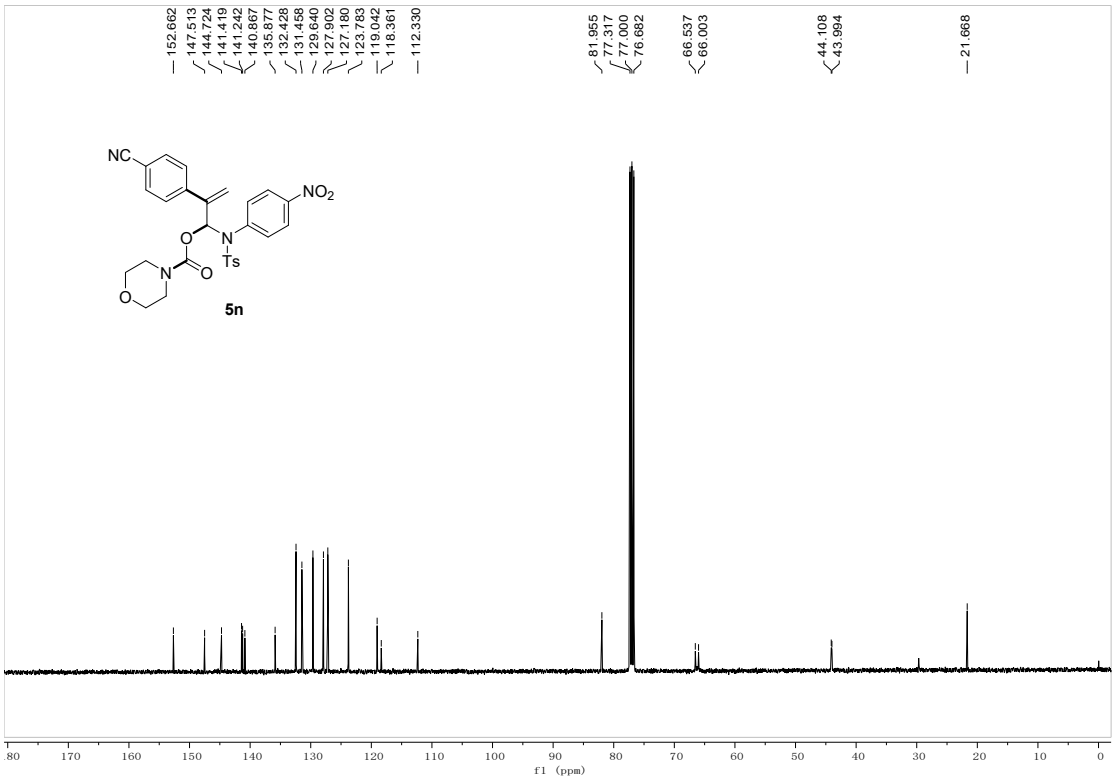
^{13}C NMR (100 MHz, $CDCl_3$)



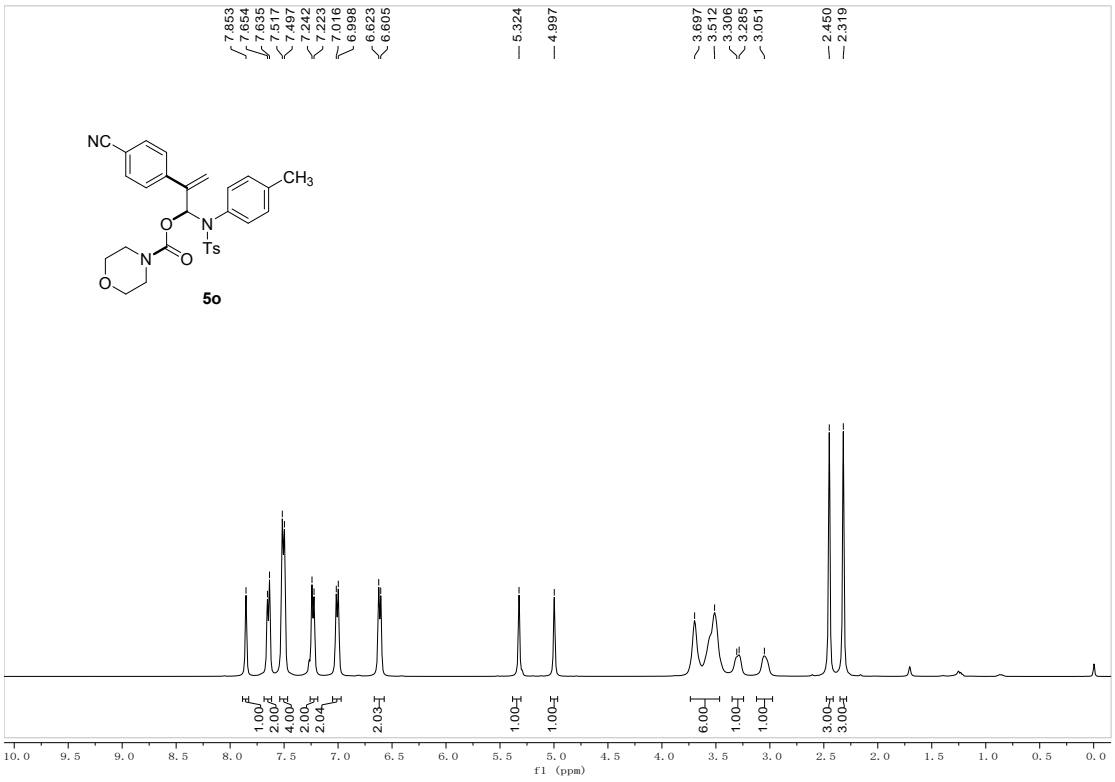
^{1}H NMR (400 MHz, $CDCl_3$)



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



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



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