Supporting Information

Switchable synthesis of sulfinylated and sulfonylated indoles and benzofurans from *o*-aminophenyl/*o*-hydroxyphenyl propargyl alcohols and β-sulfinyl esters

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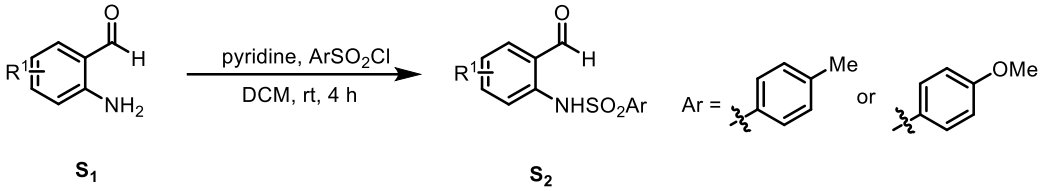
Table of Contents

General information

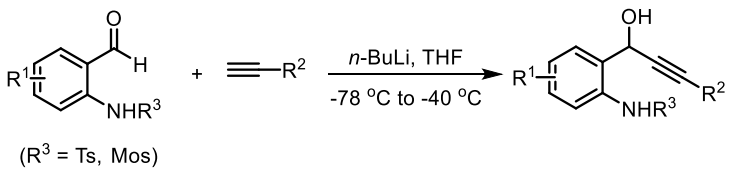
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (300 - 400 mesh). Melting points were measured using a WRS-1B digital melting point instrument. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured in $CDCl_3$ on a China Qone AS400 MHz instrument (resonance frequencies 400 MHz for ^{1}H, 101 MHz for ^{13}C and 376 MHz for ^{19}F), Bruker Advance III 400 MHz instrument (resonance frequencies 400 MHz for ^{1}H, 101 MHz for ^{13}C and 376 MHz for ^{19}F) and Bruker PLUS 500 MHz instrument (resonance frequencies 500 MHz for ^{1}H, 126 MHz for ^{13}C), with TMS as internal standard. All chemical shifts are reported in ppm scale. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, td = triple doublet, dt = double triplet, m = multiplet. Mass spectrometric data were obtained using a Bruker Solaril X70 high resolution mass spectrometer (samples were dissolved in CH_3OH and the ion source was ESI).

General procedure for the synthesis of *o*-aminophenyl propargyl alcohols



S1 **S2**

o-Aminophenyl propargyl alcohols were prepared according to known procedures.[1] To an egg-shaped flask was added 2-aminobenzaldehydes **S1** (10 mmol, 1.0 equiv.), DCM (25 mL) and pyridine (13 mmol, 1.3 equiv.). Then $ArSO_2Cl$ (12 mmol, 1.2 equiv.) was added to the above mixture under 0 °C and stirred at room temperature for about 4 h. The reaction was monitored by TLC. Upon completion, the mixture was quenched with water and extracted with DCM (30 mL × 3). The combined organic extracts were washed with water (30 mL) and brine (30 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1) to afford **S2**.

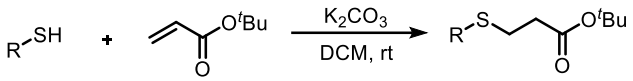


(R3 = Ts, Mos)

S2 **S3** **1**

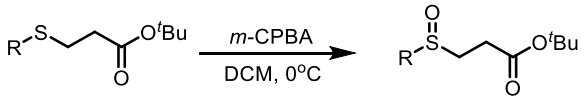
To a solution of **S3** (5.5 mmol, 2.2 equiv.) in THF (5 mL) was added *n*-BuLi dropwise (5.5 mmol, 2.5 M in THF, 2.2 equiv.) at -78 °C under nitrogen atmosphere. Then the mixture was stirred for 10 min at -78 °C. The mixture was warmed to -40 °C and allowed to continue for another 1 h. After that, the system was cooled down to -78 °C and a solution of **S2** (2.5 mmol, 1.0 equiv.) in THF (4 mL) was added slowly to the above mixture. The reaction was stirred for 1 h at -78 °C and warmed to room temperature while stirring for another 1 h (monitored by TLC). Upon completion, the reaction mixture was quenched with saturated NH_4Cl solution and extracted with EtOAc (20 mL×3) after removal of THF under vacuum. The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1) to afford **1**. The spectral data was in accordance with the reported data.[1]

General procedure for the synthesis of *β*-sulfinyl esters



S4 **S5** **S6**

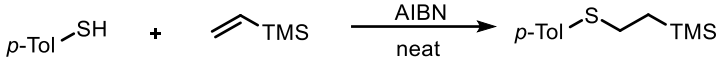
β-Sulfinyl esters were prepared according to the reported literature.[2] To a round-bottom flask (100 mL) was charged thiols **S4** (20 mmol, 1.0 equiv.) and potassium carbonate (1 mmol, 138 mg, 0.05 equiv.), followed by the addition of dichloromethane (10 mL) as the solvent. Then, *tert*-butyl acrylate **S5** (22 mmol, 1.1 equiv.) was added rapidly to the reaction mixture. The reaction was stirred at room temperature for 20 h. After completion of the reaction as monitored by TLC, the mixture was filtered and concentrated under reduced pressure to remove the solvent. The crude product was used in the next step directly without further purification due to sufficient purity.



S6 **2**

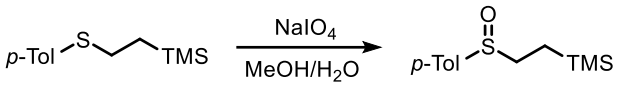
To a round-bottom flask (100 mL) was charged the crude product **S6** (20 mmol, 1.0 equiv.) from the first step, followed by the addition of dichloromethane (20 mL) as the solvent. The reaction flask was then placed in an ice bath and stirred for 10 min. A solution of *m*-chloroperoxybenzoic acid (85%, 22 mmol, 4.47 g, 1.1 equiv.) in dichloromethane (10 mL) was prepared and added dropwise to the reaction mixture. The reaction was allowed to proceed for no longer than 2 h, with the endpoint monitored by TLC. Upon completion, the reaction was quenched with saturated aqueous sodium sulfite solution. The mixture was then washed with saturated aqueous sodium sulfite solution (20 mL× 3). The aqueous layer was extracted with dichloromethane (30 mL × 3). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to remove the solvent. The residue was purified by column

chromatography to afford the product **2**. The spectral data was in accordance with the reported data.[3]



S4a **S7** **S8**

To a reaction vessel were charged *p*-tolylthiol (621.0 mg, 5.0 mmol, 1.0 equiv.) and trimethyl(vinyl)silane (601.4 mg, 6.0 mmol, 1.2 equiv.) under argon atmosphere (solvent-free). Azobisisobutyronitrile (AIBN) (20.6 mg, 0.125 mmol, 2.5 mol%) was added and the mixture was refluxed for 24 h. The resulting mixture was purified by flash chromatography to afford trimethyl[2-(p-tolylthio)ethyl]silane. The crude product was used in the next step directly without further purification due to sufficient purity.

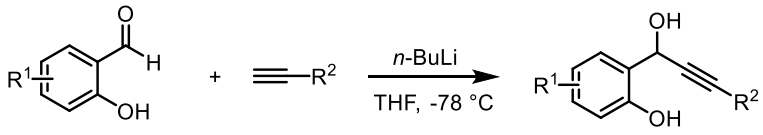


S8 **S9**

To a flask containing a cooled (0 °C) mixture of trimethyl[2-(*p*-tolylthio)ethyl]silane (**S8**, 1.12 g, 5.0 mmol), MeOH (15 mL) and H_2O (8 mL), was added solid $NaIO_4$ (1.07 g, 5.0 mmol, 1.0 equiv.) in small portions. The ice bath was removed after 30 min and the solution was stirred for 12 h. Most of the methanol was removed under reduced pressure. The inorganic solid was removed by suction filtration through Celite™, followed by washing with CH_2Cl_2 (2 × 10 mL). The filtrate was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure, and purified by column chromatography on silica gel to afford the sulfoxide **S9** (901mg, 75% yield). The spectral data was in accordance with the reported data.[4]

General procedure for the synthesis of *o*-hydroxyphenyl propargylic alcohols

o-Hydroxyphenyl propargylic alcohols were prepared according to the reported literature.[5] General synthetic route of propargylic alcohols **5** is shown below.



S10 **S3** **5**

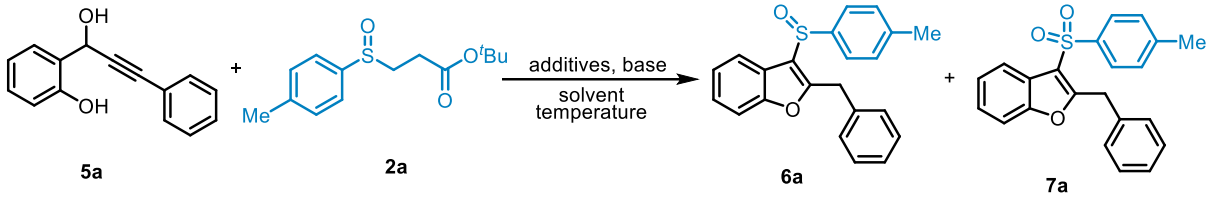
To the solution of **S3** (22 mmol, 2.2 equiv.) in dry THF (30 mL) was slowly added *n*-BuLi (22 mmol, 2.5 M in THF, 2.2 equiv.) at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at this temperature for 1 h, then a solution of the corresponding salicylaldehyde **S10** (10 mmol, 1.0 equiv.) in 4 mL of THF was added dropwise via a syringe. The reaction mixture was stirred at -78 °C for another 1-1.5 h until the disappearance of the starting material indicated by TLC analysis. Then the reaction mixture was quenched with saturated aqueous NH_4Cl solution and THF was removed under vacuum. The resulting aqueous phase

was extracted with EtOAc (30 mL × 3). The combined organic layers were washed with water (30 mL) and brine (30 mL), dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by column chromatography (petroleum ether/EtOAc = 10/1) or by crystallization with petroleum ether to give **5**. The spectral data was in accordance with the reported data.[0][5]

Screening of reaction conditions for the synthesis of benzofuran

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added *o*-hydroxyphenyl propargyl alcohol **5a** (0.3 mmol, 67.3 mg), base, *β*-sulfinyl ester **2a (**0.6 mmol, 161.0 mg), and additives, followed by solvent (2 mL). The reaction mixture was heated in an oil bath at the indicated temperature under a nitrogen atmosphere and monitored by TLC. Upon completion, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel to afford the corresponding product.

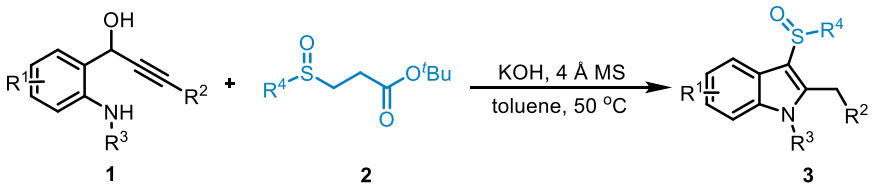
Table S1. Screening of reaction conditions[a]



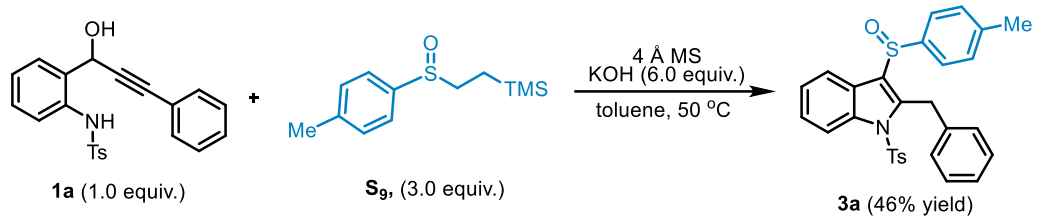
entry	base (eq.)	additives	solvent	temp/°C	time/h	yield (%)[b]	
						6a	7a
1[c]	KOH (6.0)	4 Å MS (40 mg)	toluene	50	8	nd	26
2[c]	KOH (6.0)	\	toluene	50	8	nd	24
3[c]	KOH (6.0)	\	toluene	80	5	nd	33
4	KOH (4.0)	\	toluene	80	8	nd	46
5	K_2CO_3 (4.0)	\	toluene	80	5	nd	57
6	*n*-BuLi (4.0)	\	toluene	-78	8	nd	59
7	Cs_2CO_3 (4.0)	\	toluene	80	8	nd	62
8	DMAP (4.0)	\	toluene	80	8	nd	21
9	DABCO (4.0)	\	toluene	80	8	nd	nd
10	DBU (4.0)	\	toluene	80	8	nd	34
11	Cs_2CO_3 (4.0)	\	toluene	80	8	nd	65
12	Cs_2CO_3 (4.0)	\	THF	70	8	nd	29
13	Cs_2CO_3 (4.0)	\	CH_3CN	80	8	nd	57
14	Cs_2CO_3 (4.0)	\	DCE	80	8	nd	39
15	Cs_2CO_3 (4.0)	\	DMF	80	8	nd	17
16	Cs_2CO_3 (4.0)	\	dioxane	80	8	nd	45
17	Cs_2CO_3 (4.0)	\	PhCl	80	8	nd	56
18	Cs_2CO_3 (4.0)	\	EA	80	8	nd	20
19	Cs_2CO_3 (4.0)	\	DCM	30	8	nd	11
20	Cs_2CO_3 (4.0)	\	toluene	rt	8	nd	32
21	Cs_2CO_3 (4.0)	\	toluene	30	8	nd	49
22	Cs_2CO_3 (4.0)	\	toluene	50	8	nd	53
23	Cs_2CO_3 (4.0)	\	toluene	100	8	nd	61
24	Cs_2CO_3 (4.0)	CuI (5 mol%)	toluene	80	8	nd	86
25	Cs_2CO_3 (4.0)	CuBr (5 mol%)	toluene	80	8	nd	66

[a]Reaction conditions: **5a** (0.3 mmol, 67.3 mg), **2a** (0.6 mmol, 161.0 mg), base, and additives were stirred in solvent (2 mL) at indicated temperature; [b]Yield of the isolated product; [c]0.9 mmol of **2a** was used; nd: not detected.

Procedure for synthesis of 3



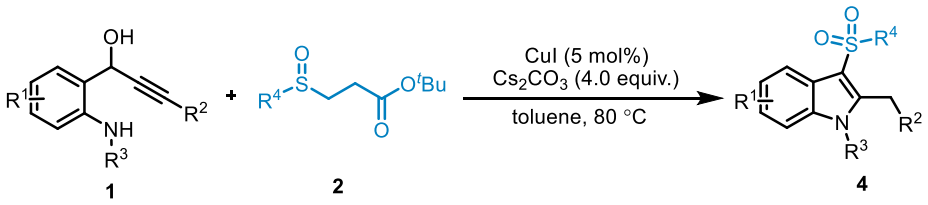
To a reaction tube containing activated molecular sieves (20 mg) and *o*-aminophenyl propargyl alcohol **1** (0.15 mmol, 1.0 equiv.) under an argon (or nitrogen) atmosphere was added KOH (0.9 mmol, 50.5 mg, 6.0 equiv.). The system was purged with argon (or nitrogen) three times, followed by the addition of toluene (1 mL). The mixture was stirred at room temperature for 15 minutes. A solution of *β*-sulfinyl ester **2** (0.45 mmol, 3.0 equiv.) in toluene (1 mL) was added dropwise to the reaction mixture. The temperature was gradually increased to 50 °C and the reaction was continued at this temperature until the disappearance of the starting material as indicated by TLC analysis. The reaction mixture was filtered through diatomaceous earth. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give the product **3**.



1a (1.0 equiv.) **S9,** (3.0 equiv.) **3a** (46% yield)

Alternative RSO- source: To a reaction tube containing activated molecular sieves (20 mg) and *o*-aminophenyl propargyl alcohol **1a** (0.15 mmol, 56.6 mg, 1.0 equiv.) under an argon atmosphere was added KOH (0.9 mmol, 50.5 mg, 6.0 equiv.). The system was purged with argon three times, followed by the addition of toluene (1 mL). The mixture was stirred at room temperature for 15 minutes. A solution of *β*-sulfinyl reagent **S9** (0.45 mmol, 101.9 mg, 3.0 equiv.) in toluene (1 mL) was added dropwise to the reaction mixture. The temperature was gradually increased to 50 °C and the reaction was continued at this temperature until the disappearance of the starting material as indicated by TLC analysis. The reaction mixture was filtered through diatomaceous earth. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give the product **3a** (34.5 mg, 46% yield).

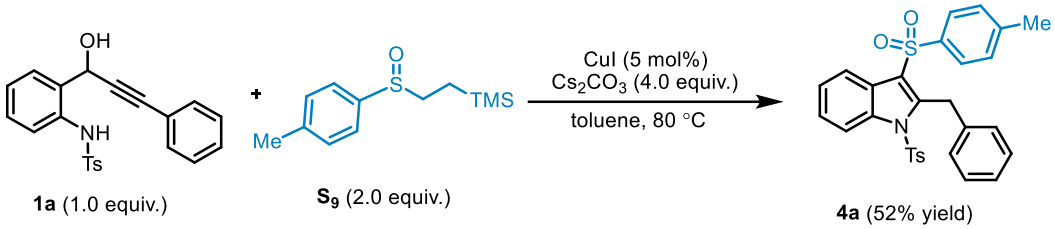
Procedure for synthesis of 4



1 **2** **4**

To the reaction tube containing *o*-aminophenyl propargyl alcohol **1** (0.3 mmol, 1.0 equiv.) and cesium carbonate (1.2 mmol, 391.0 mg, 4.0 equiv.) under a nitrogen atmosphere was added *β*-sulfinyl ester **2** (0.6 mmol, 2.0 equiv.), followed by CuI (0.015 mmol, 2.9 mg, 0.05 equiv.) and toluene (2 mL). The mixture was stirred at 80 °C until the disappearance of the starting material as indicated by TLC analysis. After completion of the reaction, the solvent was evaporated under reduced pressure. The residue was purified by column

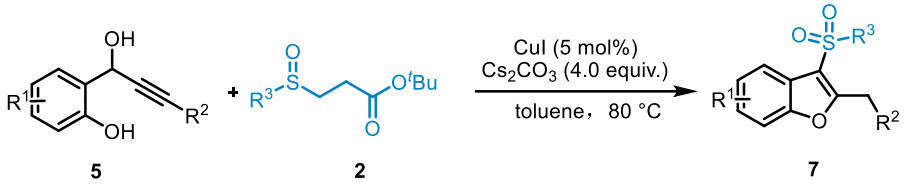
chromatography to give the product **4** (The spectral data was in accordance with the reported data[6,7]).



1a (1.0 equiv.) **S9** (2.0 equiv.) **4a** (52% yield)

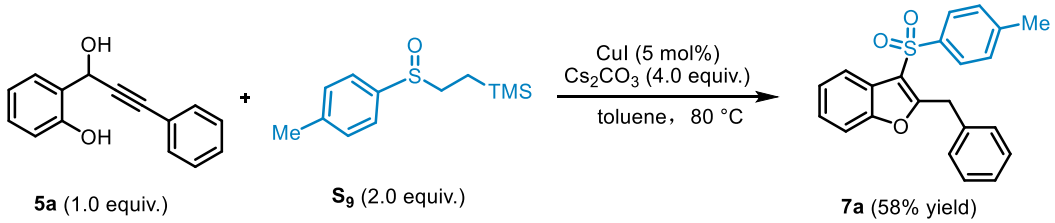
Alternative RSO- source: To the reaction tube containing *o*-aminophenyl propargyl alcohol **1a** (0.3 mmol, 113.2 mg, 1.0 equiv.) and cesium carbonate (1.2 mmol, 391.0 mg, 4.0 equiv.) under a nitrogen atmosphere was added *β*-sulfinyl reagent **S9** (0.6 mmol, 135.8 mg, 2.0 equiv.), followed by CuI (0.015 mmol, 2.9 mg, 0.05 equiv.) and toluene (2 mL). The mixture was stirred at 80 °C until the disappearance of the starting material as indicated by TLC analysis. After completion of the reaction, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give the product **4a** (80 mg, 52%yield). The spectral data was in accordance with the reported data[6]).

Procedure for synthesis of 7



5 **2** **7**

To the reaction tube containing *o*-hydroxy propargyl alcohol **5** (0.3 mmol, 1.0 equiv.) and cesium carbonate (1.2 mmol, 391.0 mg, 4.0 equiv.) under a nitrogen atmosphere was added *β*-sulfinyl ester **2** (0.6 mmol, 2.0 equiv.), followed by CuI (0.015 mmol, 2.9 mg, 0.05 equiv.) and toluene (2 mL). The mixture was stirred at 80 °C until the disappearance of the starting material as indicated by TLC analysis. After completion of the reaction, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give the product **7**. (The spectral data was in accordance with the reported data[8]).

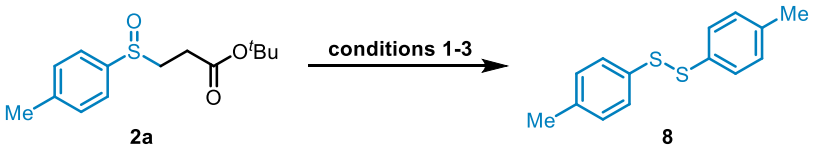


5a (1.0 equiv.) **S9** (2.0 equiv.) **7a** (58% yield)

Alternative RSO- source: To the reaction tube containing o-hydroxy propargyl alcohol **5a** (0.3 mmol, 67.3 mg, 1.0 equiv.) and cesium carbonate (1.2 mmol, 391.0 mg, 4.0 equiv.) under a nitrogen atmosphere was added *β*-sulfinyl reagent **S9** (0.6 mmol, 135.8 mg, 2.0 equiv.), followed by CuI (0.015 mmol, 2.9 mg, 0.05 equiv.) and toluene (2 mL). The mixture was stirred at 80 °C until the disappearance of the starting material as indicated by TLC analysis. After completion of the reaction, the solvent was evaporated under

reduced pressure. The residue was purified by column chromatography to give the product **7a** (63.1 mg, 58% yield). (The spectral data was in accordance with the reported data[8]).

Control experiment



2a **8**

Condition **1**: To a reaction tube containing activated molecular sieves (10 mg) and *β*-sulfinyl ester **2** (0.2 mmol, 53.6 mg, 1.0 equiv.) under an argon atmosphere was added KOH (0.4 mmol, 22.4 mg, 2.0 equiv.). The system was purged with argon three times, followed by the addition of toluene (1 mL). The temperature was gradually increased to 50 °C. The reaction mixture was filtered through diatomaceous earth. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give the product **8**.

Time	**15 min**	**30 min**	**60 min**	**90 min**	**120 min**	**180 min**	**210 min**	**240 min**
mg	2.7 mg	3.7 mg	5.4 mg	9.4 mg	13.4 mg	19.2 mg	21.9 mg	24.2 mg
yield (%)	11	15	22	38	55	78	89	98

Condition **2**: To the reaction tube containing cesium carbonate (0.4 mmol, 130.3 mg, 2.0 equiv.) under a nitrogen atmosphere was added *β*-sulfinyl ester **2** (0.2 mmol, 53.6 mg, 1.0 equiv.), followed by CuI (0.005 mmol, 1.0 mg, 0.025 equiv.) and toluene (2 mL). The mixture was stirred at 80 °C until the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give the product **8**.

Time	**15 min**	**30 min**	**60 min**	**90 min**	**120 min**	**180 min**	**210 min**	**240 min**
mg	3.9 mg	7.4 mg	12.8 mg	18.0 mg	21.9 mg	23.6 mg	23.6 mg	24.1 mg
yield (%)	16	30	52	73	89	96	96	98

Condition **3**: To the reaction tube containing cesium carbonate (0.4 mmol, 130.3 mg, 2.0 equiv.) under a nitrogen atmosphere was added *β*-sulfinyl ester **2** (0.2 mmol, 53.6 mg, 1.0 equiv.) and toluene (1 mL). The mixture was stirred at 80 °C until the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give the product **8**.

Time	**15 min**	**30 min**	**60 min**	**90 min**	**120 min**	**180 min**	**210 min**	**240 min**
mg	2.9 mg	3.9 mg	7.1 mg	11.8	15.8 mg	20.2 mg	23.4 mg	23.7 mg
yield (%)	12	16	29	48	64	82	95	96

According to the control experiments, a reaction conversion curves were drawn (Fig. S1). In our reaction system, complete conversion of *β*-sulfinyl ester **2a** to diaryl disulfide **8** was achieved within approximately 4 hours. This process could reflect the disproportionation of sulfenate anion (sulfinyl anion). This

transformation proceeded to completion with comparable efficiency when using either strong (KOH) or relatively mild base (Cs_2CO_3). Notably, the process was significantly accelerated in the presence of catalytic CuI (reaction 2 *vs* reactions 1 and 3), a finding consistent with the results reported by Zeng, (*J. Org. Chem.*, 2021, **86**, 7806). Yang, (*Org. Biomol. Chem.*, 2024, **22**, 3381). and Zhao (*Org. Chem. Front.*, 2023, **10**, 3975). These results suggest that *aza-o*-QMs might exhibit markedly higher reactivity toward the weakly nucleophilic sulfinyl anion prior to its disproportionation, compared to conventional *o*-QMs, rationalizing the distinct reactivity patterns observed between *o*-aminophenyl and *o*-hydroxyphenyl propargyl alcohols.

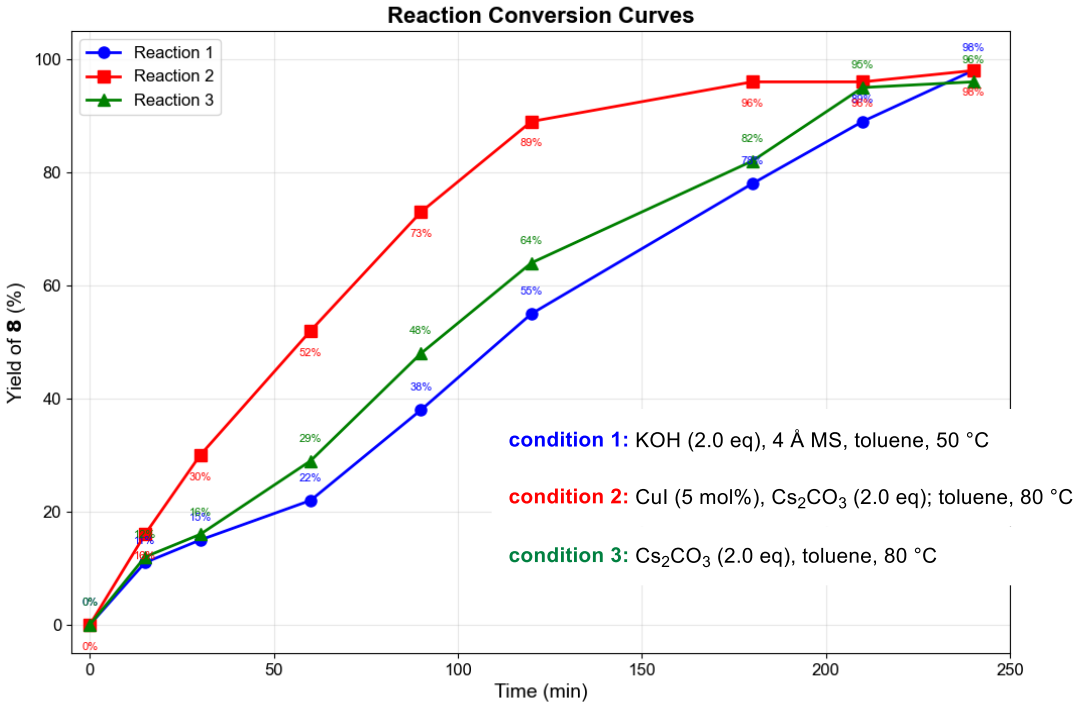
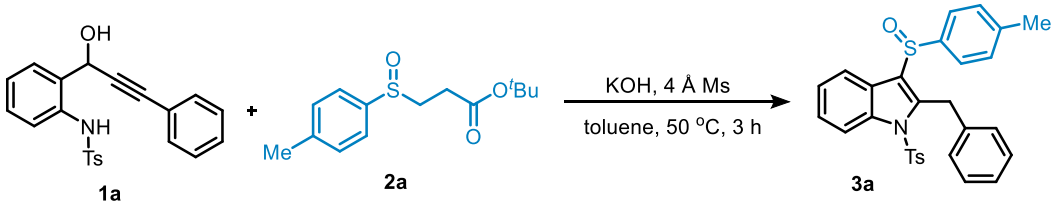


Fig. S1

Synthetic utility

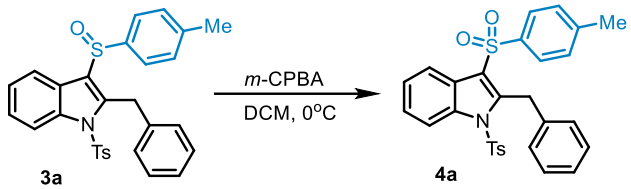
(a) Gram-scale experiment



To a reaction tube containing activated molecular sieves (400 mg) and *o*-aminophenyl propargyl alcohol **1a** (3.0 mmol, 1.13 g, 1.0 equiv.) under an argon atmosphere was added KOH (18 mmol, 1.01 g, 6.0 equiv.). The system was purged with argon three times, followed by the addition of toluene (20 mL). The mixture

was stirred at room temperature for 30 minutes. A solution of *β*-sulfinyl ester **2a** (9.0 mmol, 2.42 g, 3.0 equiv.) in toluene (20 mL) was added dropwise to the reaction mixture. The temperature was gradually increased to 50 °C and the reaction was continued at this temperature (for about 3 h) until the disappearance of the starting material as indicated by TLC analysis. The formation of diaryl disulfide 8 was observed by TLC. The reaction mixture was filtered through diatomaceous earth. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give the product **3a** (1.26 g, 84% yield).

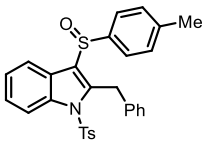
(b) Representative transformation



To a 50 mL round-bottom flask containing **3a** (0.2 mmol, 99.9 mg, 1.0 equiv.) and dichloromethane (5 mL) under a nitrogen atmosphere was added a solution of m-chloroperbenzoic acid (85%, *m*-CPBA, 0.22 mmol, 44.7 mg, 1.1 equiv.) in dichloromethane (10 mL) dropwise at 0 °C (ice bath).The reaction mixture was stirred at this temperature for 10 minutes, then allowed to warm to room temperature and stirred for up to 2 hours until the disappearance of the starting material as indicated by TLC analysis. After completion of the reaction, the mixture was quenched with saturated aqueous sodium sulfite (Na_2SO_3) solution. The resulting mixture was washed with saturated aqueous sodium sulfite solution (5 mL × 3). The combined aqueous layers were extracted with dichloromethane (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography to give the product **4a** (80.4 mg, 78% yield). (The spectral data was in accordance with the reported data[6])

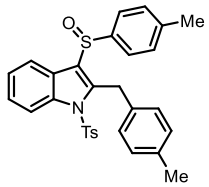
Characterization data

2-benzyl-3-(*p*-tolylsulfinyl)-1-tosyl-1*H*-indole (3a)



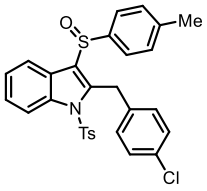
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3a** (white solid, 63.6 mg, 85% yield, Melting point: 168.2-170.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz , 1H), 7.53 (d, *J* = 8.0 Hz , 1H), 7.35 (d, *J* = 8.4 Hz , 2H), 7.30 – 7.24 (m, 8H), 7.17 (d, *J* = 8.0 Hz , 2H), 7.11 (t, *J* = 8.0 Hz , 1H), 7.06 (d, *J* = 8.0 Hz , 2H), 5.00 (d, *J* = 15.6 Hz, 1H), 4.80 (d, *J* = 16.0 Hz, 1H), 2.32 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.5, 143.0, 140.7, 139.5, 137.8, 136.6, 135.2, 129.9, 129.9, 128.8, 128.8, 126.8, 126.8, 125.5, 124.8, 124.6, 124.3, 123.3, 120.4, 115.0, 32.0, 21.6, 21.4. **HRMS (ESI)** m/z calculated for $C_{29}H_{25}NNaO_3S_2^+$ $[M+Na]^+$: 522.1168 found: 522.1177.

2-(4-methylbenzyl)-3-(*p*-tolylsulfinyl)-1-tosyl-1*H*-indole (3b)



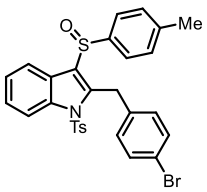
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3b** (yellow solid, 63.1 mg, 82% yield, Melting point: 136.9-138.5 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.25 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.14 – 7.09 (m, 3H), 7.06 – 7.04 (m, 3H), 4.93 (d, *J* = 16.0 Hz, 1H), 4.75 (d, *J* = 16.0 Hz, 1H), 2.33 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.7, 153.5, 144.2, 136.7, 132.7, 129.8, 129.4, 129.0, 126.9, 125.4, 124.3, 124.3, 120.6, 118.2, 118.2, 111.5, 32.8, 21.5, 21.1, 21.0. **HRMS (ESI)** m/z calculated for $C_{30}H_{27}NNaO_3S_2^+$ $[M+Na]^+$: 536.1325 found: 536.1330.

2-(4-chlorobenzyl)-3-(*p*-tolylsulfinyl)-1-tosyl-1*H*-indole (3d)



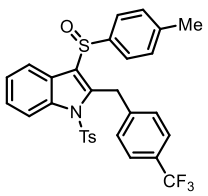
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3d** (yellow solid, 69.6 mg, 87% yield, Melting point: 155.8-157.5 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz , 1H) , 7.55 (d, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 4H), 7.31 – 7.26 (m, 1H), 7.19 (t, *J* = 6.8 Hz, 3H), 7.15 (d, *J* = 2.0 Hz, 2H), 7.13 – 7.07 (m, 4H) , 4.92 (d, *J* = 16.0 Hz , 1H), 4.77 (d, *J* = 16.0 Hz, 1H), 2.35 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.7, 142.1, 141.0, 139.4, 136.8, 136.0, 135.2, 132.8, 130.1, 130.0, 128.7, 126.6, 126.5, 125.8, 124.8, 124.6, 124.5, 123.6, 120.4, 115.0, 31.3, 21.7, 21.4. **HRMS (ESI)** m/z calculated for $C_{29}H_{25}ClNO_3S_2^+$ $[M+H]^+$: 534.0959 found: 534.0957.

2-(4-bromobenzyl)-3-(*p*-tolylsulfinyl)-1-tosyl-1H-indole (3e)



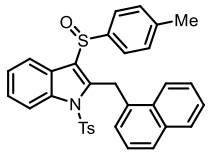
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3e** (yellow solid, 76.4 mg, 88% yield, Melting point: 165.2-167.5 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 3H), 7.30 (d, *J* = 8.0 Hz, 4H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.08 – 7.03 (m, 5H), 4.90 (d, *J* = 16.0 Hz, 1H), 4.74 (d, *J* = 16.0 Hz, 1H), 2.35 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 141.9, 140.9, 136.8, 136.5, 135.3, 131.6, 130.4, 129.9, 129.9, 126.4, 125.7, 124.8, 124.6, 124.4, 123.6, 120.8, 120.4, 115.0, 31.4, 21.7, 21.4. **HRMS (ESI)** m/z calculated for $C_{29}H_{25}BrNO_3S_2^+$ $[M+H]^+$: 578.0454, 580.0434 found: 578.0453, 580.0428.

3-(p-tolylsulfinyl)-1-tosyl-2-(4-(trifluoromethyl)benzyl)-1*H*-indole (3f)



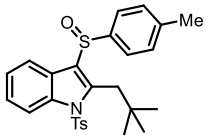
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3f** (yellow solid, 75.7 mg, 89% yield, Melting point: 148.2-149.9 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.0, 5.6 Hz, 1H), 7.59 (t, *J* = 6.4 Hz, 1H), 7.43 (t, *J* = 6.0 Hz, 2H), 7.34 – 7.30 (m, 4H), 7.27 (d, *J* = 6.0 Hz, 3H), 7.19 (t, *J* = 6.0 Hz, 3H), 7.04 (t, *J* = 5.6 Hz, 2H), 5.01 (dd, *J* = 16.0, 4.2 Hz, 1H), 4.86 (dd, *J* = 16.0, 4.2 Hz, 1H), 2.35 (d, *J* = 5.6 Hz, 3H), 2.32 (d, *J* = 5.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.7, 114.5, 141.3, 114.1, 139.4, 136.8, 135.3, 129.9, 129.9, 129.0, 126.4, 125.8, 125.5 (q, *J* = 3.8 Hz), 124.8, 124.6, 124.5, 123.8, 120.4, 115.0, 31.7, 21.5, 21.3. Due to severe signal overlap in the ^{13}C NMR spectrum, only the quartet signal at 125.5 ppm (attributable to the CF_3 group) could be unambiguously assigned, while other C-F coupling signals remained unresolved. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.36 (s). **HRMS (ESI)** m/z calculated for $C_{30}H_{24}F_3NNaO_3S_2^+$ $[M+Na]^+$: 590.1042 found: 590.1047.

2-(naphthalen-1-ylmethyl)-3-(*p*-tolylsulfinyl)-1-tosyl-1*H*-indole (3g)



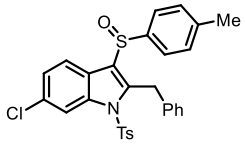
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3g** (yellow solid, 58.5 mg, 71% yield, Melting point: 126.8-128.1°C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.4 Hz , 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.31 (m, 8H), 7.22 – 7.11 (m, 5H), 7.12 (d, *J* = 16.0 Hz, 1H), 7.37 4.94 (d, *J* = 16.4 Hz, 1H), 2.28 (s, 3H), 2.07 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.2, 142.3, 140.8, 139.7, 137.0, 135.2, 134.9, 133.4, 132.3, 129.9, 129.6, 129.5, 128.3, 127.8, 127.5, 127.1, 126.3, 126.1, 125.8, 125.6, 124.9, 124.7, 124.3, 123.5, 120.5, 115.1, 32.0, 21.4, 21.3. **HRMS (ESI)** m/z calculated for $C_{33}H_{27}NNaO_3S_2^+$ $[M+Na]^+$: 572.1325 found: 572.1330.

2-neopentyl-3-(*p*-tolylsulfinyl)-1-tosyl-1*H*-indole (3i)



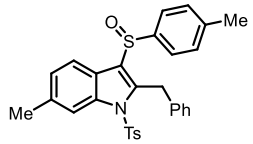
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3i** (yellow solid, 61.2 mg, 85% yield, Melting point: 124.4-126.1°C).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.20 (m, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.88 (d, *J* = 13.2 Hz, 1H), 3.61 (d, *J* = 13.6 Hz, 1H), 2.36 (s, 3H), 2.28 (s, 3H), 1.10 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.9, 145.0, 143.6, 140.3, 136.9, 134.7, 129.6, 129.4, 126.8, 126.4, 126.1, 125.6, 125.3, 123.8, 120.5, 116.7, 36.9, 34.1, 30.2, 21.6. **HRMS (ESI)** m/z calculated for $C_{27}H_{29}NNaO_3S_2^+$ $[M+H]^+$: 502.1482 found: 502.1475.

2-benzyl-6-chloro-3-(*p*-tolylsulfinyl)-1-tosyl-1*H*-indole (3l)



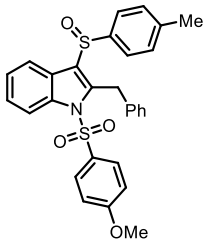
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3l** (yellow solid, 68.7 mg, 86% yield, Melting point: 154.5-156.4 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz , 1H) , 7.55 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 4H), 7.29 (d, *J* = 8.0 Hz , 1H), 7.20 – 7.17 (m, 3H), 7.15 – 7.06 (m, 6H), 4.91 (d, *J* = 16.0 Hz , 1H), 4.76 (d, *J* = 16.0 Hz, 1H), 2.34 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 142.1, 140.9, 139.5, 136.8, 136.0, 135.3, 132.7, 130.1, 129.9, 129.9, 128.7, 126.5, 125.7, 124.8, 124.6, 124.4, 123.6, 120.4, 115.0, 31.3, 21.6, 21.3. **HRMS (ESI)** m/z calculated for $C_{29}H_{24}ClNNaO_3S_2^+$ $[M+Na]^+$: 556.0778 found: 556.0784.

2-benzyl-6-methyl-3-(*p*-tolylsulfinyl)-1-tosyl-1*H*-indole (3n)



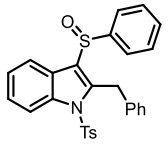
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3n** (yellow solid, 63.9 mg, 83% yield, Melting point: 167.0-169.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.8 Hz , 1H), 7.35 (d, *J* = 8.0 Hz, 3H), 7.31 – 7.23 (m, 7H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.10 – 7.05 (m, 3H), 4.97 (d, *J* = 16.0 Hz , 1H), 4.77 (d, *J* = 16.0 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 142.8, 140.7, 139.6, 137.8, 135.3, 134.9, 134.1, 129.9, 129.8, 128.8, 128.7, 126.9, 126.8, 126.7, 125.1, 124.7, 122.9, 120.2, 114.7, 32.0, 21.6, 21.3, 21.3. **HRMS (ESI)** m/z calculated for $C_{30}H_{27}NNaO_3S_2^+$ $[M+Na]^+$: 536.1325 found: 536.1330.

2-benzyl-1-((4-methoxyphenyl)sulfonyl)-3-(*p*-tolylsulfinyl)-1*H*-indole (3p)



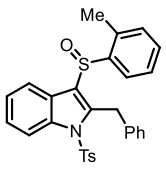
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain (**3p*)***. (yellow oil,62.6mg,81% yield, Melting point: 187.0-189.0 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz , 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.5 Hz , 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.24 (m, 6H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 2H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.81 (d, *J* = 15.5 Hz, 1H), 3.78 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.0, 142.8, 140.6, 139.6, 137.8, 136.5, 129.8, 129.6, 129.0, 128.8, 128.7, 126.8, 125.4, 124.8, 124.6, 124.2, 123.1, 120.4, 114.9, 114.4, 55.7, 31.9, 21.3. **HRMS (ESI)** m/z calculated for $C_{29}H_{25}NNaO_4S_2^+$ $[M+Na]^+$: 538.1118 found: 538.1123.

2-benzyl-3-(phenylsulfinyl)-1-tosyl-1*H*-indole (3q)



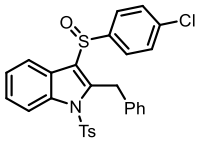
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3q** (yellow solid, 62.6 mg, 86% yield, Melting point: 157.8-158.9 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz , 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.41 (m, 2 H) 7.38 – 7.34 (m, 5H), 7.28 – 7.25 (m, 6H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.02 (d, *J* = 15.6 Hz, 1H), 4.81(d, *J* = 16.0 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 143.2, 142.8, 137.8, 136.6, 135.2, 130.4, 129.9, 129.1, 128.8, 126.9, 126.8, 125.5, 124.9, 124.8, 124.7, 124.4, 123.1, 120.3, 115.0, 32.0, 21.7. **HRMS (ESI)** m/z calculated for $C_{28}H_{23}NNaO_3S_2^+$ $[M+Na]^+$: 508.1012 found: 508.1017.

2-benzyl-3-(*o*-tolylsulfinyl)-1-tosyl-1*H*-indole (3r)



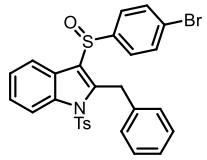
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3r** (yellow solid, 56.1 mg, 75% yield, Melting point: 157.5-159.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (t, *J* = 5.2 Hz, 1H), 8.07 (dd, *J* = 8.0, 5.2 Hz, 1H), 7.51 (dd, *J* = 12.4, 7.2 Hz, 1H), 7.38 (t, *J* = 6.0 Hz, 2H), 7.32 (d, *J* = 4.4 Hz, 2H), 7.28 – 7.23 (m, 4H), 7.21 – 7.19 (m, 2H), 7.10 (d, *J* = 6.0 Hz, 2H), 7.00 (d, *J* = 4.8 Hz, 2H), 4.99 (dd, *J* = 15.6, 3.5 Hz, 1H), 4.85(dd, *J* = 15.6, 4.4 Hz, 1H), 2.30 (d, *J* = 4.0 Hz, 3H), 2.01 (d, *J* = 4.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 143.2, 139.7, 136.9, 136.4, 135.1, 135.0, 131.3, 130.8, 129.8, 129.0, 128.7, 126.8, 126.6, 125.4, 125.4, 124.9, 124.5, 124.2, 121.1, 119.9, 114.9, 31.9, 21.6, 18.8. **HRMS (ESI)** m/z calculated for $C_{29}H_{25}NNaO_3S_2^+$ $[M+Na]^+$: 522.1169 found: 522.1170.

2-benzyl-3-((4-chlorophenyl)sulfinyl)-1-tosyl-1*H*-indole (3s)



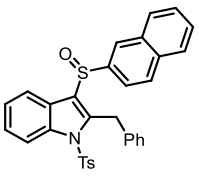
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3s** (yellow solid, 59.3 mg, 76% yield, Melting point: 156.7-157.9 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 8.4 Hz , 2H), 7.34 – 7.30 (m, 4H), 7.28 – 7.26 (m, 6H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.03 (d, *J* = 16.0 Hz, 1H), 4.78(d, *J* = 16.0 Hz, 1H), 2.33(s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.6, 143.3, 141.4, 137.7, 136.6, 136.6, 135.2, 129.9, 129.3, 128.8, 128.7, 126.9, 126.7, 126.1, 125.6, 124.6, 124.4, 122.5, 120.1, 115.1, 31.9, 21.6. **HRMS (ESI)** m/z calculated for $C_{28}H_{22}ClNO_3S_2Na^+$ $[M+Na]^+$: 542.0622 found: 542.0627.

2-benzyl-3-((4-bromophenyl)sulfinyl)-1-tosyl-1*H*-indole (3t)



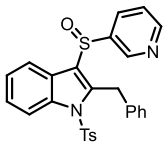
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3t** (yellow solid, 66.0 mg, 78% yield, Melting point: 147.2-149.3 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 3H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.21 (m, 10H), 7.14 (d, *J* = 8,0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2 H), 5.02 (d, *J* = 16.0 Hz, 1H), 4.77 (d, *J* = 16.0 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.7, 143.4, 142.0, 137.8, 136.6, 135.2, 132.3, 130.0, 128.9, 128.7, 127.0, 126.8, 126.3, 125.7, 124.9, 124.6, 124.5, 122.4, 120.14, 115.1, 32.0, 21.7. **HRMS (ESI)** m/z calculated for $C_{28}H_{23}BrNO_3S_2^+$ $[M+H]^+$: 564.0298, 566.0277 found: 564.0295, 566.0272.

2-benzyl-3-(naphthalen-2-ylsulfinyl)-1-tosyl-1*H*-indole (3v)



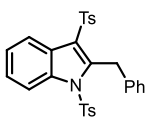
The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3v** (yellow solid, 54.6 mg, 68% yield, Melting point: 156.0-158.0 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 9.2 Hz, 2H), 7.84 – 7.80 (m, 2H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.29 (m, 4H), 7.26 – 7.23 (m, 2H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.2 Hz, 1H), 5.09 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 16.0 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.5, 143.2, 134.0, 137.9, 136.6, 135.2, 134.0, 132.8, 129.9, 129.2, 128.8, 128.5, 127.9, 127.6, 127.1, 126.8, 126.7, 125.5, 125.1, 124.8, 124.4, 122.8, 120.6, 120.3, 115.0, 32.0, 21.6. **HRMS (ESI)** m/z calculated for $C_{32}H_{25}NO_3S_2Na^+$ $[M+Na]^+$: 558.1169 found: 558.1174.

2-benzyl-3-(pyridin-3-ylsulfinyl)-1-tosyl-1*H*-indole (3w)



The crude product was purified by flash chromatography (PE/DCM=1:4) to obtain **3w** (yellow solid, 55.4 mg, 76 % yield, Melting point: 145.0-147.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.8 Hz, 1H), 8.22 (d, *J* = 8.0 Hz , 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.92 (t, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.36 (m, 2H), 7.24 – 7.20 (m, 7H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.92 (d, *J* = 16.0 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4, 150.0, 145.2, 143.9, 137.6, 137.4, 136.3, 135.3, 129.7, 129.0, 128.5, 126.8, 126.6, 125.3, 125.0, 124.4, 124.1, 122.4, 120.5, 119.8, 114.9, 32.0, 21.5. **HRMS (ESI)** m/z calculated for $C_{27}H_{22}N_2NaO_3S_2^+$ $[M+Na]^+$: 509.0965 found: 509.0970.

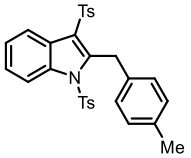
2-benzyl-1,3-ditosyl-1*H*-indole (4a)[6]



The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4a** (white solid, 133.0 mg, 86% yield, Melting point: 184.5-186.6 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (t, *J* = 9.6 Hz, 2H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.38 – 7.35 (m, 2H), 7.28 (s, 1H), 7.18 –

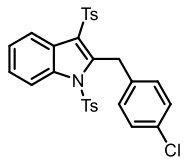
7.09 (m, 6H), 7.04 – 7.02 (m, 4H), 5.07 (s, 2H), 2.32 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 144.1, 143.6, 139.3, 137.2, 135.6, 135.1, 129.9, 129.7, 128.8, 128.4, 126.8, 126.3, 125.7, 125.5, 124.8, 122.8, 121.3, 120.8, 114.8, 31.0, 21.6, 21.5.

2-(4-methylbenzyl)-1,3-ditosyl-1*H*-indole (4b)[6]



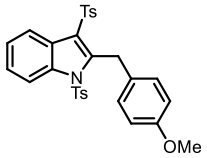
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4b** (white solid, 120.7 mg, 76% yield, Melting point: 181.5-183.6 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 – 8.16 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.38 (m, 2H), 7.28 – 7.26 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 5.0 (s, 2H), 2.33 (s, 3H), 2.31 (s, 6H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ145.5, 144.1, 144.0, 135.8, 135.7, 135.1, 134.1, 129.8, 129.6, 129.0, 128.7, 126.8, 125.7, 125.5, 124.8, 120.8, 114.8, 30.7, 21.6, 21.6, 21.1.

2-(4-chlorobenzyl)-1,3-ditosyl-1*H*-indole (4c)[6]



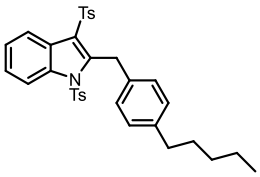
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4c** (white solid, 117.2 mg, 71% yield, Melting point: 197.5-199.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 – 8.20 (m, 2H),7.62 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.38 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.06 – 7.03 (m, 4H), 6.87 (d, *J* = 8.0 Hz, 2H); 5.0 (s, 2H), 2.33 (s, 6H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 145.8, 144.4, 142.7, 139.2, 135.8, 135.5, 135,1, 132.3, 130.0, 129.9, 129.7, 128.4, 126.7, 126.5, 126.0, 125.3, 125.0, 120.9, 114., 30.5, 21.7, 21.6.

2-(4-methoxybenzyl)-1,3-ditosyl-1*H*-indole (4d)



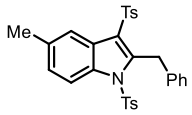
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4d** (white solid, 137.4 mg, 84% yield, Melting point: 164.5-166.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 – 8.15 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.35 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 16.0 Hz, 2H), 4.98 (s, 2H), 3.77 (s, 3H), 2.32 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 158.3 145.5, 144.1, 139.4, 135.7, 135.1, 129.9, 129.9, 129.7, 129.2, 126.8, 125.8, 125.5, 124.8, 121.1, 120.8, 114.8, 113.8, 55.4., 30.2, 21.6, 21.6. **HRMS (ESI)** m/z calculated for $C_{30}H_{28}NO_5S_2^+$ $[M+H]^+$: 546.1403 found: 546.1407.

2-(4-pentylbenzyl)-1,3-ditosyl-1H-indole (4e)



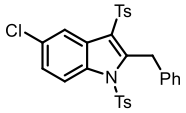
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4e** (white solid, 124.8 mg, 71% yield, Melting point: 134.5-135.9 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 – 8.16 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.02 – 6.96 (m, 6H), 5.02 (s, 2H), 2.56 (t, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 2.29 (S, 3H), 1.61– 1.58 (m, 2H), 1.36 – 1.33 (m, 4H), 0.92 – 0.89 (m, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 145.6, 144.10, 141.07, 139.4, 135.6, 135.1, 134.3, 129.9, 129.7, 128.8, 128.4, 126.9, 126.8, 125.7, 125.5, 124.8, 121.1, 120.8, 114.8, 35.6, 31.7, 31.6, 30.7, 22.7, 21.6, 21.6, 14.1. **HRMS (ESI)** m/z calculated for $C_{34}H_{36}NO_4S_2^+$ $[M+H]^+$: 586.2081 found: 586.2080.

2-benzyl-5-methyl-1,3-ditosyl-1*H*-indole (4f)



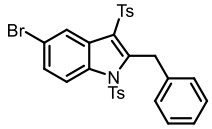
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4f** (white solid, 134.9 mg, 85% yield, Melting point: 156.1-157.3 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 – 8.11 (m, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.28 (s, 1H), 7.26 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.94 – 6.87 (m, 4H), 5.00 (s, 2H), 2.33 (s, 3H), 2.31 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.5, 144.0, 143.9, 139.3, 135.8, 135.6, 135.1, 134.0, 129.7, 129.6, 128.9, 128.6, 126.8, 125.7, 125.4, 124.7, 121.1, 120.7, 114.8, 30.6, 21.6, 21.5, 21.0. **HRMS (ESI)** m/z calculated for $C_{30}H_{28}NO_4S_2^+$ $[M+H]^+$: 530.1455 found: 530.1446.

2-benzyl-5-chloro-1,3-ditosyl-1*H*-indole (4g)



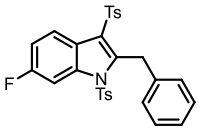
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4g** (white solid,136.7 mg, 83% yield, Melting point: 147.6-149.4 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) 8.23 – 8.20 (m, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.06 – 7.03 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 5.00 (s, 2H), 2.33 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8, 144.3, 142.7, 139.1, 135.8, 135.5, 135.0, 132.2, 130.0, 129.9, 129.7, 128.3, 126.7, 126.5, 126.0, 125.2, 124.9, 121.6, 120.8, 114.8, 30.4, 21.6, 21.5. **HRMS (ESI)** m/z calculated for $C_{29}H_{25}ClNO_4S_2^+$ $[M+H]^+$: 550.0908 found: 550.0899.

2-benzyl-5-bromo-1,3-ditosyl-1*H*-indole (4h)



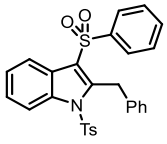
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4h** (white solid, 144.4 mg, 81% yield, Melting point: 154.5-156.3 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.39 (m, 1H), 7.19 – 7.16 (m, 3H), 7.11 – 7.04 (m, 5 H), 6.96 (d, *J* = 8.0 Hz, 2H); 6.90 (d, *J* = 8.0 Hz, 2H), 4.95 (s, 2H), 2.26 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 146.0, 144.6, 144.4, 139.0, 136.8, 134.7, 134.3, 130.0, 129.8, 128.8, 128.7, 128.5, 127.1, 126.8, 126.8, 126.4, 123.4, 120.8, 118.6, 116.2, 31.1, 21.6, 21.6. **HRMS (ESI)** m/z calculated for $C_{29}H_{25}BrNO_4S_2^+$ $[M+H]^+$: 594.0403, 596.0383 found: 594.0398, 596.0377.

2-benzyl-6-fluoro-1,3-ditosyl-1*H*-indole (4i)



The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4i** (white solid, 126.4 mg, 79% yield, Melting point: 157.5-159.8 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 – 8.05 (m, 1H), 7.85 – 7.82 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.18 (m, 2H), 7.11 – 7.02 (m, 6H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H); 4.94 (s, 2H), 2.25 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 161.3 (d, *J* = 242.0 Hz), 145.9, 144.3, 143.9 (d, *J* = 4.0 Hz) 139.1, 137.0, 135.9, 135.8, 134.7, 130.0, 129.7, 128.8, 128.4, 126.9 (d, *J* = 6.0 Hz), 126.3, 121.9 (d, *J* = 10.0 Hz), 121.7, 121.2, 113.4 (d, *J* = 24.0 Hz), 102.3 (d, *J* = 29.0 Hz), 31.1, 21.63, 21.55. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.18 (q, *J* = 7.5 Hz). **HRMS (ESI)** m/z calculated for $C_{29}H_{25}FNO_4S_2^+$ $[M+H]^+$: 534.1209 found: 534.1205.

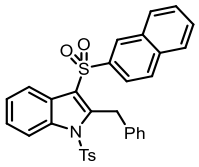
2-benzyl-3-(phenylsulfonyl)-1-tosyl-1*H*-indole (4j)[6]



The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4j** (white solid, 129.3 mg, 86% yield, Melting point: 179.4-181.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 – 8.16 (m, 2H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.39 – 7.37 (m, 2H), 7.33 – 7.27 (m, 4H), 7.14 (dd, *J* = 16.0, 8.4 Hz, 3H), 7.04 – 7.01 (m, 4H), 5.08 (s, 2H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.7, 144.0, 142.2, 137.1, 135.6, 135.0, 133.1, 129.9, 129.1, 128.8,

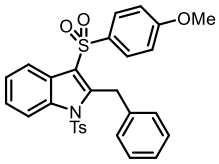
128.4, 126.8, 126.7, 126.3, 125.8, 125.5, 124.9, 120.9, 120.8, 114.9, 31.1, 21.6.

2-benzyl-3-(naphthalen-2-ylsulfonyl)-1-tosyl-1*H*-indole (4k)



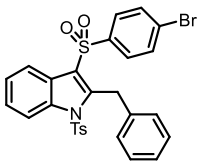
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4k** (white solid, 125.6 mg, 76% yield, Melting point: 143.7-145.6 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) 8.31 – 8.27 (m, 2H), 8.19 (s, 1H), 7.80 – 7.38 (m, 3H), 7.70 – 7.66 (m, 1H), 7.62 – 7.52 (m, 2H), 7.42 – 7.32 (m, 4H), 7.12 – 7.02 (m, 7H), 5.15 (s, 2 H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ147.2, 145.7, 143.9, 139.0, 137.1, 135.1, 132.1, 130.0, 129.6, 129.6, 129.4, 129.0, 128.7, 128.4, 128.3, 127.8, 127.4, 126.8, 126.4, 125.8, 124.94, 124.93, 121.9, 121.9, 120.8, 114.9, 31.1, 21.6. **HRMS (ESI)** m/z calculated for $C_{32}H_{25}NS_2O_4Na^+$ $[M+Na]^+$: 574.1118 found: 574.1123.

2-benzyl-3-((4-methoxyphenyl)sulfonyl)-1-tosyl-1H-indole (4l)



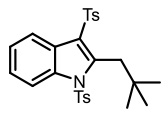
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4l** (white solid, 124.4 mg, 78% yield, Melting point: 155.5-157.3 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 – 8.16 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 4.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.13 (m, 3H), 7.04 – 7.01 (m, 4H), 6.75 (d, *J* = 8.0 Hz, 2H), 5.07 (s, 2H), 3.77 (s, 3H), 2.30 (s, 3H) . **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 163.3, 145.7, 143.3, 137.2, 135.6, 135.0, 133.9, 129.9, 129.0, 128.8, 128.4, 126.8, 126.3, 125.8, 125.4, 124.8, 121.7, 120.8, 114.8, 114.2, 55.64, 31.0, 21.6. **HRMS (ESI)** m/z calculated for $C_{29}H_{26}NO_5S_2^+$ $[M+H]^+$: 532.1247 found: 532.1249.

2-benzyl-3-((4-bromophenyl)sulfonyl)-1-tosyl-1*H*-indole (4m)



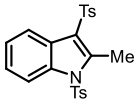
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4m** (white solid, 125.4 mg, 72% yield, Melting point: 197.5-199.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 – 8.16 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.38 (m, 4H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.12 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.06 (s, 2H), 2.32 (s, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 145.9, 144.08, 141.07, 136.9, 135.6, 135.0, 132,3, 130.0, 128.7, 128.5, 128.3, 128.2, 126.9, 126.4, 126.0, 125.3, 125.0, 120.6, 120.3, 115.0, 31.0, 21.6. **HRMS (ESI)** m/z calculated for $C_{28}H_{23}BrNO_4S_2^+$ $[M+H]^+$: 580.0247, 582.0226, found: 580.0244, 582.0219.

2-neopentyl-1,3-ditosyl-1*H*-indole (4n)



The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4n** (white solid, 105.6 mg, 71% yield, Melting point: 117.5-119.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.11 (m, 3H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 8.0 Hz, 2H), 3.32 (s, 2H), 2.35 (s, 3H), 2.22 (s, 3H), 1.05 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 144.6, 137.9, 134.9, 134.7, 132.8, 131.8, 129.5, 129.4, 126.5, 126.4, 125.0, 124.7, 119.9, 117.0, 116.2, 38.6, 34.4, 30.1, 21.6, 20.9. **HRMS (ESI)** m/z calculated for $C_{27}H_{30}NO_4S_2^+$ $[M+H]^+$: 496.1611 found: 496.1588 (Δ = -4.6 ppm).

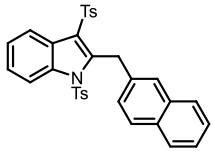
2-methyl-1,3-ditosyl-1*H*-indole (4o)[7]



The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4o** (colorless oli, 89.7 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 – 8,20 (m, 1H), 8.12 – 8,09 (m,1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.32 (m, 2H), 7.25

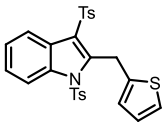
(d, *J* = 8.0 Hz, 3H), 2.98 (s, 3H), 2.39 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.1, 144.2, 142.4, 139.8, 135.6, 135.5, 130.3, 129.9, 126.7, 126.5, 125.5, 125.5, 124.8, 120.4, 119.9, 114.5, 21.7, 21.6, 13.1.

2-(naphthalen-2-ylmethyl)-1,3-ditosyl-1*H*-indole (4p)



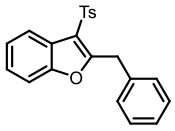
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4p** (white solid, 139.2 mg, 82% yield, Melting point: 196.5-198.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 – 8.26 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.45-7.41 (m, 2H), 7.40 – 7.36 (m, 1H), 7.33 – 7.26 (m, 2H), 7.22 – 7.17(m, 3H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.74 (s, 1H), 6.66 (d, *J* = 8.0 Hz 2H), 5.21 (s, 2H), 2.14 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 145.8, 144.4, 142.7, 139.2, 135.8, 135.5, 135,1, 132.3, 130.0, 129.9, 129.7, 128.4, 126.7, 126.5, 126.0, 125.3, 125.0, 120.9, 114., 30.5, 21.7, 21.6. **HRMS (ESI)** m/z calculated for $C_{33}H_{28}NO_4S_2^+$ $[M+H]^+$: 566.1455 found: 566.1453.

2-(thiophen-2-ylmethyl)-1,3-ditosyl-1*H*-indole (4q)[6]



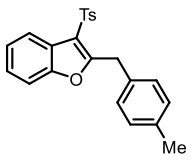
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **4q** (white solid, 65.7 mg, 84% yield, Melting point: 214.5-216.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (t, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.26 (m, 4H), 7.08 – 7.06 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.72 (t, *J* = 4.0 Hz, 1H), 6.58 (d, *J* = 4.0 Hz, 1H), 5.16 (s, 2H), 2.26 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 145.8, 144.2, 143.1, 139.7, 139.3, 135.5, 135,0, 130.0, 129.7, 126.8, 126.62, 126.58, 125.9, 125.4, 124.9, 124.4, 120.9, 120.7, 114.9, 26.1, 21.6, 21.6.

2-benzyl-3-tosylbenzofuran (7a)[8]



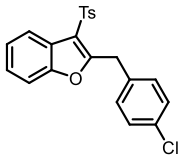
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7a** (white solid, 93.4 mg, 86% yield, Melting point 183.8-185.2 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (t, *J* = 4.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.32 (m, 1H), 7.26 – 7.20 (m, 6H), 7.18 (d, *J* = 6.5 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.50 (s, 2H), 2.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.4, 153.5, 144.3, 139.4, 135.8, 129.8, 129.1, 128.7, 127.1, 126.9, 125.5, 124.4, 124.2, 120.6, 118.3, 111.5, 33.2, 21.6. **HRMS (ESI)** m/z calculated for $C_{22}H_{19}SO_3^+$ $[M+H]^+$: 363.1049 found: 363.1046.

2-(4-methylbenzyl)-3-tosylbenzofuran (7b)[8]



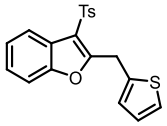
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7b** (white solid, 98.1 mg, 87% yield, Melting point: 157.9-159.2 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.30 – 7.28 (m, 2H), 7.23 – 7.19 (m, 4H), 7.10 (d, *J* = 7.2 Hz, 2H), 4.53 (s, 2H), 2.37 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4, 153.5, 144.3, 139.4, 135.8, 131.8, 130.8, 129.8, 129.1, 128.7, 127.0, 126.9, 125.5, 124.4, 120.6, 111.5, 33.2, 21.6, 21.5. **HRMS (ESI):** m/z calculated for $C_{23}H_{21}O_3S^+$ $[M + H]^+$: 377.1206 found: 377.1201.

2-(4-chlorobenzyl)-3-tosylbenzofuran (7c)[8]



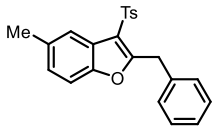
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7c** (white solid, 95.1 mg, 80% yield, Melting point: 142.5-143.9 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 3.2 Hz, 1H), 7.79 (t, *J* = 6.4 Hz, 2H), 7.42 – 7.40 (m, 1H), 7.33 – 7.30 (m, 2H), 7.27-7.22 (m, 6H), 4.54 (d, *J* = 5.2 Hz, 2H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.8, 153.6, 144.5, 139.4, 134.3, 133.1, 130.5, 129.9, 128.9, 126.9, 125.7, 124.6, 124.2, 120.7, 118.7, 111.5, 32.6, 21.6. **HRMS (ESI)** m/z calculated for $C_{22}H_{18}ClSO_3^+$ $[M+H]^+$: 397.0660 found: 397.0651.

2-(thiophen-2-ylmethyl)-3-tosylbenzofuran (7d)[6]



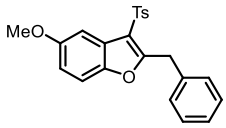
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7d** (white solid, 79.5 mg, 72% yield, Melting point: 173.7-175.3 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 4.2 Hz, 3H), 7.44 – 7.42 (m, 1H), 7.31 (d, *J* = 3.6 Hz, 2H), 7.25 (t, *J* = 6.0 Hz, 2H), 7.19 (t, *J* = 5.2 Hz, 1H), 6.98 (d, *J* = 4.8 Hz, 1H), 6.95 (t, *J* = 5.2 Hz, 1H), 4.80 (s, 2H), 2.37 (s, 3H). **^{13}CNMR** (101 MHz, $CDCl_3$) δ 160.1, 153.6, 144.4, 139.3, 137.2, 129.9, 127.1, 127.0, 126.9, 125.7, 125.0, 124.5, 124.1, 120.7, 118.2, 111.6, 27.6, 21.6. **HRMS (ESI)** m/z calculated for $C_{20}H_{17}O_3S_2^+$ $[M+H]^+$: 369.0614 found: 369.0613.

2-benzyl-5-methyl-3-tosylbenzofuran (7e)[8]



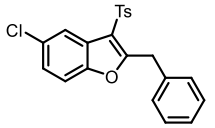
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7e** (white solid, 95.9 mg, 85% yield, Melting point: = 153.5-154.6 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.67 (s, 1H), 7.30 – 7.26 (m, 6H), 7.22 (d, *J*= 8.0 Hz, 2H), 7.10 (d, *J*= 8.5 Hz, 1H), 4.55 (s, 2H), 2.44 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.5, 152.0, 144.1, 139.5, 135.9, 134.2, 129.8, 129.1, 128.7, 127.0, 126.8, 126.7, 124.3, 120.3, 118.0, 111.0, 33.2, 21.5, 21.5.

2-benzyl-5-methoxy-3-tosylbenzofuran (7f)[8]



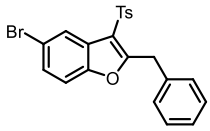
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7f** (white solid, 97.6 mg, 83% yield, Melting point: 169.2-170.9 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.30 – 7.25 (m, 6H), 7.22 (d, *J* =8.0 Hz, 2H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.54 (s, 2H), 3.85 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0, 157.0, 148.4, 144.2, 139.5, 135.8, 129.8, 129.1, 128.7, 127.0, 126.8, 124.9, 118.2, 114.3, 112.1, 102.9, 56.0, 33.3, 21.6. **HRMS (ESI)** m/z calculated for $C_{23}H_{21}O_4S^+$ $[M+H]^+$: 393.1155 found: 393.1151.

2-benzyl-5-chloro-3-tosylbenzofuran (7g)[8]



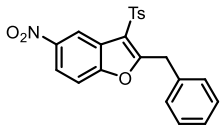
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7g** (white solid, 92.7 mg, 78% yield, Melting point: 144.8-145.9 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.29 (m, 5H), 7.27-7.23 (m, 4H), 4.55 (s, 2H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8, 151.9, 144.6, 139.1, 135.4, 130.3, 130.0, 129.1, 128.9, 127.2, 126.8, 125.9, 125.6, 120.3, 118.3, 112.6, 33.3, 21.6. **HRMS (ESI)** m/z calculated for $C_{22}H_{18}ClSO_3$ $[M+H]^+$: 397.0660 found: 397.0659.

2-benzyl-5-bromo-3-tosylbenzofuran (7h)[8]



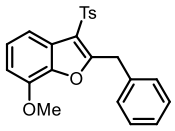
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7h** (white solid, 99.0 mg, 75% yield, Melting point: 152.0-153.5 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (t, *J*= 2.4 Hz, 1H), 7.76 (d, *J* = 6.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.30 – 7.23 (m, 8H), 6.54 (s, 2H), 2.37 (s, 3H). **^{13}CNMR** (126 MHz, $CDCl_3$) δ 162.7, 152.3, 144.7, 139.1, 135.4, 130.1, 129.2, 128.9, 128.7, 127.3, 126.9, 126.2, 123.3, 118.2, 117.8, 113.1, 33.3, 21.7. **HRMS (ESI)** m/z calculated for $C_{22}H_{18}BrSO_3$ $[M+H]^+$: 441.0155 found: 441.0162.

2-benzyl-5-nitro-3-tosylbenzofuran (7i)[8]



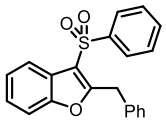
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7i** (white solid, 102.58 mg, 84% yield, Melting point: 153.2-154.5 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (t, *J* = 2.8 Hz, 1H), 8.23 – 8.20 (m, 1H), 7.83 – 7.80 (m, 2H), 7.50 (dd, *J* = 9.2, 3.2 Hz, 1H), 7.33 – 7.27 (m, 7H), 4.60 (s, 2H), 2.38 (s, 3H). **^{13}CNMR** (101 MHz, $CDCl_3$) δ 164.6, 156.1, 145.2, 145.2, 138.6, 134.9, 130.3, 129.2, 129.0, 127.5, 127.1, 125.0, 121.5, 119.6, 117.2, 112.3, 33.4, 21.7. **HRMS (ESI)** m/z calculated for $C_{22}H_{18}NO_5S^+$ $[M+H]^+$: 408.0901 found: 408.0906.

2-benzyl-7-methoxy-3-tosylbenzofuran (7j)[8]



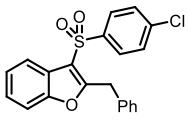
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7j**(white solid, 88.2 mg, 75% yield, Melting point: 179.2-181.1 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.25 (s, 1H), 7.22 – 7.13 (m, 8H), 6.81 (d, *J* = 9.0 Hz, 1H), 4.46 (s, 2H), 3.77 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.0, 157.0, 148.4, 144.2, 139.5, 135.8, 129.8, 129.1, 128.7, 127.0, 126.8, 124.9, 118.3, 114.3, 112.1, 103.0, 56.0, 33.3, 21.5. **HRMS (ESI)** m/z calculated for $C_{23}H_{21}O_4S^+$ $[M+H]^+$: 393.1156 found: 393.1151.

2-benzyl-3-(phenylsulfonyl)benzofuran (7k)[8]



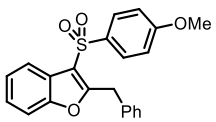
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7k** (white solid, 92.9 mg, 89% yield, Melting point: 180.0-182.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 4.4 Hz, 3H), 7.44 (t, *J* = 6.8 Hz, 1H), 7.35 – 7.32 (m, 3H), 7.24 – 7.18 (m, 7H), 4.50 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.8, 153.6, 142.3, 135.8, 133.4, 129.3, 129.2, 128.8, 127.2, 126.8, 125.6, 124.5, 124.3, 120.6, 118.1, 111.6, 33.3.

2-benzyl-3-((4-chlorophenyl)sulfonyl)benzofuran (7l)[8]



The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7l** (white solid, 97.4 mg, 85% yield, Melting point: 140.1-142.0 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 – 7.84 (m, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 4.8 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.33 – 7.29 (m, 7H), 4.57 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.1, 153.6, 140.7, 140.0, 135.7, 129.5, 129.1, 128.9, 128.3, 127.2, 125.8, 124.7, 124.1, 120.4, 117.7, 111.7, 33.3.

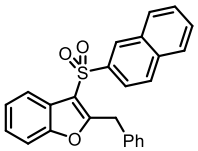
2-benzyl-3-((4-methoxyphenyl)sulfonyl)benzofuran (7m)[8]



The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7m** (white solid, 98.7 mg, 87% yield, Melting point: 142.1-144.0 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 6.0, 3.2 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.41 (dd, *J* = 6.0, 3.2 Hz, 1H), 7.33 – 7.28 (m, 6H), 7.25 (s, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.58 (s, 2H), 3.81 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.4, 161.1, 153.5, 135.9, 134.0, 129.1, 129.1, 128.7, 127.0, 125.5,

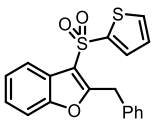
124.4, 124.2, 120.6, 118.7, 114.4, 111.5, 55.6, 33.2.

2-benzyl-3-(naphthalen-2-ylsulfonyl)benzofuran (7n)[8]



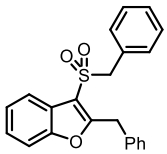
The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7n** (white solid, 94.3 mg, 79% yield, Melting point: 174.8-176.8 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.8 Hz, 1H), 8.52 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 8.4 Hz, 2H), 7.29 – 7.21 (m, 7H), 4.64 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.6, 153.5, 136.8, 135.4, 135.2, 134.2, 129.2, 129.2, 129.1, 128.8, 128.5, 128.4, 127.2, 127.0, 125.5, 124.4, 124.3, 124.3, 124.0, 120.5, 118.1, 111.6, 33.5.

2-benzyl-3-(thiophen-2-ylsulfonyl)benzofuran (7o)[8]



The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7o** (white solid, 62.7 mg, 59% yield, Melting point: 161.8-163.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (t, *J* = 4.0 Hz, 1H), 7.61 (d, *J* = 3.6 Hz, 1H), 7.56 (d, *J* = 4.8 Hz, 1H), 7.43 (t, *J* = 4.0 Hz, 1H), 7.36 – 7.27 (m, 7H), 7.01 (t, *J* = 4.8 Hz, 1H), 4.58 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.5, 153.5, 143.9, 135.6, 133.2, 132.6, 129.2, 128.7, 127.7, 127.1, 125.6, 124.5, 123.9, 120.6, 118.5, 111.5, 33.3.

2-benzyl-3-(benzylsulfonyl)benzofuran (7p)[8]



The crude product was purified by flash chromatography (PE/EA=10:1) to obtain **7p** (white solid, 60.8 mg, 56% yield, Melting point: 90.3-92.0 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (t, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.33 – 7.24 (m, 7H), 7.23 – 7.18 (m, 3H), 7.05 (t, *J* = 8.4 Hz, 2H), 4.33 (d, *J* = 10.0 Hz, 2H), 3.94 (d, *J* = 10.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.7, 153.4, 135.6, 131.0, 129.2, 129.0, 128.7, 128.3, 127.1, 125.6, 125.6, 124.6, 124.5, 120.5, 113.9, 111.5, 63.0, 32.6. **HRMS (ESI)** m/z calculated for $C_{22}H_{19}SO_3^+$ $[M+H]^+$: 363.1049 found: 363.1046.

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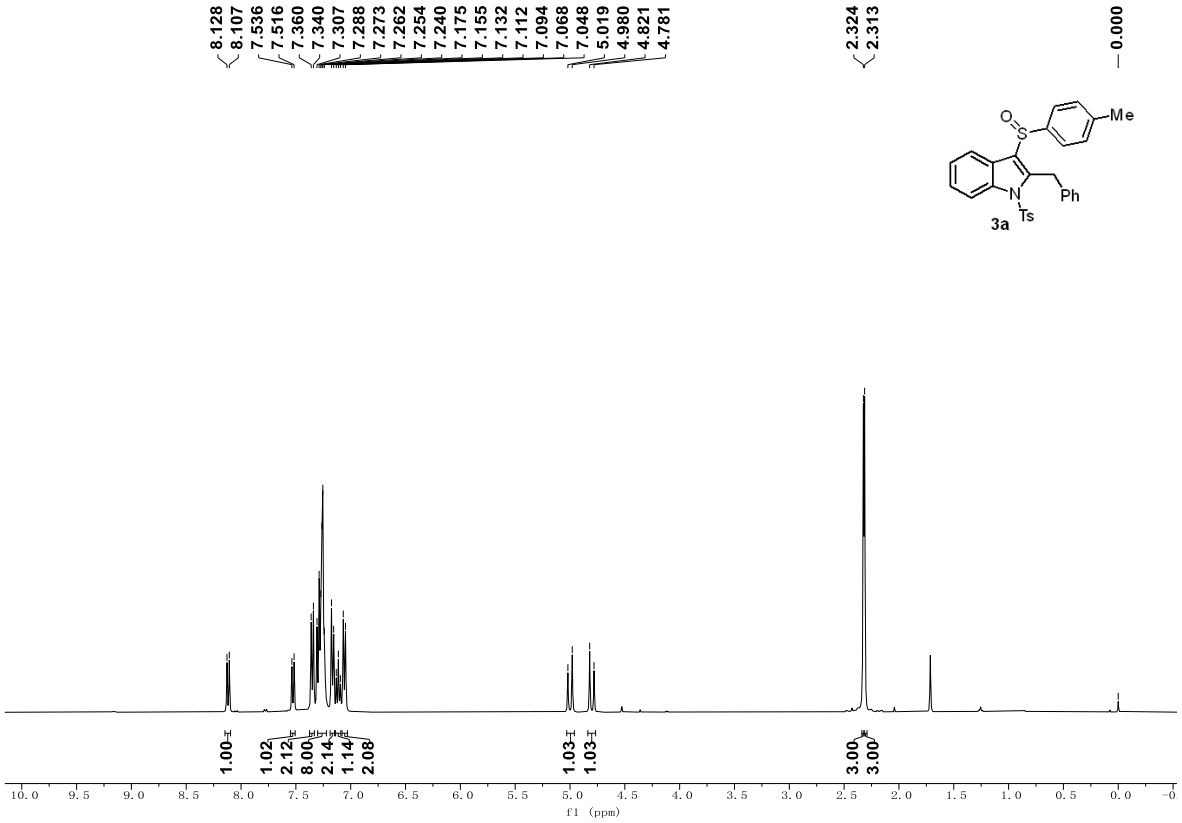
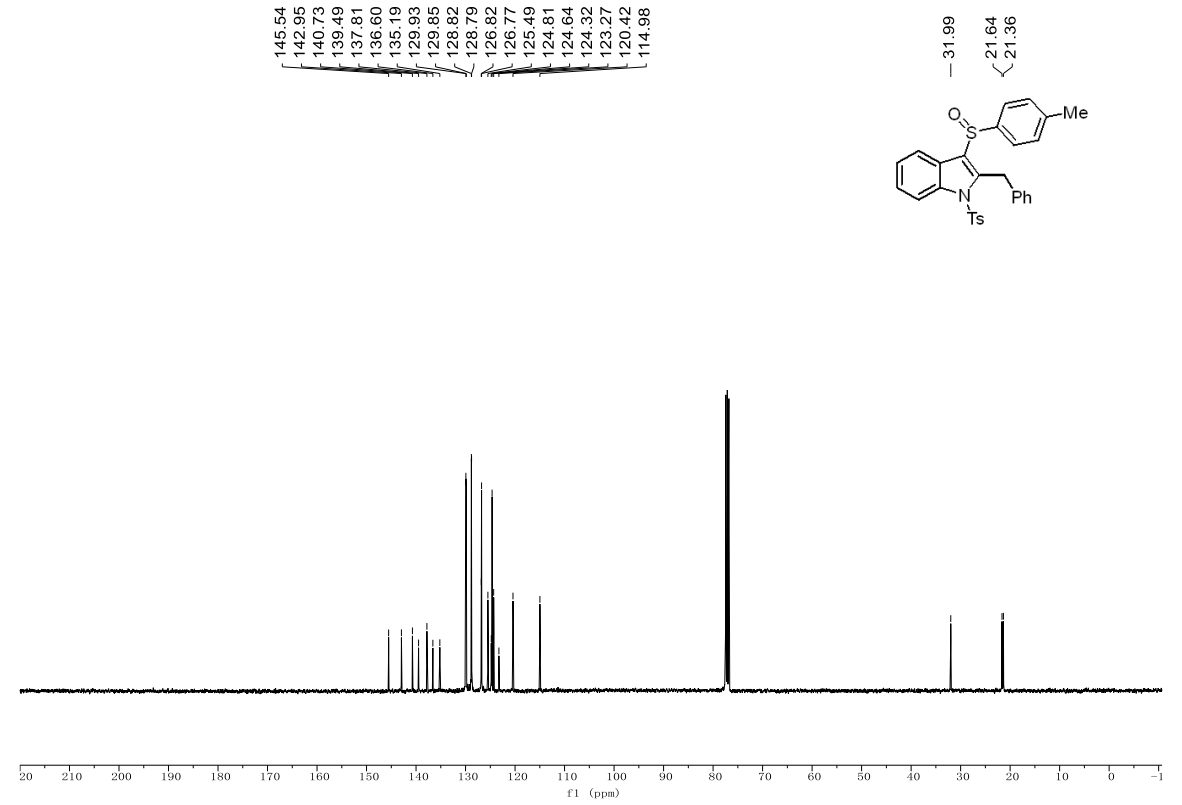
Copies of NMR spectra

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



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



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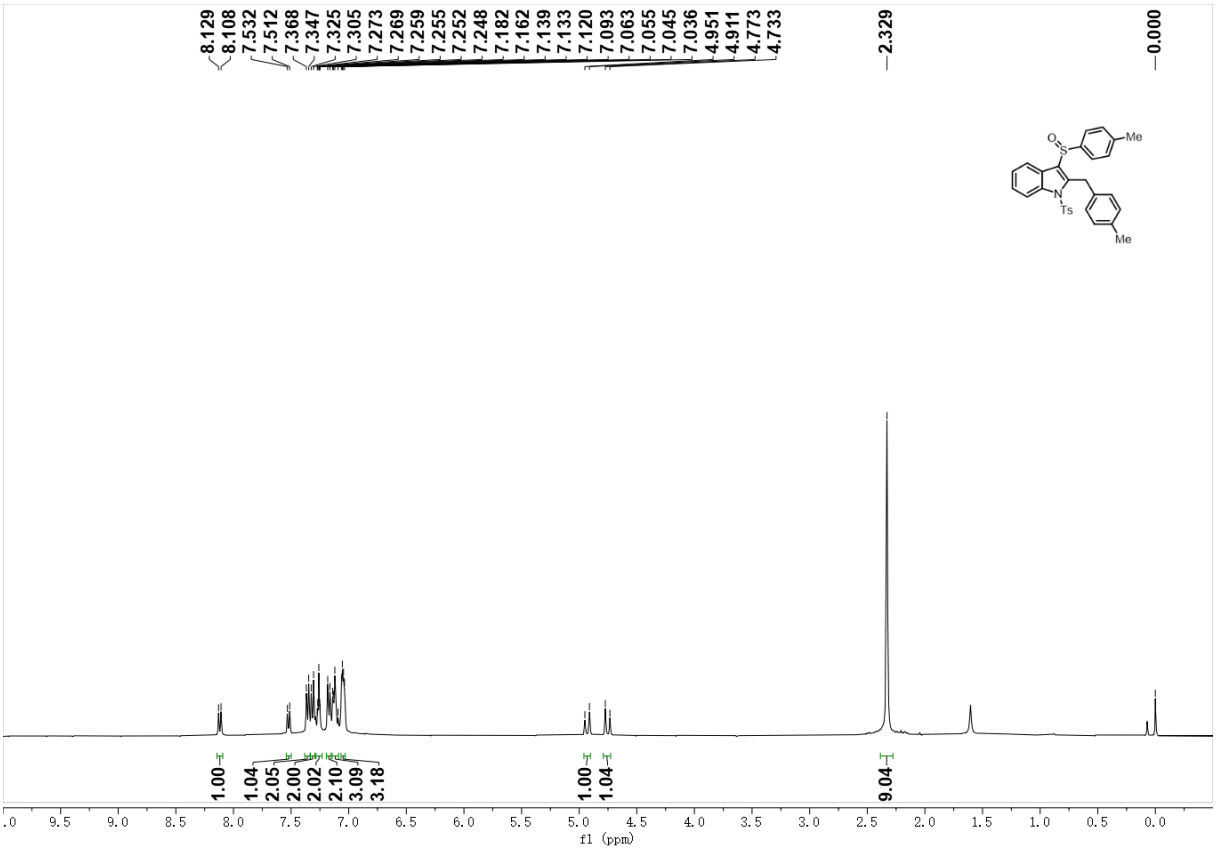

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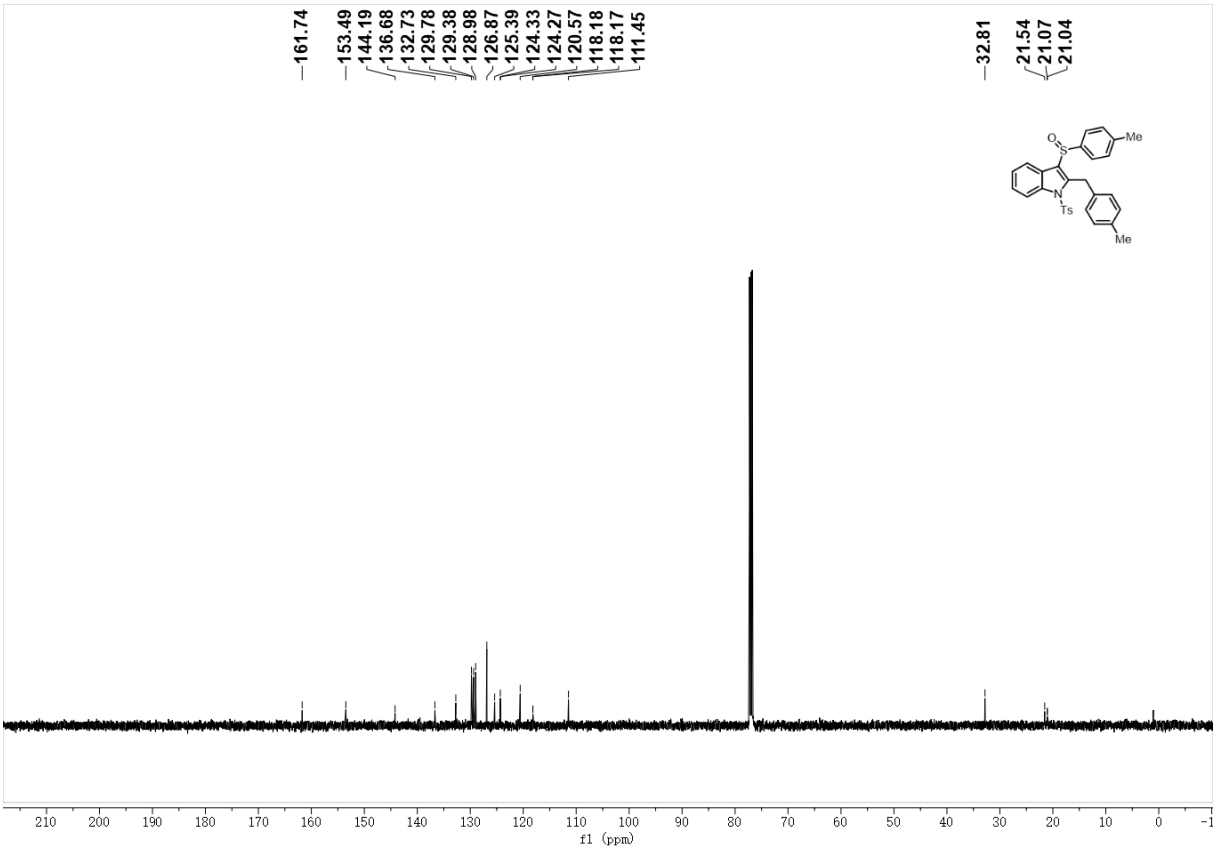

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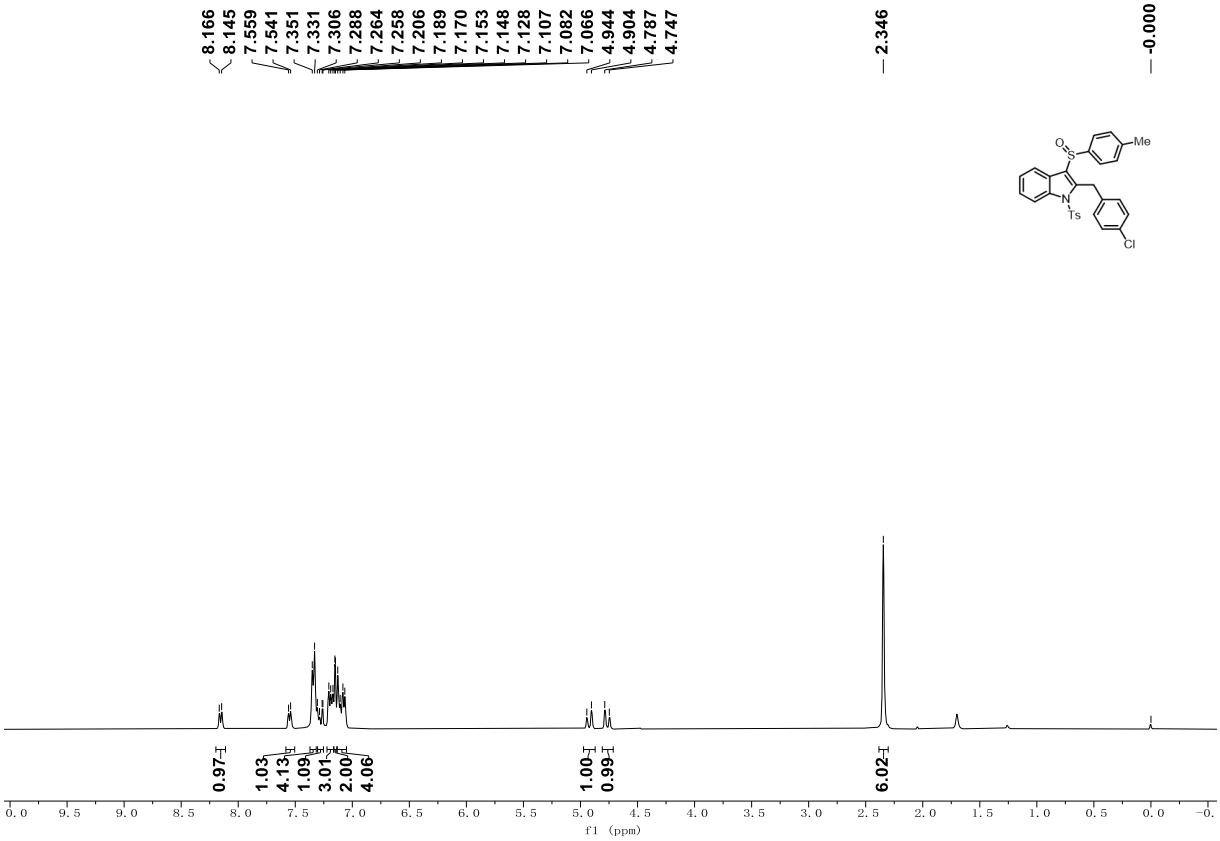

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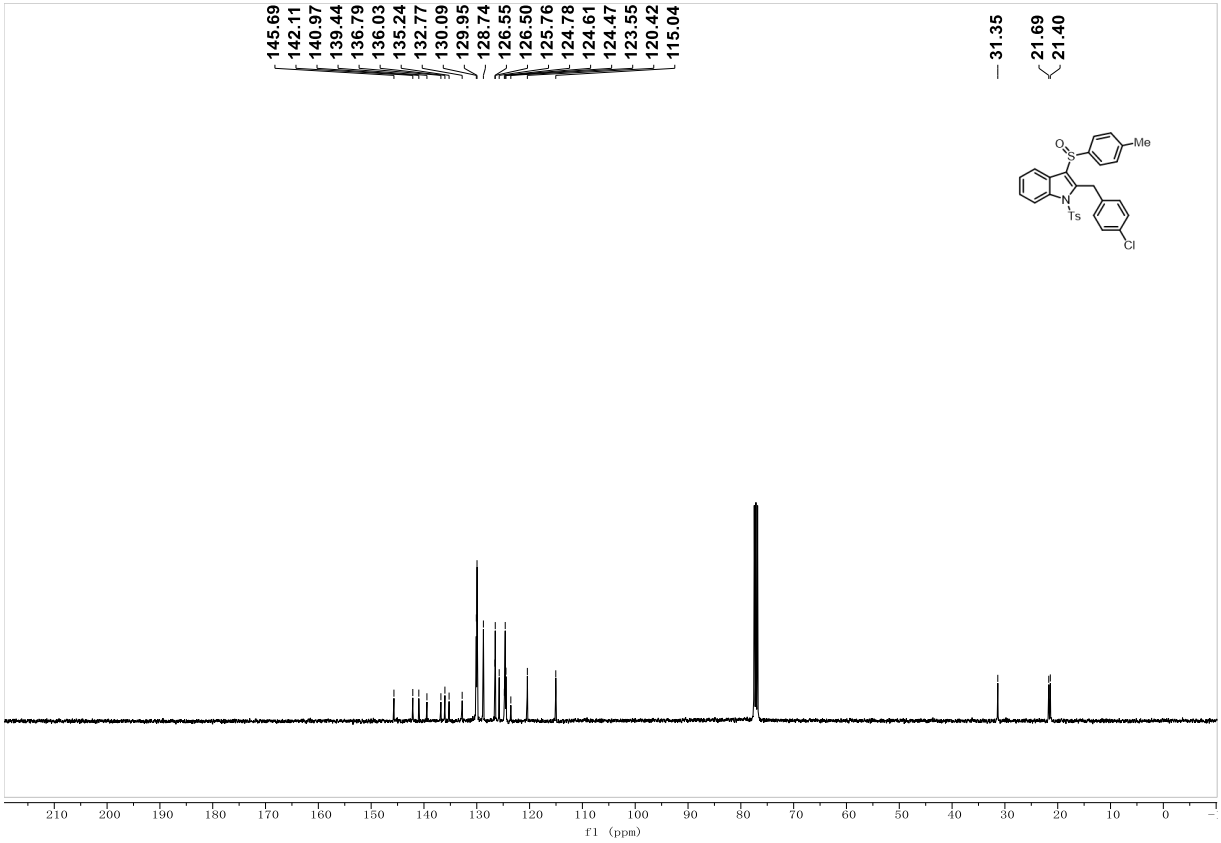

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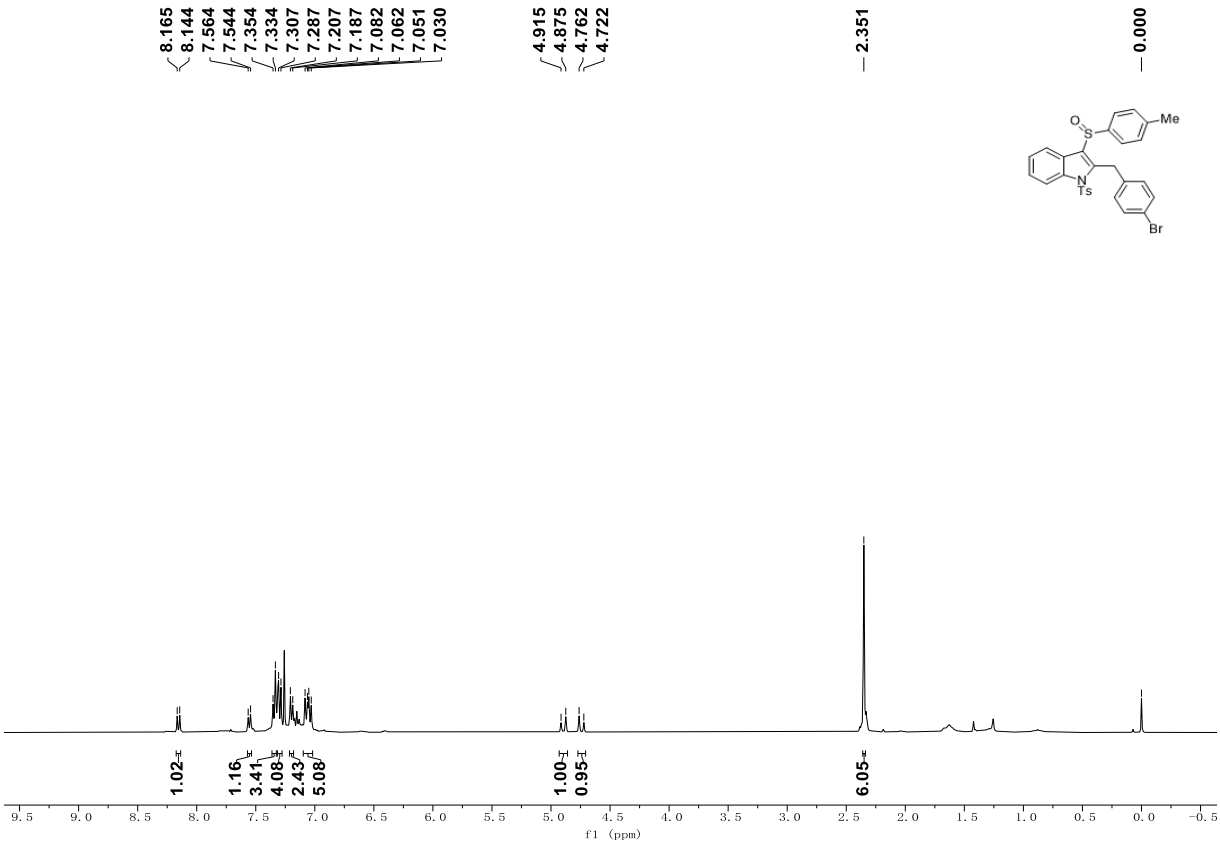

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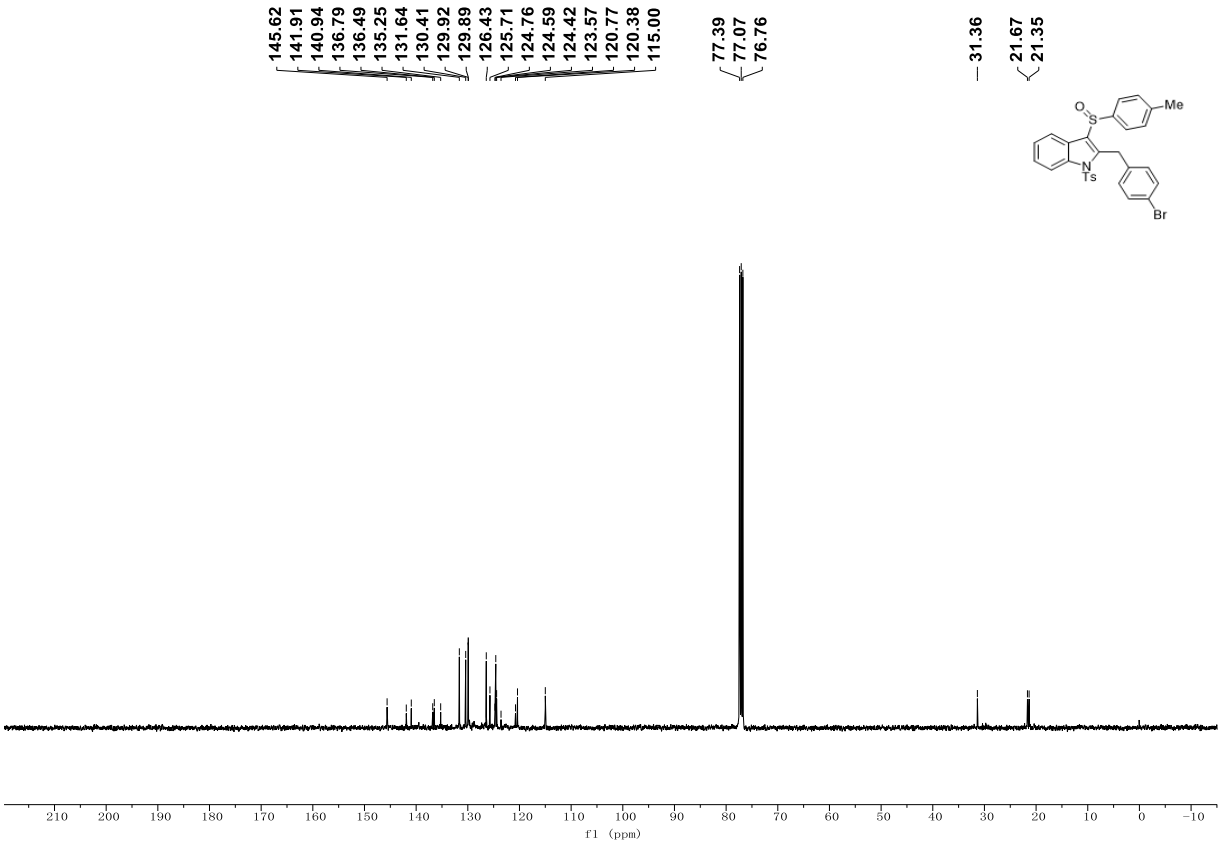
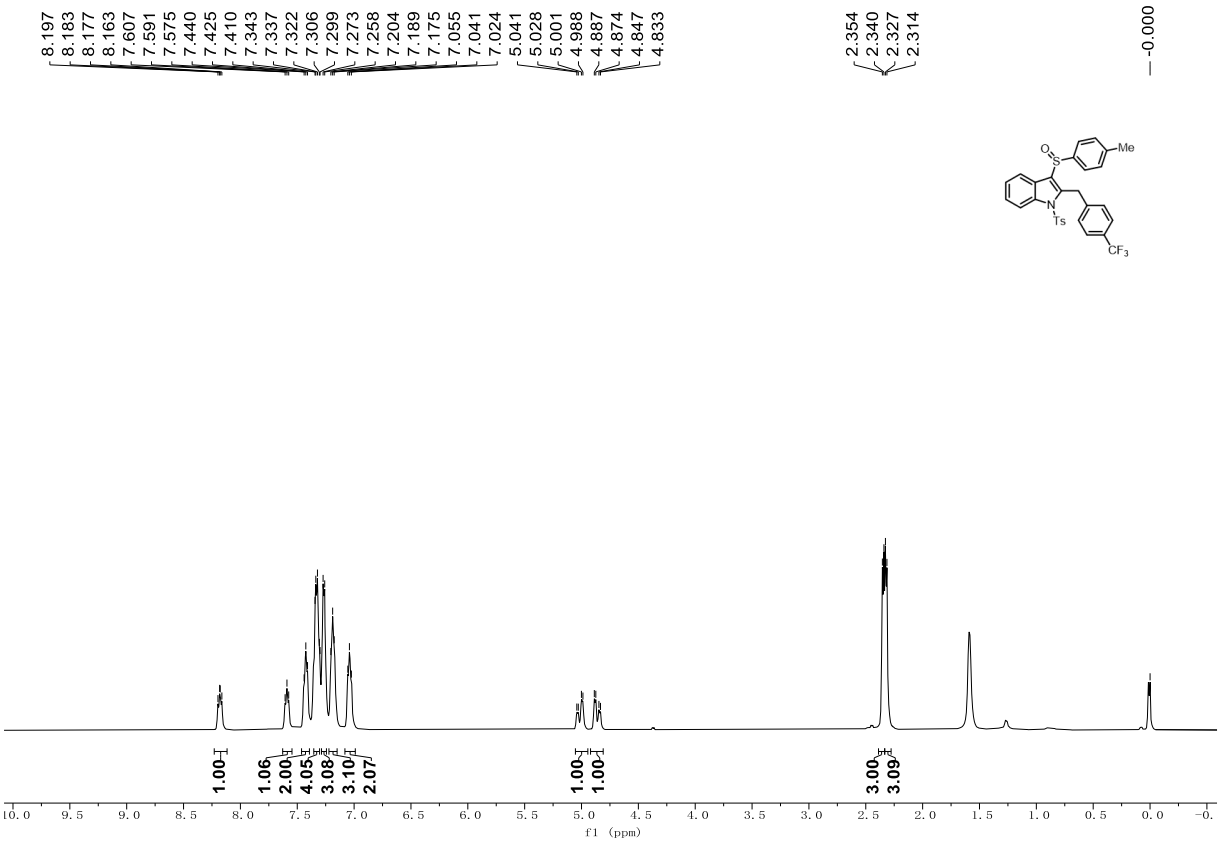
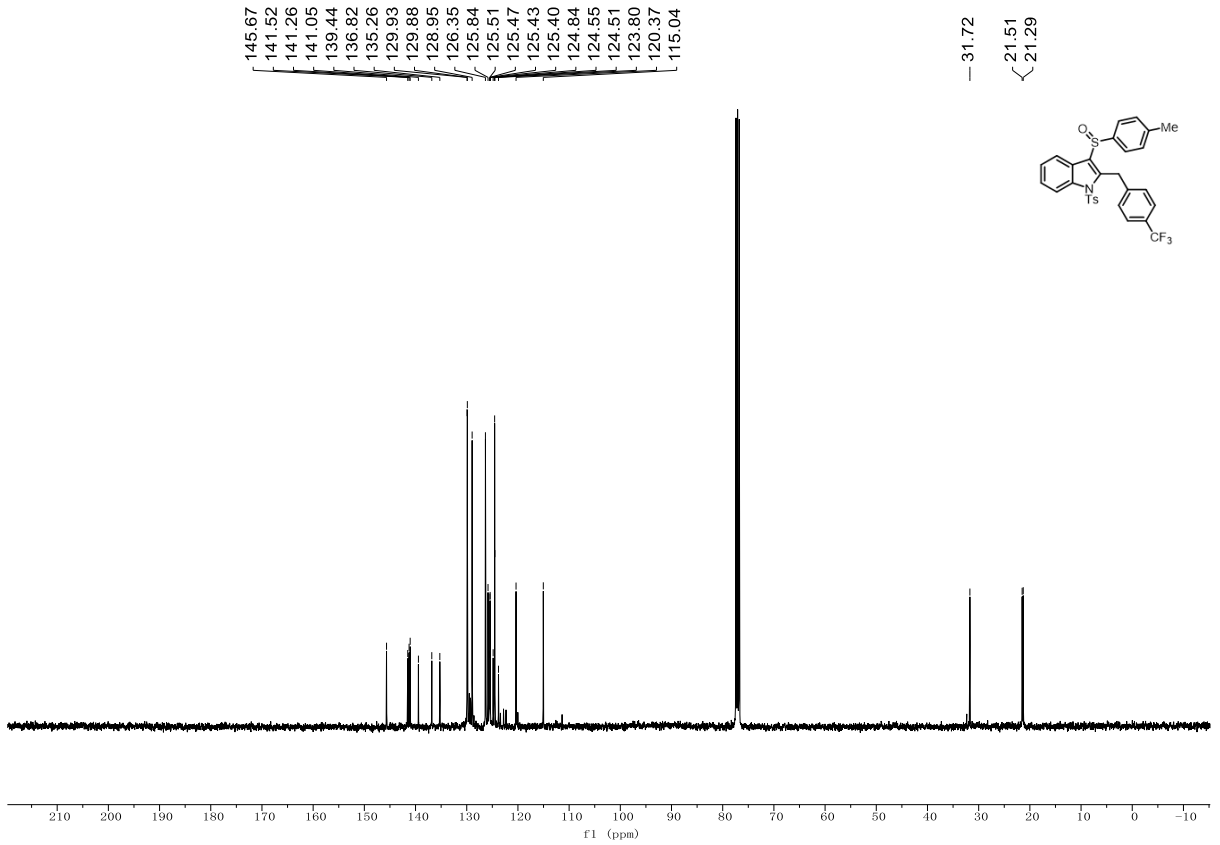


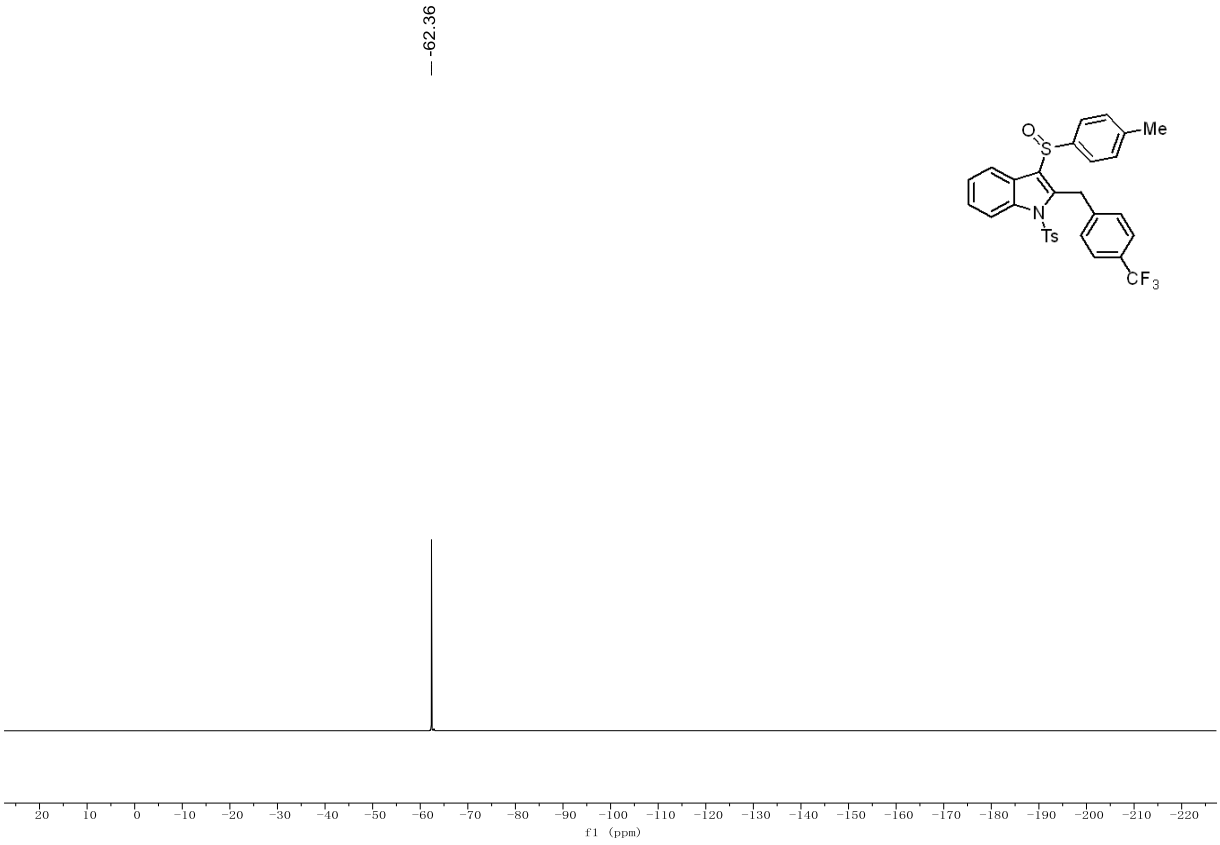
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **3f**



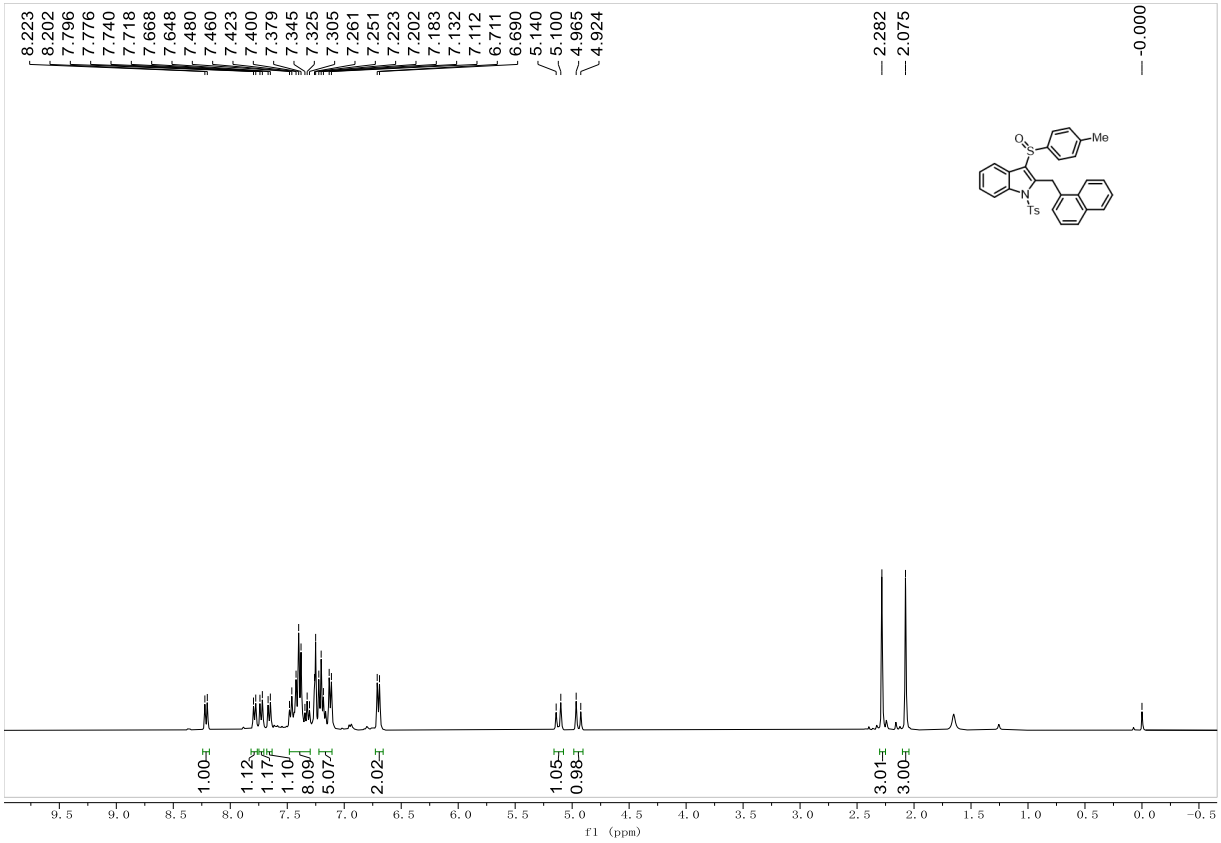
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **3f**



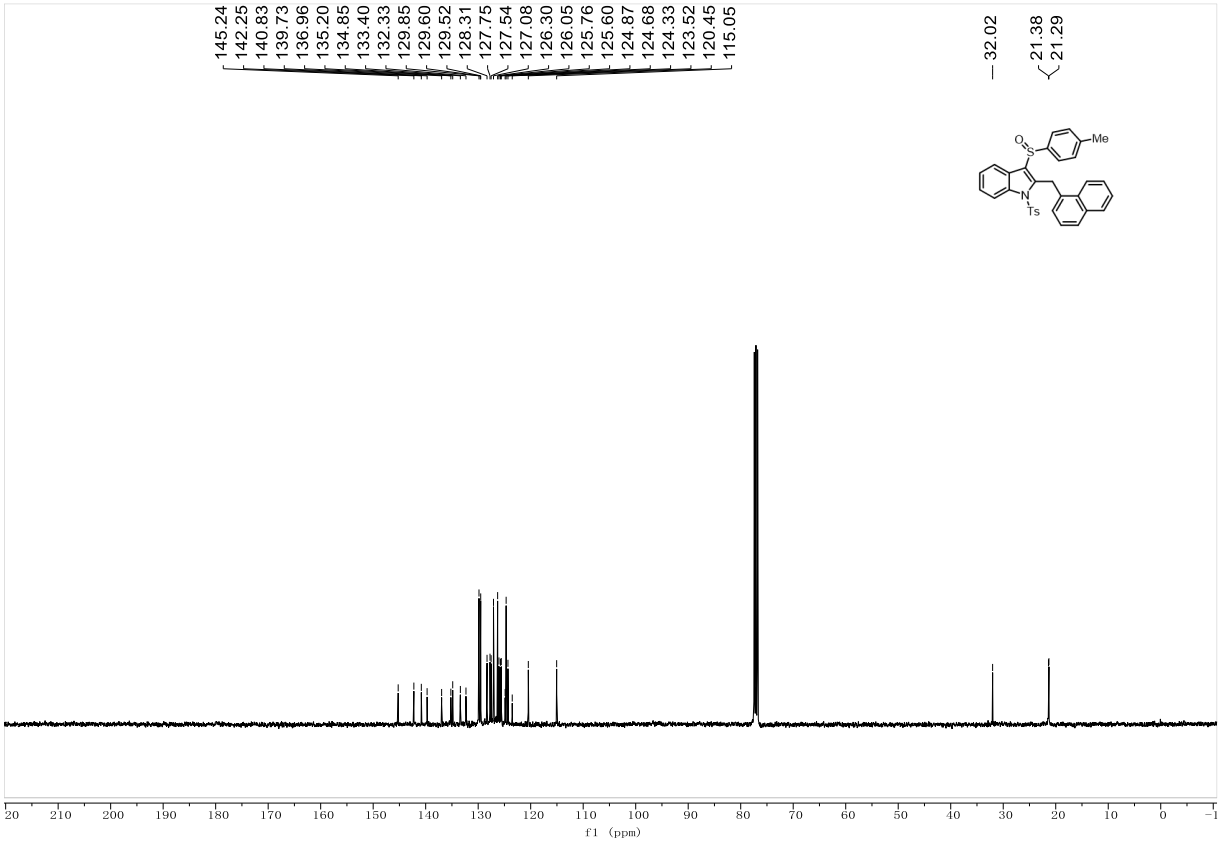
^{19}F NMR (376 MHz, $CDCl_3$) spectroscopy of **3f**



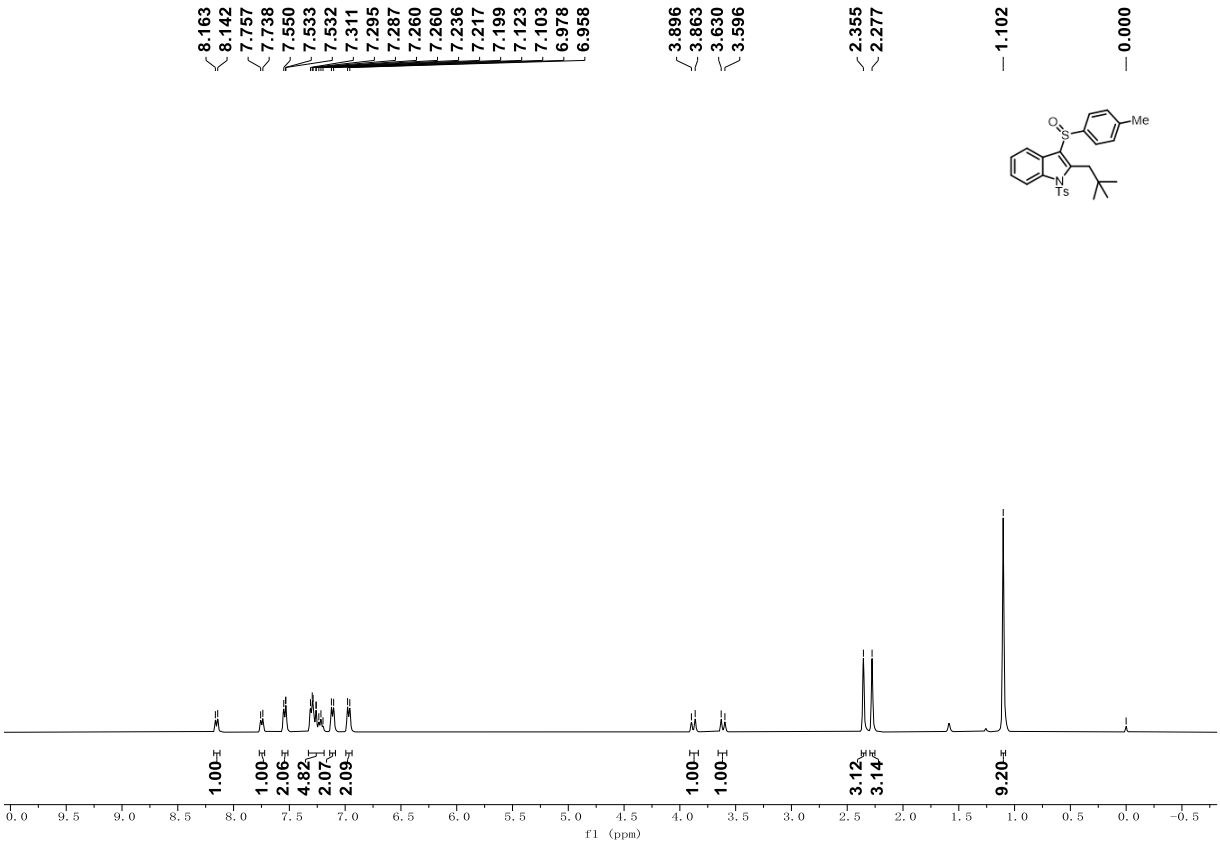
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **3g**



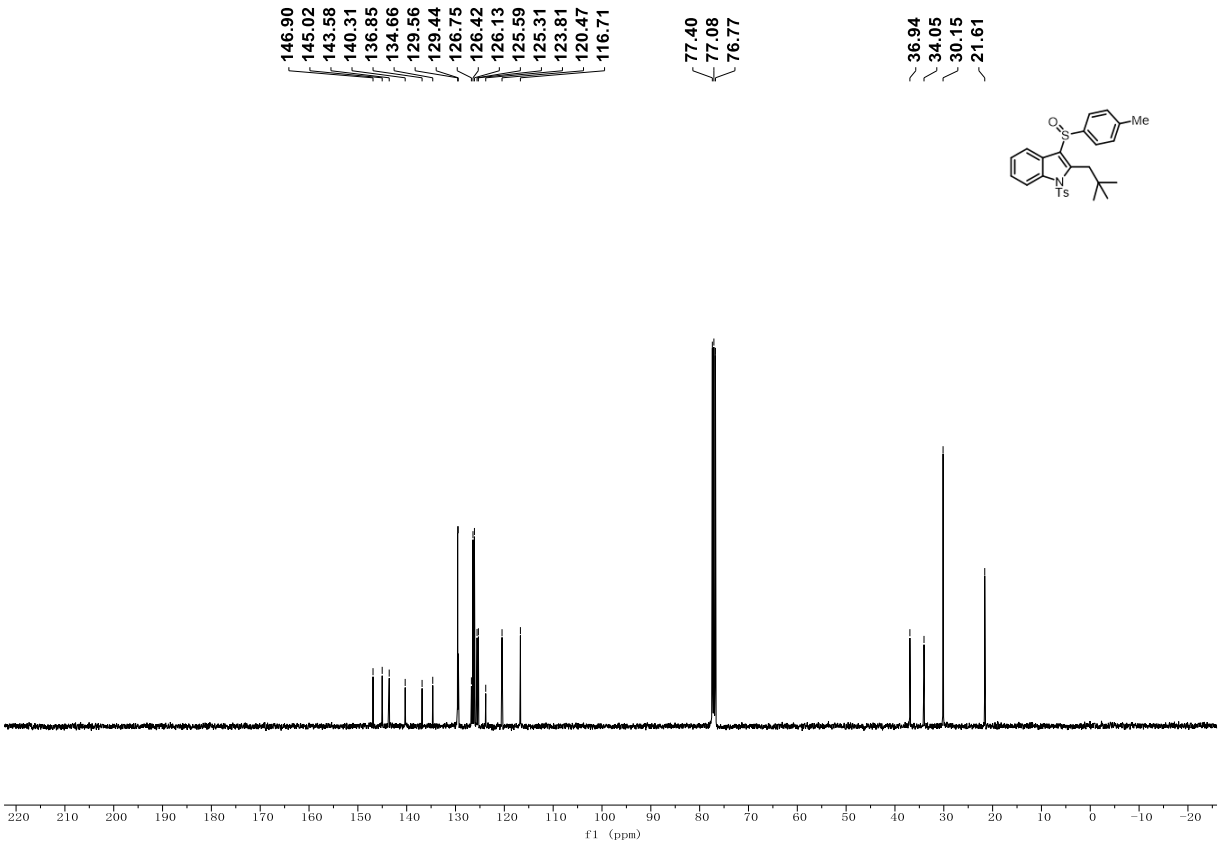
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **3g**



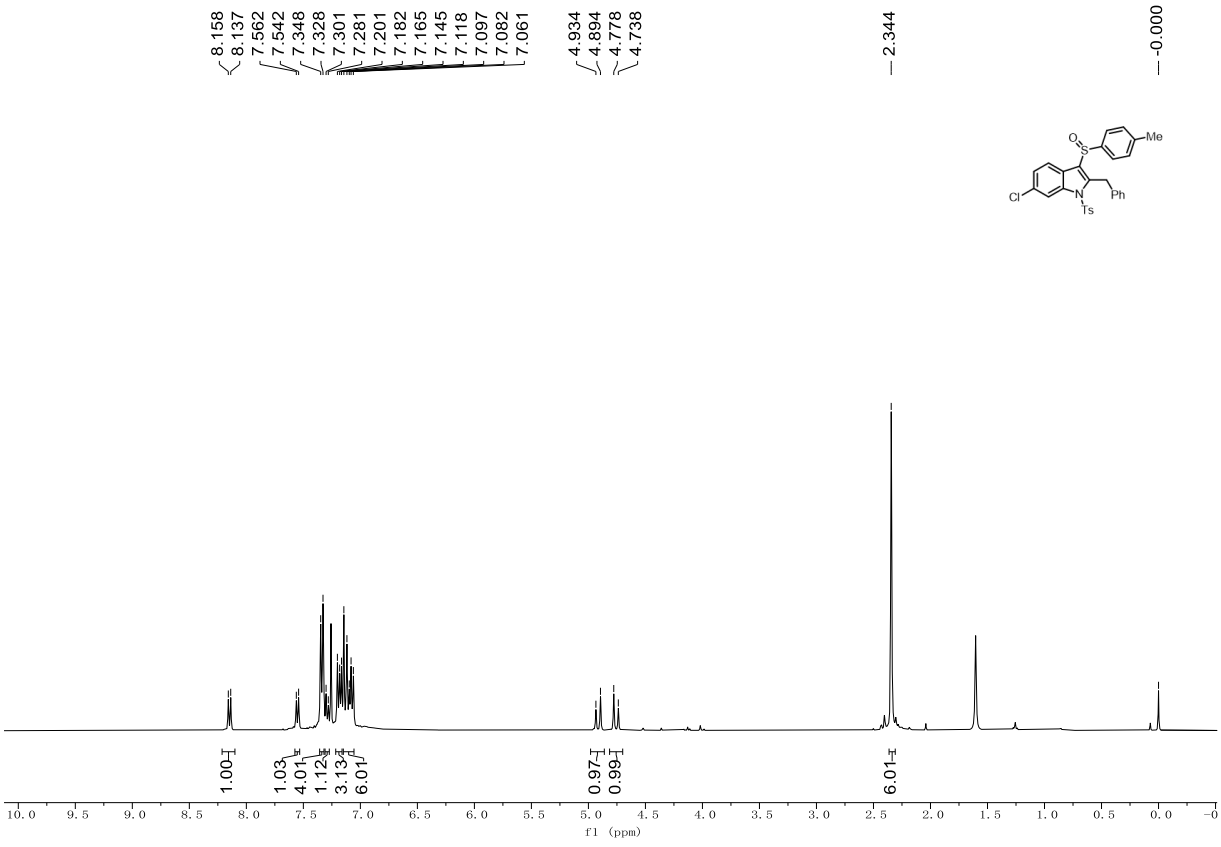
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **3i**



^{13}C NMR ($CDCl_3$) spectroscopy of **3i**



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



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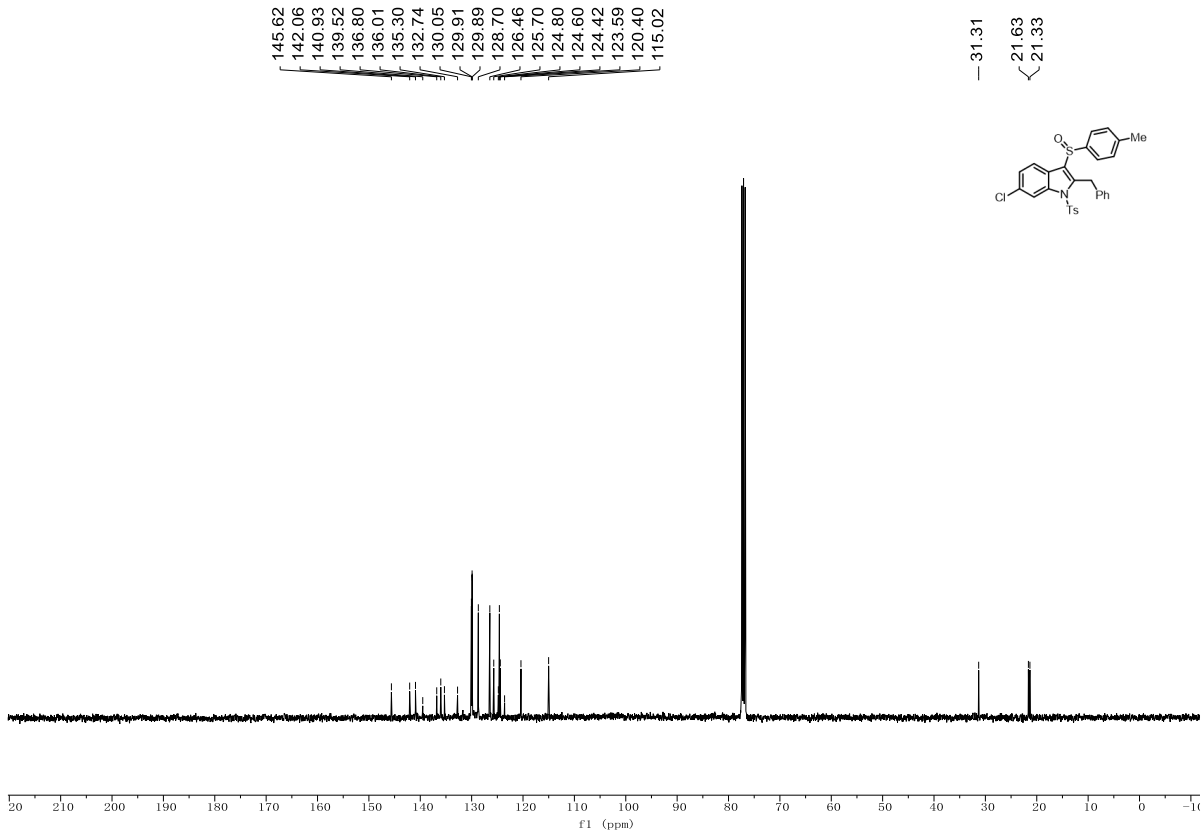

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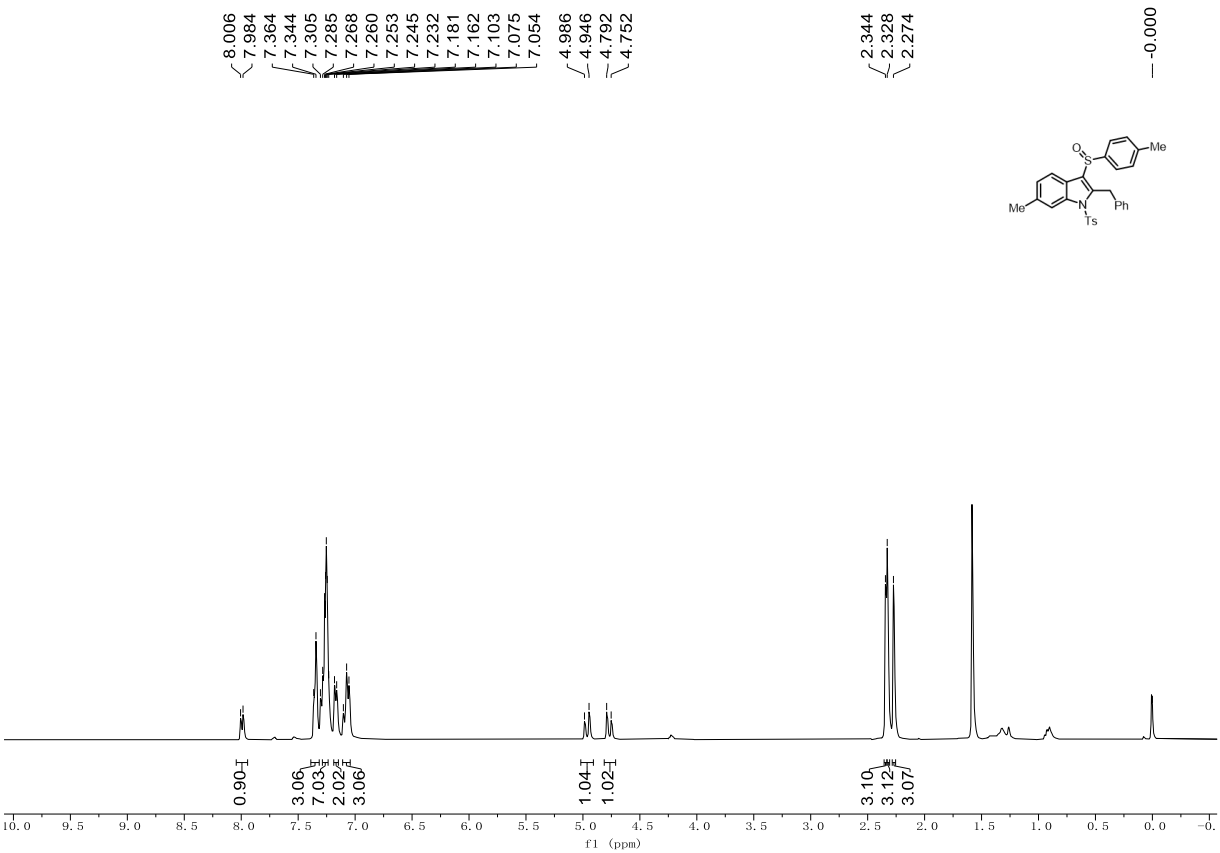
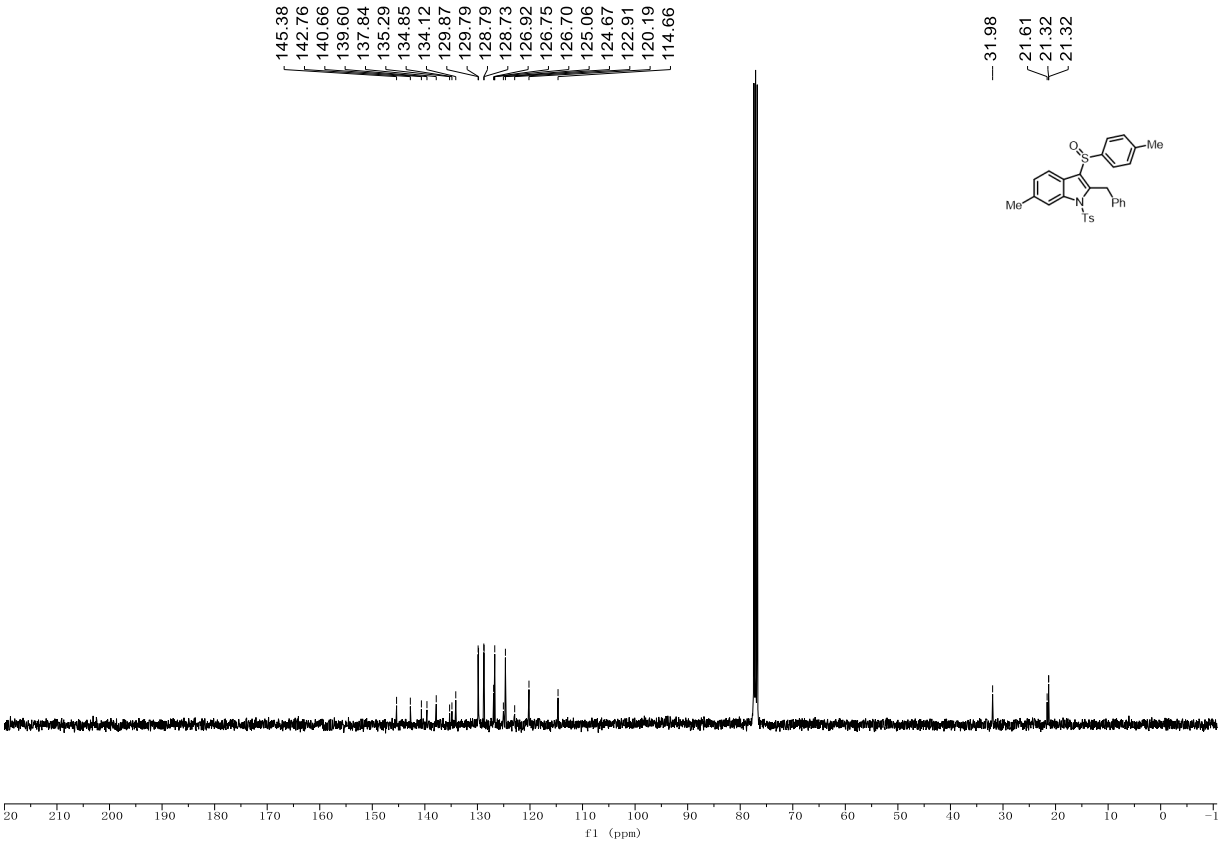
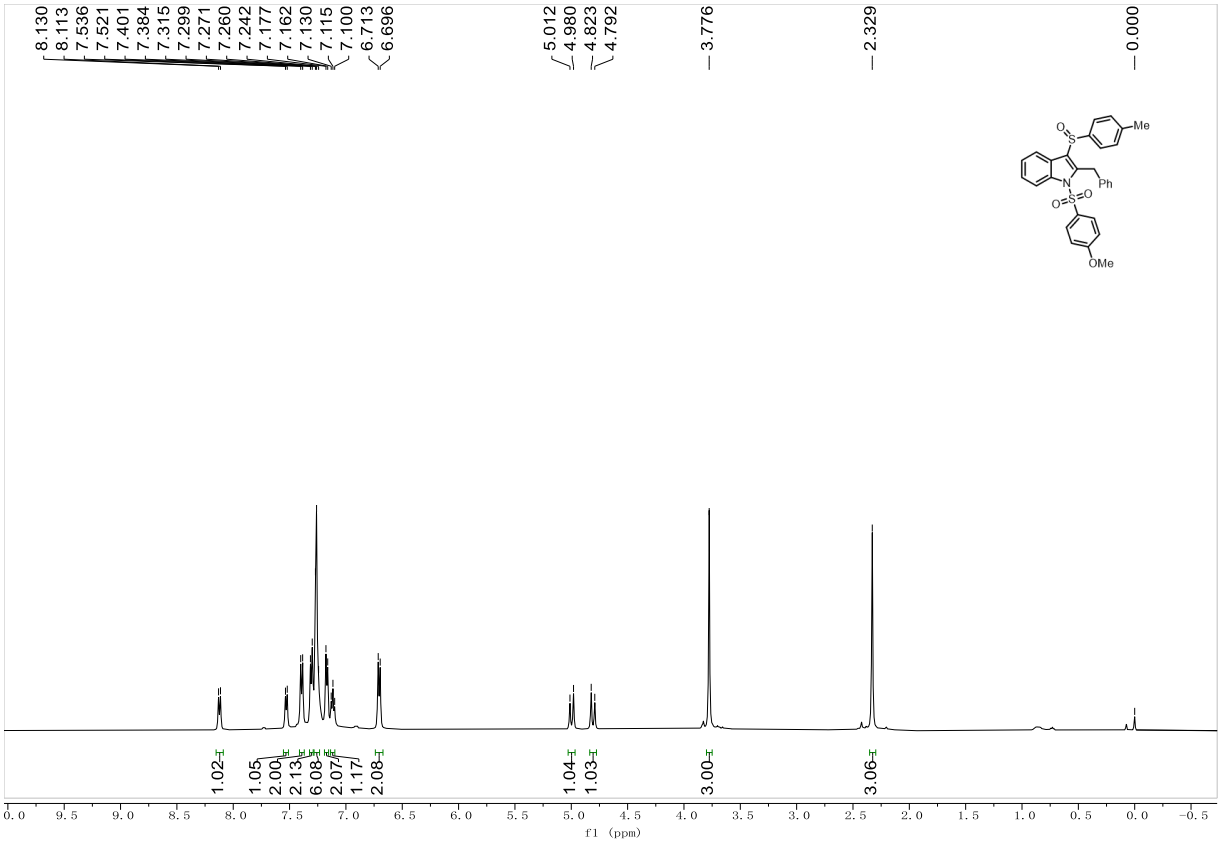


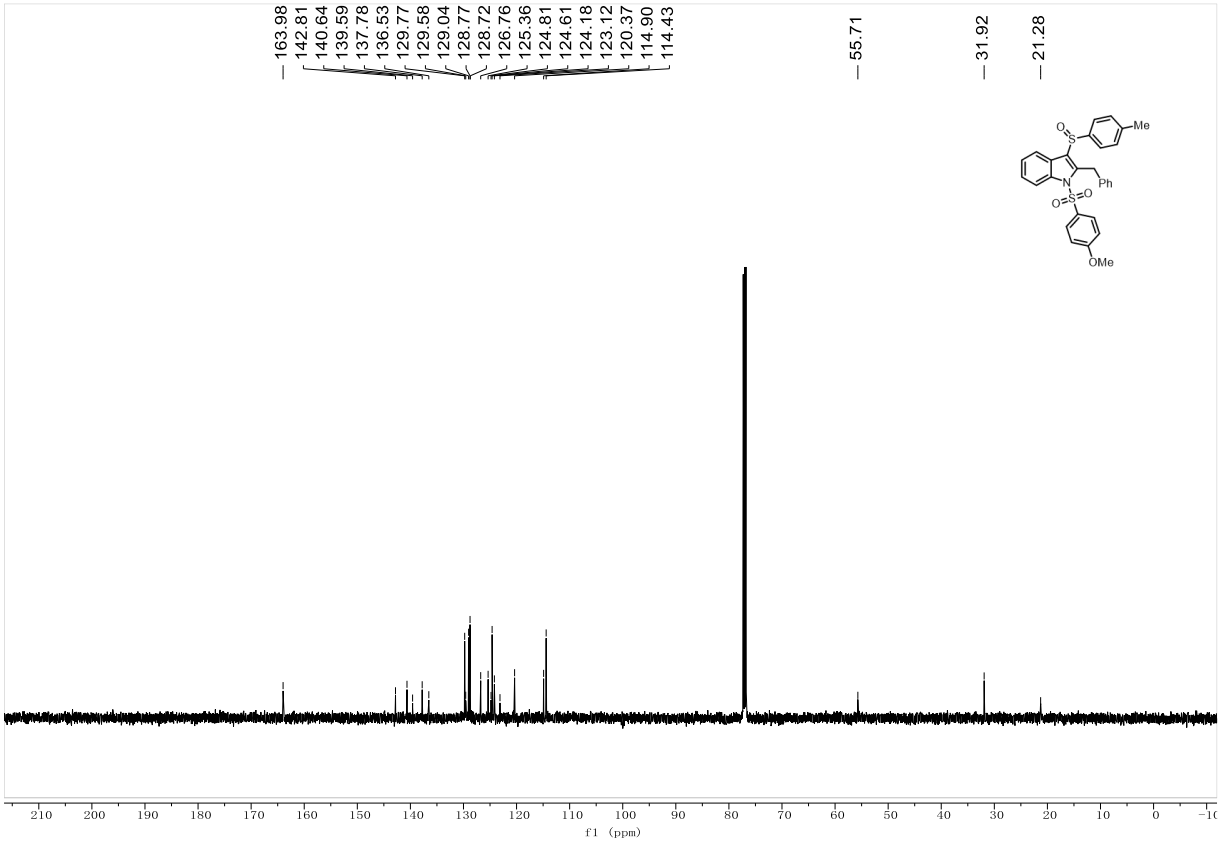
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **3n**



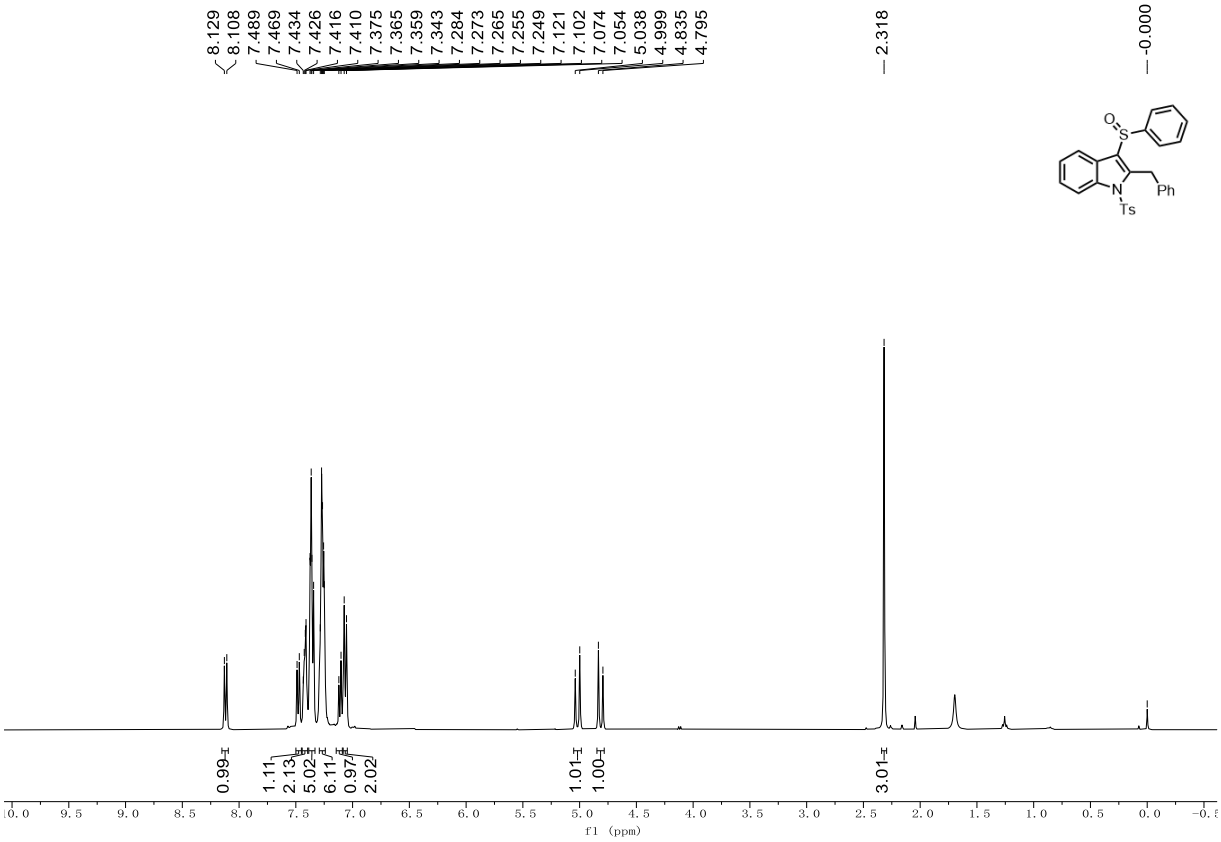
^{1}H NMR (500 MHz, $CDCl_3$) spectroscopy of **3p**



^{13}C NMR (126 MHz, $CDCl_3$) spectroscopy of **3p**



^{1}H NMR (500 MHz, $CDCl_3$) spectroscopy of **3q**



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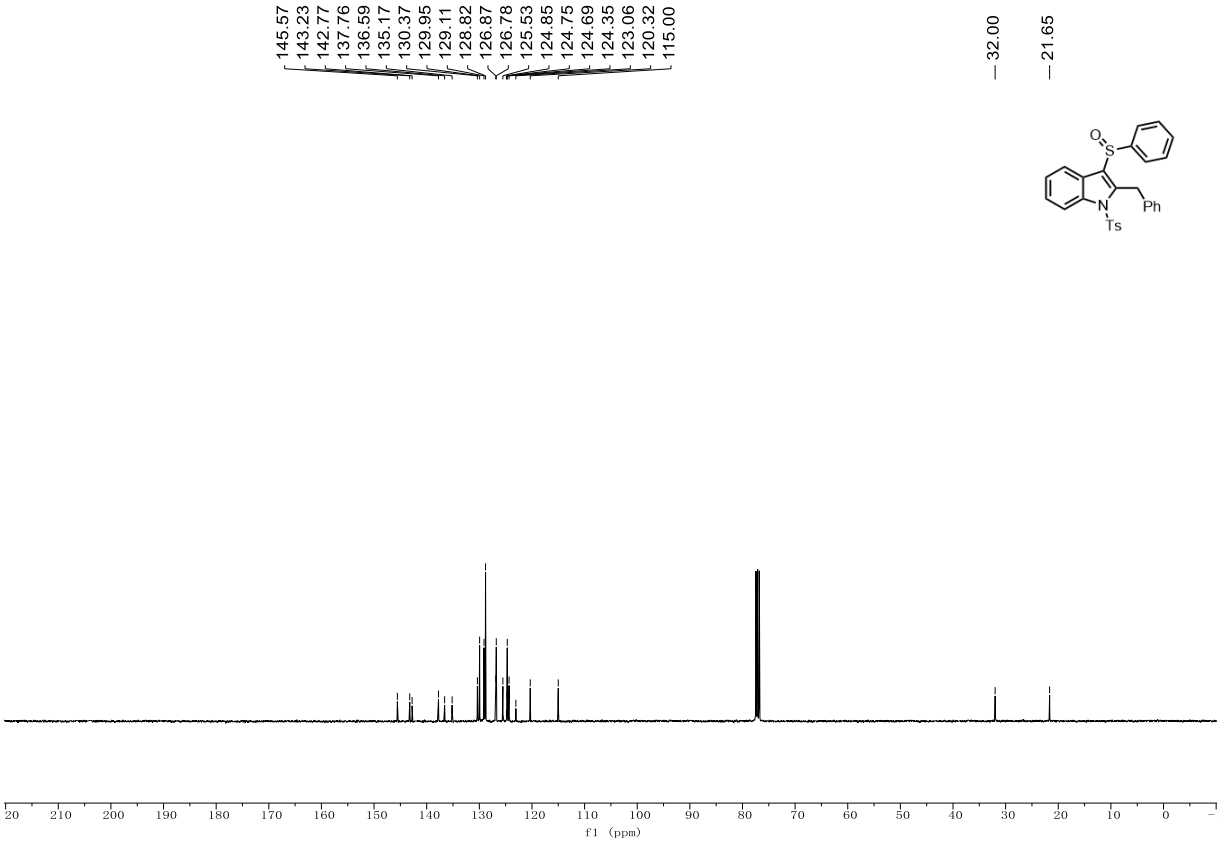

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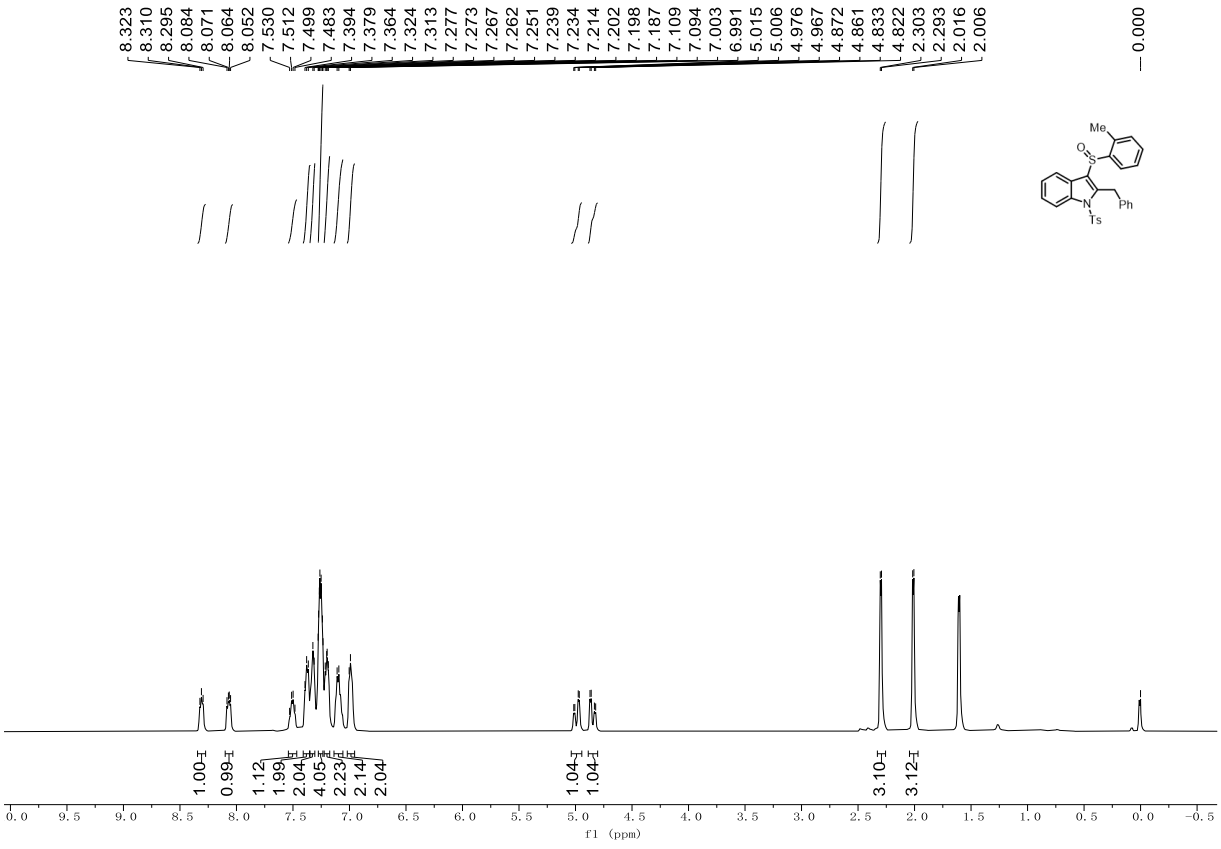

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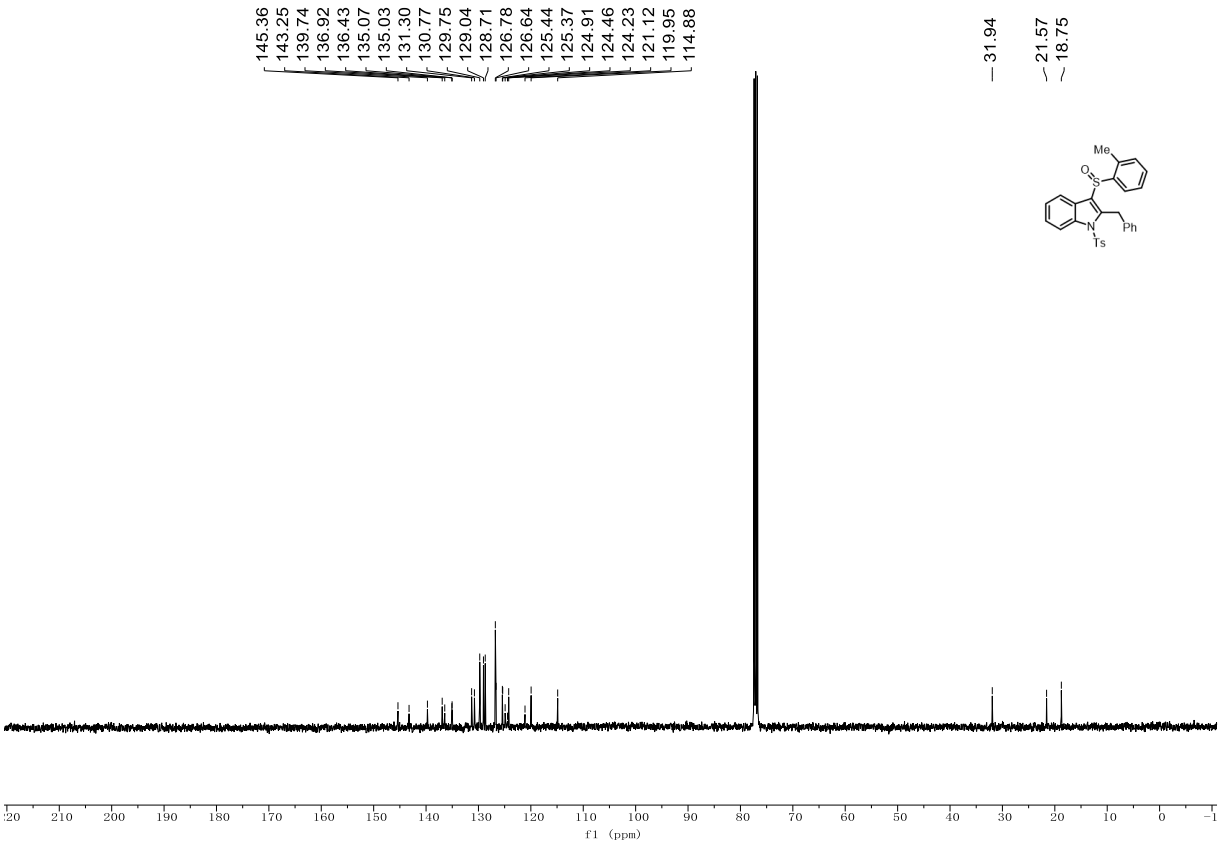
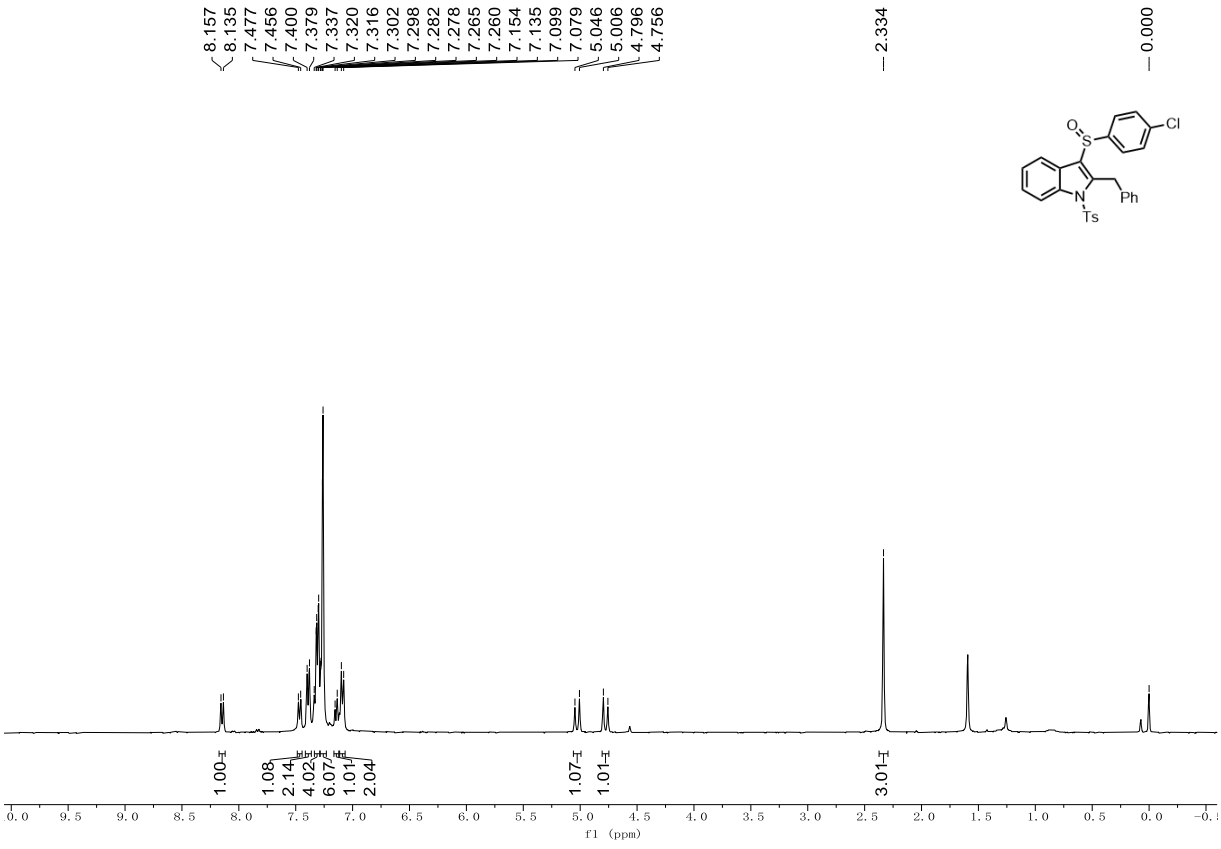


^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **3s**



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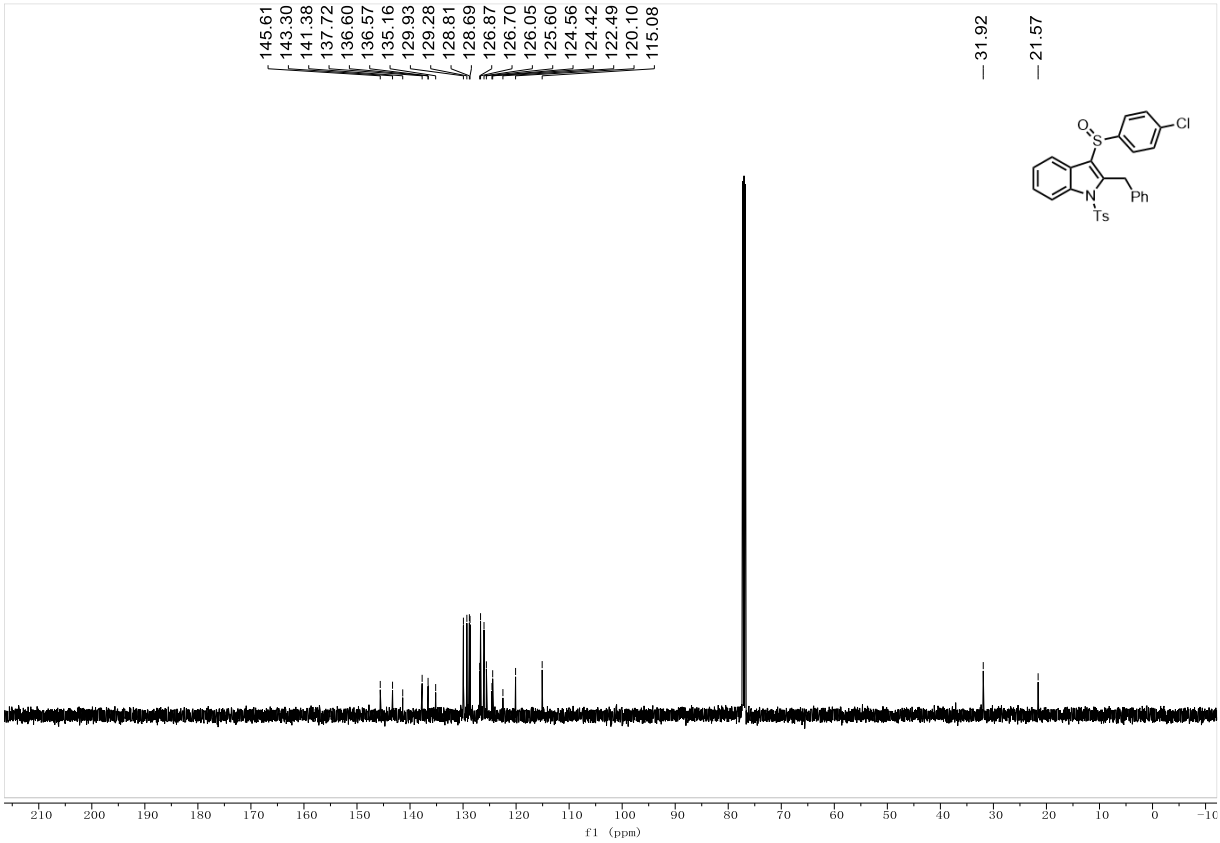

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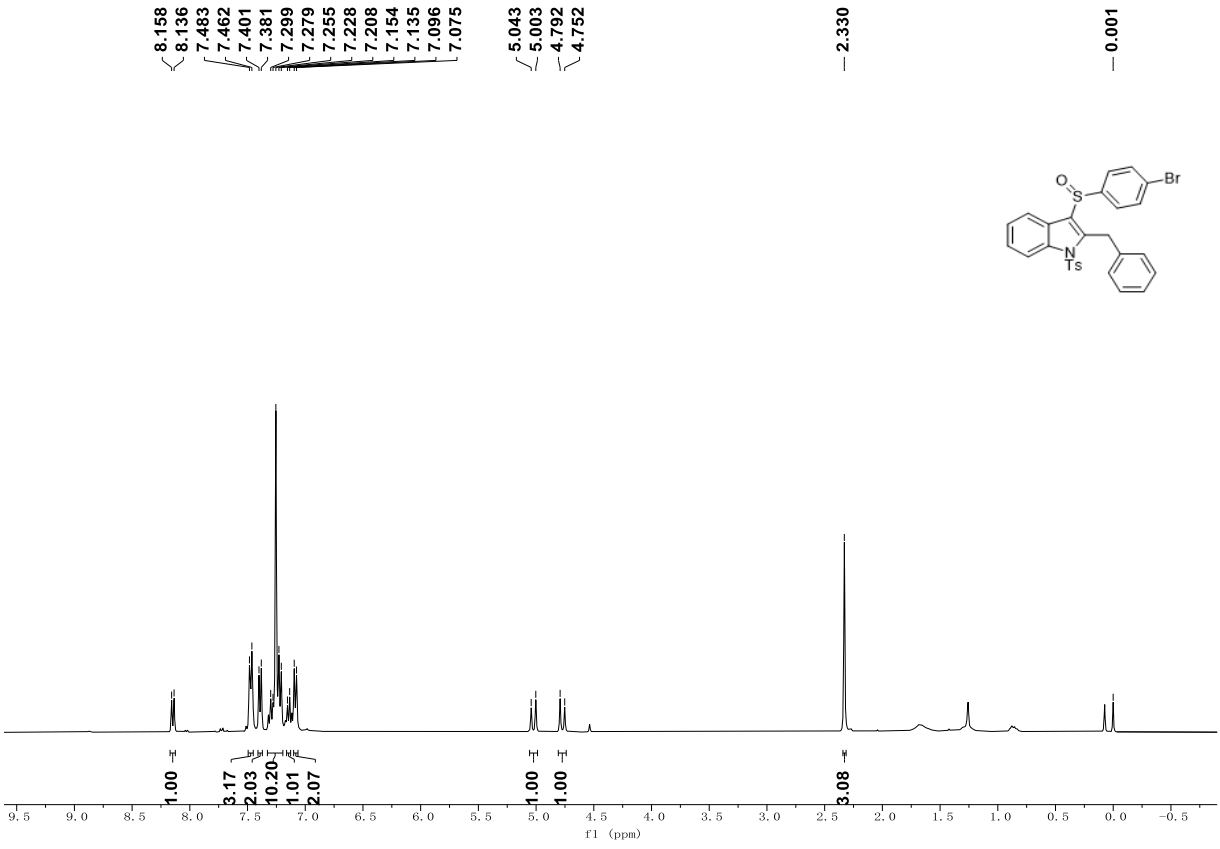
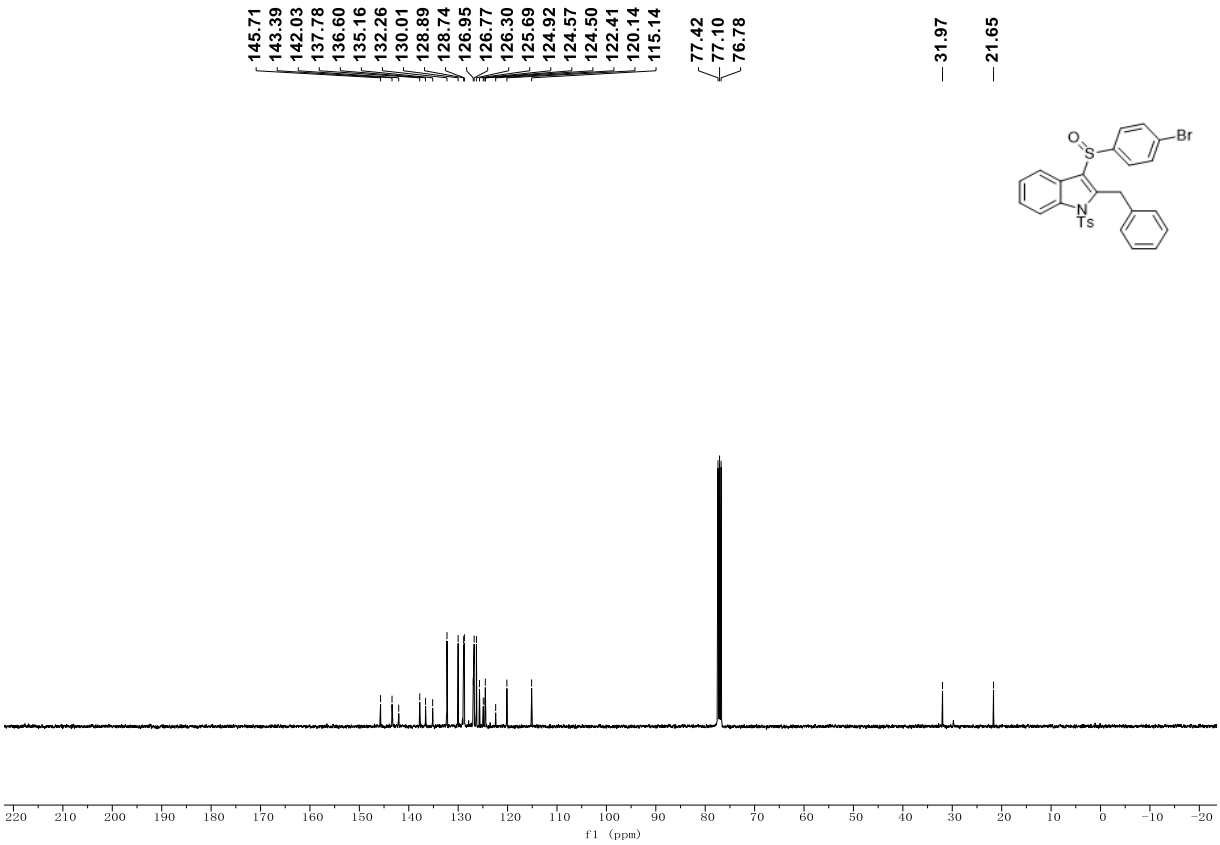
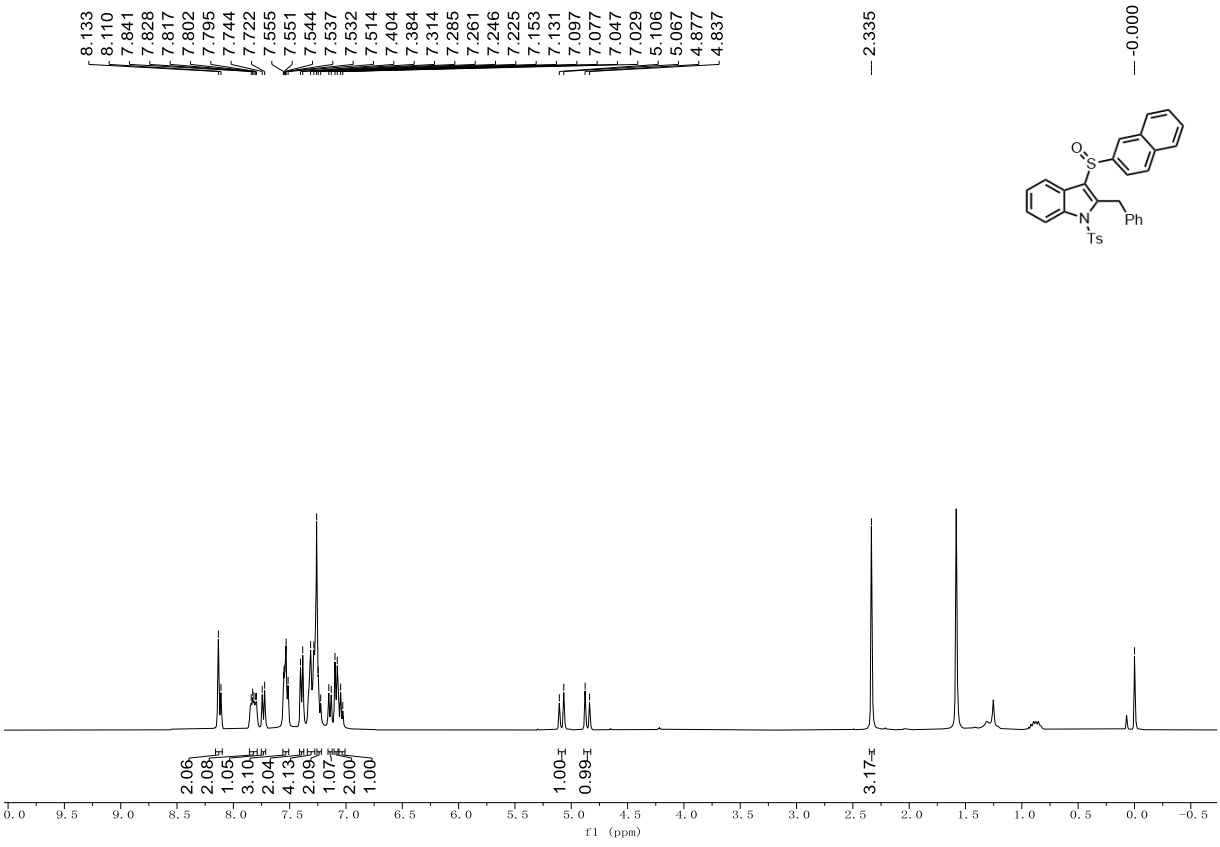


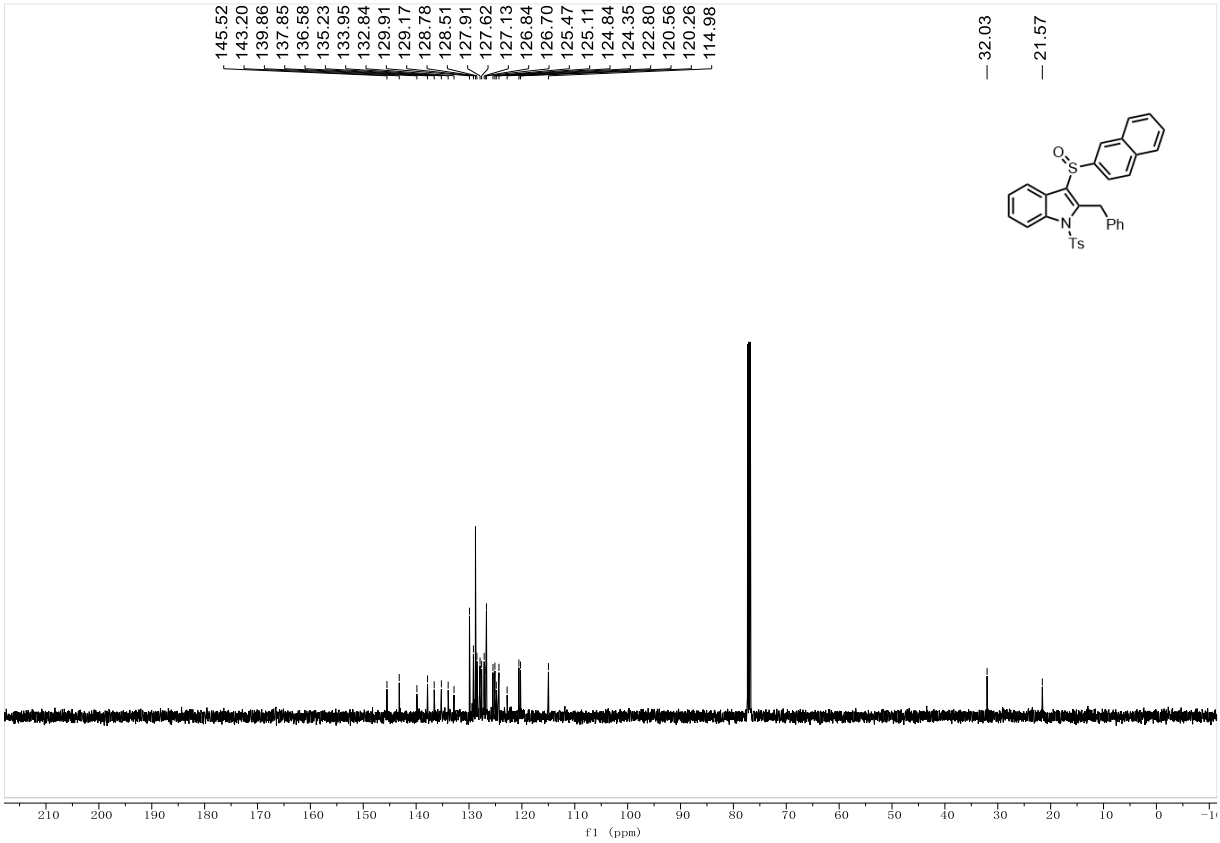
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **3t**



^{1}H NMR (500 MHz, $CDCl_3$) spectroscopy of **3v**



^{13}C NMR (126 MHz, $CDCl_3$) spectroscopy of **3v**



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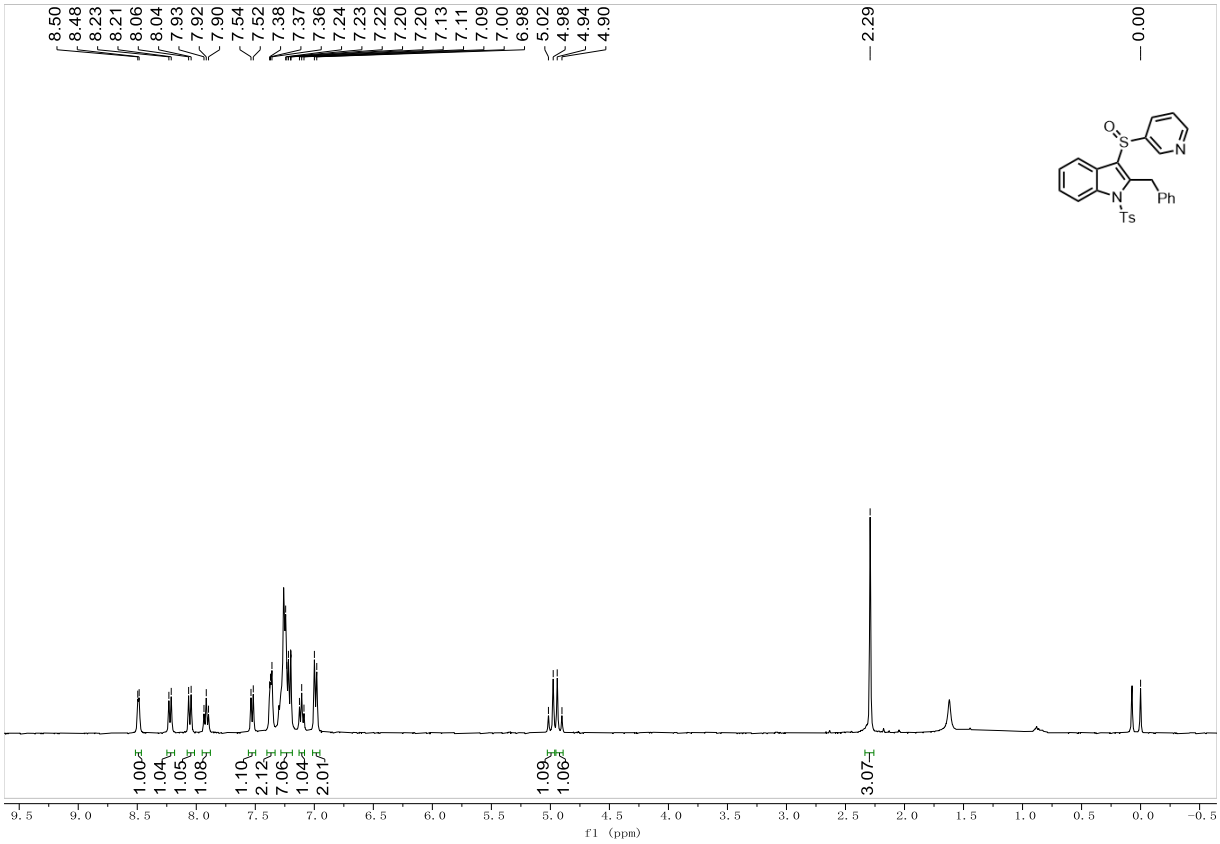

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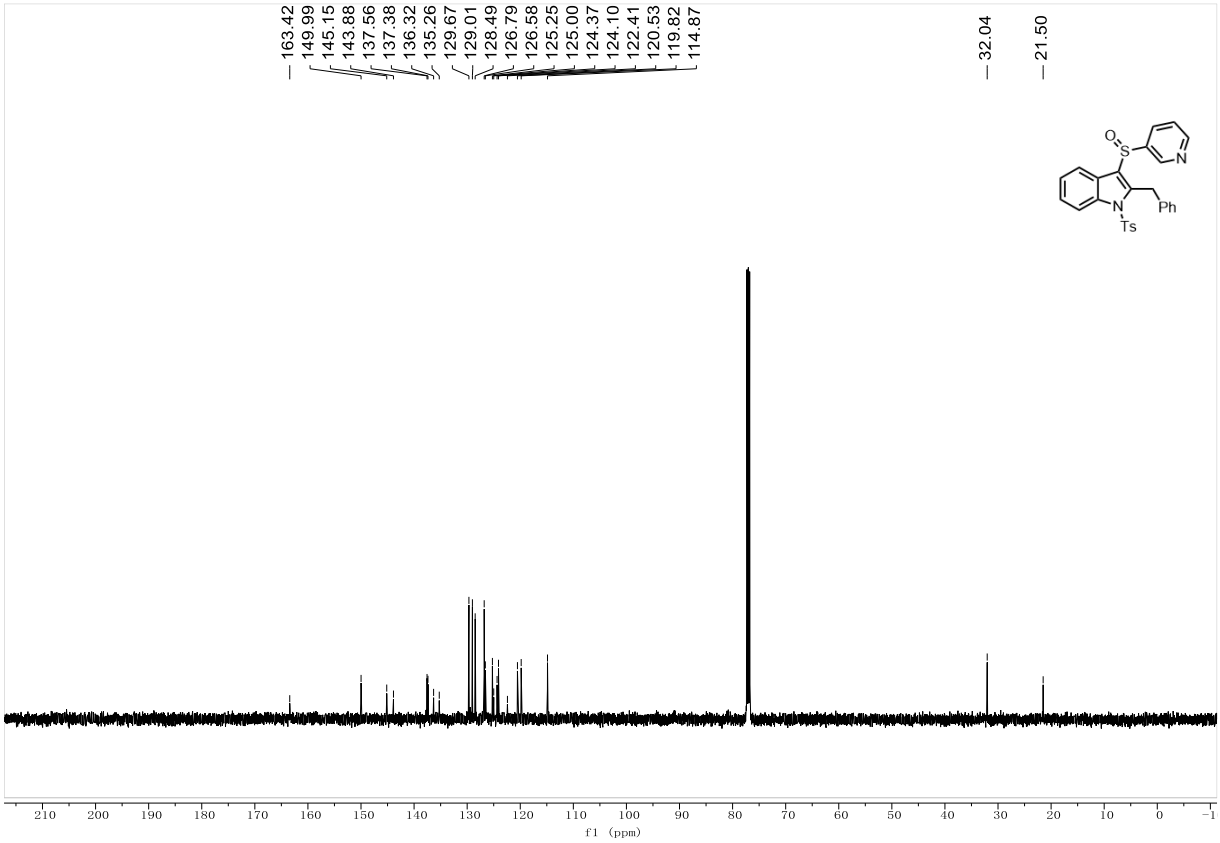

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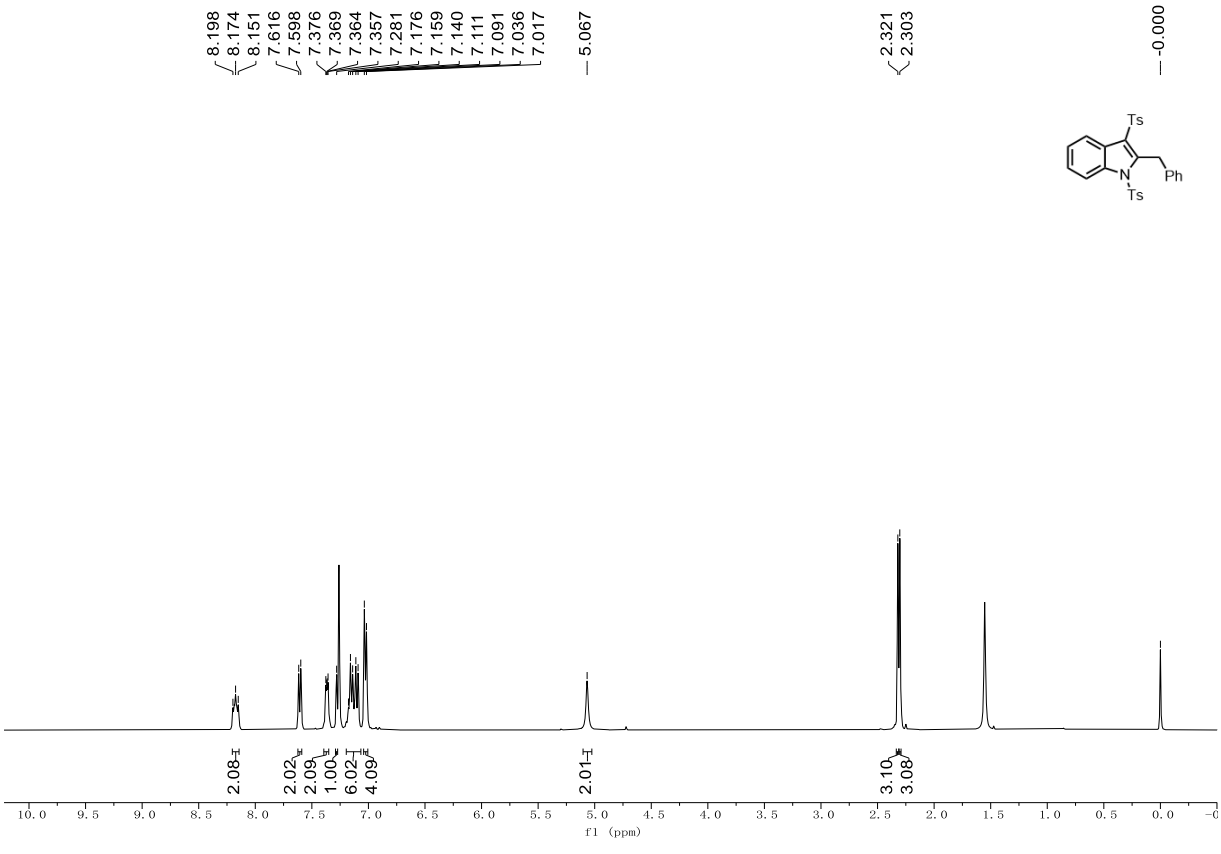

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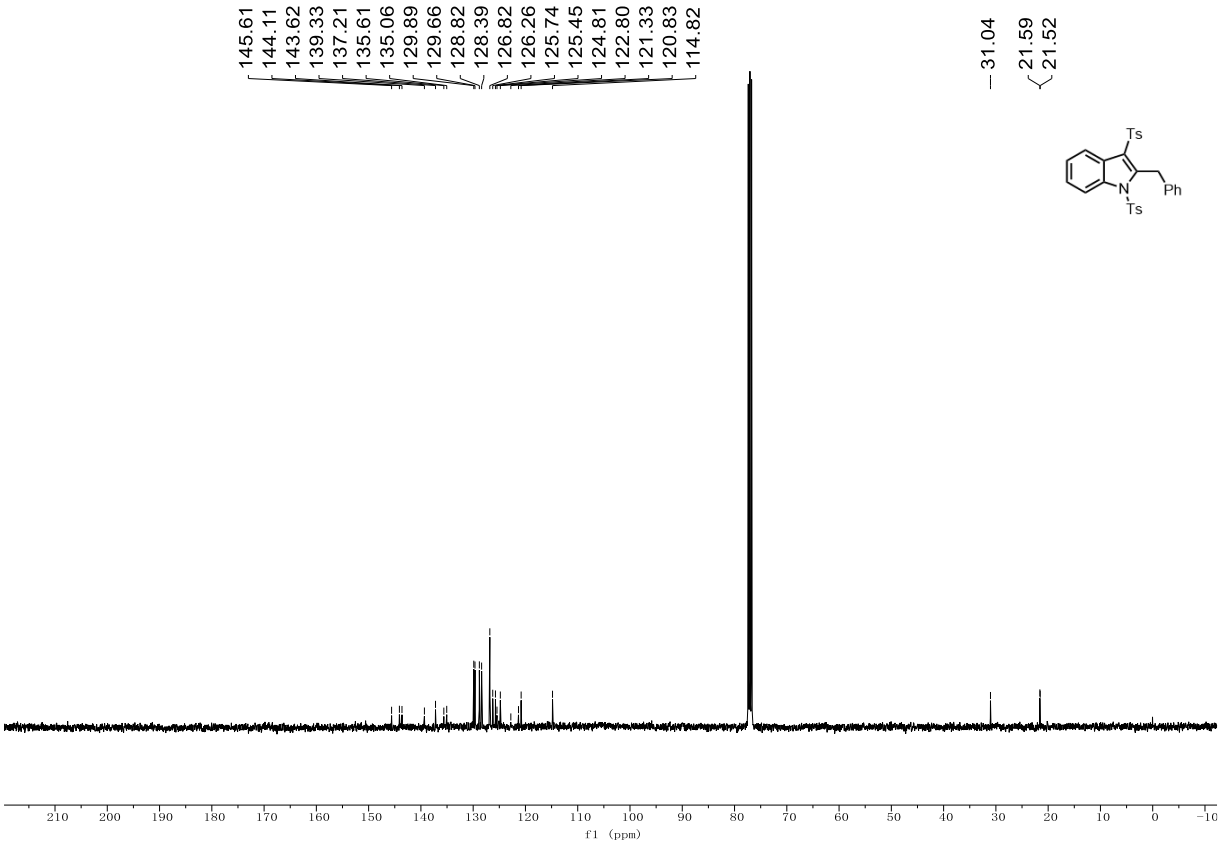
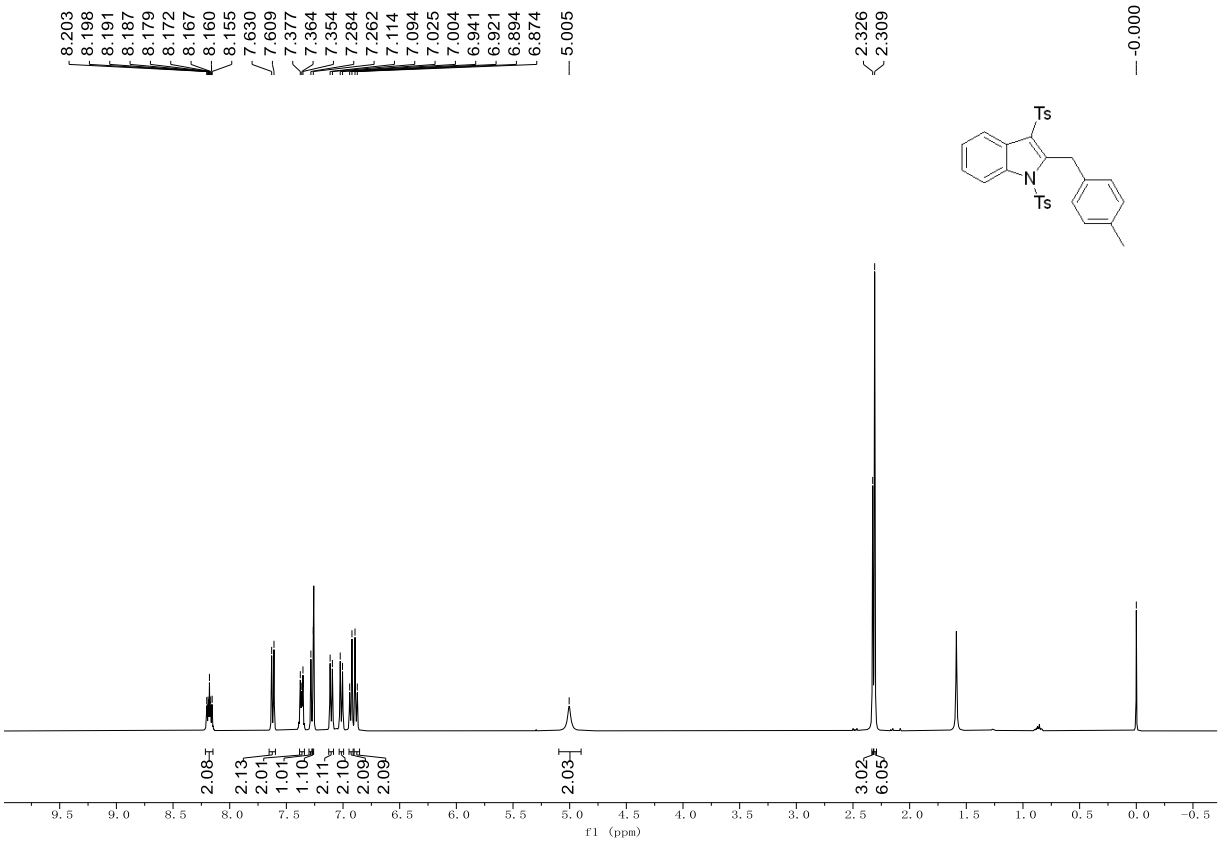
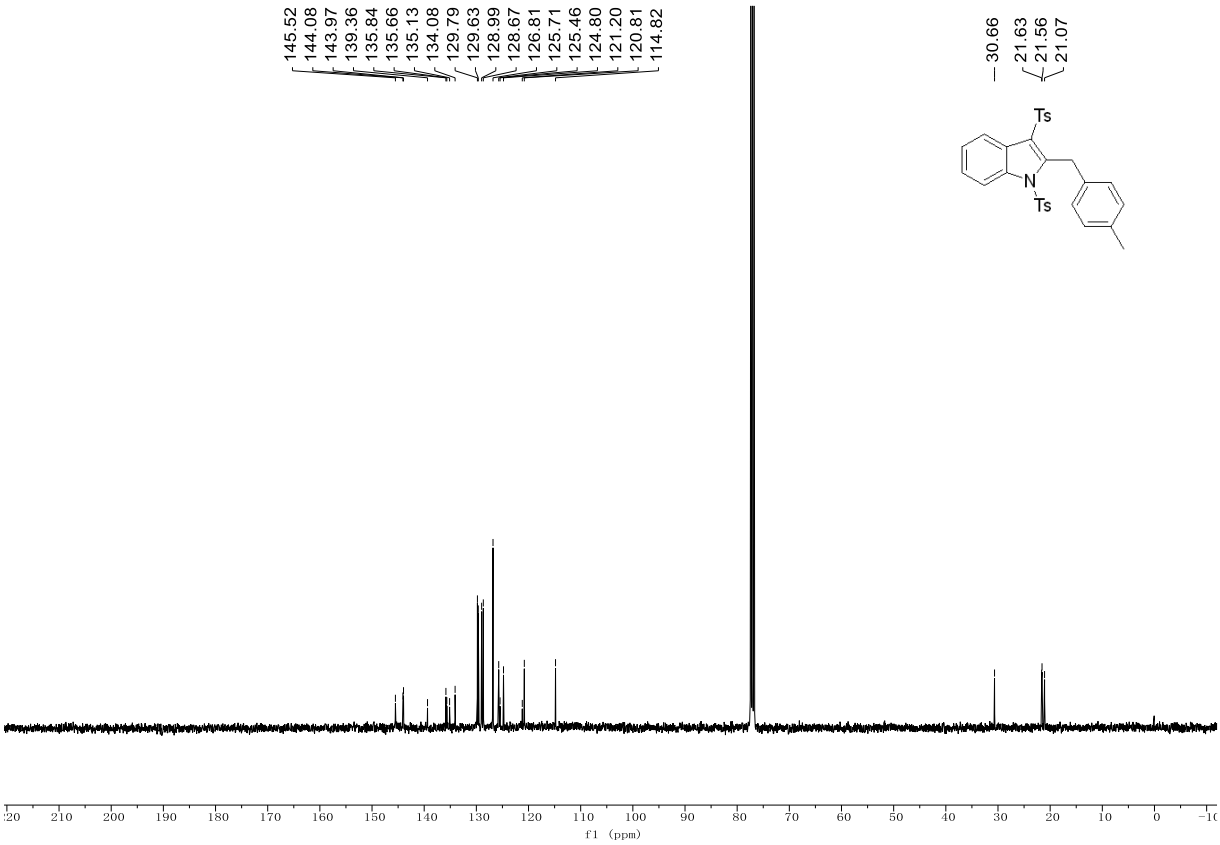


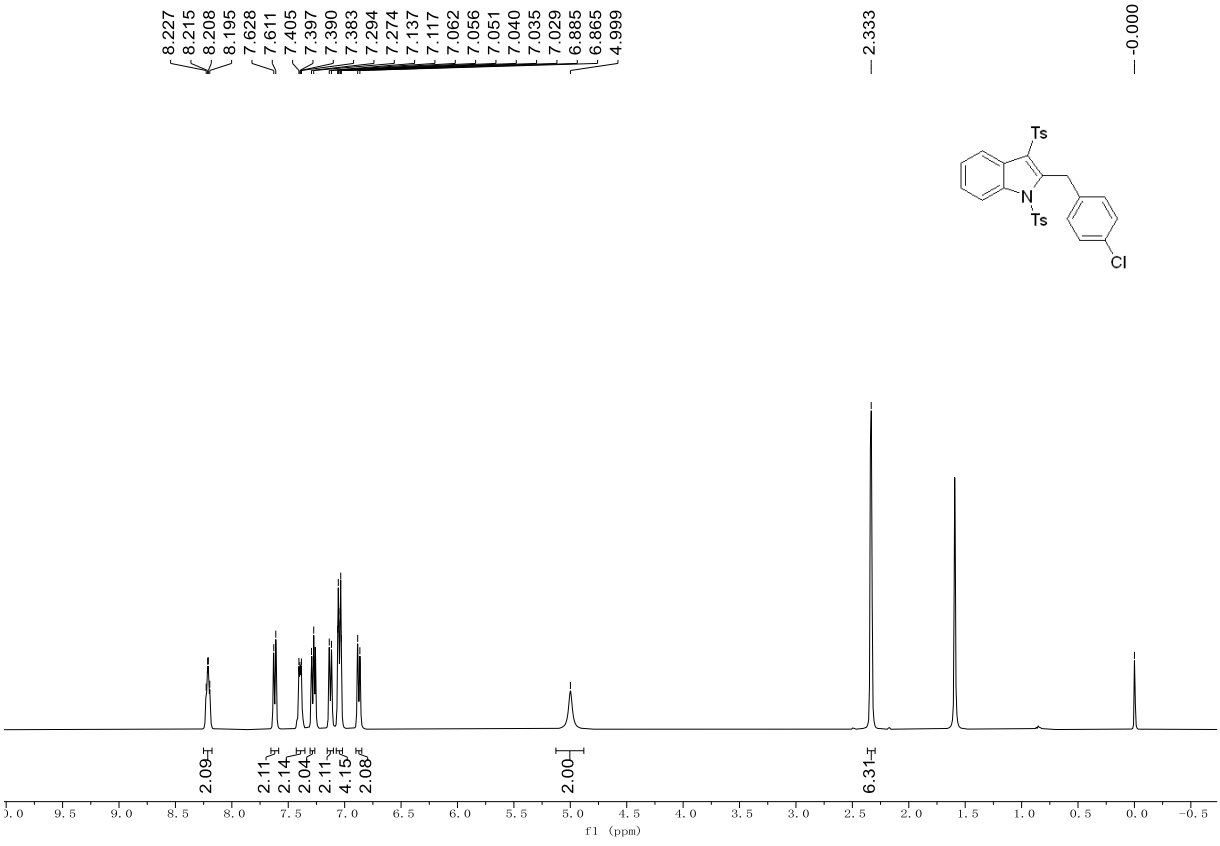
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4b**



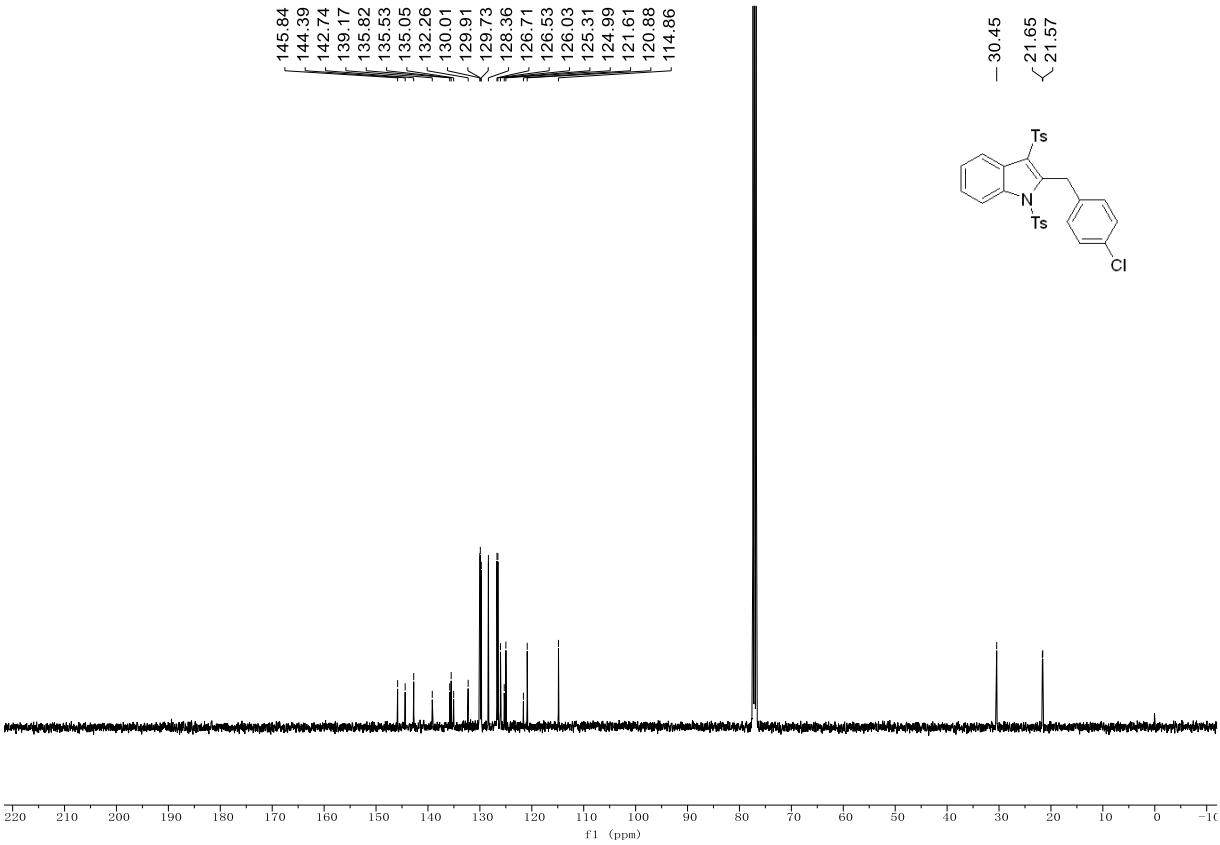
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4b**



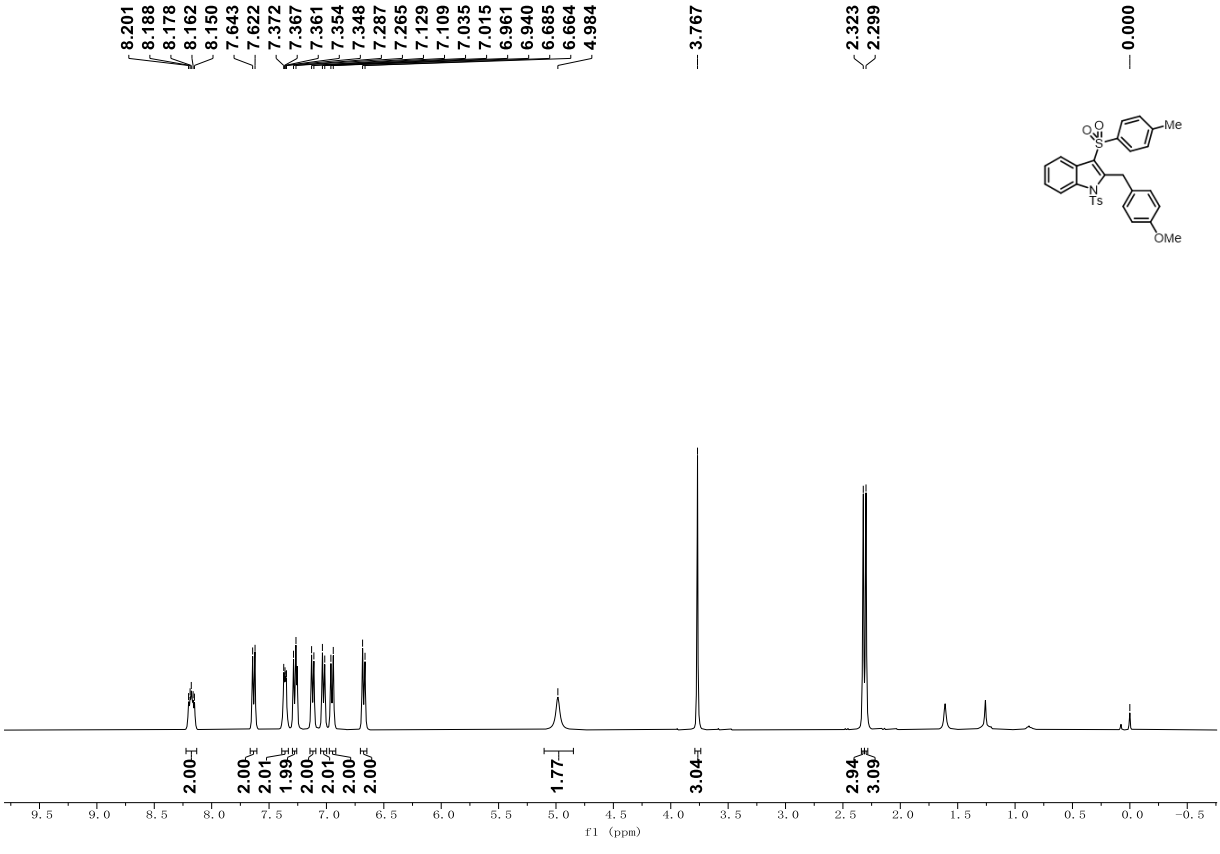
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4c**



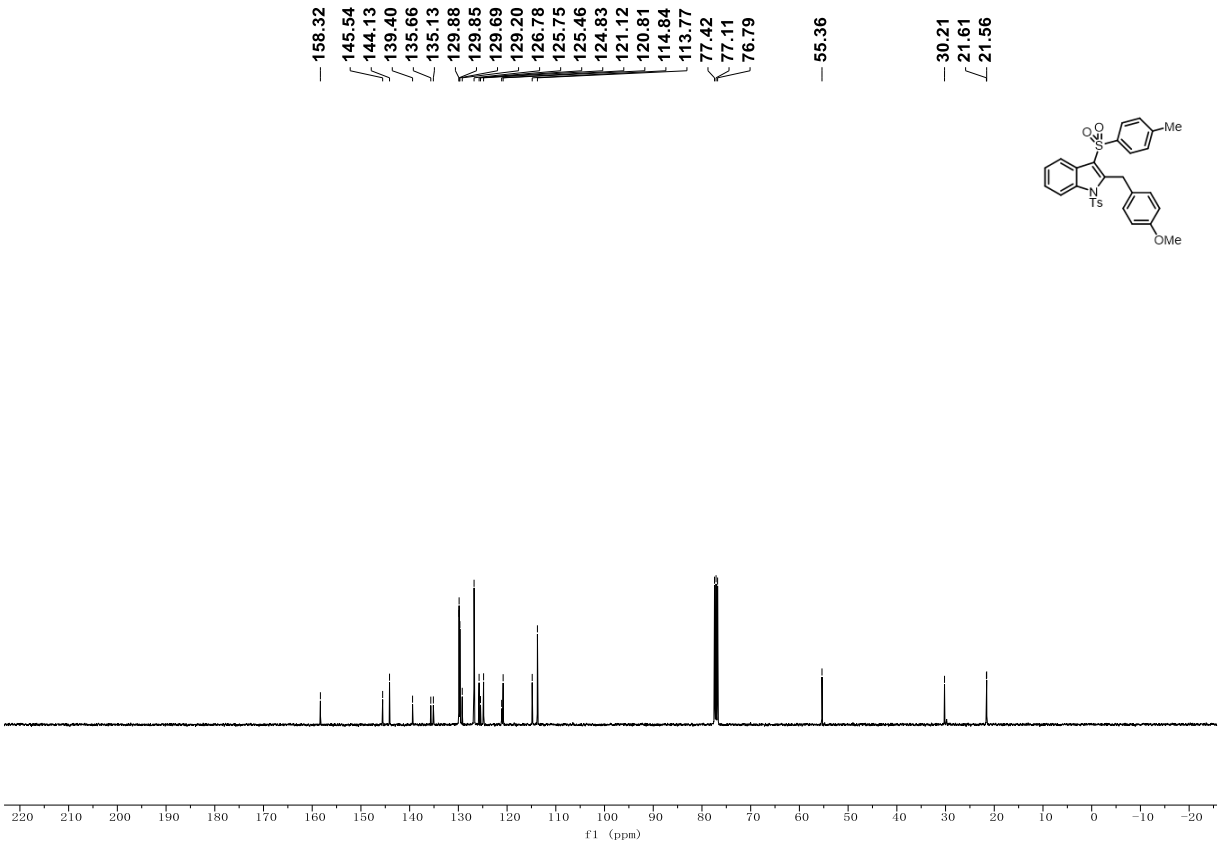
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4c**



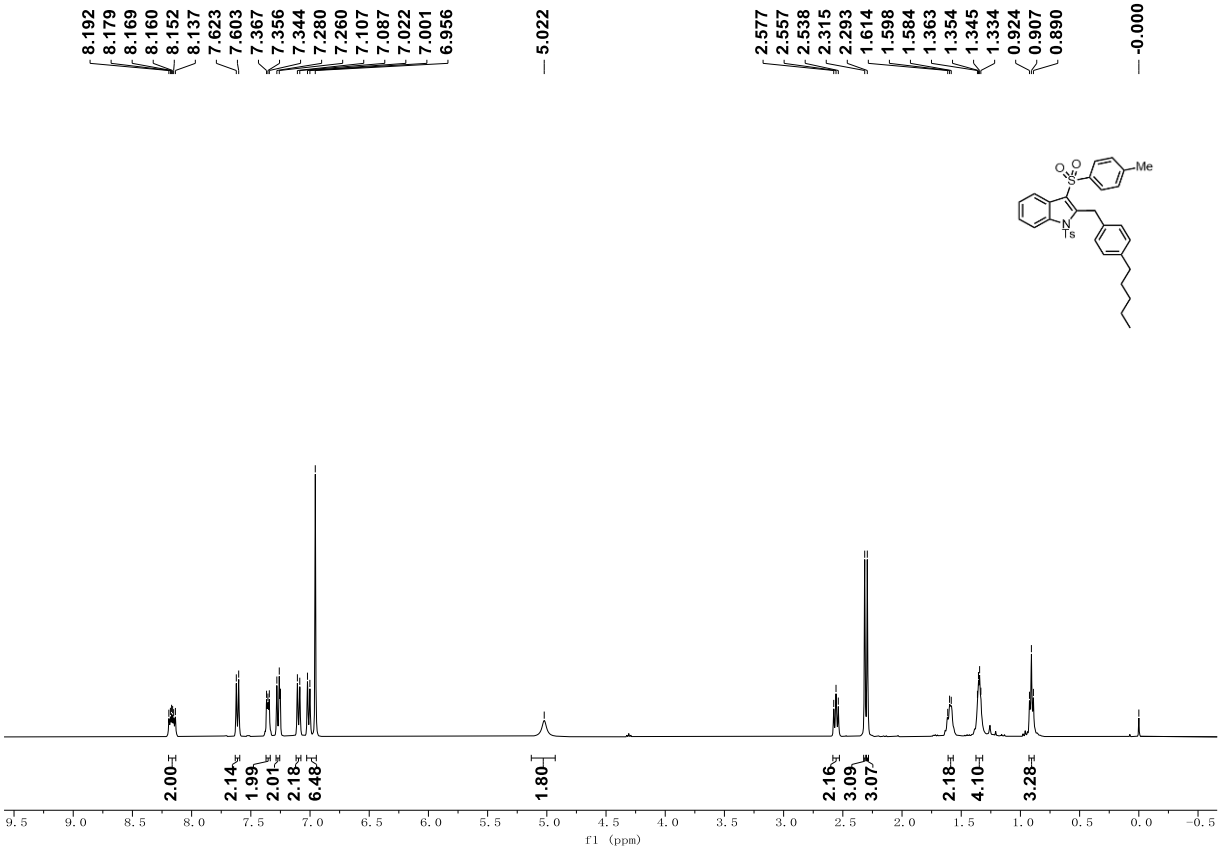
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4d**



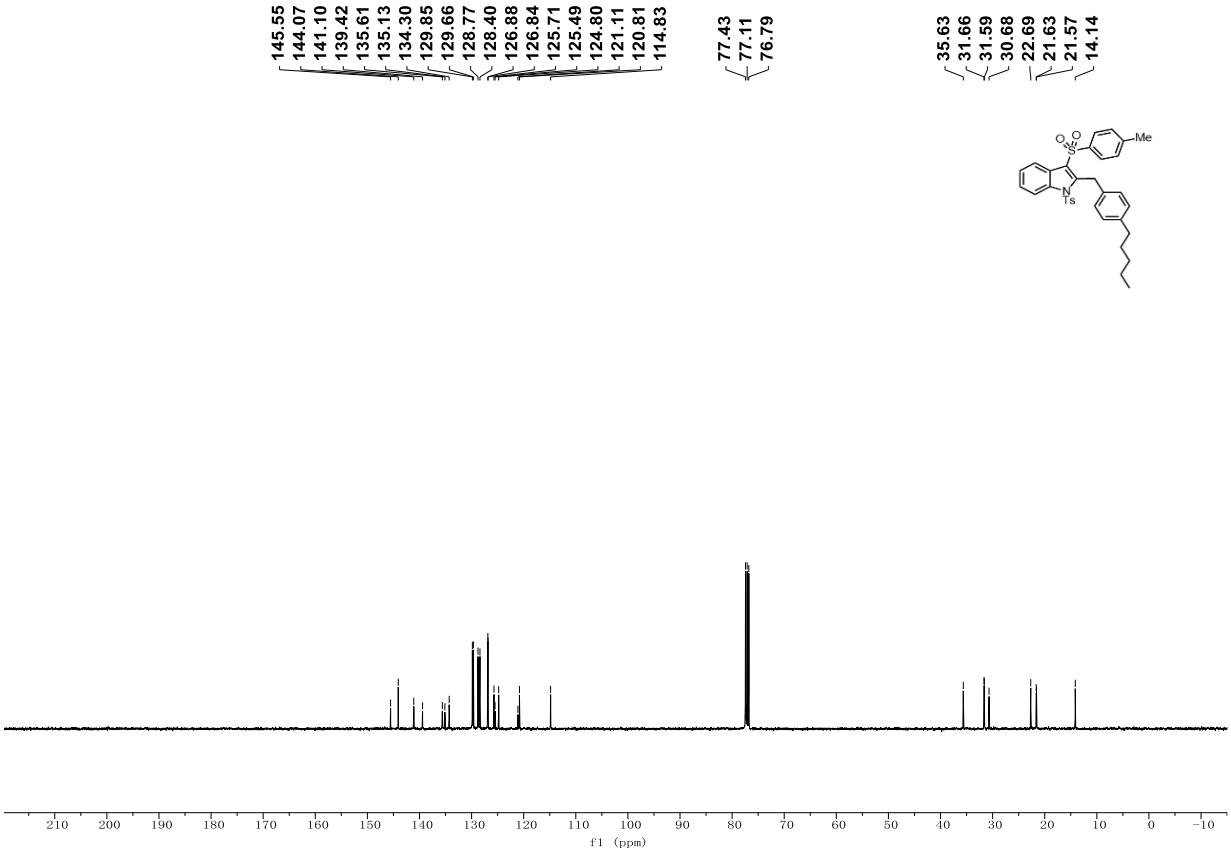
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4d**



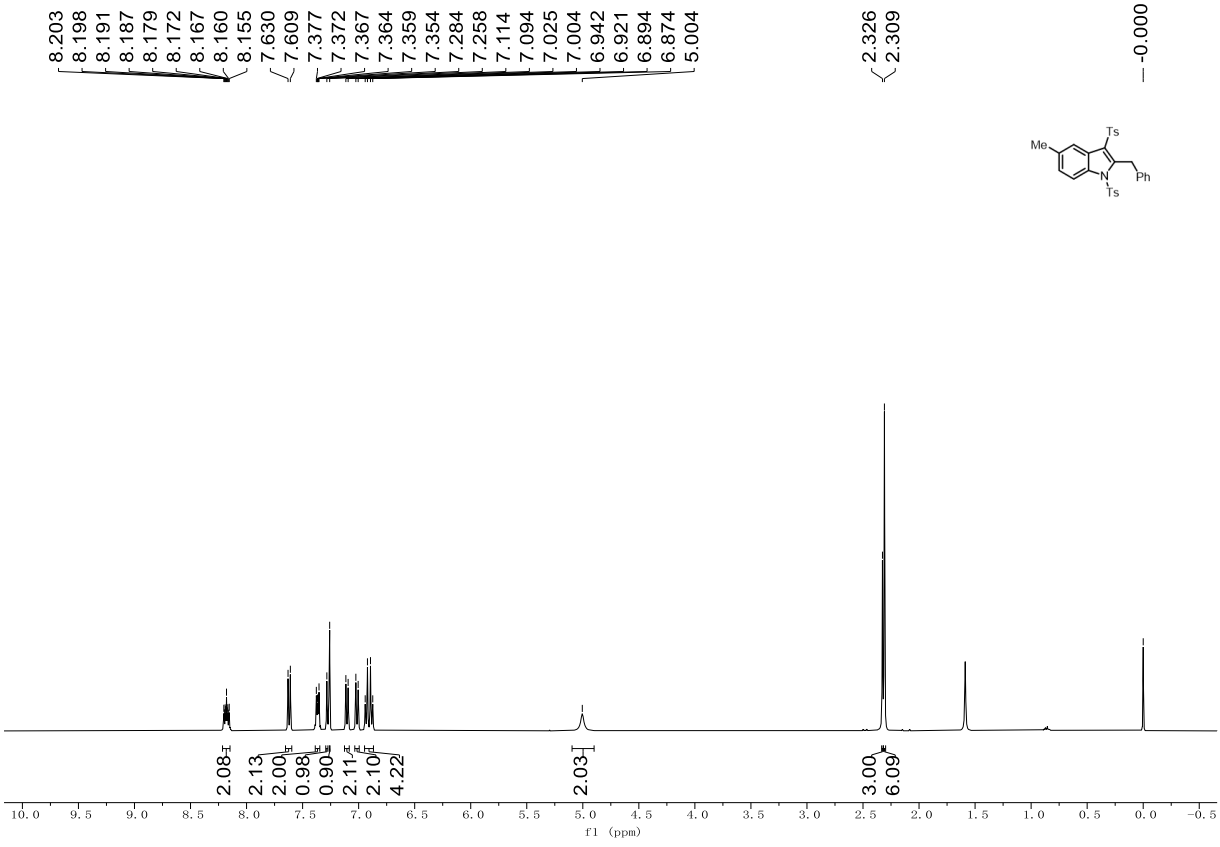
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4e**



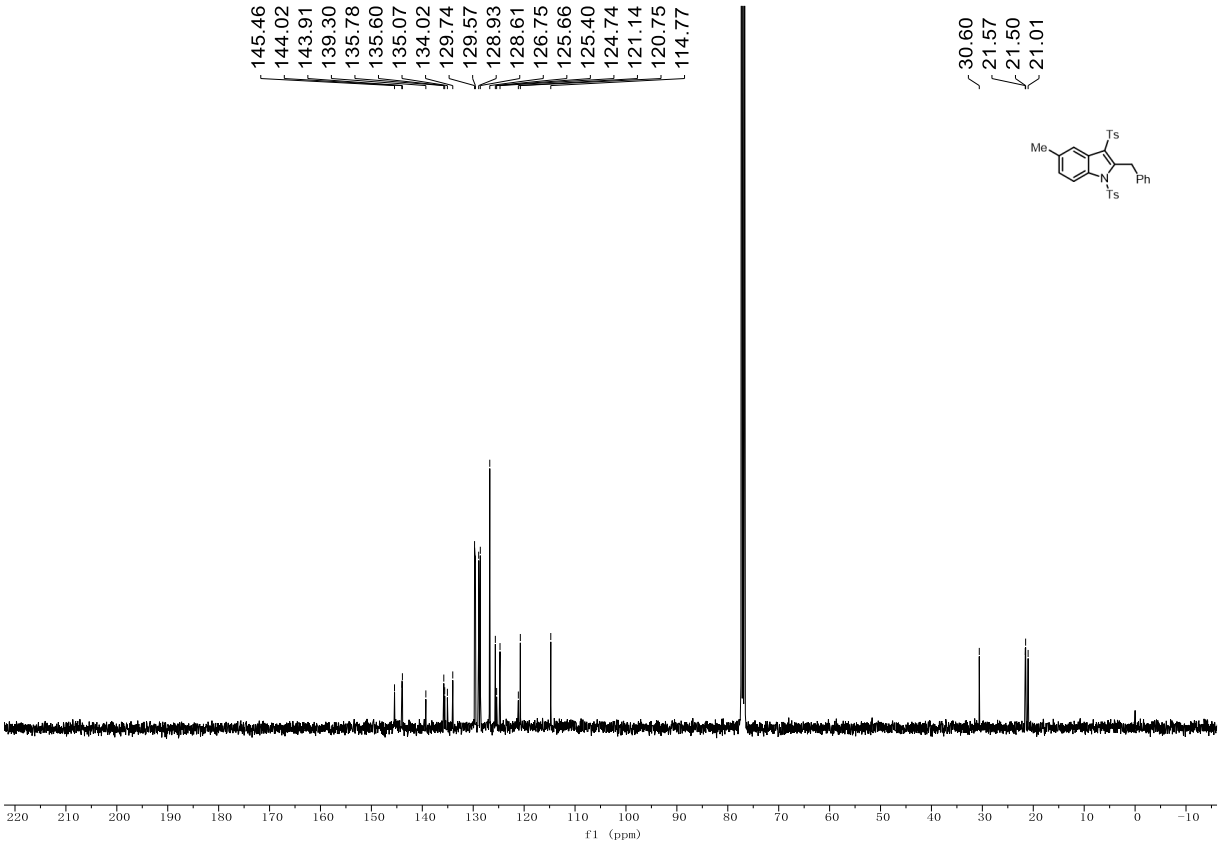
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4e**



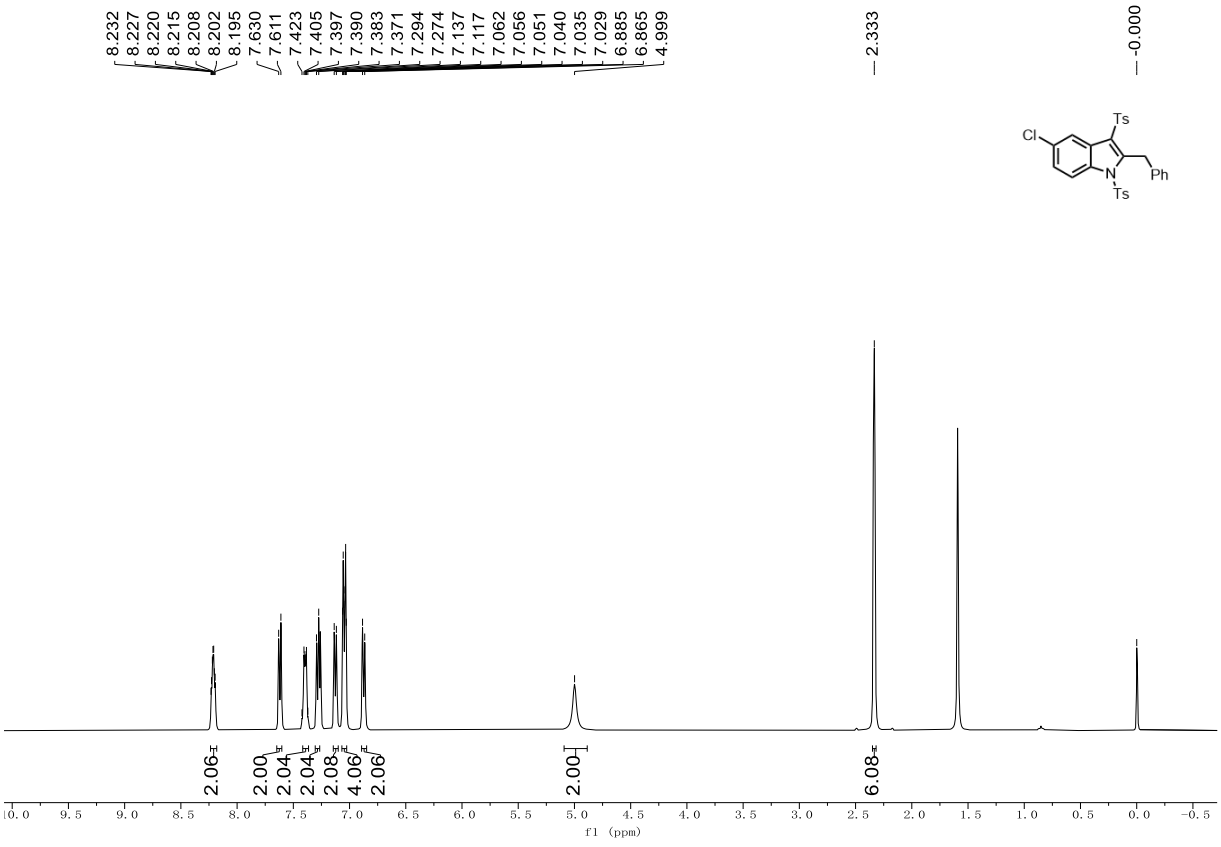
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4f**



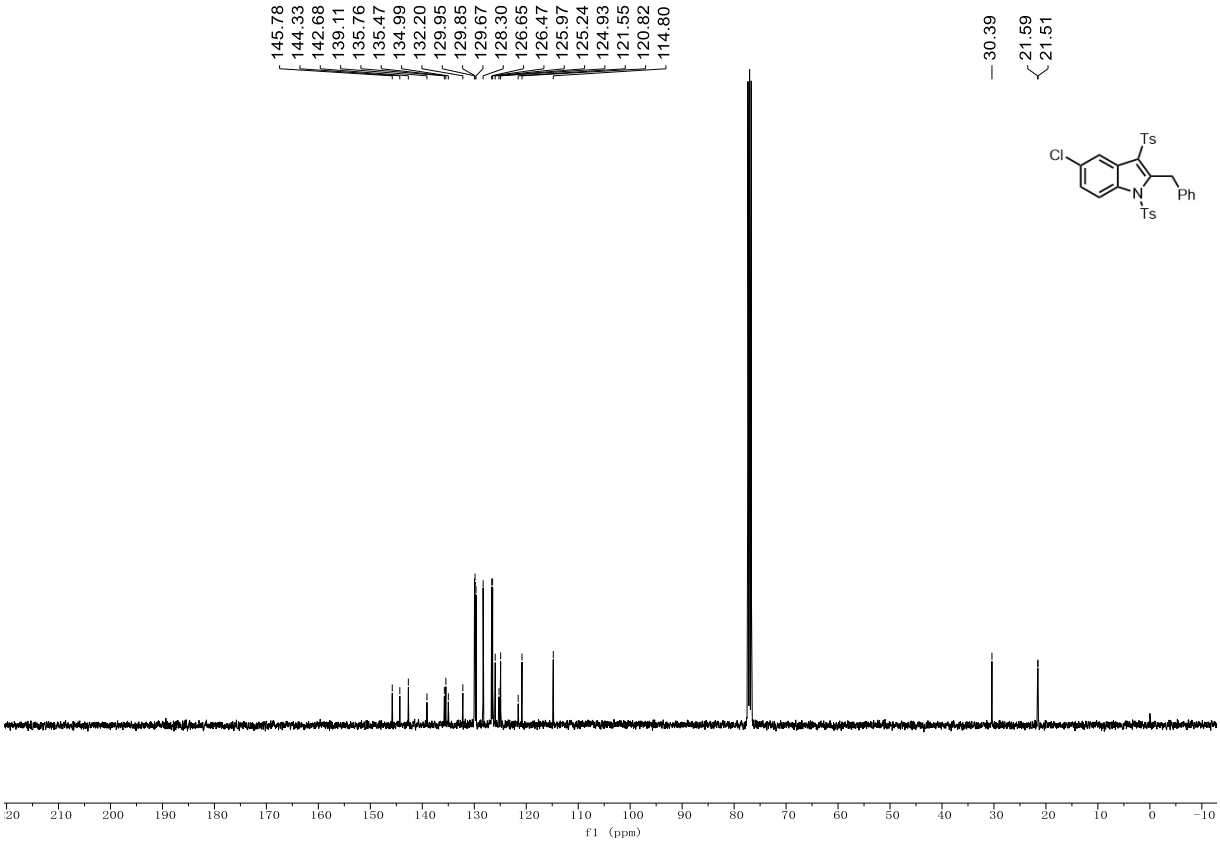
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4f**



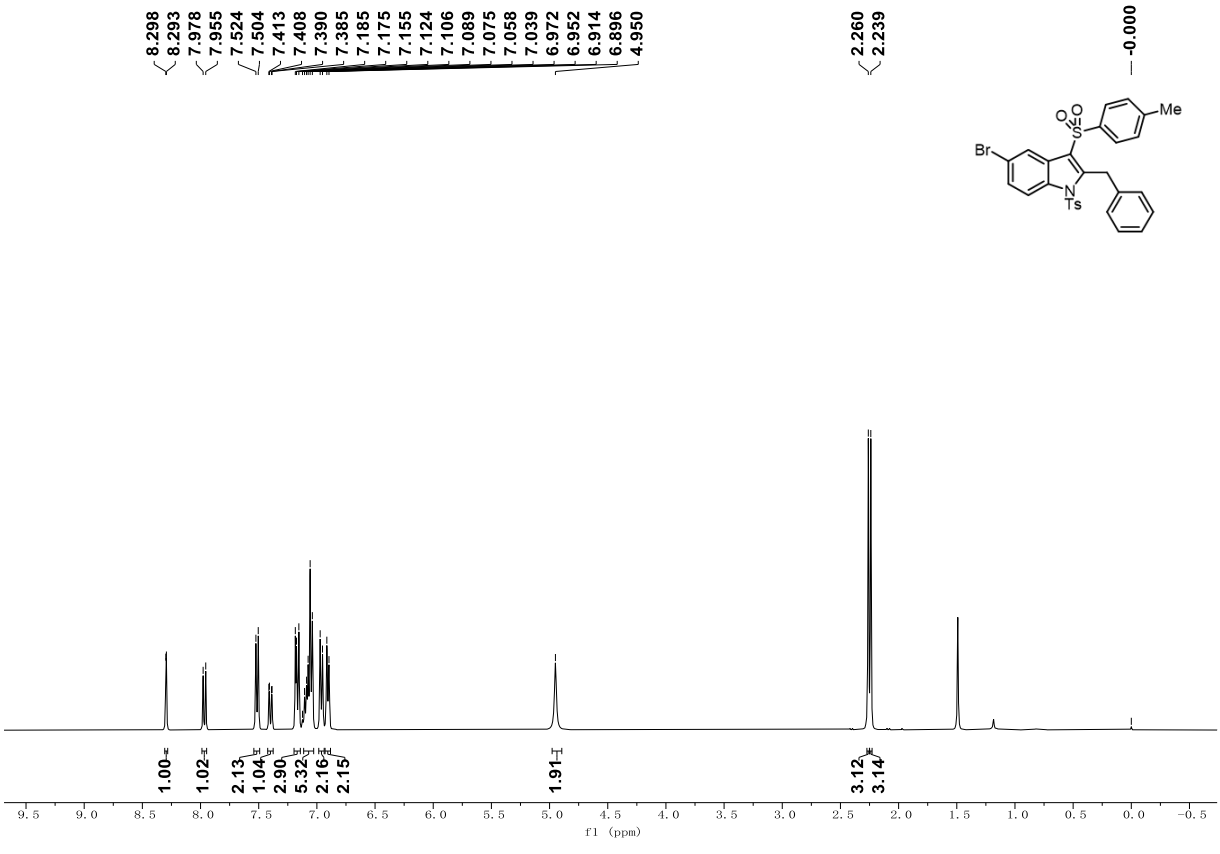
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4g**



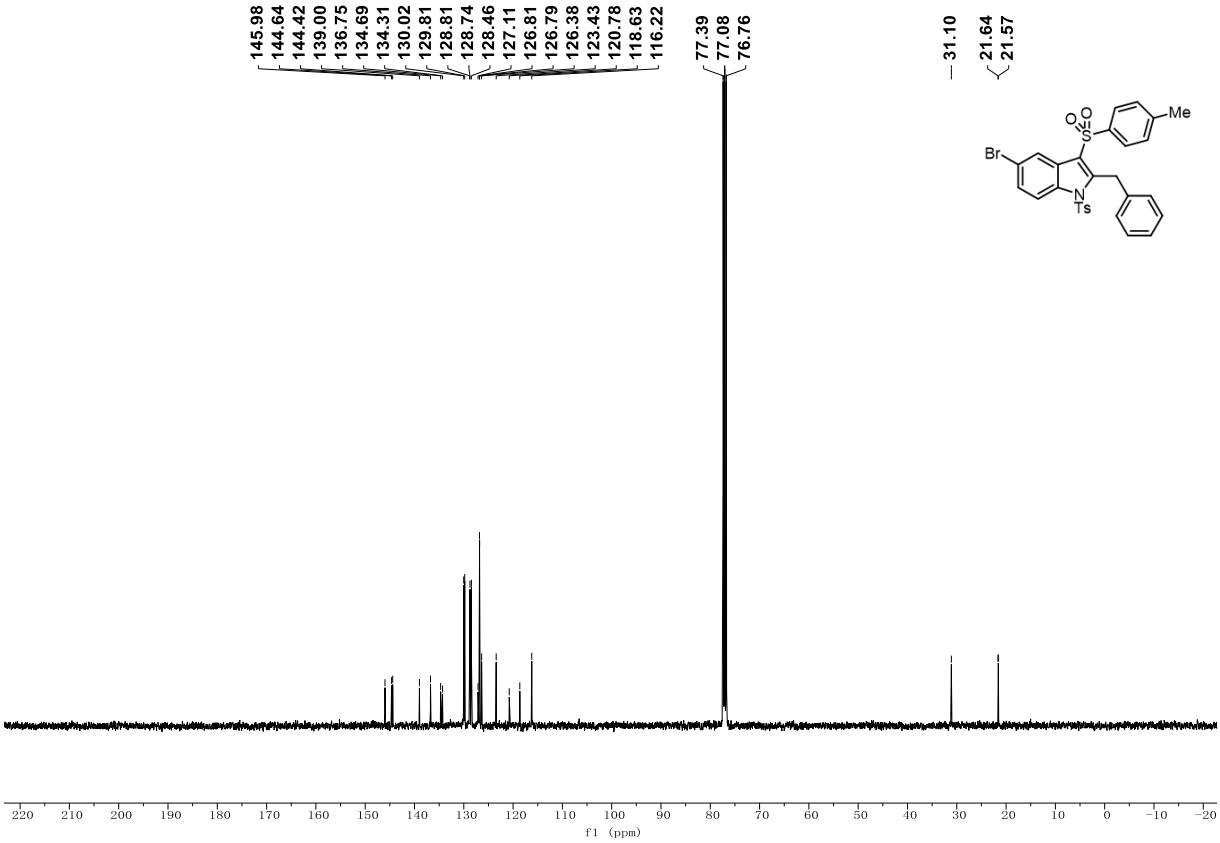
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4g**



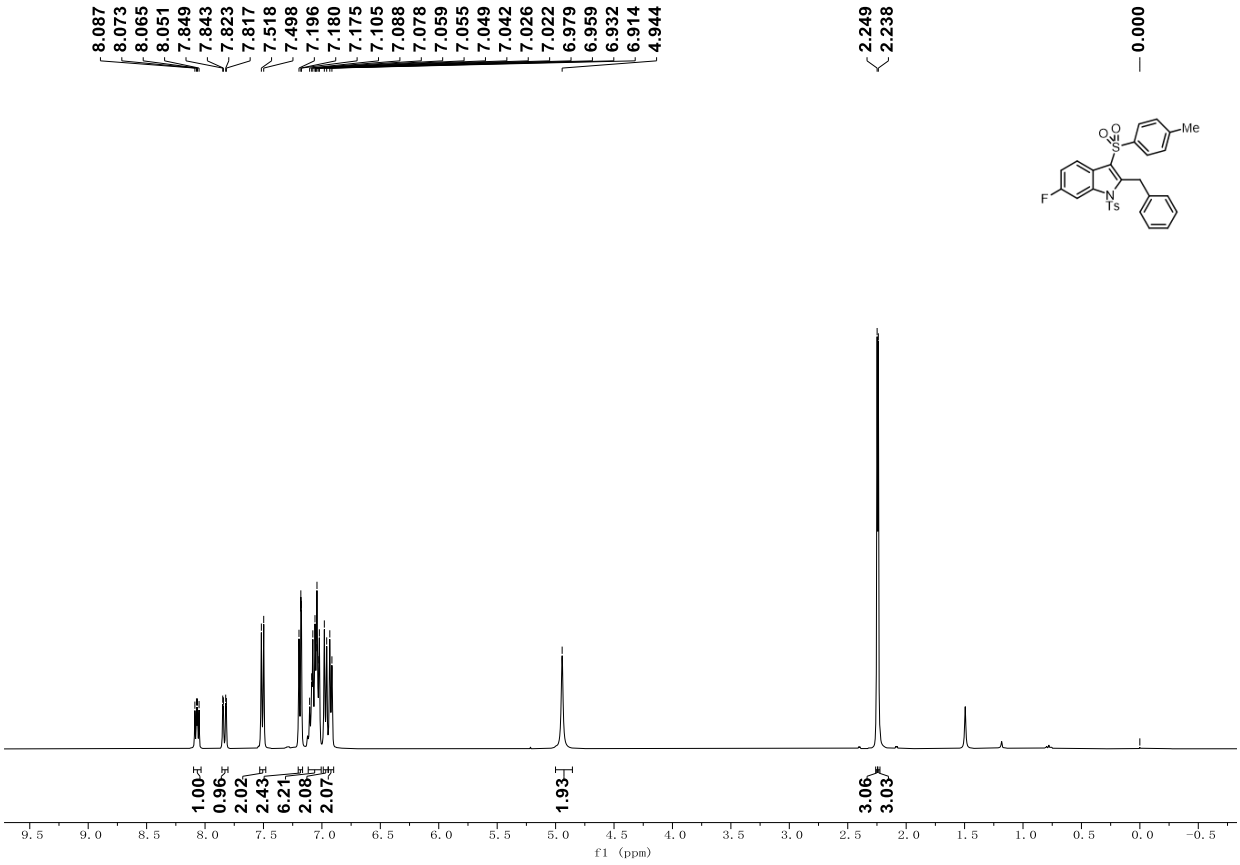
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4h**



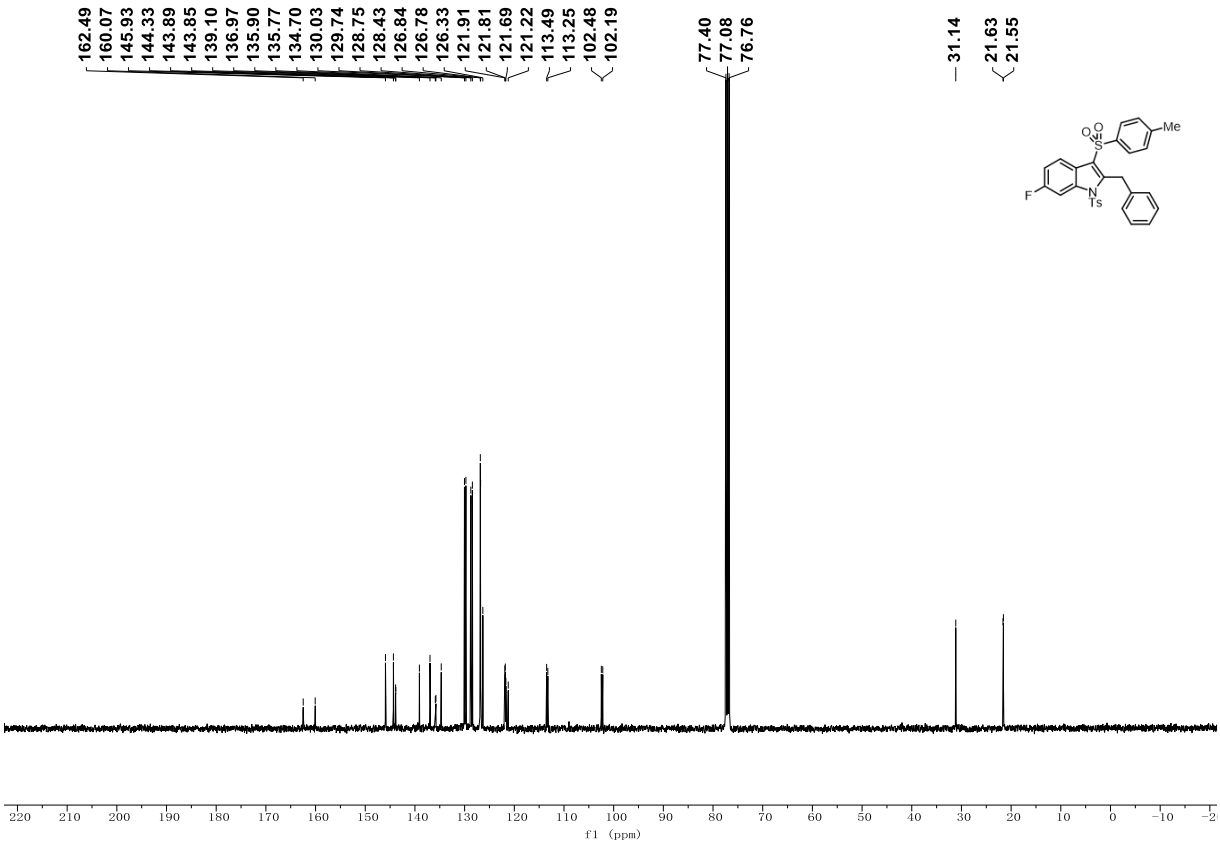
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4h**



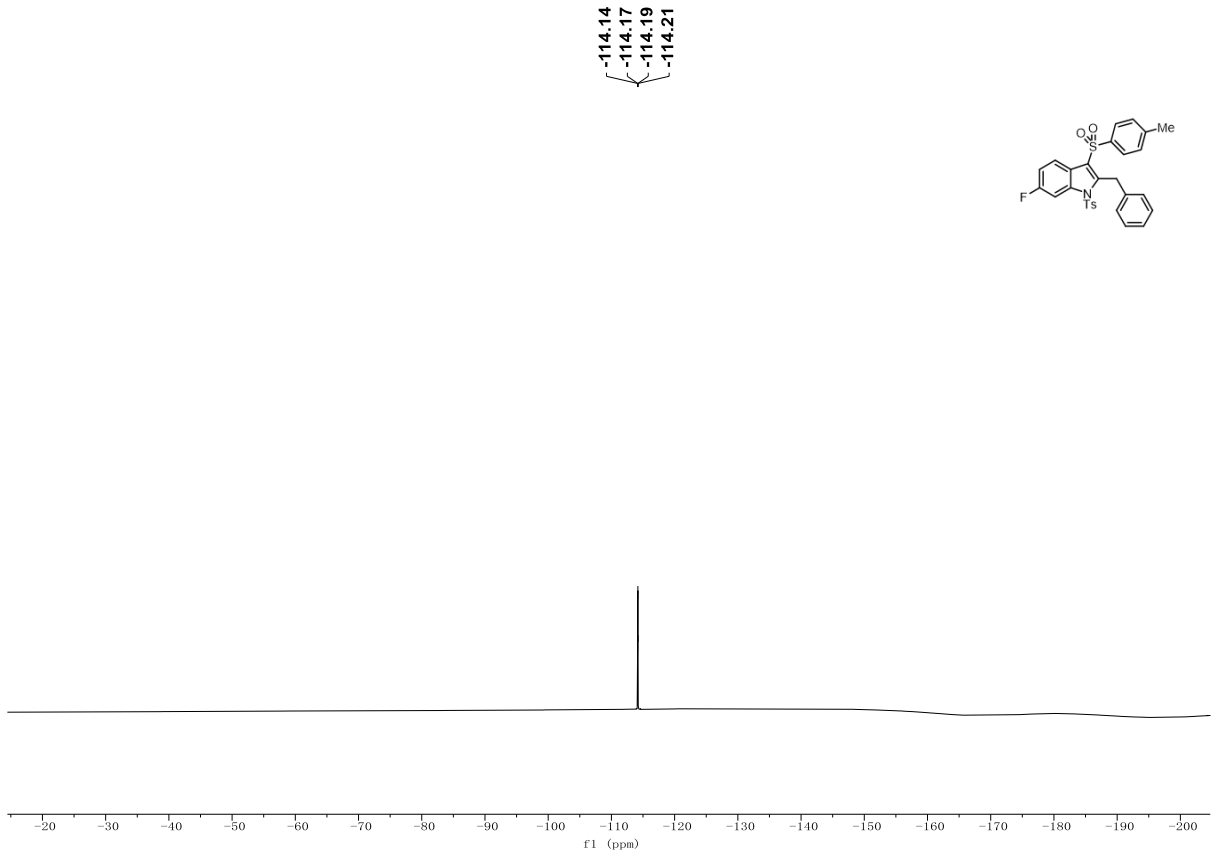
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4i**



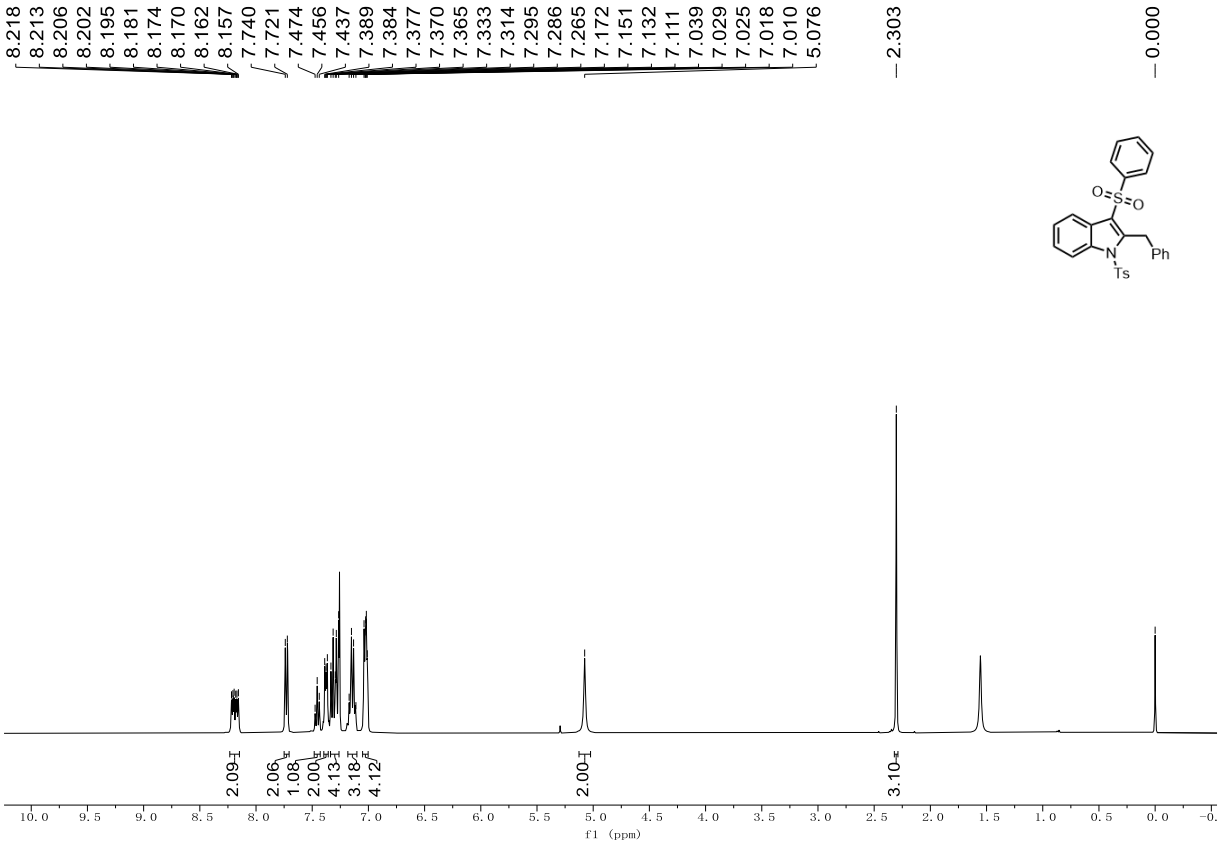
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4i**



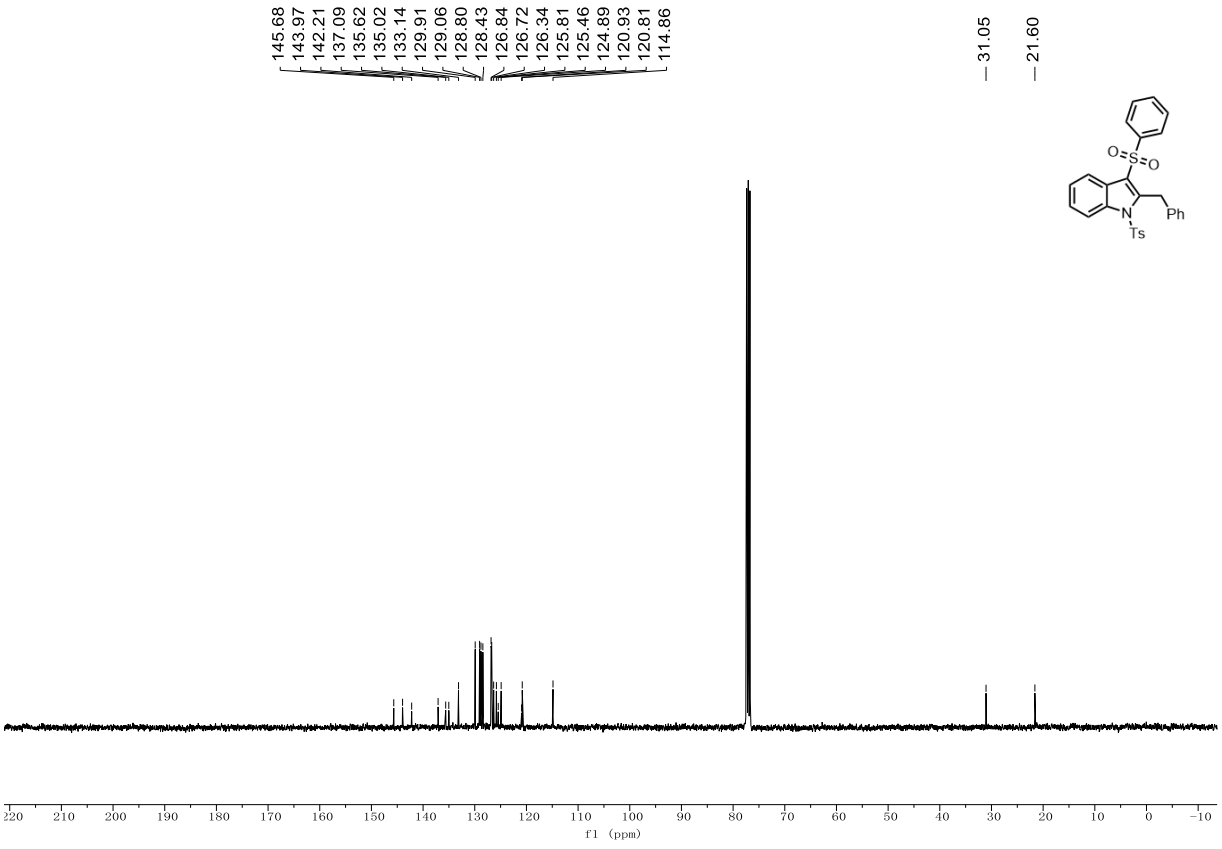
^{19}F NMR (376 MHz, $CDCl_3$) spectroscopy of **4i**



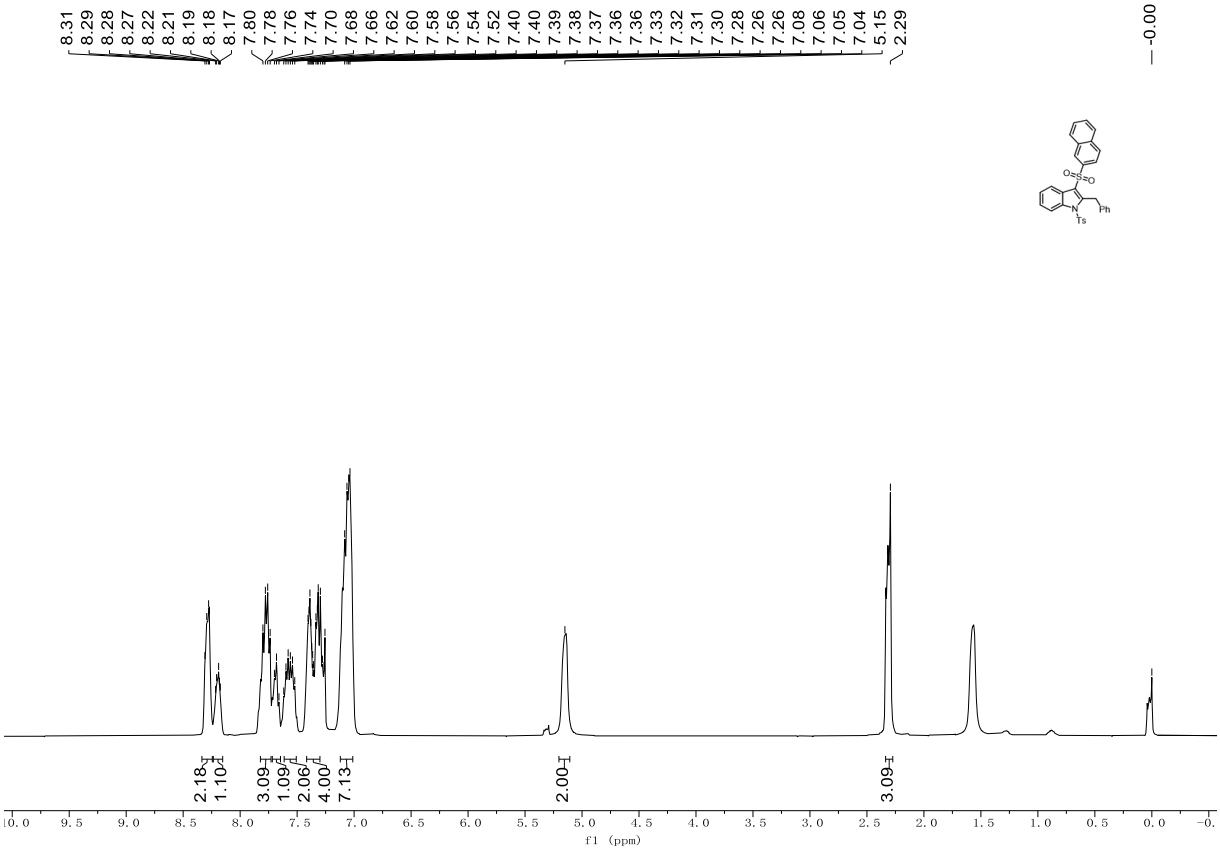
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4j**



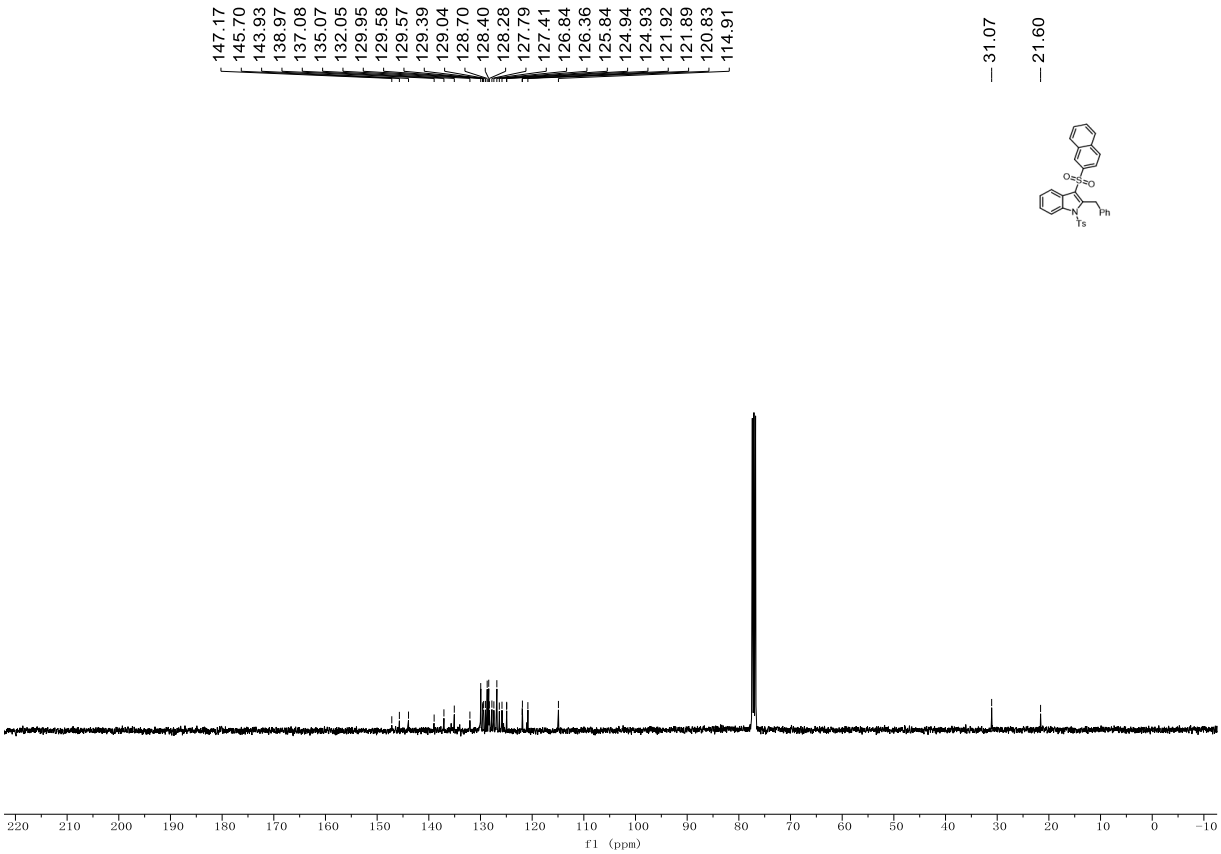
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4j**



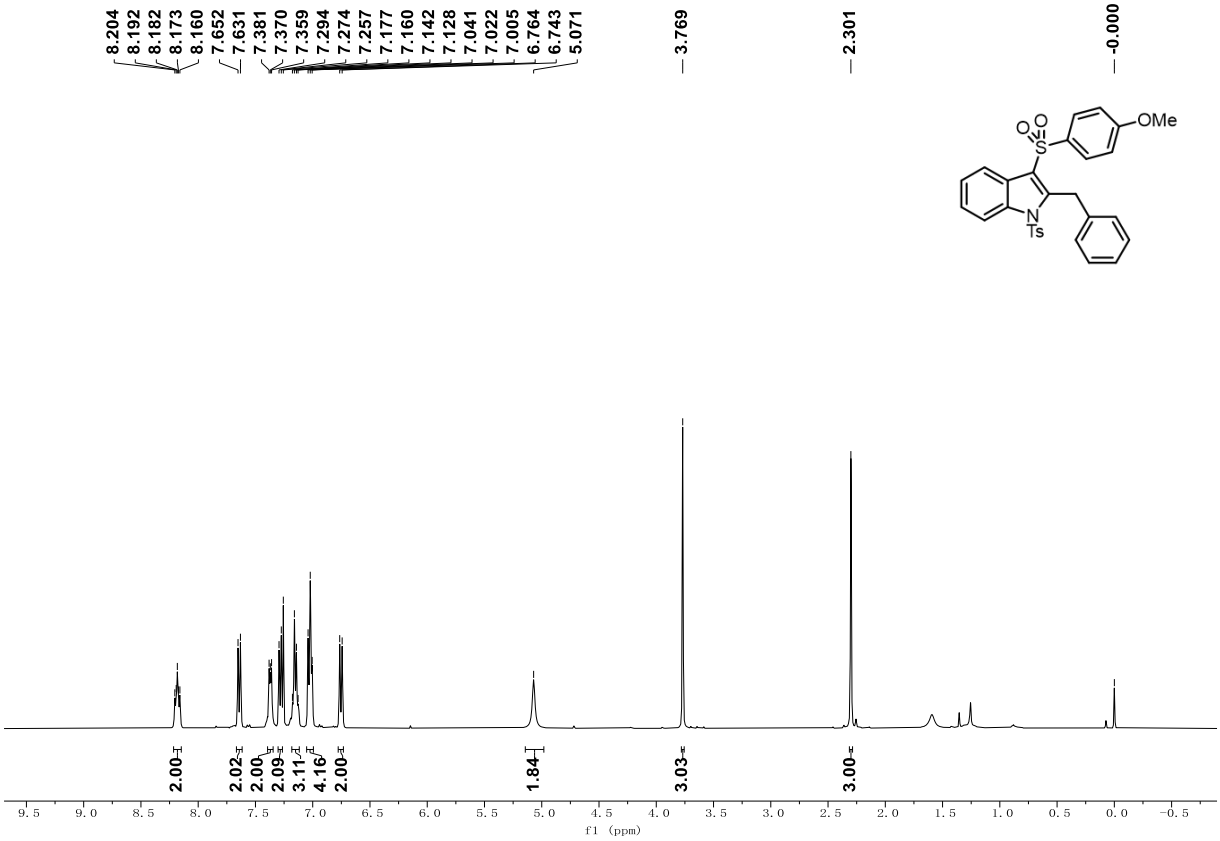
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4k**



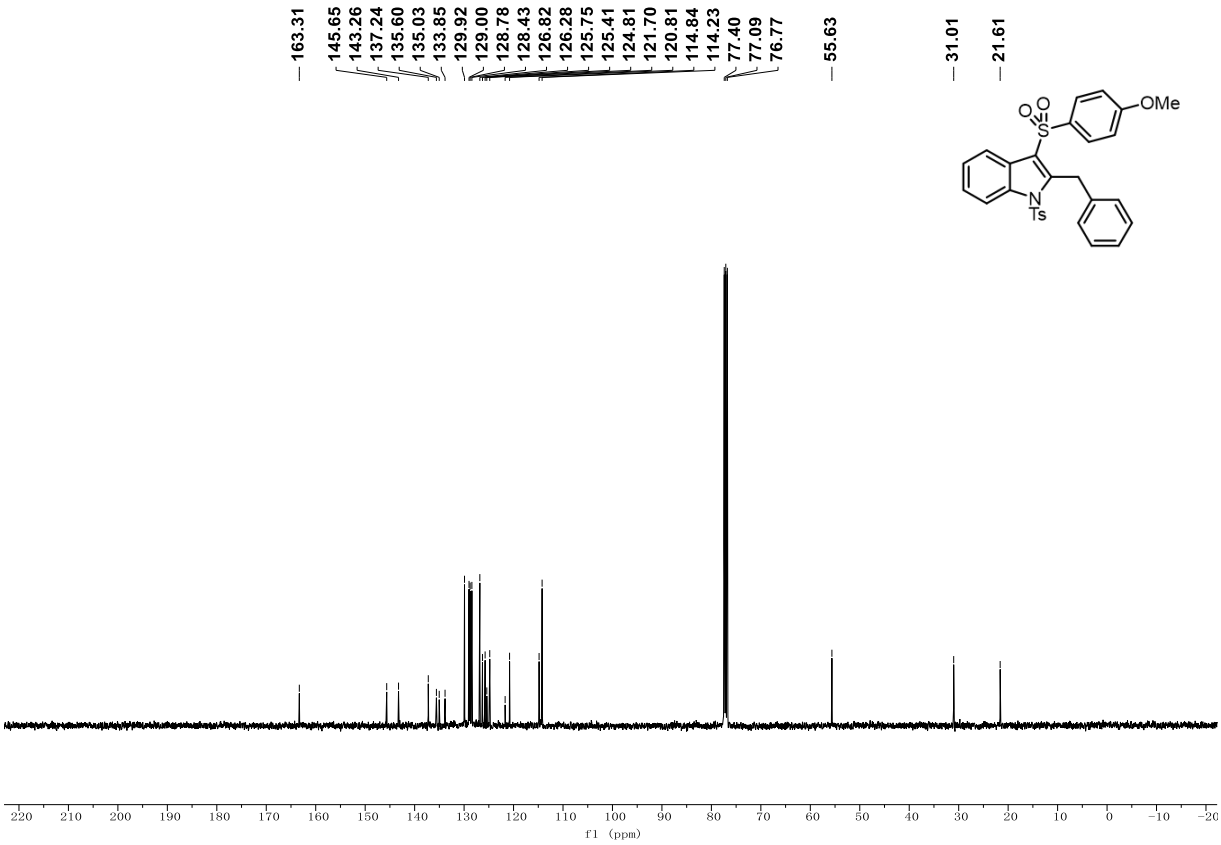
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4k**



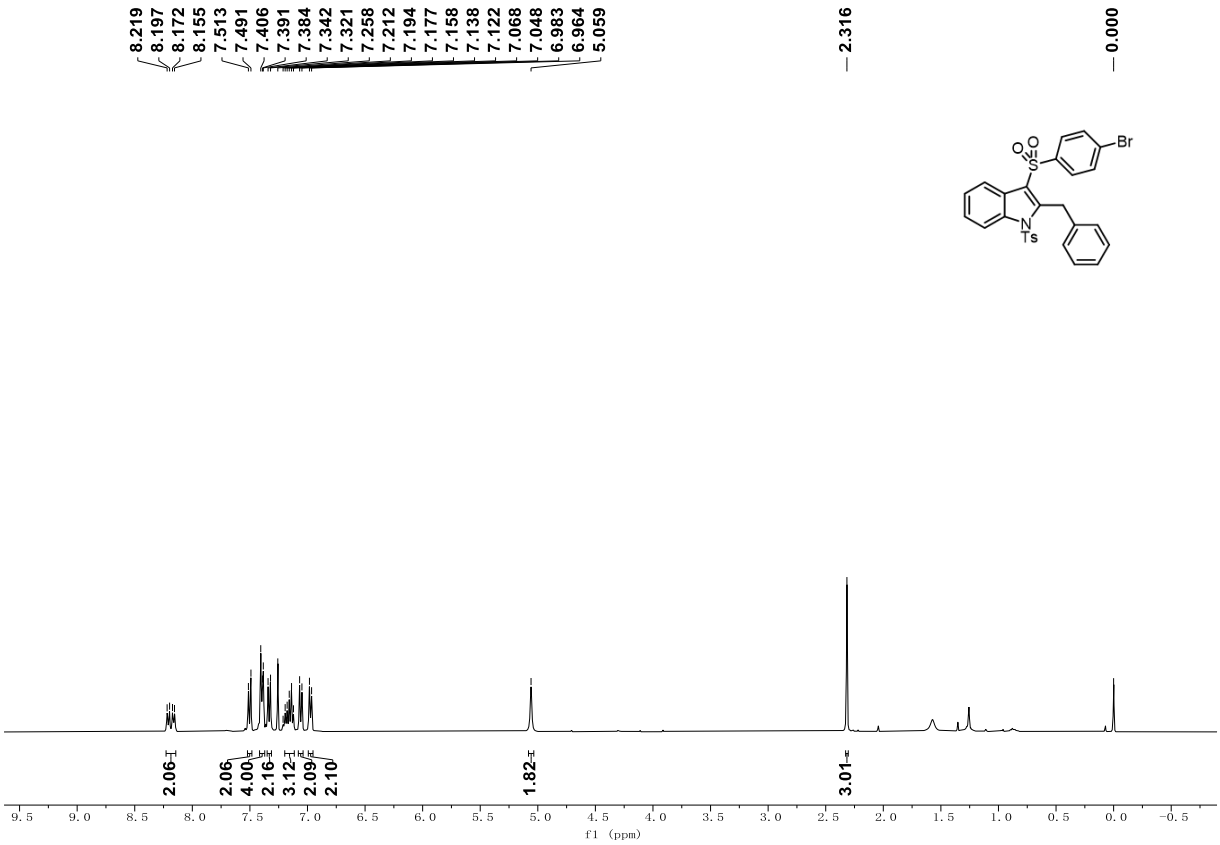
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4l**



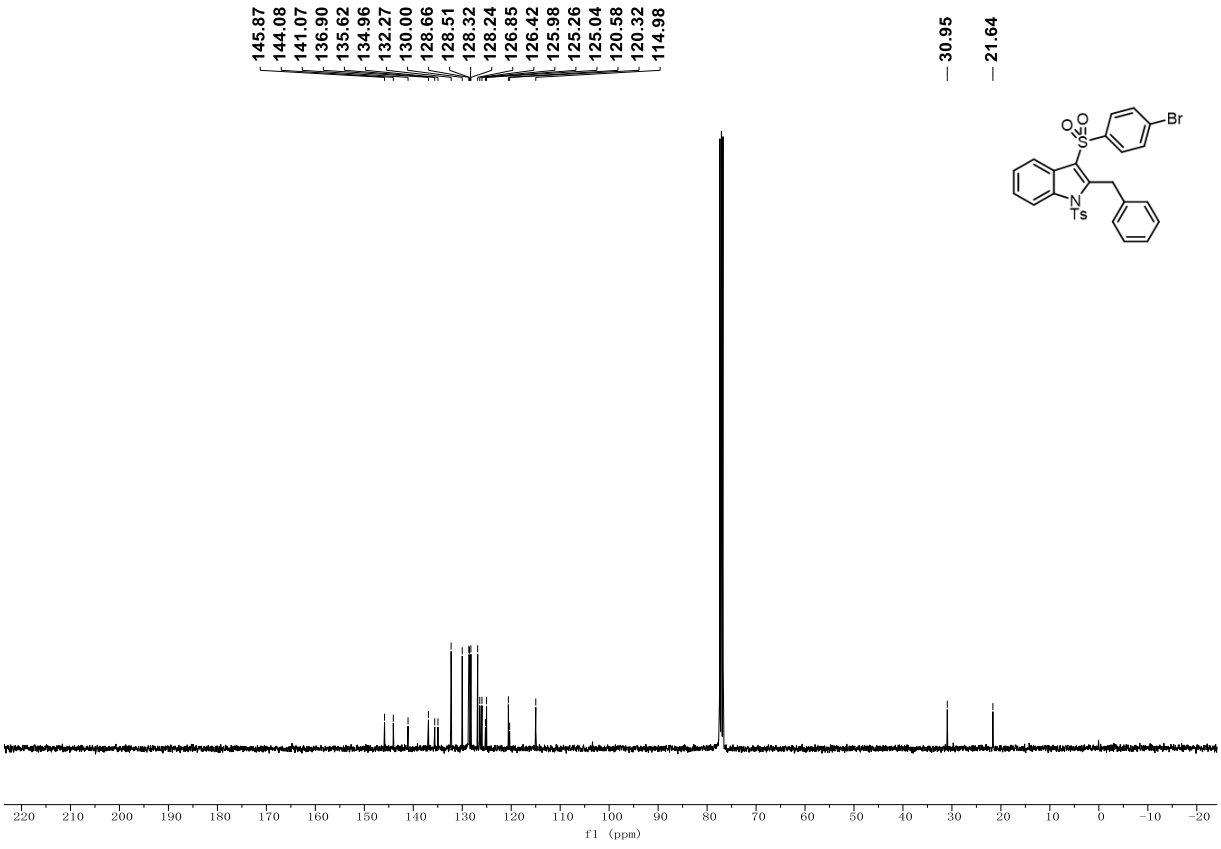
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4l**



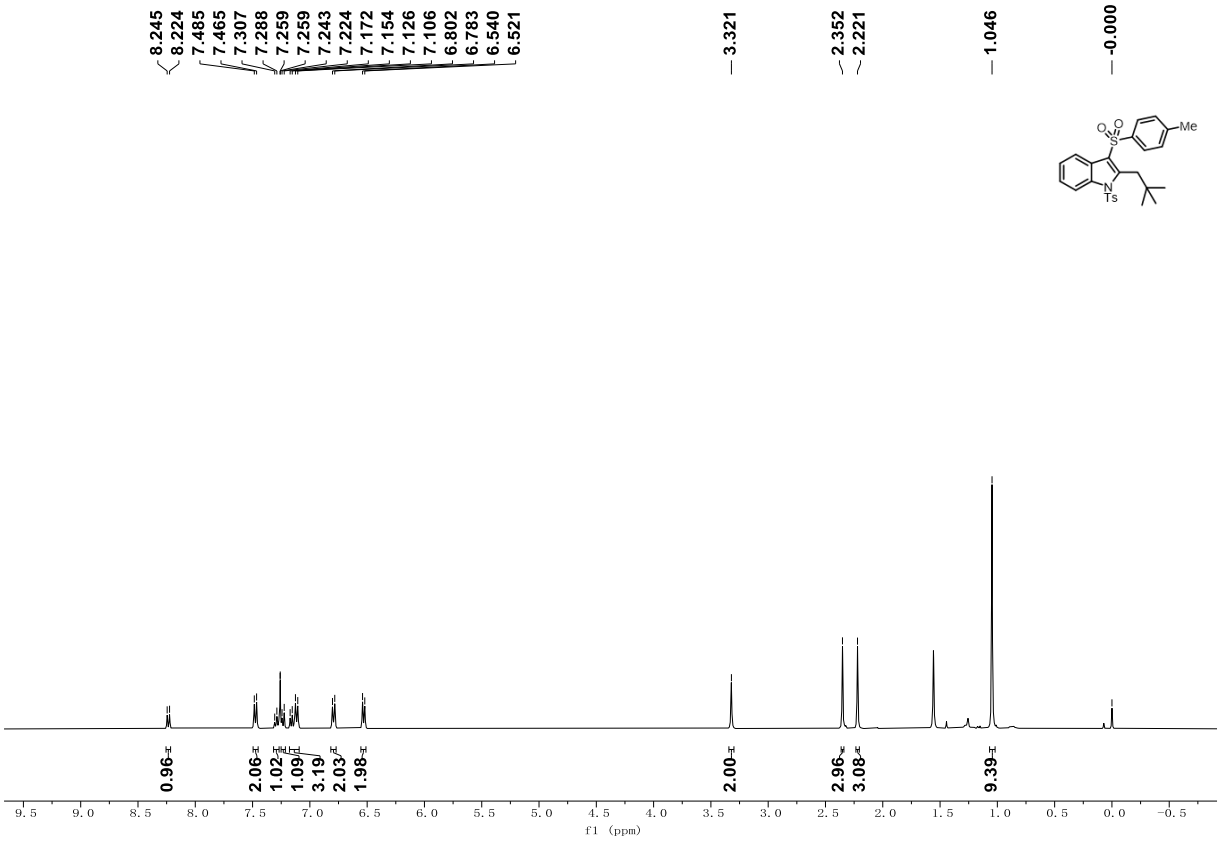
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4m**



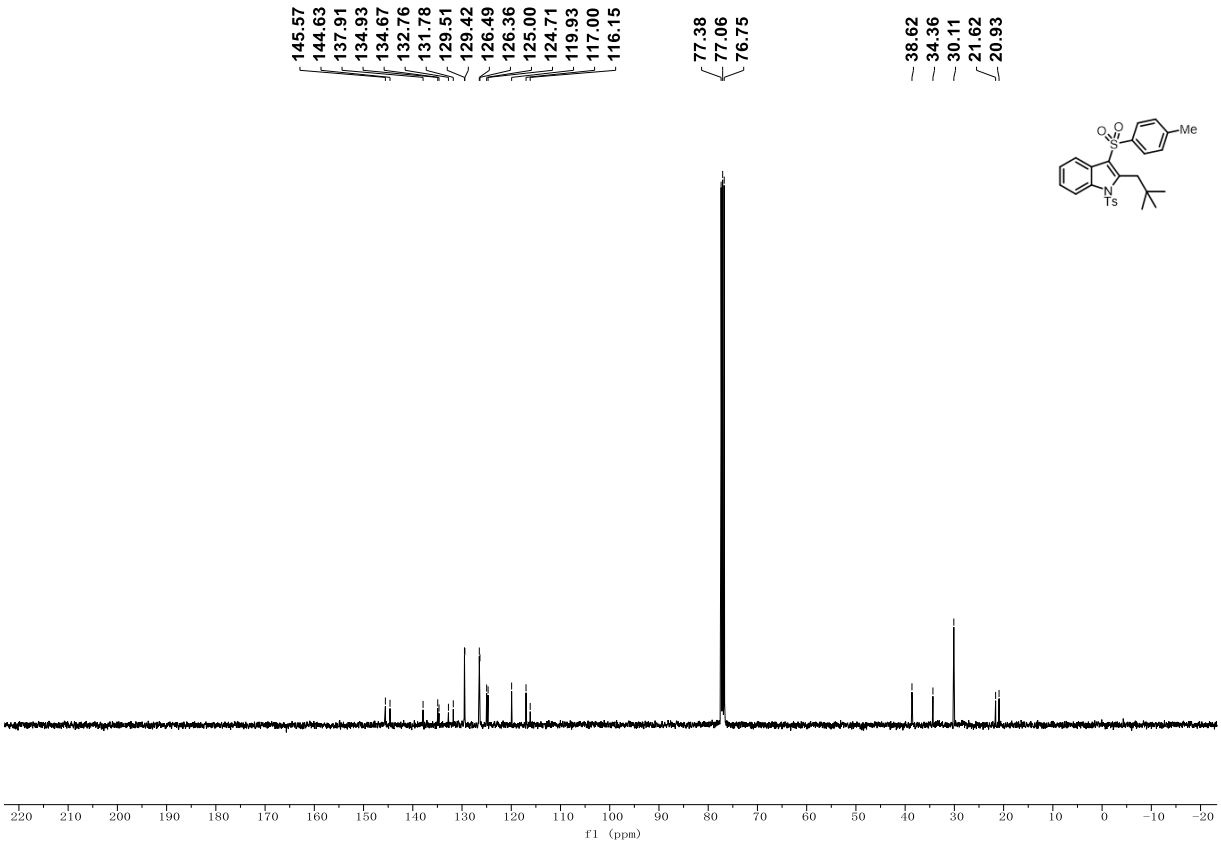
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4m**



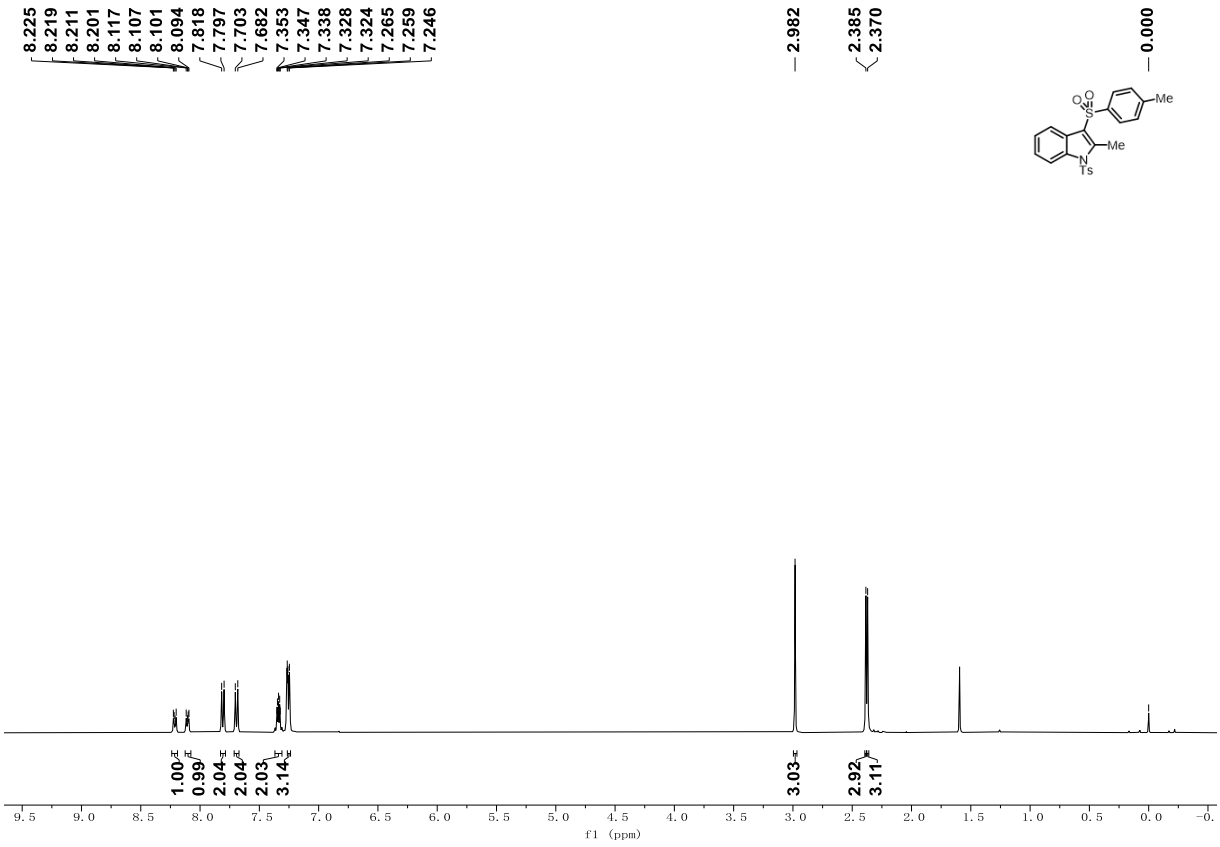
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4n**



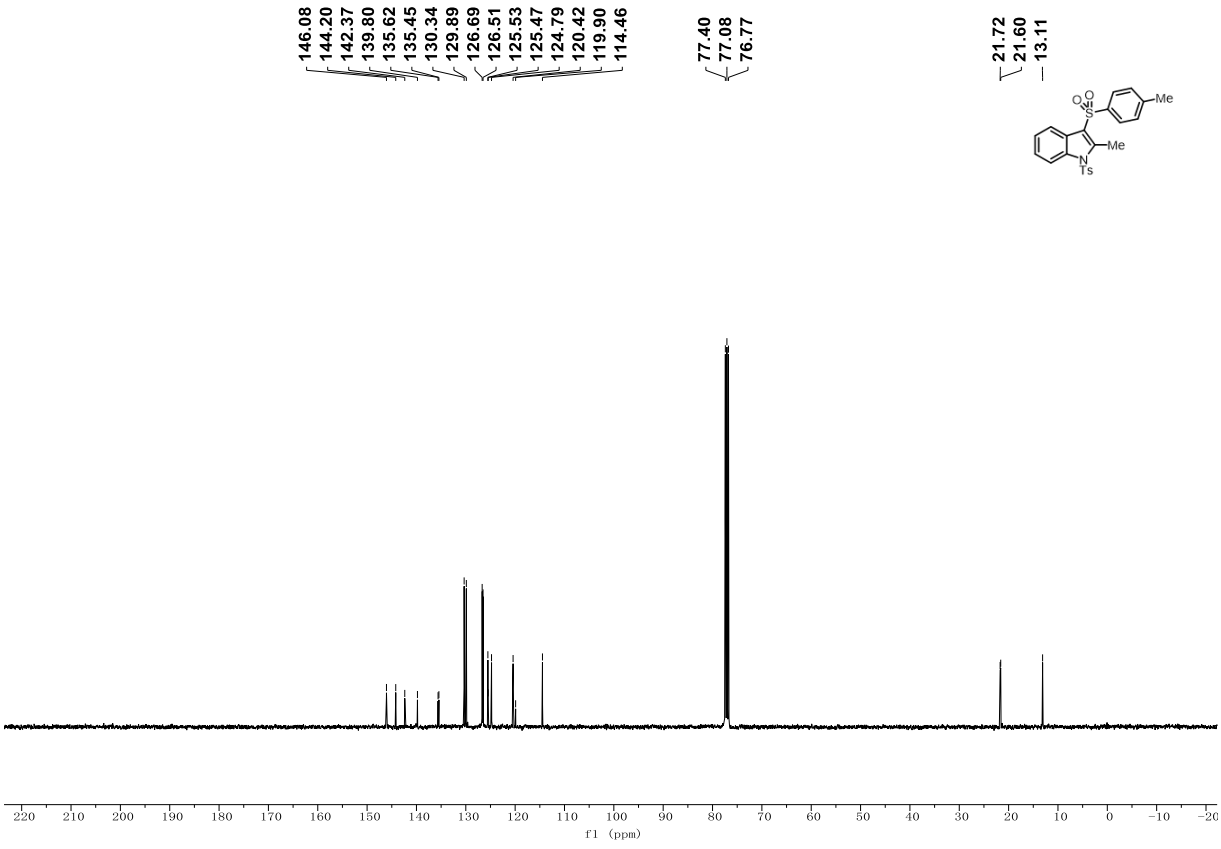
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4n**



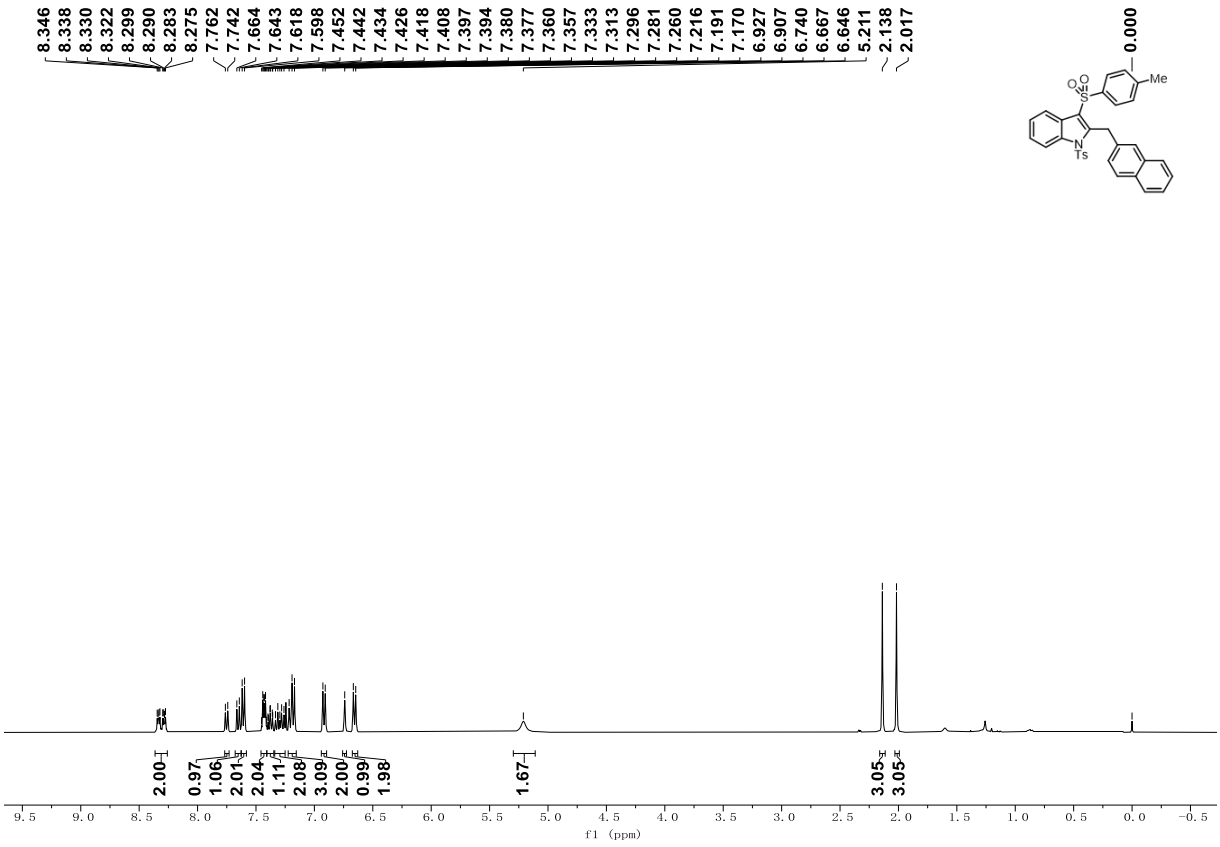
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4o**



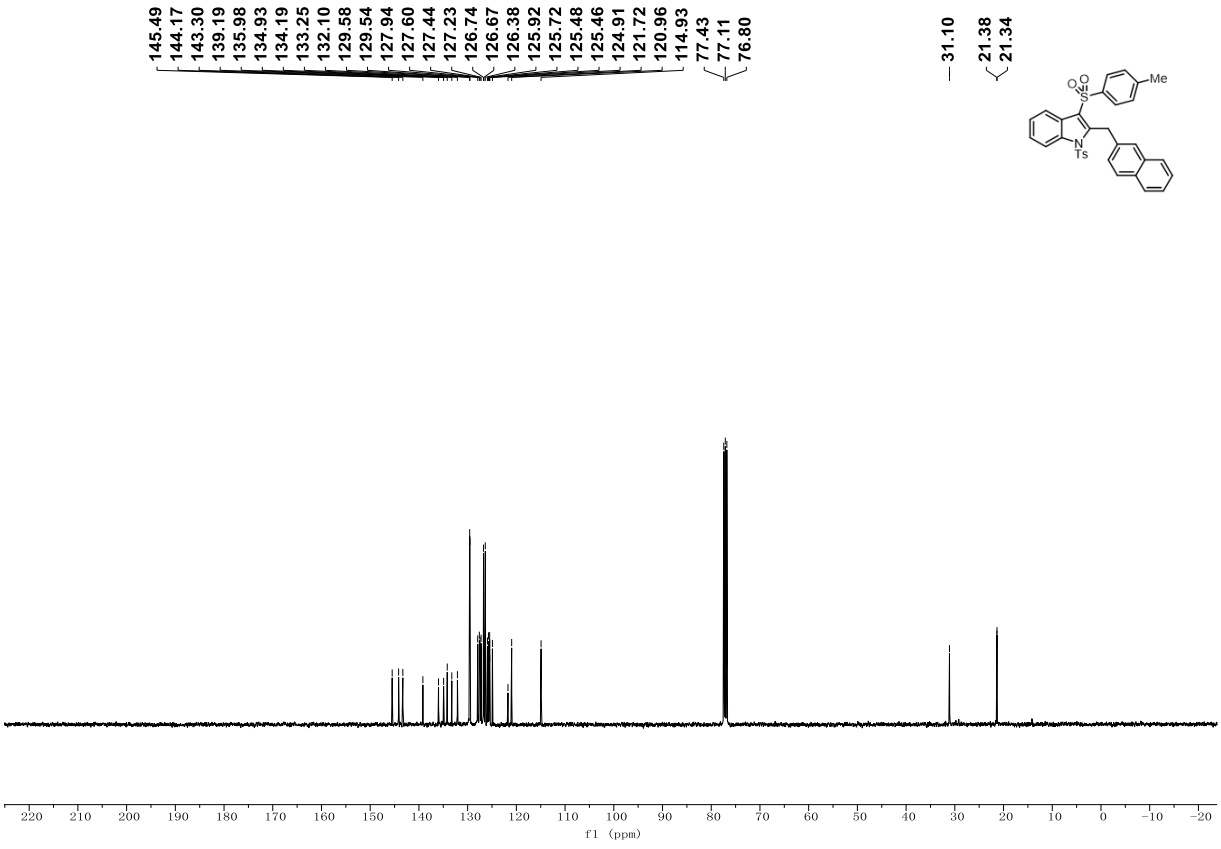
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4o**



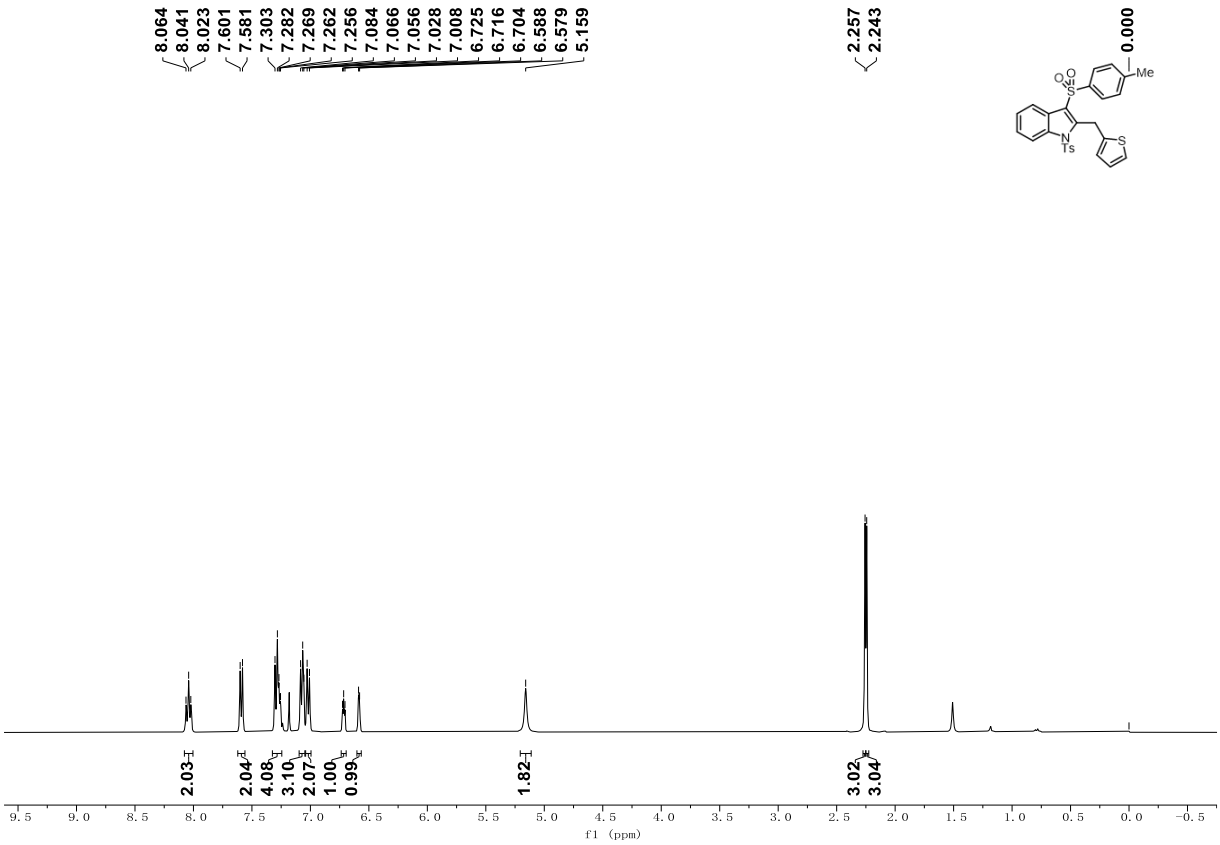
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4p**



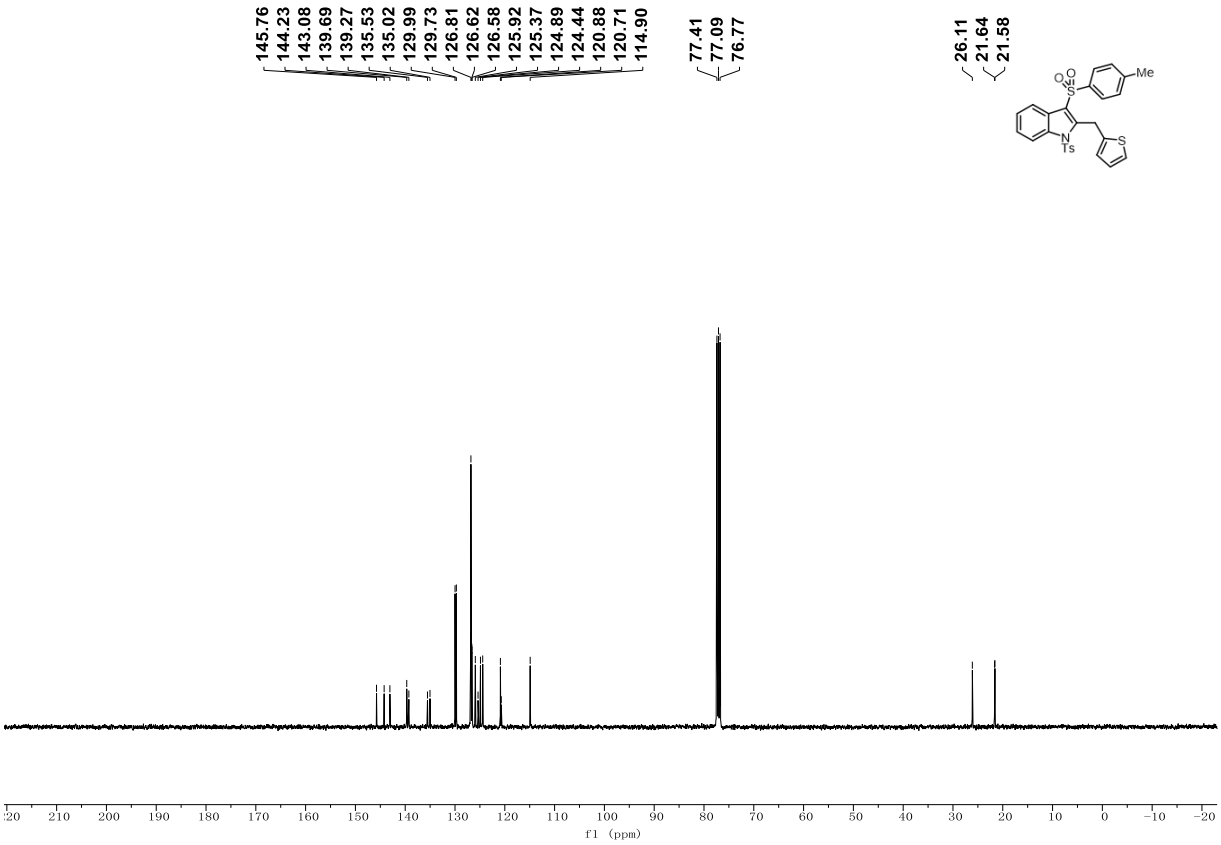
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4p**



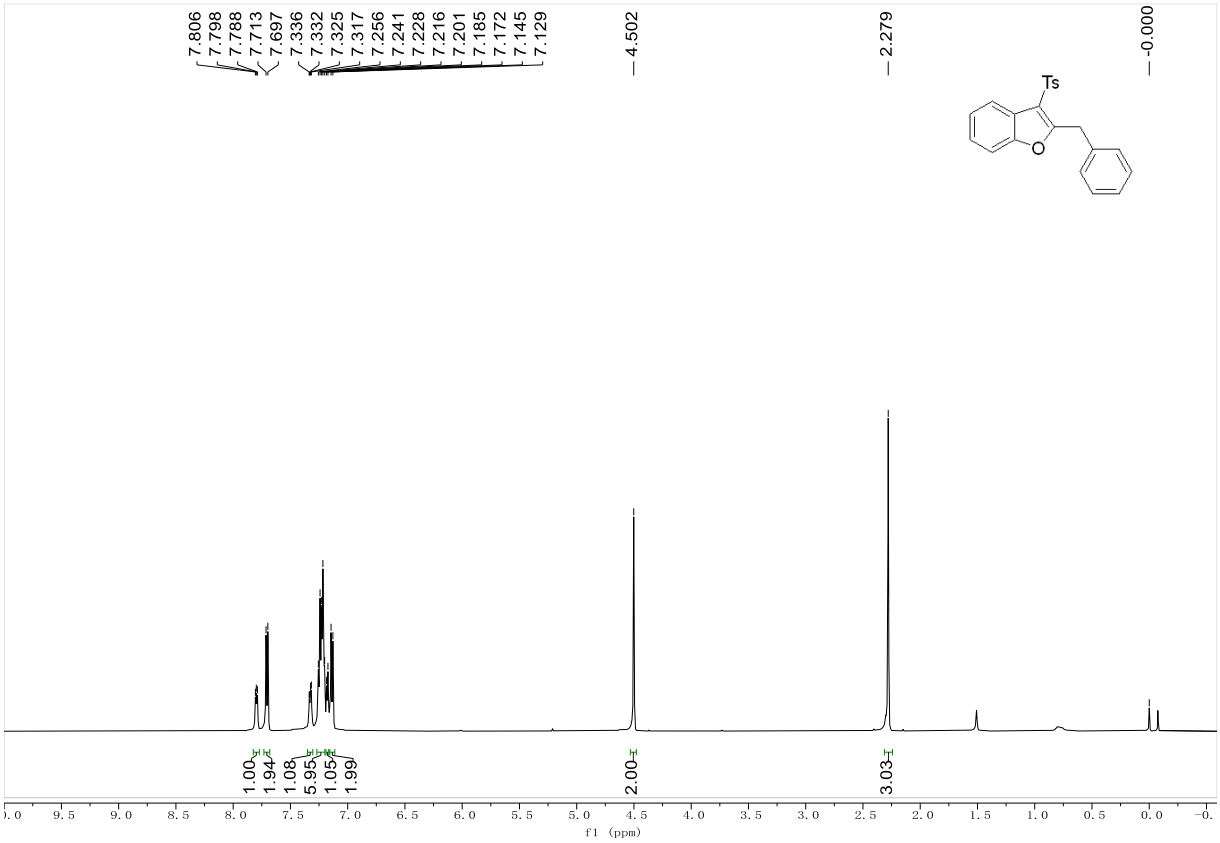
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **4q**



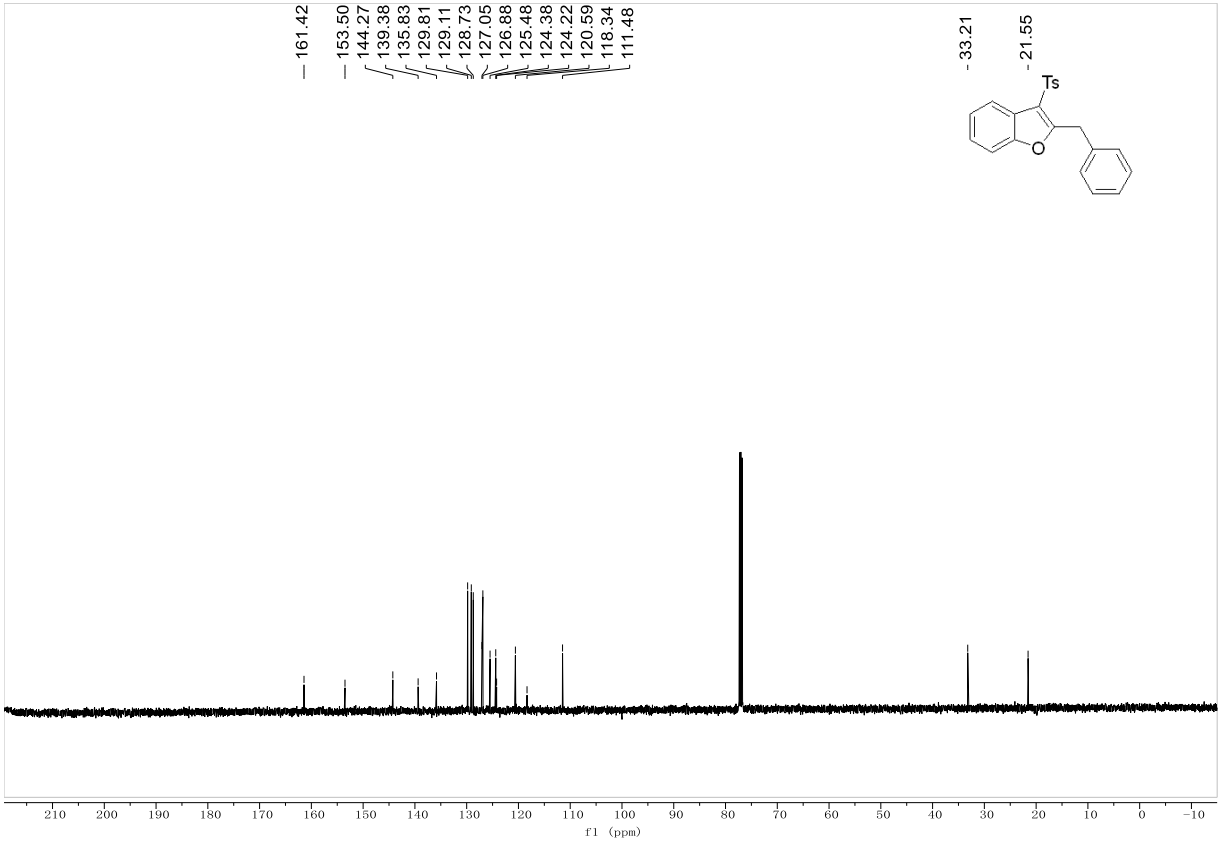
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **4q**



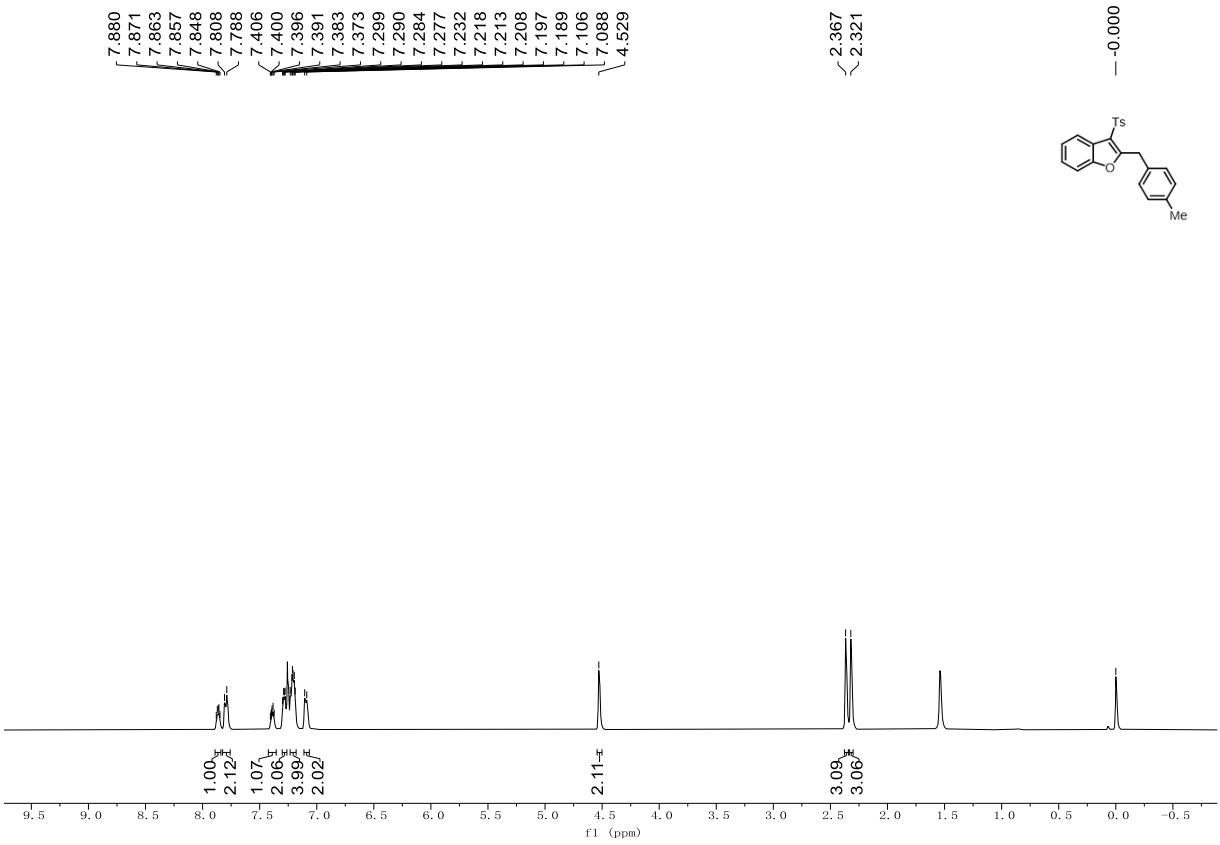
^{1}H NMR (500 MHz, $CDCl_3$) spectroscopy of **7a**



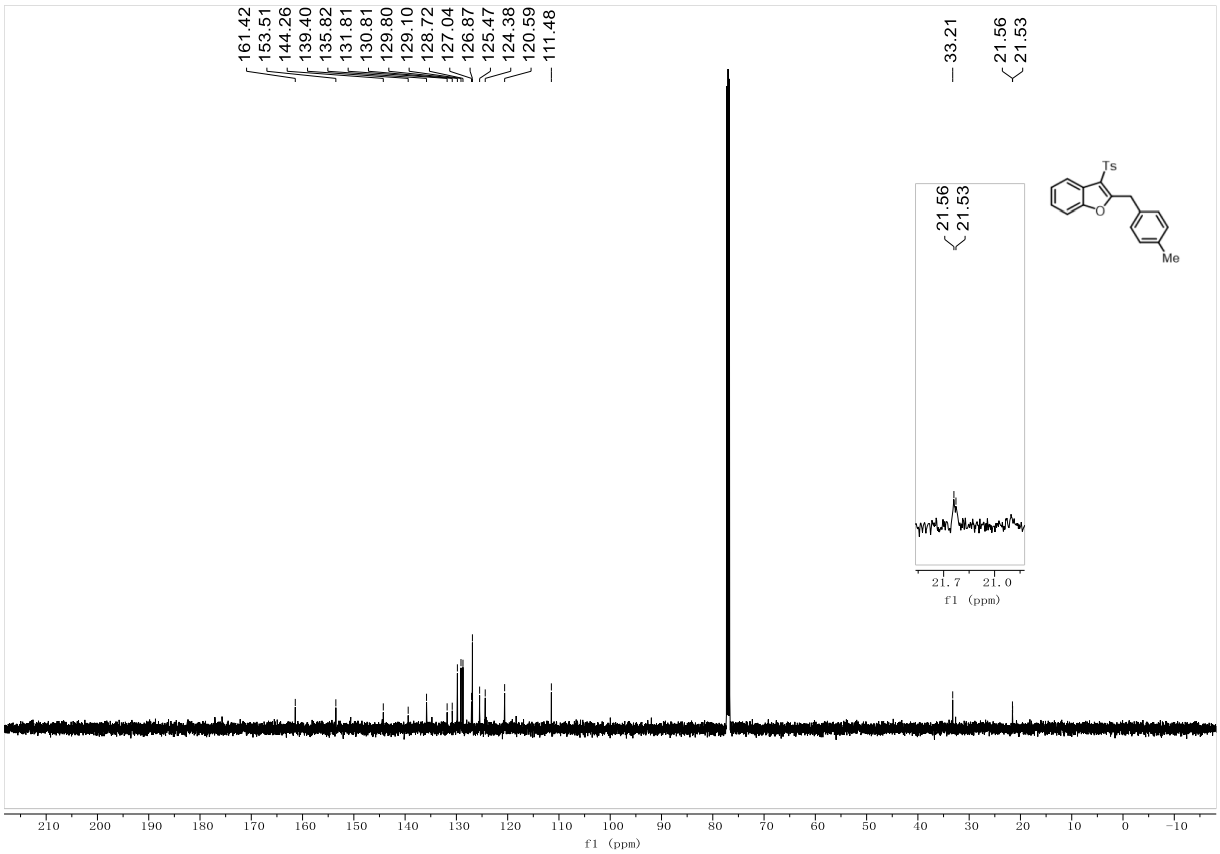
^{13}C NMR (126 MHz, $CDCl_3$) spectroscopy of **7a**



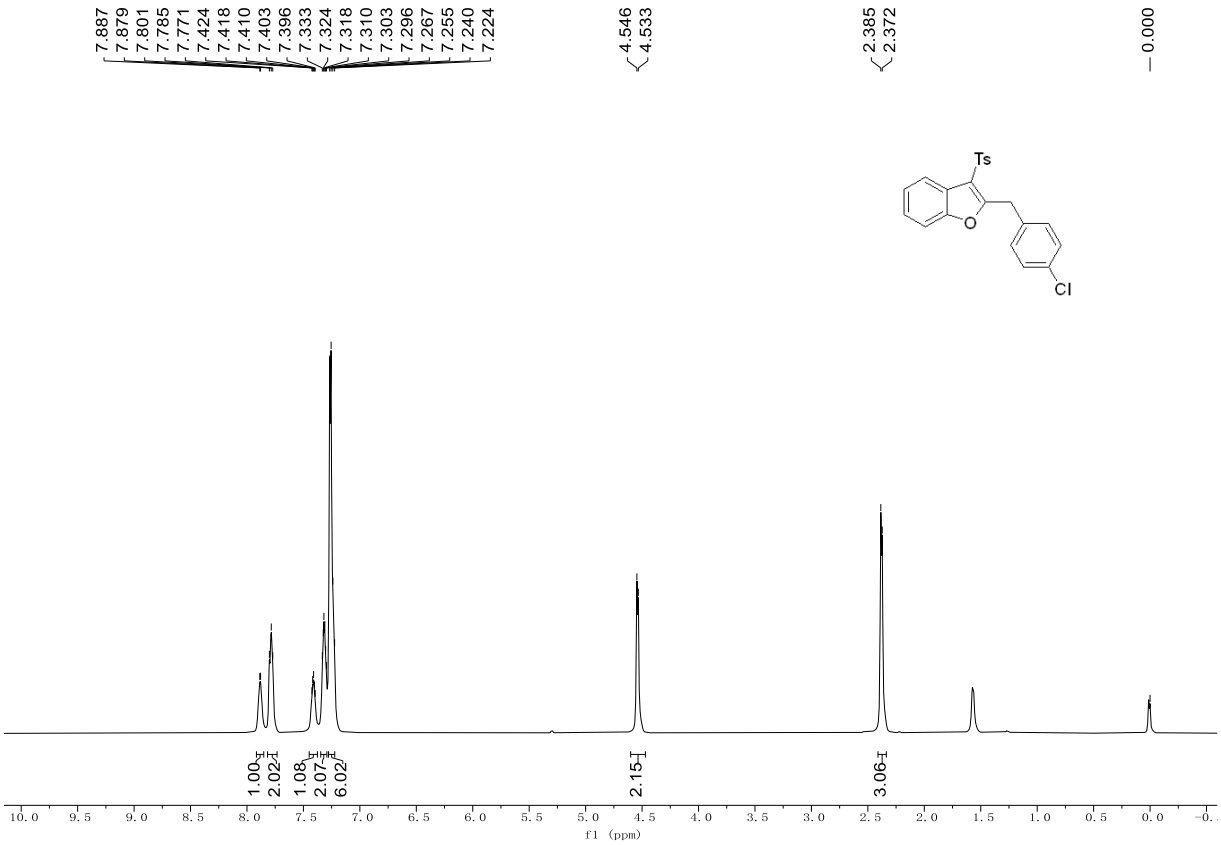
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **7b**



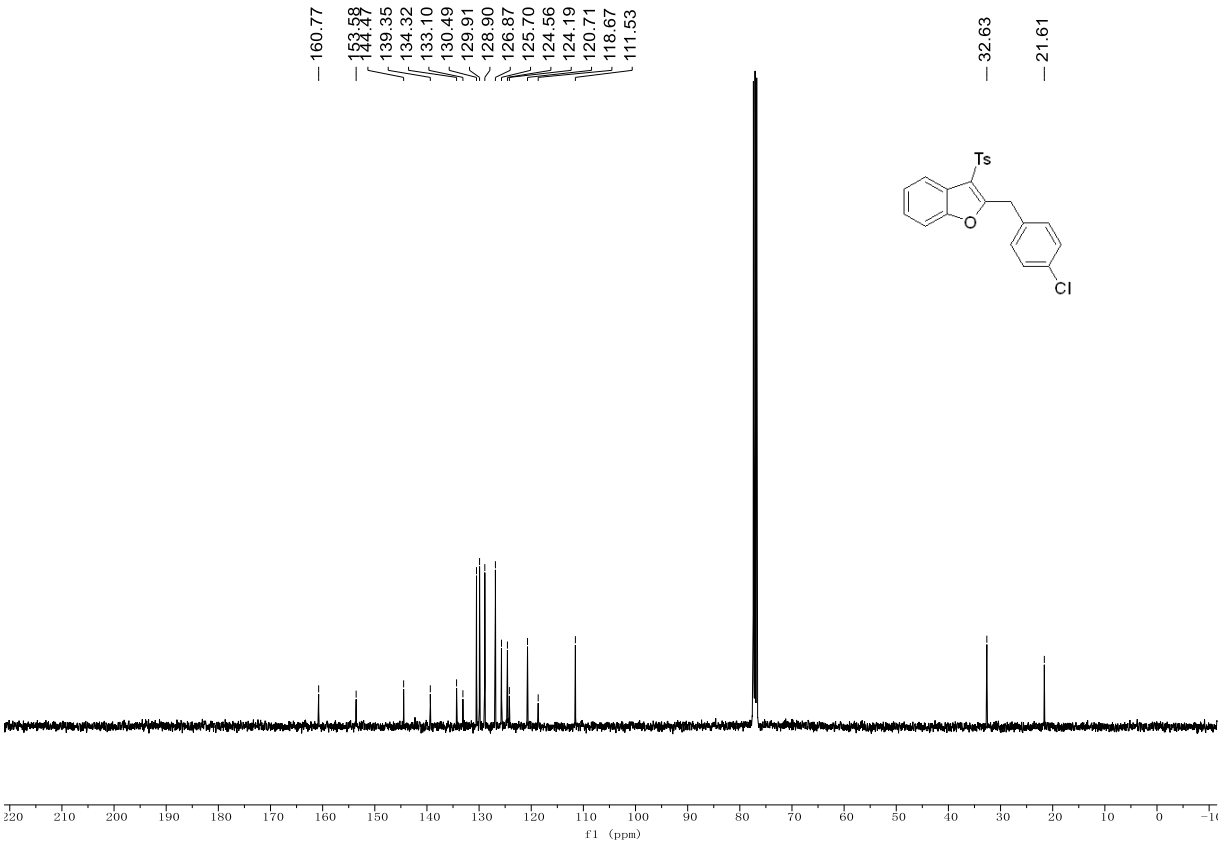
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **7b**



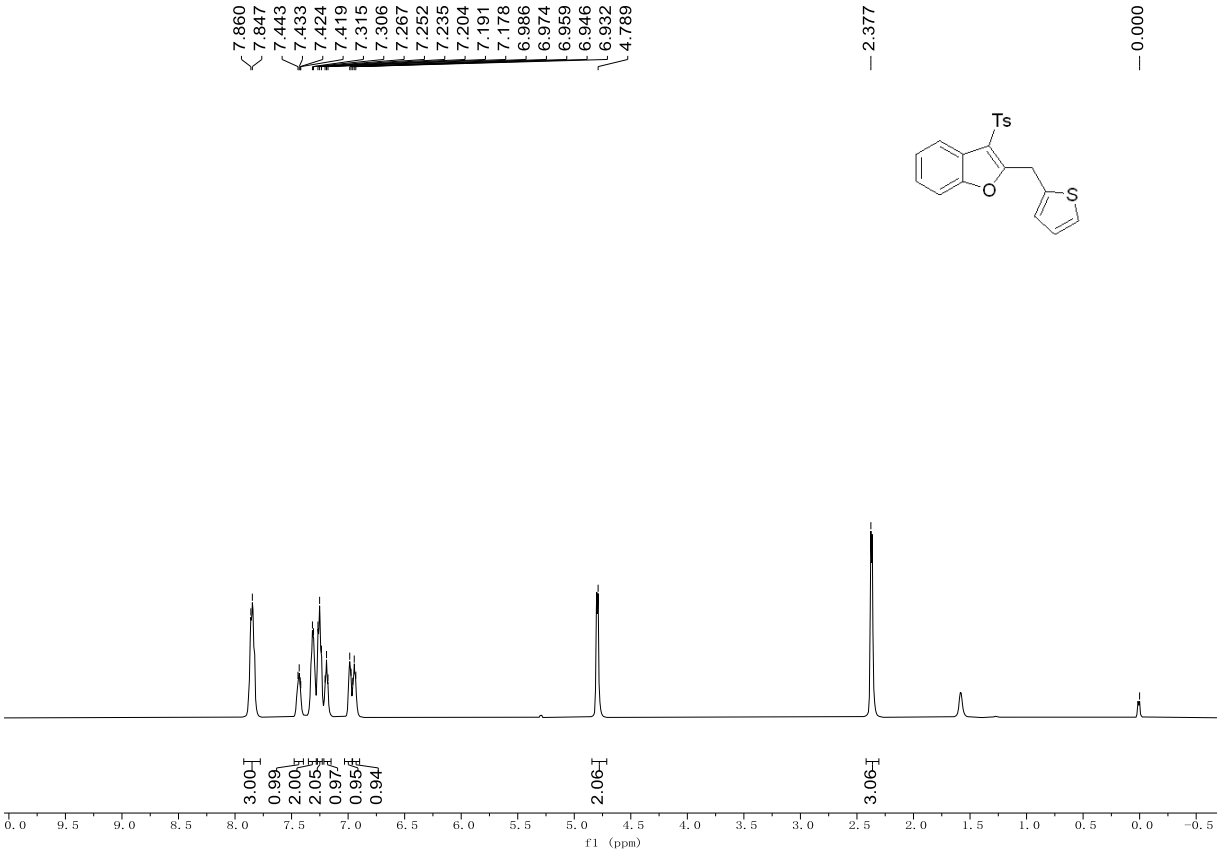
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **7c**



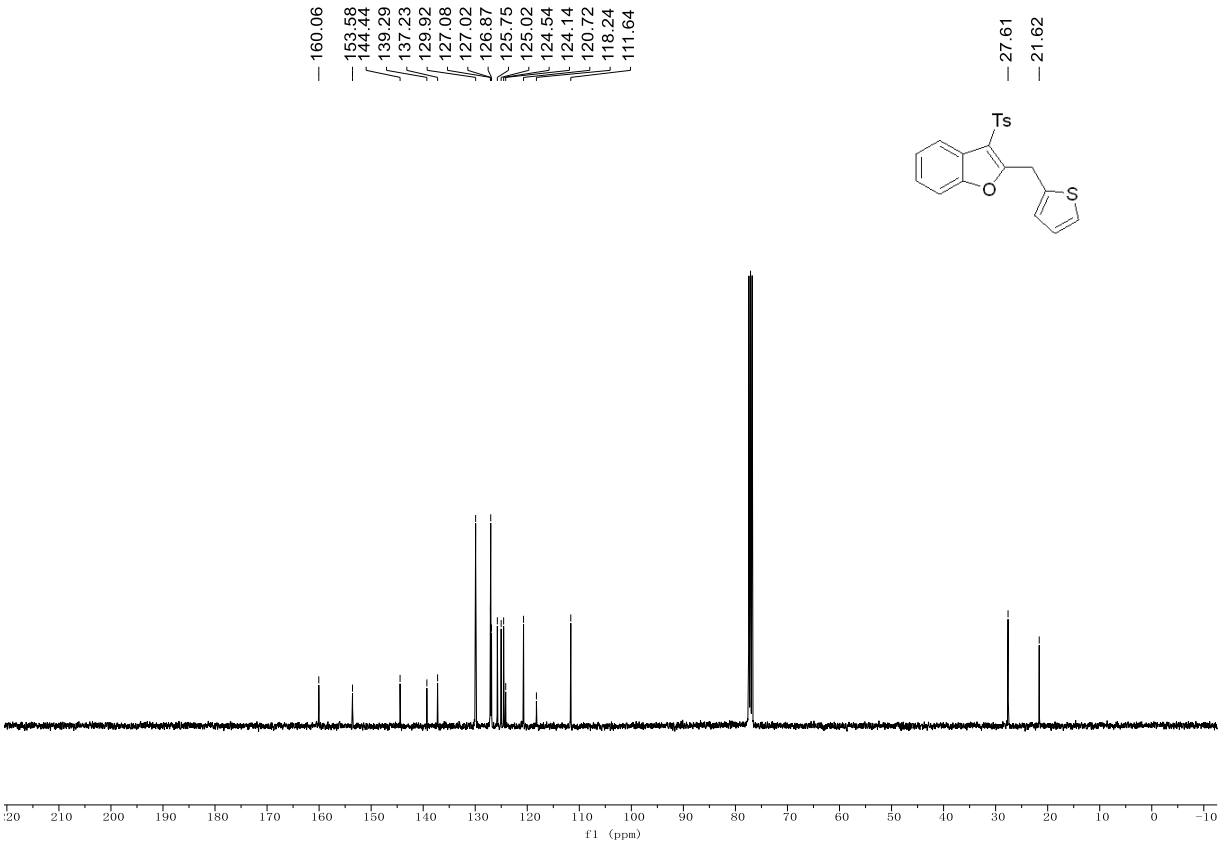
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **7c**



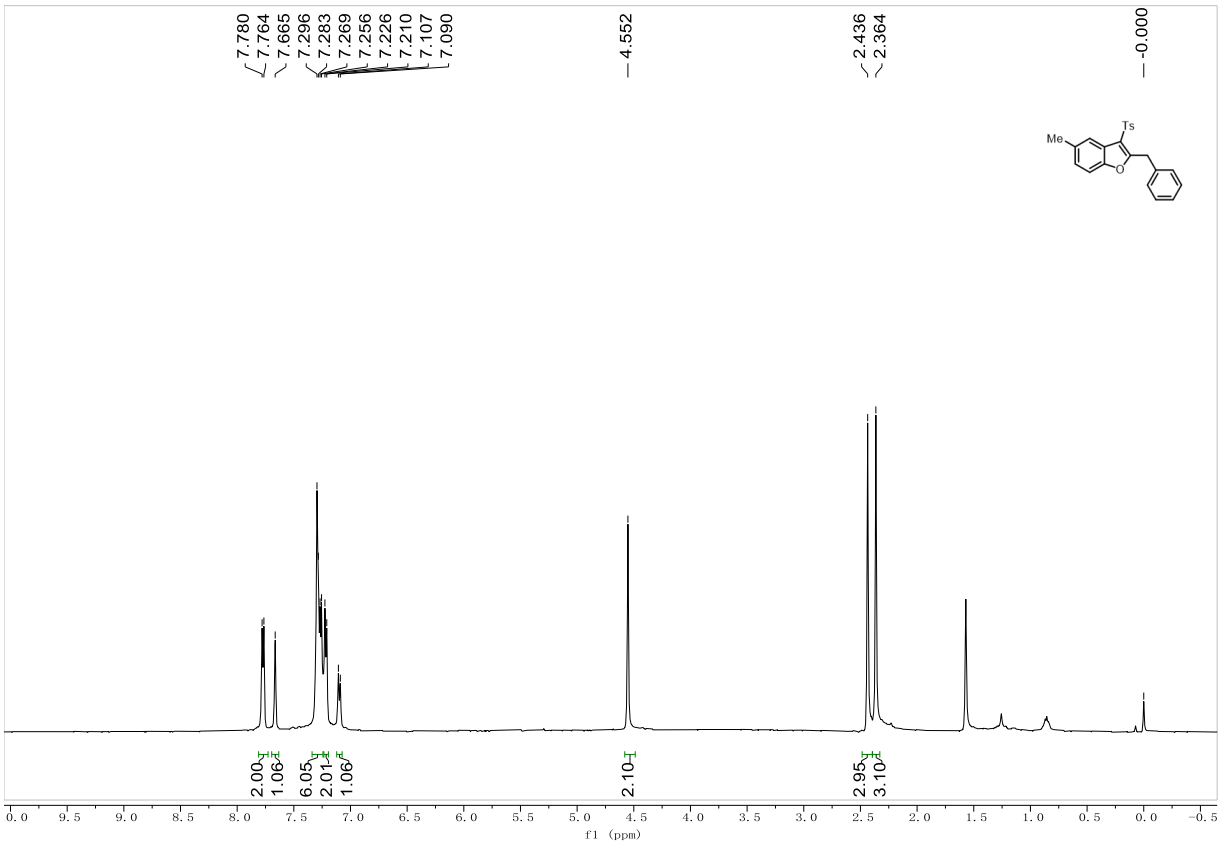
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **7d**



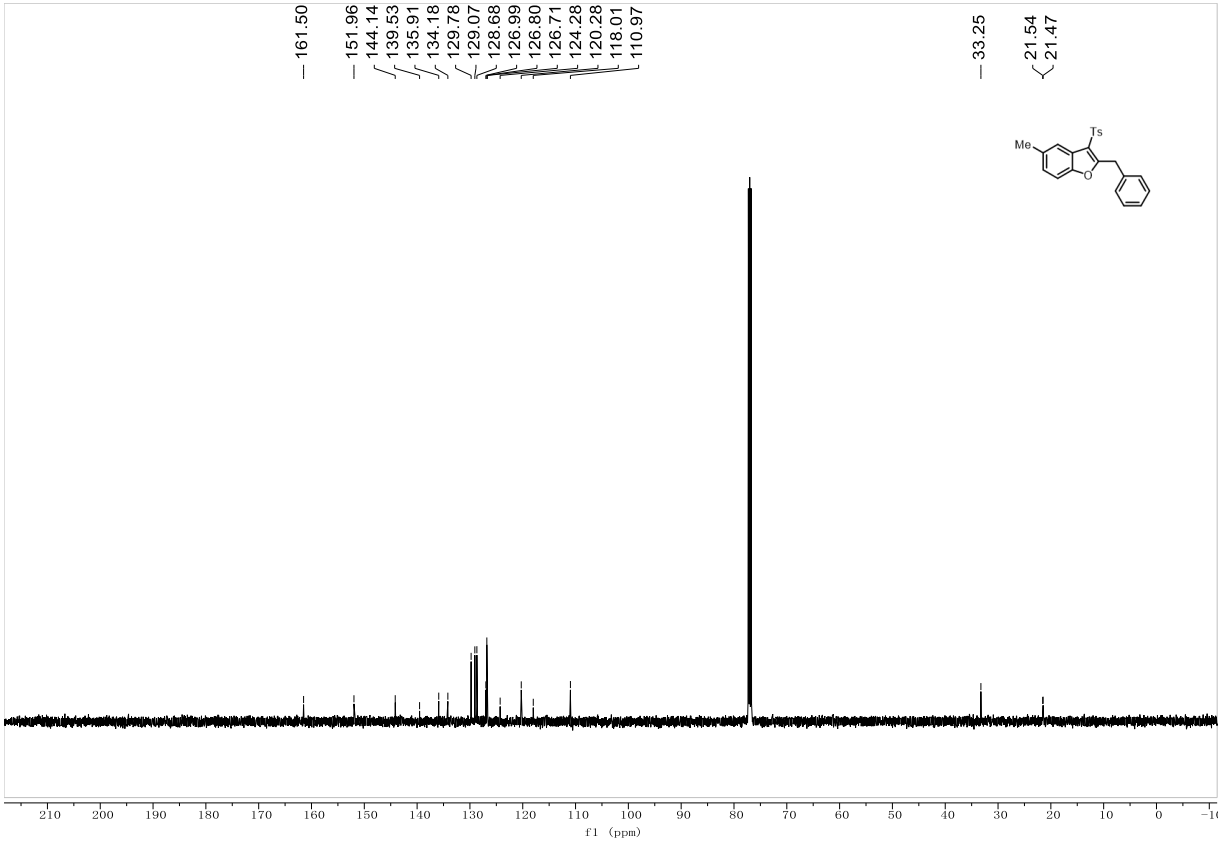
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **7d**



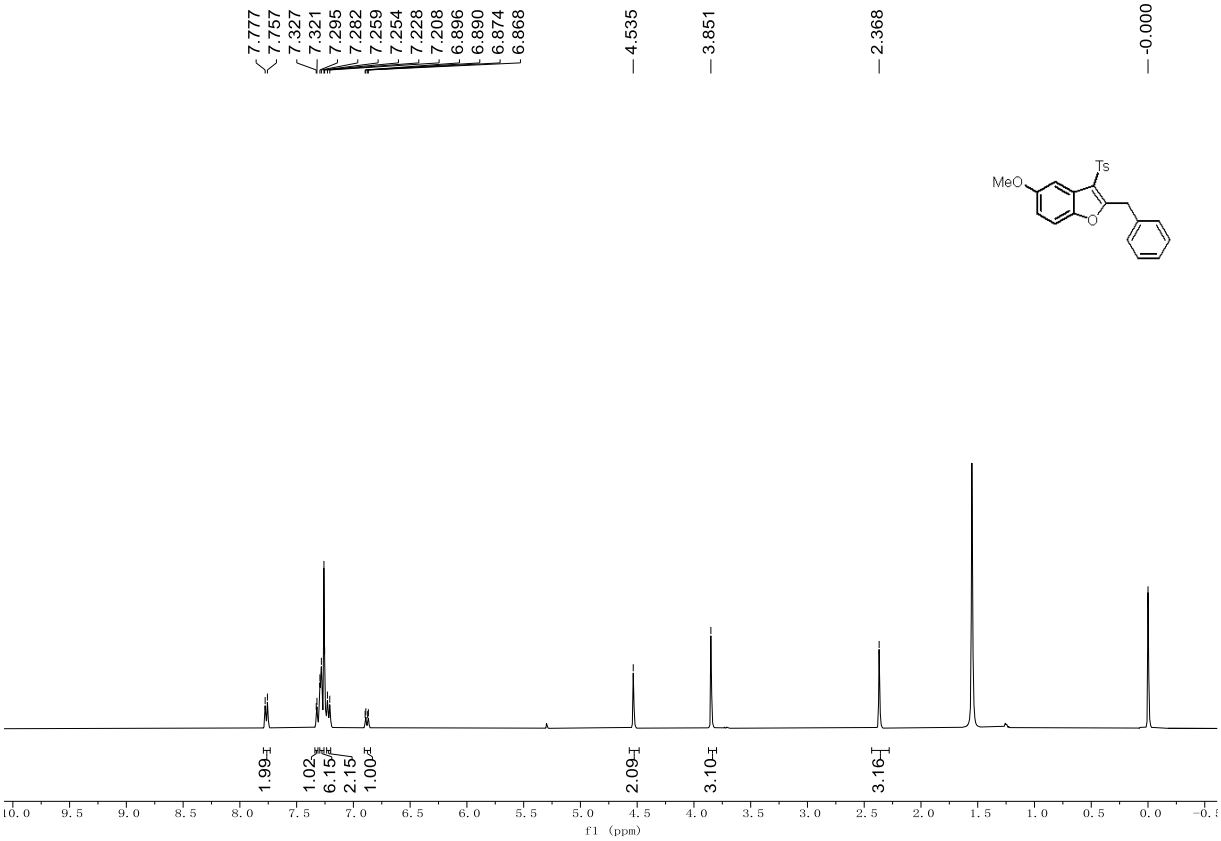
^{1}H NMR (500 MHz, $CDCl_3$) spectroscopy of **7e**



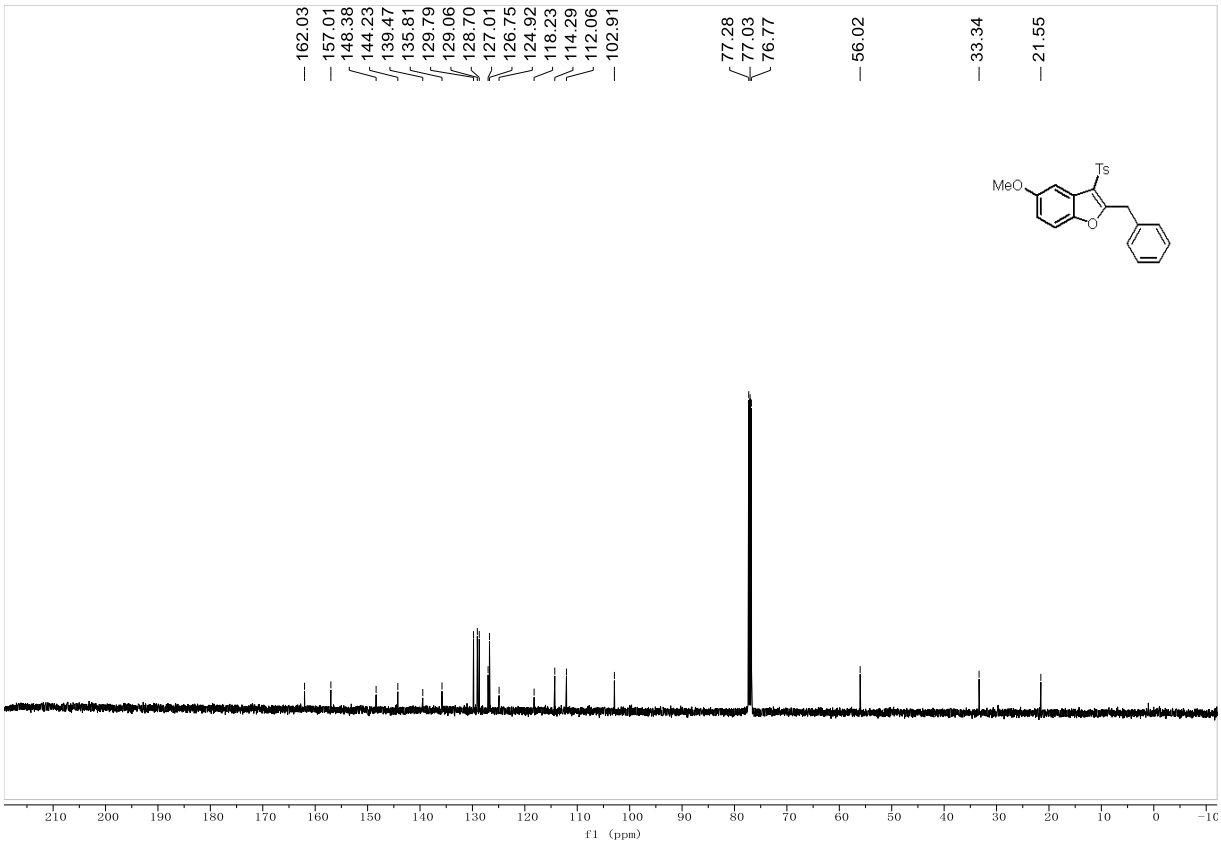
^{13}C NMR (126 MHz, $CDCl_3$) spectroscopy of **7e**



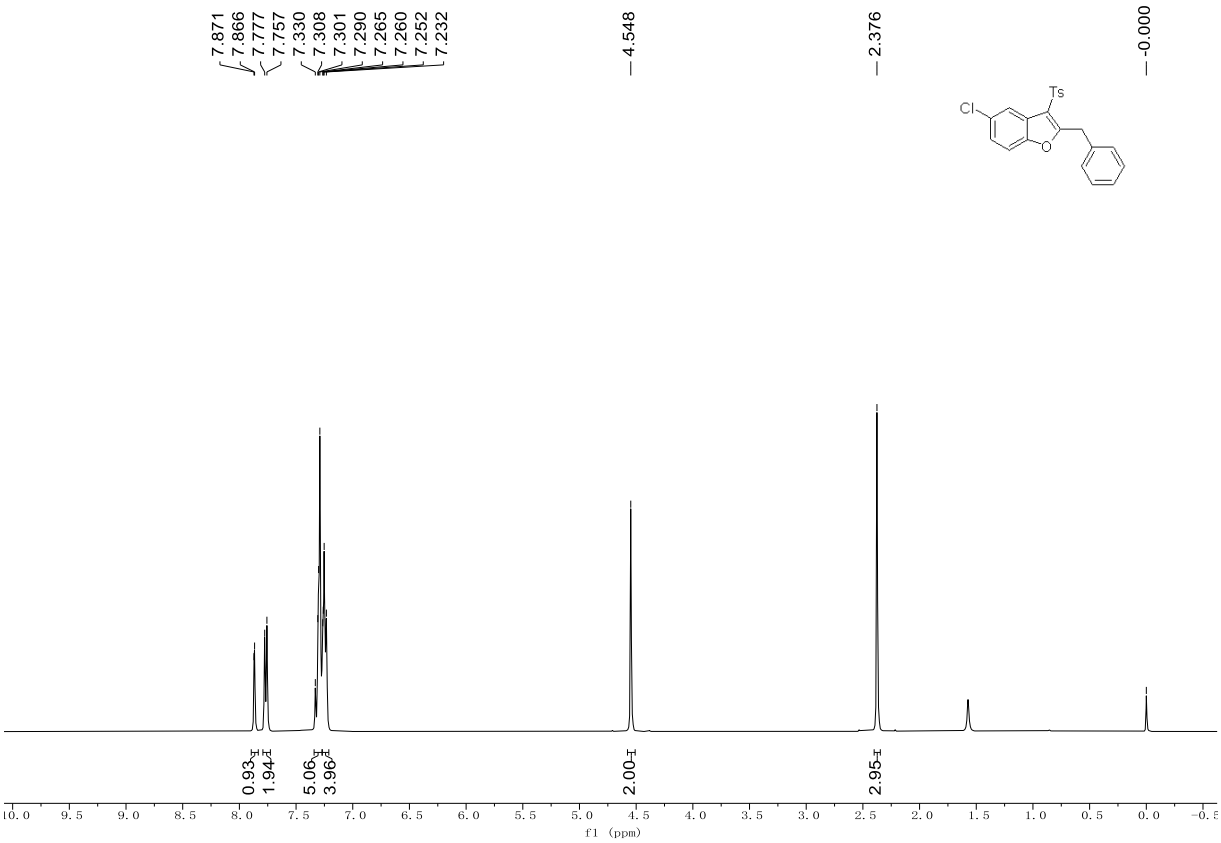
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **7f**



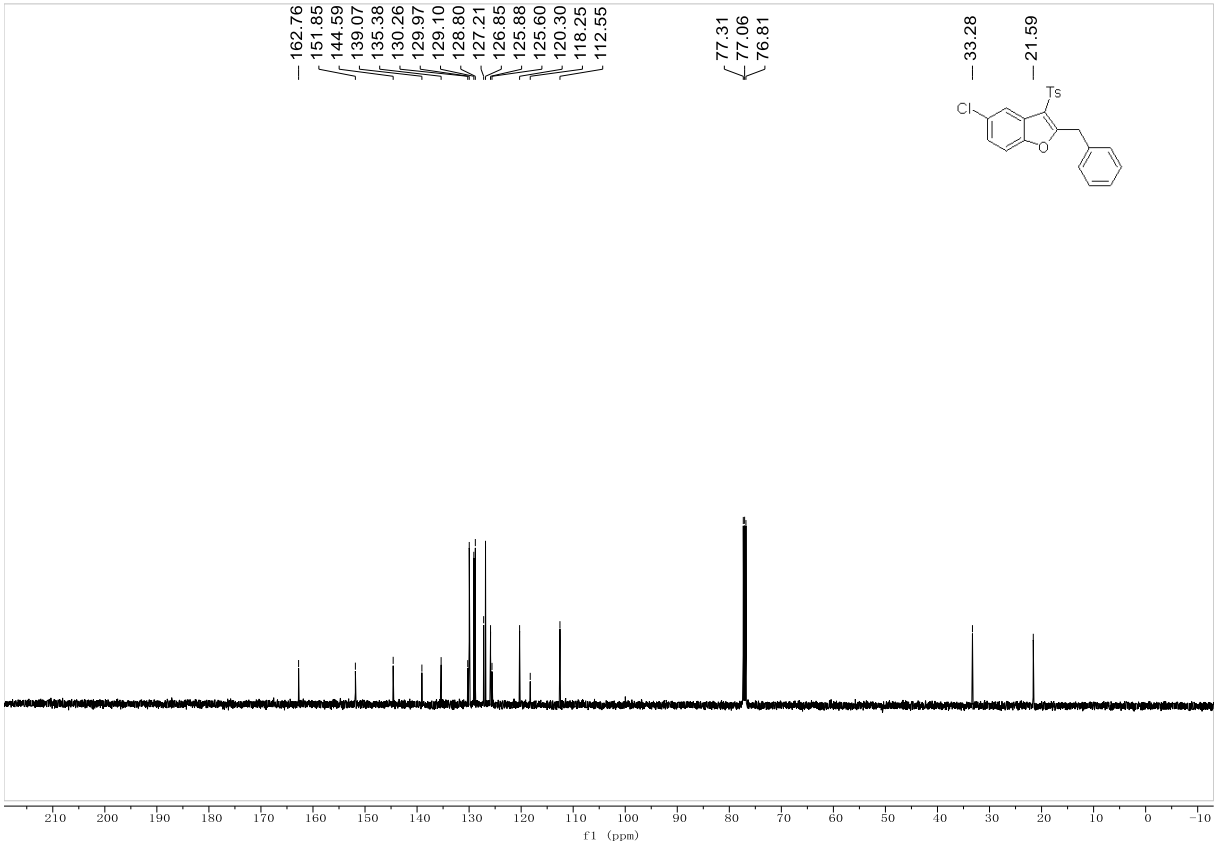
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **7f**



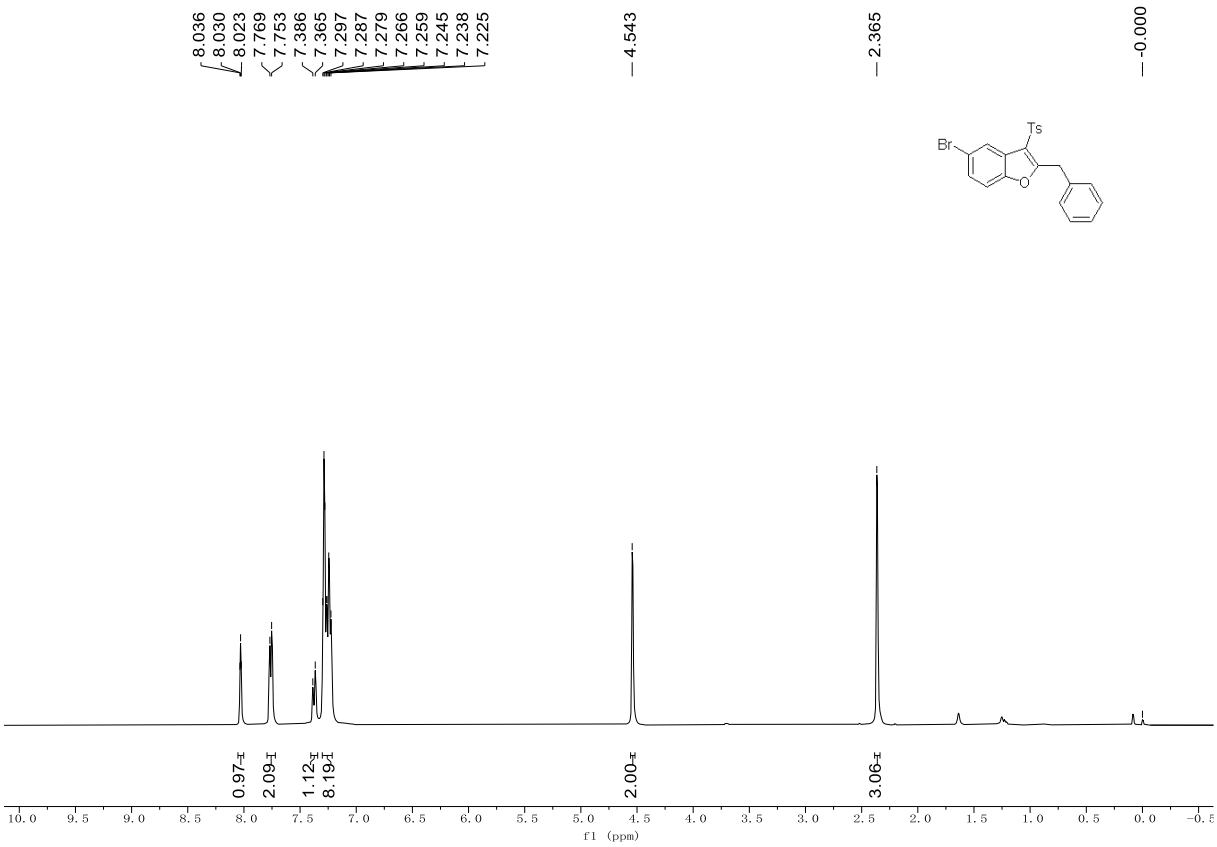
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **7g**



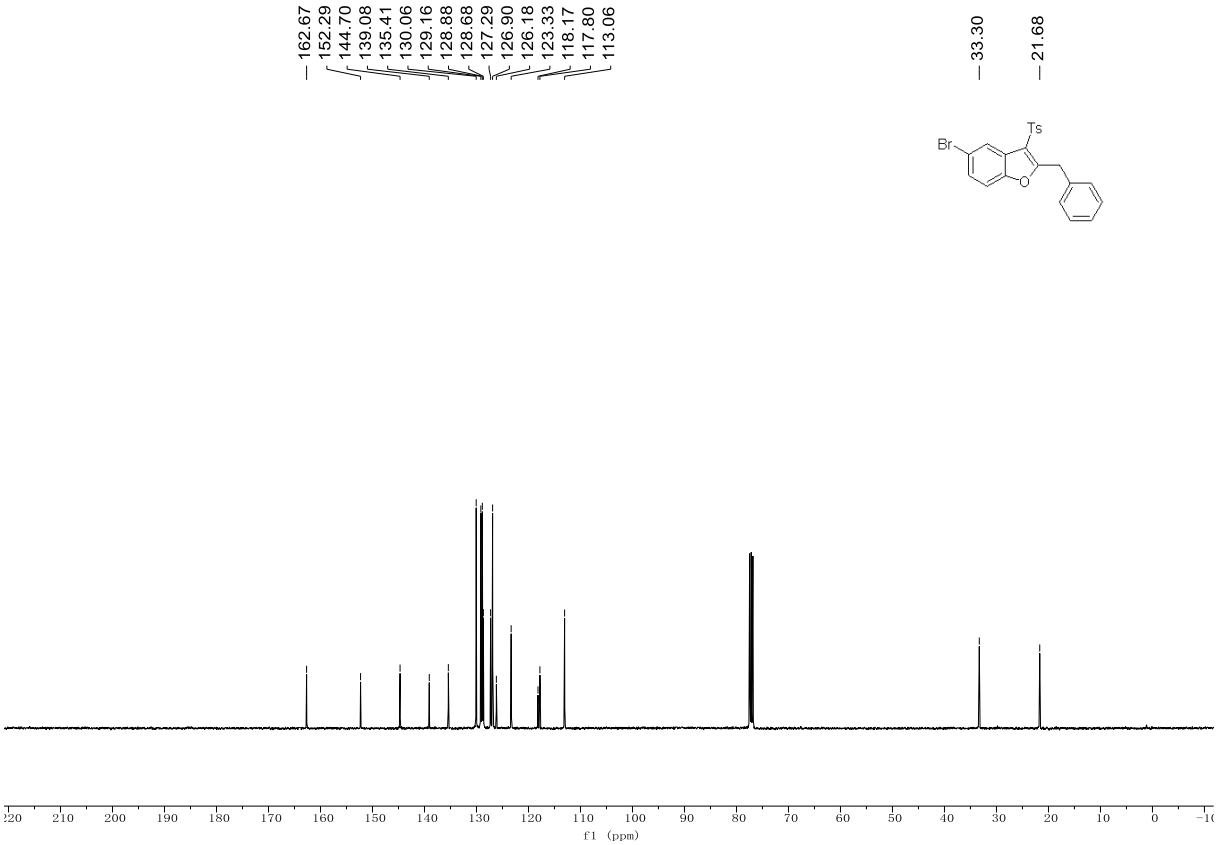
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **7g**



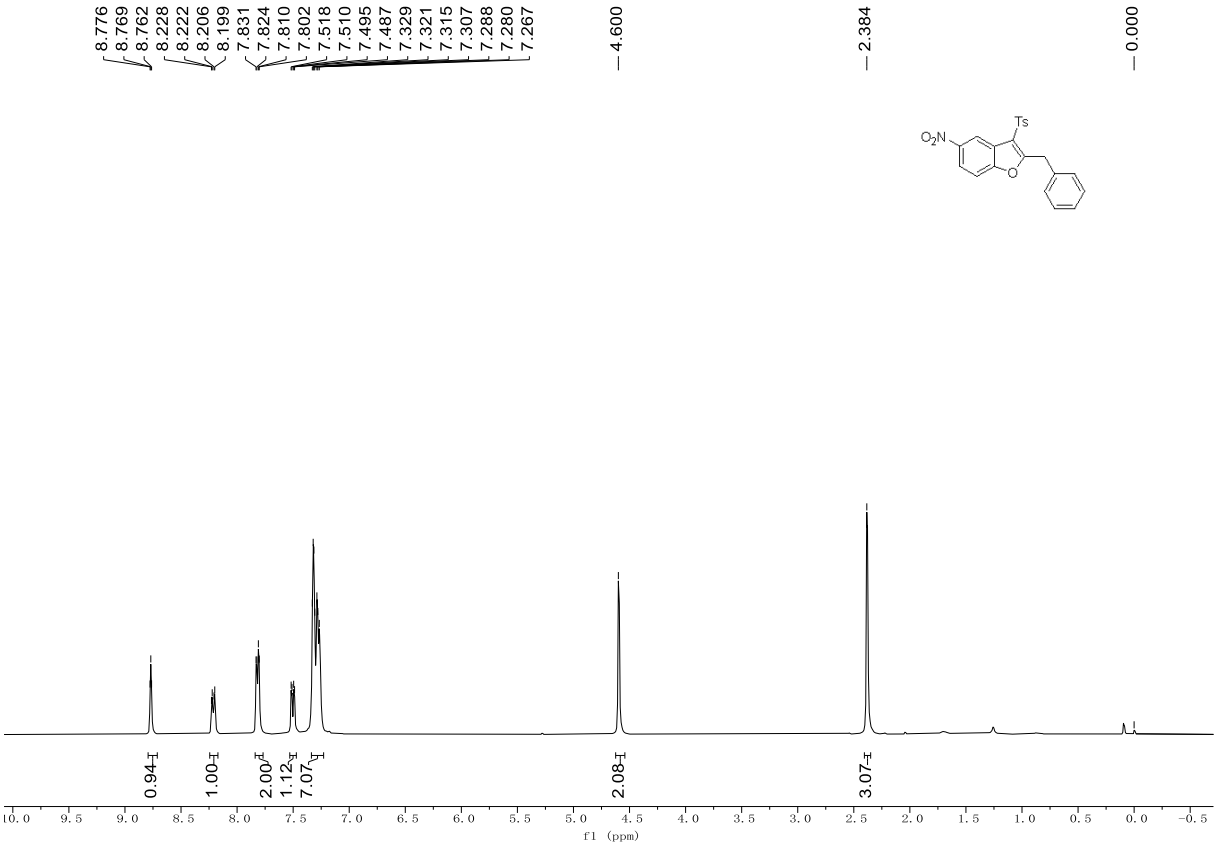
^{1}H NMR (500 MHz, $CDCl_3$) spectroscopy of **7h**



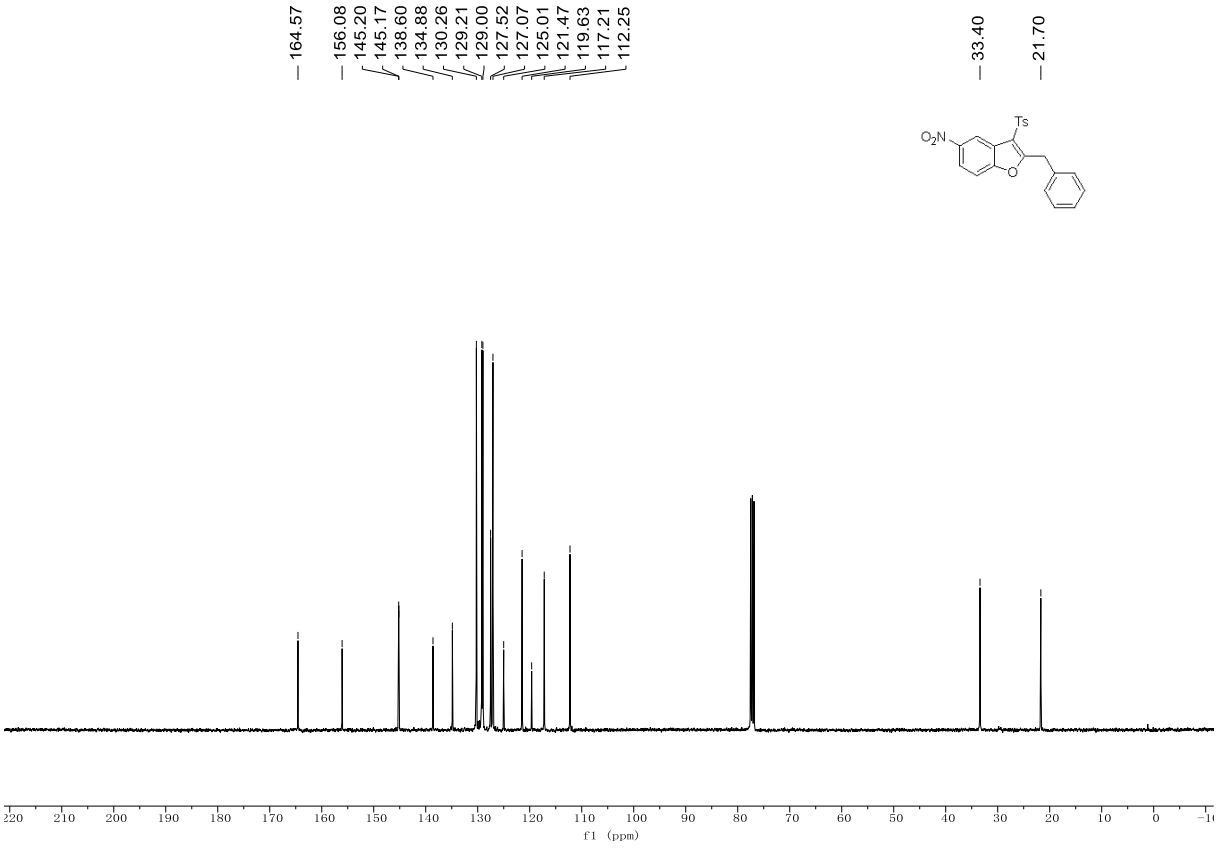
^{13}C NMR (126 MHz, $CDCl_3$) spectroscopy of **7h**



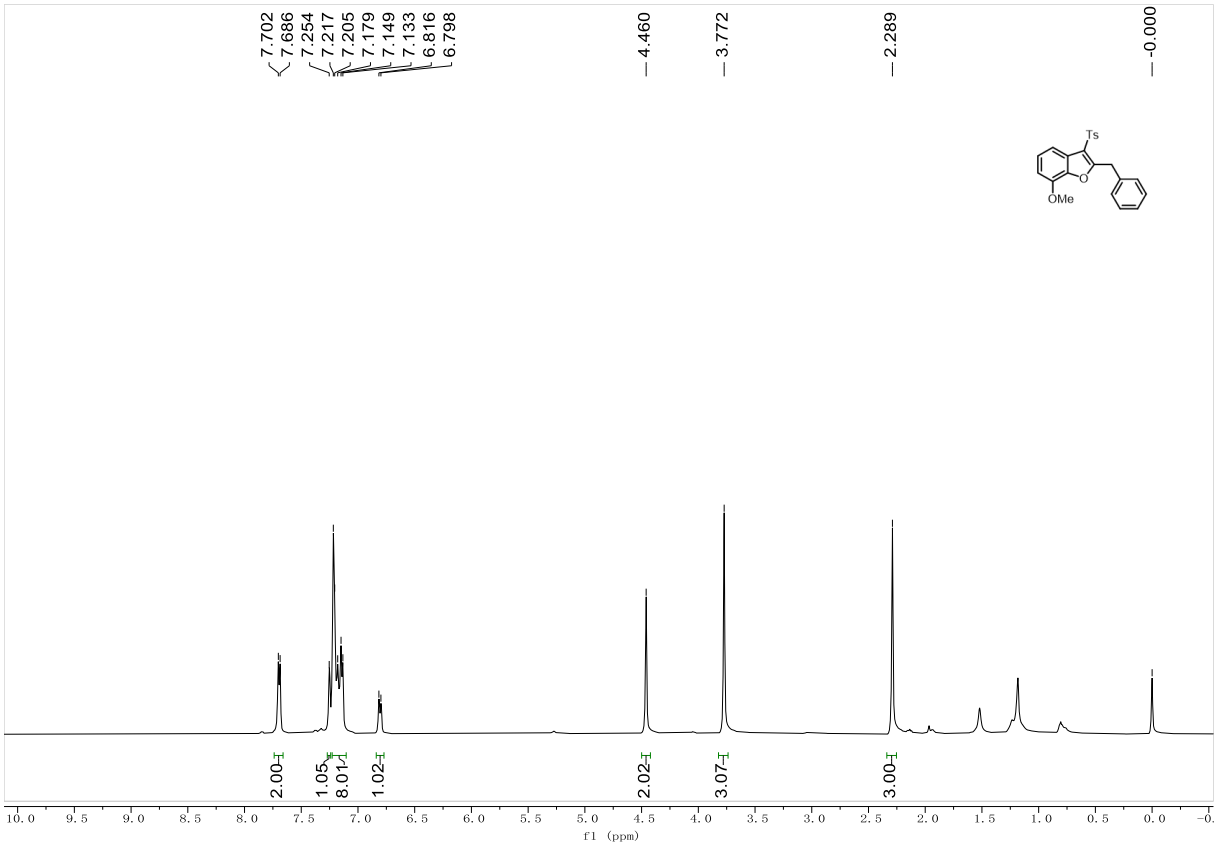
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **7i**



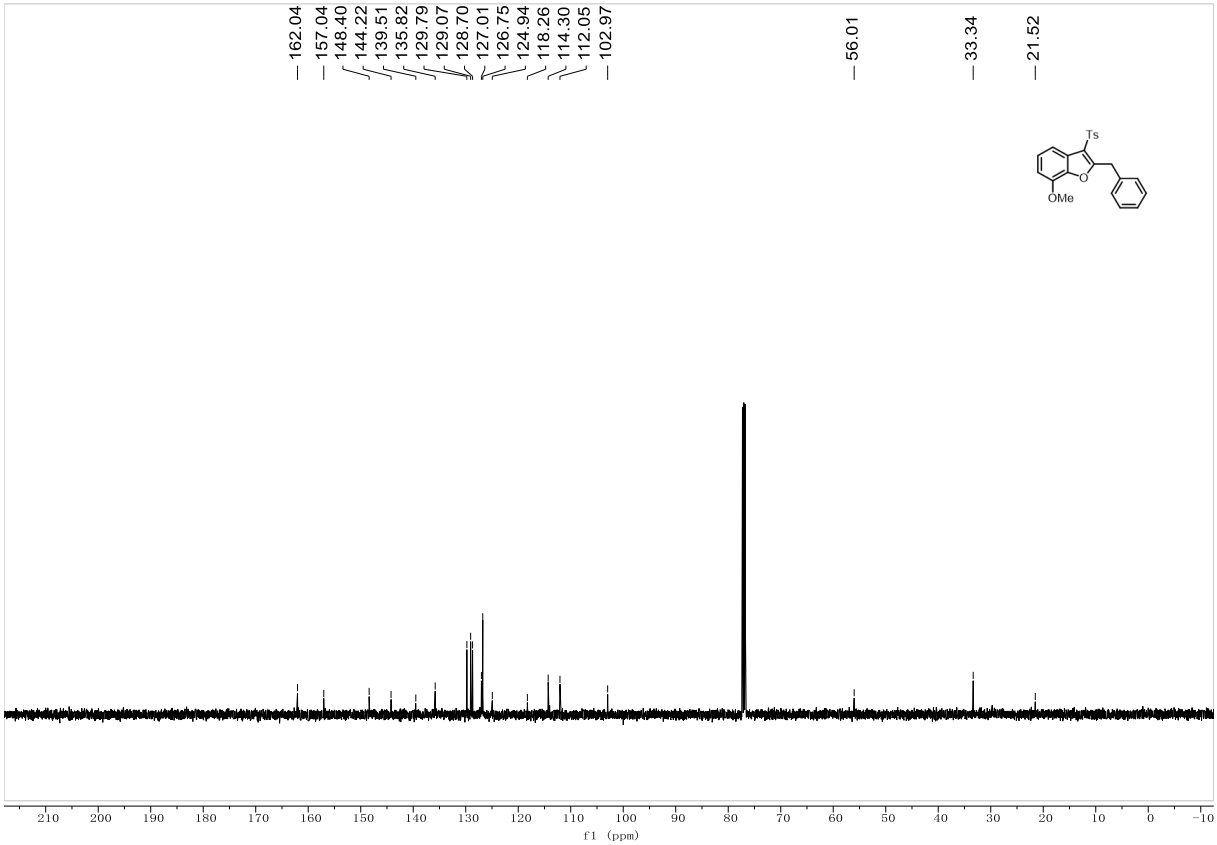
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **7i**



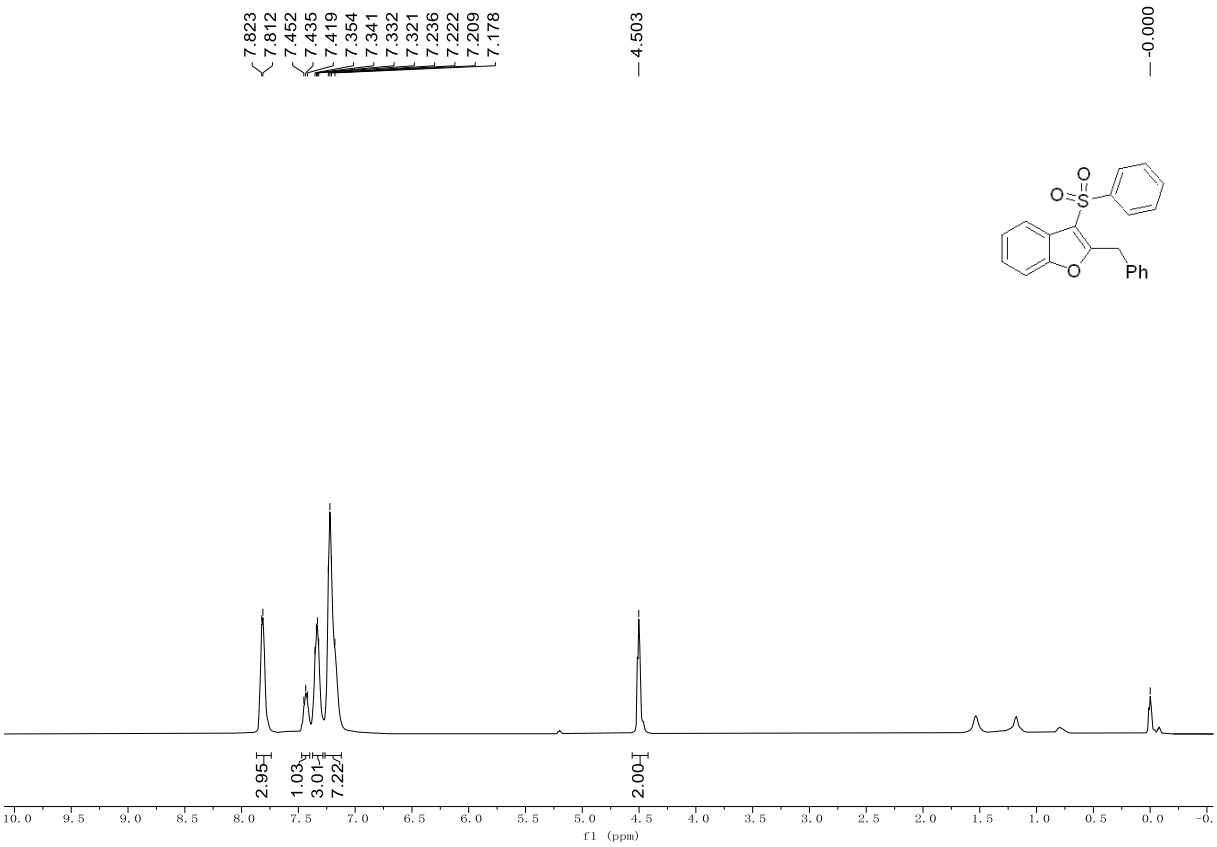
^{1}H NMR (500 MHz, $CDCl_3$) spectroscopy of **7j**



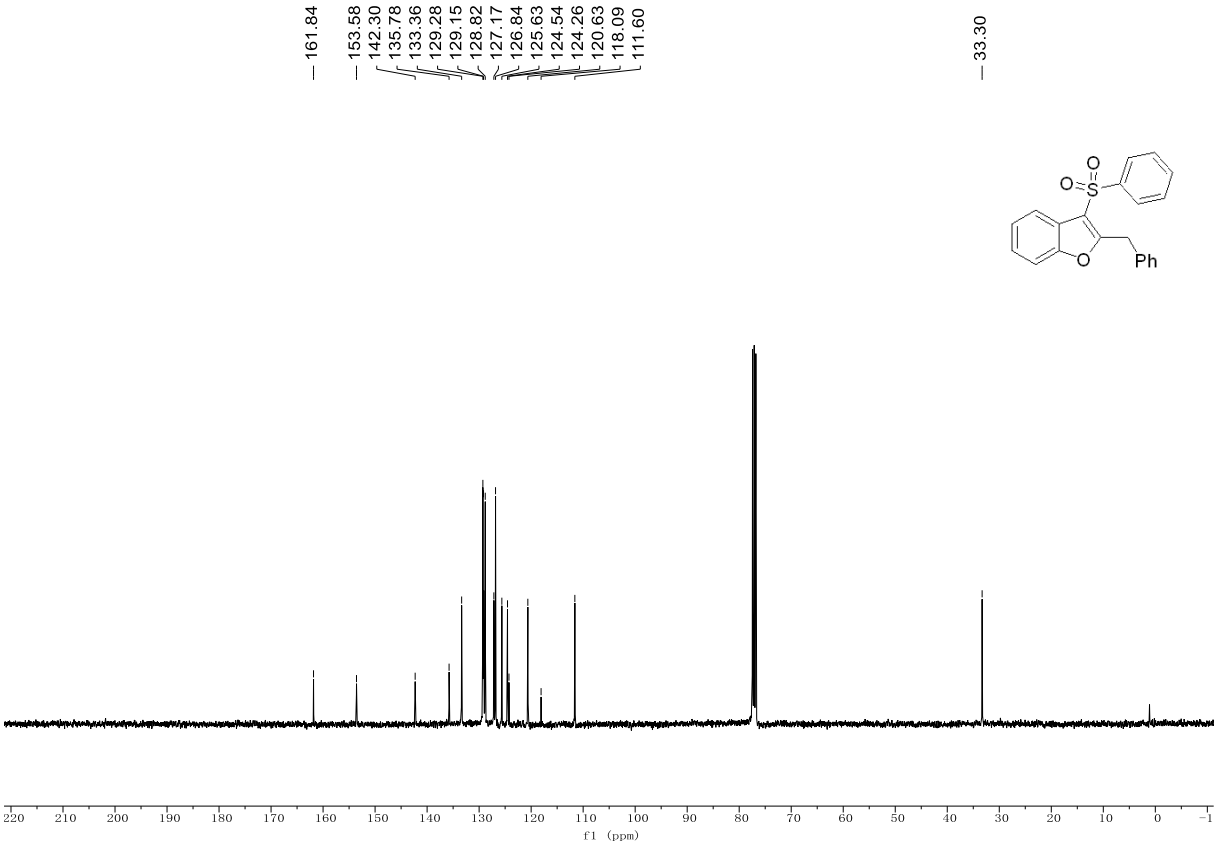
^{13}C NMR (126 MHz, $CDCl_3$) spectroscopy of **7j**



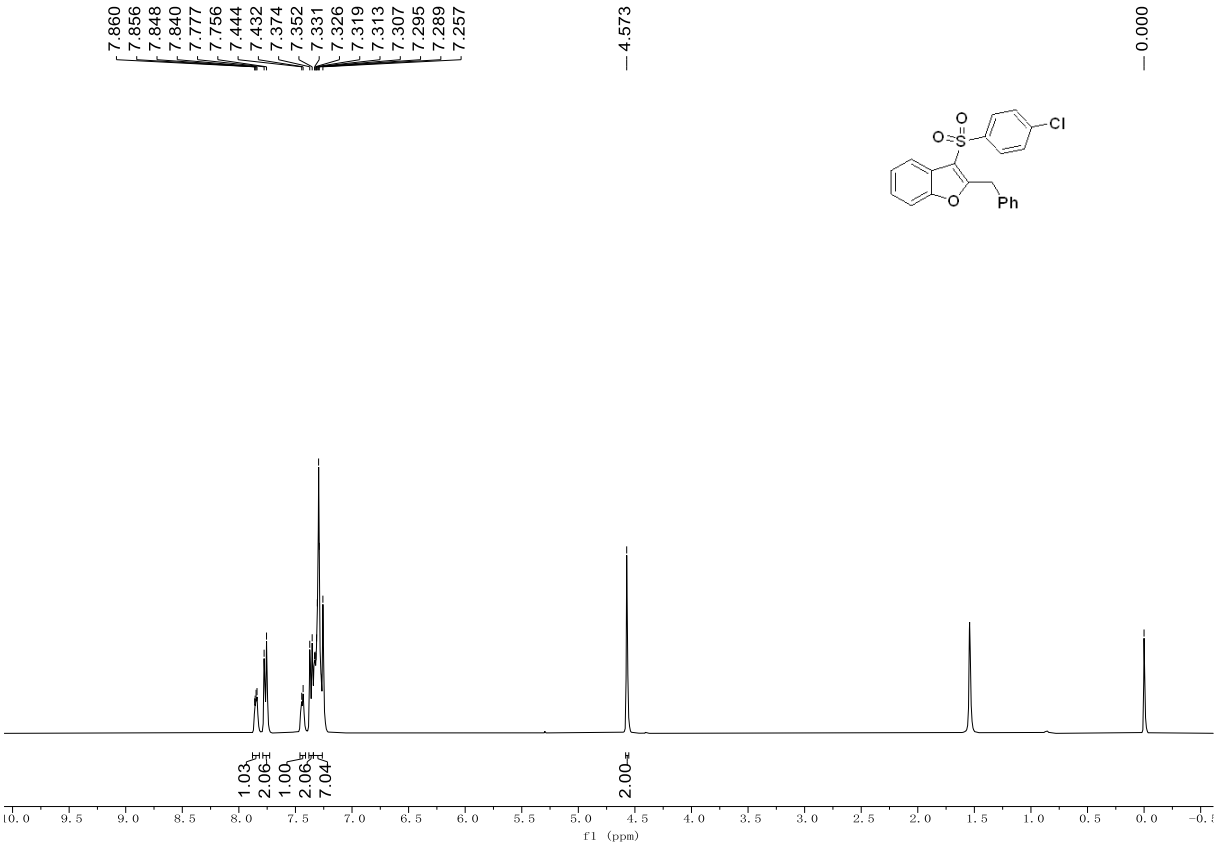
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **7k**



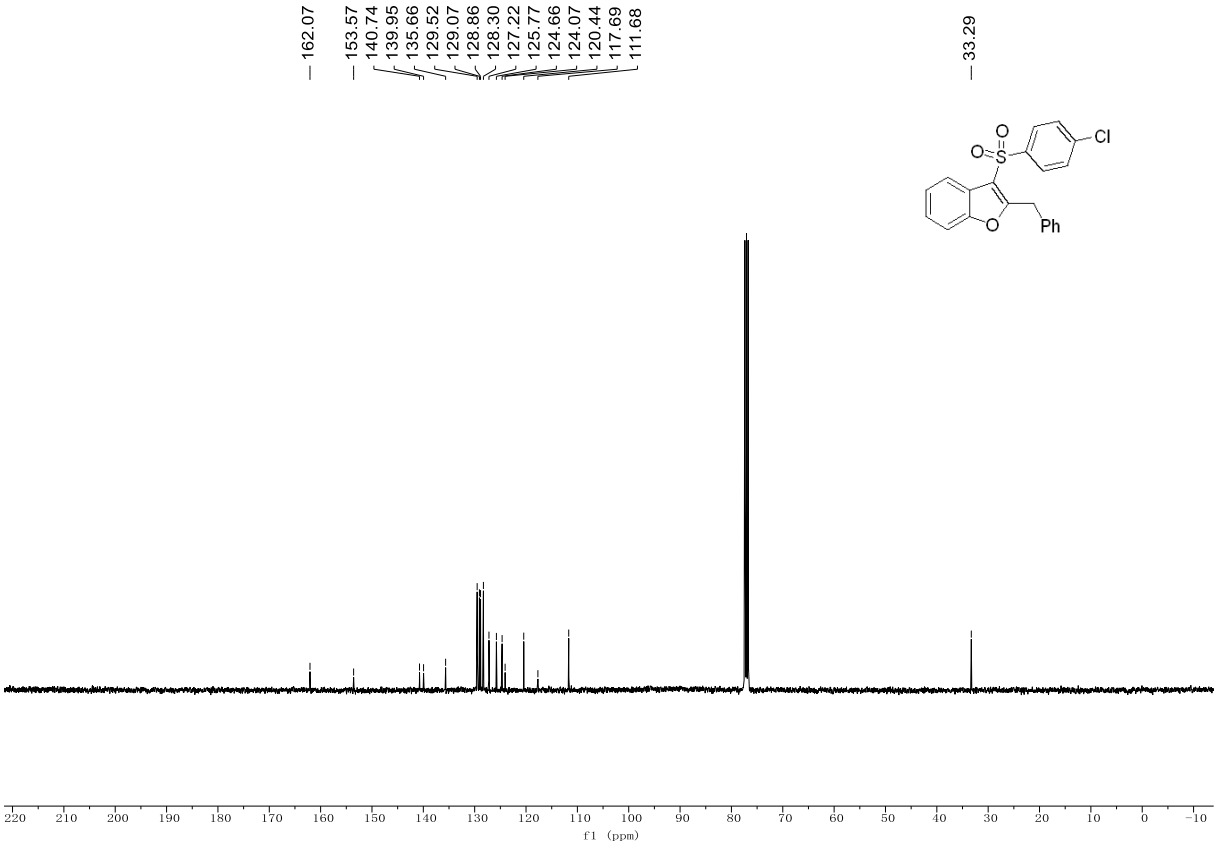
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **7k**



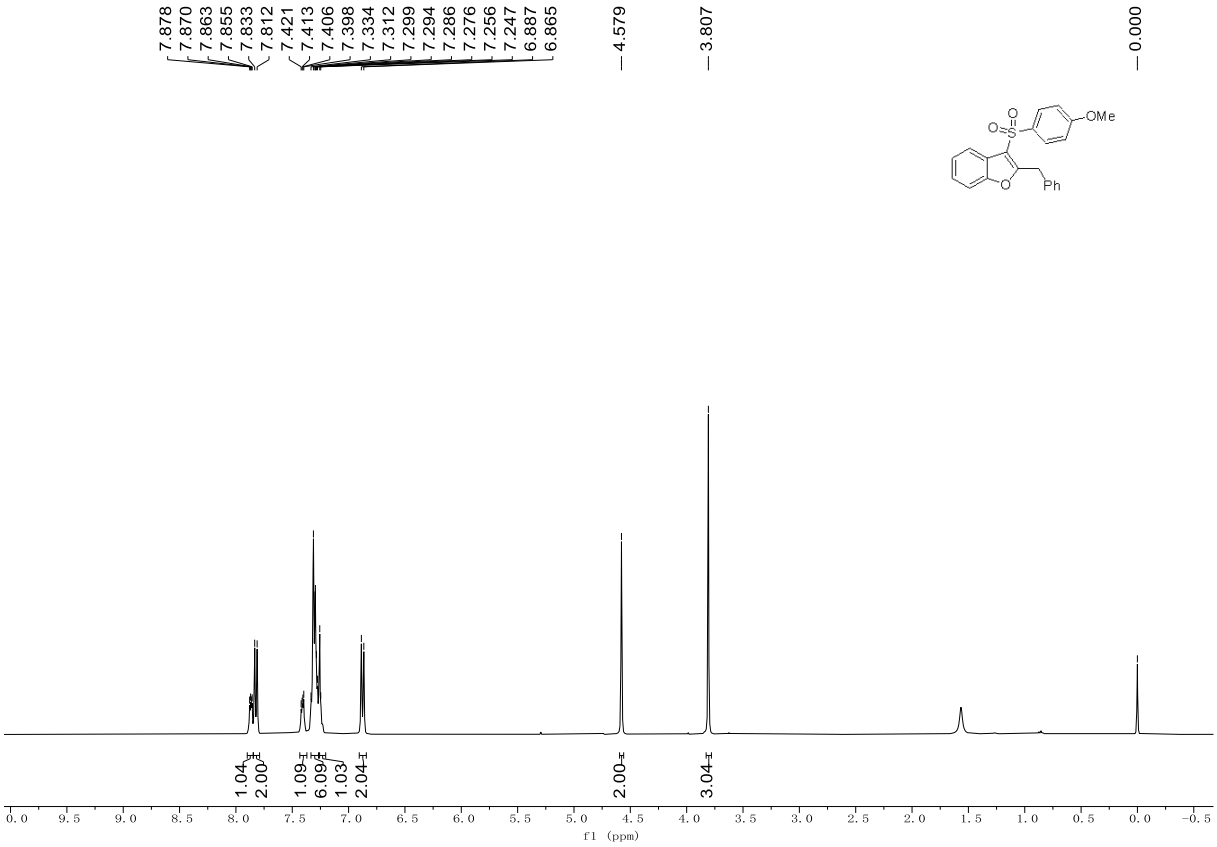
^{1}H NMR (500 MHz, $CDCl_3$) spectroscopy of **7l**



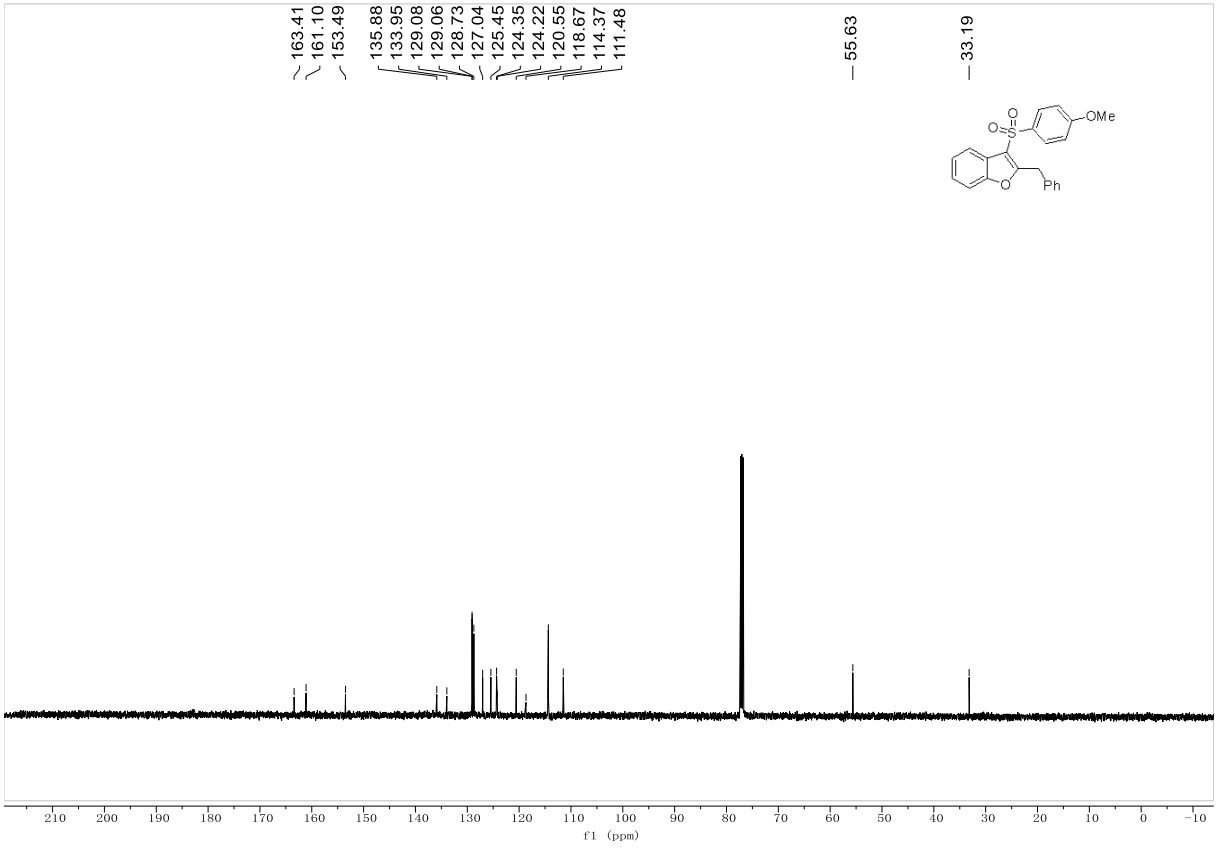
^{13}C NMR (126 MHz, $CDCl_3$) spectroscopy of **7l**



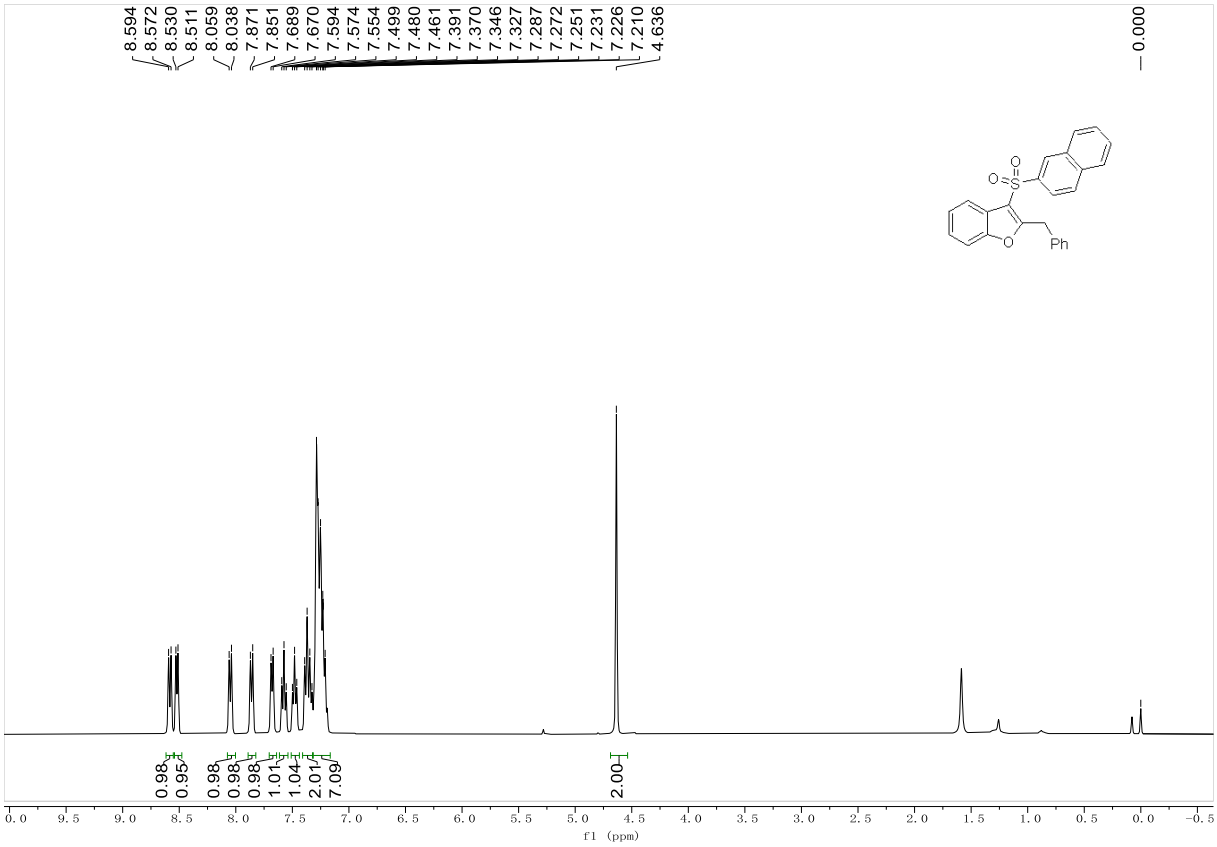
^{1}H NMR (500 MHz, $CDCl_3$) spectroscopy of **7m**



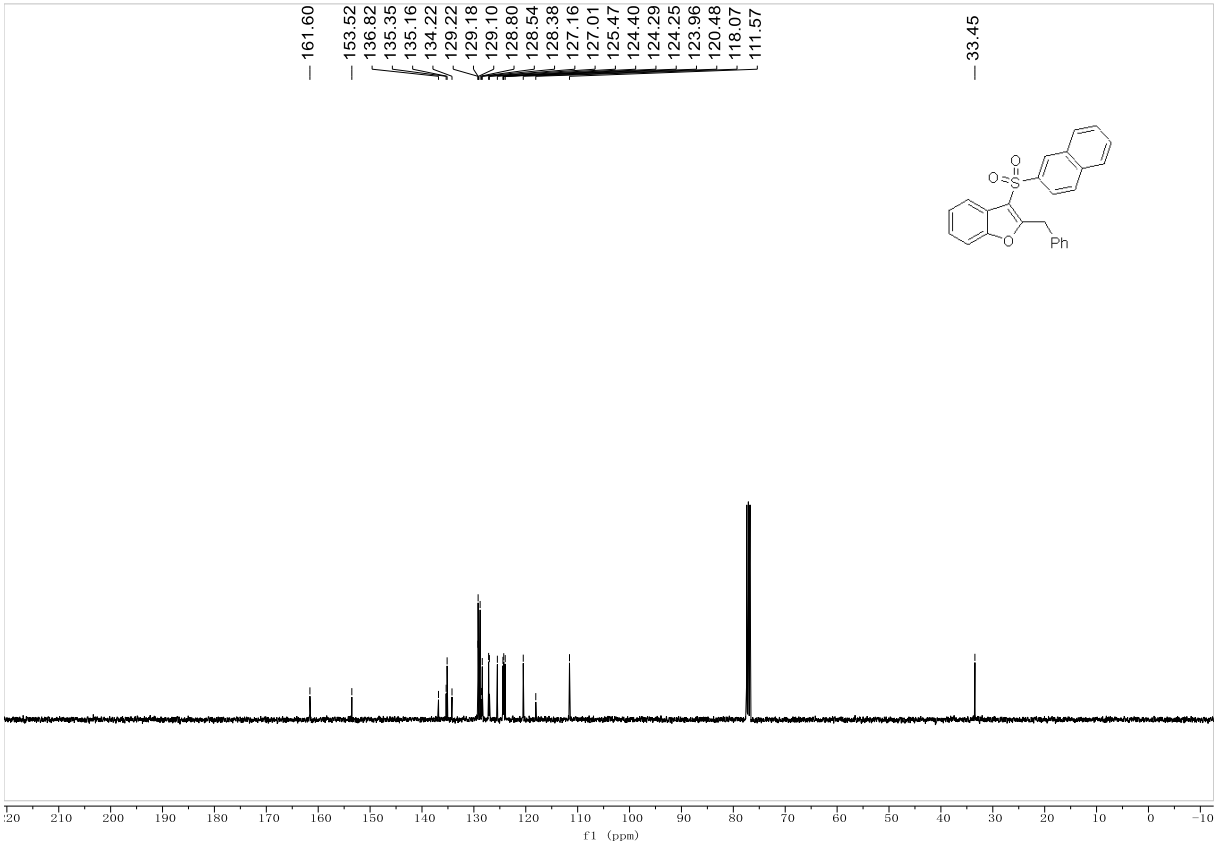
^{13}C NMR (126 MHz, $CDCl_3$) spectroscopy of **7m**



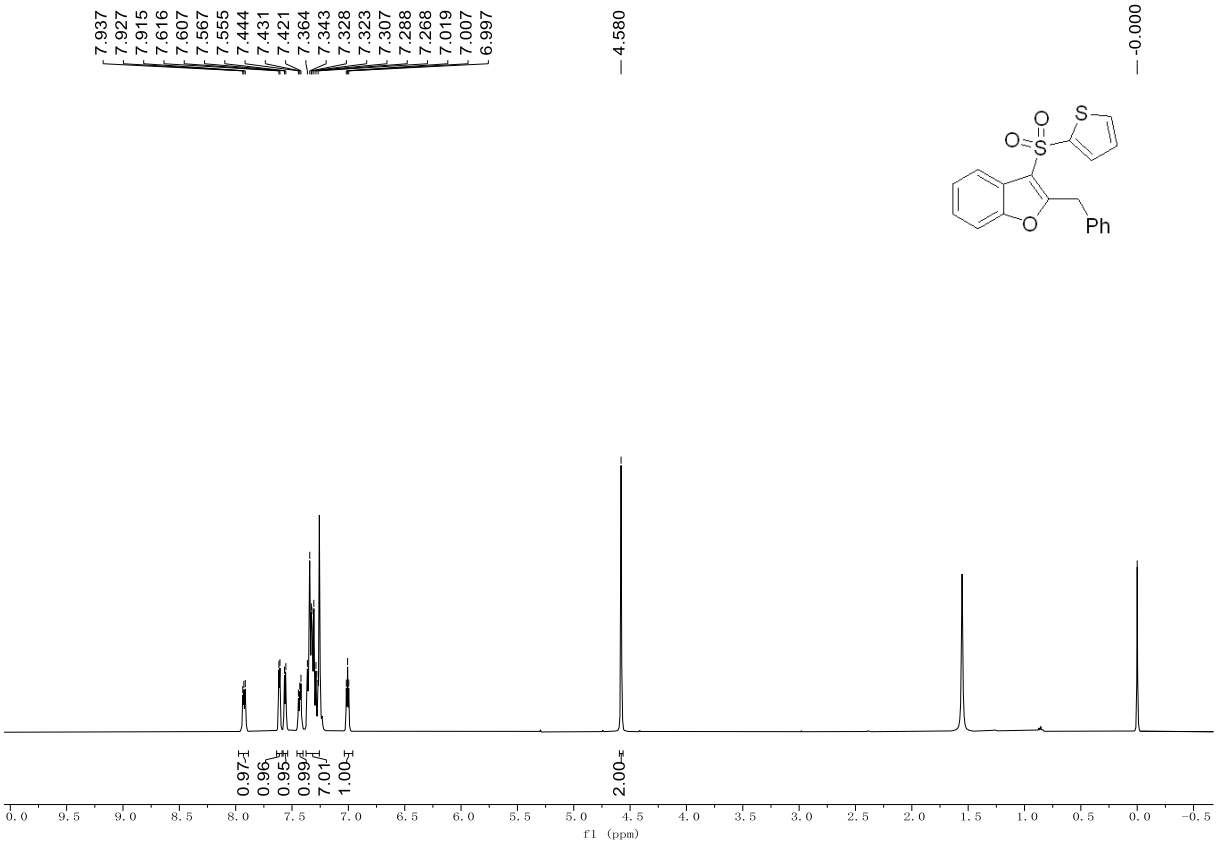
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **7n**



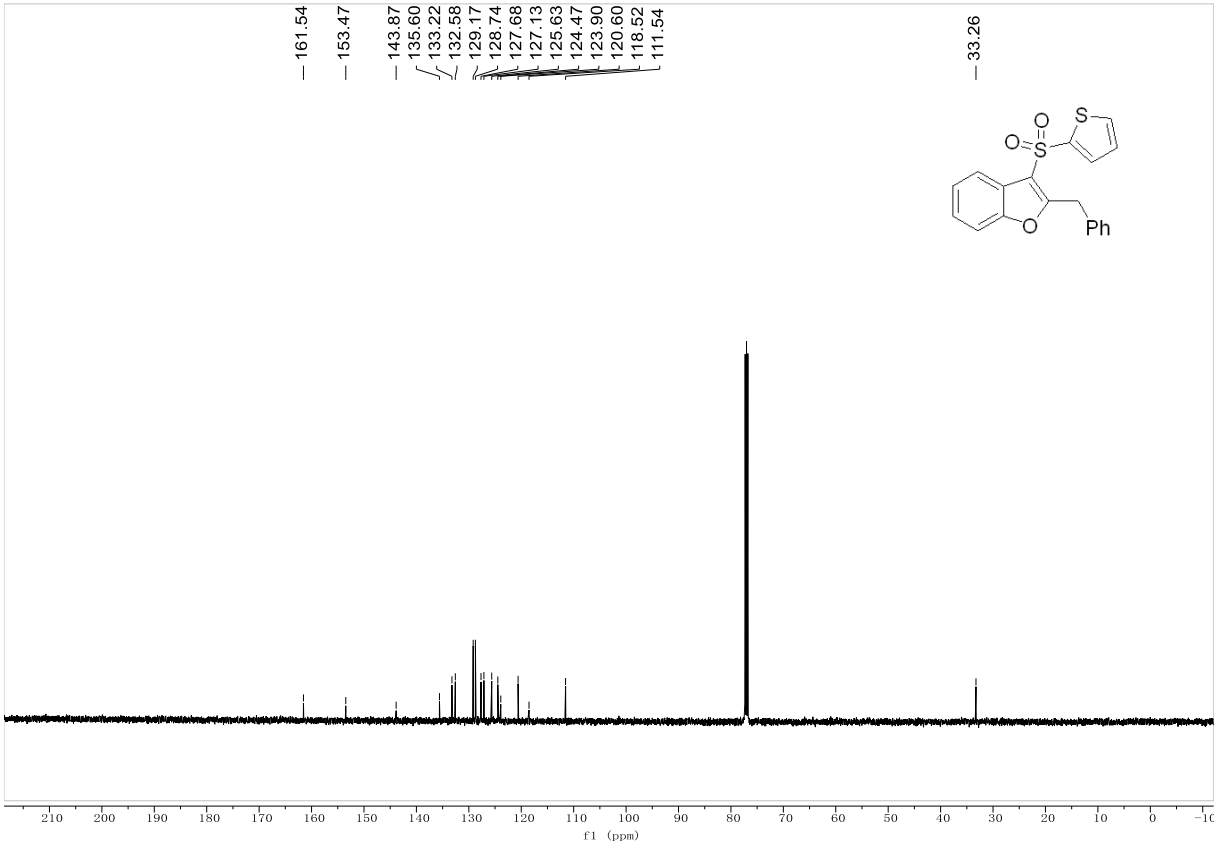
^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **7n**



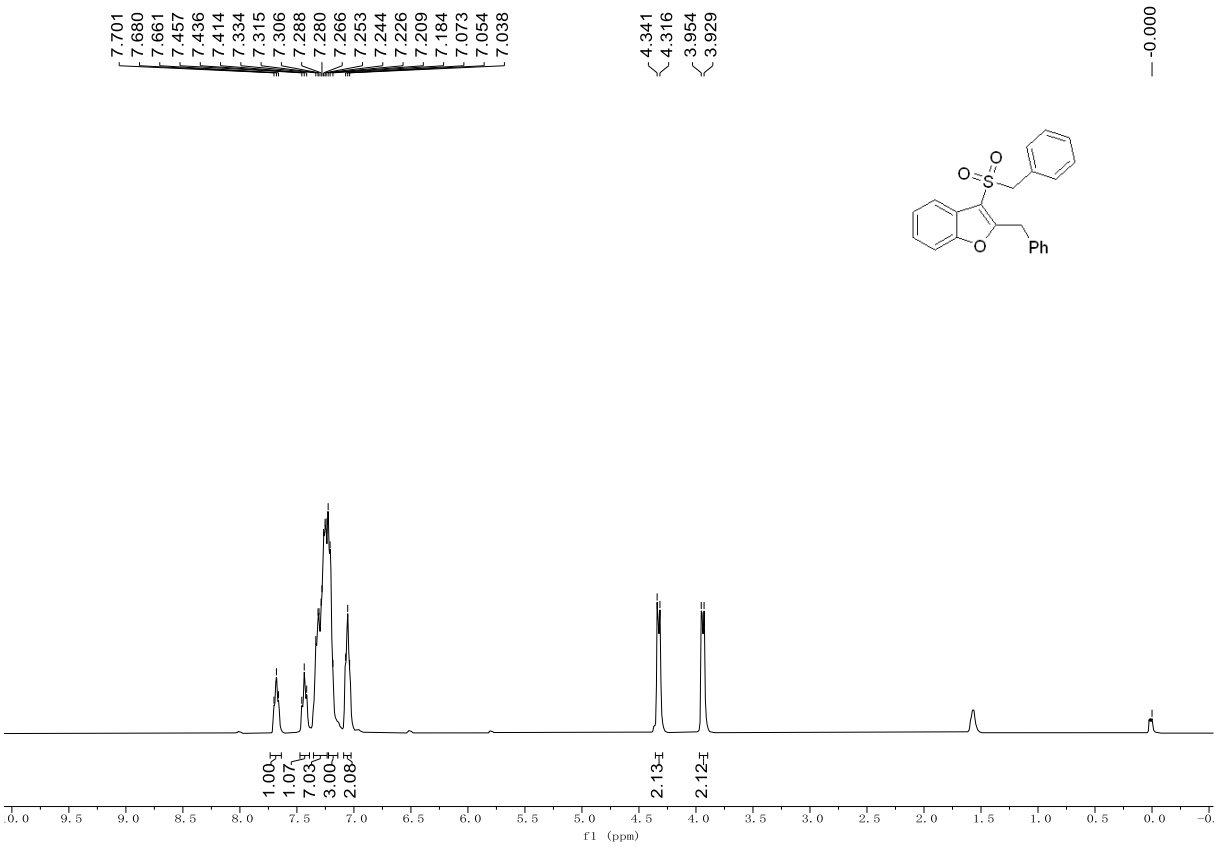
^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **7o**



^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **7o**



^{1}H NMR (400 MHz, $CDCl_3$) spectroscopy of **7p**



^{13}C NMR (101 MHz, $CDCl_3$) spectroscopy of **7p**