Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Rh(III)-catalysed C–H/C–H cross-coupling of *S*-Aryl sulfoximines with thiophenes: facile access to [1]benzothieno[3,2-*b*][1]benzothiophene (BTBT) and benzothiazines

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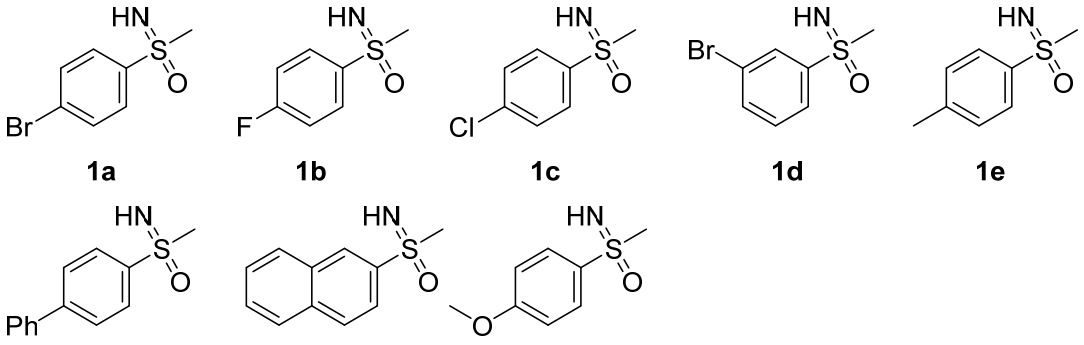
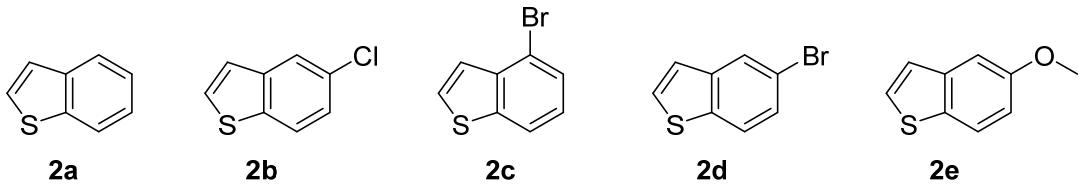
I. General remarks

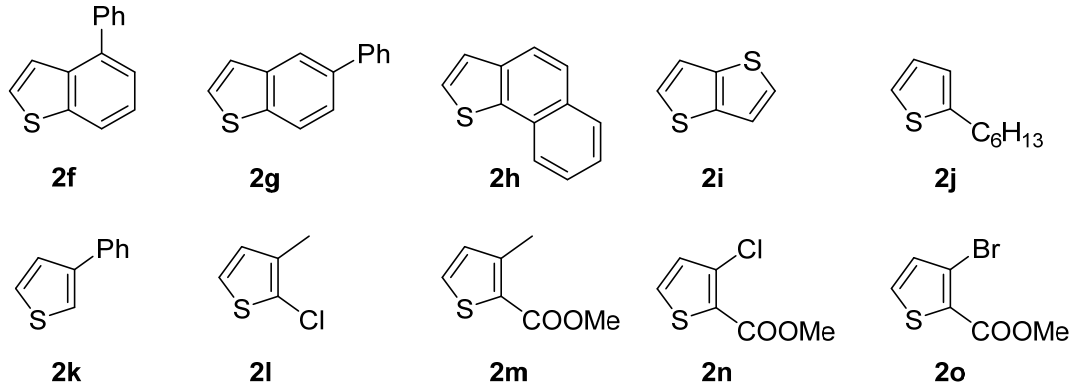
NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ as the internal reference ($CDCl_3$: δ = 7.26). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini single-crystal diffractometer. Absorption spectra were obtained on a HITACHI U-2910 spectrometer. Fluorescence spectra and absolute quantum yields were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system. The excited state lifetimes were obtained using an HORIBA TEMPRO-01 instrument. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification.

(1) List of sulfoximine derivatives 1



(2) List of thiophene derivatives 2





Synthesis of sulfoximine derivatives 1: 1a-h[1] were prepared according to literature procedures.

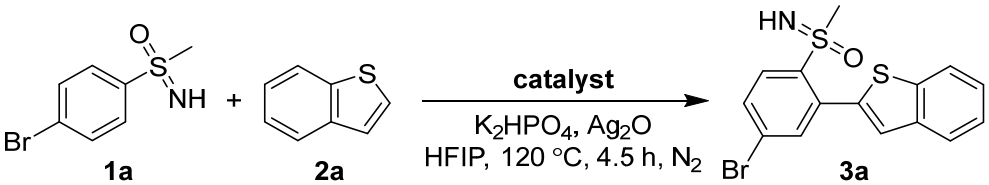
Synthesis of thiophene derivatives 2: 2e[2], **2f**[3], **2g**[4] were prepared according to literature procedures.

2a-2d, 2h-2o were purchased from Energy Chemistry.

II. Optimization of reaction conditions

A flame-dried Schlenk tube with a magnetic stir bar was charged with *S*-(4-bromophenyl)-*S*-methyl sulfoximine (**1a**, 0.3 mmol), benzo[*b*]thiophene (**2a**, 0.1 mmol), catalyst (5.0 mol%), oxidant (3.0 equiv), additive and solvent (1.0 mL). The resulting mixture was stirred at indicated temperature in oil bath for 4.5 h. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product **3a**.

Table S1. Screening of catalyst[a]

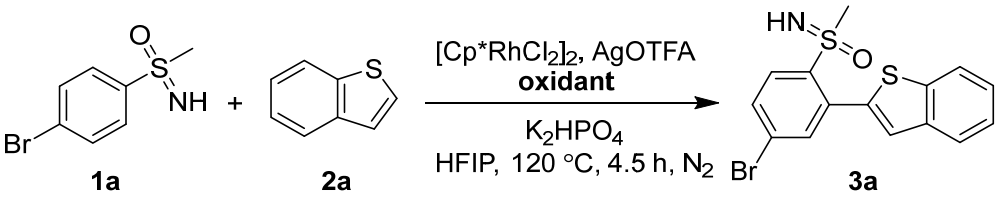


entry	catalyst	yield (%)[b]
1	$[Cp^*RhCl_2]_2/AgSbF_6$	21

2	$[Cp^*IrCl_2]_2/AgSbF_6$	trace
3	$Cp^*Co(CO)I_2$ (10%)	n.d.
4	$[Rh(cod)Cl]_2/AgSbF_6$	trace
5	$[Ru(p\text{-cymene})Cl_2]_2/AgSbF_6$	n.d.
6	$RhCl_3$	n.d.
7	$[Cp^*RhCl_2]_2$	14
8	$[Cp^*RhCl_2]_2$/AgOTFA (20%)	31
9	**$[Cp^*RhCl_2]_2$/AgOTFA (30%)**	**38**
10	$[Cp^*RhCl_2]_2$/AgOTFA (50%)	34
11	AgOTFA (30%)	n.d.
12[c]	AgOTFA (30%)/Ag_2CO_3	n.d.

[a]Reaction conditions: *S*-(4-bromophenyl)-*S*-methyl sulfoximine (**1a**, 0.3 mmol), benzo[*b*]thiophene (**2a**, 0.1 mmol), catalyst, Ag_2O (3.0 equiv), K_2HPO_4 (4.0 equiv), HFIP (1.0 mL) at 120 ºC in oil bath for 4.5 h. [b]Isolated yield. n.d. = not detected. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol. [c] Ag_2CO_3 (3.0 equiv) was used instead of Ag_2O (3.0 equiv) as the oxidant.

Table S2. Screening of oxidant[a]

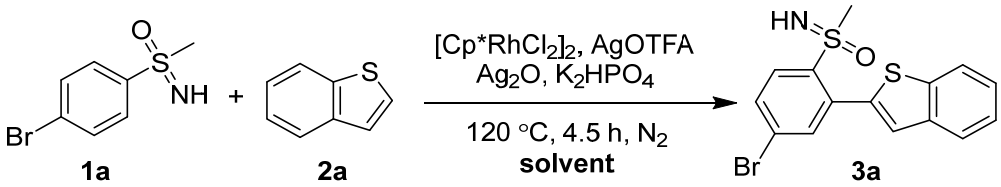


entry	oxidant (equiv)	yield (%)[b]
1	Ag_2CO_3 (3.0)	24
2	**Ag_2O (3.0)**	**38**
3	$Cu(OAc)_2$ (3.0)	n.d.
4	$Cu(OAc)_2$ (3.0) + O_2	trace
5	Ag_2O (2.0)	29
6	AgOTFA (6.0)	trace
7	AgOAc (6.0)	trace
8	$PhI(OAc)_2$ (3.0)	n.d.

9	$Na_2S_2O_8$ (3.0)	n.d.
10	MnO_2 (3.0)	n.d.
11	$AgNO_3$ (6.0)	n.d.
12	AgOTf (6.0)	n.d.
13	$Cu(OTf)_2$ (3.0)	n.d.
14	$Cu(OTFA)_2$ (3.0)	n.d.
15	BQ	n.d.
16	$Cu(OAc)_2$ (2.0) + Ag_2O (1.0)	trace
17	$Cu(OAc)_2$ (1.5) + Ag_2O (1.5)	trace

[a]Reaction conditions: *S*-(4-bromophenyl)-*S*-methyl sulfoximine (**1a**, 0.3 mmol), benzo[*b*]thiophene (**2a**, 0.1 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 μmol), AgOTFA (6.6 mg, 30 μmol), oxidant, K_2HPO_4 (4.0 equiv), HFIP (1.0 mL) at 120 ºC in oil bath for 4.5 h. [b]Isolated yield. n.d. = not detected. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol. BQ = benzoquinone.

Table S3. Screening of solvent[a]

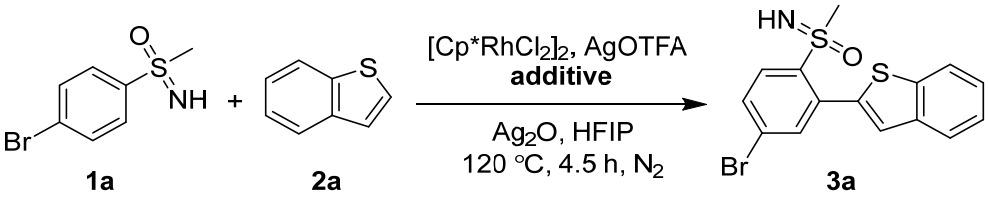


entry	solvent	yield (%)[b]
1	**HFIP**	**38**
2[c]	HFIP	trace
3[d]	HFIP	29
4	TFE	17
5	DCE	trace
6	toluene	n.d.
7	THF	n.d.
8	dioxane	n.d.
9	DMSO	n.d.
10	MeOH	n.d.
11	CH_3CN	n.d.

12	*i*-PrOH	n.d.

[a]Reaction conditions: *S*-(4-bromophenyl)-*S*-methyl sulfoximine (**1a**, 0.3 mmol), benzo[*b*]thiophene (**2a**, 0.1 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5.0 μmol), AgOTFA (6.6 mg, 30.0 μmol), Ag_2O (3.0 equiv), K_2HPO_4 (4.0 equiv), solvent (1.0 mL) at 120 ºC in oil bath for 4.5 h. [b]Isolated yield. n.d. = not detected. [c]HFIP (2.0 mL). [d]HFIP (0.5 mL). HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, TFE = 2,2,2-trifluoroethanol, DCE = 1,2-dichloroethane, THF = tetrahydrofuran, DMSO = dimethyl sulfoxide, *i*-PrOH = isopropyl alcohol.

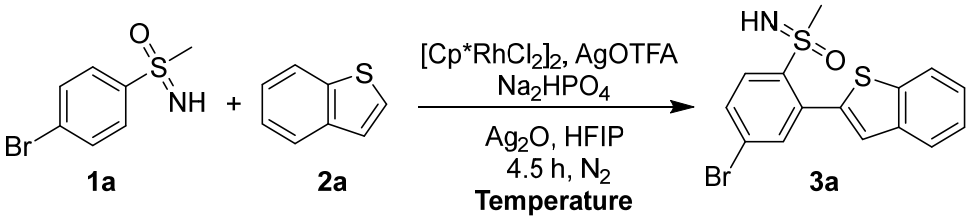
Table S4. Screening of additive[a]



entry	additive (equiv)	yield (%)[b]
1	K_2HPO_4 (4.0)	38
2	**Na_2HPO_4 (4.0)**	**41**
3	Na_2HPO_4 (2.0)	26
4	Na_2HPO_4 (1.0)	19
5	NaOAc (1.0)	trace
6	$Zn(OAc)_2$ (1.0)	trace
7	K_3PO_4 (1.0)	16
8	KH_2PO_4 (2.0)	trace
9	$NaHCO_3$ (2.0)	14
10	Na_2CO_3 (1.0)	trace
11	HOAc (1.0)	trace
12	PivOH (1.0)	trace
13	-	24

[a]Reaction conditions: *S*-(4-bromophenyl)-*S*-methyl sulfoximine (**1a**, 0.3 mmol), benzo[*b*]thiophene (**2a**, 0.1 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 μmol), AgOTFA (6.6 mg, 30.0 μmol), Ag_2O (3.0 equiv), additive, HFIP (1.0 mL) at 120 ºC in oil bath for 4.5 h. [b]Isolated yield. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

Table S5. Screening of temperature[a]



entry	temperature	yield (%)[b]
1	120 ºC	41
2	100 ºC	28
3	130 ºC	43
4	**150 ºC**	**69**
5[c]	150 ºC	61
6[d]	150 ºC	58

[a]Reaction conditions: *S*-(4-bromophenyl)-*S*-methyl sulfoximine (**1a**, 0.3 mmol), benzo[*b*]thiophene (**2a**, 0.1 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5.0 μmol), AgOTFA (6.6 mg, 30.0 μmol), Ag_2O (3.0 equiv), Na_2HPO_4 (4.0 equiv), HFIP (1.0 mL) at indicated temperature in oil bath for 4.5 h. [b]Isolated yield. [c]3 h. [d]6 h. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

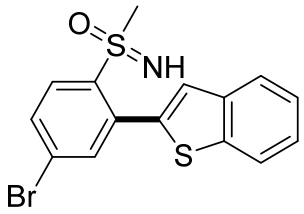
III. General procedure for heteroarylation of sulfoximines

A flame-dried Schlenk with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 5.0 μmol), Ag_2O (69.5 mg, 0.3 mmol), AgOTFA (6.6 mg, 30.0 μmol), Na_2HPO_4 (56.8 mg, 0.4 mmol), sulfoximines **1** (0.3 mmol), and thiophenes **2** (0.1 mmol) in HFIP (1.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at 150 ºC in oil bath for 4.5 h and then diluted with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product **3**.

IV. Procedure for the synthesis of 3a on 1.0 mmol scale

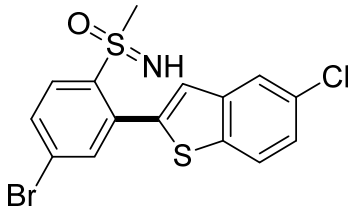
A flame-dried Schlenk with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (31 mg, 50.0 μmol), Ag_2O (695 mg, 3.0 mmol), AgOTFA (66 mg, 0.3 mmol), Na_2HPO_4 (568 mg, 4.0 mmol), *S*-(4-bromophenyl)-*S*-methyl sulfoximine **1a** (699 mg, 3.0 mmol), and

benzo[*b*]thiophene **2a** (134 mg, 1.0 mmol) in HFIP (10.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at 150 ºC in oil bath for 4.5 h and then diluted with 50 mL of dichloromethane. The solution was filtered through a celite pad and washed with 100-200 mL of dichloromethane. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to provide the desired product **3a** (182 mg, 50% yield).



2-(5-Bromo-2-(*S*-methylsulfonimidoyl)phenyl)benzo[*b*]thiophene (3a)

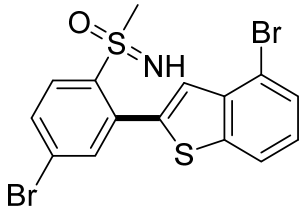
Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3a** as a yellow solid (25.2 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.4 Hz, 1H), 7.87-7.83 (m, 2H), 7.74-7.67 (m, 3H), 7.44-7.38 (m, 2H), 2.94 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.6, 140.6, 139.5, 137.2, 136.8, 135.3, 132.1, 130.4, 127.7, 127.1, 125.4, 125.1, 124.6, 122.1, 44.1 ppm. HRMS (ESI): calcd for $C_{15}H_{13}{}^{81}BrNOS_2$ $[M+H]^+$ 367.9596, found 367.9588; calcd for $C_{15}H_{13}{}^{79}BrNOS_2$ $[M+H]^+$ 365.9616, found 395.9611.



2-(5-Bromo-2-(*S*-methylsulfonimidoyl)phenyl)-5-chlorobenzo[*b*]thiophene (3b)

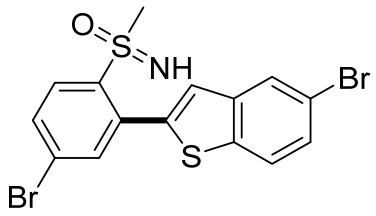
Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3b** as a gray solid (22.3 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 8.8 Hz, 1H), 7.82-7.72 (m, 4H), 7.58 (s, 1H), 7.36 (d, J = 8.8 Hz, 1H), 2.94 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.5, 138.6, 136.7, 135.7, 134.4, 132.4, 131.4, 130.6, 130.2, 127.2, 126.8, 125.8, 124.0,

123.2, 45.1 ppm. HRMS (ESI): calcd for $C_{15}H_{12}{}^{81}Br^{37}ClNOS_2$ $[M+H]^+$ 403.9177, found 403.9171; calcd for $C_{15}H_{12}{}^{81}Br^{35}ClNOS_2$ $[M+H]^+$ 401.9206, found 401.9197; calcd for $C_{15}H_{12}{}^{79}Br^{35}ClNOS_2$ $[M+H]^+$ 399.9227, found 399.9227.



2-**Bromo-2-(5-bromo-2-(*S*-methylsulfonimidoyl)phenyl)benzo[*b*]thiophene (3c)**

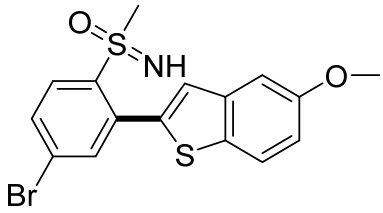
Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3c** as a yellow solid (20.7 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 8.4 Hz, 1H), 7.79-7.73 (m, 3H), 7.67 (s, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.27-7.23 (m, 1H), 3.02 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 138.9, 137.4, 132.64, 132.61, 130.8, 129.6, 128.3, 127.2, 126.2, 125.5, 121.3, 115.9, 115.3, 47.8 ppm. HRMS (ESI): calcd for $C_{15}H_{12}{}^{81}Br^{81}BrNOS_2$ $[M+H]^+$ 447.8681, found 447.8680; calcd for $C_{15}H_{12}{}^{81}Br^{79}BrNOS_2$ $[M+H]^+$ 445.8701, found 445.8701; calcd for $C_{15}H_{12}{}^{79}Br^{79}BrNOS_2$ $[M+H]^+$ 443.8722, found 443.8722.



2-Bromo-2-(5-bromo-2-(*S*-methylsulfonimidoyl)phenyl)benzo[*b*]thiophene (3d)

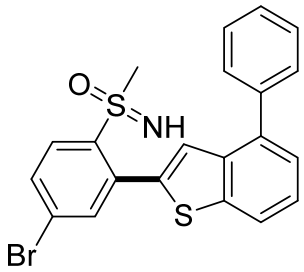
Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3d** as a yellow solid (18.9 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 9.2 Hz, 1H), 7.98 (s, 1H), 7.74-7.70 (m, 3H), 7.58 (s, 1H), 7.49 (d, J = 8.4 Hz, 1H), 2.93 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.9, 139.2, 136.7, 134.8, 134.3, 132.5, 130.6, 130.2, 128.5, 127.2, 127.1, 126.6, 123.5, 119.1, 44.3 ppm. HRMS (ESI): calcd for $C_{15}H_{12}{}^{81}Br^{81}BrNOS_2$ $[M+H]^+$

447.8681, found 447.8678; calcd for $C_{15}H_{12}{}^{81}Br^{79}BrNOS_2$ $[M+H]^+$ 445.8701, found 445.8698; calcd for $C_{15}H_{12}{}^{79}Br^{79}BrNOS_2$ $[M+H]^+$ 443.8722, found 443.8723.



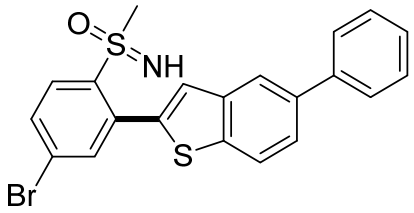
2-(5-Bromo-2-(*S*-methylsulfonimidoyl)phenyl)-5-methoxybenzo[*b*]thiophene (3e)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3e** as a yellow solid (27.7 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.8 Hz, 1H), 7.74-7.69 (m, 3H), 7.63 (s, 1H), 7.28 (d, J = 2.0 Hz, 1H), 7.05 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 3.88 (s, 3H), 2.93 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 140.6, 138.2, 137.4, 136.7, 135.3, 133.0, 132.0, 130.3, 127.6, 127.1, 122.8, 116.0, 106.2, 55.7, 43.9 ppm. HRMS (ESI): calcd for $C_{16}H_{15}{}^{81}BrNO_2S_2$ $[M+H]^+$ 397.9702, found 397.9692; calcd for $C_{16}H_{15}{}^{79}BrNO_2S_2$ $[M+H]^+$ 395.9722, found 395.9720.



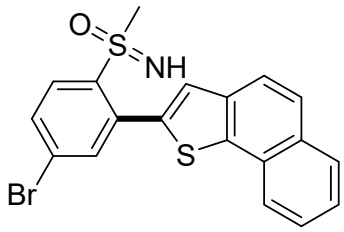
2-(5-Bromo-2-(*S*-methylsulfonimidoyl)phenyl)-4-phenylbenzo[*b*]thiophene (3f)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3f** as a yellow solid (30.3 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.70-7.68 (m, 3H), 7.61-7.59 (m, 2H), 7.49-7.37 (m, 5H), 2.97 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 141.3, 140.5, 138.7, 137.6, 137.1, 136.7, 135.6, 132.2, 130.5, 129.2, 128.7, 127.8, 127.2, 127.1, 125.5, 121.2, 118.1, 44.5 ppm. HRMS (ESI): calcd for $C_{21}H_{17}{}^{81}BrNOS_2$ $[M+H]^+$ 443.9909, found 443.9907; calcd for $C_{21}H_{17}{}^{79}BrNOS_2$ $[M+H]^+$ 441.9929, found 441.9929.



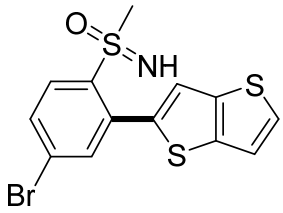
2-(5-Bromo-2-(*S*-methylsulfonimidoyl)phenyl)-5-phenylbenzo[*b*]thiophene (3g)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3g** as a yellow solid (29.9 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.4 Hz, 1H), 8.04 (s, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.76-7.72 (m, 3H), 7.67-7.64 (m, 3H), 7.50-7.46 (m, 2H), 7.40-7.36 (m, 1H), 2.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 167.9, 167.5, 159.2, 142.7, 138.7, 136.8, 132.2, 131.6, 130.9, 130.4, 129.3, 129.1, 127.9, 127.5, 125.1, 122.9, 112.4, 43.4 ppm. HRMS (ESI): calcd for $C_{21}H_{17}{}^{81}BrNOS_2$ $[M+H]^+$ 443.9909, found 443.9908; calcd for $C_{21}H_{17}{}^{79}BrNOS_2$ $[M+H]^+$ 441.9929, found 441.9928.



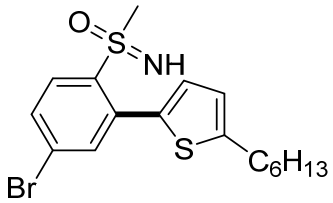
2-(5-Bromo-2-(*S*-methylsulfonimidoyl)phenyl)naphtho[1,2-*b*]thiophene (3h)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3h** as a yellow solid (28.0 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.8 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.84-7.77 (m, 4H), 7.73 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.62-7.54 (m, 2H), 2.92 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.6, 138.6, 137.4, 136.9, 136.2, 135.2, 132.0, 131.2, 130.3, 129.1, 129.0, 128.6, 127.11, 127.06, 126.4, 126.2, 123.8, 122.5, 43.9 ppm. HRMS (ESI): calcd for $C_{19}H_{15}{}^{81}BrNOS_2$ $[M+H]^+$ 417.9752, found 417.9745; calcd for $C_{19}H_{15}{}^{79}BrNOS_2$ $[M+H]^+$ 415.9773, found 415.9773.



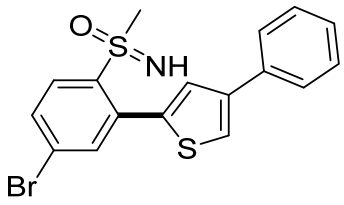
2-(5-Bromo-2-(*S*-methylsulfonimidoyl)phenyl)thieno[3,2-*b*]thiophene (3i)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3i** as a yellow solid (21.9 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.8 Hz, 1H), 7.73-7.68 (m, 3H), 7.46 (d, J = 6.0 Hz, 1H), 7.29 (d, J = 5.2 Hz, 1H), 2.92 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4, 140.6, 139.4, 138.4, 136.9, 135.2, 131.9, 130.2, 128.5, 127.1, 123.3, 119.4, 43.7 ppm. HRMS (ESI): calcd for $C_{13}H_{11}{}^{81}BrNOS_3$ $[M+H]^+$ 373.9160, found 373.9153; calcd for $C_{13}H_{11}{}^{79}BrNOS_3$ $[M+H]^+$ 371.9181, found 371.9176.



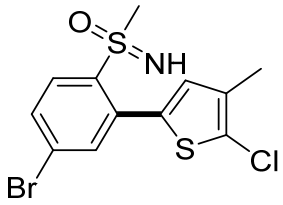
2-(5-Bromo-2-(*S*-methylsulfonimidoyl)phenyl)-5-hexylthiophene (3j)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3j** as a yellow solid (21.2 mg, 53% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 8.4 Hz, 1H), 7.65-7.61 (m, 2H), 7.28 (d, J = 3.2 Hz, 1H), 6.78 (d, J = 3.6 Hz, 1H), 2.87 (s, 3H), 2.84 (t, J = 7.6 Hz, 2H), 1.73-1.66 (m, 2H), 1.40-1.25 (m, 6H), 0.91-0.88 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.0, 142.2, 136.7, 135.7, 134.2, 131.2, 130.8, 130.0, 126.9, 124.7, 43.4, 31.7, 31.7, 30.2, 28.9, 22.7, 14.2 ppm. HRMS (ESI): calcd for $C_{17}H_{23}{}^{81}BrNOS_2$ $[M+H]^+$ 402.0378, found 402.0378; calcd for $C_{17}H_{23}{}^{79}BrNOS_2$ $[M+H]^+$ 400.0399, found 400.0399.



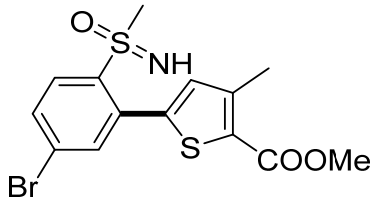
3-(5-Bromo-2-(*S*-methylsulfonimidoyl)phenyl)-4-phenylthiophene (3k)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3k** as a yellow solid (18.8 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 1.2 Hz, 1H), 7.72-7.68 (m, 2H), 7.62-7.58 (m, 3H), 7.43-7.40 (m, 2H), 7.34-7.30 (m, 1H), 2.92 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.6, 142.3, 138.0, 136.6, 135.3, 135.2, 131.8, 130.24, 130.15, 129.1, 127.7, 127.1, 126.6, 122.4, 43.8 ppm. HRMS (ESI): calcd for $C_{17}H_{15}{}^{81}BrNOS_2$ $[M+H]^+$ 393.9752, found 391.9736; calcd for $C_{17}H_{15}{}^{79}BrNOS_2$ $[M+H]^+$ 391.9773, found 391.9770.



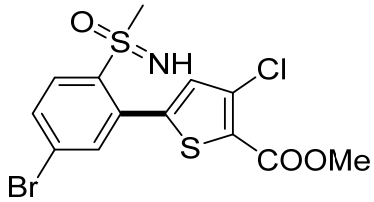
2-(5-Bromo-2-(*S*-methylsulfonimidoyl)phenyl)-2-chloro-3-methylthiophene (3l)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3l** as a yellow solid (22.4 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.8 Hz, 1H), 7.66 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.61 (d, J = 2.0 Hz, 1H), 7.12 (s, 1H), 2.95 (s, 3H), 2.22 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.2, 136.7, 134.9, 134.6, 133.4, 132.4, 131.9, 130.3, 127.5, 127.2, 43.8, 13.8 ppm. HRMS (ESI): calcd for $C_{12}H_{11}{}^{81}Br^{37}ClNNaOS_2$ $[M+Na]^+$ 389.8996, found 389.8999; calcd for $C_{12}H_{11}{}^{81}Br^{35}ClNNaOS_2$ $[M+Na]^+$ 387.9026, found 387.9028; calcd for $C_{12}H_{11}{}^{79}Br^{37}ClNNaOS_2$ $[M+Na]^+$ 387.9017, found 387.9018; calcd for $C_{12}H_{11}{}^{79}Br^{35}ClNNaOS_2$ $[M+Na]^+$ 385.9046, found 385.9045.



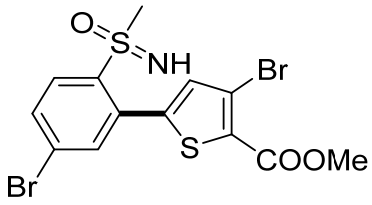
Methyl 5-(5-bromo-2-(*S*-methylsulfonimidoyl)phenyl)-3-methylthiophene-2-carboxylate (3m)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3m** as a yellow solid (18.2 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 8.8 Hz, 1H), 7.71 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.20 (s, 1H), 3.88 (s, 3H), 2.94 (s, 3H), 2.58 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 152.8, 146.2, 142.3, 141.6, 136.5, 134.9, 134.5, 132.4, 130.6, 127.2, 52.1, 44.4, 16.2 ppm. HRMS (ESI): calcd for $C_{14}H_{15}{}^{81}BrNO_3S_2$ $[M+H]^+$ 389.9651, found 389.9641; calcd for $C_{14}H_{15}{}^{79}BrNO_3S_2$ $[M+H]^+$ 387.9671, found 387.9670.



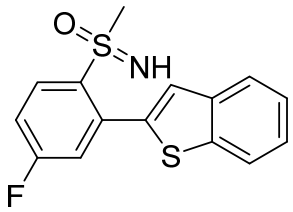
Methyl 5-(5-bromo-2-(*S*-methylsulfonimidoyl)phenyl)-3-chlorothiophene-2-carboxylate (3n)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3n** as a yellow solid (23.8 mg, 58% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.63 (s, 1H), 7.30 (s, 1H), 3.91 (s, 3H), 2.97 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 142.3, 142.2, 136.4, 133.3, 133.1, 132.8, 131.1, 131.0, 127.5, 127.2, 52.6, 44.8 ppm. HRMS (ESI): calcd for $C_{13}H_{12}{}^{81}Br^{37}ClNO_3S_2$ $[M+H]^+$ 411.9075, found 411.9062; calcd for $C_{13}H_{12}{}^{79}Br^{37}ClNO_3S_2$ $[M+H]^+$ 409.9096, found 409.9091; calcd for $C_{13}H_{12}{}^{79}Br^{35}ClNO_3S_2$ $[M+H]^+$ 407.9125, found 407.9125.



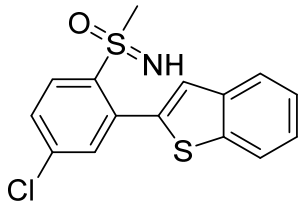
Methyl 3-bromo-5-(5-bromo-2-(*S*-methylsulfonimidoyl)phenyl)thiophene-2-carboxylate (3o)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3o** as a yellow solid (29.3 mg, 65% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.8 Hz, 1H), 7.75 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.35 (s, 1H), 3.92 (s, 3H), 2.97 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9, 143.2, 142.3, 136.4, 135.4, 133.2, 133.1, 131.0, 128.8, 127.5, 116.6, 52.6, 44.8 ppm. HRMS (ESI): calcd for $C_{13}H_{12}{}^{81}Br^{81}BrNO_3S_2$ $[M+H]^+$ 455.8579, found 455.8578; calcd for $C_{13}H_{12}{}^{81}Br^{79}BrNO_3S_2$ $[M+H]^+$ 453.8599, found 453.8600; calcd for $C_{13}H_{12}{}^{79}Br^{79}BrNO_3S_2$ $[M+H]^+$ 451.8620, found 451.8619.



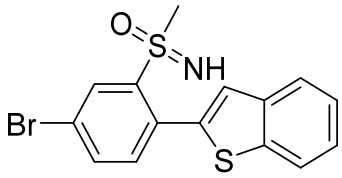
2-(5-Fluoro-2-(*S*-methylsulfonimidoyl)phenyl)benzo[*b*]thiophene (3p)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3p** as a yellow solid (10.4 mg, 34% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32-8.29 (m, 1H), 7.87-7.84 (m, 2H), 7.70 (s, 1H), 7.44-7.38 (m, 2H), 7.31-7.24 (m, 2H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0 (d, $J_{C–F}$ = 249.9 Hz), 141.7, 140.3, 139.3 (d, $J_{C–F}$ = 9.6 Hz), 131.7 (d, $J_{C–F}$ = 9.3 Hz), 130.6, 127.3, 125.2, 125.1, 124.9, 124.4 122.0, 121.1 (d, $J_{C–F}$ = 22.8 Hz), 115.7 (d, $J_{C–F}$ = 21.2 Hz), 44.0. HRMS (ESI): calcd for $C_{15}H_{12}FNNaOS_2$ $[M+Na]^+$ 328.0237, found 328.0240.



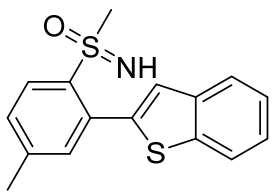
2-(5-Chloro-2-(*S*-methylsulfonimidoyl)phenyl)benzo[*b*]thiophene (3q)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3q** as a yellow solid (24.1 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, J = 8.8 Hz, 1H), 7.85 (t, J = 6.4 Hz, 2H), 7.68 (s, 1H), 7.58-7.53 (m, 2H), 7.44-7.38 (m, 2H), 2.93 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 140.5, 139.5, 138.7, 137.3, 135.2, 133.9, 130.4, 129.0, 127.6, 125.4, 125.1, 124.6, 122.1, 44.1 ppm. HRMS (ESI): calcd for $C_{15}H_{13}{}^{37}ClNOS_2$ $[M+H]^+$ 324.0092, found 324.0091; calcd for $C_{15}H_{13}{}^{35}ClNOS_2$ $[M+H]^+$ 322.0122, found 322.0119.



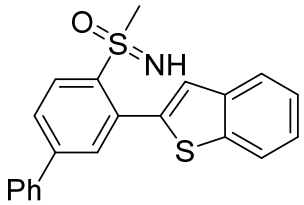
2-(4-Bromo-2-(*S*-methylsulfonimidoyl)phenyl)benzo[*b*]thiophene (3r)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3r** as a yellow solid (18.6 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 2.0 Hz, 1H), 7.86-7.83 (m, 2H), 7.74 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.66 (s, 1H), 7.46-7.37 (m, 3H), 2.95 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6, 135.4, 131.7, 130.3, 130.3, 127.5, 125.3, 125.1, 124.9, 124.6, 124.5, 123.3, 122.5, 122.1, 53.7 ppm. HRMS (ESI): calcd for $C_{15}H_{13}{}^{81}BrNOS_2$ $[M+H]^+$ 367.9596, found 367.9570; calcd for $C_{15}H_{13}{}^{79}BrNOS_2$ $[M+H]^+$ 365.9616, found 365.9614.



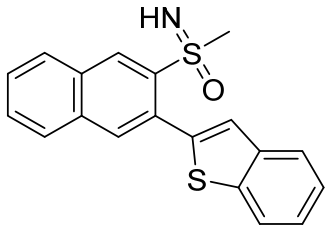
2-(5-Methyl-2-(*S*-methylsulfonimidoyl)phenyl)benzo[*b*]thiophene (3s)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3s** as a yellow solid (19.3 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 8.0 Hz, 1H), 7.86-7,82 (m, 2H), 7.64 (s, 1H), 7.42-7.35 (m, 4H), 2.94 (s, 3H), 2.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2, 140.48, 140.45, 139.7, 139.1, 134.8, 133.3, 129.6, 128.9, 126.9, 125.0, 124.8, 124.3, 122.0, 44.2, 21.4 ppm. HRMS (ESI): calcd for $C_{16}H_{16}NOS_2$ $[M+H]^+$ 302.0668, found 302.0683.



2-(4-(*S*-Methylsulfonimidoyl)-[1,1'-biphenyl]-3-yl)benzo[*b*]thiophene (3t)

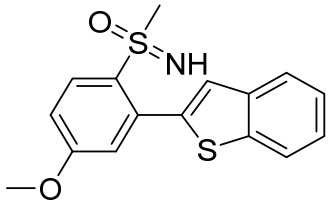
Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3t** as a yellow solid (23.1 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, J = 8.4 Hz, 1H), 7.87-7.82 (m, 2H), 7.80-7.77 (m, 2H), 7.71 (s, 1H), 7.63 (d, J = 7.6 Hz, 2H), 7.50-7.37 (m, 5H), 3.00 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.4, 142.8, 141.8, 138.9, 138.0, 134.0, 132.9, 129.5, 129.3, 128.9, 127.5, 127.4, 127.2, 125.1, 125.0, 124.4, 122.1, 120.6, 44.3 ppm. $C_{21}H_{18}NOS_2$ $[M+H]^+$ 364.0824, found 364.0826.



2-(3-(*S*-Methylsulfonimidoyl)naphthalen-2-yl)benzo[*b*]thiophene (3u)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3u** as a yellow solid (22.3 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (s, 1H), 8.06-8.04 (m, 2H), 7.92 (d, J = 7.2 Hz, 1H), 7.88-7.85 (m, 2H), 7.73 (s, 1H), 7.72-7.65 (m, 2H), 7.44-7.38 (m, 2H), 3.01 (s, 3H)

ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.5, 139.8, 139.5, 139.1, 134.3, 134.2, 131.9, 130.3, 129.7, 129.3, 128.9, 128.4, 127.9, 127.4, 125.0, 124.9, 124.4, 122.0, 44.1 ppm. HRMS (ESI): calcd for $C_{19}H_{16}NOS_2$ $[M+H]^+$ 338.0668, found 338.0667.

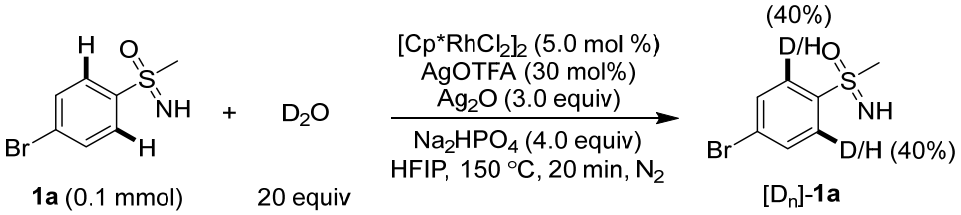


2-(5-Methoxy-2-(*S*-methylsulfonimidoyl)phenyl)benzo[*b*]thiophene (3v)

Following the general procedure. Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3v** as a yellow solid (16.5 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, J = 8.8 Hz, 1H), 7.85-7.82 (m, 2H), 7.64 (s, 1H), 7.42-7.35 (m, 2H), 7.07-7.02 (m, 2H), 3.89 (s, 3H), 2.93 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 140.4, 139.6, 138.9, 135.4, 135.1, 131.3, 126.8, 125.0, 124.9, 124.4, 122.1, 119.7, 113.7, 55.9, 44.6 ppm. HRMS (ESI): calcd for $C_{16}H_{15}NNaO_2S_2$ $[M+Na]^+$ 340.0436, found 340.0433.

V. Mechanistic studies

Scheme S1. H/D exchange experiments of **1a**



A flame-dried Schlenk with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 5 μmol), Ag_2O (69.5 mg, 0.3 mmol), AgOTFA (6.6 mg, 30 $u$mol), Na_2HPO_4 (56.8 mg, 0.4 mmol), *S*-(4-bromophenyl)-*S*-methyl sulfoximine **(1a**, 0.1 mmol) and D_2O (20 equiv) in HFIP (1 mL) under an N_2 atmosphere. The resulting mixture was stirred at 150 ºC in oil bath for 20 min and then diluted with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product. The deuterated ratio was

calculated from ^{1}H NMR analysis.

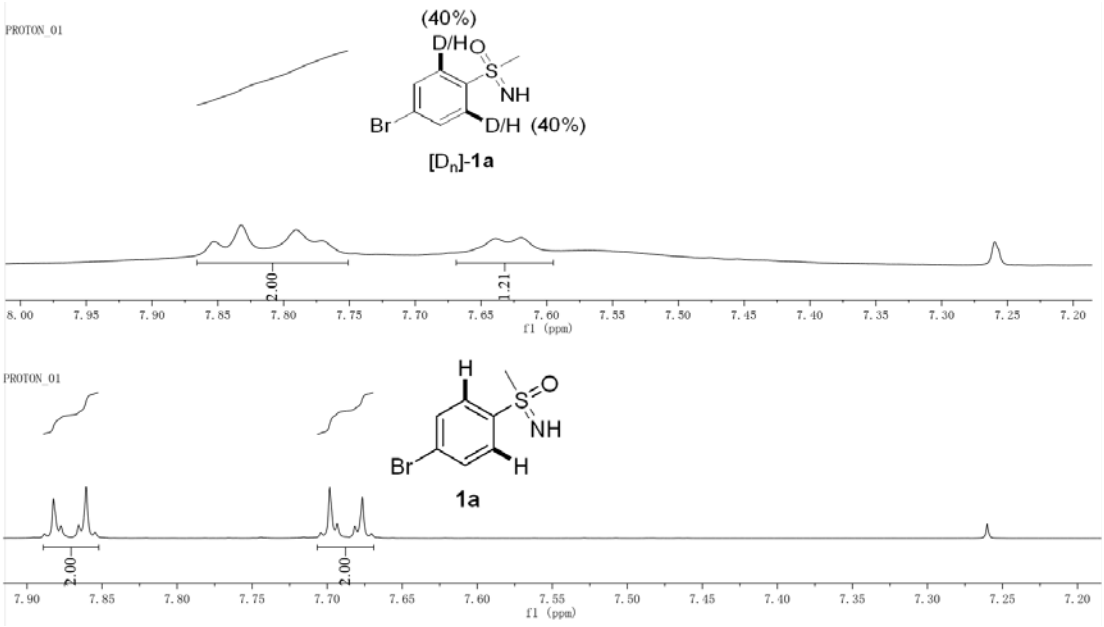
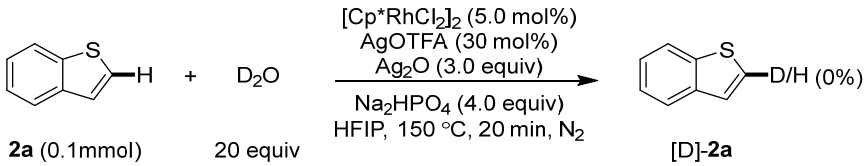


Fig. S1. H/D exchange experiments of **1a**

Scheme S2. H/D exchange experiments of **2a**



A flame-dried Schlenk with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 5.0 μmol), Ag_2O (69.5 mg, 0.3 mmol), AgOTFA (6.6 mg, 30.0 μmol), Na_2HPO_4 (56.8 mg, 0.4 mmol), benzo[*b*]thiophene (**2a**, 0.1 mmol) and D_2O (20.0 equiv) in HFIP (1.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at 150 ºC in oil bath for 20 min and then diluted with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product. The deuterated ratio was calculated from ^{1}H NMR analysis.

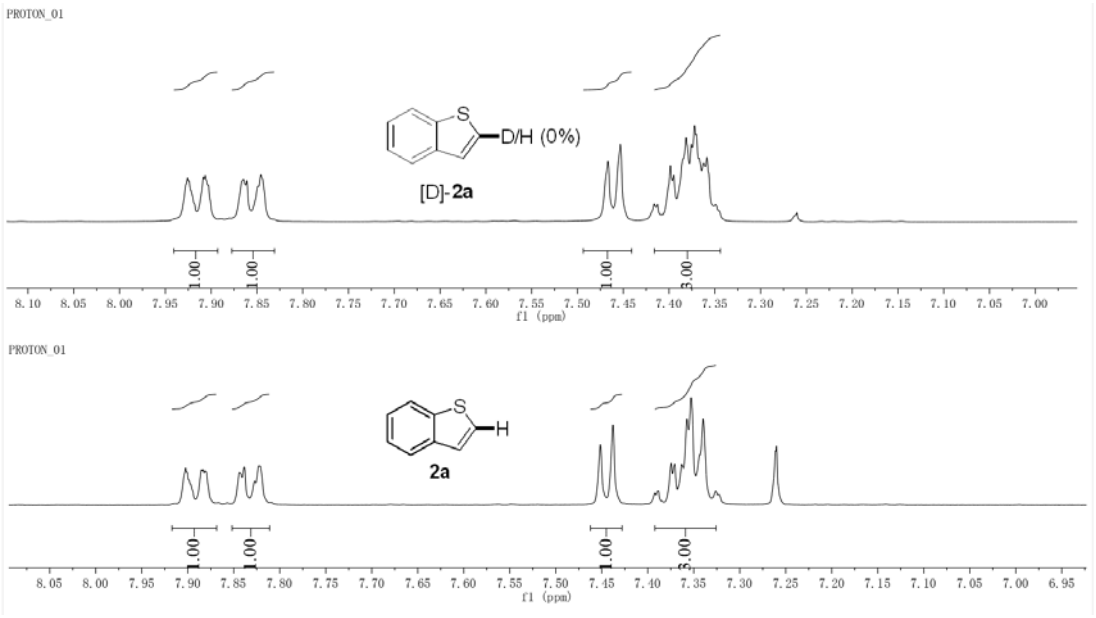
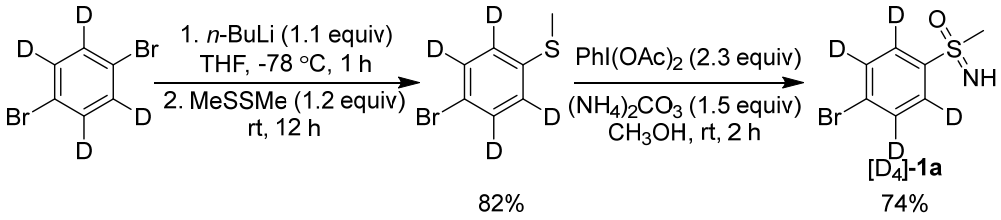


Fig. S2. H/D exchange experiments of **2a**

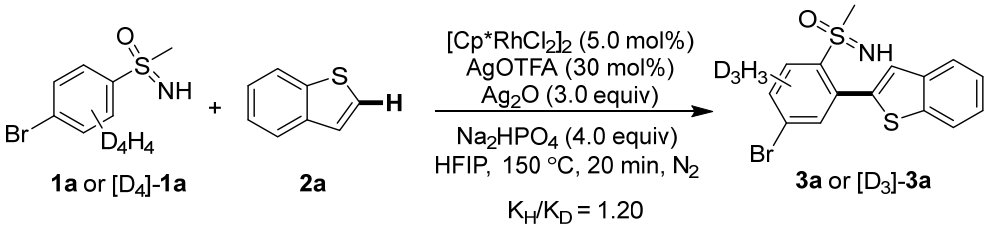


Synthesis of [D_4]-**1a**: A flame-dried two-neck round-bottom flask with a magnetic stir bar was charged with 1,4-dibromobenzene-d_4 (10.0 mmol) and THF (20.0 mL) under an N_2 atmosphere. The solution was cooled to -78 ºC and *n*-BuLi (2.5 mol/L in hexane, 11.0 mmol, 1.1 equiv) was added dropwise. After stirring for 1 h at -78 ºC, dimethyl disulfide (12.0 mmol, 1.2 equiv) was added. The mixture was allowed to stir overnight, and 1.0 M HCl aq. was added. The organic layer was separated, washed with H_2O and saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4, and concentrated in vacuo. Column chromatography (eluent: hexane) was performed to give 4-bromothioanisole-d_4 as white solid (1.7 g, 82% yield).

To a 50 mL round bottom flask equipped with a suitable magnetic stir bar, $(NH_4)_2CO_3$ (0.288 g, 1.5 equiv) was added the stirred solution of 4-bromothioanisole-d_4 (2.0 mmol, 1.0 equiv) in MeOH (20.0 mL). After stirred five minutes, $PhI(OAc)_2$ (1.482 g, 2.3 equiv) was added and the solution was stirred at room temperature for 2 h. After disappearance of the raw material detected by TLC (petroleum ether/EtOAc =

1:1), the solvent was removed under reduced pressure. Column chromatography (eluent: petroleum ether/EtOAc = 1/1) was performed to give [D_4]-**1a** as white solid (348 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.10 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4, 132.2 (t, J_{C-D} = 24.9 Hz), 129.0 (t, J_{C-D} = 25.9 Hz), 128.2, 46.2 ppm. HRMS (ESI): calcd for $C_7H_5D_4{}^{81}BrNOS_2$ $[M+H]^+$ 239.9813, found 239.9794; calcd for $C_7H_5D_4{}^{79}BrNOS_2$ $[M+H]^+$ 237.9834, found 237.9815.

Scheme S3. Kinetic isotope experiments of **1a**



A flame-dried Schlenk with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 5.0 μmol), Ag_2O (69.5 mg, 0.3 mmol), AgOTFA (6.6 mg, 30.0 μmol), Na_2HPO_4 (56.8 mg, 0.4 mmol), **1a** or [D_4]**-1a** (0.3 mmol), benzo[*b*]thiophene (**2a**, 0.1 mmol) in HFIP (1.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at 150 ºC in oil bath for indicated time and then diluted with 5.0 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to provide the desired product. The yield of **3a** was determined by ^{1}H NMR analysis of the crude product using dibromomethane (0.15 mmol, 10.5 μL) as internal standard. A kinetic isotope effect (KIE) value (k_H/k_D = 0.024/0.020 = 1.20) was obtained.

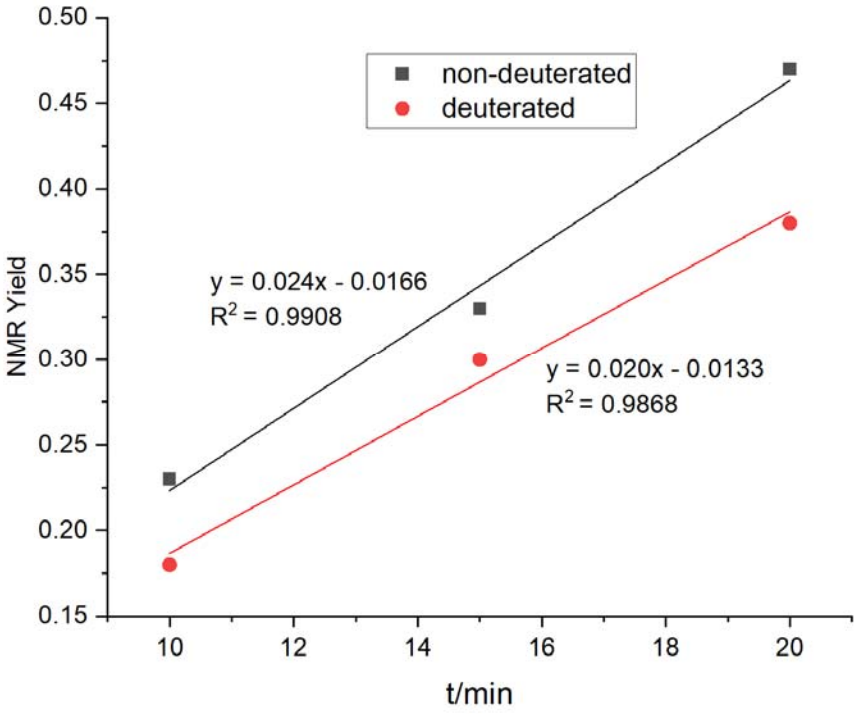
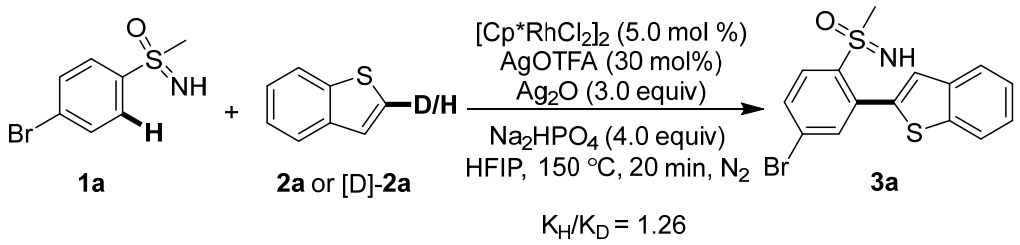


Fig. S3. Kinetic isotope experiments of **1a**

Scheme S4. Kinetic isotope experiments of **2a**



A flame-dried Schlenk with a magnetic stir bar was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 5.0 μmol), Ag_2O (69.5 mg, 0.3 mmol), AgOTFA (6.6 mg, 30.0 μmol), Na_2HPO_4 (56.8 mg, 0.4 mmol), *S*-(4-bromophenyl)-*S*-methyl sulfoximine (**1a**, 0.3 mmol), benzo[*b*]thiophene (**2a**, 0.1 mmol) or deuterated benzothiophene ([D_1]-**2a**, 0.1 mmol) in HFIP (1.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at 150 ºC in oil bath for indicated time and then diluted with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to provide the desired product. The yield of **3a** was determined by ^{1}H NMR analysis of the crude product using dibromomethane (0.15 mmol, 10.5 μL) as internal standard. A kinetic isotope effect (KIE) value (k_H/k_D =

0.024/0.019 = 1.26) was obtained.

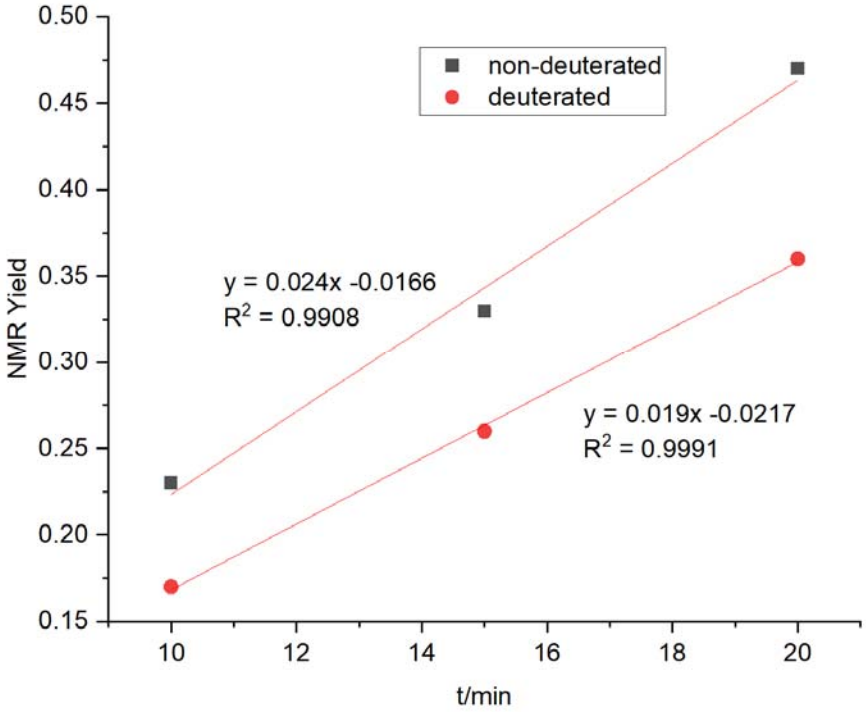
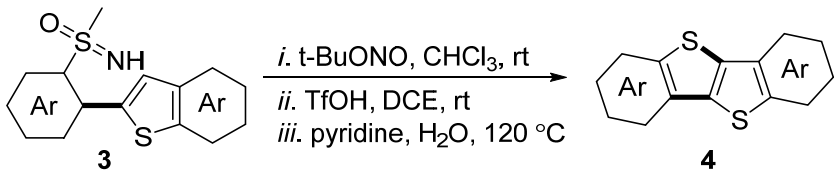


Fig. S4. Kinetic isotope experiments of **2a**

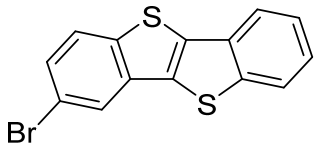
VI. Synthesis of BTBT derivatives



Synthesis of 4: **3** (0.1 mmol, 1.0 equiv) was dissolved in $CHCl_3$ (2.0 mL) under air and *t*-BuONO (1.1 equiv) was added. The mixture was stirred at room temperature for 2 h. the solvent and *t*-BuONO were removed under reduced pressure. The residue was subjected to the next reaction without further purification.[5]

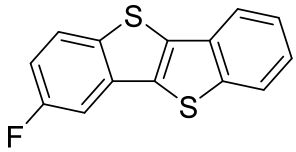
The corresponding crude sulfoxide was placed in a Schlenk tube and DCE (1.5 mL) was added. With continuous N_2 streaming into the tube, TfOH (0.75 mL) was added dropwise. After stirring 24 hours at room temperature, H_2O (2.65 mL) and pyridine (0.35 mL) was charged, and the resulting mixture was stirred for 1 hour at 120 ºC. The mixture was poured into 2.5 mL of 2 M aqueous HCl and diluted with H_2O and dichloromethane. The organic layer was separated, and the aqueous layer was extracted

with dichloromethane three times. The combined organic extracts was washed with H_2O and brine, dried over Na_2SO_4, and concentrated in vacuo. The obtained crude material was purified through column chromatography (eluent: petroleum ether/EtOAc = 40/1) to give the cyclized product.[6]



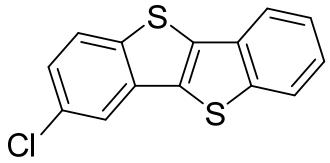
3-Bromobenzo[*b*]benzo[4,5]thieno[2,3-*d*]thiophene (4a)

Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 40/1, v/v) afforded **4a** as a white solid (20.4 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 9.2 Hz, 1H), 7.51-7.42 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 140.9, 137.6, 135.0, 134.8, 132.9, 128.0, 125.6, 125.4, 125.2, 124.4, 124.2, 121.9, 119.0 ppm. HRMS (ESI): calcd for $C_{14}H_8{}^{79}BrS_2$ $[M+H]^+$ 318.9245, found 318.9251.



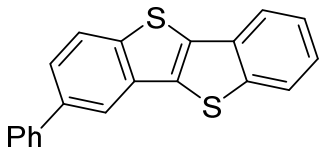
3-Fluorobenzo[*b*]benzo[4,5]thieno[2,3-*d*]thiophene (4b)

Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 40/1, v/v) afforded **4b** as a white solid (16.3 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.84 (dd, *J* = 8.8 Hz, 4.8 Hz, 1H), 7.55 (dd, *J* = 9.2 Hz, 2.4 Hz, 1H), 7.49-7.41 (m, 2H), 7.16 (td, *J* = 8.8 Hz, 2.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1 (d, $J_{C–F}$ = 241.7 Hz), 142.4, 137.5, 135.7, 134.1 (d, $J_{C–F}$ = 9.9 Hz), 133.0, 132.8 (d, $J_{C–F}$ = 4.3 Hz), 125.6, 125.2 (d, $J_{C–F}$ = 9.3 Hz), 125.1, 124.2, 121.9, 113.6 (d, $J_{C–F}$ = 24.8 Hz), 107.8 (d, $J_{C–F}$ = 24.0 Hz) ppm. HRMS (ESI): calcd for $C_{14}H_8FS_2$ $[M+H]^+$ 259.0046, found 259.0046. The ^{1}H NMR and ^{13}C NMR of **4b** are consistent with the previous report.[7]



3-Chlorobenzo[*b*]benzo[4,5]thieno[2,3-*d*]thiophene (4c)

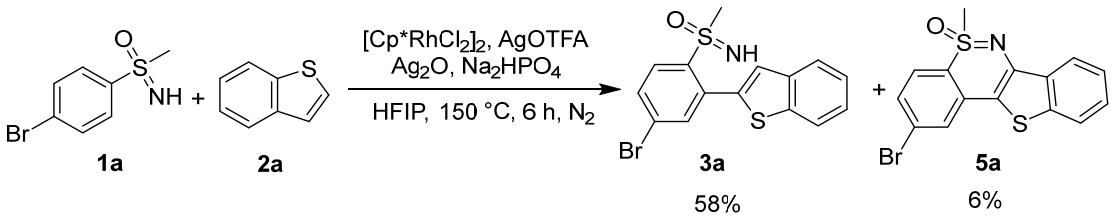
Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 40/1, v/v) afforded **4c** as a yellow solid (11.8 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94-7.81 (m, 4H), 7.49-7.41 (m, 2H), 7.36 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H). ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 140.4, 135.2, 134.3, 132.9, 132.5, 131.3, 125.6, 125.4, 125.2, 125.1, 124.2, 121.9, 121.4 ppm. The ^{1}H NMR and ^{13}C NMR of **4c** are consistent with the previous report.[8]



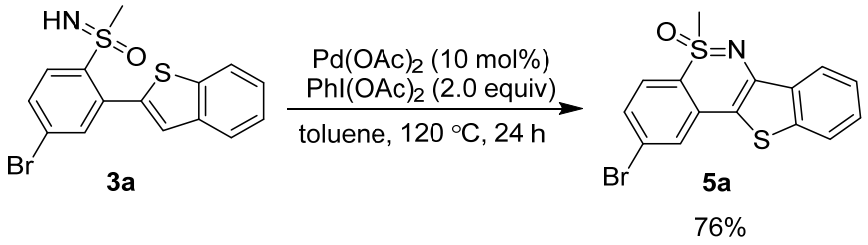
3-Phenylbenzo[*b*]benzo[4,5]thieno[2,3-*d*]thiophene (4d)

Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 40/1, v/v) afforded **4d** as a white solid (17.1 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (s, 1H), 7.97-7.88 (m, 3H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.50-7.36 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4, 141.4, 141.0, 140.3, 138.6, 134.2, 133.8, 133.6, 133.2, 129.0, 127.6, 125.2, 125.1, 124.7, 124.4, 124.2, 121.8, 120.1 ppm. HRMS (ESI): calcd for $C_{20}H_{13}S_2$ $[M+H]^+$ 317.0453, found 317.0451.

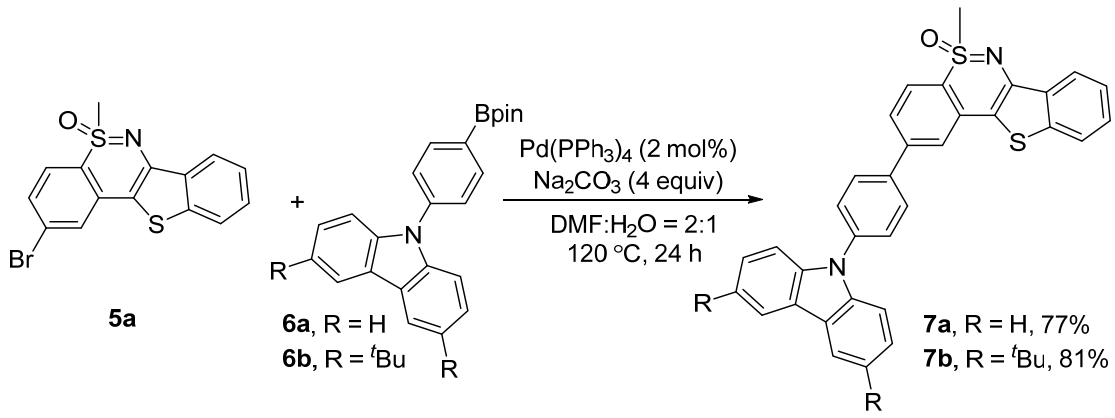
VII. Synthesis of thermally activated delayed fluorescence molecules



According to the conditions (Table S5, Entry 6). Purification *via* column chromatography on silica gel (petroleum ether/EtOAc) afforded **3a** as a yellow solid (21.2 mg, 58% yield) and **5a** as a yellow solid (2.2 mg, 6%).

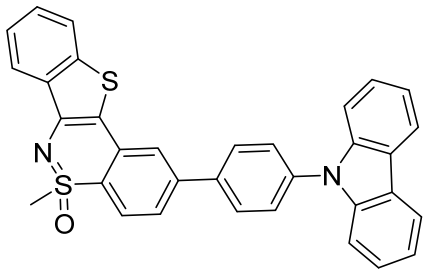


Intramolecular annulation of 3a: a Schlenk tube (25 mL) equipped with a stir bar was loaded with 2-(5-bromo-2-(*S*-methylsulfonimidoyl)phenyl)benzo[*b*]thiophene **3a** (36.5 mg, 0.1 mmol), $Pd(OAc)_2$ (10 mol%) and $PhI(OAc)_2$ (2.0 equiv). Then, dry toluene (2.0 mL) was added, and the mixture was allowed to stir at 120 ºC in oil bath for 24 h. After cooling to room temperature, the mixture was filtered through a short celite pad and washed with dichloromethane (3 × 20 mL). The filtrate was concentrated, and the product was purified by column chromatography using silica gel as stationary phase and a mixture of hexane and ethyl acetate as eluent to give pure product 2-bromo-5-methylbenzo[*e*]benzo[4,5]thieno[3,2-*c*][1,2]thiazine 5-oxide (**5a**) as a yellow solid (27.5 mg, 76% yield).[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06-8.04 (m, 1H), 7.79-7.73 (m, 3H), 7.57 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.46-7.39 (m, 2H), 3.63 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.5, 138.2, 135.5, 134.2, 130.0, 128.4, 127.4, 126.8, 126.1, 124.7, 123.0, 122.9, 119.2, 109.5, 45.8 ppm. HRMS (ESI): calcd for $C_{15}H_{11}{}^{79}BrNOS_2$ $[M+H]^+$ 363.9460, found 363.9462.



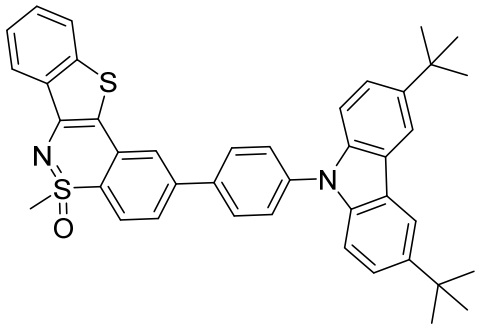
Synthesis of 7: a Schlenk tube with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (2.3 mg, 2.0 mol%), Na_2CO_3 (42.4 mg, 4.0 equiv), **5a** (36.3 mg, 0.1 mmol, 1.0 equiv), aryl borates **6** (1.1 equiv, 0.11 mmol), DMF (1.4 mL) and H_2O (0.7 mL) under an N_2 atmosphere. The resulting mixture was stirred at 120 ºC in oil bath for 24 h and then

removes solvent under vacuum. The solution was filtered through a celite pad and washed with 10-25 mL of dichloromethane. The filtrate was concentrated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to provide the desired product.[10]



2-(4-(9*H*-Carbazol-9-yl)phenyl)-5-methylbenzo[*e*]benzo[4,5]thieno[3,2-*c*][1,2]Thazine 5-oxide (7a)

Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **7a** as a yellow solid (38.9 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, J = 7.6 Hz, 2H), 8.11-8.09 (m, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.94-7.92 (m, 2H), 7.84-7.75 (m, 5H), 7.53-7.43 (m, 6H), 7.33 (t, J = 7.6 Hz, 2H), 3.72 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.9, 145.6, 141.0, 141.0, 140.8, 129.2, 129.1, 127.8, 127.7, 127.1, 126.3, 126.2, 126.0, 125.5, 124.6, 123.7, 123.4, 123.0, 122.6, 120.61, 120.58, 120.4, 109.9, 109.8, 45.9 ppm. HRMS (ESI): calcd for $C_{33}H_{23}N_2OS_2$ $[M+H]^+$ 527.1246, found 527.1245.



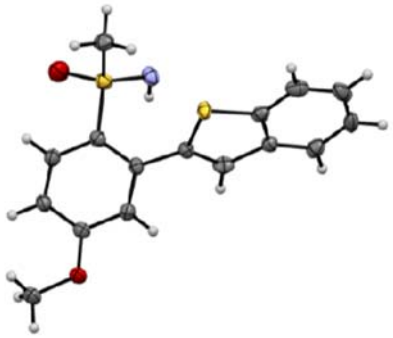
2-(4-(3,6-Di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)-5-methylbenzo[*e*]benzo[4,5]thieno[3,2-*c*][1,2]thiazine 5-oxide (7b)

Purification *via* column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **7b** as a yellow solid (51.7 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (s, 2H), 8.11-8.08 (m, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 2H),

7.84-7.78 (m, 3H), 7.74 (d, J = 8.4 Hz, 2H), 7.52-7.42 (m, 6H), 3.72 (s, 3H), 1.49 (s, 18H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.6, 145.5, 143.2, 138.9, 137.8, 137.5, 135.7, 133.1, 131.8, 128.8, 127.0, 126.9, 125.8, 125.2, 124.4, 123.9, 123.7, 123.6, 122.9, 122.8, 122.4, 119.4, 116.3, 109.2, 45.7, 34.8, 32.0 ppm. HRMS (ESI): calcd for $C_{41}H_{39}N_2OS_2$ $[M+H]^+$ 639.2498, found 639.2493.

VIII. Single-crystal X-ray structure of 3v

Table S6. Crystaldata and structure refinement for **3v**



Identification code	**3v**
Empirical formula	$C_{16}H_{15}NO_2S_2$
Formula weight	317.41
Temperature/K	150.0
Crystal system	monoclinic
Space group	P21/c
a/Å	7.9599(3)
b/Å	11.6425(4)
c/Å	15.6846(4)
α/°	90
β/°	95.3910(10)
γ/°	90
Volume/Å^3	1447.11(8)
Z	4
ρ_{calc}g/cm^3	1.457

μ/mm^{-1}	0.371
F(000)	664.0
Crystal size/mm^3	0.43 × 0.25 × 0.17
Radiation	MoKa (λ = 0.71073)
2Θ range for data collection/°	6.22 to 55.054
Index ranges	$-10 \leq h \leq 10$, $-15 \leq k \leq 15$, $-19 \leq l \leq 20$
Reflections collected	39620
Independent reflections	3292 [Rint = 0.0821，Rsigma = 0.0370]
Data/restraints/parameters	3292/7/215
Goodness-of-fit on F_2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0399， wR_2 = 0.0877
Final R indexes [all data]	R_1 = 0.0628， wR_2 = 0.0967
Largest diff. peak/hole / e $Å^{-3}$	0.45/-0.36

IX. References

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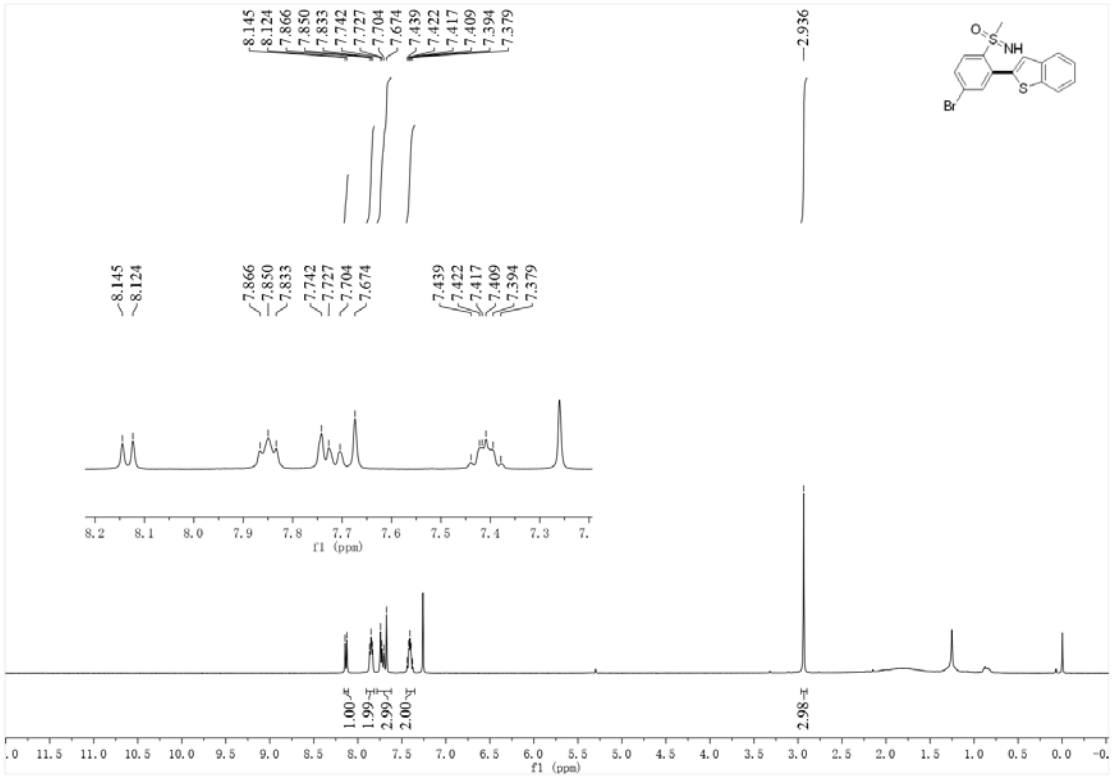
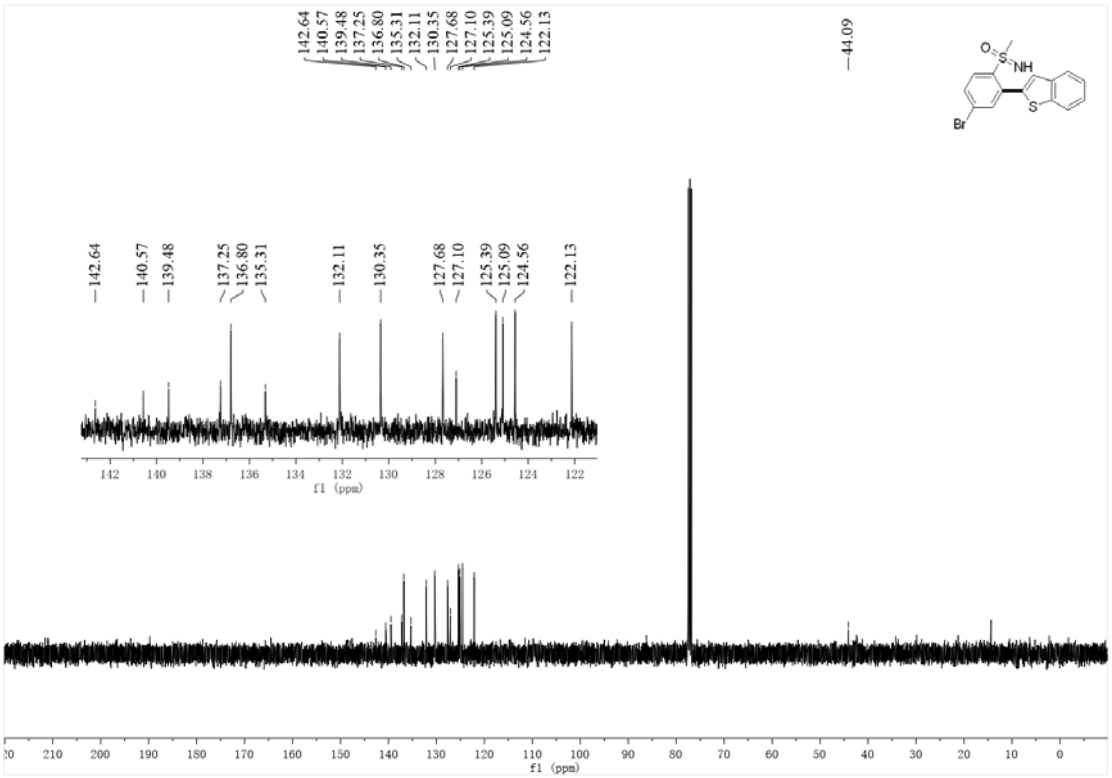
(10) M. Wang, M. Zhang, Y. Luo, Z. Liu, C. Yang, J. Lan, D. Wu and J. You, *Org. Lett.,* **2020**, *22*, 135-139.

X. Copies of ^{1}H and ^{13}C NMR spectra

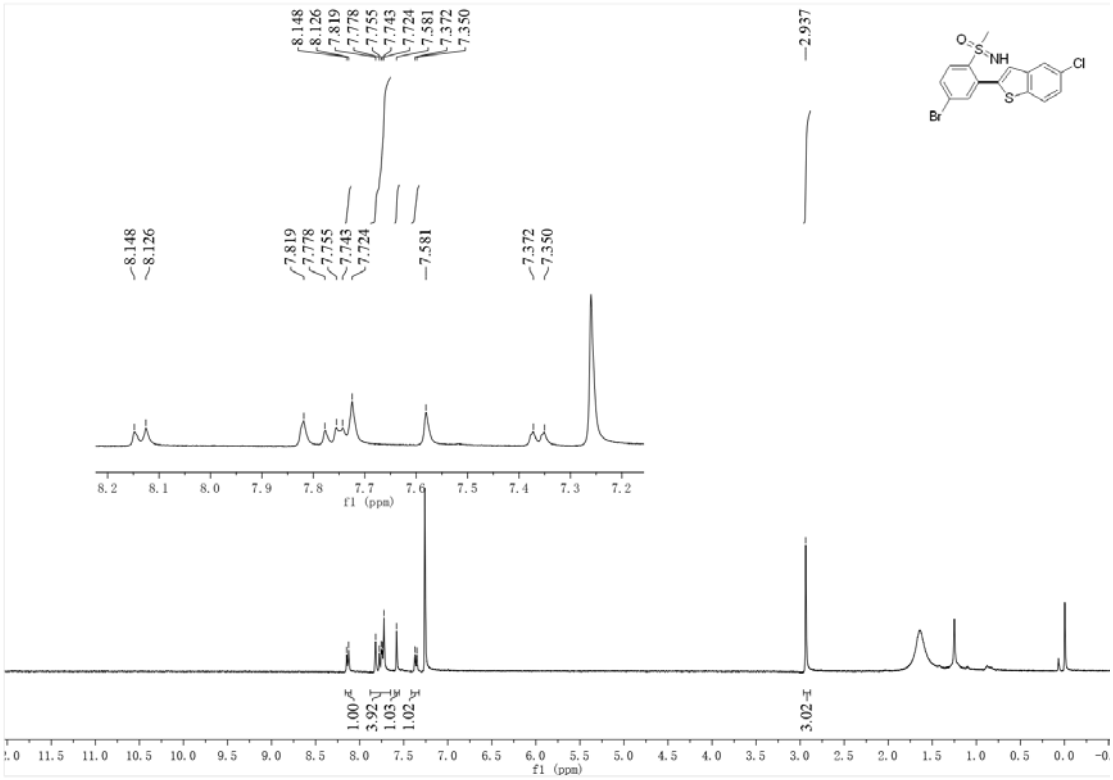
^{1}H NMR (400 MHz) spectrum of **3a** in $CDCl_3$



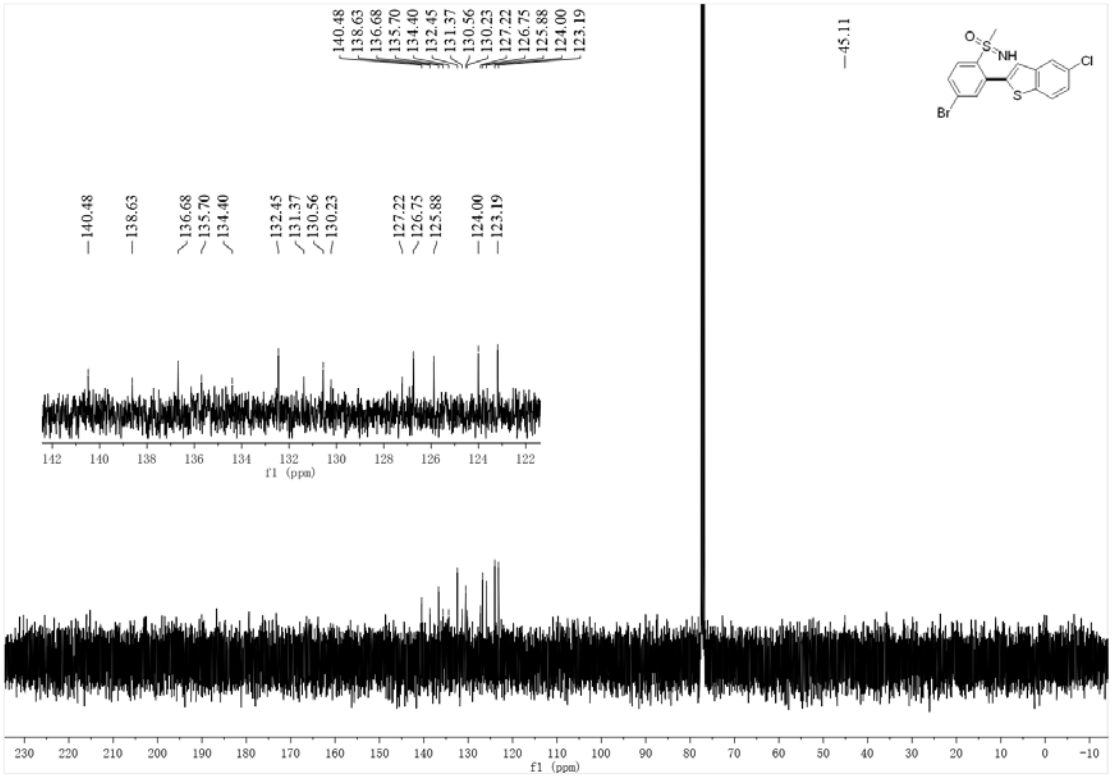
^{13}C NMR (100 MHz) spectrum of **3a** in $CDCl_3$



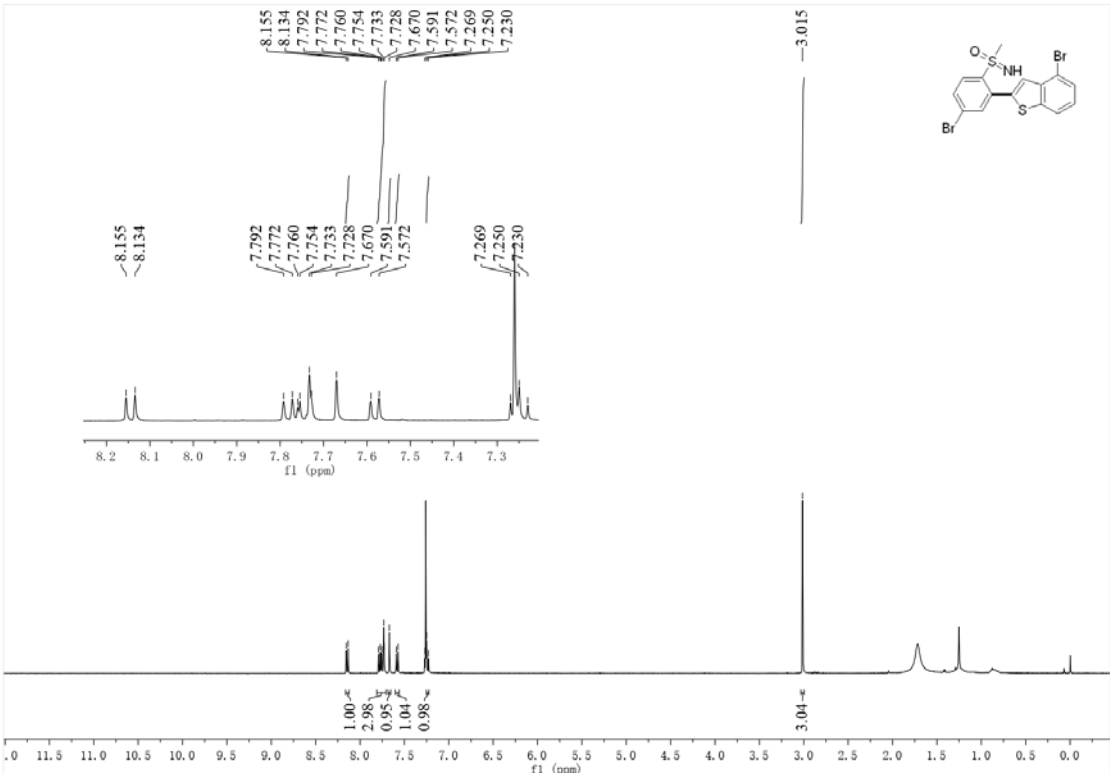
^{1}H NMR (400 MHz) spectrum of **3b** in $CDCl_3$



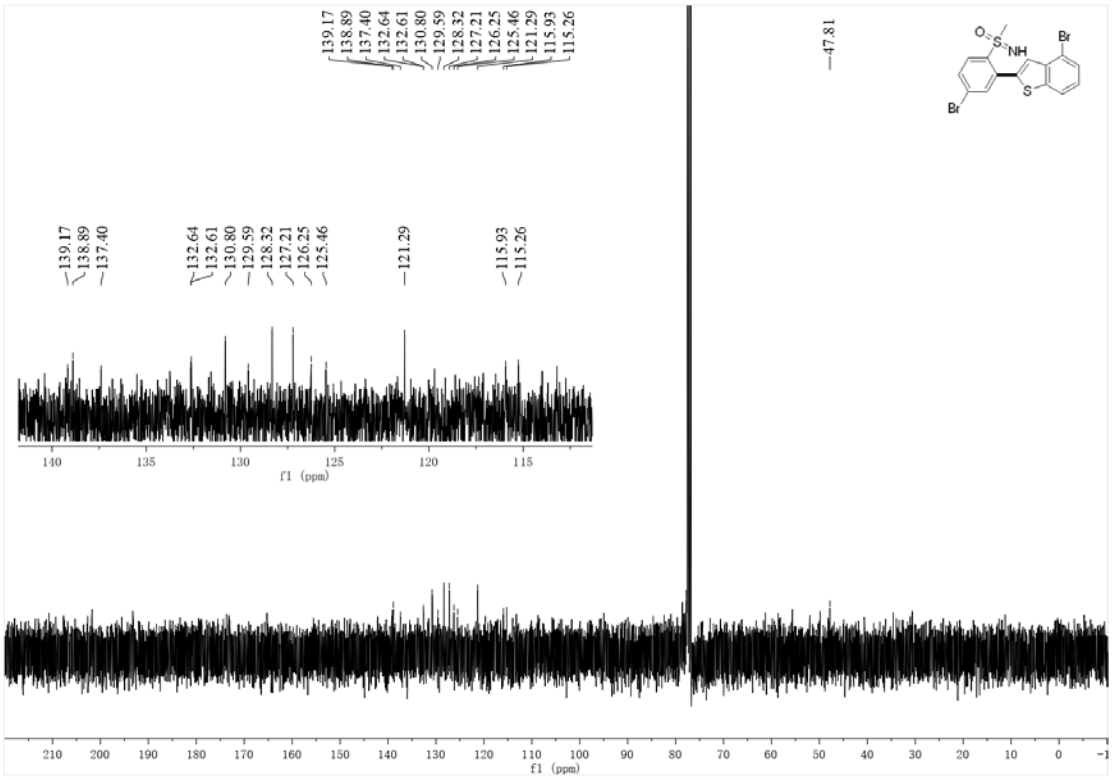
^{13}C NMR (100 MHz) spectrum of **3b** in $CDCl_3$



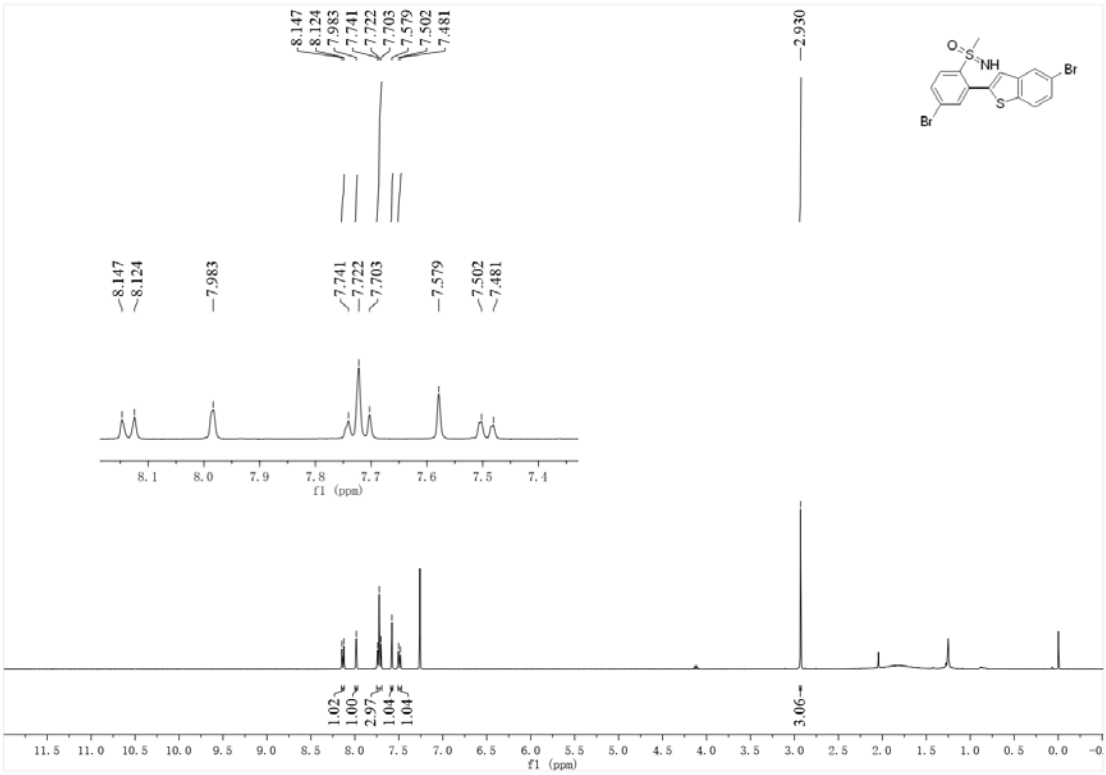
^{1}H NMR (400 MHz) spectrum of **3c** in $CDCl_3$



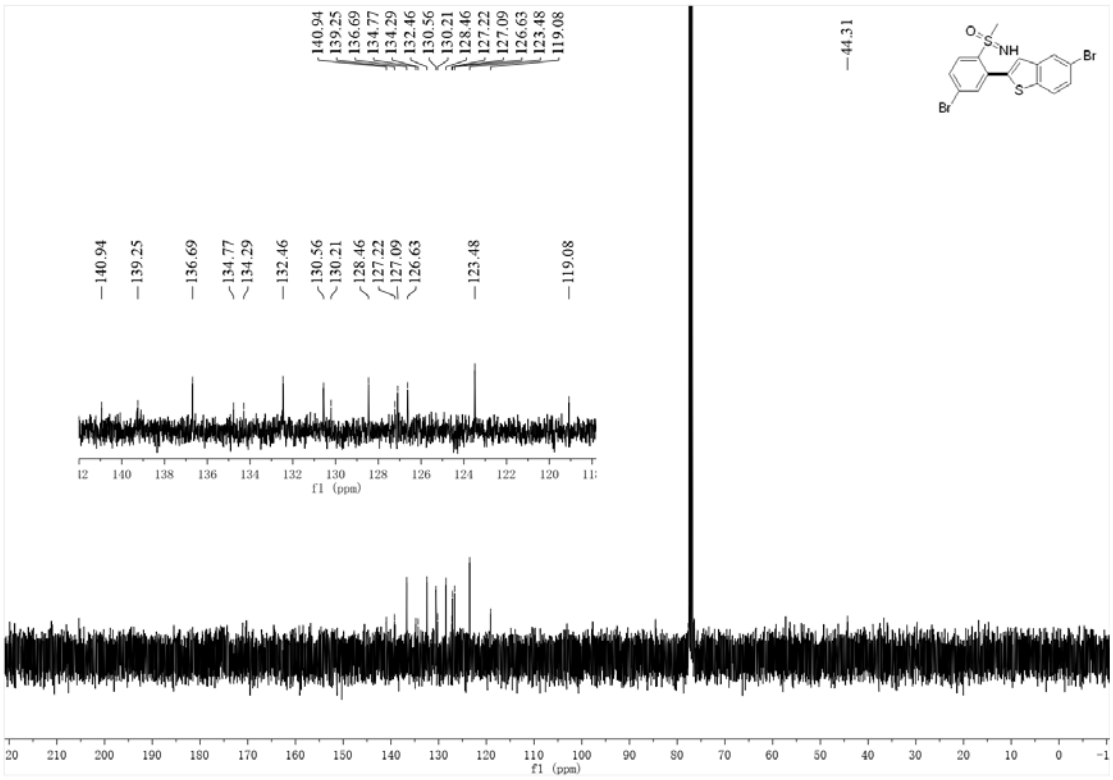
^{13}C NMR (100 MHz) spectrum of **3c** in $CDCl_3$



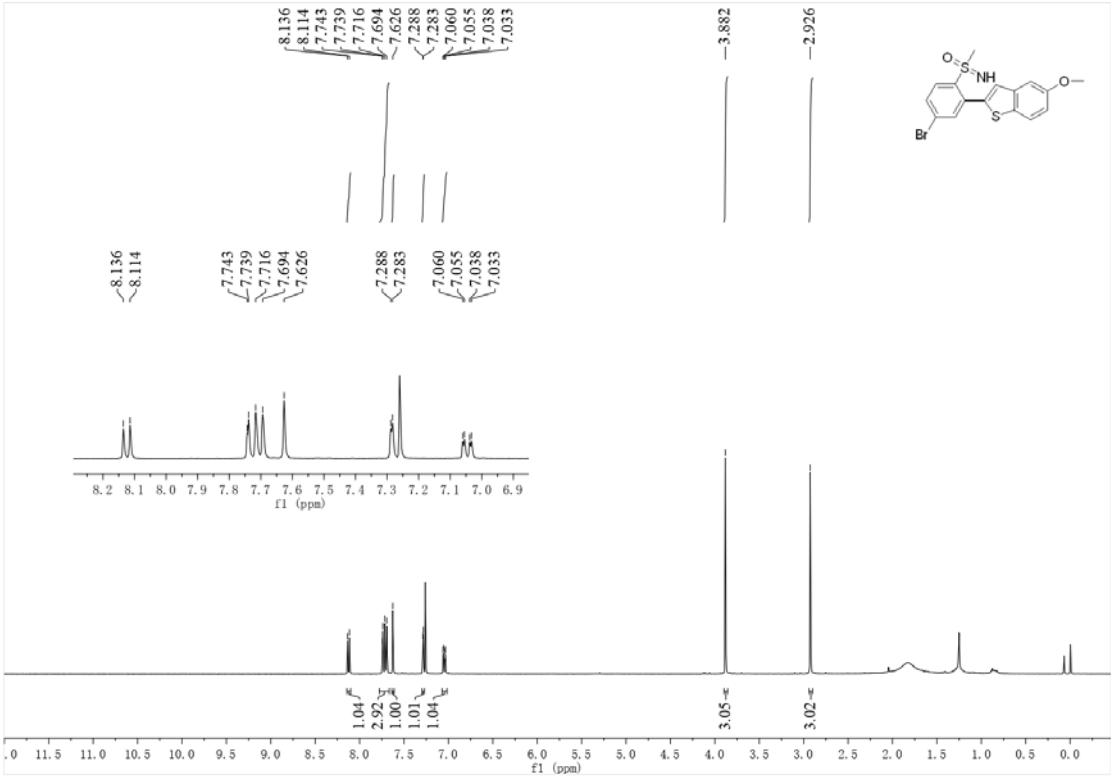
^{1}H NMR (400 MHz) spectrum of **3d** in $CDCl_3$



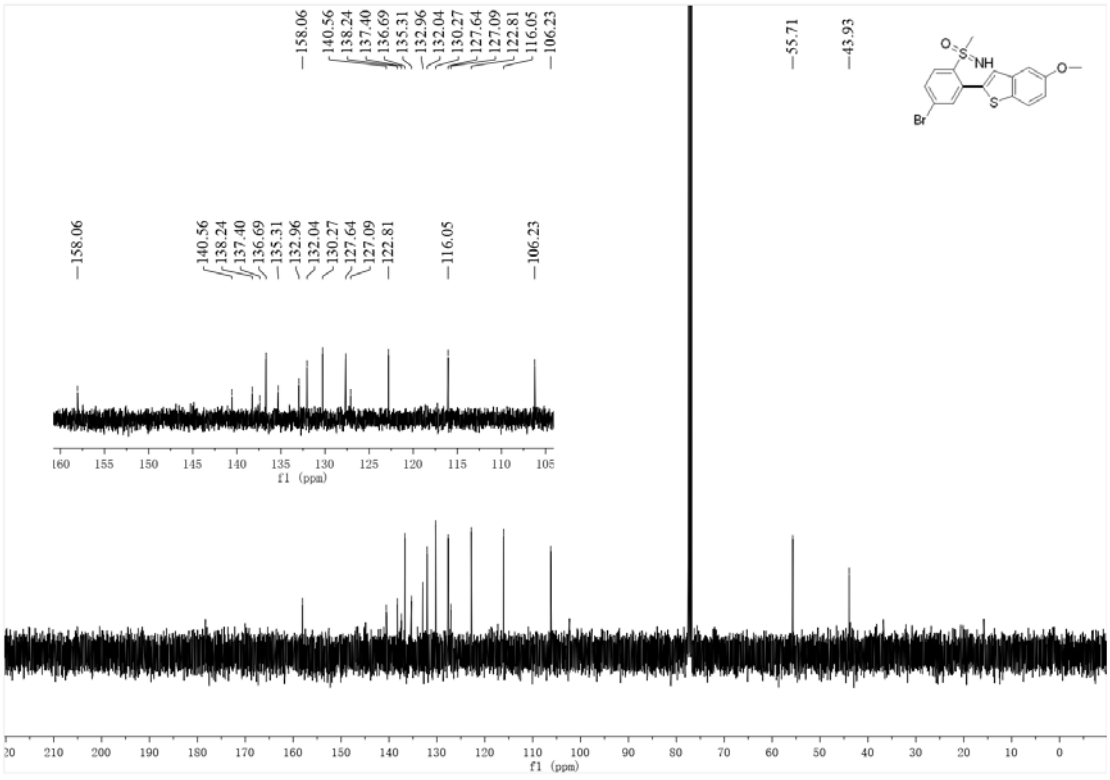
^{13}C NMR (100 MHz) spectrum of **3d** in $CDCl_3$



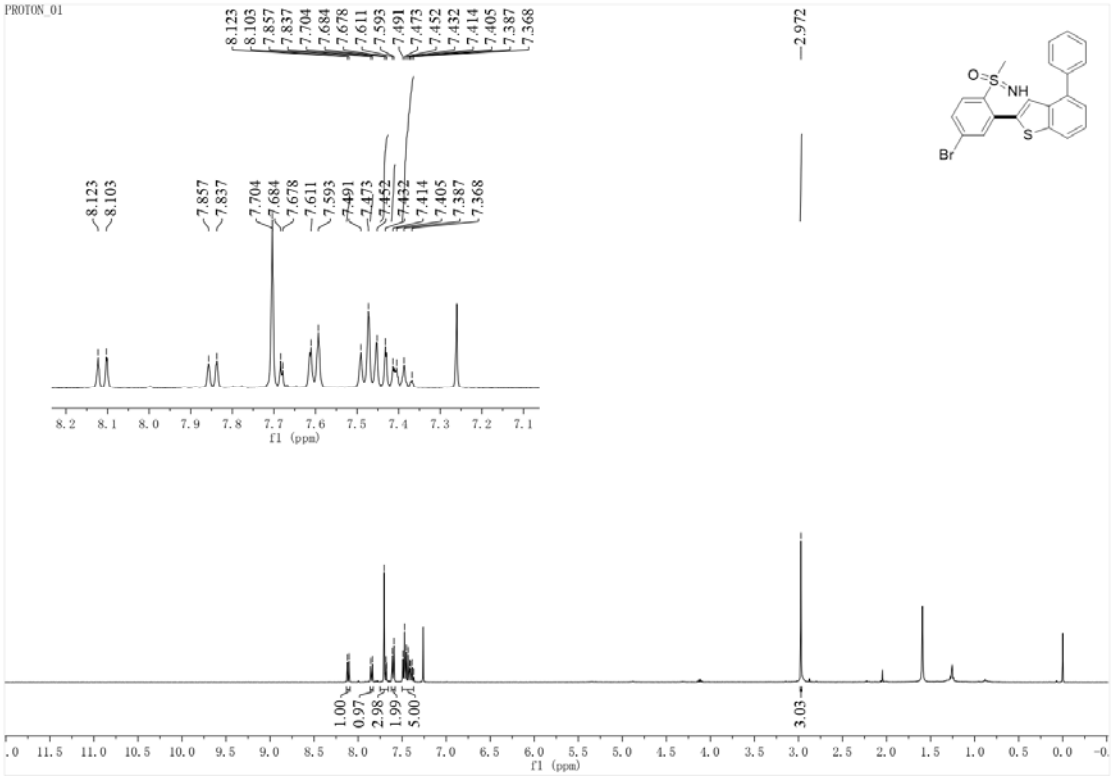
^{1}H NMR (400 MHz) spectrum of **3e** in $CDCl_3$



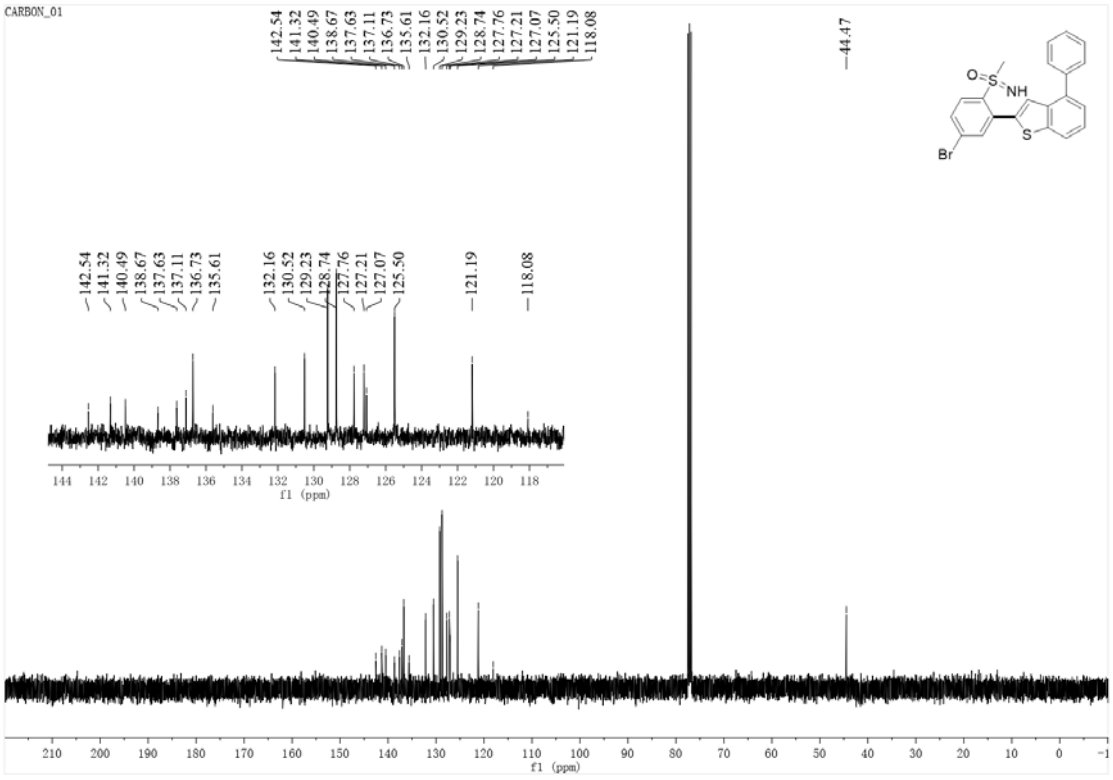
^{13}C NMR (100 MHz) spectrum of **3e** in $CDCl_3$



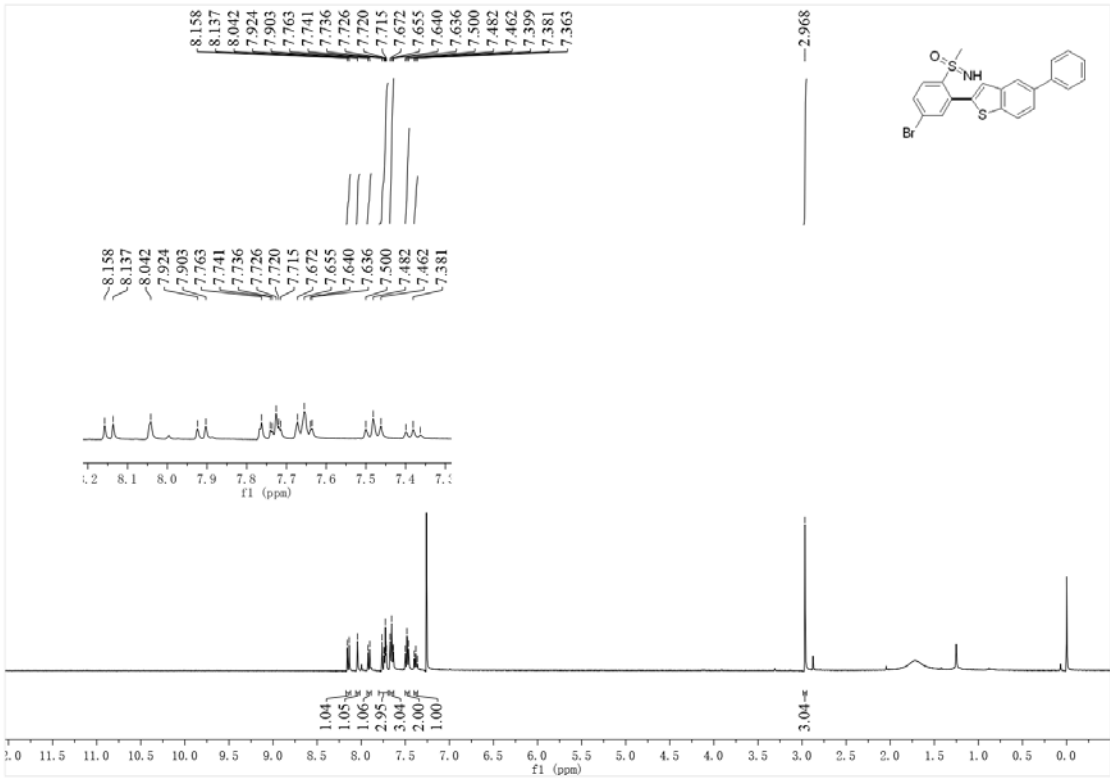
^{1}H NMR (400 MHz) spectrum of **3f** in $CDCl_3$



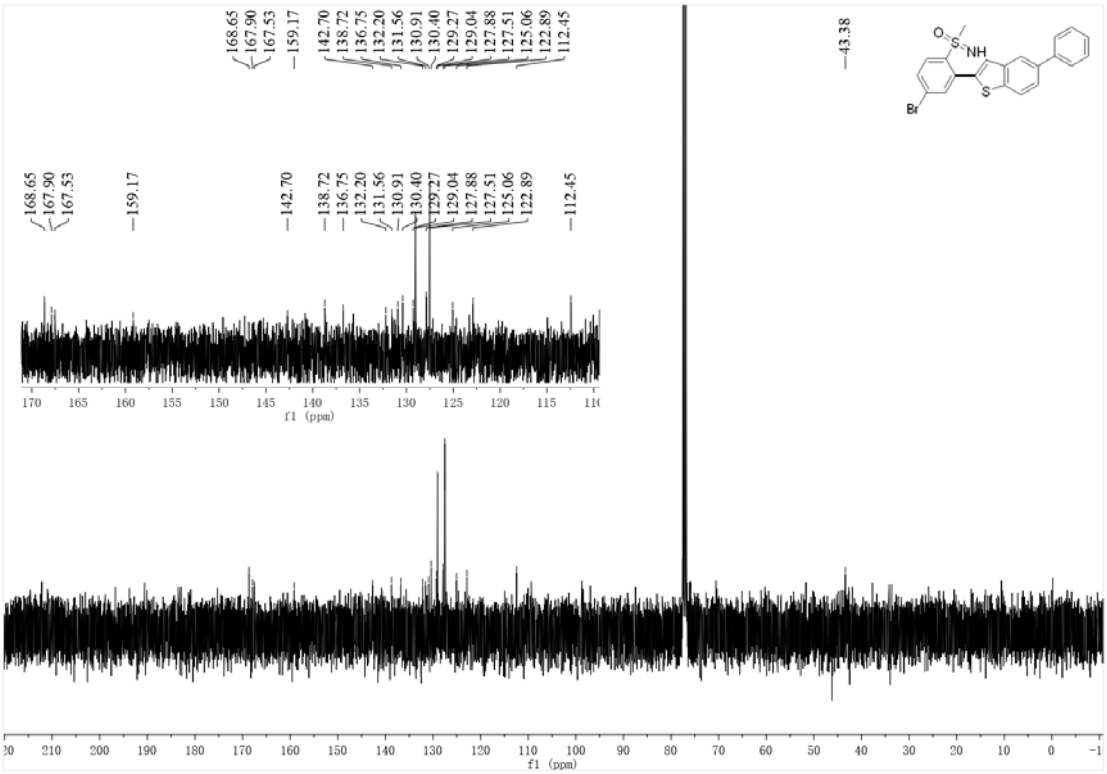
^{13}C NMR (100 MHz) spectrum of **3f** in $CDCl_3$



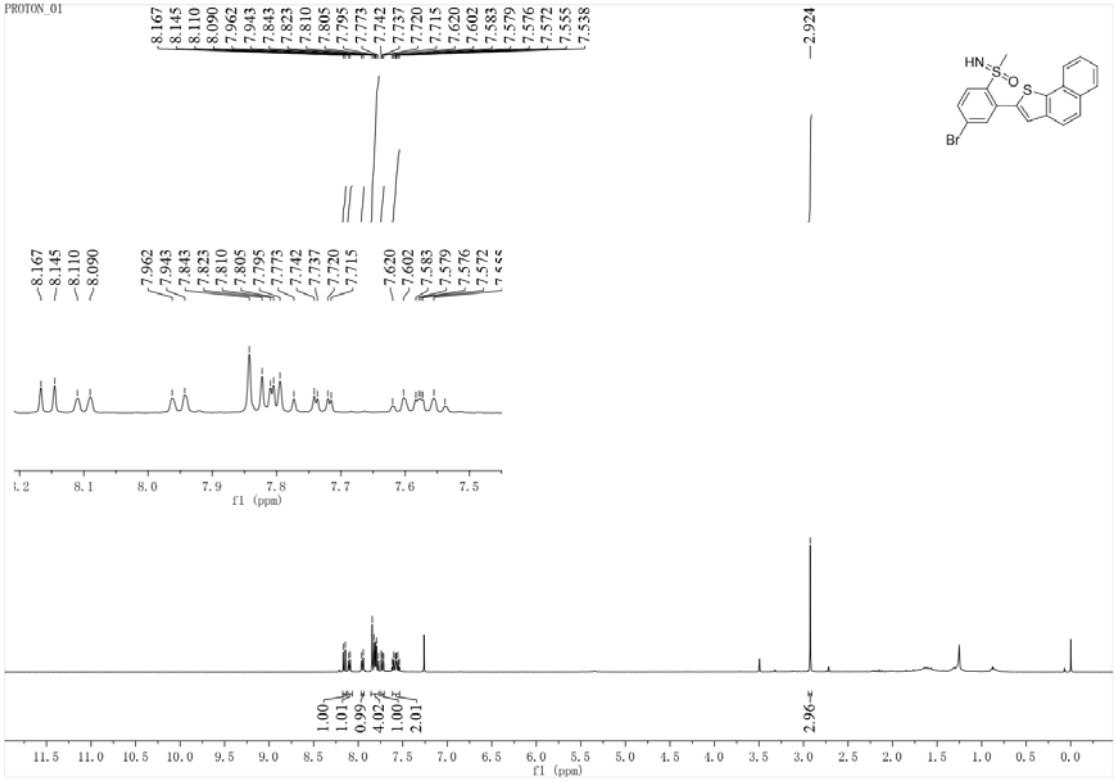
^{1}H NMR (400 MHz) spectrum of **3g** in $CDCl_3$



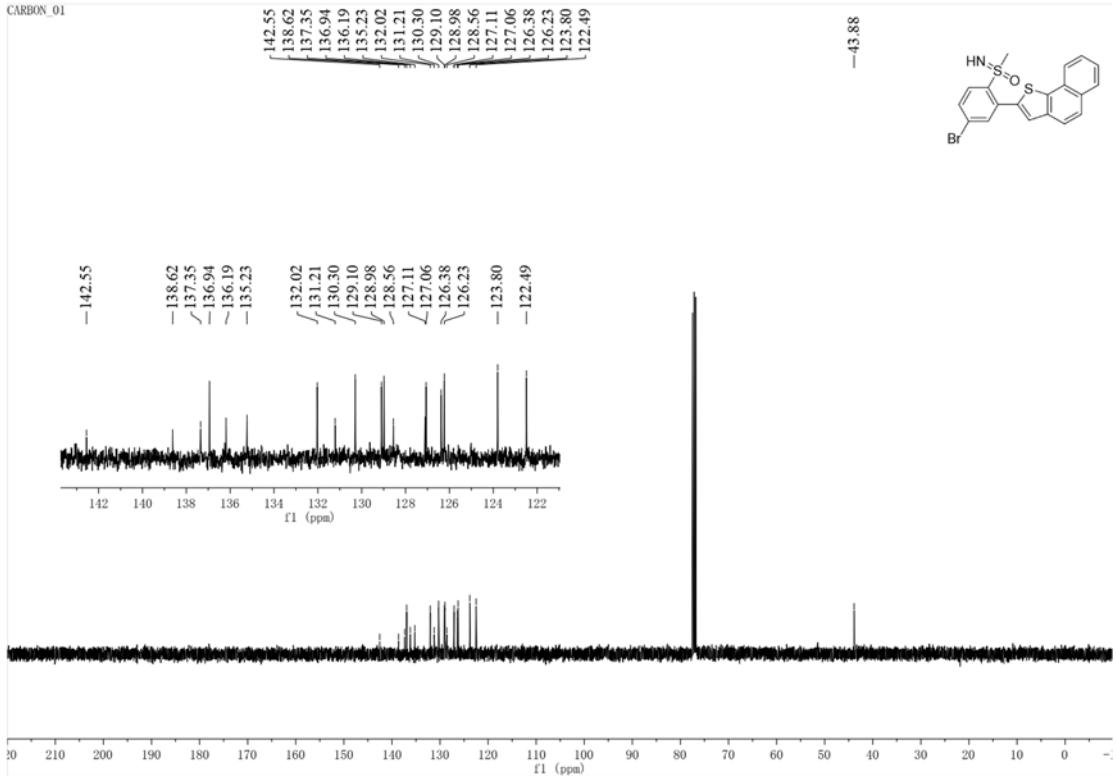
^{13}C NMR (100 MHz) spectrum of **3g** in $CDCl_3$



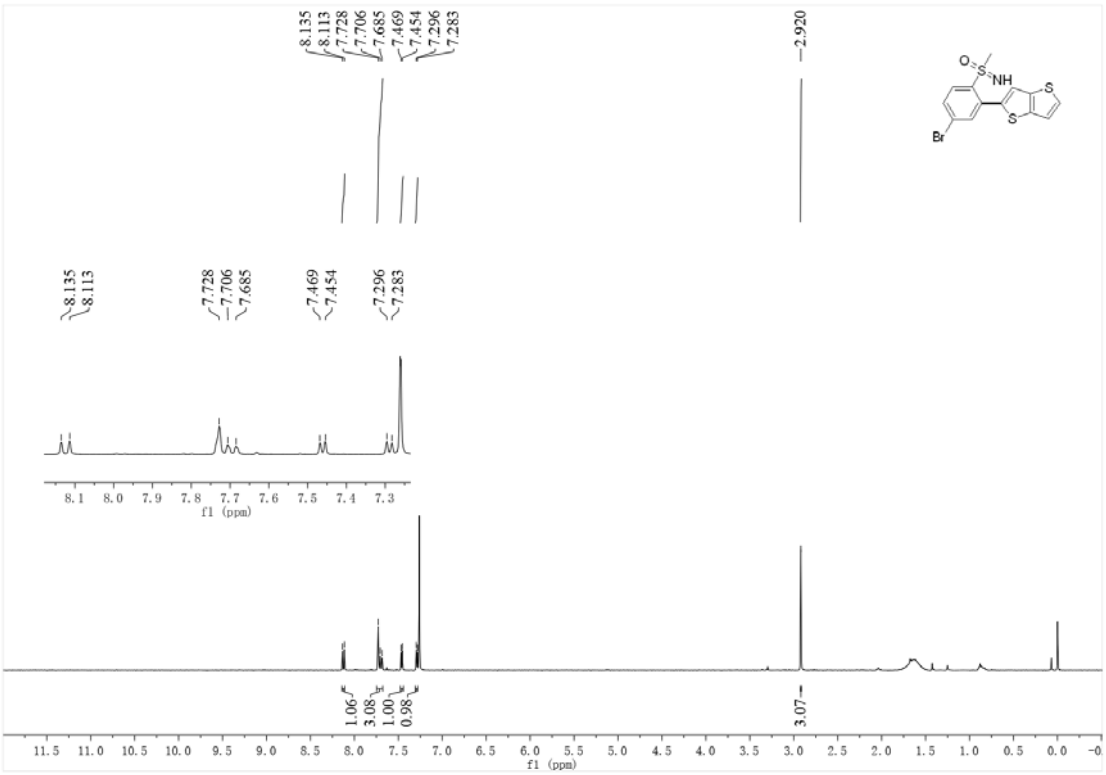
^{1}H NMR (400 MHz) spectrum of **3h** in $CDCl_3$



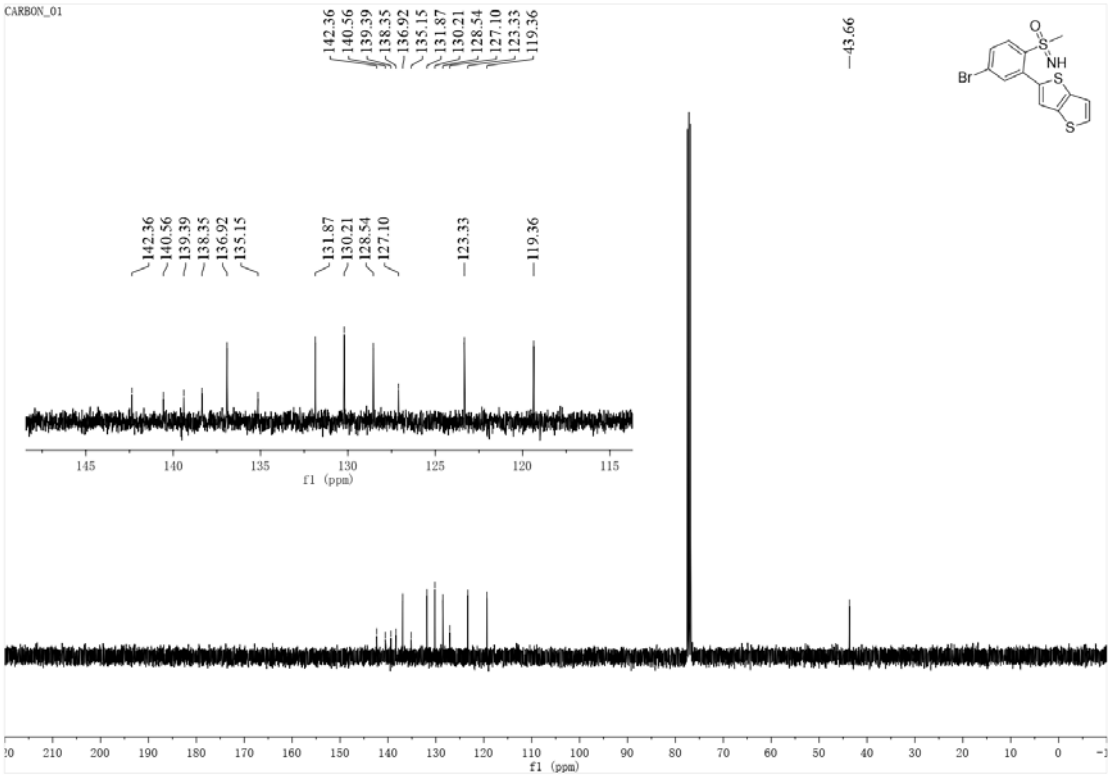
^{13}C NMR (100 MHz) spectrum of **3h** in $CDCl_3$



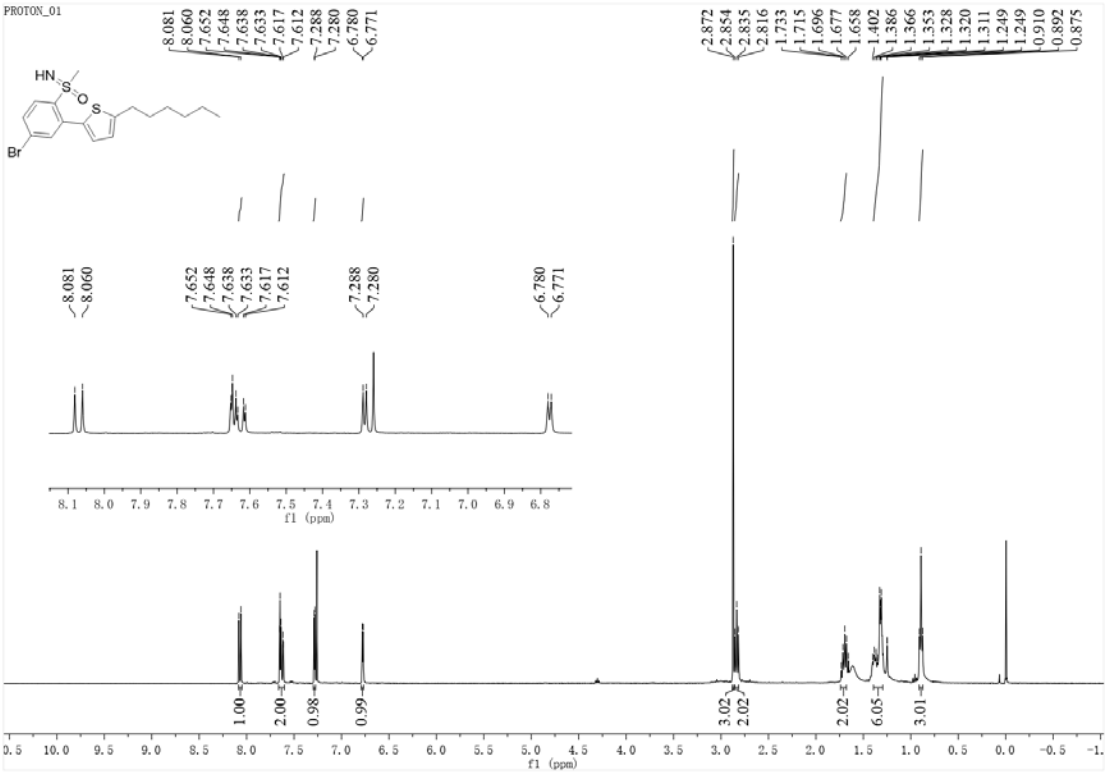
^{1}H NMR (400 MHz) spectrum of **3i** in $CDCl_3$



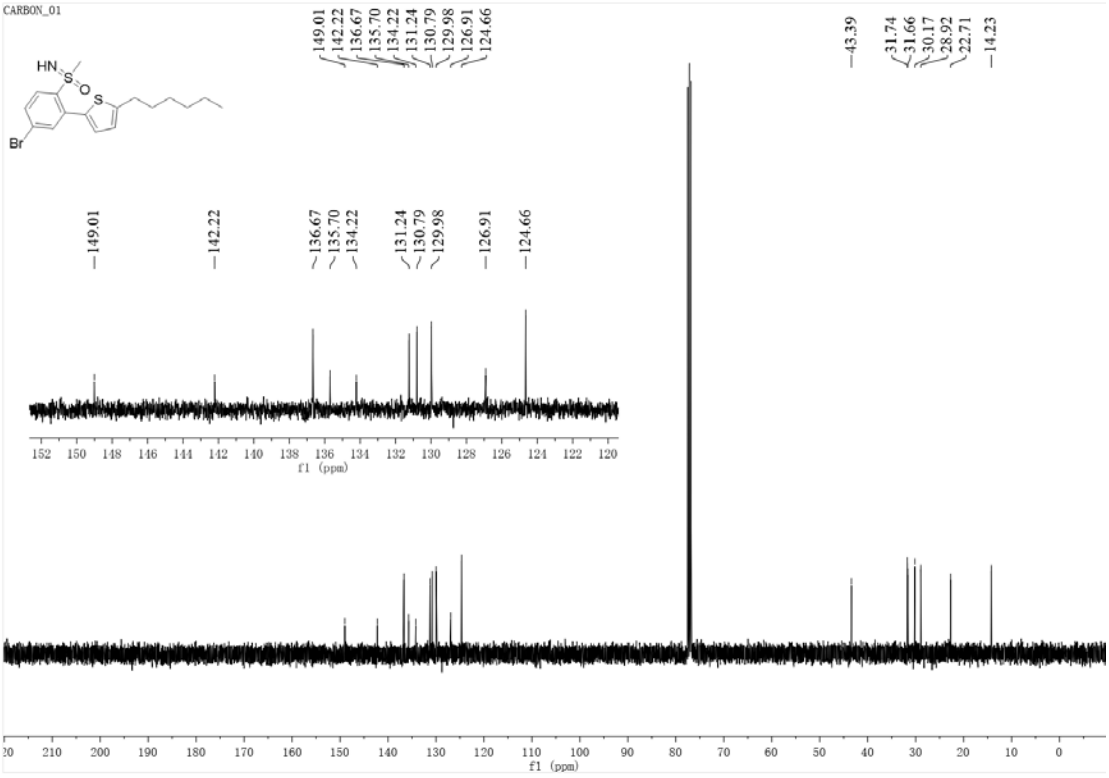
^{13}C NMR (100 MHz) spectrum of **3i** in $CDCl_3$



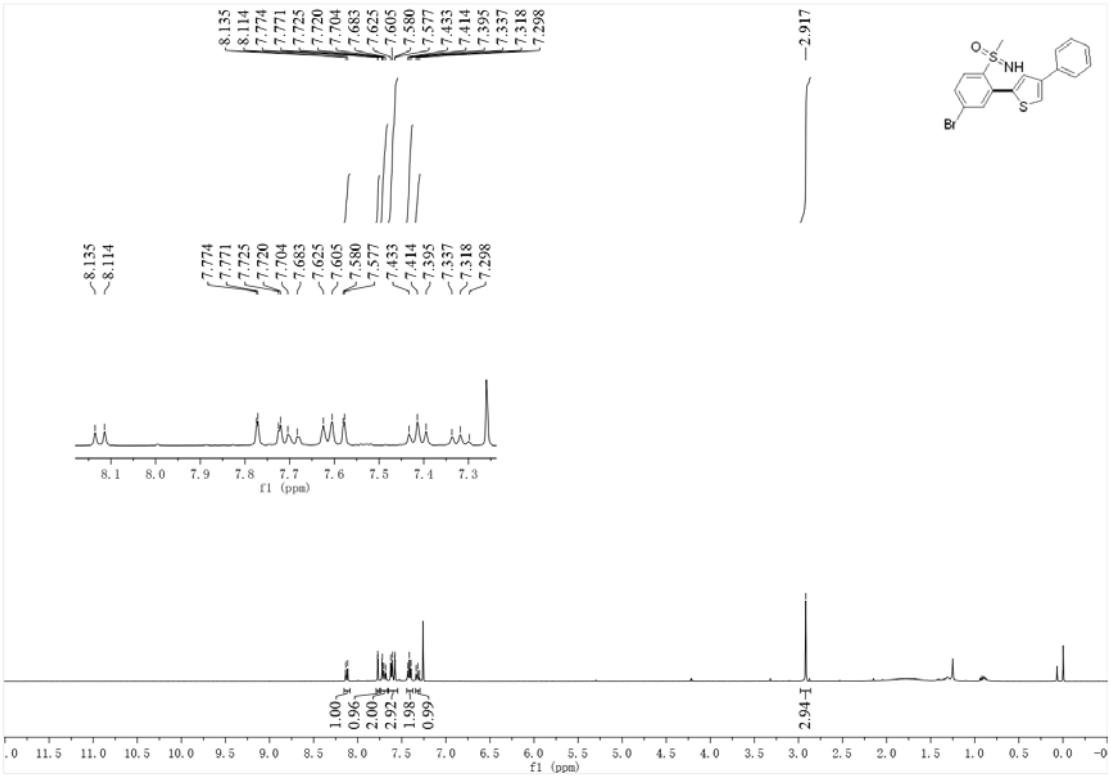
^{1}H NMR (400 MHz) spectrum of **3j** in $CDCl_3$



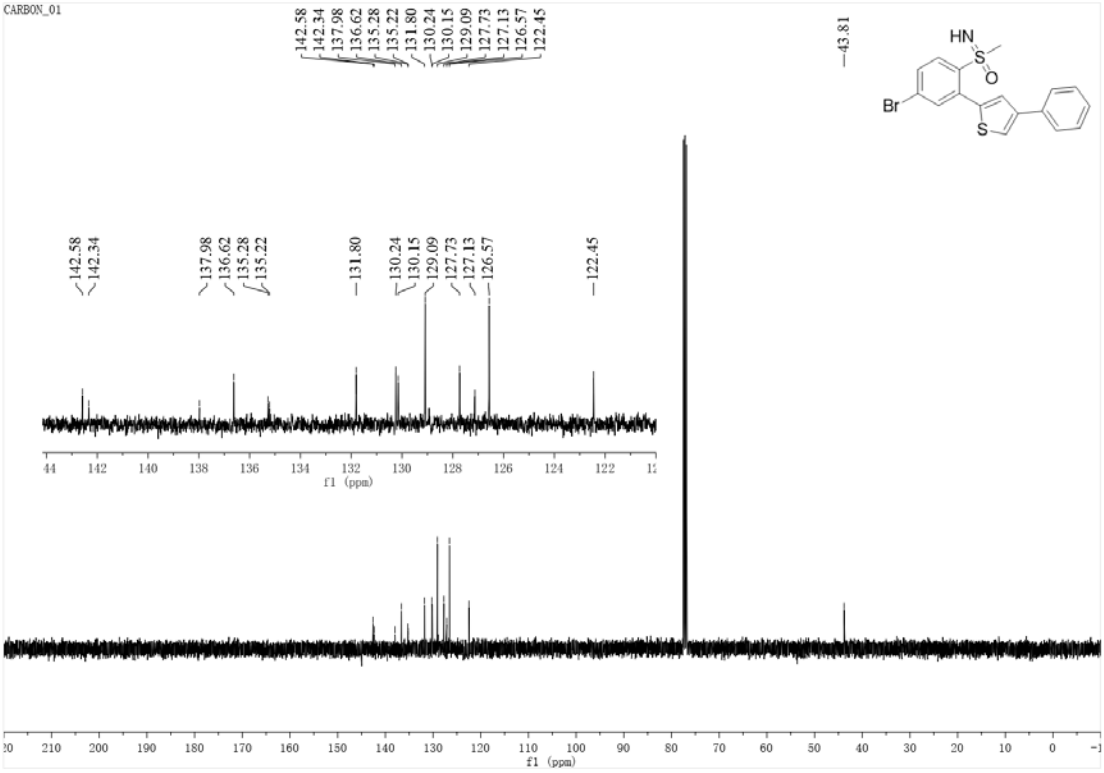
^{13}C NMR (100 MHz) spectrum of **3j** in $CDCl_3$



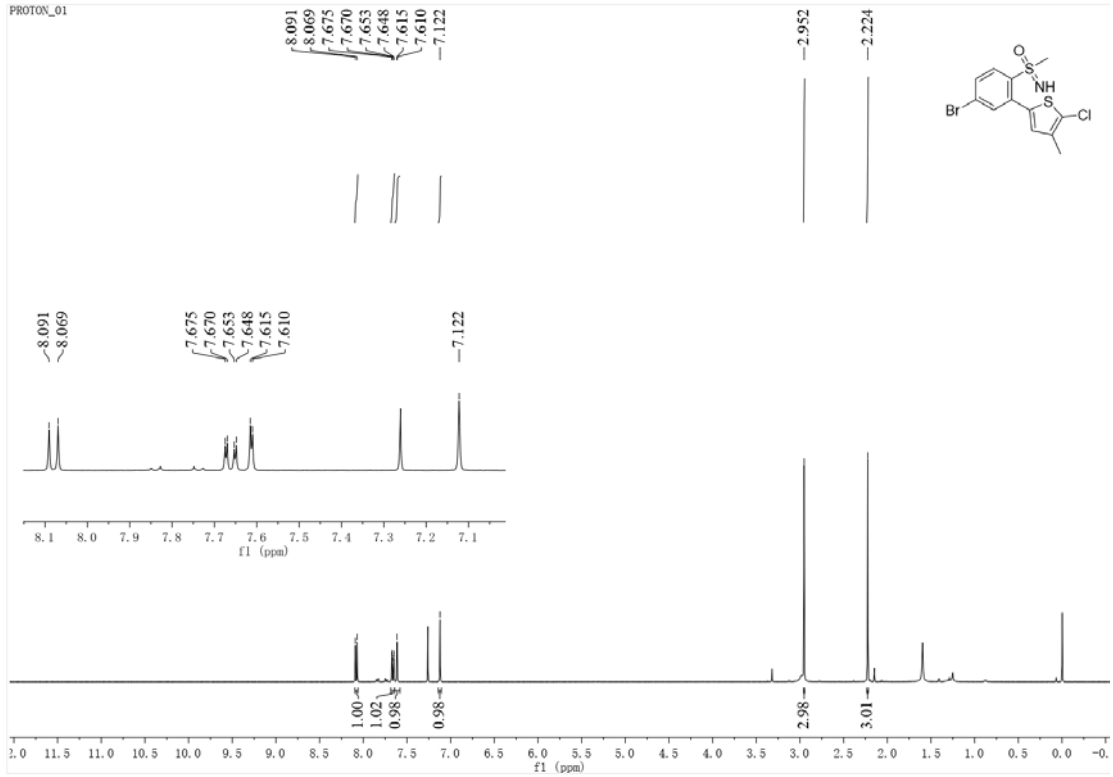
^{1}H NMR (400 MHz) spectrum of **3k** in $CDCl_3$



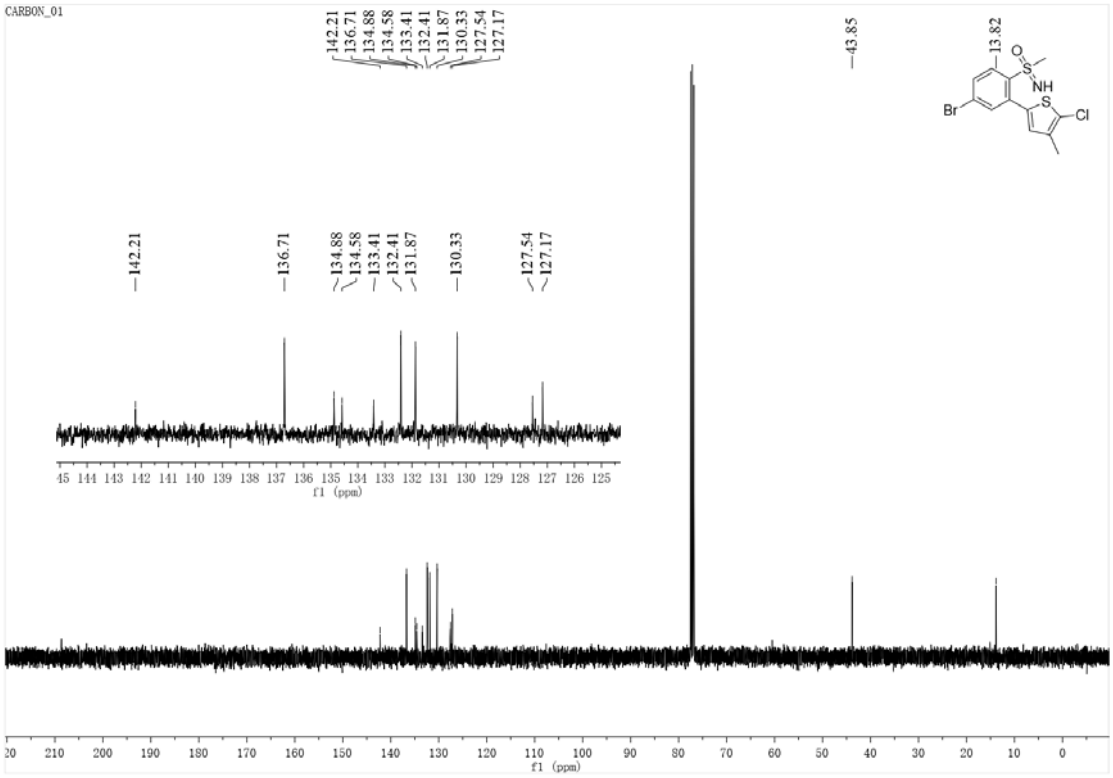
^{13}C NMR (100 MHz) spectrum of **3k** in $CDCl_3$



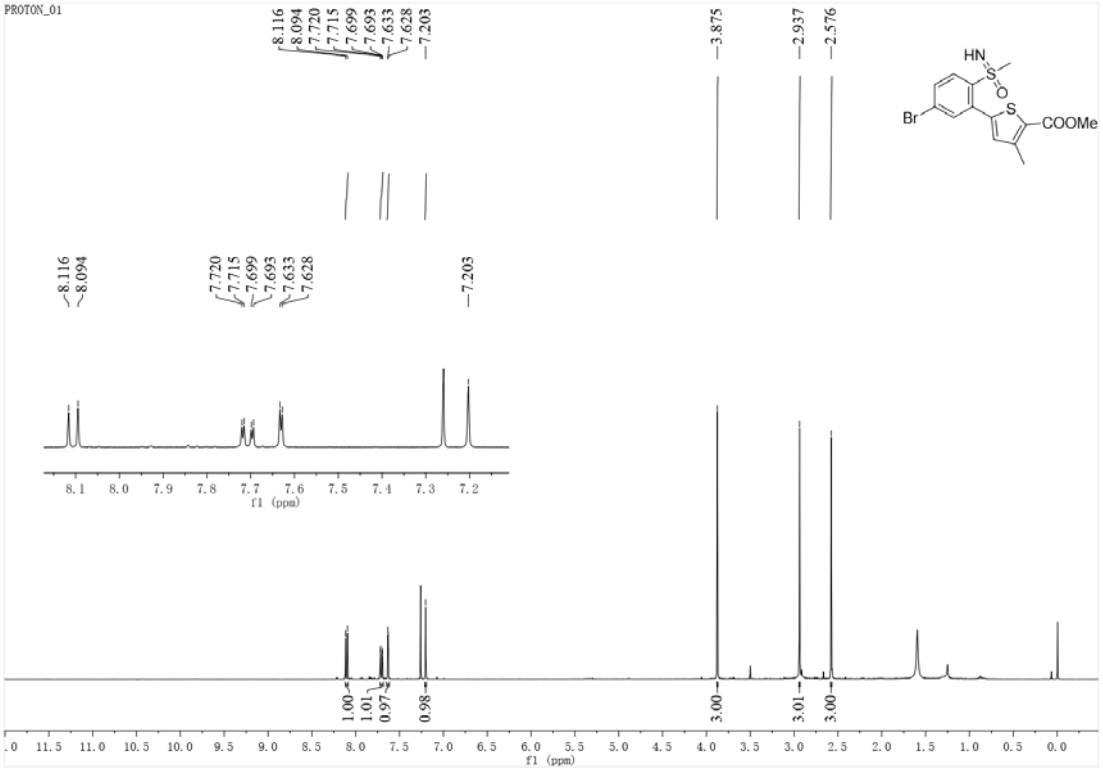
^{1}H NMR (400 MHz) spectrum of **3l** in $CDCl_3$



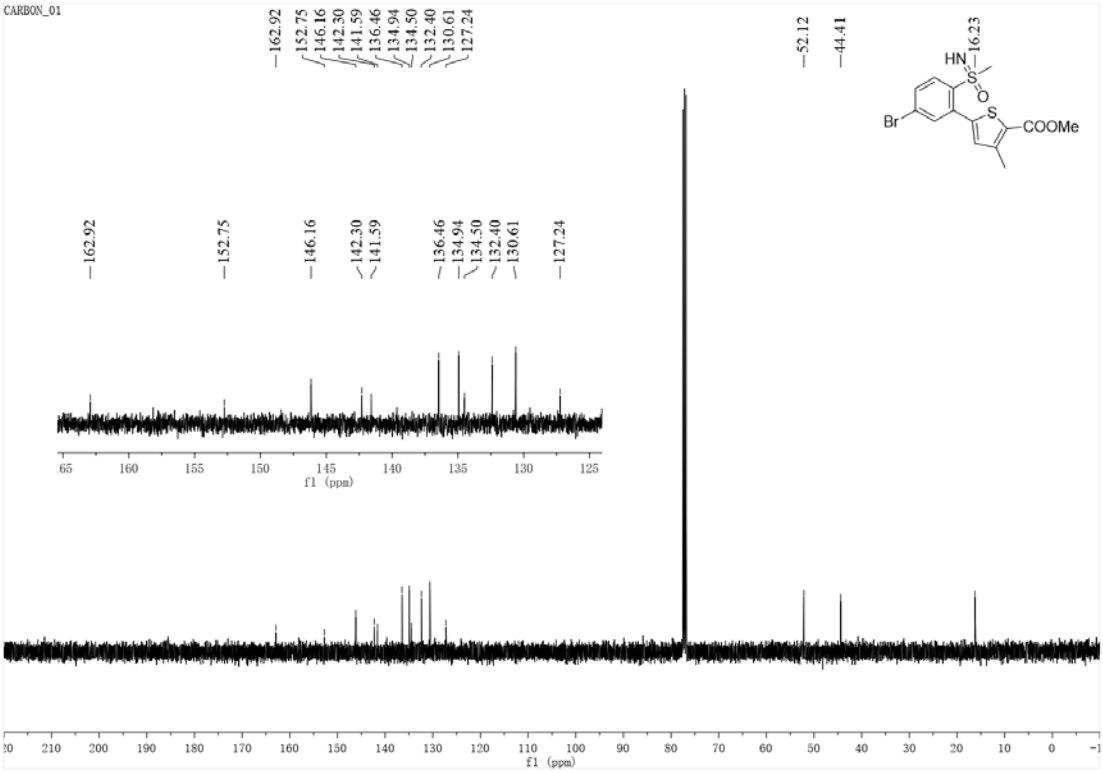
^{13}C NMR (100 MHz) spectrum of **3l** in $CDCl_3$



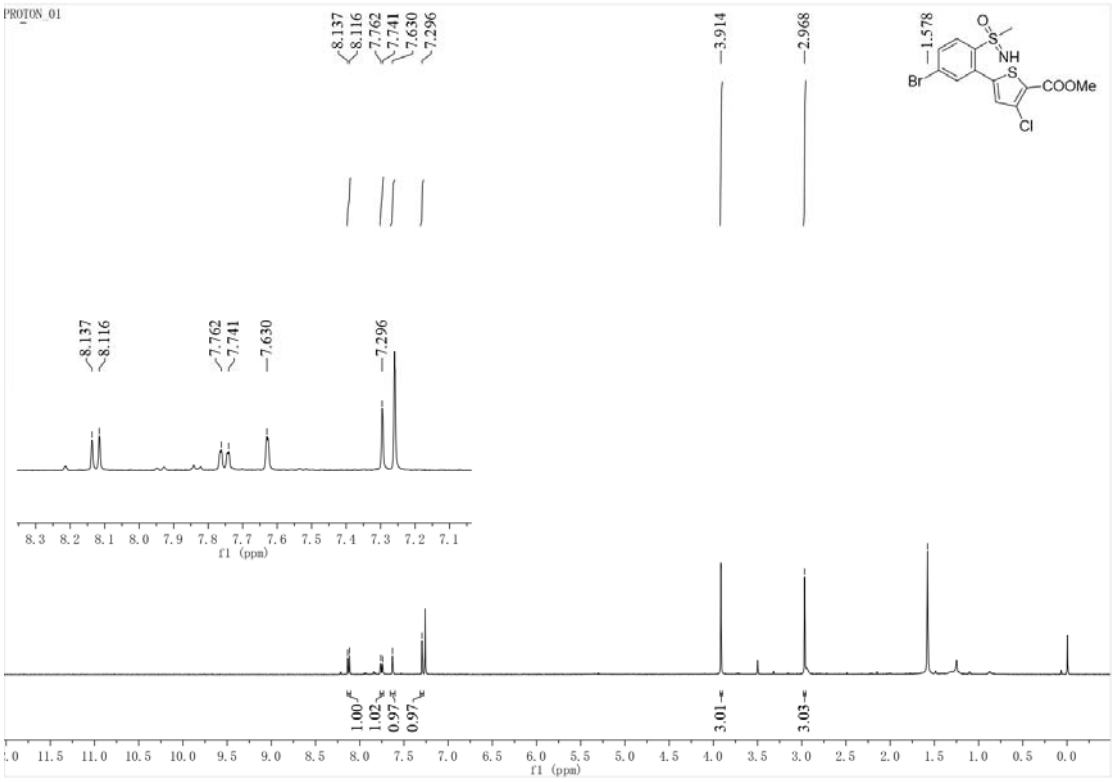
^{1}H NMR (400 MHz) spectrum of **3m** in $CDCl_3$



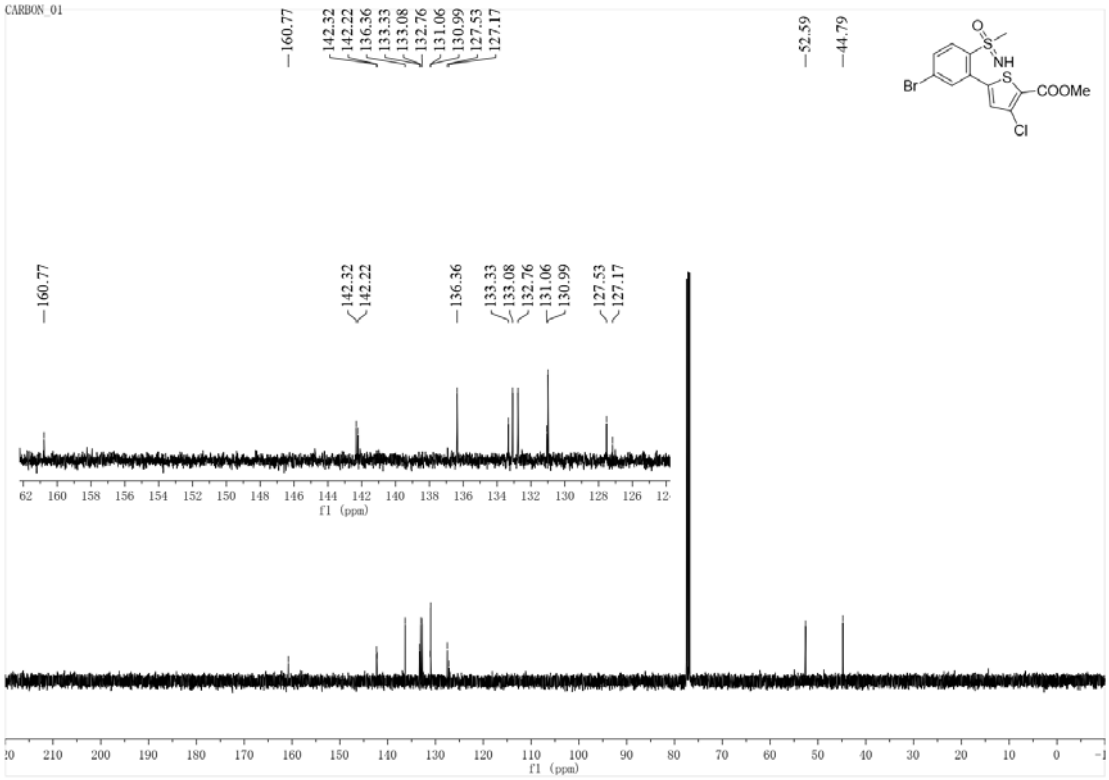
^{13}C NMR (100 MHz) spectrum of **3m** in $CDCl_3$



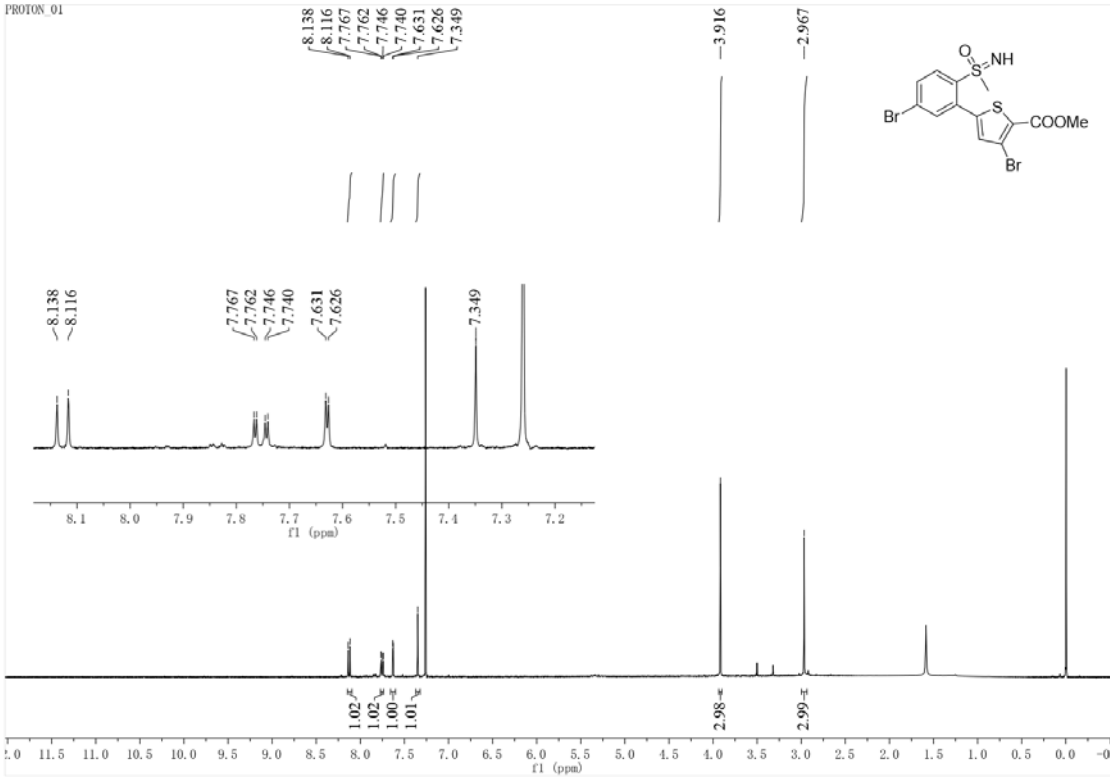
^{1}H NMR (400 MHz) spectrum of **3n** in $CDCl_3$



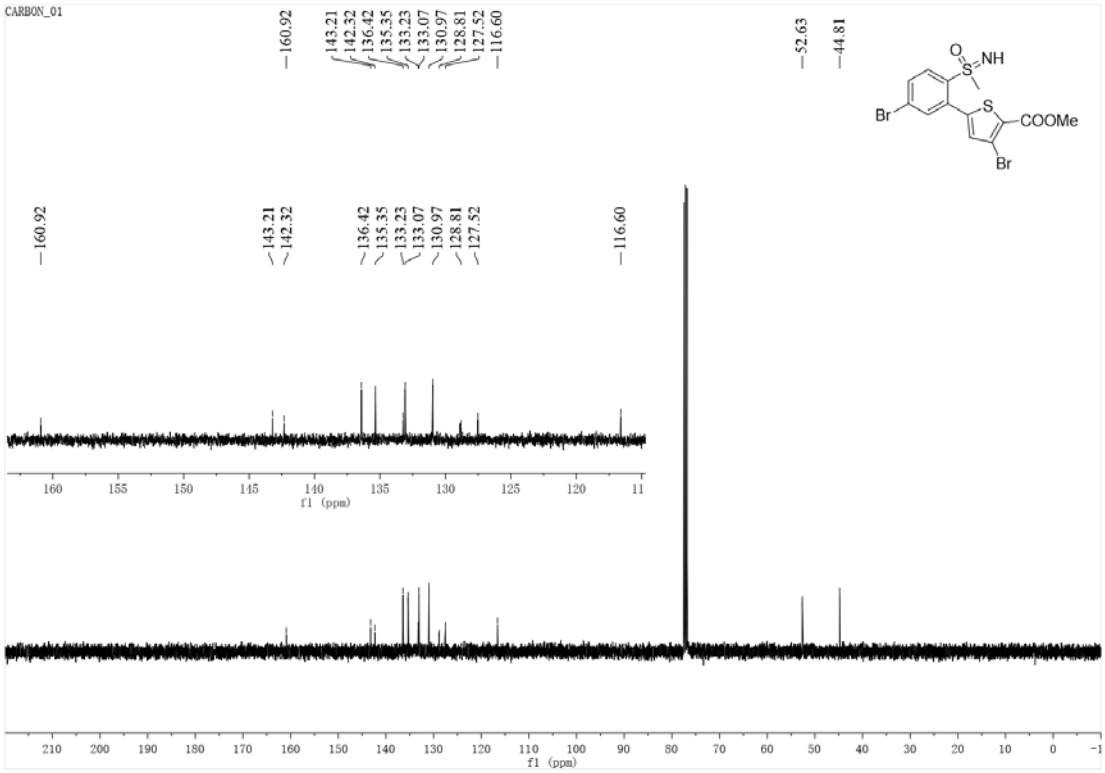
^{13}C NMR (100 MHz) spectrum of **3n** in $CDCl_3$



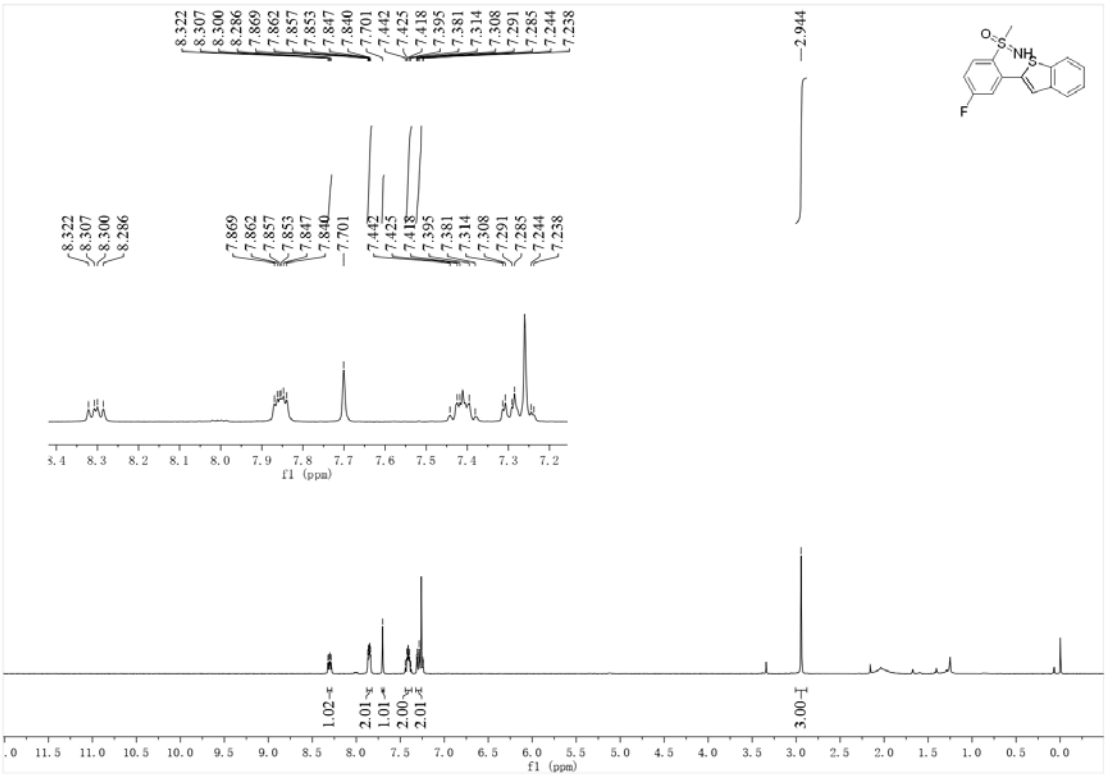
^{1}H NMR (400 MHz) spectrum of **3o** in $CDCl_3$



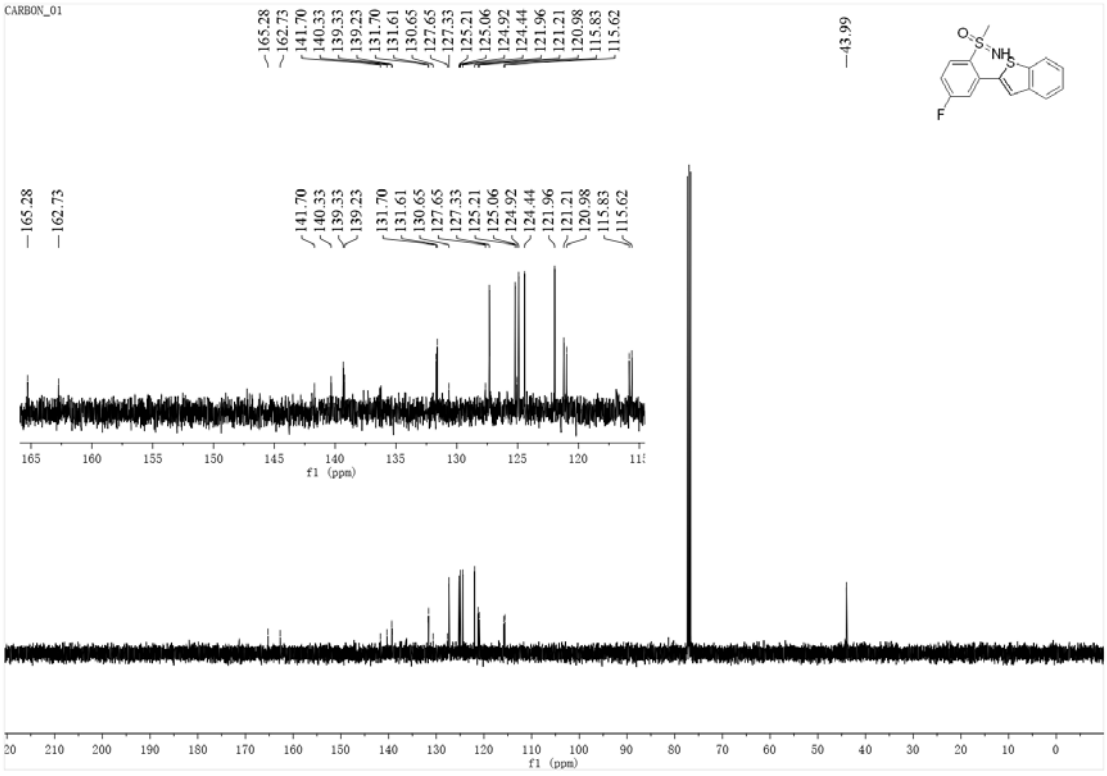
^{13}C NMR (100 MHz) spectrum of **3o** in $CDCl_3$



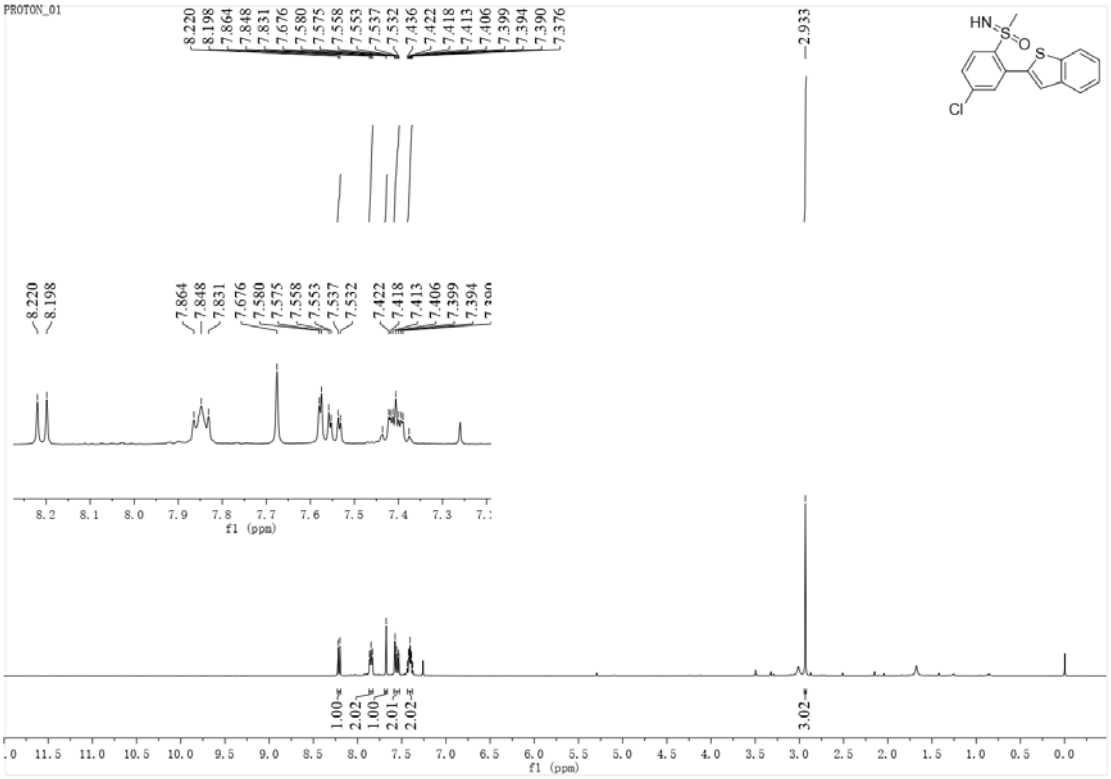
^{1}H NMR (400 MHz) spectrum of **3p** in $CDCl_3$



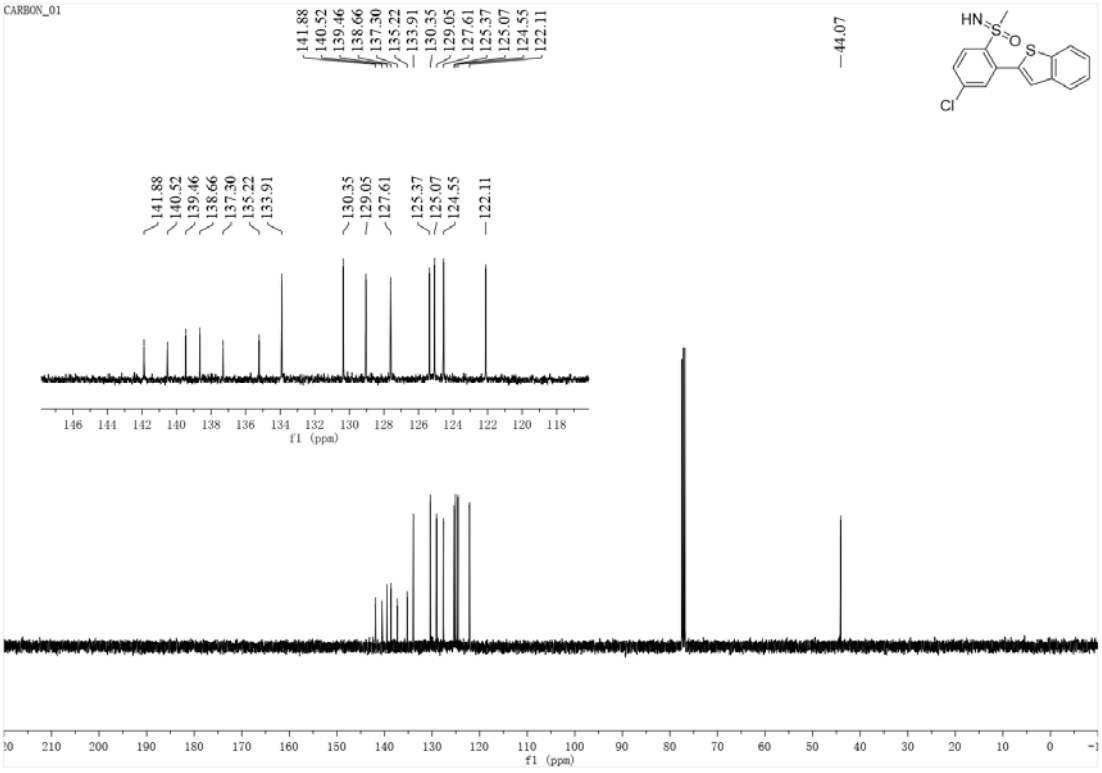
^{13}C NMR (100 MHz) spectrum of **3p** in $CDCl_3$



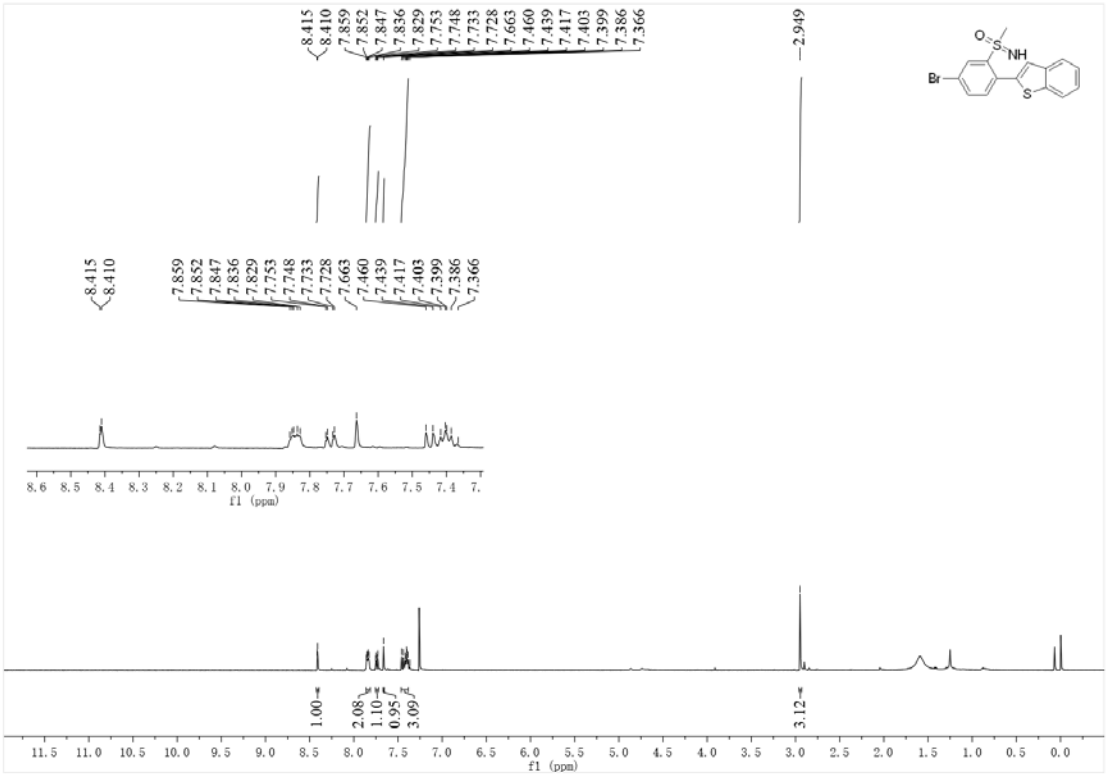
^{1}H NMR (400 MHz) spectrum of **3q** in $CDCl_3$



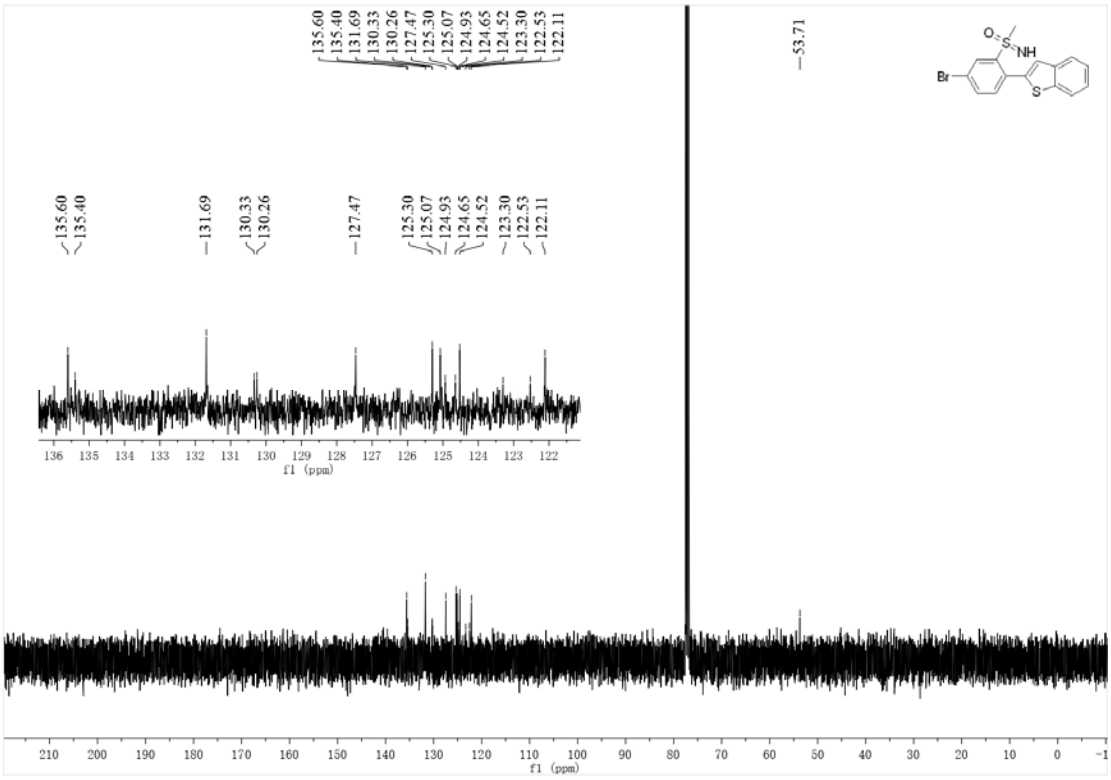
^{13}C NMR (100 MHz) spectrum of **3q** in $CDCl_3$



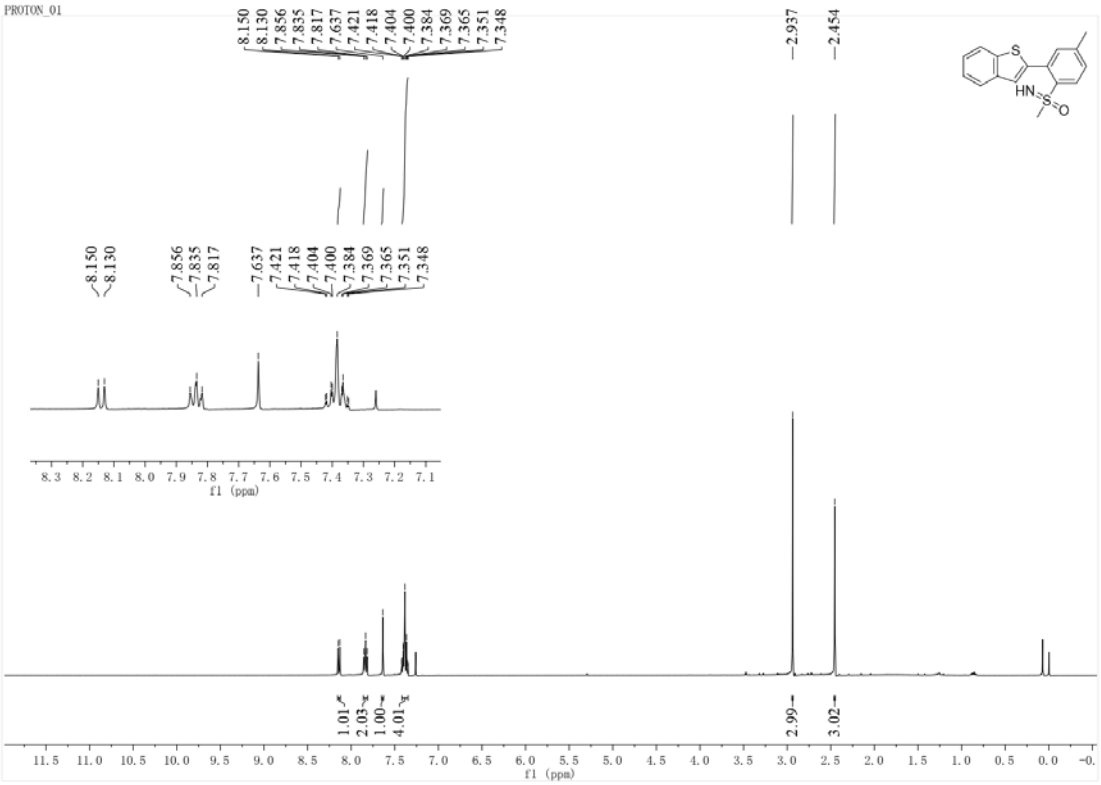
^{1}H NMR (400 MHz) spectrum of **3r** in $CDCl_3$



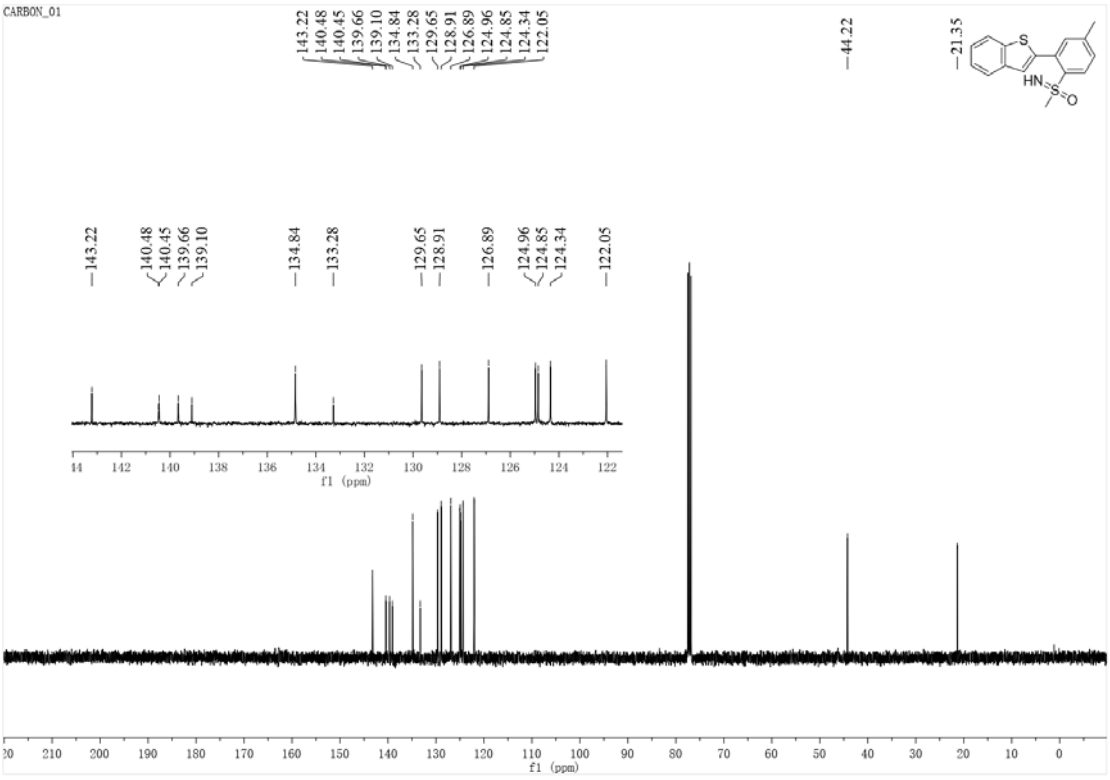
^{13}C NMR (100 MHz) spectrum of **3r** in $CDCl_3$



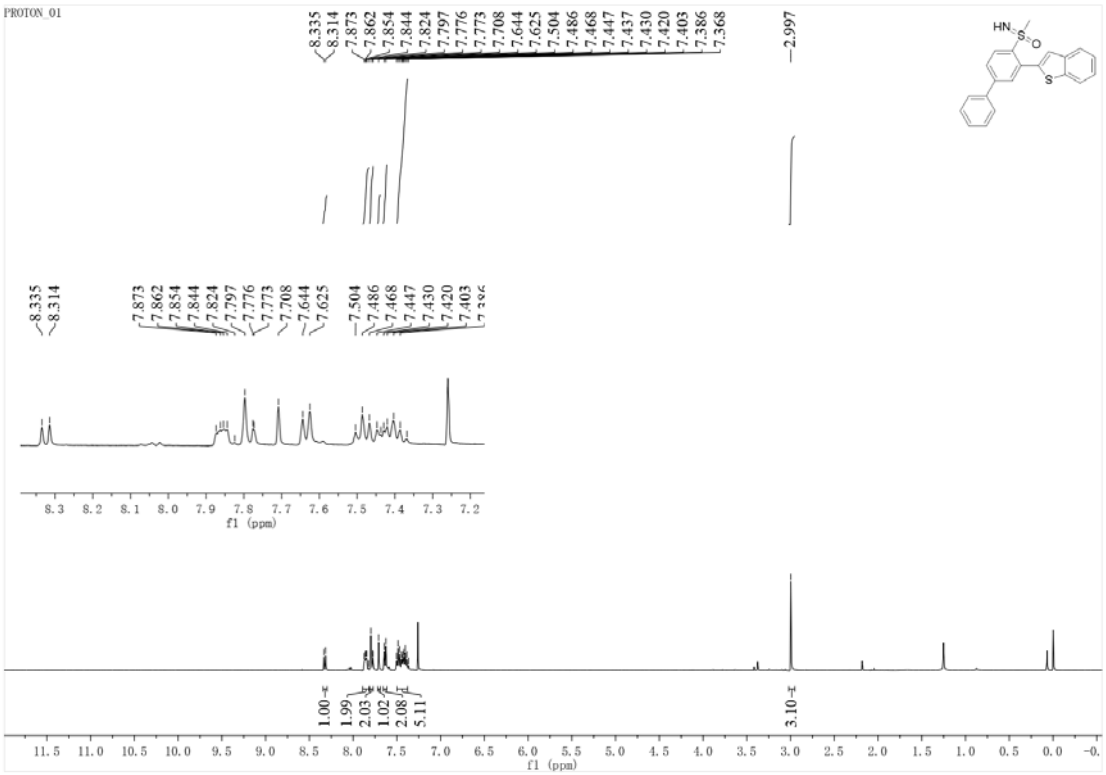
^{1}H NMR (400 MHz) spectrum of **3s** in $CDCl_3$



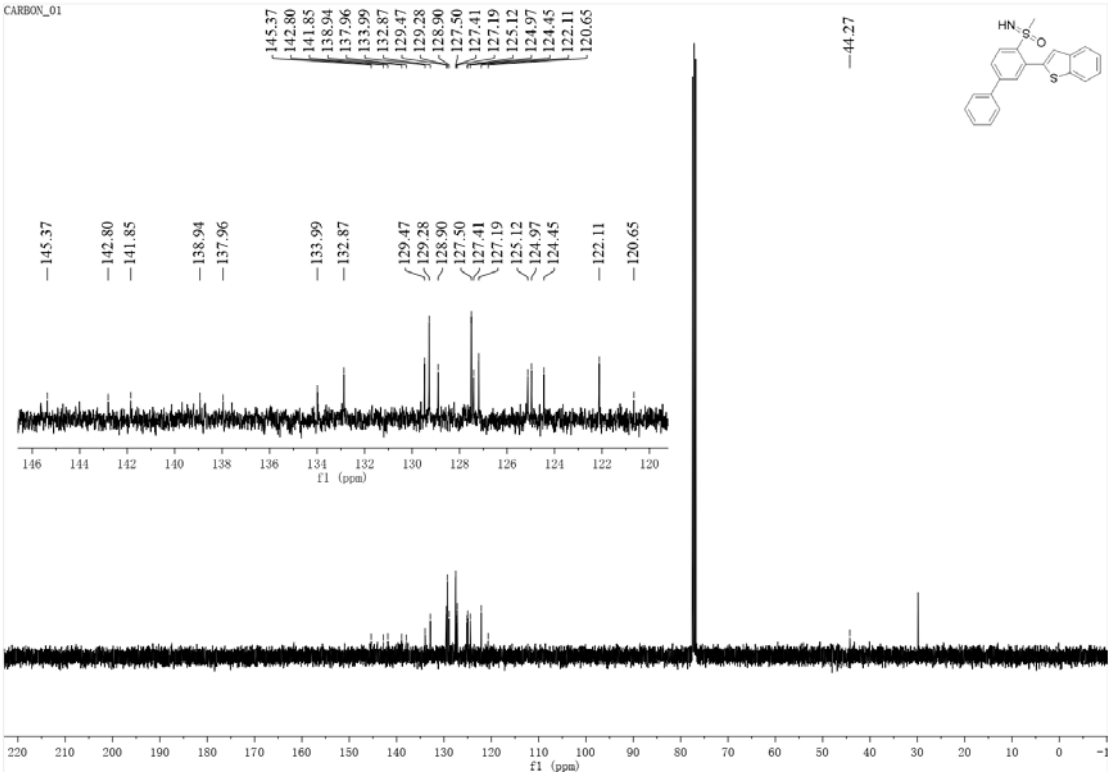
^{13}C NMR (100 MHz) spectrum of **3s** in $CDCl_3$



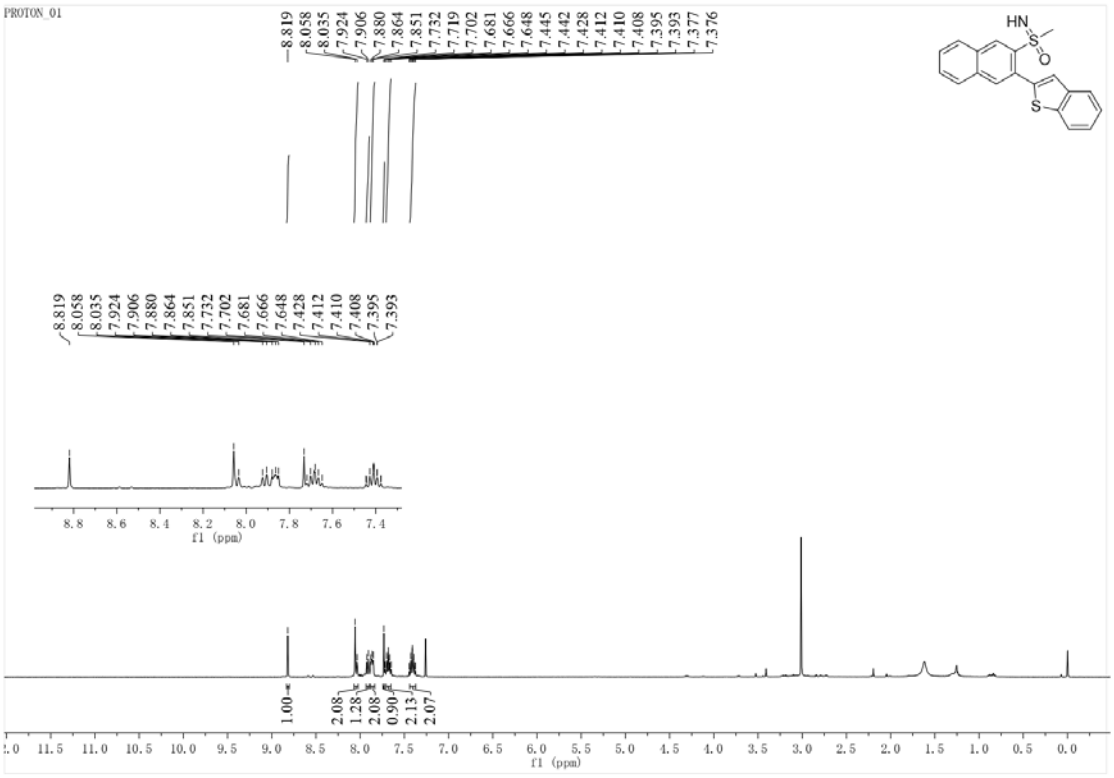
^{1}H NMR (400 MHz) spectrum of **3t** in $CDCl_3$



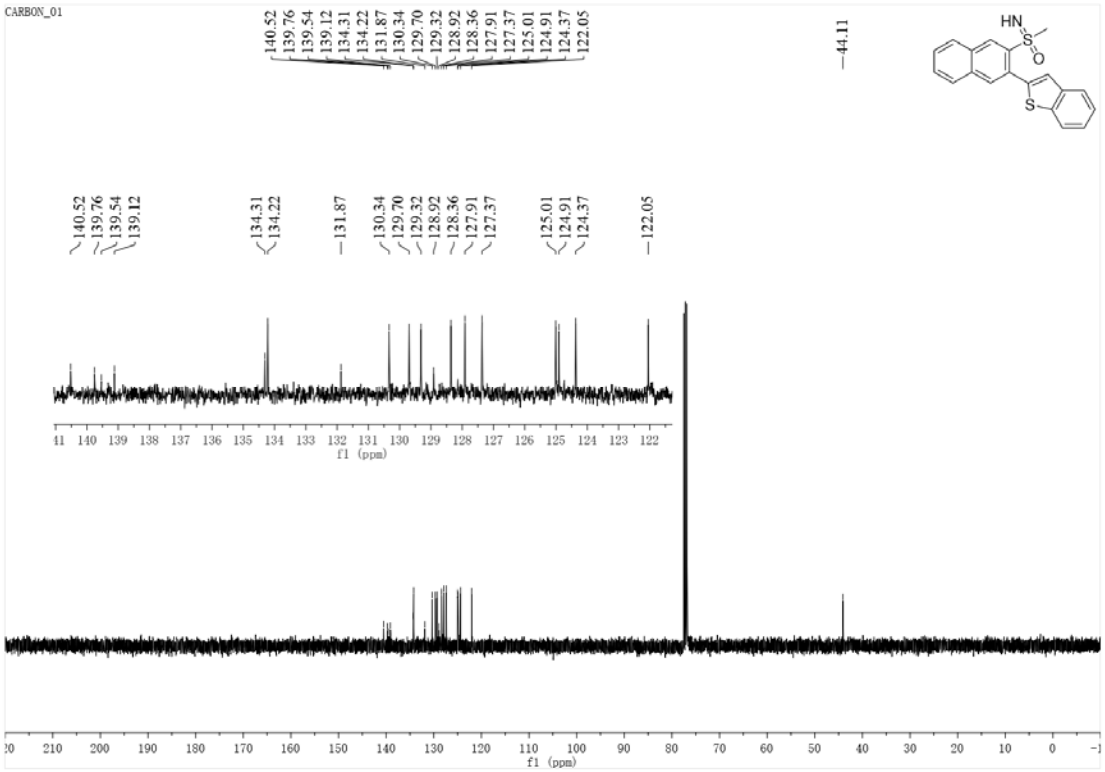
^{13}C NMR (100 MHz) spectrum of **3t** in $CDCl_3$



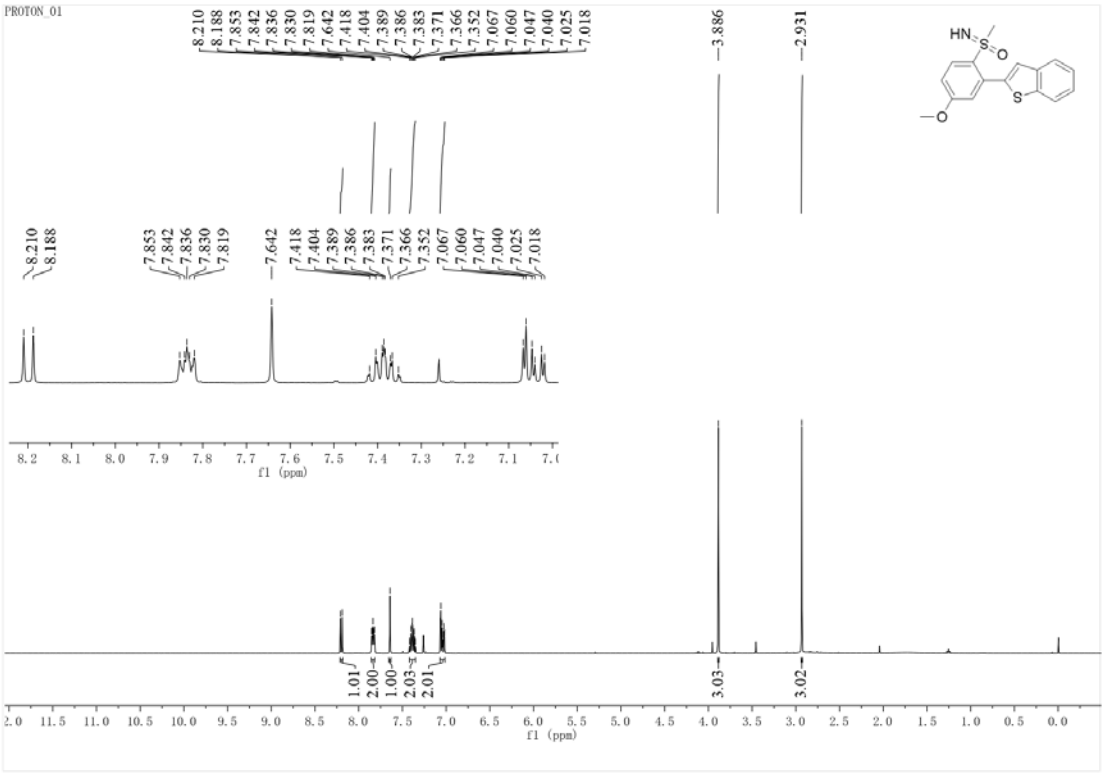
^{1}H NMR (400 MHz) spectrum of **3u** in $CDCl_3$



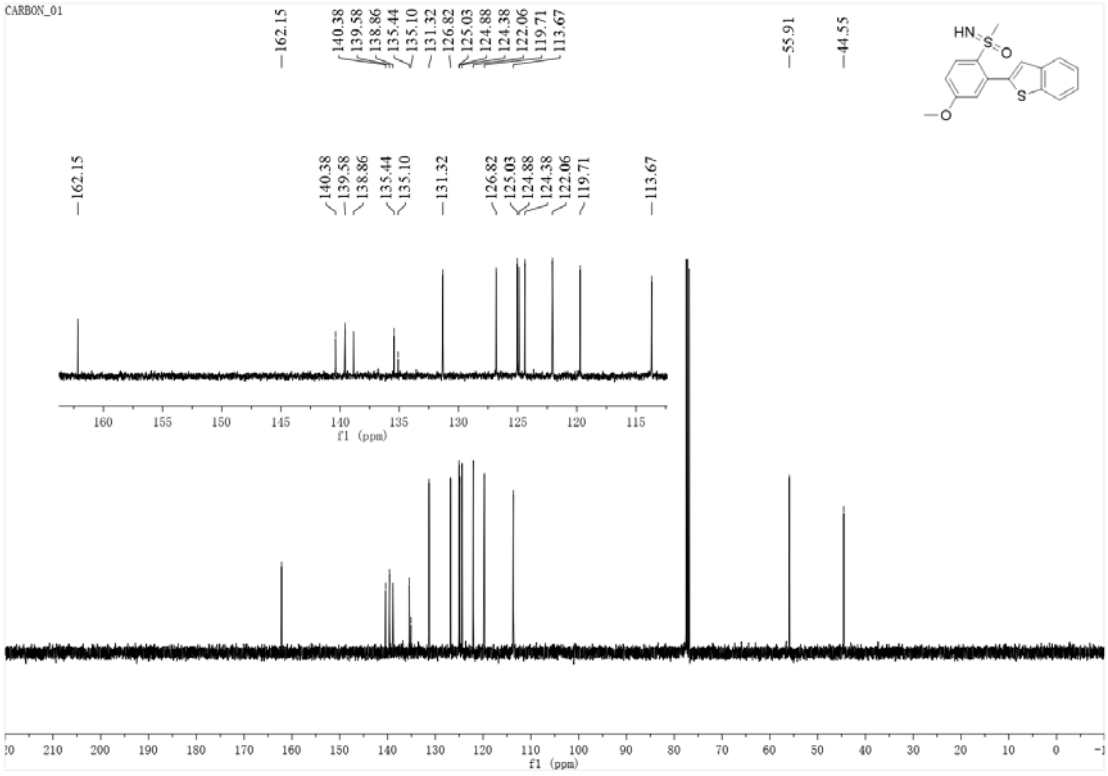
^{13}C NMR (100 MHz) spectrum of **3u** in $CDCl_3$



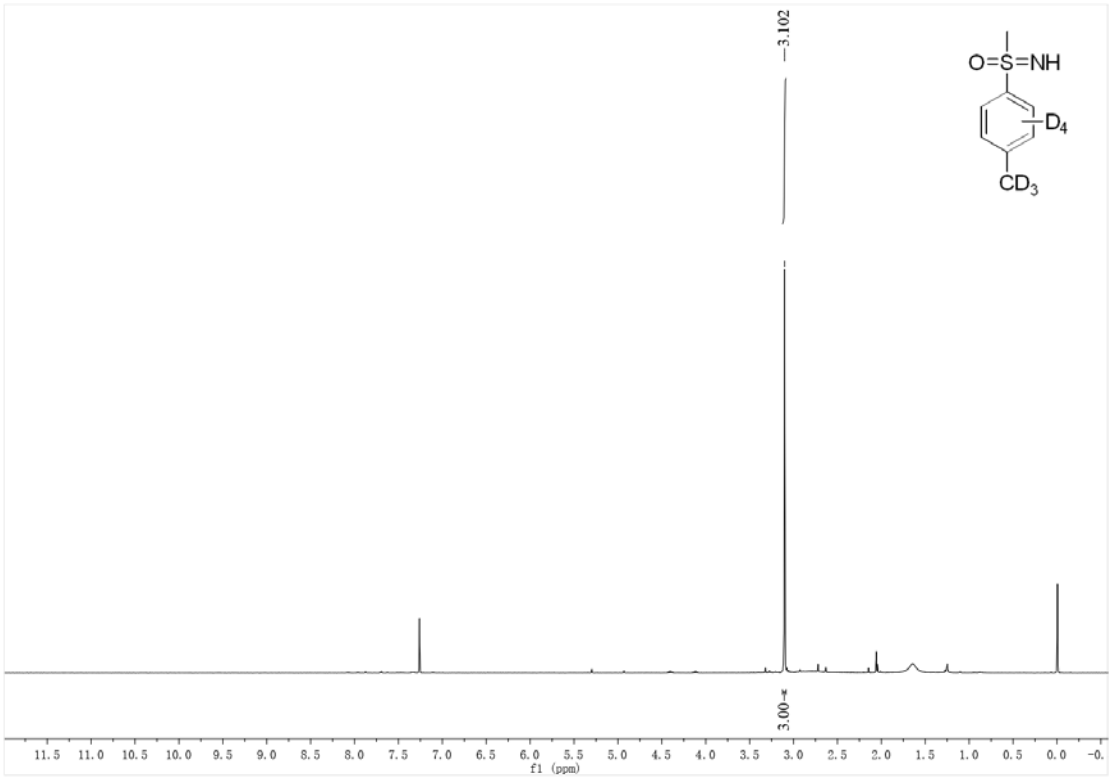
^{1}H NMR (400 MHz) spectrum of **3v** in $CDCl_3$



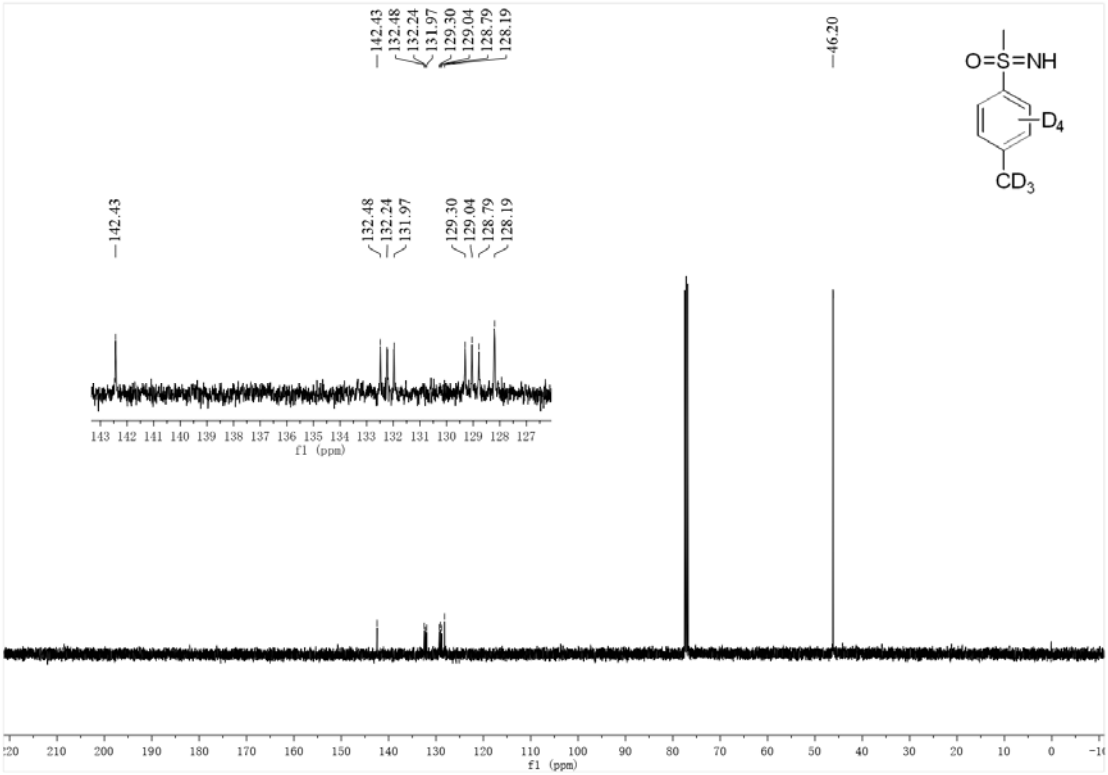
^{13}C NMR (100 MHz) spectrum of **3v** in $CDCl_3$



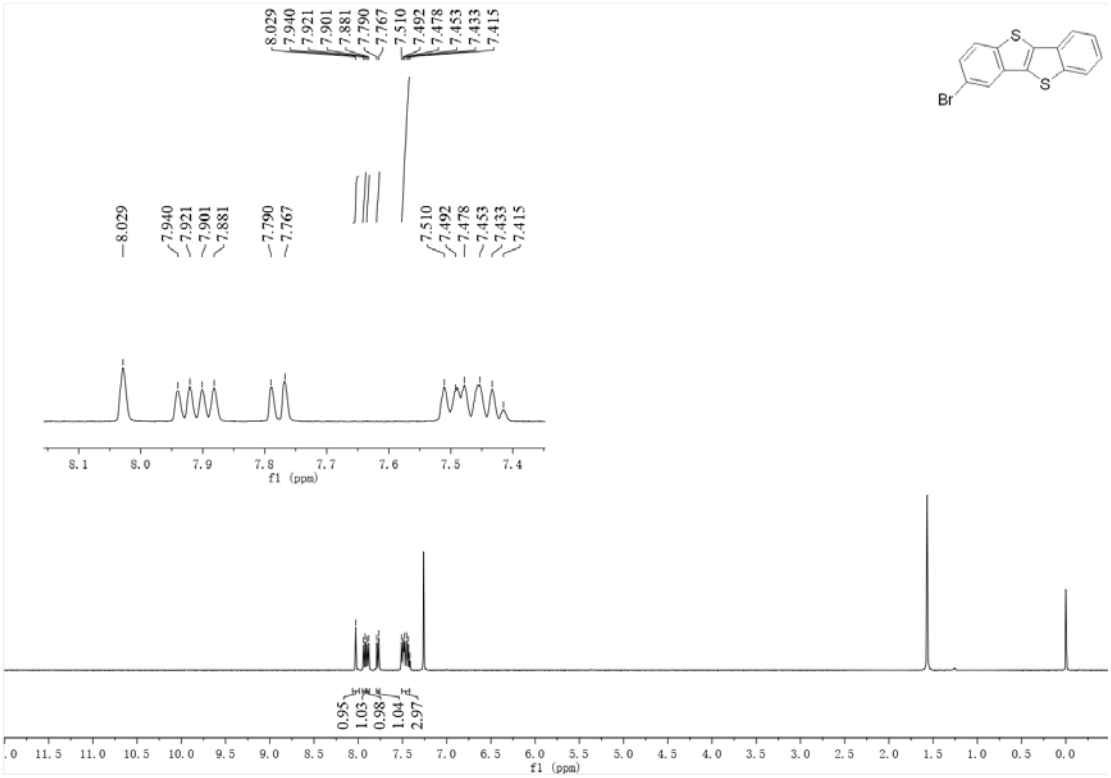
^{1}H NMR (400 MHz) spectrum of [D_4]-**1a** in $CDCl_3$



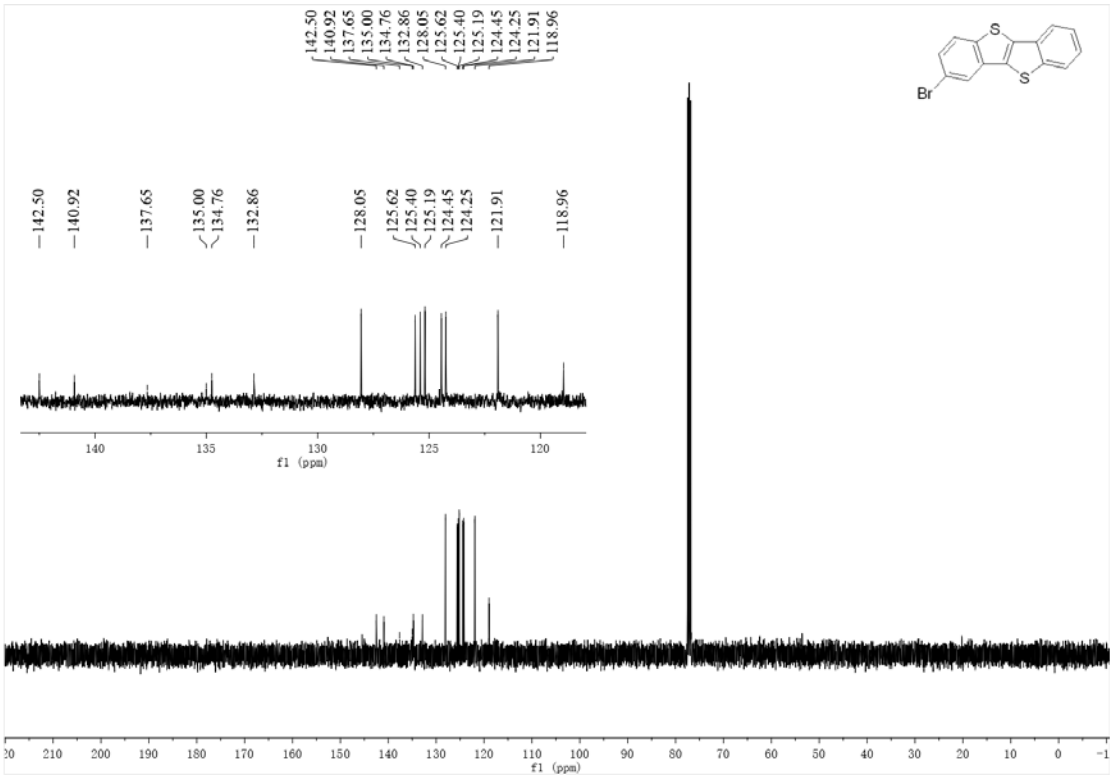
^{13}C NMR (100 MHz) spectrum of [D_4]-**1a** in $CDCl_3$



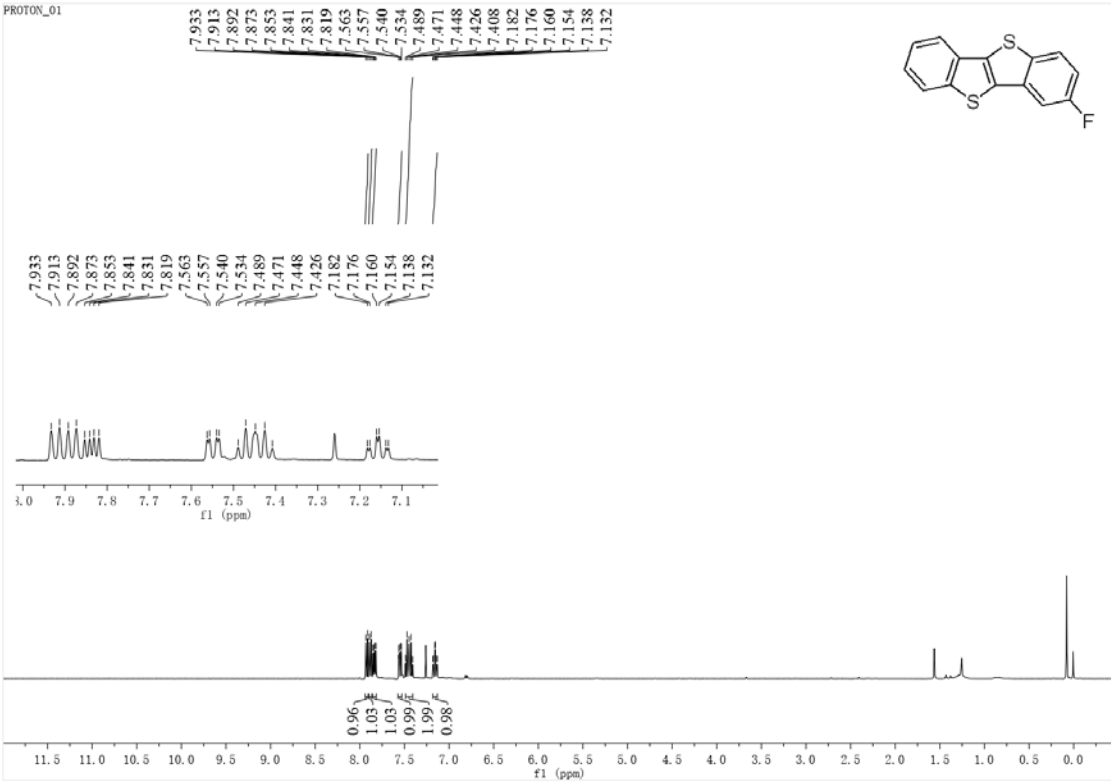
^{1}H NMR (400 MHz) spectrum of **4a** in $CDCl_3$



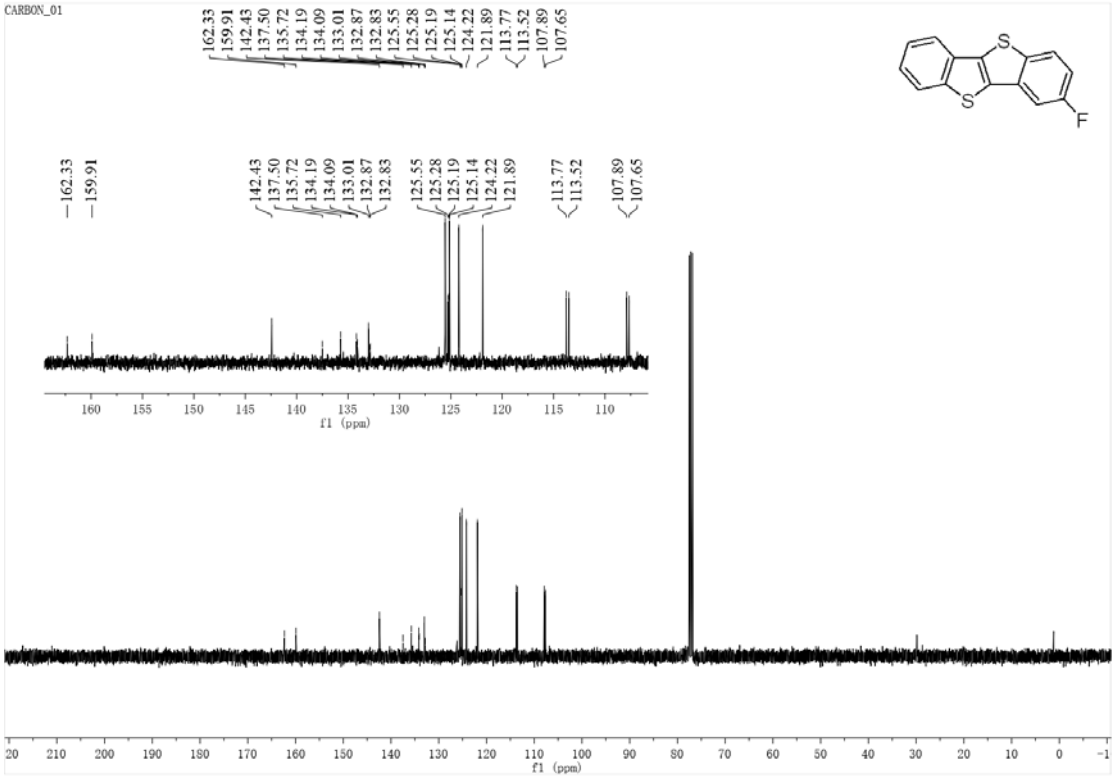
^{13}C NMR (100 MHz) spectrum of **4a** in $CDCl_3$



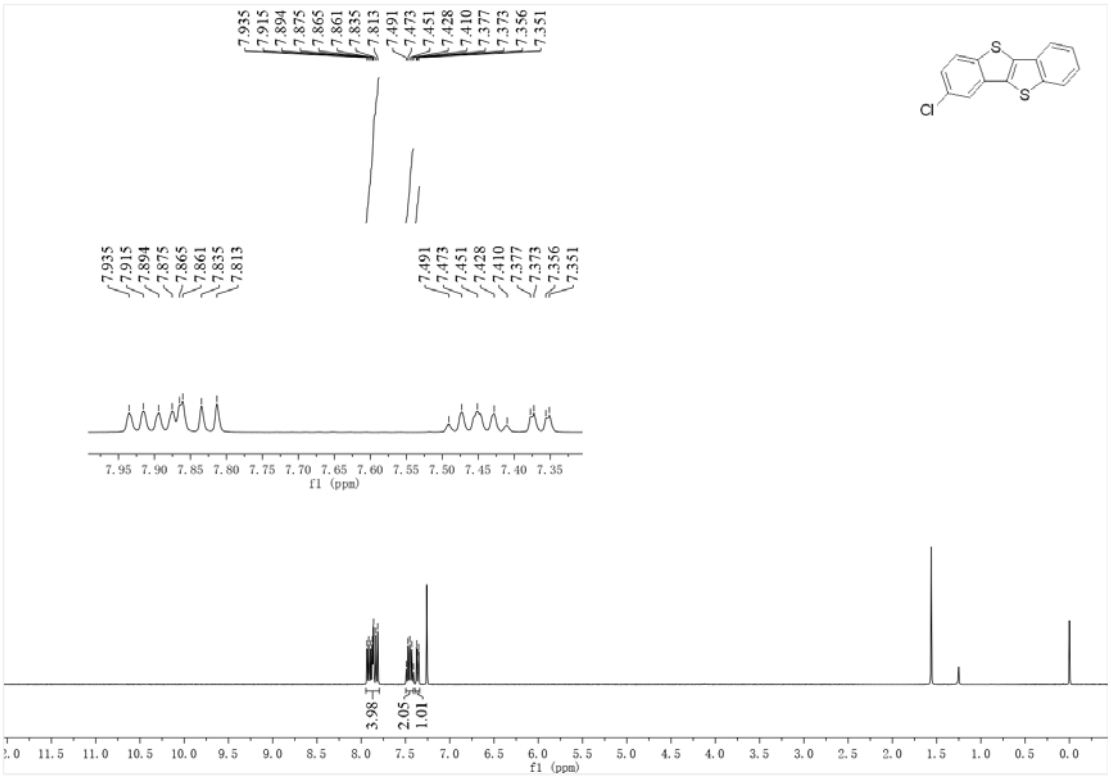
^{1}H NMR (400 MHz) spectrum of **4b** in $CDCl_3$



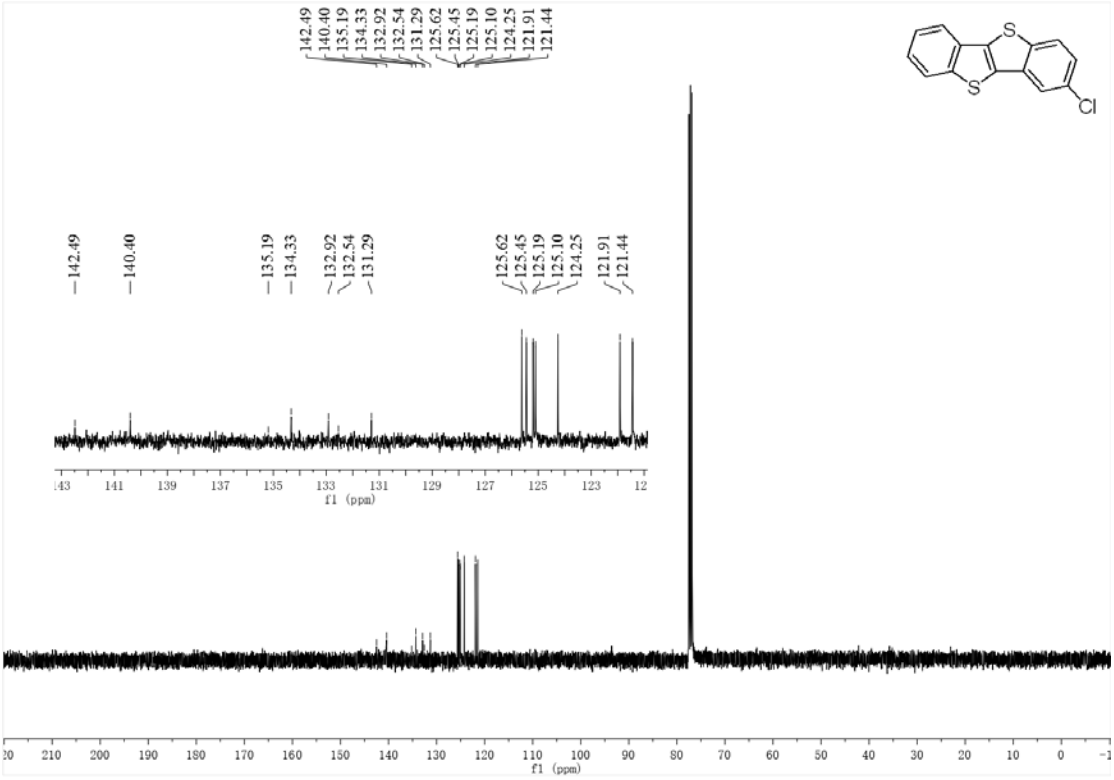
^{13}C NMR (100 MHz) spectrum of **4b** in $CDCl_3$



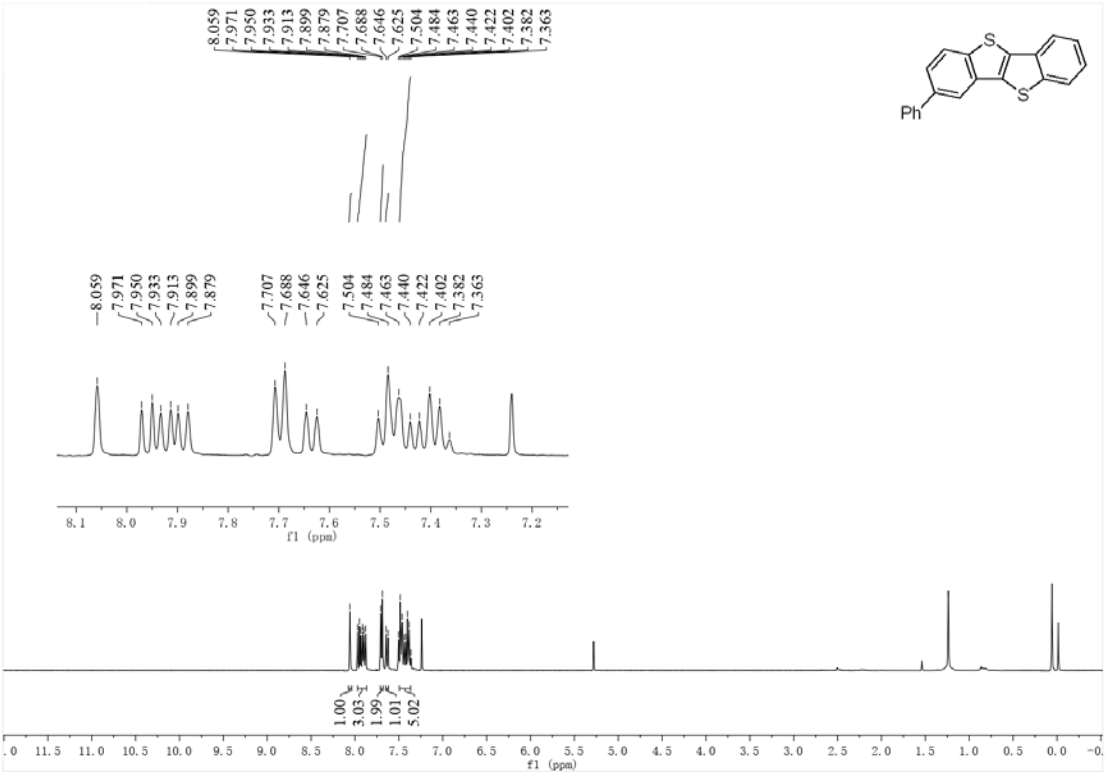
^{1}H NMR (400 MHz) spectrum of **4c** in $CDCl_3$



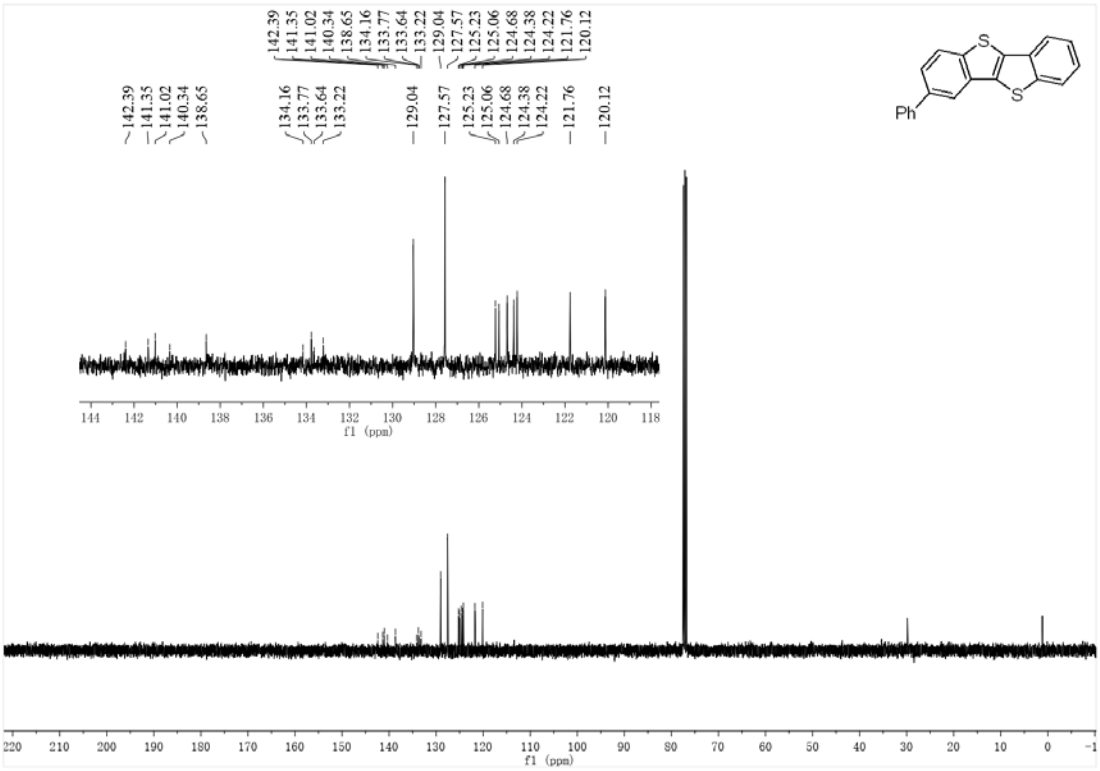
^{13}C NMR (100 MHz) spectrum of **4c** in $CDCl_3$



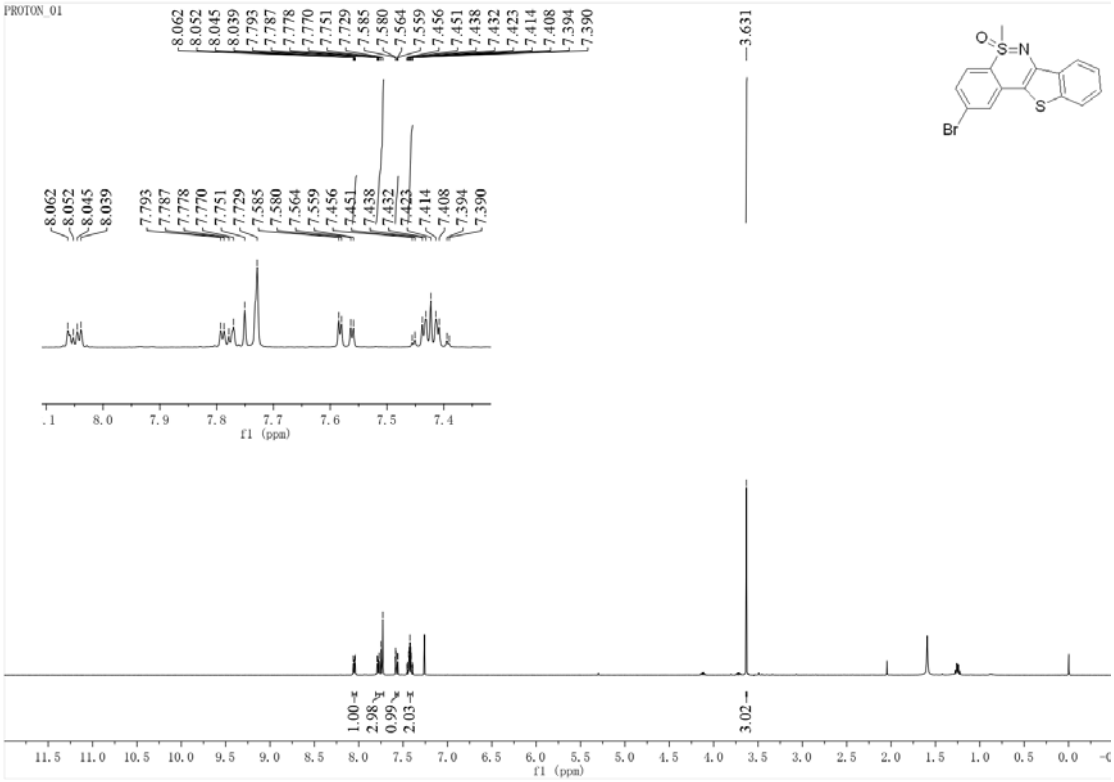
^{1}H NMR (400 MHz) spectrum of **4d** in $CDCl_3$



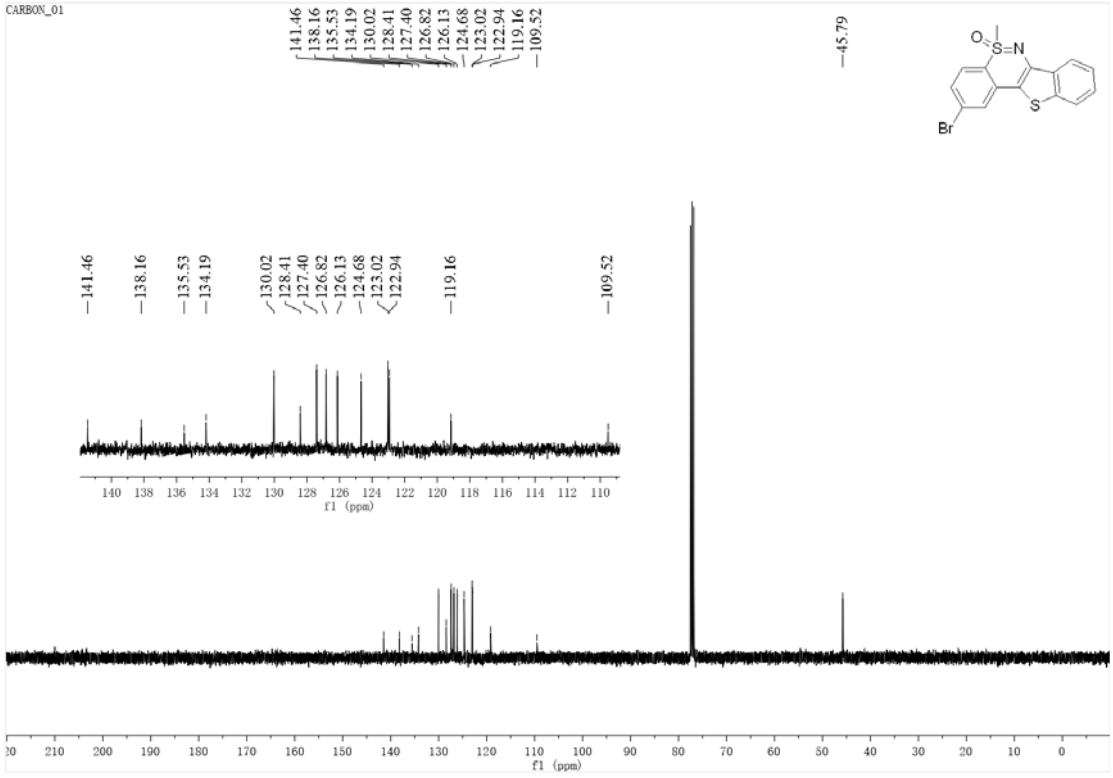
^{13}C NMR (100 MHz) spectrum of **4d** in $CDCl_3$



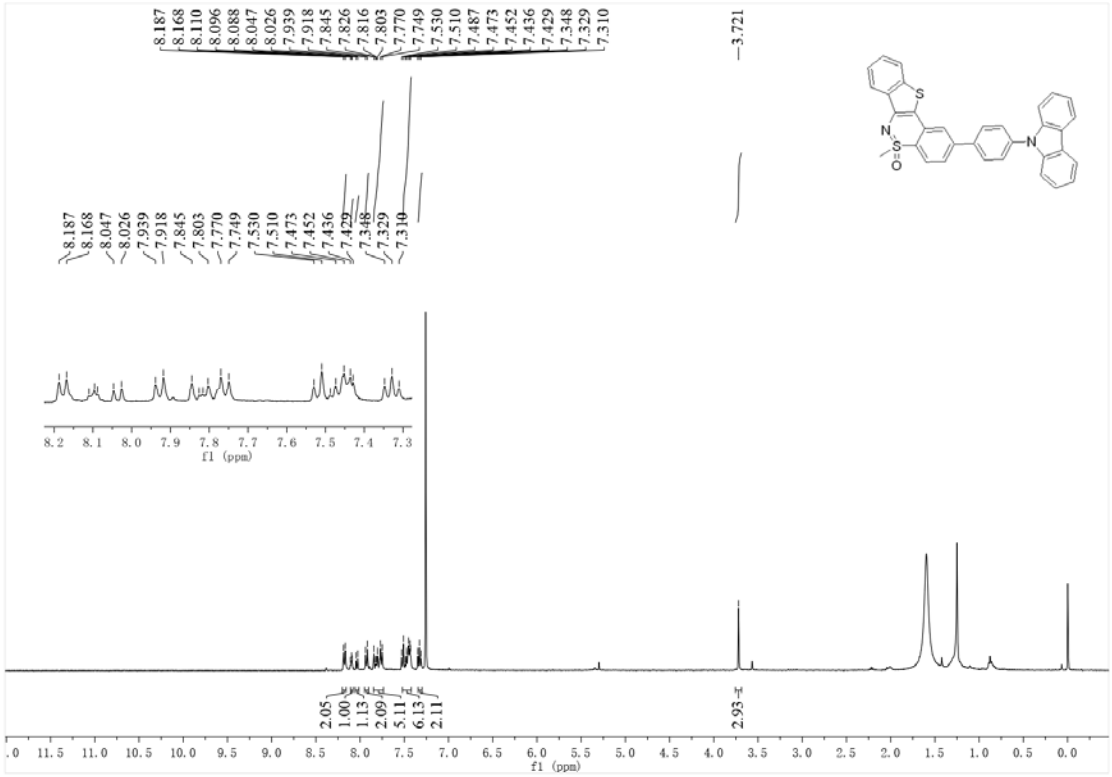
^{1}H NMR (400 MHz) spectrum of **5a** in $CDCl_3$



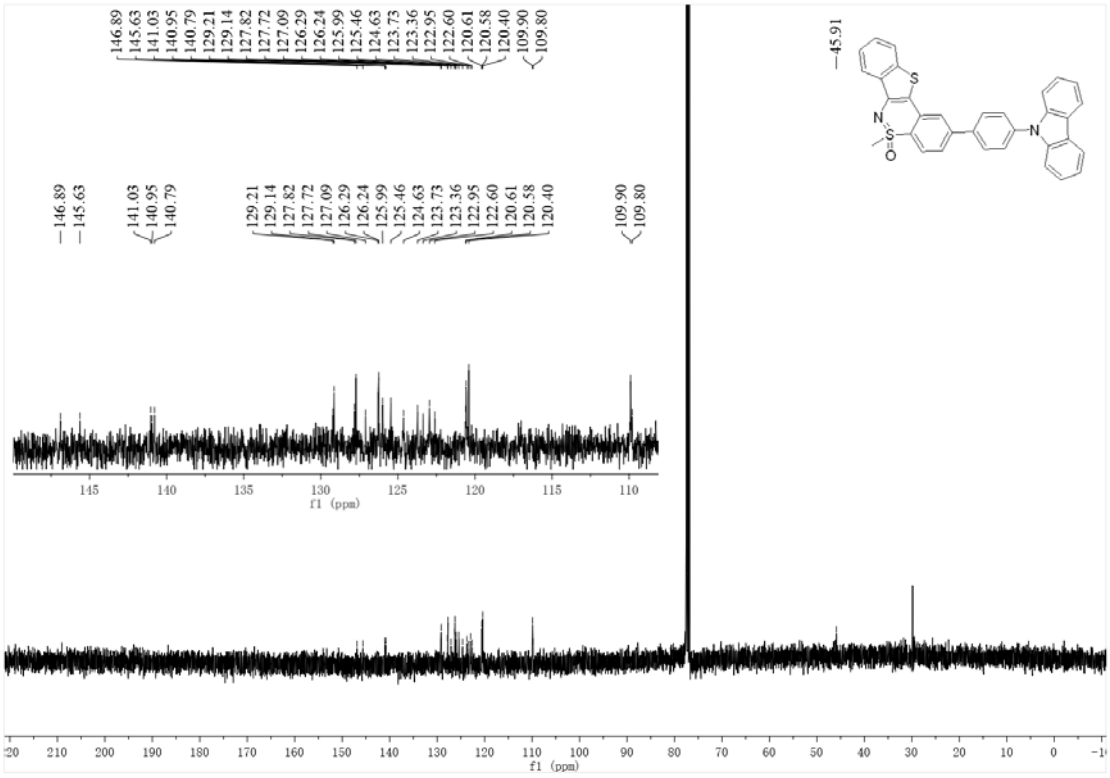
^{13}C NMR (100 MHz) spectrum of **5a** in $CDCl_3$



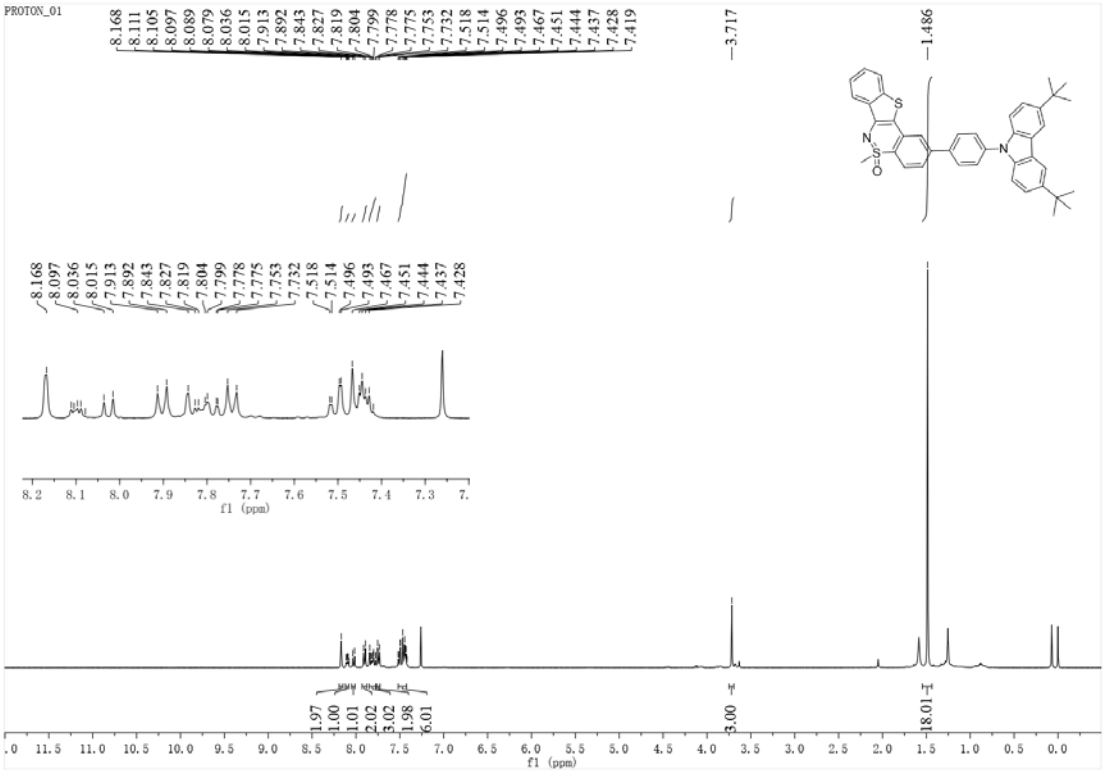
^{1}H NMR (400 MHz) spectrum of **7a** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of **7a** in $CDCl_3$



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



^{13}C NMR (100 MHz) spectrum of **7b** in $CDCl_3$