Supporting Information

$RhCl_3$-Catalyzed Oxidative C–H/C–H Cross-Coupling of (Hetero)aromatic Sulfonamides with (Hetero)arenes

You Ran, Yudong Yang, Huansha You and Jingsong You*

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu 610064, PR China

E-mail: jsyou@scu.edu.cn

Table of contents

I. General remarks

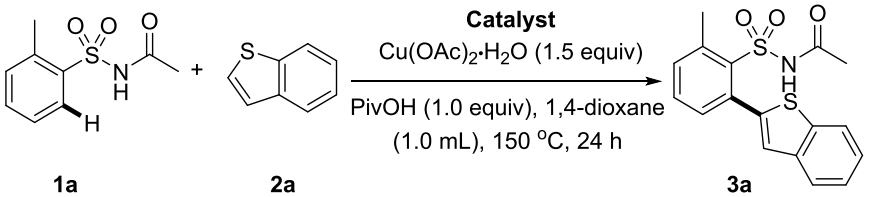
NMR spectra were obtained on an Agilent 400-MR DD2 or a Bruker AV II-400 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-*d*6 as the internal reference ($CDCl_3$: δ = 7.26 ppm, DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO as the internal standard ($CDCl_3$: δ = 77.16 ppm, DMSO-d_6: δ = 39.52 ppm). High resolution mass spectra (HR-MS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). Melting points were determined with XRC-1 and are uncorrected. **5b** and **5b'** were separated by Water 2489 UV/Visible Detector. Absolute quantum yield was collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Sulfonamide derivatives were prepared according to the literature procedures.[1] 1,4-dioxane, dichloroethane (DCE), tetrahydrofuran (THF), and *N,N*-dimethylformamide (DMF) were dried with an innovative technology solvent purification system (model no.:PS-MD-5).

II. Optimization of the reaction conditions

A Schlenk tube with a magnetic stir bar was charged with catalyst, oxidant, additive, *N*-(*o*-tolylsulfonyl)acetamide **1a** (42.7 mg, 0.2 mmol, 1.0 equiv.) and benzothiophene **2a** (80.6 mg, 0.6 mmol, 3.0 equiv.) under air. Then the Schlenk tube was evacuated and refilled with O_2 or N_2 three times. Next, solvent (1.0 mL) was added. The Schlenk tube was then sealed with a Teflon lined cap. The resulting solution was stirred at the indicated temperature for 24 hours and then diluted with 5 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The yield of **3a** was determined by ^{1}H NMR analysis of the crude product using dibromomethane (0.3 mmol, 21 μL) as internal standard.

Table S1. Screening of catalysts[a]



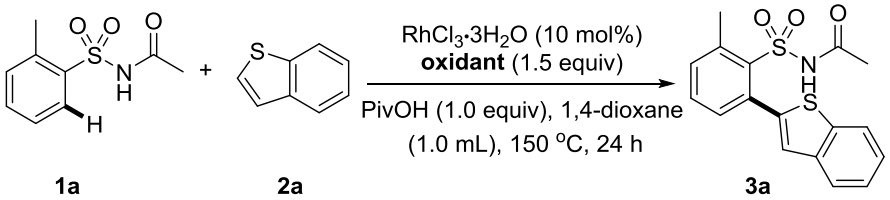
1a **2a** **3a**

Entry	Catalyst (mol%)	Yield (%)[b]	Entry	Catalyst (mol%)	Yield (%)[b]
1	$RhCl_3·3H_2O$ (10)	9	6	$[Cp^*IrCl_2]_2$ (5)	nd
2	$[Cp^*RhCl_2]_2$ (5)	12	7	$[CoCp^*(CO)I_2]$ (5)	nd
3	$[Rh(cod)Cl]_2$ (10)	12	8	$[Ru(p\text{-cymene})Cl_2]_2$ (10)	nd
4	$Rh(PPh_3)_3Cl$ (10)	15	9	-	nd

5	$Pd(OAc)_2$ (5)	nd

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), catalyst (5-10 mol%), $Cu(OAc)_2 \cdot H_2O$ (1.5 equiv), PivOH (1.0 equiv), 1,4-dioxane (1.0 mL), 150°C, under N_2 for 24 hours. [b]yields were determined based on ^1H NMR with dibromomethane as internal standard. nd = not detected. Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl. cod = 1,5-cyclooctadien. PivOH = pivalic acid

Table S2. Screening of oxidants[a]

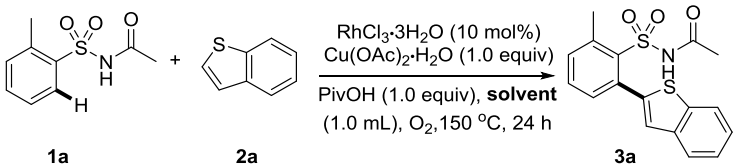


1a **2a** **3a**

Entry	oxidants (equiv)	Yield (%)[b]	Entry	oxidants (equiv)	Yield (%)[b]
1	$Cu(NO_3)_2$ (1.5)	nd	7	BQ (1.5)	nd
2	$Cu(acac)_2$ (1.5)	nd	8	O_2	nd
3	$Cu(OTf)_2$ (1.5)	nd	9	$Cu(OAc)_2 \cdot H_2O$ (1.0) /O_2	46
4	Ag_2O (1.5)	nd	10	$Cu(OAc)_2 \cdot H_2O$ (0.5) /O_2	37
5	Ag_2CO_3 (1.5)	nd	11	$Cu(OAc)_2 \cdot H_2O$ (1.0) /air	15
6	Oxone (1.5)	nd			

Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), $RhCl_3 \cdot 3H_2O$ (10 mol%), oxidant (1.5 equiv), PivOH (1.0 equiv), 1,4-dioxane (1.0 mL), 150°C, under N_2 for 24 hours. [b]yields were determined based on ^1H NMR with dibromomethane as internal standard. nd = not detected. BQ = 1,4-Benzoquinone.

Table S3. Screening of solvents[a]



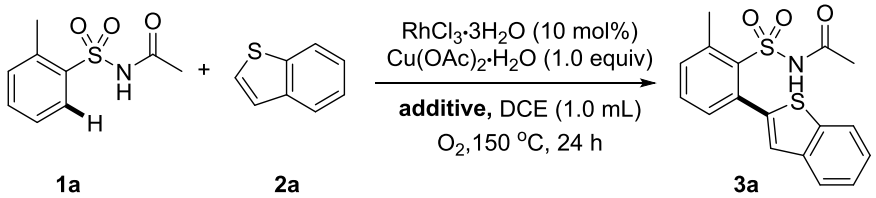
1a **2a** **3a**

Entry	solvent	Yield (%)[b]	Entry	solvent	Yield (%)[b]
1	DCE	55	4	DMSO	nd
2[c]	THF	36	5	*t*-AmylOH	trace

3	DMF	25	

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), $RhCl_3·3H_2O$ (10 mol%), $Cu(OAc)_2·H_2O$ (1.0 equiv), PivOH (1.0 equiv), solvent (1.0 mL), 150 °C, under O_2 for 24 hours. [b]yields were determined based on ^1H NMR with dibromomethane as internal standard. [c]120 °C. nd = not detected. DCE = 1,2-dichloroethane. THF = tetrahydrofuran. DMF = *N*,*N*-dimethylformamide. *t*-AmylOH = *tert*-amyl alcohol

Table S4. Screening of additives[a]

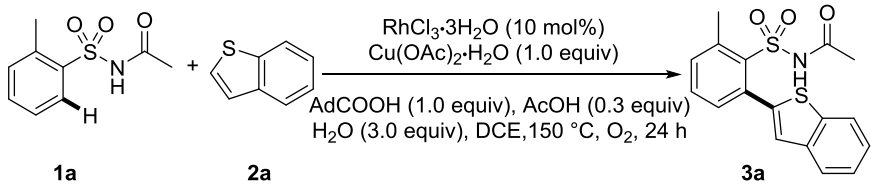


1a **2a** **3a**

Entry	additive (equiv)	Yield (%)[b]	Entry	additive (equiv)	Yield (%)[b]
1	PivOH (1.0)/$AgSbF_6$ (0.2)	trace	7	MesCOOH (1.0)	52
2	K_2HPO_4 (1.0)	trace	8	AdCOOH (1.0)	68
3	K_2CO_3 (1.0)	trace	9	AdCOOH (1.0)/CsOPiv (0.3)	<10
4	-	45	10	AdCOOH (1.0)/AcOH (0.3)	72
5	TFA (1.0)	39	11	AdCOOH (1.0)/AcOH (0.5)	66
6	AcOH (1.0)	64	12	AdCOOH (1.0)/AcOH (0.3)/ H_2O (3.0)	76/72[c]

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), $RhCl_3·3H_2O$ (10 mol%), $Cu(OAc)_2·H_2O$ (1.0 equiv), additive, DCE (1.0 mL), 150 °C, under O_2 for 24 hours. [b]yields were determined based on ^1H NMR with dibromomethane as internal standard. [c]isolated yield. TFA = trifluoroacetic acid. AcOH = acetic acid. MesCOOH = 2,4,6-trimethylbenzoic acid. AdCOOH = 1-adamantanecarboxylic acid

Table S5. Optimization of other reaction parameters[a]

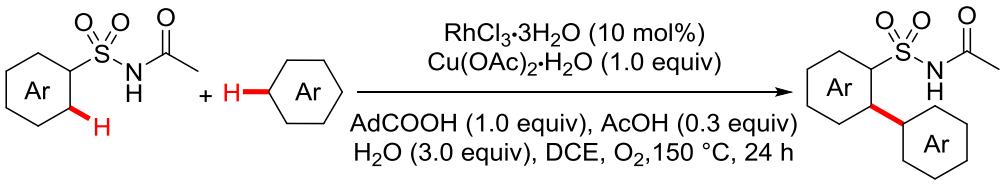


1a **2a** **3a**

Entry	Variation	Yield (%)[b]	Entry	Variation	Yield (%)[b]
1	DCE (0.5 mL)	46	5	140 °C	33
2	DCE (2.0 mL)	63	6	$RhCl_3·3H_2O$ (5 mol%)	44
3	12 h	55	7	**2a** (2.0 equiv)	61
4	36 h	70	8[c]	*N*-(*o*-tolylsulfonyl)pivalamide	n.d.

[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), $RhCl_3{\cdot}3H_2O$ (10 mol%), $Cu(OAc)_2{\cdot}H_2O$ (1.0 equiv), AdCOOH (1.0 equiv), AcOH (0.3 equiv), H_2O (3.0 equiv), DCE (1.0 mL), 150°C, under O_2 for 24 hours. [b]yields were determined based on ^1H NMR with dibromomethane as internal standard. [c]The replacement of **1a** with *N*-(*o*-tolylsulfonyl)pivalamide. n.d. = no detected.

III. General procedure for the $RhCl_3$-catalyzed oxidative C–H/C–H cross-coupling of (hetero)aromatic sulfonamides with (hetero)arenes



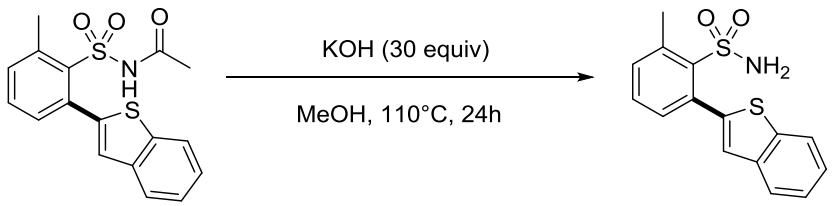
Procedure A:

A Schlenk tube with a magnetic stir bar was charged with aryl sulfonamide **1** (0.2 mmol), **2** (0.6 mmol), $RhCl_3{\cdot}3H_2O$ (5.3 mg, 0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (40.0 mg, 0.2 mmol), and AdCOOH (36.0 mg, 0.2 mmol) under air. Then the Schlenk tube was evacuated and refilled with O_2 three times. Next, AcOH (3.4 μL, 0.06 mmol), H_2O (10.8 μL, 0.6 mmol) and DCE (1.0 mL) were added. The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 150 °C for 24 hours. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product **3** or **4**.

Procedure B:

A Schlenk tube with a magnetic stir bar was charged with aryl sulfonamide **1** (0.2 mmol), **2** (10.0 mmol or 0.5 mL), $RhCl_3{\cdot}3H_2O$ (5.3 mg, 0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (40.0 mg, 0.2 mmol), and AdCOOH (36.0 mg, 0.2 mmol), under air. Then the Schlenk tube was evacuated and refilled with O_2 three times. Next, AcOH (3.4 μL, 0.06 mmol), H_2O (10.8 μL, 0.6 mmol) and DCE (1.0 mL or 0.5 mL) were added. The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 150 °C for 24 hours. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product **5**

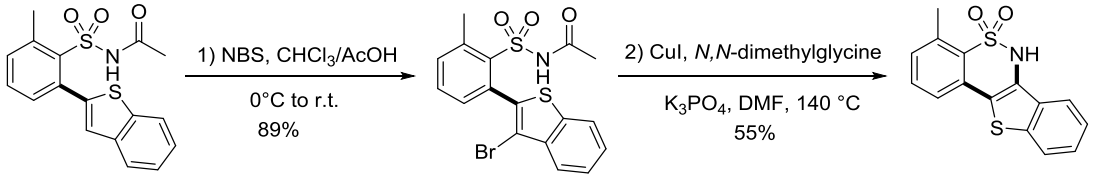
IV. General procedure for the removal of acetyl group



3a **6,** 87%

A Schlenk tube with a magnetic stirring bar was charged with *N*-((2-(benzo[*b*]thiophen-2-yl)-6-methylphenyl)sulfonyl)acetamide **3a** (33.8 mg, 0.1 mmol), and KOH (168.3 mg, 3.0 mmol) under air. Then the Schlenk tube was evacuated and refilled with N_2 three times. Next, MeOH (1.5 mL) was added. The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 110 °C for 24 hours. After being cooled to room temperature, the reaction was diluted with dichloromethane (15 mL). And then 2M HCl aqueous solution (15 mL) was added. Organic phase was separated, dried over $MgSO_4$, filtered, and evaporated under vacuum. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 6/1, v/v) afforded the desired product **6** as a white solid (26.3 mg, 87% yield).

V. Synthesis of compound 7



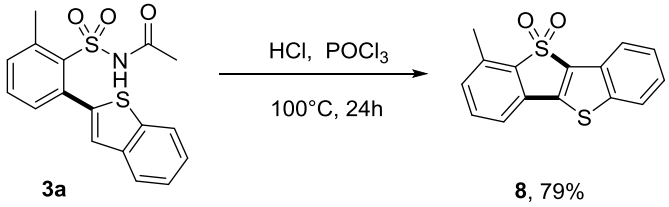
3a **7'** **7**

N-bromosuccinimide (89 mg, 0.5 mmol) was added stepwise to a solution of *N*-((2-(benzo[*b*]thiophen-2-yl)-6-methylphenyl)sulfonyl)acetamide **3a** (138 mg, 0.4 mmol) in chloroform (3.0 mL) and acetic acid (3.0 mL). Then the mixture was stirred at 0 °C for 4 h and allowed to stir at room temperature for 24 h. Then chloroform was added and the resulting mixture was successively washed with saturated sodium thiosulfate solution, saturated sodium carbonate solution and water. The organic layer was then dried over $MgSO_4$, filtered and evaporated. Purification via silica gel column chromatography (petroleum ether/ethyl acetate/methanol = 10/1/0.05, v/v/v) afforded the desired product **7'** as a light yellow solid (150.2 mg, 89% yield).

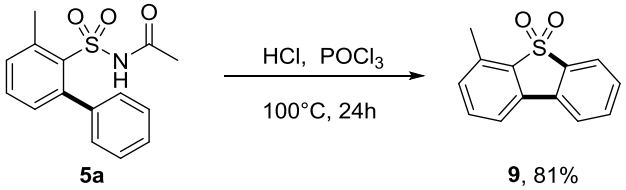
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with *N*-((2-(3-bromobenzo[*b*]thiophen-2-yl)-6-methylphenyl)sulfonyl)acetamide (84.9 mg, 0.2 mmol), CuI (7.6 mg, 0.04 mmol), *N,N*-dimethylglycine hydrochloride (5.6 mg, 0.04 mmol), K_3PO_4 (89.2 mg, 0.42 mmol) under air. Then the Schlenk tube was evacuated and refilled with N_2 three times. Next, DMF (1.5 mL) was added. The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 140 °C for 24 hours. The resulting solution was cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The organic extract was washed with water, dried over Na_2SO_4 and concentrated under reduced pressure. Purification via silica gel

column chromatography (petroleum ether/ethyl acetate/methanol = 10/1/0.05, v/v/v) afforded the desired product **7** as a white solid (33.1 mg, 55% yield).

VI. Synthesis of compounds 8 and 9



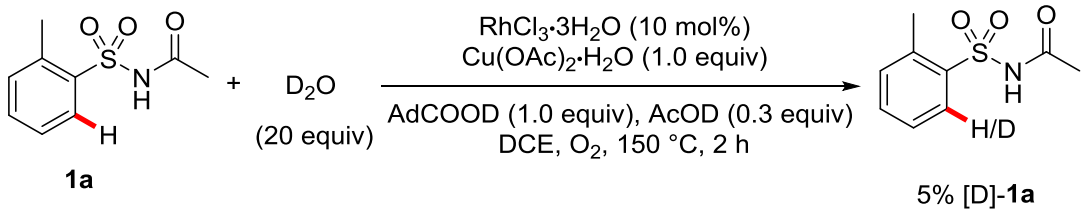
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with *N*-((2-(benzo[*b*]thiophen-2-yl)-6-methylphenyl)sulfonyl)acetamide **3a** (34.5 mg, 0.1 mmol), concentrated hydrochloric acid (0.2 mL) and $POCl_3$ (1.8 mL) under air. The resulting mixture was stirred for 5 min at room temperature, and then heated at 100 °C for 24 h. Then the mixture was cooled and carefully poured on crushed ice. Organic phase was separated, dried over $MgSO_4$, filtered, and evaporated. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) afforded the desired product **8** as a yellow solid (22.5 mg, 79% yield).



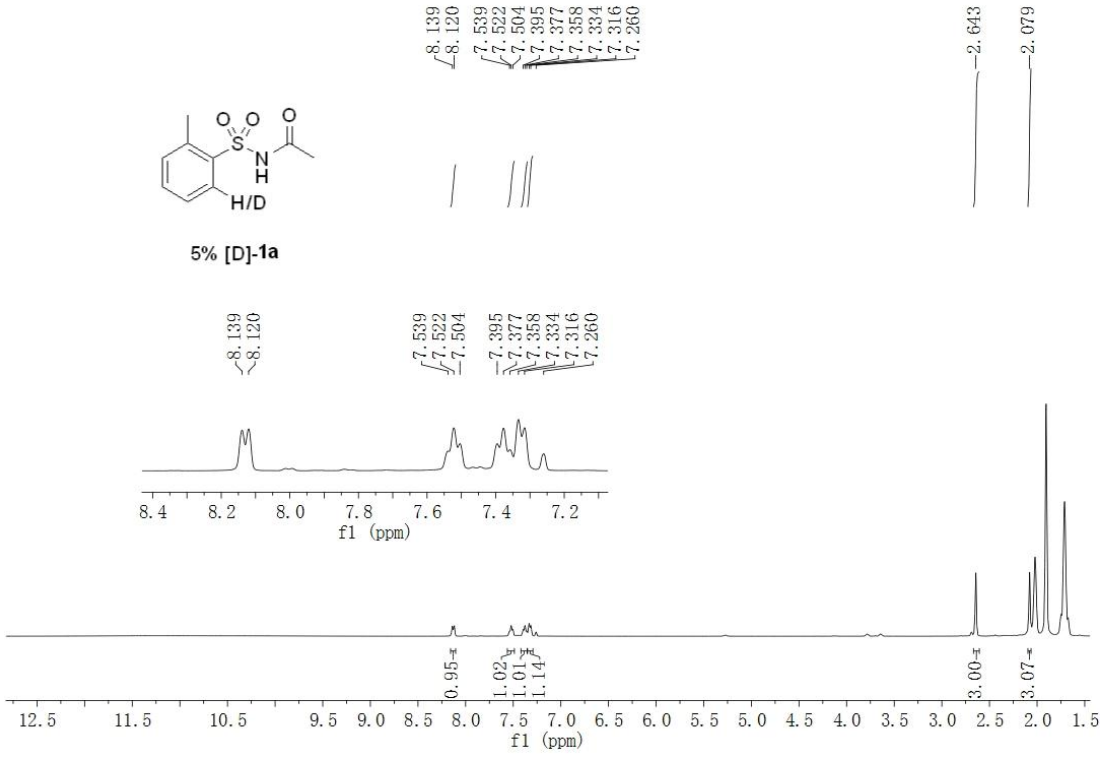
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with *N*-((3-methyl-[1,1'-biphenyl]-2-yl)sulfonyl)acetamide **5a** (29 mg, 0.1 mmol), concentrated hydrochloric acid (0.2 mL) and $POCl_3$ (1.8 mL) under air. The resulting mixture was stirred for 5 min at room temperature, and then heated at 100 °C for 24 h. Then the mixture was cooled and carefully poured on crushed ice. Organic phase was separated, dried over $MgSO_4$, filtered, and evaporated. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) afforded the desired product **9** as a white solid (18.7 mg, 81% yield).

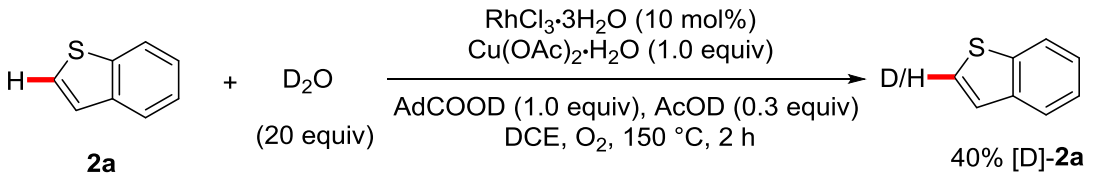
VII. Mechanism study

(i) The H/D exchange experiments for the coupling partners 1a and 2a



A Schlenk tube with a magnetic stir bar was charged with *N*-(*o*-tolylsulfonyl)acetamide **1a** (42.7 mg, 0.2 mmol), $RhCl_3{\cdot}3H_2O$ (5.3 mg, 0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (40.0 mg, 0.2 mmol), and AdCOOD (36.0 mg, 0.2 mmol) under air. Then the Schlenk tube was evacuated and refilled with O_2 three times. Next, AcOD (3.4 μL, 0.06 mmol), D_2O (72 μL, 4.0 mmol) and DCE (1.0 mL) were added. The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 150 °C for 2 hours. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 2/1/0.1, v/v/v) to provide [D]-**1a**. The deuterium incorporation was calculated from ^{1}H NMR analysis.

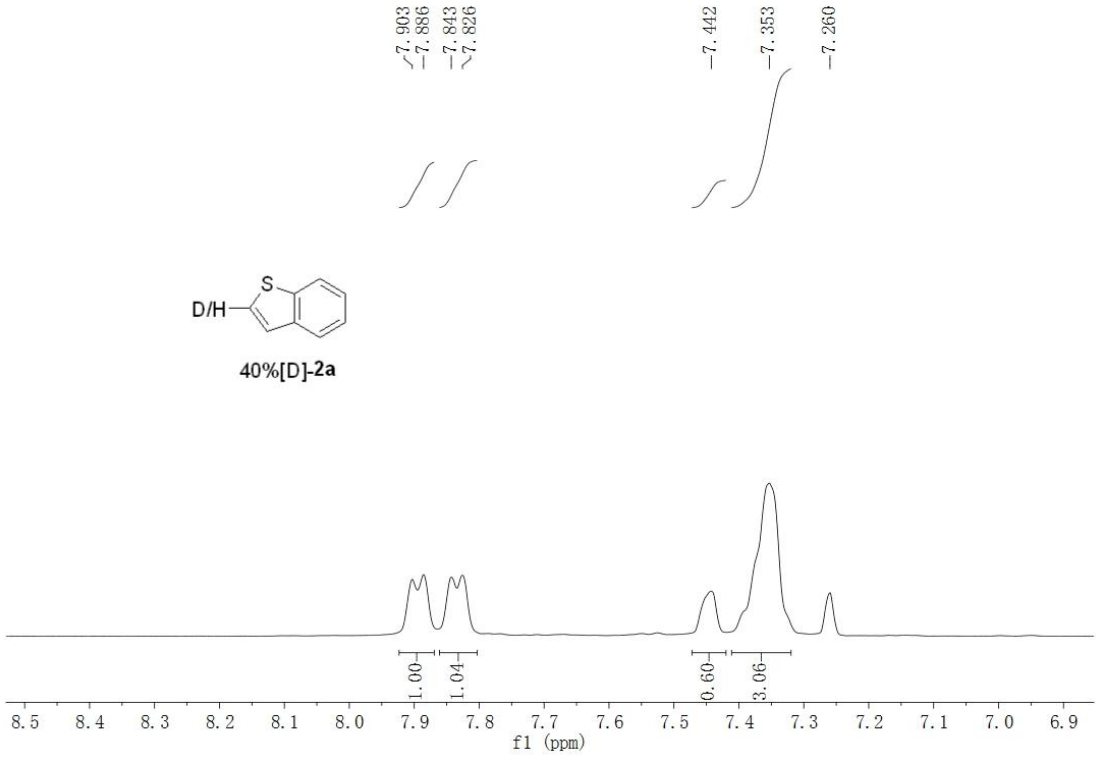


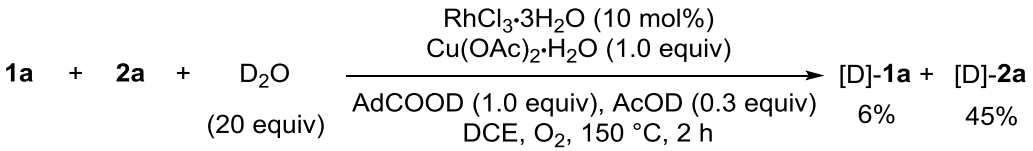


2a 40% [D]-**2a**

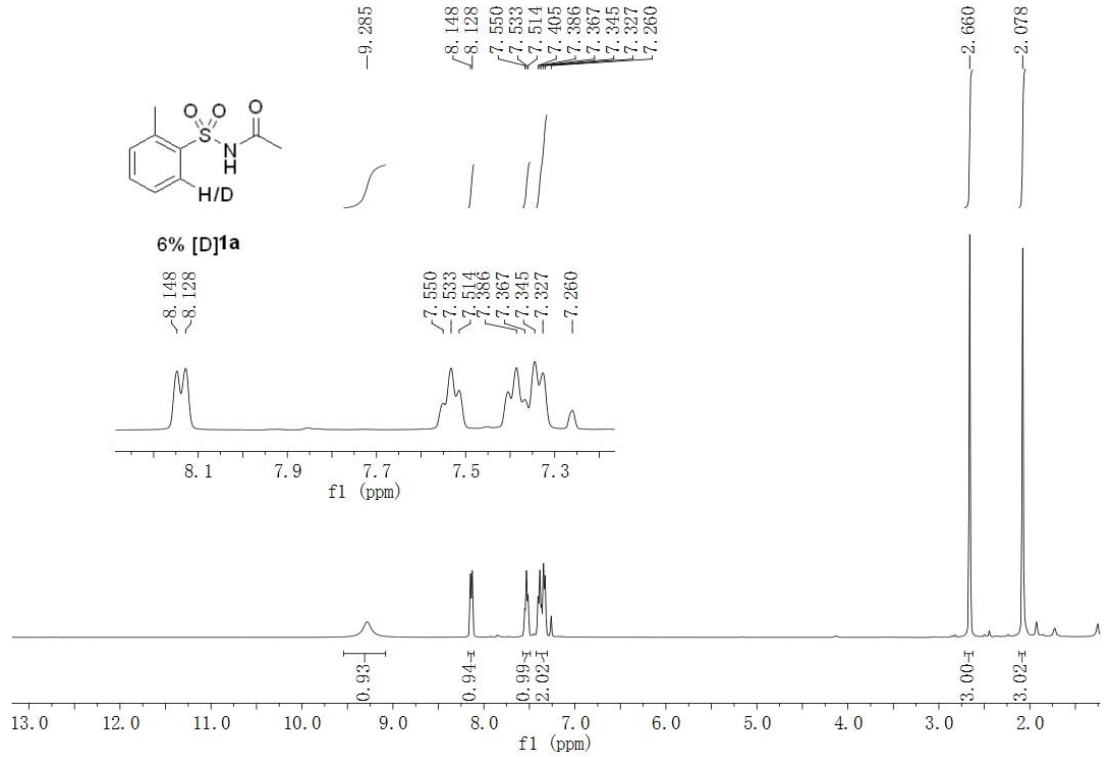
A Schlenk tube with a magnetic stir bar was charged with benzothiophene **2a** (80.6 mg, 0.6 mmol), $RhCl_3{\cdot}3H_2O$ (5.3 mg, 0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (40.0 mg, 0.2 mmol), AdCOOD (36.0 mg, 0.2 mmol) under air. Then the Schlenk tube was evacuated and refilled with O_2 three times. Next, AcOD (3.4 μL, 0.06 mmol), D_2O (72 μL, 4.0 mmol) and DCE (1.0 mL) were added. The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 150 °C for 2 hours. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1, v/v)

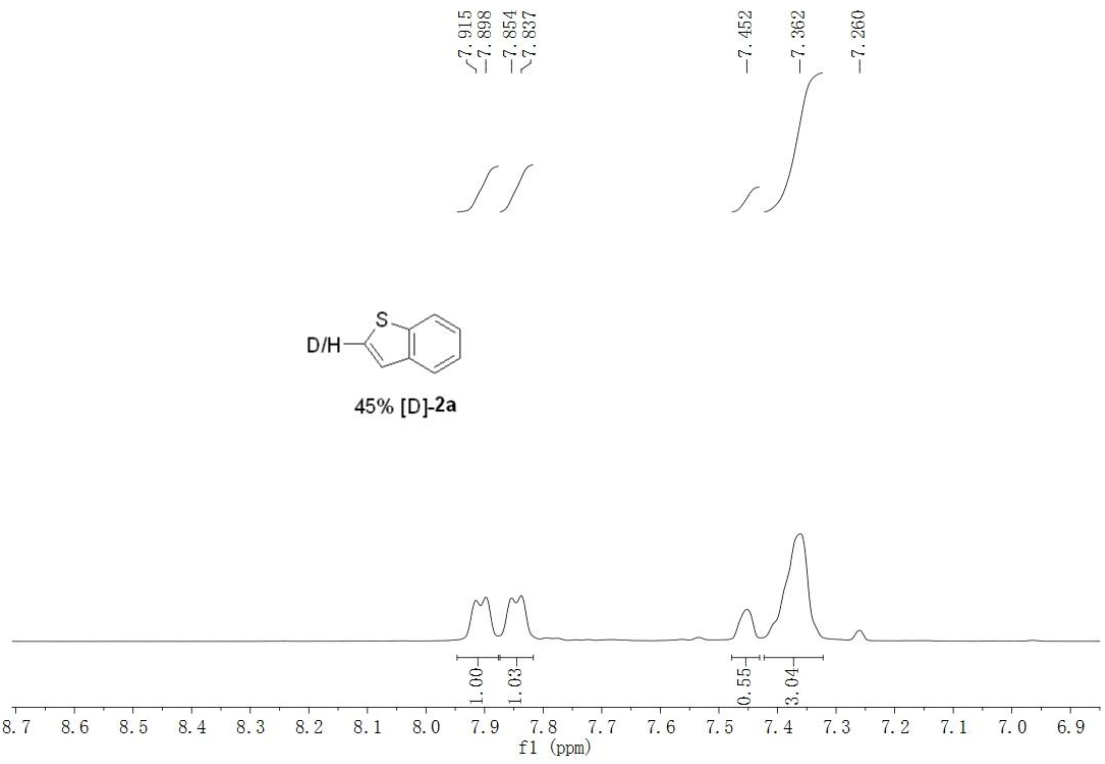
to provide [D]-**2a**. The deuterium incorporation was calculated from ^{1}H NMR analysis.



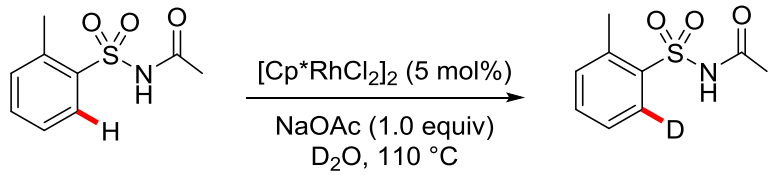


A Schlenk tube with a magnetic stir bar was charged with *N*-(*o*-tolylsulfonyl)acetamide **1a** (42.7 mg, 0.2 mmol), benzothiophene **2a** (80.6 mg, 0.6 mmol), $RhCl_3{\cdot}3H_2O$ (5.3 mg, 0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (40.0 mg, 0.2 mmol), AdCOOD (36.0 mg, 0.2 mmol) under air. Then the Schlenk tube was evacuated and refilled with O_2 three times. Next, AcOD (3.4 μL, 0.06 mmol), D_2O (72 μL, 4.0 mmol) and DCE (1.0 mL) were added. The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 150 °C for 2 hours. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide [D]-**1a** and [D]-**2a** and **3a** (20.7 mg, 30% yield). The deuterium incorporation was calculated from ^{1}H NMR analysis.



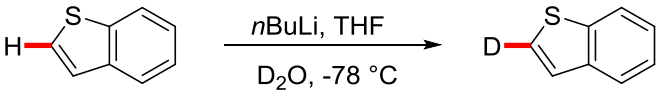


(ii) Kinetic isotope experiments



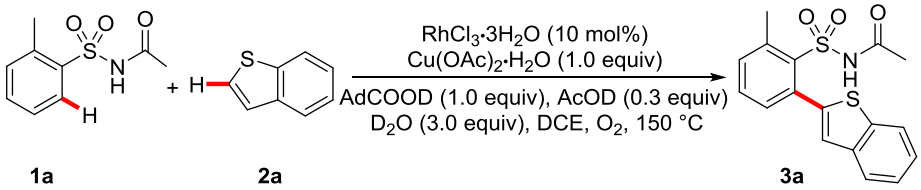
1a [D]-**1a**, 84%

Preparation of *N*-((2-methylphenyl-6-*d*)sulfonyl)acetamide ([D]-1a) : A flame-dried Schlenk test tube with a magnetic stirring bar was charged with *N*-(*o*-tolylsulfonyl)acetamide **1a** (42.7 mg, 0.2 mmol), NaOAc (16.4 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (6.3 mg, 0.01 mmol) under air. Then the Schlenk tube was evacuated and refilled with N_2 three times. Next, D_2O (0.5 mL) was added. The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 110 °C for 24 hours. The resulting solution was cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The organic extract was washed with water, dried over Na_2SO_4 and concentrated under reduced pressure. Purification via silica gel column chromatography (petroleum ether/ethyl acetate/methanol = 4/1/0.1, v/v/v) afforded the desired product [D]-**1a** as a white solid (36.0 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07 (s, 3H), 2.66 (s, 3H), 7.33 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 7.2 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.4, 23.5, 126.5, 132.6, 132.8, 134.3, 136.5, 137.7, 168.6 ppm.

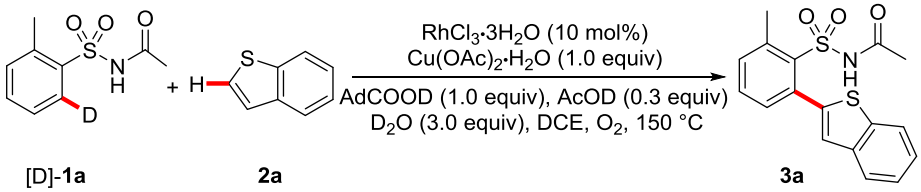


2a **[D]-2a**

Preparation of 2-deutero-benzothiophene ([D]-2a)[2] **:** A stirred solution of benzothiophene **2a** (20 mmol) in dry THF (40 mL) under nitrogen was cooled to -78 °C and *n*BuLi (2.5 M solution in hexane, 30 mmol) was added dropwise. The resulting mixture was stirred for 2 hours at -78 °C. D_2O (9 mL) was added to the reaction system and allowed to stir at room temperature for 2 hours. The suspension was extracted with water extracted with ethyl acetate three times. The organic extract was dried over Na_2SO_4 and concentrated under reduced pressure. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded the desired product [D]-**2a** as a white solid (2.2 g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.40 (m, 3H), 7.84 (d, J = 7.2 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H) ppm.

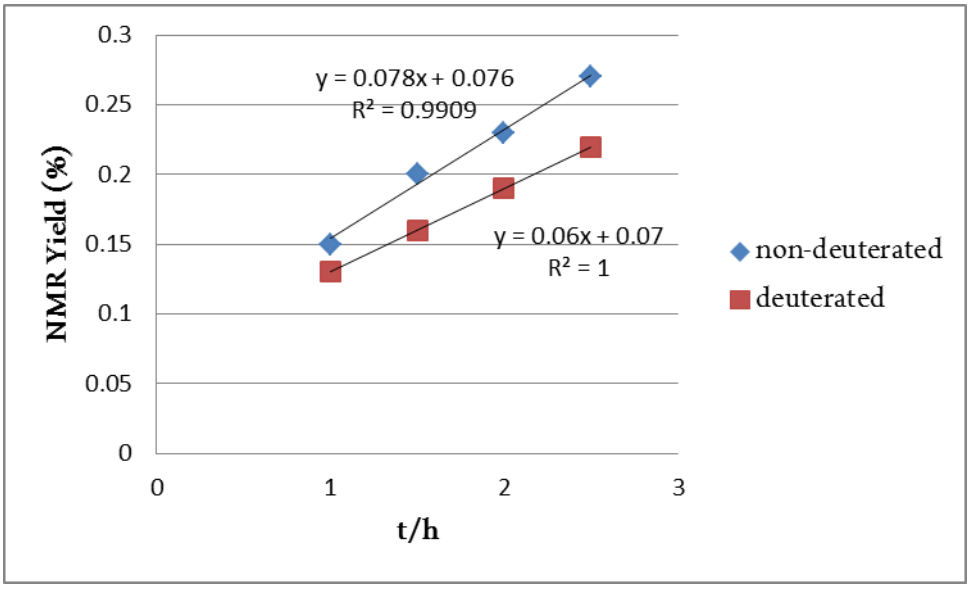


1a **2a** **3a**

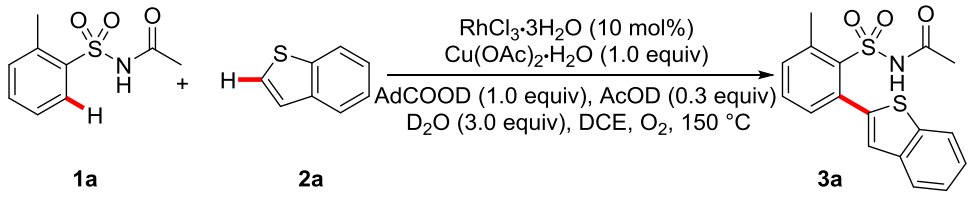


[D]-**1a** **2a** **3a**

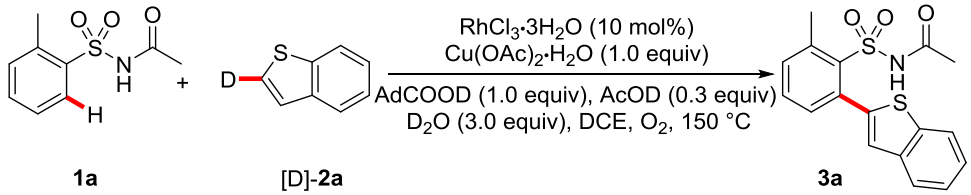
A Schlenk tube with a magnetic stir bar was charged with *N*-(*o*-tolylsulfonyl)acetamide **1a** (42.7 mg, 0.2 mmol) or [D]-**1a** (42.9 mg, 0.2 mmol), benzothiophene **2a** (80.6 mg, 0.6 mmol), $RhCl_3{\cdot}3H_2O$ (5.3 mg, 0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (40.0 mg, 0.2 mmol), AdCOOD (36.0 mg, 0.2 mmol) under air. Then the Schlenk tube was evacuated and refilled with O_2 three times. Next, AcOD (3.4 μL, 0.06 mmol), D_2O (10.8 μL, 0.6 mmol) and DCE (1.0 mL) were added. The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 150 °C for designated time (1.0 hour, 1.5 hours, 2.0 hours, 2.5 hours). The reaction solution was then cooled to ambient temperature, diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the yield of **3a** was determined by ^1H NMR of the crude product using CH_2Br_2 as internal standard.



KIE = 0.078/0.06 = 1.3



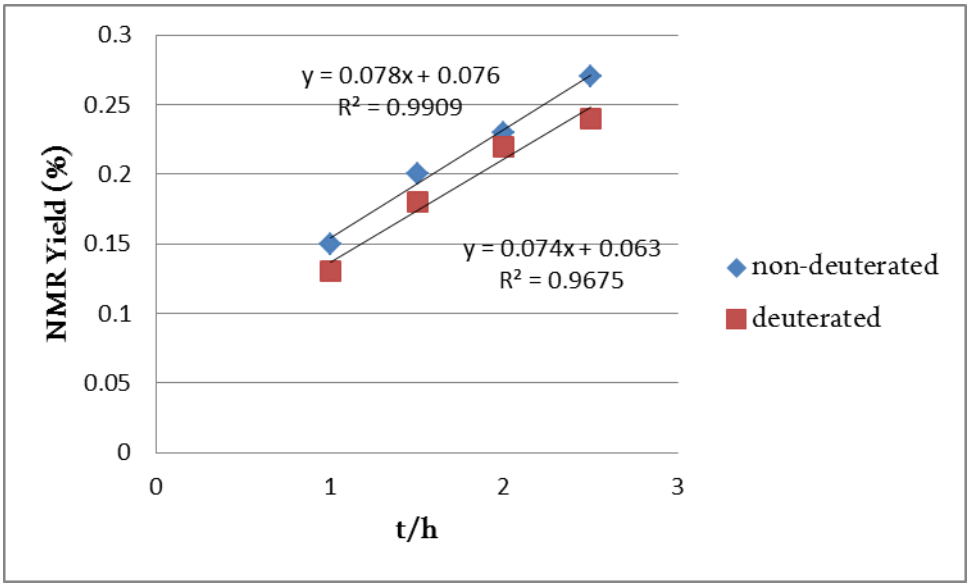
1a **2a** **3a**



1a [D]-**2a** **3a**

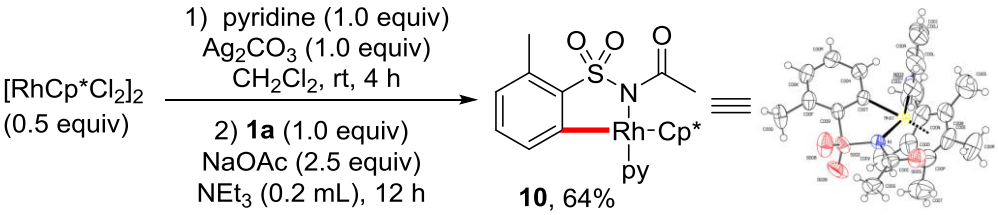
A Schlenk tube with a magnetic stir bar was charged with *N*-(*o*-tolylsulfonyl)acetamide **1a** (42.7 mg, 0.2 mmol), benzothiophene **2a** (80.6 mg, 0.6 mmol) or [D]-**2a** (81.1 mg, 0.6 mmol), $RhCl_3{\cdot}3H_2O$ (5.3 mg, 0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (40.0 mg, 0.2 mmol), AdCOOD (36.0 mg, 0.2 mmol) under air. Then the Schlenk tube was evacuated and refilled with O_2 three times. Next, AcOD (3.4 μL, 0.06 mmol), D_2O (10.8 μL, 0.6 mmol) and DCE (1.0 mL) were added. The Schlenk tube was then sealed with a Teflon lined cap and the mixture was

heated at 150 °C for designated time (1.0 hour, 1.5 hours, 2.0 hours, 2.5 hours). The reaction solution was then cooled to ambient temperature, diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the yield of **3a** was determined by ^{1}H NMR of the crude product using CH_2Br_2 as internal standard.



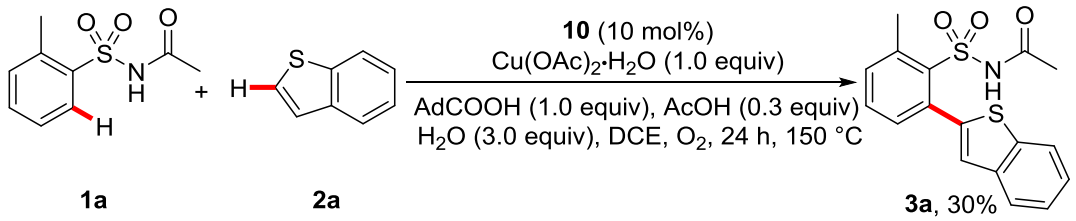
KIE = 0.078/0.74 = 1.1

(iii) Synthesis of cyclometalated Rh(III) complex 10[3]



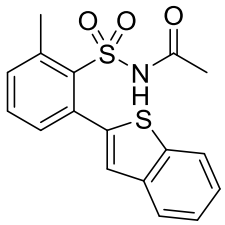
A Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (31.3 mg, 0.05 mmol), Ag_2CO_3 (27.5 mg, 0.10 mmol), pyridine (8 μL, 0.10 mmol), and CH_2Cl_2 (1 mL) at room temperature for 4 h. NaOAc (34.0 mg. 0.25 mmol) and *N*-(*o*-tolylsulfonyl)acetamide **1a** (21.4 mg, 0.1 mmol) were added to the solution with TEA (0.2 ml) and the resulting mixture was stirred at room temperature for 12 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 alumina (petroleum ether/EtOAc/methanol = 3/1/0.1, v/v/v) to provide the complex **10** as a red orange solid (33.5 mg, 64% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.57 (s, 15H), 2.42 (s, 3H), 2.46 (s, 3H), 7.01 (d, J = 7.2 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H), 7.25-7.40 (m, 3H), 7.78 (tt, J = 7.6 Hz, 2.0 Hz, 1H), 8.57 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 8.8, 17.1, 27.5, 100.2, 100.3, 123.9, 127.9, 129.7, 134.4, 134.9, 136.1, 146.7, 149.6, 151.6, 151.9, 174.8 ppm.

(iv) Complex 10-catalyzed heteroarylation of *N*-(*o*-tolylsulfonyl)acetamide 1a



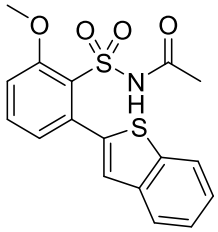
A Schlenk tube with a magnetic stir bar was charged with aryl sulfonamide **1a** (42.7 mg, 0.2 mmol), **2a** (80.6 mg, 0.6 mmol), complex **10** (10.5 mg, 0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (40.0 mg, 0.2 mmol), and AdCOOH (36.0 mg, 0.2 mmol) under air. Then the Schlenk tube was evacuated and refilled with O_2 three times. Next, AcOH (3.4 μL, 0.06 mmol), H_2O (10.8 μL, 0.6 mmol) and DCE (1.0 mL) were added. The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 150 °C for 24 hours. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was collected and concentrated. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3a** as a white solid (20.7 mg, 30% yield).

VIII. Experimental data for the described substances



***N*-((2-(Benzo[*b*]thiophen-2-yl)-6-methylphenyl)sulfonyl)acetamide (3a)**

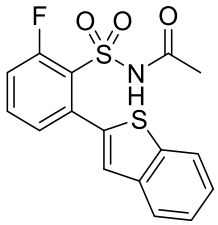
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3a** as a white solid (49.6 mg, 72% yield). M.p.: 197-199 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.84 (s, 3H), 2.72 (s, 3H), 7.34-7.40 (m, 4H), 7.52-7.57 (m, 2H), 7.85 (d, J = 7.2 Hz, 1H), 7.96 (d, J = 7.2 Hz, 1H), 11.88 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 22.1, 23.1, 121.9, 123.8, 124.2, 124.4, 124.7, 131.9, 132.1, 133.8, 135.0, 137.2, 139.36, 139.40, 139.7, 140.9, 168.9 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{15}NNaO_3S_2$ [M+Na]$^+$ 368.0386, found 368.0385.



***N*-((2-(Benzo[*b*]thiophen-2-yl)-6-methoxyphenyl)sulfonyl)acetamide (3b)**

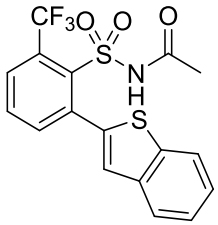
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3b** as a white solid (54.2 mg, 75% yield). M.p.: 232-234 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.92 (s, 3H), 3.97 (s, 3H), 7.09 (d, J

= 7.6 Hz, 1H), 7.34 (s, 1H), 7.35-7.41 (m, 3H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 11.85 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.1, 56.9, 114.0, 122.0, 123.6, 124.15, 124.21, 124.4, 125.4, 126.8, 133.5, 136.1, 139.3, 139.7, 140.9, 157.3, 169.1 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{15}NNaO_4S_2$ [M+Na]$^+$ 384.0335, found 384.0331.



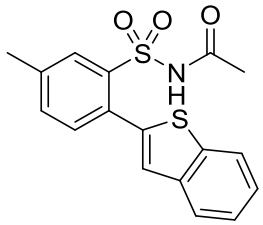
N-((2-(Benzo[*b*]thiophen-2-yl)-6-fluorophenyl)sulfonyl)acetamide (3c)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3c** as a white solid (50.6 mg, 72% yield). M.p.: 161-163 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.91 (s, 3H), 7.40-7.42 (m, 3H), 7.46 (s, 1H), 7.55-7.60 (m, 1H), 7.74-7.79 (m, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 12.37 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.1, 118.0 (d, *J* = 23 Hz), 122.1, 124.0, 124.6 (d, *J* = 4 Hz), 125.5, 127.0 (d, *J* = 12 Hz), 129.8 (d, *J* = 3 Hz), 131.2, 134.6 (d, *J* = 10 Hz), 136.1, 138.4 (d, *J* = 3 Hz), 139.2, 139.8, 159.2 (d, *J* = 254 Hz), 169.3 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{12}FNNaO_3S_2$ [M+Na]$^+$ 372.0135, found 372.0131.



N-((2-(Benzo[*b*]thiophen-2-yl)-6-(trifluoromethyl)phenyl)sulfonyl)acetamide (3d)

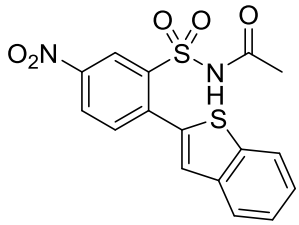
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3d** as a white solid (59.0 mg, 74% yield). M.p.: 210-212 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.65 (s, 3H), 7.44-7.48 (m, 3H), 7.86-7.94 (m, 3H), 8.04 (d, *J* = 6.8 Hz, 1H), 8.11 (d, *J* = 6.8 Hz, 1H), 11.75 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.2, 122.3, 123.1 (q, *J* = 273 Hz), 124.4, 124.8, 125.1, 126.7, 129.0 (q, *J* = 32 Hz), 129.3 (q, *J* = 6 Hz), 132.7, 135.3, 138.1, 138.6, 139.5, 140.0, 169.0 ppm. HRMS (ESI$^-$): calcd for $C_{17}H_{11}F_3NO_3S_2$ [M-H]$^-$ 398.0138, found 398.0124.



N-((2-(Benzo[*b*]thiophen-2-yl)-5-methylphenyl)sulfonyl)acetamide (3e)

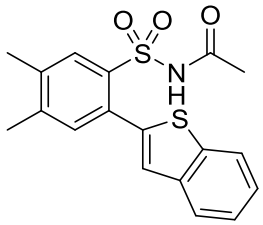
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol= 8/1/0.05, v/v/v) afforded **3e** as a white solid (45.0 mg, 65% yield). M.p.: 201-203 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.77 (s, 3H), 2.47 (s, 3H), 7.40-7.47 (m,

4H), 7.57 (d, J = 7.2 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 7.95 (s, 1H), 8.00 (d, J = 6.8 Hz, 1H), 11.79 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.7, 23.1, 122.1, 124.2, 124.5, 124.6, 125.7, 129.7, 130.5, 133.5, 133.7, 138.1, 138.2, 139.1, 139.6, 139.8, 168.7 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{15}NNaO_3S_2$ [M+Na]$^+$ 368.0386, found 368.0380.



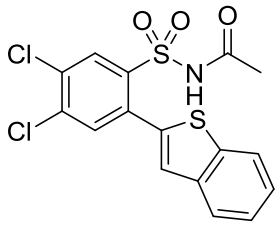
***N*-((2-(Benzo[*b*]thiophen-2-yl)-5-nitrophenyl)sulfonyl)acetamide (3f)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3f** as a yellow solid (30.8 mg, 41% yield). M.p.: 198-200 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.82 (s, 3H), 7.47-7.48 (m, 2H), 7.63 (s, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 4.4 Hz, 1H), 8.07 (d, J = 5.2 Hz, 1H), 8.55 (d, J = 8.0 Hz, 1H), 8.84 (s, 1H), 12.28 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.2, 122.3, 124.7, 124.9, 125.3, 125.7, 127.2, 127.6, 135.6, 135.8, 139.2, 139.4, 139.6, 140.1, 146.9, 169.2 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{12}N_2NaO_5S_2$ [M+Na]$^+$ 399.0080, found 399.0078.



***N*-((2-(Benzo[*b*]thiophen-2-yl)-4,5-dimethylphenyl)sulfonyl)acetamide (3g)**

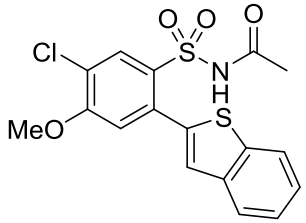
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3g** as a white solid (51.8 mg, 72% yield). M.p.: 188-190 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.76 (s, 3H), 2.32 (s, 3H), 2.37 (s, 3H), 7.36 (s, 1H), 7.37-7.43 (m, 3H), 7.88-7.90 (m, 2H), 7.99 (d, J = 7.6 Hz, 1H), 11.71 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 19.1, 23.1, 122.0, 124.2, 124.5, 124.6, 125.6, 129.9, 131.0, 134.4, 135.4, 137.8, 138.3, 139.6, 139.7, 142.6, 168.6 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{17}NNaO_3S_2$ [M+Na]$^+$ 382.0542, found 382.0546.



***N*-((2-(Benzo[*b*]thiophen-2-yl)-4,5-dichlorophenyl)sulfonyl)acetamide (3h)**

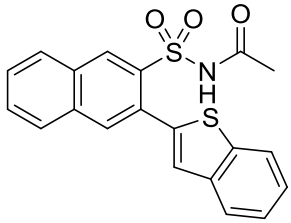
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3h** as a white solid (54.4 mg, 68% yield). M.p.: 203-205 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.83 (s,3H), 7.42-7.48 (m, 2H), 7.54 (s, 1H), 7.92-7.94 (m, 2H), 8.04 (d, J = 7.6 Hz, 1H), 8.26 (s, 1H), 12.12 (s, 1H) ppm.

^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.2, 122.2, 124.5, 124.7, 125.1, 126.9, 131.9, 132.1, 133.2, 135.1, 135.3, 136.2, 138.3, 139.3, 140.0, 169.1 ppm. HRMS (ESI$^-$): calcd for $C_{16}H_{10}{}^{35}Cl_2NO_3S_2$ [M-H]$^-$ 397.9485, found 397.9476; calcd for $C_{16}H_{10}{}^{35}Cl^{37}ClNO_3S_2$ [M-H]$^-$ 399.9455, found 399.9459; calcd for $C_{16}H_{10}{}^{37}Cl_2NO_3S_2$ [M-H]$^-$ 401.9426, found 401.9429.



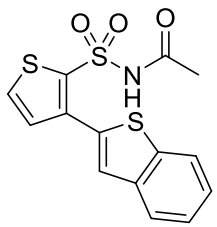
***N*-((2-(Benzo[*b*]thiophen-2-yl)-5-chloro-4-methoxyphenyl)sulfonyl)acetamide (3i)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3i** as a white solid (41.5 mg, 53% yield). M.p.: 170-172 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.82 (s, 3H), 3.97 (s, 3H), 7.28 (s, 1H), 7.41-7.47 (m, 2H), 7.51 (s, 1H), 7.93 (d, J = 6.8 Hz, 1H), 8.03 (d, J = 7.2 Hz, 1H), 8.10 (s, 1H), 11.92 (s, 1H) ppm.^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.2, 57.2, 117.3, 121.0, 122.1, 124.4, 124.7, 124.9, 126.2, 130.6, 132.2, 134.0, 137.1, 139.4, 139.9, 157.4, 168.8 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{14}{}^{35}ClNNaO_3S_2$ [M+Na]$^+$ 417.9945, found 417.9942; calcd for $C_{17}H_{14}{}^{37}ClNNaO_3S_2$ [M+Na]$^+$ 419.9915, found 419.9918.



***N*-((3-(Benzo[*b*]thiophen-2-yl)naphthalen-2-yl)sulfonyl)acetamide (3j)**

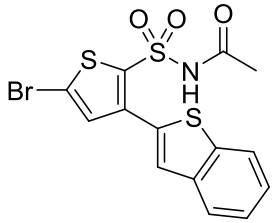
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3j** as a white solid (44.5mg, 58% yield). M.p.: 181-183 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.80 (s, 3H), 7.44 (m, 2H), 7.54 (s, 1H), 7.75-7.80 (m, 2H), 7.93 (d, J = 6.8 Hz, 1H), 8.03 (d, J = 6.8 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H), 8.18 (s, 1H), 8.31 (d, J = 7.6 Hz, 1H), 8.85 (s, 1H), 11.87 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.2, 122.1, 124.2, 124.6, 124.7, 126.2, 127.87, 127.94, 128.5, 129.3, 130.0, 131.1, 132.3, 133.5, 133.9, 135.4, 138.3, 139.6, 139.8, 168.7 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{15}NNaO_3S_2$ [M+Na]$^+$ 404.0386, found 404.0381.



***N*-((3-(Benzo[*b*]thiophen-2-yl)thiophen-2-yl)sulfonyl)acetamide (3k)**

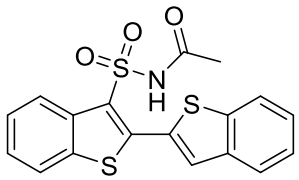
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3k** as a white solid (39.1mg, 58% yield). M.p.:

75-77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85 (s, 3H), 7.28 (d, J = 5.2 Hz, 1H), 7.37-7.42 (m, 2H), 7.69-7.70 (m, 2H), 7.83-7.85 (m, 2H), 8.30 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.3, 122.3, 124.6, 125.1, 125.6, 126.4, 131.8, 132.2, 133.6, 134.8, 138.3, 139.8, 140.4, 168.1 ppm. HRMS (ESI$^+$): calcd for $C_{14}H_{11}NNaO_3S_3$ $[M+Na]^+$ 359.9794, found 359.9795.



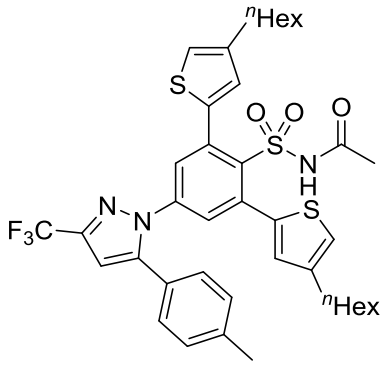
***N*-((3-(Benzo[*b*]thiophen-2-yl)-5-bromothiophen-2-yl)sulfonyl)acetamide (3l)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3l** as a white solid (41.3mg, 50% yield). M.p.: 196-198 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.85 (s, 3H), 7.42-7.48 (m, 2H), 7.62 (s, 1H), 7.80 (s, 1H), 7.92-7.94 (m, 1H), 8.02-8.04 (m, 1H), 12.55 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.1, 119.6, 122.3, 124.7, 125.0, 125.6, 126.8, 132.1, 134.3, 136.0, 137.5, 139.4, 139.8, 168.8 ppm. HRMS (ESI$^+$): calcd for $C_{14}H_{10}{}^{79}BrNNaO_3S_3$ $[M+Na]^+$ 437.8898, found 437.8899; calcd for $C_{14}H_{10}{}^{81}BrNNaO_3S_3$ $[M+Na]^+$ 439.8878, found 439.8881.



***N*-([2,2'-Bibenzo[*b*]thiophen]-3-ylsulfonyl)acetamide (3m)**

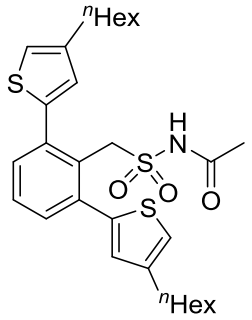
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3m** as a white solid (34.7mg, 45% yield). M.p.: 2129-231 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.86 (s, 3H), 7.46-7.48 (m, 2H), 7.54-7.64 (m, 2H), 7.97 (m, 2H), 8.05-8.06 (m, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 12.45 (s, 1H) ppm.^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.1, 122.4, 122.7, 124.1, 124.8, 125.2, 125.8, 126.28, 126.31, 128.2, 128.8, 130.9, 135.7, 137.6, 139.2, 140.5, 143.9, 169.4 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{13}NNaO_3S_3$ $[M+Na]^+$ 409.9955, found 409.9951.



***N*-((2,6-Bis(4-hexylthiophen-2-yl)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl**

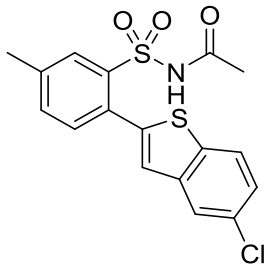
)phenyl)sulfonyl)acetamide (3n)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3n** as a white solid (68.1mg, 45% yield). M.p.: 60-62 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.86 (t, J = 6.8 Hz, 6H), 1.28 (m, 12H), 1.52-1.57 (m, 7H), 2.37 (s, 3H), 2.55 (t, J = 7.6 Hz, 4H), 6.90 (d, J = 1.2 Hz, 2H), 7.20-7.28 (m, 7H), 7.31 (s, 2H), 11.24 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 14.0, 20.9, 22.1, 23.2, 28.4, 29.80, 29.85, 31.2, 106.4, 121.2 (q, J = 267 Hz), 122.6, 125.4, 127.7, 129.1, 129.5, 130.1, 136.5, 139.2 (m), 139.3, 139.4 (m), 142.6 (q, J = 38 Hz), 142.7, 145.4, 168.9 ppm. HRMS (ESI$^+$): calcd for $C_{39}H_{44}F_3N_3NaO_3S_3$ [M+Na]$^+$ 778.2389, found 778.2386.



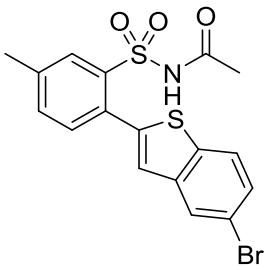
***N*-((2,6-Bis(4-hexylthiophen-2-yl)benzyl)sulfonyl)acetamide (3o)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **3o** as a white solid (50.6 mg, 44% yield). M.p.: 87-89 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.87 (m, 6H), 1.30 (m, 12H), 1.58-1.63 (m, 4H), 1.65 (s, 3H), 2.57 (t, J = 7.6 Hz, 4H), 5.18 (s, 2H), 7.12 (s, 2H), 7.21 (s, 2H), 7.38-7.46 (m, 3H), 11.36 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 14.0, 22.1, 23.0, 28.5, 29.8, 30.0, 31.2, 53.3, 121.4, 125.7, 128.6, 129.1, 131.2, 137.5, 141.1, 142.9, 168.8 ppm. HRMS (ESI$^-$): calcd for $C_{29}H_{38}NO_3S_3$ [M-H]$^-$ 544.2019, found 544.2018.



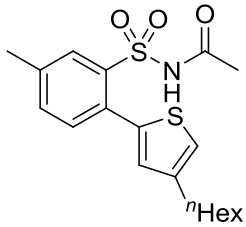
***N*-((2-(5-Chlorobenzo[*b*]thiophen-2-yl)-5-methylphenyl)sulfonyl)acetamide (4a)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **4a** as a white solid (50.4 mg, 66% yield). M.p.: 190-192 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.76 (s, 3H), 2.47 (s, 3H), 7.43-7.48 (m, 3H), 7.58 (d, J = 7.6 Hz, 1H), 7.96 (s, 1H), 8.00 (s, 1H), 8.04 (d, J = 8.8 Hz, 1H), 11.73 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.7, 23.1, 123.5, 123.8, 124.6, 125.2, 129.2, 129.5, 130.5, 133.4, 133.8, 138.1, 138.3, 139.5, 140.5, 140.9, 168.7 ppm. HRMS (ESI$^-$): calcd for $C_{17}H_{13}{}^{35}ClNO_3S_2$ [M-H]$^-$ 378.0031, found 378.0032; calcd for $C_{17}H_{13}{}^{37}ClNO_3S_2$ [M-H]$^-$ 380.0001, found 379.9999.



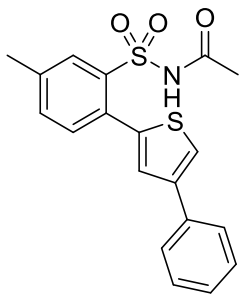
***N*-((2-(5-Bromobenzo[*b*]thiophen-2-yl)-5-methylphenyl)sulfonyl)acetamide (4b)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **4b** as a white solid (51.5 mg, 61% yield). M.p.: 208-210 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.77 (s, 3H), 2.47 (s, 3H), 7.43 (s, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.53-7.59 (m, 2H), 7.96 (s, 1H), 7.99 (d, J = 8.4 Hz, 1H), 8.14 (s, 1H), 11.72 (s, 1H) ppm. NMR (400 MHz, DMSO-d_6): δ = 20.7, 23.1, 117.7, 124.1, 125.0, 126.5, 127.1, 129.1, 130.5, 133.3, 133.7, 138.1, 138.6, 139.4, 140.2, 141.4, 168.6 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{14}{}^{79}BrNNaO_3S_2$ [M+Na]$^+$ 445.9491, found 445.9494; calcd for $C_{17}H_{14}{}^{81}BrNNaO_3S_2$ [M+Na]$^+$ 447.9471, found 447.9477.



***N*-((2-(4-Hexylthiophen-2-yl)-5-methylphenyl)sulfonyl)acetamide (4c)**

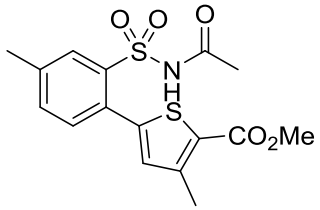
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **4c** as a white solid (65.5 mg, 84% yield). M.p.: 118-120 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.87 (t, J = 6.0 Hz, 3H), 1.30-1.35 (m, 6H), 1.57-1.64 (m, 2H), 1.74 (s, 3H), 2.43 (s, 3H), 2.60 (t, J = 8.0 Hz, 2H), 7.00 (s, 1H), 7.23 (s, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.89 (s, 1H), 11.60 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 14.0, 20.6, 22.1, 23.0, 28.5, 29.7, 29.9, 31.1, 121.4, 130.07, 130.14, 130.2, 133.4, 133.6, 137.5, 137.6, 138.4, 142.6, 168.4 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{25}NNaO_3S_2$ [M+Na]$^+$ 402.1168, found 402.1173.



***N*-((5-Methyl-2-(4-phenylthiophen-2-yl)phenyl)sulfonyl)acetamide (4d)**

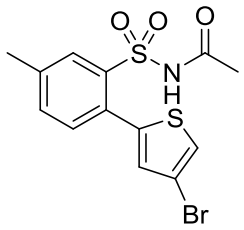
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **4d** as a white solid (50.0 mg, 67% yield). M.p.: 96-98 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.82 (s, 3H), 2.70 (s, 3H), 7.27-7.33 (m, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.46 (d, J = 1.2 Hz, 1H), 7.48 (d, J = 6.8 Hz, 1H), 7.55 (t, J

= 7.6 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 1.6 Hz, 1H), 11.77 (s, 1H) ppm.^{13}C NMR (100 MHz, DMSO-d_6): δ = 22.3, 23.1, 121.3, 126.0, 127.0, 127.1, 128.9, 131.9, 132.3, 133.6, 134.8, 135.2, 137.2, 139.4, 140.5, 141.1, 168.8 ppm. HRMS (ESI$^-$): calcd for $C_{19}H_{16}NO_3S_2$ [M-H]$^-$ 370.0577, found 370.0569.



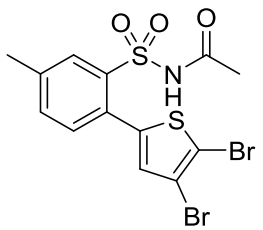
Methyl 5-(2-(*N*-acetylsulfamoyl)-4-methylphenyl)-3-methylthiophene-2-carboxylate (4e)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **4e** as a white solid (54.0 mg, 74% yield). M.p.: 173-175 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.78 (s, 3H), 2.45 (s, 3H), 2.52 (s, 3H), 3.81 (s, 3H), 7.06 (s, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.92 (s, 1H), 11.75 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 15.8, 20.6, 23.0, 51.9, 126.1, 128.5, 130.4, 133.1, 133.6, 133.8, 137.9, 139.5, 142.5, 145.6, 162.3, 168.6 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{17}NNaO_5S_2$ [M+Na]$^+$ 390.0440, found 390.0436.



***N*-((2-(4-Bromothiophen-2-yl)-5-methylphenyl)sulfonyl)acetamide (4f)**

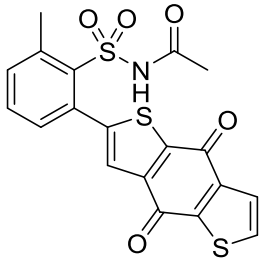
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **4f** as a white solid (50.7 mg, 68% yield). M.p.: 158-160 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.78 (s, 3H), 2.44 (s, 3H), 7.12 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.80 (s, 1H), 7.91 (s, 1H), 11.83 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.6, 23.0, 108.7, 124.8, 128.4, 130.4, 130.8, 133.5, 133.8, 137.9, 139.4, 139.5, 168.6 ppm. HRMS (ESI$^+$): calcd for $C_{13}H_{12}{}^{79}BrNNaO_3S_2$ [M+Na]$^+$ 395.9334, found 395.9340; calcd for $C_{13}H_{12}{}^{81}BrNNaO_3S_2$ [M+Na]$^+$ 397.9314, found 397.9311.



***N*-((2-(4,5-Dibromothiophen-2-yl)-5-methylphenyl)sulfonyl)acetamide (4g)**

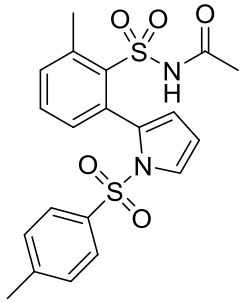
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **4g** as a white solid (65.7 mg, 75% yield). M.p.: 185-187 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.83 (s, 3H), 2.44 (s, 3H), 7.09 (s, 1H),

7.41 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.92 (s, 1H), 11.94 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.7, 23.1, 111.6, 113.5, 127.7, 130.6, 131.2, 133.6, 133.9, 138.0, 139.8, 139.9, 168.7 ppm. HRMS (ESI$^+$): calcd for $C_{13}H_{11}{}^{79}Br^{81}BrNNaO_3S_2$ [M+Na]$^+$ 475.8419, found 475.8422; calcd for $C_{13}H_{11}{}^{81}Br_2NNaO_3S_2$ [M+Na]$^+$ 477.8398, found 477.8400.



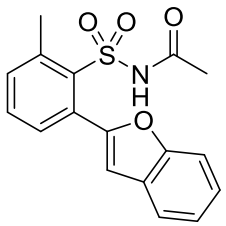
_N_-((2-(4,8-Dioxo-4,8-dihydrobenzo[1,2-_b_:4,5-_b'_]dithiophen-2-yl)-6-methylphenyl)sulfonyl)acetamide (4h)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **4h** as a white solid (39.1 mg, 45% yield). M.p.: > 250 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.89 (s, 3H), 2.71 (s, 3H), 7.38 (dd, J = 7.2 Hz, 1.6 Hz, 1H), 7.53 (s, 1H), 7.58-7.60 (m, 1H), 7.62 (d, J = 7.2 Hz, 1 H), 7.67 (d, J = 5.2 Hz, 1H), 8.19 (d, J = 5.2 Hz, 1H), 12.07 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.6, 23.1, 126.4, 126.8, 131.6, 132.5, 133.1, 134.8, 136.1, 136.9, 139.6, 141.5, 142.3, 143.4, 144.1, 150.1, 169.2, 174.20, 174.24 ppm. HRMS (ESI$^-$): calcd for $C_{19}H_{12}NO_5S_3$ [M-H]$^-$ 429.9883, found 429.9878.



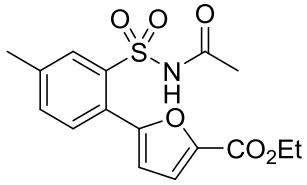
_N_-((2-Methyl-6-(1-tosyl-1H-pyrrol-3-yl)phenyl)sulfonyl)acetamide (4i)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **4i** as a white solid (58.4 mg, 68% yield). M.p.: 150-152 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.72 (s, 3H), 2.39 (s, 3H), 2.64 (s, 3H), 6.48 (q, J = 1.6 Hz, 1H), 7.07 (dd, J = 7.2 Hz, 0.8 Hz, 1H), 7.28-7.29 (m, 1H), 7.35 (t, J = 2.0 Hz, 1H), 7.37-7.40 (m, 1H), 7.42-7.47 (m, 3H), 7.87 (d, J = 8.4 Hz, 2H), 11.73 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.1, 22.2, 22.8, 116.4, 119.0, 120.0, 126.9, 128.0, 130.3, 131.7, 132.0, 132.6, 135.1, 135.4, 136.6, 138.8, 145.3, 168.8 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{20}N_2NaO_5S_2$ [M+Na]$^+$ 455.0706, found 455.0710.



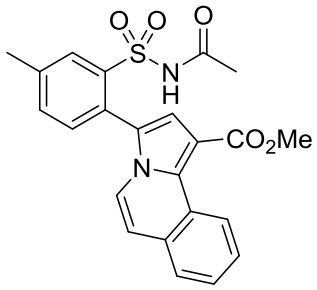
_N_-((2-(Benzofuran-2-yl)-6-methylphenyl)sulfonyl)acetamide (4k)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **4k** as a white solid (41.8 mg, 63% yield). M.p.: 128-130 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.84 (s, 3H), 2.72 (s, 3H), 6.95 (s, 1H), 7.26-7.34 (m, 2H), 7.47 (d, J = 7.2 Hz, 1H), 7.56-7.58 (m, 2H), 7.62 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 11.96 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ =21.7, 23.0, 106.0, 111.3, 121.2, 122.8, 124.1, 128.6, 131.43, 131.45, 132.3, 134.5, 137.2, 139.3, 153.9, 154.3, 168.8 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{15}NNaO_4S$ [M+Na]$^+$ 352.0614, found 352.0617.



Ethyl 5-(2-(_N_-acetylsulfamoyl)-4-methylphenyl)furan-2-carboxylate (4l)

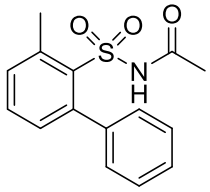
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **4l** as a white solid (32.2 mg, 46% yield). M.p.: 134-136 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.30 (t, J = 7.2 Hz, 3H), 1.88 (s, 3H), 2.47 (s, 3H), 4.31 (q, J = 7.2 Hz, 2H), 6.92 (d, J = 3.6 Hz, 1H), 7.41 (d, J = 3.6 Hz, 1H), 7.57-7.63 (m, 2H), 7.95 (s, 1H), 11.82 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 14.2, 20.8, 23.0, 60.7, 113.2, 119.4, 125.2, 130.9, 131.9, 134.0, 137.4, 140.1, 144.0, 152.7, 158.0, 168.7 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{17}NNaO_6S$ [M+Na]$^+$ 374.0669, found 374.0666.



Methyl 3-(2-(_N_-acetylsulfamoyl)-4-methylphenyl)pyrrolo[2,1-_a_]isoquinoline-1-carboxylate (4m)

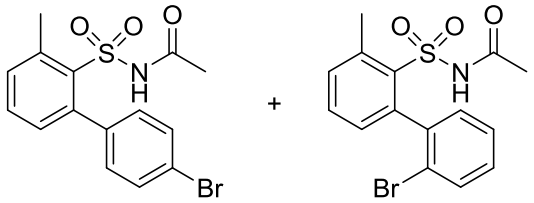
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **4m** as a yellow solid (53.0 mg, 61% yield). M.p.: 133-135 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.70 (s, 3H), 2.46 (s, 3H), 3.33 (s, 3H), 7.18-7.22 (m, 2H), 7.48 (dd, J = 8.0 Hz, 0.4 Hz, 1H), 7.55-7.58 (m, 3H), 7.79-7.81 (m, 1H), 7.90 (s, 1H), 8.27 (d, J = 7.2 Hz, 1H), 9.27-9.29 (m, 1H), 11.27 (s, 1H) ppm. ^{13}C NMR

(100 MHz, DMSO-d_6): δ = 20.6, 23.0, 50.5, 108.4, 112.9, 117.7, 124.86, 124.87, 125.2, 125.4, 127.15, 127.17, 127.4, 128.8, 129.7, 130.0, 132.5, 132.9, 133.0, 136.6, 137.3, 165.4, 168.2 ppm. HRMS (ESI$^+$): calcd for $C_{23}H_{20}NNaO_5S$ [M+Na]$^+$ 459.0986, found 459.0984.



N-((3-Methyl-[1,1'-biphenyl]-2-yl)sulfonyl)acetamide (5a)

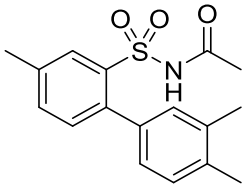
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **5a** as a white solid (42.5 mg, 74% yield). M.p.: 196-198 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.76 (s, 3H), 2.69 (s, 3H), 7.06 (d, J = 7.2 Hz, 1H), 7.25 (d, J = 6.4 Hz, 2H), 7.34 (m, 3H), 7.43 (d, J = 7.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 11.60 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.9, 22.9, 126.9, 127.3, 128.6, 131.0, 131.8, 132.4, 136.2, 138.4, 141.1, 142.8, 168.6 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_{15}NNaO_3S$ [M+Na]$^+$ 312.0665, found 312.0661.



5b 1.3 : **5b'** 1

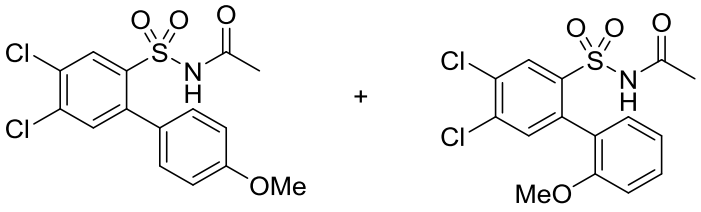
N-((4'-bromo-3-methyl-[1,1'-biphenyl]-2-yl)sulfonyl)acetamide (5b) and N-((2'-bromo-3-methyl-[1,1'-biphenyl]-2-yl)sulfonyl)acetamide (5b')

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded the mixture of **5b** and **5b'** as a white solid (42.4 mg, 58% yield). The ratio of **5b**/**5b'** was 1.3/1 as determined by ^{1}H NMR, and the compounds were separated by preparative HPLC. ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of two isomers): δ = 1.84 (C<u>H</u>$_3$, major isomer), 1.86 (C<u>H</u>$_3$, minor isomer), 2.81-2.82 (C<u>H</u>$_3$, major + minor isomer), 7.07-7.11 (m, Ar<u>H</u>, major + minor isomer), 7.23 (d, J = 6.8 Hz, Ar<u>H</u>, major isomer), 7.29-7.35 (m, Ar<u>H</u>, minor isomer), 7.37-7.39 (m, Ar<u>H</u>, major + minor isomer), 7.44-7.48 (m, Ar<u>H</u>, major + minor isomer), 7.56 (d, J = 8.0 Hz, Ar<u>H</u>, major isomer) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, **5b'**): δ = 1.86 (s, 3H), 2.82 (s, 3H), 7.11 (d, J = 7.6 Hz, 1H), 7.29-7.35 (m, 2H), 7.38 (d, J = 7.6 Hz, 1H), 7.45-7.48 (m, 2H), 7.56 (dt, J = 7.2 Hz, 2.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of two isomers): δ = 23.2, 23.5, 122.0, 122.4, 128.2, 129.6, 130.9, 131.0, 131.2, 132.0, 132.38, 132.41, 133.4, 133.5, 136.2, 139.7, 140.4, 141.4, 167.8 ppm. ^{13}C NMR (100 MHz, $CDCl_3$, **5b'**):δ = 23.3, 23.5, 122.0, 128.2, 129.6, 130.9, 132.0, 133.5, 140.6, 140.7, 142.8, 167.7 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_{14}{}^{79}BrNNaO_3S$ [M+Na]$^+$ 389.9770, found 389.9770; $C_{15}H_{14}{}^{81}BrNNaO_3S$ [M+Na]$^+$ 391.9750, found 391.9746.



***N*-((3',4,4'-Trimethyl-[1,1'-biphenyl]-2-yl)sulfonyl)acetamide (5e)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **5e** as a white solid (39.2 mg, 62% yield). M.p.: 174-176 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.72 (s, 3H), 2.24 (s, 3H), 2.27 (s, 3H), 2.43 (s, 3H), 6.96-6.98 (m, 2H), 7.14-7.18 (m, 2H), 7.48 (d, J = 7.6 Hz, 1H), 7.86 (s, 1H), 11.37 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 19.3, 19.6, 20.6, 23.0, 126.4, 128.9, 129.8, 130.0, 132.5, 133.6, 135.4, 135.5, 136.2, 137.2, 137.3, 138.0, 168.5 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{19}NNaO_3S$ [M+Na]$^+$ 340.0978, found 340.0975.

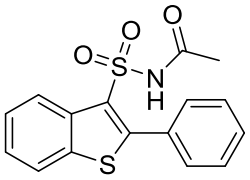


5f : **5f'**

10 : 1

***N*-((4,5-Bichloro-4'-methoxy-[1,1'-biphenyl]-2-yl)sulfonyl)acetamide (5f) and *N*-((4,5-Bichloro-2'-methoxy-[1,1'-biphenyl]-2-yl)sulfonyl)acetamide (5f')**

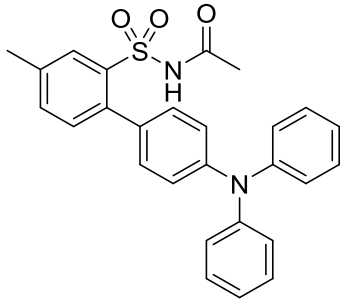
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded the mixture of **5f** and **5f'** as a white solid (56.3 mg, 75% yield). The ratio of **5c**/**5c'** was 10/1 as determined by ^{1}H NMR. ^{1}H NMR (400 MHz, DMSO-d_6, a mixture of two isomers): δ = 1.76 (C$\underline{H}_3$, major + minor isomer), 3.78 (OC$\underline{H}_3$, minor isomer), 3.81 (OC$\underline{H}_3$, major isomer), 6.86 (d, J = 7.6 Hz, Ar$\underline{H}$, minor isomer), 6.89-6.90 (m, Ar$\underline{H}$, minor isomer), 7.00-7.02 (m, Ar$\underline{H}$, major + minor isomer), 7.26 (d, J = 8.8 Hz, Ar$\underline{H}$, major isomer), 7.36 (t, J = 8.0 Hz, Ar$\underline{H}$, minor isomer), 7.62 (s, Ar$\underline{H}$, major isomer), 7.66 (s, Ar$\underline{H}$, minor isomer), 8.18 (s, Ar$\underline{H}$, major isomer), 8.20 (s, Ar$\underline{H}$, minor isomer), 11.75 (s, N$\underline{H}$Ac, major + minor isomer) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.0, 55.2, 113.5, 128.3, 130.2, 130.3, 131.5, 134.4, 135.9, 137.6, 140.8, 159.4, 168.8 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_{13}{}^{35}Cl_2NNaO_4S$ [M+Na]$^+$ 395.9835, found 395.9836; calcd for $C_{15}H_{13}{}^{35}Cl^{37}ClNNaO_4S$ [M+Na]$^+$ 397.9805, found 397.9805; calcd for $C_{15}H_{13}{}^{37}Cl_2NNaO_4S$ [M+Na]$^+$ 399.9776, found 399.9775.



***N*-((2-Phenylbenzo[*b*]thiophen-3-yl)sulfonyl)acetamide (5g)**

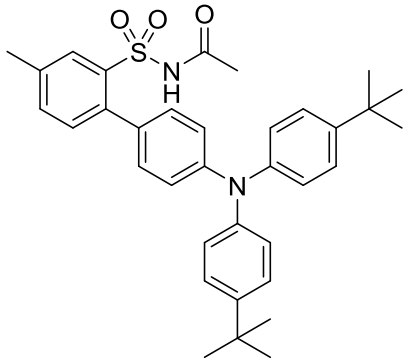
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **5g** as a white solid (35.6 mg, 54% yield).

M.p.: 98-100 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.81 (s, 3H), 7.46-7.52 (m, 3H), 7.55 (d, J = 8.0 Hz, 1H), 7.58-7.62 (m, 1H), 7.66-7.69 (m, 2H), 8.12 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 12.26 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.0, 122.6, 123.5, 125.7, 125.9, 126.7, 127.9, 129.4, 130.2, 131.5, 135.3, 137.2, 152.0, 169.0 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{13}NNaO_3S_2$ [M+Na]$^+$ 354.0229, found 354.0223.



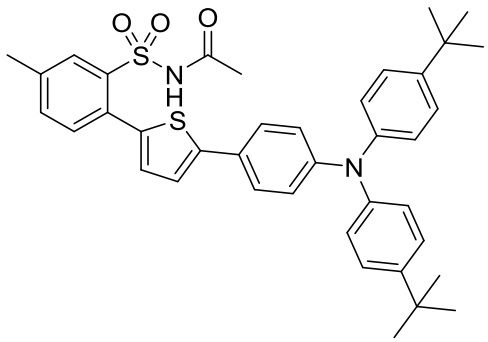
_N_-((4'-(Diphenylamino)-4-methyl-[1,1'-biphenyl]-2-yl)sulfonyl)acetamide (5h)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **5h** as a white solid (62.2 mg, 68% yield). M.p.: 179-181 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.69 (s, 3H), 2.44 (s, 3H), 7.00 (d, J = 8.4 Hz, 2H), 7.07 (t, J = 7.2 Hz, 2H), 7.13 (d, J = 7.6 Hz, 4H), 7.17 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 8.0 Hz, 4H), 7.50 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 11.47 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.5, 22.8, 122.2, 123.2, 124.2, 129.4, 129.5, 129.9, 132.4, 132.5, 133.6, 137.2, 137.3, 137.5, 146.8, 147.1, 168.3 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{24}N_2NaO_3S$ [M+Na]$^+$ 479.1400, found 479.1403.



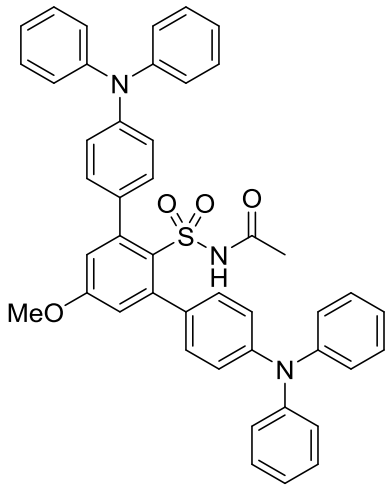
_N_-((4'-(Bis(4-(*tert*-butyl)phenyl)amino)-4-methyl-[1,1'-biphenyl]-2-yl)sulfonyl)acetamide (5i)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **5i** as a white solid (69.4 mg, 61% yield). M.p.: 134-136 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.28 (s, 18H), 1.70 (s, 3H), 2.43 (s, 3H), 6.92 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 4H), 7.14 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.8 Hz, 4H), 7.49 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 11.48 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.5, 22.9, 31.2, 34.1, 121.1, 124.1, 126.2, 129.4, 129.8, 131.5, 132.6, 133.6, 137.2, 137.30, 137.33, 144.5, 145.6, 147.0, 168.3 ppm. HRMS (ESI$^+$): calcd for $C_{35}H_{40}N_2NaO_3S$ [M+Na]$^+$ 591.2652, found 591.2645.



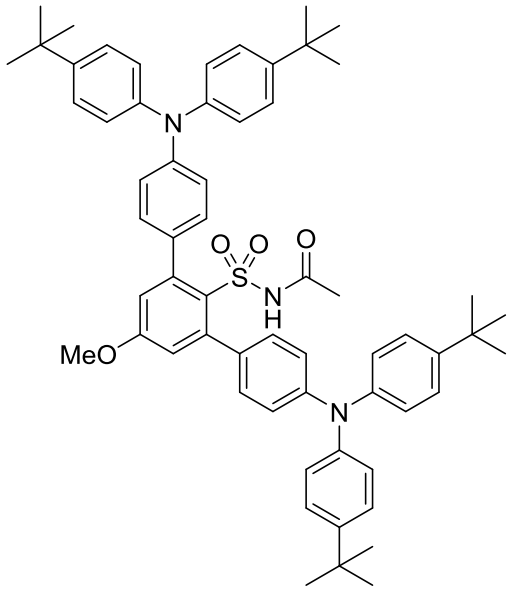
***N*-((2-(5-(4-(Bis(4-(*tert*-butyl)phenyl)amino)phenyl)thiophen-2-yl)-5-methylphenyl)sulfonyl)acetamide (5j)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **5j** as a yellow solid (57.5 mg, 44% yield). M.p.: 208-210 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.28 (s, 18H), 1.77 (s, 3H), 2.44 (s, 3H), 6.93 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 4H), 7.14 (d, J = 3.6 Hz, 1H), 7.34-7.37 (m, 5H), 7.42 (d, J = 8.0 Hz, 1H), 7.52-7.56 (m, 3H), 7.92 (s, 1H), 11.70 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 23.6, 31.6, 34.5, 122.3, 122.5, 124.5, 126.3, 126.4, 126.5, 130.1, 130.6, 131.1, 133.7, 134.2, 136.2, 137.7, 139.4, 144.7, 146.4, 146.5, 148.4, 167.7 ppm. HRMS (ESI$^+$): calcd for $C_{39}H_{43}N_2O_3S_2$ [M+H]$^+$ 651.2710, found 651.2711.



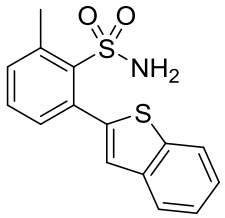
***N*-((4,4''-Bis(diphenylamino)-5'-methoxy-[1,1':3',1''-terphenyl]-2'-yl)sulfonyl)acetamide (5k)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **5k** as a white solid (33.0 mg, 46% yield). M.p.: 243-245 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.55 (s, 3H), 3.87 (s, 3H), 6.82 (s, 2H), 7.00 (d, J = 8.4 Hz, 4H), 7.05-7.11 (m, 12H), 7.31-7.35 (m, 12H), 10.92 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 22.8, 55.8, 109.6, 116.7, 122.4, 123.2, 124.2, 129.5, 129.7, 135.0, 144.4, 146.7, 147.1, 160.1, 167.8 ppm. HRMS (ESI$^+$): calcd for $C_{45}H_{37}N_3NaO_4S$ [M+Na]$^+$ 738.2397, found 738.2399.



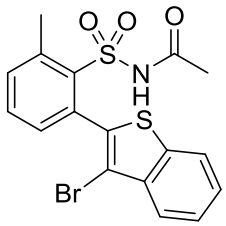
***N*-((4,4''-Bis(bis(4-(*tert*-butyl)phenyl)amino)-5'-methoxy-[1,1':3',1''-terphenyl]-2'-yl)sulfonyl)acetamide (5l)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate/methanol = 8/1/0.05, v/v/v) afforded **5l** as a white solid (45.9 mg, 49% yield). M.p.: 119-121 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.28 (s, 36H), 1.55 (s, 3H), 3.87 (s, 3H), 6.79 (s, 2H), 6.93 (d, J = 8.0 Hz, 4H), 7.03 (d, J = 8.0 Hz, 8H), 7.28 (d, J = 8.0 Hz, 4H), 7.34 (d, J = 8.0 Hz, 8H), 10.89 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.1, 31.6, 34.5, 55.8, 110.2, 117.1, 121.5, 124.7, 126.3, 129.7, 133.5, 144.8, 145.6, 146.4, 148.4, 161.0, 167.9 ppm. HRMS (ESI$^+$): calcd for $C_{61}H_{69}N_3NaO_4S$ [M+Na]$^+$ 962.4901, found 962.4903.



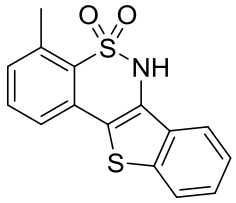
2-(Benzo[*b*]thiophen-2-yl)-6-methylbenzenesulfonamide (6)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1, v/v) afforded **6** as a white solid (26.3 mg, 87% yield). M.p.: 212-214 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.80 (s, 3H), 4.52 (s, 2H), 7.36-7.42 (m, 5H), 7.54 (s, 1H), 7.82-7.87 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.4, 122.2, 124.5, 125.3, 125.4, 126.2, 130.7, 131.6, 132.8, 133.8, 138.9, 139.6, 140.2, 141.1, 141.4 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_{13}NNaO_2S_2$ [M+Na]$^+$ 326.0280, found 326.0285.



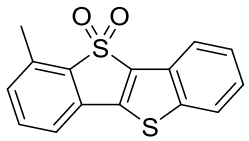
***N*-((2-(3-Bromobenzo[*b*]thiophen-2-yl)-6-methylphenyl)sulfonyl)acetamide (7')**

Purification via silica gel column chromatography (petroleum ether/ethyl acetate/CH_3OH = 10/1/0.05, v/v/v) afforded the desired product **7'** as a light yellow solid (150.2 mg, 89% yield). M.p.: 200-202 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.91 (s, 3H), 2.74 (s, 3H), 7.29 (d, J = 6.4 Hz, 1H), 7.46-7.59 (m, 3H), 7.64 (t, J = 7.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 12.08 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.6, 23.2, 108.0, 122.5, 122.6, 125.2, 125.5, 131.9, 132.5, 134.0, 134.5, 136.9, 137.4, 138.2, 138.3, 139.5, 168.9 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{14}{}^{79}BrNNaO_3S_2$ [M+Na]$^+$ 445.9491, found 445.9483; calcd for $C_{17}H_{14}{}^{81}BrNNaO_3S_2$ [M+Na]$^+$ 447.9470, found 447.9462.



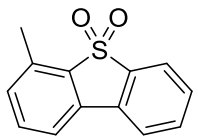
4-Methyl-6*H*-benzo[*e*]benzo[4,5]thieno[3,2-*c*][1,2]thiazine 5,5-dioxide (7)

Purification via silica gel column chromatography (petroleum ether/ethyl acetate/CH_3OH = 10/1/0.05, v/v/v) afforded the desired product **7** as a white solid (33.1 mg, 55% yield). M.p.: 240-242 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.70 (s, 3H), 7.45 (d, J = 7.2 Hz, 1H), 7.50-7.53 (m, 2H), 7.57 (d, J = 7.6 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.97-7.99 (m, 1H), 8.04-8.08 (m, 1H), 11.87 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 19.9, 118.7, 121.5, 123.4, 123.5, 125.3, 126.9, 129.8, 130.2, 131.1, 131.6, 132.3, 132.4, 134.7, 136.4 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_{11}NNaO_2S_2$ [M+Na]$^+$ 324.0123, found 324.0124.



6-Methylbenzo[*b*]benzo[4,5]thieno[2,3-*d*]thiophene 5,5-dioxide (8)

Purification by column chromatography on silica gel (petroleum ether/ ethyl acetate = 8/1, v/v) afforded **8** as a white solid (22.5mg, 79% yield). M.p.: 172-174 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.71 (s, 3H), 7.25-7.27 (m, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.45 (m, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 17.0, 119.8, 122.5, 123.9, 126.5, 126.8, 128.6, 130.5, 132.6, 133.5, 133.9, 135.8, 140.3, 142.8, 143.9 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_{10}NaO_2S_2$ [M+Na]$^+$ 309.0014, found 309.0015.



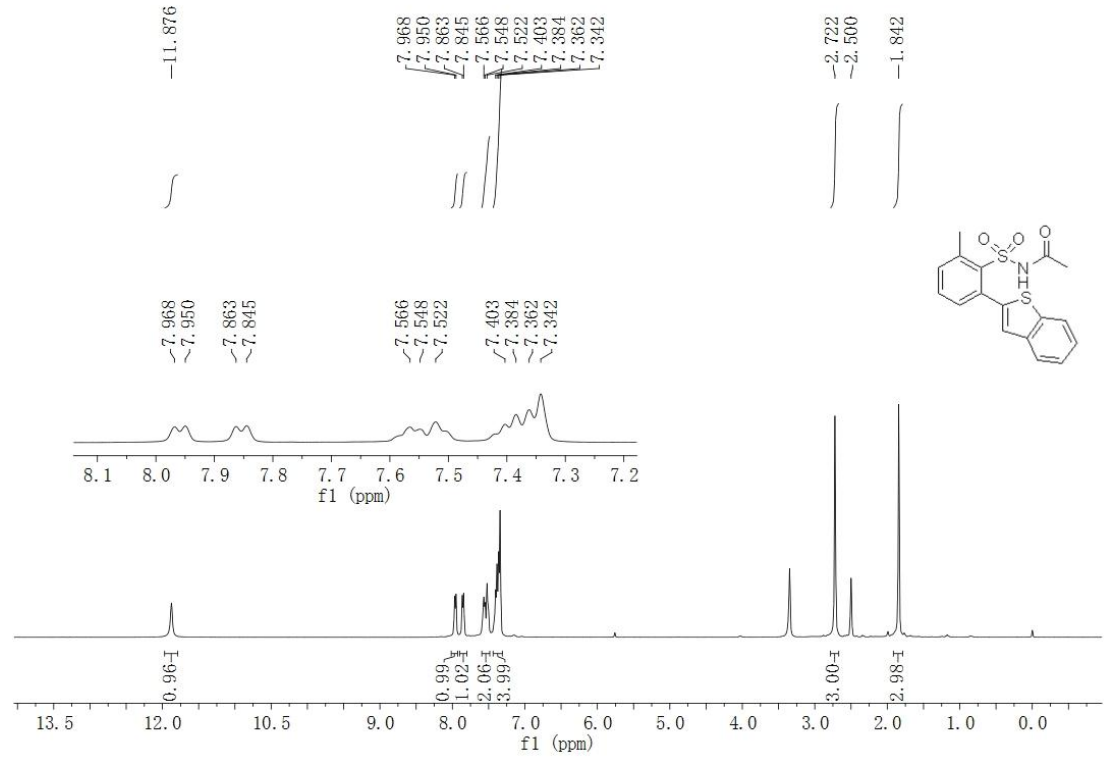
4-Methyldibenzo[*b*,*d*]thiophene 5,5-dioxide (9)

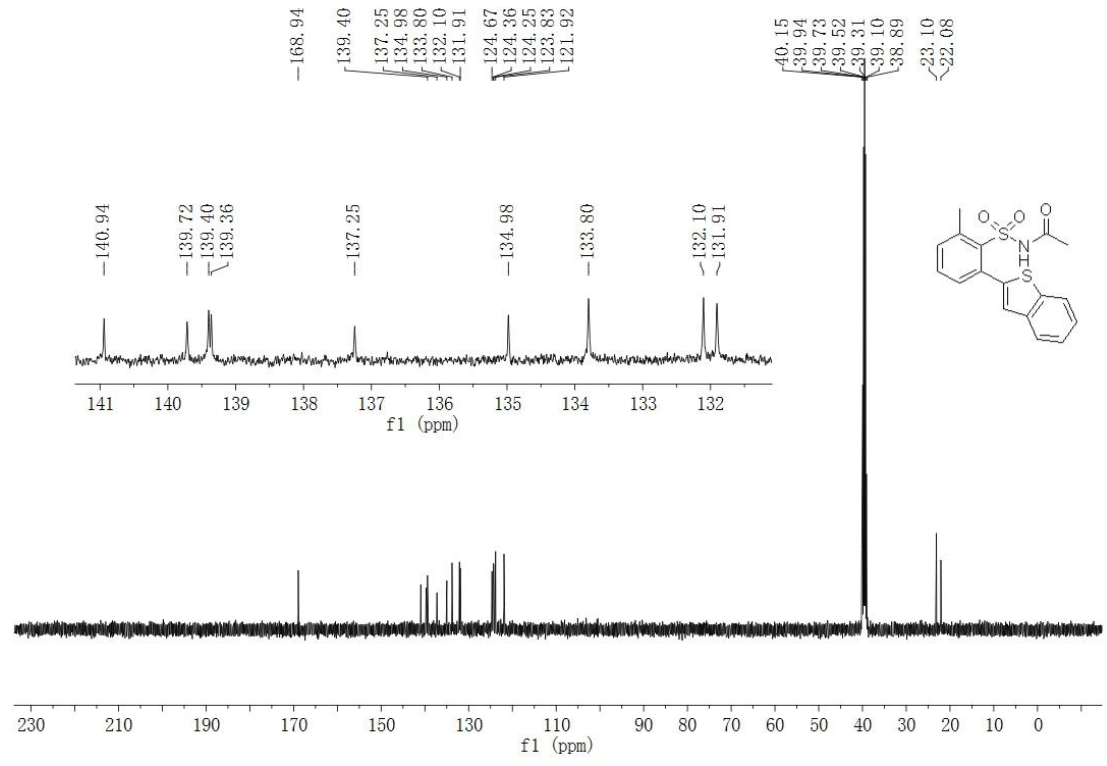
Purification by column chromatography on silica gel (petroleum ether/ ethyl acetate = 8/1, v/v) afforded **9** as a white solid (18.7mg, 81% yield). M.p.: 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.71 (s, 3H), 7.26 (d, J = 7.2 Hz, 1H), 7.47-7.53 (m, 2H), 7.59-7.64 (m, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H) ppm. ^{13}NMR ($CDCl_3$, 100 MHz): δ = 17.1, 119.0, 121.6, 122.1, 130.3, 131.8, 132.0, 132.4, 133.7, 133.9, 135.8, 136.0, 137.9 ppm. HRMS (ESI$^+$): calcd for $C_{13}H_{10}NaO_2S$ [M+Na]$^+$ 253.0294, found 253.0286.

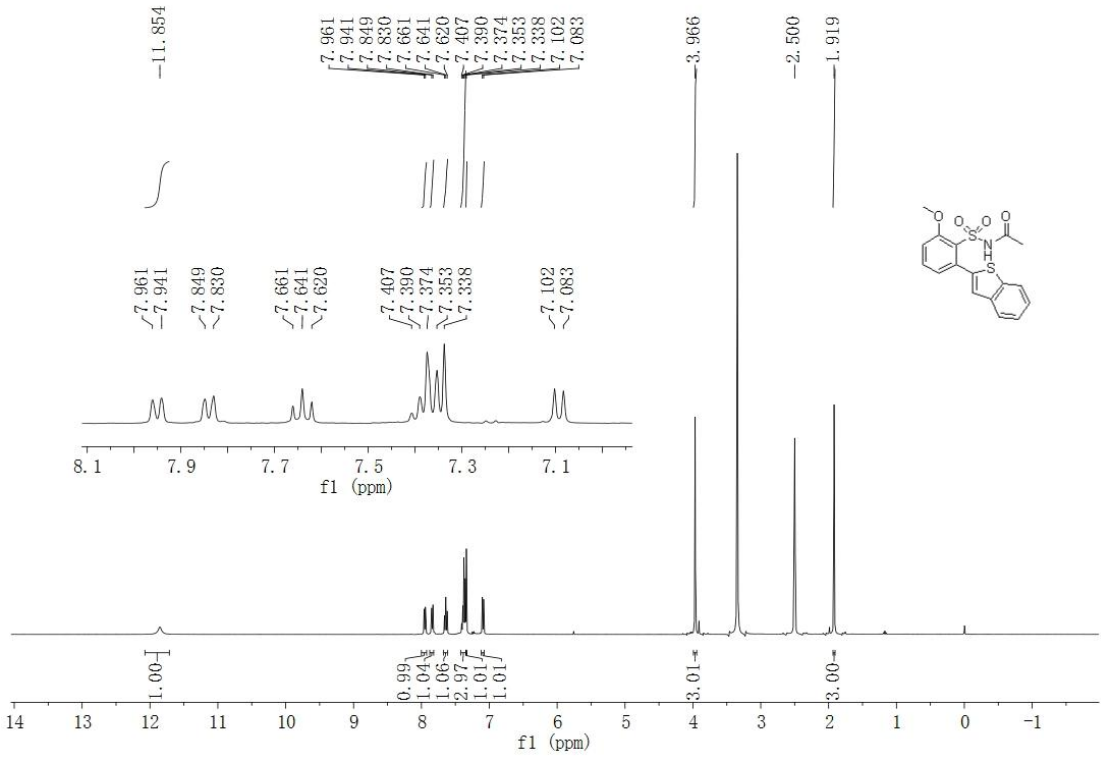
IX. References

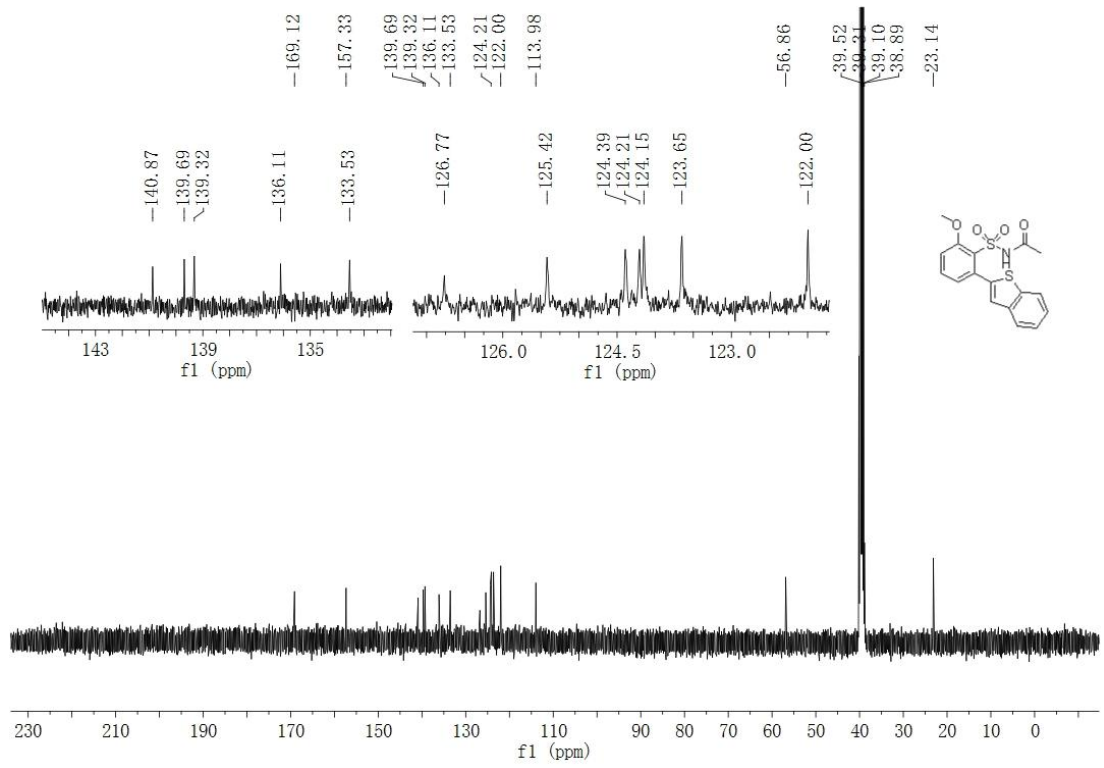
1) (a) Pham, M. V.; Ye, B.; Cramer, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 10610–10614. (b) Xie, W.; Yang, J.; Wang, B.; Li, B. *J. Org. Chem.* **2014**, *79*, 8278–8287. (c) Li, X.; Dong, Y.; Qu, F.; Liu, G. *J. Org. Chem.* **2015**, *80*, 790–798.
2) Colletto, C.; Islam, S.; Juliá-Hernández, F.; Larrosa, I. *J. Am. Chem. Soc.* **2016**, *138*, 1677–1683.
3) Duan, P.; Lan, X.; Chen, Y.; Qian, S.-S.; Li, J. J.; Lu, L.; Lu, Y.; Chen, B.; Hong, M.; Zhao, J. *Chem. Commun.* **2014**, *50*, 12135–12138.

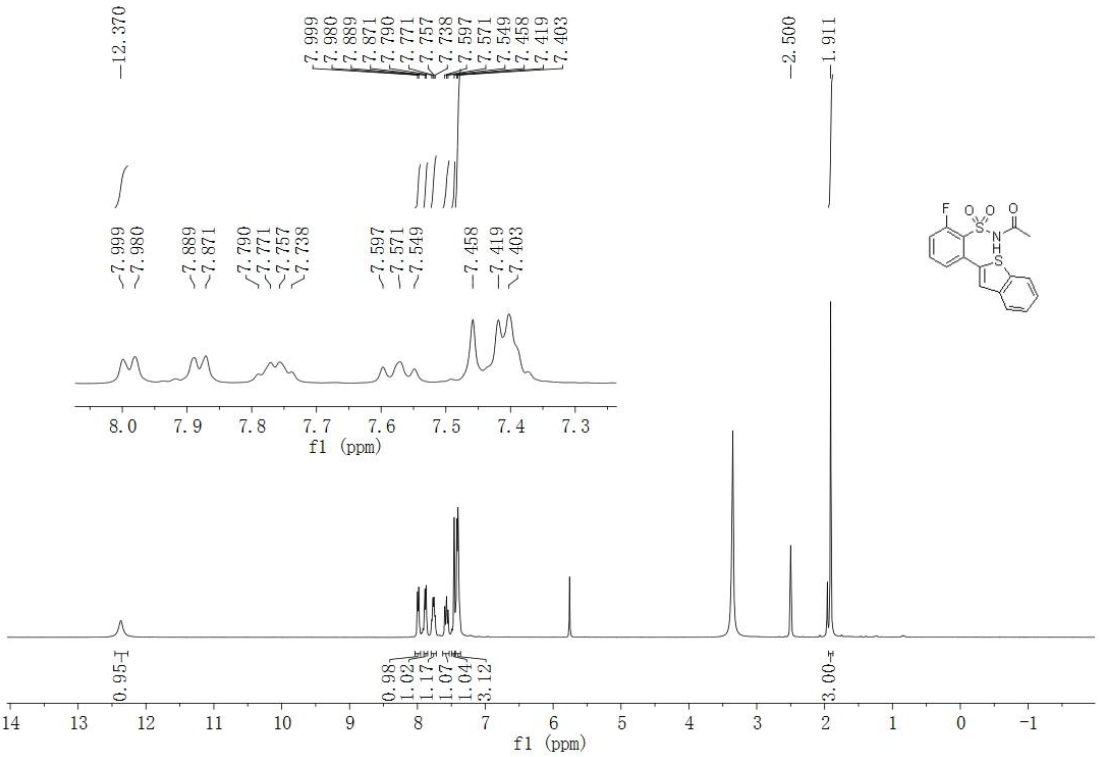
X. Copies of ^{1}H and ^{13}C spectra

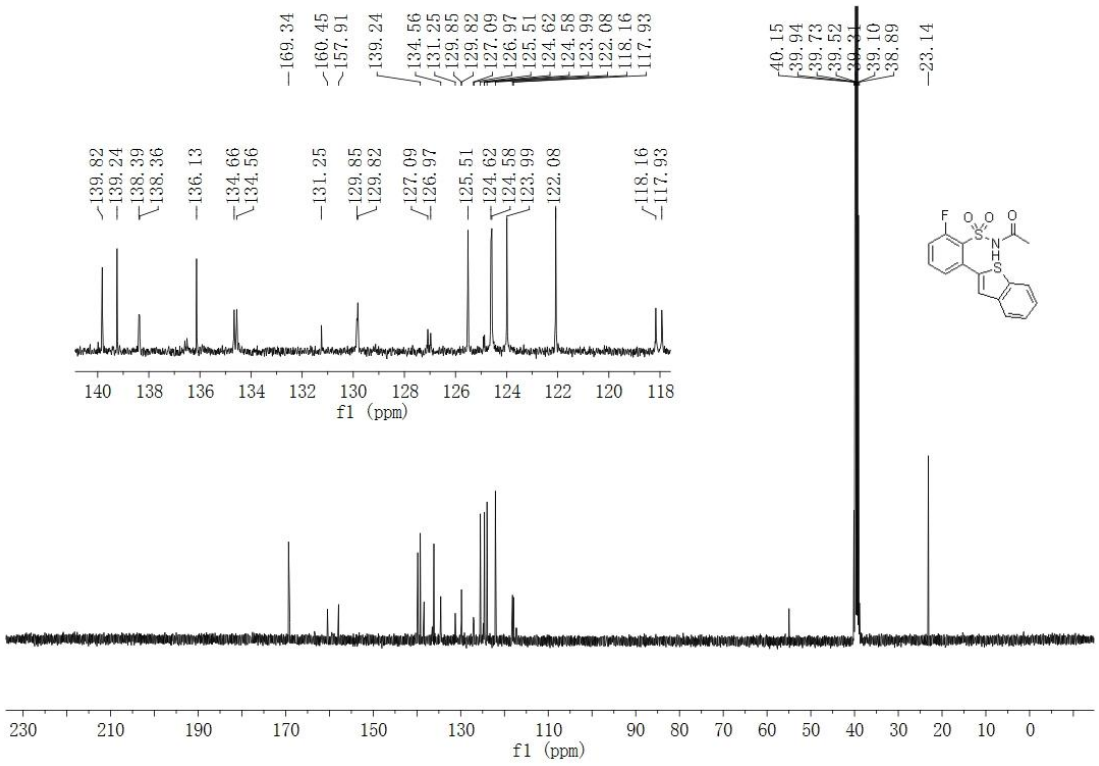


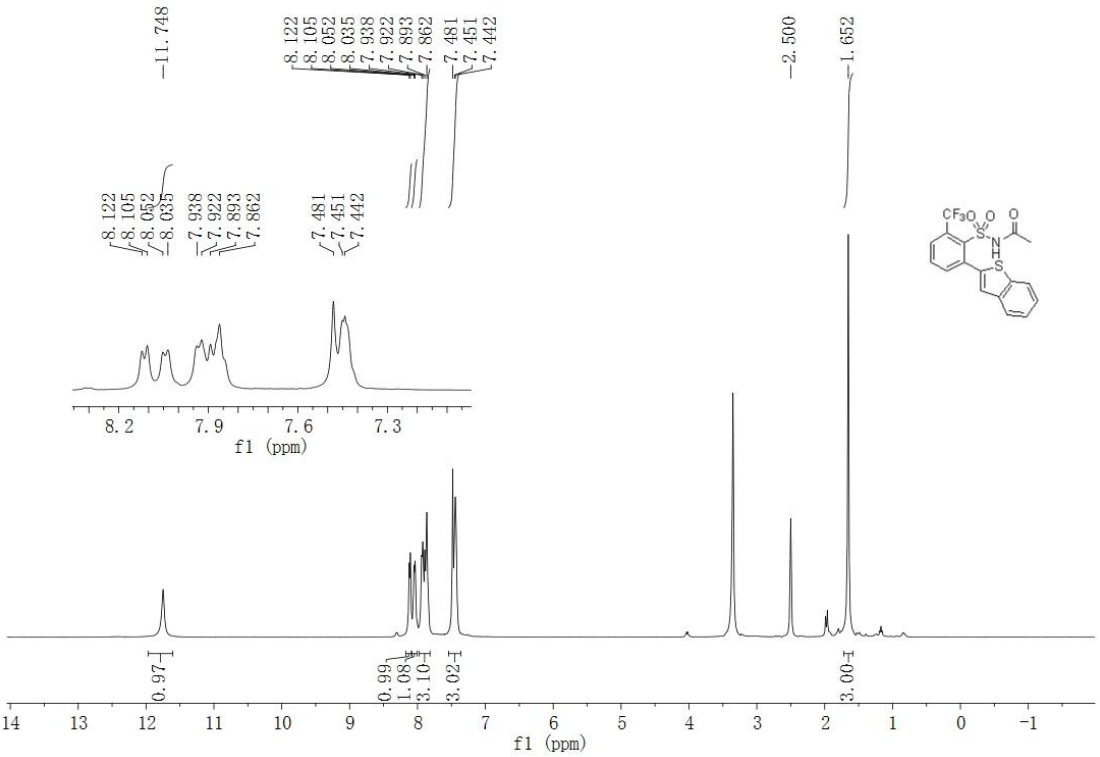


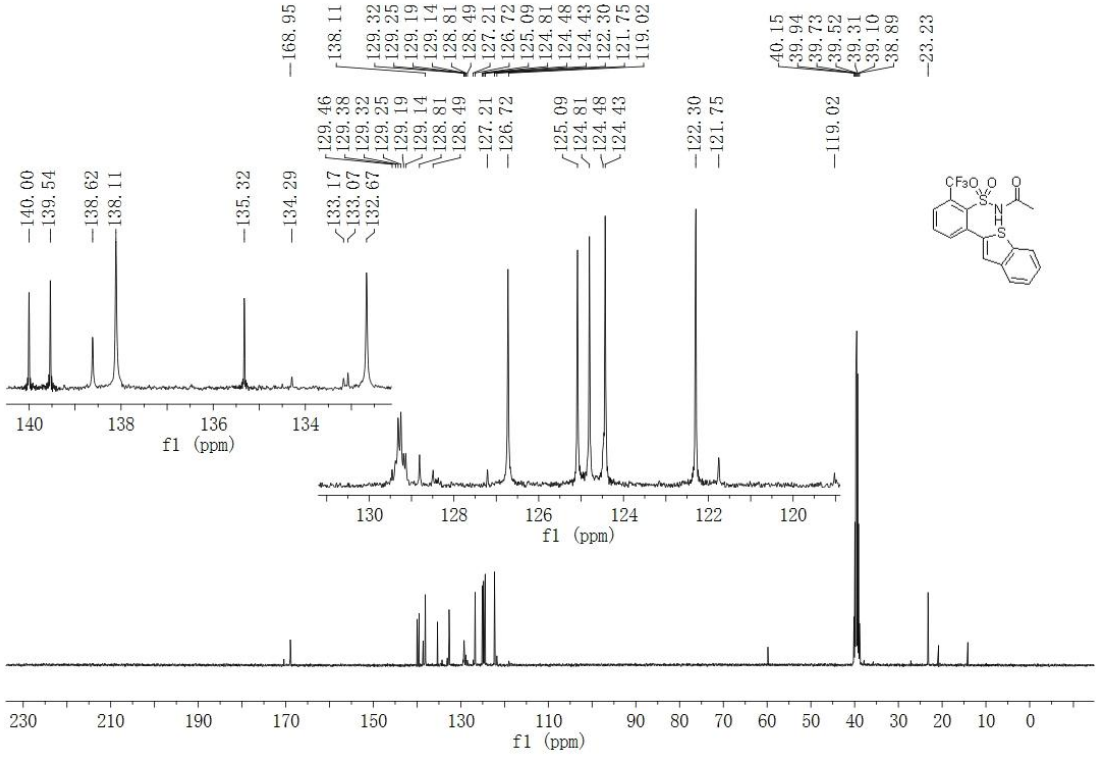

11.854
7.961
7.941
7.849
7.830
7.661
7.641
7.620
7.407
7.390
7.374
7.353
7.338
7.102
7.083
3.966
2.500
1.919
f1 (ppm)

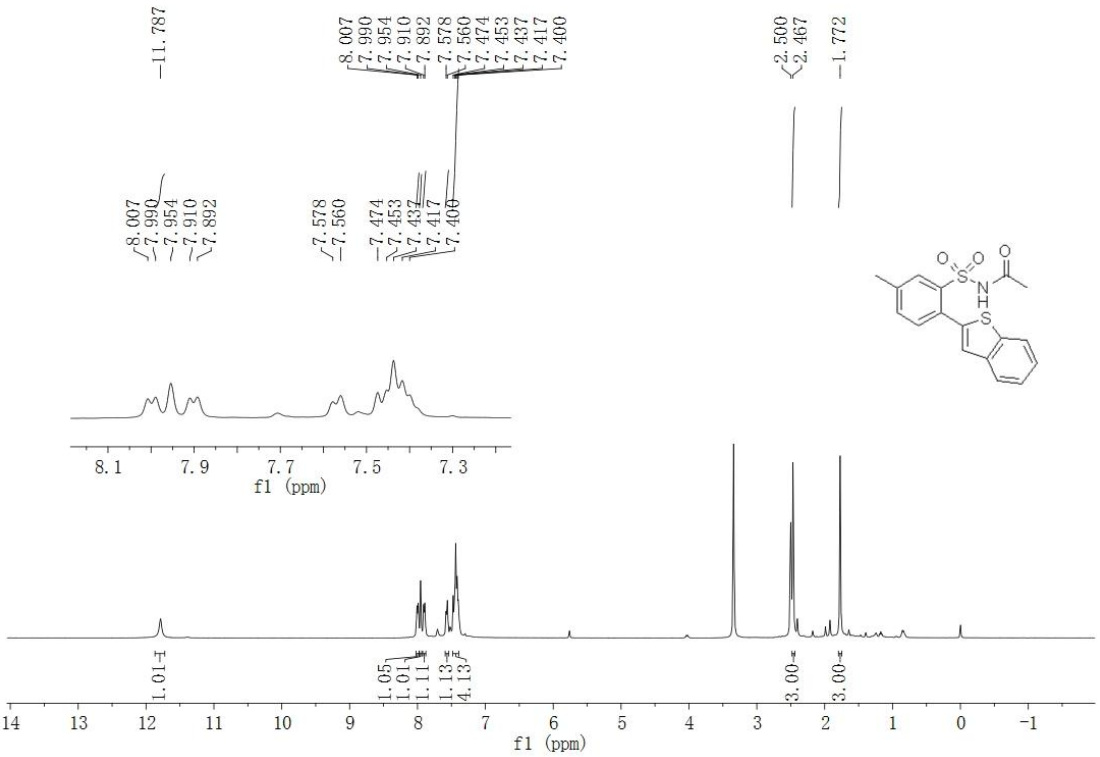

169.12
157.33
139.69
139.32
136.11
133.53
124.21
122.00
113.98
56.86
39.52
39.31
39.10
38.89
23.14
f1 (ppm)

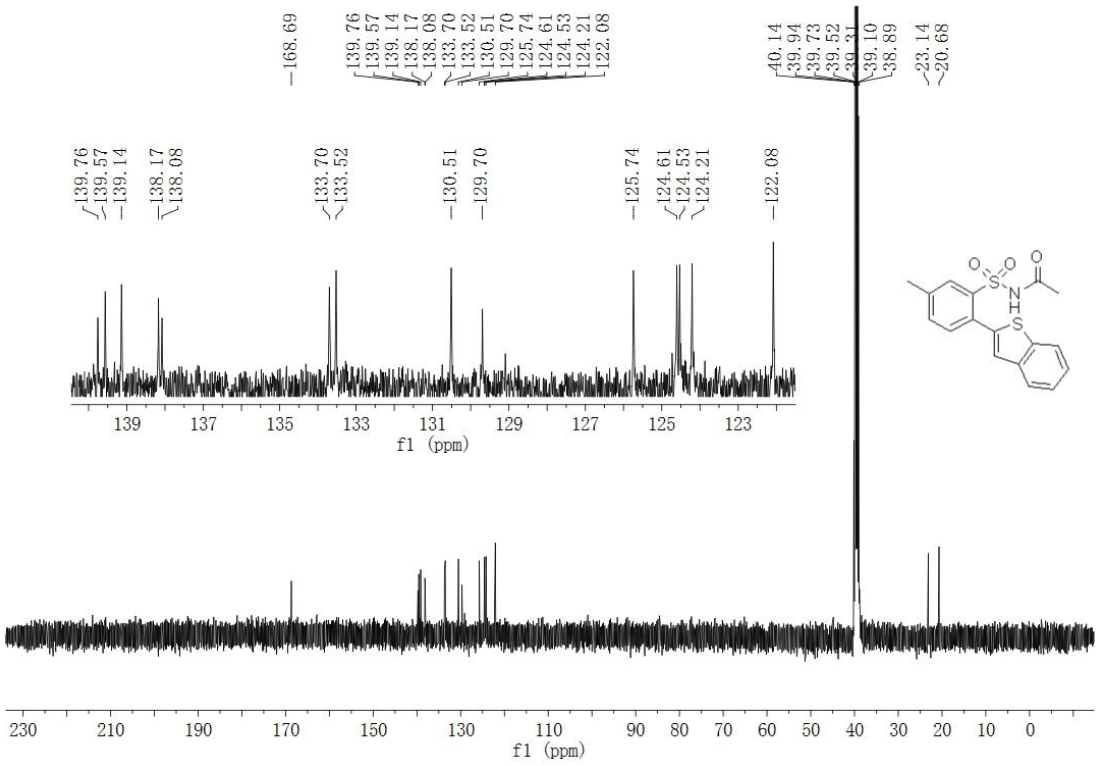

12.370
7.999
7.980
7.889
7.871
7.790
7.771
7.757
7.738
7.597
7.571
7.549
7.458
7.419
7.403
2.500
1.911
0.95
0.98
1.02
1.17
1.07
1.04
3.12
3.00
f1 (ppm)

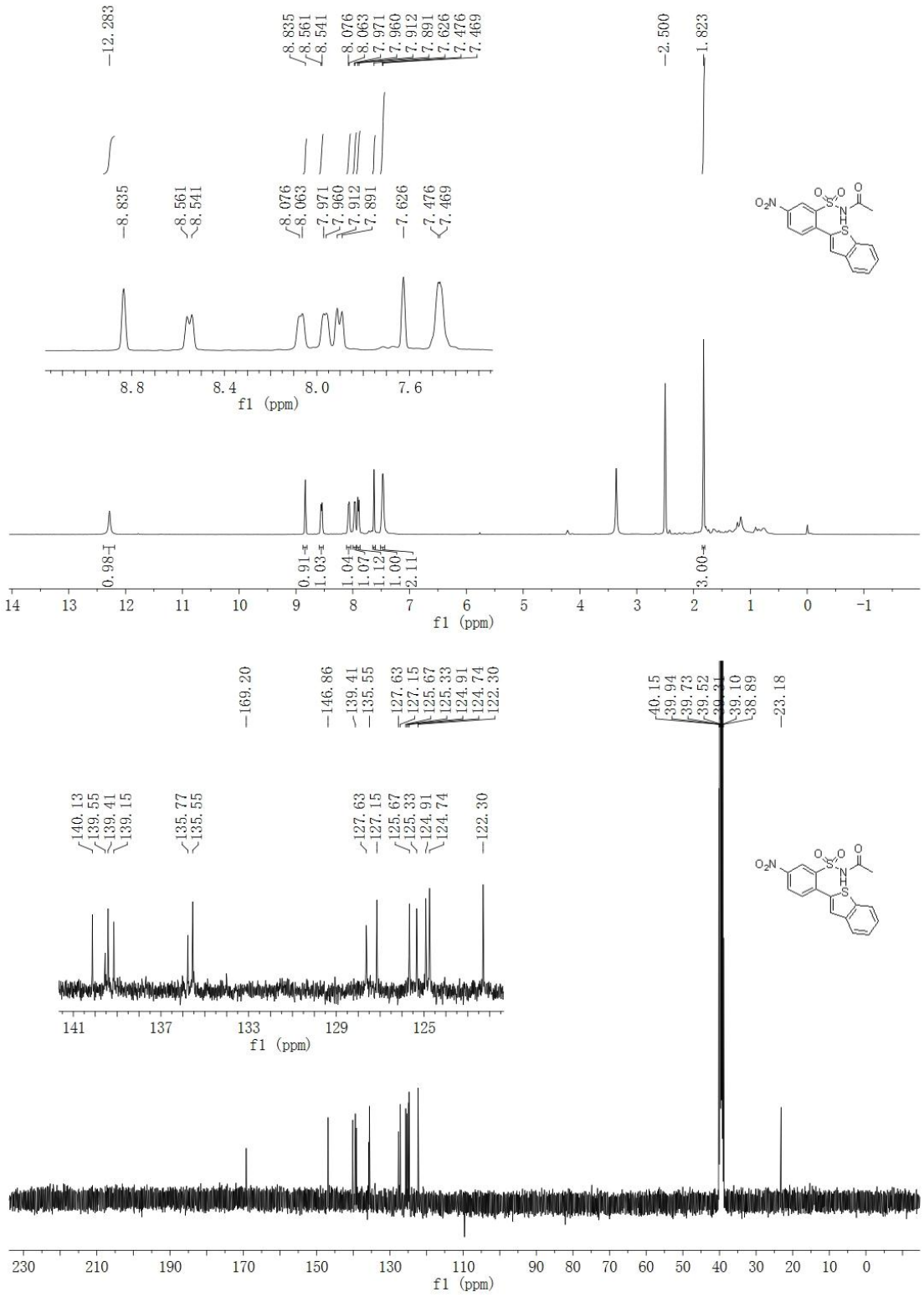

169.34
160.45
157.91
139.24
134.56
131.25
129.85
129.82
127.09
126.97
125.51
124.62
124.58
123.99
122.08
118.16
117.93
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.14
f1 (ppm)

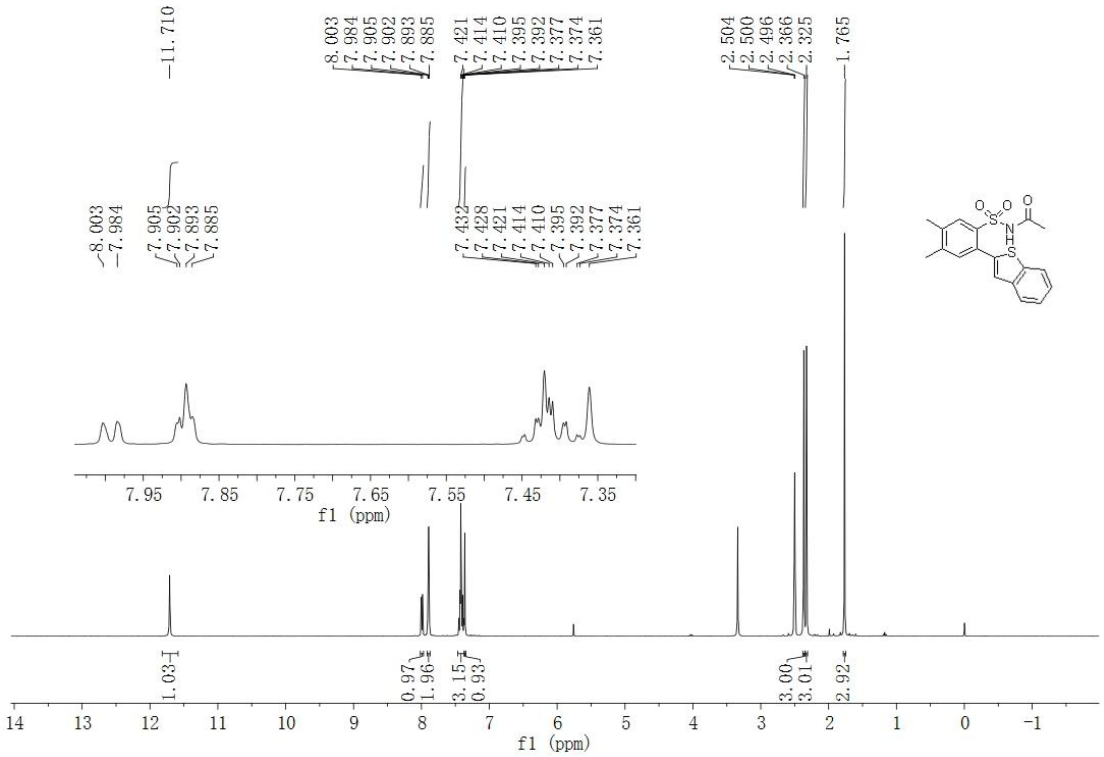

11.748
8.122
8.105
8.052
8.035
7.938
7.922
7.893
7.862
7.481
7.451
7.442
2.500
1.652
0.97
0.99
1.08
3.10
3.02
3.00
f1 (ppm)

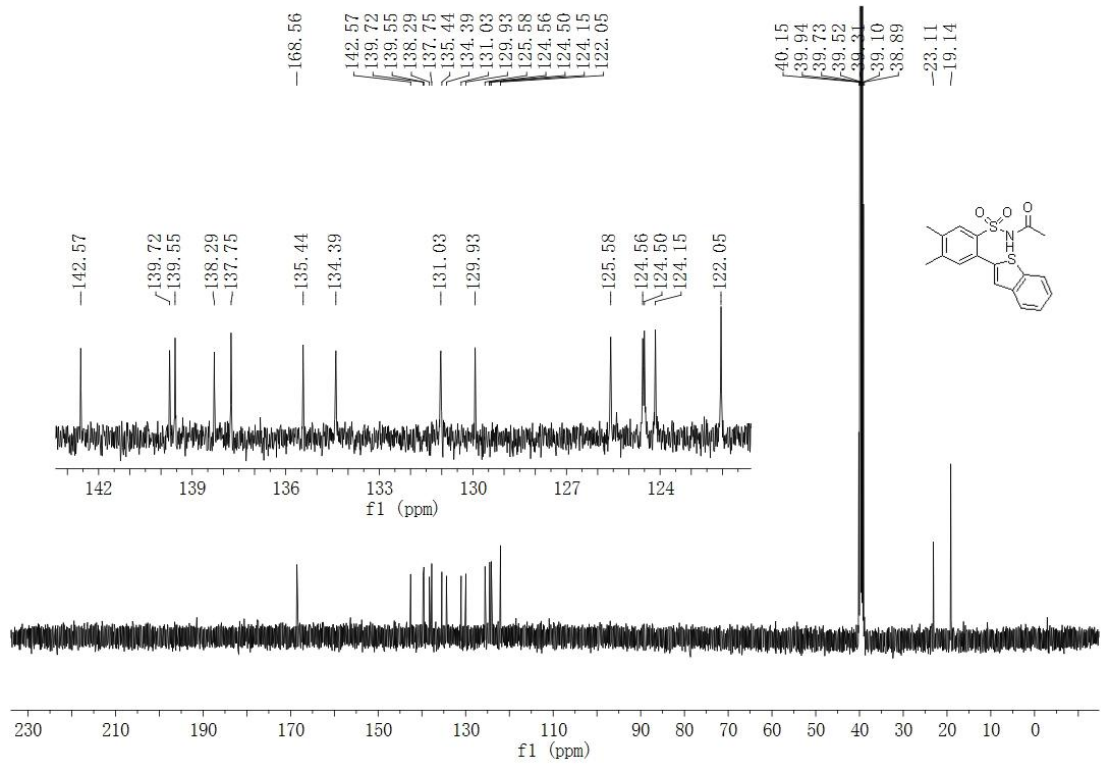

168.95
140.00
139.54
138.62
138.11
135.32
134.29
133.17
133.07
132.67
129.46
129.38
129.32
129.25
129.19
129.14
128.81
128.49
127.21
126.72
125.09
124.81
124.48
124.43
122.30
121.75
119.02
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.23
f1 (ppm)

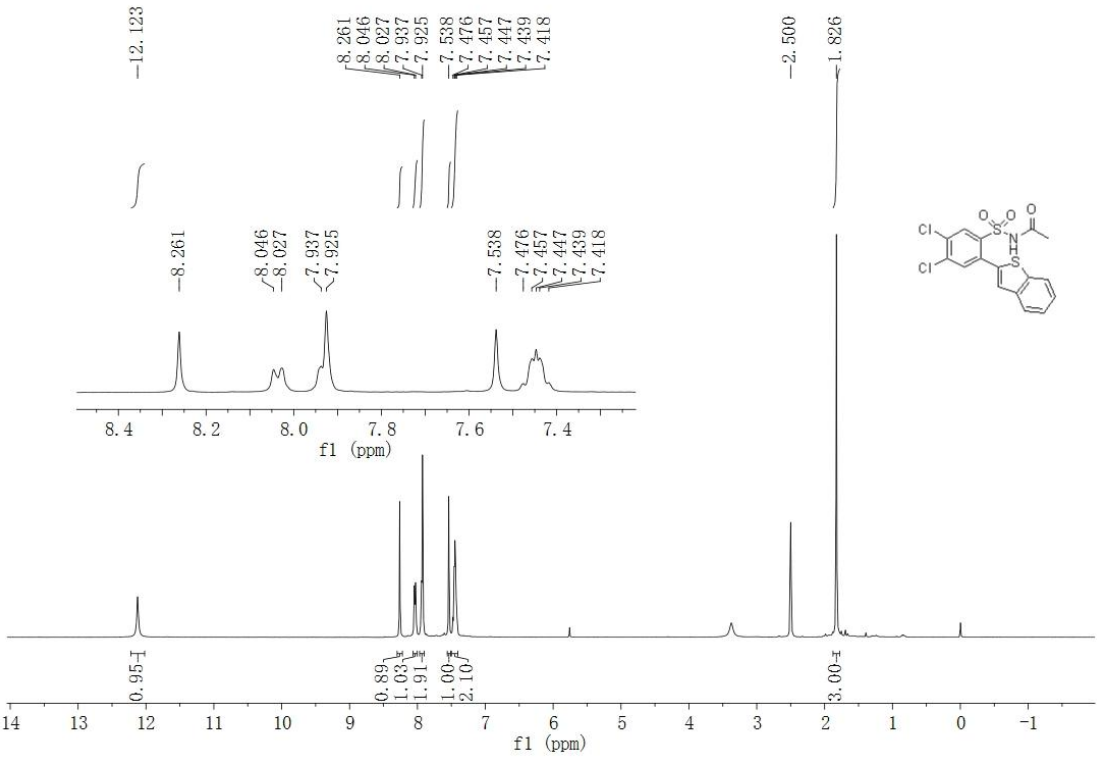

11.787
8.007
7.990
7.954
7.910
7.892
7.578
7.560
7.474
7.453
7.437
7.417
7.400
2.500
2.467
1.772
1.01
1.05
1.01
1.11
1.13
4.13
3.00
3.00
f1 (ppm)

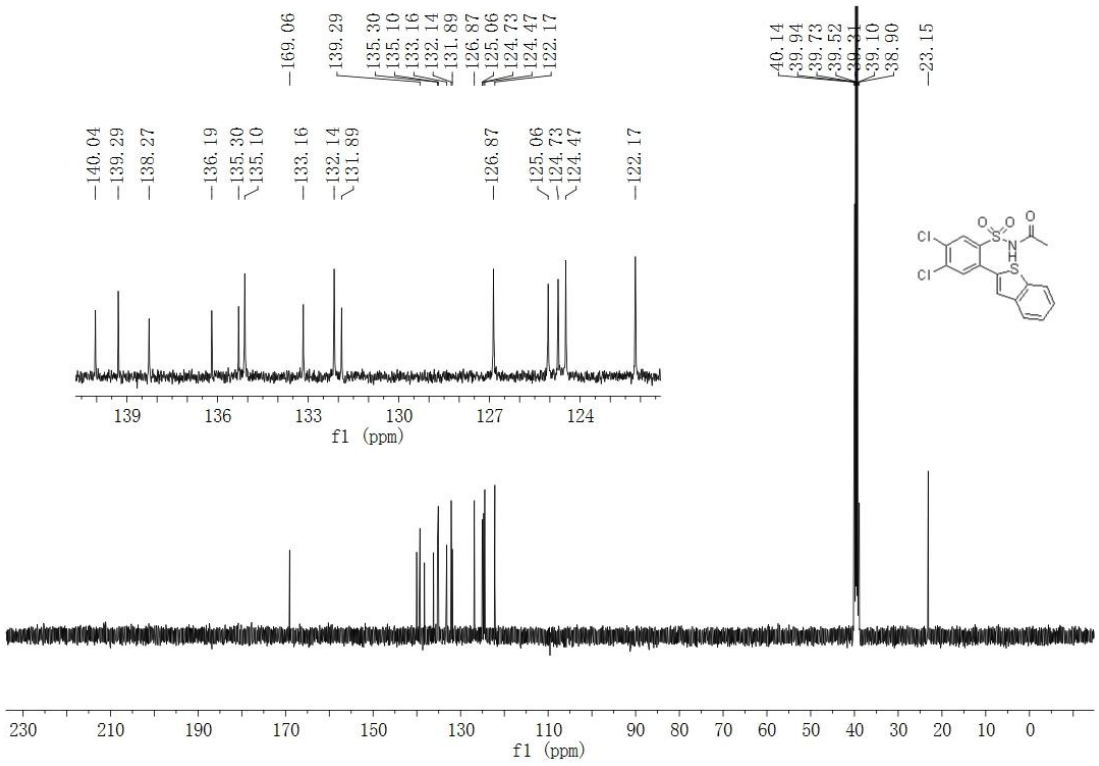

168.69
139.76
139.57
139.14
138.17
138.08
133.70
133.52
130.51
129.70
125.74
124.61
124.53
124.21
122.08
40.14
39.94
39.73
39.52
39.31
39.10
38.89
23.14
20.68
f1 (ppm)

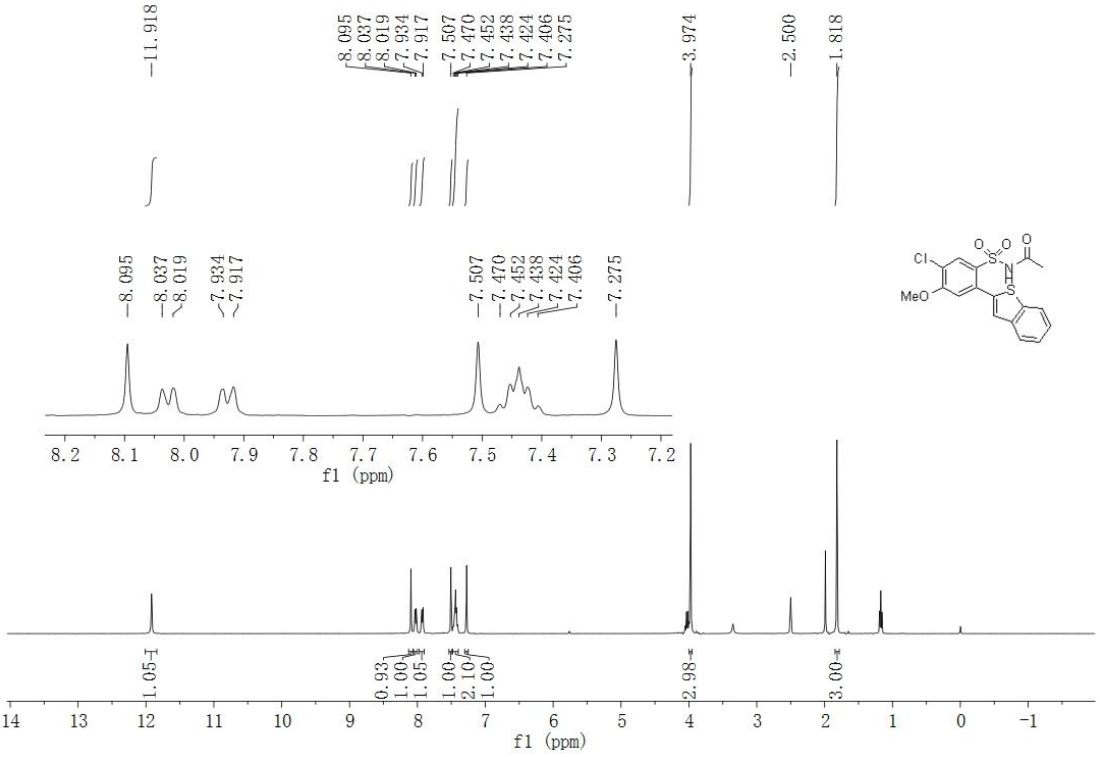

12.283
8.835
8.561
8.541
8.076
8.063
7.971
7.960
7.912
7.891
7.626
7.476
7.469
2.500
1.823
f1 (ppm)
0.98
0.91
1.03
1.04
1.07
1.12
1.00
2.11
3.00
169.20
146.86
139.41
135.55
127.63
127.15
125.67
125.33
124.91
124.74
122.30
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.18
140.13
139.55
139.41
139.15
135.77
135.55
127.63
127.15
125.67
125.33
124.91
124.74
122.30

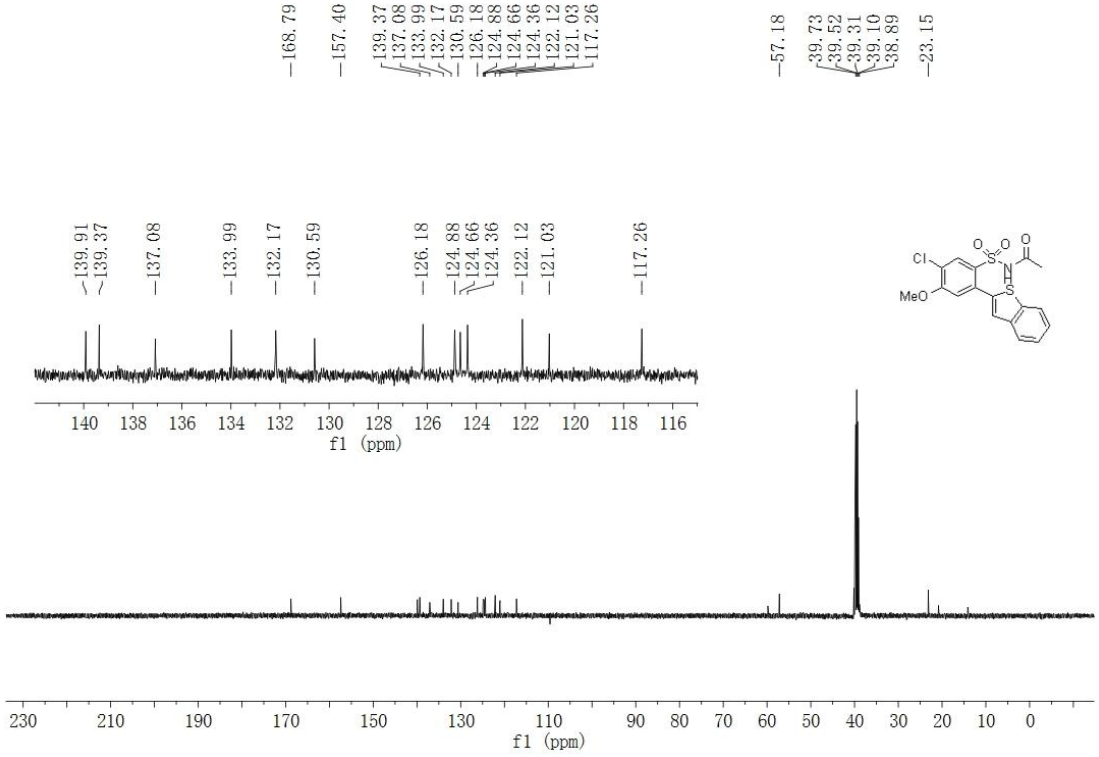

11.710
8.003
7.984
7.905
7.902
7.893
7.885
7.421
7.414
7.410
7.395
7.392
7.377
7.374
7.361
2.504
2.500
2.496
2.366
2.325
1.765
f1 (ppm)
1.03
0.97
1.96
3.15
0.93
3.00
3.01
2.92

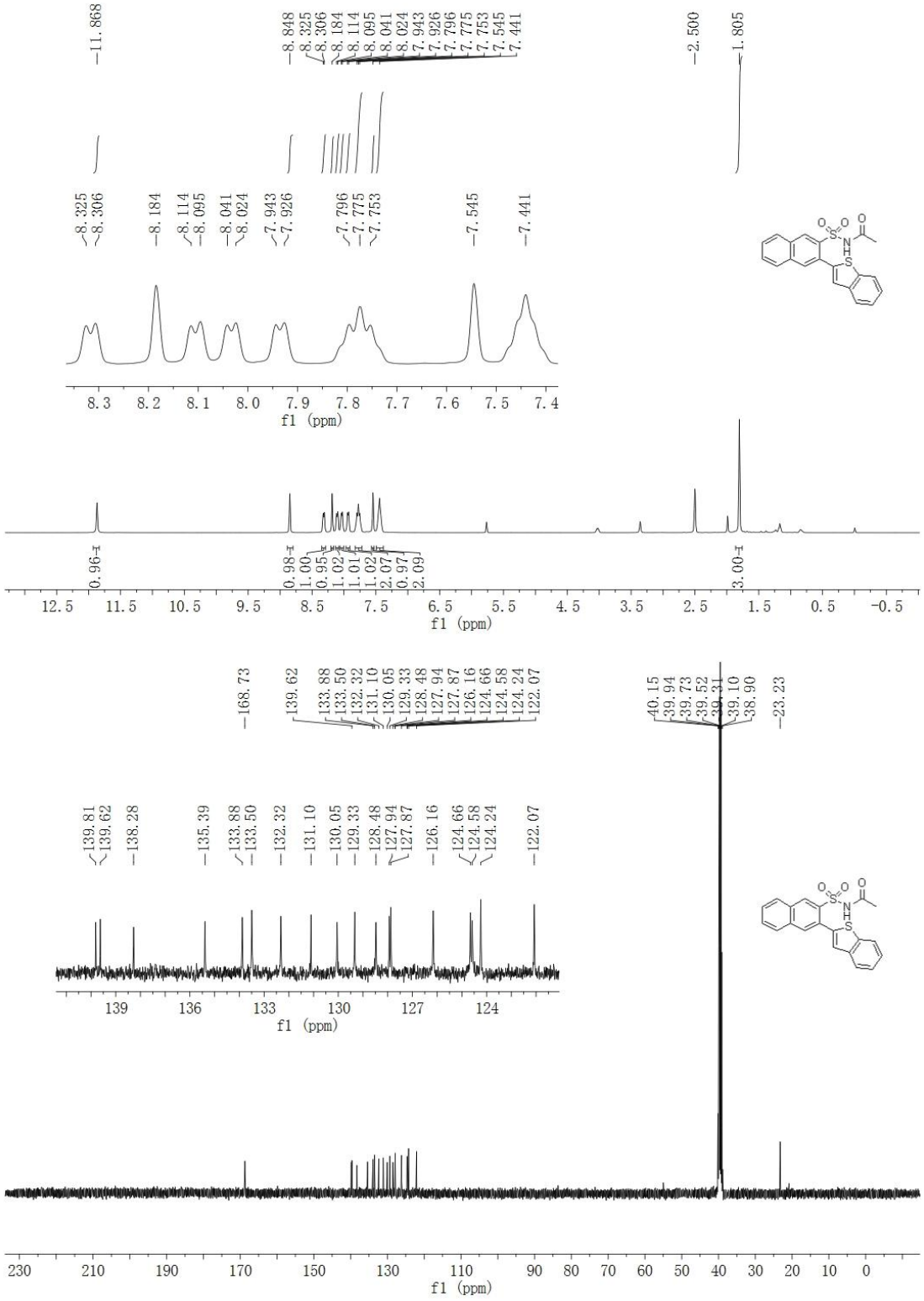

168.56
142.57
139.72
139.55
138.29
137.75
135.44
134.39
131.03
129.93
125.58
124.56
124.50
124.15
122.05
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.11
19.14
f1 (ppm)

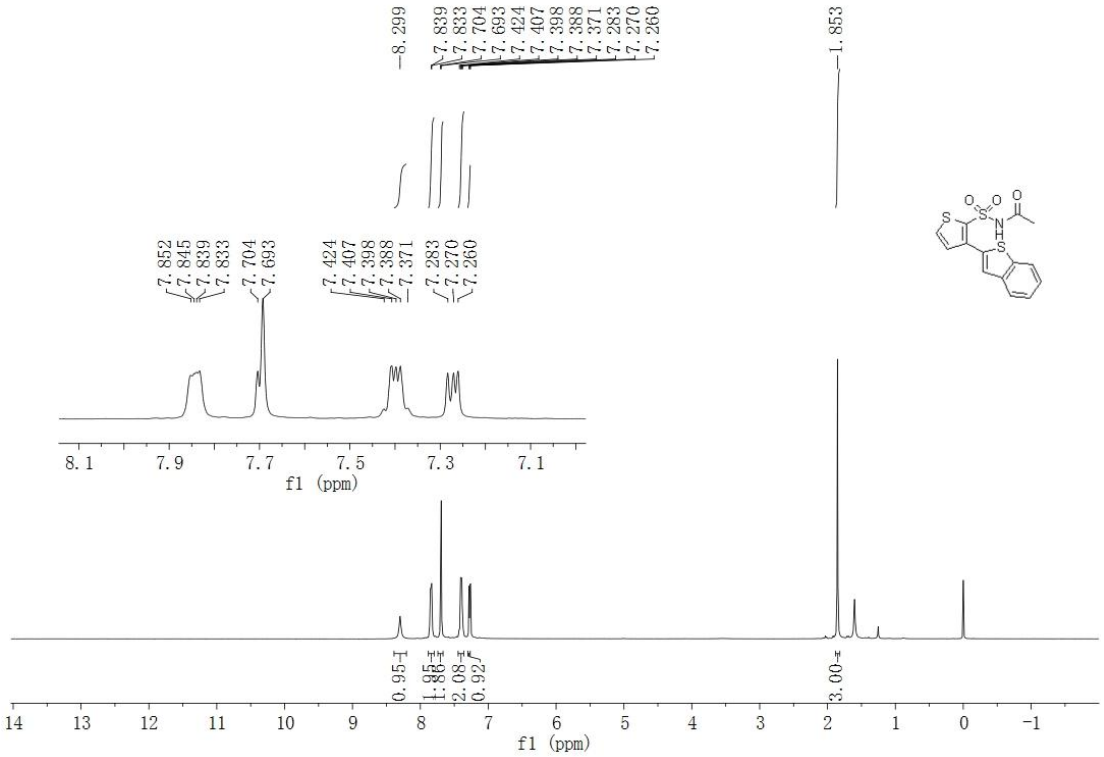

12.123
8.261
8.046
8.027
7.937
7.925
7.538
7.476
7.457
7.447
7.439
7.418
2.500
1.826
f1 (ppm)
0.95
0.89
1.03
1.91
1.00
2.10
3.00

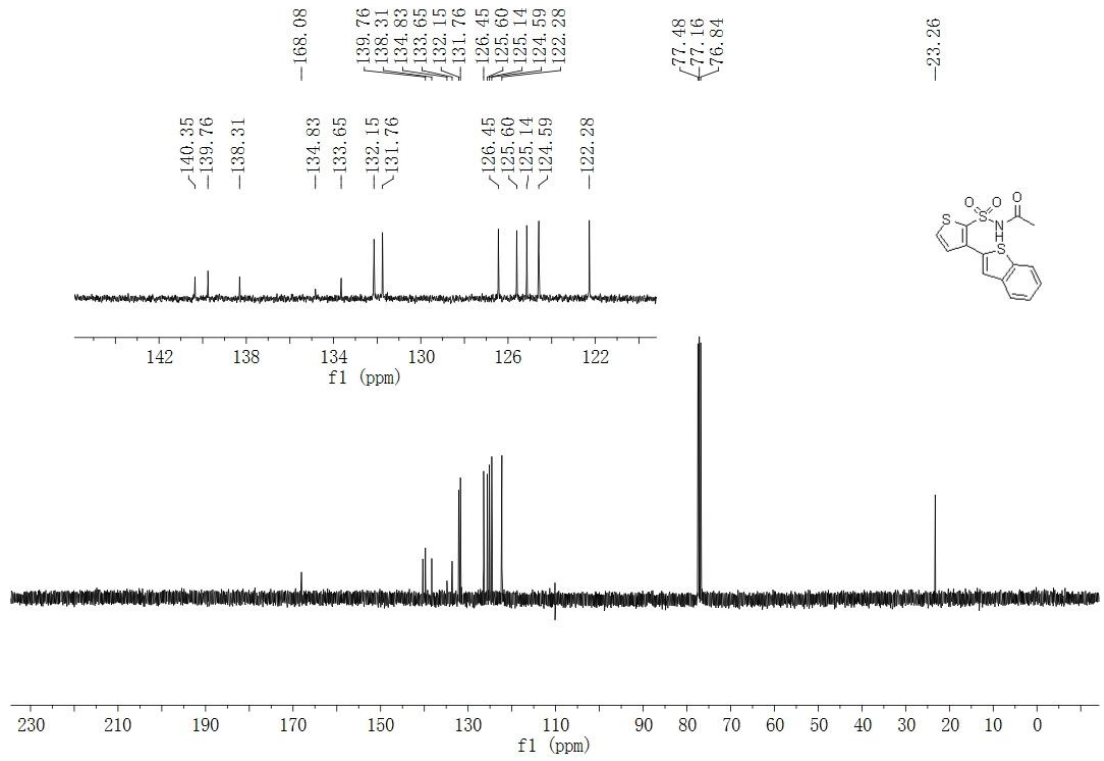

169.06
139.29
135.30
135.10
133.16
132.14
131.89
126.87
125.06
124.73
124.47
122.17
40.14
39.94
39.73
39.52
39.31
39.10
38.90
23.15
f1 (ppm)

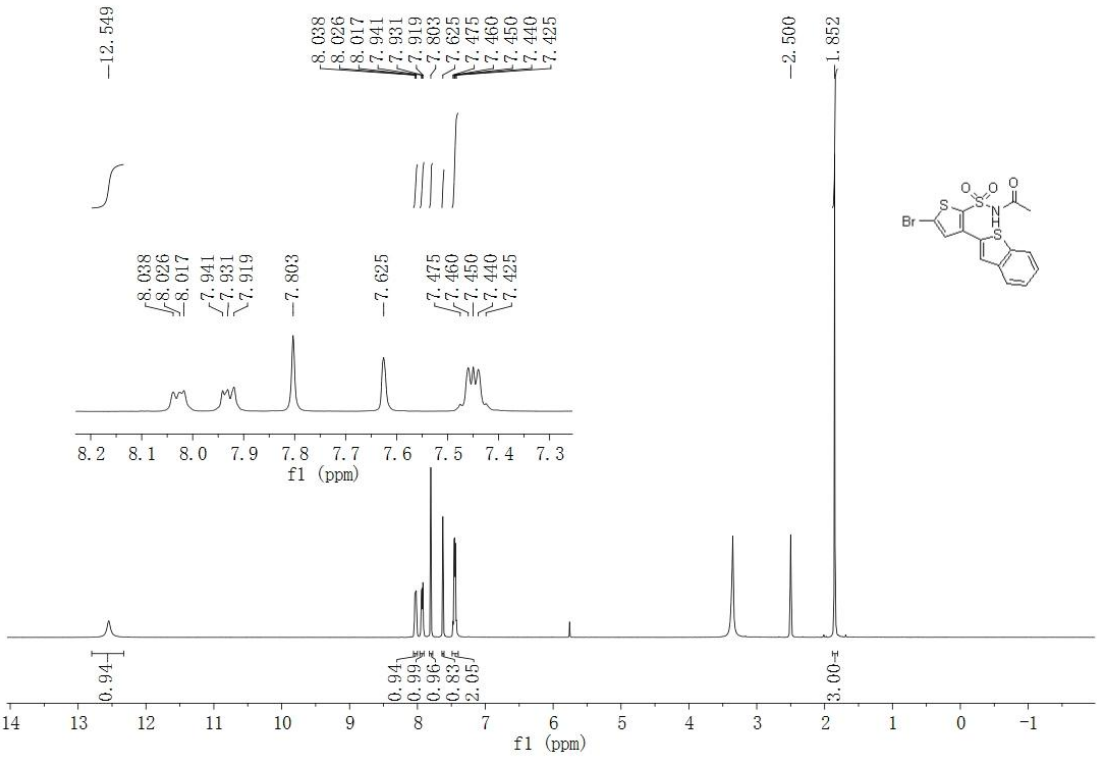

11.918
8.095
8.037
8.019
7.934
7.917
7.507
7.470
7.452
7.438
7.424
7.406
7.275
3.974
2.500
1.818
Cl
MeO
f1 (ppm)
1.05
0.93
1.00
1.05
1.00
2.10
1.00
2.98
3.00

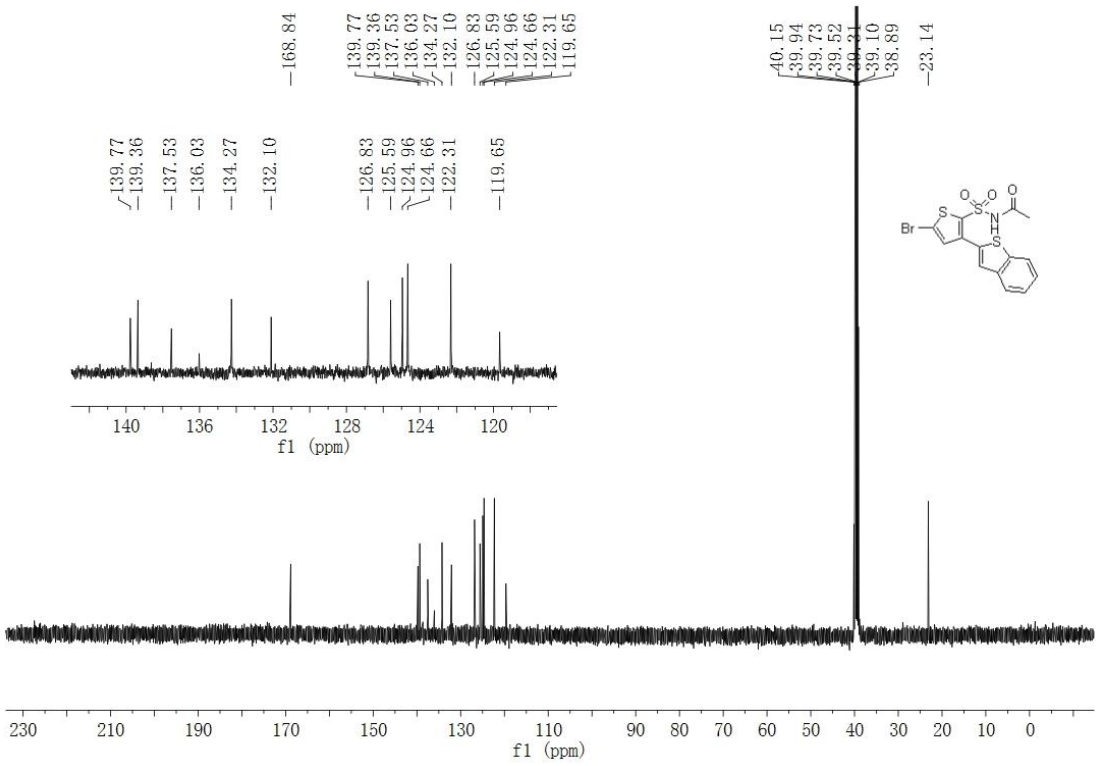

168.79
157.40
139.37
137.08
133.99
132.17
130.59
126.18
124.88
124.66
124.36
122.12
121.03
117.26
57.18
39.73
39.52
39.31
39.10
38.89
23.15
Cl
MeO
f1 (ppm)

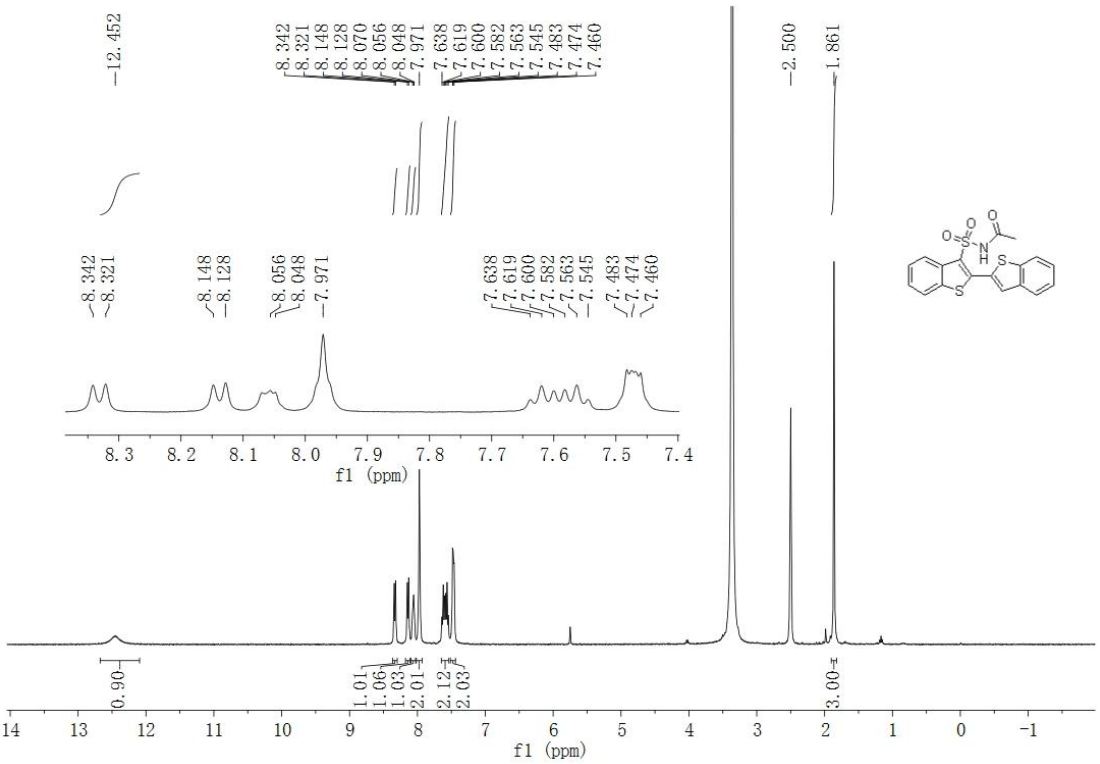

11.868
8.848
8.325
8.306
8.184
8.114
8.095
8.041
8.024
7.943
7.926
7.796
7.775
7.753
7.545
7.441
2.500
1.805
f1 (ppm)
0.96
0.98
1.00
0.95
1.02
1.01
1.02
2.07
0.97
2.09
3.00
168.73
139.62
133.88
133.50
132.32
131.10
130.05
129.33
128.48
127.87
126.16
124.66
124.58
124.24
122.07
40.15
39.94
39.73
39.52
39.31
39.10
38.90
23.23
139.81
138.28
135.39
f1 (ppm)

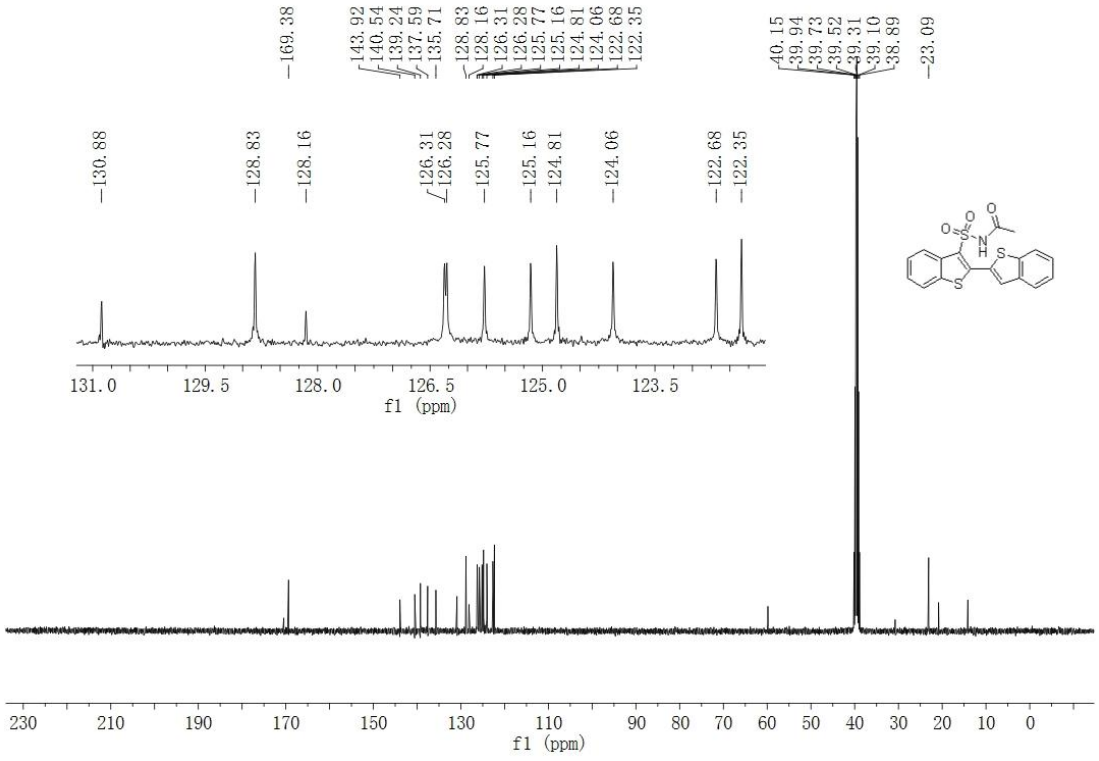

8.299
7.839
7.833
7.704
7.693
7.424
7.407
7.398
7.388
7.371
7.283
7.270
7.260
1.853
7.852
7.845
7.839
7.833
7.704
7.693
7.424
7.407
7.398
7.388
7.371
7.283
7.270
7.260
8.1
7.9
7.7
7.5
7.3
7.1
f1 (ppm)
0.95
1.95
2.08
0.92
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

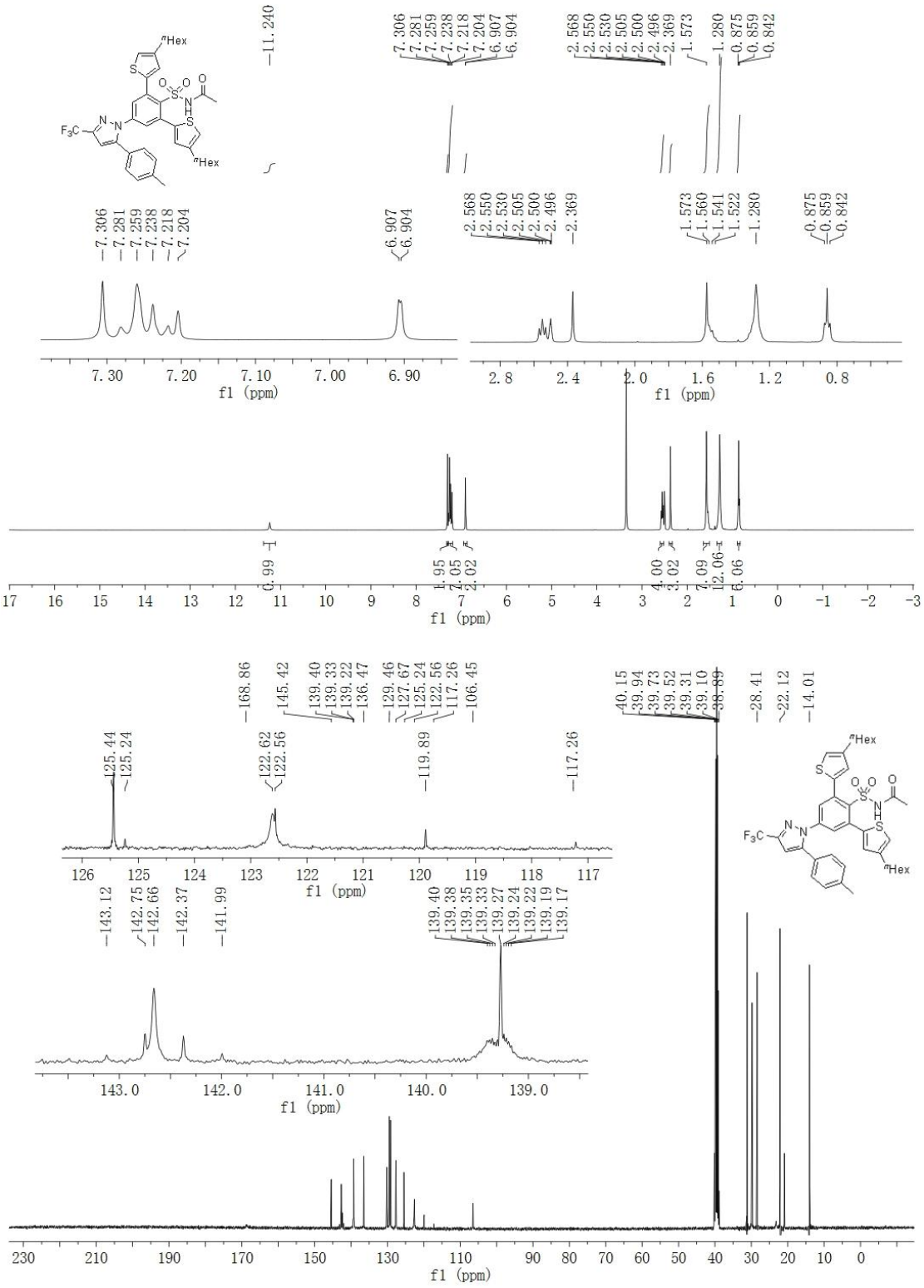

168.08
139.76
138.31
134.83
133.65
132.15
131.76
126.45
125.60
125.14
124.59
122.28
77.48
77.16
76.84
23.26
140.35
139.76
138.31
134.83
133.65
132.15
131.76
126.45
125.60
125.14
124.59
122.28
142
138
134
130
126
122
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

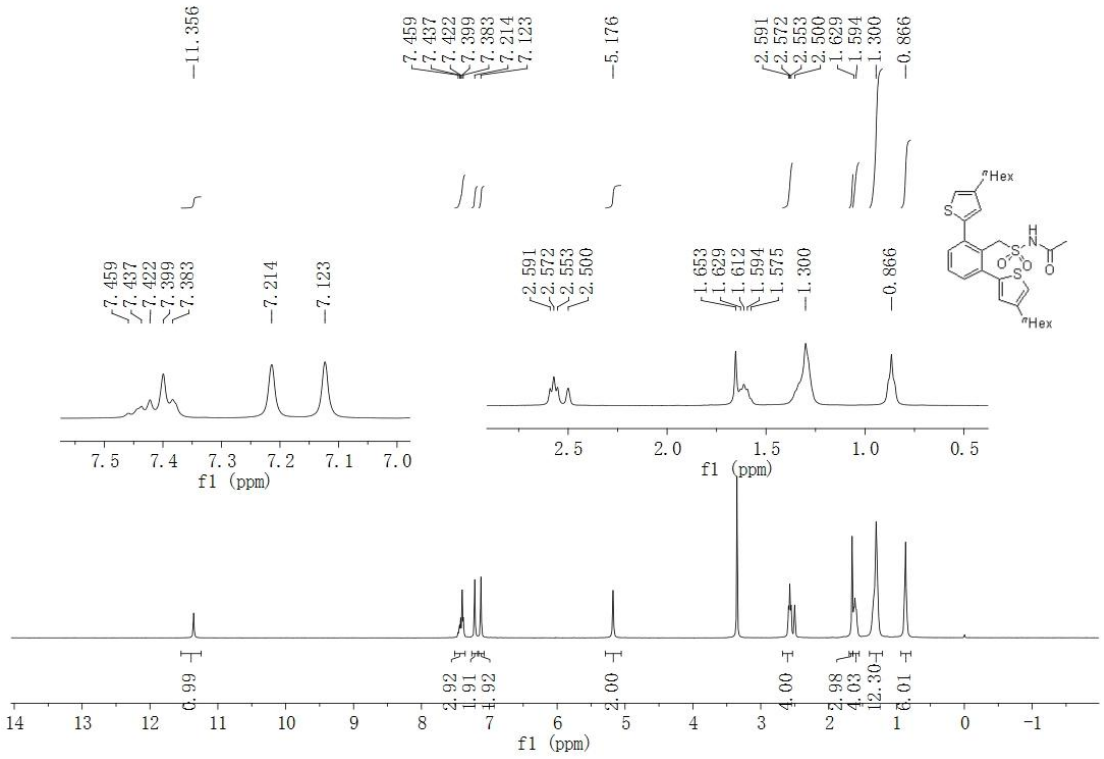

12.549
8.038
8.026
8.017
7.941
7.931
7.919
7.803
7.625
7.475
7.460
7.450
7.440
7.425
2.500
1.852
Br
f1 (ppm)
0.94
0.99
0.96
0.83
2.05
3.00

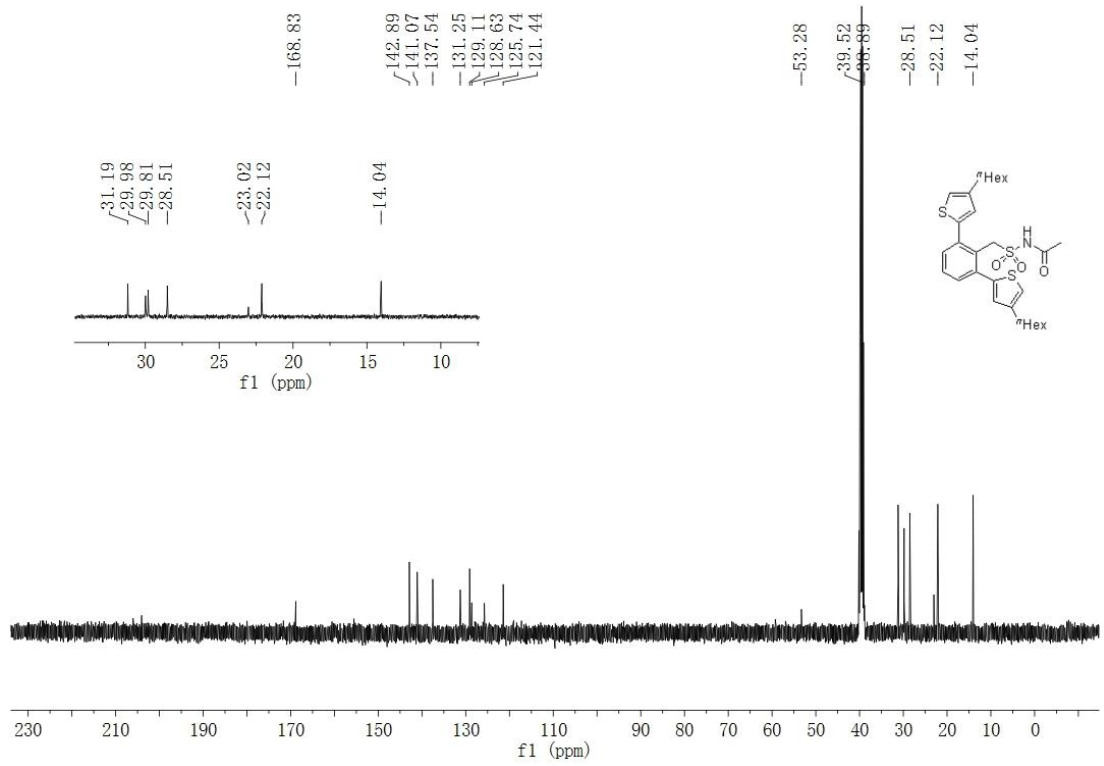

168.84
139.77
139.36
137.53
136.03
134.27
132.10
126.83
125.59
124.96
124.66
122.31
119.65
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.14
Br
f1 (ppm)

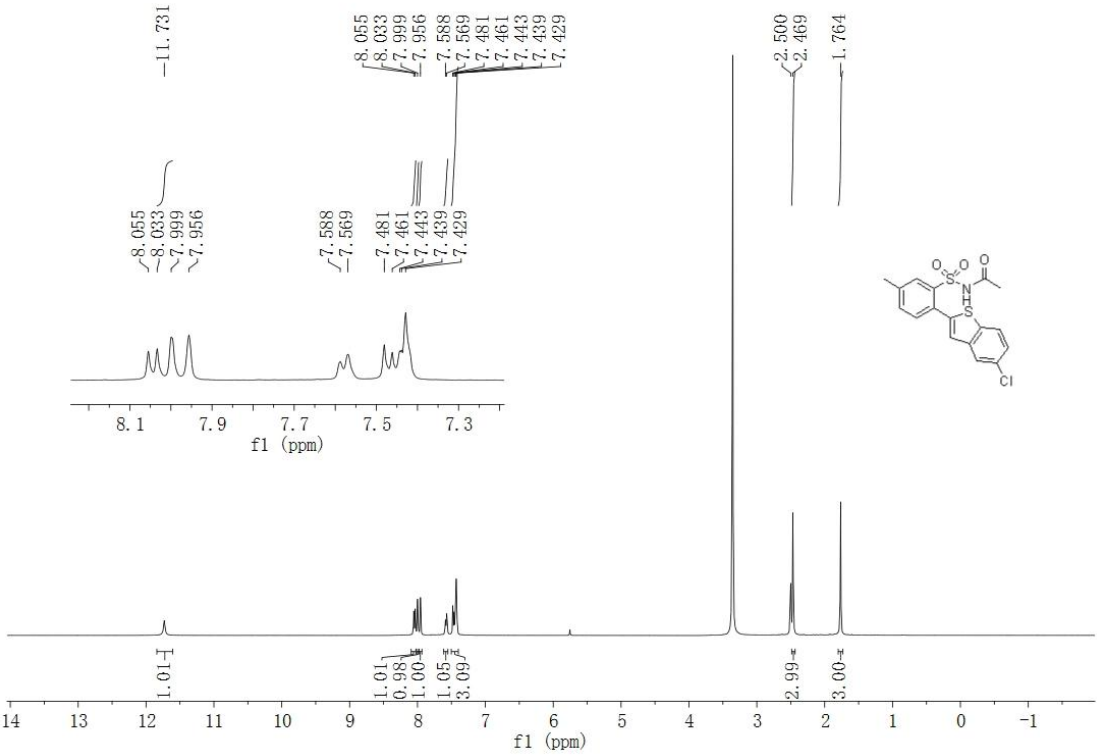

12.452
8.342
8.321
8.148
8.128
8.070
8.056
8.048
7.971
7.638
7.619
7.600
7.582
7.563
7.545
7.483
7.474
7.460
2.500
1.861
f1 (ppm)
0.90
1.01
1.06
1.03
2.01
2.12
2.03
3.00

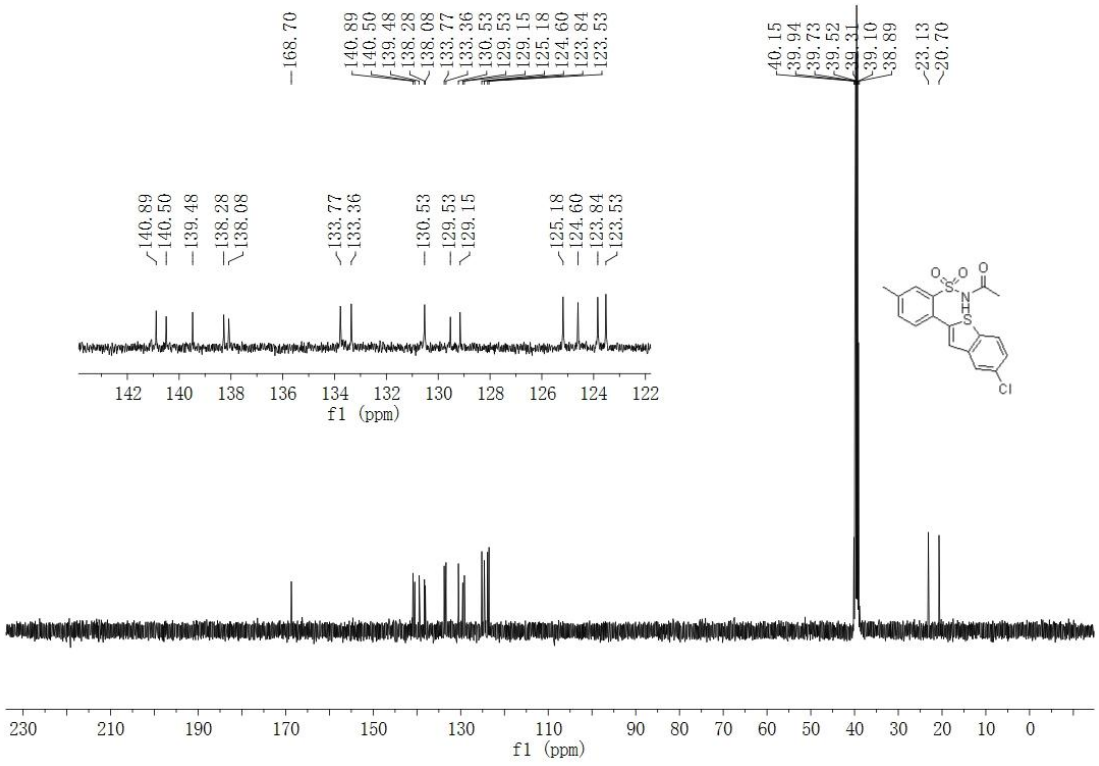

169.38
143.92
140.54
139.24
137.59
135.71
128.83
128.16
126.31
126.28
125.77
125.16
124.81
124.06
122.68
122.35
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.09
f1 (ppm)

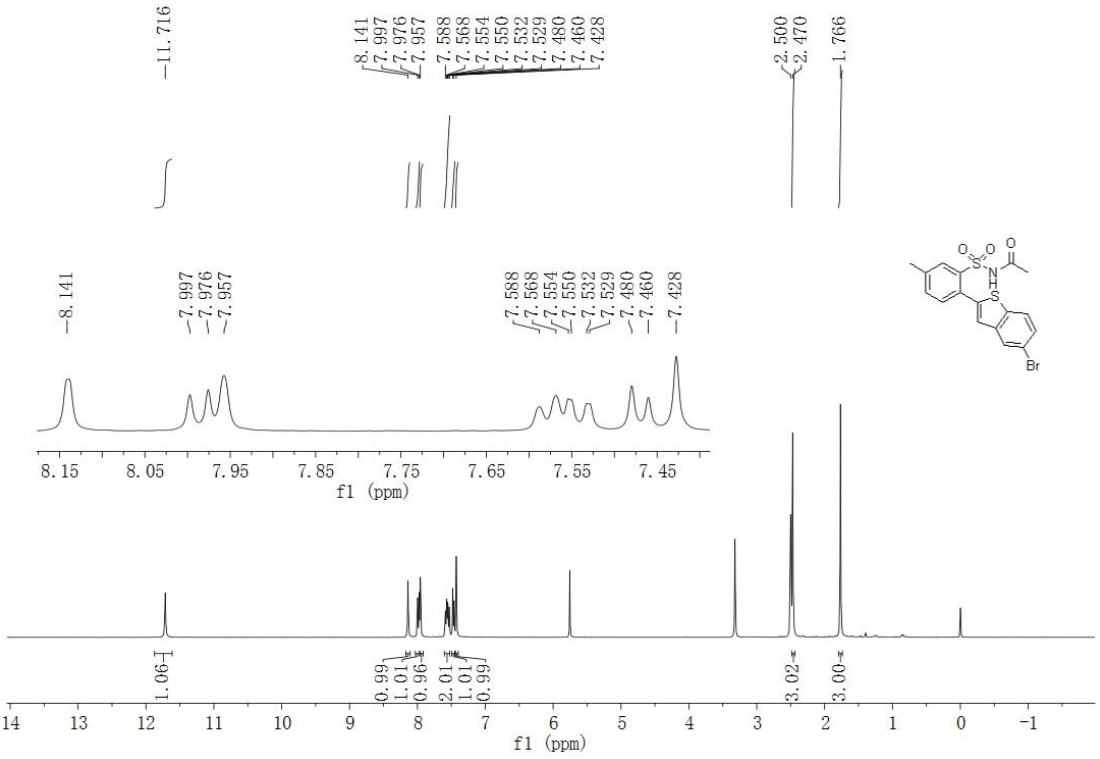

nHex
F3C
O
S
N
11.240
7.306
7.281
7.259
7.238
7.218
7.204
6.907
6.904
2.568
2.550
2.530
2.505
2.500
2.496
2.369
1.573
1.560
1.541
1.522
1.280
0.875
0.859
0.842
f1 (ppm)
6.99
1.95
2.05
2.02
4.00
3.02
7.09
12.06
6.06
168.86
145.42
139.40
139.33
139.22
136.47
129.46
127.67
125.24
122.56
117.26
106.45
125.44
125.24
122.62
122.56
119.89
117.26
40.15
39.94
39.73
39.52
39.31
39.10
38.89
28.41
22.12
14.01
143.12
142.75
142.66
142.37
141.99
139.40
139.38
139.35
139.33
139.27
139.24
139.22
139.19
139.17

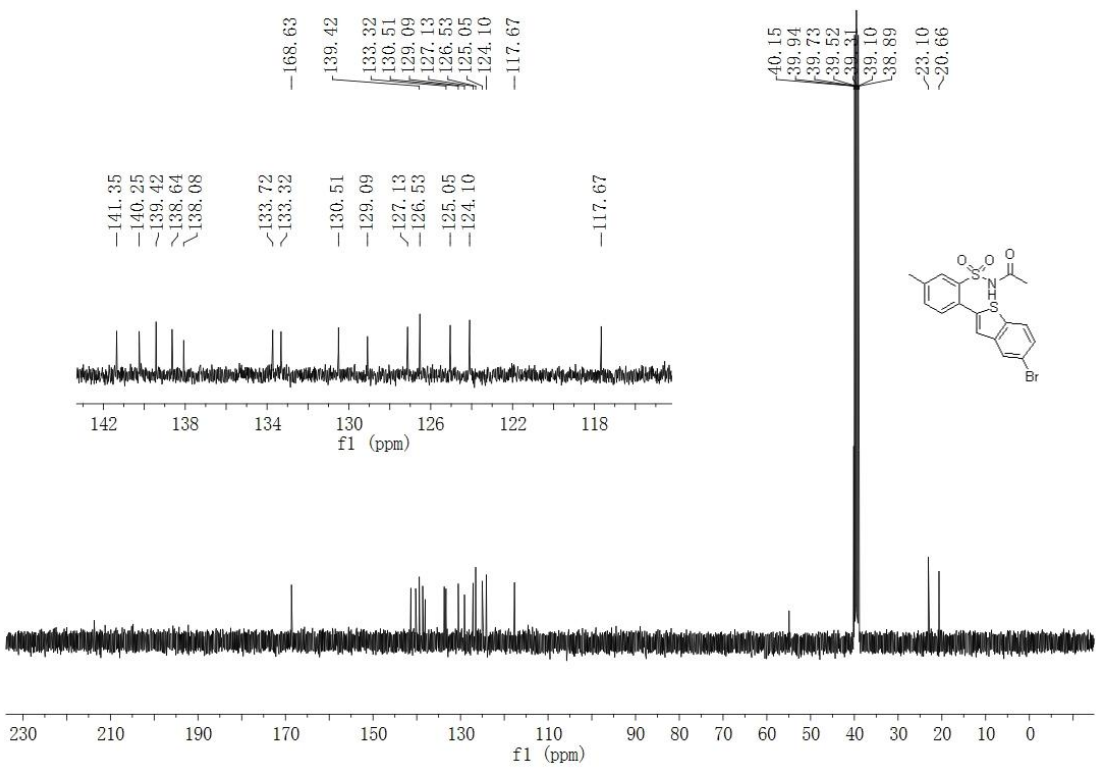

11.356
7.459
7.437
7.422
7.399
7.383
7.214
7.123
5.176
2.591
2.572
2.553
2.500
1.629
1.594
1.300
0.866
nHex
nHex
f1 (ppm)
0.99
2.92
1.91
1.92
2.00
4.00
2.98
4.03
12.30
6.01

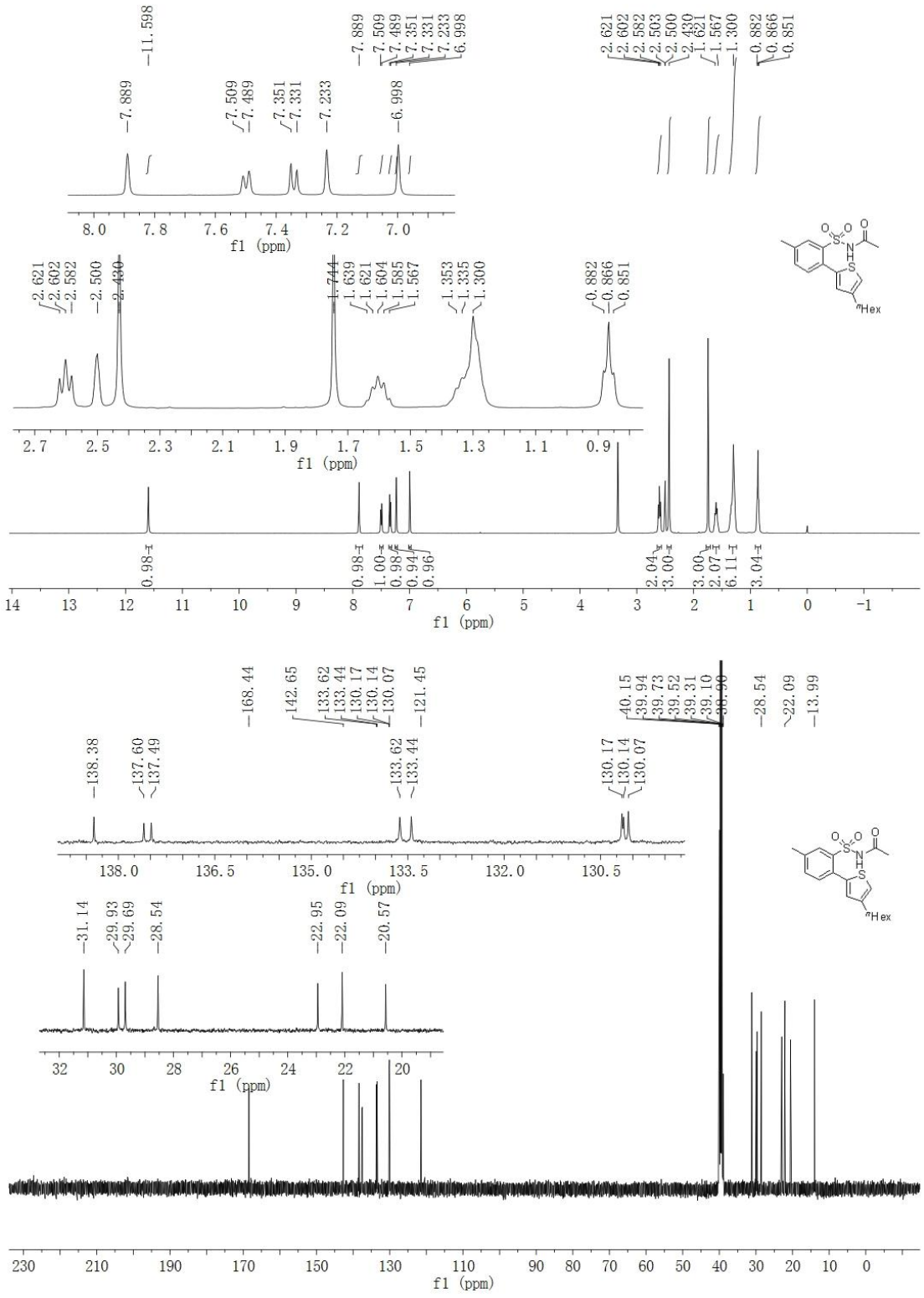

168.83
142.89
141.07
137.54
131.25
129.11
128.63
125.74
121.44
53.28
39.52
38.89
28.51
22.12
14.04
31.19
29.98
29.81
28.51
23.02
22.12
14.04
nHex
nHex
f1 (ppm)

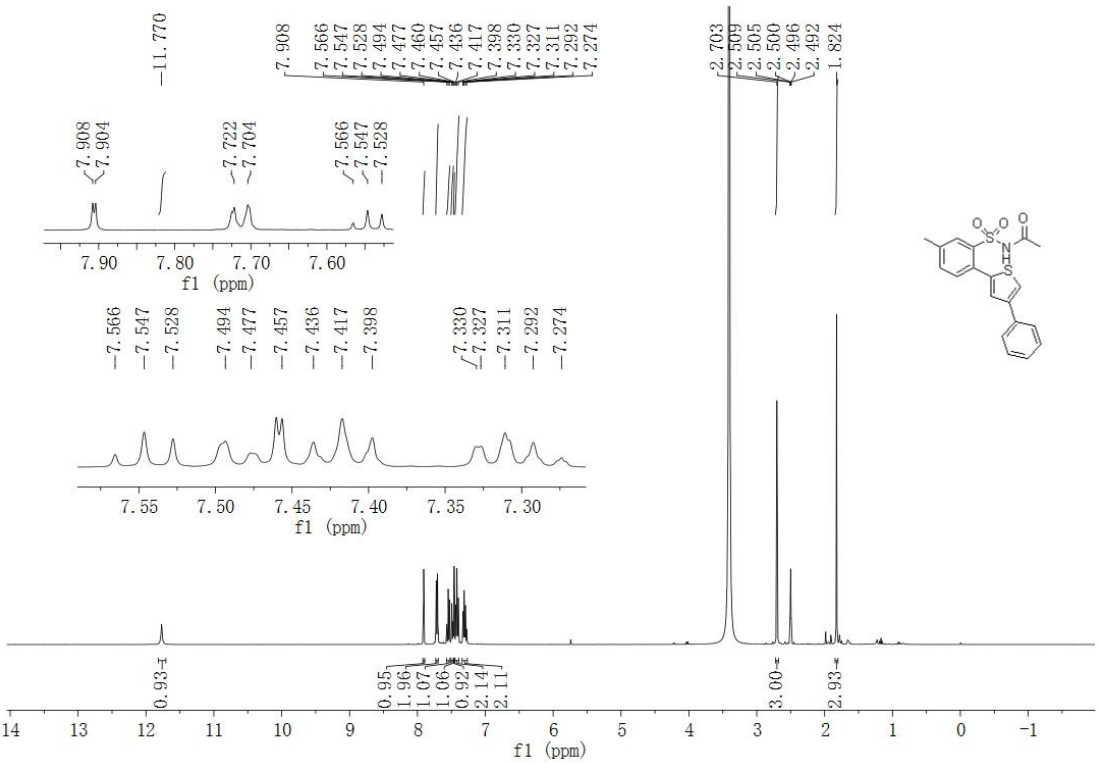

11.731
8.055
8.033
7.999
7.956
7.588
7.569
7.481
7.461
7.443
7.439
7.429
2.500
2.469
1.764
1.01
0.98
1.00
1.05
3.09
2.99
3.00
f1 (ppm)

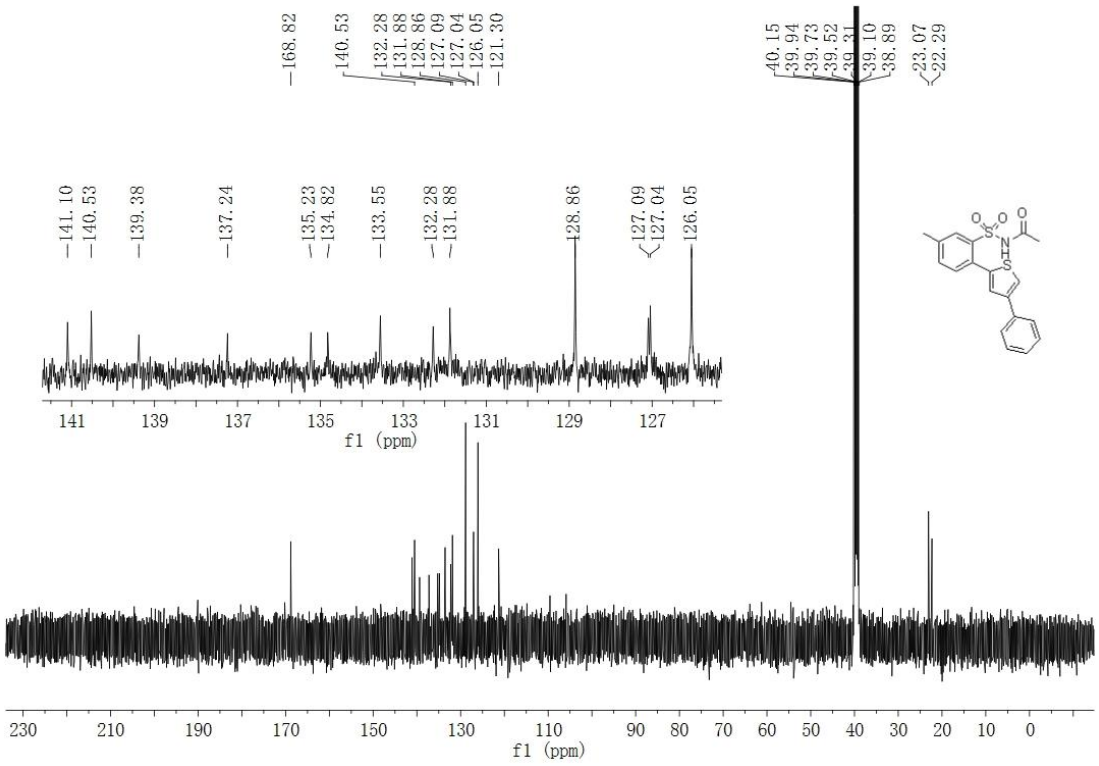

168.70
140.89
140.50
139.48
138.28
138.08
133.77
133.36
130.53
129.53
129.15
125.18
124.60
123.84
123.53
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.13
20.70
f1 (ppm)

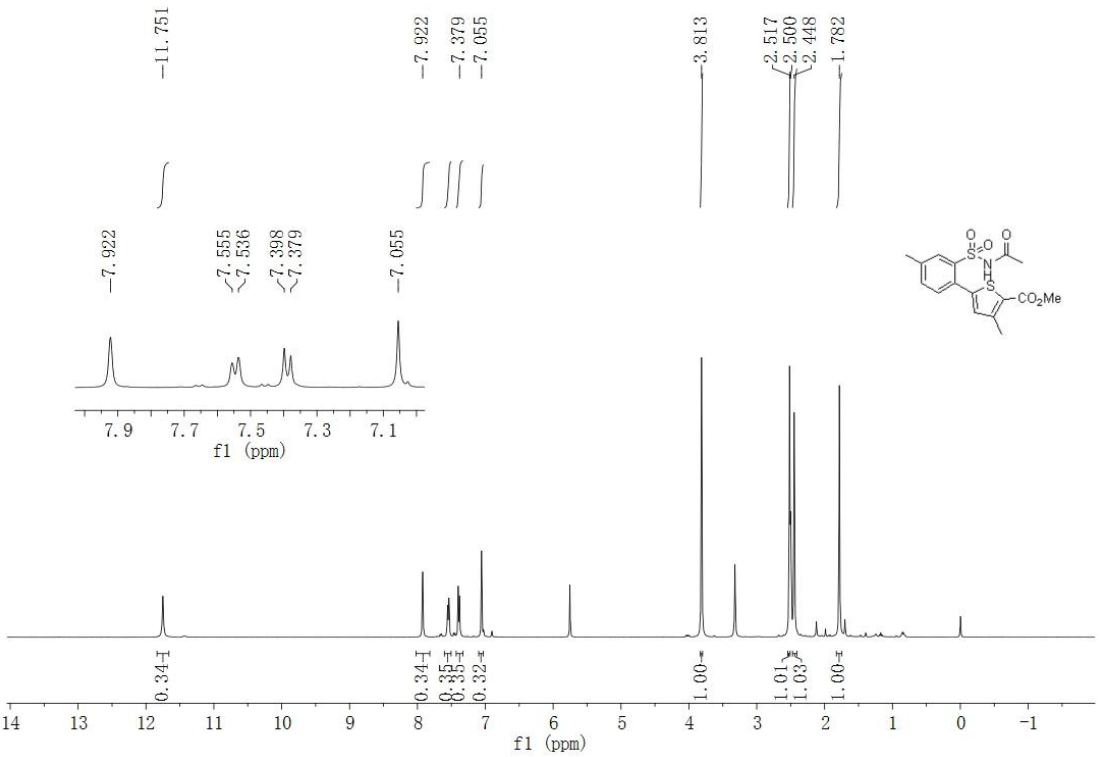

11.716
8.141
7.997
7.976
7.957
7.588
7.568
7.554
7.550
7.532
7.529
7.480
7.460
7.428
2.500
2.470
1.766
f1 (ppm)
1.06
0.99
1.01
0.96
2.01
1.01
0.99
3.02
3.00
Br

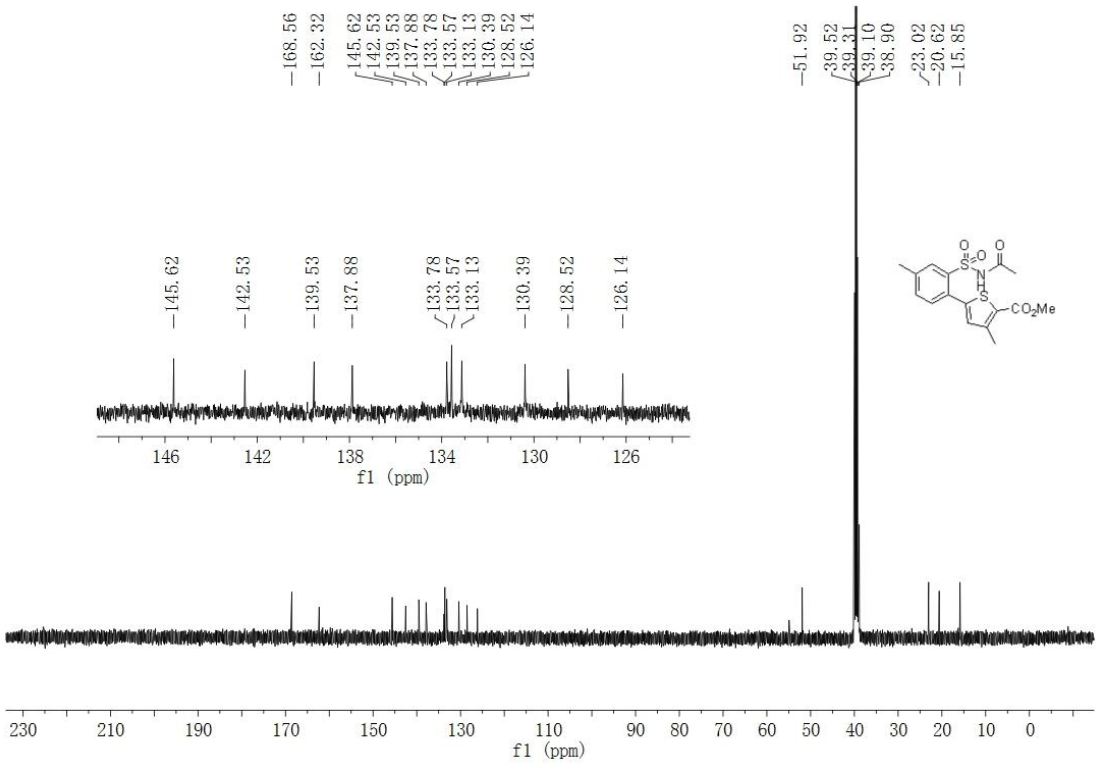

168.63
139.42
133.32
130.51
129.09
127.13
126.53
125.05
124.10
117.67
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.10
20.66
141.35
140.25
139.42
138.64
138.08
133.72
133.32
130.51
129.09
127.13
126.53
125.05
124.10
117.67
f1 (ppm)
Br

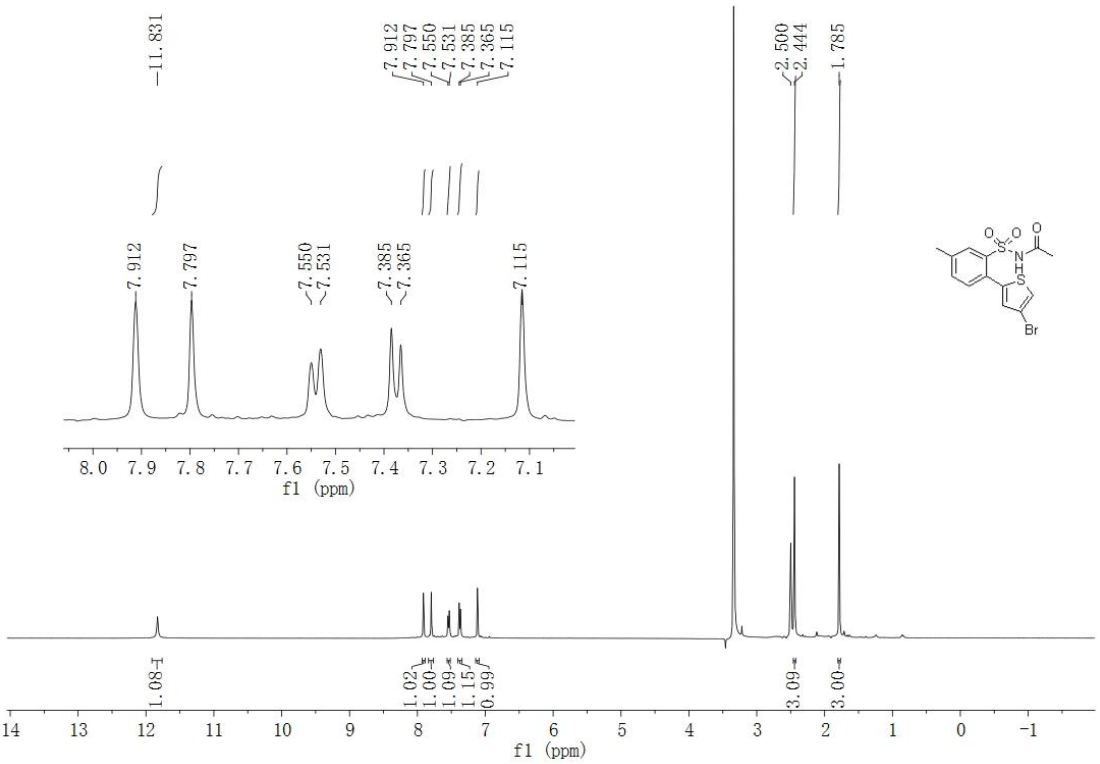

11.598
7.889
7.509
7.489
7.351
7.331
7.233
6.998
2.621
2.602
2.582
2.503
2.500
2.430
1.621
1.567
1.300
0.882
0.866
0.851
nHex
f1 (ppm)
168.44
142.65
133.62
133.44
130.17
130.14
130.07
121.45
40.15
39.94
39.73
39.52
39.31
39.10
38.90
28.54
22.09
13.99
138.38
137.60
137.49
31.14
29.93
29.69
22.95
22.09
20.57

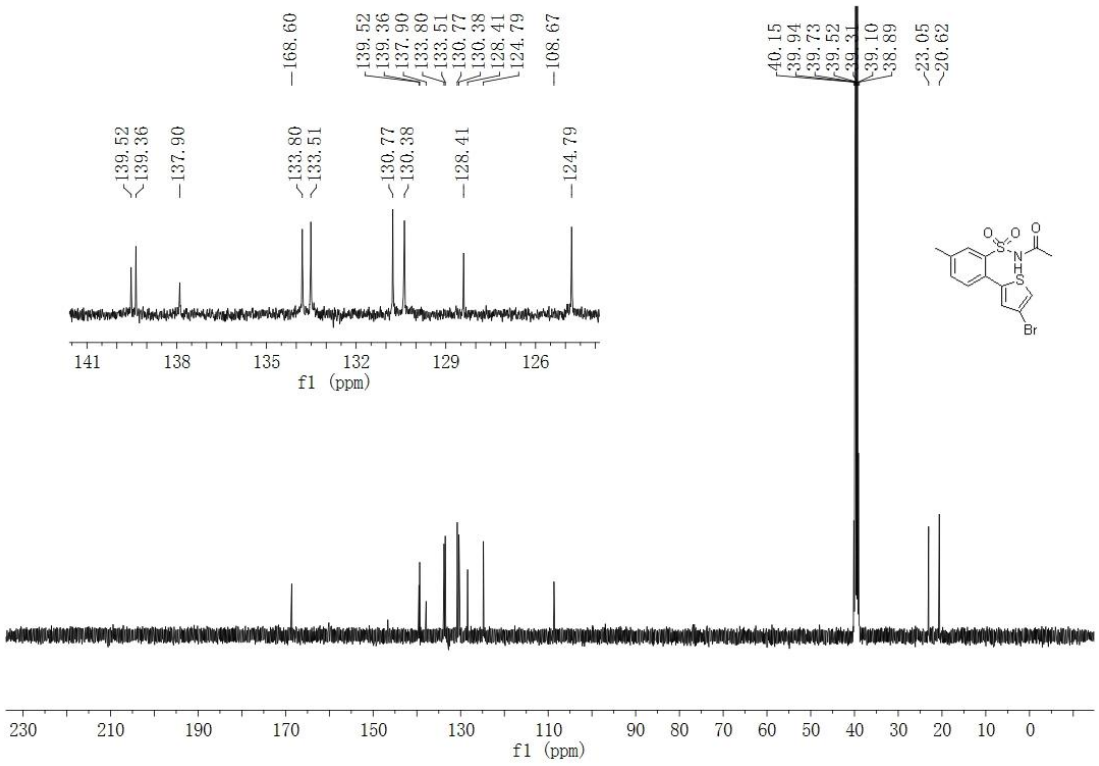

11.770
7.908
7.904
7.722
7.704
7.566
7.547
7.528
7.494
7.477
7.457
7.436
7.417
7.398
7.330
7.327
7.311
7.292
7.274
2.703
2.509
2.505
2.500
2.496
2.492
1.824
f1 (ppm)
0.93
0.95
1.96
1.07
1.06
0.92
2.14
2.11
3.00
2.93

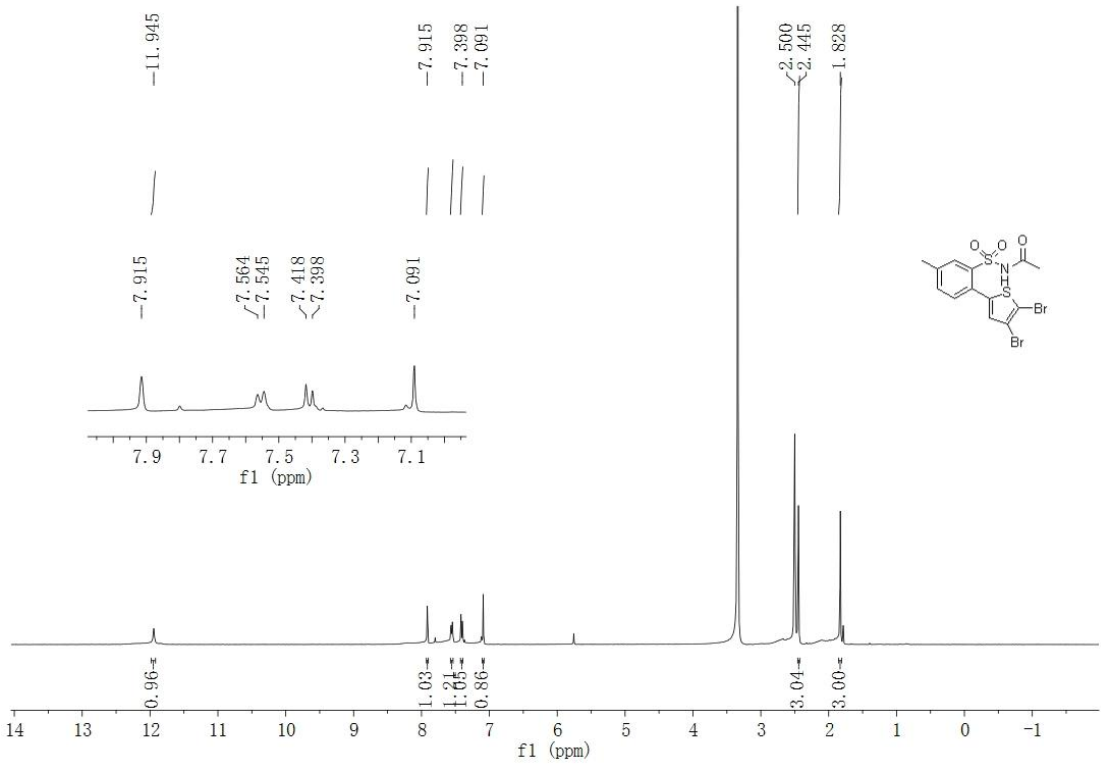

168.82
140.53
132.28
131.88
128.86
127.09
127.04
126.05
121.30
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.07
22.29
141.10
140.53
139.38
137.24
135.23
134.82
133.55
132.28
131.88
128.86
127.09
127.04
126.05
f1 (ppm)

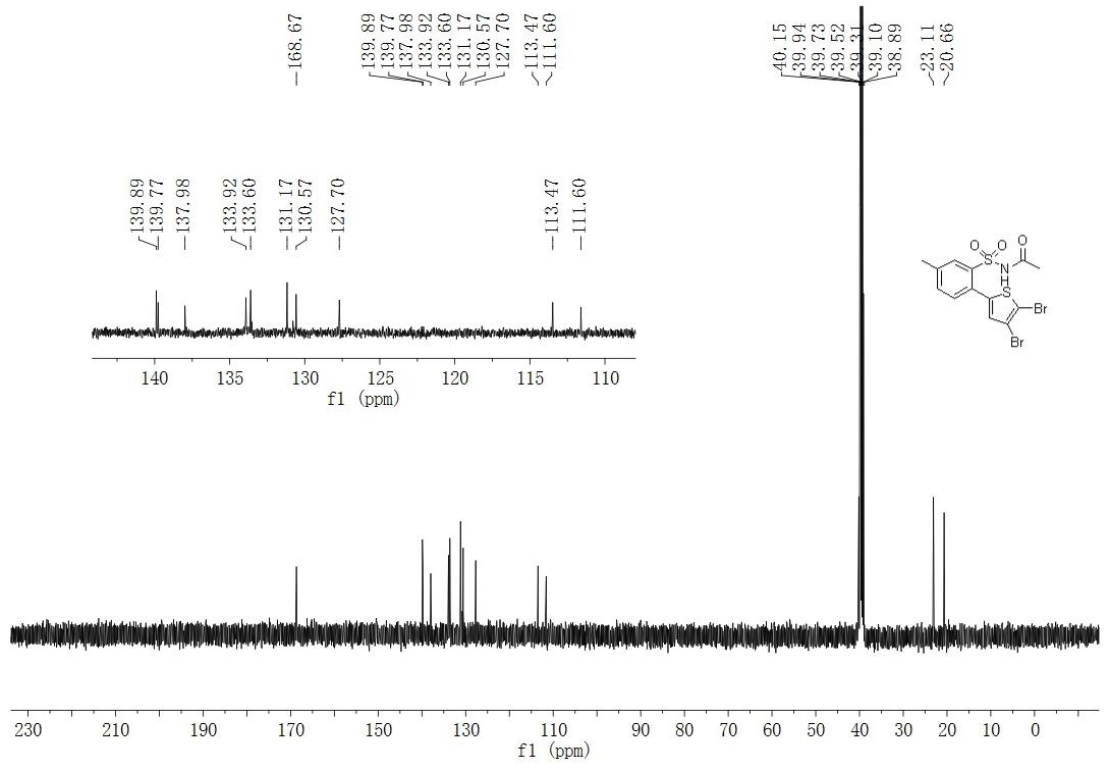

11.751
7.922
7.379
7.055
3.813
2.517
2.500
2.448
1.782
7.922
7.555
7.536
7.398
7.379
7.055
f1 (ppm)
0.34
0.34
0.35
0.32
1.00
1.01
1.03
1.00
f1 (ppm)

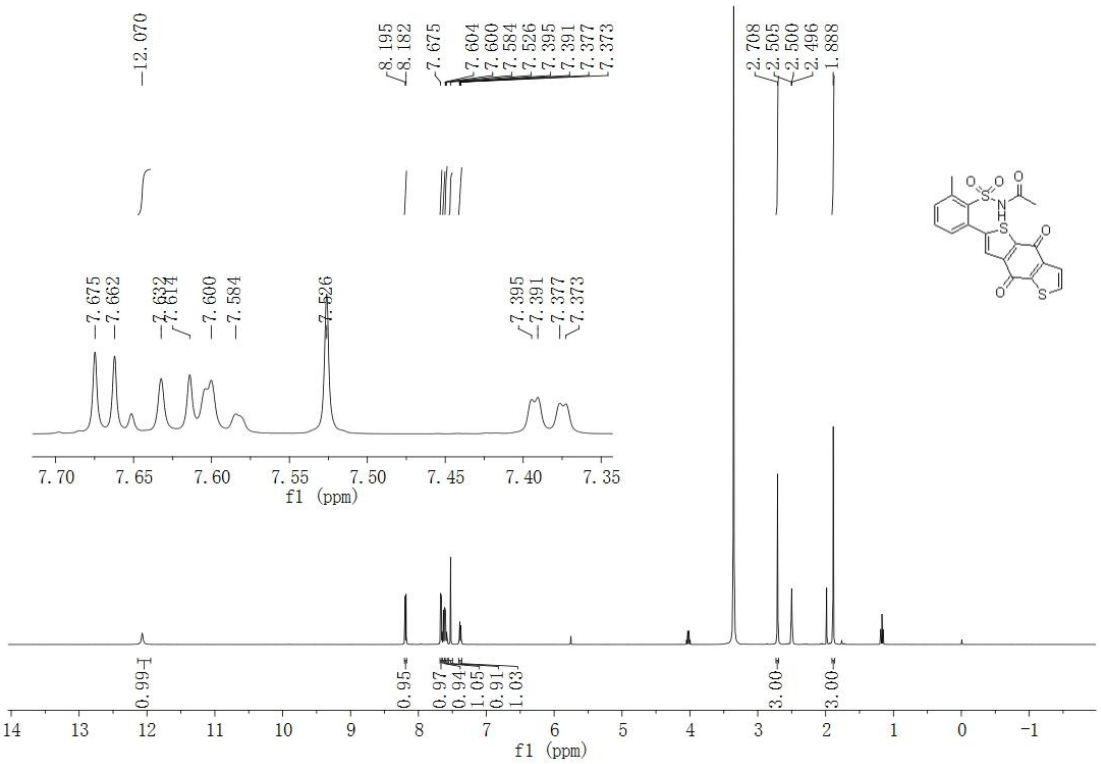

168.56
162.32
145.62
142.53
139.53
137.88
133.78
133.57
133.13
130.39
128.52
126.14
51.92
39.52
39.31
39.10
38.90
23.02
20.62
15.85
145.62
142.53
139.53
137.88
133.78
133.57
133.13
130.39
128.52
126.14
f1 (ppm)
f1 (ppm)

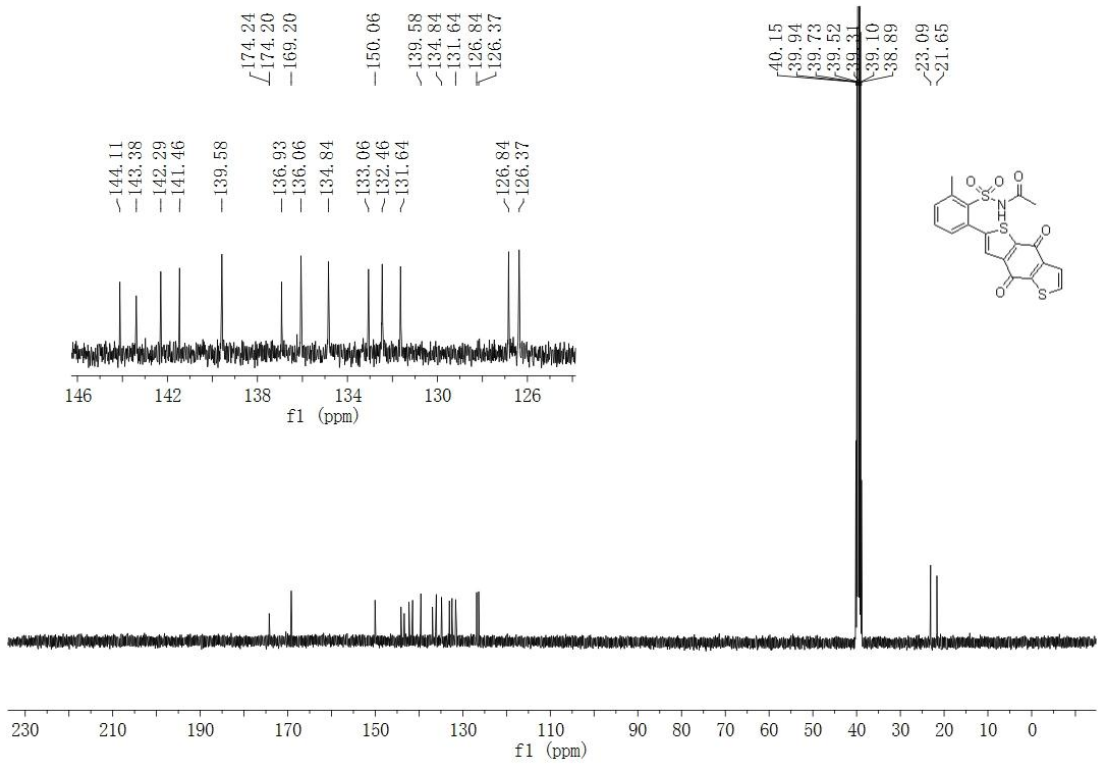

11.831
7.912
7.797
7.550
7.531
7.385
7.365
7.115
2.500
2.444
1.785
1.08
1.02
1.00
1.09
1.15
0.99
3.09
3.00
f1 (ppm)
Br

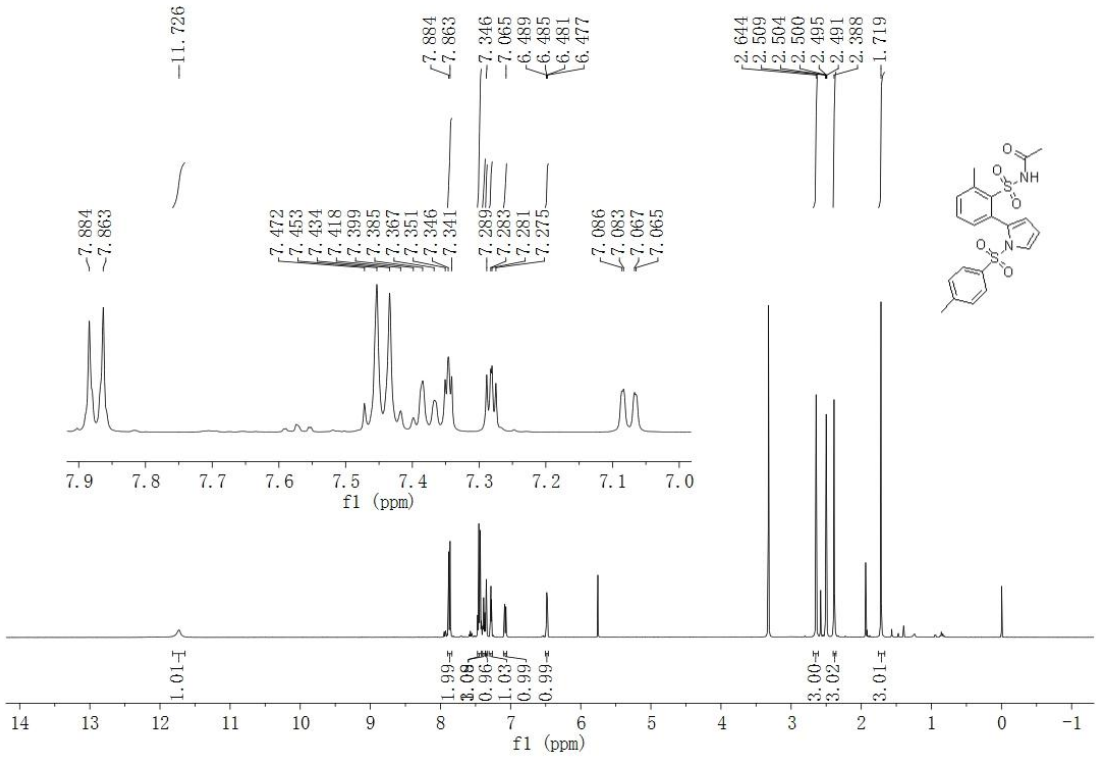

168.60
139.52
139.36
137.90
133.80
133.51
130.77
130.38
128.41
124.79
108.67
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.05
20.62
f1 (ppm)
Br

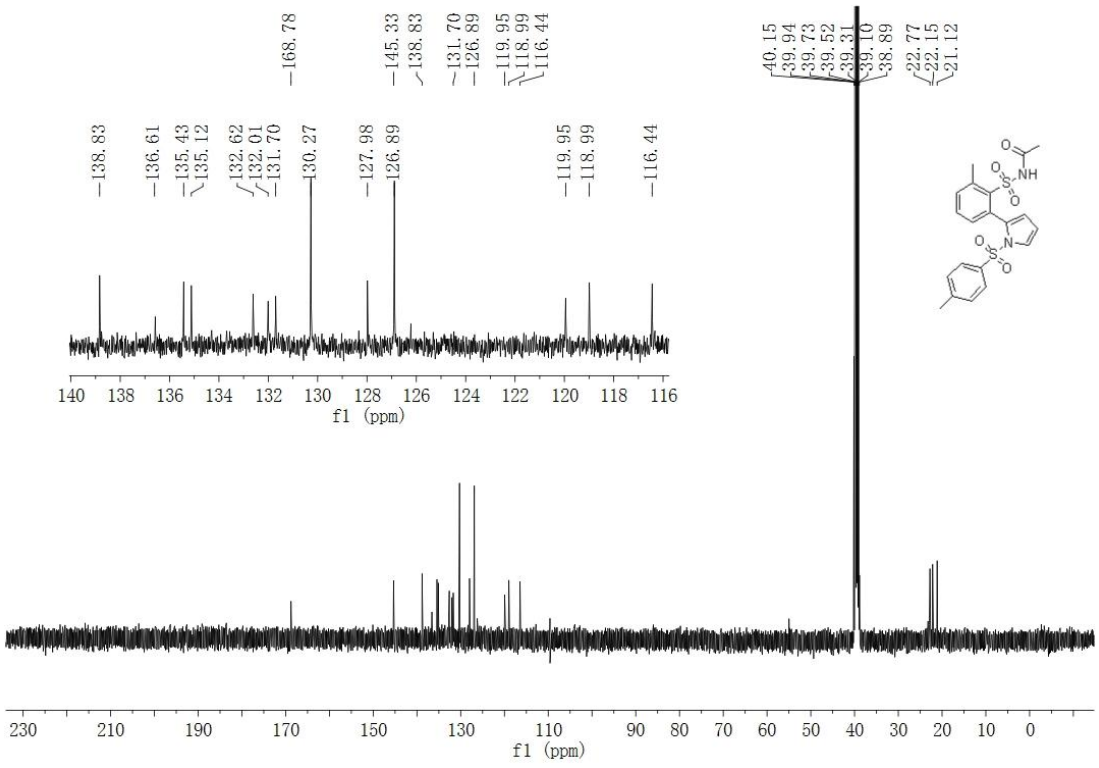

11.945
7.915
7.398
7.091
2.500
2.445
1.828
7.915
7.564
7.545
7.418
7.398
7.091
7.9
7.7
7.5
7.3
7.1
f1 (ppm)
0.96
1.03
1.21
1.05
0.86
3.04
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)
Br
Br

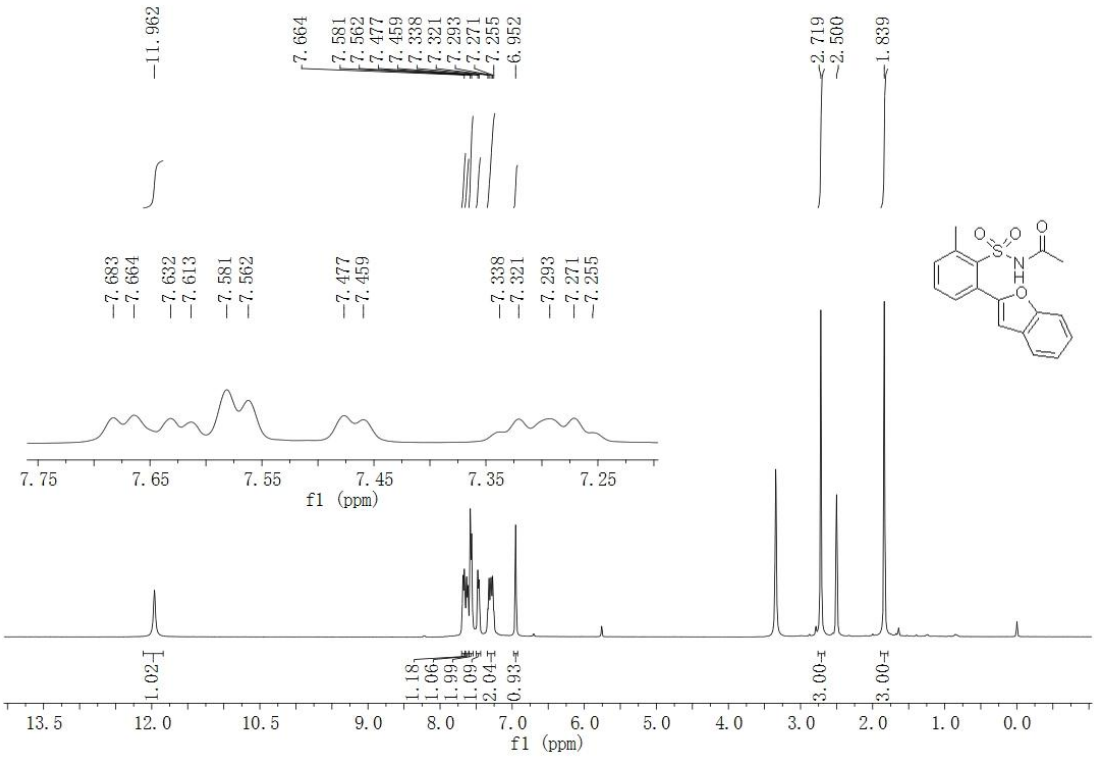

168.67
139.89
139.77
137.98
133.92
133.60
131.17
130.57
127.70
113.47
111.60
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.11
20.66
139.89
139.77
137.98
133.92
133.60
131.17
130.57
127.70
113.47
111.60
140
135
130
125
120
115
110
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
Br
Br

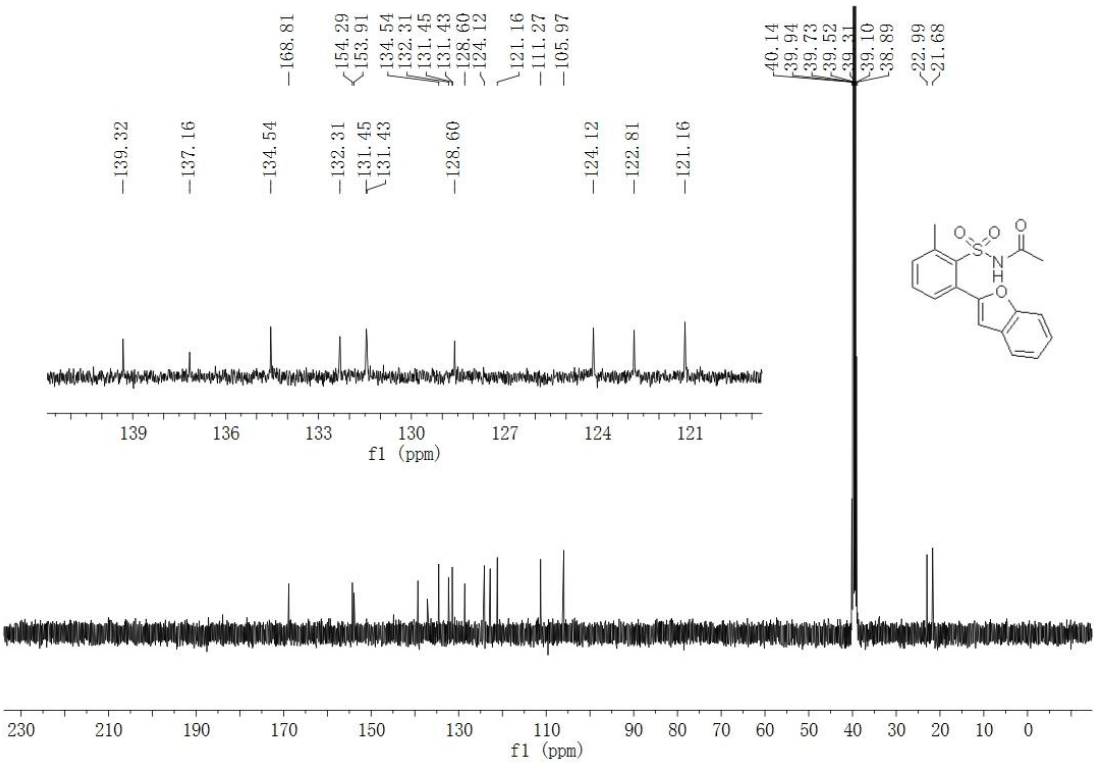

12.070
8.195
8.182
7.675
7.604
7.600
7.584
7.526
7.395
7.391
7.377
7.373
2.708
2.505
2.500
2.496
1.888
7.675
7.662
7.632
7.614
7.600
7.584
7.526
7.395
7.391
7.377
7.373
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
0.99
0.95
0.97
0.94
1.05
0.91
1.03
3.00
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

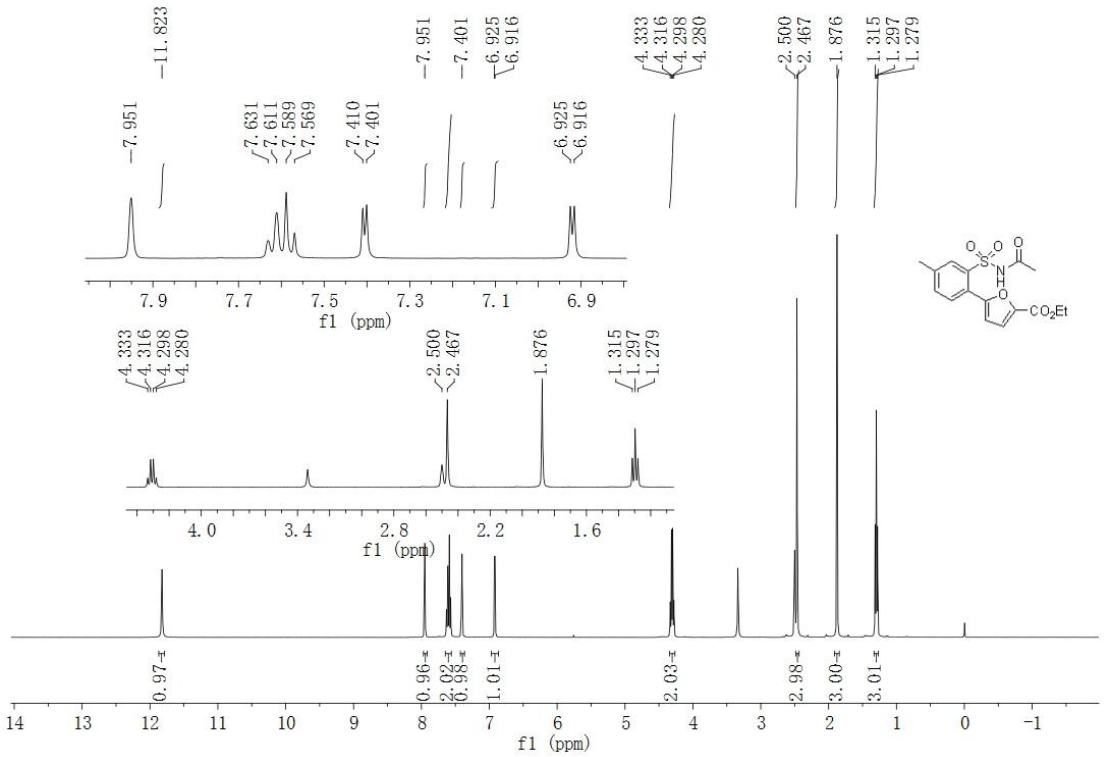

174.24
174.20
169.20
150.06
139.58
134.84
131.64
126.84
126.37
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.09
21.65
144.11
143.38
142.29
141.46
139.58
136.93
136.06
134.84
133.06
132.46
131.64
126.84
126.37
146 142 138 134 130 126
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

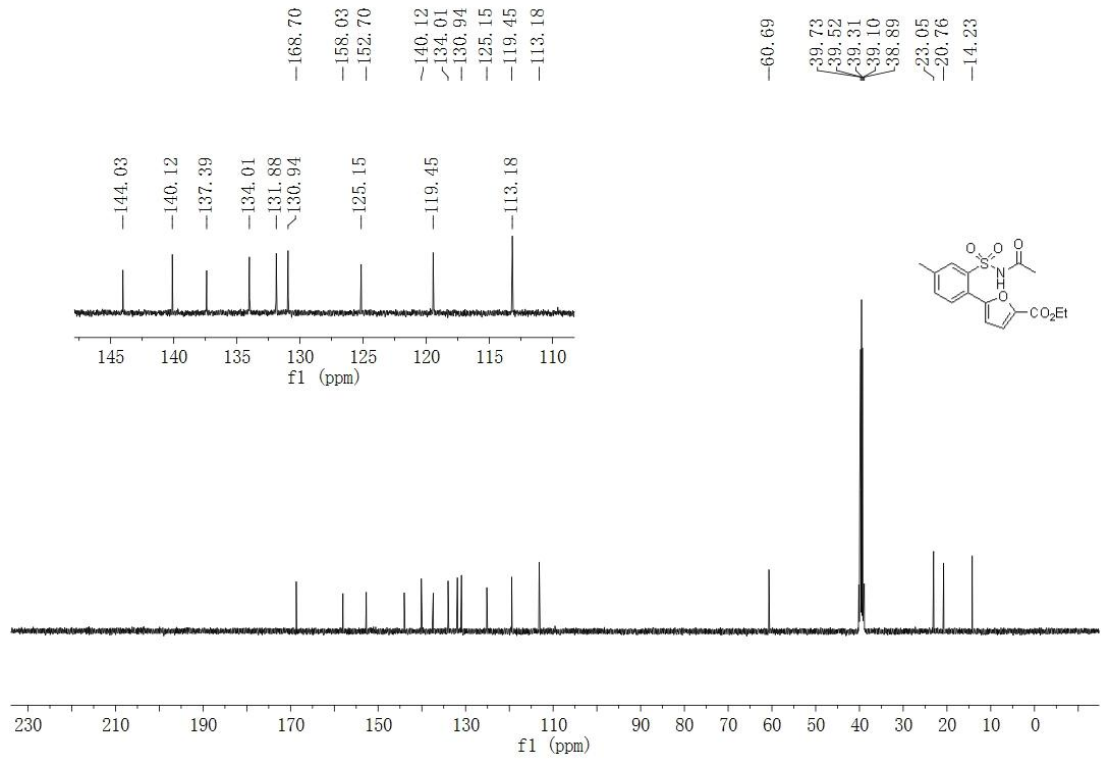

11.726
7.884
7.863
7.472
7.453
7.434
7.418
7.399
7.385
7.367
7.351
7.346
7.341
7.346
7.289
7.283
7.281
7.275
7.065
6.489
6.485
6.481
6.477
7.086
7.083
7.067
7.065
2.644
2.509
2.504
2.500
2.495
2.491
2.388
1.719
f1 (ppm)
1.01
1.99
1.08
0.96
1.03
0.99
0.99
3.00
3.02
3.01

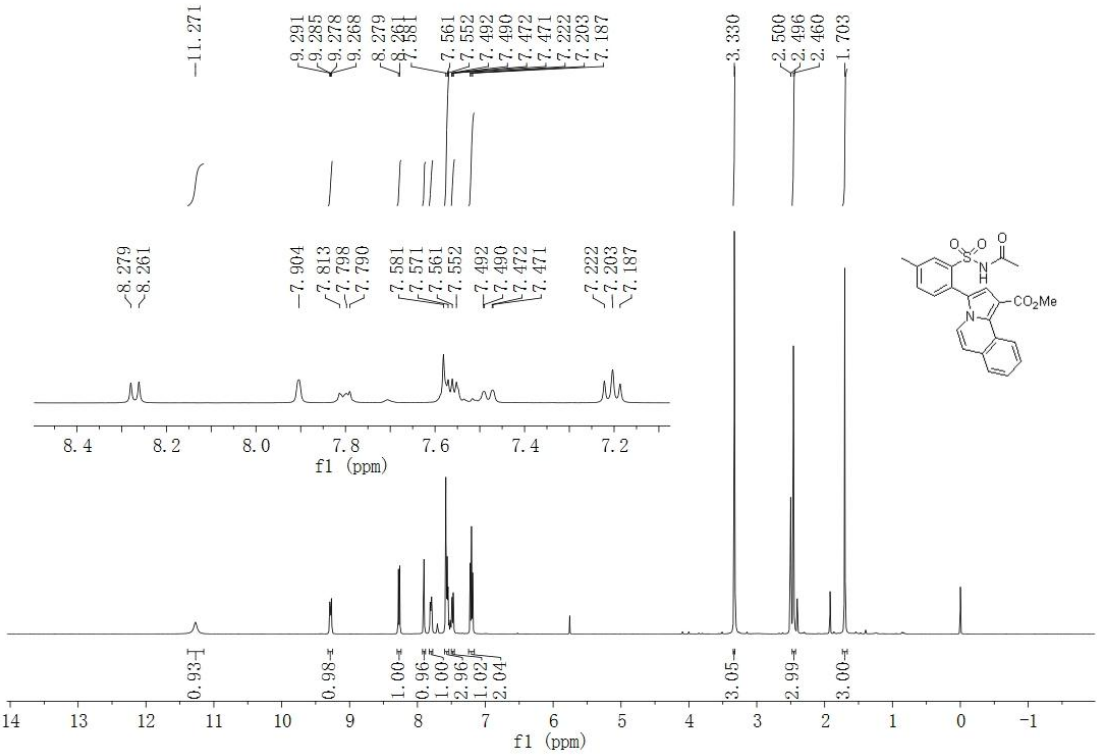

168.78
145.33
138.83
131.70
126.89
119.95
118.99
116.44
40.15
39.94
39.73
39.52
39.31
39.10
38.89
22.77
22.15
21.12
138.83
136.61
135.43
135.12
132.62
132.01
131.70
130.27
127.98
126.89
119.95
118.99
116.44
f1 (ppm)

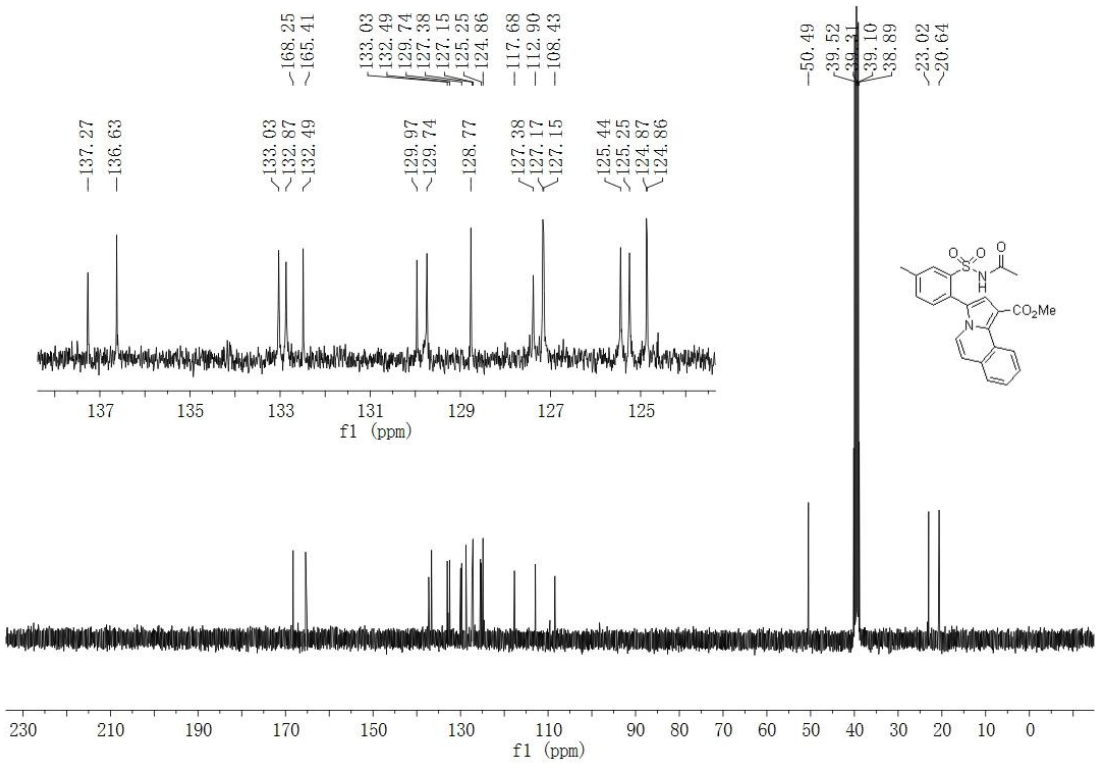

11.962
7.664
7.581
7.562
7.477
7.459
7.338
7.321
7.293
7.271
7.255
6.952
2.719
2.500
1.839
7.683
7.664
7.632
7.613
7.581
7.562
7.477
7.459
7.338
7.321
7.293
7.271
7.255
7.75
7.65
7.55
7.45
7.35
7.25
f1 (ppm)
1.02
1.18
1.06
1.99
1.09
2.04
0.93
3.00
3.00
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

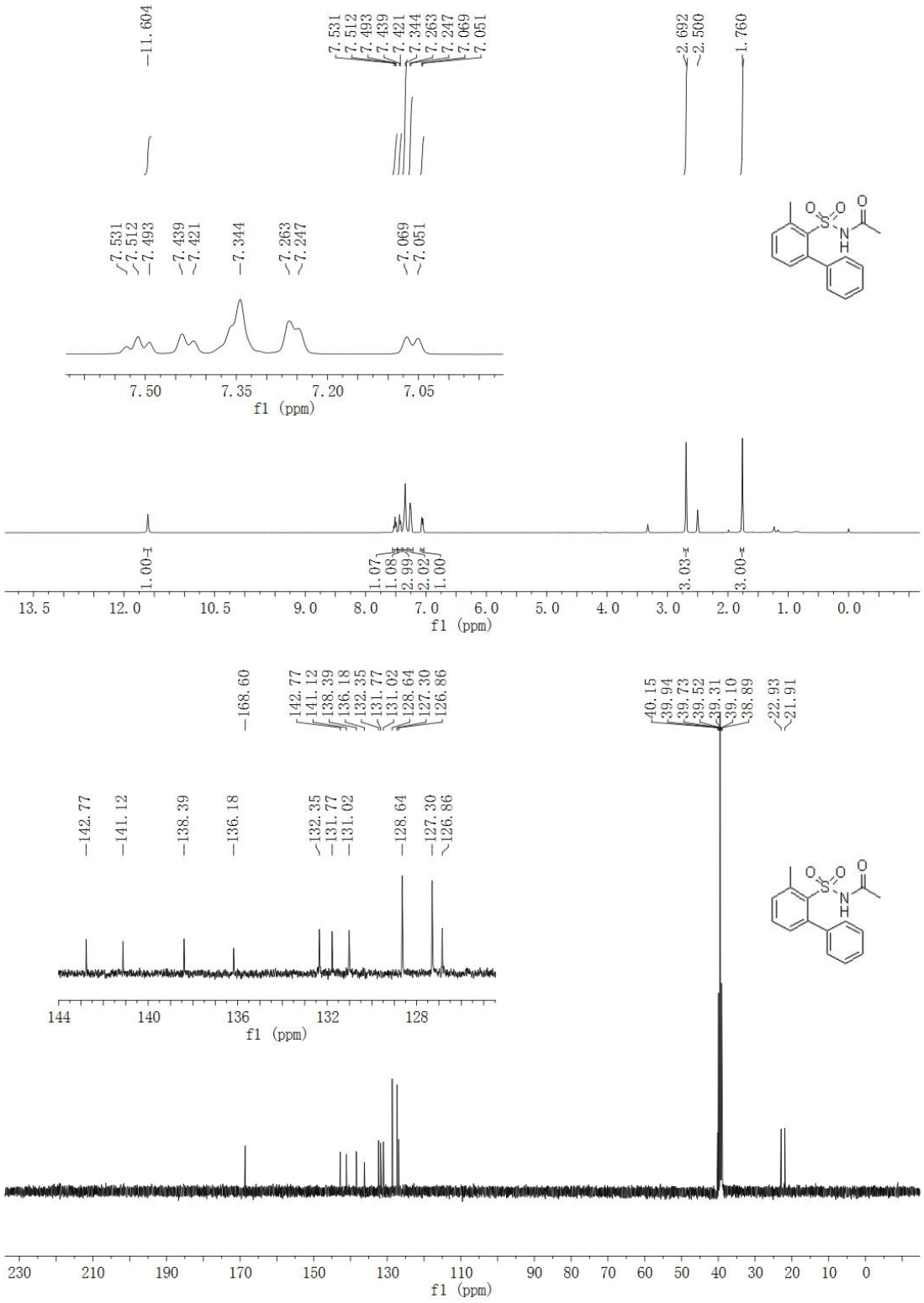

168.81
154.29
153.91
134.54
132.31
131.45
131.43
128.60
124.12
121.16
111.27
105.97
40.14
39.94
39.73
39.52
39.31
39.10
38.89
22.99
21.68
139.32
137.16
134.54
132.31
131.45
131.43
128.60
124.12
122.81
121.16
139
136
133
130
127
124
121
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

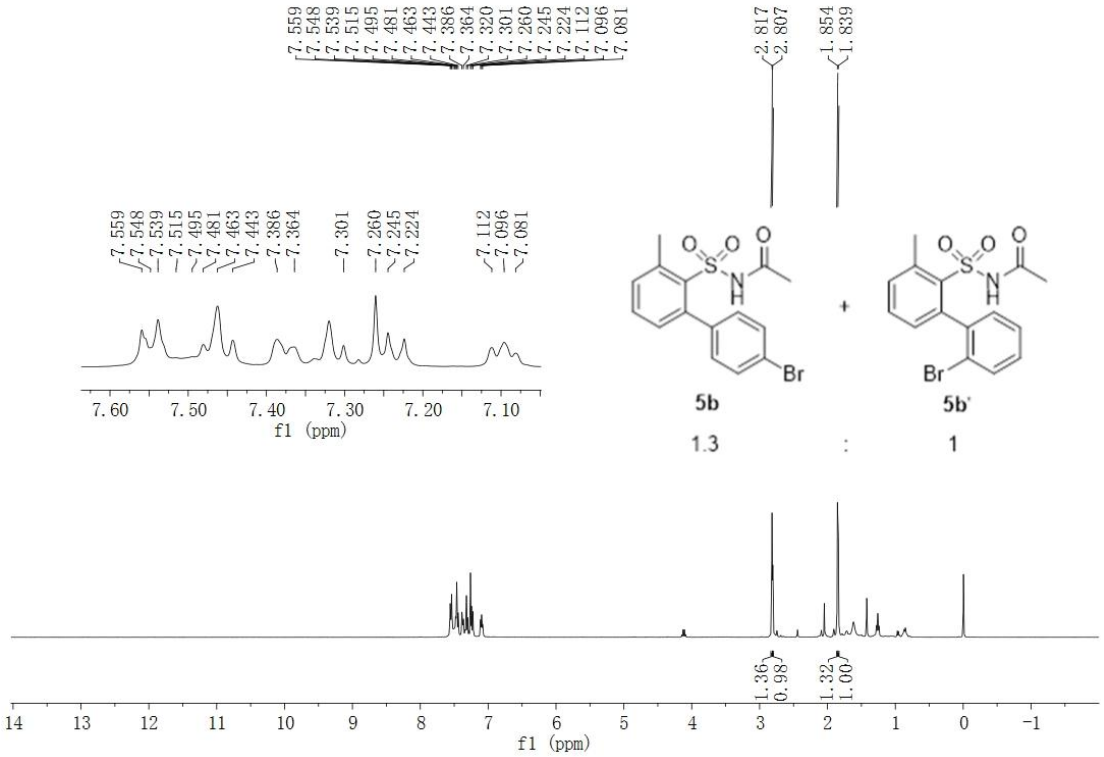

11.823
7.951
7.631
7.611
7.589
7.569
7.410
7.401
6.925
6.916
4.333
4.316
4.298
4.280
2.500
2.467
1.876
1.315
1.297
1.279
f1 (ppm)
0.97
0.96
2.02
0.98
1.01
2.03
2.98
3.00
3.01

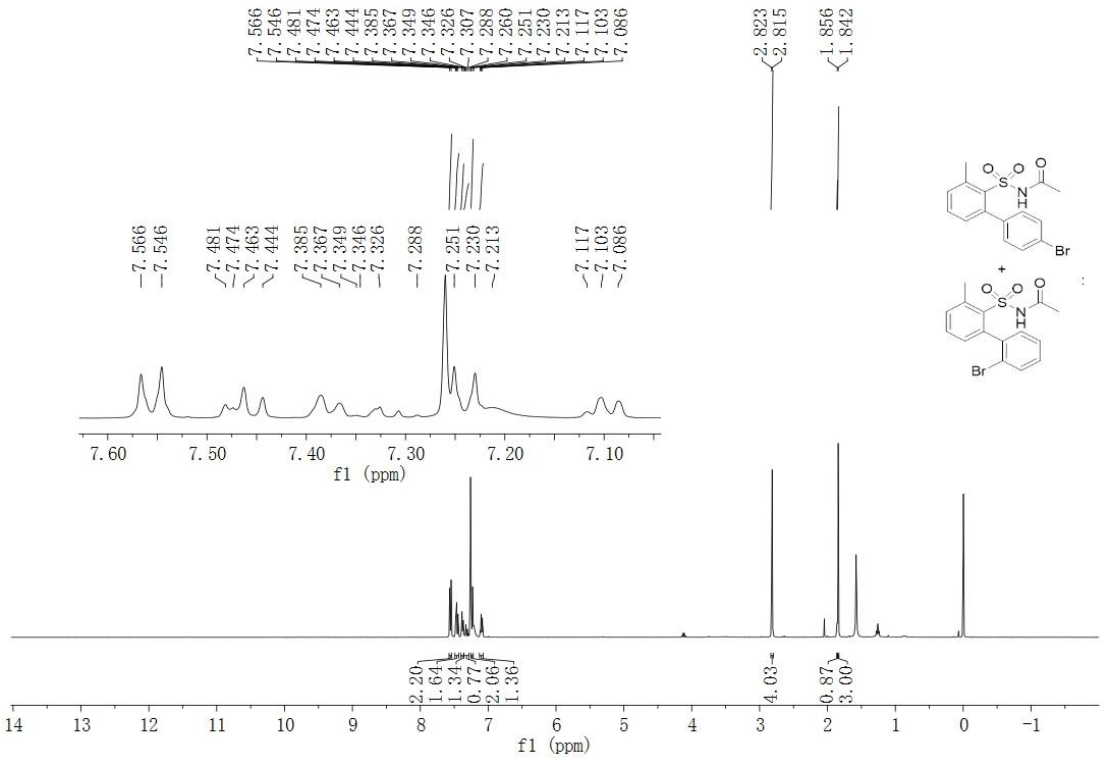

168.70
158.03
152.70
140.12
134.01
130.94
125.15
119.45
113.18
60.69
39.73
39.52
39.31
39.10
38.89
23.05
20.76
14.23
144.03
140.12
137.39
134.01
131.88
130.94
125.15
119.45
113.18
f1 (ppm)

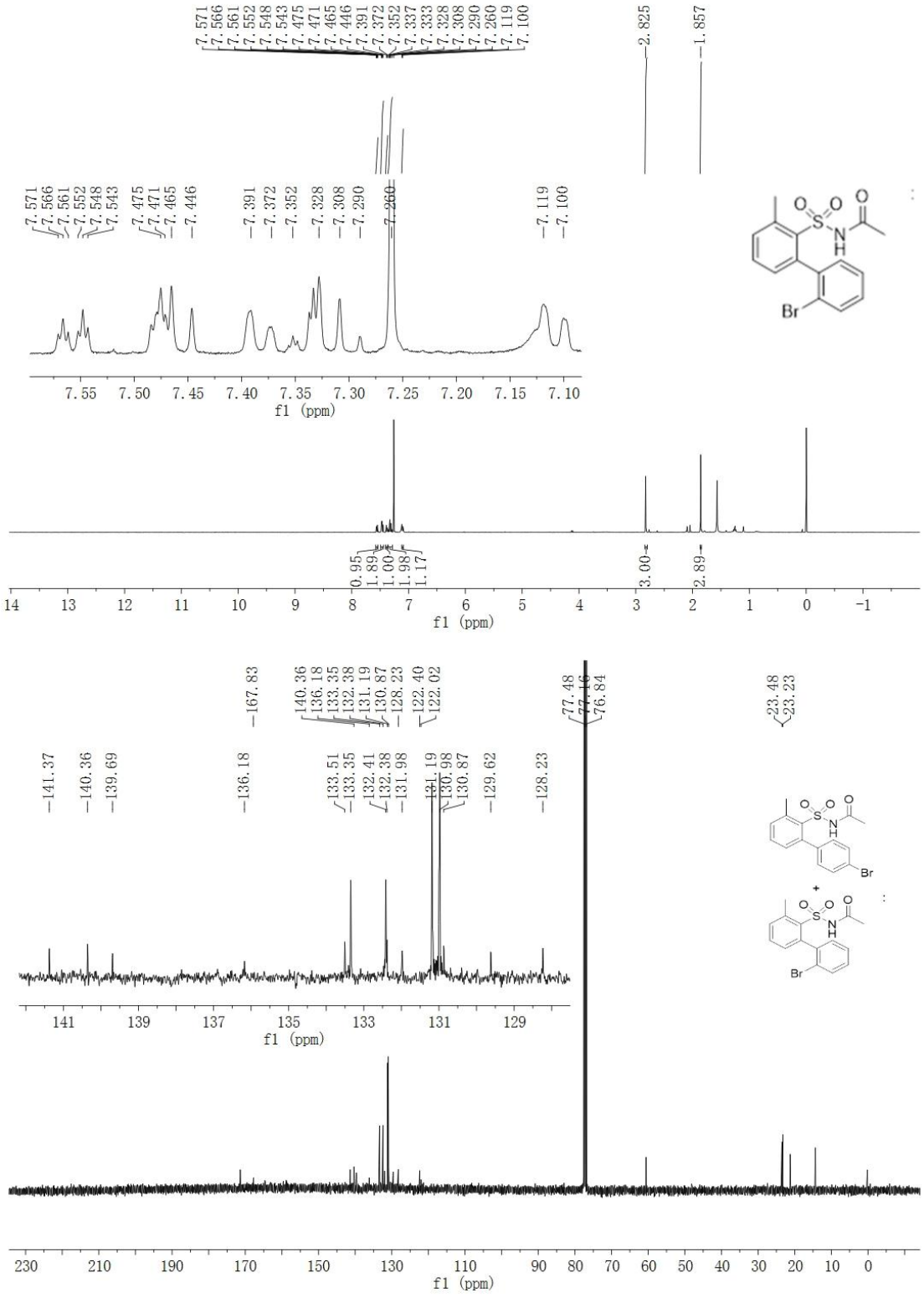

11.271
9.291
9.285
9.278
9.268
8.279
8.261
7.581
7.571
7.561
7.552
7.492
7.490
7.472
7.471
7.222
7.203
7.187
3.330
2.500
2.496
2.460
1.703
0.93
0.98
1.00
0.96
1.00
2.96
1.02
2.04
3.05
2.99
3.00
f1 (ppm)
CO2Me

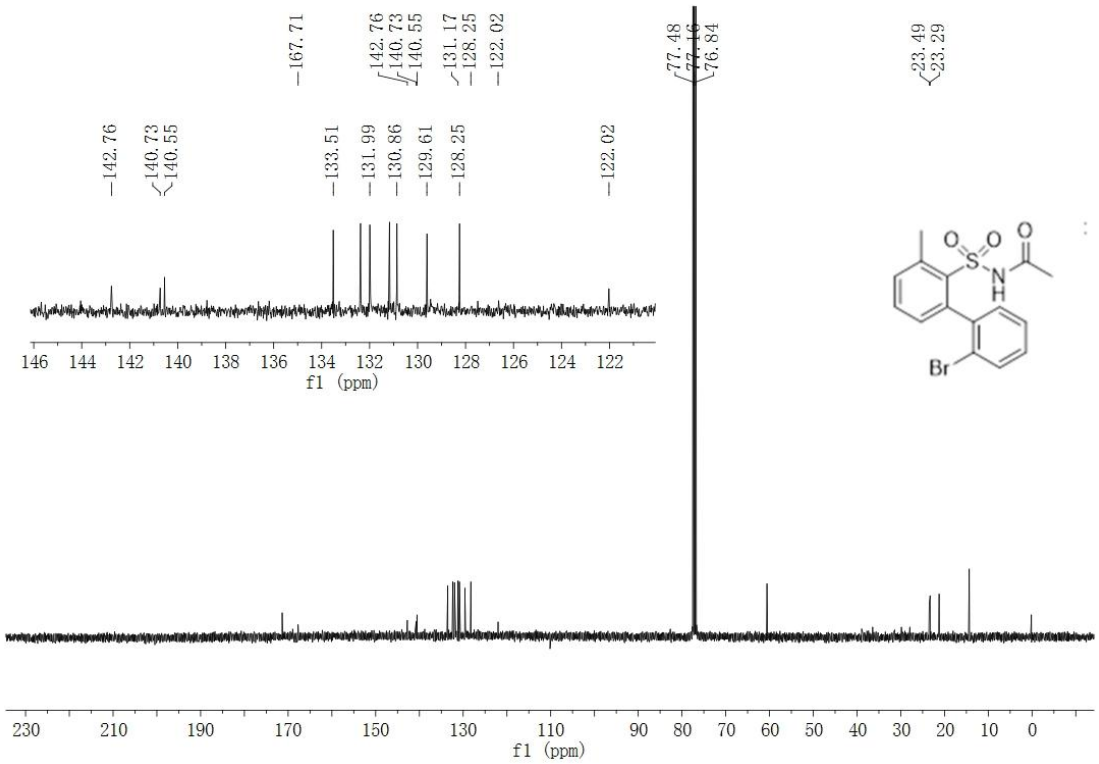

168.25
165.41
133.03
132.49
129.74
127.38
127.15
125.25
124.86
117.68
112.90
108.43
50.49
39.52
39.31
39.10
38.89
23.02
20.64
137.27
136.63
f1 (ppm)
CO2Me

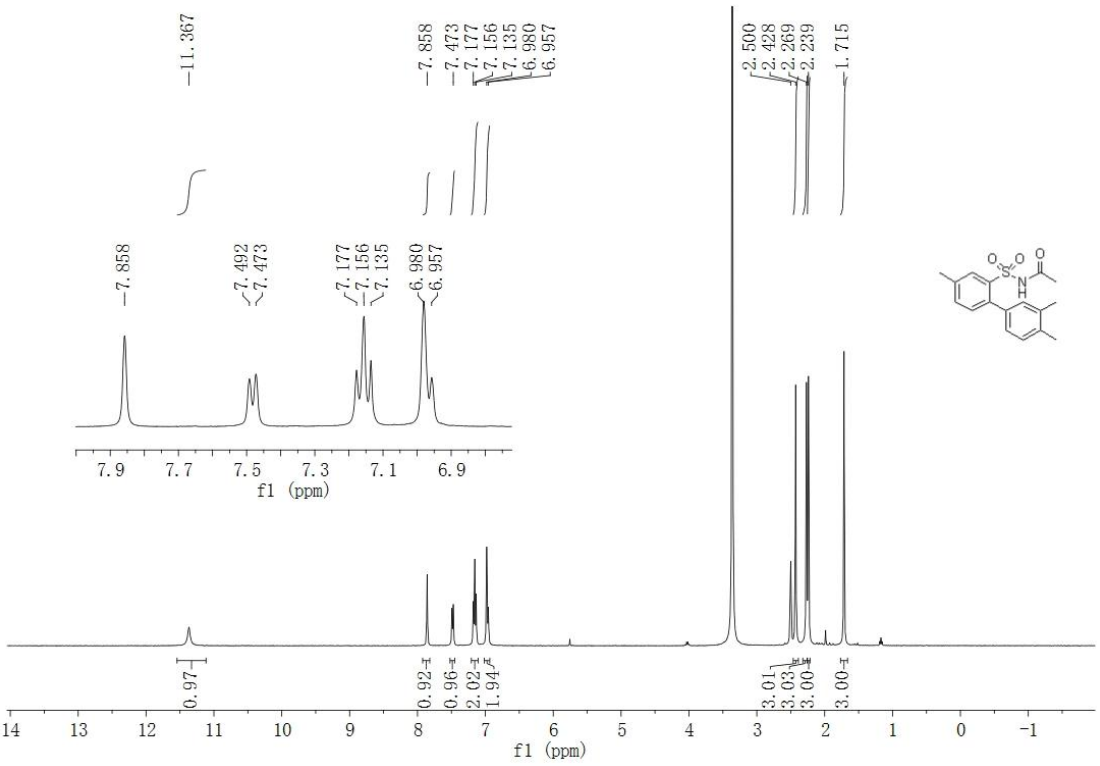

11.604
7.531
7.512
7.493
7.439
7.421
7.344
7.263
7.247
7.069
7.051
2.692
2.500
1.760
1.00
1.07
1.08
2.99
2.02
1.00
3.03
3.00
f1 (ppm)
168.60
142.77
141.12
138.39
136.18
132.35
131.77
131.02
128.64
127.30
126.86
40.15
39.94
39.73
39.52
39.31
39.10
38.89
22.93
21.91
f1 (ppm)

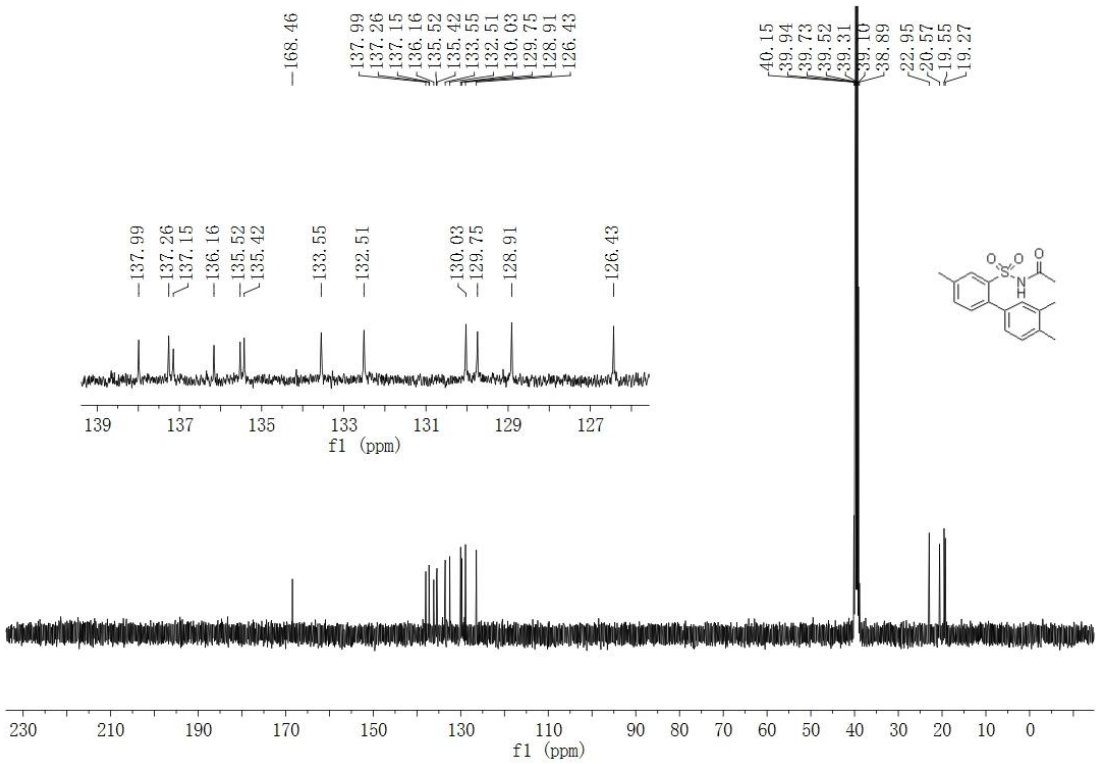

7.559
7.548
7.539
7.515
7.495
7.481
7.463
7.443
7.386
7.364
7.320
7.301
7.260
7.245
7.224
7.112
7.096
7.081
2.817
2.807
1.854
1.839
7.60
7.50
7.40
7.30
7.20
7.10
f1 (ppm)
5b
1.3
:
5b'
1
1.36
0.98
1.32
1.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

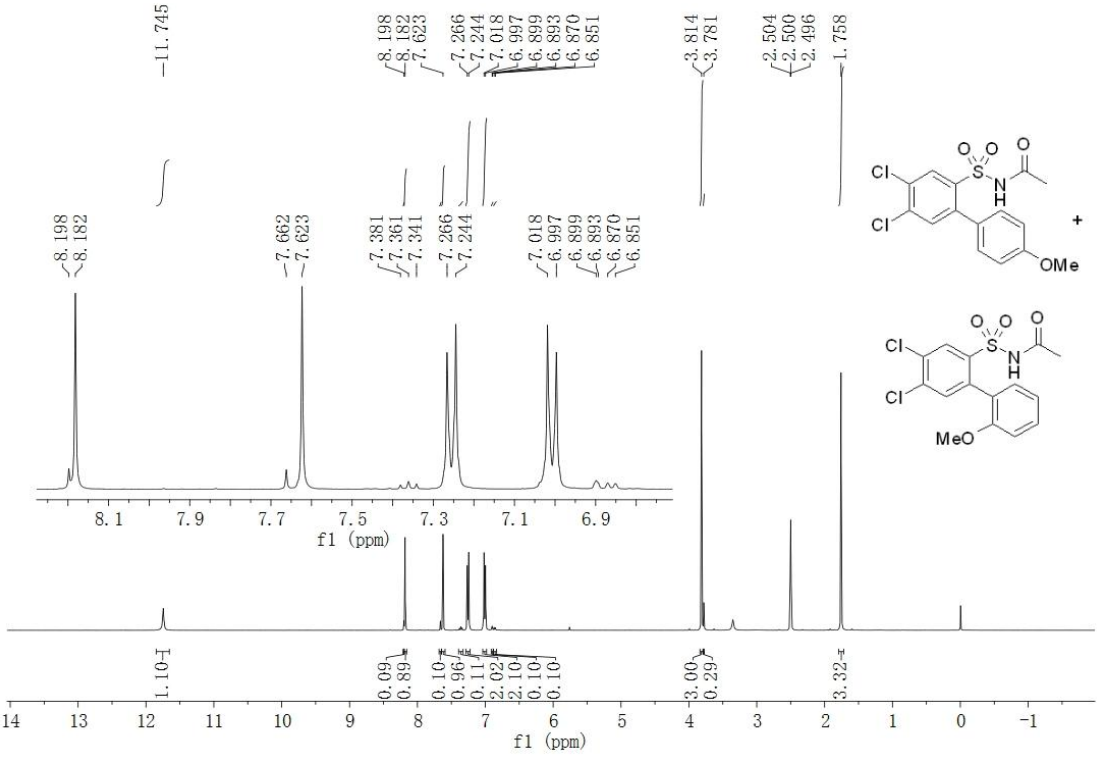

7.566
7.546
7.481
7.474
7.463
7.444
7.385
7.367
7.349
7.346
7.326
7.307
7.288
7.260
7.251
7.230
7.213
7.117
7.103
7.086
2.823
2.815
1.856
1.842
7.60
7.50
7.40
7.30
7.20
7.10
f1 (ppm)
2.20
1.64
1.34
0.77
2.06
1.36
4.03
0.87
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

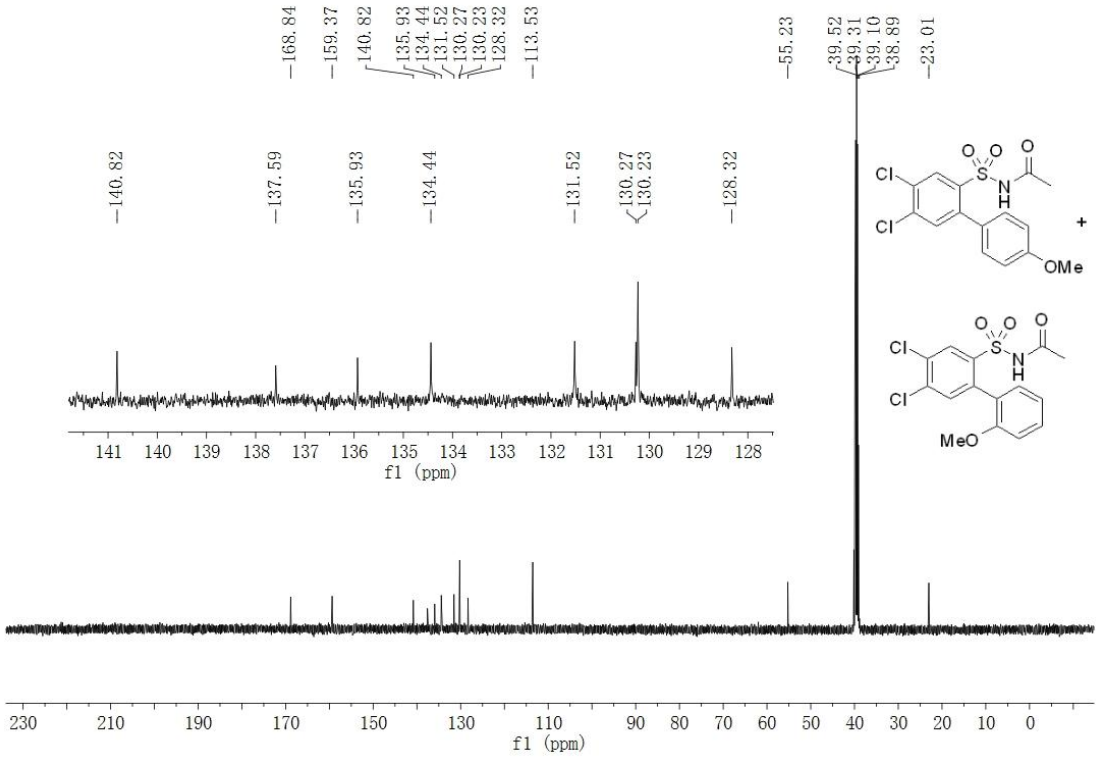

7.571
7.566
7.561
7.552
7.548
7.543
7.475
7.471
7.465
7.446
7.391
7.372
7.352
7.328
7.308
7.290
7.260
7.119
7.100
2.825
1.857
f1 (ppm)
0.95
1.89
1.00
1.98
1.17
3.00
2.89
f1 (ppm)
167.83
140.36
136.18
133.35
132.38
131.19
130.87
128.23
122.40
122.02
77.48
77.16
76.84
23.48
23.23
141.37
140.36
139.69
136.18
133.51
133.35
132.41
132.38
131.98
131.19
130.98
130.87
129.62
128.23
f1 (ppm)
f1 (ppm)

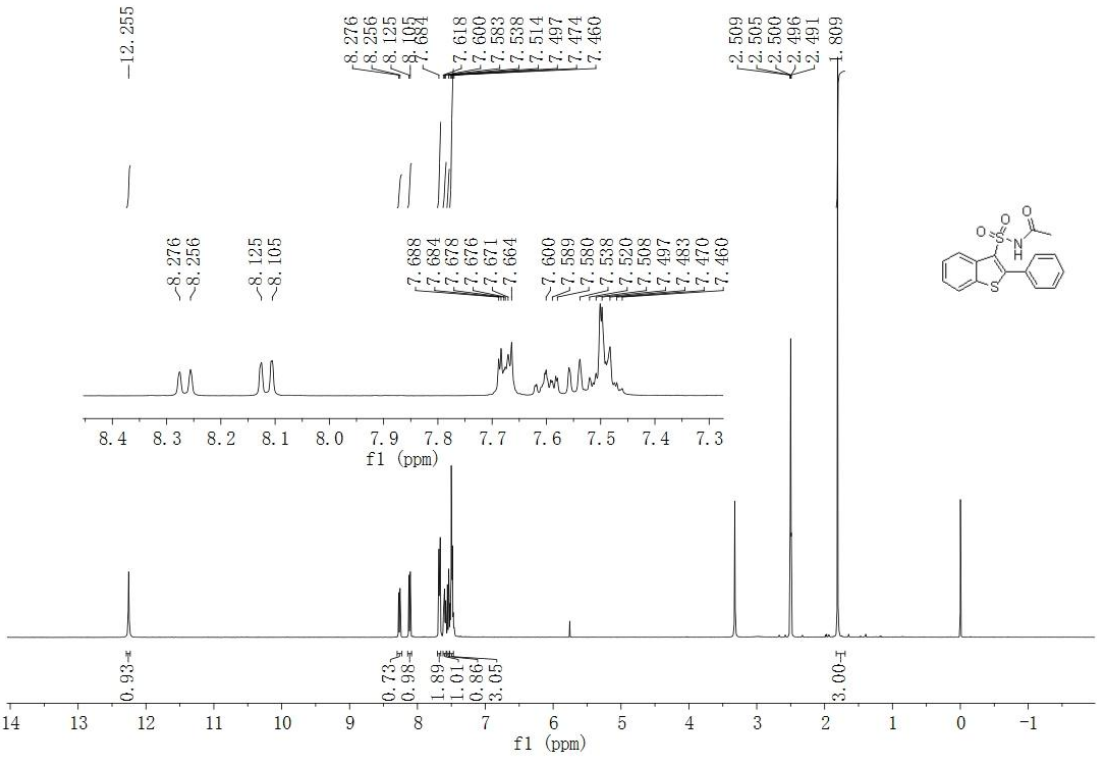

167.71
142.76
140.73
140.55
131.17
128.25
122.02
77.48
77.16
76.84
23.49
23.29
142.76
140.73
140.55
133.51
131.99
130.86
129.61
128.25
122.02
f1 (ppm)
Br
f1 (ppm)

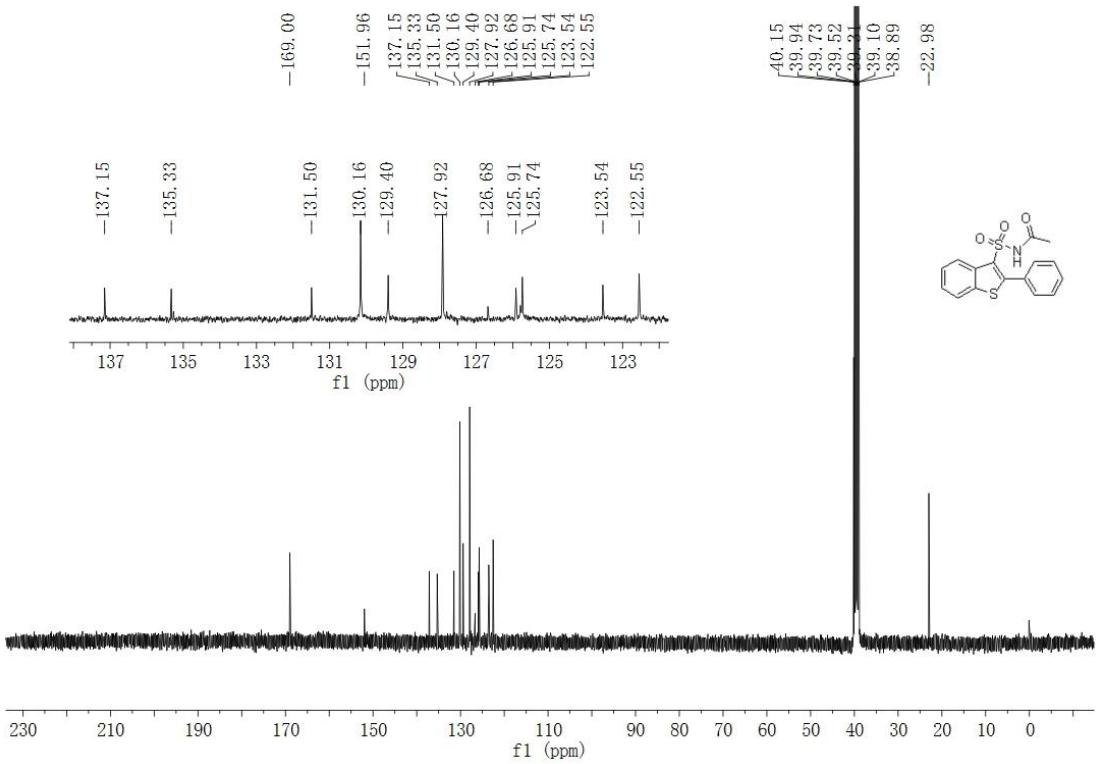

11.367
7.858
7.473
7.177
7.156
7.135
6.980
6.957
2.500
2.428
2.269
2.239
1.715
7.858
7.492
7.473
7.177
7.156
7.135
6.980
6.957
f1 (ppm)
0.97
0.92
0.96
2.02
1.94
3.01
3.03
3.00
3.00
f1 (ppm)

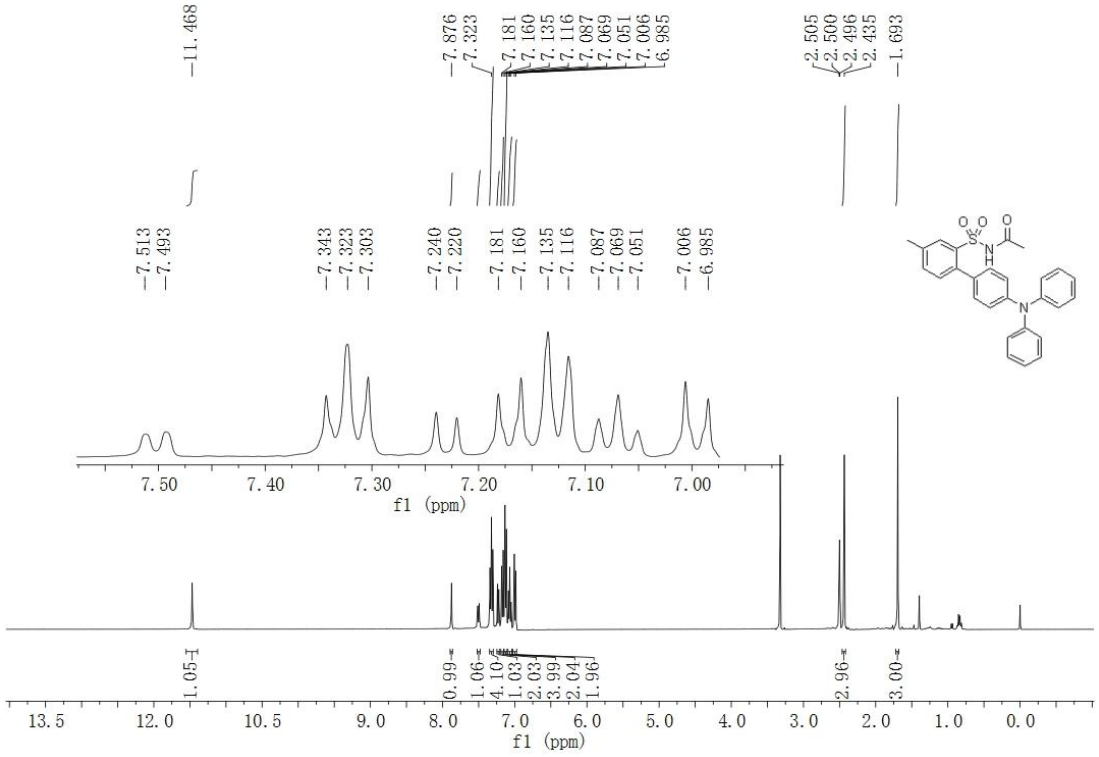

168.46
137.99
137.26
137.15
136.16
135.52
135.42
133.55
132.51
130.03
129.75
128.91
126.43
40.15
39.94
39.73
39.52
39.31
39.10
38.89
22.95
20.57
19.55
19.27
f1 (ppm)

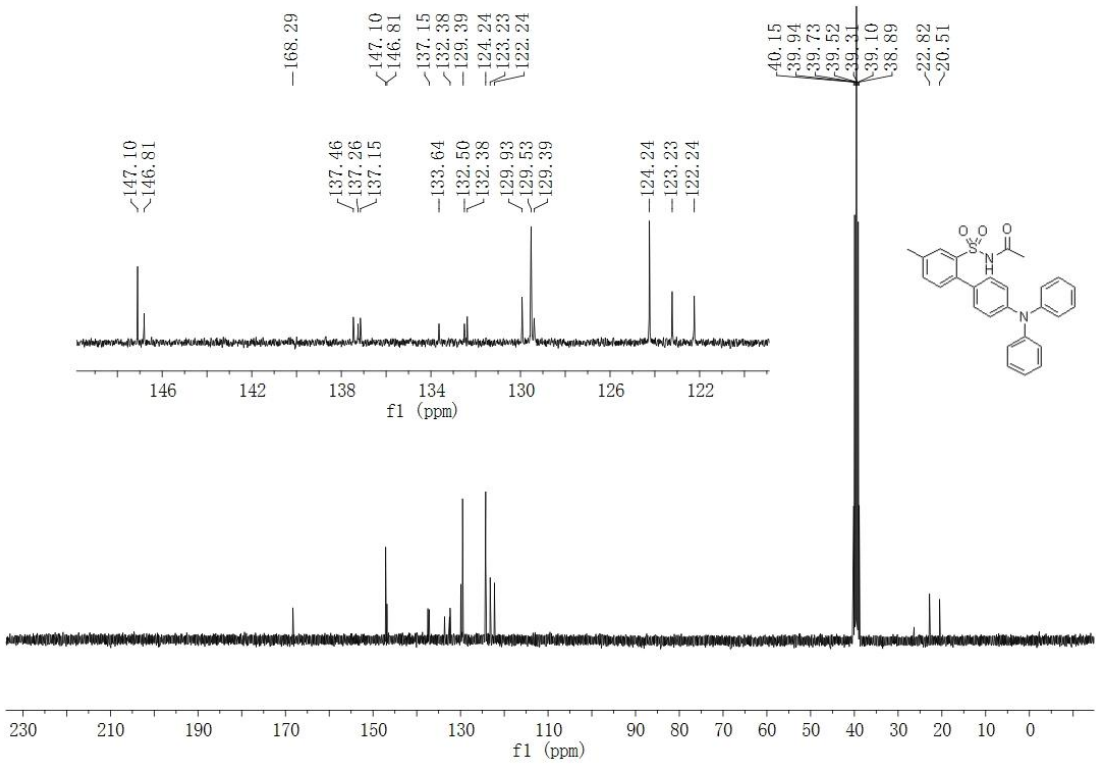

11.745
8.198
8.182
7.662
7.623
7.381
7.361
7.341
7.266
7.244
7.018
6.997
6.899
6.893
6.870
6.851
3.814
3.781
2.504
2.500
2.496
1.758
Cl
Cl
OMe
MeO
f1 (ppm)

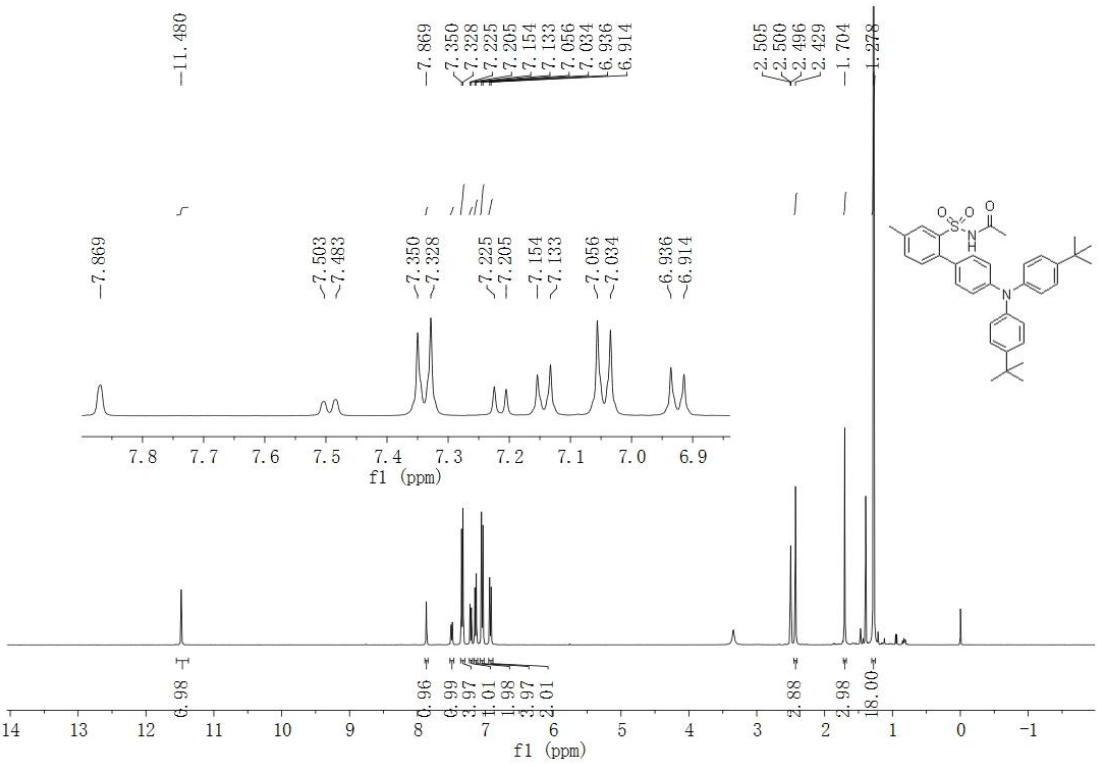

168.84
159.37
140.82
135.93
134.44
131.52
130.27
130.23
128.32
113.53
55.23
39.52
39.31
39.10
38.89
23.01
f1 (ppm)
Cl
Cl
OMe
MeO

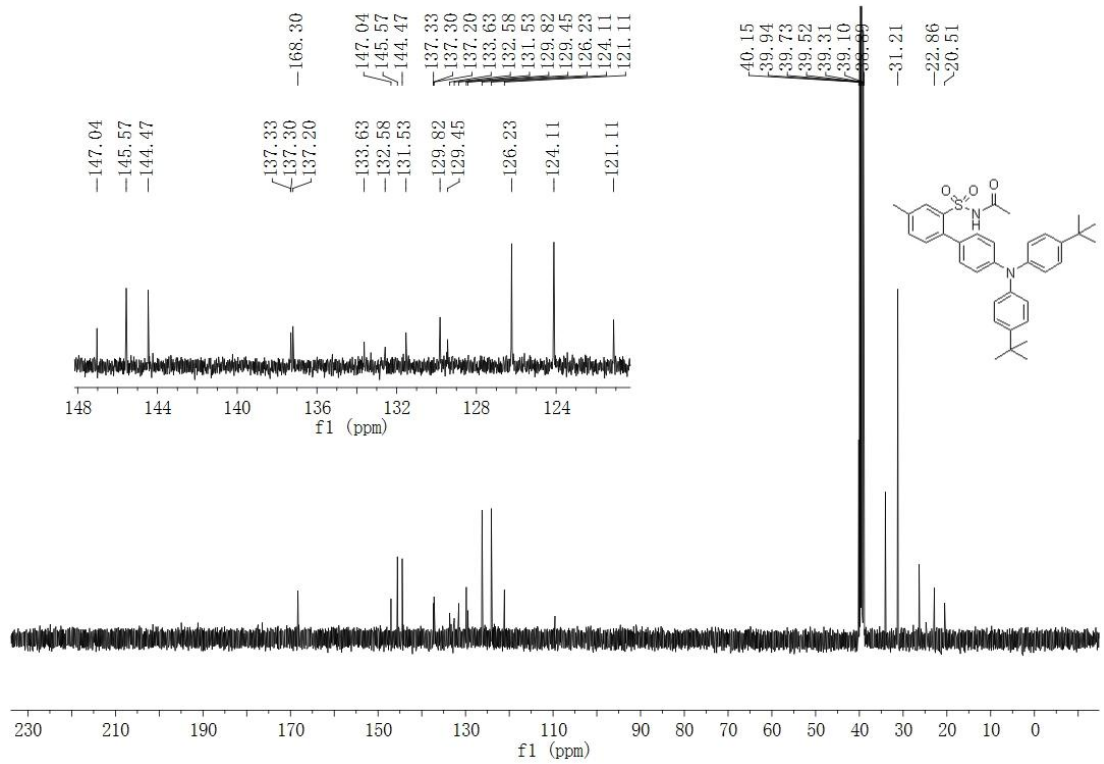

12.255
8.276
8.256
8.125
8.105
7.684
7.618
7.600
7.583
7.538
7.514
7.497
7.474
7.460
2.509
2.505
2.500
2.496
2.491
1.809
7.688
7.684
7.678
7.676
7.671
7.664
7.589
7.580
7.538
7.520
7.508
7.497
7.483
7.470
0.93
0.73
0.98
1.89
1.01
0.86
3.05
3.00
f1 (ppm)

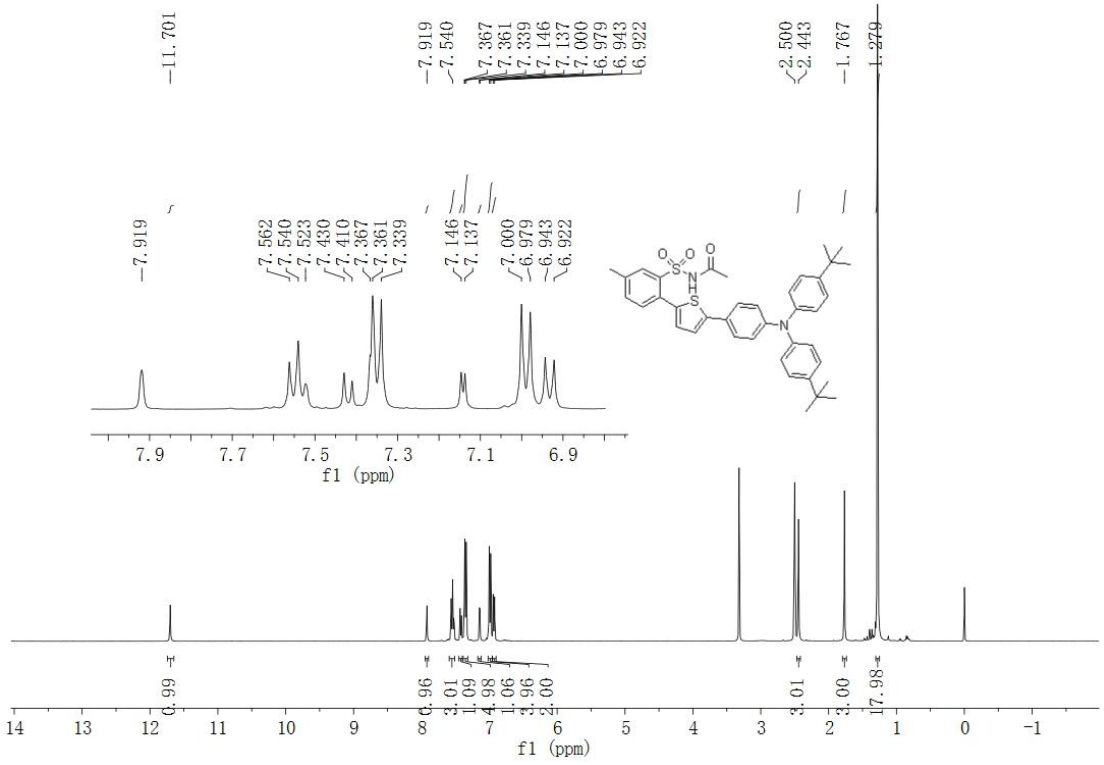

169.00
151.96
137.15
135.33
131.50
130.16
129.40
127.92
126.68
125.91
125.74
123.54
122.55
40.15
39.94
39.73
39.52
39.31
39.10
38.89
22.98
f1 (ppm)
f1 (ppm)

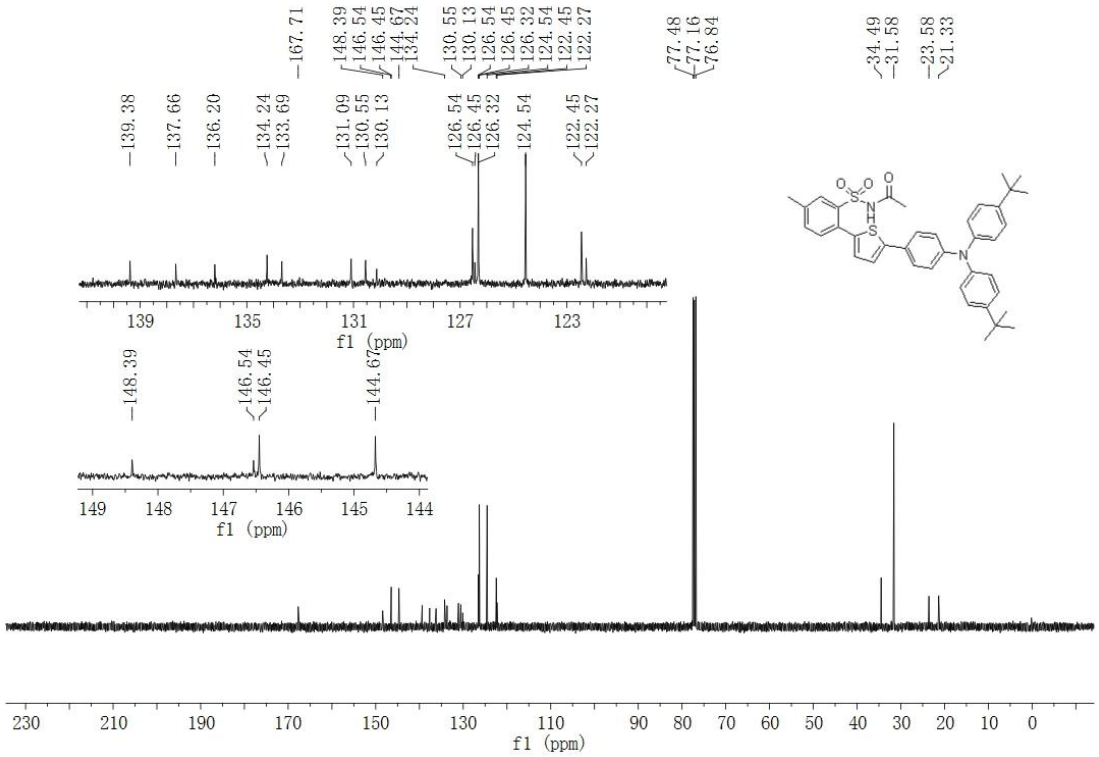

11.468
7.876
7.323
7.181
7.160
7.135
7.116
7.087
7.069
7.051
7.006
6.985
2.505
2.500
2.496
2.435
1.693
7.513
7.493
7.343
7.323
7.303
7.240
7.220
7.181
7.160
7.135
7.116
7.087
7.069
7.051
7.006
6.985
1.05
0.99
1.06
4.10
1.03
2.03
3.99
2.04
1.96
2.96
3.00
f1 (ppm)
f1 (ppm)

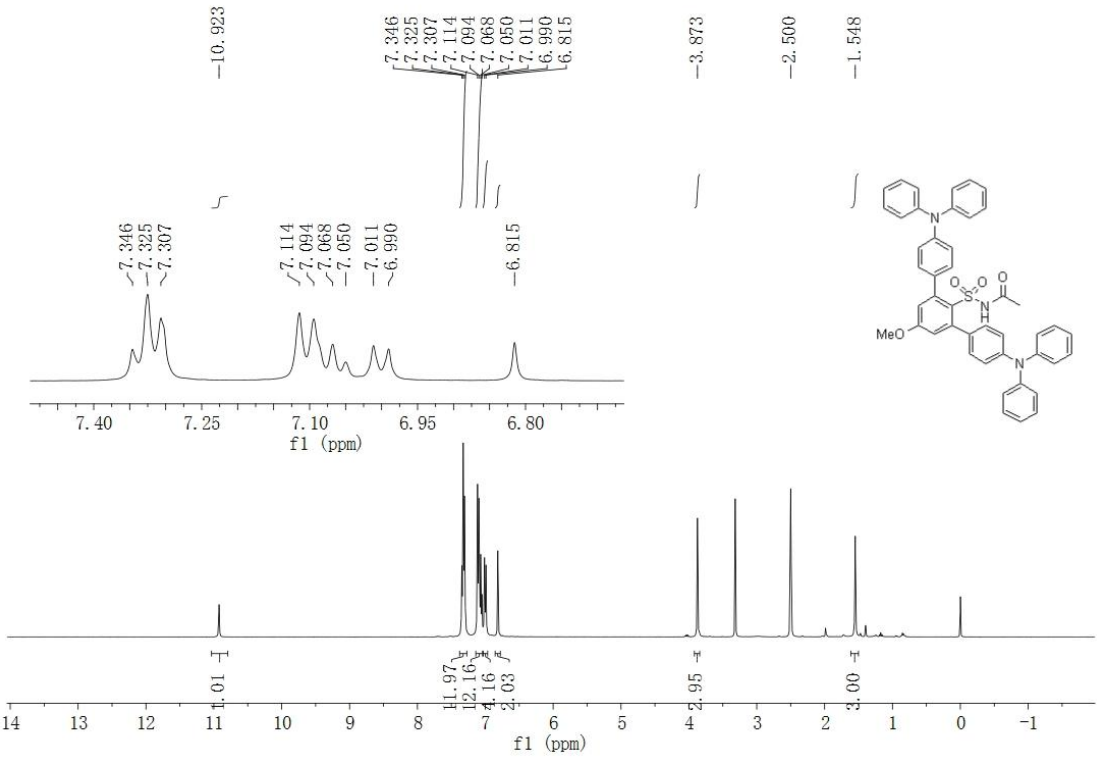

168.29
147.10
146.81
137.15
132.38
129.39
124.24
123.23
122.24
40.15
39.94
39.73
39.52
39.31
39.10
38.89
22.82
20.51
f1 (ppm)

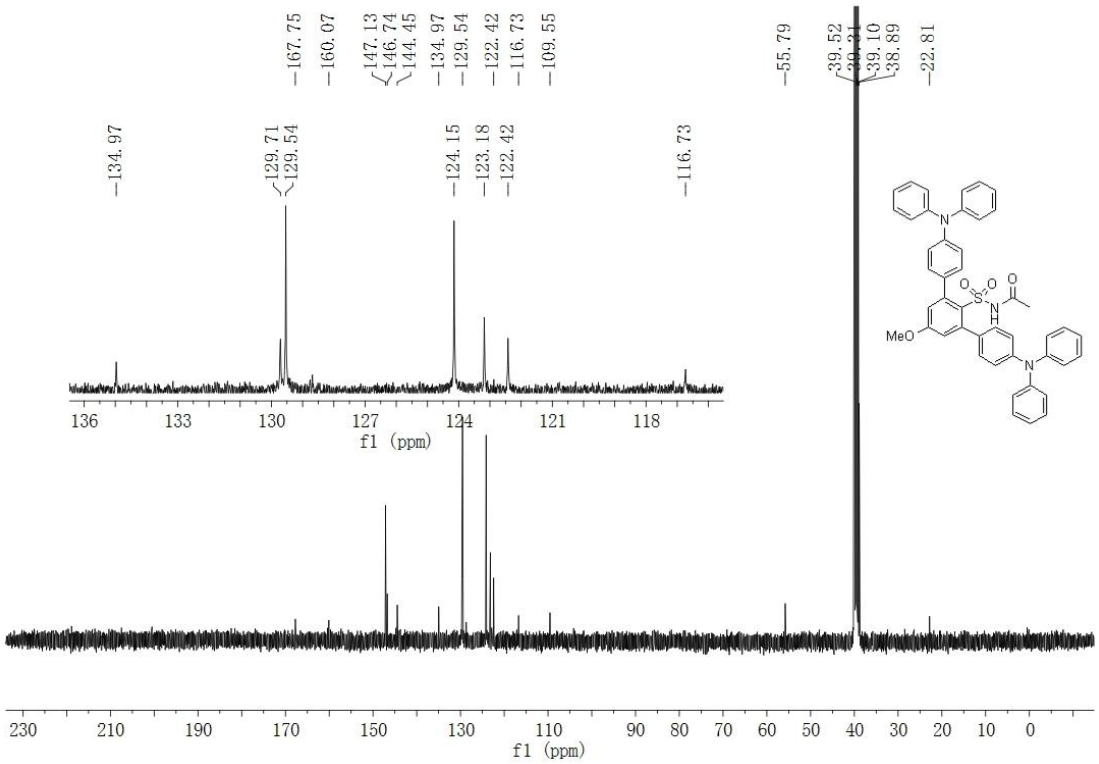

11.480
7.869
7.350
7.328
7.225
7.205
7.154
7.133
7.056
7.034
6.936
6.914
2.505
2.500
2.496
2.429
1.704
1.278
6.98
6.96
6.99
3.97
4.01
1.98
3.97
2.01
2.88
2.98
18.00
f1 (ppm)

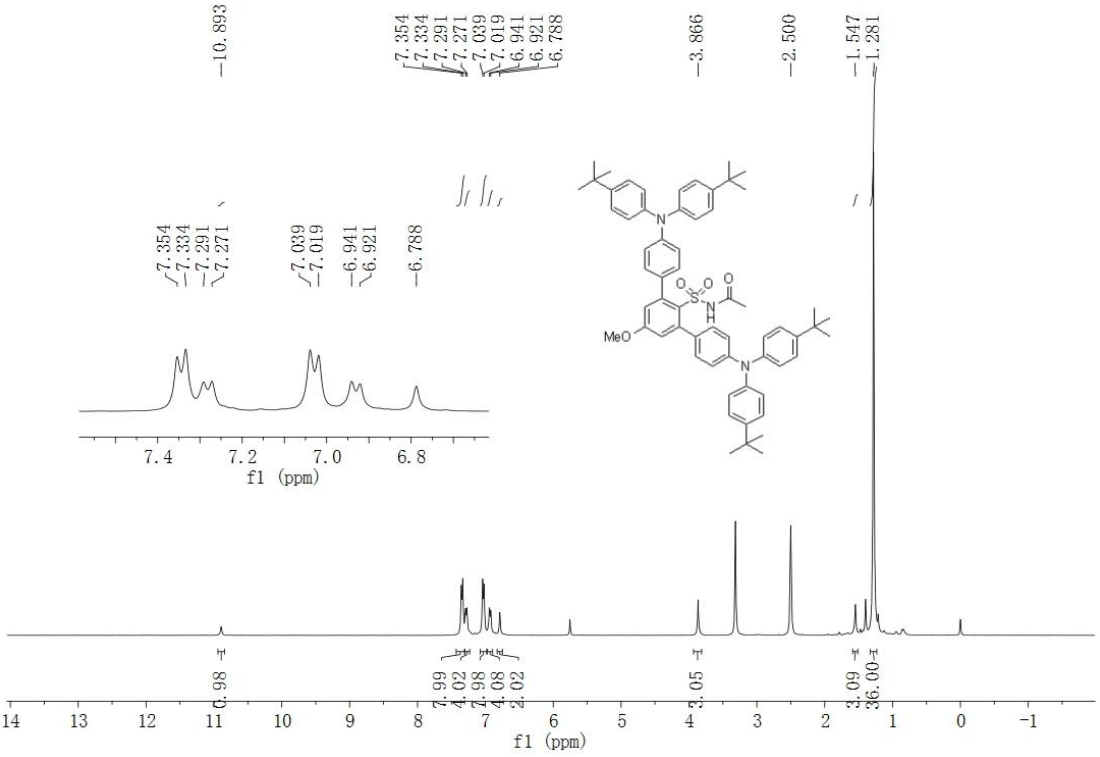

168.30
147.04
145.57
144.47
137.33
137.30
137.20
133.63
132.58
131.53
129.82
129.45
126.23
124.11
121.11
40.15
39.94
39.73
39.52
39.31
39.10
31.21
22.86
20.51
f1 (ppm)

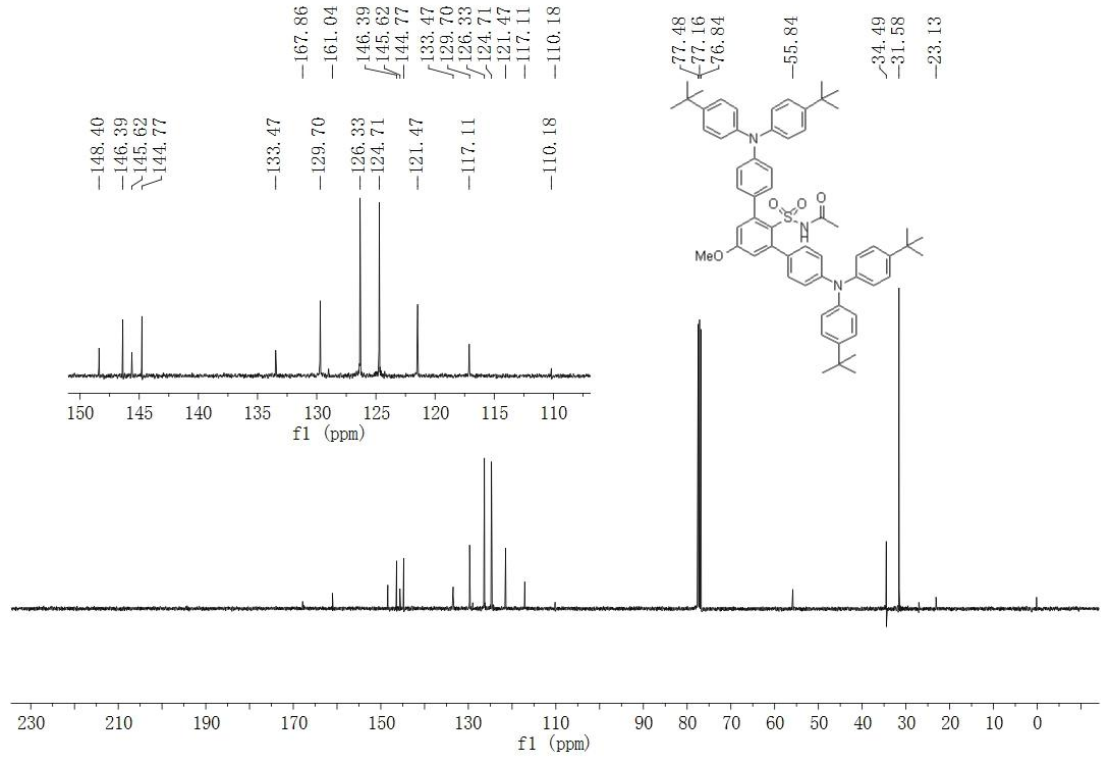

11.701
7.919
7.540
7.367
7.361
7.339
7.146
7.137
7.000
6.979
6.943
6.922
2.500
2.443
1.767
1.279
f1 (ppm)

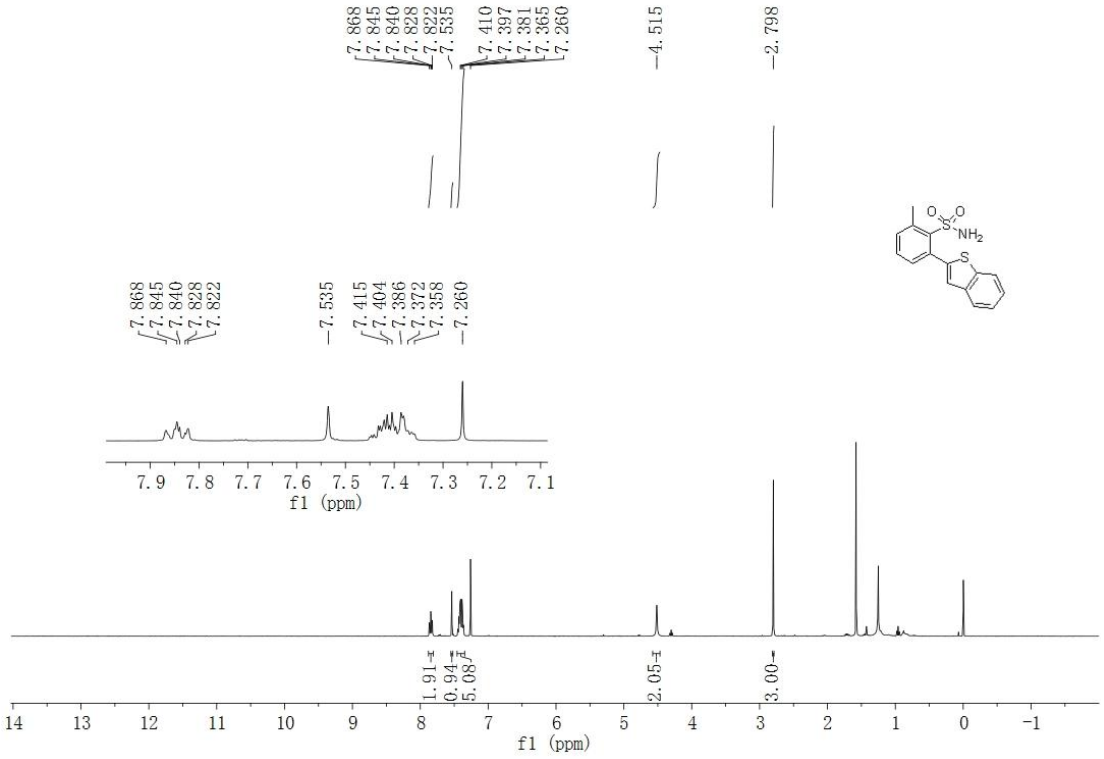

167.71
148.39
146.54
146.45
144.67
134.24
130.55
130.13
126.54
126.45
126.32
124.54
122.45
122.27
77.48
77.16
76.84
34.49
31.58
23.58
21.33
139.38
137.66
136.20
134.24
133.69
131.09
130.55
130.13
126.54
126.45
126.32
124.54
122.45
122.27
f1 (ppm)
148.39
146.54
146.45
144.67
f1 (ppm)
f1 (ppm)

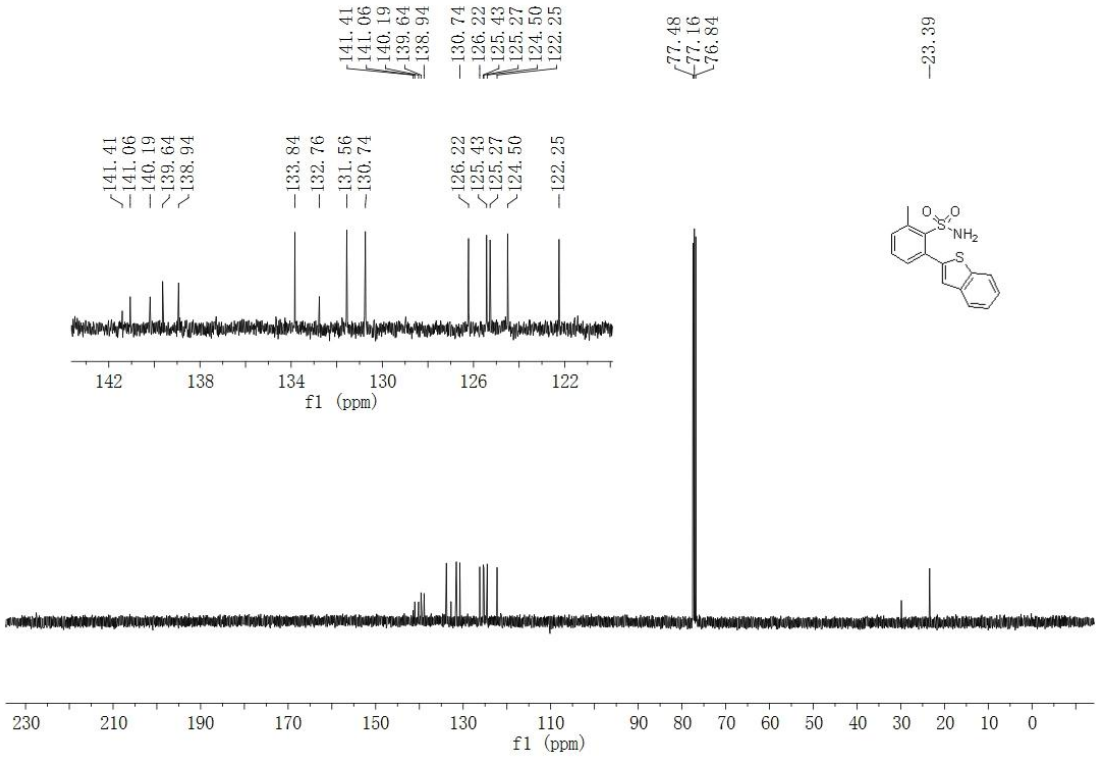

10.923
7.346
7.325
7.307
7.114
7.094
7.068
7.050
7.011
6.990
6.815
3.873
2.500
1.548
MeO
f1 (ppm)
1.01
11.97
12.16
4.16
2.03
2.95
3.00
f1 (ppm)

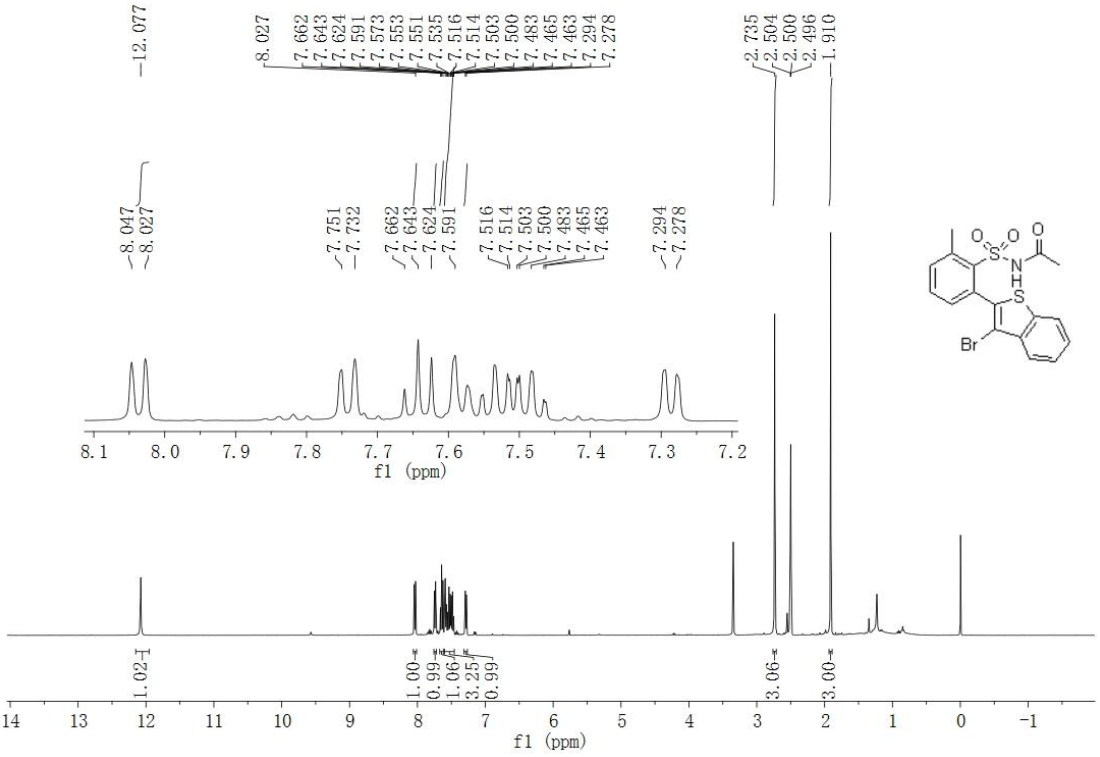

167.75
160.07
147.13
146.74
144.45
134.97
129.54
122.42
116.73
109.55
55.79
39.52
39.31
39.10
38.89
22.81
134.97
129.71
129.54
124.15
123.18
122.42
116.73
MeO
f1 (ppm)

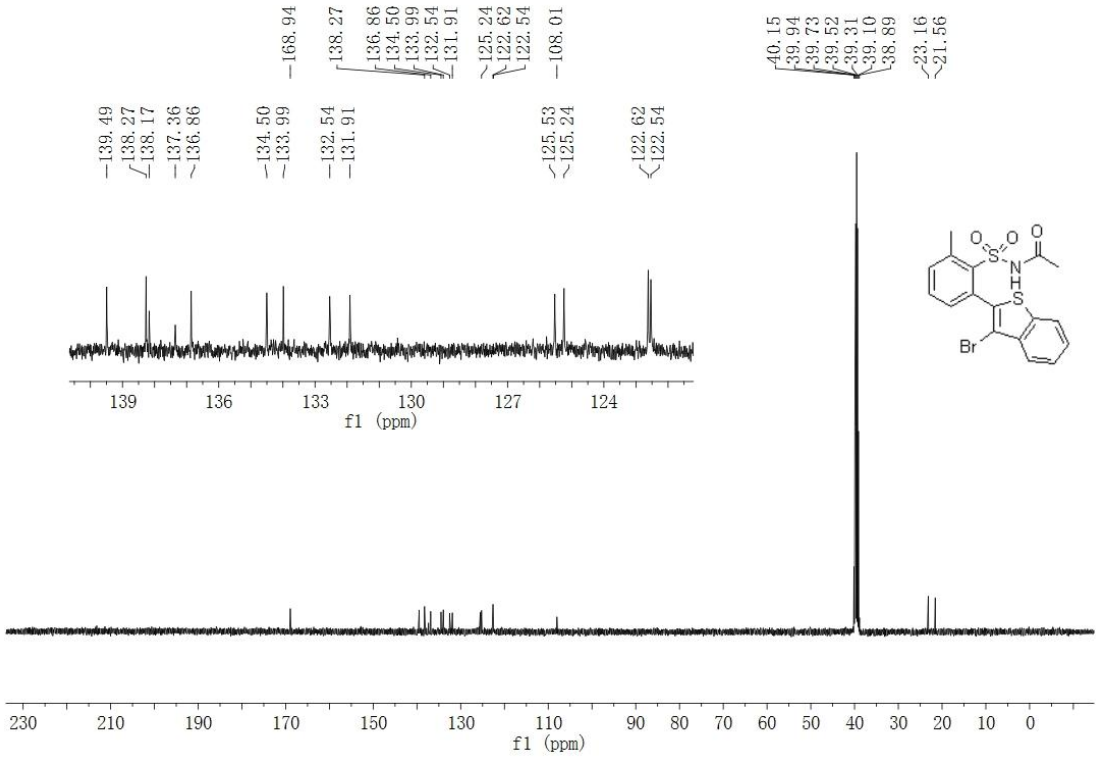

10.893
7.354
7.334
7.291
7.271
7.039
7.019
6.941
6.921
6.788
3.866
2.500
1.547
1.281
MeO
f1 (ppm)

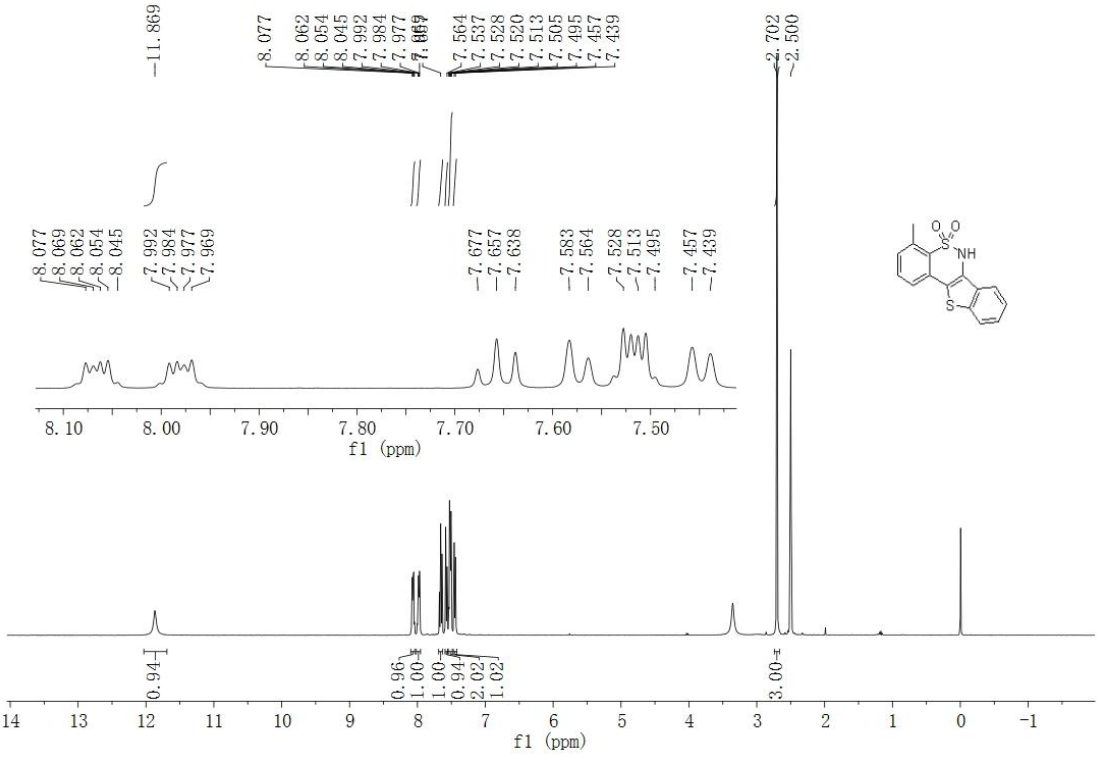

167.86
161.04
146.39
145.62
144.77
133.47
129.70
126.33
124.71
121.47
117.11
110.18
77.48
77.16
76.84
55.84
34.49
31.58
23.13
MeO
f1 (ppm)

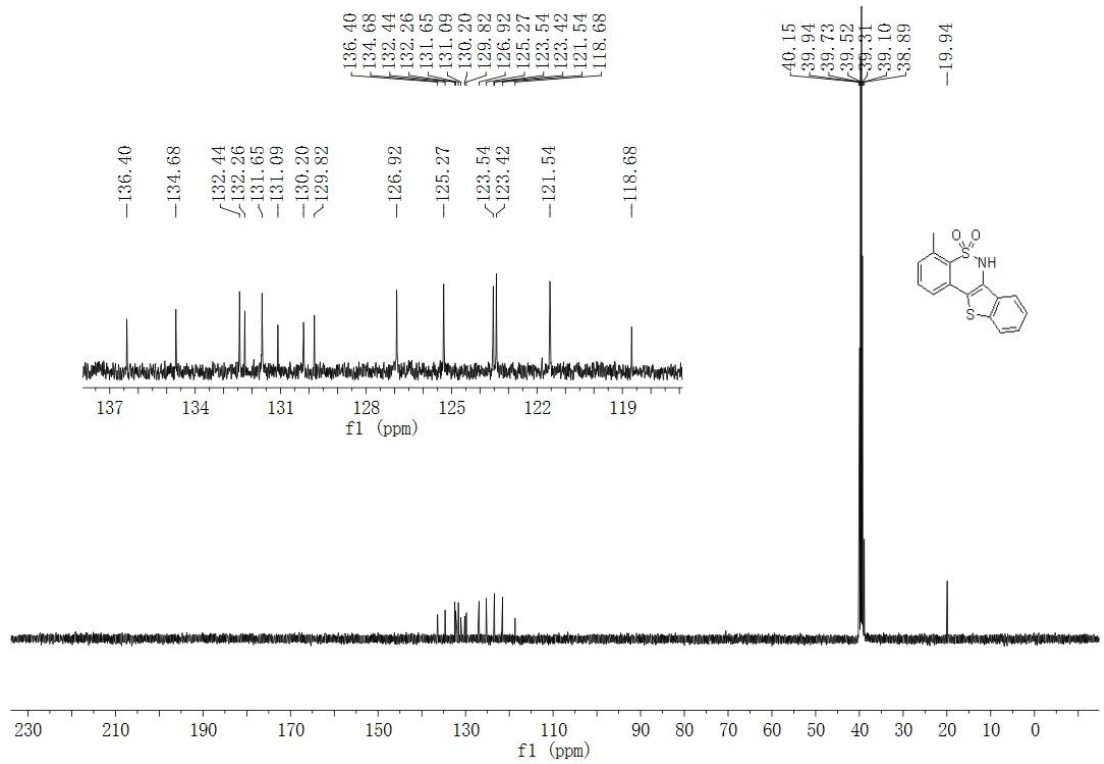

7.868
7.845
7.840
7.828
7.822
7.535
7.410
7.397
7.381
7.365
7.260
4.515
2.798
NH2
f1 (ppm)
1.91
0.94
5.08
2.05
3.00

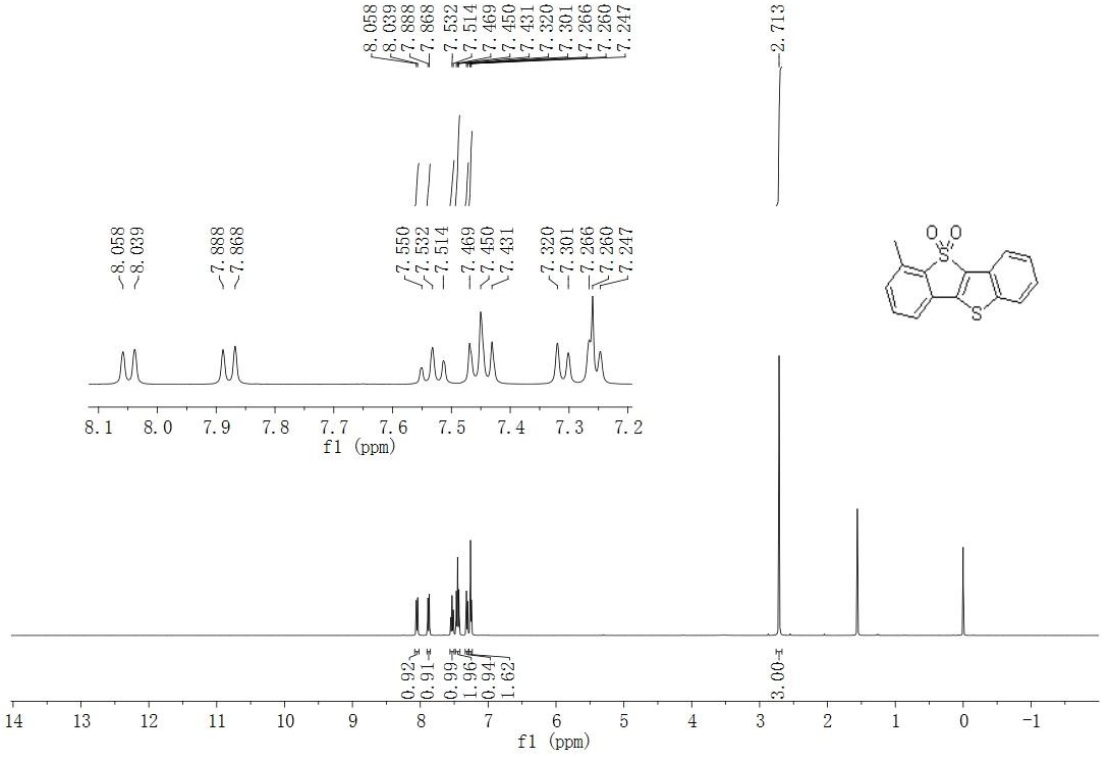

141.41
141.06
140.19
139.64
138.94
130.74
126.22
125.43
125.27
124.50
122.25
77.48
77.16
76.84
23.39
133.84
132.76
131.56
130.74
126.22
125.43
125.27
124.50
122.25
142
138
134
130
126
122
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

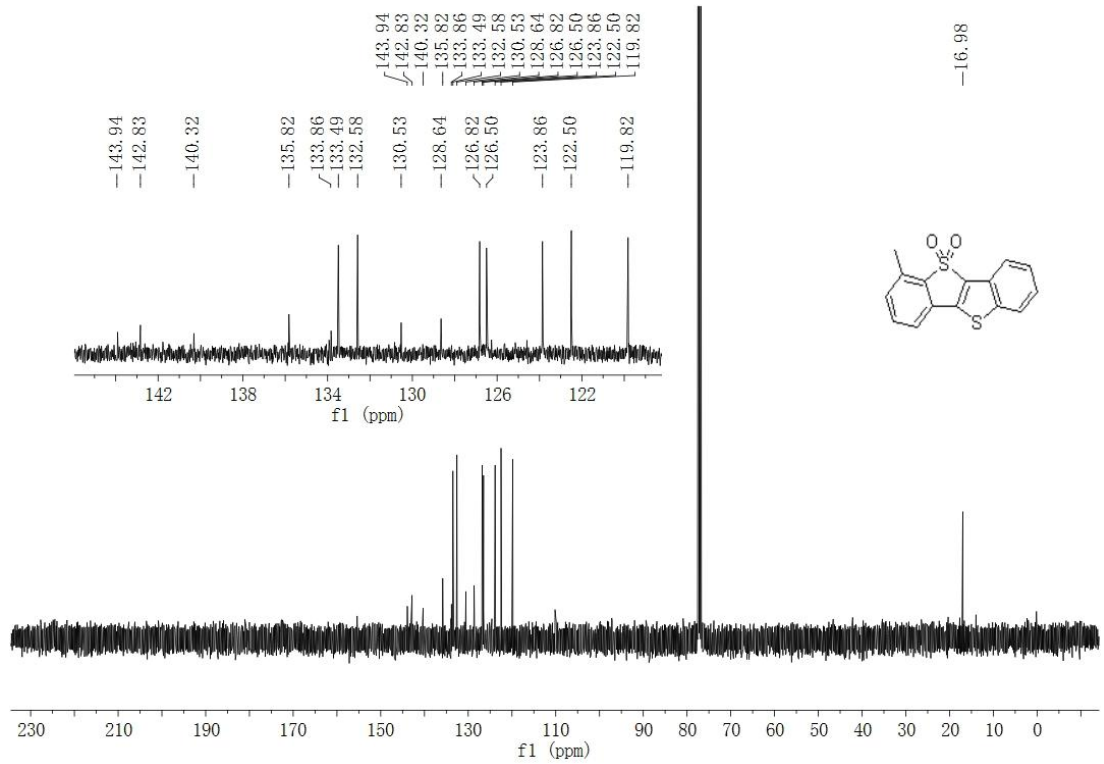

12.077
8.027
7.662
7.643
7.624
7.591
7.573
7.553
7.551
7.535
7.516
7.514
7.503
7.500
7.483
7.465
7.463
7.294
7.278
2.735
2.504
2.500
2.496
1.910
8.047
8.027
7.751
7.732
7.662
7.643
7.624
7.591
7.516
7.514
7.503
7.500
7.483
7.465
7.463
7.294
7.278
Br
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
1.02
1.00
0.99
1.06
3.25
0.99
3.06
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

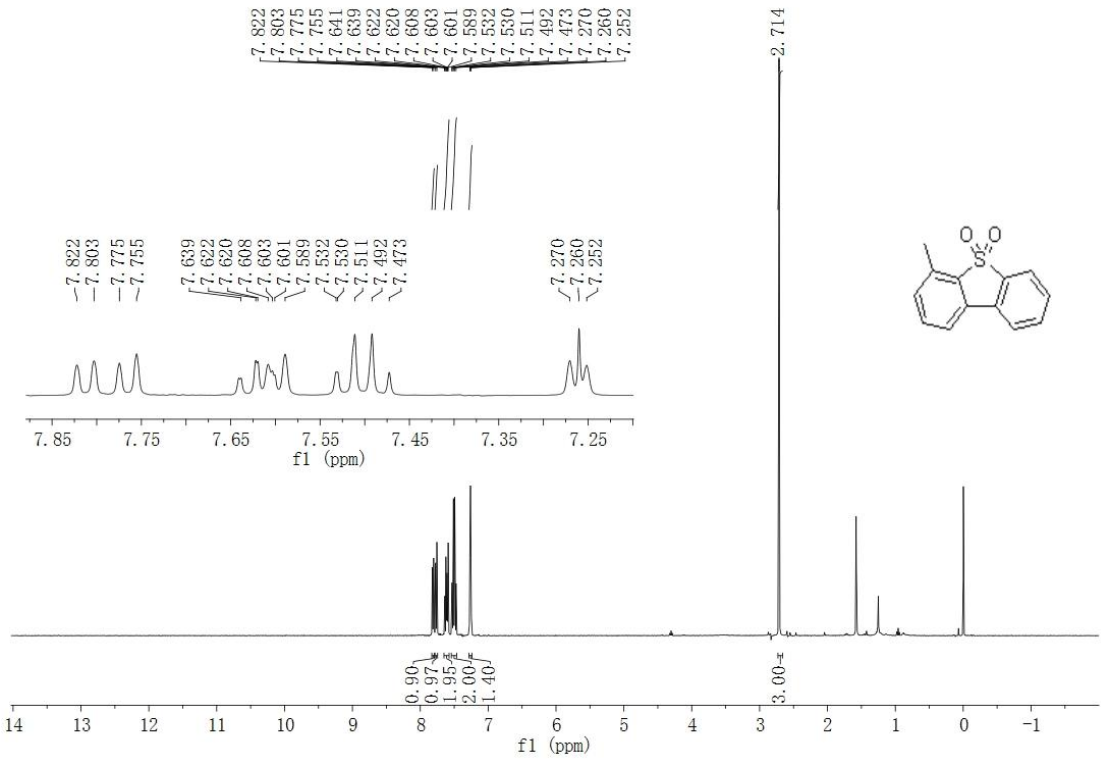

168.94
138.27
136.86
134.50
133.99
132.54
131.91
125.24
122.62
122.54
108.01
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.16
21.56
f1 (ppm)

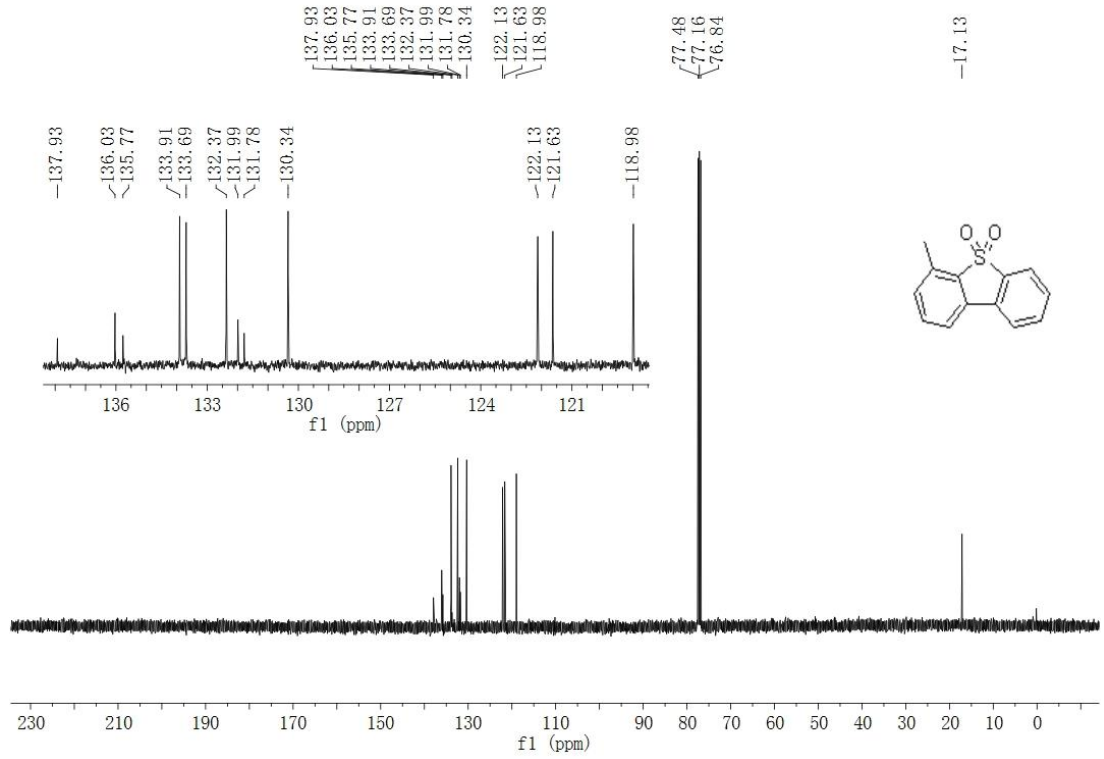

11.869
8.077
8.062
8.054
8.045
7.992
7.984
7.977
7.969
7.677
7.657
7.638
7.583
7.564
7.528
7.513
7.495
7.457
7.439
2.702
2.500
0.94
0.96
1.00
1.00
0.94
2.02
1.02
3.00
f1 (ppm)

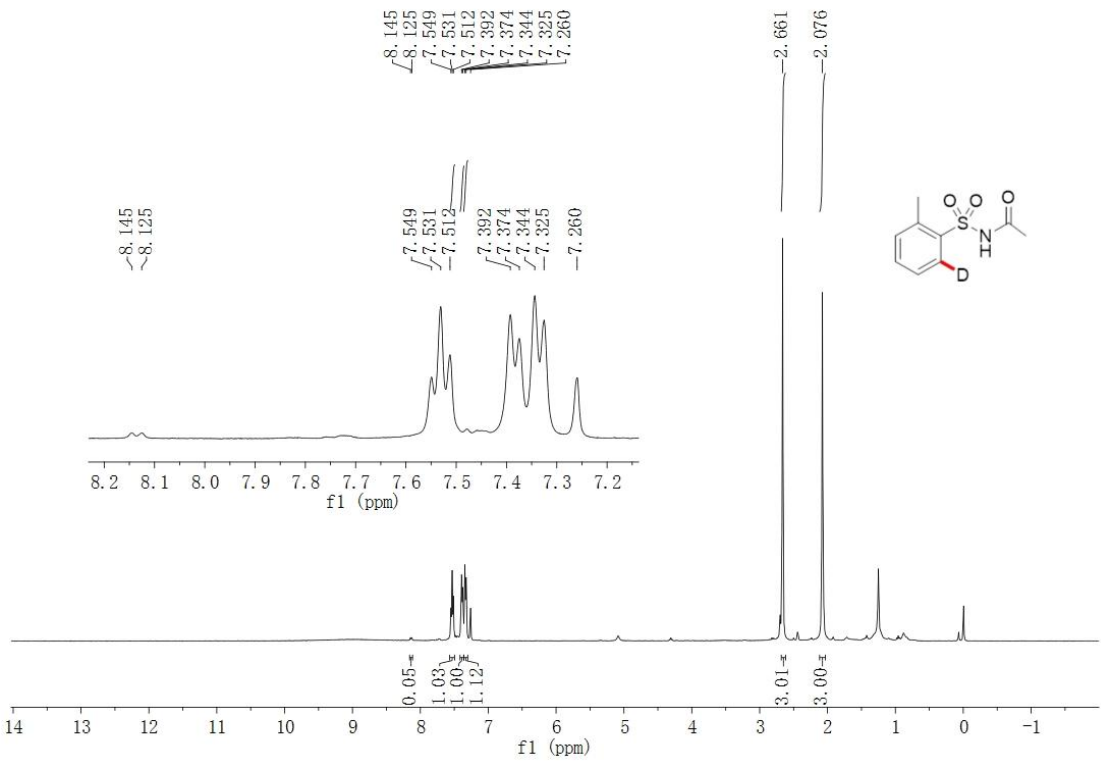

136.40
134.68
132.44
132.26
131.65
131.09
130.20
129.82
126.92
125.27
123.54
123.42
121.54
118.68
40.15
39.94
39.73
39.52
39.31
39.10
38.89
19.94
NH
S
f1 (ppm)
f1 (ppm)

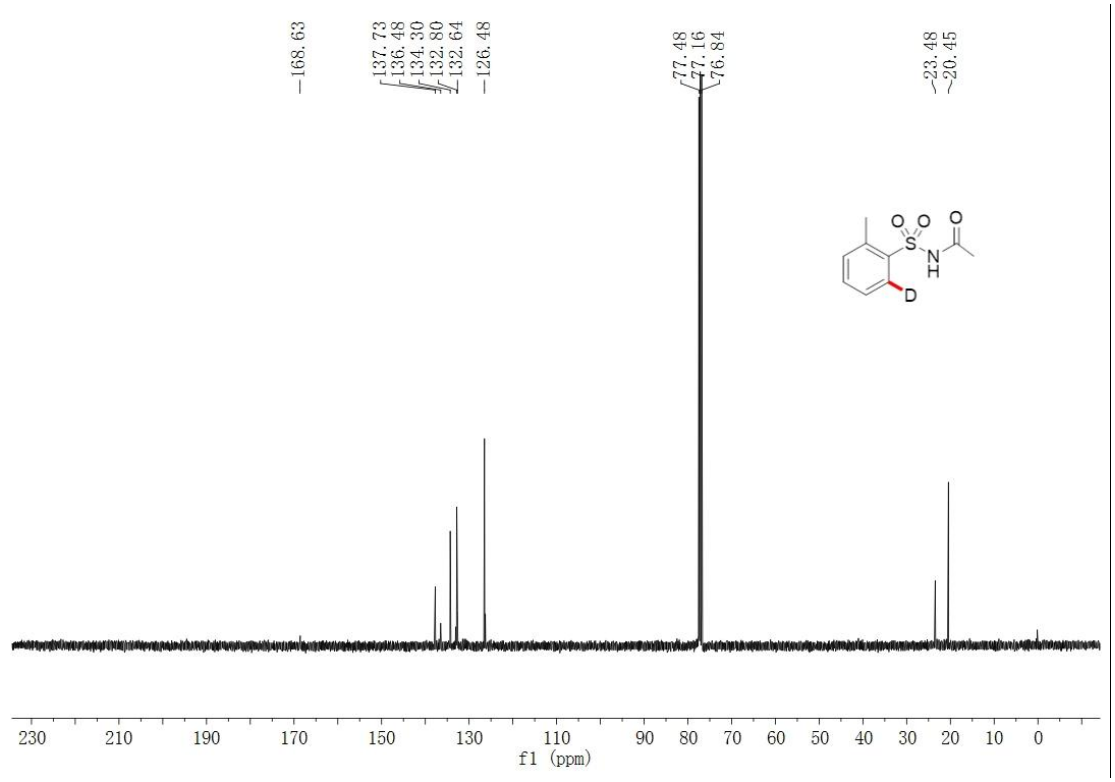

8.058
8.039
7.888
7.868
7.532
7.514
7.469
7.450
7.431
7.320
7.301
7.266
7.260
7.247
2.713
S
0.92
0.91
0.99
1.96
0.94
1.62
3.00
f1 (ppm)
f1 (ppm)

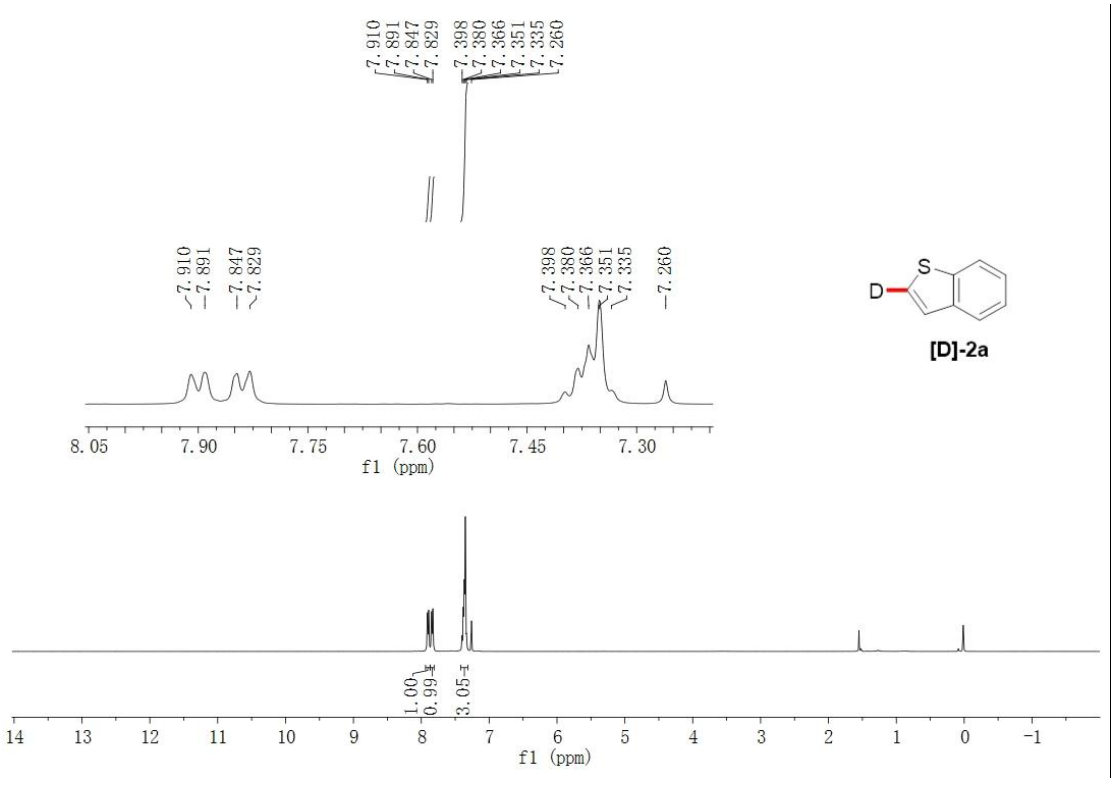

143.94
142.83
140.32
135.82
133.86
133.49
132.58
130.53
128.64
126.82
126.50
123.86
122.50
119.82
16.98
f1 (ppm)
f1 (ppm)

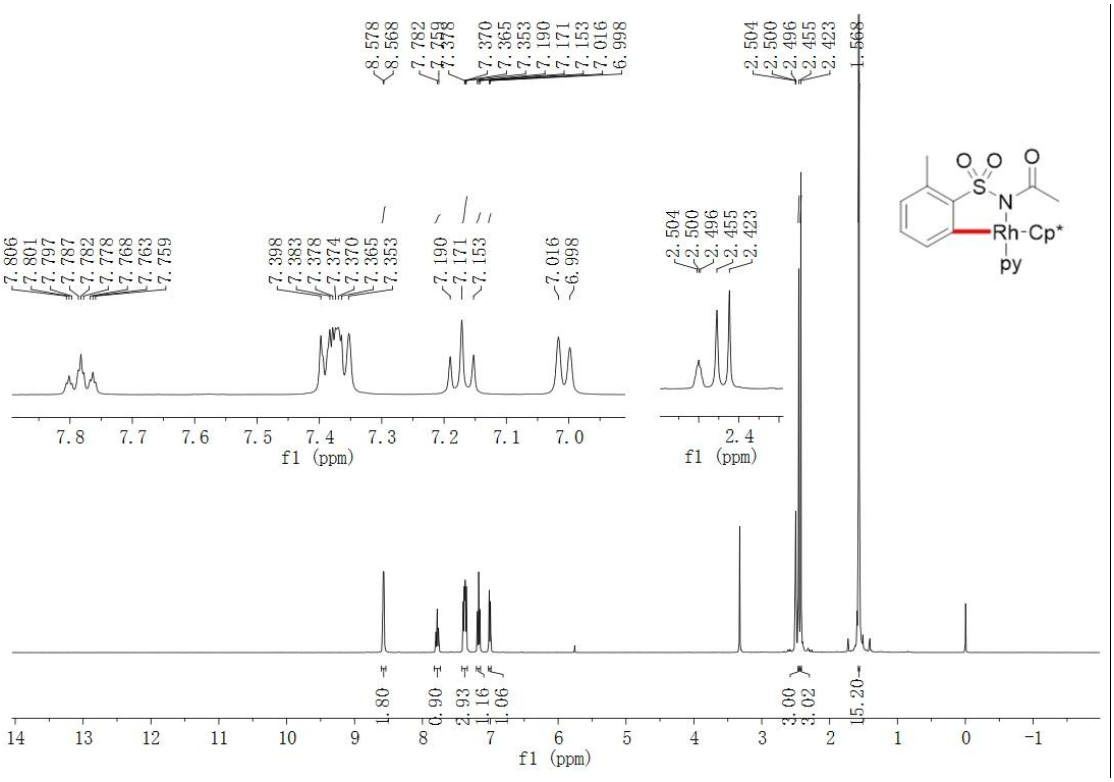

7.822
7.803
7.775
7.755
7.641
7.639
7.622
7.620
7.608
7.603
7.601
7.589
7.532
7.530
7.511
7.492
7.473
7.270
7.260
7.252
2.714
0.90
0.97
1.95
2.00
1.40
3.00
f1 (ppm)
f1 (ppm)

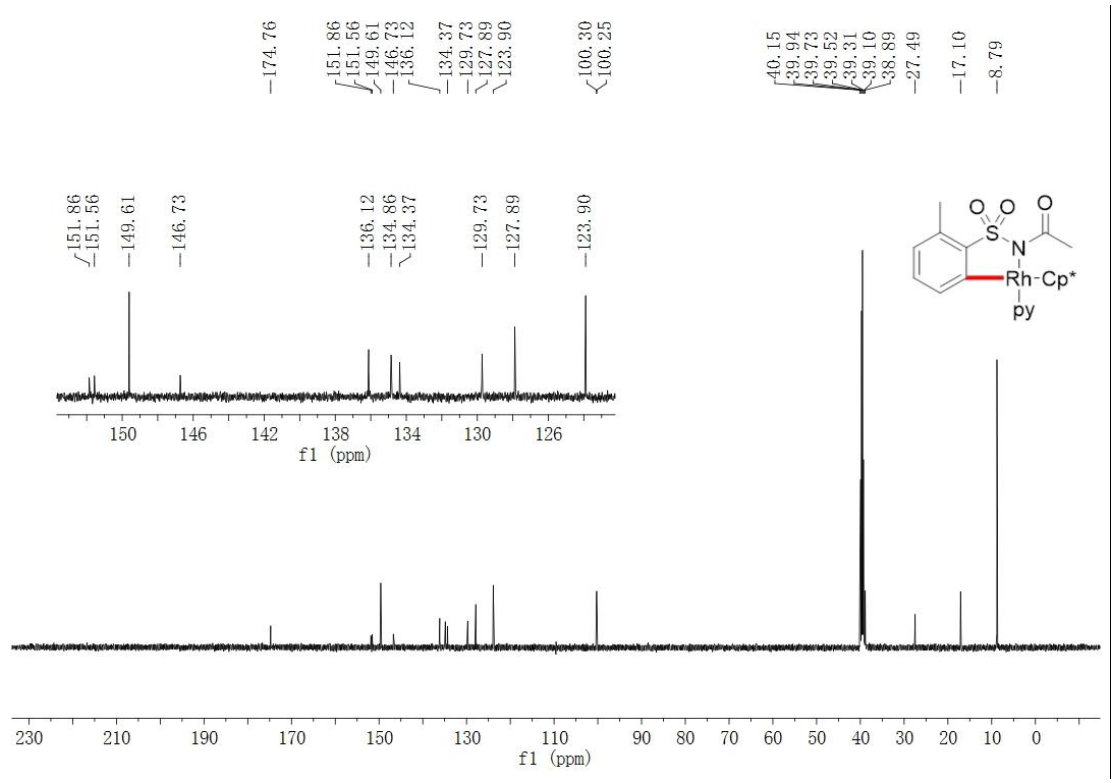

137.93
136.03
135.77
133.91
133.69
132.37
131.99
131.78
130.34
122.13
121.63
118.98
77.48
77.16
76.84
17.13
f1 (ppm)
f1 (ppm)


8.145
8.125
7.549
7.531
7.512
7.392
7.374
7.344
7.325
7.260
2.661
2.076
0.05
1.03
1.00
1.12
3.01
3.00
f1 (ppm)
f1 (ppm)


168.63
137.73
136.48
134.30
132.80
132.64
126.48
77.48
77.16
76.84
23.48
20.45
O
O
S
N
H
O
D
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.910
7.891
7.847
7.829
7.398
7.380
7.366
7.351
7.335
7.260
8.05
7.90
7.75
7.60
7.45
7.30
f1 (ppm)
S
D
[D]-2a
1.00
0.99
3.05
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


8.578
8.568
7.782
7.759
7.378
7.370
7.365
7.353
7.190
7.171
7.153
7.016
6.998
2.504
2.500
2.496
2.455
2.423
1.568
7.806
7.801
7.797
7.787
7.782
7.778
7.768
7.763
7.759
7.398
7.383
7.378
7.374
7.370
7.365
7.353
7.190
7.171
7.153
7.016
6.998
2.504
2.500
2.496
2.455
2.423
O
O
O
S
N
Rh-Cp*
py
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
2.4
f1 (ppm)
1.80
0.90
2.93
1.16
1.06
3.00
3.02
5.20
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


174.76
151.86
151.56
149.61
146.73
136.12
134.37
129.73
127.89
123.90
100.30
100.25
40.15
39.94
39.73
39.52
39.31
39.10
38.89
27.49
17.10
8.79
151.86
151.56
149.61
146.73
136.12
134.86
134.37
129.73
127.89
123.90
O
O
O
S
N
Rh-Cp*
py
150
146
142
138
134
130
126
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)