Supporting Information

Transient directing ligand- and solvent-controlled C−H/C−H cross-coupling/quaternization cyclization/dequaternization of benzaldehydes with thiophenes

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I. General remarks

NMR spectra were recorded on an Agilent 400-MR DD2 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$, DMSO-d_6 or CD_3CN as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm; CD_3CN: δ = 1.94 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-*d* as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). Melting points were determined with XRC-1 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $RhCl_3 \cdot 3H_2O$ was purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd. Ag salts were purchased from Tianjin Yin Li Da Chemical Engineering (China) CO., Ltd. $[Cp^*RhCl_2]_2$ was prepared according to the literature procedures.[1] Unless otherwise noted, all reactions were carried out under air atmosphere.

II. Optimization of the C–H/C–H cross-coupling/quaternization cyclization/dequaternization of benzaldehydes with thiophenes

(a) Optimization of the C–H/C–H cross-coupling of benzaldehydes with thiophenes

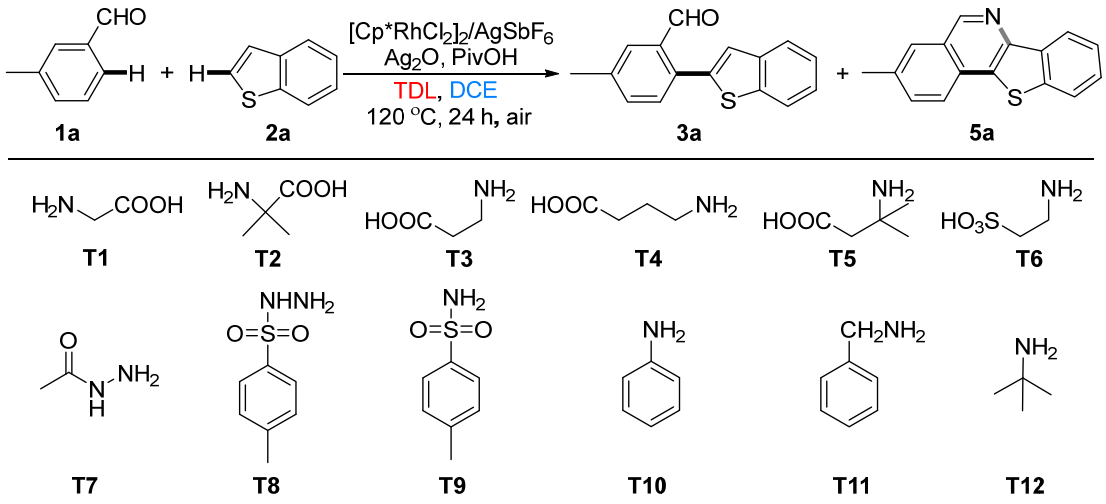
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 3-methylbenzaldehyde (**1a**, 0.20 mmol), benzothiophene (**2a**, 2.0 equiv), transient directing ligand (TDL, 40 mol%), the catalyst (5.0 mol%), $AgSbF_6$ (20 mol%), oxidant (2.0 equiv), PivOH (1.0 equiv), and solvent. The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 24 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were

concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 35/1, v/v) to provide the desired product **3a**.

(b) Optimization of the cascade *ortho*-heteroarylation/quaternization cyclization/dequaternization

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 3-methylbenzaldehyde (**1a**, 0.20 mmol), benzothiophene (**2a**, 2.0 equiv), transient directing ligand (TDL, 1.0 equiv), the catalyst (5.0 mol%), $AgSbF_6$ (20 mol%), oxidant (2.0 equiv), PivOH (1.0 equiv), and solvent. The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 36 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 35/1, v/v) to provide the desired product **5a**.

Table S1. Optimization of the reaction of **1a** with **2a**[a]



TDL	T1	T2	T3	T3[a]	T4	T4[a]	T5	T6	T7	T8	T9	T10	T11	T12
3a	trace	trace	18%	8%	trace	5%	trace	nd	trace	nd	nd	nd	15%	10%
5a	nd	nd	nd	20%	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Entry	Catalyst	TDL	Oxidant (equiv)	Solvent	Temp. (^{o}C)	Time (h)	**3a**[b] (%)	**5a**[b] (%)
1	$Pd(OAc)_2$ (10 mol%)	**T1**	Ag_2O (1.0)	DCE	120	24	nd	nd
2	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T1**	Ag_2O (1.0)	DCE	120	24	trace	nd
3	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T2**	Ag_2O (1.0)	DCE	120	24	trace	nd
4	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T3**	Ag_2O (1.0)	DCE	120	24	18	nd
5	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T4**	Ag_2O (1.0)	DCE	120	24	trace	nd
6	$Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T5**	Ag_2O (1.0)	DCE	120	24	trace	nd
7	$Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T6**	Ag_2O (1.0)	DCE	120	24	nd	nd
8	$Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T7**	Ag_2O (1.0)	DCE	120	24	nd	nd
9	$Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T8**	Ag_2O (1.0)	DCE	120	24	nd	nd
10	$Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T9**	Ag_2O (1.0)	DCE	120	24	nd	nd
11	$Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T10**	Ag_2O (1.0)	DCE	120	24	nd	nd
12	$Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T11**	Ag_2O (1.0)	DCE	120	24	15	nd
13	$Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T12**	Ag_2O (1.0)	DCE	120	24	10	nd
14	$Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T3**	Ag_2O (1.0)	dioxane	120	24	trace	nd
15	$Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T3**	Ag_2O (1.0)	DMF	120	24	8	nd
16	$Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T3**	Ag_2O (1.0)	HFIP	120	24	8	20
17	$Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T3**	Ag_2O (1.0)	TFE	120	24	10	12
18	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T4**	Ag_2O (1.0)	HFIP	120	24	5	nd
19	$Cp^*RhCl_2]_2$ (5.0 mol%) /$AgSbF_6$ (20 mol%)	**T11**	Ag_2O (2.0)	DCE	120	24	30	nd
20	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgBF_4$ (20 mol%)	**T11**	Ag_2O (2.0)	DCE	120	24	35	nd

21	$[Cp^*RhCl_2]_2$ (5.0 mol%) / $AgBF_4$ (50 mol%)	**T11**	Ag_2O (2.0)	DCE	120	24	40	nd
22	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgBF_4$ (50 mol%)	**T11**	Ag_2O (2.0)	MeOH	120	24	40	nd
23	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgBF_4$ (50 mol%)	**T11**	Ag_2O (2.0)	*t*-BuOH	120	24	55	nd
24	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgBF_4$ (50 mol%)	**T11**	Ag_2O (2.0)	*t*-AmylOH	120	24	75	nd
25[c]	**$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgBF_4$ (50 mol%)**	**T11**	**Ag_2O (2.0)**	***t*-AmylOH/DCE**	**80**	**24**	**81**	**nd**
26[d]	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgBF_4$ (50 mol%)	**T3**	Ag_2O (1.0)	HFIP	120	24	trace	30
27[d,e]	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgBF_4$ (50 mol%)	**T3**	Ag_2O/ $Cu(OTf)_2$	HFIP	120	24	trace	32
28[d,f]	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgBF_4$ (50 mol%)	**T3**	Ag_2O/ AgOPiv	HFIP	120	24	trace	42
29[d]	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgBF_4$ (50 mol%)	**T3**	Ag_2O (2.0)	HFIP	120	24	trace	48
30[d]	$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgBF_4$ (50 mol%)	**T3**	Ag_2O (3.0)	HFIP	120	24	trace	55
31[d]	**$[Cp^*RhCl_2]_2$ (5.0 mol%) /$AgBF_4$ (50 mol%)**	**T3**	**Ag_2O (3.0)**	**HFIP (0.5 mL)**	**120**	**36**	**trace**	**65**

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgSbF_6$ (20 mol%), TDL (40 mol%) , Ag_2O (1.0 equiv), PivOH (1.0 equiv), solvent (1.0 mL) under air at 120 °C for 24 h. [b]Isolated yield. [c]*t*-AmylOH/DCE (2/1, v/v, 1.0 mL). [d]Ligand (1.0 equiv). [e]Ag_2O (1.0 equiv)/$Cu(OTf)_2$ (1.0 equiv). [f]Ag_2O (1.0 equiv)/AgOPiv (1.0 equiv). DCE = 1,2-dichloroethane, DMF = *N*,*N*-dimethylformamide, *t*-AmylOH = *t*-amyl alcohol, HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, TFE = 2,2,2-trifluoroethanol, nd = not detected.

III. General procedure for the C–H/C–H cross-coupling of benzaldehydes with thiophenes

Condition A: A flame-dried Schlenk test tube with a magnetic stirring bar was charged with benzaldehydes (**1**, 0.20 mmol), benzothiophene (**2a**, 2.0 equiv), benzylamine (40 mol%), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgBF_4$ (50 mol%), Ag_2O (2.0 equiv), PivOH (1.0 equiv), and *t*-AmylOH/DCE (1.0 mL, 2/1, V/V). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 80 °C in a pre-heated oil bath for 24 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a

celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1~20/1, v/v) to provide the desired product **3**.

Condition B: A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 3-methylbenzaldehyde (**1a**, 0.20 mmol), thiophenes (**2**, 2.0 equiv), benzylamine (40 mol%), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgBF_4$ (50 mol%), Ag_2O (2.0 equiv), TFA (1.0 equiv), and *t*-AmylOH (1.0 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 24 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1~20/1, v/v) to provide the desired product **4**.

IV. General procedure for the cascade *ortho*-heteroarylation/quaternization cyclization/dequaternization

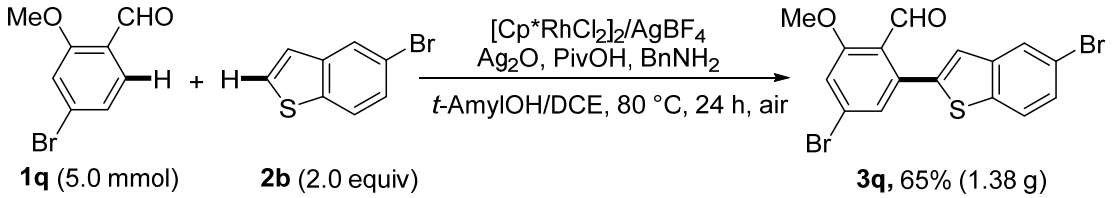
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with benzaldehydes (**1**, 0.20 mmol), benzothiophene (**2a**, 2.0 equiv), *β*-alanine (1.0 equiv), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgBF_4$ (50 mol%), Ag_2O (3.0 equiv)，PivOH (1.0 equiv) and HFIP (0.5 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 36 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1~5/1, v/v) to provide the desired product **5**.

V. General procedure for the cascade *ortho*-heteroarylation/quaternization cyclization

Condition A: A flame-dried Schlenk test tube with a magnetic stirring bar was charged with benzaldehyde (**1h** or **1k**, 0.20 mmol), benzothiophene (**2a**, 2.0 equiv), γ-aminobutyric acid (1.0 equiv), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgBF_4$ (1.2 equiv), Ag_2O (3.0 equiv)，PivOH (1.0 equiv) and HFIP (0.5 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 48 h. The reaction mixture was then cooled to room temperature, 1.0 mL of HBF_4 (40% aqueous solution) was added and the mixture was stirred at room temperature for another 0.5 h in air, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel dichloromethane/ methanol = 5/1, v/v) to provide the desired products **6b** and **6c**.

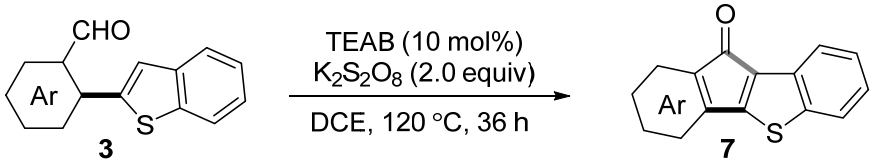
Condition B: A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 2-fluorobenzaldehyde (**1j**, 0.20 mmol), benzothiophene (**2a**, 2.0 equiv), benzylamine (1.0 equiv), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgBF_4$ (1.2 equiv), Ag_2O (3.0 equiv), PivOH (1.0 equiv) and HFIP (0.5 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 48 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (dichloromethane/methanol = 5/1, v/v) to provide the desired product **6d**.

VI. Gram-scale synthesis of 3q



A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 4-bromo-2-methoxybenzaldehyde (**1q**, 5.0 mmol), 5-bromobenzo[*b*]thiophene (**2b**, 2.0 equiv), benzylamine (40 mol%), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgBF_4$ (50 mol%), Ag_2O (2.0 equiv), PivOH (1.0 equiv), and *t*-AmylOH/DCE (10.0 mL, 2/1, V/V). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 80 °C in a pre-heated oil bath for 24 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1, v/v) to provide the desired product **3q** in 65% yield (1.38 g).

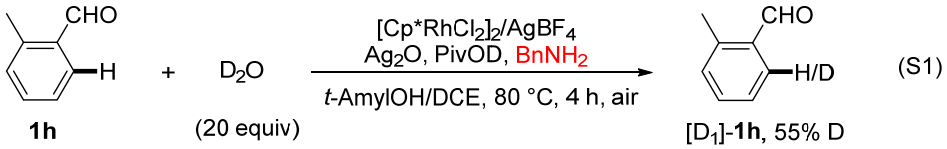
VII. General procedure for the construction of fluorenone-type polycyclic structures



To a 10 mL Schlenk tube was added tetraethylammonium bromide (TEAB, 4.2 mg, 10 mol%), $K_2S_2O_8$ (108 mg, 2.0 equiv) and the tube was purged with N_2 for three times, followed by addition of **3** (0.20 mmol) and DCE (1.0 mL). The formed mixture was stirred at 120 ºC under N_2 for 36 h. The solution was then cooled to rt, and DCE was removed under vacuum directly. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) to provide the desired product **7**.

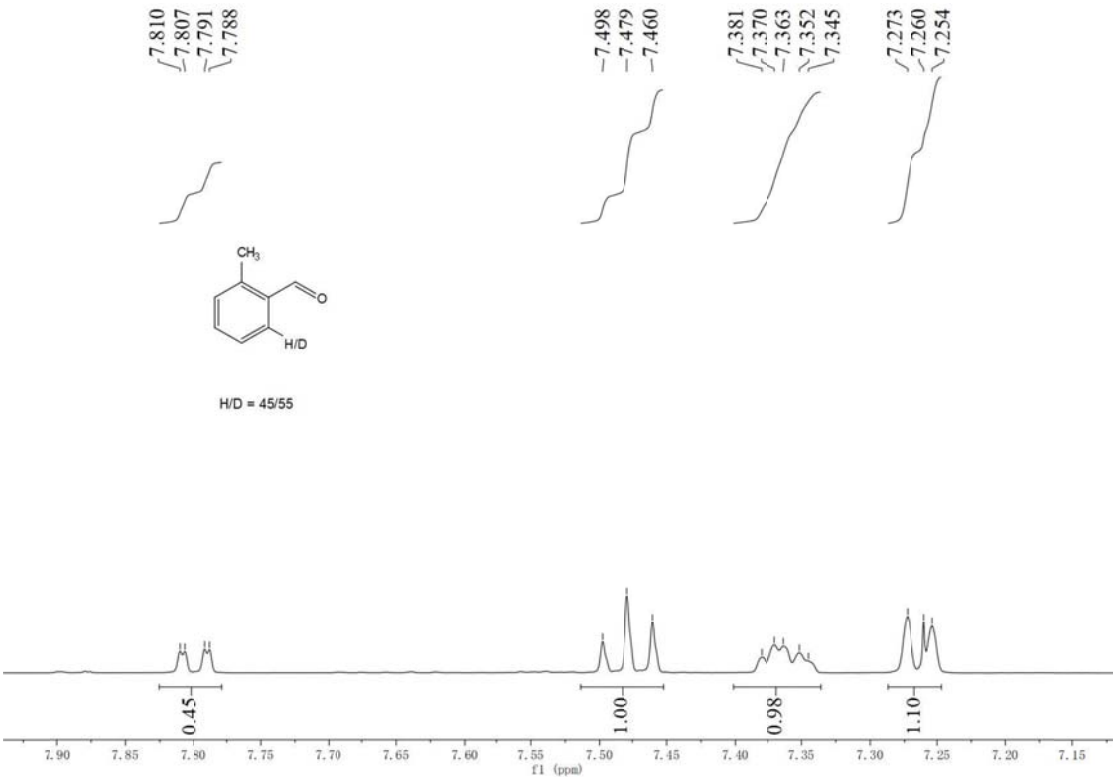
VIII. Mechanistic study

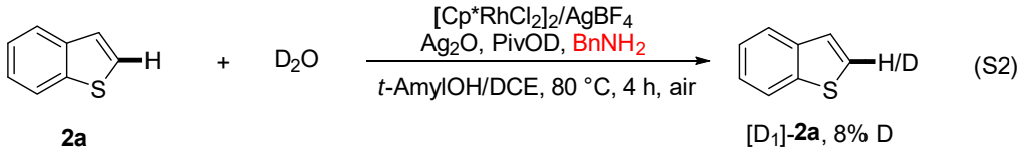
(a) H/D exchange experiments



(S1)

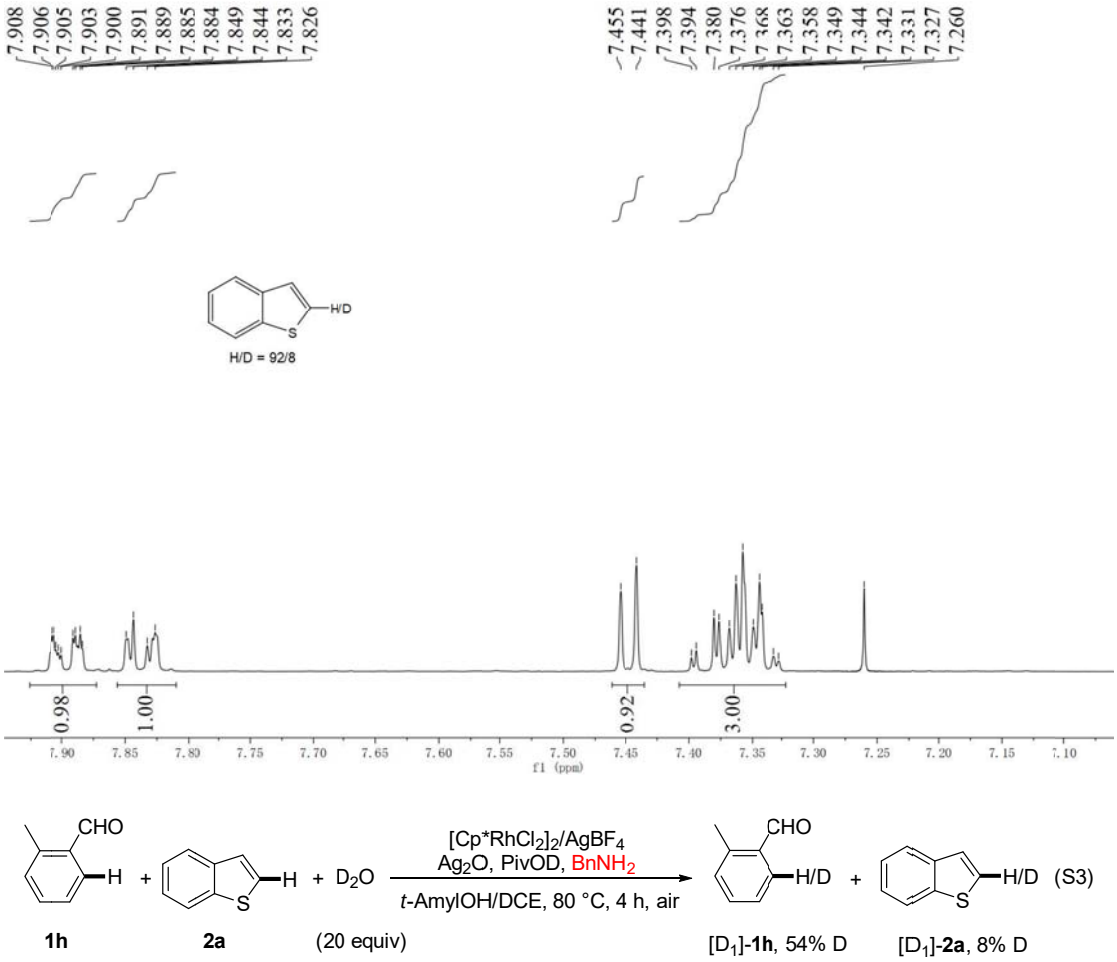
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **1h** (24.0 mg, 0.20 mmol), D_2O (73 μL, 20.0 equiv), benzylamine (40 mol%), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgBF_4$ (50 mol%), Ag_2O (2.0 equiv), PivOD (1.0 equiv) and *t*-AmylOH/DCE (1.0 mL, 2/1, V/V). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 80 °C in a pre-heated oil bath for 4 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) to provide the desired product. The deuterated ratio was calculated from ^{1}H NMR analysis. The ^{1}H NMR analysis showed that 55% hydrogen at the *ortho*-position of the benzaldehyde ring of **1h** was deuterated.



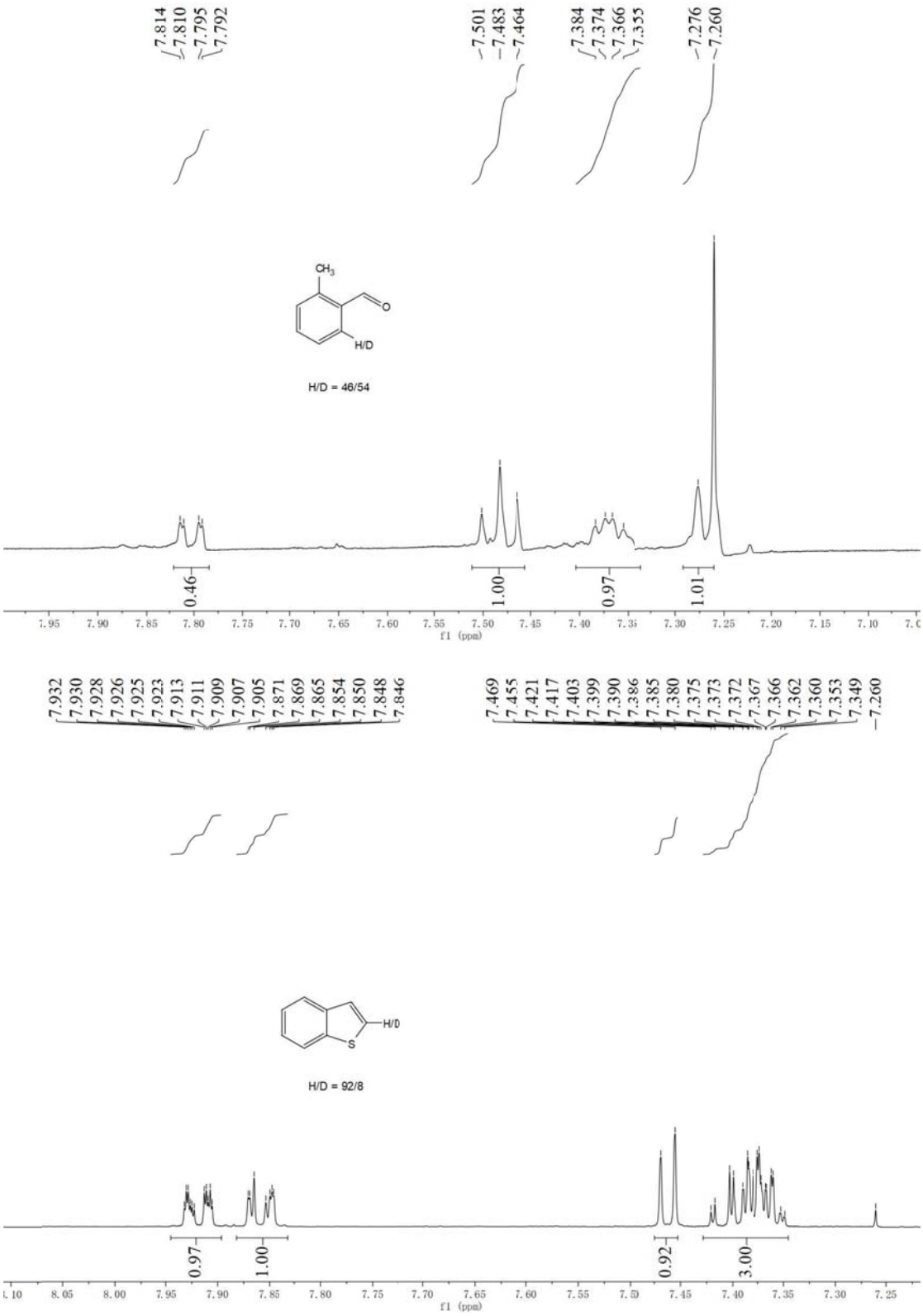


2a [D1]-**2a**, 8% D

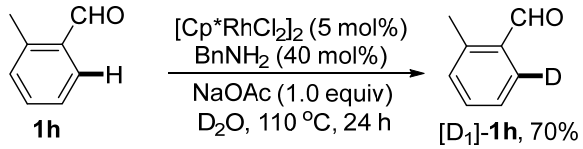
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **2a** (53.6 mg, 0.40 mmol), D_2O (73 μL, 4.0 mmol), benzylamine (40 mol%), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgBF_4$ (50 mol%), Ag_2O (2.0 equiv), PivOD (1.0 equiv) and *t*-AmylOH/DCE (1.0 mL, 2/1, V/V). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 80 °C in a pre-heated oil bath for 4 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether) to provide the desired product. The deuterated ratio was calculated from ^{1}H NMR analysis. The ^{1}H NMR analysis showed that 8% hydrogen at the 2-position of **2a** was deuterated.



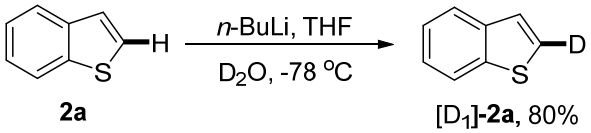
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **1h** (24.0 mg, 0.20 mmol), **2a** (2.0 equiv), D_2O (73 μL, 20.0 equiv), benzylamine (40 mol%), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgBF_4$ (50 mol%), Ag_2O (2.0 equiv), PivOD (1.0 equiv) and *t*-AmylOH/DCE (1.0 mL, 2/1, V/V). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 80 °C in a pre-heated oil bath for 4 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel to provide $[D_1]$-**1h** and $[D_1]$-**2a**. The deuterated ratio was calculated from ^1H NMR analysis. The ^1H NMR analysis showed that 54% hydrogen at the *ortho*-position of the phenyl ring of **1h** and 8% hydrogen at the 2-position of **2a** were deuterated.



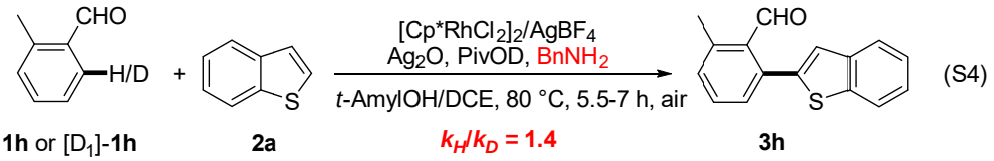
(b) Kinetic isotope experiments



Preparation of [D_1]-1h: A flame-dried Schlenk test tube with a magnetic stirring bar was charged with [Cp*$RhCl_2$]$_2$ (5.0 mol%), NaOAc (1.0 equiv) under air. Then the Schlenk test tube was evacuated and refilled with N_2 three times. Next, **1h** (24.0 mg, 0.20 mmol), benzylamine (40 mol%), and D_2O (0.5 mL) were added. The reaction mixture was allowed to stir for 15 min at room temperature, and then heated at 110 °C in a pre-heated oil bath for 24 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1, v/v) to provide [D_1]-**1h** (16.8 mg, 70%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.68 (s, 3H), 7.26 (d, J = 7.6 Hz, 1H), 7.36 (d, J = 7.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 10.28 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.8, 126.3, 131.9, 133.8, 134.2, 140.7, 193.0 ppm.



Preparation of [D_1]-2a[2]: A stirred solution of **2a** (0.67 g, 5.0 mmol) in dry THF (10.0 mL) under nitrogen was cooled to -78 °C, and *n*-BuLi (2.5 M solution in hexane, 7.5 mmol) was added dropwise. The reaction mixture was stirred for 2 h at -78 °C. D_2O (4.0 mL) was added to the reaction system and allowed to stir at room temperature for 2 h. The suspension was extracted with ethyl acetate three times. The organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether) to provide [D_1]-**2a** (0.54 g, 80%) as a white solid.



A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **1h** (24.0 mg, 0.20 mmol) or [D_1]-**1h** (24.2 mg, 0.20 mmol), **2a** (2.0 equiv), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgBF_4$ (50 mol%), benzylamine (40 mol%), Ag_2O (2.0 equiv), PivOD (1.0 equiv) and *t*-AmylOH/DCE (1.0 mL, 2/1, V/V). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 80 °C in a pre-heated oil bath for 5.5 h, 6 h, 6.5 h and 7 h. The reaction was stopped in the indicated reaction time and quickly cooled to room temperature before dilution with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. Then the filtrate was concentrated under a reduced pressure and the resulting residue was purified by column chromatography on silica gel. The k_{obs} = 0.072 h^{-1} for **1h** and k_{obs} = 0.051 h^{-1} for [D_1]-**1h** were determined from the pseudo-first-order plots of $ln(C_0/C_t)$ *vs.* time (C_0 = initial concentrations of **1h** or [D_1]-**1h**; C_t = concentrations of **1h** or [D_1]-**1h** after a time). Therefore, the KIE (for **1h** and [D_1]-**1h**) was calculated to be k_H/k_D = 0.072 h^{-1}/0.051 h^{-1} ≈ 1.4.

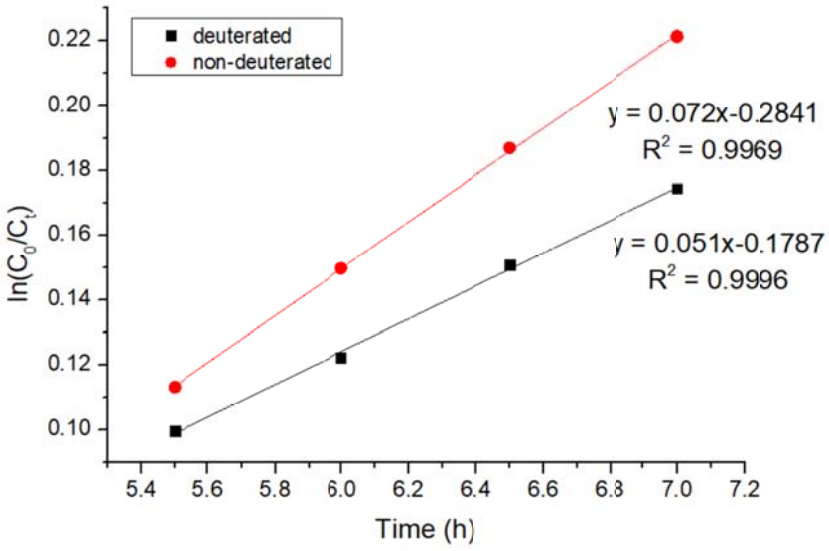
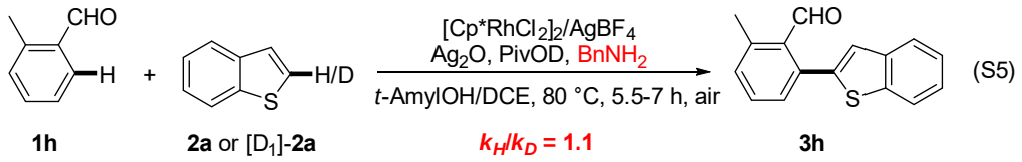


Figure S1. The Pseudo-First Order Plots for the Reaction of **2a** with **1h** and with [D_1]-**1h**.



A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **1h** (24.0 mg, 0.20 mmol), **2a** (2.0 equiv) or [D_1]-**2a** (2.0 equiv), [Cp*$RhCl_2$]$_2$ (5.0 mol%), $AgBF_4$ (50 mol%), benzylamine (40 mol%), Ag_2O (2.0 equiv), PivOD (1.0 equiv) and *t*-AmylOH/DCE (1.0 mL, 2/1, V/V). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 80 °C in a pre-heated oil bath for 5.5 h, 6 h, 6.5 h and 7 h. The reaction was stopped in the indicated reaction time and quickly cooled to room temperature before dilution with 5 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. Then the filtrate was concentrated under a reduced pressure and the resulting residue was purified by column chromatography on silica gel. The k_{obs} = 0.072 h^{-1} for **1h** reacting with **2a** and k_{obs} = 0.066 h^{-1} for **1h** reacting with [D_1]-**2a** were determined from the pseudo-first-order plots of $ln(C_0/C_t)$ *vs.* time (C_0 = initial concentrations of **1h**; C_t = concentrations of **1h** after a time). Therefore, the KIE (for **1h** reacting with **2a** and [D_1]-**2a**, respectively) was calculated to be k_H/k_D = 0.072 h^{-1}/0.066 h^{-1} ≈ 1.1.

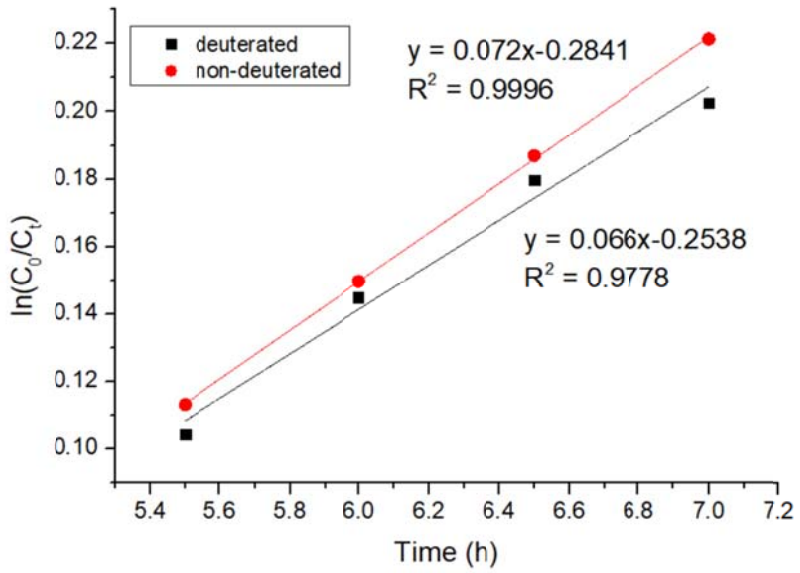
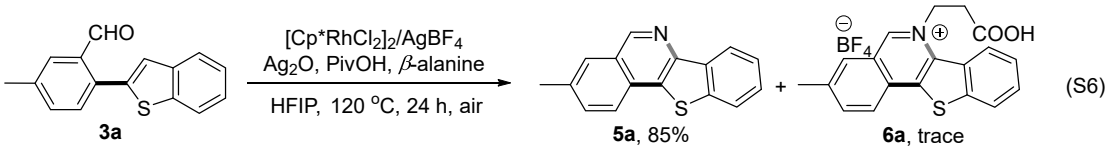


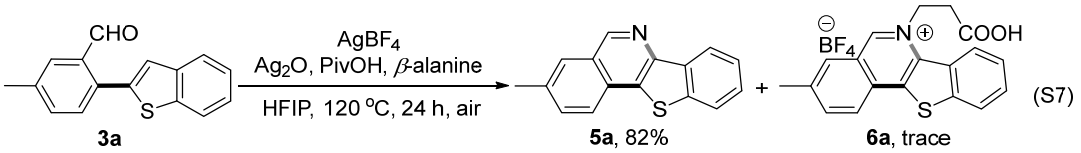
Figure S2. The Pseudo-First Order Plots for the Reaction of **1h** with **2a** and with [D_1]-**2a**.

(c) Control experiments of quaternization cyclization/dequaternization



(S6)

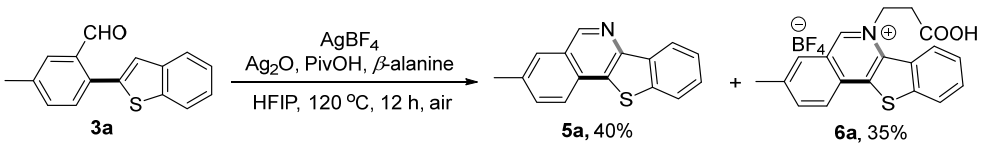
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 2-(benzo[*b*]thiophen-2-yl)-5-methylbenzaldehyde (**3a**, 0.20 mmol), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgBF_4$ (50 mol%), Ag_2O (3.0 equiv), *β*-alanine (1.0 equiv), PivOH (1.0 equiv) and HFIP (0.5 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 24 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to provide the desired product **5a** as a white solid (42.4 mg, 85%). A trace amount of **6a** was also observed in this reaction system.



(S7)

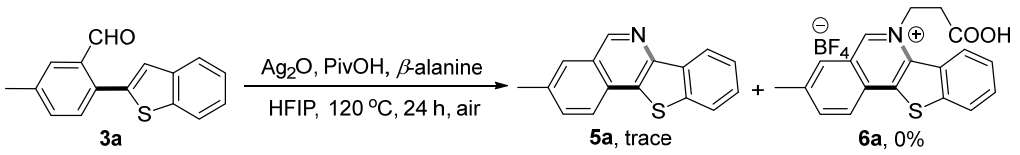
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 2-(benzo[*b*]thiophen-2-yl)-5-methylbenzaldehyde (**3a**, 0.20 mmol), *β*-alanine (1.0 equiv), $AgBF_4$ (50 mol%), Ag_2O (3.0 equiv), PivOH (1.0 equiv) and HFIP (0.5 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 24 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1,

v/v) to provide the desired product **5a** as a white solid (40.9 mg, 82%). A trace amount of **6a** was also observed in this reaction system.



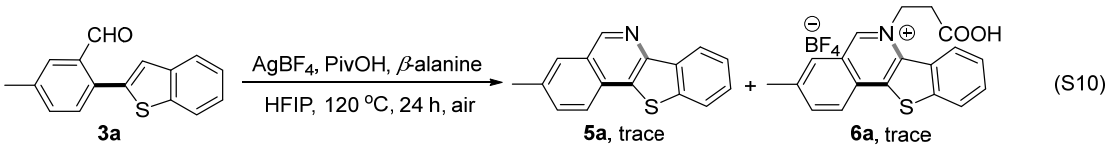
(S8)

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 2-(benzo[*b*]thiophen-2-yl)-5-methylbenzaldehyde (**3a**, 0.20 mmol), *β*-alanine (1.0 equiv), $AgBF_4$ (50 mol%), Ag_2O (3.0 equiv), PivOH (1.0 equiv) and HFIP (0.5 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 12 h. The reaction mixture was then cooled to room temperature, 1.0 mL of HBF_4 (40% aqueous solution) was added and the mixture was stirred at room temperature for another 0.5 h in air, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to provide **5a** as a white solid (19.9 mg, 40%) and (dichloromethane/methanol = 5/1, v/v) to provide **6a** (28.6 mg, 35%) as a yellow solid.



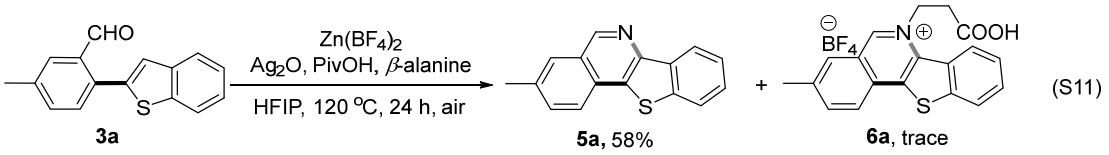
(S9)

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 2-(benzo[*b*]thiophen-2-yl)-5-methylbenzaldehyde (**3a**, 0.20 mmol), *β*-alanine (1.0 equiv), Ag_2O (3.0 equiv), PivOH (1.0 equiv) and HFIP (0.5 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 24 h. Only a trace amount of **5a** was observed and **6a** was not detected in this reaction system.



(S10)

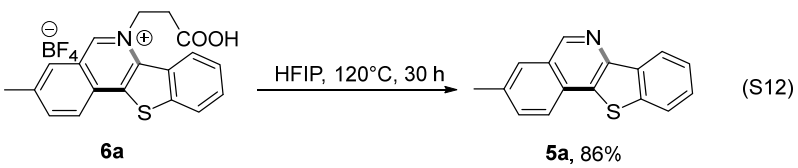
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 2-(benzo[*b*]thiophen-2-yl)-5-methylbenzaldehyde (**3a**, 0.20 mmol), *β*-alanine (1.0 equiv), $AgBF_4$ (50 mol%), PivOH (1.0 equiv) and HFIP (0.5 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 24 h. Only trace amounts of **5a** and **6a** were observed in this reaction system.



(S11)

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 2-(benzo[*b*]thiophen-2-yl)-5-methylbenzaldehyde (**3a**, 0.20 mmol), *β*-alanine (1.0 equiv), $Zn(BF_4)_2$ (25 mol%), Ag_2O (3.0 equiv), PivOH (1.0 equiv) and HFIP (0.5 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 24 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to provide the desired product **5a** as a white solid (28.9 mg, 58%). A trace amount of **6a** was also observed in this reaction system.

(d) The dequaternization of the phenanthridinium 6a

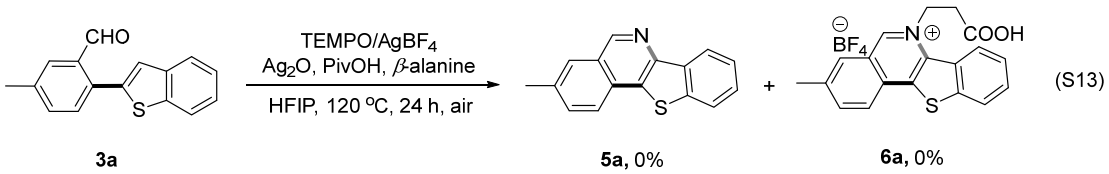


(S12)

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **6a**

(0.20 mmol) and HFIP (0.5 mL). The reaction mixture was heated at 120 °C in a pre-heated oil bath for 30 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to provide **5a** as a white solid (42.7 mg, 86%).

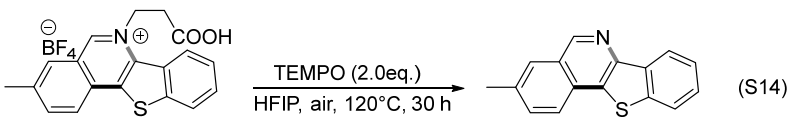
(e) The quaternization cyclization/dequaternization of 3a in the presence of 2 equiv of TEMPO



3a **5a,** 0% **6a,** 0% (S13)

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 2-(benzo[*b*]thiophen-2-yl)-5-methylbenzaldehyde (**3a**, 0.20 mmol), TEMPO (2.0 equiv), *ß*-alanine (1.0 equiv), $AgBF_4$ (50 mol%), Ag_2O (3.0 equiv), PivOH (1.0 equiv) and HFIP (0.5 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 24 h. The reaction mixture was then cooled to room temperature, **5a** and **6a** were not found in the reaction mixture.

(f) The dequaternization of the phenanthridinium-type polycycle 6a in the presence of radical scavenger

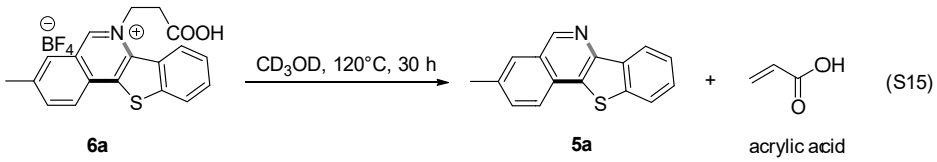


6a **5a,** 78% (S14)

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **6a** (0.20 mmol), TEMPO (2.0 equiv) and HFIP (0.5 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then

heated at 120 °C in a pre-heated oil bath for 30 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to provide **5a** as a white solid (38.8 mg, 78%).

(g) The in-situ ^{1}H NMR monitoring of dequaternization of the phenanthridinium-type polycycle 6a



6a **5a** acrylic acid

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with **6a** (0.20 mmol), and CD_3OD (0.5 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 30 h. The reaction mixture was then cooled to room temperature and analyzed by ^{1}H NMR.

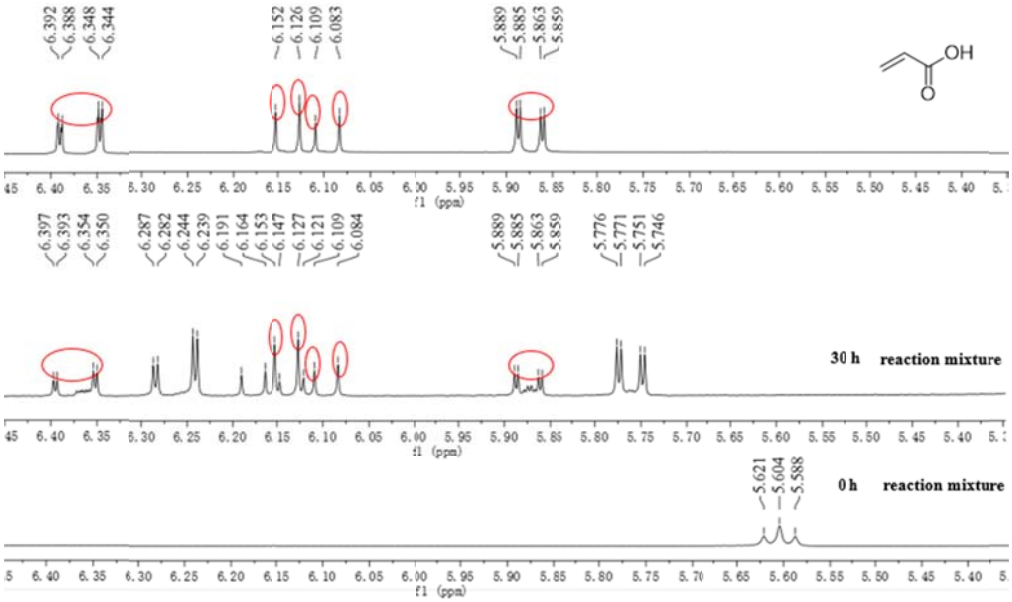
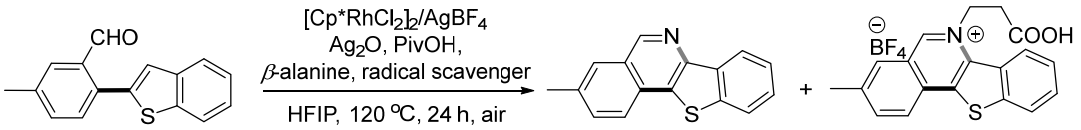


Figure S3. ^{1}H NMR spectra of acrylic acid in CD_3OD and ^{1}H NMR spectra of reaction mixture taken at different time points.

(h) General procedure for the quaternizationcyclization/dequaternization of 3a in the presence of radical scavenger

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with 2-(benzo[*b*]thiophen-2-yl)-5-methylbenzaldehyde (**3a**, 0.20 mmol), *ß*-alanine (1.0 equiv), $AgBF_4$ (50 mol%), Ag_2O (3.0 equiv), radical scavenger and HFIP (0.5 mL). The reaction mixture was allowed to stir for 15 min at room temperature under an air atmosphere, and then heated at 120 °C in a pre-heated oil bath for 24 h. The reaction mixture was then cooled to room temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 25-35 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to provide **5a**.

***Table S2*. The quaternization cyclization/dequaternization of 3a in the presence of radical scavenger**[a]

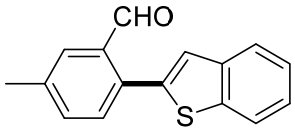


3a **5a** **6a**

Entry	Radical Scavenger	Equivalent	**5a**[b] (%)	**6a**[b] (%)
1	TEMPO	0.5	trace	trace
2	BHT	0.5	10	trace
3	ascorbic acid	0.5	25	trace
4	TEMPO	1.0	nd	nd
5	BHT	1.0	trace	nd
6	ascorbic acid	1.0	trace	nd

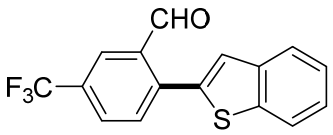
[a]Reaction condition: 2-(benzo[*b*]thiophen-2-yl)-5-methylbenzaldehyde **3a** (0.2 mmol), *ß*-alanine (1.0 equiv), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgBF_4$ (50 mol%), Ag_2O (3.0 equiv), radical scavenger, and PivOH (1.0 equiv) in HFIP (0.5 mL) under air at 120 °C for 24 h. [b]Yield of isolated products. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy, BHT = 2,6-di-*tert*-butyl-4-methylphenol, nd = not detected.

IX. Experimental data for the described substances



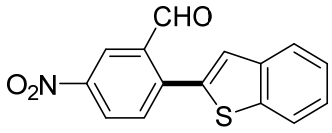
2-(Benzo[*b*]thiophen-2-yl)-5-methylbenzaldehyde (3a)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **3a** as a yellow solid (40.8 mg, 81%). M.p.: 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3H), 7.25 (s, 1H), 7.37-7.44 (m, 2H), 7.46-7.48 (m, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.81-7.83 (m, 1H), 7.85-7.88 (m, 2H), 10.24 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 122.3, 124.0, 125.0, 126.2, 128.3, 131.5, 134.4, 134.6, 135.5, 139.1, 139.2, 140.1, 140.7, 192.2 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{12}NaOS$ $[M+Na]^+$ 275.0507, found 275.0506.



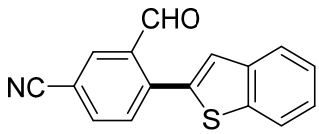
2-(Benzo[*b*]thiophen-2-yl)-5-(trifluoromethyl)benzaldehyde (3b)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **3b** as a yellow solid (45.9 mg, 75%). M.p.: 100-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (s, 1H), 7.42-7.48 (m, 2H), 7.78 (d, J = 8.0 Hz, 1H), 7.85-7.91 (m, 3H), 8.30-8.31 (m, 1H), 10.27 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.4, 123.6 (q, J_{CF} = 271.1 Hz), 124.4, 125.3 (q, J_{CF} = 3.8 Hz), 125.4, 125.7, 127.5, 129.9 (q, J_{CF} = 3.4 Hz), 131.2 (q, J_{CF} = 33.5 Hz), 132.2, 134.8, 137.2, 139.9, 141.0, 141.2 (d, J_{CF} = 1.1 Hz), 190.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.97 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_9F_3NaOS$ $[M+Na]^+$ 329.0224, found 329.0224.



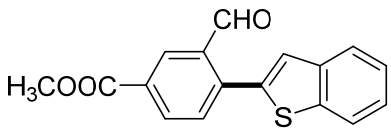
2-(Benzo[*b*]thiophen-2-yl)-5-nitrobenzaldehyde (3c)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate= 50/1, v/v) afforded **3c** as a yellow solid (39.6 mg, 70%)**.** M.p.: 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 1H), 7.45-7.50 (m, 2H), 7.85 (d, J = 8.4 Hz, 1H), 7.88-7.93 (m, 2H), 8.48 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 8.86 (d, J = 2.4 Hz, 1H), 10.29 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.5, 123.6, 124.6, 125.6, 126.1, 127.5, 128.2, 132.8, 135.3, 136.4, 139.8, 141.2, 143.5, 147.9, 189.6 ppm. HRMS (ESI^+): calcd for $C_{15}H_9NNaO_3S$ $[M+Na]^+$ 306.0201, found 306.0205.



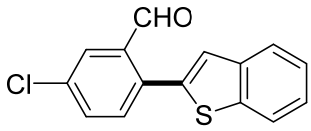
4-(Benzo[*b*]thiophen-2-yl)-3-formylbenzonitrile (3d)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **3d** as a yellow solid (31.6 mg, 60%). M.p.: 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (s, 1H), 7.43-7.47 (m, 2H), 7.78 (d, J = 8.4 Hz, 1H), 7.86-7.92 (m, 3H), 8.31 (d, J = 2.0 Hz, 1H), 10.24 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.9, 117.7, 122.4, 124.5, 125.5, 126.0, 128.0, 132.3, 132.4, 135.0, 136.0, 136.7, 139.9, 141.1, 141.9, 189.8 ppm. HRMS (ESI^+): calcd for $C_{16}H_9NNaOS$ $[M+Na]^+$ 286.0303, found 286.0304.



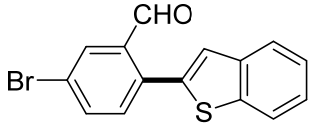
Methyl 4-(benzo[*b*]thiophen-2-yl)-3-formylbenzoate (3e)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3e** as a yellow solid (38.5 mg, 65%). M.p.: 86-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.99 (s, 3H), 7.35 (s, 1H), 7.41-7.47 (m, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.84-7.91 (m, 2H), 8.30 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 8.68 (d, J = 1.6 Hz, 1H), 10.28 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.7, 122.4, 124.3, 125.3, 125.6, 127.4, 129.6, 130.6, 131.8, 134.1, 134.6, 137.9, 140.0, 141.0, 141.9, 166.0, 191.1 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{12}NaO_3S$ $[M+Na]^+$ 319.0405, found 319.0417.



2-(Benzo[*b*]thiophen-2-yl)-5-chlorobenzaldehyde (3f)

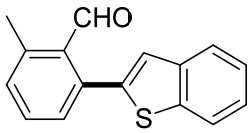
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **3f** as a yellow solid (30.0 mg, 55%). M.p.: 94-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (s, 1H), 7.43-7.48 (m, 2H), 7.78 (d, J = 8.8 Hz, 1H), 7.86-7.92 (m, 3H), 8.30 (d, J = 1.2 Hz, 1H), 10.24 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.9, 117.7, 122.4, 124.5, 125.5, 126.0, 128.0, 132.4, 135.0, 136.0, 136.7, 139.8, 141.1, 141.9, 189.8 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_9{}^{35}ClNaOS$ $[M+Na]^+$ 294.9960, found 294.9962, and $C_{15}H_9{}^{37}ClNaOS$ $[M+Na]^+$ 296.9931, found 296.9935.



2-(Benzo[*b*]thiophen-2-yl)-5-bromobenzaldehyde (3g)

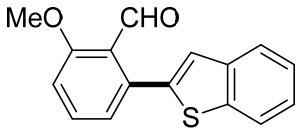
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =

50/1, v/v) afforded **3g** as a yellow solid (32.9 mg, 52%). M.p.: 61-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (s, 1H), 7.40-7.46 (m, 2H), 7.52 (d, J = 8.4 Hz, 1H), 7.77 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.83-7.85 (m, 1H), 7.87-7.89 (m, 1H), 8.16 (d, J = 2.4 Hz, 1H), 10.18 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.3, 123.5, 124.2, 125.2, 125.4, 126.9, 131.0, 133.1, 135.7, 136.5, 136.9, 137.7, 140.0, 140.8, 190.5 ppm. HRMS (ESI^+): calcd for $C_{15}H_9{}^{79}BrNaOS$ $[M+Na]^+$ 338.9455, found 338.9454, and $C_{15}H_9{}^{81}BrNaOS$ $[M+Na]^+$ 340.9435, found 340.9443.



2-(Benzo[b]thiophen-2-yl)-6-methylbenzaldehyde (3h)

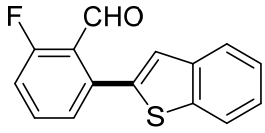
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3h** as a yellow solid (31.2 mg, 62%). M.p.: 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.66 (s, 3H), 7.22 (s, 1H), 7.32-7.34 (m, 1H), 7.38-7.42 (m, 2H), 7.47-7.51 (m, 2H), 7.80-7.82 (m, 1H), 7.85-7.88 (m, 1H), 10.20 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 122.2, 124.0, 124.9, 125.0, 126.7, 129.2, 132.1, 132.2, 133.7, 138.9, 140.0, 140.1, 140.2, 140.7, 194.1 ppm. HRMS (ESI^+): called for $C_{16}H_{12}NaOS$ $[M+Na]^+$ 275.0507, found 275.0508.



2-(Benzo[*b*]thiophen-2-yl)-6-methoxybenzaldehyde (3i)

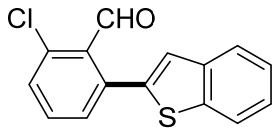
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3i** as a yellow solid (34.8 mg, 65%). M.p.: 120-122°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.97 (s, 3H), 7.05 (d, J = 8.4 Hz, 1H), 7.19 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.24 (s, 1H), 7.35-7.41 (m, 2H), 7.53-7.57 (m, 1H), 7.78-7.81 (m, 1H),

7.83-7.86 (m, 1H), 10.22 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.3, 111.9, 122.2, 123.7, 124.1, 124.5, 124.8, 125.0, 126.2, 133.9, 138.7, 139.9, 140.0, 140.6, 159.9, 191.2 ppm. HRMS (ESI^+): called for $C_{16}H_{12}NaO_2S$ $[M+Na]^+$ 291.0456, found 291.0448.



2-(Benzo[*b*]thiophen-2-yl)-6-fluorobenzaldehyde (3j)

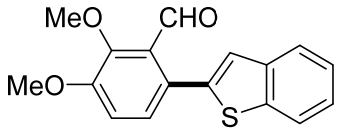
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **3j** as a yellow solid (35.8 mg, 70%). M.p.: 90-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19-7.24 (m, 1H), 7.27 (s, 1H), 7.38-7.44 (m, 3H), 7.57-7.62 (m, 1H), 7.81-7.83 (m, 1H), 7.86-7.88 (m, 1H), 10.14 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.9 (d, J_{CF} = 21.4 Hz), 122.3, 123.6 (d, J_{CF} = 8.5 Hz), 124.2, 125.1, 125.4, 126.9, 127.3 (d, J_{CF} = 3.6 Hz), 134.3 (d, J_{CF} = 10.2 Hz), 138.2 (d, J_{CF} = 2.9 Hz), 139.0 (d, J_{CF} = 2.1 Hz), 139.9, 140.7, 161.7 (d, J_{CF} = 261.8 Hz), 189.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -115.14 ~ -115.18 (m, 1F) ppm. HRMS (ESI^+): calcd for $C_{15}H_9FNaOS$ $[M+Na]^+$ 279.0256, found 279.0254.



2-(Benzo[*b*]thiophen-2-yl)-6-chlorobenzaldehyde (3k)

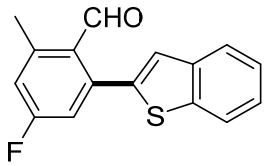
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **3k** as a yellow solid (32.7 mg, 60%). M.p.: 92-94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (s, 1H), 7.37-7.43 (m, 2H), 7.50-7.55 (m, 3H), 7.80-7.83 (m, 1H), 7.85-7.87 (m, 1H), 10.18 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.3, 124.2, 125.1, 125.3, 126.8, 130.1, 131.2, 132.7, 133.0, 134.4, 138.6, 138.7,

139.9, 140.7, 190.7 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_9{}^{35}ClNaOS$ $[M+Na]^+$ 294.9960, found 294.9957, and $C_{15}H_9{}^{37}ClNaOS$ $[M+Na]^+$ 296.9931, found 296.9921.



6-(Benzo[*b*]thiophen-2-yl)-2,3-dimethoxybenzaldehyde (3l)

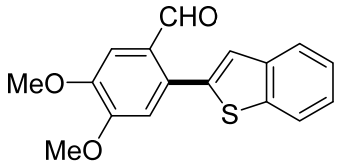
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3l** as a yellow solid (38.7 mg, 65%). M.p.: 116-118 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.95 (s, 3H), 3.98 (s, 3H), 7.14 (d, J = 8.4 Hz, 1H), 7.16 (s, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.34-7.40 (m, 2H), 7.76-7.78 (m, 1H), 7.82-7.84 (m, 1H), 10.21 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.3, 62.6, 116.0, 122.2, 123.9, 124.7, 124.8, 125.3, 127.3, 128.7, 130.2, 140.0, 140.1, 140.4, 149.7, 153.5, 191.4 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{14}NaO_3S$ $[M+Na]^+$ 321.0561, found 321.0557.



2-(Benzo[*b*]thiophen-2-yl)-4-fluoro-6-methylbenzaldehyde (3m)

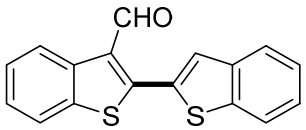
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3m** as a yellow solid (34.0 mg, 63%). M.p.:125-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.67 (s, 3H), 7.03 (dd, J = 9.2 Hz, 2.4 Hz, 1H), 7.17 (dd, J = 8.8 Hz, 2.8 Hz, 1H), 7.25 (s, 1H), 7.40-7.45 (m, 2H), 7.81-7.83 (m, 1H), 7.86-7.88 (m, 1H), 10.12 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.8 (d, J_{CF} = 1.4 Hz), 115.9 (d, J_{CF} = 22.2 Hz), 119.0 (d, J_{CF} = 20.9 Hz), 122.3, 124.2, 125.2, 125.4, 127.1, 130.2 (d, J_{CF} = 2.8 Hz), 138.7 (d, J_{CF} = 2.2 Hz), 139.8, 140.7, 142.0 (d, J_{CF} = 10.0 Hz), 144.2 (d, J_{CF} = 9.5 Hz), 163.7 (d, J_{CF} = 254.3 Hz), 192.6 ppm. ^{19}F NMR (376 MHz,

$CDCl_3$): δ = -105.73 ~ -105.78 (m, 1F) ppm. HRMS (ESI^+): called for $C_{16}H_{11}FNaOS$ $[M+Na]^+$ 293.0412, found 293.0411.



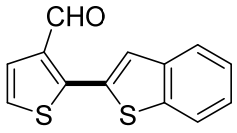
2-(Benzo[*b*]thiophen-2-yl)-4,5-dimethoxybenzaldehyde (3n)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **3n** as a yellow solid (35.8 mg, 60%). M.p.: 156-158 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.00 (d, J = 0.8 Hz, 6H), 7.03 (s, 1H), 7.28 (s, 1H), 7.37-7.45 (m, 2H), 7.55 (s, 1H), 7.81-7.83 (m, 1H), 7.86-7.88 (m, 1H), 10.12 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.4, 56.5, 109.0, 113.2, 122.2, 124.0, 125.1, 126.3, 128.1, 133.3, 138.8, 139.9, 140.6, 149.7, 153.5, 190.6 ppm. HRMS (ESI^+): calcd for $C_{17}H_{15}O_3S$ $[M+H]^+$ 299.0742, found 299.0742.



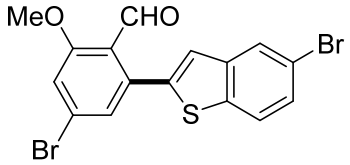
[2,2'-Bibenzo[*b*]thiophene]-3-carbaldehyde (3o)

Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **3o** as a yellow solid (29.4 mg, 50%). M.p.: 126-128 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.44-7.49 (m, 3H), 7.52-7.55 (m, 1H), 7.62 (s, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.88-7.90 (m, 2H), 8.78 (d, J = 8.0 Hz, 1H), 10.44 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.7, 122.4, 124.7, 125.5, 125.6, 126.1, 126.5, 126.7, 127.7, 131.1, 132.6, 137.3, 138.5, 139.7, 141.4, 152.0, 186.5 ppm. HRMS (ESI^+): calcd for $C_{17}H_{10}NaOS_2$ $[M+Na]^+$ 317.0071, found 317.0068.



2-(Benzo[*b*]thiophen-2-yl)thiophene-3-carbaldehyde (3p)

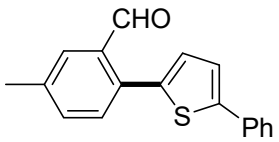
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =50/1, v/v) afforded **3p** as a yellow solid (24.4 mg, 50%). M.p.: 77-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (dd, J = 5.6 Hz, 1.2 Hz, 1H), 7.39-7.45 (m, 2H), 7.52 (s, 1H), 7.58 (d, J = 5.2 Hz, 1H), 7.83-7.87 (m, 2H), 10.21 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.3, 124.4, 125.3, 125.7, 126.1, 126.3, 127.5, 132.5, 138.2, 139.8, 140.9, 147.5, 185.4 ppm. HRMS (ESI^+): calcd for $C_{13}H_8NaOS_2$ $[M+Na]^+$ 266.9914, found 266.9911.



4-Bromo-2-(5-bromobenzo[*b*]thiophen-2-yl)-6-methoxybenzaldehyde (3q)

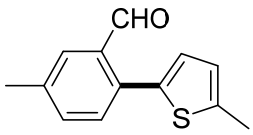
Following the general procedure, the reaction mixture was heated at 80 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 30/1, v/v) afforded **3q** as a yellow solid (61.3 mg, 72%). M.p.: 167-169°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.96 (s, 3H), 7.18 (s, 1H), 7.21 (d, J = 1.6 Hz, 1H), 7.31 (d, J = 1.6 Hz, 1H), 7.46 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 2.0 Hz, 1H), 10.17 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.7, 115.8, 118.9, 123.3, 123.6, 125.2, 126.7, 128.2, 139.0, 139.2, 140.6, 141.3, 160.7, 189.8 ppm. HRMS (ESI^+): called for $C_{16}H_{10}{}^{79}Br_2NaO_2S$ $[M+Na]^+$ 446.8666, found 446.8658, $C_{16}H_{10}{}^{79}Br^{81}BrNaO_2S$ $[M+Na]^+$ 448.8645, found 448.8639, and $C_{16}H_{10}{}^{81}Br_2NaO_2S$ $[M+Na]^+$ 450.8626, found 450.8630.

Alternatively, product **3q** can be obtained in 65% yield (1.38 g) using 4-bromo-2-methoxybenzaldehyde **1q** (1.08 g, 5.0 mmol) for 24 h.



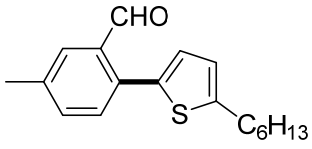
5-Methyl-2-(5-phenylthiophen-2-yl)benzaldehyde (4a)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **4a** as a yellow solid (40.0 mg, 72%). M.p.: 95-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3H), 7.00 (d, J = 3.6 Hz, 1H), 7.30-7.34 (m, 2H), 7.39-7.46 (m, 3H), 7.49 (d, J = 8.0 Hz, 1H), 7.63-7.65 (m, 2H), 7.83 (s, 1H), 10.26 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 123.8, 125.9, 128.1, 128.3, 129.2, 130.4, 131.2, 139.9, 134.0, 134.7, 135.4, 138.3, 138.5, 146.3, 192.4 ppm. HRMS (ESI^+): calcd for $C_{18}H_{15}OS$ $[M+H]^+$ 279.0844, found 279.0836.



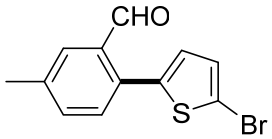
5-Methyl-2-(5-methylthiophen-2-yl)benzaldehyde (4b)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **4b** as a yellow liquid (29.4 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3H), 2.54 (s, 3H), 6.78-6.79 (m, 1H), 6.81 (d, J = 3.2 Hz, 1H), 7.40 (d, J = 1.2 Hz, 2H), 7.79 (s, 1H), 10.19 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.5, 21.2, 126.1, 128.1, 129.5, 131.2, 134.0, 134.6, 135.9, 136.6, 138.1, 142.0, 192.6 ppm. HRMS (ESI^+): calcd for $C_{13}H_{13}OS$ $[M+H]^+$ 217.0687, found 217.0680.



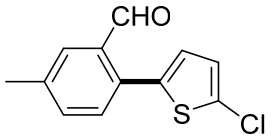
2-(5-Hexylthiophen-2-yl)-5-methylbenzaldehyde (4c)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **4c** as a yellow liquid (34.3 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89-0.92 (m, 3H), 1.31-1.43 (m, 6H), 1.68-1.73 (m, 2H), 2.43 (s, 3H), 2.85 (t, J = 7.6 Hz, 2H), 6.79-6.80 (m, 1H), 6.83 (d, J = 3.6 Hz, 1H), 7.39-7.43(m, 2H), 7.79 (s, 1H), 10.20 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 21.2, 22.7, 29.0, 30.3, 31.7, 31.8, 124.9, 128.1, 129.2, 131.2, 133.9, 134.6, 136.1, 136.2, 138.0, 148.3, 192.7 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{23}OS$ $[M+H]^+$ 287.1470, found 287.1468.



2-(5-Bromothiophen-2-yl)-5-methylbenzaldehyde (4d)

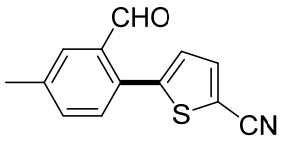
Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **4d** as a yellow solid (33.7 mg, 60%). M.p.: 42-44°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 6.78 (d, J = 3.6 Hz, 1H), 7.09 (d, J = 3.6 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.42-7.44 (m, 1H), 7.80 (s, 1H), 10.16 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 113.7, 128.4, 129.6, 130.7, 131.2, 134.0, 134.4, 134.7, 139.1, 140.6, 191.9 ppm. HRMS (ESI$^+$): called for $C_{12}H_9{}^{79}BrNaOS$ $[M+Na]^+$ 302.9455, found 302.9452, and $C_{12}H_9{}^{81}BrNaOS$ $[M+Na]^+$ 304.9435, found 304.9435.



2-(5-Chlorothiophen-2-yl)-5-methylbenzaldehyde (4e)

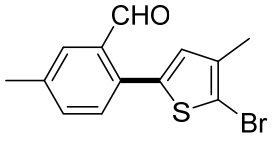
Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =

50/1, v/v) afforded **4e** as a yellow solid (33.1 mg, 70%). M.p.: 30-32 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 6.80 (dd, J = 3.6 Hz, 0.8 Hz, 1H), 6.95 (dd, J = 4.0 Hz, 0.8 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.81 (s, 1H), 10.16 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 126.9, 128.4, 128.6, 131.3, 131.5, 134.1, 134.5, 134.7, 137.6, 139.0, 191.9 ppm. HRMS (ESI^+): calcd for $C_{12}H_9{}^{35}ClNaOS$ $[M+Na]^+$ 258.9960, found 258.9952, and calcd for $C_{12}H_9{}^{37}ClNaOS$ $[M+Na]^+$ 260.9931, found 260.9935.



5-(2-Formyl-4-methylphenyl)thiophene-2-carbonitrile (4f)

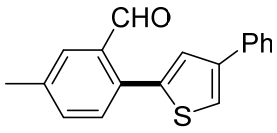
Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **4f** as a yellow solid (25.0 mg, 55%). M.p.: 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.48 (s, 3H), 7.05 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.47-7.50 (m, 1H), 7.64 (d, J = 3.6 Hz, 1H), 7.85 (s, 1H), 10.11 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 113.9, 129.2, 131.5, 132.5, 134.2, 134.9, 137.8, 140.5, 146.8, 191.0 ppm. HRMS (ESI^+): calcd for $C_{13}H_{10}NOS$ $[M+H]^+$ 228.0483, found 228.0480.



2-(5-Bromo-4-methylthiophen-2-yl)-5-methylbenzaldehyde (4g)

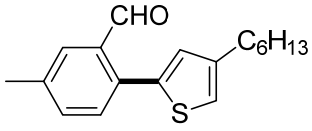
Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **4g** as a yellow solid (44.3 mg, 75%). M.p.: 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 2.44 (s, 3H), 6.71 (s, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.41-7.43 (m, 1H), 7.80 (s, 1H), 10.18 (s, 1H) ppm. ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 15.4, 21.3, 110.9, 128.3, 131.1, 131.3, 134.0, 134.7, 134.8, 138.2, 138.4, 138.9, 192.1 ppm. HRMS (ESI^+): calcd for $C_{13}H_{11}{}^{79}BrNaOS$ $[M+Na]^+$ 316.9612, found 316.9605, and $C_{13}H_{11}{}^{81}BrNaOS$ $[M+Na]^+$ 318.9591, found 318.9597.



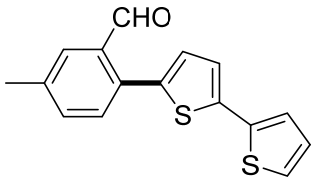
5-Methyl-2-(4-phenylthiophen-2-yl)benzaldehyde (4h)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **4h** as a yellow solid (38.9 mg, 70%). M.p.: 94-96 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3H), 7.30-7.35 (m, 2H), 7.40-7.47 (m, 3H), 7.49 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 1.6 Hz, 1H), 7.59-7.60 (m, 1H), 7.61-7.62 (m, 1H), 7.84 (s, 1H), 10.27 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 121.9, 126.5, 127.7, 128.2, 128.6, 129.1, 131.3, 134.1, 134.7, 135.4, 135.5, 138.8, 139.9, 143.0, 192.4 ppm. HRMS (ESI^+): calcd for $C_{18}H_{15}OS$ $[M+H]^+$ 279.0844, found 279.0842.



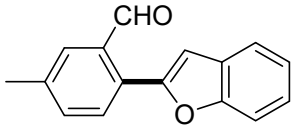
2-(4-Hexylthiophen-2-yl)-5-methylbenzaldehyde (4i)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **4i** as a yellow liquid (37.1 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88-0.91 (m, 3H), 1.31-1.39 (m, 6H), 1.60-1.68 (m, 2H), 2.44 (s, 3H), 2.63 (t, J = 7.6 Hz, 2H), 6.86 (d, J = 1.2 Hz, 1H), 7.02 (s, 1H), 7.40-7.45 (m, 2H), 7.80 (s, 1H), 10.19 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 21.2, 22.8, 29.2, 30.5, 30.6, 31.8, 121.8, 128.0, 130.9, 131.2, 133.9, 134.6, 136.0, 138.3, 138.7, 144.2, 192.7 ppm. HRMS (ESI^+): calcd for $C_{18}H_{22}NaOS$ $[M+Na]^+$ 309.1289, found 309.1285.



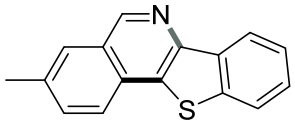
2-([2,2'-Bithiophen]-5-yl)-5-methylbenzaldehyde (4j)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **4j** as a yellow solid (33.0 mg, 58%). M.p.: 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 6.93 (d, J = 3.6 Hz, 1H), 7.05 (dd, J = 5.2 Hz, 3.6 Hz, 1H), 7.19 (d, J = 3.6 Hz, 1H), 7.22 (dd, J = 3.6 Hz, 1.2 Hz, 1H), 7.26 (dd, J = 5.2 Hz, 1.2 Hz, 1H), 7.42-7.47 (m, 2H), 7.82 (s, 1H), 10.24 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 124.2, 124.3, 125.1, 128.1, 128.4, 130.2, 131.2, 134.0, 134.7, 135.1, 136.9, 137.8, 138.6, 139.3, 192.3 ppm. HRMS (ESI^+): calcd for $C_{16}H_{12}NaOS_2$ $[M+Na]^+$ 307.0227, found 307.0225.



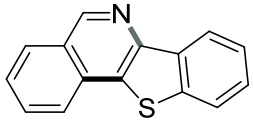
2-(Benzofuran-2-yl)-5-methylbenzaldehyde (4k)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 50/1, v/v) afforded **4k** as a yellow solid (23.6 mg, 50%). M.p.: 65-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3H), 6.94 (d, J = 0.8 Hz, 1H), 7.27-7.31 (m, 1H), 7.33-7.37 (m, 1H), 7.49-7.51 (m, 1H), 7.54-7.57 (m, 1H), 7.63-7.66 (m, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.85 (s, 1H), 10.47 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 107.4, 111.5, 121.4, 123.5, 125.1, 128.6, 128.8, 129.4, 130.7, 134.6, 139.5, 192.5 ppm. HRMS (ESI^+): calcd for $C_{16}H_{12}NaO_2$ $[M+Na]^+$ 259.0375, found 233.0579.



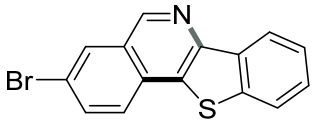
3-Methylbenzo[4,5]thieno[3,2-*c*]isoquinoline (5a)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **5a** as a white solid (32.4 mg, 65%). M.p.: 102-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.60 (s, 3H), 7.52-7.60 (m, 2H), 7.65 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.89-7.90 (m, 1H), 7.93-7.95 (m, 1H), 7.98 (d, J = 8.4 Hz, 1H), 8.51-8.54 (m, 1H), 9.22 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.0, 122.6, 123.1, 123.5, 125.2, 127.2, 127.3, 128.0, 130.0, 130.1, 133.3, 136.2, 137.5, 138.3, 145.8, 150.2 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{12}NS$ $[M+H]^+$ 250.0690, found 250.0683.



Benzo[4,5]thieno[3,2-*c*]isoquinoline (5b)

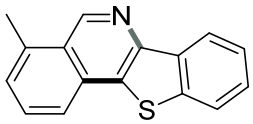
Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **5b** as a yellow solid (29.1 mg, 62%). M.p.: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54-7.61 (m, 2H), 7.66-7.70 (m, 1H), 7.80-7.84 (m, 1H), 7.95-7.97 (m, 1H), 8.08 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.54-8.56(m, 1H), 9.30 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.8, 123.1, 123.7, 125.2, 127.1, 127.3, 127.4, 129.1, 130.0, 131.1, 131.9, 136.1, 138.5, 146.3, 150.7 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_{10}NS$ $[M+H]^+$ 236.0534, found 236.0525.



3-Bromobenzo[4,5]thieno[3,2-*c*]isoquinoline (5c)

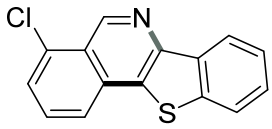
Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **5c** as a yellow solid (30.8 mg, 49%). M.p.: 210-212 °C. ^{1}H NMR

(400 MHz, $CDCl_3$): δ = 7.55-7.62 (m, 2H), 7.89 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.95-7.99 (m, 2H), 8.30 (d, J = 1.6 Hz, 1H), 8.53-8.55 (m, 1H), 9.22 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.9, 122.9, 123.2, 125.4, 125.5, 127.8, 128.0, 130.4, 131.2, 134.5, 135.9, 138.5, 146.8, 149.4 ppm. HRMS (ESI^+): calcd for $C_{15}H_9{}^{79}BrNS$ $[M+H]^+$ 313.9639, found 313.9640, and $C_{15}H_9{}^{81}BrNS$ $[M+H]^+$ 315.9619, found 315.9610.



4-Methylbenzo[4,5]thieno[3,2-*c*]isoquinoline (5d)

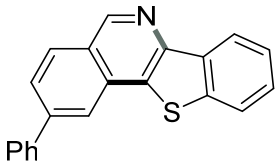
Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **5d** as a yellow solid (27.4 mg, 55%). M.p.: 96-98 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.87 (s, 3H), 7.42-7.44 (m, 1H), 7.53-7.60 (m, 2H), 7.64-7.69 (m, 1H), 7.90-7.95 (m, 2H), 8.54 (d, J = 7.6 Hz, 1H), 9.50 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 122.0, 122.7, 123.1, 125.2, 125.9, 127.4, 128.4, 130.5, 130.9, 132.1, 136.1, 137.0, 138.6, 146.2, 147.4 ppm. HRMS (ESI^+): calcd for $C_{16}H_{12}NS$ $[M+H]^+$ 250.0690, found 250.0679.



4-Chlorobenzo[4,5]thieno[3,2-*c*]isoquinoline (5e)

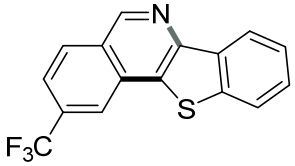
Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **5e** as a yellow solid (26.9 mg, 50%). M.p.: 208-210 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.55-7.61 (m, 2H), 7.65-7.70 (m, 2H), 7.93-7.98 (m, 2H), 8.53-8.56 (m, 1H), 9.70 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.8, 123.0, 123.1, 124.1, 125.4, 127.7, 127.9, 129.7, 131.1, 133.1, 134.0, 135.8, 138.8, 147.2,

147.4 ppm. HRMS (ESI$^+$): calcd for $C_{15}H_9{}^{35}ClNS$ $[M+H]^+$ 270.0144, found 270.0145, and $C_{15}H_9{}^{37}ClNS$ $[M+H]^+$ 272.0115, found 272.0120.



2-Phenylbenzo[4,5]thieno[3,2-*c*]isoquinoline (5f)

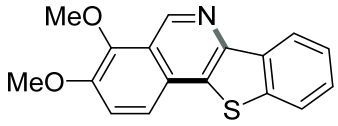
Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **5f** as a yellow solid (42.3 mg, 68%). M.p.: 205-207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.49 (m, 1H), 7.54-7.62 (m, 4H), 7.78 (s, 1H), 7.79-7.80 (s, 1H), 7.91-7.93 (m, 1H), 7.96-7.98 (m, 1H), 8.19 (d, J = 8.4 Hz, 1H), 8.23 (m, 1H), 8.55-8.57 (m, 1H), 9.31 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.5, 122.8, 123.2, 125.3, 126.1, 127.1, 127.5, 127.9, 128.6, 129.3, 129.6, 130.1, 132.3, 136.1, 138.5, 140.2, 144.0, 146.7, 150.4 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{14}NS$ $[M+H]^+$ 312.0847, found 312.0847.



2-(Trifluoromethyl)benzo[4,5]thieno[3,2-*c*]isoquinoline (5g)

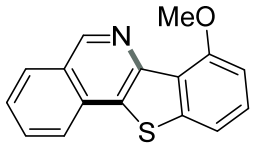
Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **5g** as a yellow solid (33.3 mg, 55%). M.p.: 176-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58-7.63(m, 2H), 7.84 (d, J = 8.4 Hz, 1H), 7.96-7.99 (m, 1H), 8.25 (d, J = 8.4 Hz, 1H), 8.36 (s, 1H), 8.54-8.56 (m, 1H), 9.35 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.4 (q, J_{CF} = 4.3 Hz), 123.0, 123.1 (q, J_{CF} = 3.0 Hz), 123.2, 125.5, 126.5 (q, J_{CF} = 271.5 Hz), 128.1, 130.2, 131.1, 132.4, 132.7, 135.7, 138.6, 147.5, 150.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.76 ppm. HRMS (ESI$^+$): calcd

for $C_{16}H_9F_3NS$ $[M+H]^+$ 304.0408, found 304.0408.



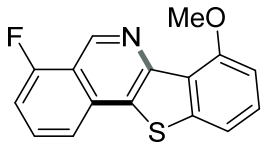
3,4-Dimethoxybenzo[4,5]thieno[3,2-*c*]isoquinoline (5h)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **5h** as a yellow solid (38.9 mg, 66%). M.p.: 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.05 (s, 3H), 4.13 (s, 3H), 7.50-7.59 (m, 3H), 7.81 (dd, J = 8.8 Hz, 0.8 Hz, 1H), 7.91-7.93 (m, 1H), 8.51-8.53 (m, 1H), 9.61 (d, J = 0.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 57.2, 62.0, 119.7, 120.1, 122.5, 122.7, 123.0, 125.2, 127.1, 127.2, 129.8, 136.3, 138.1, 145.1, 145.5, 145.6, 149.6 ppm. HRMS (ESI^+): calcd for $C_{17}H_{14}NO_2S$ $[M+H]^+$ 296.0745, found 296.0735.



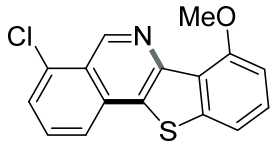
7-Methoxybenzo[4,5]thieno[3,2-*c*]isoquinoline (5i)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) afforded **5i** as a yellow solid (26.5 mg, 50%). M.p.: 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20 (s, 3H), 7.04 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.82 (t, J = 8.0 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 9.41 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.5, 106.6, 115.6, 123.6, 124.6, 126.0, 127.3, 128.1, 128.9, 129.1, 131.0, 131.5, 141.0, 146.6, 150.7, 157.5 ppm. HRMS (ESI^+): calcd for $C_{16}H_{12}NOS$ $[M+H]^+$ 266.0640, found 266.0638.



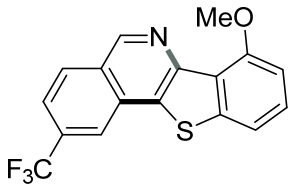
4-Fluoro-7-methoxybenzo[4,5]thieno[3,2-*c*]isoquinoline (5j)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) afforded **5j** as a yellow solid (23.8 mg, 42%). M.p.: 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20 (s, 3H), 7.06 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.72-7.78 (m, 1H), 7.86 (d, J = 8.4 Hz, 1H), 9.69 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.5, 106.8, 111.4 (d, J_{CF} = 19.3 Hz), 115.5, 116.3 (d, J_{CF} = 15.5 Hz), 119.6 (d, J_{CF} = 4.4 Hz), 124.5, 128.6, 131.6 (d, J_{CF} = 8.9 Hz), 132.8 (d, J_{CF} = 3.9 Hz), 140.5, 144.1 (d, J_{CF} = 5.4 Hz), 157.7, 160.2 (d, J_{CF} = 255.7 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -120.50 ~ -120.54 (m, 1F) ppm. HRMS (ESI^+): calcd for Chemical Formula: $C_{16}H_{11}FNOS$ $[M+H]^+$ 284.0545, found 284.0541.



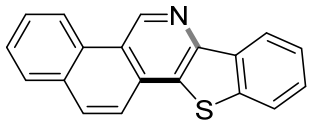
4-Chloro-7-methoxybenzo[4,5]thieno[3,2-*c*]isoquinoline (5k)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) afforded **5k** as a yellow solid (33.0 mg, 55%). M.p.: 205-207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20 (s, 3H), 7.06 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.67-7.73 (m, 2H), 7.99 (d, J = 7.2 Hz, 1H), 9.85 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.5, 106.8, 115.5, 122.8, 123.1, 127.6, 128.6, 131.0, 132.8, 134.0, 140.5, 140.6, 147.6, 157.7 ppm. HRMS (ESI^+): calcd for $C_{16}H_{11}{}^{35}ClNOS$ $[M+H]^+$ 300.0250, found 300.0253, and $C_{16}H_{11}{}^{37}ClNOS$ $[M+H]^+$ 302.0220, found 302.0223.



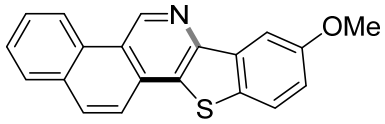
7-Methoxy-2-(trifluoromethyl)benzo[4,5]thieno[3,2-*c*]isoquinoline (5l)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 5/1, v/v) afforded **5l** as a yellow solid (38.6 mg, 58%). M.p.: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20 (s, 3H), 7.07 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 8.36 (s, 1H), 9.48 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.5, 106.9, 115.6, 121.4 (q, J_{CF} = 4.3 Hz), 122.5, 123.0 (d, J_{CF} = 3.1 Hz), 125.5 (q, J_{CF} = 248.6 Hz), 128.8, 130.1, 130.8, 132.2, 132.6, 140.4, 147.8, 150.3, 157.7 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{11}F_3NOS$ $[M+H]^+$ 334.0513, found 334.0513.



Benzo[*h*]benzo[4,5]thieno[3,2-*c*]isoquinoline (5m)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **5m** as a yellow solid (34.2 mg, 60%). M.p.: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.62 (m, 2H), 7.68 (t, J = 7.2 Hz, 1H), 7.78 (t, J = 7.2 Hz, 1H), 7.93-7.98 (m, 3H), 8.07 (d, J = 8.8 Hz, 1H), 8.57-8.59 (m, 1H), 8.88 (d, J = 8.4 Hz, 1H), 10.12 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.1, 121.5, 121.9, 122.2, 124.3, 126.5, 126.9, 127.5, 128.4, 129.2, 130.0, 130.4, 131.3, 131.6, 134.9, 138.1, 143.7, 147.2 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{12}NS$ $[M+H]^+$ 286.0690, found 286.0683.

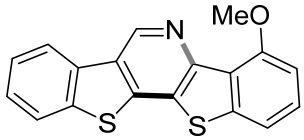


10-Methoxybenzo[*h*]benzo[4,5]thieno[3,2-*c*]isoquinoline (5n)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 5/1, v/v) afforded **5n** as a yellow solid (30.2 mg, 48%). M.p.: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.00 (s, 3H), 7.17 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.74-7.78 (m, 2H), 7.88 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 2.0 Hz, 1H), 8.02 (d, J = 8.8 Hz, 1H), 8.83 (d, J = 8.4 Hz, 1H), 10.04 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.9, 104.5, 118.3, 122.0, 122.4, 122.7, 123.8, 127.4, 128.4, 129.4, 130.2, 130.9, 131.5, 132.2, 132.5, 136.8, 144.4, 147.8, 158.3 ppm. HRMS (ESI^+): calcd for $C_{20}H_{14}NOS$ $[M+H]^+$316.0796, found 316.0795.

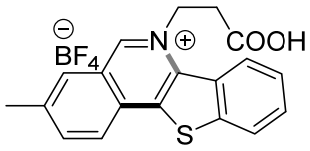
Benzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*d*]pyridine (5o)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) afforded **5o** as a yellow solid (30.8 mg, 53%). M.p.: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54-7.56 (m, 4H), 7.90-7.94 (m, 2H), 8.31-8.33 (m, 1H), 8.54-8.56 (m, 1H), 9.46 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.0, 123.1, 123.2, 123.4, 125.5, 125.8, 127.6, 127.7, 128.4, 129.7, 134.4, 135.2, 138.4, 138.8, 140.8, 142.0, 149.1 ppm. HRMS (ESI^+): calcd for $C_{17}H_{10}NS_2$ $[M+H]^+$ 292.0255, found 292.0248.



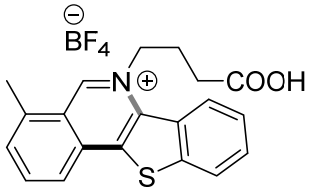
4-Methoxybenzo[4,5]thieno[3,2-*b*]benzo[4,5]thieno[2,3-*d*]pyridine (5p)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 5/1, v/v) afforded **5p** as a yellow solid (38.5 mg, 60%). M.p.: >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20 (s, 3H), 7.02-7.07 (m, 1H), 7.51-7.58 (m, 4H), 7.92-7.94 (m, 1H), 8.33-8.35 (m, 1H), 9.61 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.5, 107.0, 115.6, 122.1, 123.2, 123.5, 125.8, 126.9, 127.7, 128.5, 129.1, 134.4, 138.4, 140.6, 140.8, 141.7, 149.0, 157.9 ppm. HRMS (ESI$^+$): calcd for $C_{18}H_{12}NOS_2$ $[M+H]^+$ 322.0360, found 322.0359.



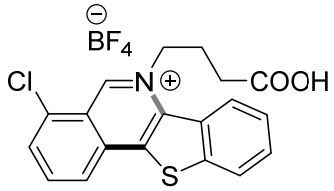
6-(2-Carboxyethyl)-3-methylbenzo[4,5]thieno[3,2-*c*]isoquinolin-6-ium tetrafluoroborate (6a)

A yellow solid, M.p.: >250 °C. ^{1}H NMR (400 MHz, CD_3CN): δ = 2.70 (s, 3H), 3.27 (t, J = 6.8 Hz, 2H), 5.54 (t, J = 6.8 Hz, 2H), 7.82-7.86 (m, 2H), 8.19 (d, J = 8.8 Hz, 1H), 8.31 (d, J = 8.8 Hz, 1H), 8.35 (s, 1H), 8.39 (d, J = 8.4 Hz, 1H), 8.47 (d, J = 8.4 Hz, 1H), 9.70 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.3, 32.6, 55.4, 123.7, 123.9, 124.8, 125.0, 127.0, 128.1, 129.1, 130.0, 131.0, 133.6, 136.4, 138.3, 140.2, 141.7, 150.8, 170.4 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ = -148.17, -148.22 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{16}NO_2S^+$ $[M-BF_4^-]^+$ 322.0896, found 322.0890.



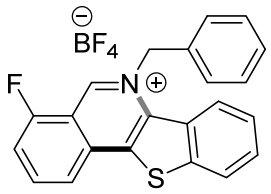
6-(3-Carboxypropyl)-4-methylbenzo[4,5]thieno[3,2-*c*]isoquinolin-6-ium tetrafluoroborate (6b)

Following the general procedure, the reaction mixture was heated at 120 ºC for 48 h. Purification via silica gel column chromatography (dichloromethane/methanol = 5/1, v/v) afforded the desired product **6b** as a yellow solid (54.1 mg, 64%). M.p.: > 250 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.37-2.42 (m, 2H), 2.66 (t, J = 7.2 Hz, 2H), 2.96 (s, 1H), 5.47 (t, J = 7.2 Hz, 2H), 7.81-7.88 (m, 2H), 7.94 (d, J = 7.2 Hz, 1H), 8.24 (t, J = 8.0 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 8.48 (d, J = 7.6 Hz,1H), 8.75 (d, J = 8.4 Hz, 1H),10.11 (s, 1H), 12.28 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.6, 24.5, 30.3, 59.2, 121.8, 123.4, 124.7, 125.3, 127.1, 128.0, 129.3, 131.7, 133.2, 133.8, 137.0, 137.8, 138.6, 140.9, 148.2, 173.8 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ = -148.20, -148.26 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{18}NO_2S^+$ [M-BF_4^-]$^+$ 336.1053, found 336.1056.



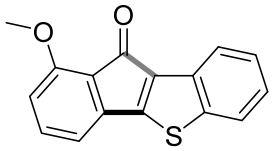
6-(3-Carboxypropyl)-4-chlorobenzo[4,5]thieno[3,2-*c*]isoquinolin-6-ium tetrafluoroborate (6c)

Following the general procedure, the reaction mixture was heated at 120 ºC for 48 h. Purification via silica gel column chromatography (dichloromethane/methanol = 5/1, v/v) afforded the desired product **6c** as a yellow solid (51.4 mg, 58%). M.p.: > 250 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.33-2.40 (m, 2H), 2.65 (t, J = 7.2 Hz, 2H), 5.56 (t, J = 7.2 Hz, 2H), 7.85-7.94 (m, 2H), 8.29-8.36 (m, 2H), 8.55 (d, J = 8.0 Hz,1H), 8.60 (d, J = 7.6 Hz,1H), 8.81 (d, J = 7.6 Hz,1H), 10.23 (s, 1H), 12.38 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 24.4, 30.2, 59.5, 122.3, 123.4, 124.9, 125.7, 127.3, 127.7, 129.8, 131.4, 134.4, 134.5, 135.2, 137.4, 138.2, 139.0, 147.4, 173.8 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ = -148.18, -148.23 ppm. HRMS (ESI$^+$): calcd for $C_{19}H_{15}{}^{35}ClNO_2S^+$ [M-BF_4^-]$^+$ 356.0507, found 356.0508, and $C_{19}H_{15}{}^{37}ClNO_2S^+$ [M-BF_4^-]$^+$ 358.0477, found 358.0478.



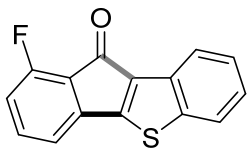
6-Benzyl-4-fluorobenzo[4,5]thieno[3,2-*c*]isoquinolin-6-ium tetrafluoroborate (6d)

Following the general procedure, the reaction mixture was heated at 120 ºC for 48 h. Purification via silica gel column chromatography (dichloromethane/methanol = 5/1, v/v) afforded the desired product **6d** as a yellow solid (24.1 mg, 28%). M.p.: > 250 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.81 (s, 2H), 7.31-7.41 (m, 5H), 7.64 (t, J = 8.4 Hz, 1H), 7.79 (t, J = 8.0 Hz, 1H), 8.03 (t, J = 8.0 Hz, 1H), 8.41-8.53 (m, 4H), 10.44 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 62.6, 115.3 (d, J_{CF} = 12.5 Hz), 115.5 (d, J_{CF} = 10.0 Hz), 120.5 (d, J_{CF} = 4.2 Hz), 124.7, 125.8, 126.3, 126.7, 127.5, 128.5, 129.3, 129.6, 133.5, 133.8, 135.2, 137.0 (d, J_{CF} = 2.8 Hz), 138.8, 140.0 (d, J_{CF} = 9.5 Hz), 146.2 (d, J_{CF} = 4.8 Hz), 160.1 (d, J_{CF} = 261.7 Hz) ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ = -113.80 ~ -113.84 (m, 1F), -148.21, -148.26 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{15}FNS^+$ [M-BF_4^-]$^+$ 344.0904, found 344.0899.



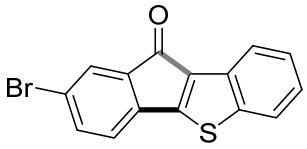
1-Methoxy-10*H*-benzo[*b*]indeno[2,1-*d*]thiophen-10-one (7a)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) afforded the desired product **7a** as a yellow solid (46.8 mg, 88%). M.p.: 218-220 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.98 (s, 3H), 6.83-6.86 (m, 2H), 7.28-7.35 (m, 2H), 7.42 (t, J = 7.2 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.2, 113.8, 115.2, 121.4, 123.1, 123.5, 125.3, 126.5, 132.7, 135.1, 135.9, 140.8, 144.2, 157.0, 159.5, 186.2 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{11}O_2S$ [M+H]$^+$ 267.0480, found 267.0476.



1-Fluoro-10*H*-benzo[*b*]indeno[2,1-*d*]thiophen-10-one (7b)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) afforded the desired product **7b** as a yellow solid (36.6 mg, 72%). M.p.: 115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (t, J = 8.8 Hz, 1H), 7.01 (d, J = 7.2 Hz, 1H), 7.32-7.37 (m, 2H), 7.45 (t, J = 8.0 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.7 (d, J_{CF} = 2.6 Hz), 119.2 (d, J_{CF} = 21.5 Hz), 121.6 (d, J_{CF} = 12.8 Hz), 123.2, 123.6, 125.8, 126.8, 132.3, 135.1 (d, J_{CF} = 1.3 Hz), 136.3 (d, J_{CF} = 8.5 Hz), 140.6 (d, J_{CF} = 4.5 Hz), 144.3, 158.0 (d, J_{CF} = 261.9 Hz), 160.4 (d, J_{CF} = 4.4 Hz), 183.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -115.00 ~ -115.03 (m, 1F) ppm. HRMS (ESI^+): calcd for $C_{15}H_8FOS$ $[M+H]^+$ 255.0280, found 255.0278.



2-Bromo-10*H*-benzo[*b*]indeno[2,1-*d*]thiophen-10-one (7c)

Following the general procedure, the reaction mixture was heated at 120 ºC for 36 h. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) afforded the desired product **7c** as a red solid (37.6 mg, 60%). M.p.: 97-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, J = 8.0 Hz, 1H), 7.31-7.36 (m, 1H), 7.42-7.46 (m, 1H), 7.50 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.57 (d, J = 2.0 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.5, 123.1, 123.7, 125.7, 126.8, 126.9, 132.4, 132.9, 134.9, 136.0, 137.4, 138.5, 144.2, 161.7, 185.8 ppm. HRMS (ESI^+): calcd for $C_{15}H_8{}^{79}BrOS$ $[M+H]^+$314.9479, found 314.9474, and $C_{15}H_8{}^{81}BrOS$ $[M+H]^+$316.9459, found 316.9

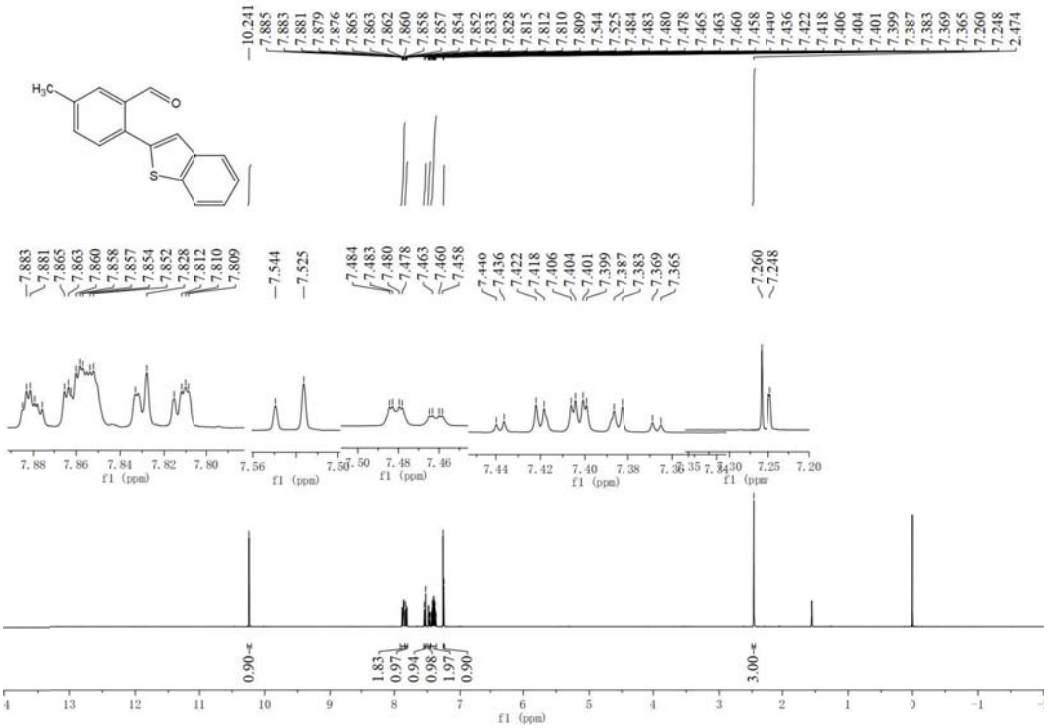
X. References

1. (a) J. W. Kang, K. Moseley and P. M. Maitlis, *J. Am. Chem. Soc.,* 1969, **91**, 5970; (b) K. Fujita, Y. Takahashi, M. Owaki, K. Yamamoto and R. Yamaguchi, *Org. Lett.,* 2004, **6**, 2785.

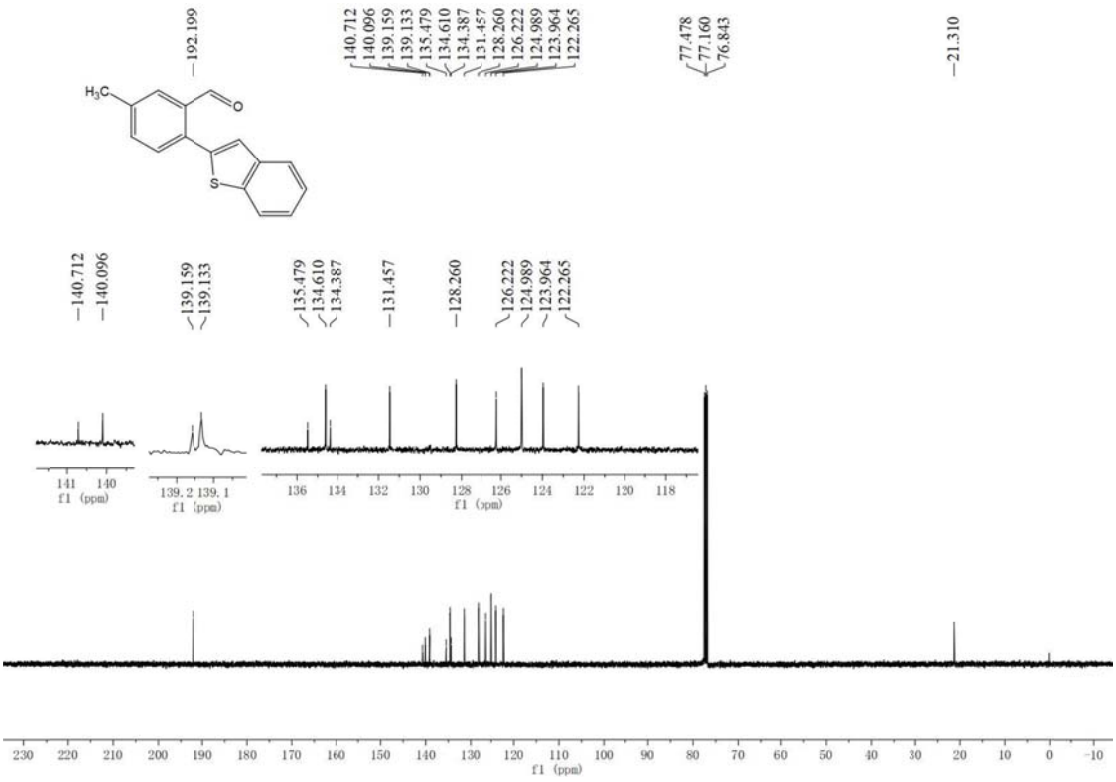
2. C. Colletto, S. Islam, F. Juliá-Hernández and I. Larrosa, *J. Am. Chem. Soc.,* 2016, **138**, 1677.

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

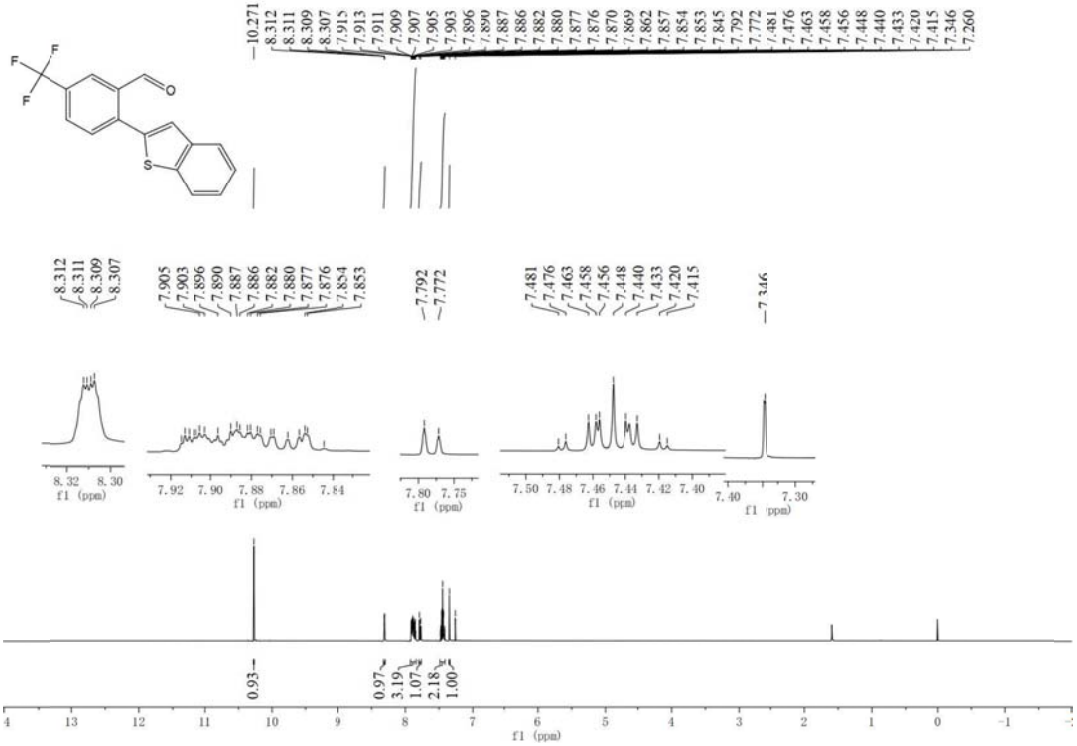
^{1}H NMR spectra of **3a** ($CDCl_3$)



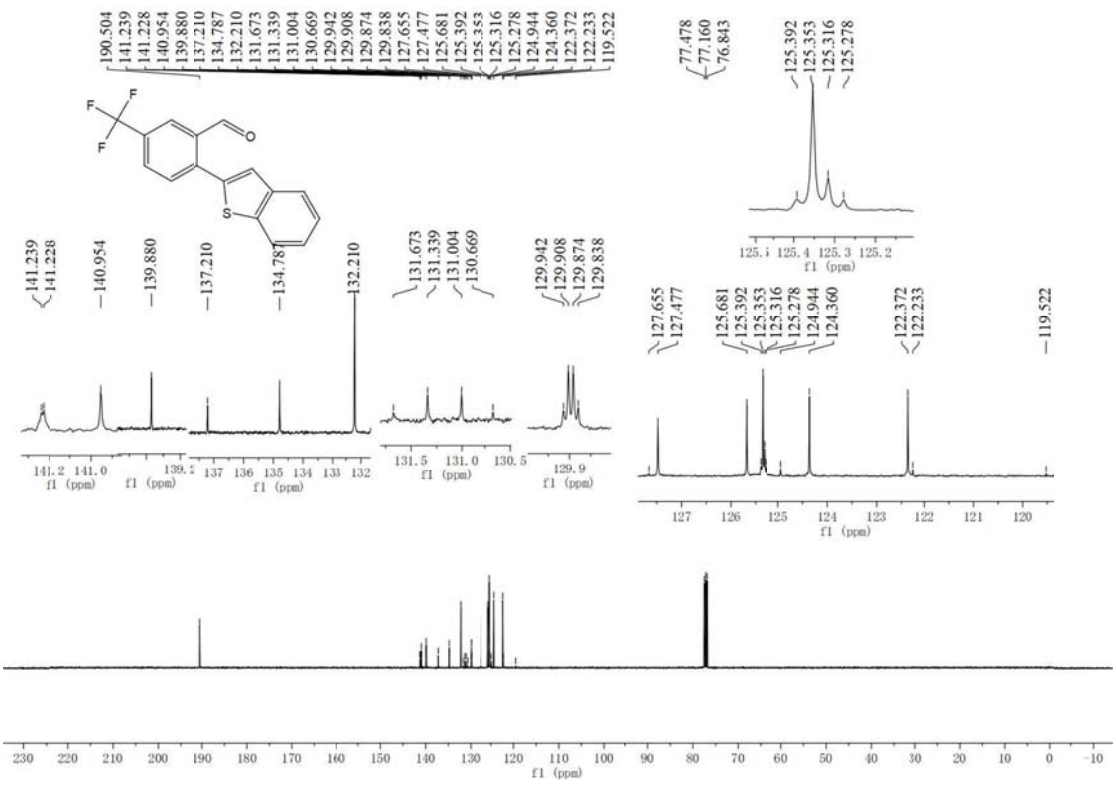
^{13}C NMR spectra of **3a** ($CDCl_3$)



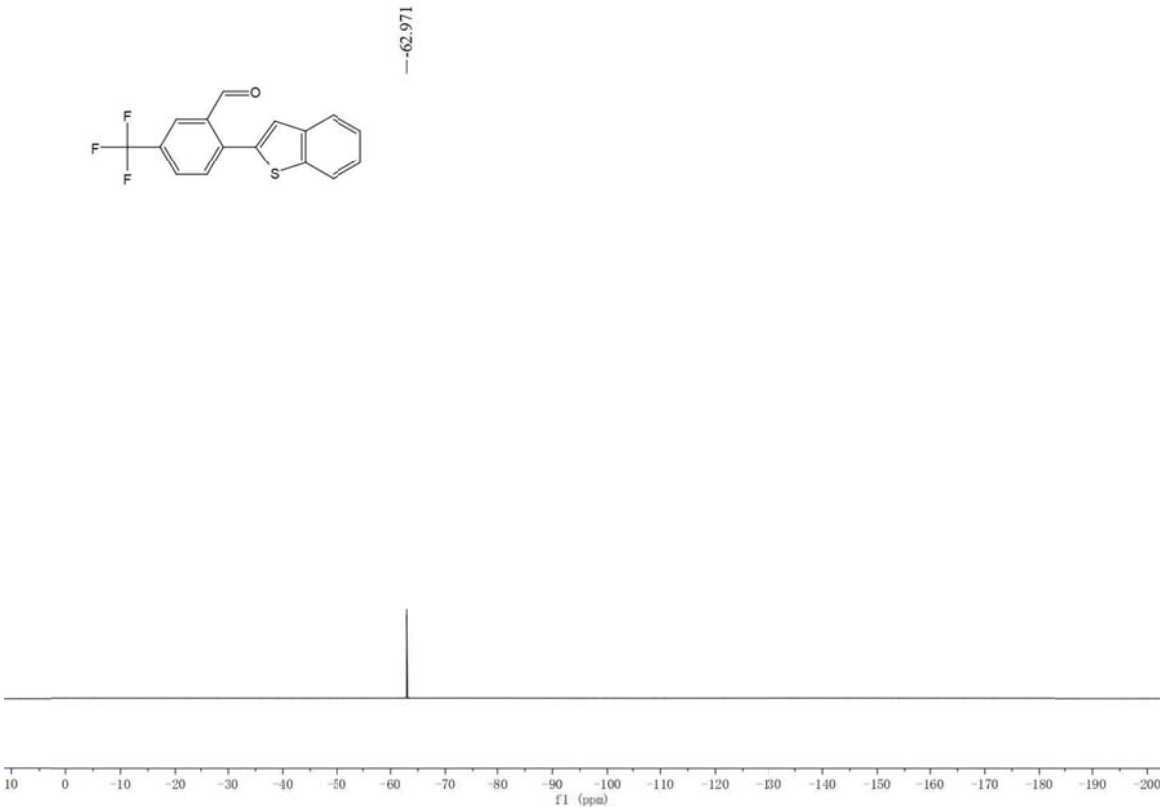
^{1}H NMR spectra of **3b** ($CDCl_3$)



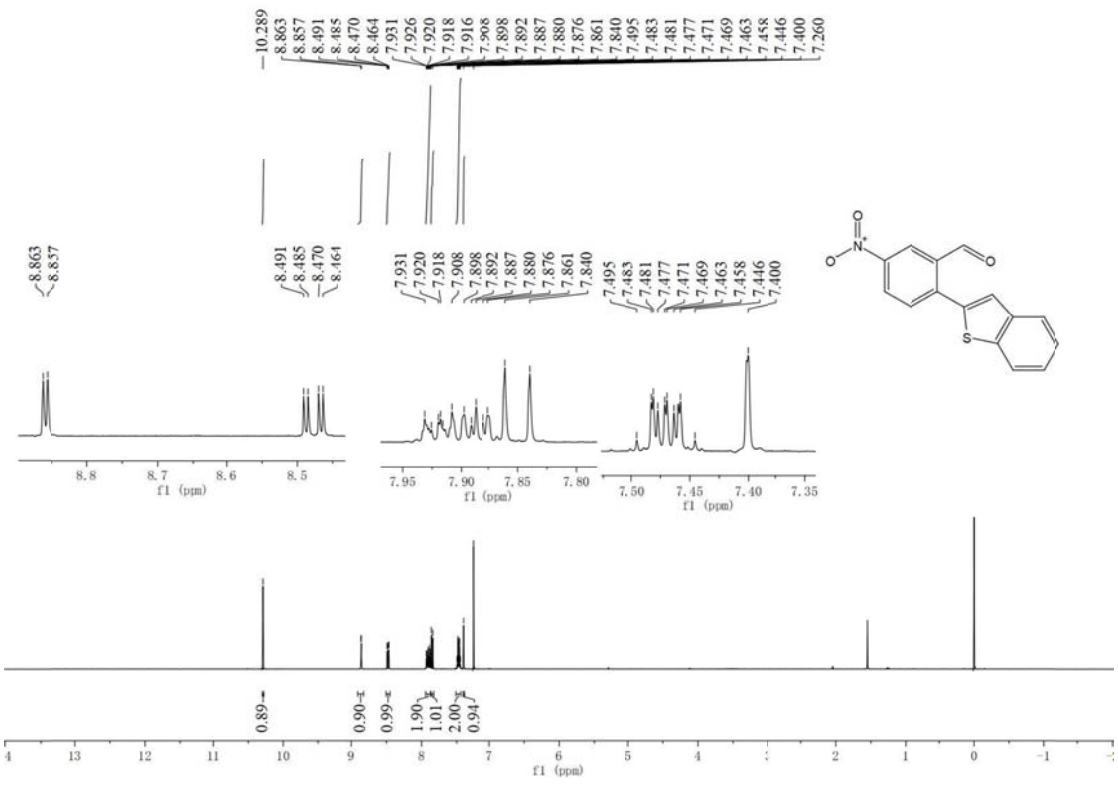
^{13}C NMR spectra of **3b** ($CDCl_3$)



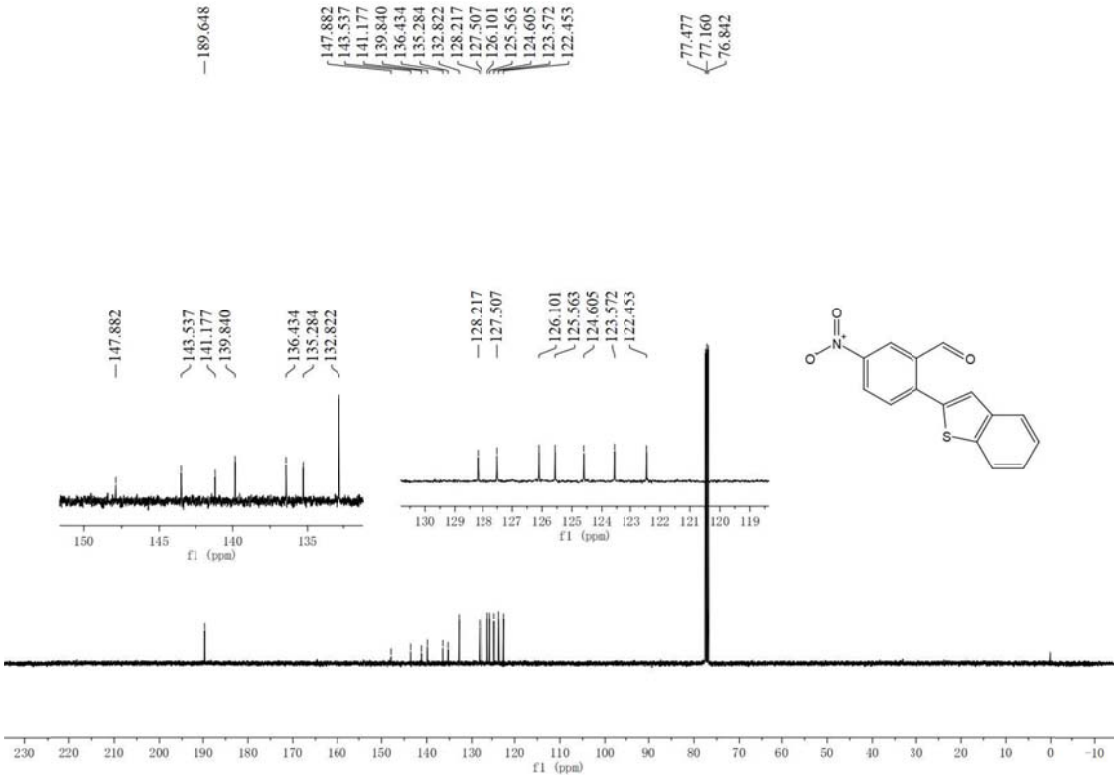
^{19}F NMR spectra of **3b** ($CDCl_3$)



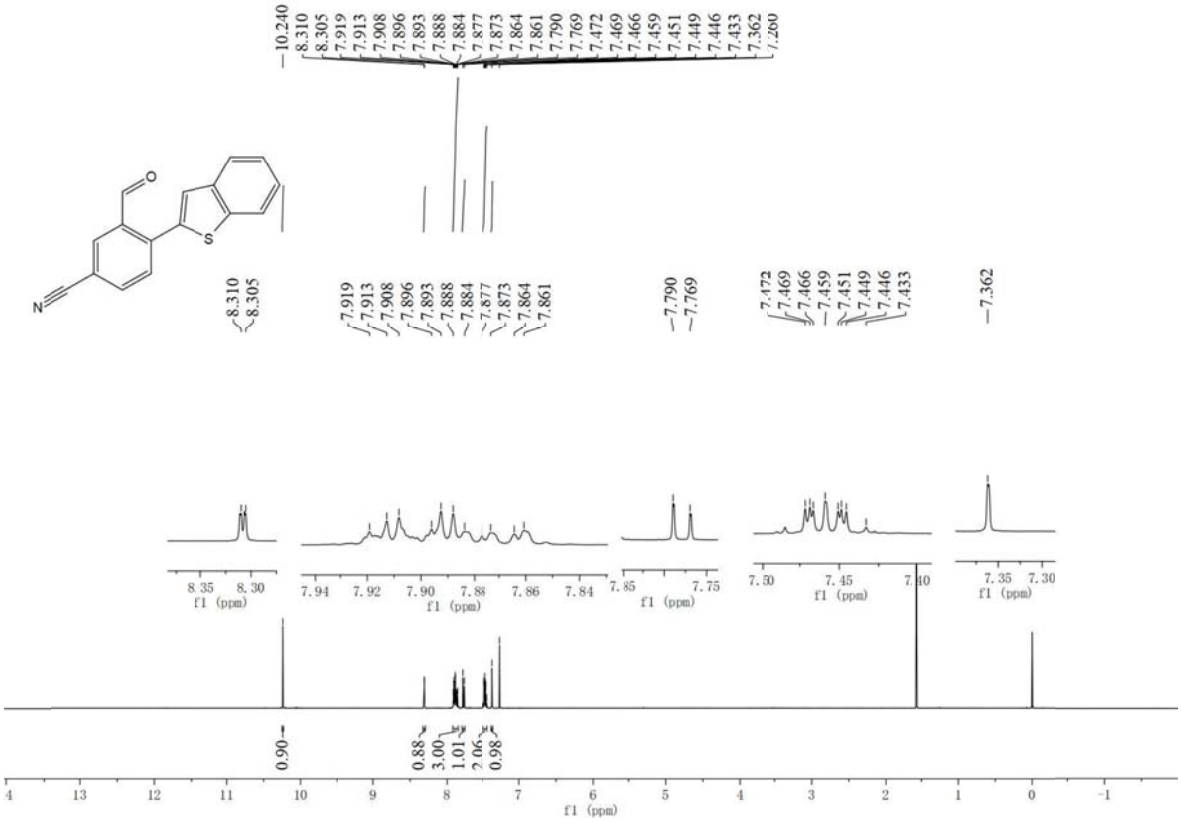
^{1}H NMR spectra of **3c** ($CDCl_3$)



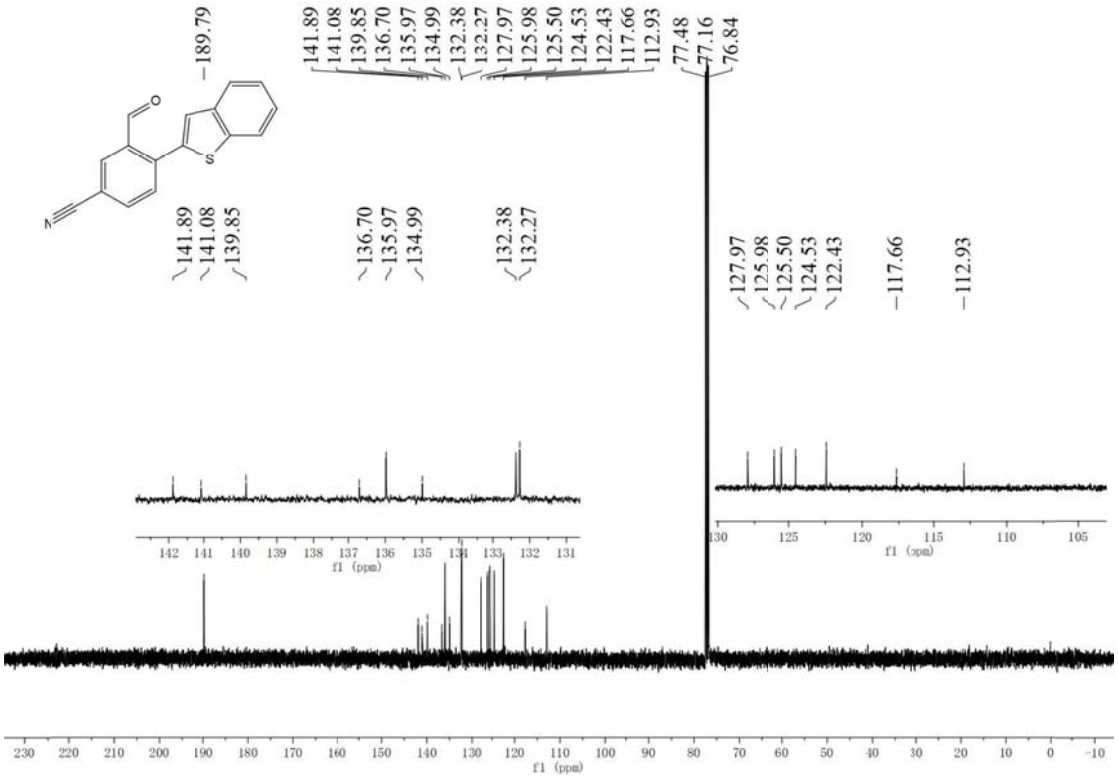
^{13}C NMR spectra of **3c** ($CDCl_3$)



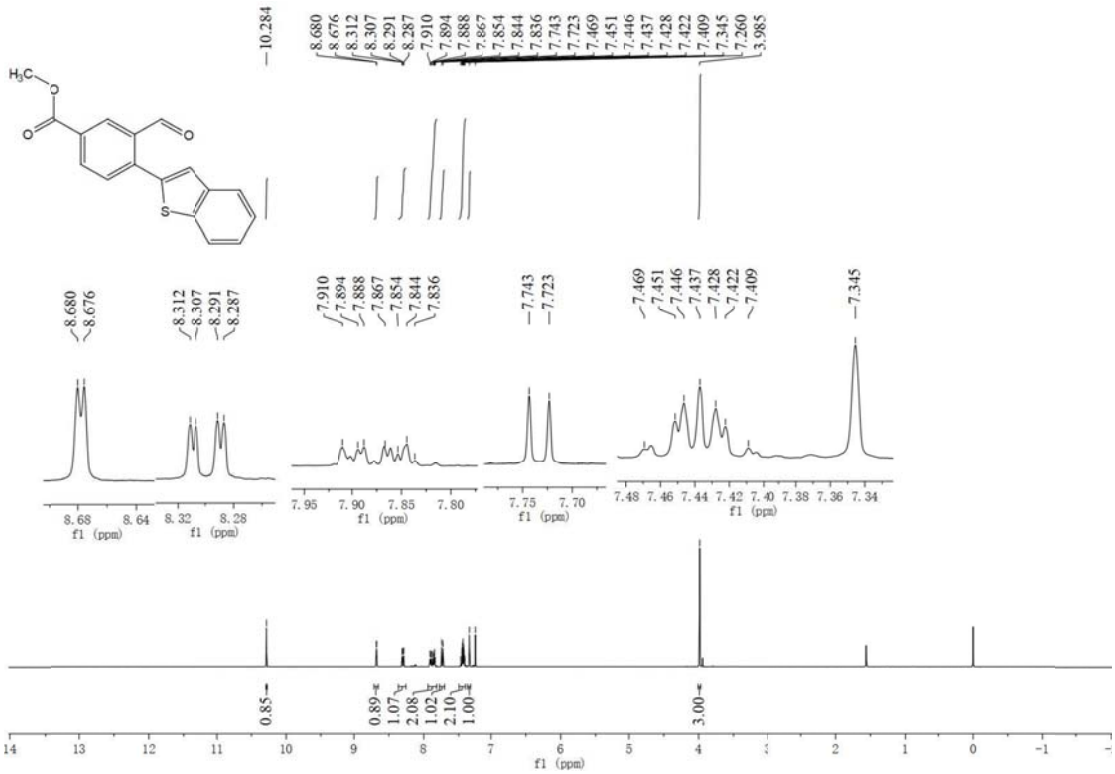
^{1}H NMR spectra of **3d** ($CDCl_3$)



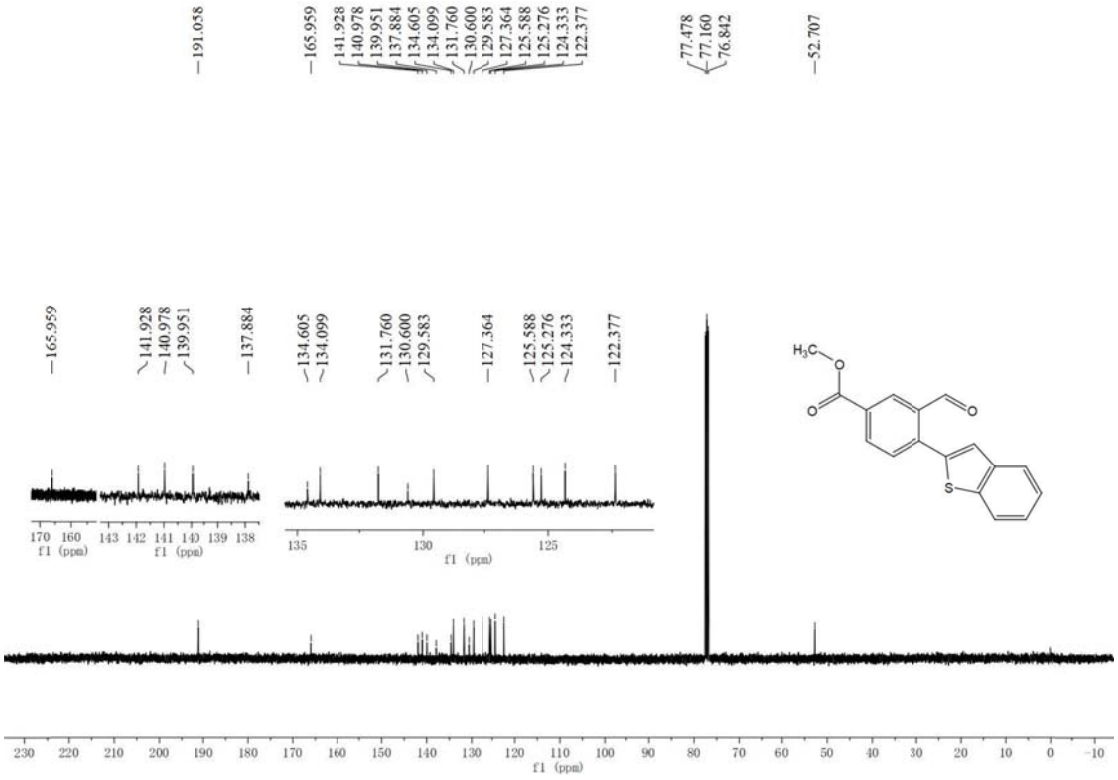
^{13}C NMR spectra of **3d** ($CDCl_3$)



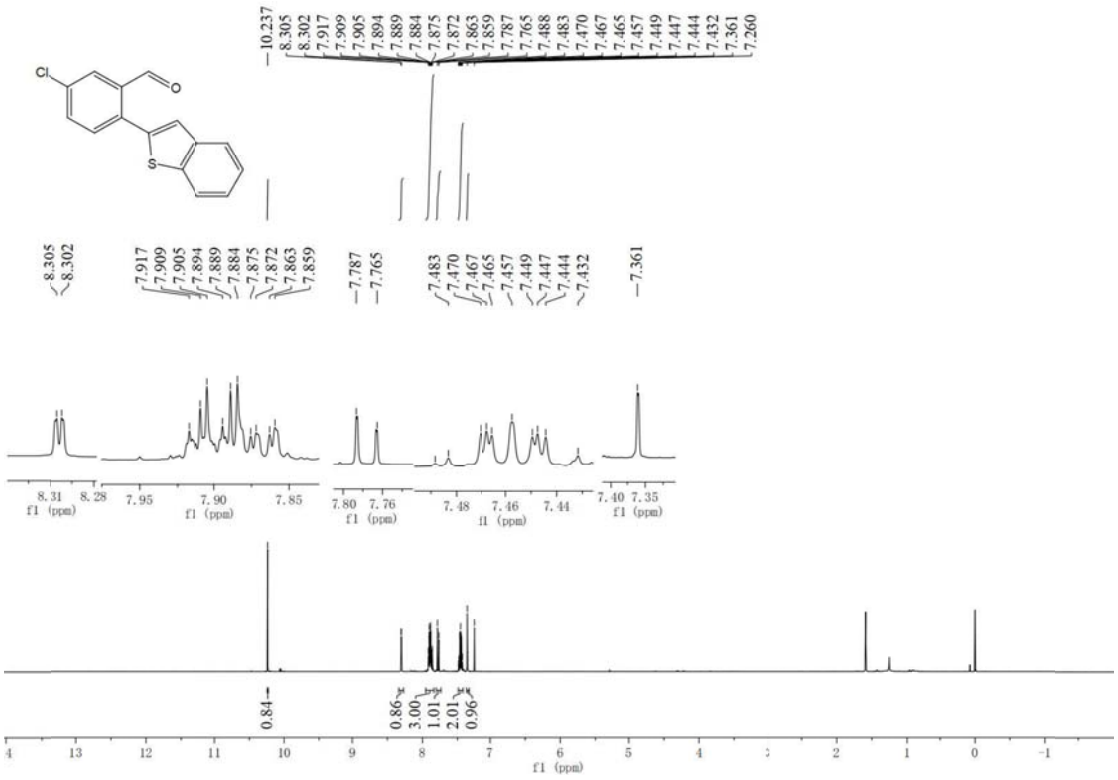
^{1}H NMR spectra of **3e** ($CDCl_3$)



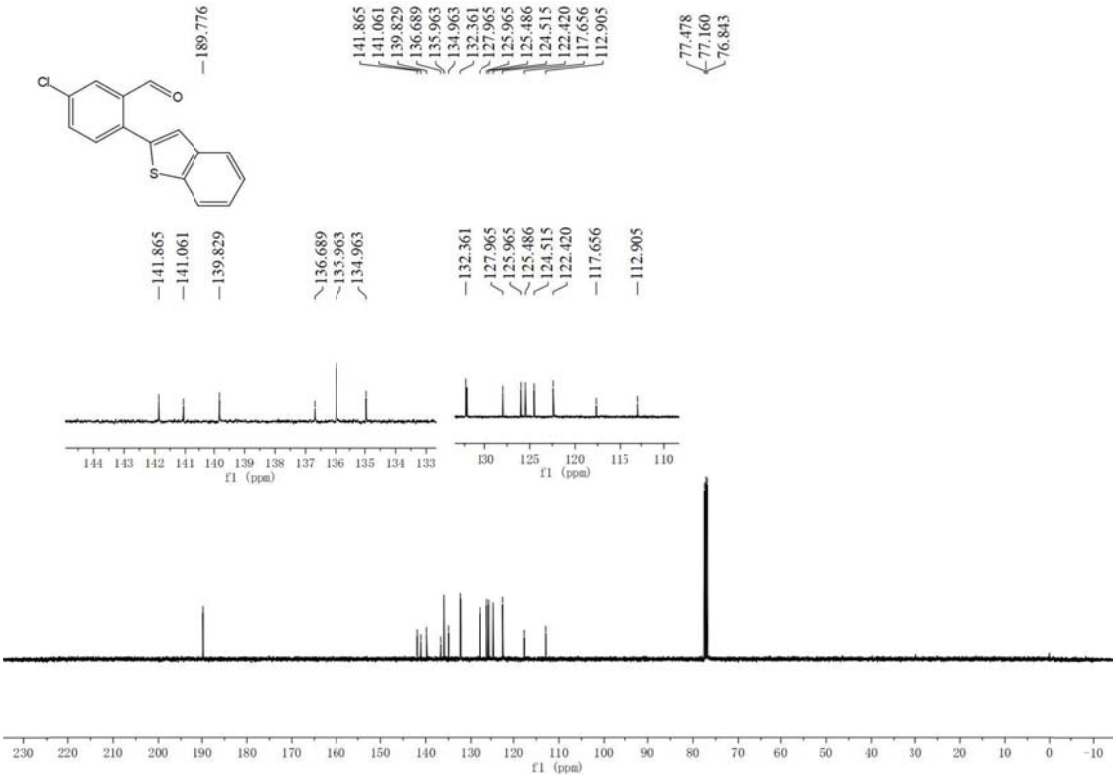
^{13}C NMR spectra of **3e** ($CDCl_3$)



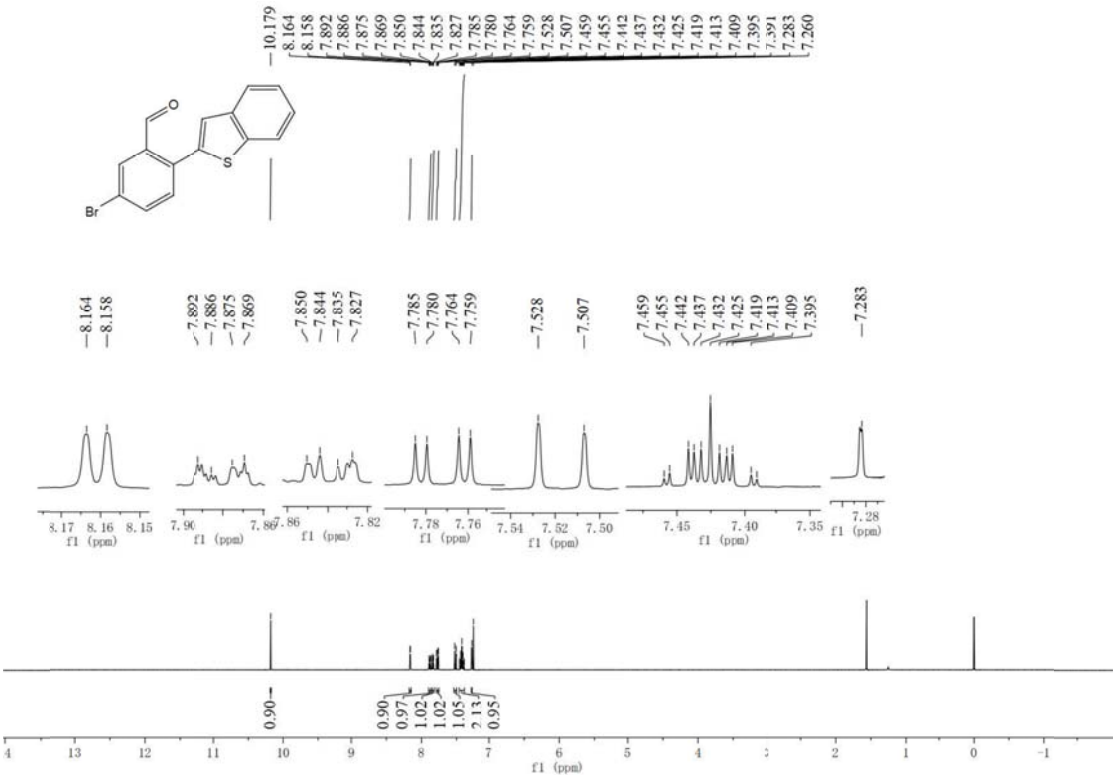
^{1}H NMR spectra of **3f** ($CDCl_3$)



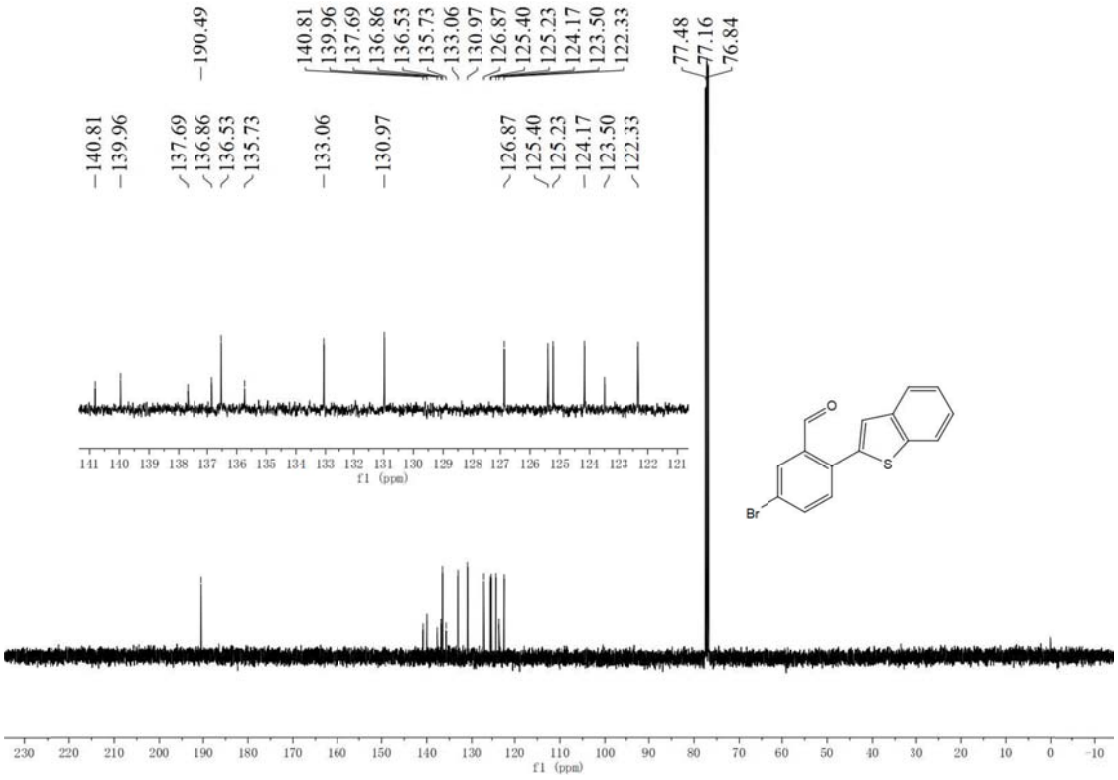
^{13}C NMR spectra of **3f** ($CDCl_3$)



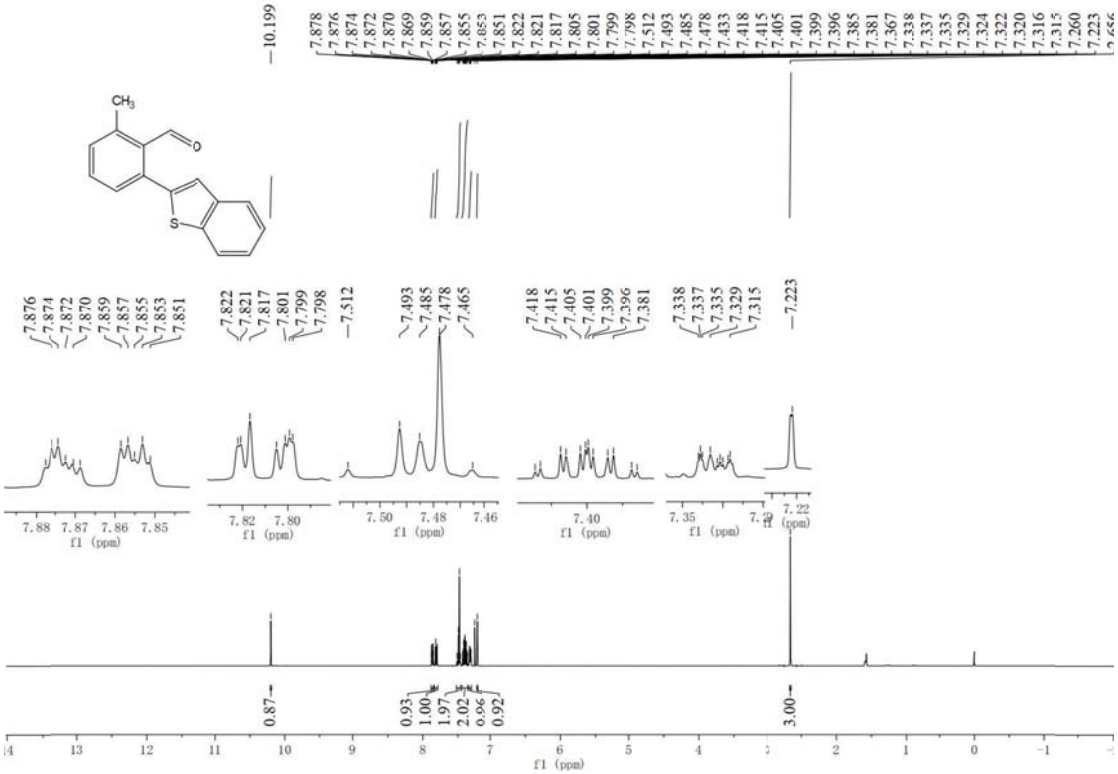
^{1}H NMR spectra of **3g** ($CDCl_3$)



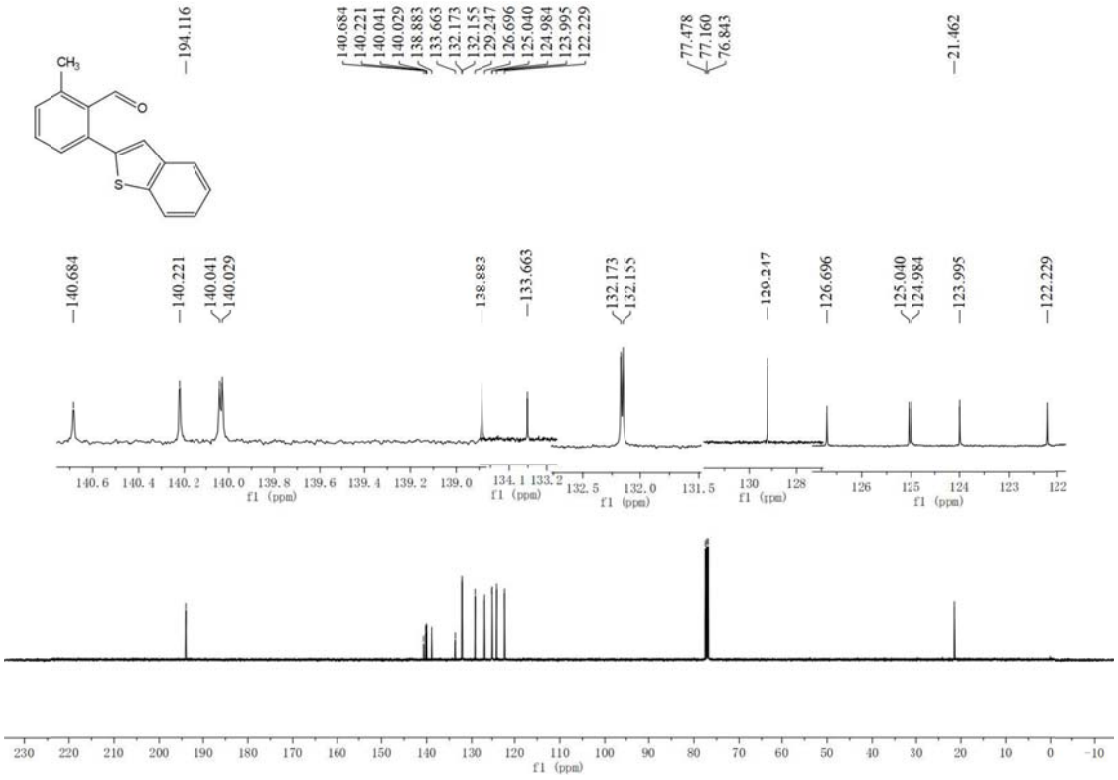
^{13}C NMR spectra of **3g** ($CDCl_3$)



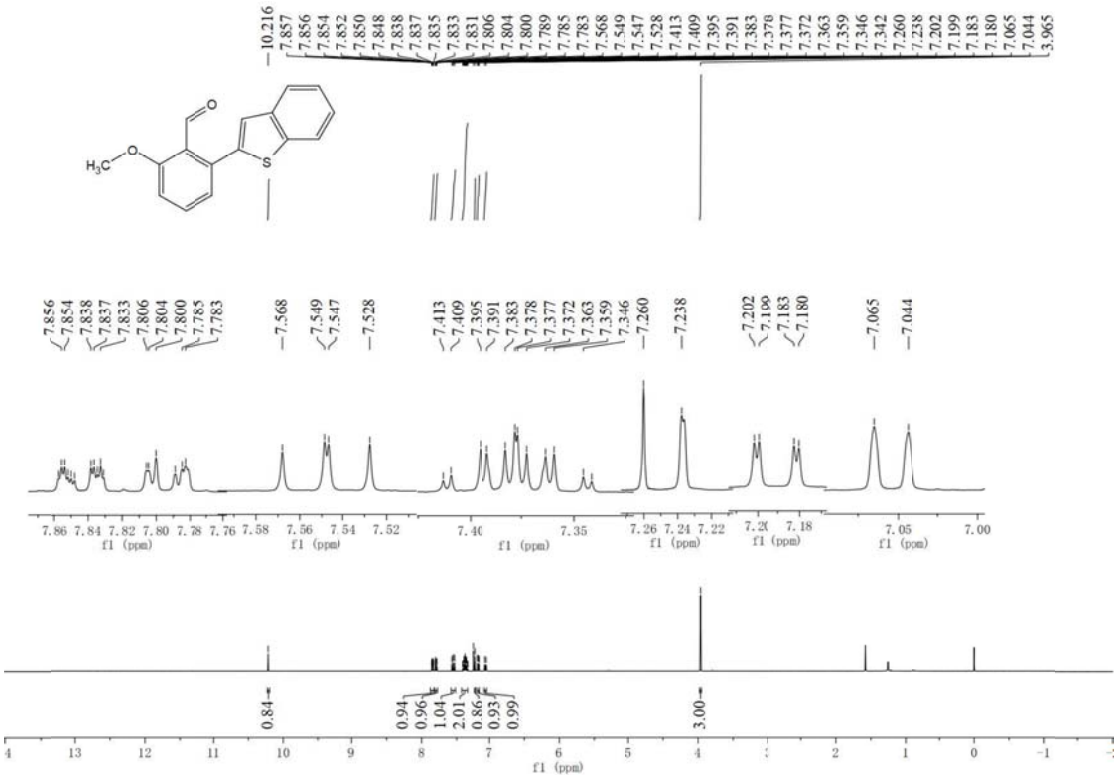
^{1}H NMR spectra of **3h** ($CDCl_3$)



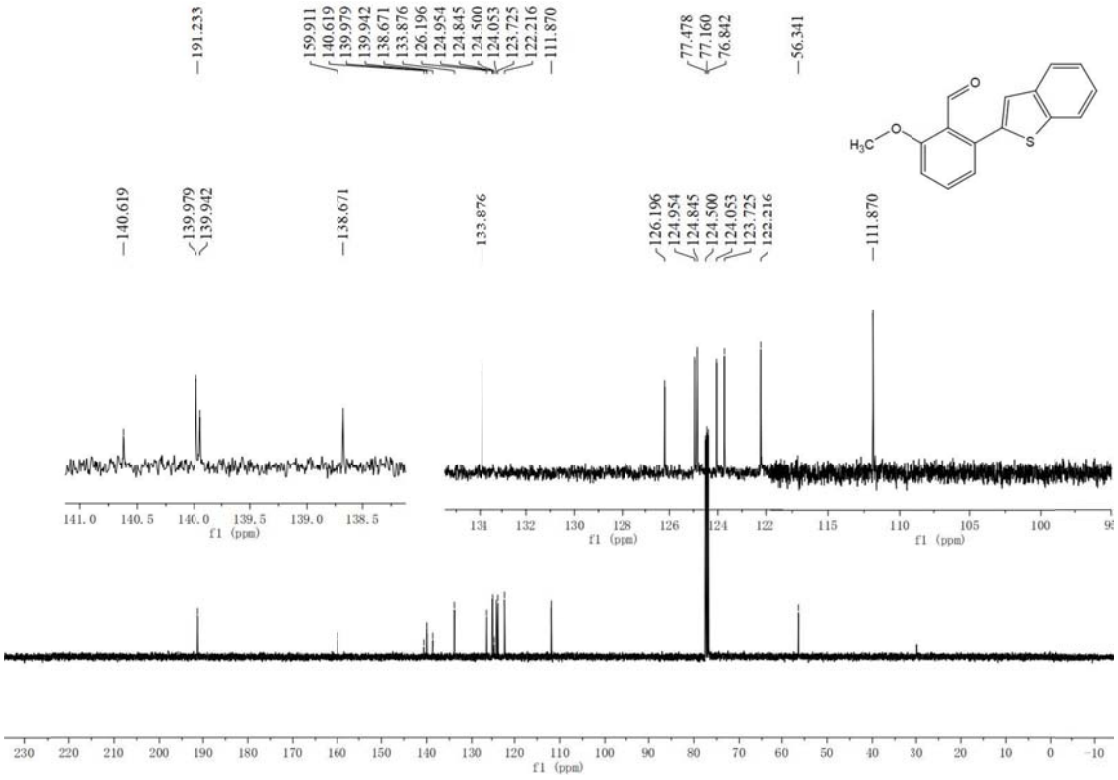
^{13}C NMR spectra of **3h** ($CDCl_3$)



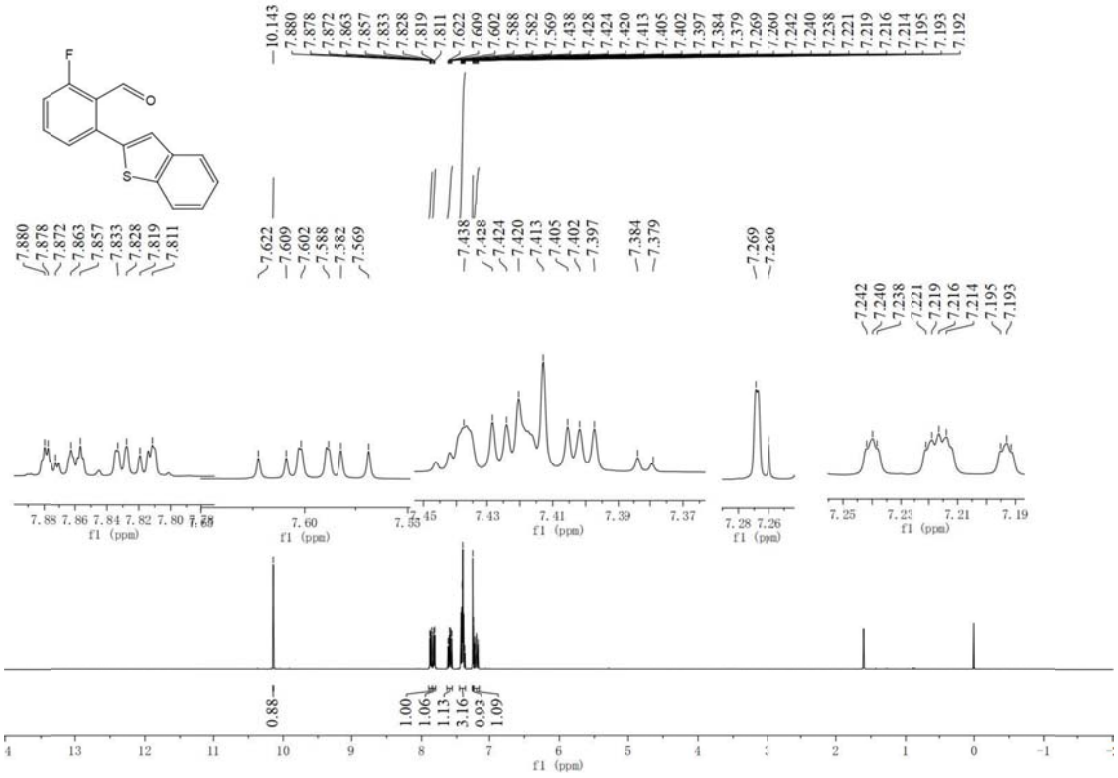
^{1}H NMR spectra of **3i** ($CDCl_3$)



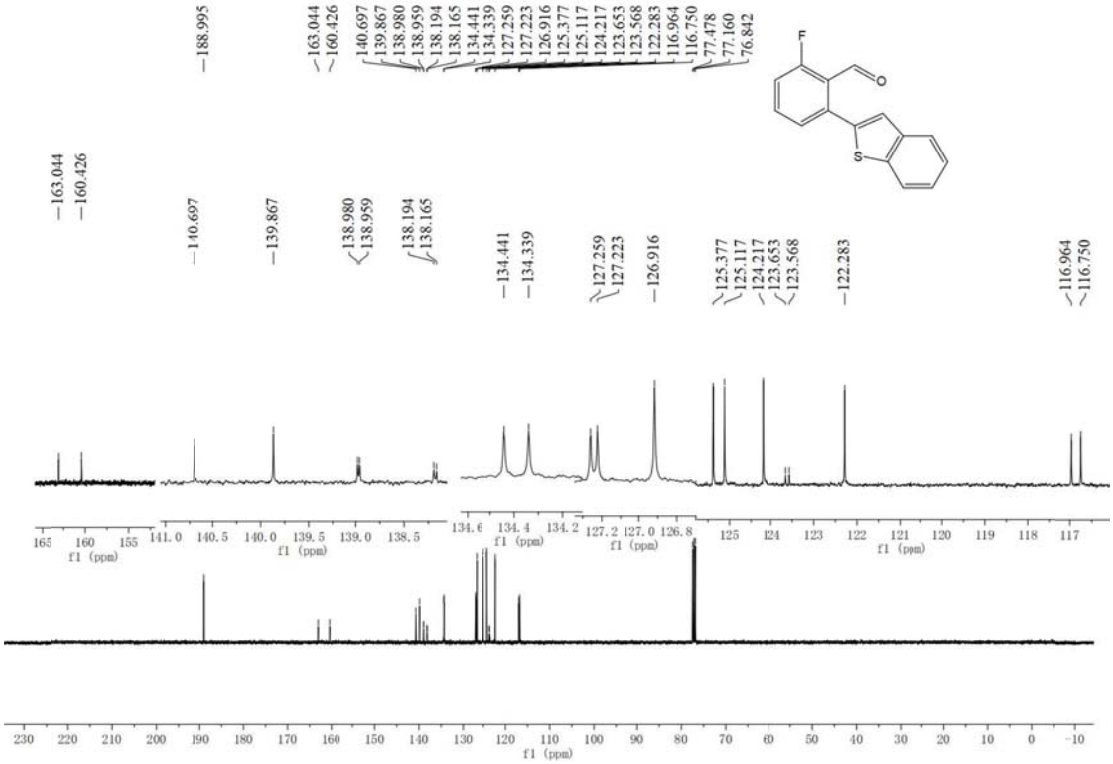
^{13}C NMR spectra of **3i** ($CDCl_3$)



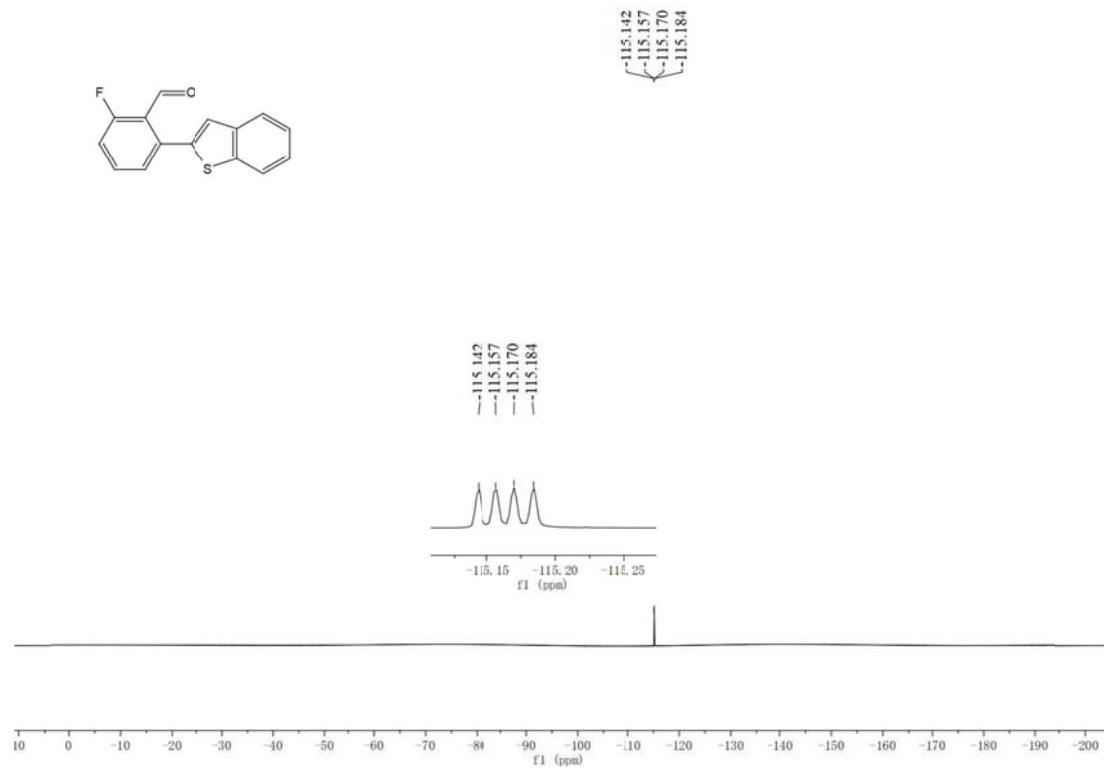
^{1}H NMR spectra of **3j** ($CDCl_3$)



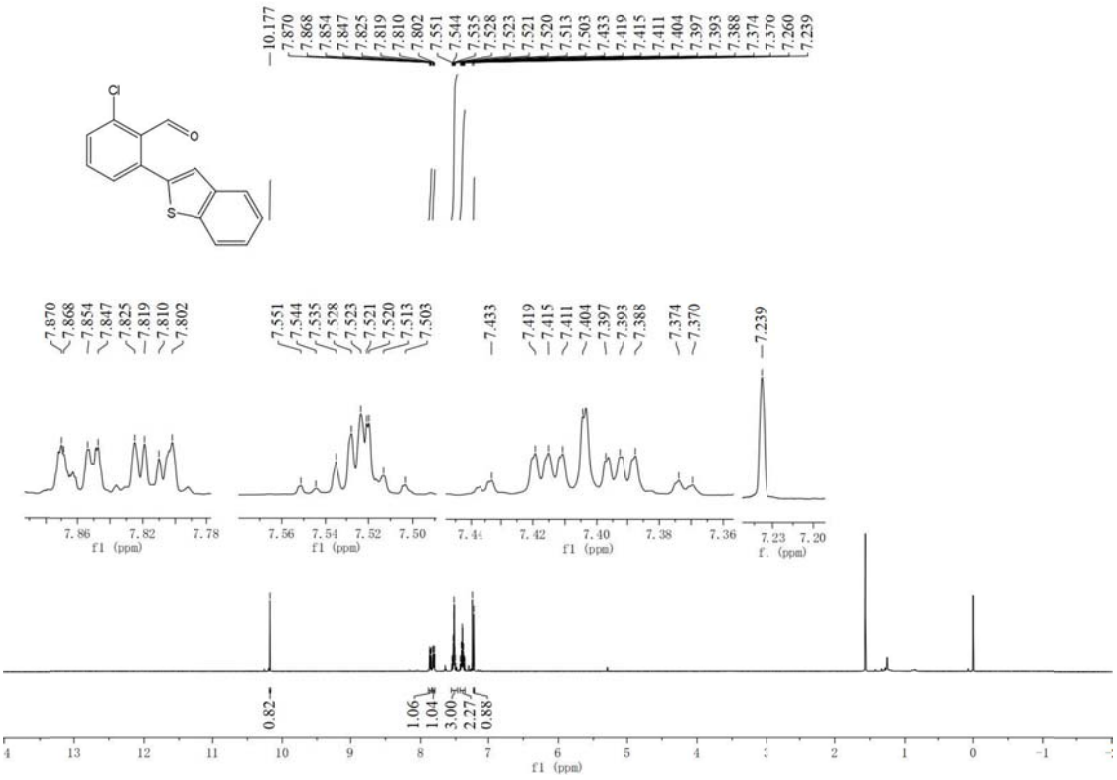
^{13}C NMR spectra of **3j** ($CDCl_3$)



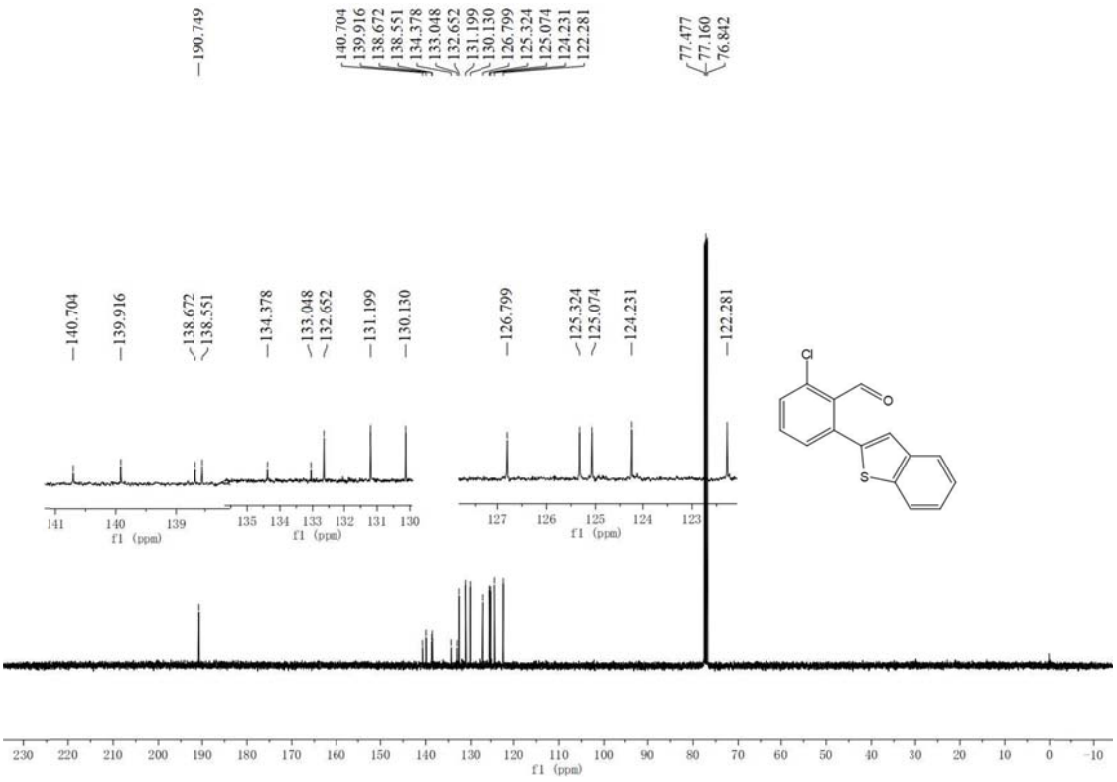
^{19}F NMR spectra of **3j** ($CDCl_3$)



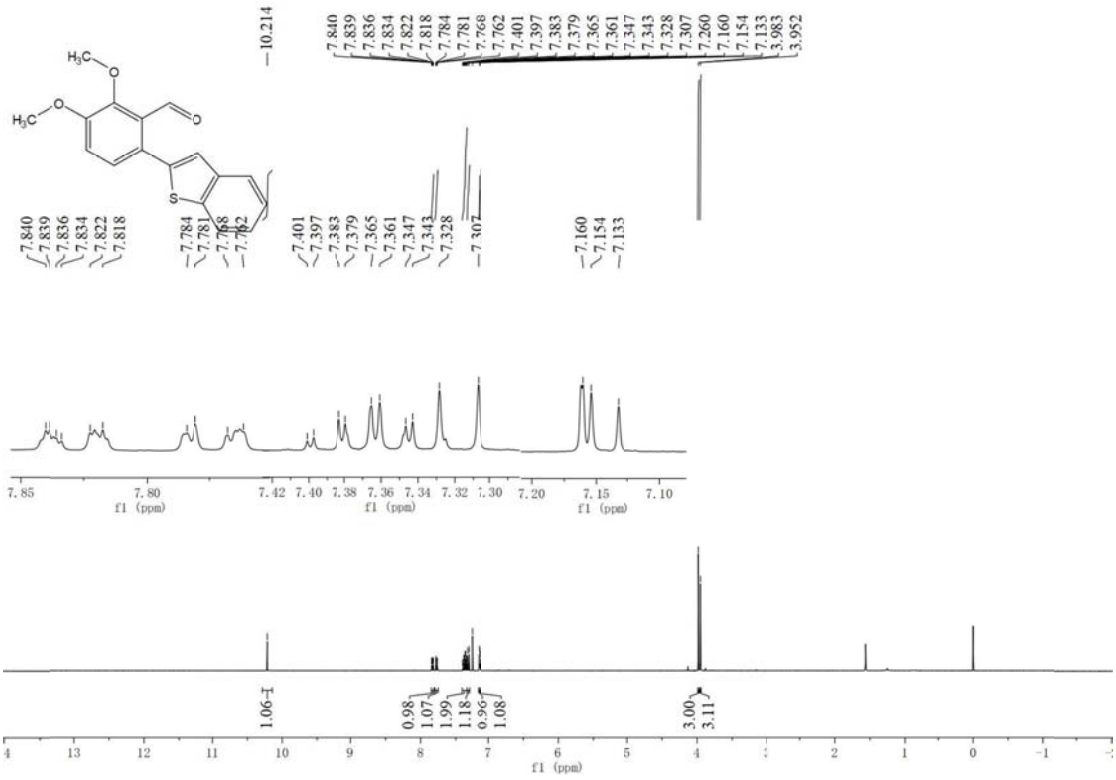
^{1}H NMR spectra of **3k** ($CDCl_3$)



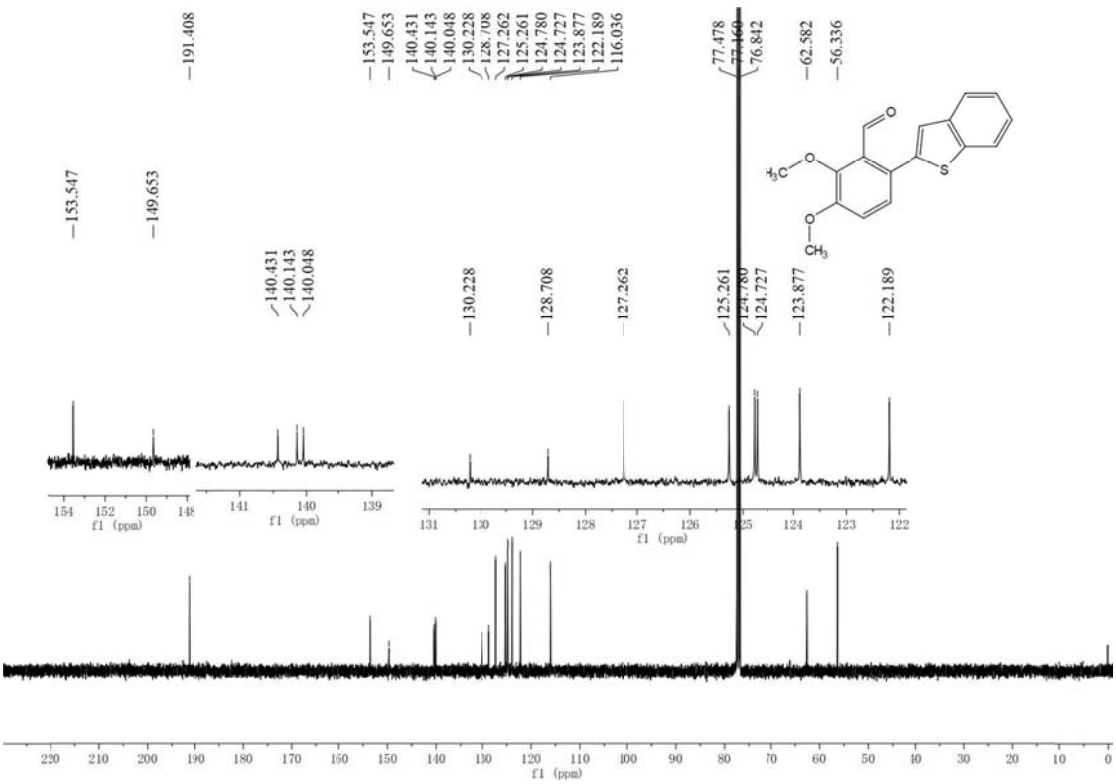
^{13}C NMR spectra of **3k** ($CDCl_3$)



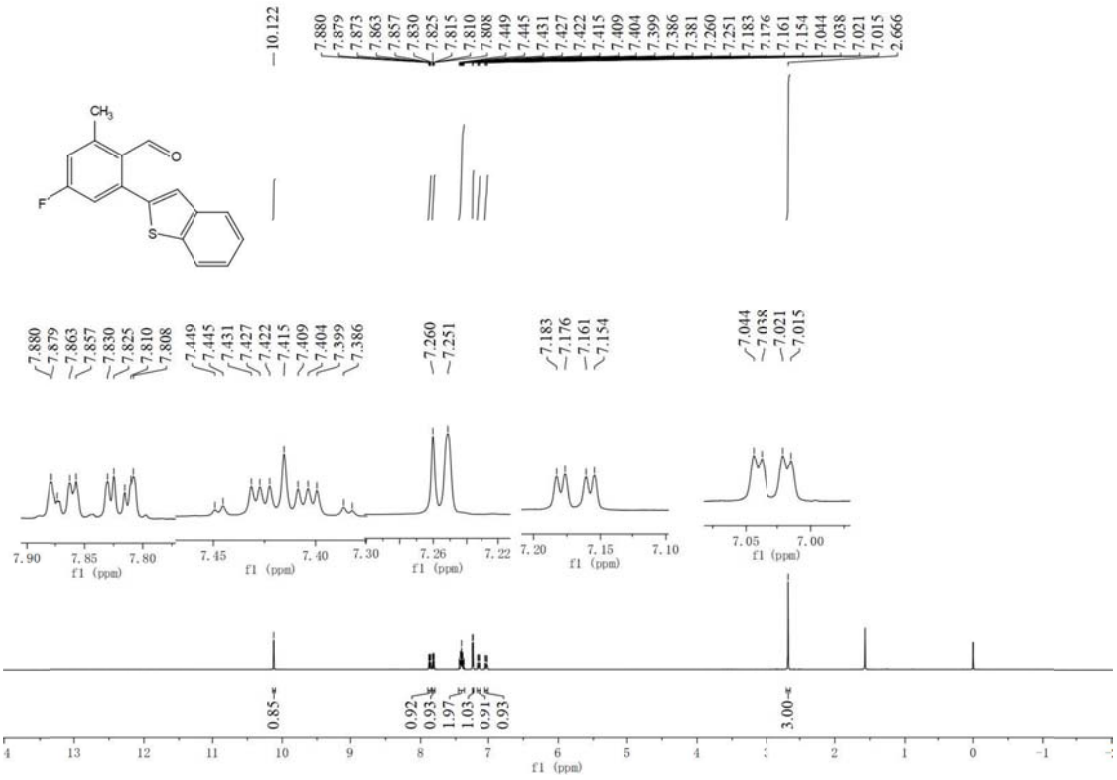
^{1}H NMR spectra of **3l** ($CDCl_3$)



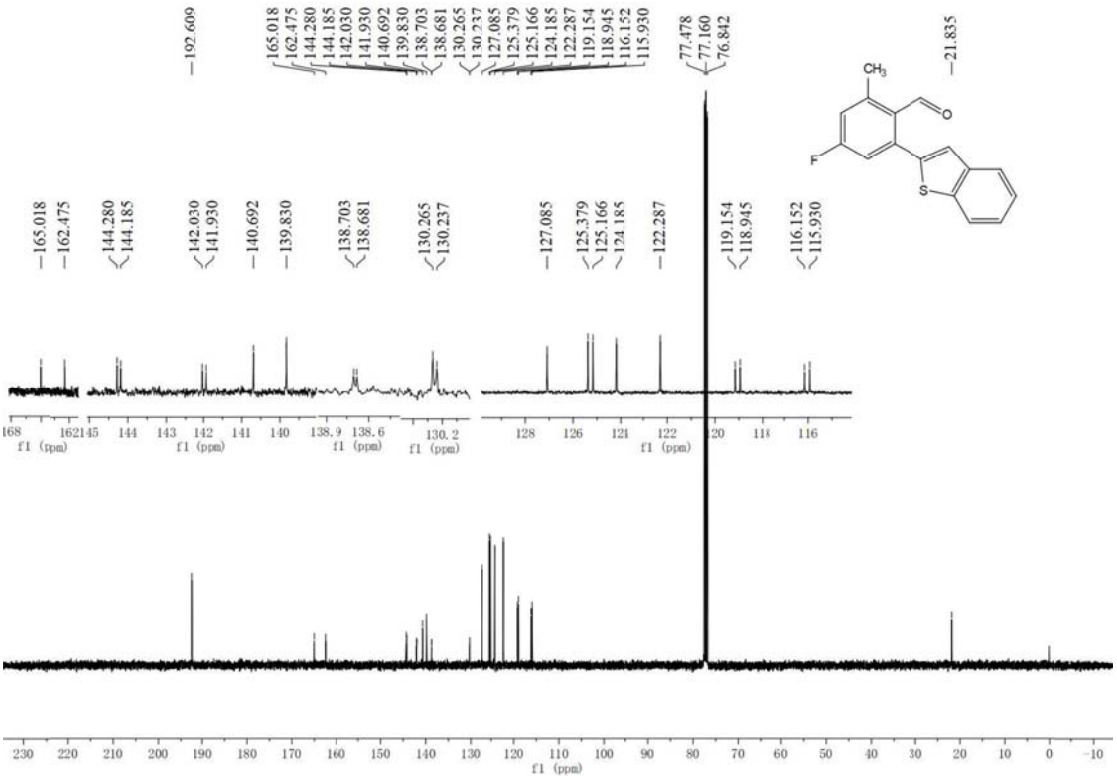
^{13}C NMR spectra of **3l** ($CDCl_3$)



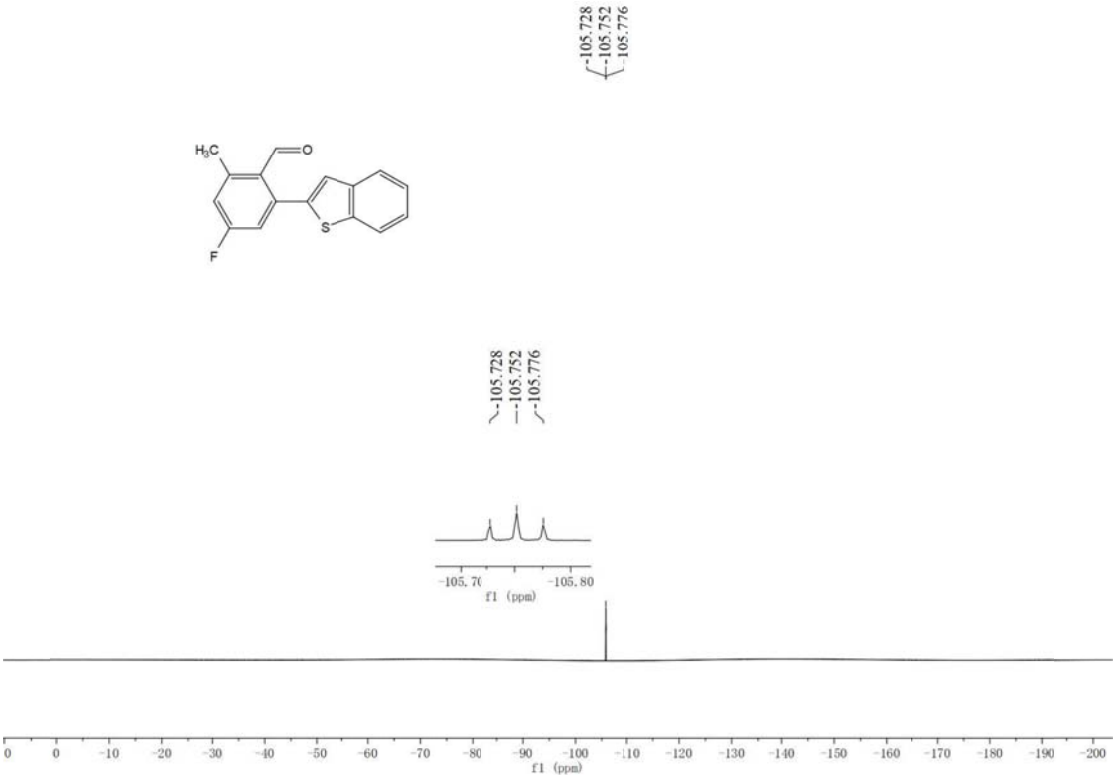
^{1}H NMR spectra of **3m** ($CDCl_3$)



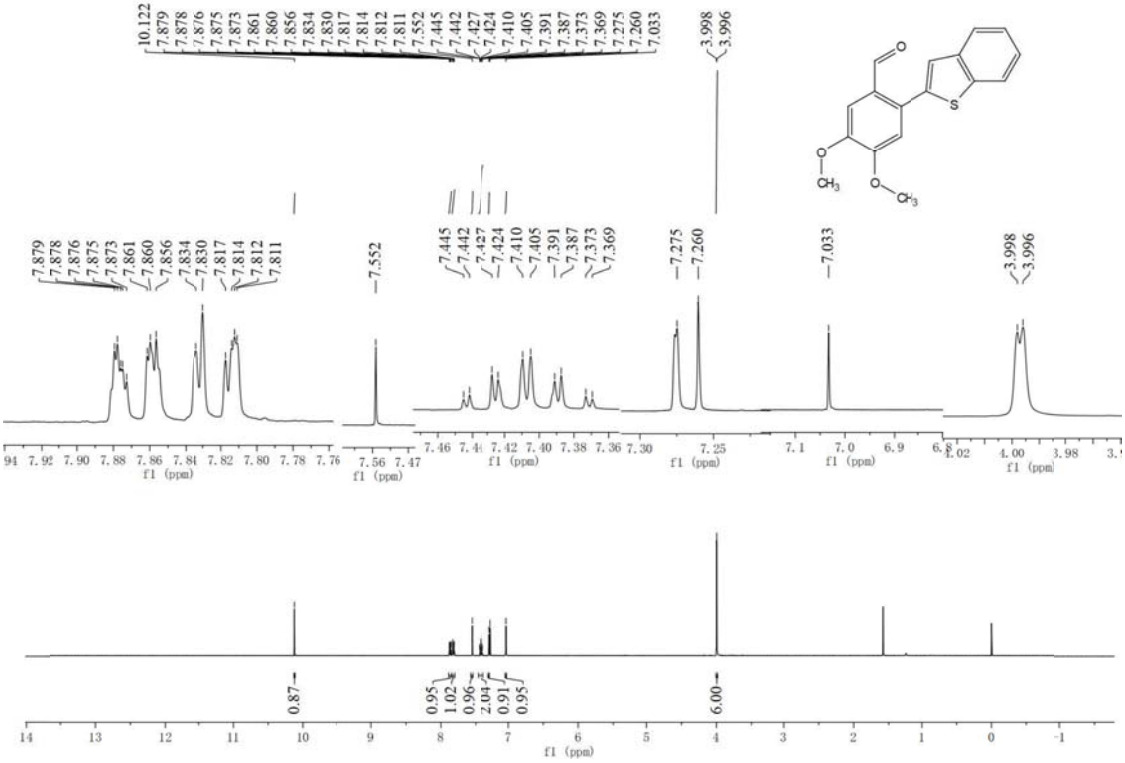
^{13}C NMR spectra of **3m** ($CDCl_3$)



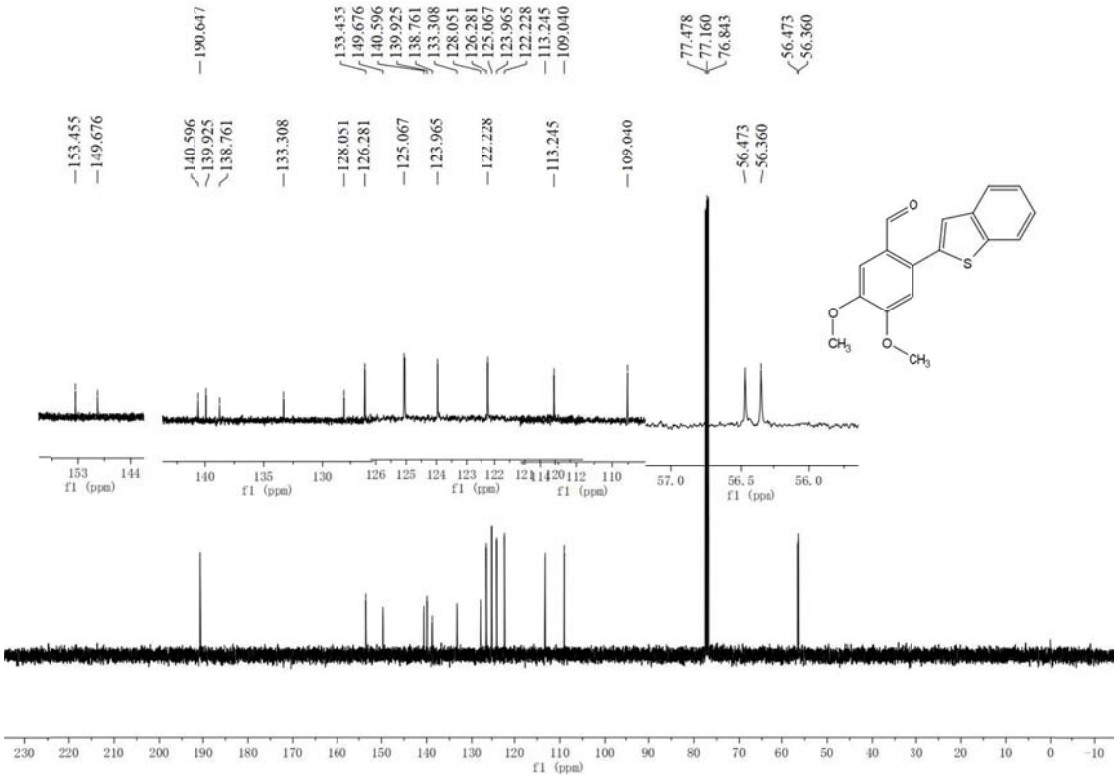
^{19}F NMR spectra of **3m** ($CDCl_3$)



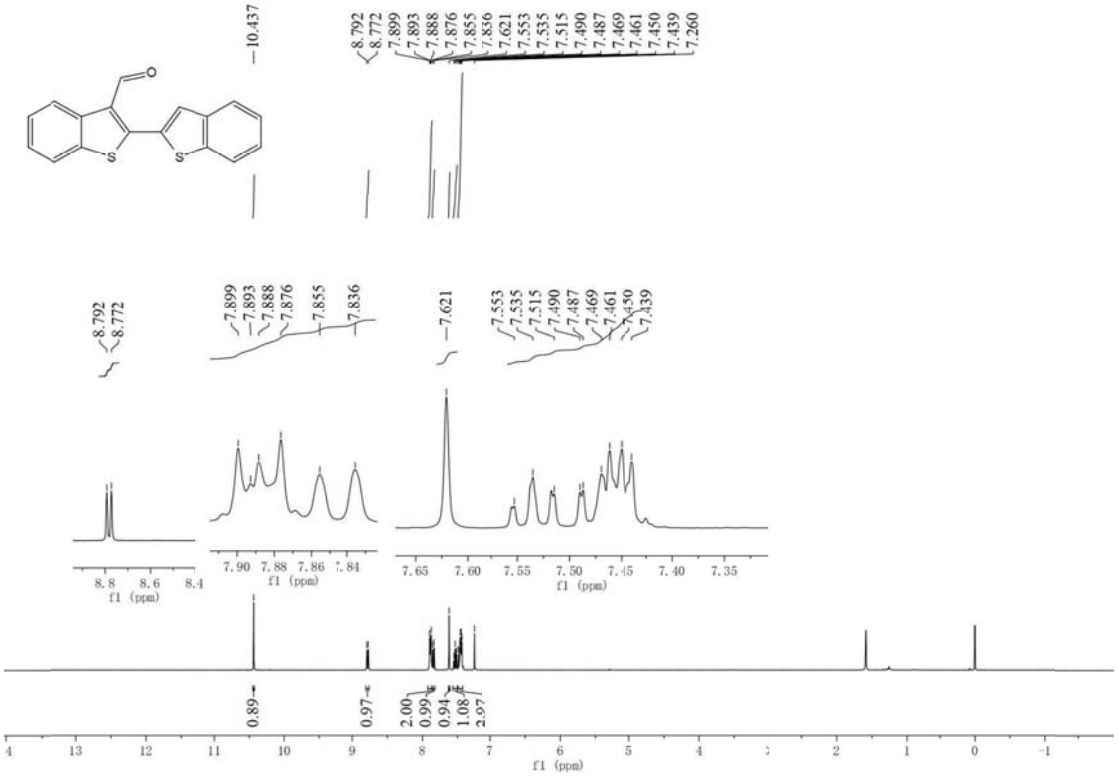
^{1}H NMR spectra of **3n** ($CDCl_3$)



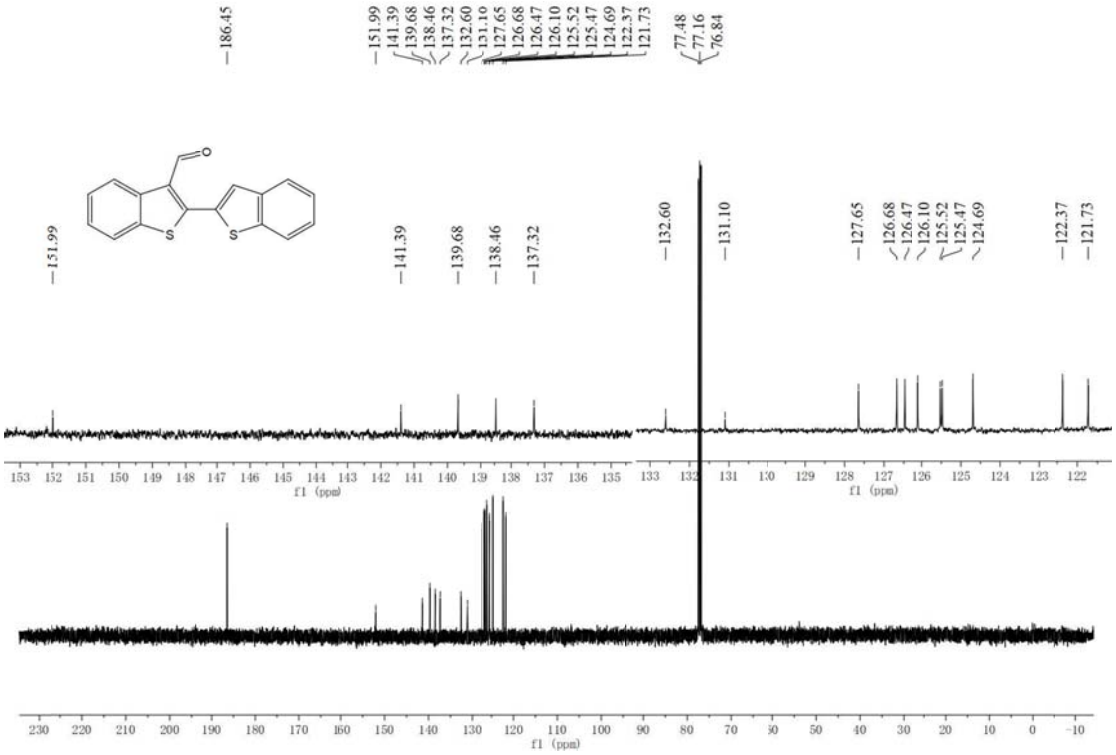
^{13}C NMR spectra of **3n** ($CDCl_3$)



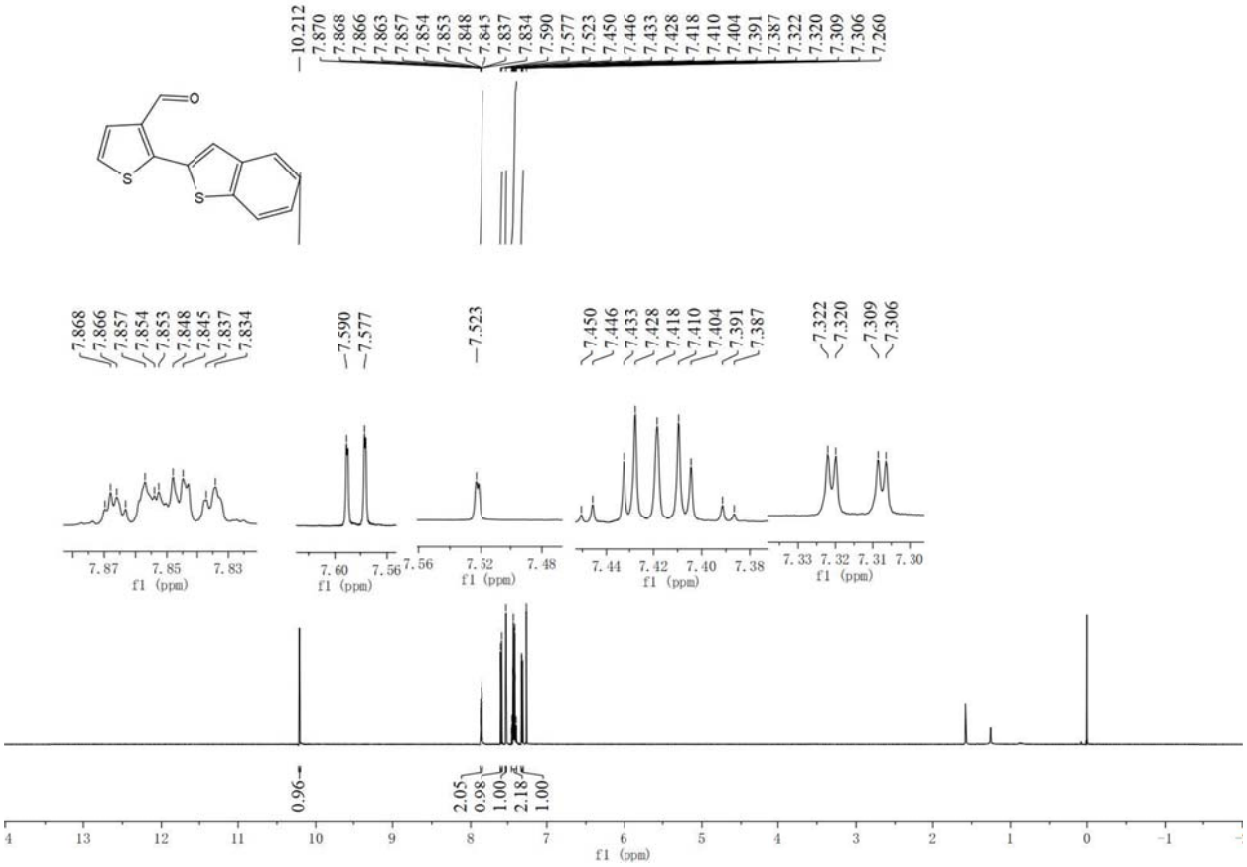
^{1}H NMR spectra of **3o** ($CDCl_3$)



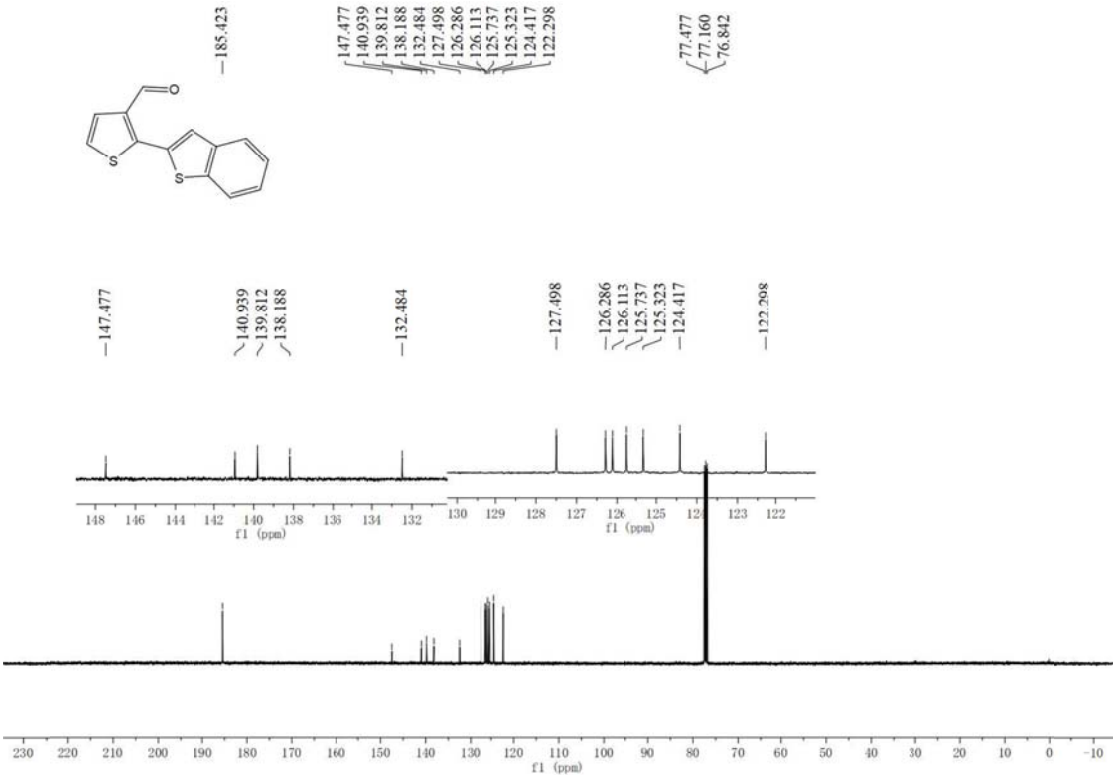
^{13}C NMR spectra of **3o** ($CDCl_3$)



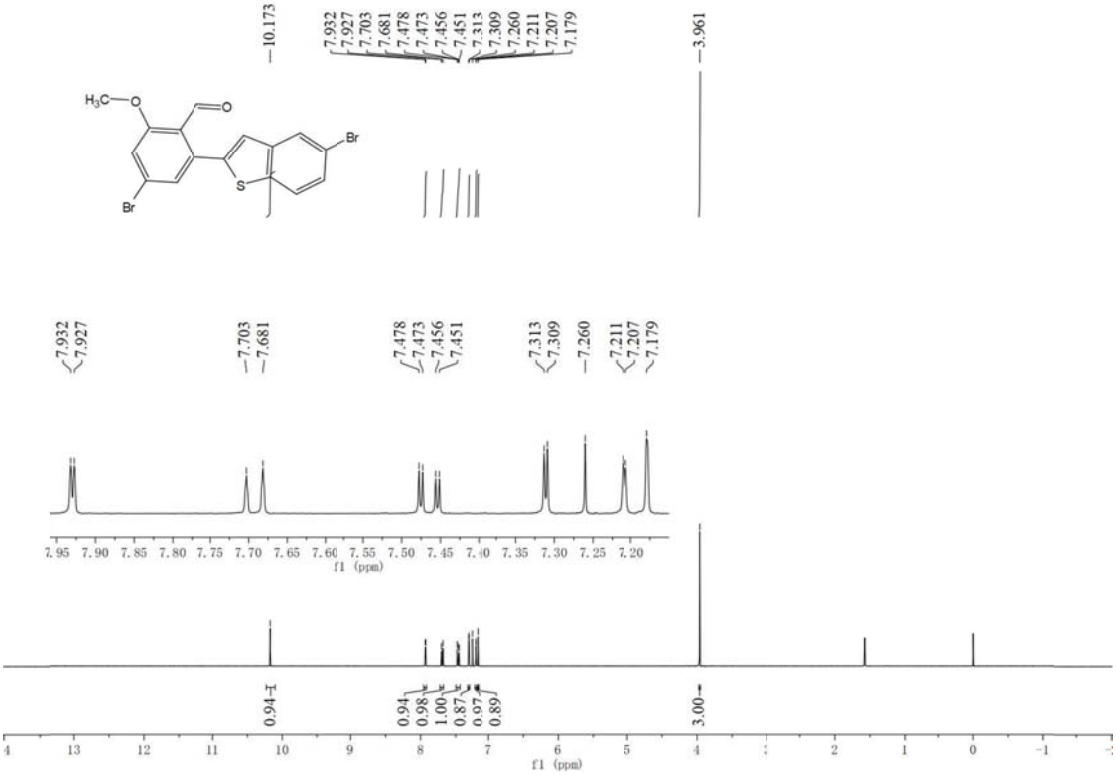
^{1}H NMR spectra of **3p** ($CDCl_3$)



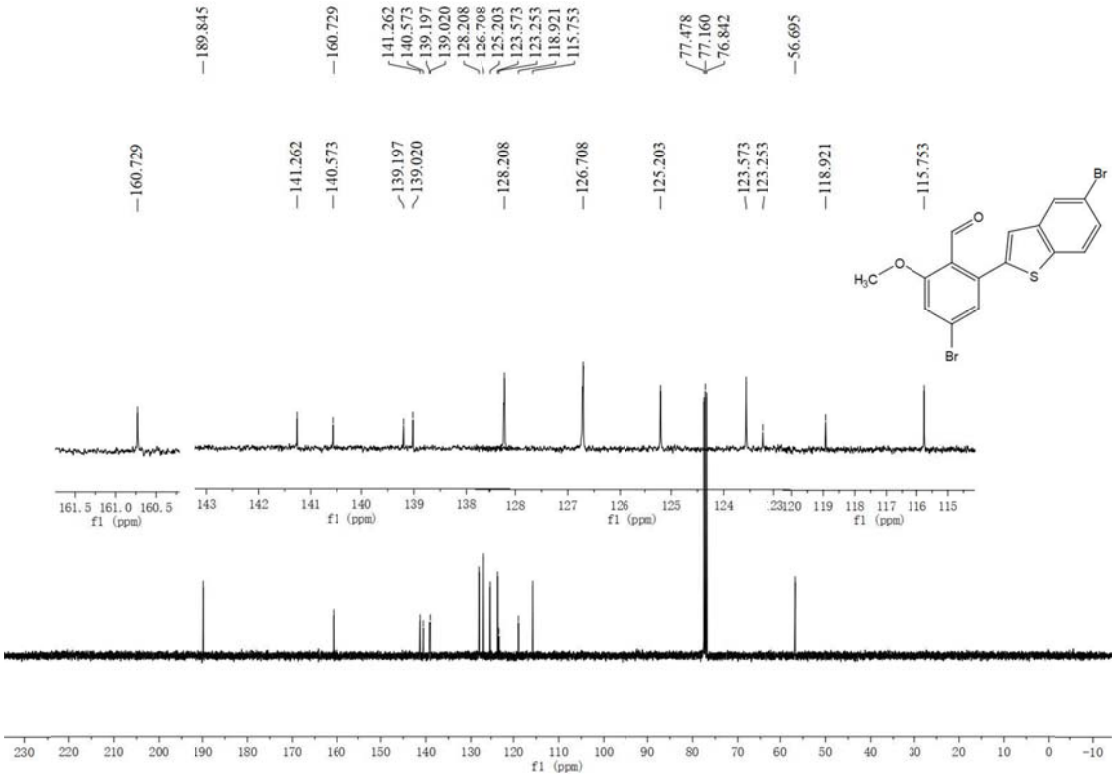
^{13}C NMR spectra of **3p** ($CDCl_3$)



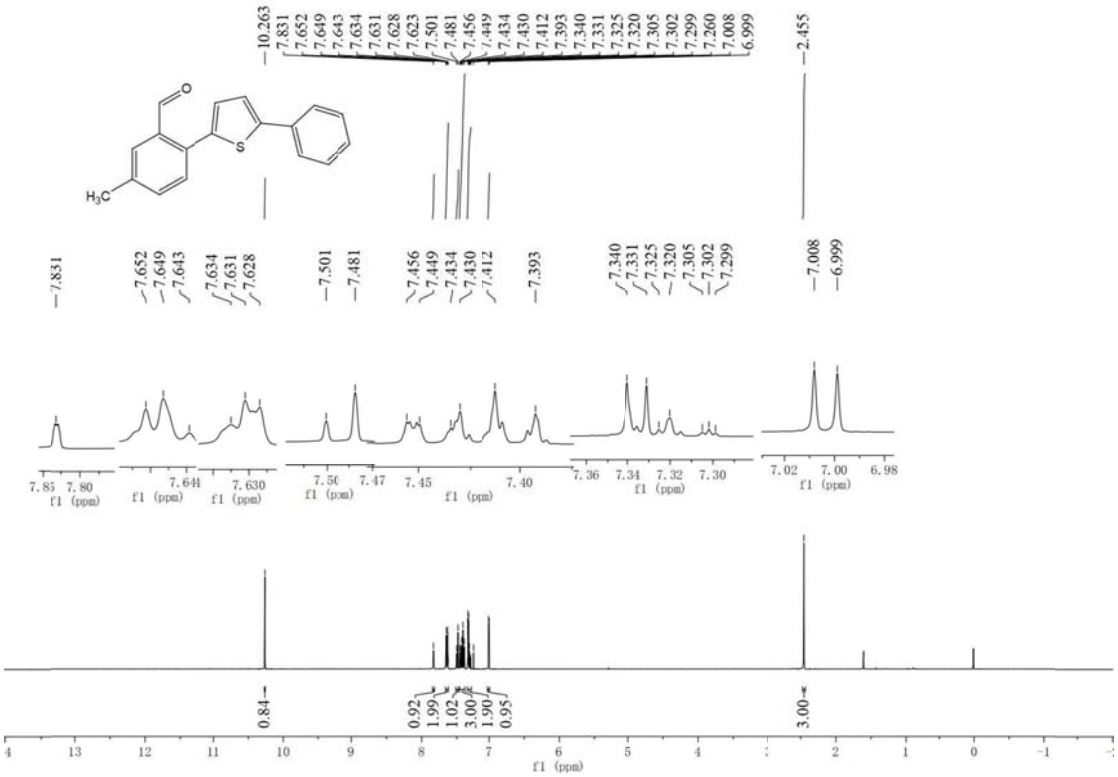
^{1}H NMR spectra of **3q** ($CDCl_3$)



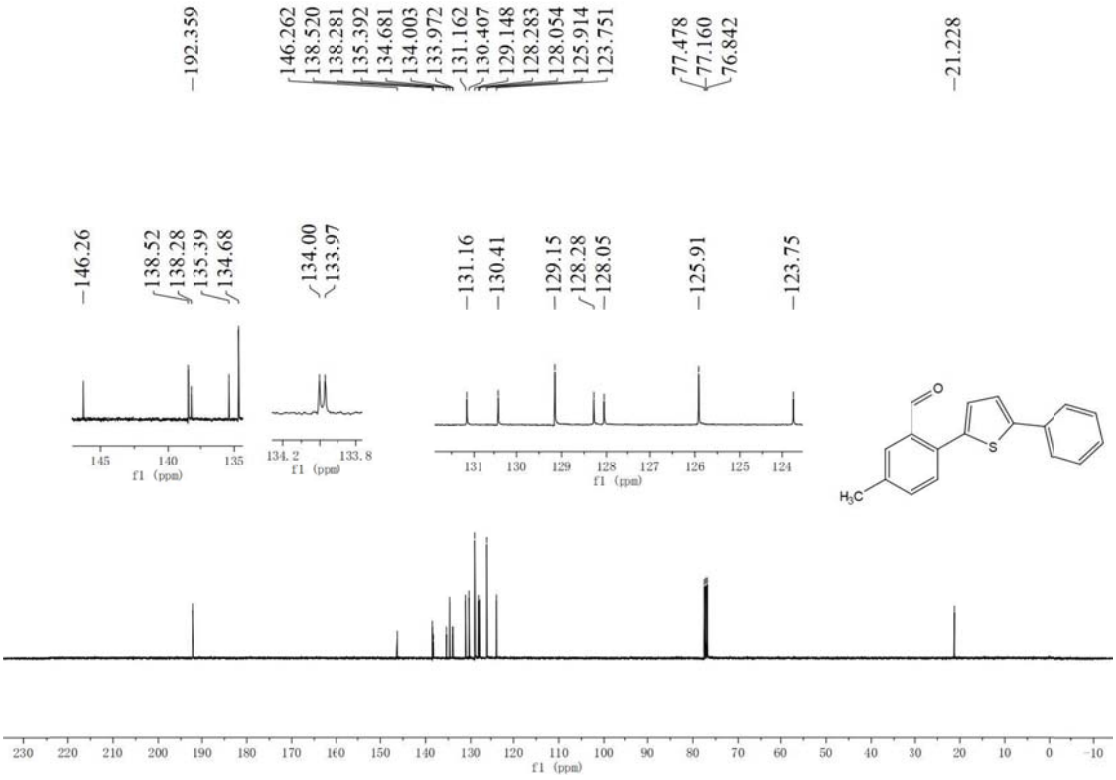
^{13}C NMR spectra of **3q** ($CDCl_3$)



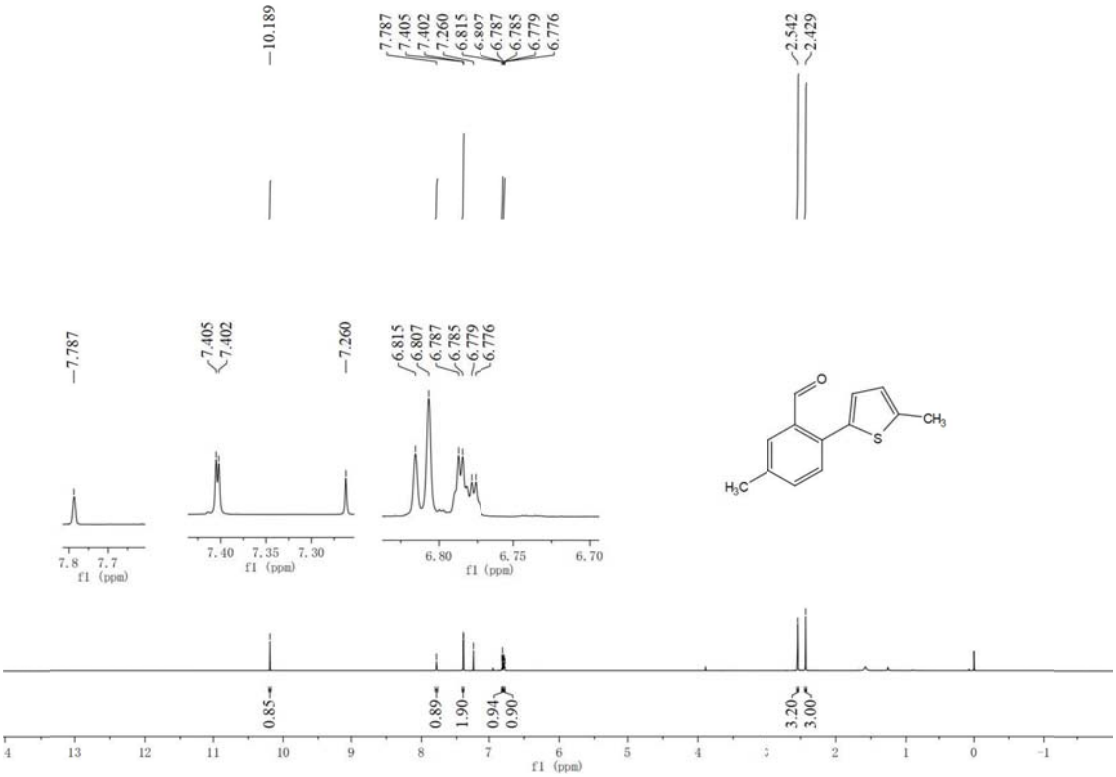
^{1}H NMR spectra of **4a** ($CDCl_3$)



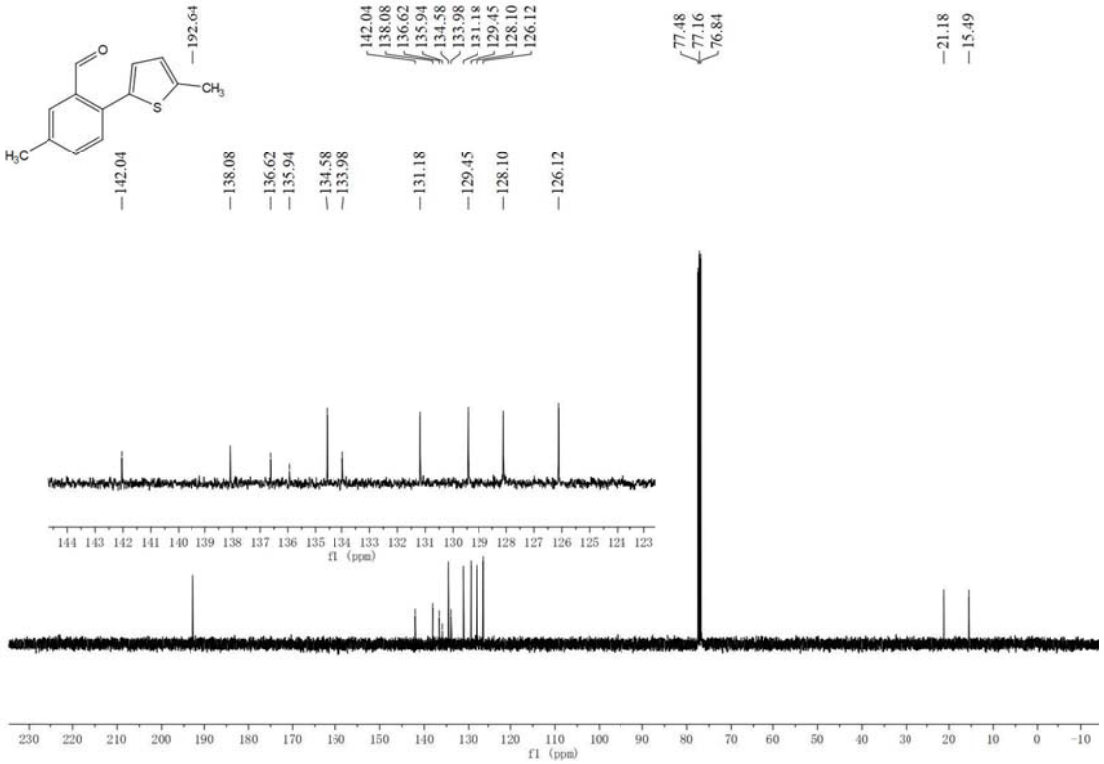
^{13}C NMR spectra of **4a** ($CDCl_3$)



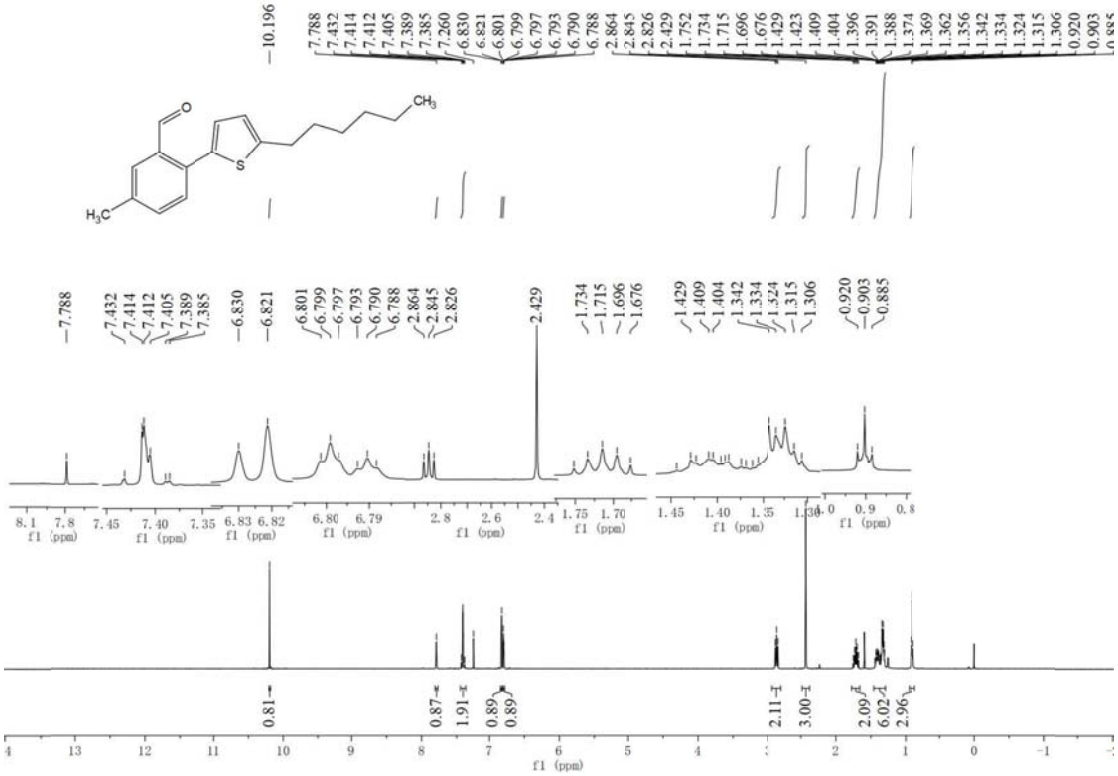
^{1}H NMR spectra of **4b** ($CDCl_3$)



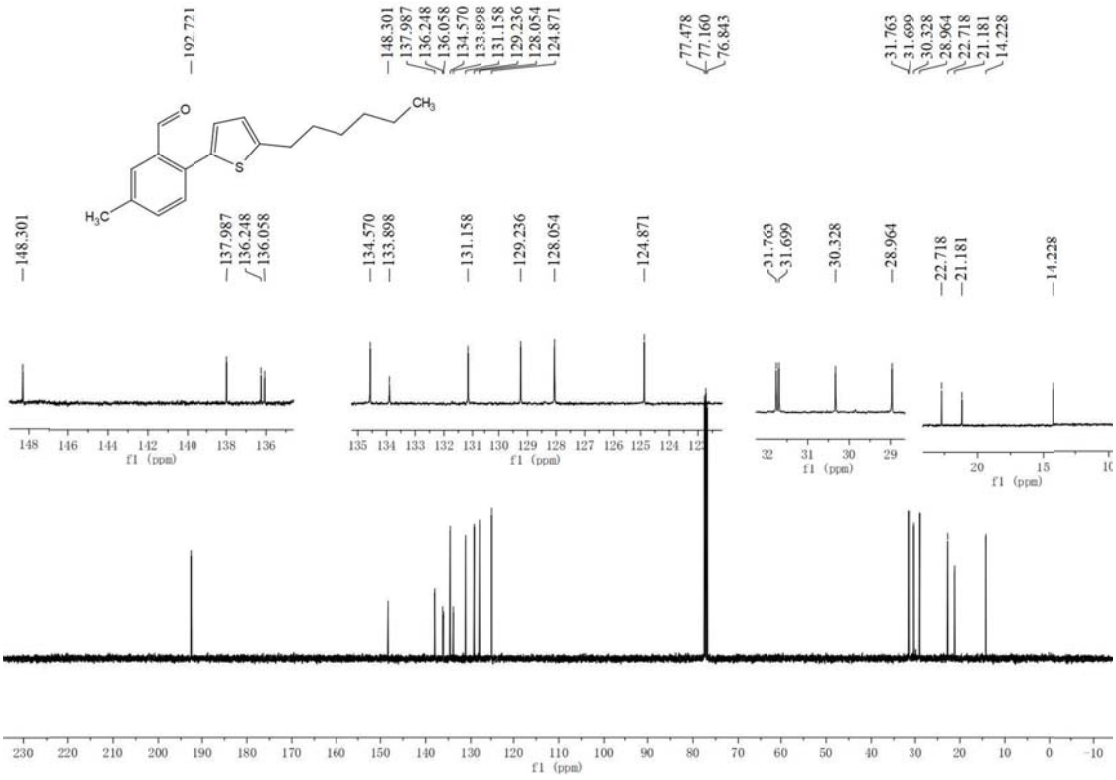
^{13}C NMR spectra of **4b** ($CDCl_3$)



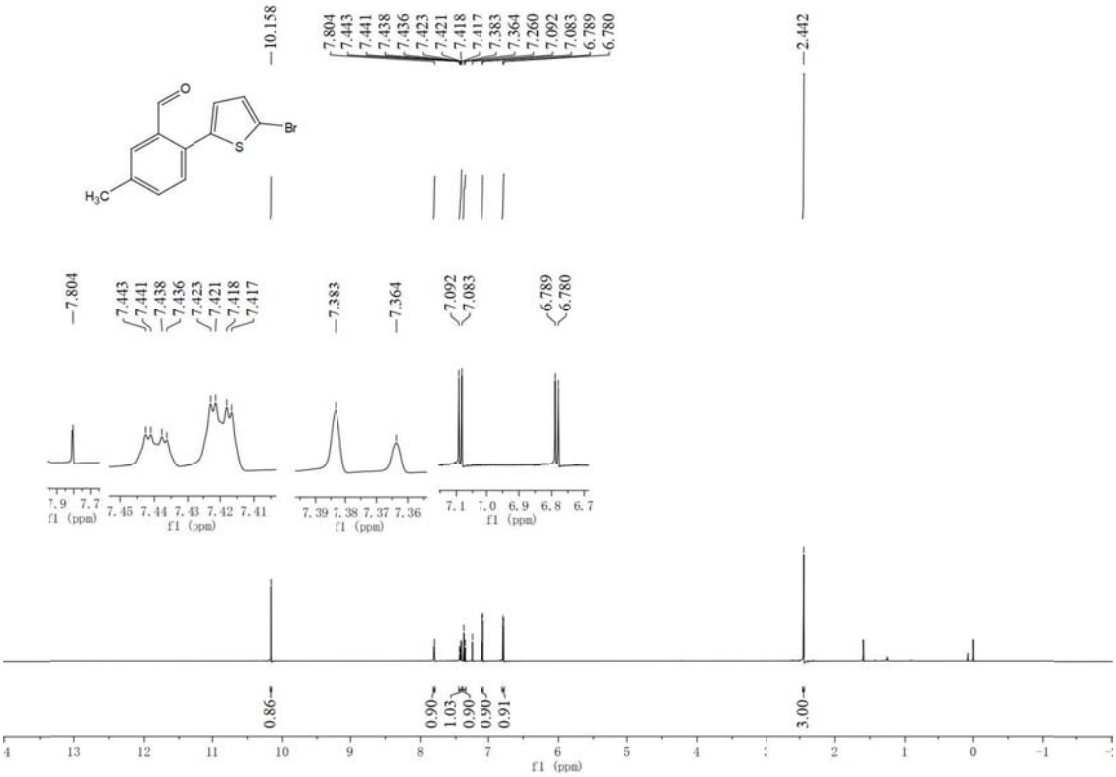
^{1}H NMR spectra of **4c** ($CDCl_3$)



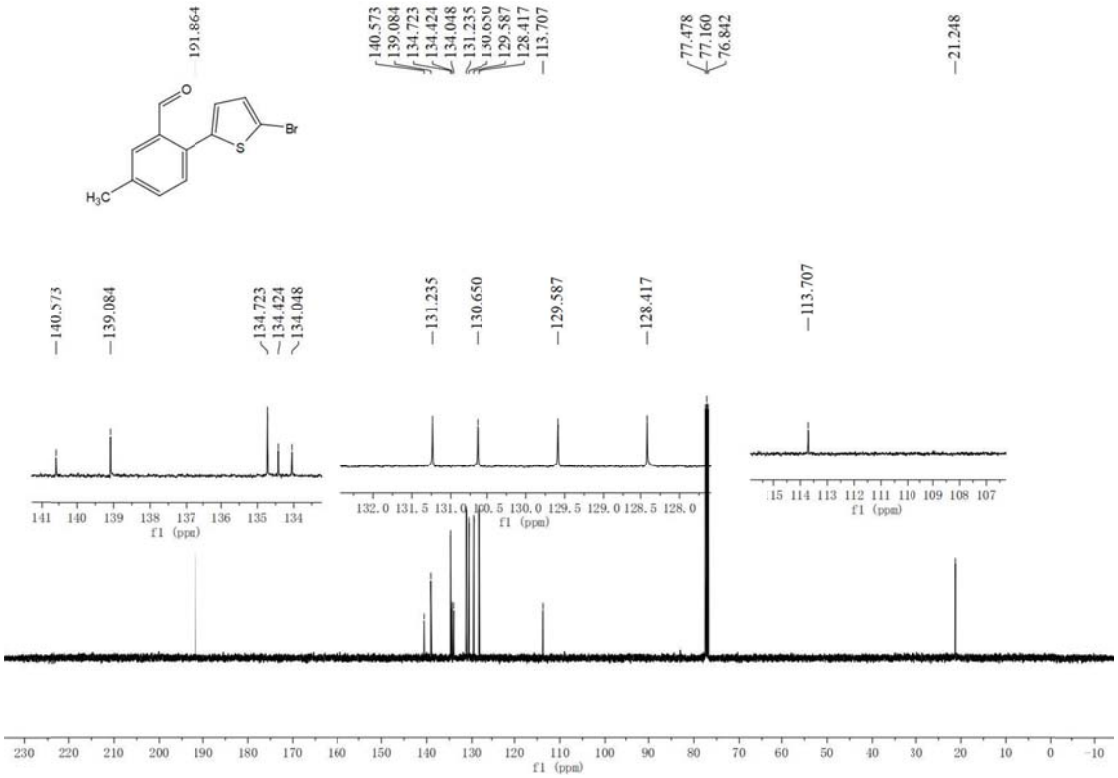
^{13}C NMR spectra of **4c** ($CDCl_3$)



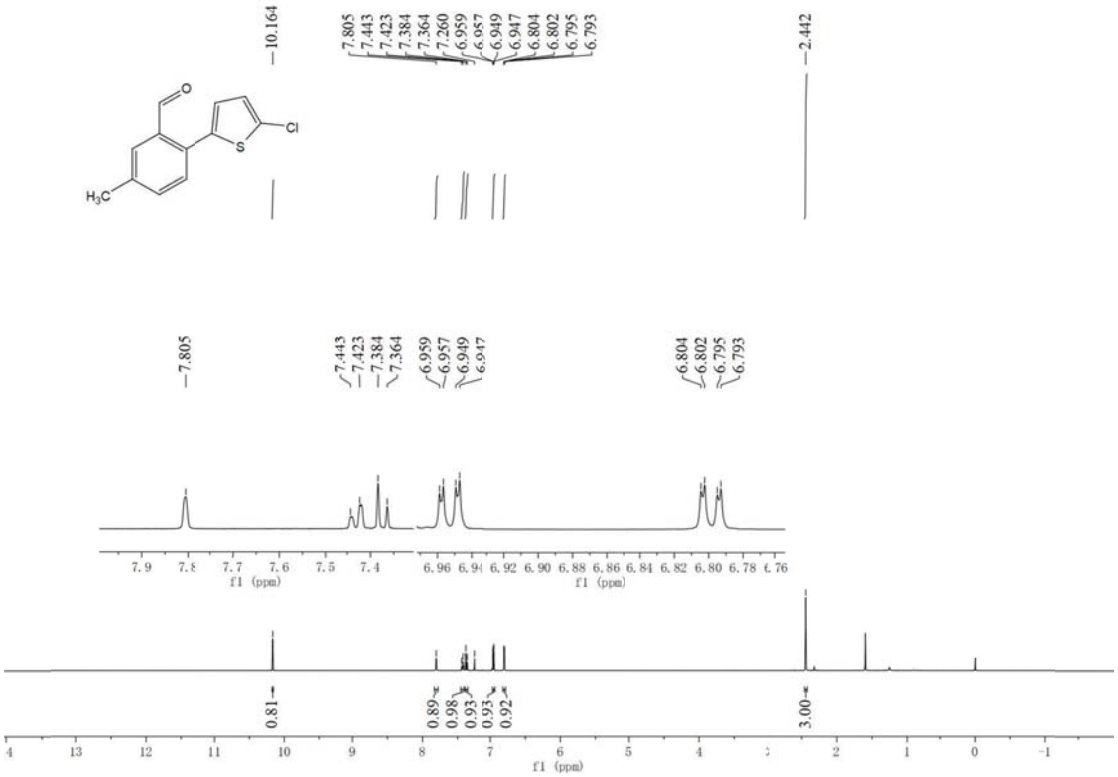
^{1}H NMR spectra of **4d** ($CDCl_3$)



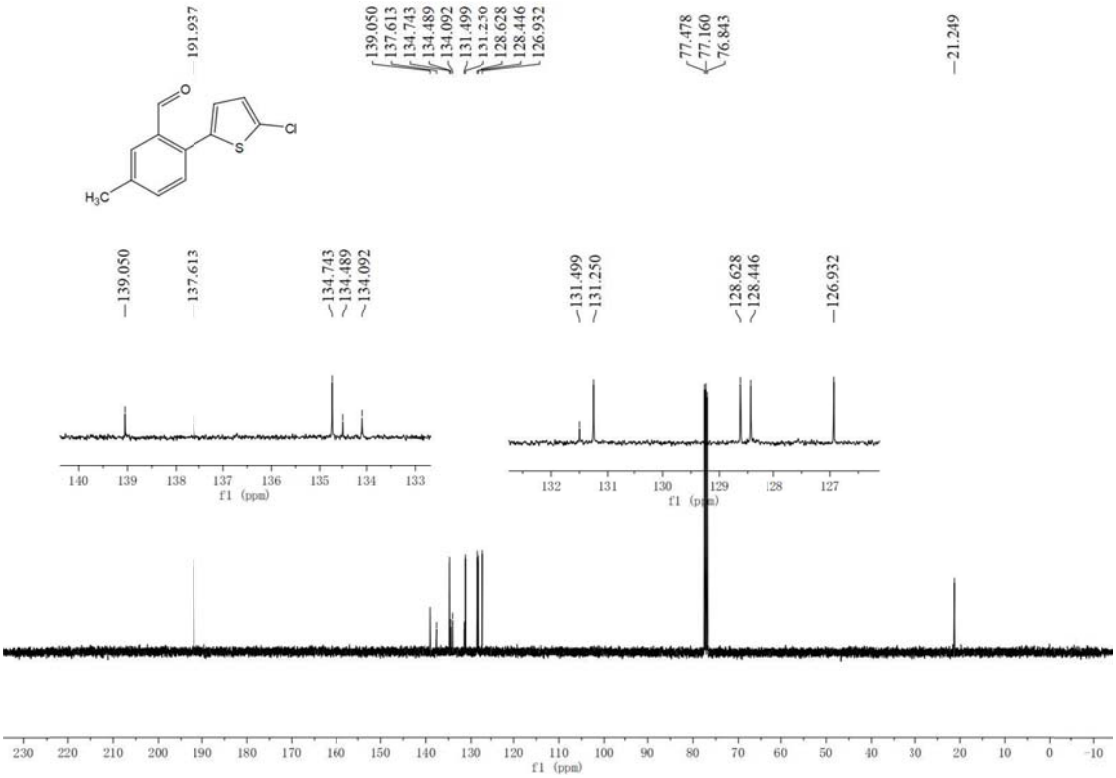
^{13}C NMR spectra of **4d** ($CDCl_3$)



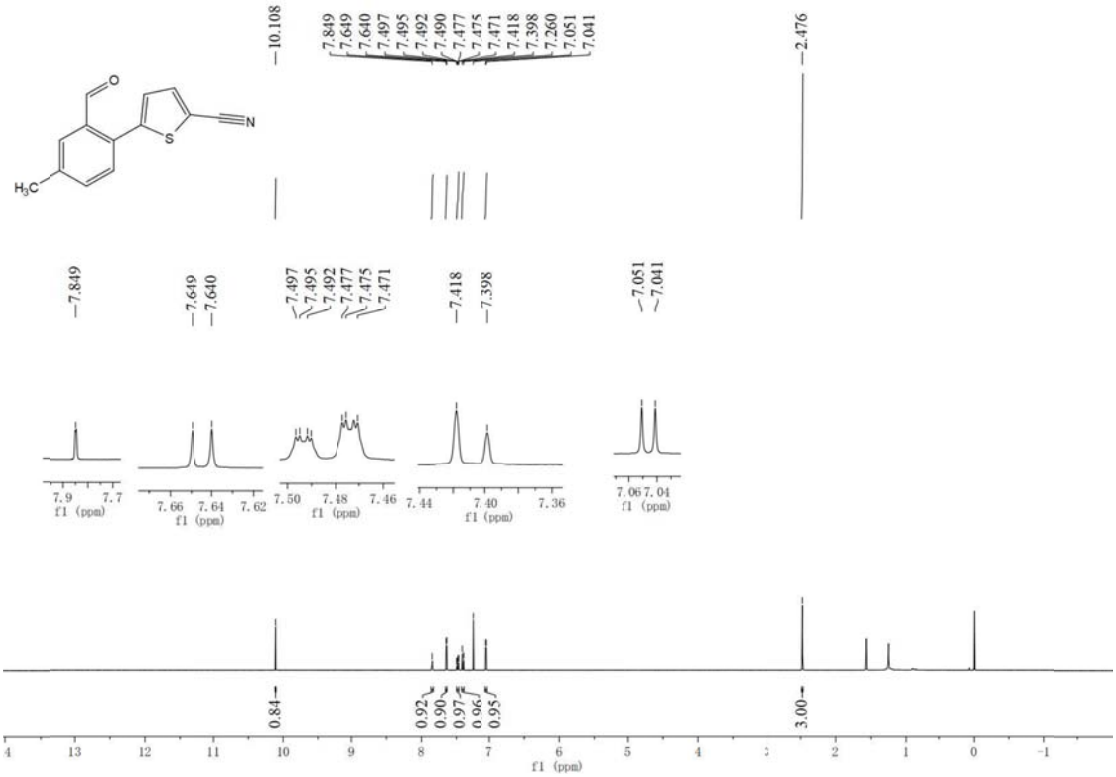
^{1}H NMR spectra of **4e** ($CDCl_3$)



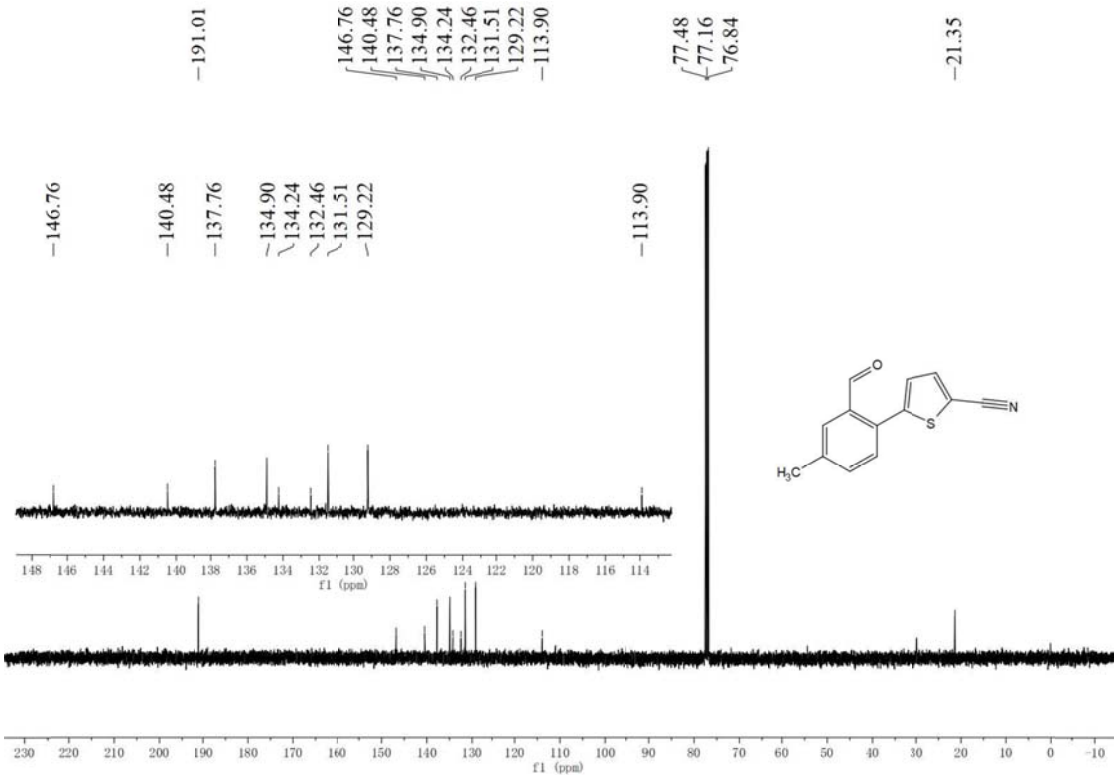
^{13}C NMR spectra of **4e** ($CDCl_3$)



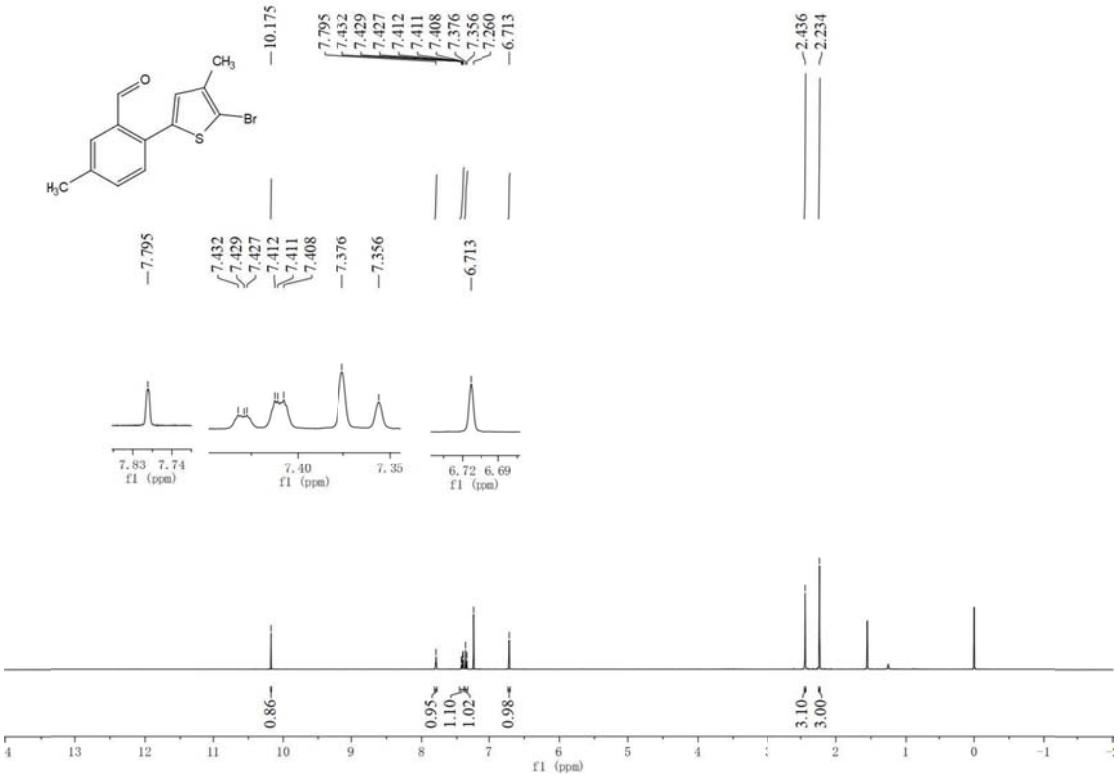
^{1}H NMR spectra of **4f** ($CDCl_3$)



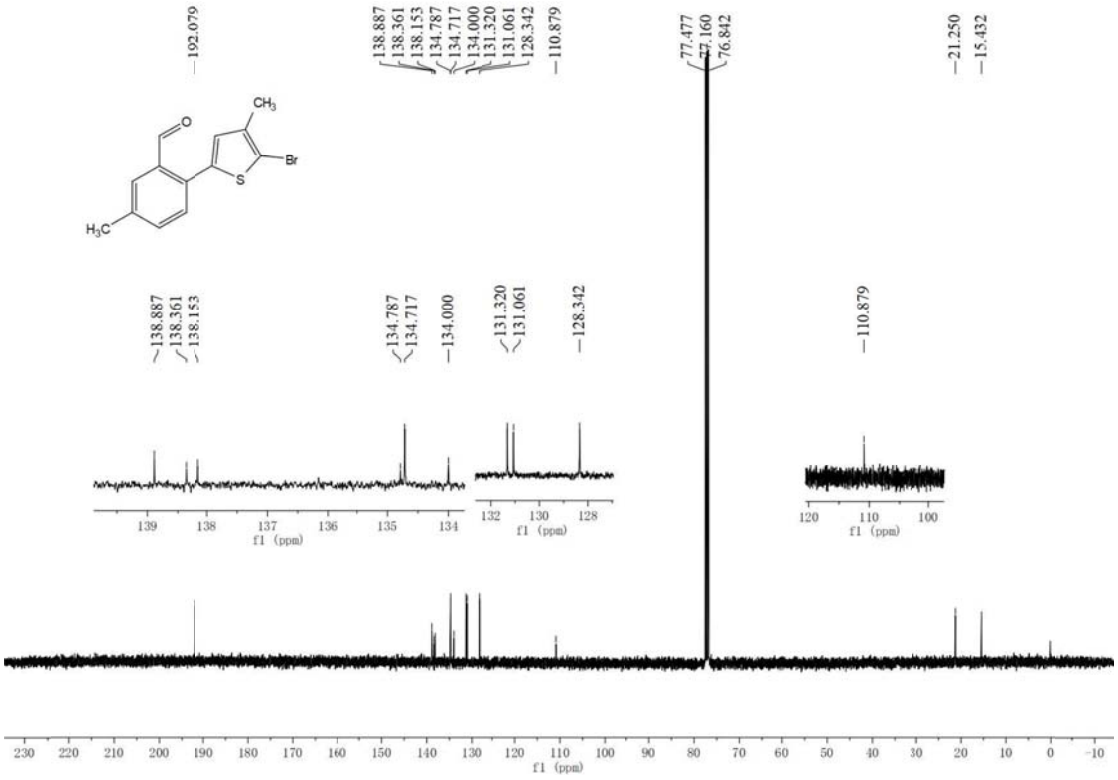
^{13}C NMR spectra of **4f** ($CDCl_3$)



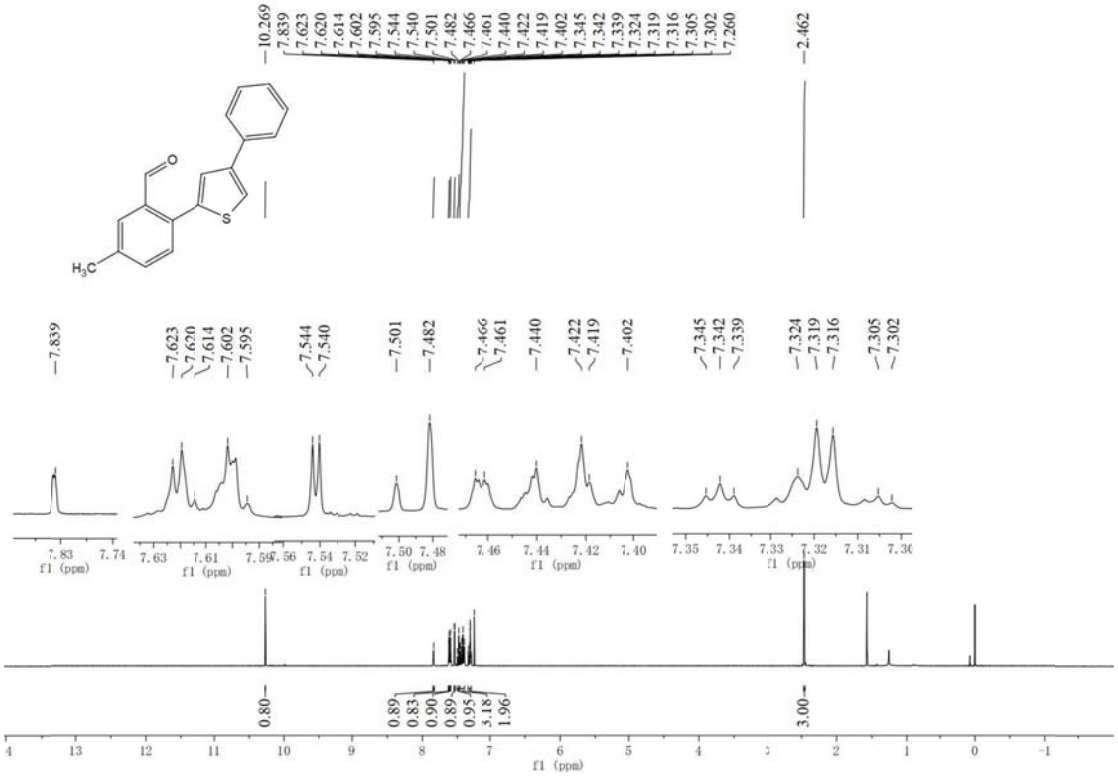
^{1}H NMR spectra of **4g** ($CDCl_3$)



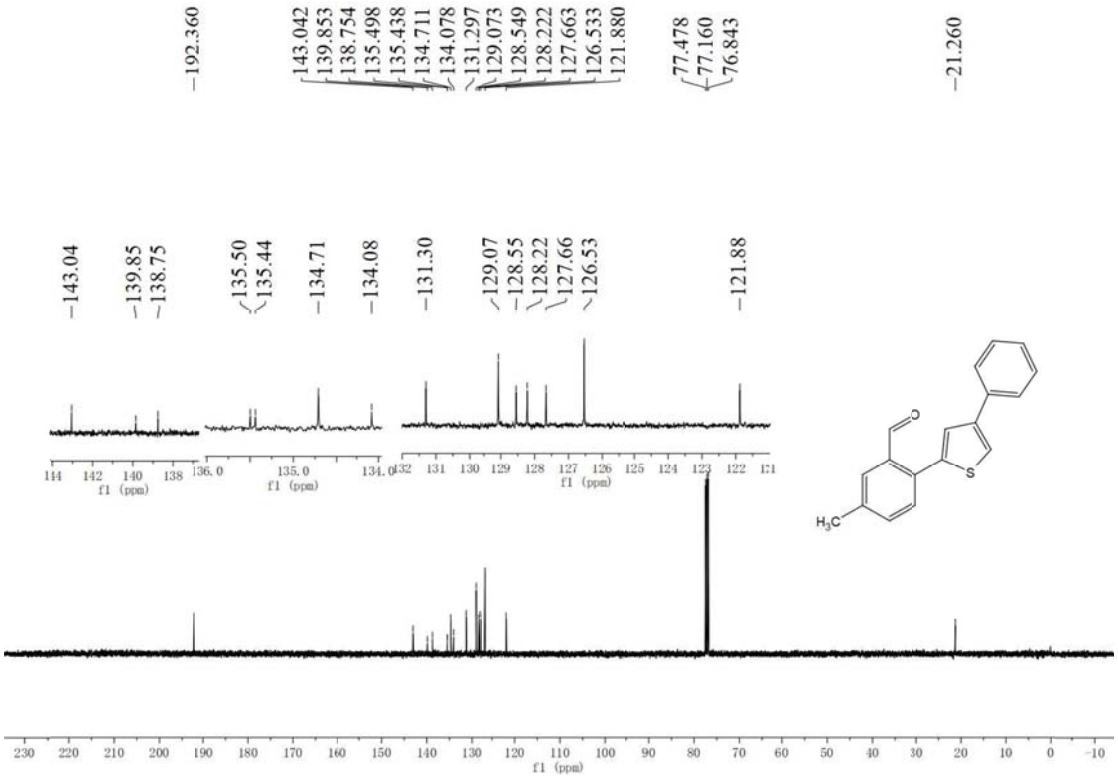
^{13}C NMR spectra of **4g** ($CDCl_3$)



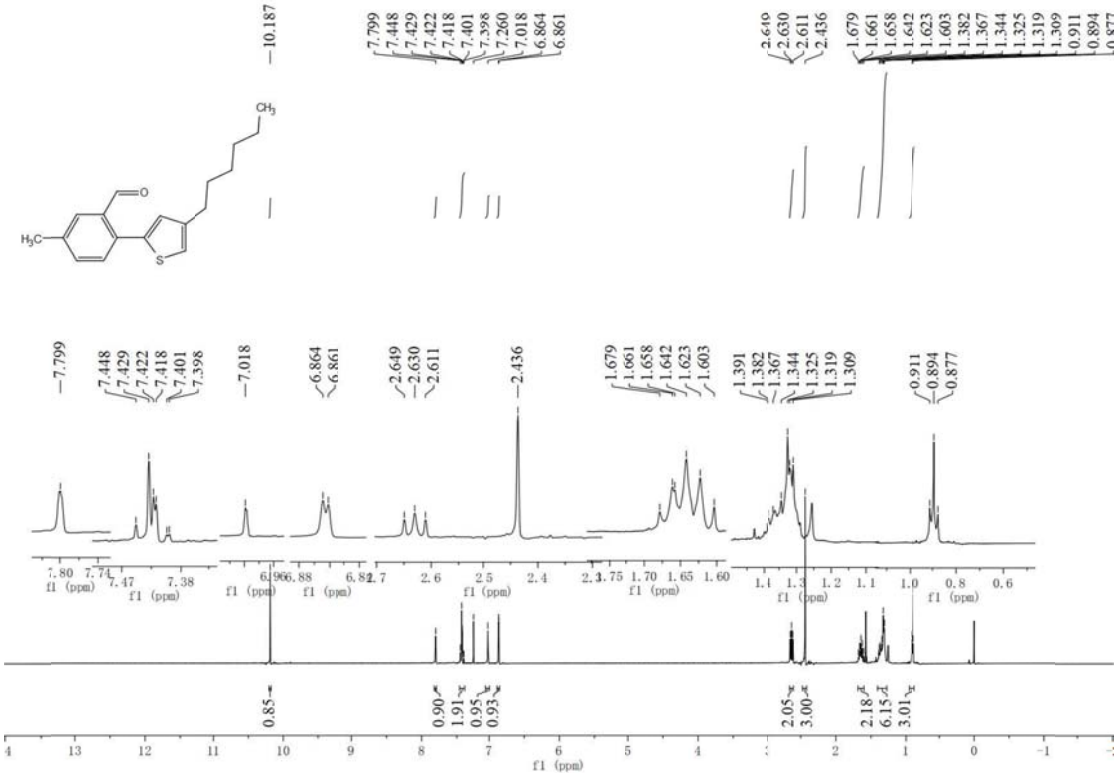
^{1}H NMR spectra of **4h** ($CDCl_3$)



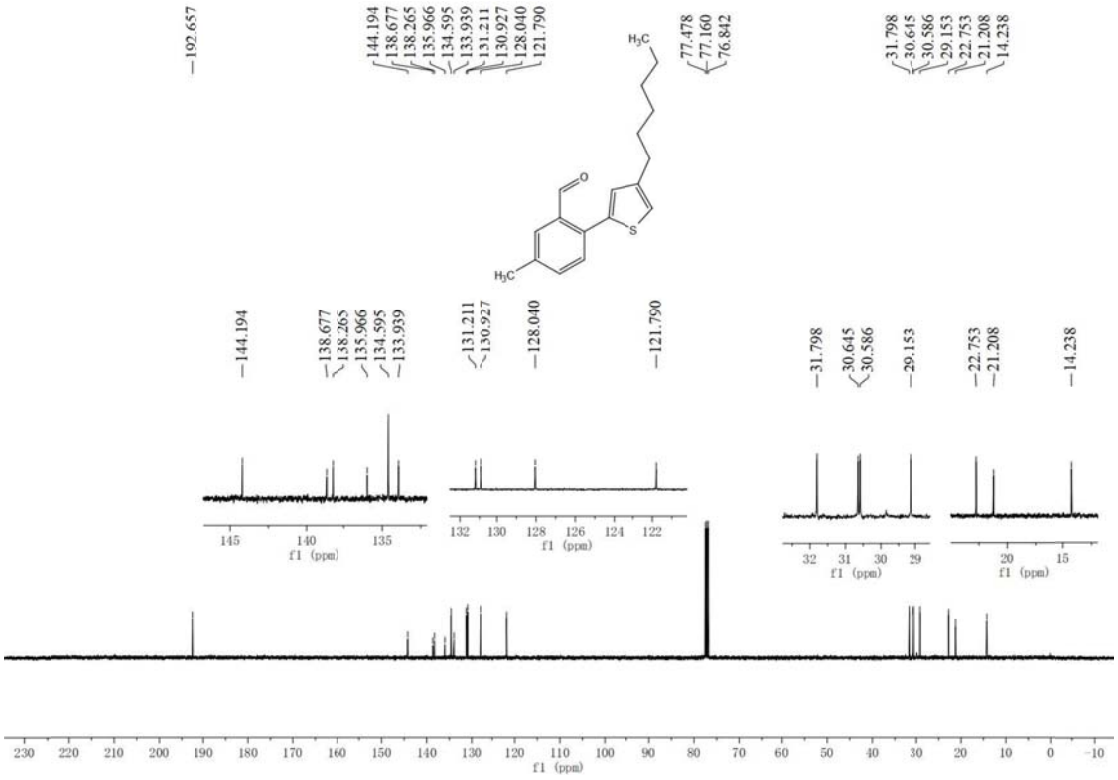
^{13}C NMR spectra of **4h** ($CDCl_3$)



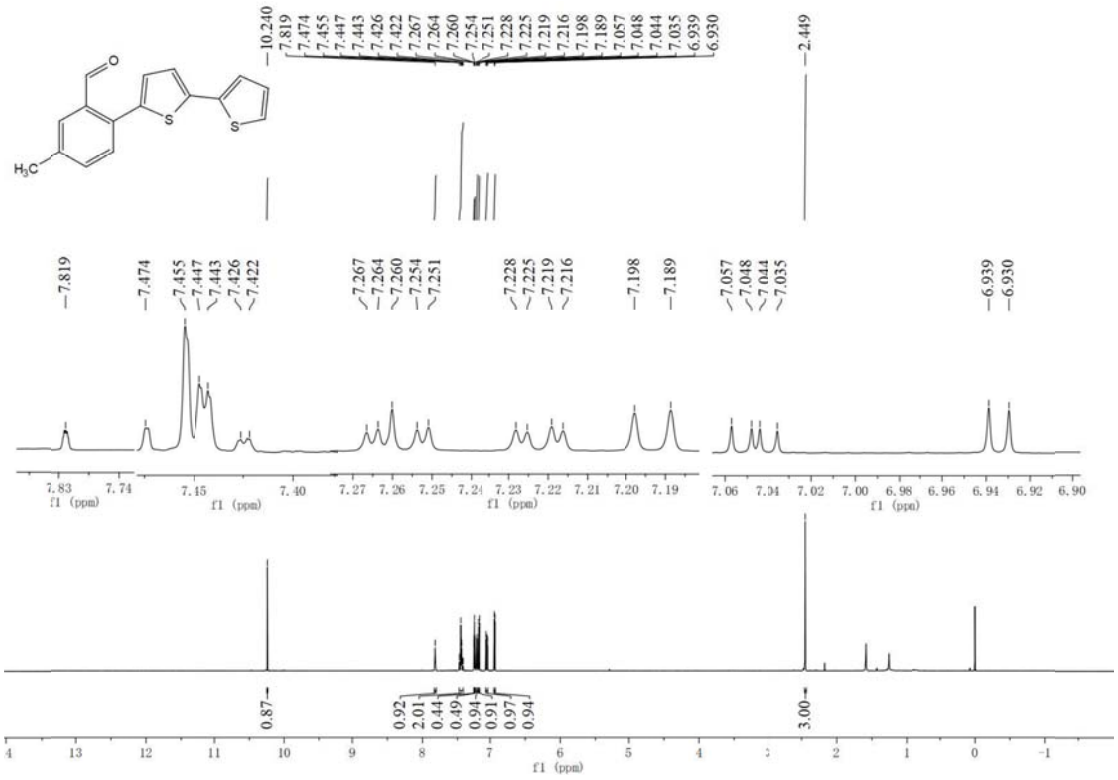
^{1}H NMR spectra of **4i** ($CDCl_3$)



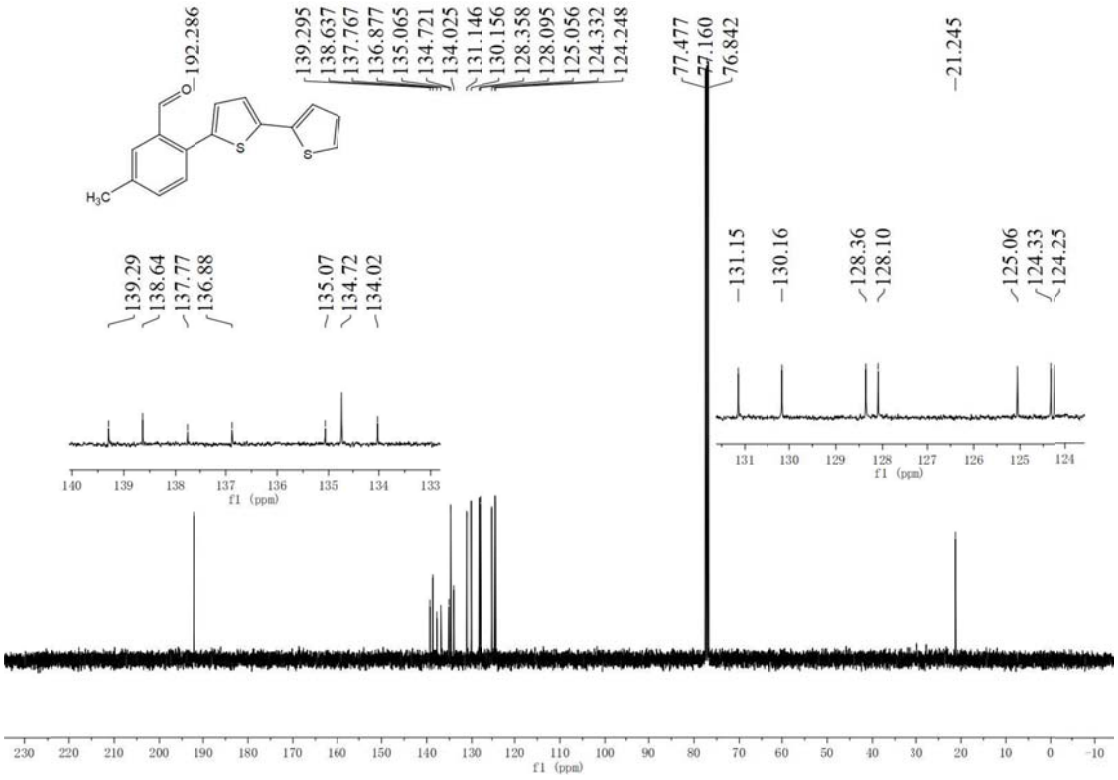
^{13}C NMR spectra of **4i** ($CDCl_3$)



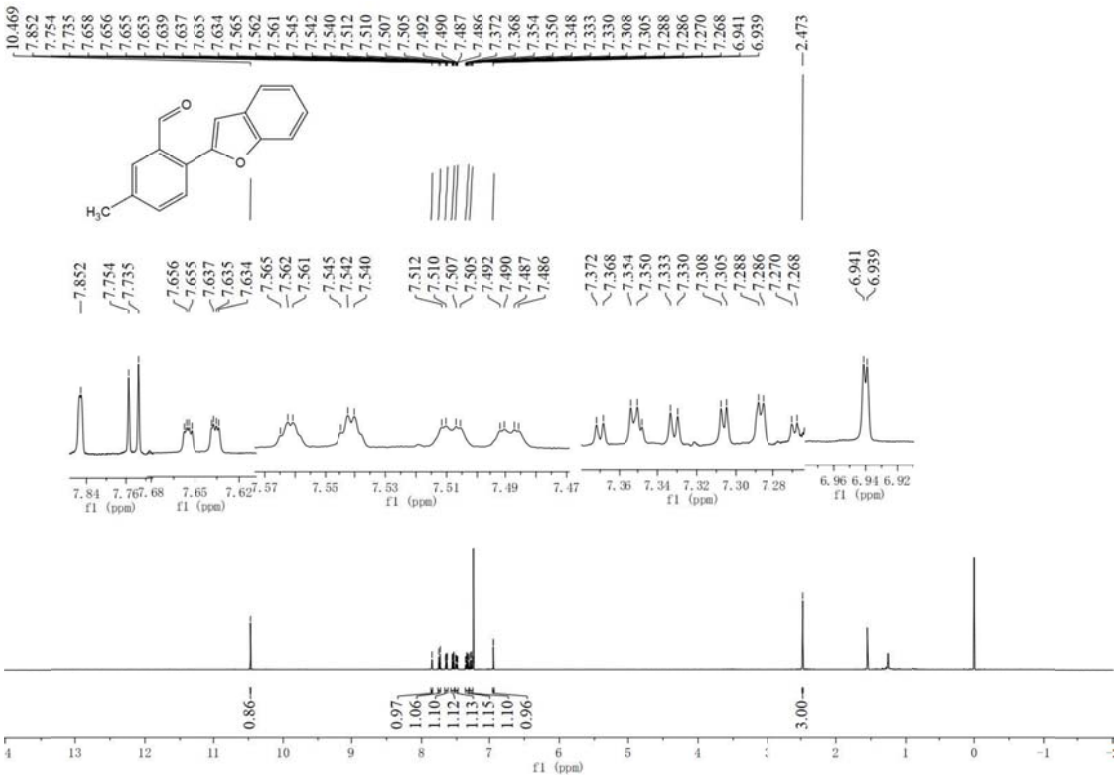
^{1}H NMR spectra of **4j** ($CDCl_3$)



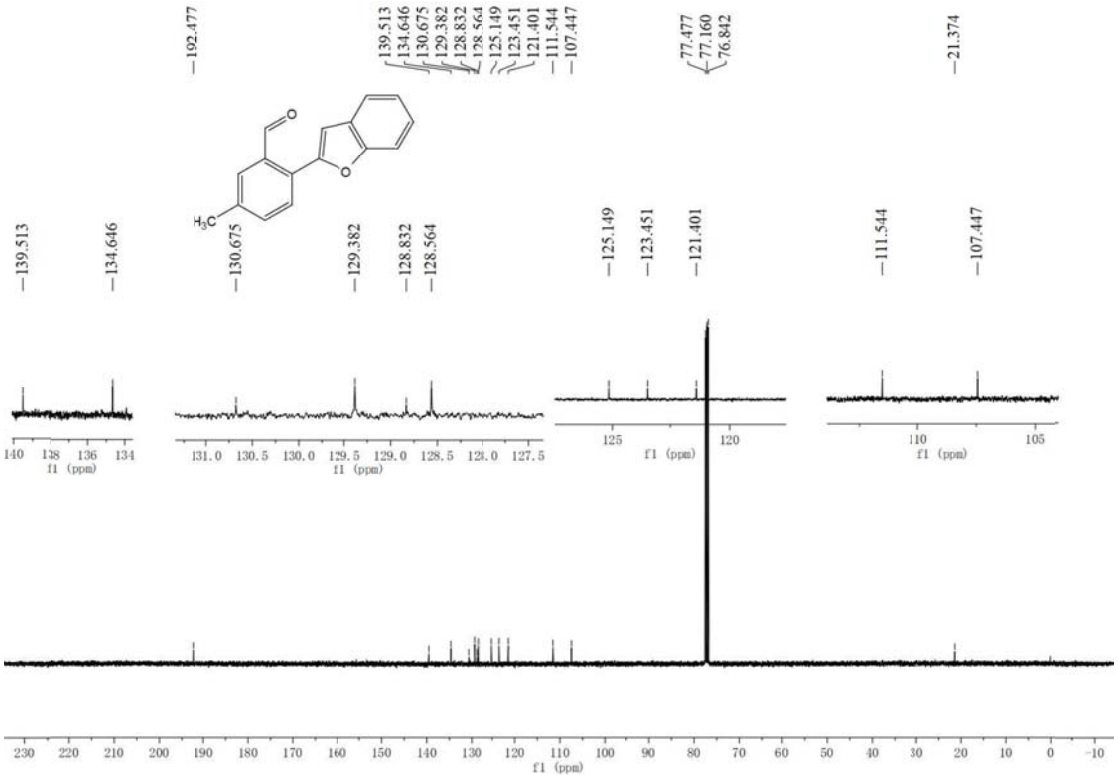
^{13}C NMR spectra of **4j** ($CDCl_3$)



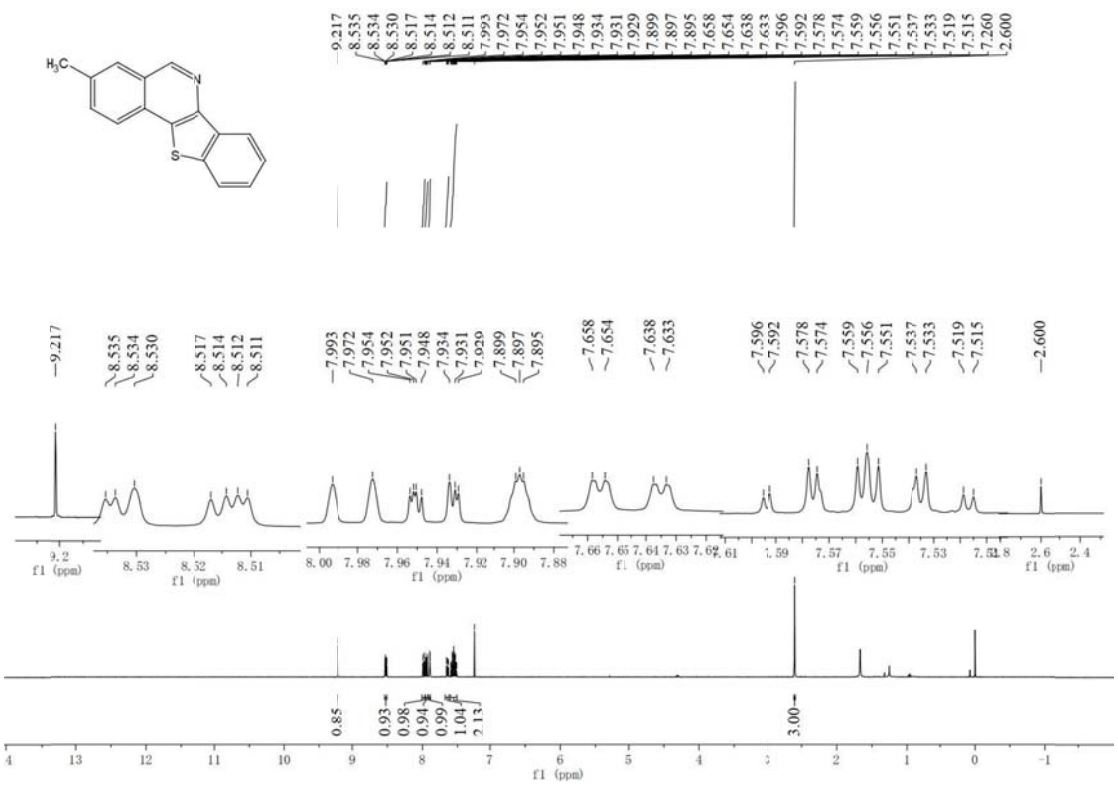
^{1}H NMR spectra of **4k** ($CDCl_3$)



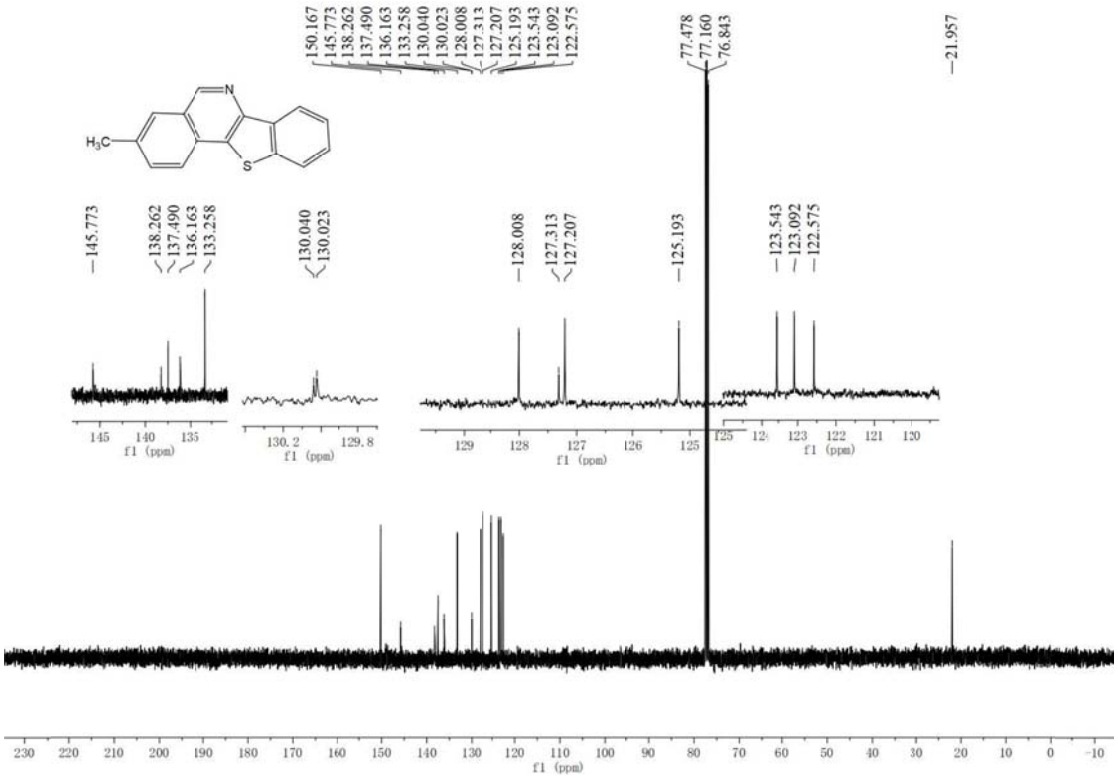
^{13}C NMR spectra of **4k** ($CDCl_3$)



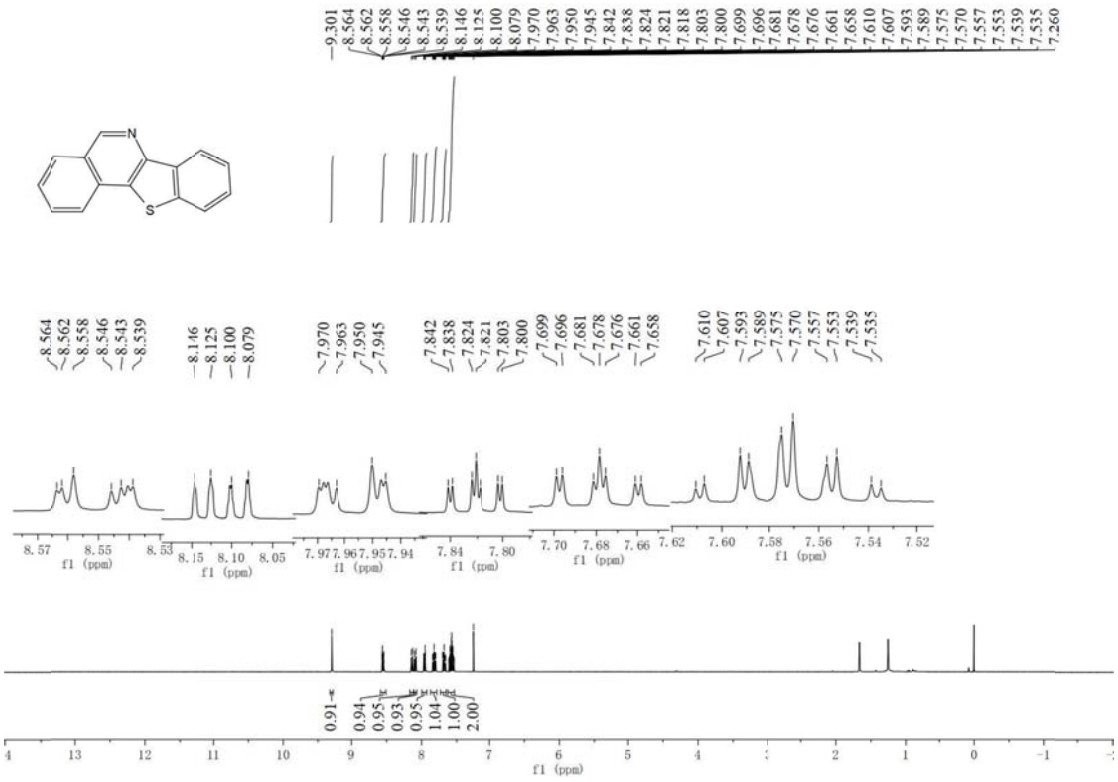
^{1}H NMR spectra of **5a** ($CDCl_3$)



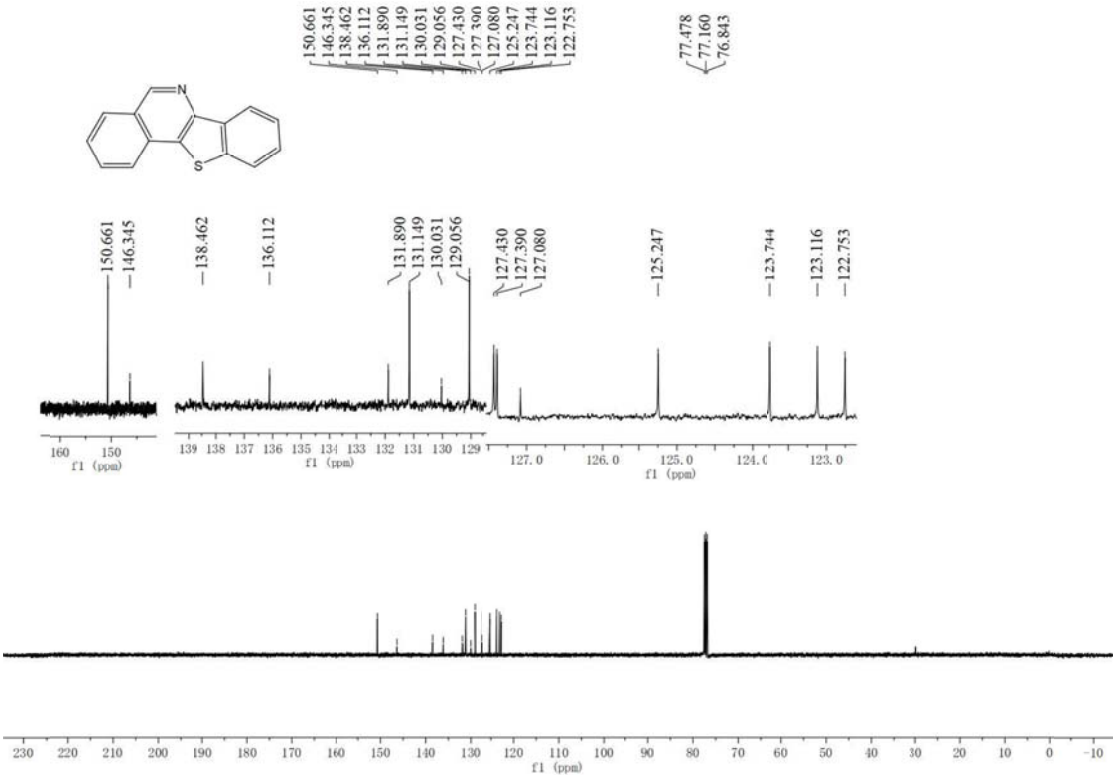
^{13}C NMR spectra of **5a** ($CDCl_3$)



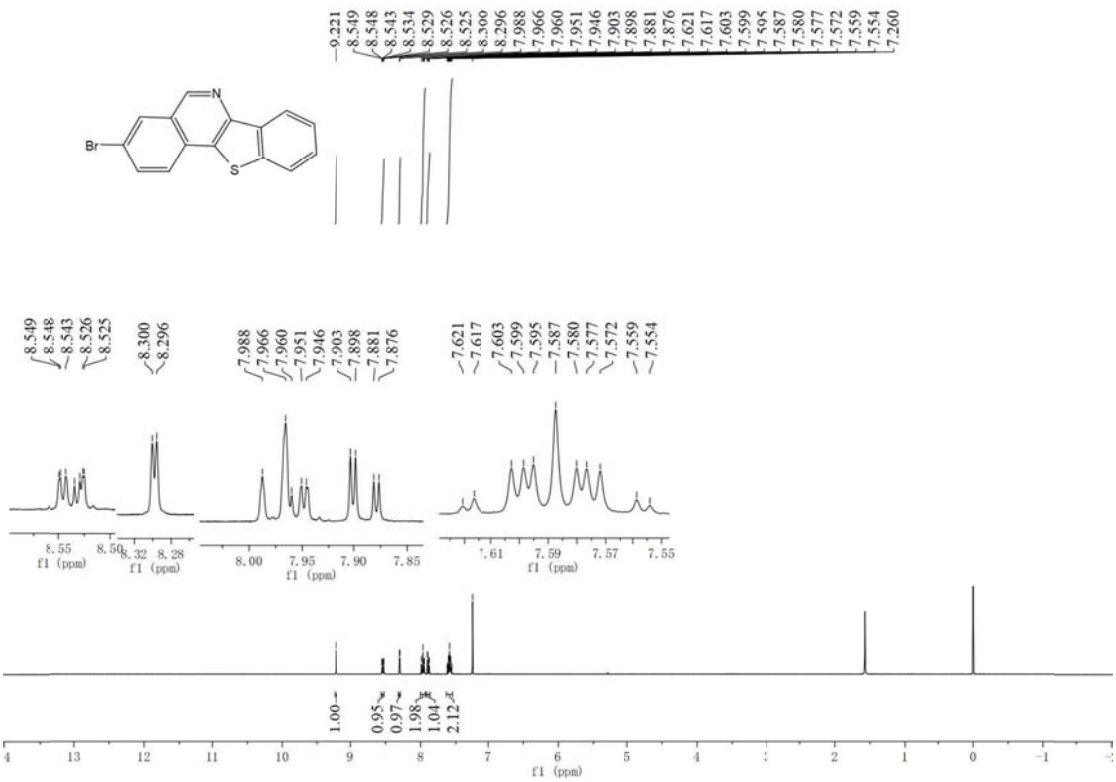
^{1}H NMR spectra of **5b** ($CDCl_3$)



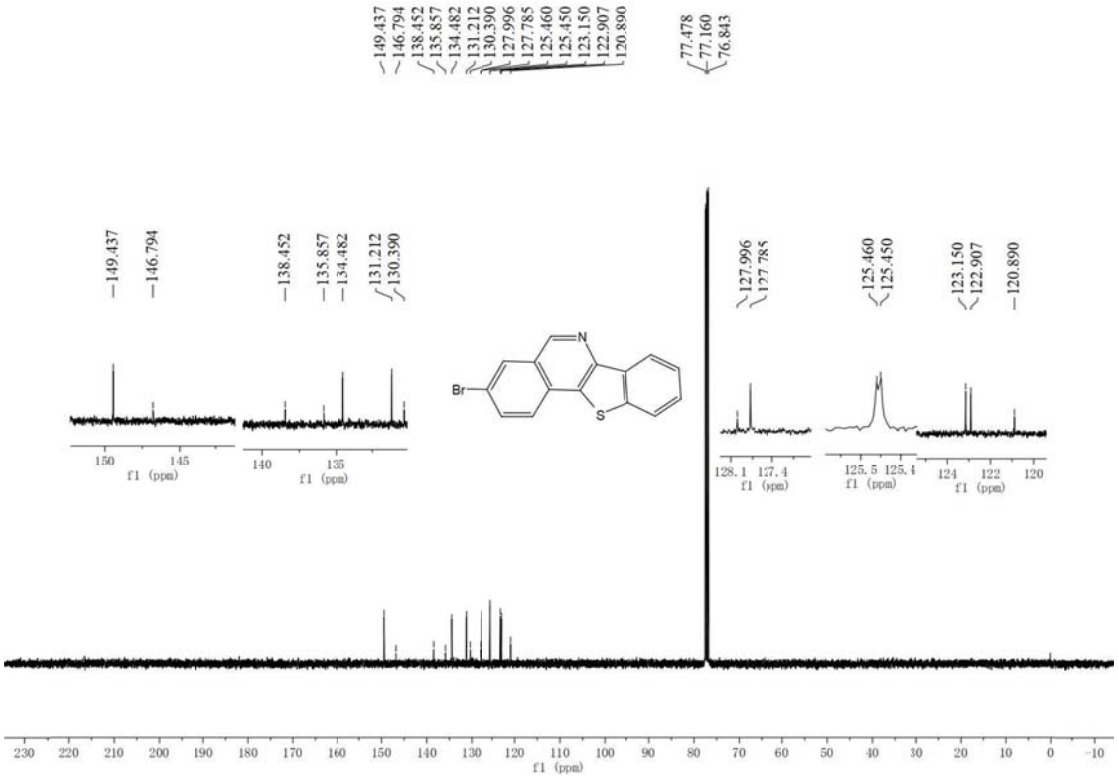
^{13}C NMR spectra of **5b** ($CDCl_3$)



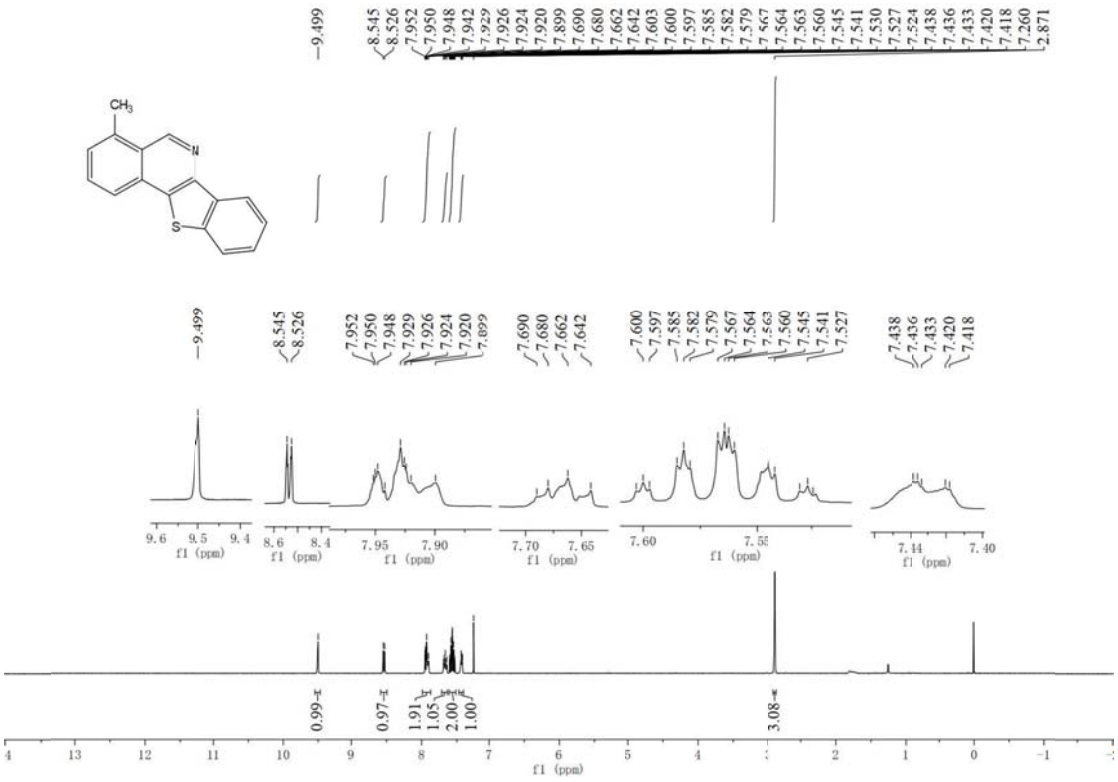
^{1}H NMR spectra of **5c** ($CDCl_3$)



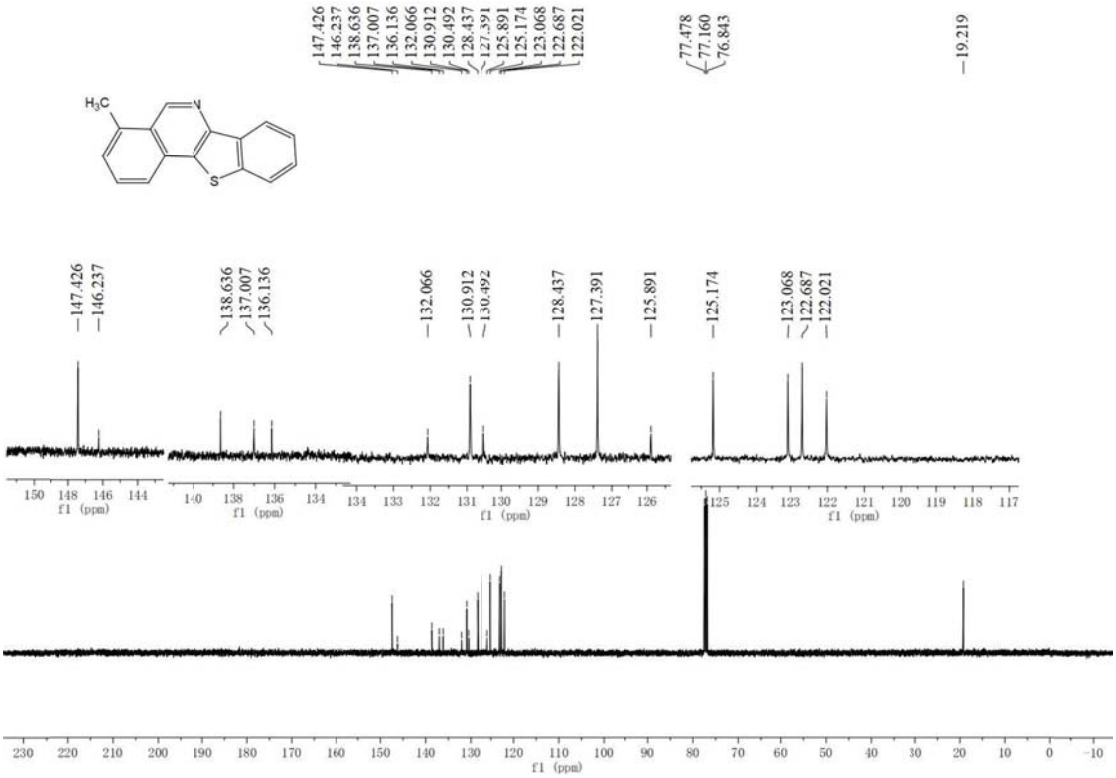
^{13}C NMR spectra of **5c** ($CDCl_3$)



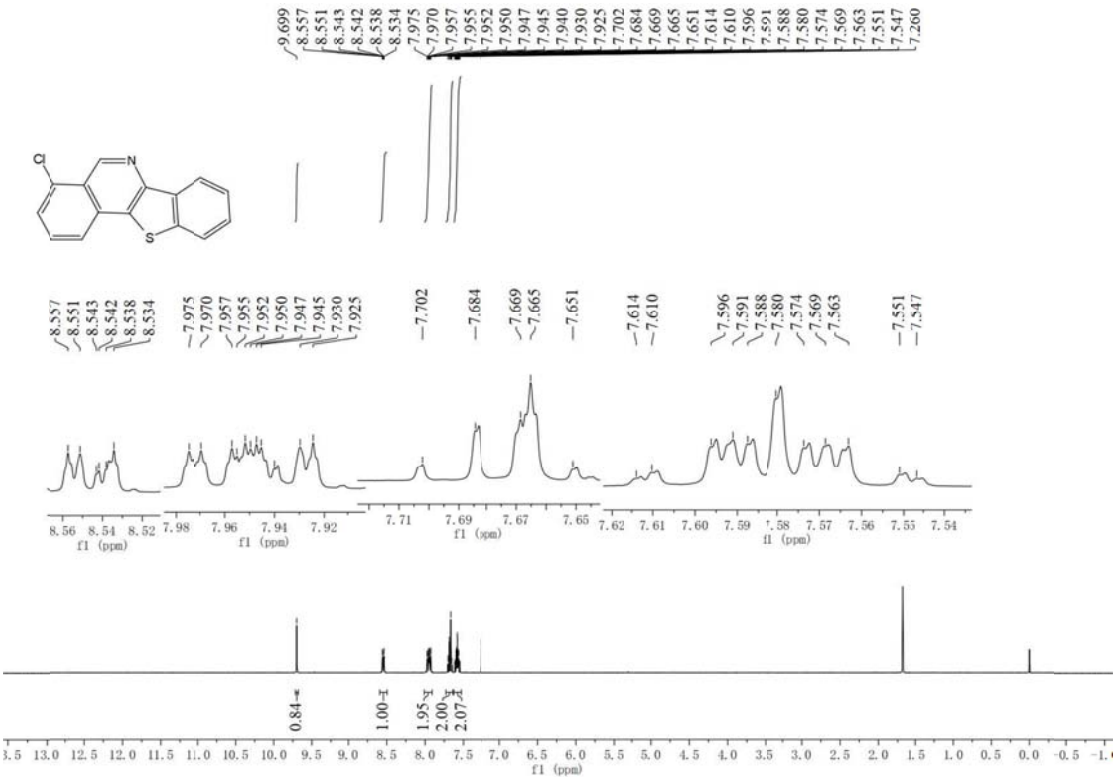
^{1}H NMR spectra of **5d** ($CDCl_3$)



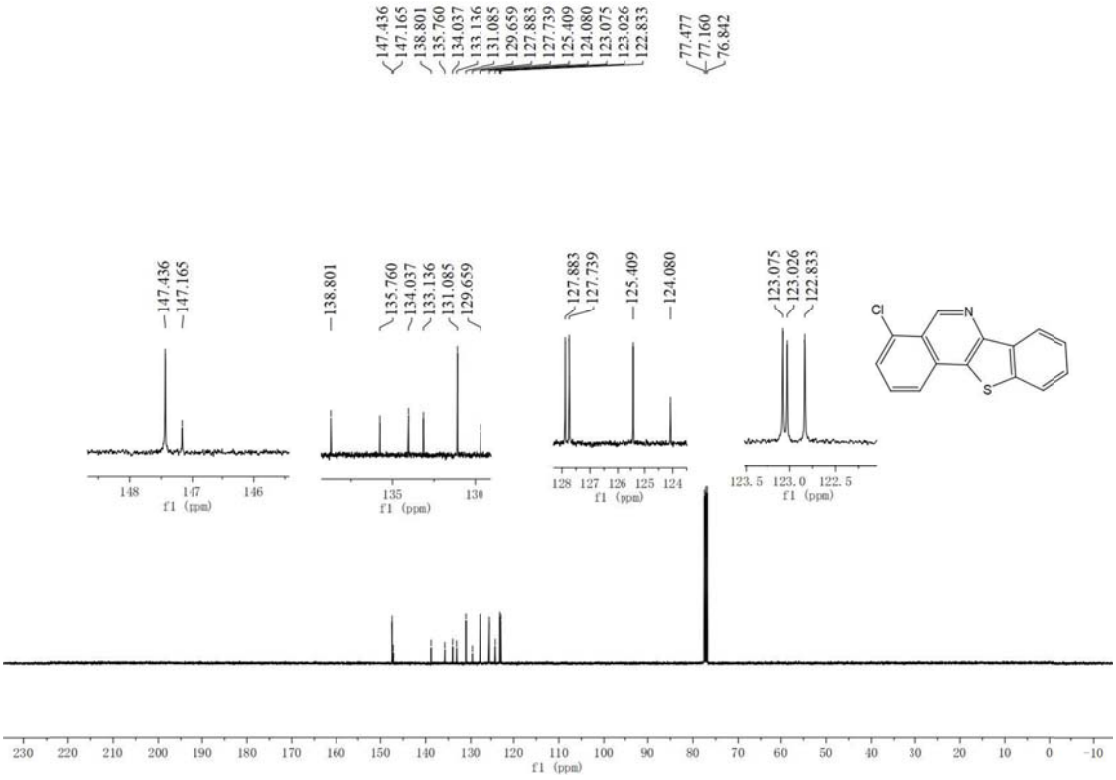
^{13}C NMR spectra of **5d** ($CDCl_3$)



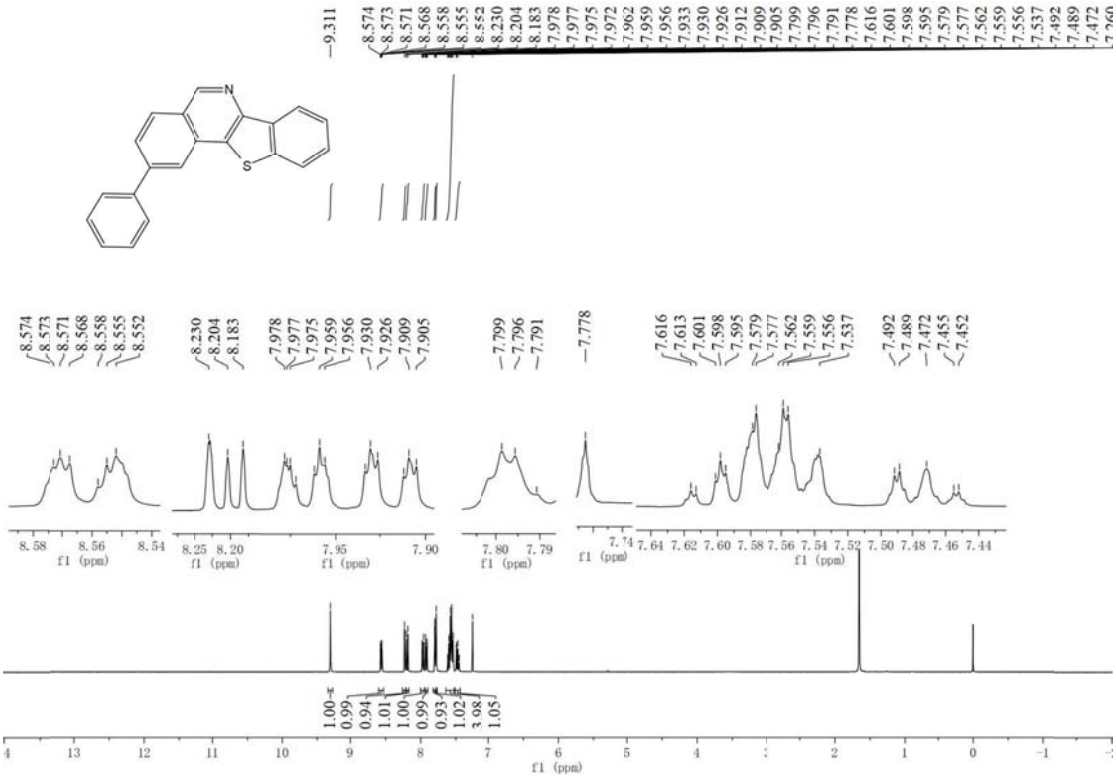
^{1}H NMR spectra of **5e** ($CDCl_3$)



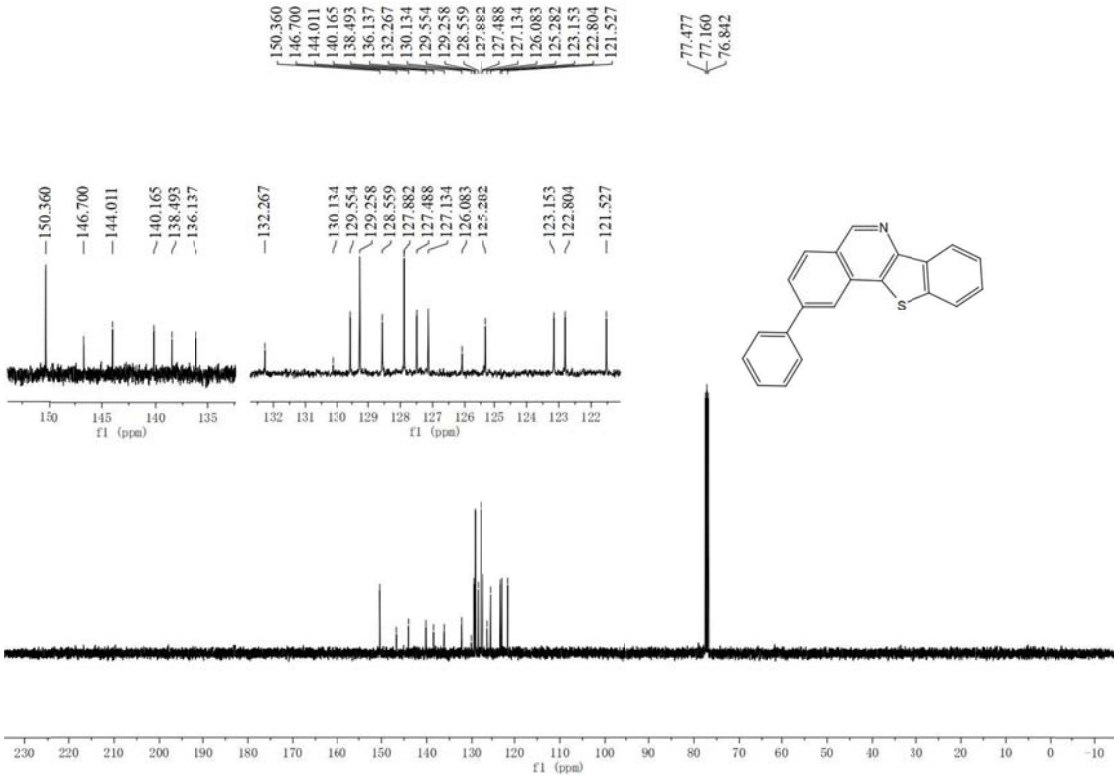
^{13}C NMR spectra of **5e** ($CDCl_3$)



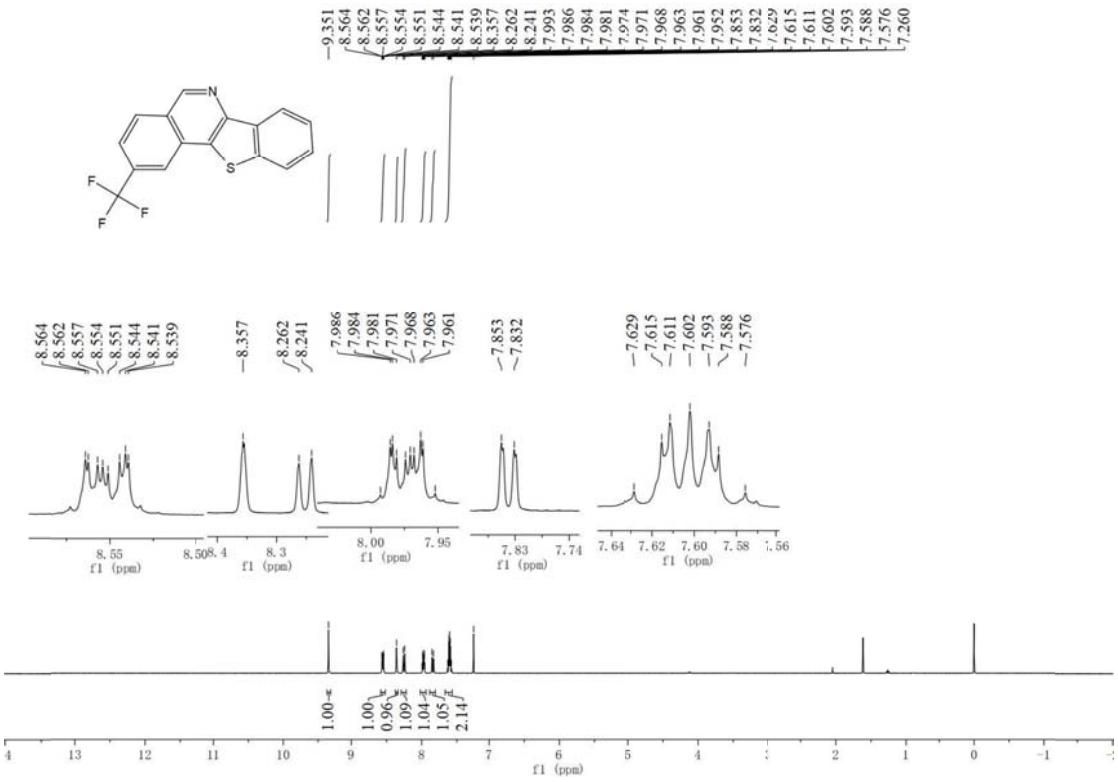
^{1}H NMR spectra of **5f** ($CDCl_3$)



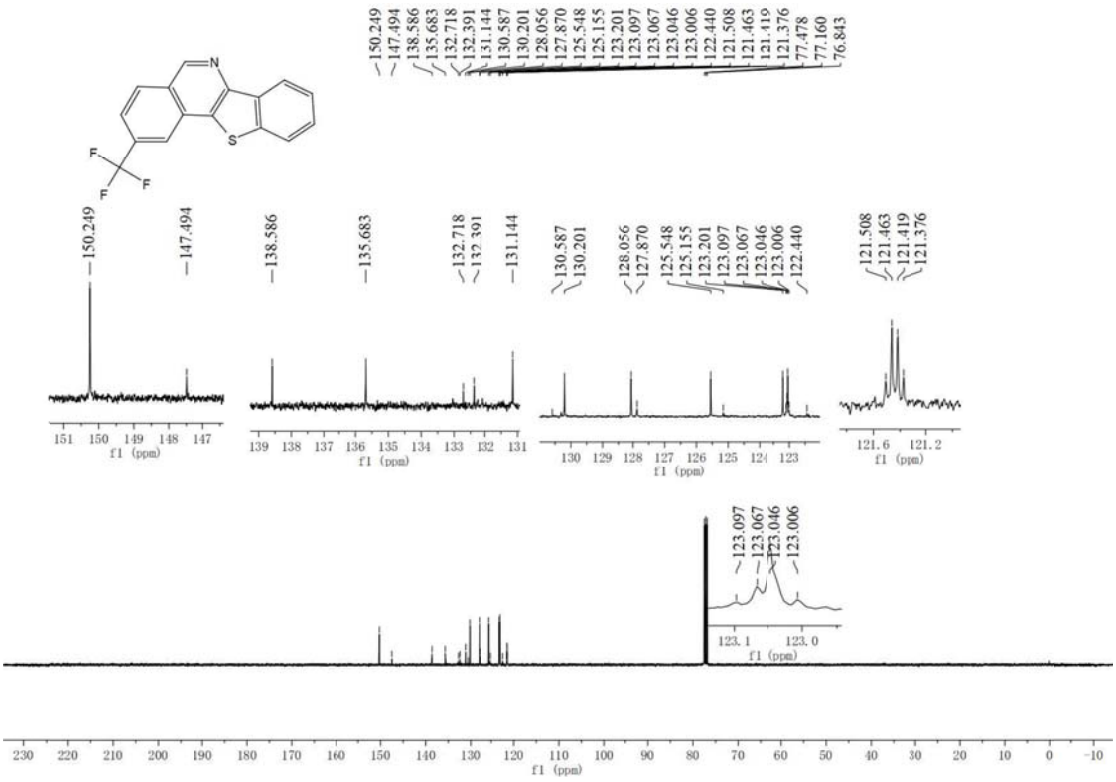
^{13}C NMR spectra of **5f** ($CDCl_3$)



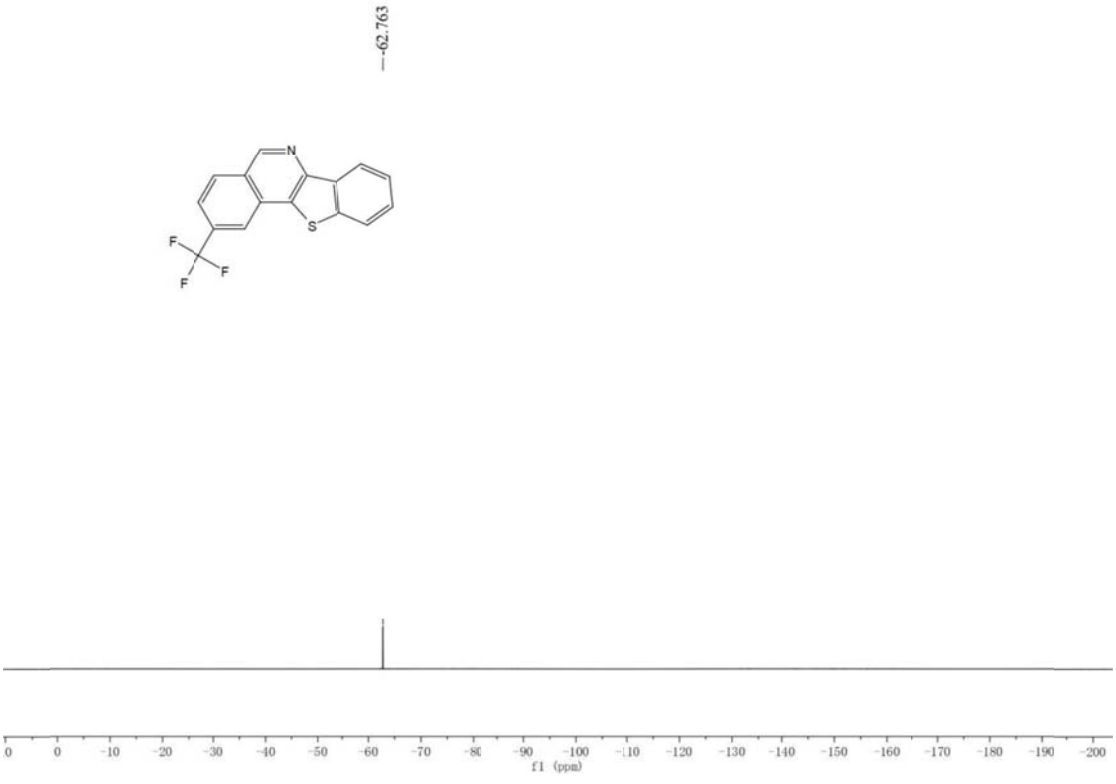
^{1}H NMR spectra of **5g** ($CDCl_3$)



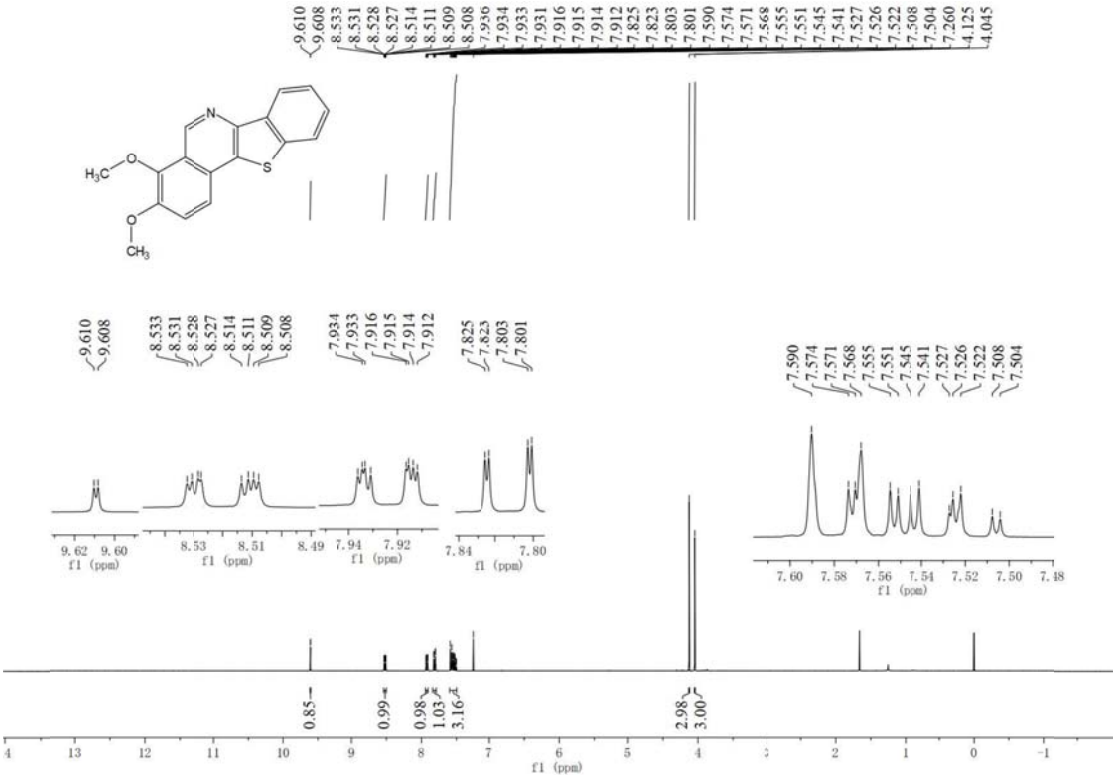
^{13}C NMR spectra of **5g** ($CDCl_3$)



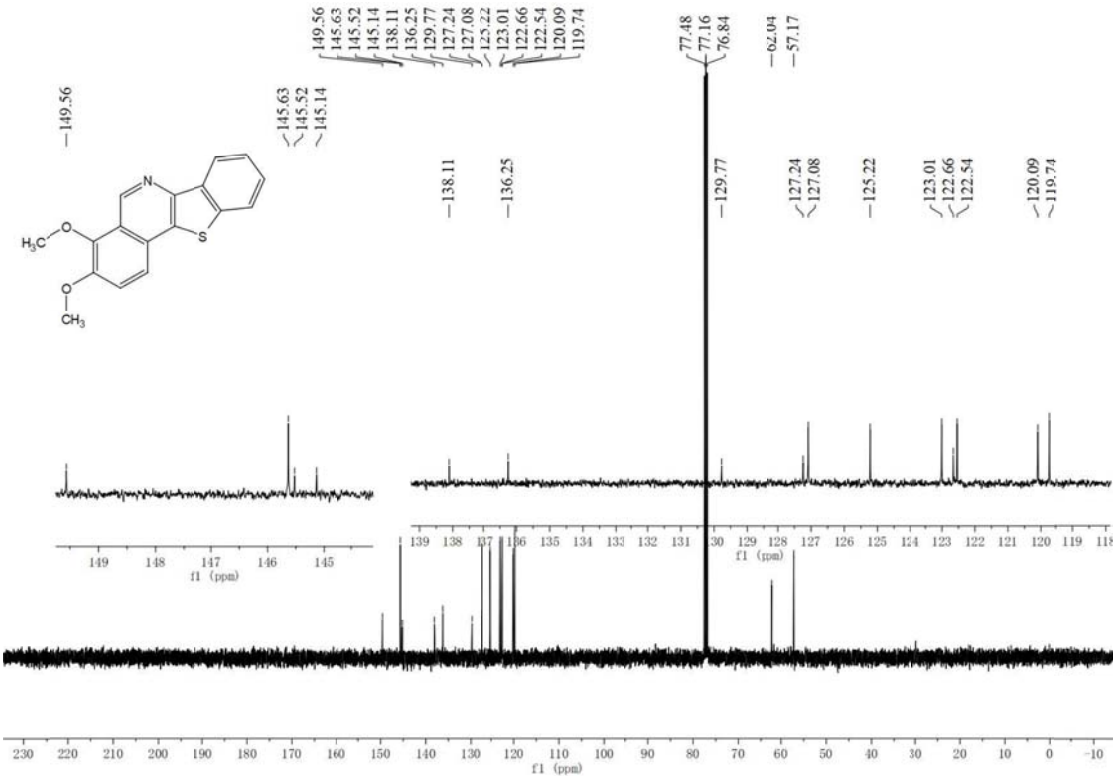
^{19}F NMR spectra of **5g** ($CDCl_3$)



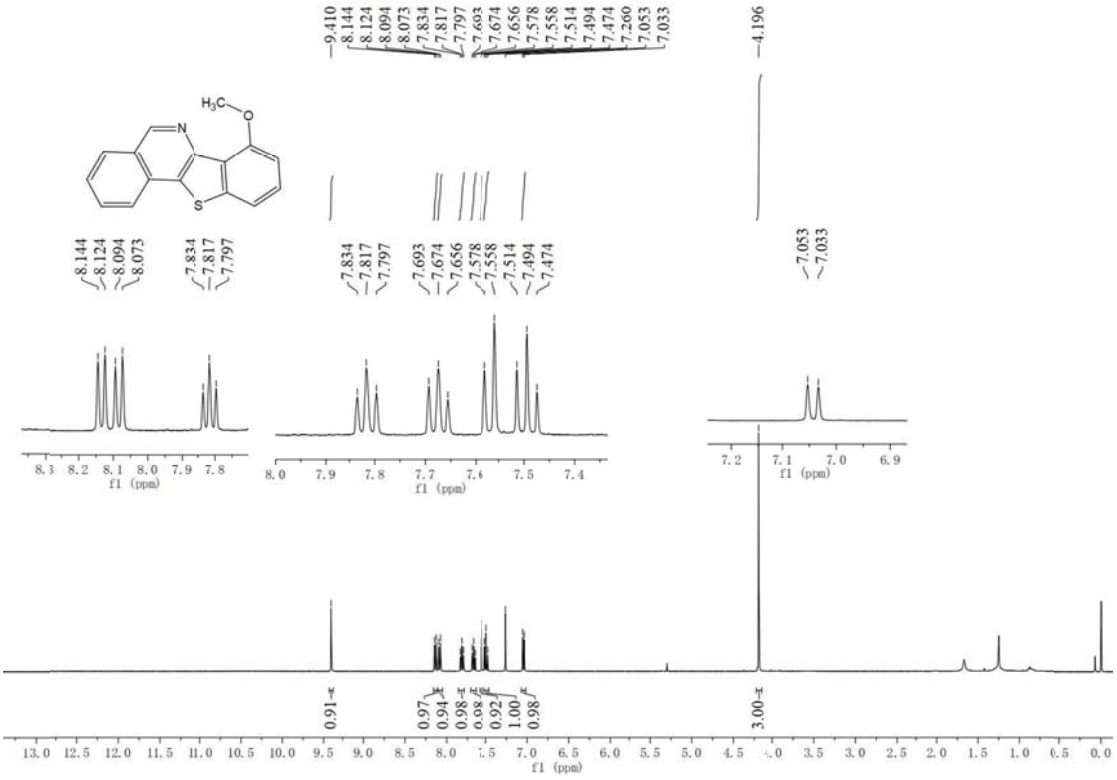
^{1}H NMR spectra of **5h** ($CDCl_3$)



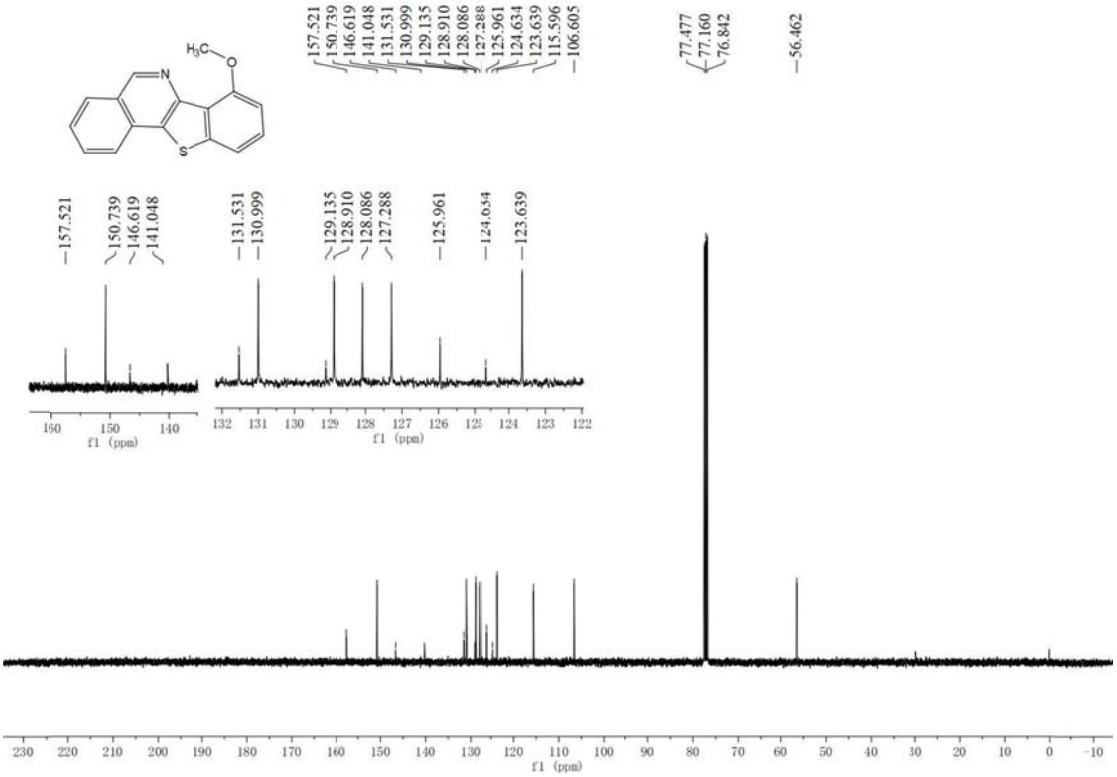
^{13}C NMR spectra of **5h** ($CDCl_3$)



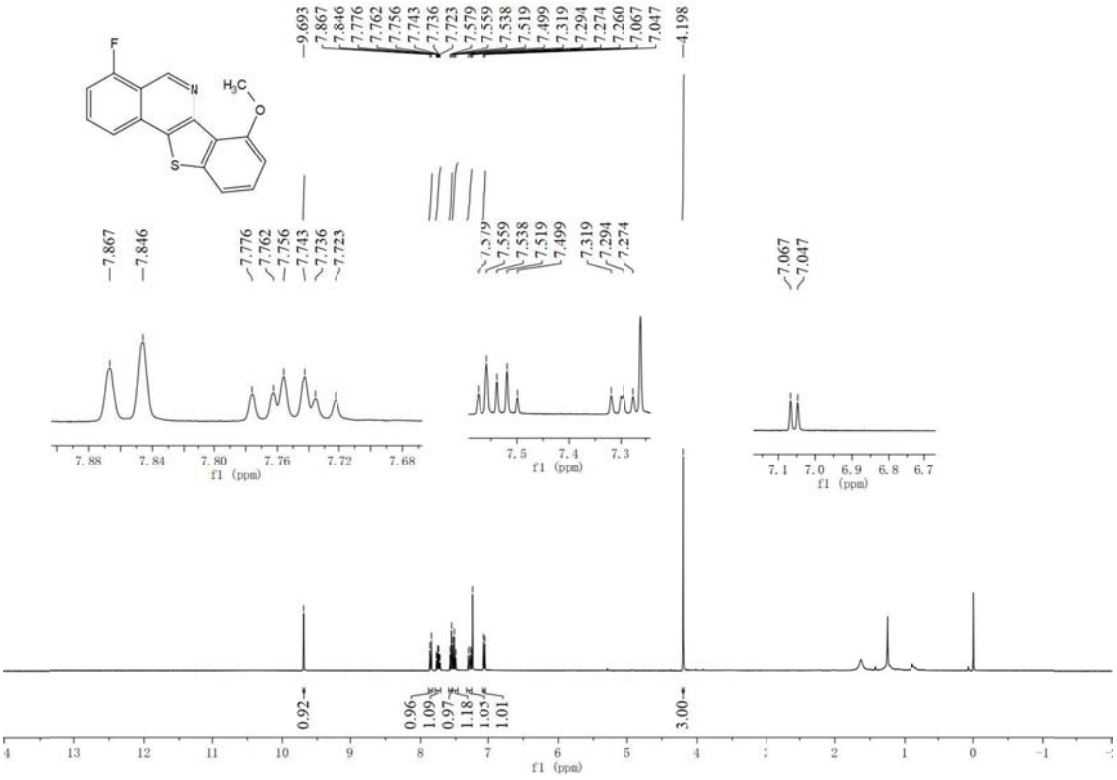
^{1}H NMR spectra of **5i** ($CDCl_3$)



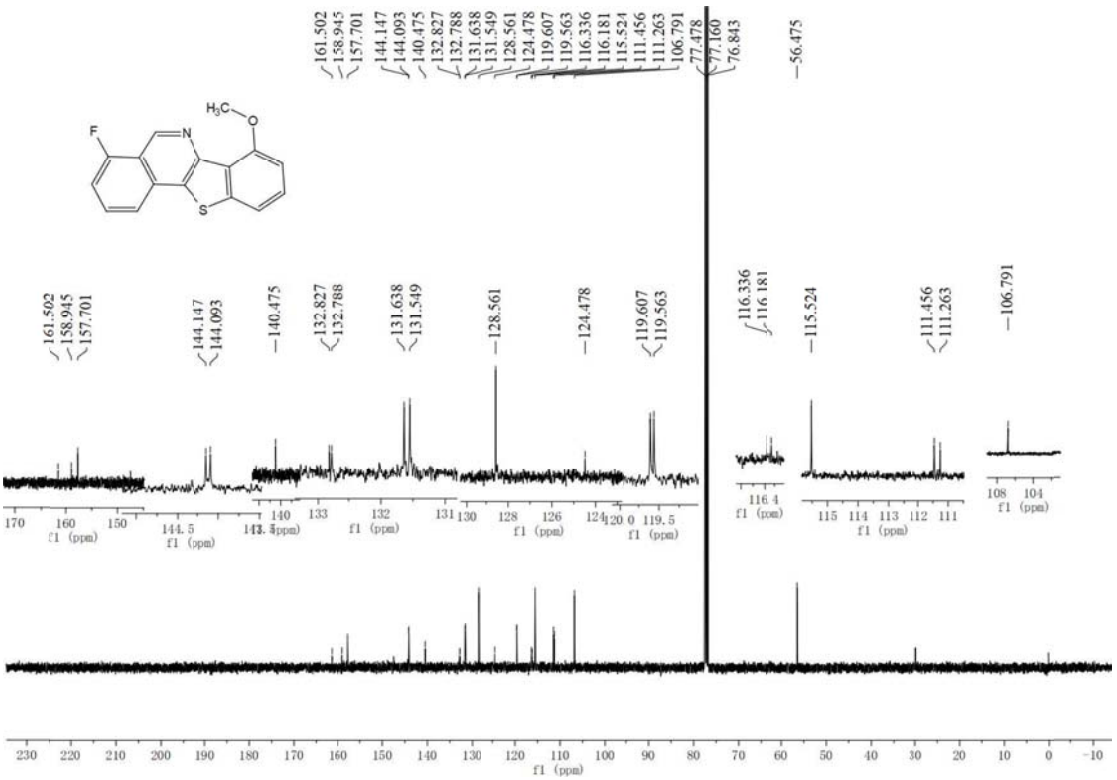
^{13}C NMR spectra of **5i** ($CDCl_3$)



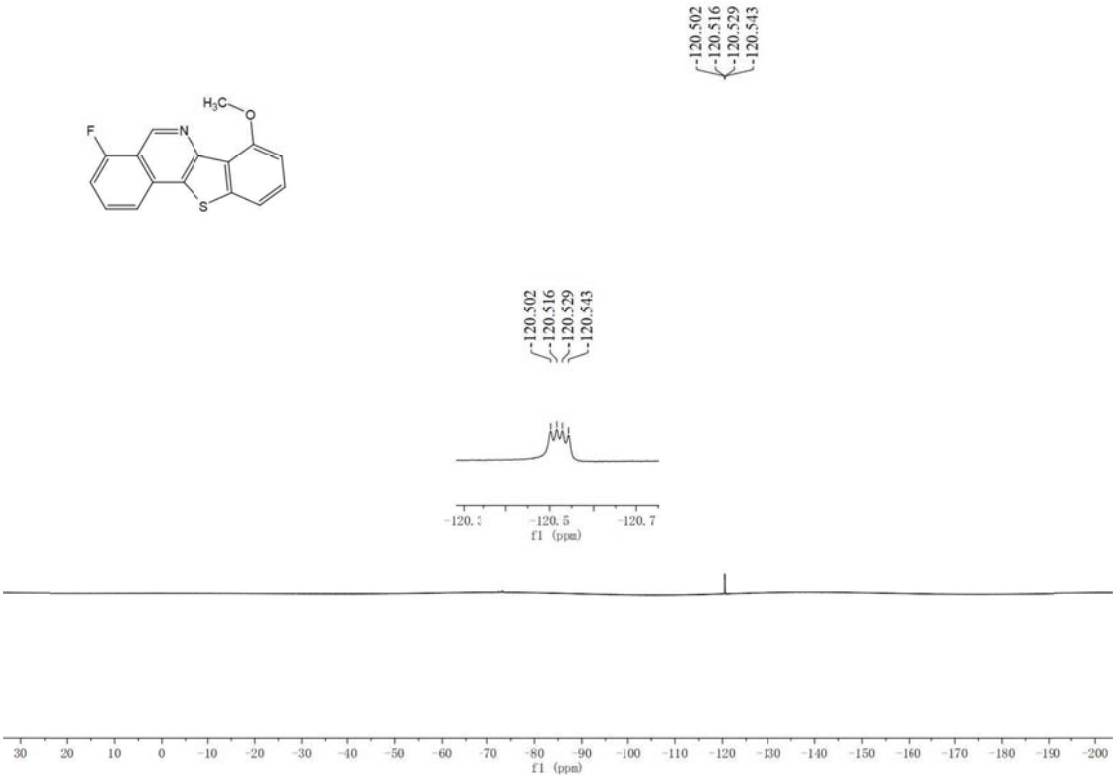
^{1}H NMR spectra of **5j** ($CDCl_3$)



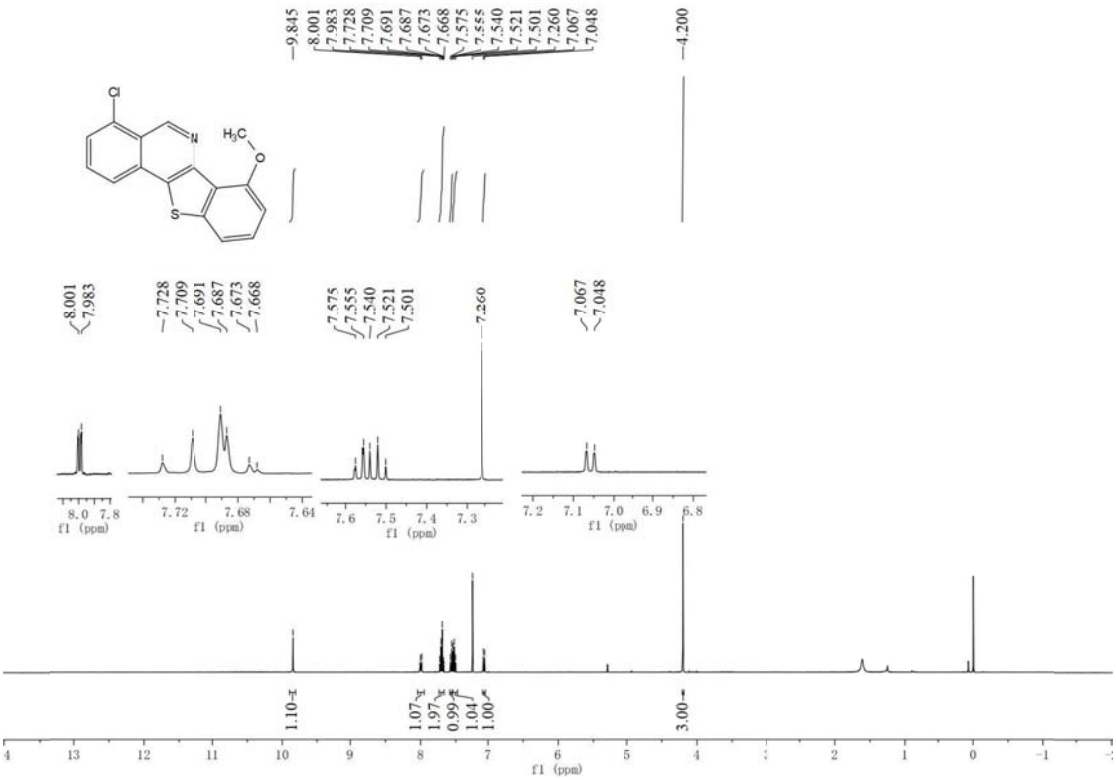
^{13}C NMR spectra of **5j** ($CDCl_3$)



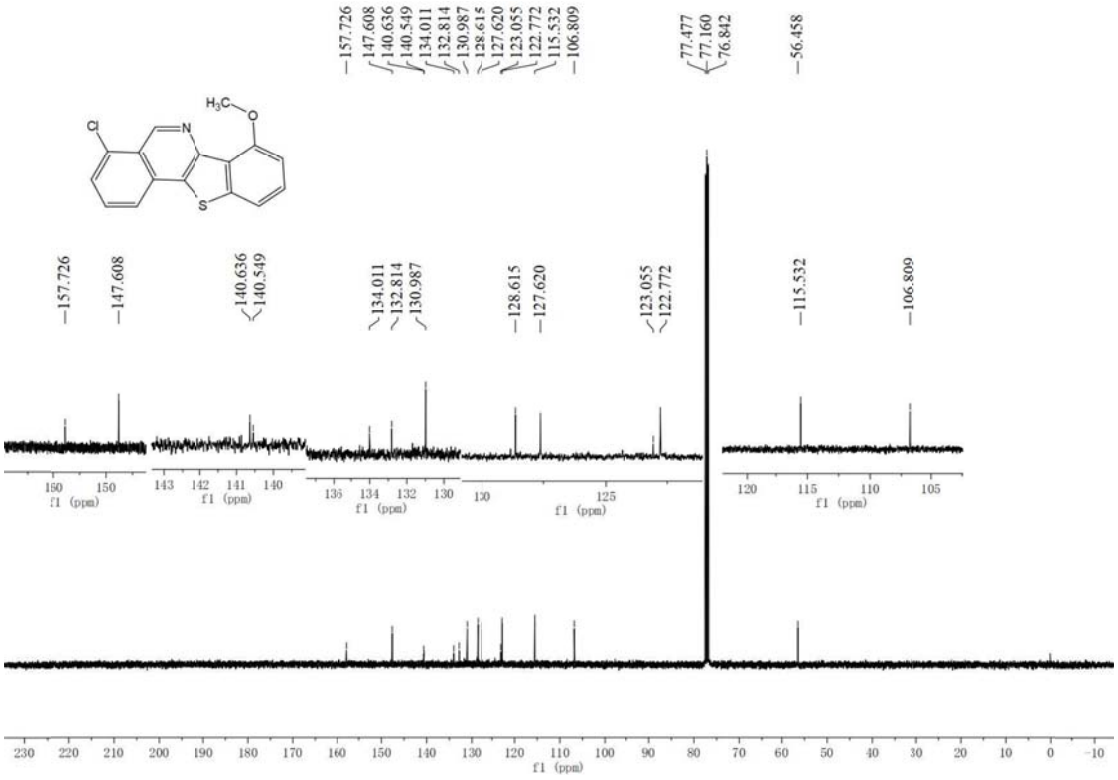
^{19}F NMR spectra of **5j** ($CDCl_3$)



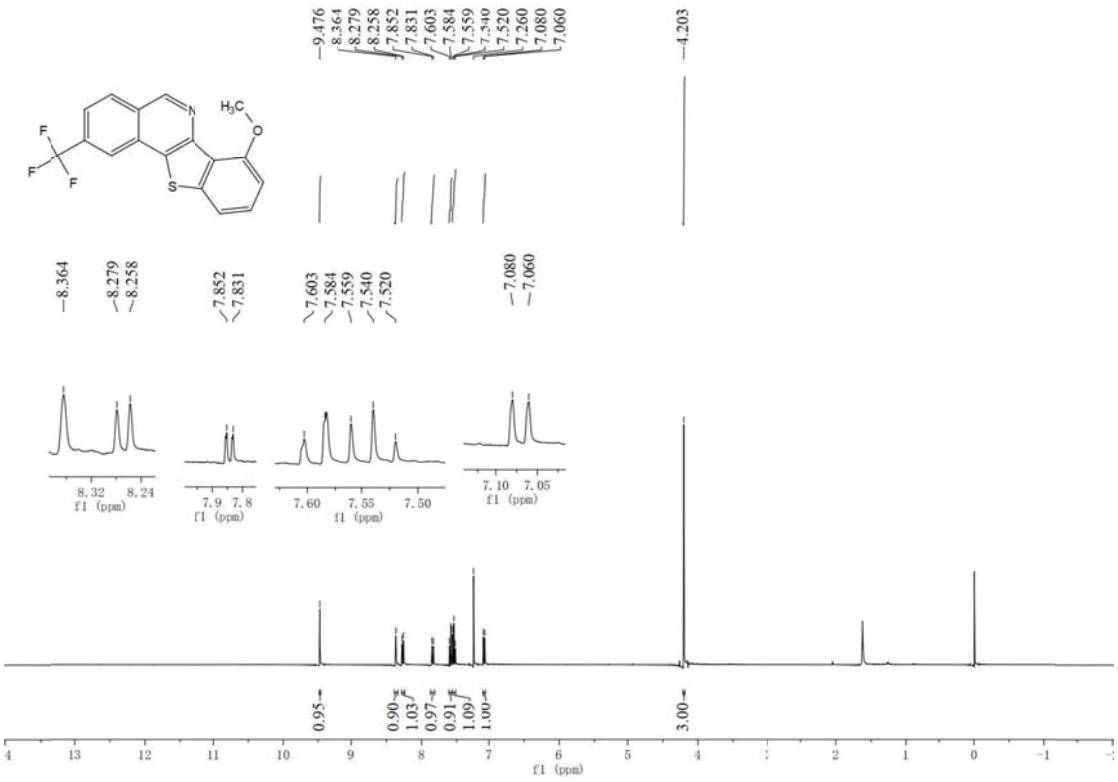
^{1}H NMR spectra of **5k** ($CDCl_3$)



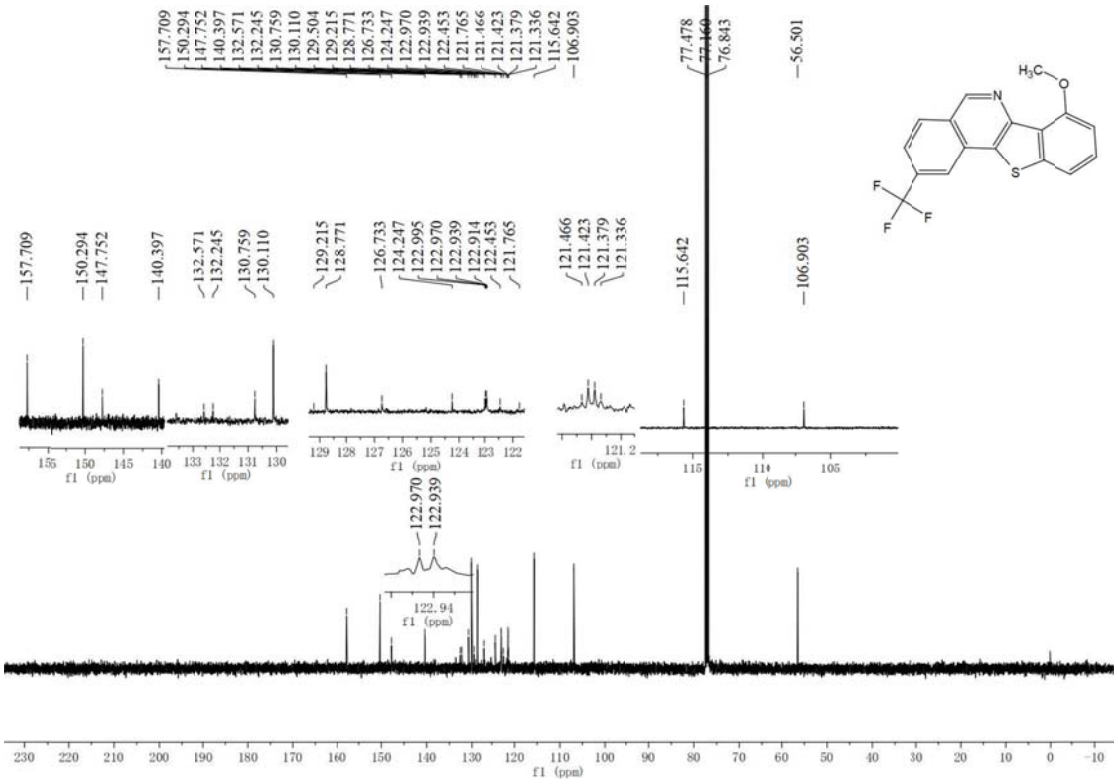
^{13}C NMR spectra of **5k** ($CDCl_3$)



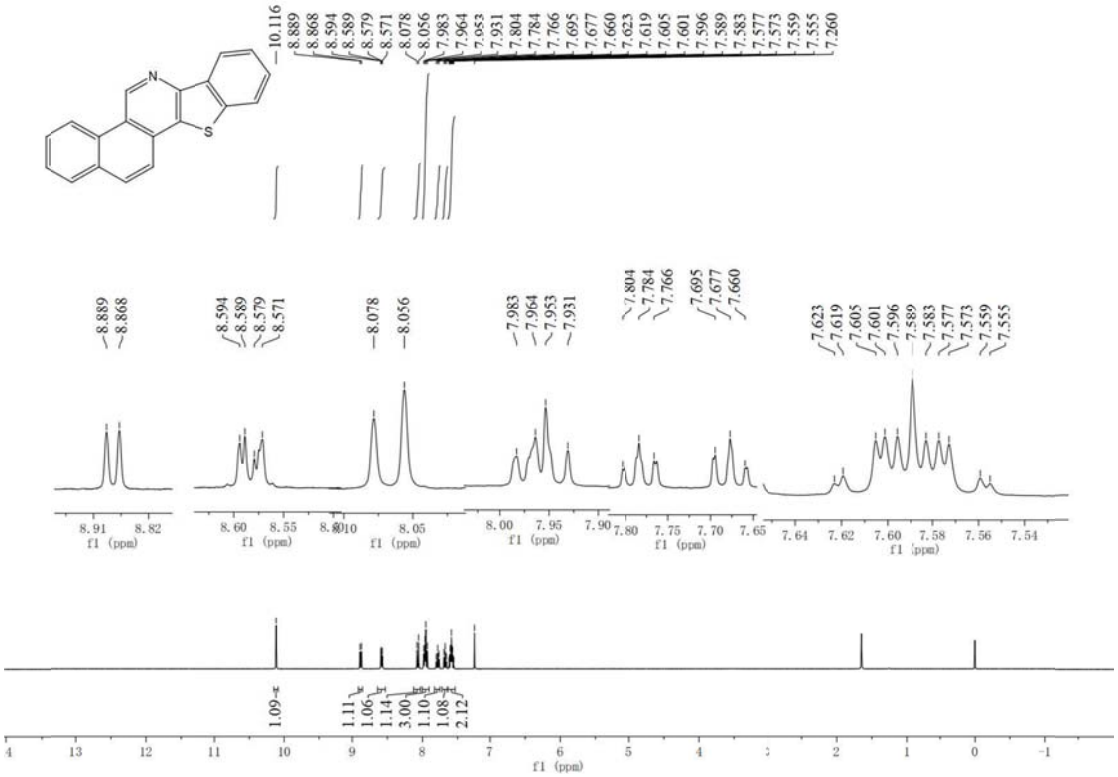
^{1}H NMR spectra of **5l** ($CDCl_3$)



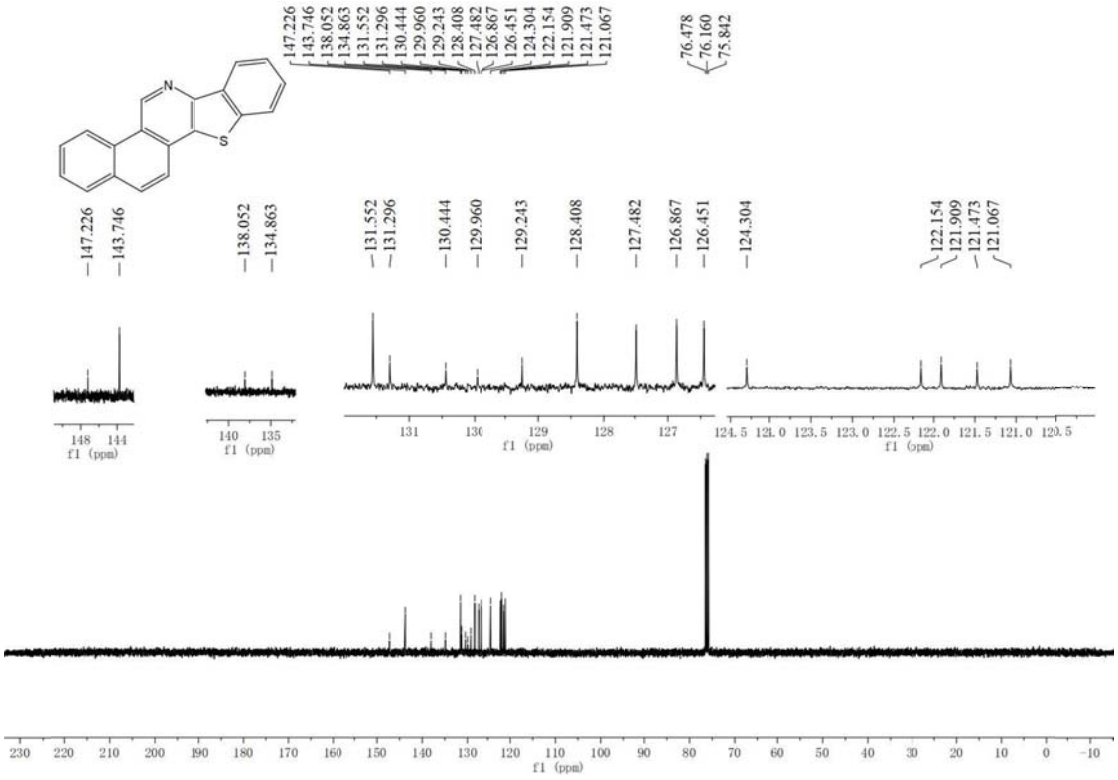
^{13}C NMR spectra of **5l** ($CDCl_3$)



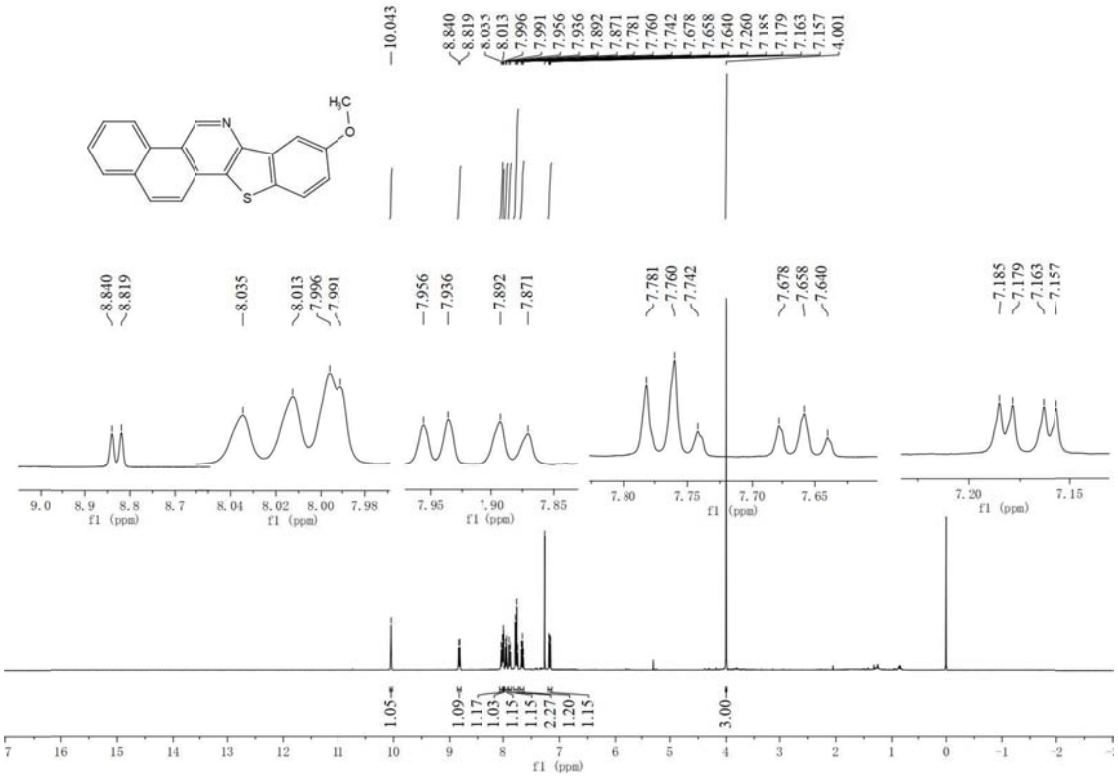
^{1}H NMR spectra of **5m** ($CDCl_3$)



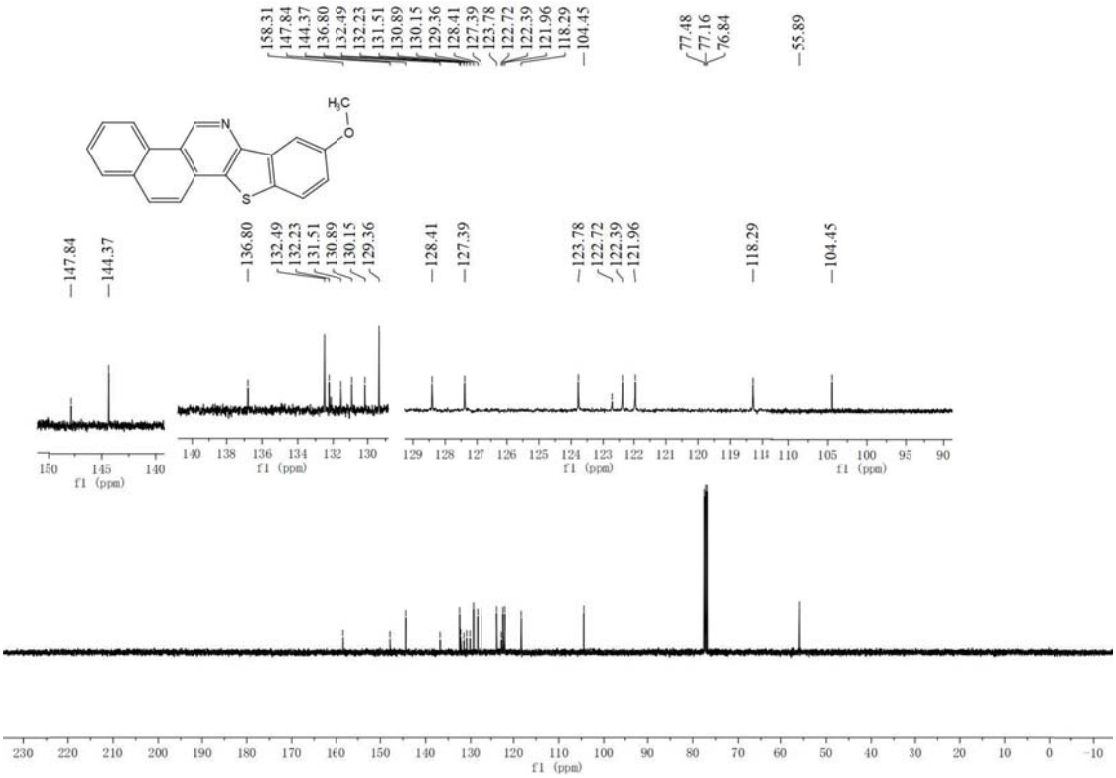
^{13}C NMR spectra of **5m** ($CDCl_3$)



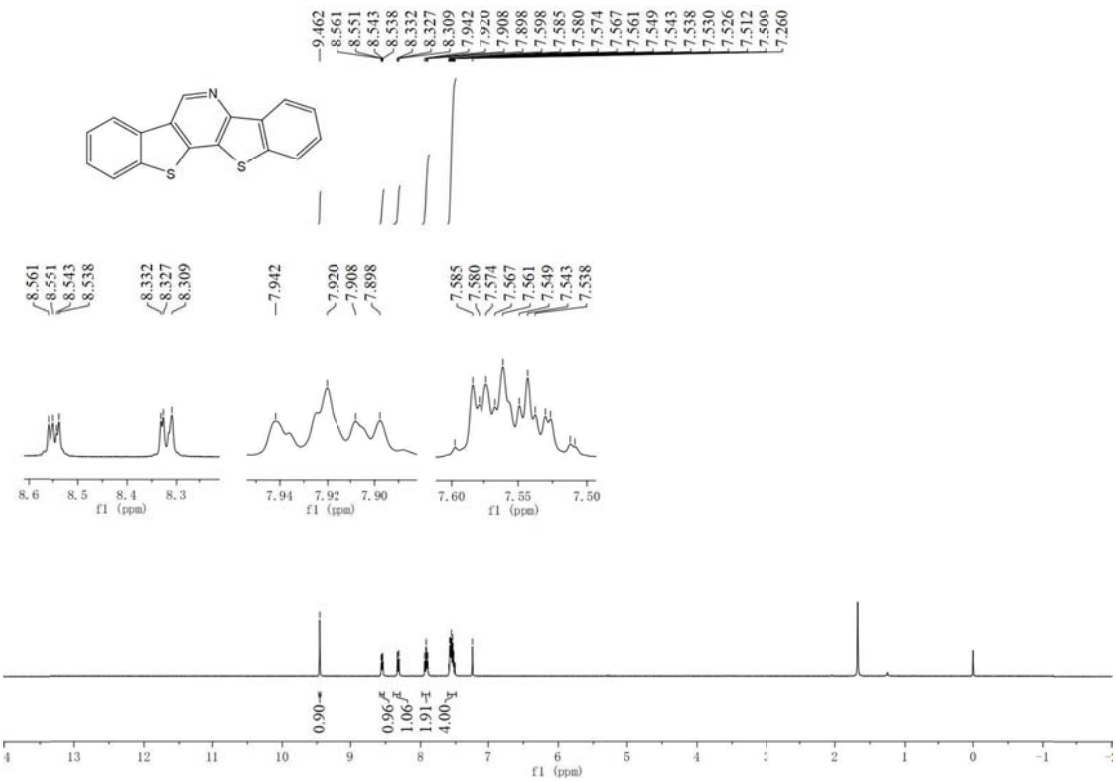
^{1}H NMR spectra of **5n** ($CDCl_3$)



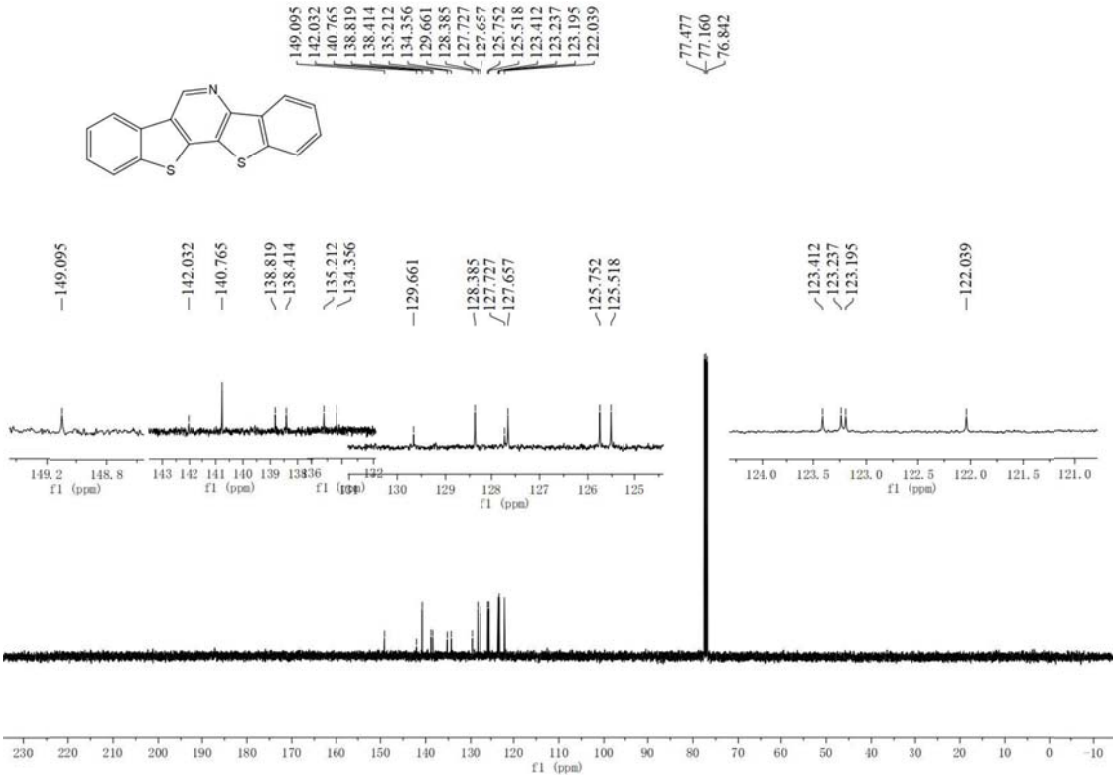
^{13}C NMR spectra of **5n** ($CDCl_3$)



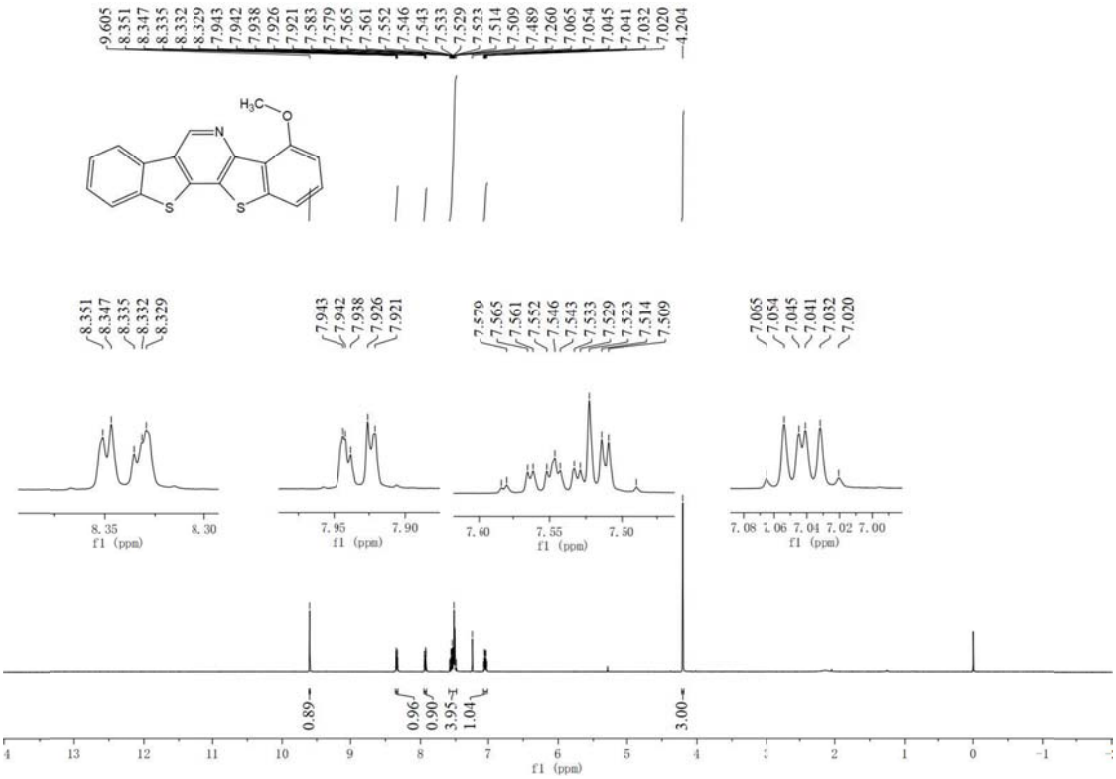
^{1}H NMR spectra of **5o** ($CDCl_3$)



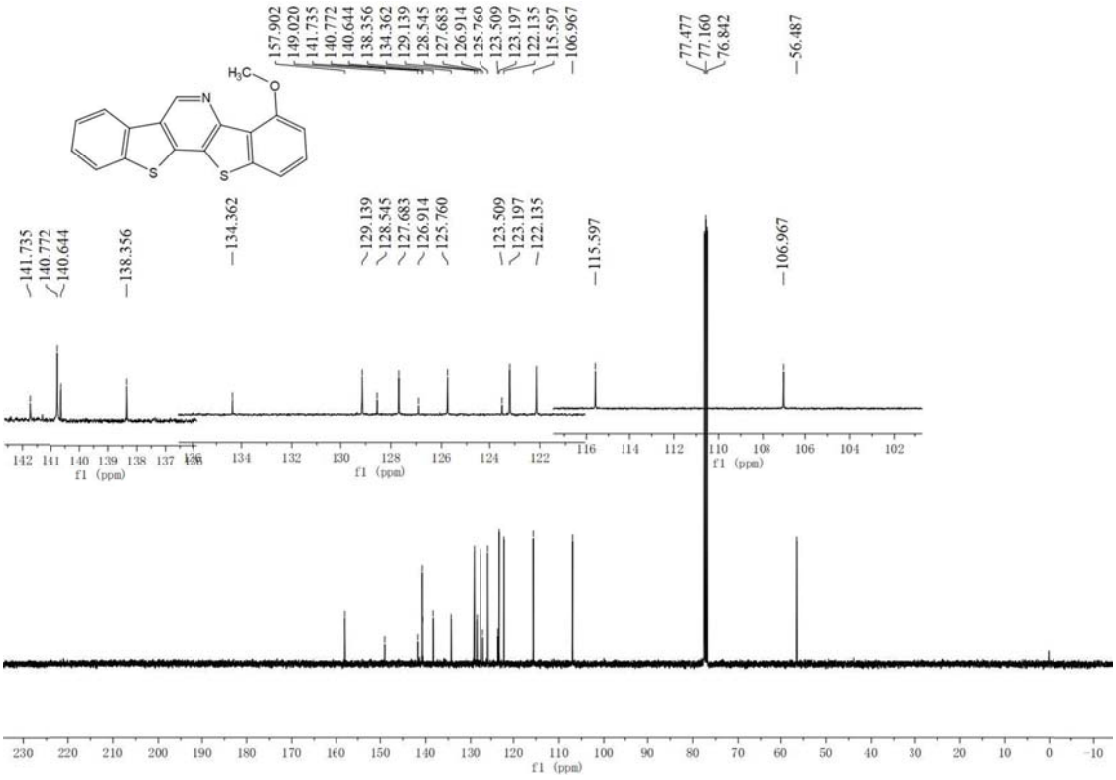
^{13}C NMR spectra of **5o** ($CDCl_3$)



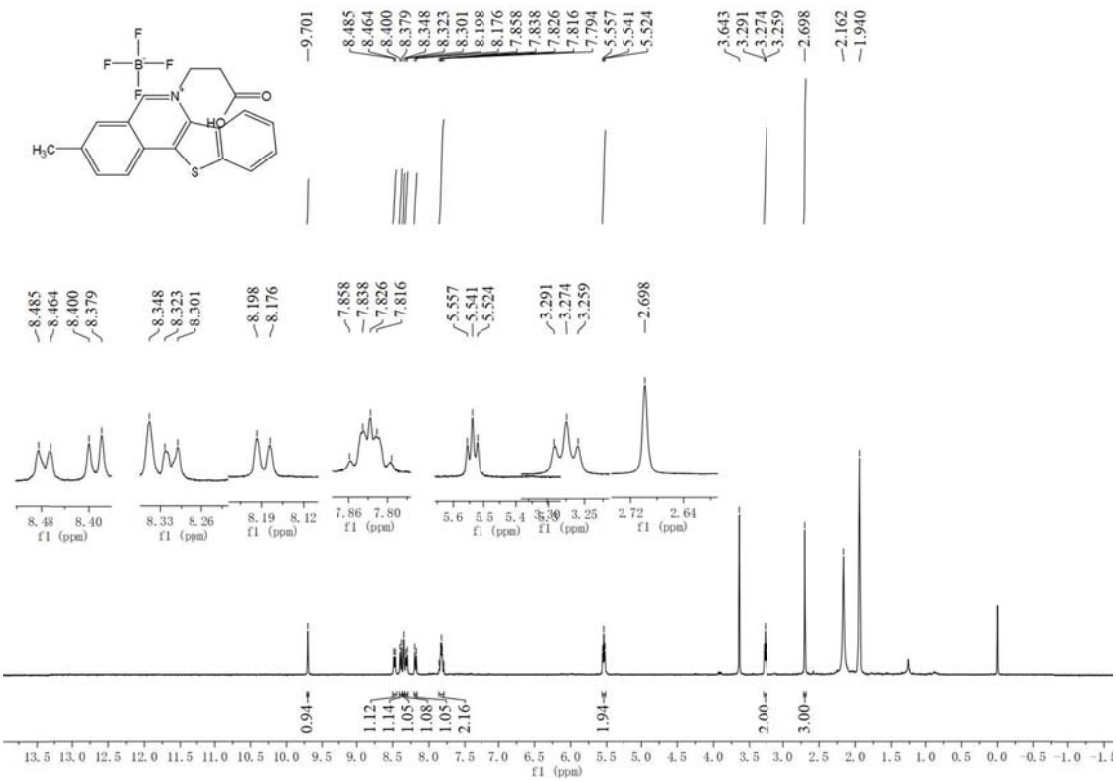
^{1}H NMR spectra of **5p** ($CDCl_3$)



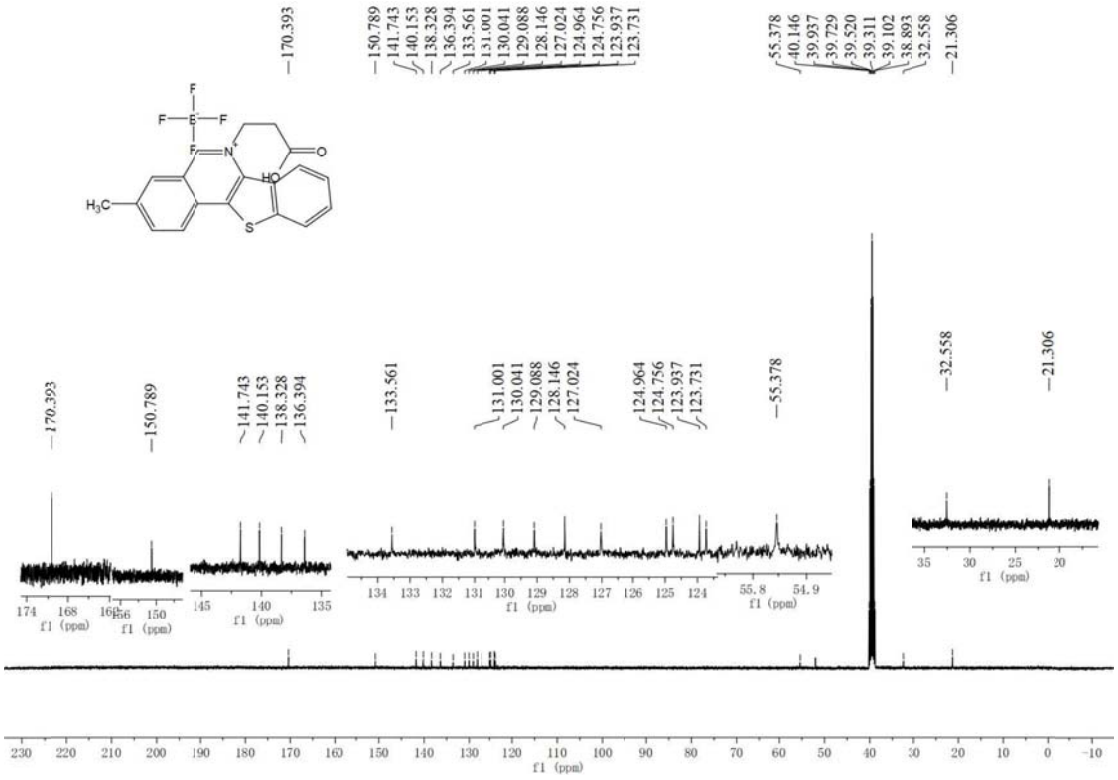
^{13}C NMR spectra of **5p** ($CDCl_3$)



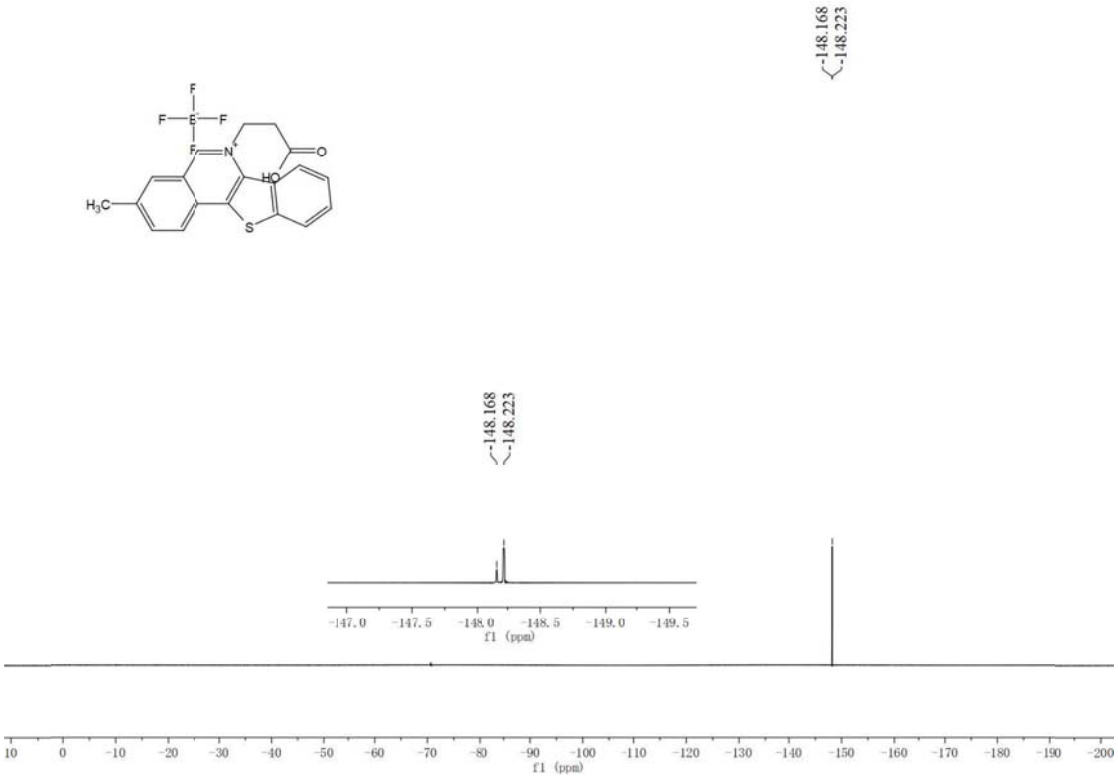
^{1}H NMR spectra of **6a** (CD_3CN)



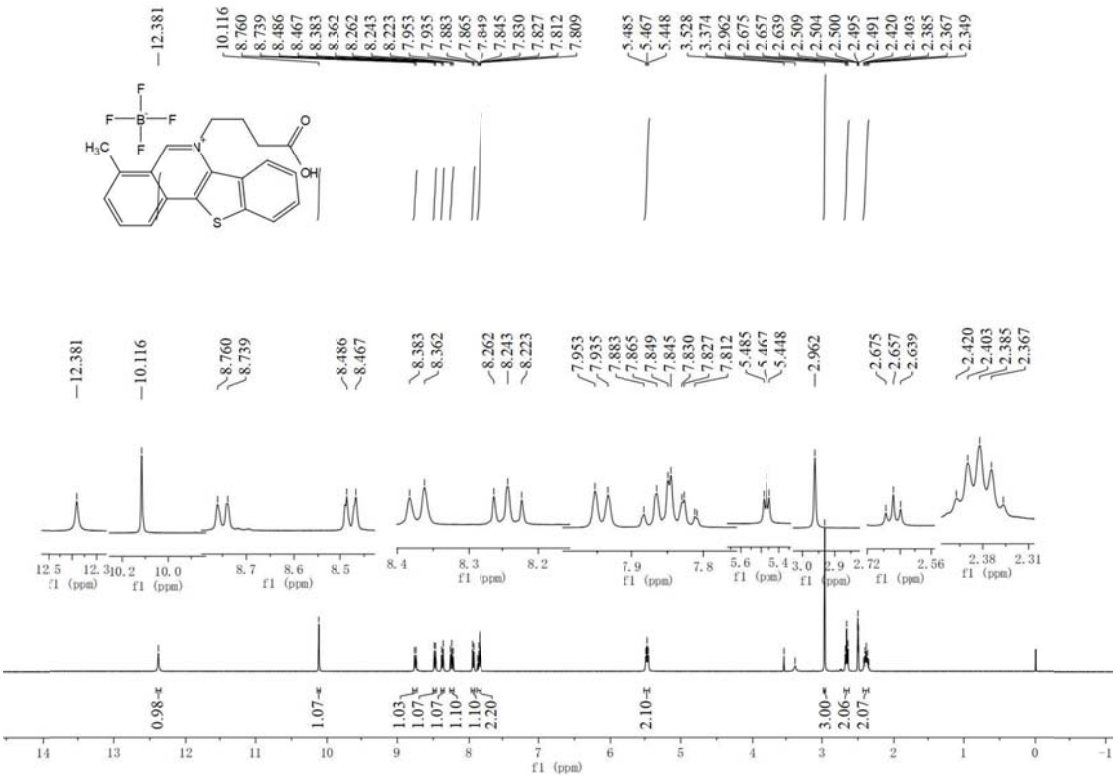
^{13}C NMR spectra of **6a** (DMSO-d_6)



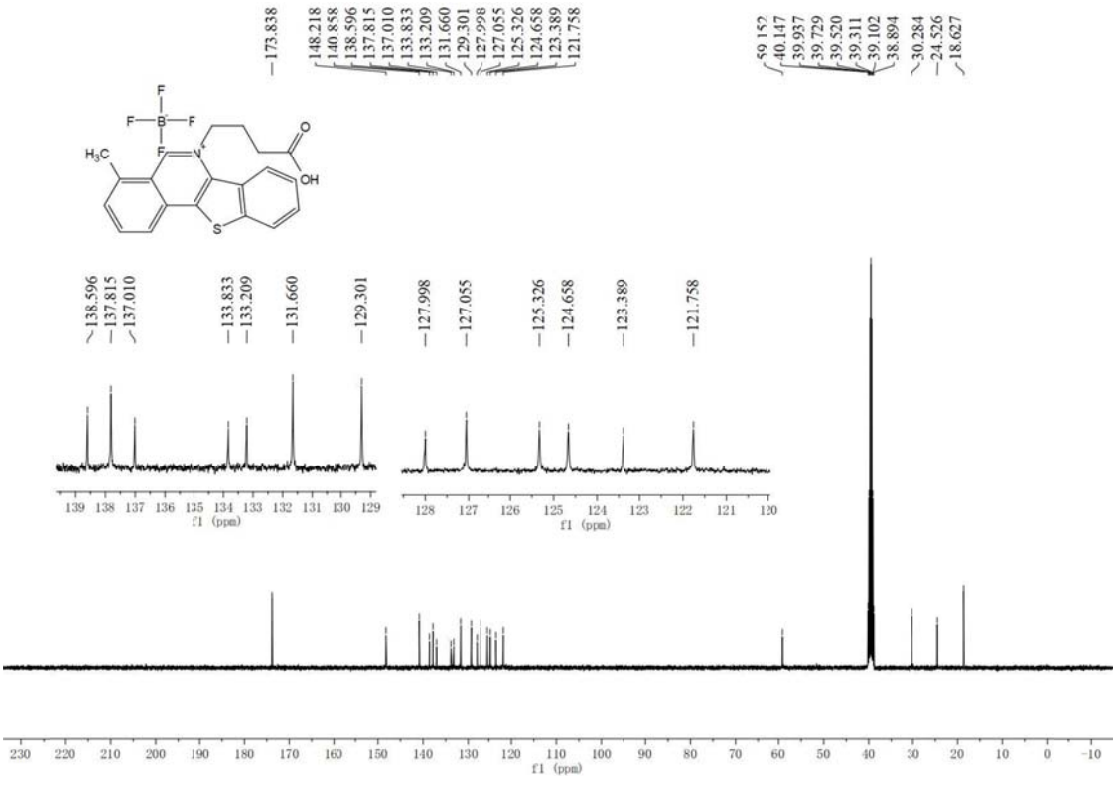
^{19}F NMR spectra of **6a** (DMSO-d_6)



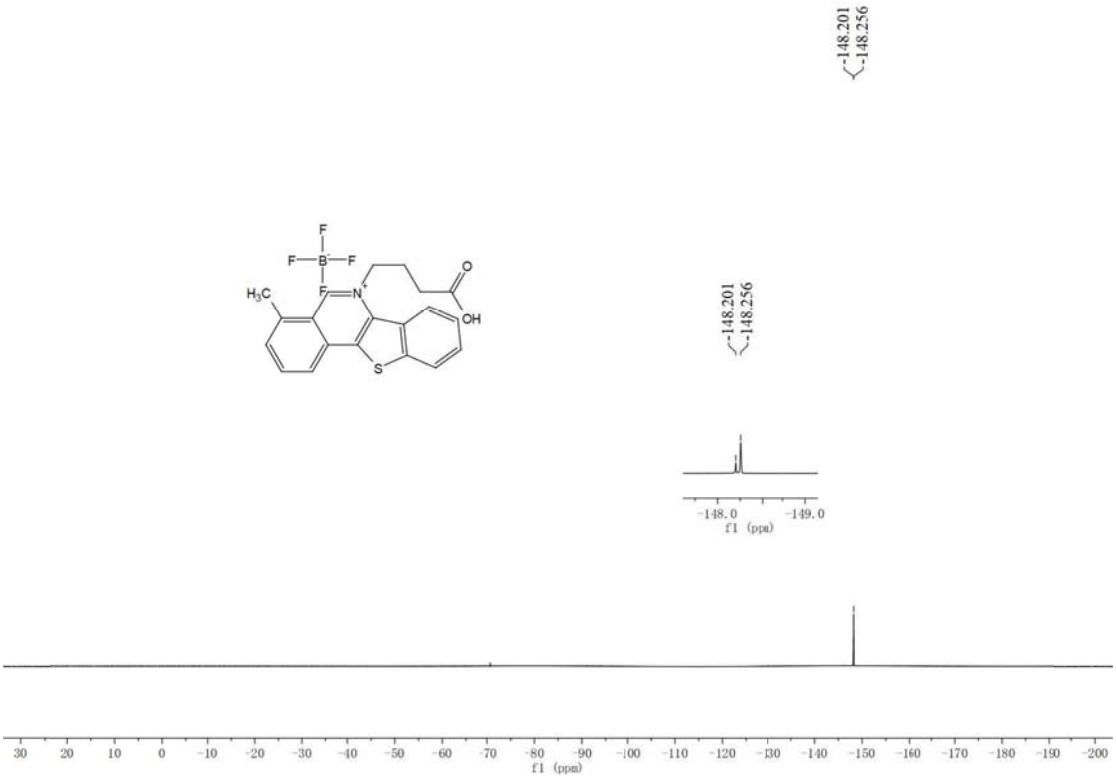
^{1}H NMR spectra of **6b** (DMSO-d_6)



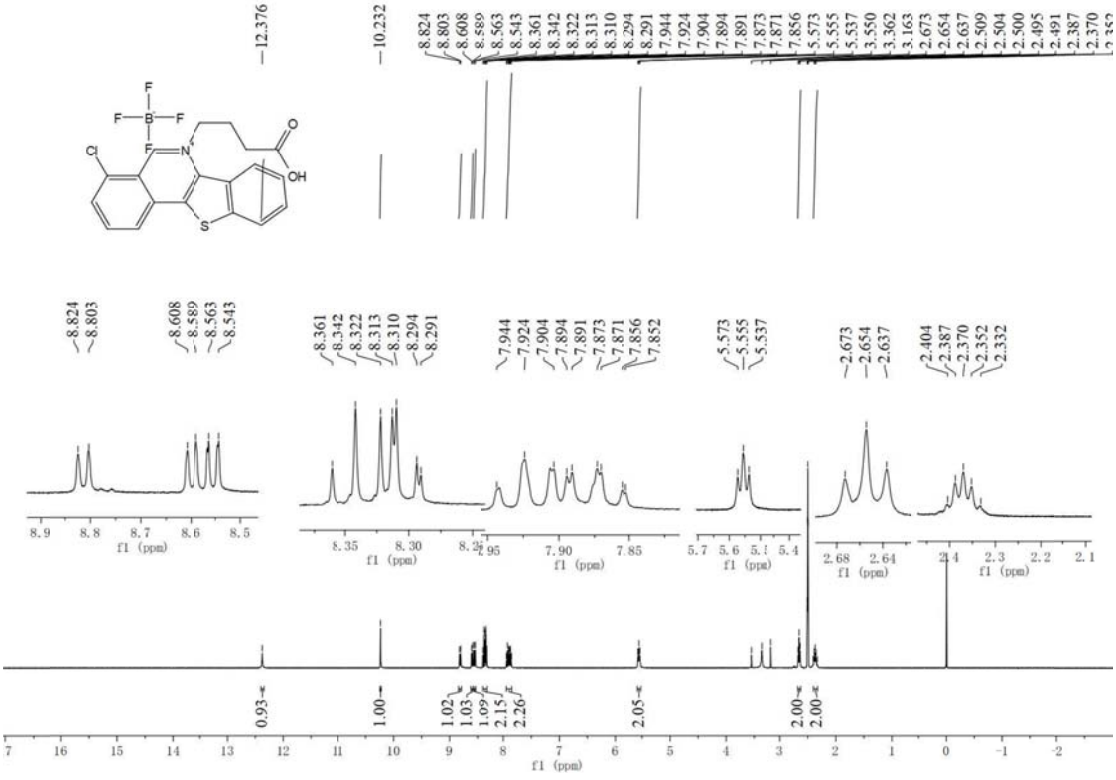
^{13}C NMR spectra of **6b** (DMSO-d_6)



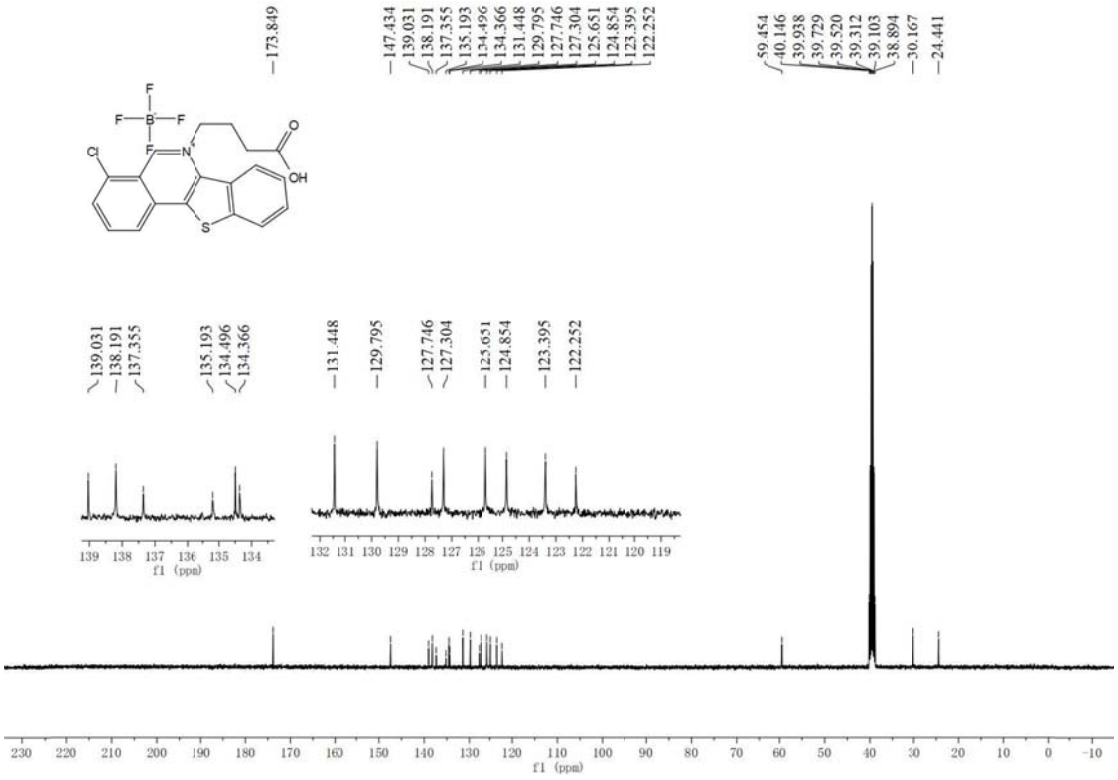
^{19}F NMR spectra of **6b** (DMSO-d_6)



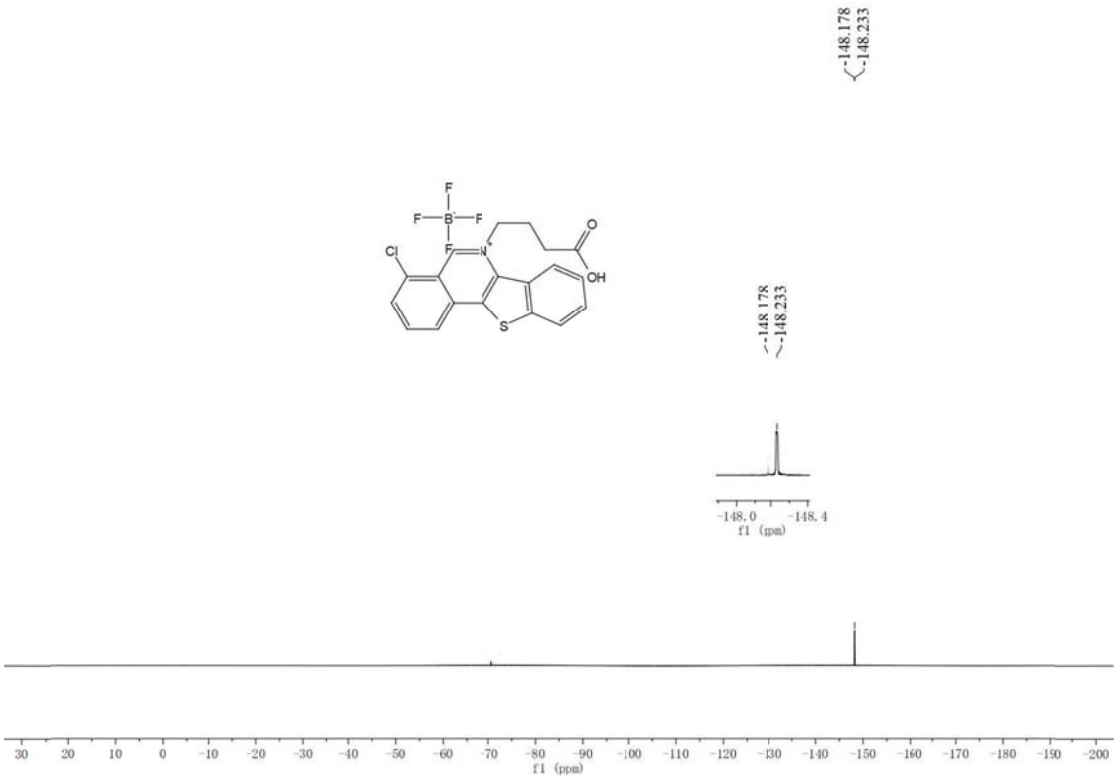
^{1}H NMR spectra of **6c** (DMSO-d_6)



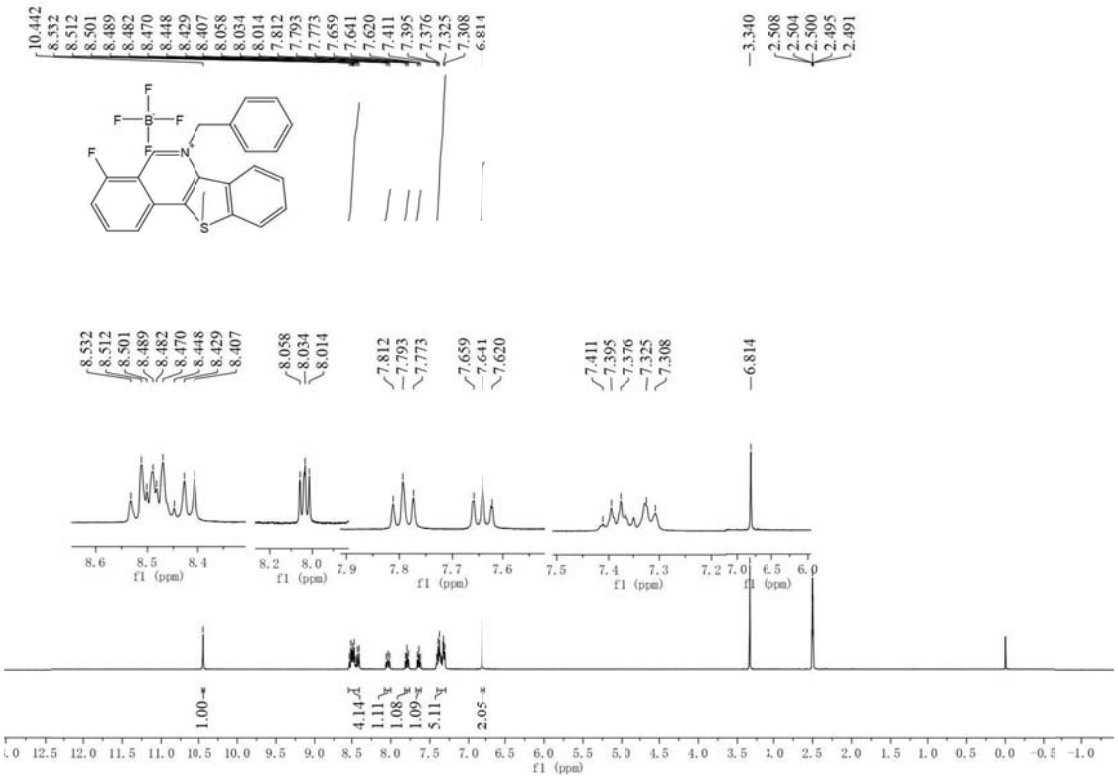
^{13}C NMR spectra of **6c** (DMSO-d_6)



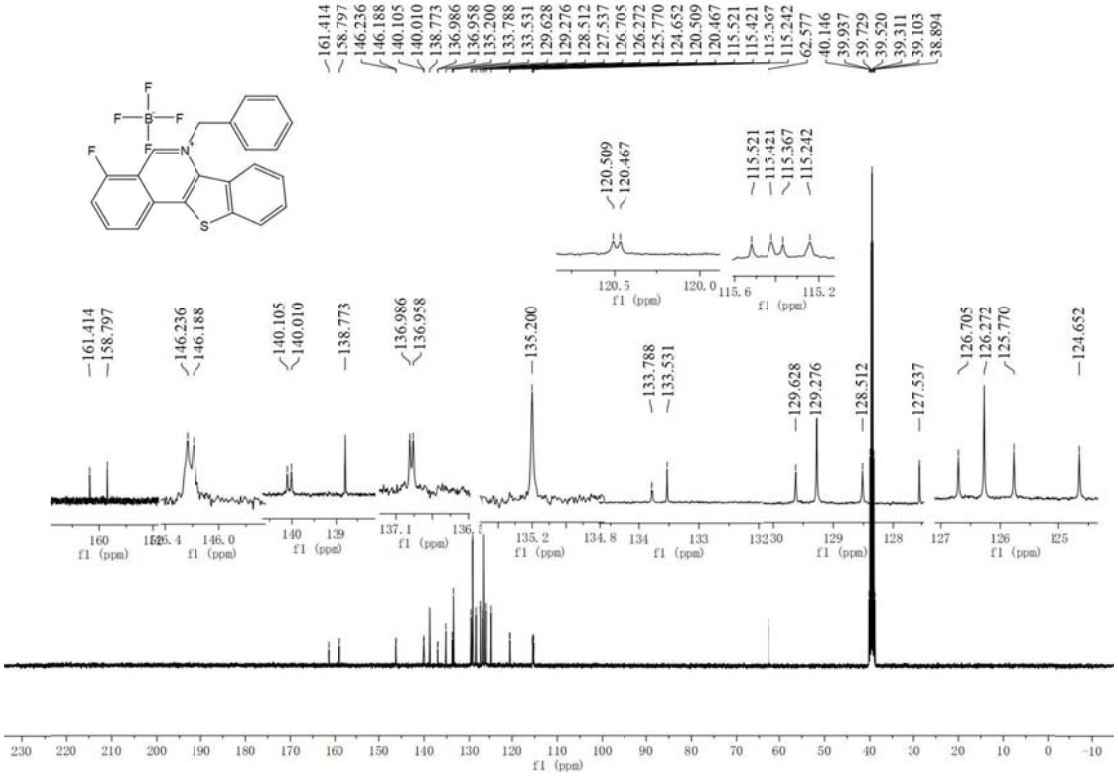
^{19}F NMR spectra of **6c** (DMSO-d_6)



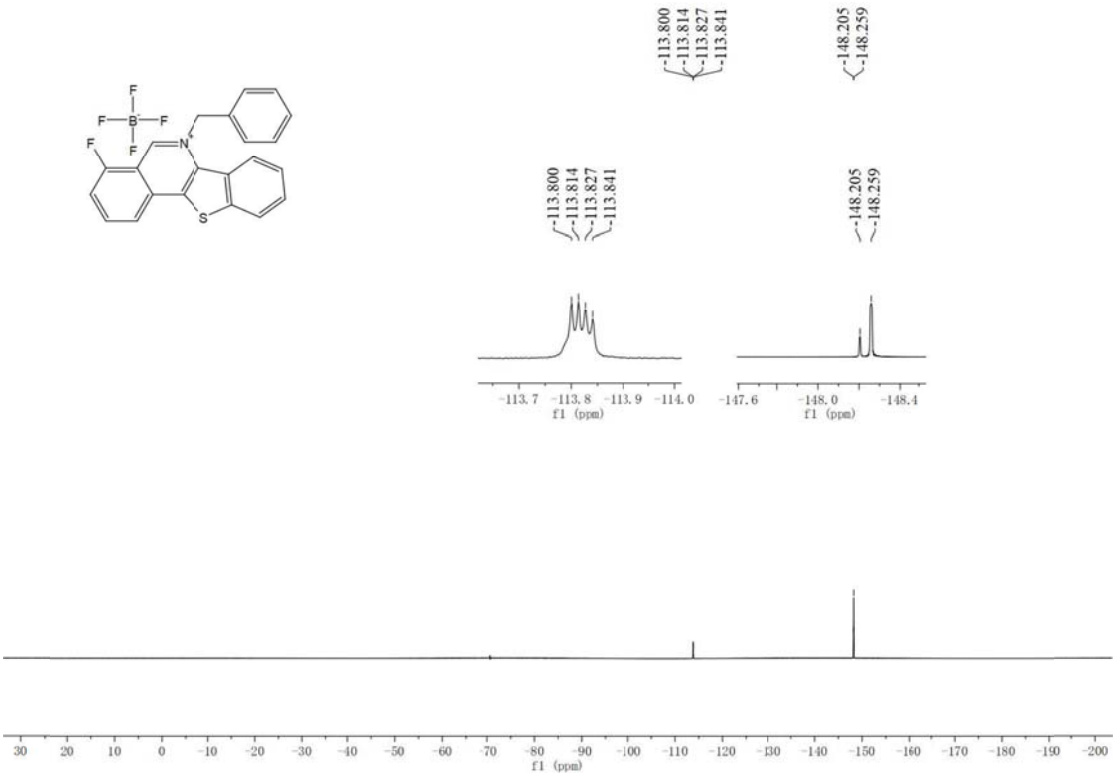
^{1}H NMR spectra of **6d** (DMSO-d_6)



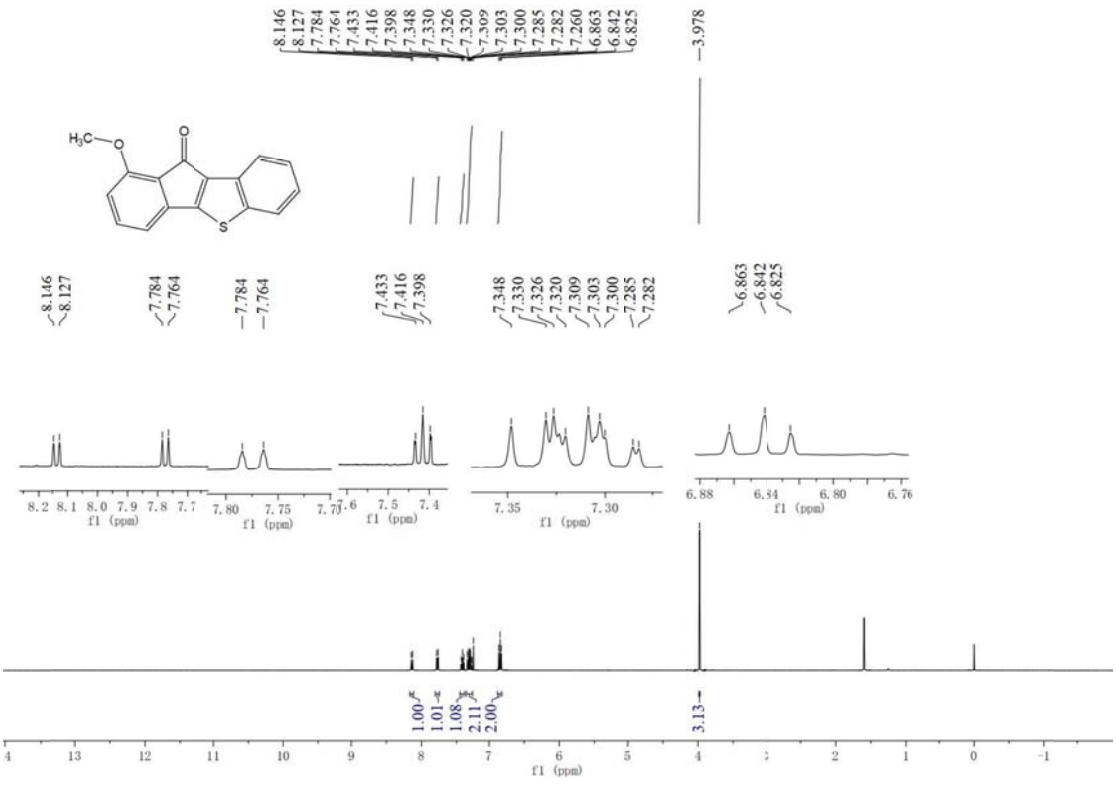
^{13}C NMR spectra of **6d** (DMSO-d_6)



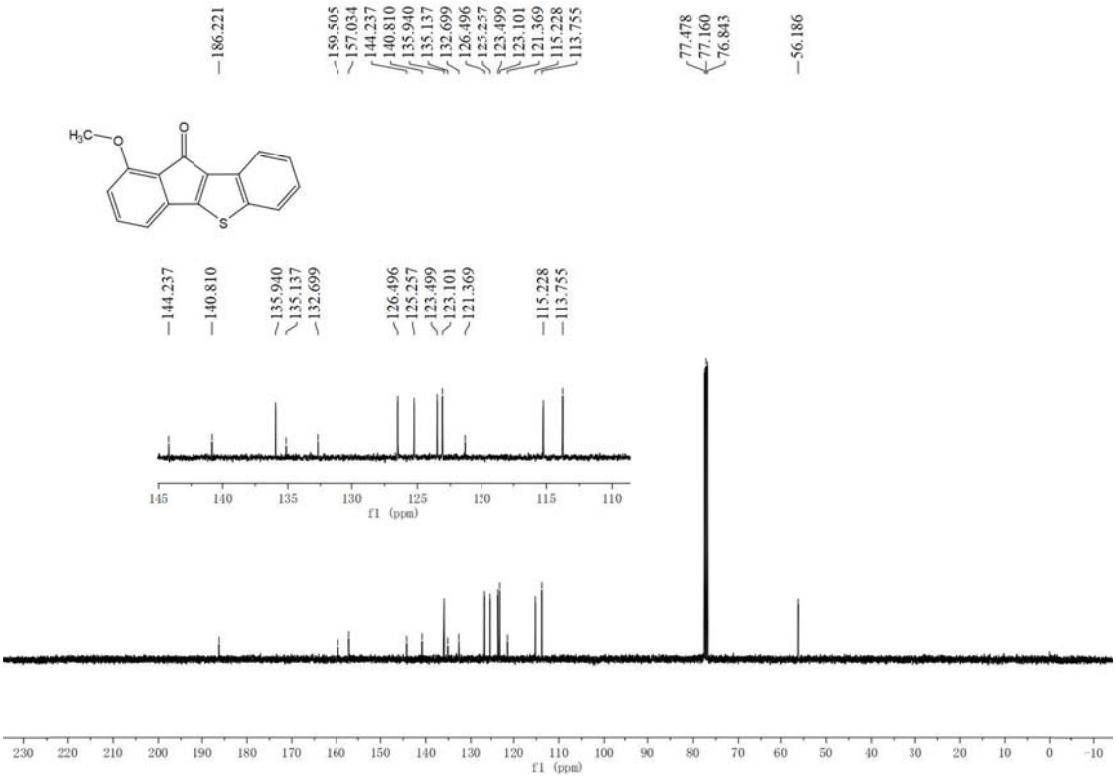
^{19}F NMR spectra of **6d** (DMSO-d_6)



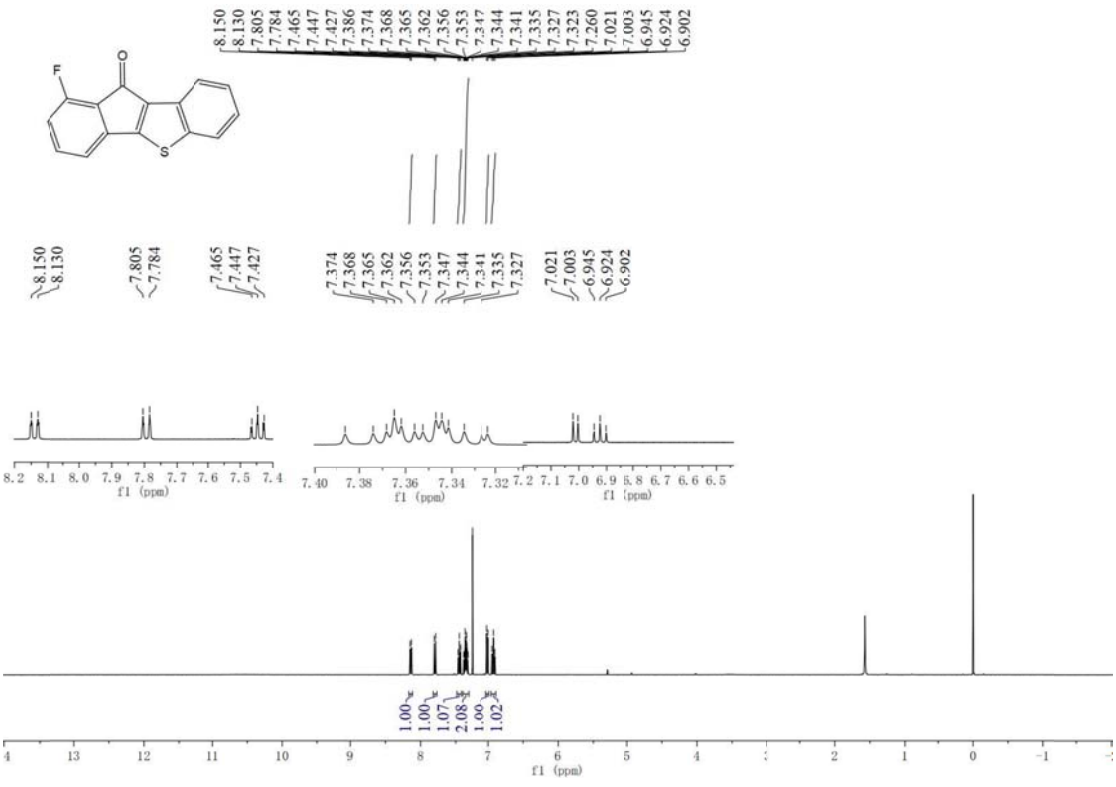
^{1}H NMR spectra of **7a** ($CDCl_3$)



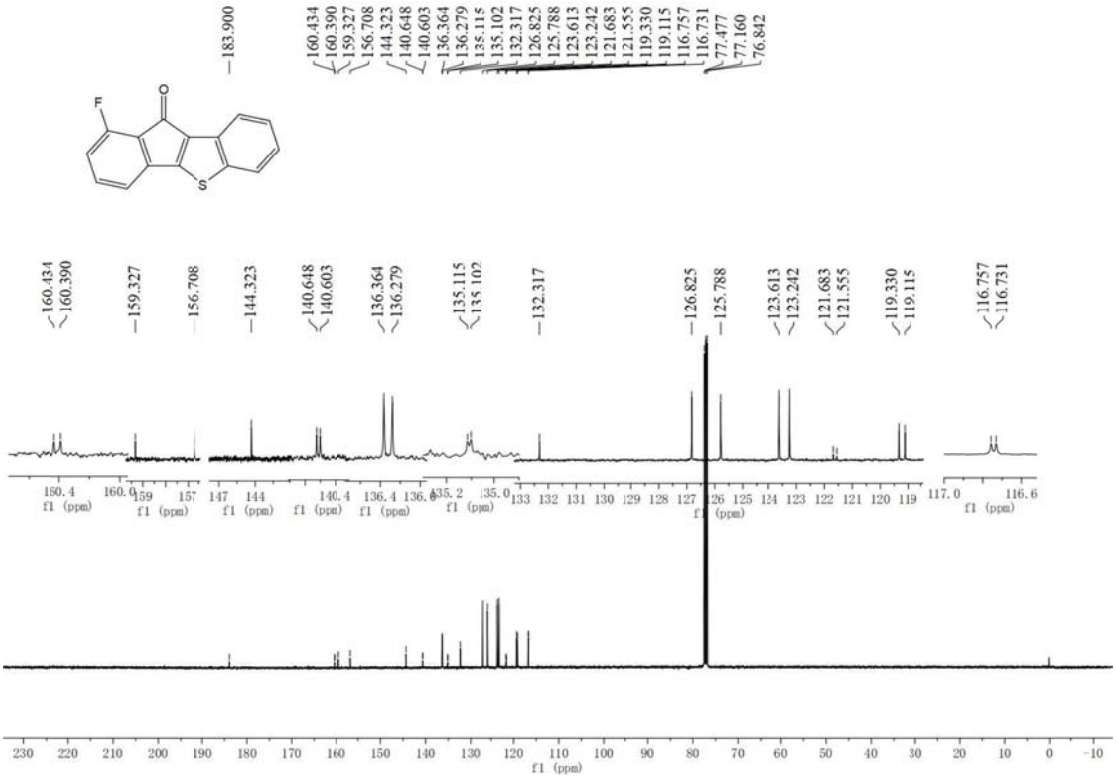
^{13}C NMR spectra of **7a** ($CDCl_3$)



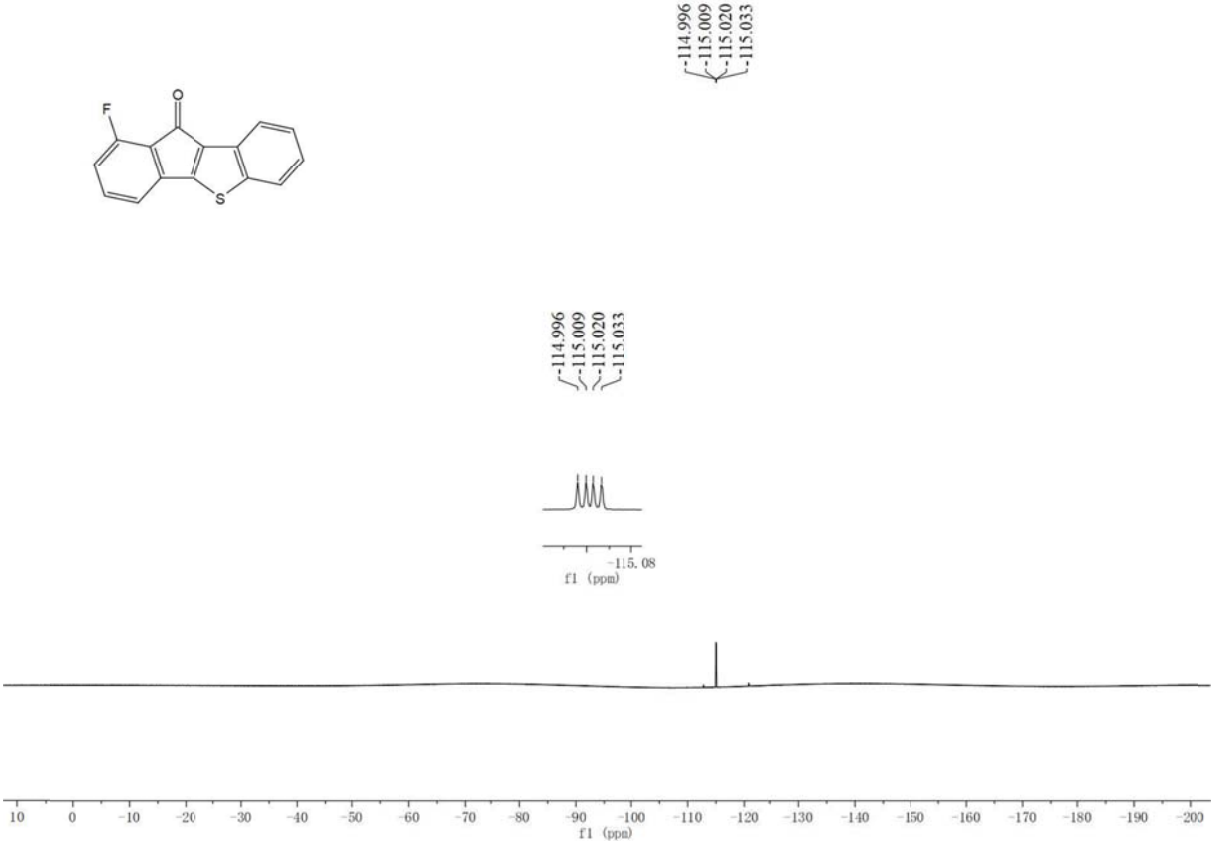
^{1}H NMR spectra of **7b** ($CDCl_3$)



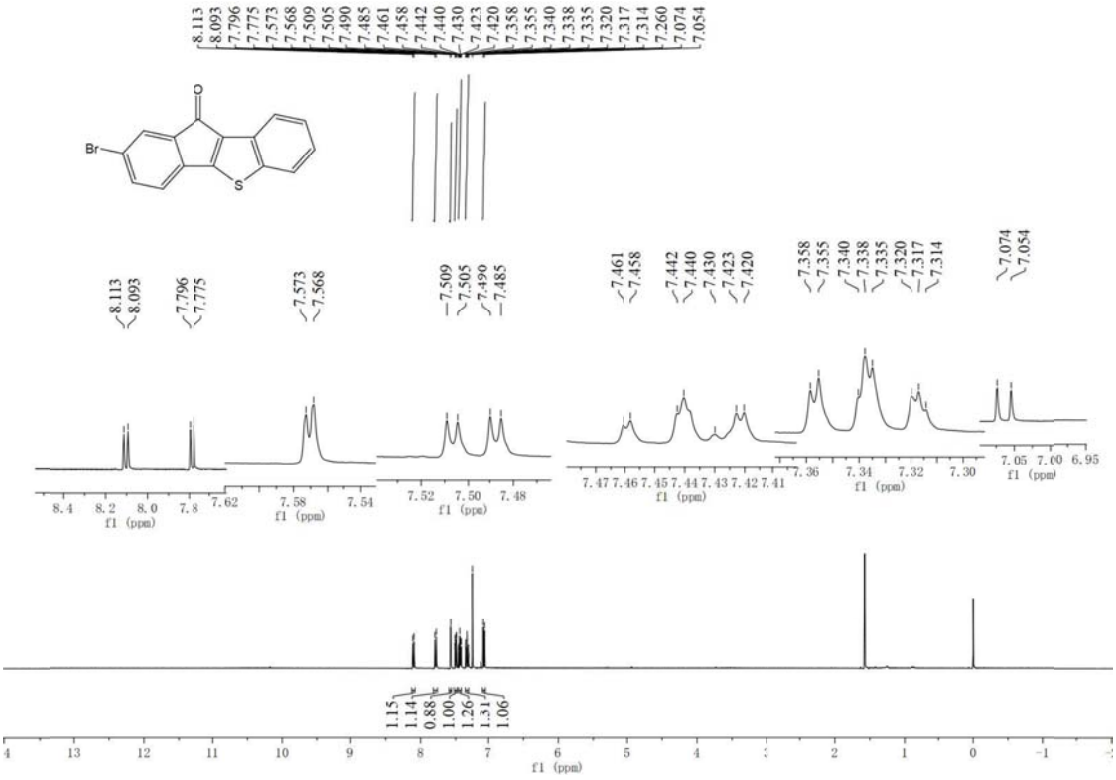
^{13}C NMR spectra of **7b** ($CDCl_3$)



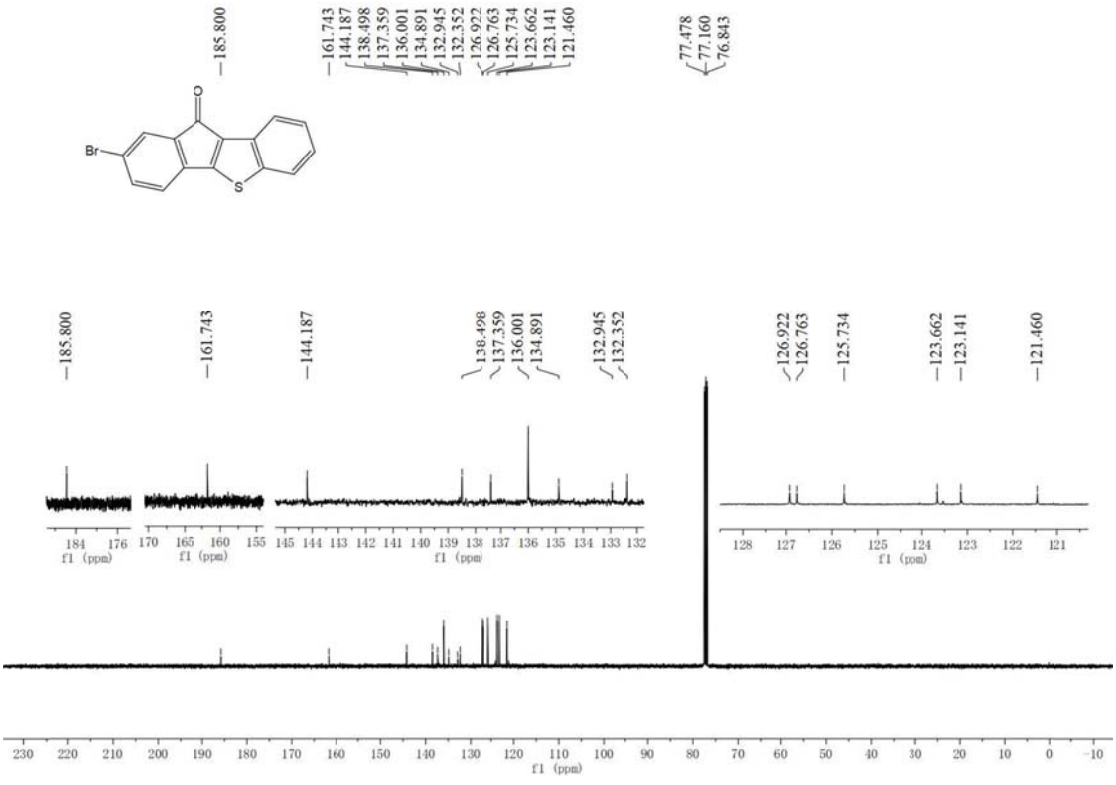
^{19}F NMR spectra of **7b** ($CDCl_3$)



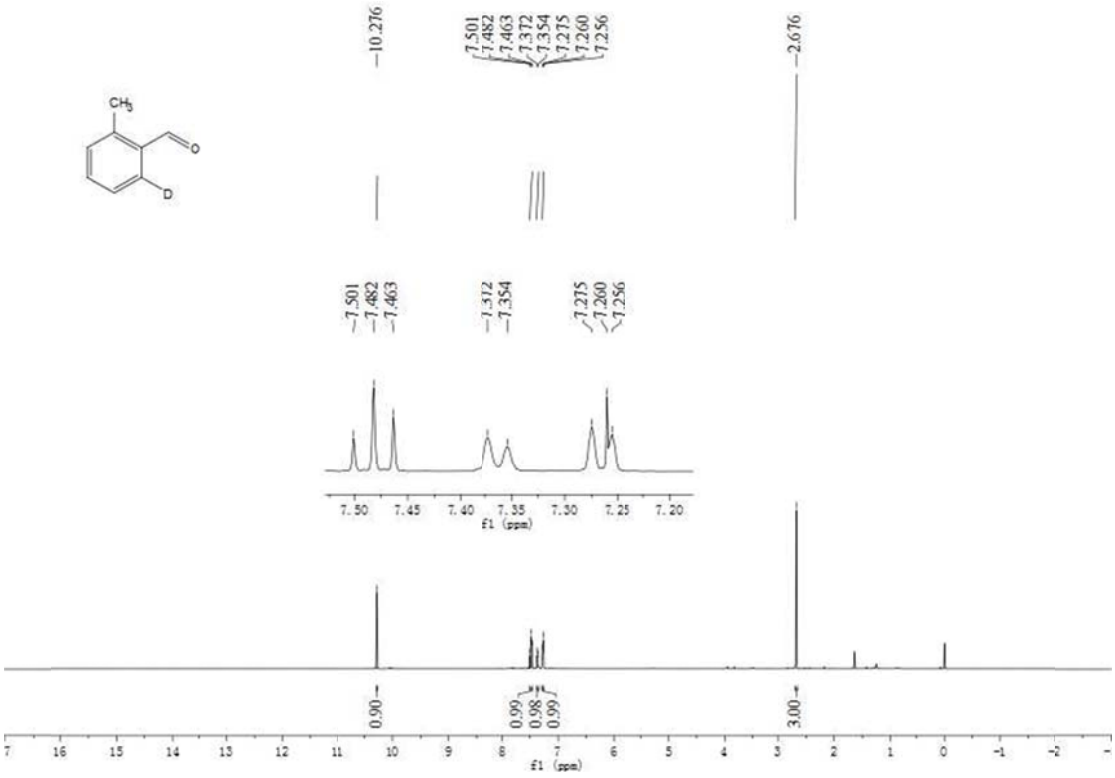
^{1}H NMR spectra of **7c** ($CDCl_3$)



^{13}C NMR spectra of **7c** ($CDCl_3$)



^{1}H NMR spectra of [D_1]-**1h** ($CDCl_3$)



^{13}C NMR spectra of [D_1]-**1h** ($CDCl_3$)