Supporting Information

Cu(I)-Catalyzed Oxidative Homo-Coupling of Thiazoline-4-Carboxylates: Synthesis of 4,4'-Bithiazoline Derivatives

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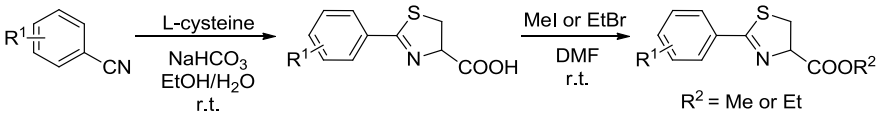
1. General Information

All chemicals and reagents were purchased from commercial suppliers and used without further purification. The products were purified by flash chromatography on silica gel. Melting point (mp) was measured on a microscopic melting point apparatus. ^{1}H NMR spectra were recorded at 300 MHz NMR spectrometer. ^{13}C NMR spectra were recorded at 75 MHz NMR spectrometer. NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. High resolution mass measurement was performed with an electrospray ionization (ESI) method on a Q-TOF mass spectrometer operating in positive ion mode.

2. General Procedure for the Preparation of Substrates

2.1 Preparation of Thiazoline-4-carboxylates

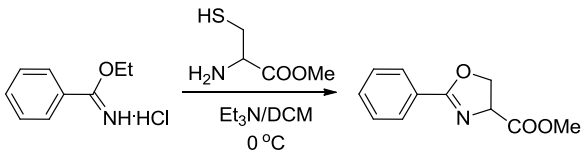
As shown in **Scheme S1**, the suspension of benzonitrile (20 mmol) and L-cysteine (40 mmol) in EtOH (30 mL) was stirred at room temperature or refluxed for 3 h, then water (20 mL) was added and the reaction mixture was stirred at room temperature overnight. EtOH was removed in vacuum. To the remaining solution was added 1N HCl to adjust to pH = 3 under 0 ℃. The resulting precipitate was filtered to yield a white solid 2-pheny-4, 5-dihydrothiazole-4-carboxylic acid, which was used directly to next step without purification. Crude 2-phenyl-4, 5-dihydrothiazole-4-carboxylic acid (4.1g, 20 mmol) was dissolved in 20 mL DMF at 0 ℃, to which potassium bicarbonate (2.0 g, 20 mmol) was added. After stirring for 30 min, iodomethane (1.86 mL, 30 mmol) was added and the solution was brought to room temperature and stirred for 3h until completion by TLC (hexanes: ethyl acetate = 10:1). The reaction mixture was then diluted in ethyl acetate (40 mL), washed with brine 3 times, and dried over Na_2SO_4. The crude product mixture was then concentrated in vacuum and purified by flash chromatography on silica gel to yield the product as a white solid (3.63 g, 82% yield, 2 steps, mp 67 ℃). Data are consistent with a previously characterized compound. All other thiazolines were prepared via a route reported by corresponding literatures.[1]



Scheme S1. Preparation of thiazoline-4-carboxylates

2.2 Preparation of Oxazoline-4-carboxylates

As shown in **Scheme S2**, to a dichloromethane solution (20 mL) of L-serine methyl ester hydrochloride (1.85 g, 10 mmol) and ethyl benzimidate hydrochloride (2.08 g, 13.4 mmol) was added triethylamine (1.9 mL, 13.4 mmol) at 0 ℃ and the reaction mixture was then stirred at room temperature overnight. After completion of the reaction, the reaction mixture was diluted with dichloromethane (30 mL), washed with saturated $NaHCO_3$ solution (40 mL) and brine (40 mL), dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the product (5.71 g, 89% yield) as a white liquid.[2]



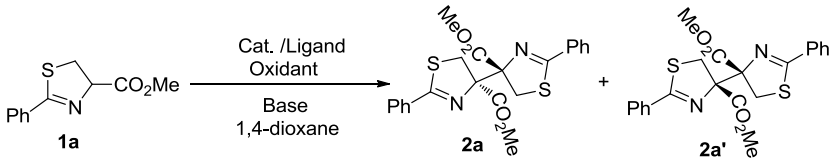
Scheme S2. Preparation of oxazoline-4-carboxylate

3. Cu(I)-catalyzed Homo-coupling of Azoline-4-carboxylates

3.1 General Procedure

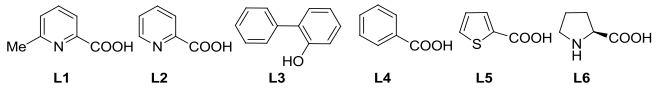
3.1.1 Optimization for Synthesis of 4,4'-Bithiazoline-4-carboxylates[a]

Table S1 Screening of Reaction Conditions[a]



Entry	Cat. (mol %)	Base	Solvent (1.0 mL)	Ligand	T (^{o}C)	Yield (%)[b]	dr[b]
1	CuI (10)	Cs_2CO_3	1,4-dioxane	**L1**	70	44	1.4:1
2	CuI (10)	CsF	1,4-dioxane	**L1**	70	trace	/
3	CuI (10)	CsOAc	1,4-dioxane	**L1**	70	60	1.2:1
4	CuI (10)	K_2CO_3	1,4-dioxane	**L1**	70	trace	/
5	CuI (10)	Na_2CO_3	1,4-dioxane	**L1**	70	trace	/
6	CuI (10)	Et_3N	1,4-dioxane	**L1**	70	trace	/
7	CuI (10)	K_3PO_4	1,4-dioxane	**L1**	70	40	1.9:1
8	CuI (10)	DIPEA	1,4-dioxane	**L1**	70	nr	/
9	Cu_2O (10)	CsOAc	DCM	**L1**	70	36	1.3:1
10	Cu_2O (10)	CsOAc	DCE	**L1**	70	30	1.5:1
11	Cu_2O (10)	CsOAc	THF	**L1**	70	39	1.3:1
12	Cu_2O (10)	CsOAc	toluene	**L1**	70	31	1.2:1
13	Cu_2O (10)	CsOAc	DMF	**L1**	70	trace	/
14	Cu_2O (10)	CsOAc	MeOH	**L1**	70	33	1.3:1
15	Cu_2O (10)	CsOAc	MeCN	**L1**	70	52	1.4:1
16	Cu_2O (10)	CsOAc	1,4-dioxane	**L2**	70	67	1.2:1
17	Cu_2O (10)	CsOAc	1,4-dioxane	**L3**	70	23	1.8:1
18	Cu_2O (10)	CsOAc	1,4-dioxane	**L4**	70	68	1.4:1
19	Cu_2O (10)	CsOAc	1,4-dioxane	**L5**	70	33	1.4:1
20	Cu_2O (10)	CsOAc	1,4-dioxane	**L6**	70	59	1.7:1
21	Cu_2O (5)	CsOAc	1,4-dioxane	**L1**	70	44	1.1:1
22	Cu_2O (15)	CsOAc	1,4-dioxane	**L1**	70	82	1.1:1
23	Cu_2O (20)	CsOAc	1,4-dioxane	L1	70	69	1.2:1
24	Cu_2O (15)	CsOAc	1,4-dioxane	L1	65	63	1.1:1

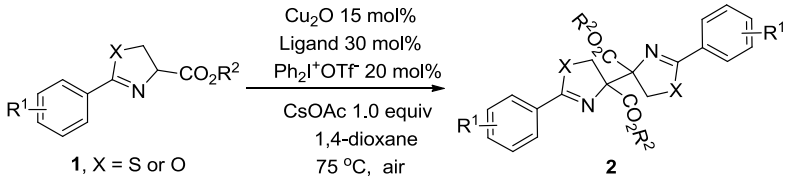
25	**Cu_2O (15)**	**CsOAc**	**1,4-dioxane**	L1	**75**	**84 (86)** [c]	**1.5:1**
26	Cu_2O (15)	CsOAc	1,4-dioxane	L1	80	65	1.2:1
27	Cu_2O (15)	NaOH	1,4-dioxane	L1	75	trace	/
28	Cu_2O (15)	KOH	1,4-dioxane	L1	75	trace	/
29[d]	Cu_2O (15)	CsOAc	1,4-dioxane	L1	75	81	1.3:1



L1 L2 L3 L4 L5 L6

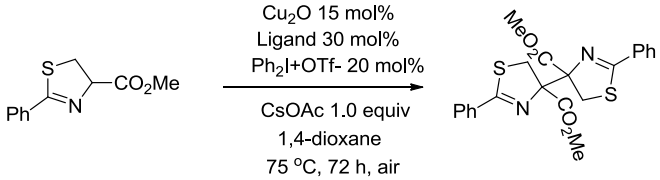
[a] Reaction conditions: **1a** (0.4 mmol, 1 equiv), catalyst, ligand (0.12 mmol), oxidant (0.08 mmol), CsOAc (0.4 mmol), 1,4-dioxane (1.0 mL), air atmosphere, 70 °C, 26 h. [b] Yield and diastereoselectivity ratio were determined by ^{1}H-NMR using dibromomethane (δ = 4.80) as an internal standard. [c] Isolated yield. [d] Under O_2 atmosphere.

3.1.2 Typical Experimental Procedure for Synthesis of 2a-2r



A reaction tube was charged with azole-4-carboxylate **1** (0.4 mmol, 1 equiv), Cu_2O (0.06 mmol, 15 mol %), Ligand (0.12 mmol, 0.3 equiv), $Ph_2I^+OTf^-$ (0.08 mmol, 0.2 equiv), CsOAc (0.4 mmol, 1 equiv) and 1,4-dioxane (1.0 mL). The reaction mixture was vigorously stirred at 75 °C (oil temperature). After stirring for 26 h, the mixture was cooled to room temperature, diluted with dichloromethane and filtered. The filtrate was washed with saturated $NaHCO_3$ solution, water and brine, dried over Na_2SO_4, and concentrated in vacuum to give dark residue, which was purified by flash chromatography on silica gel (PE:EA = 100:1-40:1; TLC: R_{f1} = 0.6-0.4, R_{f2} = 0.5-0.2, PE:EA = 20:1) to afford the desired product **2**.

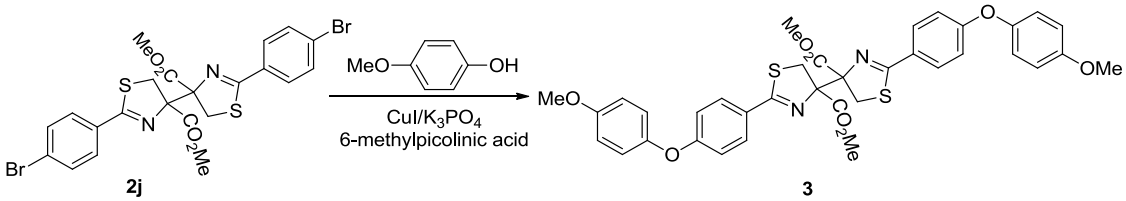
3.1.3 Gram-scale Reaction of 2a



A reaction tube was charged with azole-4-carboxylate **1** (6 mmol, 1.33 g, 1 equiv), Cu_2O (0.9 mmol, 15 mol %), Ligand (1.8 mmol, 0.3 equiv), $Ph_2I^+OTf^-$ (1.2 mmol, 0.2 equiv), CsOAc (6 mmol, 1 equiv) and 1,4-dioxane (5.0 mL). The reaction mixture was vigorously stirred at 75 °C (oil temperature). After stirring for 72 hours, the mixture was cooled to room temperature, diluted with dichloromethane and filtered. The filtrate was washed with saturated $NaHCO_3$, water and brine, dried over Na_2SO_4, and concentrated in vacuo to give dark residue, which was purified by flash chromatography on silica gel to afford 958 mg light yellow solid in 72 % yield, dr = 1.8: 1.

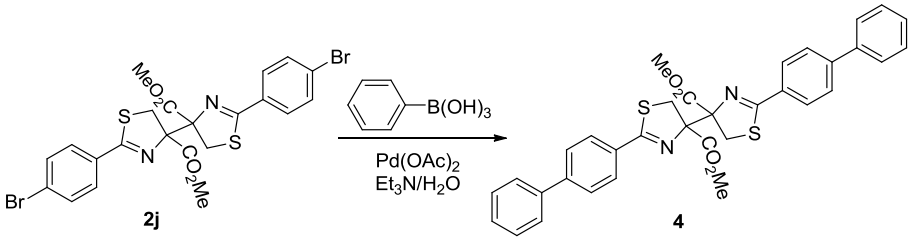
3.1.4 Further Functionalization of Generated Homo-coupling Products

General Procedure for Preparing of 3



A 25 mL flask was charged with **2j** (0.2 mmol, 1 equiv), CuI (0.04 mmol, 20 mol %), 6-methylpicolinic acid (0.08 mmol, 40 mol %), K_3PO_4 (0.8 mmol, 4 equiv) and 4-methoxyphenol (0.6 mmol, 3 equiv). The reaction mixture was then vigorously stirred at 90 ^oC (oil temperature) under argon for 12 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (20 mL) and filtered through a plug of celite. The mixture was concentrated in vacuum and purified by flash chromatography on silica gel to afford the desired product **3** in 56% yield.[3]

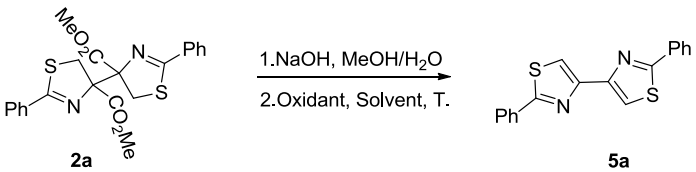
General Procedure for Preparing of 4



A 25 mL flask was charged with **2j** (0.2 mmol, 1.0 equiv), arylboronic acid (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.2 mg, 5 mol %), Et_3N (0.6 mmol, 3.0 equiv) and H_2O (3.0 mL). The reaction mixture was stirred at room temperature under air. After the reaction was stopped, the solution was diluted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, filtered and concentrated in vacuum. The residue was purified by flash chromatography on silica gel to afford the desired product **4** in 71% yield.[4]

General Procedure for Preparing of 4,4'-Bithiazoles

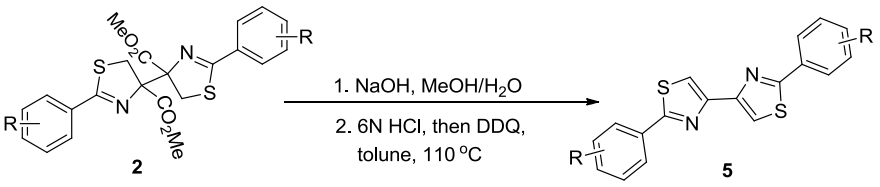
Table S2 Screening of Reaction Conditions [a]



Entry	Oxidant (equiv)	Solvent (2.0 mL)	T (^oC)	Yield (%)[b]
1	MnO_2 (1.1)	DCM	80	trace
2	DDQ (1.1)	DCM	80	31
3	TBHP (1.1)	DCM	80	0

4	DTBP (1.1)	DCM	80	0
5	IBX (1.1)	DCM	80	0
6	DDQ (1.1)	1,4-dioxane	80	<10
7	DDQ (1.1)	toluene	80	52
8	DDQ (1.1)	THF	80	<10
9	DDQ (1.1)	EA	80	41
10	DDQ (1.1)	MeCN	80	trace
11	DDQ (2.0)	toluene	80	56
12	DDQ (3.0)	toluene	80	66
13	DDQ (3.0)	toluene	rt	trace
14	DDQ (3.0)	toluene	100	68
15	**DDQ (3.0)**	**toluene**	**110**	**74 (70)** [c]

[a] Reaction conditions: (1) **2a** (0.2 mmol), NaOH (1.6 mmol, 8 equiv), MeOH/H_2O (1:1, 3.0 mL); (2) DDQ (0.6 mmol, 3 equiv), toluene (2.0 ml), 110 °C, 24 h. [b] ^{1}H NMR yields using dibromomethane (δ = 4.80) as an internal standard. [c] Isolated yield.



General Procedure. A 25 mL round bottom flask was charged with 0.2 mmol **2**, 1.6 mmol NaOH, 5 mL MeOH/H_2O (1:1), heated to reflux for 2 h.[5] MeOH was removed in vacuum. 6 N HCl was added until pH = 4, the resulting precipitate was filtered to yield a white solid 2,2'-diphenyl-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylic acid, which was used directly to next step without purification. A reaction tube was charged with the acid (0.2 mmol, 1 equiv), DDQ (0.6 mmol, 3 equiv) and toluene (2.0 mL). The reaction mixture was vigorously stirred at 110 °C (oil temperature) under air for 24 h. After cooling to room temperature, diluted with dichloromethane and filtered, the filtrate was concentrated in vacuum directly to give dark residue, which was purified by flash chromatography on silica gel to afford the desired product **5**.[6]

3.2 Characterization of the Homo-coupling and Functionalizationed Products

Crystal structure of 2a

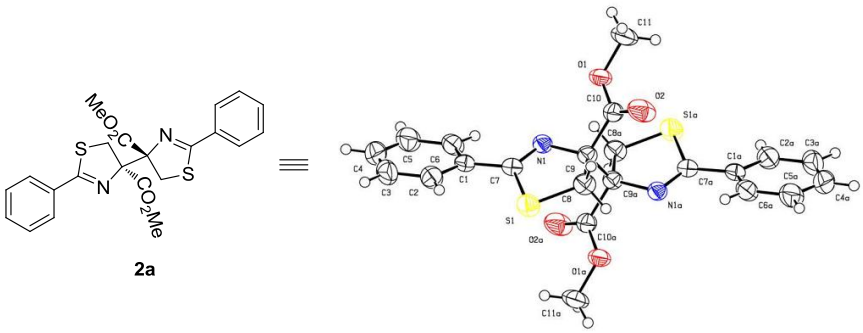


Figure S1. ORTEP plot of the crystal structure of 2a (at 30% probability level).

X-ray crystallographic data of 2a

CCDC number	1441556
Empirical formula	$C_{22}H_{20}N_2O_4S_2$
Formula weight	440.52
Temperature	296 K
Wavelength	0.71073 Å
Space group	P2(1)/c
Unit cell dimensions	a= 9.621(3) Å =90 º
	b= 14.256(5) Å =111.224(5) º
	c= 8.097(3) Å =90 º
Volume	1035.2(6) $Å^3$
Z	2
Density (calculated)	1.413 Mg/m3
F(000)	460.0
Completeness to theta = 25.010 °	99.4%
Absorption correction	MULTI-SCAN
Max. and min. transmission	0.939 and 0.923
R indices (all data)	R= 0.0324(1524) wR2(reflections)= 0.0867(1813)

Crystal structure of 2a'

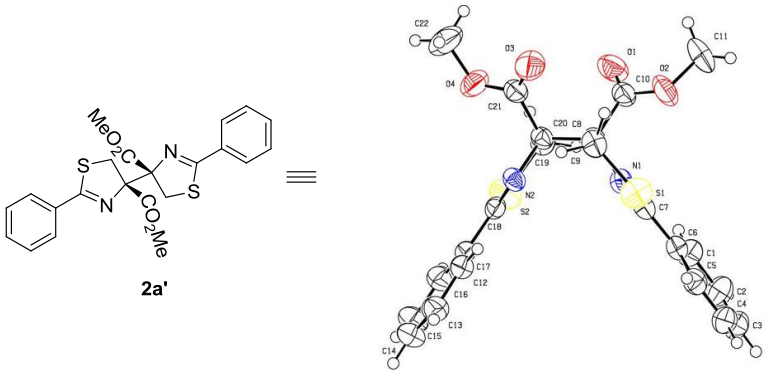


Figure S2. ORTEP plot of the crystal structure of 2a' (at 30% probability level).

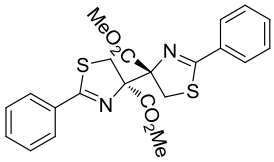
X-ray crystallographic data of 2a'

CCDC number	1444167
Empirical formula	$C_{22}H_{20}N_2O_4S_2$
Formula weight	440.52
Temperature	296 K
Wavelength	0.71073 Å
Space group	P2(1)/c
Unit cell dimensions	a= 11.3995(11) Å =90 º
	b= 15.4075(15) Å = 97.817(2) º

	c= 12.3398(12) Å =90 º
Volume	2147.2(4) Å^3
Z	4
Density (calculated)	1.363 Mg/m3
F(000)	920.0
Completeness to theta = 25.010 °	99.9%
Absorption correction	MULTI-SCAN
Max. and min. transmission	0.941 and 0.926
R indices (all data)	R= 0.0385(3191) wR2= 0.1058(3796)

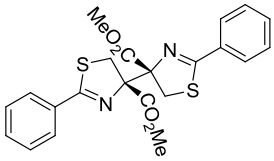
Characterization data of 2a-2r

(4R,4'S)-dimethyl 2,2'-diphenyl-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (2a)



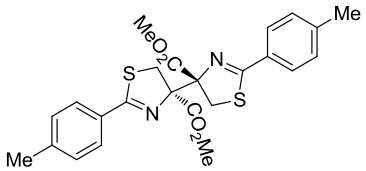
Pale white solid, 45.6 mg, 52% yield, mp 145-146 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.67 (m, 4H), 7.44-7.35 (m, 2H), 7.35-7.27 (m, 4H), 4.57 (d, J = 11.7 Hz, 2H), 4.21 (d, J = 11.7 Hz, 2H), 3.81 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 170.9, 132.8, 131.5, 128.6, 128.4, 94.7, 53.1, 38.9 ppm; HRMS (ESI) calcd for $[C_{22}H_{20}N_2O_4S_2 + H]^+$ 441.0937, found 441.0939.

(4R,4'R)-dimethyl 2,2'-diphenyl-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (2a')



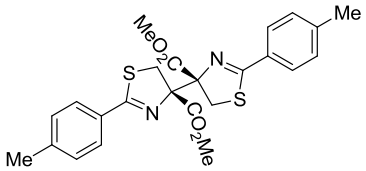
Pale yellow solid, 30.4 mg, 34% yield, mp 165-166 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01-7.76 (m, 4H), 7.61-7.45 (m, 2H), 7.40 (dd, J = 8.2, 6.4 Hz, 4H), 4.14 (d, J = 12.2 Hz, 2H), 3.91 (d, J = 12.2 Hz, 2H), 3.77 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 171.0, 132.8, 131.7, 128.8, 128.5, 92.8, 53.3, 38.6 ppm; HRMS (ESI) calcd for $[C_{22}H_{20}N_2O_4S_2 + H]^+$ 441. 0937, found 441. 0936.

(4R,4'S)-dimethyl 2,2'-di-p-tolyl-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (2b)



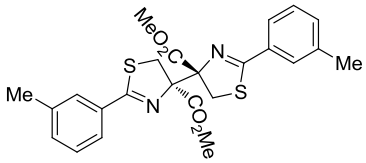
White solid, 32.0 mg, 34% yield, mp 159-160 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 8.2 Hz, 4H), 7.11 (d, J = 7.9 Hz, 4H), 4.54 (d, J = 11.7 Hz, 2H), 4.18 (d, J = 11.7 Hz, 2H), 3.80 (s, 6H), 2.32 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 171.0, 141.8, 130.2, 129.0, 128.6, 94.6, 53.0, 38.8, 21.5 ppm; HRMS (ESI) calcd for $[C_{24}H_{24}N_2O_4S_2 + H]^+$ 469.1250, found 469.1250.

(4R,4'R)-dimethyl 2,2'-di-p-tolyl-4,4',5,5'-tetrahydro-[4,4'-bithiazole]- 4,4'-dicarboxylate (2b')



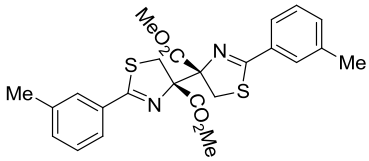
White solid, 29.0 mg, 31% yield, mp 166-167 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 4H), 7.20 (d, J = 7.9 Hz, 4H), 4.12 (d, J = 12.2 Hz, 2H), 3.89 (d, J = 12.2 Hz, 2H), 3.76 (s, 6H), 2.39 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 170.8, 142.2, 130.2, 129.1, 128.8, 92.8, 53.3, 38.5, 21.6 ppm; HRMS (ESI) calcd for $[C_{24}H_{24}N_2O_4S_2 + H]^+$ 469.1250, found 469.1257.

(4R,4'S)-dimethyl 2,2'-di-m-tolyl-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (2c)



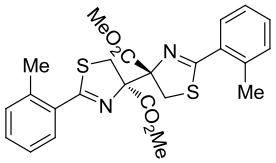
White oil liquid, 36.5 mg, 39% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J = 2.8 Hz, 4H), 7.24-7.12 (m, 4H), 4.55 (d, J = 11.7 Hz, 2H), 4.20 (d, J = 11.7 Hz, 2H), 3.80 (s, 6H), 2.31 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 171.0, 138.1, 132.8, 132.2, 129.1, 128.2, 125.8, 94.6, 53.1, 38.8, 21.3 ppm; HRMS (ESI) calcd for $[C_{24}H_{24}N_2O_4S_2 + H]^+$ 469.1250, found 469.1251.

(4R,4'R)-dimethyl 2,2'-di-m-tolyl-4,4',5,5'-tetrahydro-[4,4'-bithiazole]- 4,4'-dicarboxylate (2c')



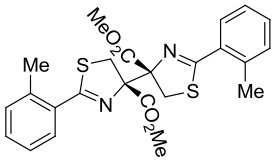
Yellow solid, 33.1 mg, 35% yield, mp 135-136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (s, 2H), 7.68-7.59 (m, 2H), 7.37-7.26 (m, 4H), 4.14 (d, J = 12.2 Hz, 2H), 3.90 (d, J = 12.2 Hz, 2H), 3.77 (s, 6H), 2.38 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 171.2, 138.2, 132.8, 132.5, 129.2, 128.3, 126.1, 92.8, 53.3, 38.5, 21.3 ppm; HRMS (ESI) calcd for $[C_{24}H_{24}N_2O_4S_2 + H]^+$ 469.1250, found 469.1250.

(4R,4'S)-dimethyl 2,2'-di-o-tolyl-4,4',5,5'-tetrahydro-[4,4'-bithiazole]- 4,4'-dicarboxylate (2d)



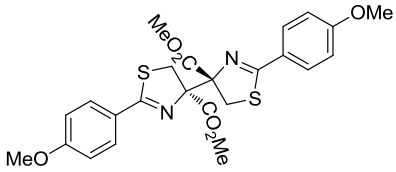
White solid, 29.3 mg, 31% yield, mp 103-104 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (dd, J = 8.0, 1.5 Hz, 2H), 7.37-7.24 (m, 2H), 7.19 (d, J = 7.2 Hz, 4H), 4.48 (d, J = 11.6 Hz, 2H), 4.18 (d, J = 11.7 Hz, 2H), 3.82 (s, 6H), 2.45 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 170.7, 137.5, 132.3, 131.3, 130.3, 129.9, 125.7, 95.5, 53.1, 39.1, 21.4 ppm; HRMS (ESI) calcd for $[C_{24}H_{24}N_2O_4S_2 + H]^+$ 469.1250, found 469.1248.

(4R,4'R)-dimethyl 2,2'-di-o-tolyl-4,4',5,5'-tetrahydro-[4,4'-bithiazole]- 4,4'-dicarboxylate (2d')



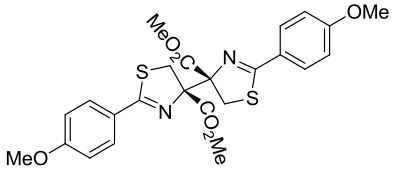
White solid, 24.4 mg, 26% yield, mp 142-143 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (dd, J = 7.6, 1.5 Hz, 2H), 7.31-7.28 (m, 2H), 7.27-7.15 (m, 4H), 4.06 (d, J = 12.1 Hz, 2H), 3.90 (d, J = 12.1 Hz, 2H), 3.80 (s, 6H), 2.58 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 171.4, 138.0, 132.3, 131.3, 130.4, 130.0, 125.6, 93.7, 53.2, 38.7, 21.2 ppm; HRMS (ESI) calcd for $[C_{24}H_{24}N_2O_4S_2 + H]^+$ 469.1250, found 469.1251.

(4R,4'S)-dimethyl 2,2'-bis(4-methoxyphenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4, 4'-dicarboxylate (2e)



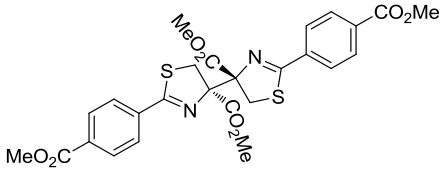
White oil liquid, 27.4 mg, 27% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J = 8.8 Hz, 4H), 6.80 (d, J = 8.7 Hz, 4H), 4.53 (d, J = 11.7 Hz, 2H), 4.17 (d, J = 11.6 Hz, 2H), 3.79 (s, 6H), 3.77 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 170.7, 161.6, 129.8, 125.1, 113.1, 94.0, 54.8, 52.5, 38.3 ppm; HRMS (ESI) calcd for $[C_{24}H_{24}N_2O_6S_2 + H]^+$ 501.1149, found 501.1151.

(4R,4'R)-dimethyl 2,2'-bis(4-methoxyphenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]- 4,4'-dicarboxylate (2e')



White solid, 22.8 mg, 23% yield, mp 175-176 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 8.5 Hz, 4H), 6.89 (d, J = 8.5 Hz, 4H), 4.11 (d, J = 12.2 Hz, 2H), 3.89-3.84 (m, 8H), 3.75 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 170.0, 162.4, 130.5, 125.7, 113.7, 92.7, 55.4, 53.2, 38.6 ppm; HRMS (ESI) calcd for $[C_{24}H_{24}N_2O_6S_2 + H]^+$ 501.1149, found 501.1151.

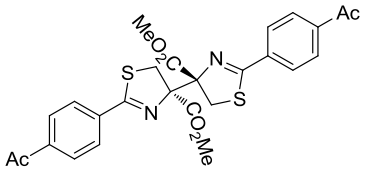
(4R,4'S)-dimethyl 2,2'-bis(4-(methoxycarbonyl)phenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]- 4,4'-dicarboxylate (2f)



White solid, 38.0 mg, 34% yield, mp 154-155 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 4H), 7.72 (d, J = 8.3 Hz, 4H), 4.51 (d, J = 11.8 Hz, 2H), 4.17 (d, J = 11.8 Hz, 2H), 3.81 (s, 6H), 3.75 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 170.5, 166.3, 136.4, 132.6, 129.6, 128.5, 94.7,

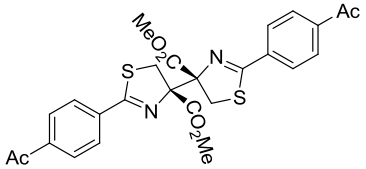
53.3, 52.3, 39.0 ppm; HRMS (ESI) calcd for $[C_{26}H_{24}N_2O_8S_2 + H]^+$ 557.1047, found 557.1048.

(4R,4'S)-dimethyl 2,2'-bis(4-acetylphenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (2g)



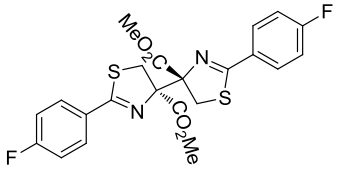
Yellow oil liquid, 32.5 mg, 31% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76-7.72 (m, 8H), 4.52 (d, J = 11.8 Hz, 2H), 4.18 (d, J = 11.8 Hz, 2H), 3.75 (s, 6H), 2.48 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 171.8, 170.4, 139.0, 136.4, 128.8, 128.3, 94.7, 53.3, 39.0, 26.7 ppm; HRMS (ESI) calcd for $[C_{26}H_{24}N_2O_6S_2 + H]^+$ 525.1149, found 525.1157.

(4R,4'R)-dimethyl 2,2'-bis(4-acetylphenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (2g')



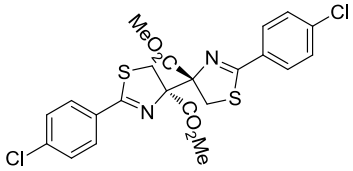
Pale yellow solid, 29.5 mg, 28% yield, mp 65-66 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45-7.53 (m, 8H), 4.08 (d, J = 12.4 Hz, 2H), 3.87 (d, J = 12.3 Hz, 2H), 3.71 (s, 6H), 2.56 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 171.4, 170.4, 139.3, 136.5, 129.0, 128.4, 92.8, 53.4, 38.8, 26.9 ppm; HRMS (ESI) calcd for $[C_{26}H_{24}N_2O_6S_2 + H]^+$ 525.1149, found 525.1145.

(4R,4'S)-dimethyl 2,2'-bis(4-fluorophenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4' -dicarboxylate (2h)



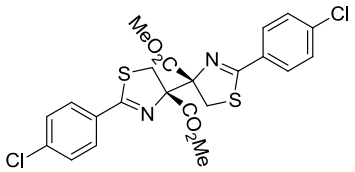
White solid, 40.7 mg, 43% yield, mp 110-111 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88-7.59 (m, 4H), 6.99-6.96 (m, 4H), 4.56 (d, J = 11.8 Hz, 2H), 4.21 (d, J = 11.7 Hz, 2H), 3.81 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 170.7, 166.4, 163.0, 130.8, 130.7, 129.0, 115.6, 115.3, 94.6, 53.2, 39.1 ppm; HRMS (ESI) calcd for $[C_{22}H_{18}F_2N_2O_4S_2 + H]^+$ 477.0749, found 477.0749.

(4R,4'S)-dimethyl 2,2'-bis(4-chlorophenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (2i)



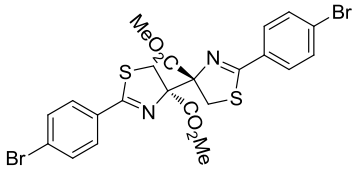
White solid, 45.8 mg, 45% yield, mp 160-161 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 8.6 Hz, 4H), 7.28 (d, J = 8.5 Hz, 4H), 4.55 (d, J = 11.7 Hz, 2H), 4.21 (d, J = 11.8 Hz, 2H), 3.81 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 170.6, 137.7, 131.1, 129.8, 128.6, 94.6, 53.2, 39.0 ppm; HRMS (ESI) calcd for $[C_{22}H_{18}Cl_2N_2O_4S_2+ H]^+$ 509.0158, found 509.0159.

(4R,4'R)-dimethyl 2,2'-bis(4-chlorophenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (2i')



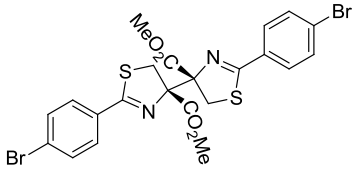
Pale yellow solid, 32.7 mg, 32% yield, mp 164-165 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J = 8.6 Hz, 4H), 7.38 (d, J = 8.5 Hz, 4H), 4.12 (d, J = 12.3 Hz, 2H), 3.90 (d, J = 12.3 Hz, 2H), 3.77 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 170.0, 138.0, 131.2, 130.0, 128.7, 92.7, 53.4, 38.8 ppm; HRMS (ESI) calcd for $[C_{22}H_{18}Cl_2N_2O_4S_2 + H]^+$ 509.0158, found 509.0162.

(4R,4'S)-dimethyl 2,2'-bis(4-bromophenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (2j)



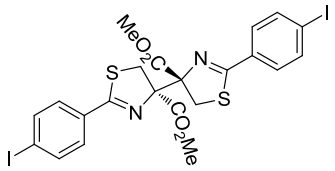
White solid, 52.5 mg, 44% yield, mp 170-171 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 8.6 Hz, 4H), 7.28 (d, J = 8.5 Hz, 4H), 4.55 (d, J = 11.7 Hz, 2H), 4.21 (d, J = 11.8 Hz, 2H), 3.81 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 170.6, 131.6, 131.5, 130.0, 126.2, 94.6, 53.2, 39.0 ppm; HRMS (ESI) calcd for $[C_{22}H_{18}Br_2N_2O_4S_2 + H]^+$ 596.9148, found 596.9149.

(4R,4'R)-dimethyl 2,2'-bis(4-bromophenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (2j')



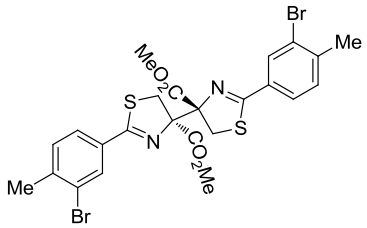
White solid, 47.8 mg, 40% yield, mp 172-173 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 8.5 Hz, 4H), 7.54 (d, J = 8.5 Hz, 4H), 4.11 (d, J = 12.3 Hz, 2H), 3.90 (d, J = 12.3 Hz, 2H), 3.77 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 170.1, 131.7, 131.6, 130.2, 126.5, 92.7, 53.4, 38.8 ppm; HRMS (ESI) calcd for $[C_{22}H_{18}Br_2N_2O_4S_2 + H]^+$ 596.9148, found 596.9146.

(4R,4'S)-dimethyl 2,2'-bis(4-iodophenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]- 4,4'-dicarboxylate (2k)



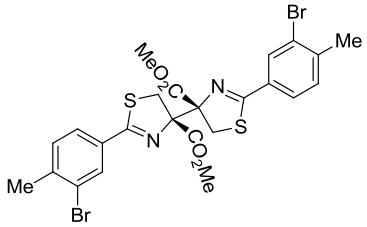
White solid, 59.7 mg, 43% yield, mp 160-161 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.59 (m, 4H), 7.52-7.39 (m, 4H), 4.54 (d, J = 11.8 Hz, 2H), 4.20 (d, J = 11.8 Hz, 2H), 3.80 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 170.6, 137.6, 132.1, 130.0, 98.6, 94.6, 53.2, 39.0 ppm; HRMS (ESI) calcd for $[C_{22}H_{18}I_2N_2O_4S_2 + H]^+$ 692.8870, found 692.8868.

(4R,4'S)-dimethyl 2,2'-bis(3-bromo-4-methylphenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4' -dicarboxylate (2l)



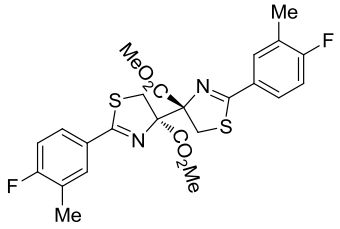
White solid, 55.6 mg, 45% yield, mp 170-171 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 1.8 Hz, 2H), 7.55 (dd, J = 7.9, 1.8 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 4.55 (d, J = 11.7 Hz, 2H), 4.20 (d, J = 11.8 Hz, 2H), 3.81 (s, 6H), 2.34 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.2, 141.1, 131.6, 131.5, 130.1, 127.0, 124.3, 94.0, 52.7, 38.5, 22.5 ppm; HRMS (ESI) calcd for $[C_{24}H_{22}Br_2N_2O_4S_2 + H]^+$ 624.9461, found 624.9462.

(4R,4'R)-dimethyl 2,2'-bis(3-bromo-4-methylphenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4' -dicarboxylate (2l')



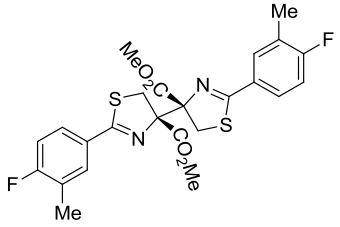
White solid, 55.4 mg, 44% yield, mp 172-173 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 1.8 Hz, 2H), 7.67 (dd, J = 7.9, 1.8 Hz, 2H), 7.25 (d, J = 7.7 Hz, 2H), 4.12 (d, J = 12.3 Hz, 2H), 3.90 (d, J = 12.3 Hz, 2H), 3.77 (s, 6H), 2.43 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 169.1, 141.4, 131.7, 131.6, 130.2, 127.1, 124.5, 92.1, 52.9, 38.2, 22.6 ppm; HRMS (ESI) calcd for $[C_{24}H_{22}Br_2N_2O_4S_2 + H]^+$ 624.9461, found 624.9463.

(4R,4'S)-dimethyl 2,2'-bis(4-fluoro-3-methylphenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4' -dicarboxylate (2m)



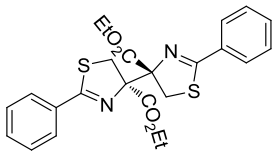
White solid, 33.9 mg, 34% yield, mp 160-161 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76-7.36 (m, 4H), 6.92 (t, J = 8.9 Hz, 2H), 4.55 (d, J = 11.7 Hz, 2H), 4.20 (d, J = 11.8 Hz, 2H), 3.81 (s, 6H), 2.22 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 170.3, 164.5, 161.1, 131.5, 131.4, 128.2, 127.6, 127.5, 124.7, 124.4, 114.7, 114.4, 94.1, 52.6, 38.5, 14.0, 13.9 ppm; HRMS (ESI) calcd for $[C_{24}H_{22}F_2N_2O_4S_2 + H]^+$ 505.1062, found 505.1059.

(4R,4'R)-dimethyl 2,2'-bis(4-fluoro-3-methylphenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4' -dicarboxylate (2m')



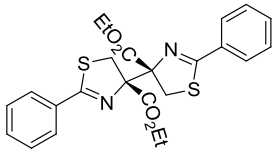
White solid, 30.8 mg, 30% yield, mp 166-167 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (dd, J = 7.4, 2.3 Hz, 2H), 7.66-6.99 (m, 2H), 7.02 (t, J = 8.9 Hz, 2H), 4.12 (d, J = 12.2 Hz, 2H), 3.89 (d, J = 12.2 Hz, 2H), 3.78 (s, 6H), 2.29 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 169.5, 164.7, 161.4, 131.6, 131.5, 128.2, 127.9, 127.8, 124.9, 124.6, 114.8, 114.5, 92.2, 52.9, 38.3, 14.0, 13.9 ppm; HRMS (ESI) calcd for $[C_{24}H_{22}F_2N_2O_4S_2 + H]^+$ 505.1062, found 505.1058.

(4R,4'S)-diethyl 2,2'-diphenyl-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (2n)



White solid, 31.3 mg, 33% yield, mp 95-96 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.73 (m, 4H), 7.52-7.17 (m, 6H), 4.60 (d, J = 11.6 Hz, 2H), 4.43-4.10 (m, 6H), 1.30 (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 169.8, 132.4, 130.9, 128.1, 127.8, 94.2, 61.6, 38.5, 13.6 ppm; HRMS (ESI) calcd for $[C_{24}H_{24}N_2O_4S_2 + H]^+$ 469.1250, found 469.1245.

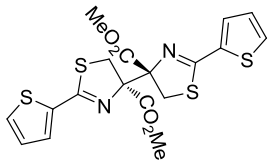
(4R,4'R)-diethyl 2,2'-diphenyl-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (2n')



Yellow solid, 26.0 mg, 28% yield, mp 48-49 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02-7.71 (m, 4H), 7.64-7.31 (m, 6H), 4.46-4.10 (m, 6H), 3.99 (d, J = 12.2 Hz, 2H), 1.21 (t, J = 7.1 Hz, 6H); ^{13}C NMR

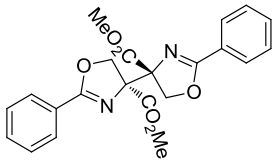
(75 MHz, $CDCl_3$) δ 170.3, 170.2, 132.4, 131.1, 128.3, 127.9, 92.3, 61.8, 38.1, 13.5 ppm; HRMS (ESI) calcd for $[C_{24}H_{24}N_2O_4S_2 + H]^+$ 469.1250, found 469.1246.

(4R,4'S)-dimethyl 2,2'-di(thiophen-2-yl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (2o)



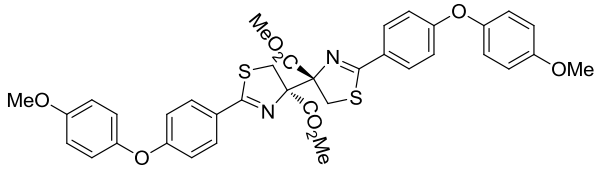
White solid, 21.7 mg, 24% yield, mp 150-151 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, J = 10.1, 4.4 Hz, 4H), 6.97 (t, J = 4.4 Hz, 2H), 4.54 (d, J = 11.6 Hz, 2H), 4.20 (d, J = 11.6 Hz, 2H), 3.80 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 165.3, 136.3, 131.2, 130.4, 127.4, 94.0, 53.1, 39.4 ppm; HRMS (ESI) calcd for $[C_{18}H_{16}N_2O_4S_4 + H]^+$ 453.0066, found 453.0065.

(4R,4'S)-dimethyl 2,2'-diphenyl-4,4',5,5'-tetrahydro-[4,4'-bioxazole]-4,4'-dicarboxylate (2r)



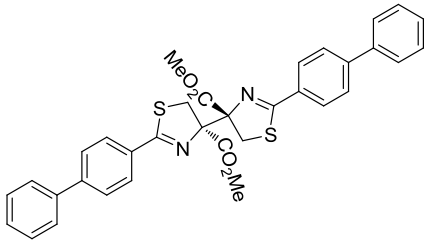
White solid, 13.3 mg, 16% yield, mp 222-223 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, J = 7.5 Hz, 4H), 7.51 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.6 Hz, 4H), 4.85 (d, J = 10.0 Hz, 2H), 4.66 (d, J = 10.0 Hz, 2H), 3.78 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 167.1, 132.1, 128.9, 128.3, 126.7, 82.3, 72.5, 53.2 ppm; HRMS (ESI) calcd for $[C_{22}H_{20}N_2O_6 + H]^+$ 409.1394, found 409.1399.

(4R,4'S)-dimethyl 2,2'-bis(4-(4-methoxyphenoxy)phenyl)-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (3)



Yellow solid, 79.1 mg, 56% yield, mp 50-51 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.82-7.55 (m, 4H), 6.94 (d, J = 9.1 Hz, 4H), 6.90-6.78 (m, 8H), 4.54 (d, J = 11.7 Hz, 2H), 4.18 (d, J = 11.7 Hz, 2H), 3.78 (s, 6H), 3.77 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 171.0, 161.5, 156.4, 148.9, 130.4, 127.0, 121.4, 116.6, 115.0, 94.6, 55.6, 53.1, 39.0 ppm; HRMS (ESI) calcd for $[C_{36}H_{32}N_2O_8S_2 + Na]^+$ 707.1492, found 707.1467.

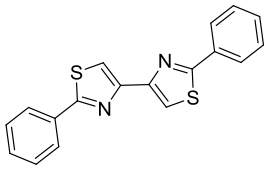
(4R,4'S)-dimethyl 2,2'-diphenyl-4,4',5,5'-tetrahydro-[4,4'-bithiazole]-4,4'-dicarboxylate (4)



White solid, 84.1 mg, 71% yield, mp 90-91 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.97-7.73 (m, 4H),

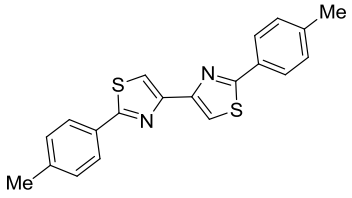
7.68-7.48 (m, 8H), 7.47-7.30 (m, 6H), 4.62 (d, J = 11.8 Hz, 2H), 4.25 (d, J = 11.7 Hz, 2H), 3.82 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 170.9, 144.2, 140.1, 131.7, 129.1, 128.9, 127.9, 127.1, 127.0, 94.7, 53.1, 39.0 ppm; HRMS (ESI) calcd for $[C_{34}H_{28}N_2O_4S_2 + H]^+$ 593.1563, found 593.1558.

2,2'-diphenyl-4,4'-bithiazole (5a)



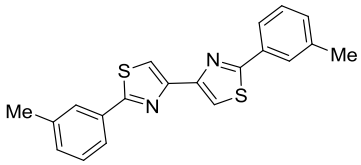
Yellow solid, 44.8 mg, 70% yield, mp 186-187 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (dd, J = 7.1, 2.5 Hz, 4H), 7.83 (s, 2H), 7.53-7.29 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 151.6, 133.6, 130.2, 129.0, 126.6, 115.3 ppm; HRMS (ESI) calcd for $[C_{18}H_{12}N_2S_2 + H]^+$ 321.0515, found 321.0520.

2,2'-di-p-tolyl-4,4'-bithiazole (5b)



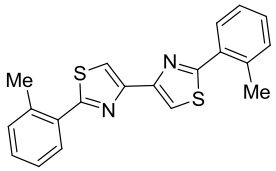
White solid, 44.8 mg, 77% yield, mp 198-199 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, J = 7.9 Hz, 4H), 7.85 (s, 2H), 7.25 (d, J = 7.8 Hz, 4H), 2.39 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 151.5, 140.4, 131.0, 129.6, 126.6, 114.8, 21.5 ppm; HRMS (ESI) calcd for $[C_{20}H_{16}N_2S_2 + H]^+$ 349.0828, found 349.0833.

2,2'-di-m-tolyl-4,4'-bithiazole (5c)



White solid, 57.8 mg, 83% yield, mp 160-161 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.87 (s, 2H), 7.81 (d, J = 7.7 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.29-7.18 (m, 2H), 2.43 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 151.5, 138.7, 133.5, 131.0, 128.9, 127.2, 123.9, 115.2, 21.4 ppm; HRMS (ESI) calcd for $[C_{20}H_{16}N_2S_2 + H]^+$ 349.0828, found 349.0831.

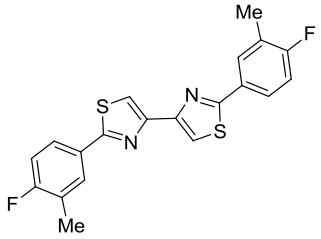
2,2'-di-o-tolyl-4,4'-bithiazole (5d)



White solid, 50.4 mg, 71% yield, mp 105-106 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.78 (d, J = 7.2 Hz, 2H), 7.33-7.25 (m, 6H), 2.68 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 151.1, 136.7, 132.9, 131.6, 129.9, 129.6, 126.1, 115.7, 21.6 ppm; HRMS (ESI) calcd for $[C_{20}H_{16}N_2S_2 +$

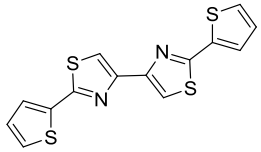
H]$^+$ 349.0828, found 349.0832.

2,2'-bis(4-fluoro-3-methylphenyl)-4,4'-bithiazole (5e)



White solid, 41.5 mg, 54% yield, m.p. 213-214 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.82 (m, 3H), 7.10 (t, J = 8.7 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 160.9, 151.5, 129.9, 129.8, 125.9, 125.8, 125.6, 115.8, 115.5, 115.1, 14.6 ppm; HRMS(ESI) calcd for [$C_{20}H_{14}F_2N_2S_2$+ Na]$^+$ 407.0459, found 407.0467.

2,2'-di(thiophen-2-yl)-4,4'-bithiazole (5f)



White solid, 44.4 mg, 67% yield, mp 185-186 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.56 (d, J = 3.7 Hz, 2H), 7.42 (d, J = 5.1 Hz, 2H), 7.20-6.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.9, 150.7, 137.2, 127.9, 127.6, 126.8, 114.9 ppm; HRMS (ESI) calcd for [$C_{14}H_8N_2S_4$ + H]$^+$ 332.9643, found 332.9641.

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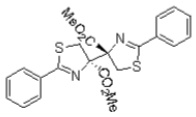
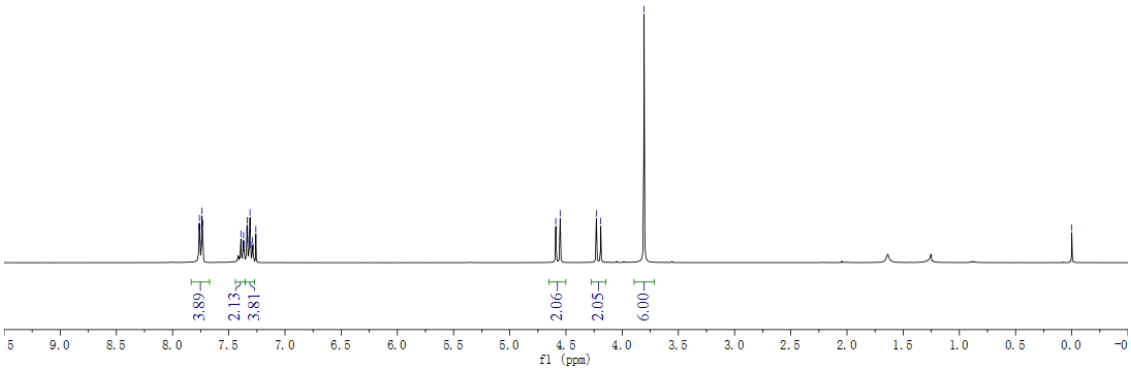
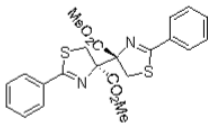
^{1}H NMR and ^{13}C NMR Spectra of Title Compounds



2a

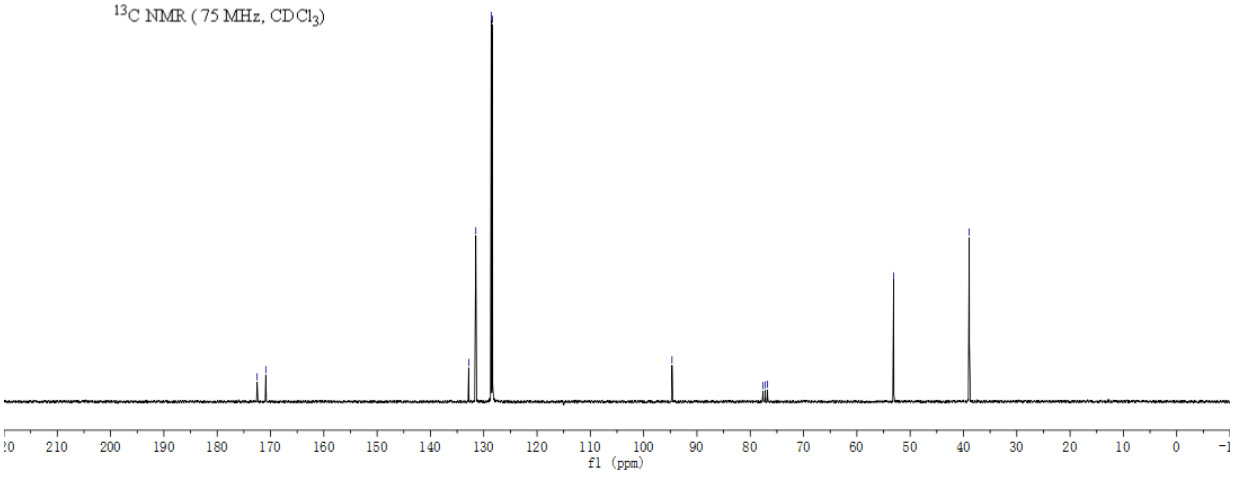
^{1}H NMR (300 MHz, $CDCl_3$)

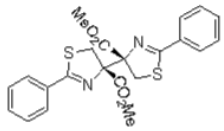




2a

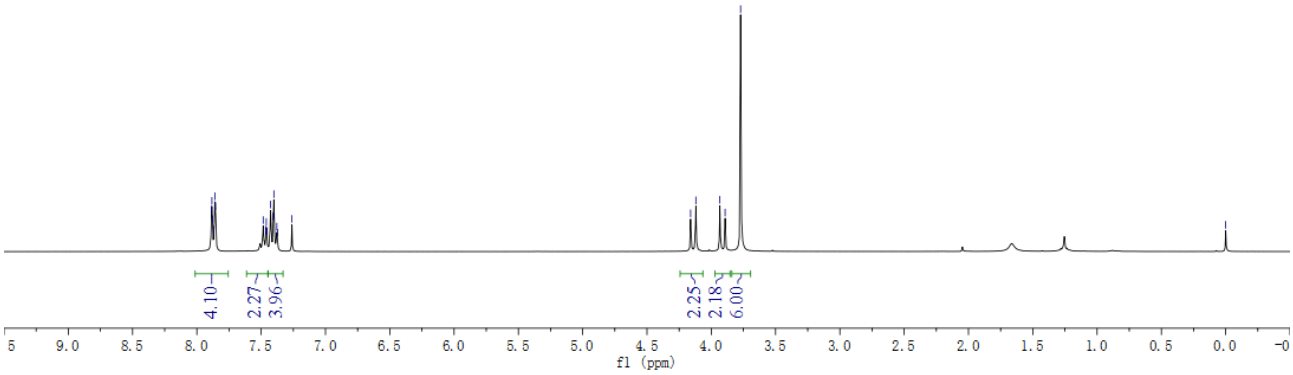
^{13}C NMR (75 MHz, $CDCl_3$)

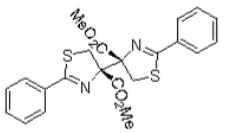




2a'

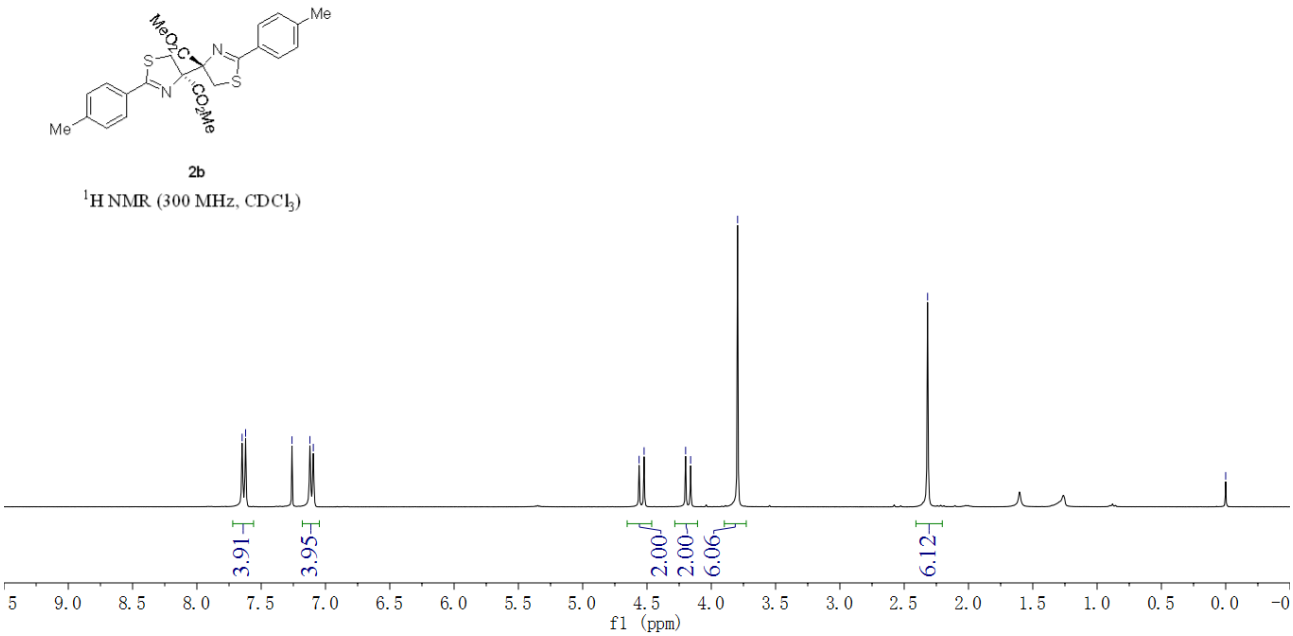
^{1}H NMR (300 MHz, $CDCl_3$)

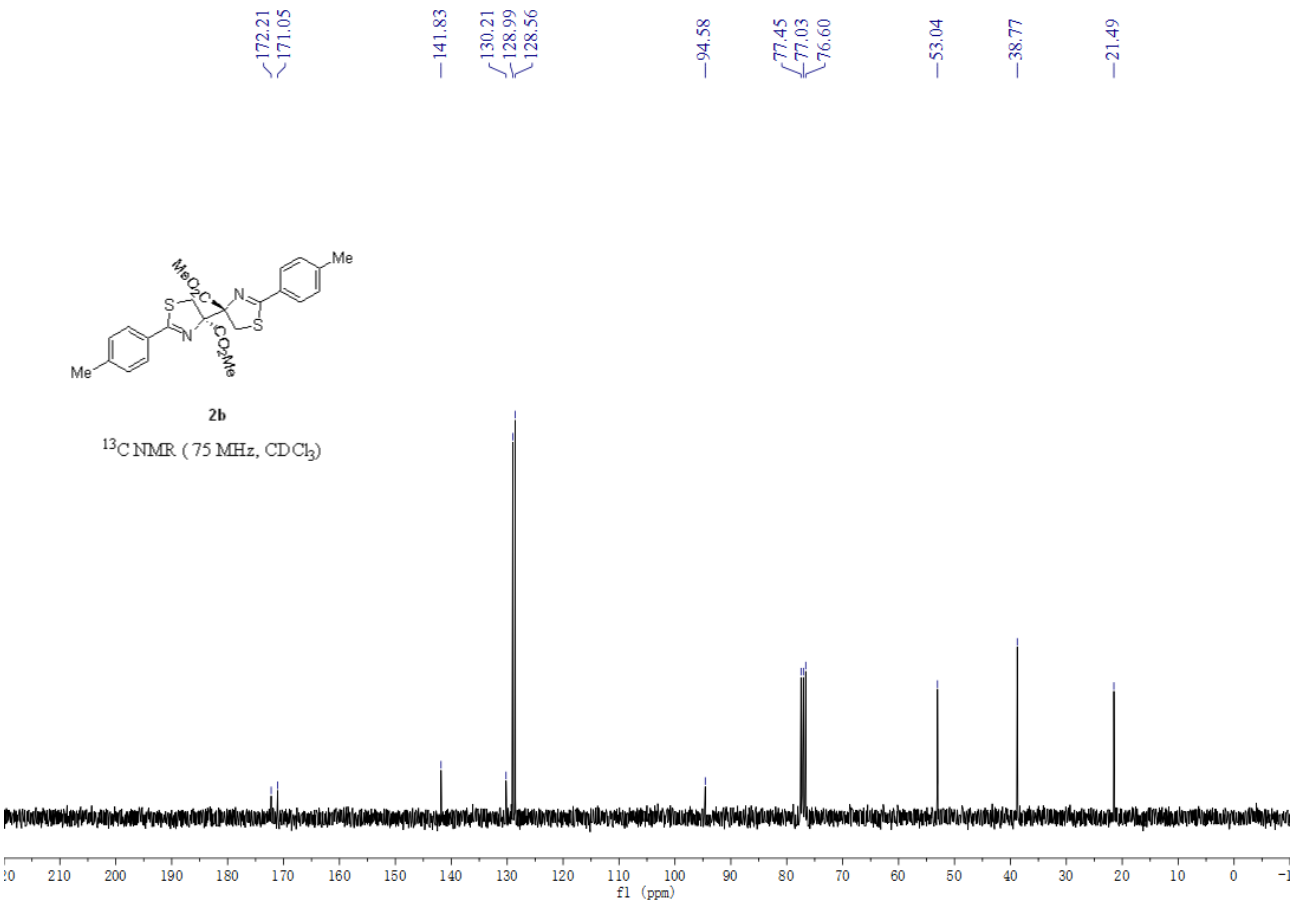


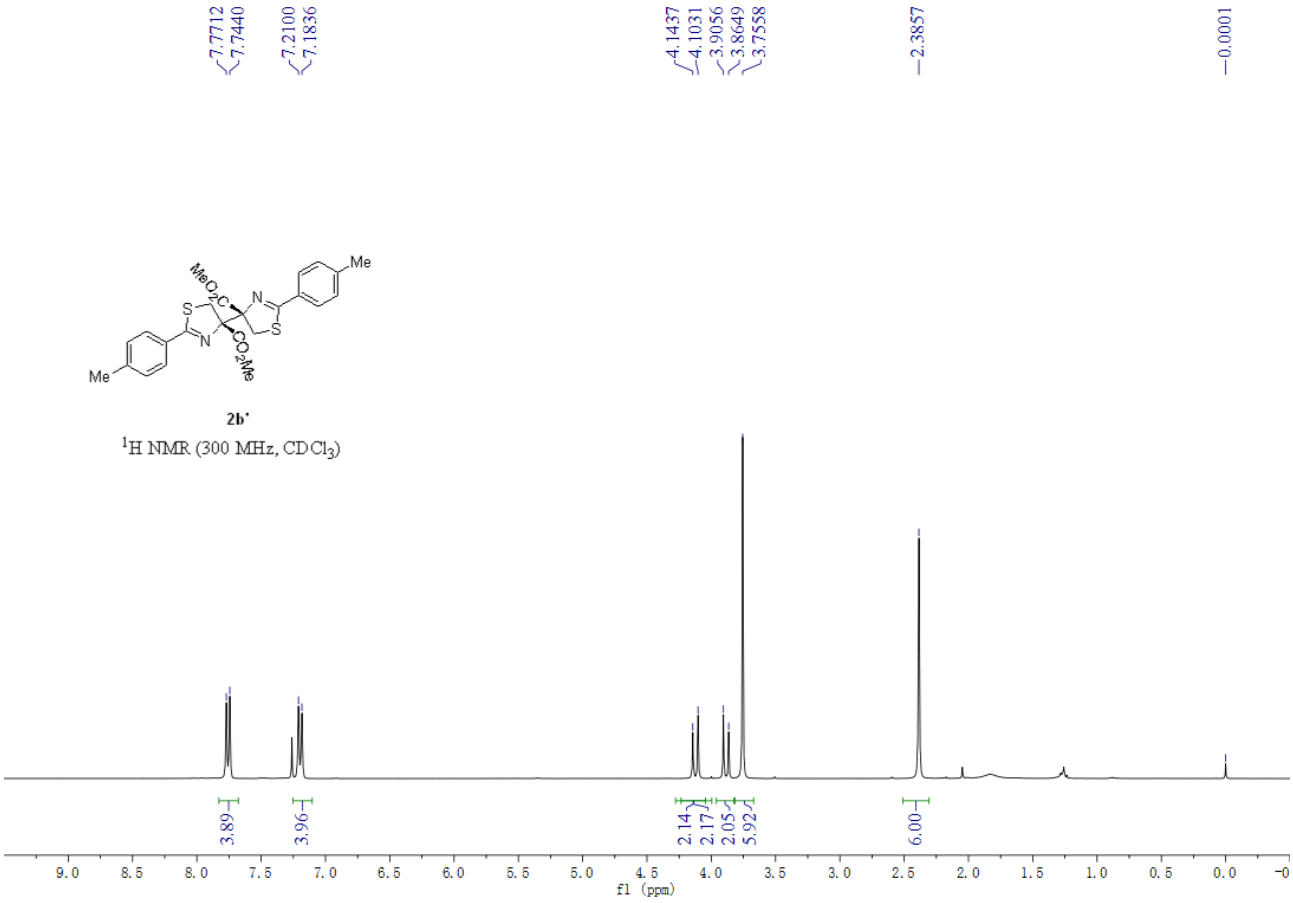


2a'

^{13}C NMR (75 MHz, $CDCl_3$)

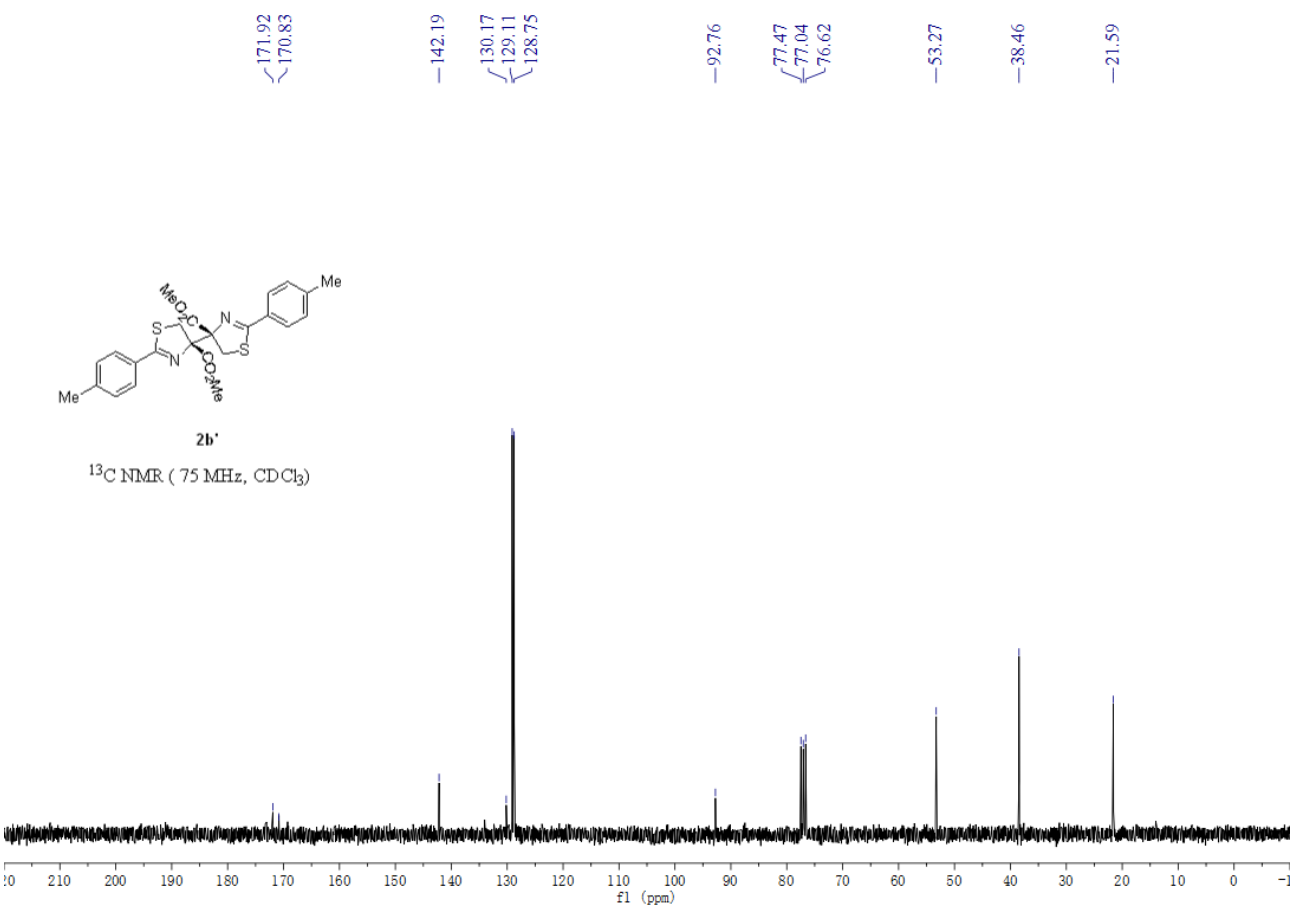

7.6484
7.6212
7.2605
7.1212
7.0948
4.5614
4.5225
4.1996
4.1607
3.7955
2.3179
0.0000
Me
MeO2C
CO2Me
Me
2b
1H NMR (300 MHz, CDCl3)
3.91
3.95
2.00
2.00
6.06
6.12
f1 (ppm)


172.21
171.05
141.83
130.21
128.99
128.56
94.58
77.45
77.03
76.60
53.04
38.77
21.49
Me
MeO2C
CO2Me
Me
2b
13C NMR (75 MHz, CDCl3)
f1 (ppm)



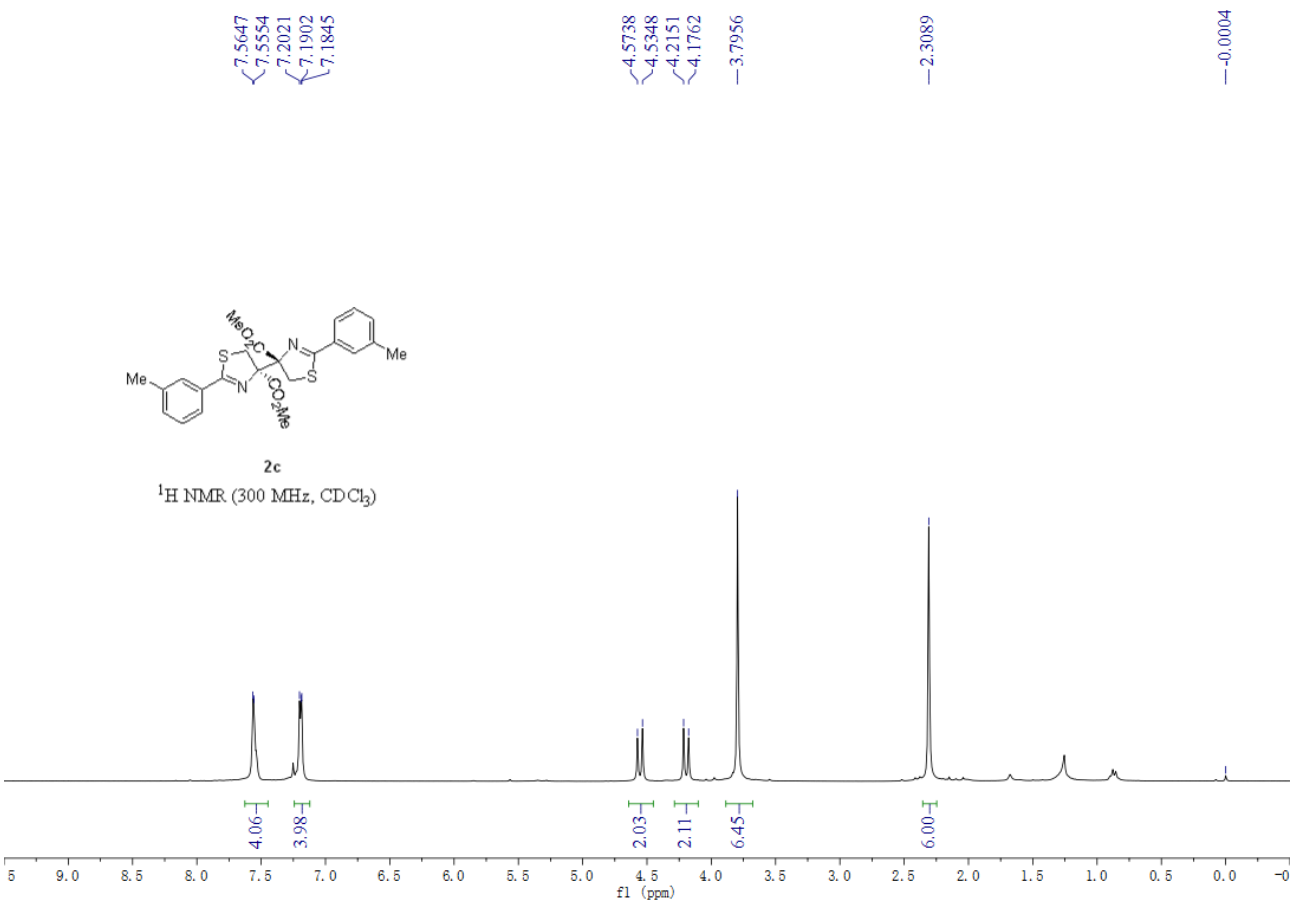
2b'

^{1}H NMR (300 MHz, $CDCl_3$)



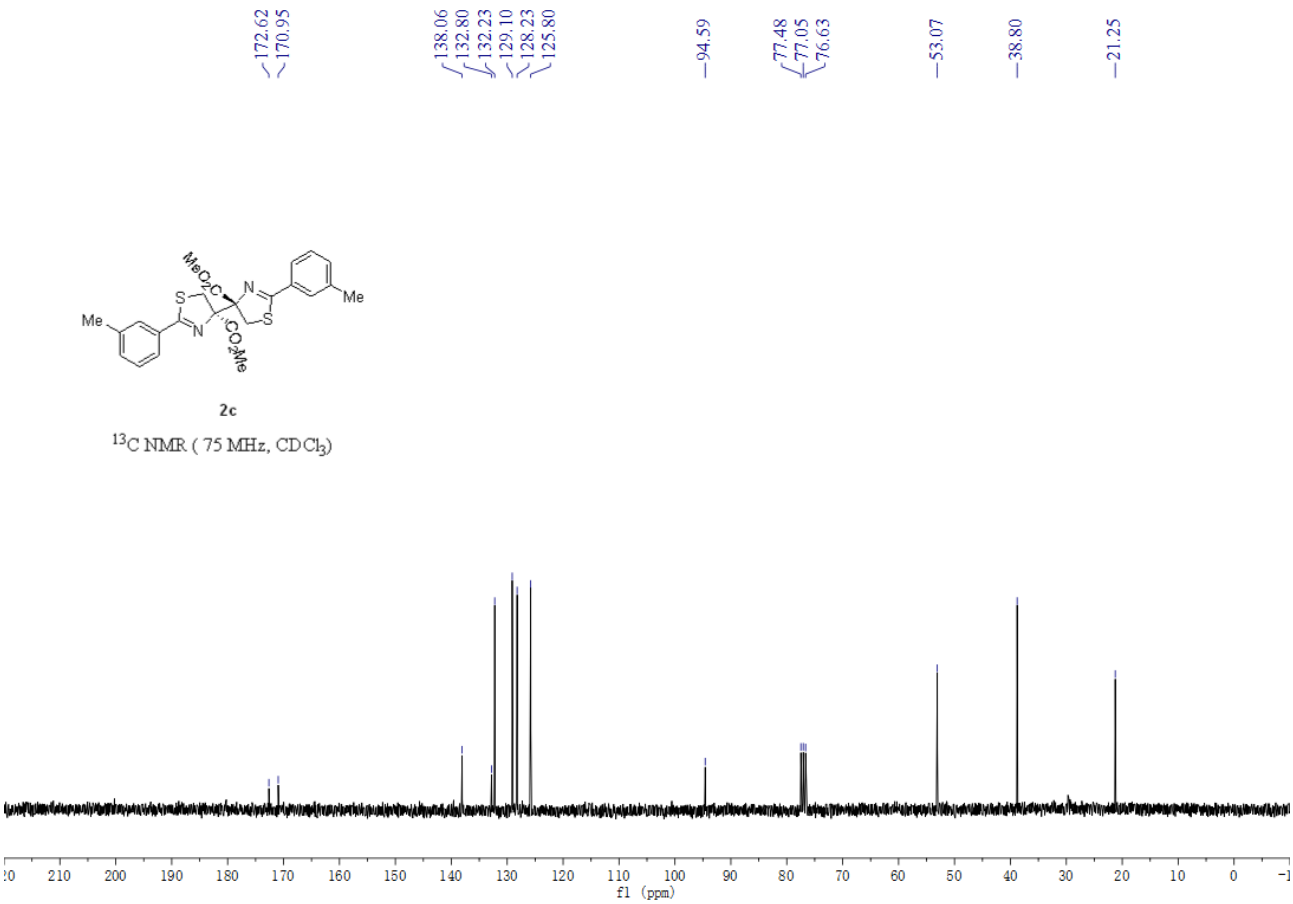
2b'

^{13}C NMR (75 MHz, $CDCl_3$)



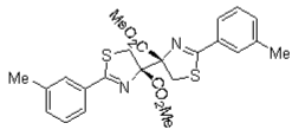
2c

^{1}H NMR (300 MHz, $CDCl_3$)



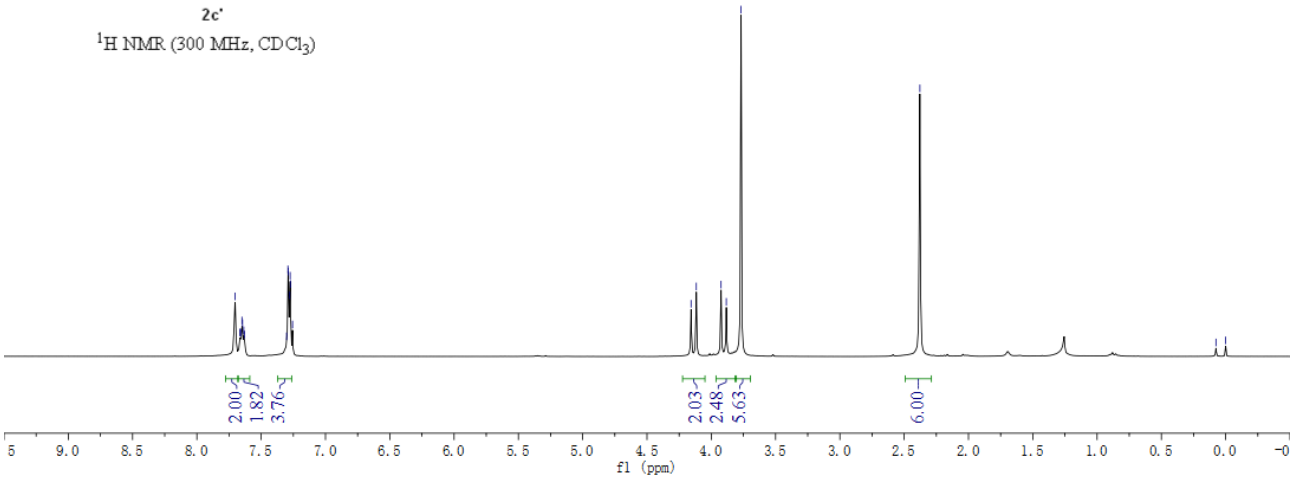
2c

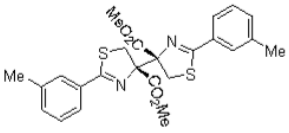
^{13}C NMR (75 MHz, $CDCl_3$)



2c'

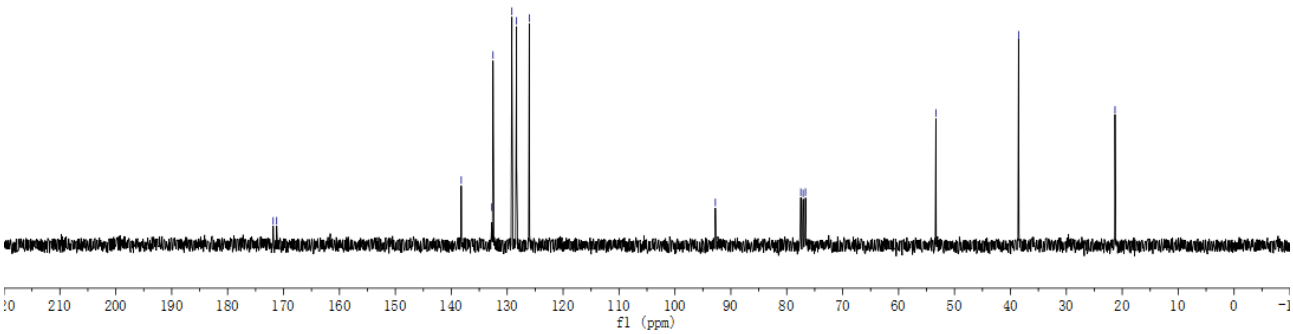
^{1}H NMR (300 MHz, $CDCl_3$)

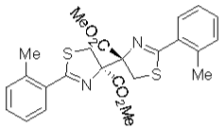




2c'

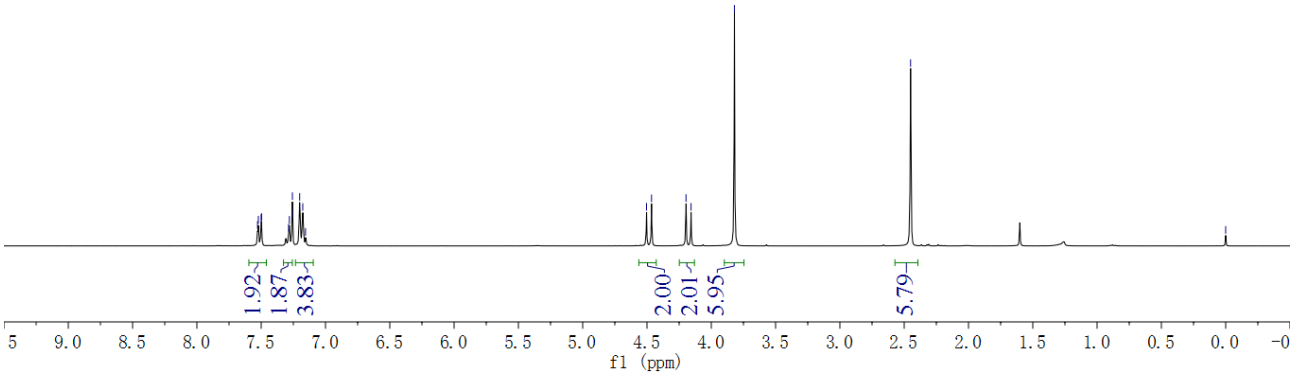
^{13}C NMR (75 MHz, $CDCl_3$)

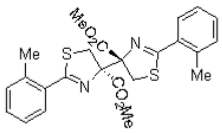




2d

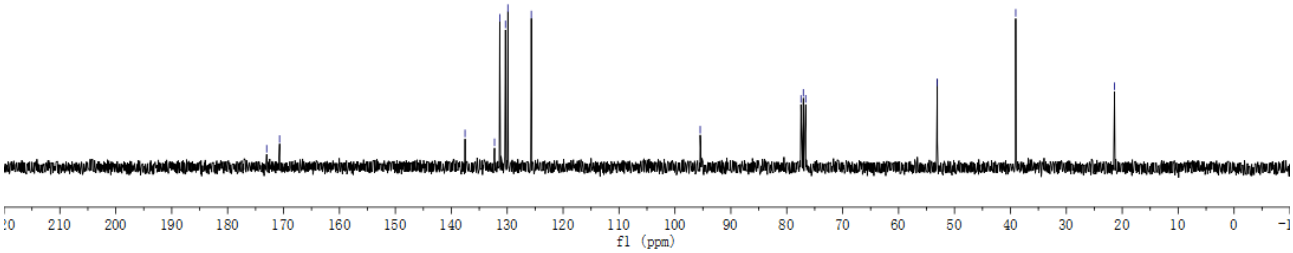
^{1}H NMR (300 MHz, $CDCl_3$)

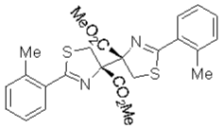




2d

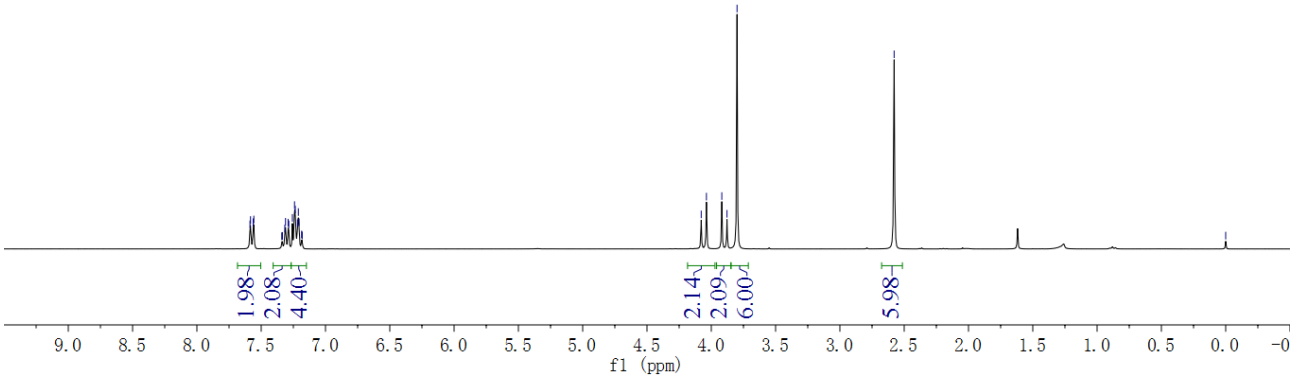
^{13}C NMR (75 MHz, $CDCl_3$)

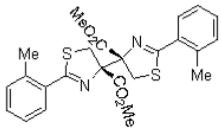




2d'

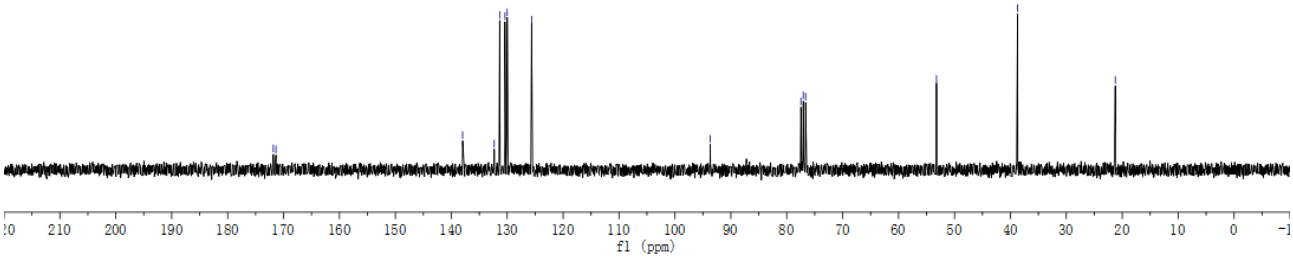
^{1}H NMR (300 MHz, $CDCl_3$)

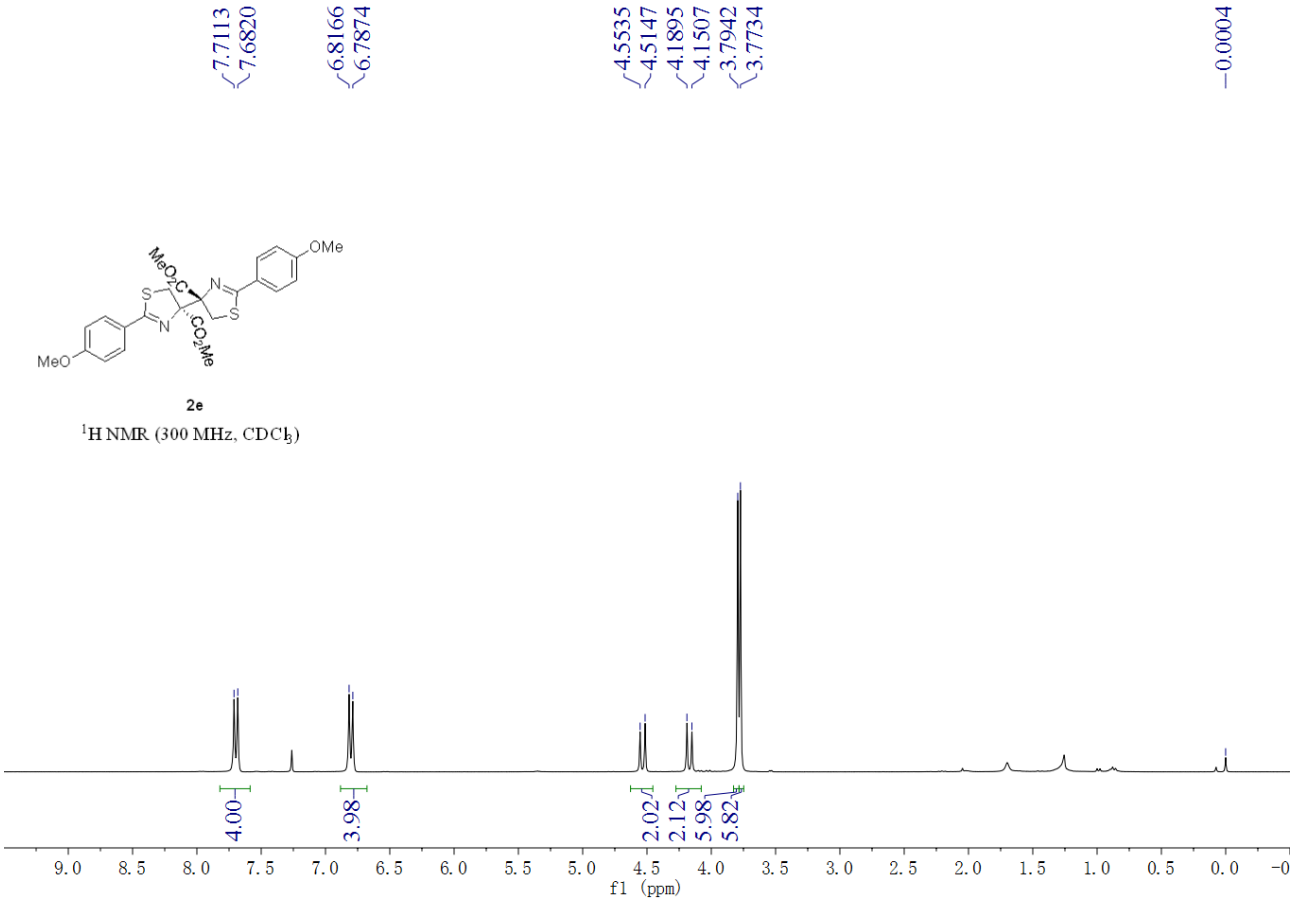




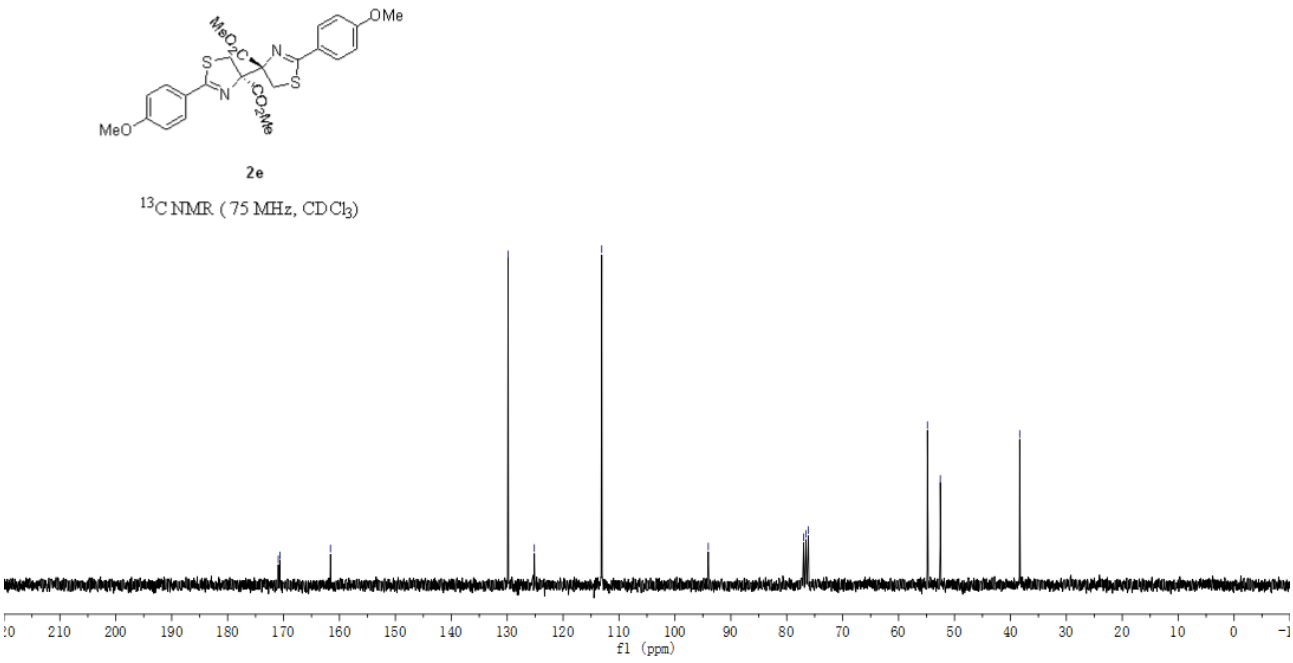
2d'

^{13}C NMR (75 MHz, $CDCl_3$)

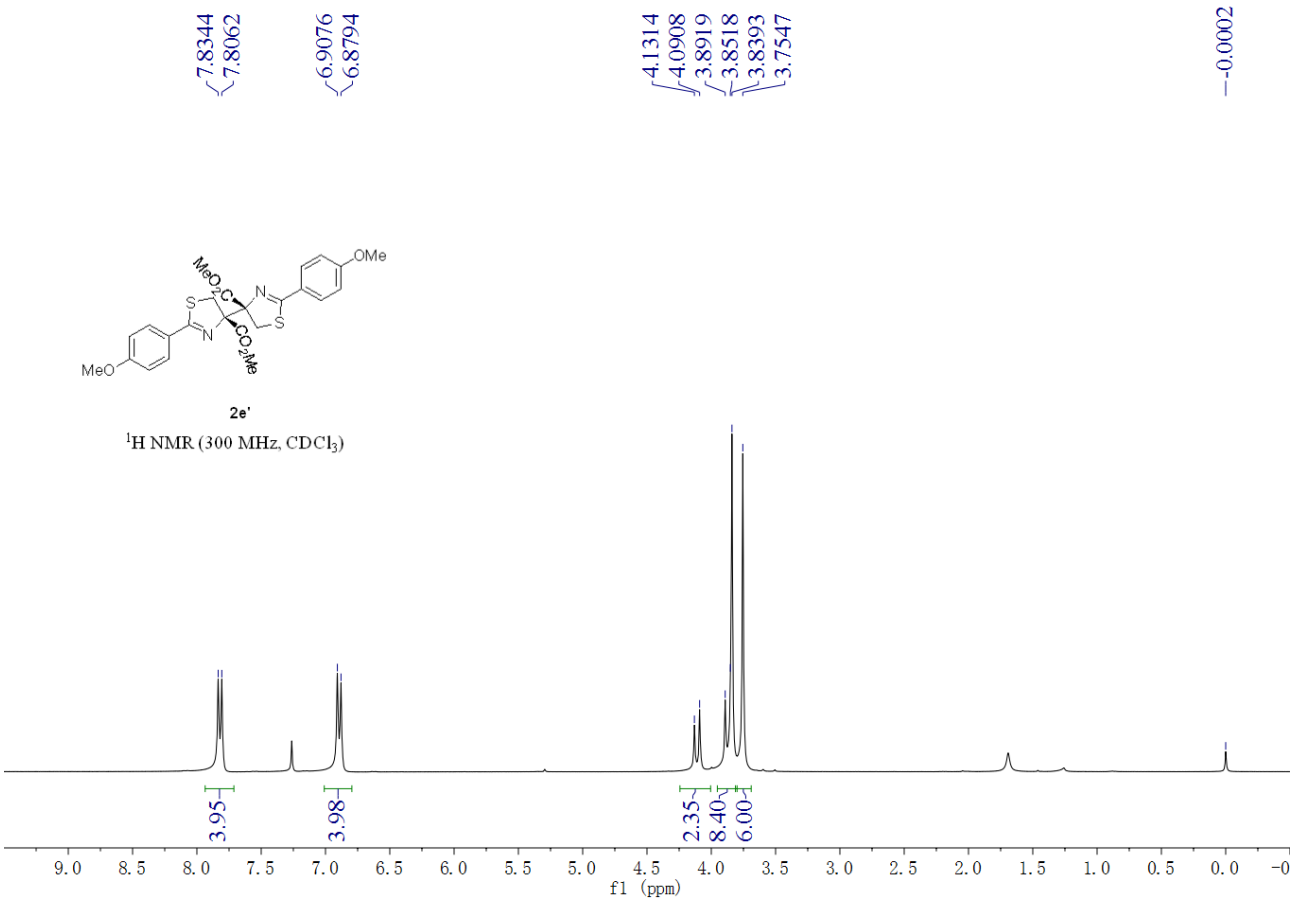


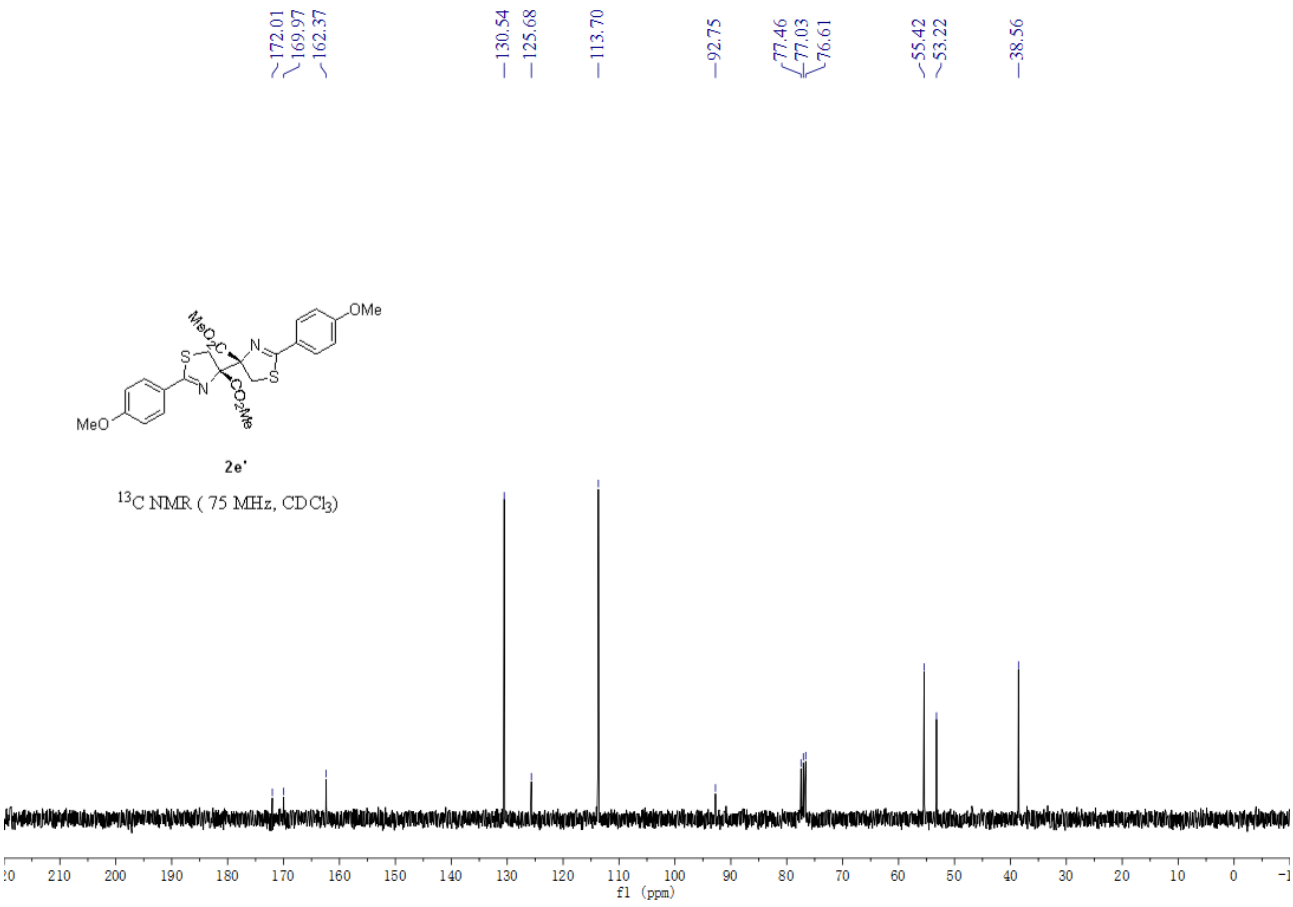


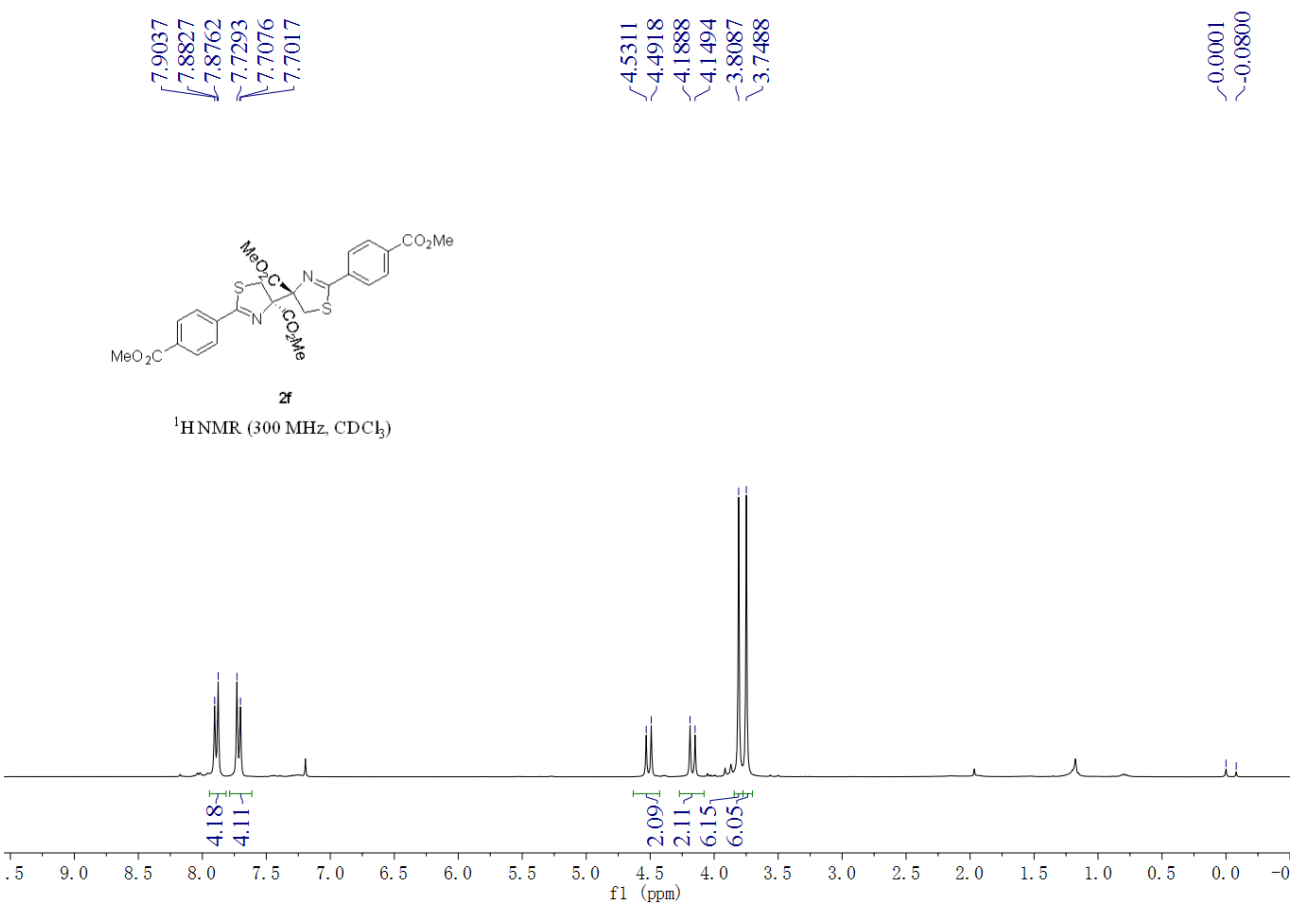
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

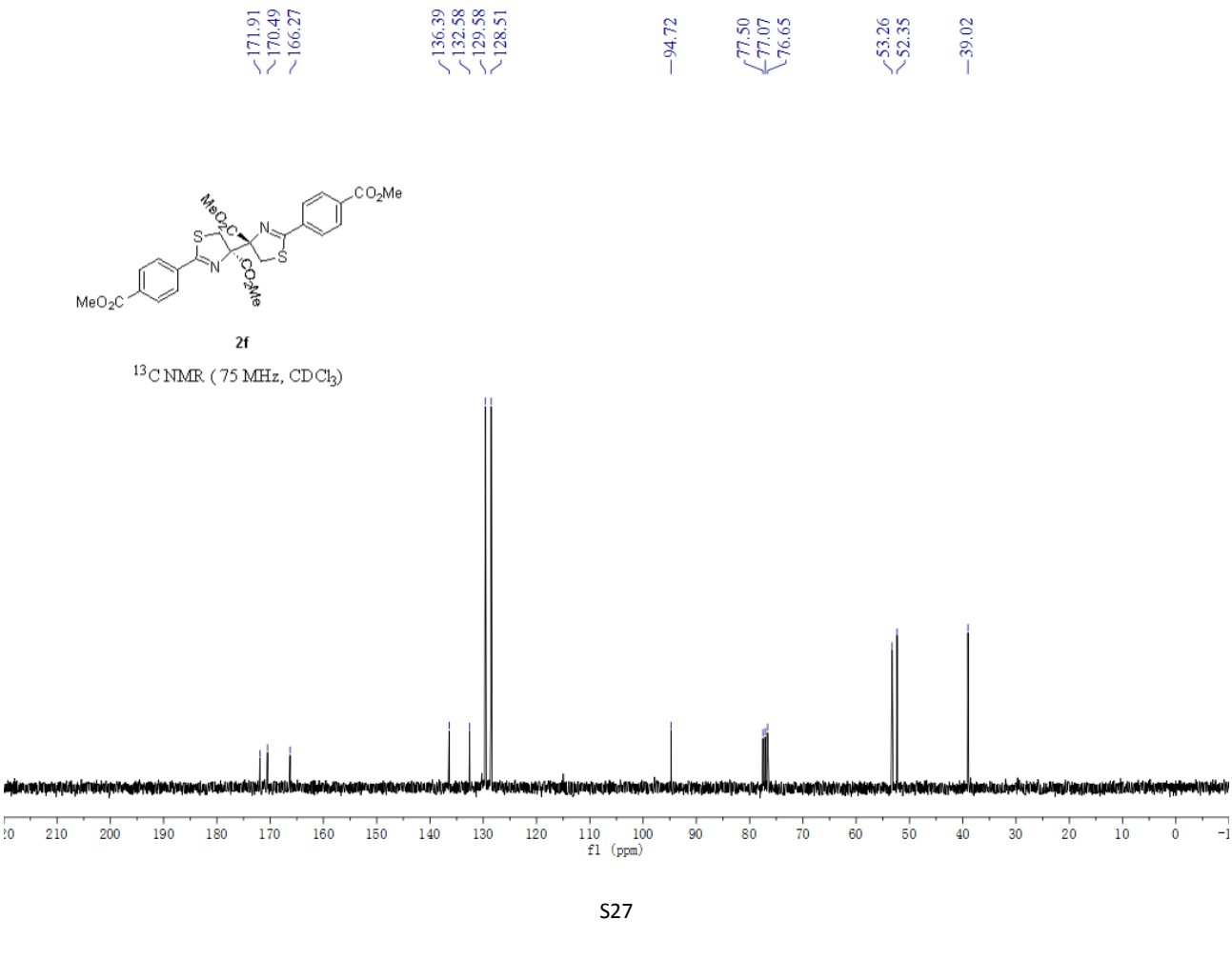

7.8344
7.8062
6.9076
6.8794
4.1314
4.0908
3.8919
3.8518
3.8393
3.7547
0.0002
OMe
MeO
MeO2C
CO2Me
2e'
1H NMR (300 MHz, CDCl3)
3.95
3.98
2.35
8.40
6.00
f1 (ppm)


172.01
169.97
162.37
130.54
125.68
113.70
92.75
77.46
77.03
76.61
55.42
53.22
38.56
OMe
MeO
MeO2C
CO2Me
2e'
13C NMR (75 MHz, CDCl3)
f1 (ppm)



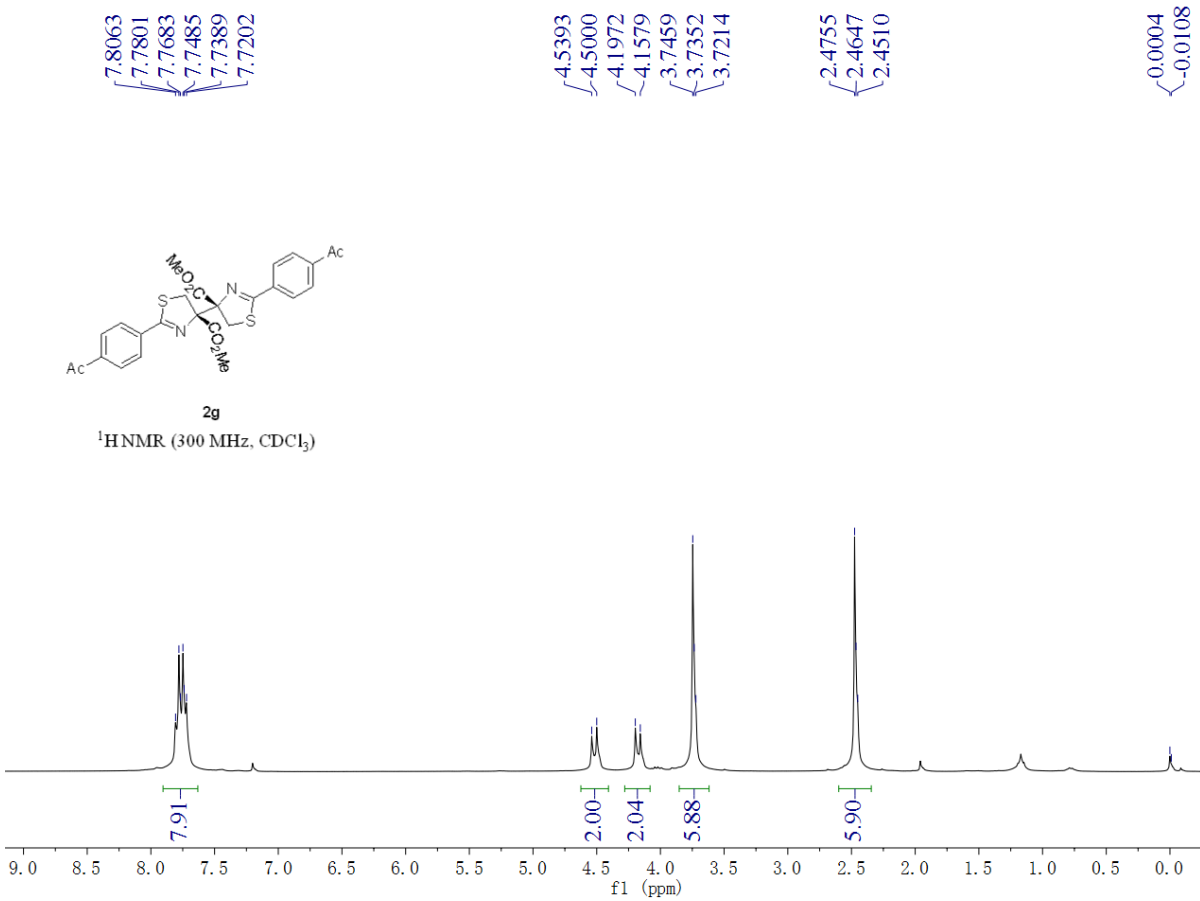
2f

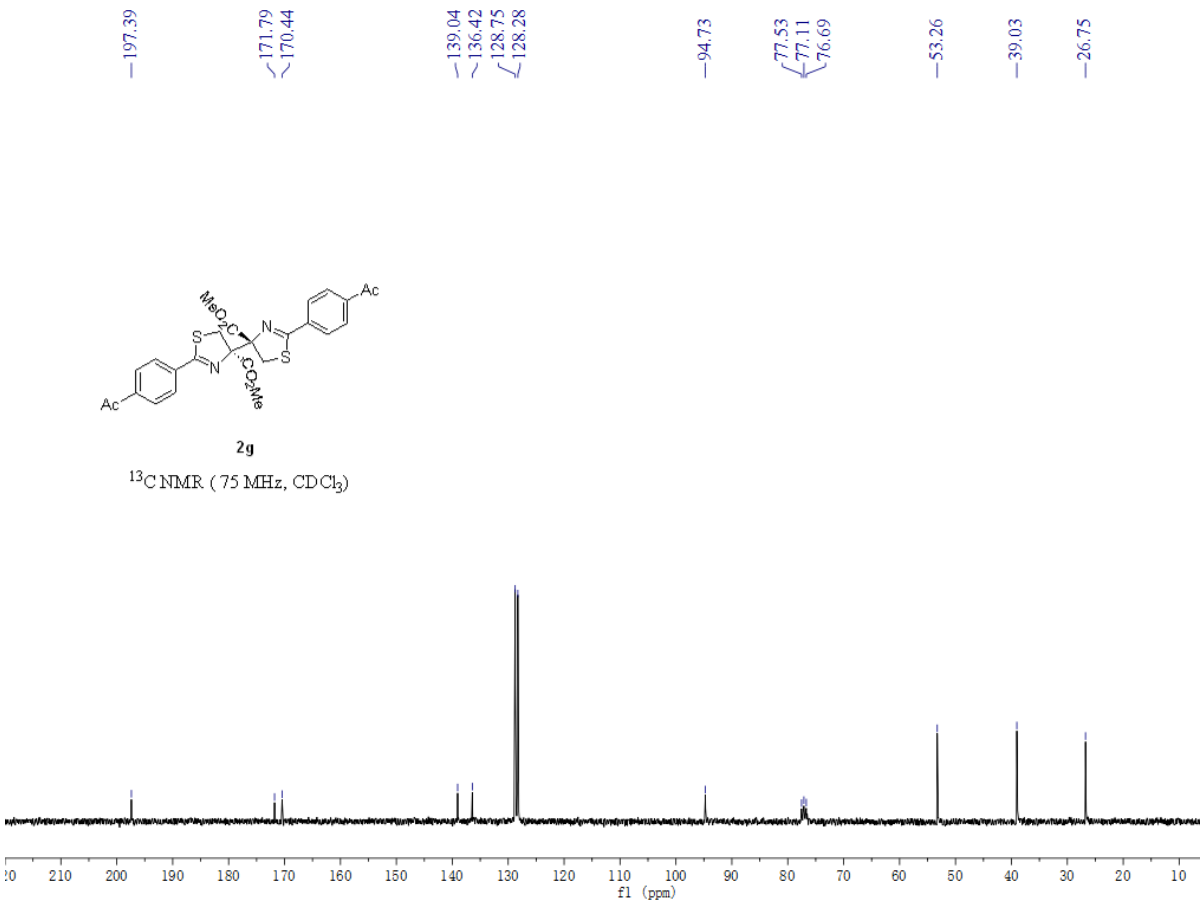
^{1}H NMR (300 MHz, $CDCl_3$)

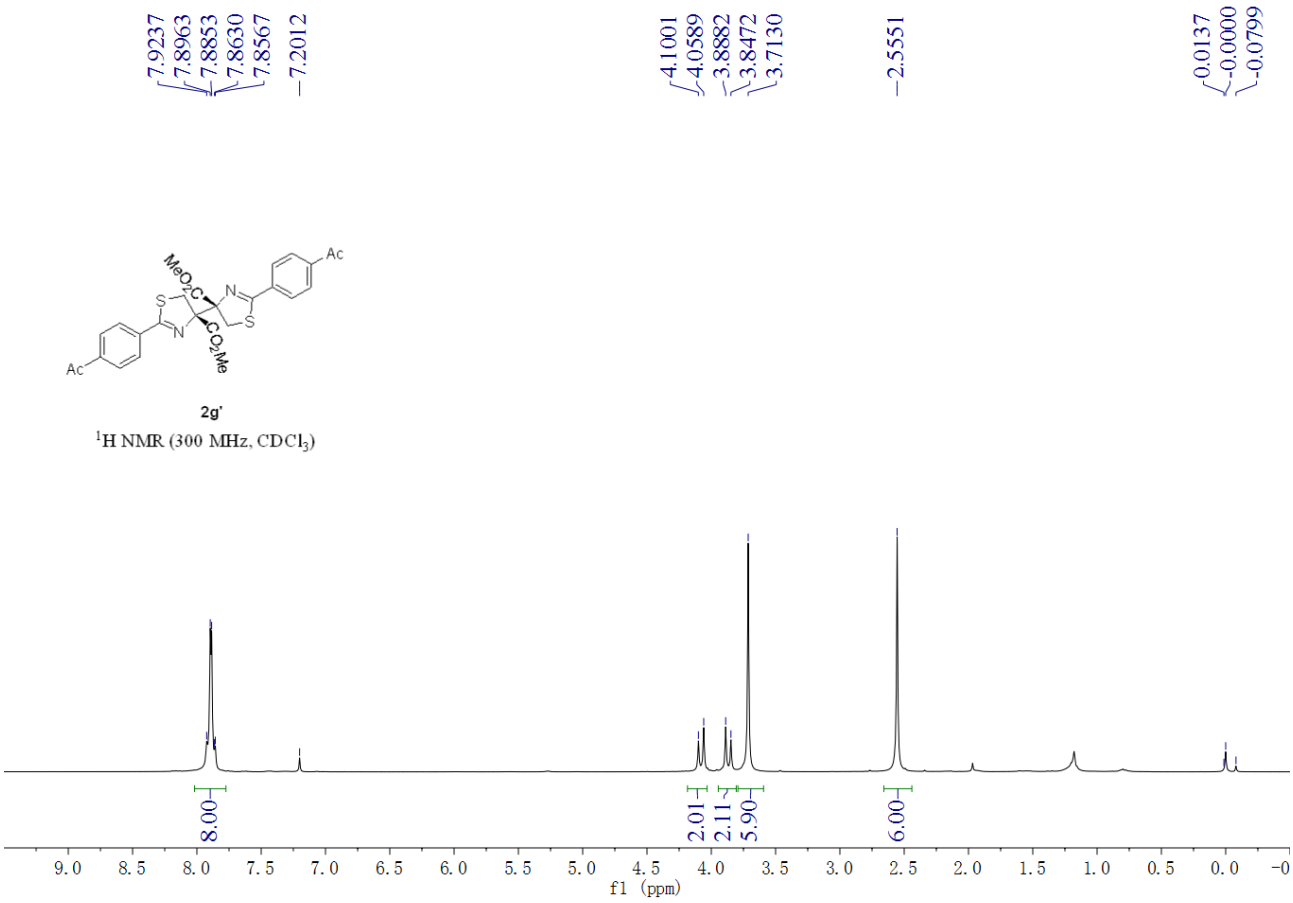


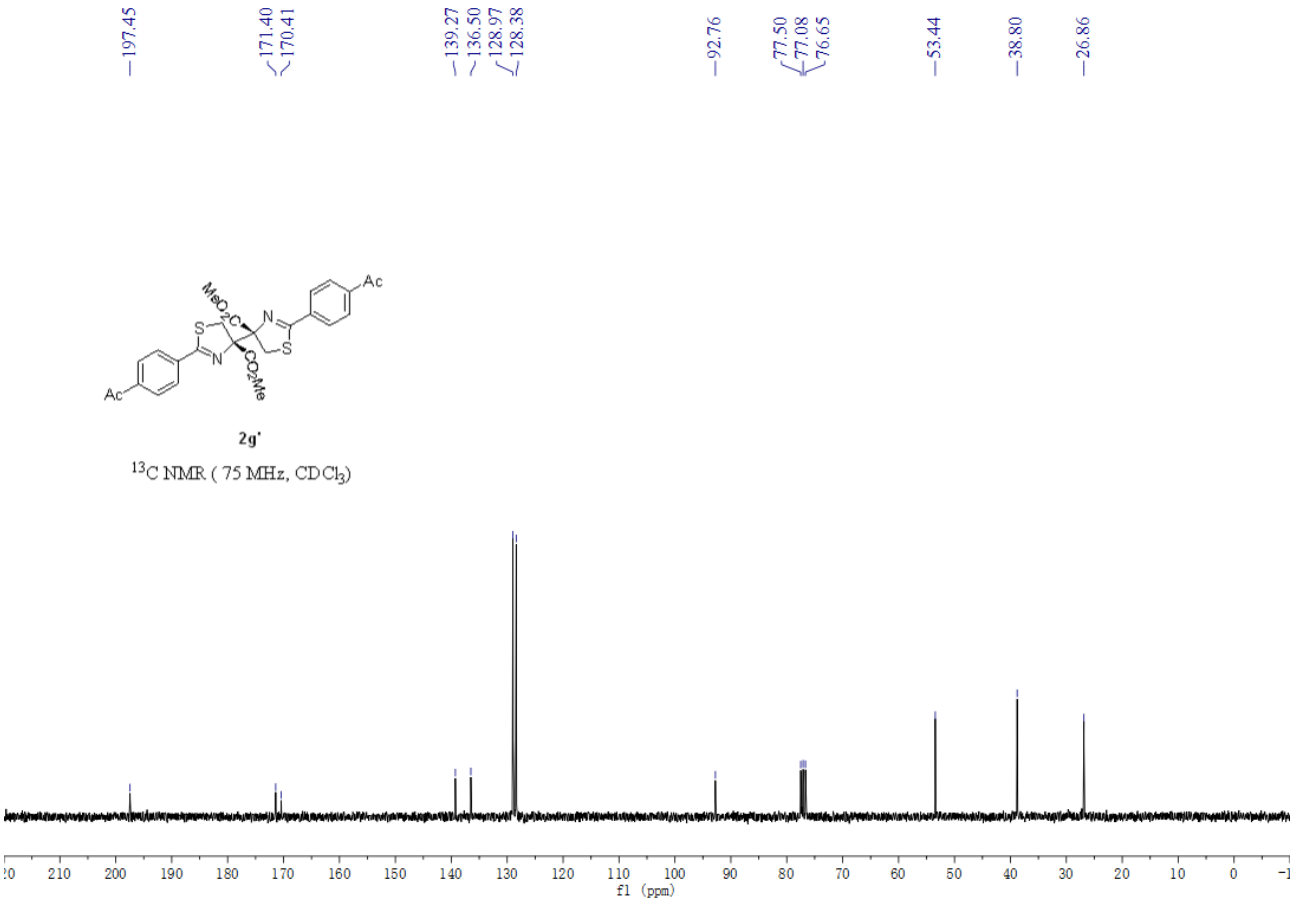
2f

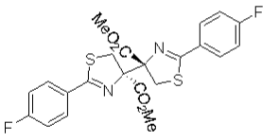
^{13}C NMR (75 MHz, $CDCl_3$)


7.8063
7.7801
7.7683
7.7485
7.7389
7.7202
4.5393
4.5000
4.1972
4.1579
3.7459
3.7352
3.7214
2.4755
2.4647
2.4510
0.0004
-0.0108
Ac
MeO2C
CO2Me
Ac
2g
1H NMR (300 MHz, CDCl3)
7.91
2.00
2.04
5.88
5.90
f1 (ppm)


197.39
171.79
170.44
139.04
136.42
128.75
128.28
94.73
77.53
77.11
76.69
53.26
39.03
26.75
Ac
MeO2C
CO2Me
Ac
2g
13C NMR (75 MHz, CDCl3)
f1 (ppm)

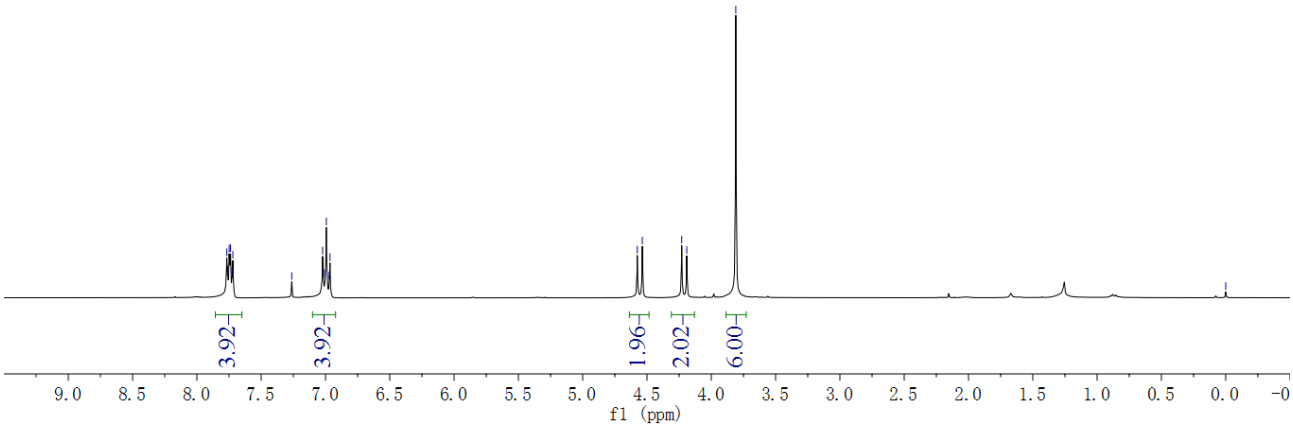

7.9237
7.8963
7.8853
7.8630
7.8567
7.2012
4.1001
4.0589
3.8882
3.8472
3.7130
2.5551
0.0137
-0.0000
-0.0799
Ac
MeO2C
CO2Me
Ac
2g'
1H NMR (300 MHz, CDCl3)
8.00
2.01
2.11
5.90
6.00
f1 (ppm)

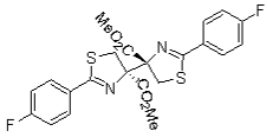

197.45
171.40
170.41
139.27
136.50
128.97
128.38
92.76
77.50
77.08
76.65
53.44
38.80
26.86
Ac
MeO2C
CO2Me
Ac
2g'
13C NMR (75 MHz, CDCl3)
f1 (ppm)



2h

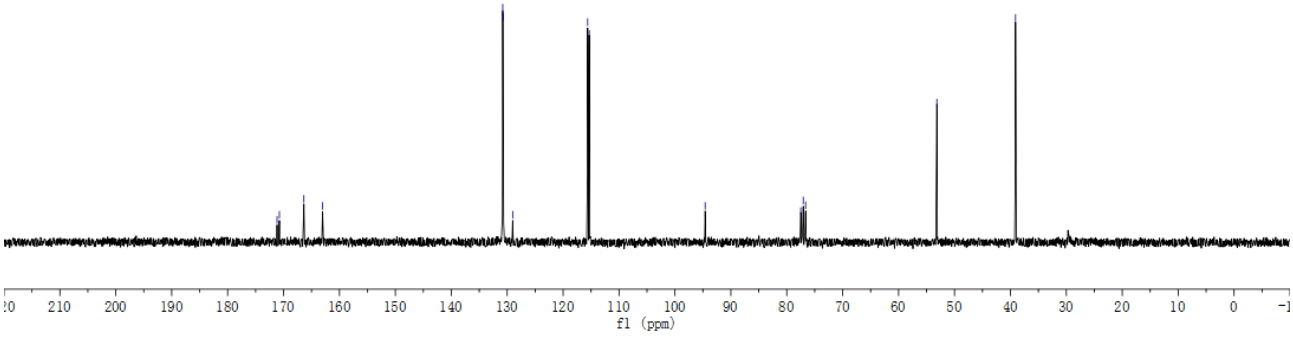
^{1}H NMR (300 MHz, $CDCl_3$)

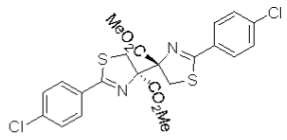




2h

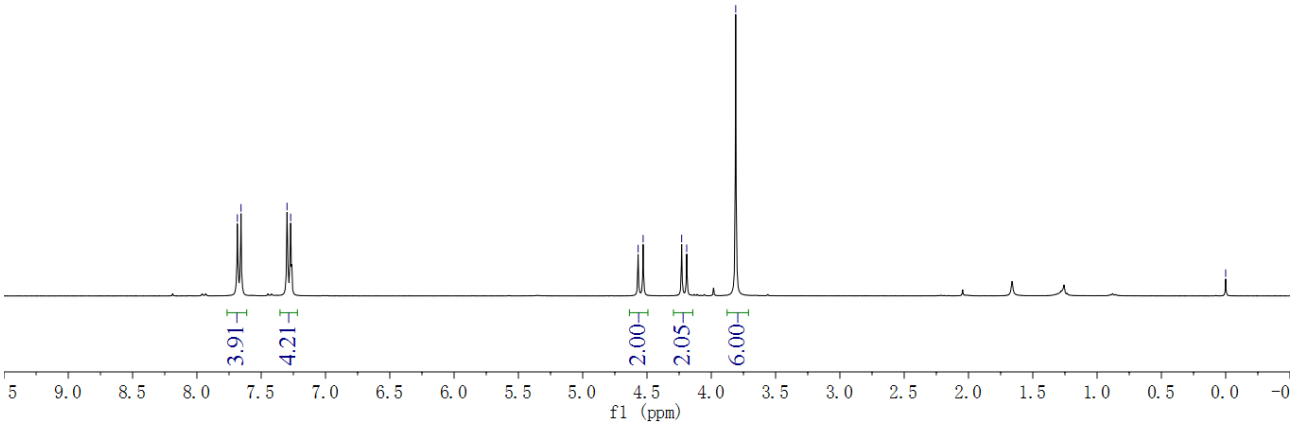
^{13}C NMR (75 MHz, $CDCl_3$)

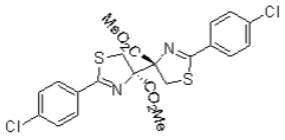




2i

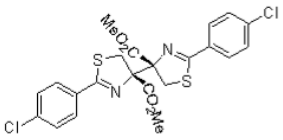
^{1}H NMR (300 MHz, $CDCl_3$)





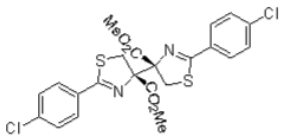
2i

^{13}C NMR (75 MHz, $CDCl_3$)



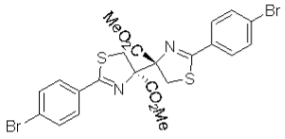
2i'

^{1}H NMR (300 MHz, $CDCl_3$)



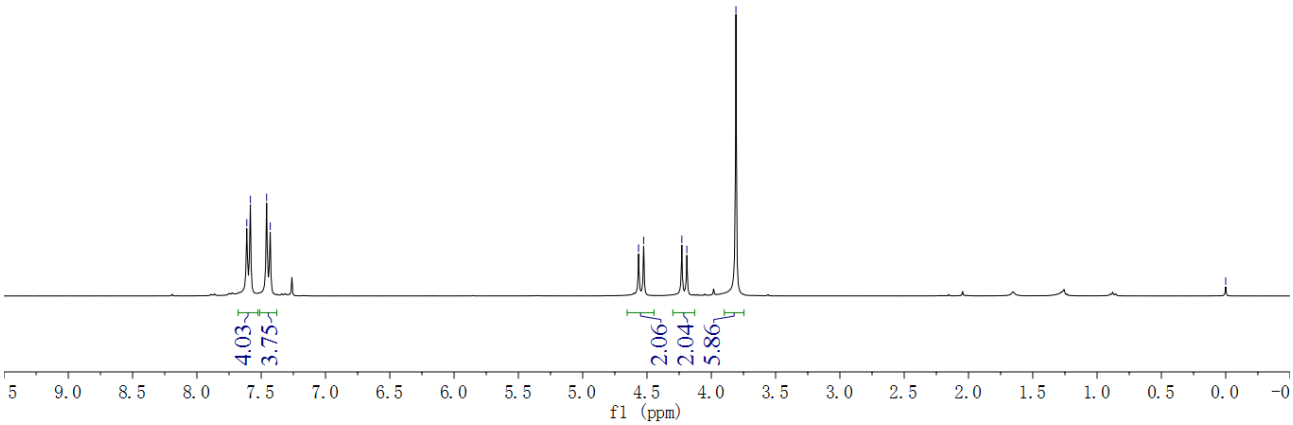
2i'

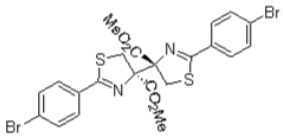
^{13}C NMR (75 MHz, $CDCl_3$)



2j

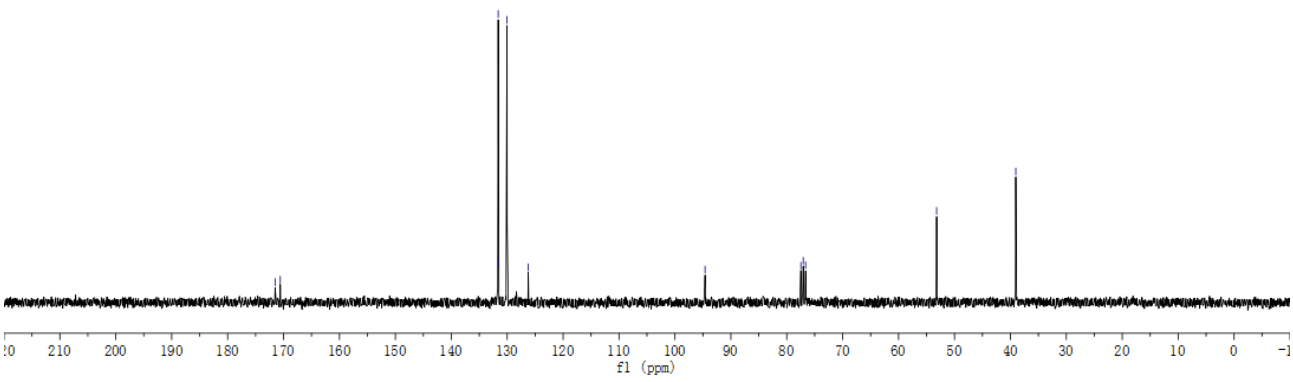
^{1}H NMR (300 MHz, $CDCl_3$)

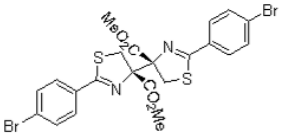




2j

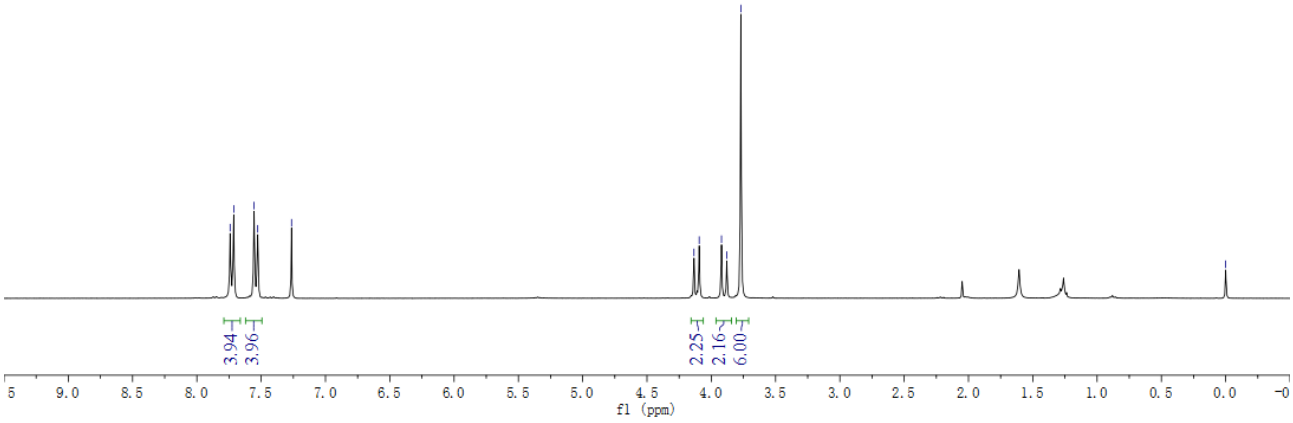
^{13}C NMR (75 MHz, $CDCl_3$)

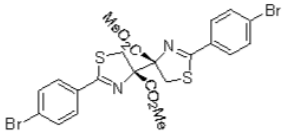




2j'

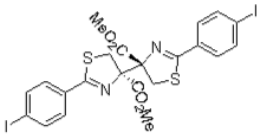
^{1}H NMR (300 MHz, $CDCl_3$)





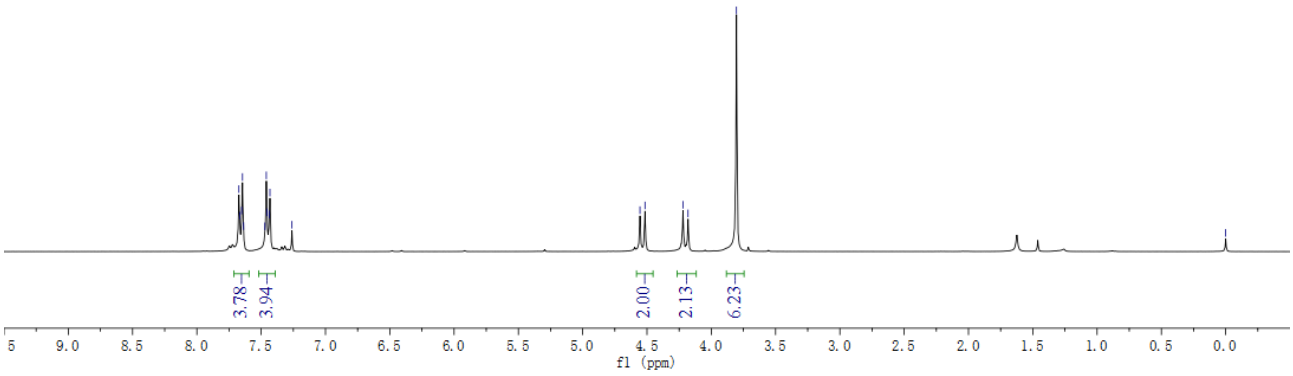
2j'

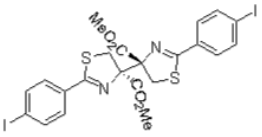
^{13}C NMR (75 MHz, $CDCl_3$)



2k

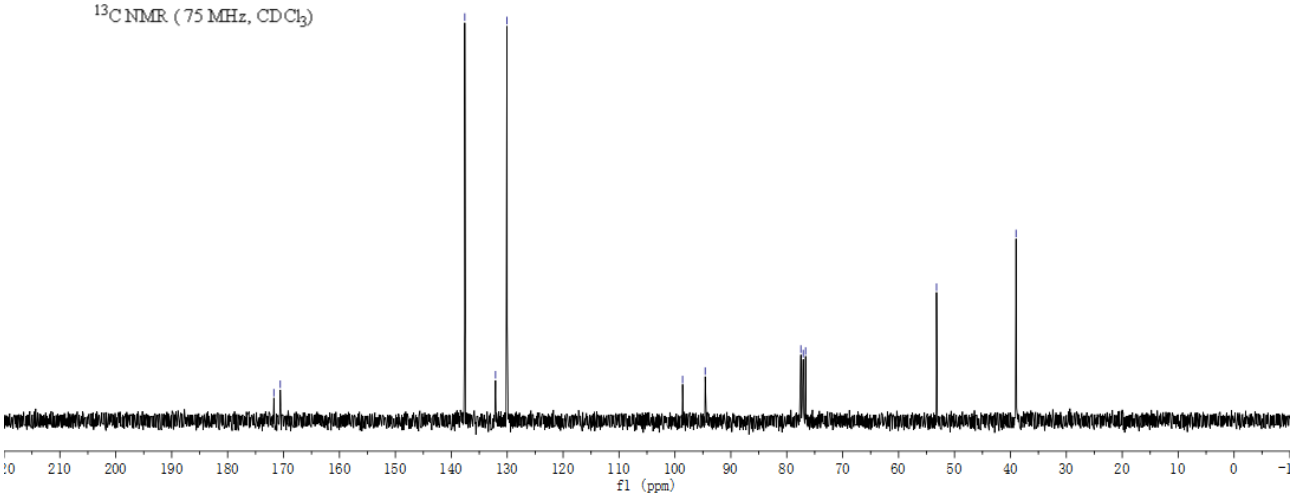
^{1}H NMR (300 MHz, $CDCl_3$)

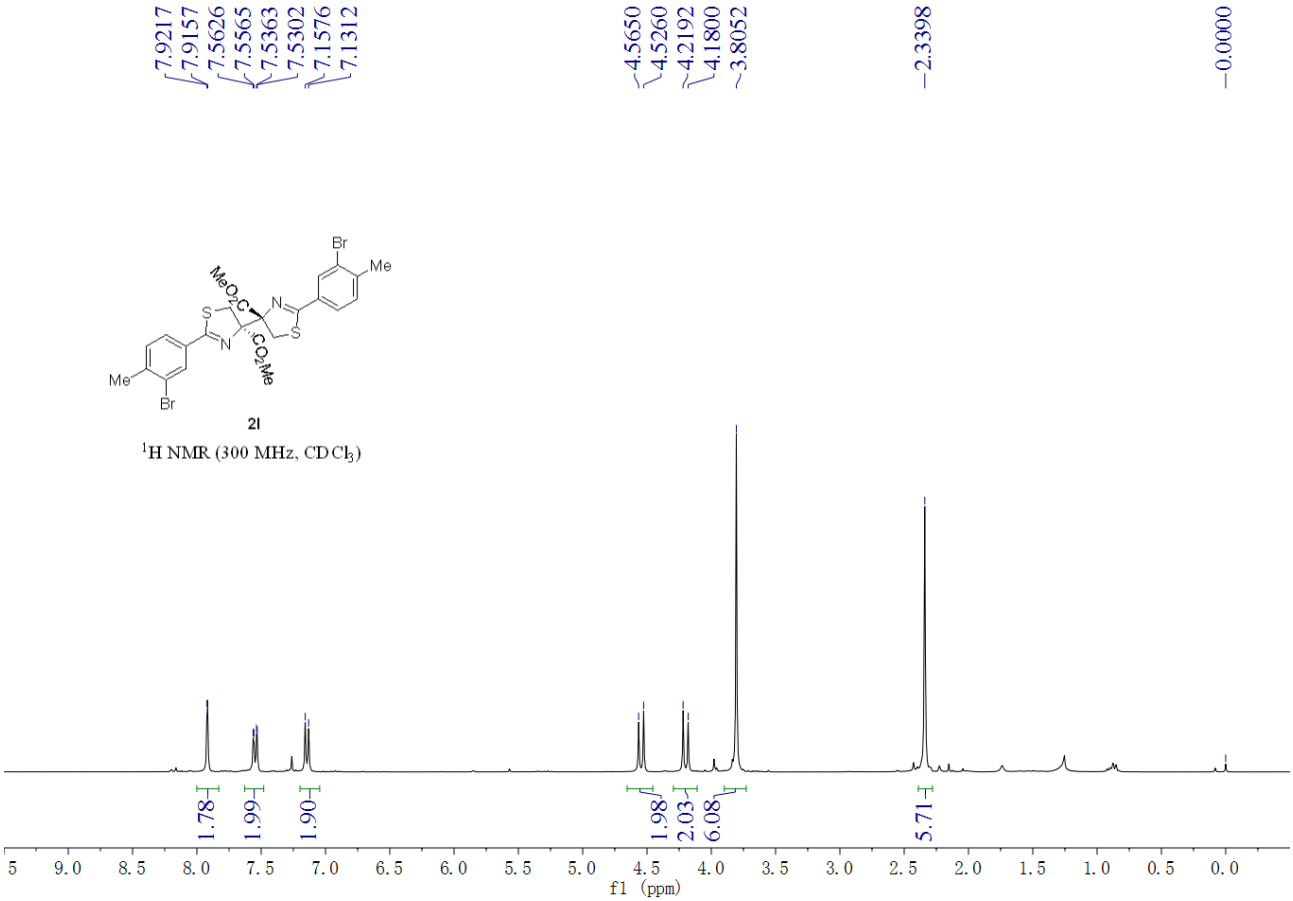




2k

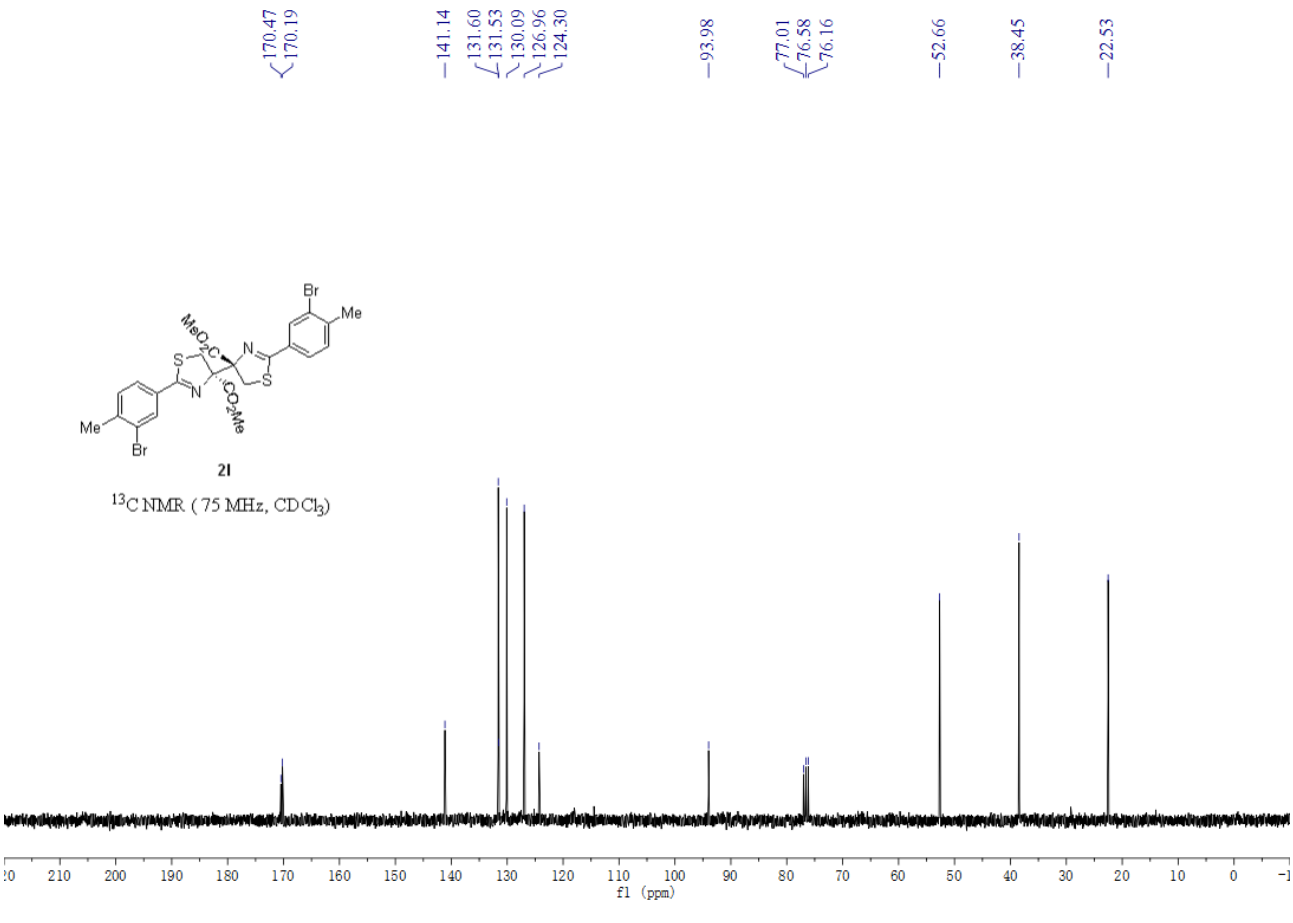
^{13}C NMR (75 MHz, $CDCl_3$)





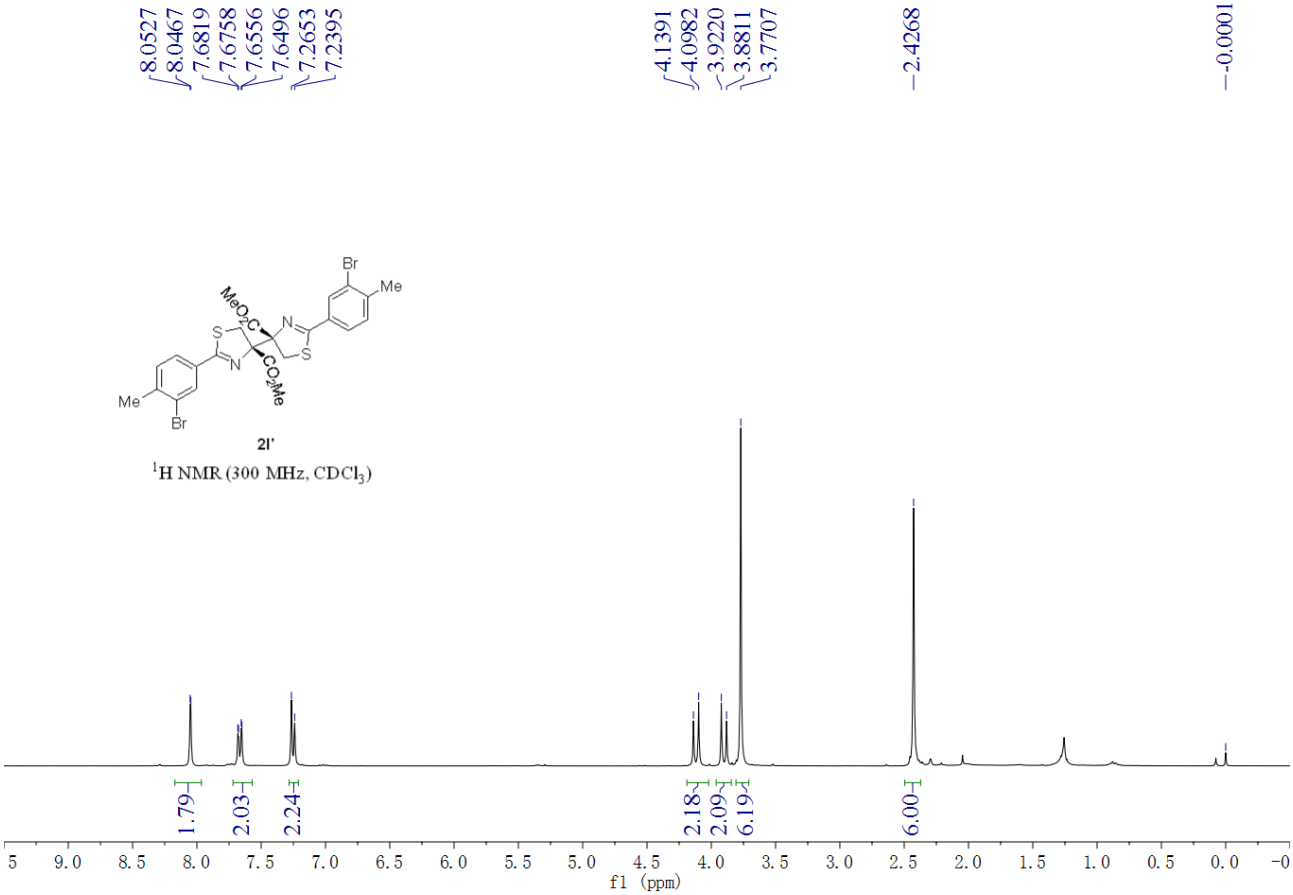
2l

^{1}H NMR (300 MHz, $CDCl_3$)



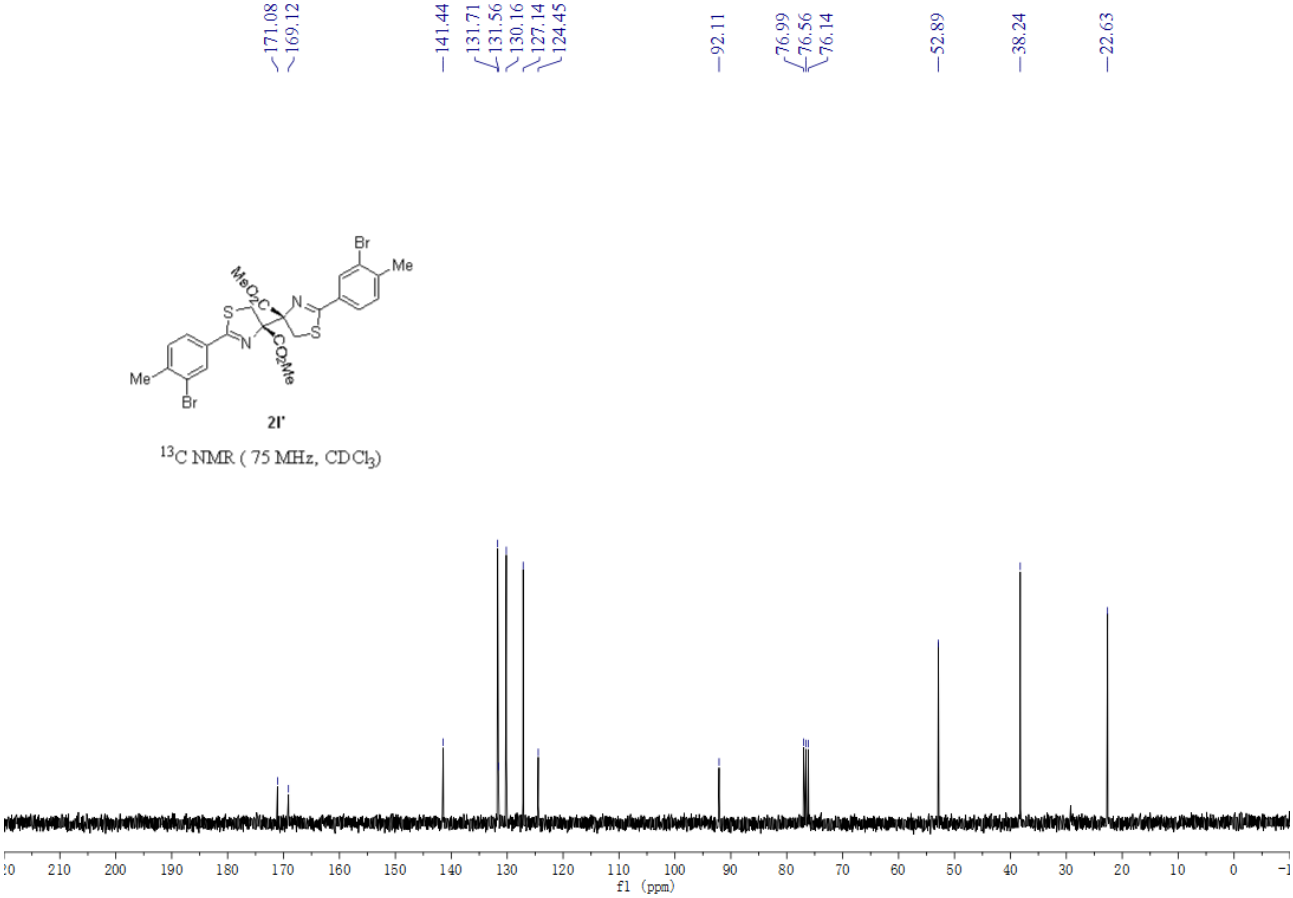
2l

^{13}C NMR (75 MHz, $CDCl_3$)



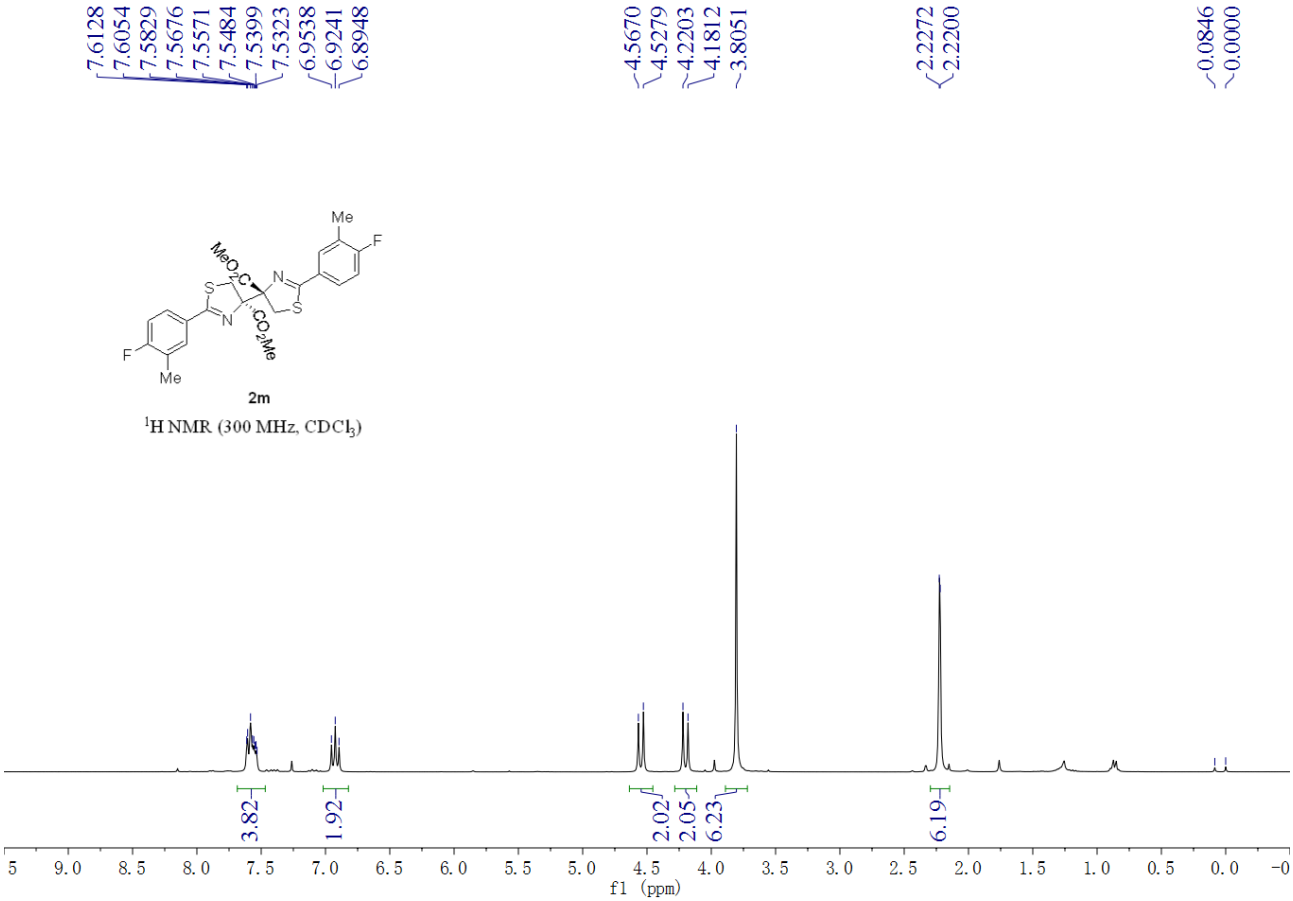
2l'

^{1}H NMR (300 MHz, $CDCl_3$)



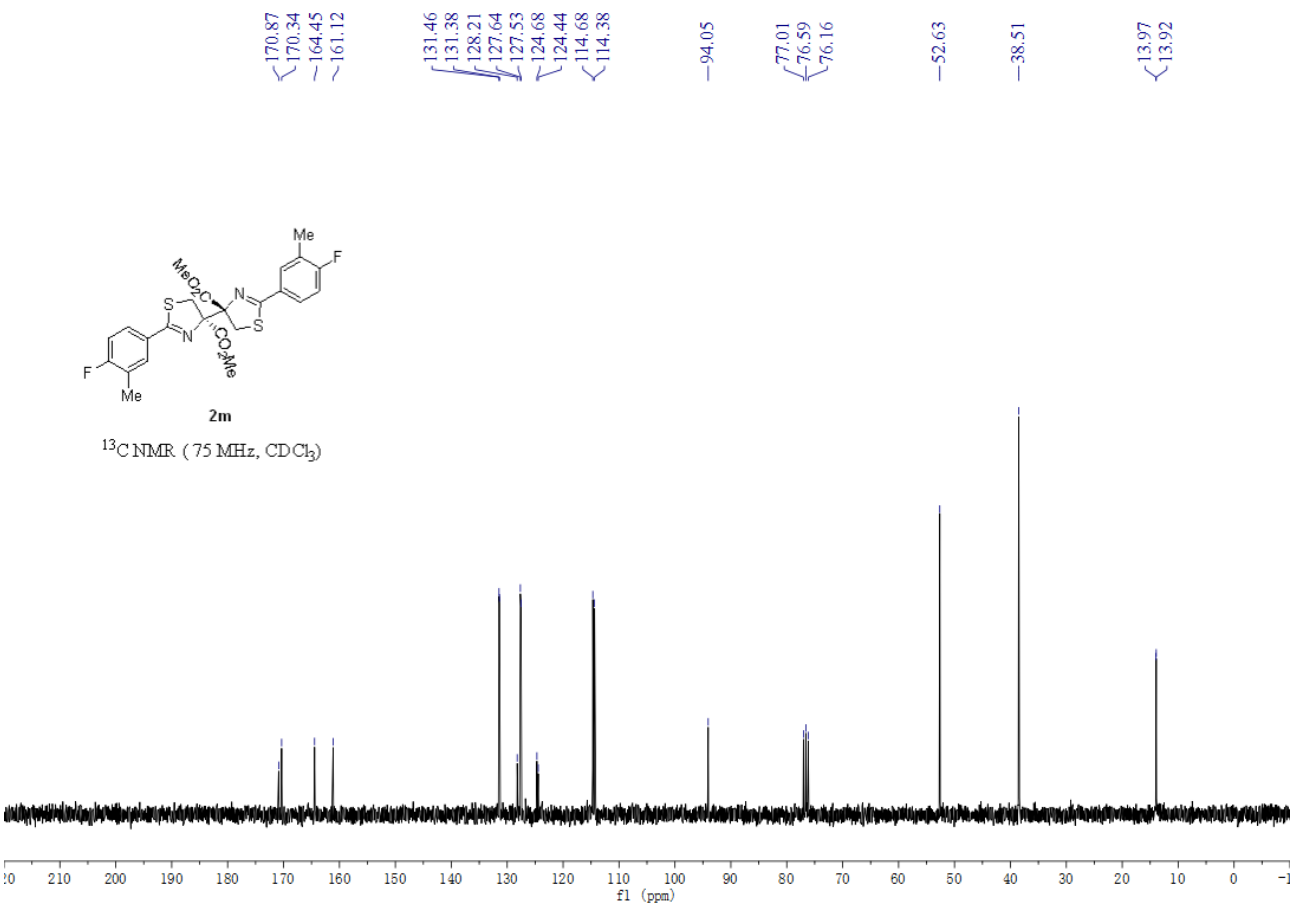
2l'

^{13}C NMR (75 MHz, $CDCl_3$)



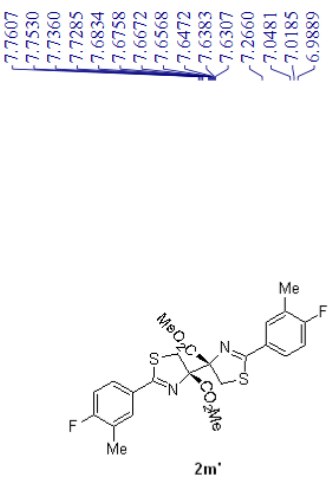
2m

^{1}H NMR (300 MHz, $CDCl_3$)



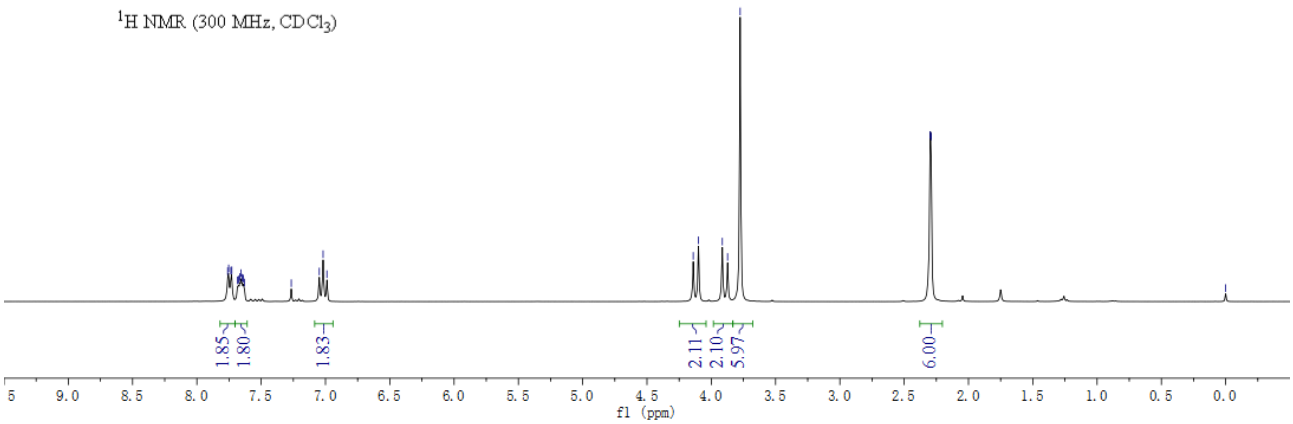
2m

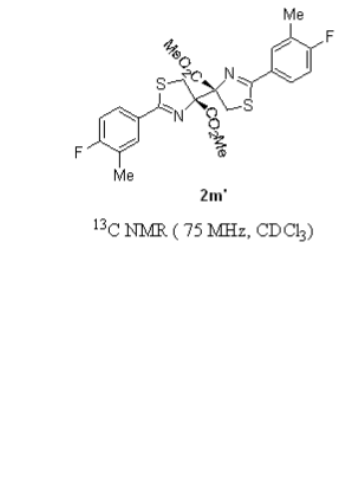
^{13}C NMR (75 MHz, $CDCl_3$)



2m'

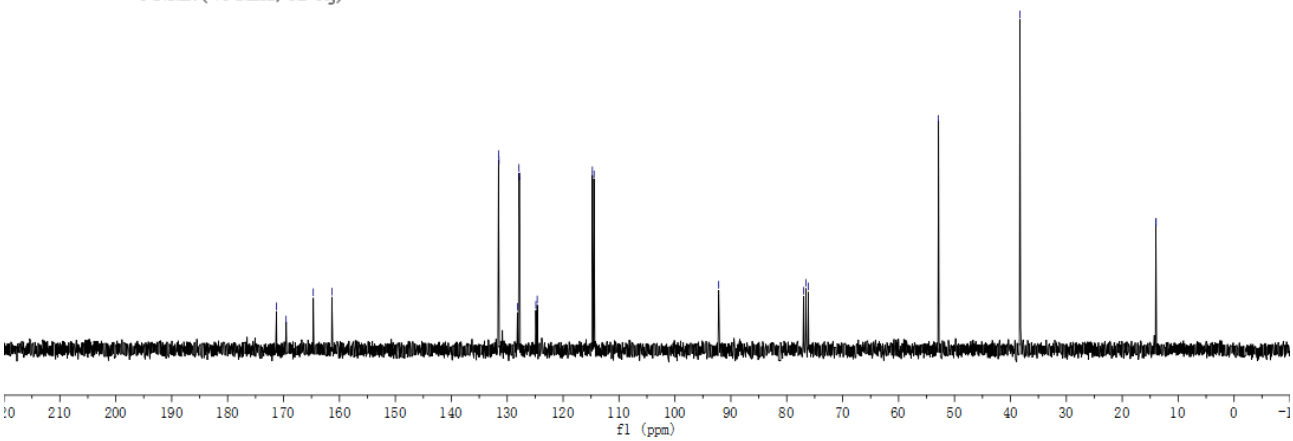
^{1}H NMR (300 MHz, $CDCl_3$)

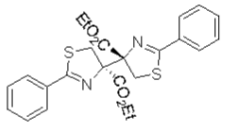




2m'

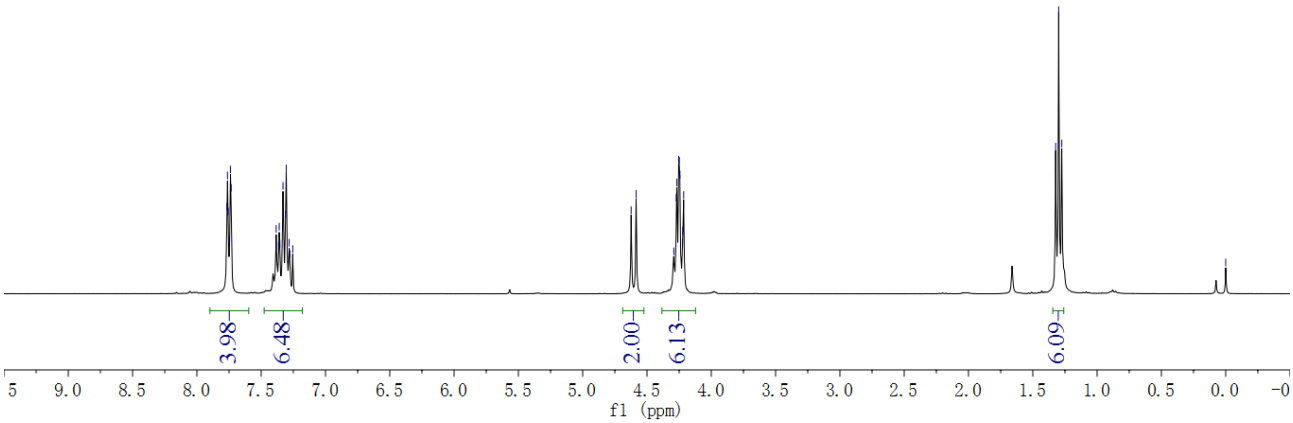
^{13}C NMR (75 MHz, $CDCl_3$)

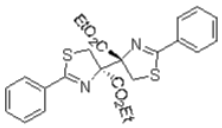




2n

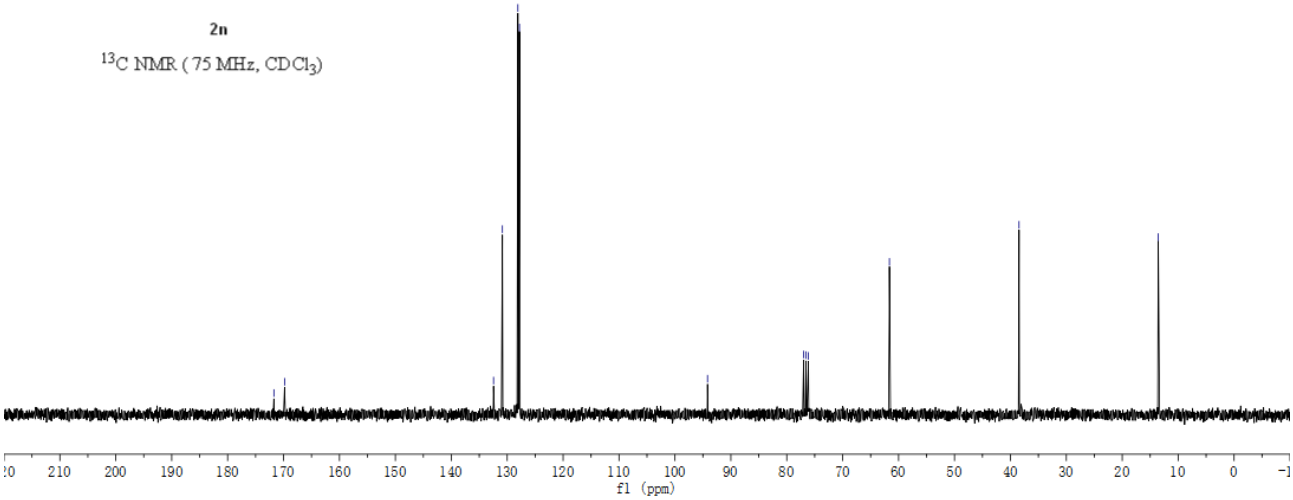
^{1}H NMR (300 MHz, $CDCl_3$)

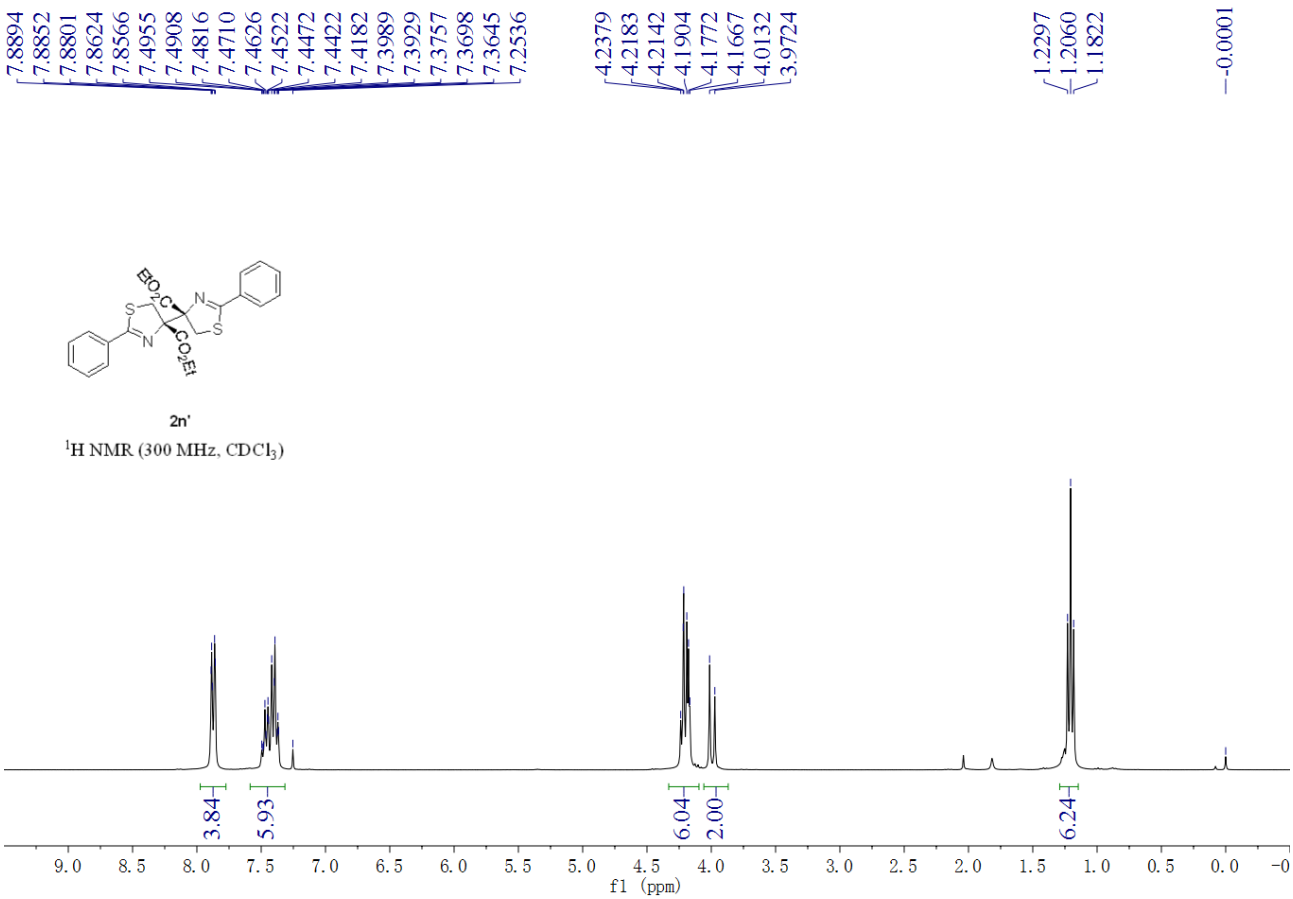




2n

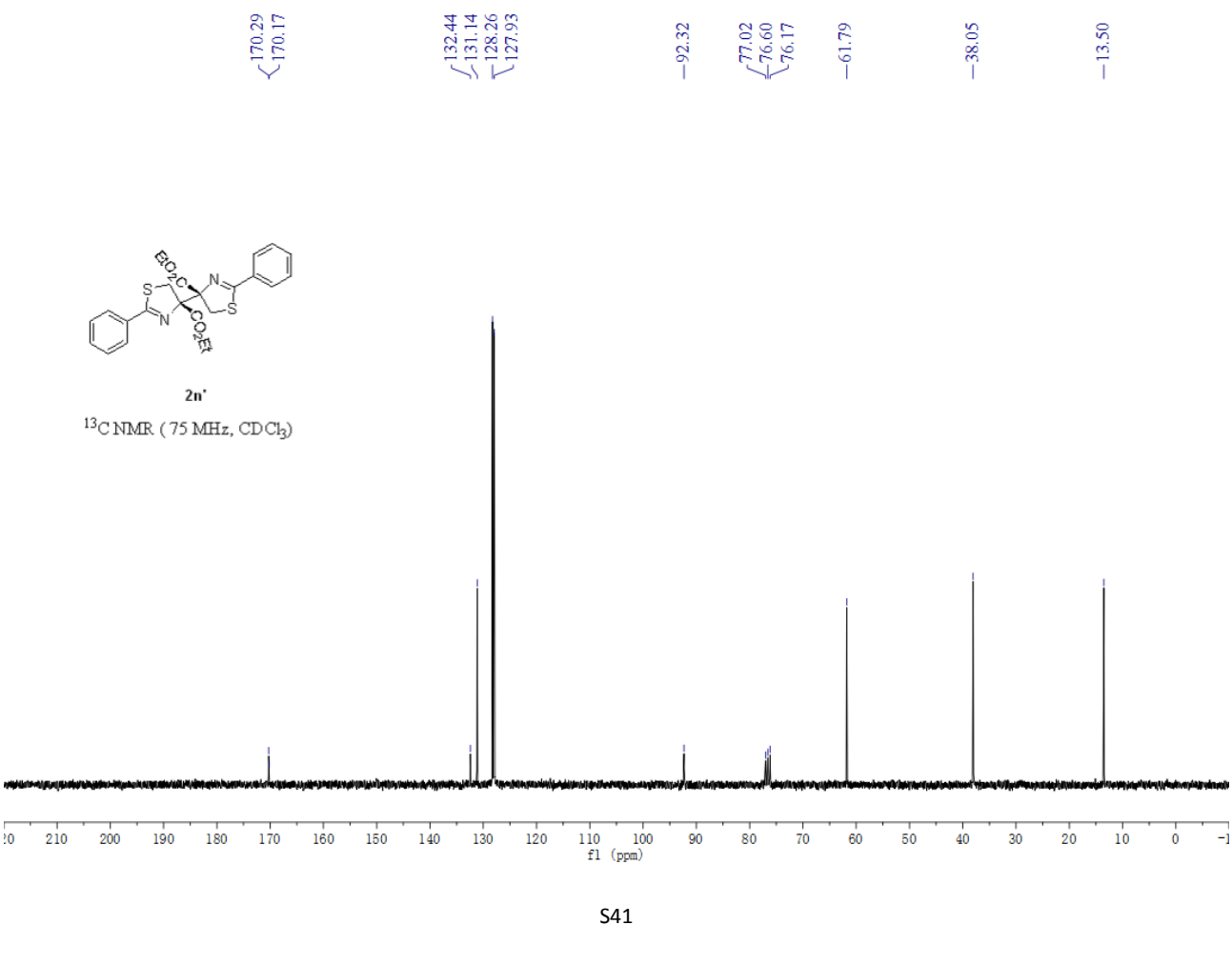
^{13}C NMR (75 MHz, $CDCl_3$)





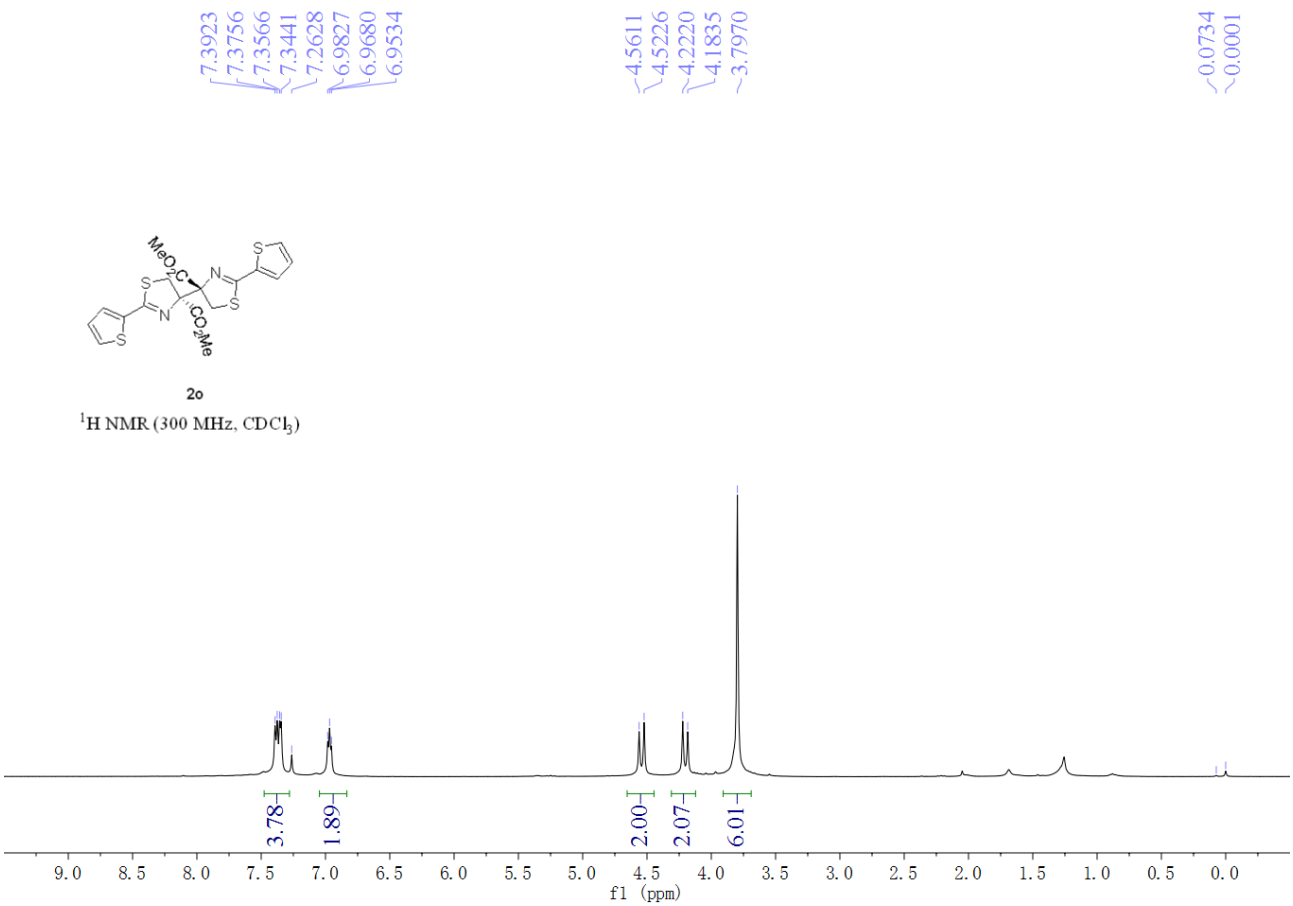
2n'

^{1}H NMR (300 MHz, $CDCl_3$)



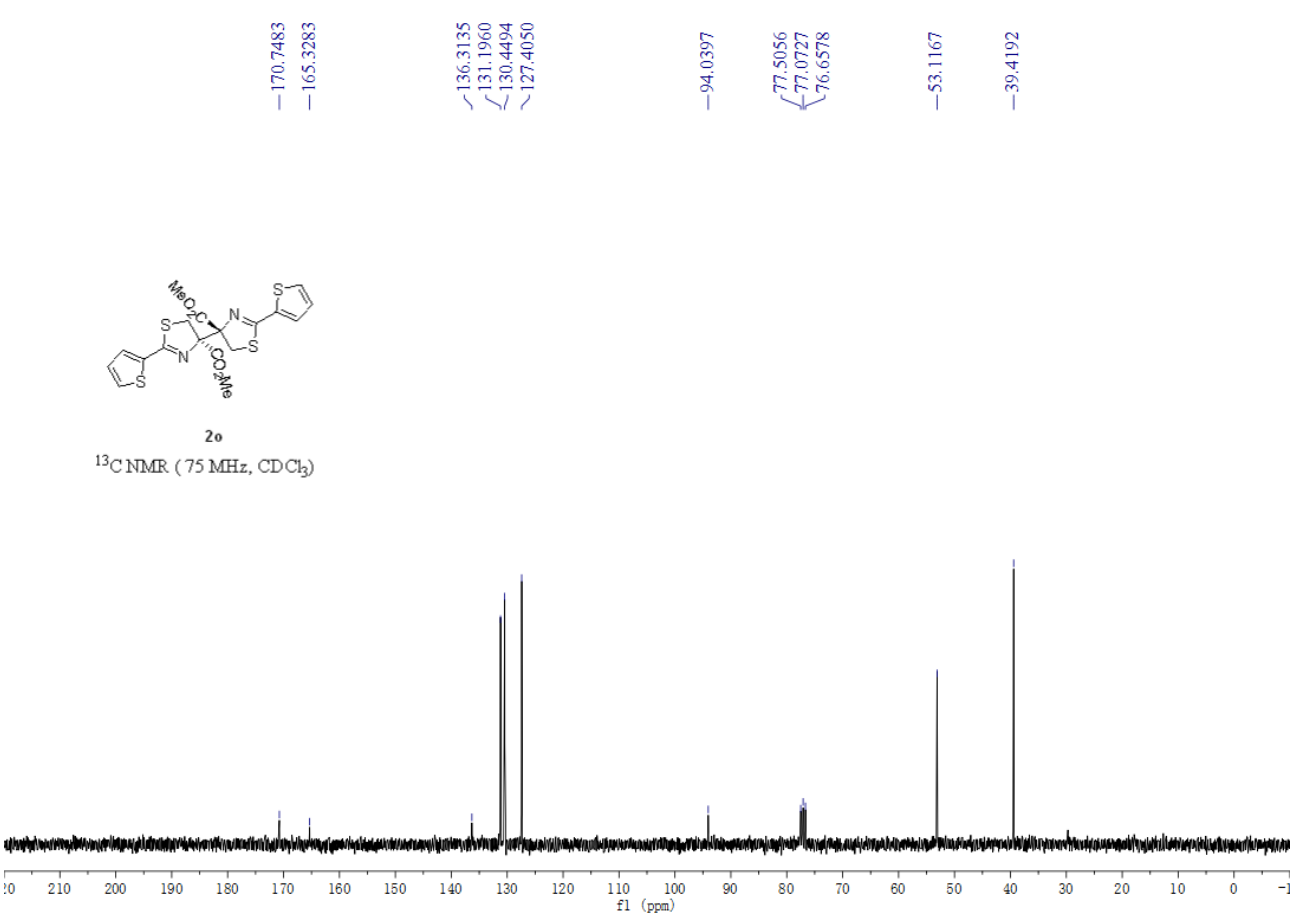
2n'

^{13}C NMR (75 MHz, $CDCl_3$)



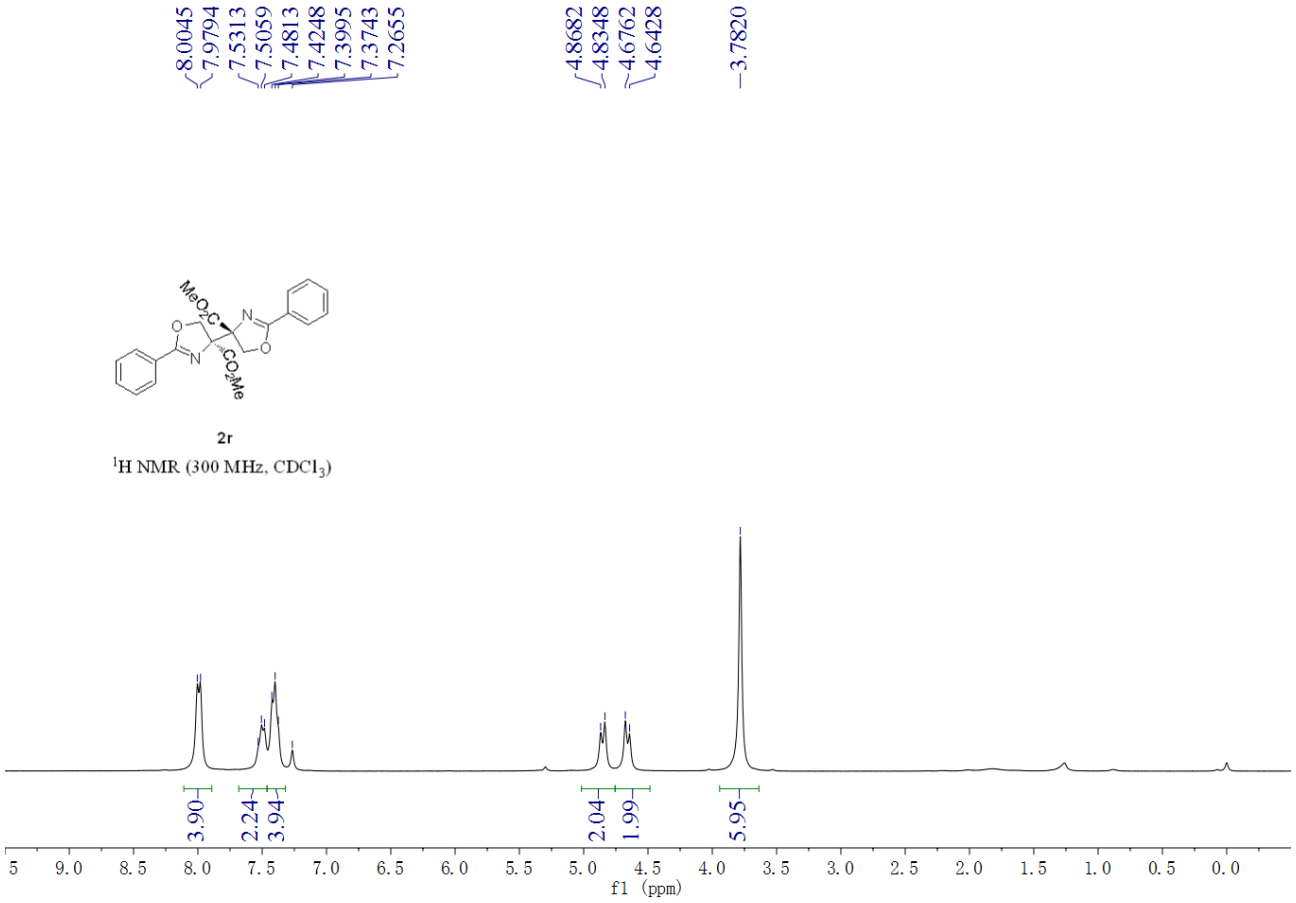
2o

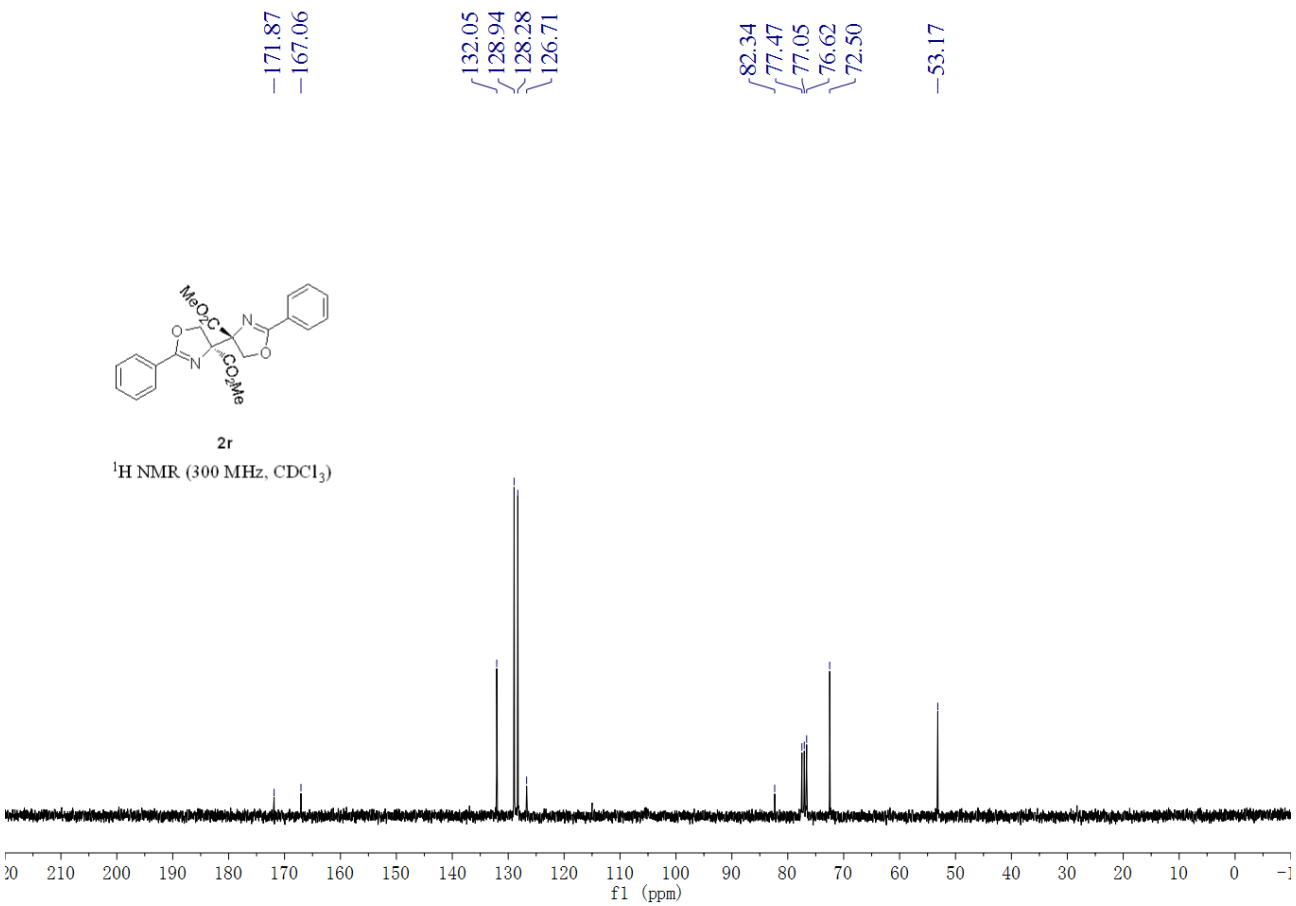
^{1}H NMR (300 MHz, $CDCl_3$)

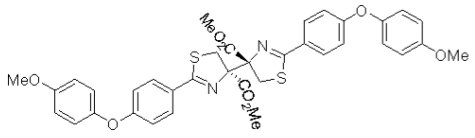


2o

^{13}C NMR (75 MHz, $CDCl_3$)

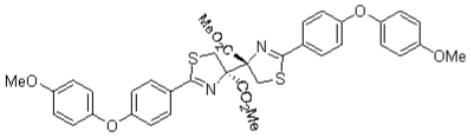

8.0045
7.9794
7.5313
7.5059
7.4813
7.4248
7.3995
7.3743
7.2655
4.8682
4.8348
4.6762
4.6428
3.7820
MeO2C
CO2Me
2r
1H NMR (300 MHz, CDCl3)
3.90
2.24
3.94
2.04
1.99
5.95
f1 (ppm)


171.87
167.06
132.05
128.94
128.28
126.71
82.34
77.47
77.05
76.62
72.50
53.17
MeO2C
CO2Me
2r
1H NMR (300 MHz, CDCl3)
f1 (ppm)



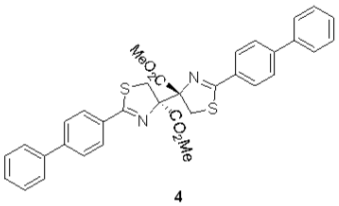
3

^{1}H NMR (300 MHz, $CDCl_3$)



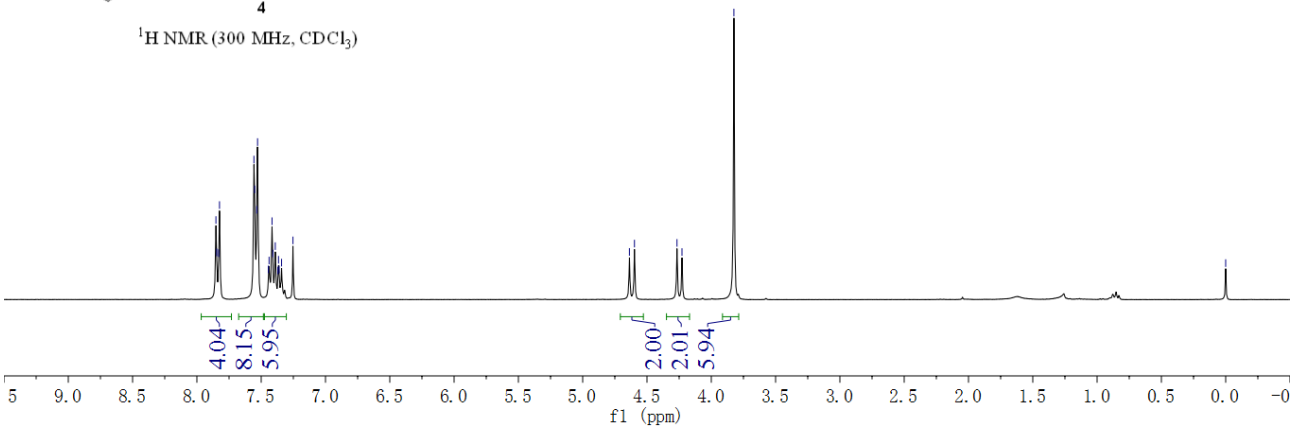
3

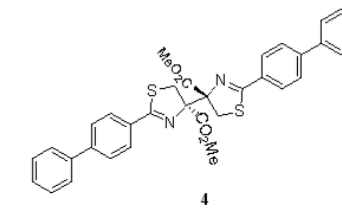
^{13}C NMR (75 MHz, $CDCl_3$)



4

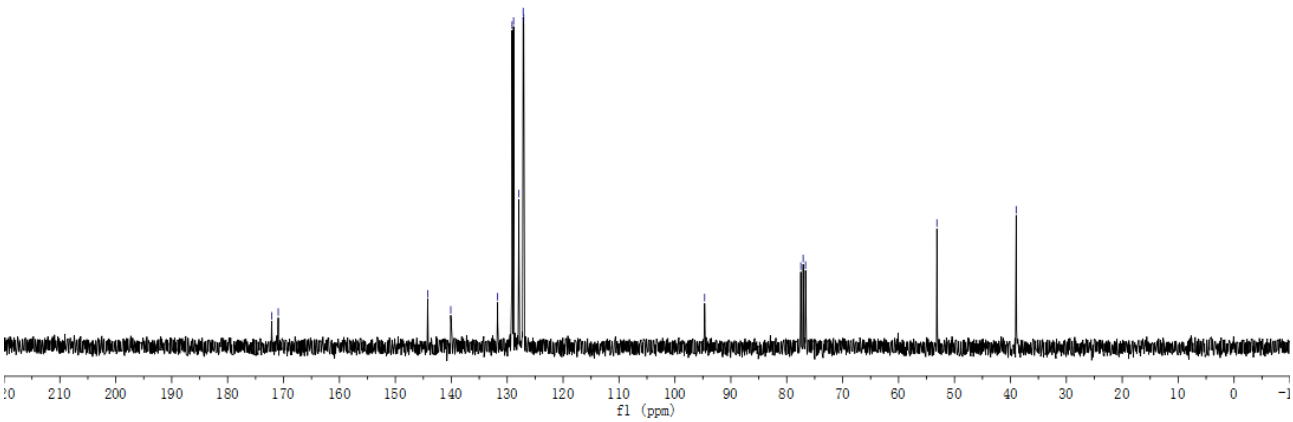
^{1}H NMR (300 MHz, $CDCl_3$)

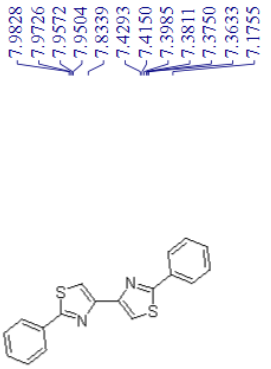




4

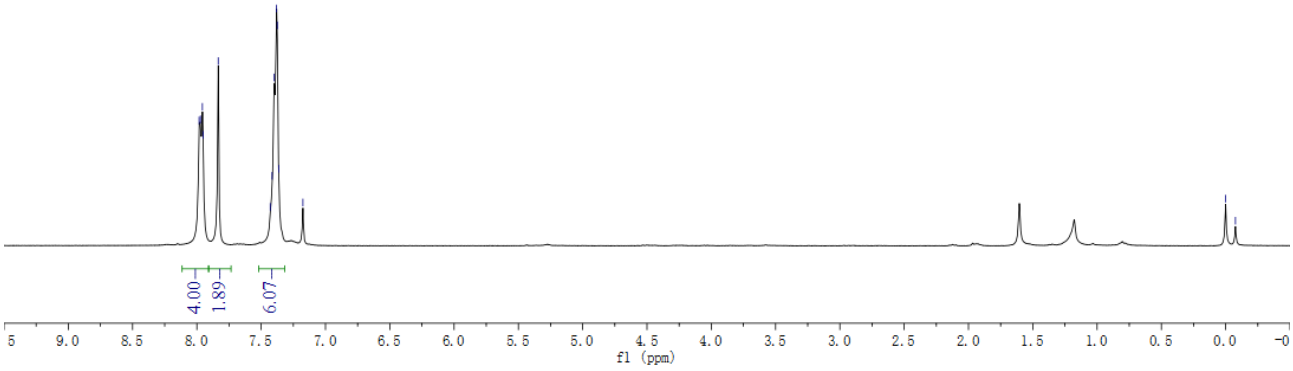
^{13}C NMR (75 MHz, $CDCl_3$)

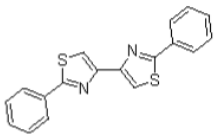




5a

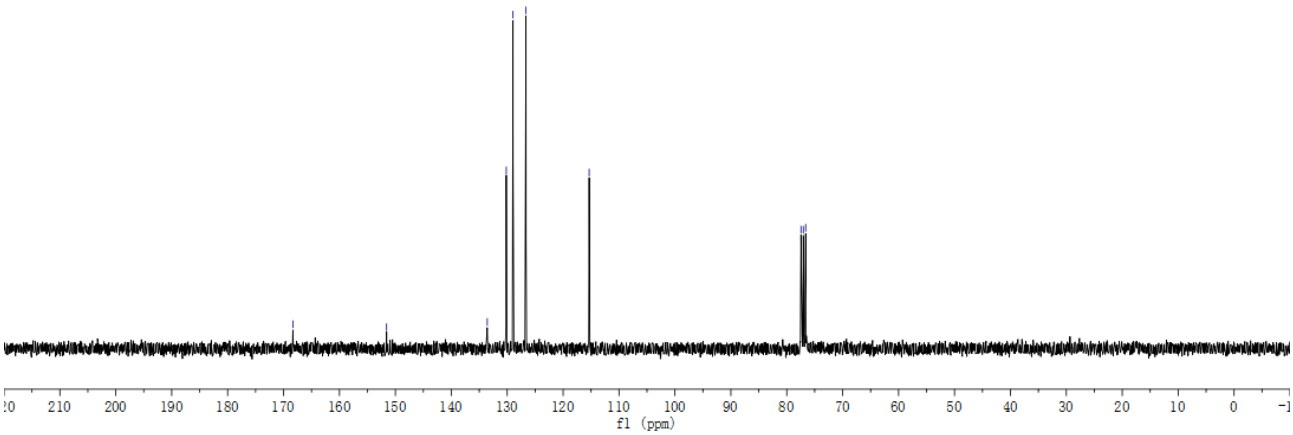
^{1}H NMR (300 MHz, $CDCl_3$)

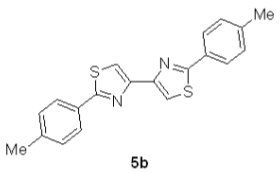




5a

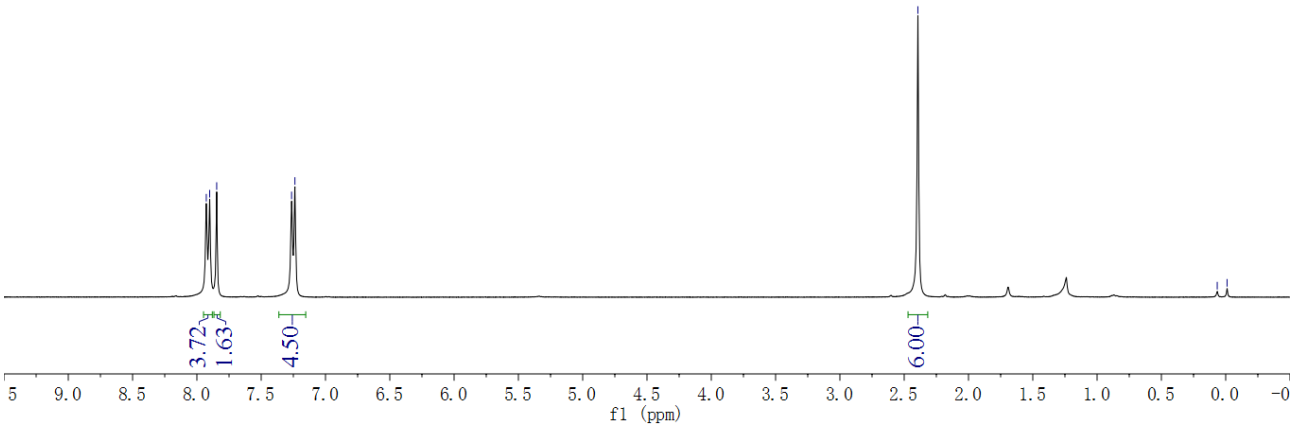
^{13}C NMR (75 MHz, $CDCl_3$)

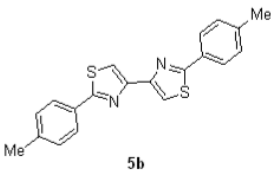




5b

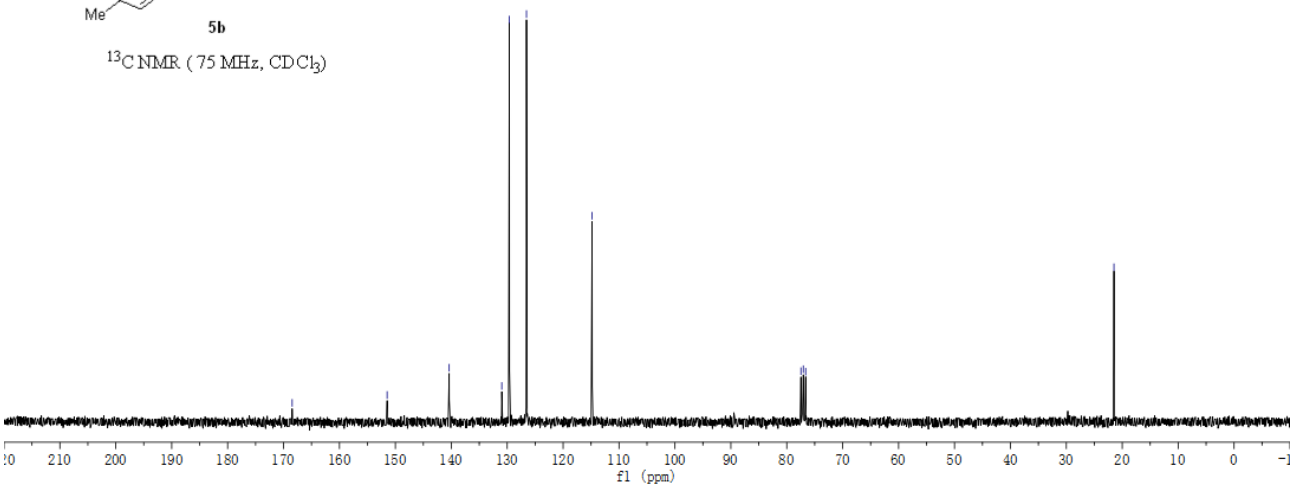
^{1}H NMR (300 MHz, $CDCl_3$)

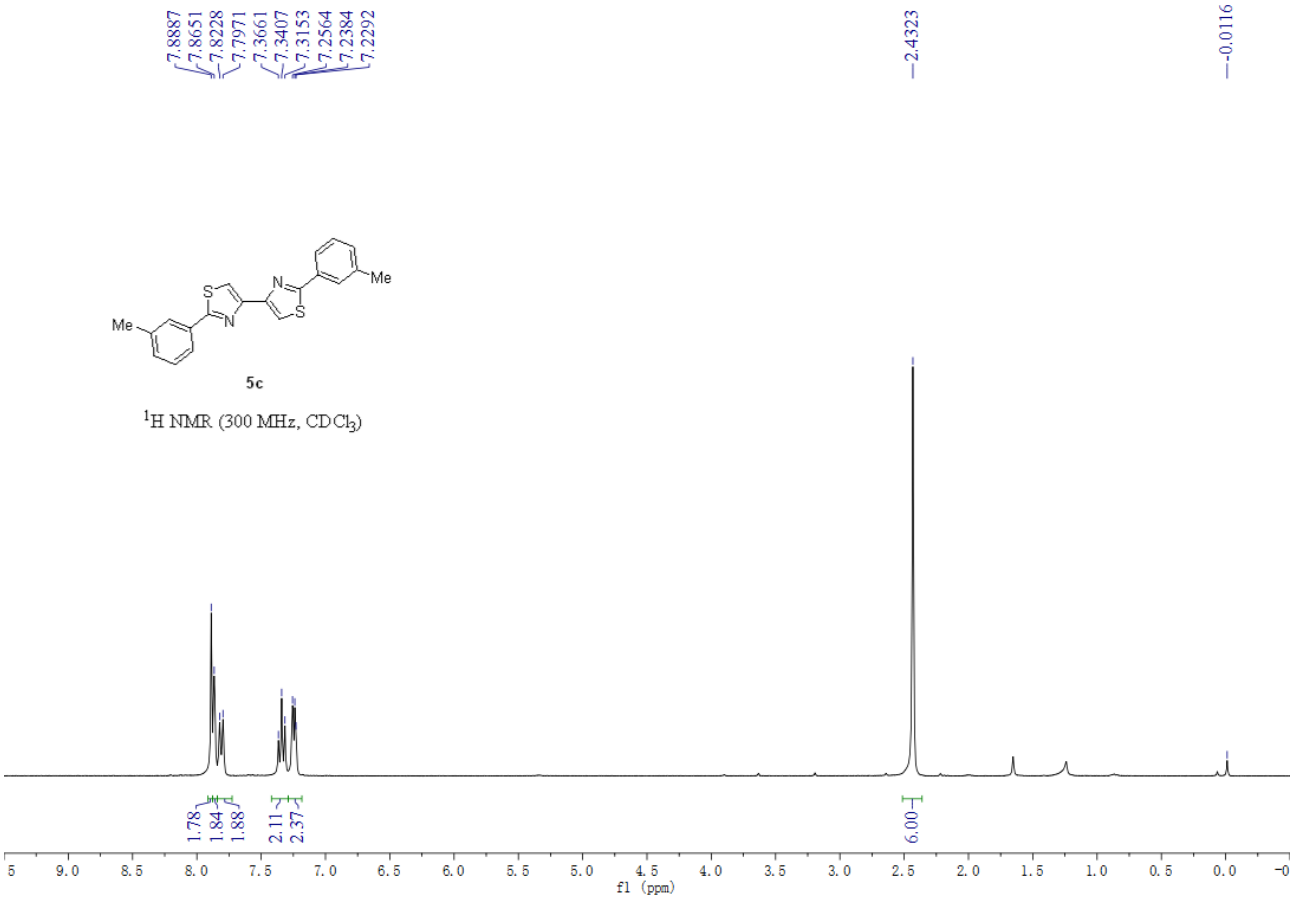




5b

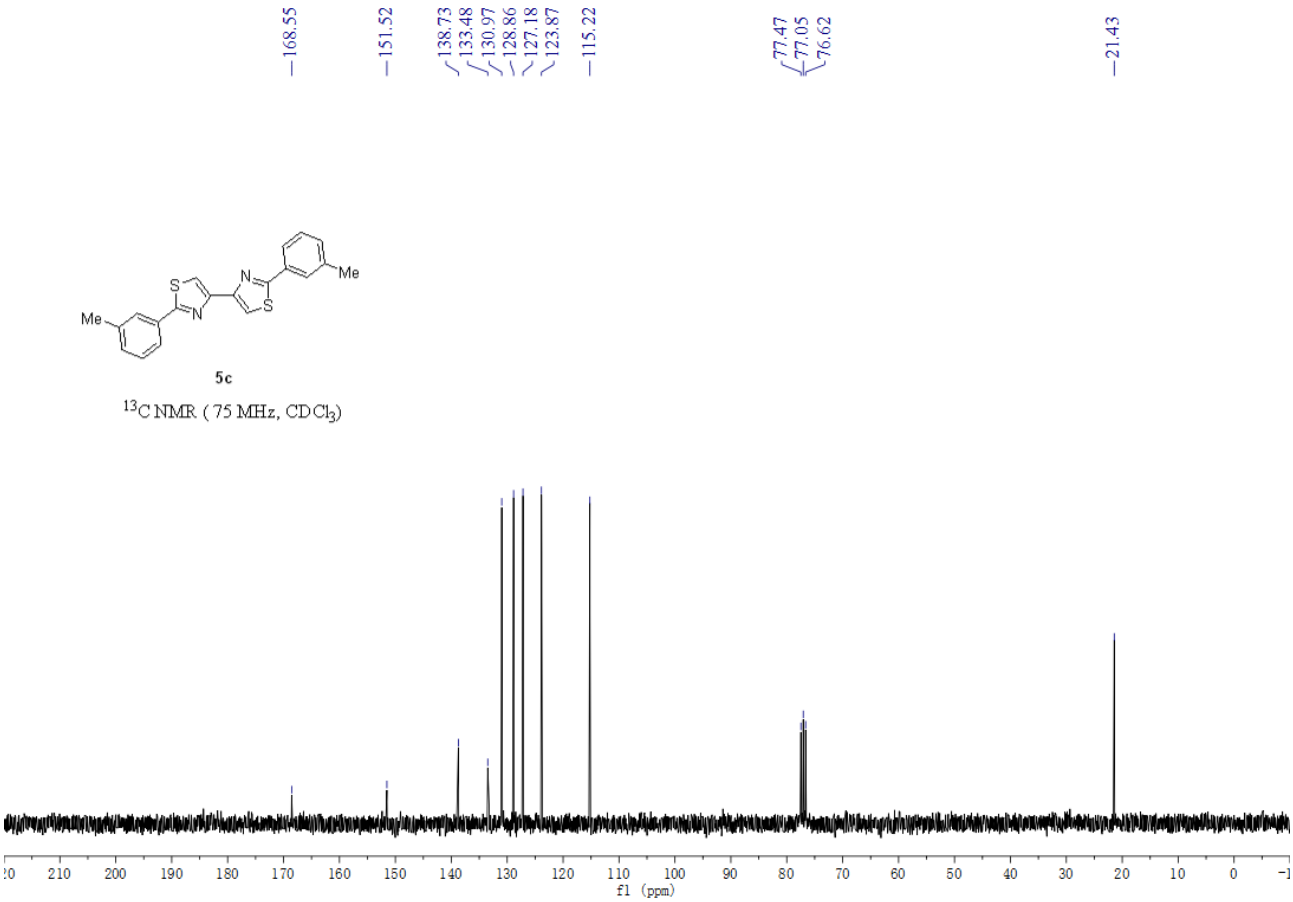
^{13}C NMR (75 MHz, $CDCl_3$)





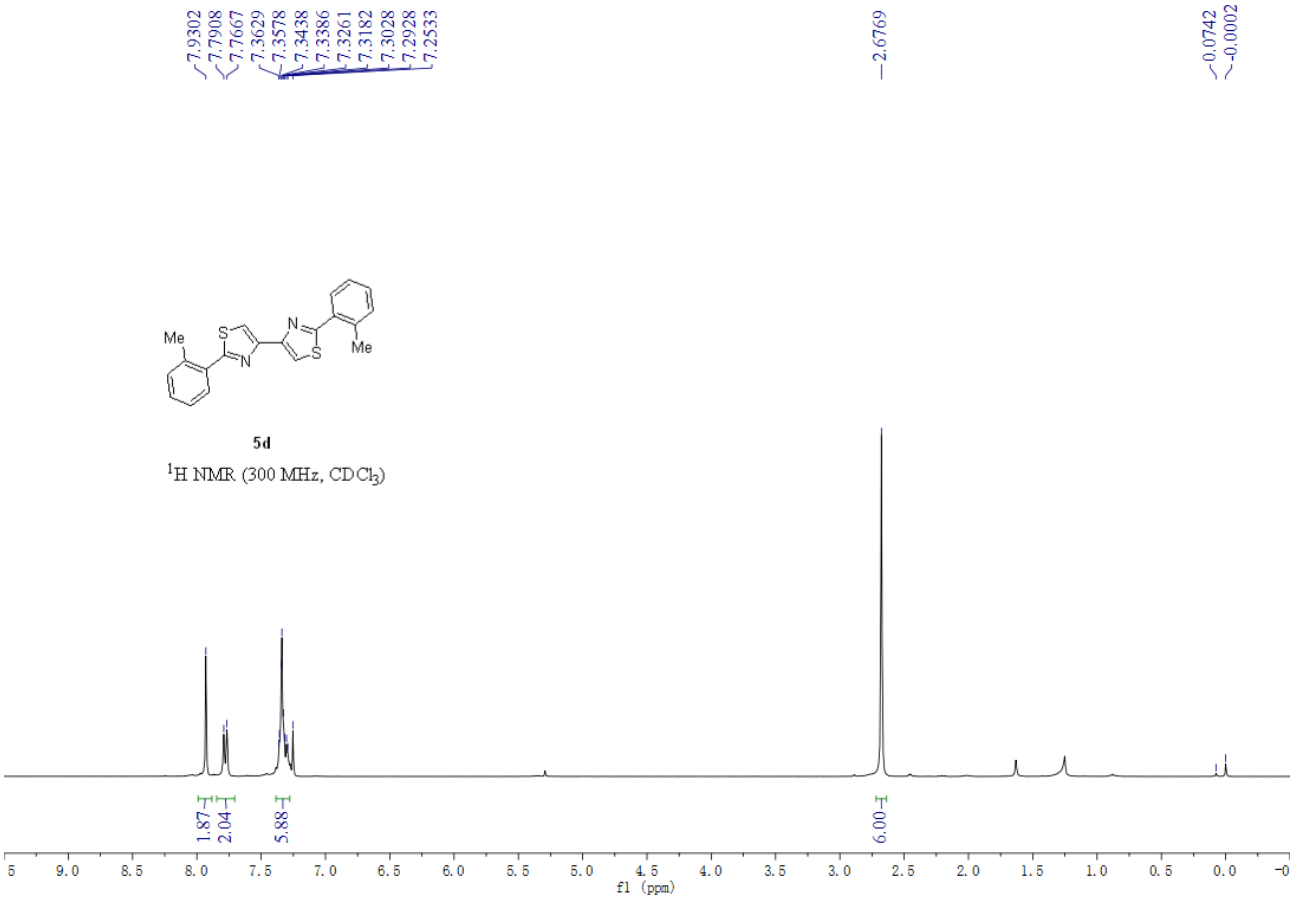
5c

^{1}H NMR (300 MHz, $CDCl_3$)



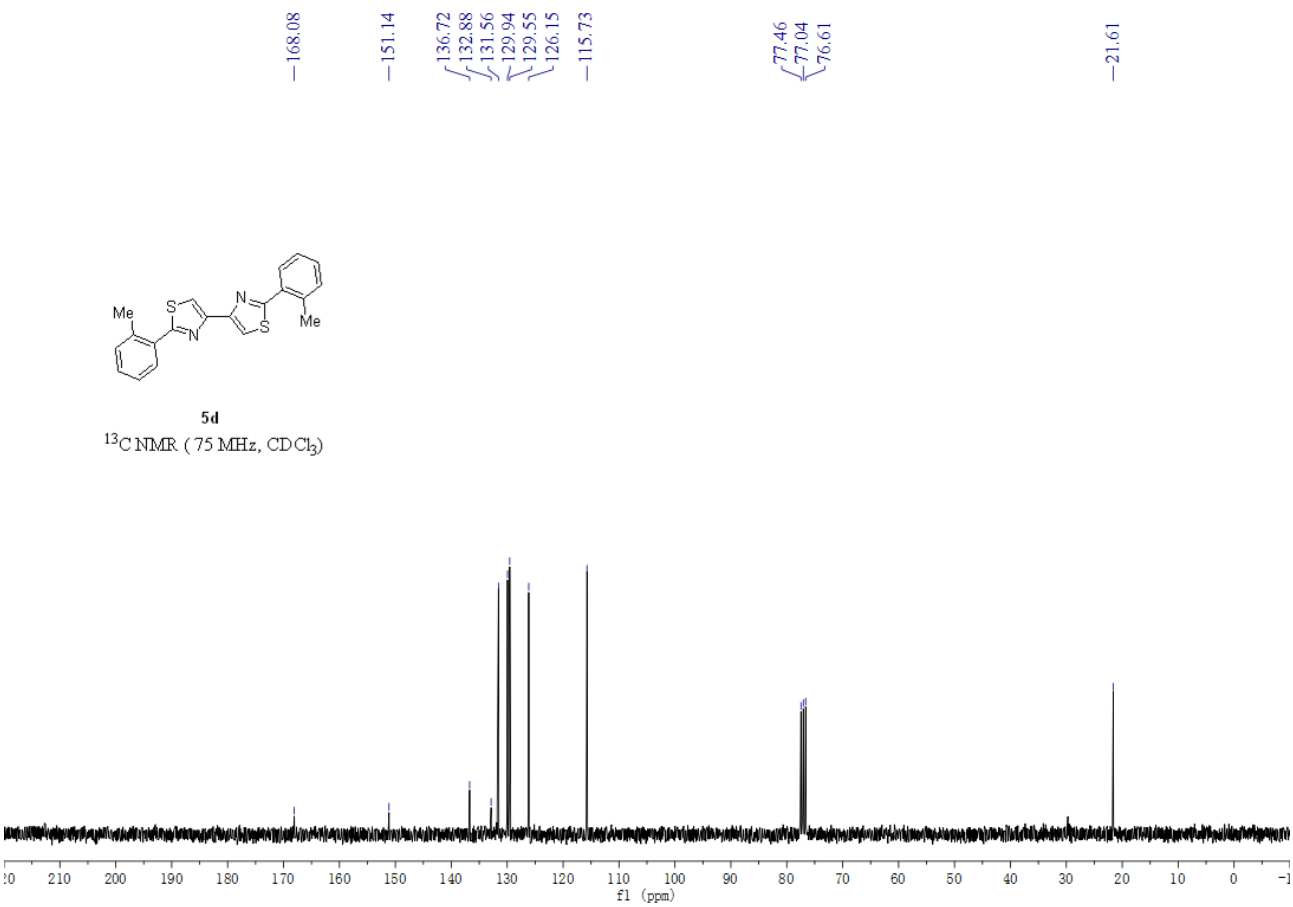
5c

^{13}C NMR (75 MHz, $CDCl_3$)



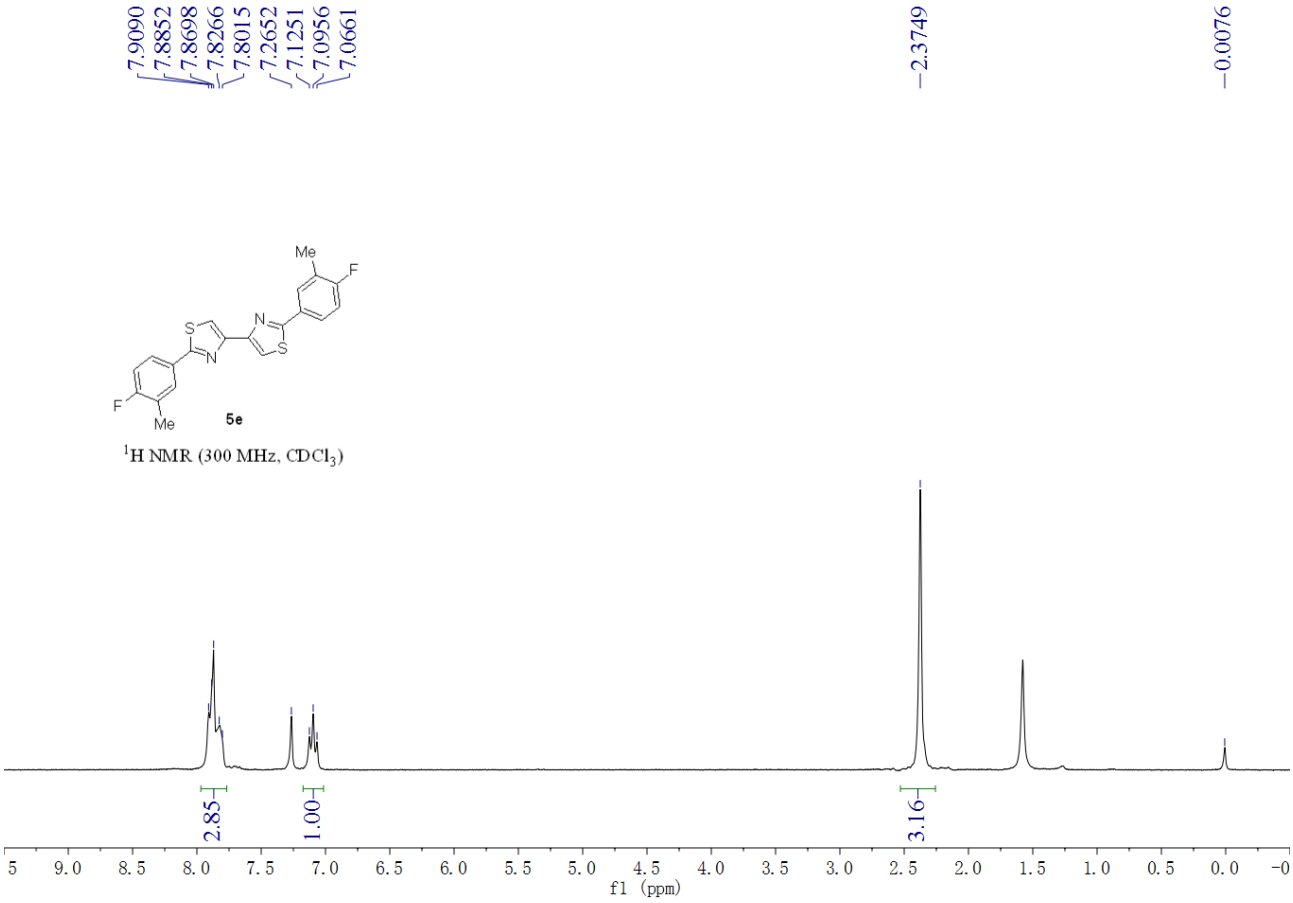
5d

^{1}H NMR (300 MHz, $CDCl_3$)

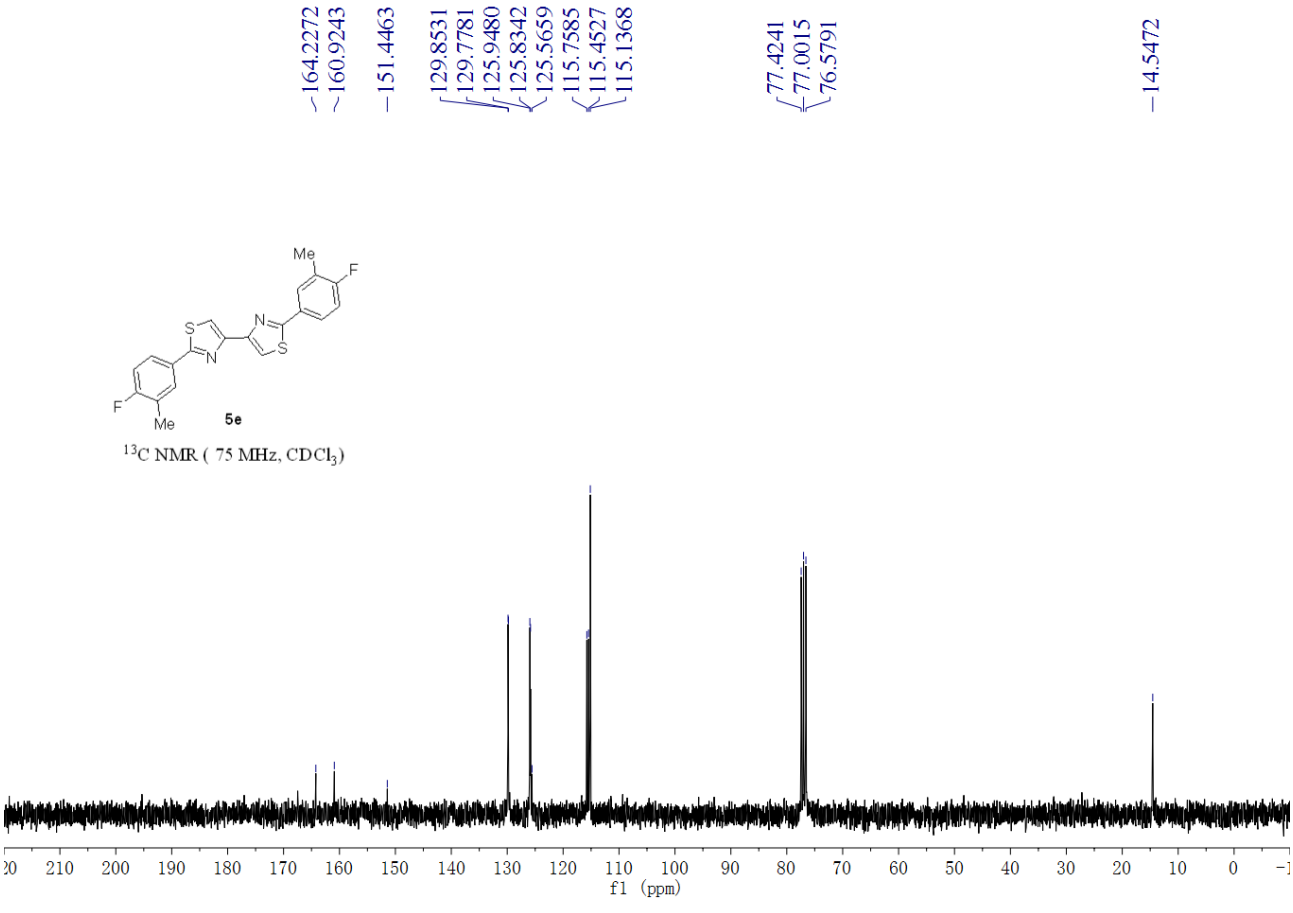


5d

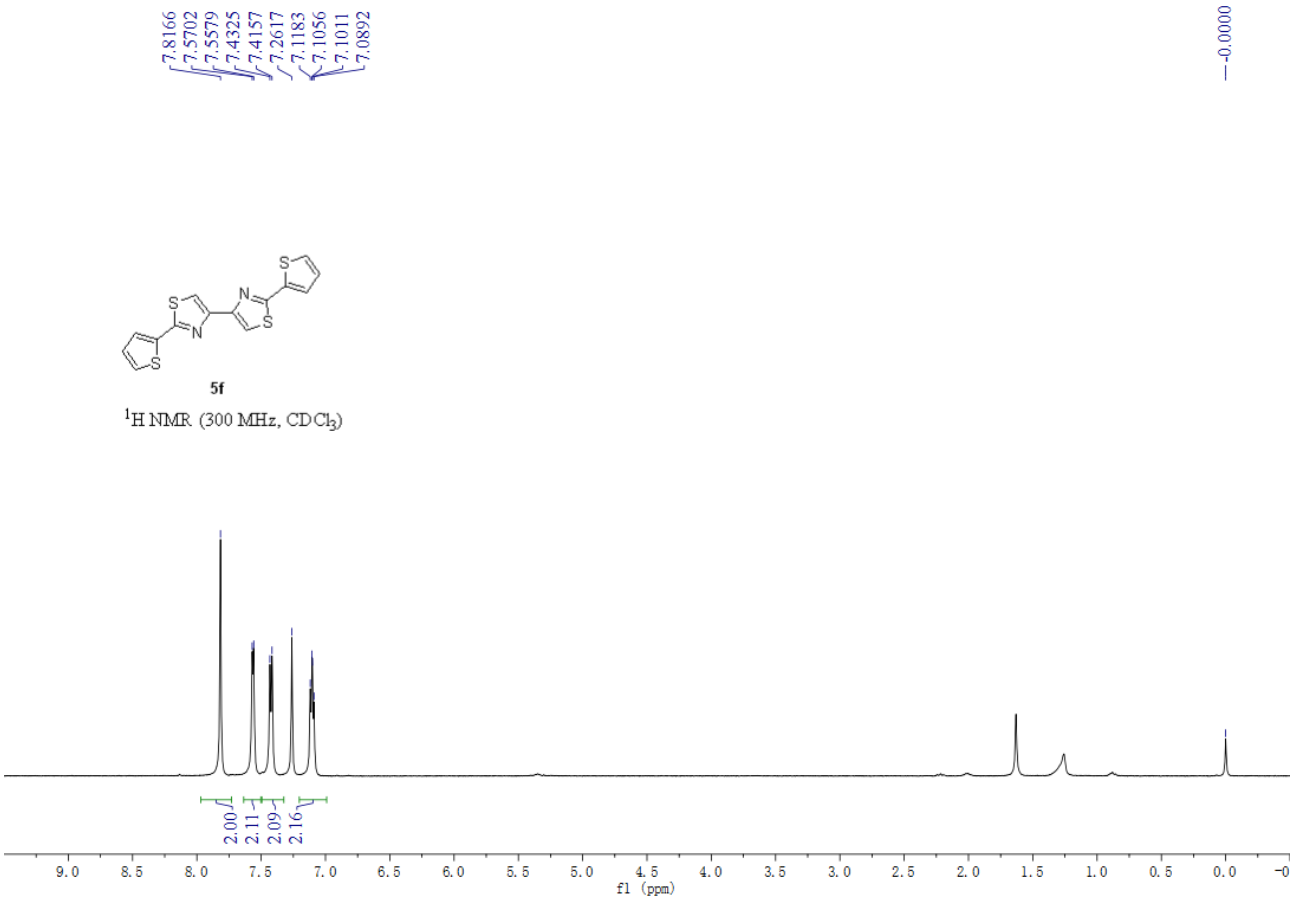
^{13}C NMR (75 MHz, $CDCl_3$)



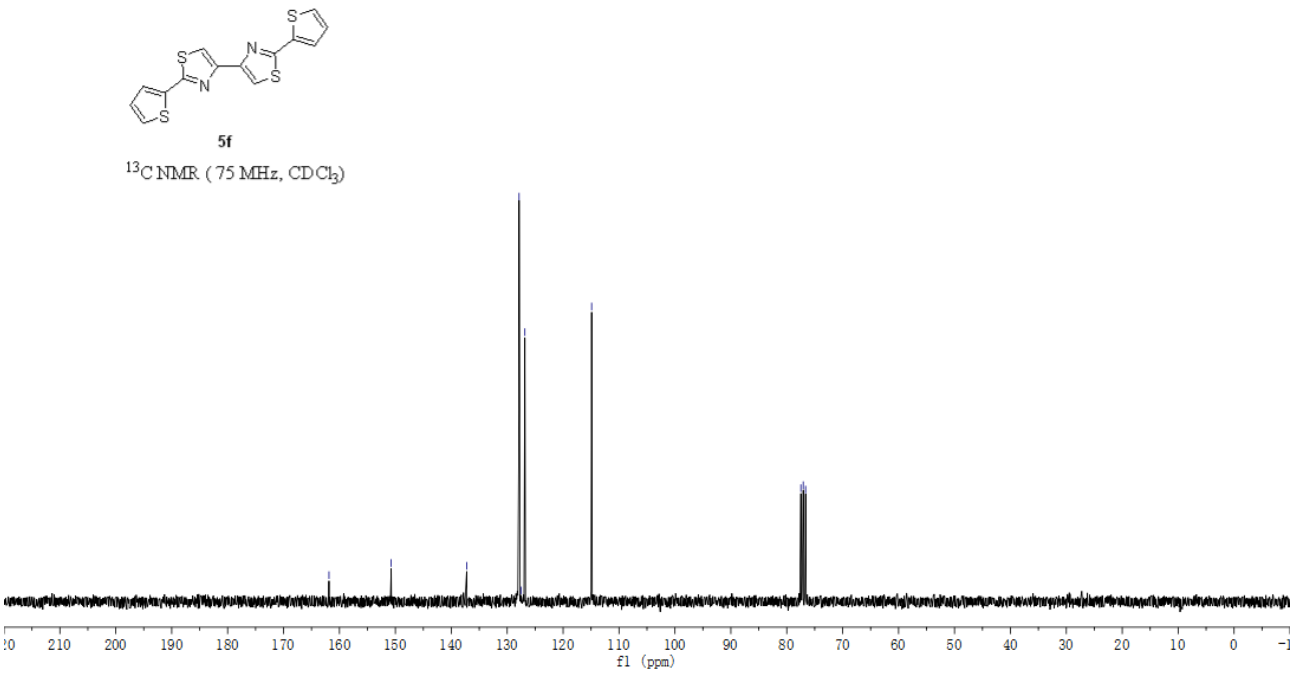
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)