Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Cascade intramolecular imidoylation and C−H activation/annulation of benzimidoyl chlorides with alkynes: one-pot synthesis of 7*H*-dibenzo[*de*,*h*]quinoline analogues

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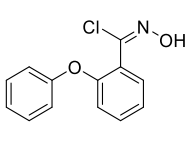
I. General remarks

NMR spectra were recorded on an Agilent 400-MR DD2 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were recorded relative to $CDCl_3$ or CD_2Cl_2 as the internal reference ($CDCl_3$: δ = 7.26 ppm; CD_2Cl_2: δ = 5.32 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or CD_2Cl_2 as the internal standard ($CDCl_3$: δ = 77.16 ppm; CD_2Cl_2: δ = 54.00 ppm). X-Ray single-crystal diffraction data were obtained on an Agilent Technologies Gemini plus single crystal diffraction. High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI) or a Waters-Q-TOF-Premier (ESI). Melting points were tested with an SGW S-4 and were uncorrected. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $[RhCp^*Cl_2]_2$ were prepared according to the literature procedures.[1] The solvents were dried and purified using an Innovative Technology PS-MD-5 Solvent Purification System. $RhCl_3 \cdot xH_2O$ was purchased from Shanxi Kaida Chemical Engineering (China) CO. Ltd.

II. List of substrates

1. List of *N*-hydroxy-2-phenoxybenzimidoyl chloride derivatives 1



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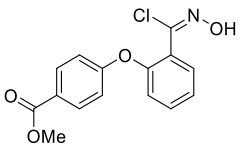

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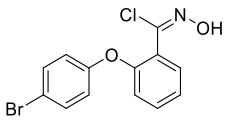

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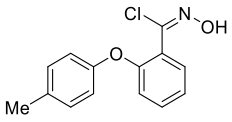

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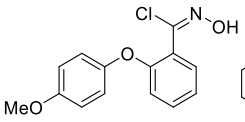

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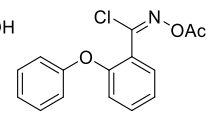

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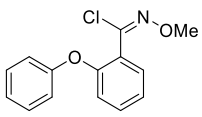

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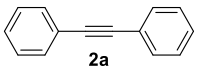
2. List of alkynes 2



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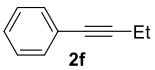

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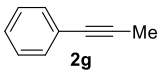

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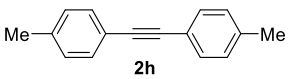

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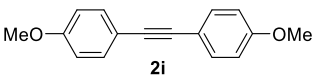

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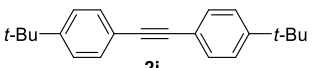

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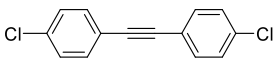

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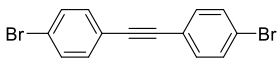

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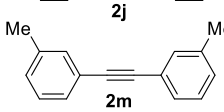

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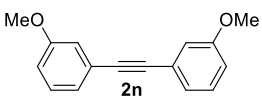
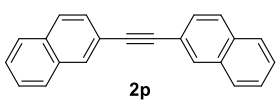


2n

2o



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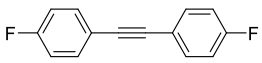

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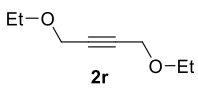
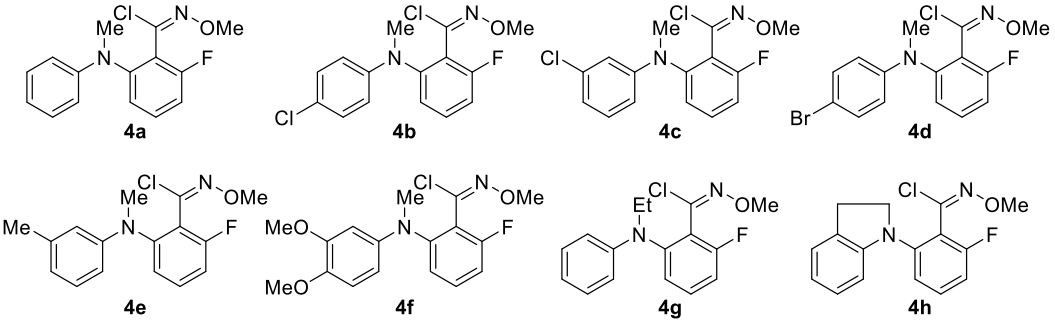


2r

3. List of 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride derivatives 4

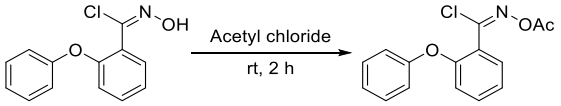


III. General procedure for the synthesis of substrates

1. General procedure for the synthesis of *N*-hydroxy-2-phenoxybenzimidoyl chlorides 1

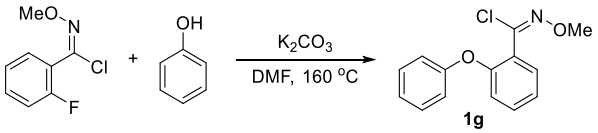
N-hydroxy-2-phenoxybenzimidoyl chloride **1a, 1b**, **1c**, **1d** and **1e** were prepared according to the literature procedures.[2]

General procedure for the synthesis of *N*-acetoxy-2-phenoxybenzimidoyl chloride **1f**:[3]



The *N*-hydroxy-2-phenoxybenzimidoyl chloride **1a** (2 mol, 494 mg) was stirred at room temperature with an excess of acetyl chloride (2 ml) for 2 h. The excess of acetylating agent was removed under reduced pressure to afford yellow oil **1f**.

General procedure for the synthesis of *N*-methoxy-2-phenoxybenzimidoyl chloride **1g**:[2]



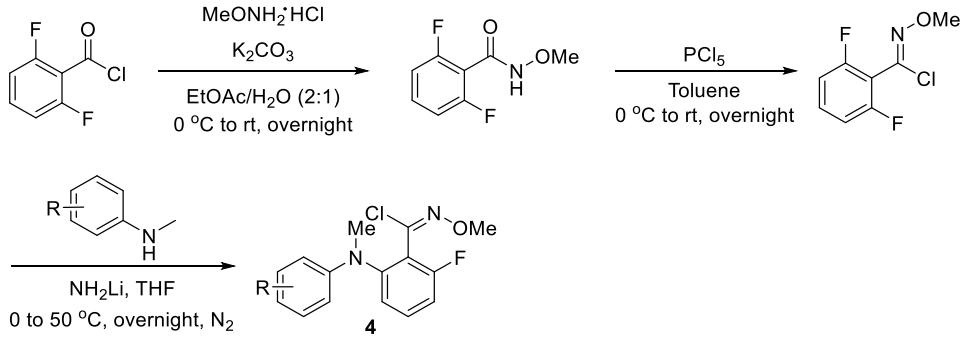
A mixture of 2-fluoro-*N*-methoxybenzimidoyl chloride (40.3 mmol, 374 mg), phenol (2.2 mmol, 207 mg) and K_2CO_3 (2.5 mmol 346) in DMF (2 mL) was refluxed for 13 h. The mixture was cooled to room temperature and diluted with EA and quenched by the addition of water. The organic layer was washed with water, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified through a silica gel column (petroleum ether/ethyl acetate = 100:1, v/v) to give *N*-methoxy-2-phenoxybenzimidoyl chloride **1g**.

2. General procedure for the synthesis of Alkynes 2

Alkynes **2a**, **2f**, **2g** and **2o** were obtained from commercial suppliers and used without further purification. Alkynes **2h**, **2i**, **2j**, **2k**, **2l**, **2m**, **2n, 2p, 2q** and **2r** were prepared according to the literature procedures.[4,5]

3. General procedure for the synthesis of 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)

benzimidoyl chloride derivatives 4[6,7]

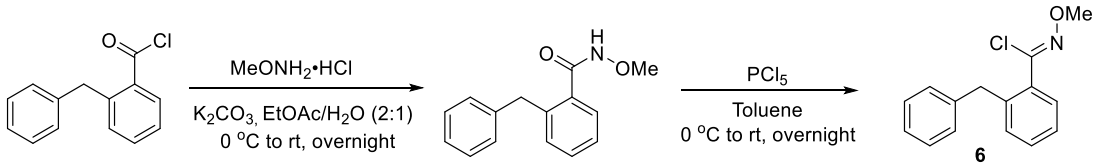


In a 250 mL round-bottom flask with a magnetic stir bar, a solution of *O*-methylhydroxylamine hydrochloride (2.00 g, 24.0 mmol, 1.2 equiv) and K_2CO_3 (5.98 g, 48.0 mmol, 2.4 equiv) in water (40 mL) was added to a solution of 2,6-difluorobenzoyl chloride (2.5 mL, 20.0 mmol, 1.0 equiv) in ethyl acetate (80 mL) drop by drop at 0 °C. Then the reaction mixture was stirred at room temperature for 8 h. After the completion of reaction, the organic layer was separated and washed with water (60 mL×2) and brine (60 mL). Then the organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting crude was recrystallized in a mixture of ethyl acetate and petroleum ether to get a white solid.

The white solid was transferred into a round-bottom flask under an N_2 atmosphere. Then dry toluene (60 mL) was added. The mixture was cooled to 0 °C and PCl_5 (6.25 g, 30.0 mmol, 1.5 equiv) was added. The reaction mixture was stirred at room temperature overnight. Then the mixture was cooled to 0 °C and stirred in a mixture of water (60 mL) and ethyl acetate (60 mL) for 10 minutes. The separated organic layer was sequentially washed with water (60 mL×2) and brine (60 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified through a silica gel column (petroleum ether/ethyl acetate = 100:1, v/v) to give 2,6-difluoro-*N*-methoxybenzimidoyl chloride.

A 100 mL Schlenk tube was evacuated and back filled with argon, *N*-alkylanilines (5.0 mmol, 1 equiv), 2,6-difluoro-*N*-methoxybenzimidoyl chloride (1.13 g, 5.5 mmol, 1.1 equiv), lithium amide (0.25 g, 11 mmol, 2.2 equiv) and THF (20 mL) were added successively at 0 °C. The reaction mixture was heated at 50 °C for 8 h and then cooled to room temperature. The reaction was quenched with saturated ammonium chloride solution (25 mL). Then the water phase was extracted with ethyl acetate (2 × 30 mL). The combined organic layer was washed with water (30 mL×2), brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified through a silica gel column (petroleum ether/ethyl acetate = 100:1, v/v) to give 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride derivatives **4**.

4. General procedure for the synthesis of 2-benzyl-*N*-methoxybenzimidoyl chloride 6[6]



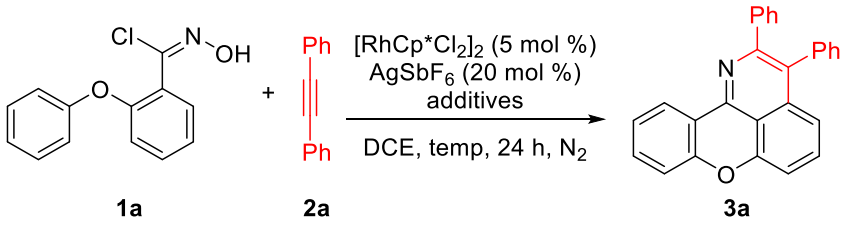
In a 250 mL round-bottom flask with a magnetic stir bar, a solution of *O*-methylhydroxylamine hydrochloride (498 mg, 6.0 mmol, 1.2 equiv) and K_2CO_3 (1.66 g, 12 mmol, 2.4 equiv) in water (10 mL) was added to a solution of 2-benzylbenzoyl chloride (1.27 g, 5.0 mmol, 1.0 equiv) in ethyl acetate (20 ml) dropwise at 0 °C. Then the reaction mixture was stirred at room temperature for 8 h. After the completion of reaction, the organic layer was separated and washed with water (15mL×2) and brine (15 mL). Then the organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting crude was recrystallized in a mixture of ethyl acetate and petroleum ether to afford 2-benzyl-*N*-methoxybenzamide as a white solid.

The white solid was transferred into a round-bottom flask under an N_2 atmosphere. Then dry toluene (15 mL) was added. The mixture was cooled to 0 °C and PCl_5 (1.54 g, 7.5 mmol, 1.5 equiv) was added. The reaction mixture was stirred at room temperature overnight. Then the mixture was cooled to 0 °C and stirred in a mixture of water (15 mL) and ethyl acetate (15 mL) for 10 minutes. The separated organic layer was sequentially washed with water (15 mL×2) and brine (15 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified through a silica gel column (petroleum ether/ethyl acetate = 100:1, v/v) to give 2-benzyl-*N*-methoxybenzimidoyl chloride **6**.

IV. Optimization of the cascade cyclization of *N*-hydroxy-2-phenoxybenzimidoyl chloride with 1,2-diphenylethyne

A 25 mL Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (3.1 mg, 5 μmol, 5 mol %), $AgSbF_6$ (7.2 mg, 20 μmol, 20 mol %), additives, *N*-hydroxy-2-phenoxybenzimidoyl chloride **1a** (0.15 mol, 37.1 mg), 1,2-diphenylethyne **2a** (0.1 mol, 17.8 mg) and DCE (2.0 mL) under an N_2 atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the indicated temperature for 24 h. Subsequently, it was diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 50 mL of dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on aluminum oxide to provide the desired product **3a**.

Table S1. Optimization of the reaction conditions for the cascade cyclization of *N*-hydroxy-2-phenoxybenzimidoyl chloride with 1,2-diphenylethyne[a]



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

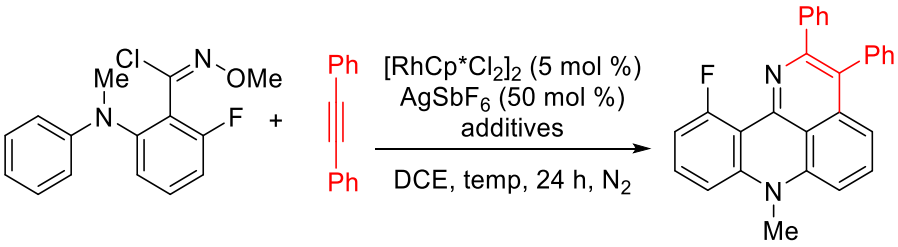
Entry	**1a** : **2a**	Additives (equiv)	Temp (°C)	Yield (%)[b]
1	1 : 1.5	$Zn(OAc)_2·2H_2O$ (1), PivOH (2)	140	35
2	1 : 1.5	$Zn(OTf)_2$ (1), PivOH (2)	140	<10
3	1 : 1.5	$Mn(OAc)_2$ (1), PivOH (2)	140	<10
4	1 : 1.5	$Ni(OAc)_2·4H_2O$ (1), PivOH (2)	140	trace
5	1 : 1.5	$Mg(OAc)_2·2H_2O$ (1), PivOH (2)	140	trace
6	1 : 1.5	LiOAc (1), PivOH (2)	140	trace
7	1 : 1.5	CsOAc (1), PivOH (2)	140	trace
8	1 : 1.5	$Zn(OAc)_2$ (1), PivOH (2)	120	40
9	1 : 1.5	$Zn(OAc)_2$ (1), PivOH (2)	100	38
10	1 : 1.5	$Zn(OAc)_2·2H_2O$ (1), PivOH (2)	80	21
11	1 : 1.5	$Zn(OAc)_2$ (1)	120	67
12	1 : 1	$Zn(OAc)_2$ (1)	120	57
13	**1.5 : 1**	**$Zn(OAc)_2$ (1)**	**120**	**87**
14[c]	1.5 : 1	$Zn(OAc)_2$ (1)	120	N.D.
15[d]	1.5 : 1	$Zn(OAc)_2$ (1)	120	N.D.
16	1.5 : 1	--	120	N.D.
17[e]	1.5 : 1	$Zn(OAc)_2$ (1)	120	trace

[a]Reaction conditions: **1a**, **2a**, $[RhCp*Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), additives and DCE at indicated temperature under N_2 for 24 h. [b]Isolated yield. [c]Without $AgSbF_6$. [d]Without $[RhCp*Cl_2]_2$. [e]$[Cp*Co(CO)I_2]_2$ (5 mol %) was used. DCE = 1,2-dichloroethane, Cp* = C_5Me_5, N.D.: not detected.

V. Optimization of the cascade cyclization of 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride with 1,2-diphenylethyne

A 25 mL Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (3.1 mg, 10 μmol, 5 mol %), $AgSbF_6$ (17.9 mg, 50.0 μmol, 50 mol %), additives 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride **4a** (29.2 mg, 0.1 mmol), 1,2-diphenylethyne **2a** (26.7 mg, 0.15 mmol), and DCE (2.0 mL) under an N_2 atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the indicated temperature for 24 h. Subsequently, it was diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 50 mL of dichloromethane. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography on aluminum oxide to provide the desired product **5a**.

Table S2. Optimization of the reaction conditions for the cascade cyclization of 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride with 1,2-diphenylethyne[a]



4a **2a** **5a**

Entry	Additives (equiv)	Temp°C	Yield (%)[b]
1	PivOH (1), $Cu(OAc)_2$ (2), $NaSbF_6$ (2)	80	55
2	PivOH (5), $Cu(OAc)_2$ (2), $NaSbF_6$ (2)	80	78
3	PivOH (5), $Cu(OAc)_2$ (2), $NaBF_4$ (2)	80	67
4	PivOH (1), $Cu(OAc)_2$ (2)	80	69
5	PivOH (5), CuO (2), $NaSbF_6$ (2)	140	82
6	PivOH (2.5), CuO (2), $NaSbF_6$ (1)	140	80
7	PivOH (2), $Zn(OAc)_2{\cdot}2H_2O$ (1)	140	87
8[c]	PivOH (2), $Zn(OAc)_2{\cdot}2H_2O$ (1)	140	88
9[c]	PivOH (2), $Zn(OAc)_2{\cdot}2H_2O$ (1)	140	89[d]

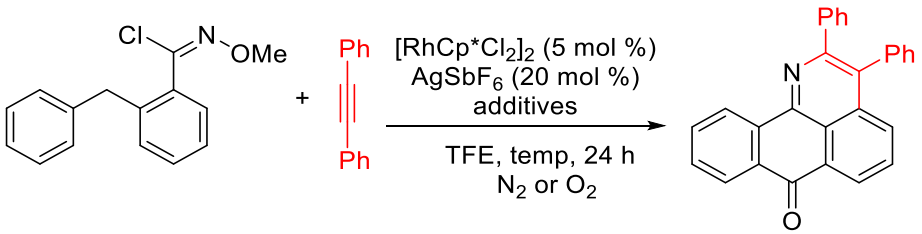
[a]Reaction conditions: **4a** (0.10 mmol), **2a** (0.15 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), $AgSbF_6$ (50 mol %), additives, and DCE at the indicated temperature under N_2 for 24 h. [b]Isolated yields. [c]$AgSbF_6$ (20

mol %) was used. [d]12 h. DCE = 1,2-dichloroethane, Cp* = C_5Me_5.

VI. Optimization of the cascade cyclization of 2-benzyl-*N*-methoxybenzimidoyl chloride with 1,2-diphenylethyne

A 25 mL Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (3.1 mg, 5 μmol, 5 mol %), $AgSbF_6$ (7.2 mg, 20 μmol, 20 mol %), additives, 2-benzyl-*N*-methoxybenzimidoyl chloride **6** (0.15 mmol, 38.9mg), 1,2-diphenylethyne **2a** (0.1 mmol, 17.8 mg) and solvent (2.0 mL) under an indicated atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the indicated temperature for 24 h. After the reaction, it was diluted with 10 mL of dichloromethane. The reaction mixture was filtered through a celite pad and washed with 50 mL of dichloromethane. Then the solution was concentrated and the residue was purified by column chromatography on aluminum oxide to provide the desired product **7a**.

Table S3: Optimization of the cascade cyclization of 2-benzyl-*N*-methoxybenzimidoyl chloride with 1,2-diphenylethyne[a]



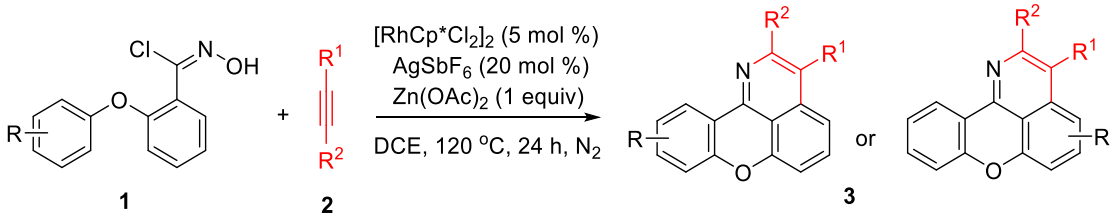
6 **2a** **7a**

Entry	Additives	solvent	Temp(°C)	Atmosphere	Yield (%)[b]
1	$Zn(OAc)_2$ (1.0), PivOH (2.0)	DCE	140	N_2	< 10
2	$Zn(OAc)_2$ (1.0)	DCE	140	N_2	< 10
3	$Cu(OAc)_2$ (2.0), PivOH (2.0)	DCE	140	N_2	27
4	$Cu(OAc)_2$ (2.0), PivOH (2.0)	TFE	140	N_2	32
5	$Cu(OAc)_2$ (2.0), PivOH (2.0)	TFE	140	O_2	62
6	$Cu(OAc)_2$ (5.0), PivOH (2.0)	TFE	140	N_2	80
7	$Cu(OAc)_2$ (4.0), PivOH (2.0)	TFE	140	N_2	47
8	$Cu(OAc)_2$ (3.0), PivOH (2.0)	TFE	140	N_2	41
9	$Cu(OAc)_2$ (3.0), PivOH (2.0)	TFE	140	O_2	78
10	$Cu(OAc)_2$ (3.0), PivOH (2.0)	TFE	120	O_2	83

[a]Reaction conditions: **6** (0.15 mmol), **2a** (0.10 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), additives, and solvent at the indicated temperature under N_2 or O_2 for 24 h. [b]Isolated yields. DCE = 1,2-dichloroethane, Cp* = C_5Me_5.

VII. General procedure for the synthesis of chromeno[2,3,4-*ij*]isoquinolines and analogues

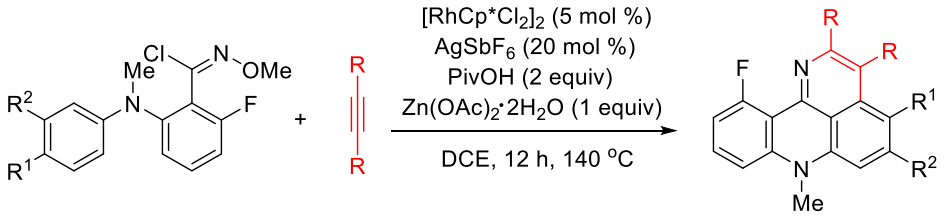
1. General procedure for the synthesis of chromeno[2,3,4-*ij*]isoquinolines (Procedure I)



1 2 3

A 25 ml Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (3.1 mg, 5 mol %), $AgSbF_6$ (7.2 mg, 20 mol %), $Zn(OAc)_2$ (18.4 mg, 0.1 mmol, 1.0 equiv), **1** (0.15 mmol), alkyne **2** (0.10 mmol), and DCE (2.0 mL) under an N_2 atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 120 °C for 24 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on aluminum oxide to provide the desired product **3**.

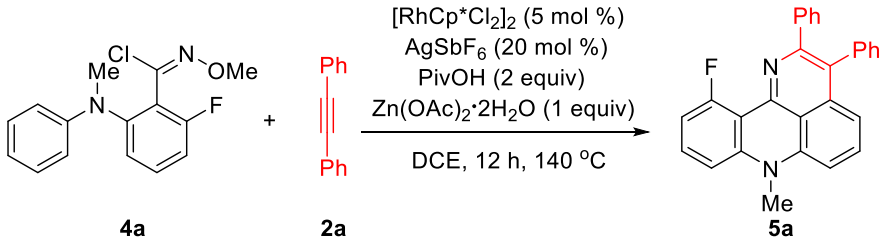
2. General procedure for the synthesis of pyrido[4,3,2-*kl*]acridine derivatives (Procedure II)



4 2 5

A 25 ml Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (3.1 mg, 5 mol %), $AgSbF_6$ (7.2 mg, 20 mol %), $Zn(OAc)_2{\cdot}2H_2O$ (21.9 mg, 0.1 mmol, 1.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), **4** (0.10 mmol), alkyne **2** (0.15 mmol), and DCE (2.0 mL) under an N_2 atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 140 °C for 12 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on aluminum oxide to provide the desired product **5**.

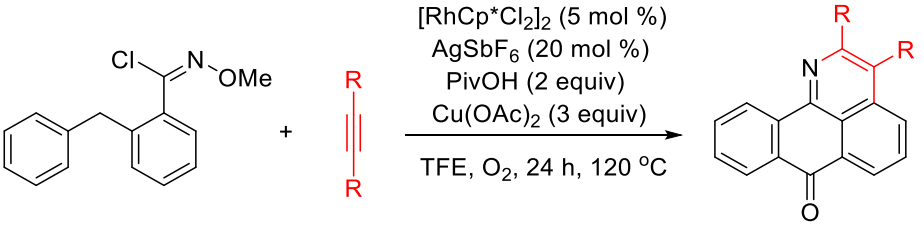
3. Procedure for the synthesis of 5a on 1 mmol scale



4a **2a** **5a**

A 100 ml Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (31.0 mg, 5 mol %), $AgSbF_6$ (71.6 mg, 20 mol %), $Zn(OAc)_2{\cdot}2H_2O$ (219.5 mg, 1.0 mmol, 1.0 equiv), PivOH (204.3 mg, 2 mmol, 2.0 equiv), **4a** (1.0 mmol, 291.1mg), 1,2-diphenylethyne **2a** (1.5 mmol, 267.1 mg), and DCE (5.0 mL) under an N_2 atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 140 °C for 12 h. The reaction mixture was cooled to ambient temperature and then diluted with 20 mL of dichloromethane. The solution was filtered through a celite pad and washed with 50-80 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) to afford **5a** as a yellow solid (349.7 mg, 87%).

4. General procedure for the synthesis of 7*H*-dibenzo[*de*,*h*]quinolin-7-one derivatives (Procedure III)

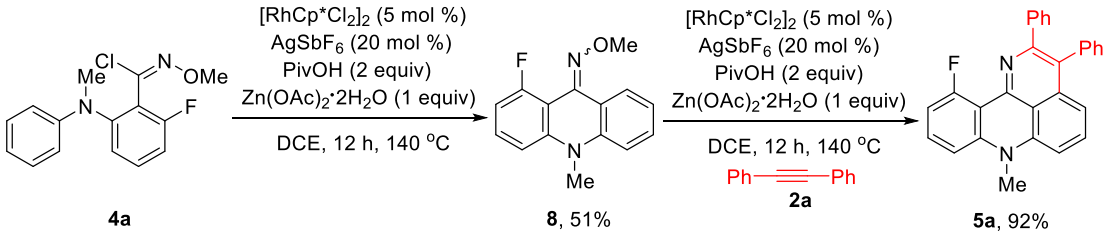


6 **2** **7**

A 25 ml Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (3.1 mg, 5 mol %), $AgSbF_6$ (7.2 mg, 20 mol %), $Cu(OAc)_2$ (54.5 mg, 0.3 mmol, 3.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), **6** (0.15 mmol), alkyne **2** (0.10 mmol), and TFE (2.0 mL) under an O_2 atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 120 °C for 24 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on aluminum oxide to provide the desired product **7**.

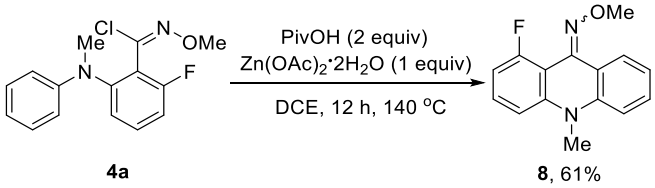
VIII. Mechanistic study

1. Control experiments for cascade cyclization of 2-Fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride 4a with 1,2-diphenylethyne 2a

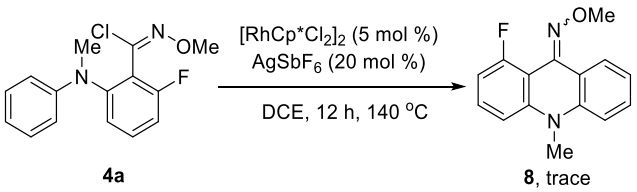


A 25 ml Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (3.1 mg, 5 mol %), $AgSbF_6$ (7.2 mg, 20 mol %), $Zn(OAc)_2 \cdot 2H_2O$ (21.9 mg, 0.1 mmol, 1.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), **4a** (0.10 mmol, 29.2 mg) and DCE (2.0 mL) under an N_2 atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 140 °C for 12 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) to provide the desired product **8** as a white solid (13.1 mg, 51%).

A 25 ml Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (3.1 mg, 5 mol %), $AgSbF_6$ (7.2 mg, 20 mol %), $Zn(OAc)_2 \cdot 2H_2O$ (21.9 mg, 0.1 mmol, 1.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), **8** (0.10 mmol, 25.6 mg), 1,2-diphenylethyne **2a** (0.15 mmol, 26.7 mg) and DCE (2.0 mL) under an N_2 atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 140 °C for 12 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) to afford the desired product **1a** as a yellow solid (36.9 mg, 92%).



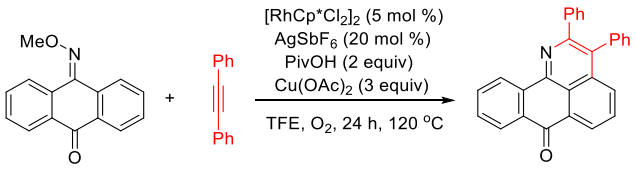
A 25 ml Schlenk tube with a magnetic stir bar was charged with $Zn(OAc)_2 \cdot 2H_2O$ (21.9 mg, 0.1 mmol, 1.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), **4a** (0.10 mmol, 29.2 mg) and DCE (2.0 mL) under an N_2 atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 140 °C for 12 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) to provide the desired product **8** as a white solid (15.6 mg, 61%).



4a **8**, trace

A 25 ml Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (3.1 mg, 5 mol %), $AgSbF_6$ (7.2 mg, 20 mol %), **4a** (29.2 mg, 0.10 mmol) and DCE (2.0 mL) under an N_2 atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 140 °C for 12 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. Trace amounts of the **8a** were detected.

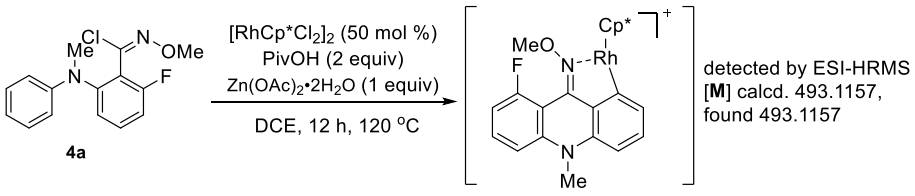
2. Control experiments for cascade cyclization of 2-benzyl-*N*-methoxybenzimidoyl chloride with 1,2-diphenylethyne



9 **2a** **7a**, 77%

A 25 ml Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (3.1 mg, 5 mol %), $AgSbF_6$ (7.2 mg, 20 mol %), $Cu(OAc)_2$ (54.5 mg, 0.3 mmol, 3.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), **9** (35.6 mg, 0.15 mmol), alkyne **2a** (17.8 mg, 0.10 mmol), and TFE (2.0 mL) under an O_2 atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 120 °C for 24 h. The reaction mixture was cooled to ambient temperature and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 30-50 mL of dichloromethane. Then it was concentrated and the residue was purified by flash column chromatography on aluminum oxide to provide the desired product **7a** (29.5 mg, 77%). Note: Oxime **9** was synthesized by the reaction of anthracene-9,10-dione (208 mg, 1 mmol) with *O*-methylhydroxylamine hydrochloride (84 mg, 1 mmol) in pyridine (1 mL) at 115 ℃ for 48 h under air.

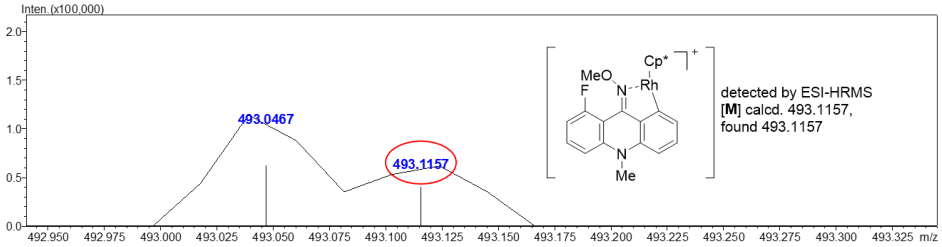
3. ESI-HRMS analysis.



4a

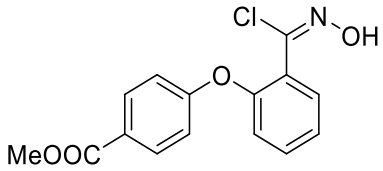
A 25 ml Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (31 mg, 50 mol %), $Zn(OAc)_2 \cdot 2H_2O$ (21.9 mg, 0.1 mmol, 1.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv), **4a** (29.2

mg, 0.10 mmol) and DCE (2.0 mL) under an N_2 atmosphere. The resulting solution was stirred at room temperature for 10 min and then stirred at the 120 °C for 12 h. The reaction mixture was cooled to ambient temperature. The ESI-HRMS analysis of the resultant solution was then performed immediately ([**M**]$^+$ calcd. 493.1157, found 493.1157).



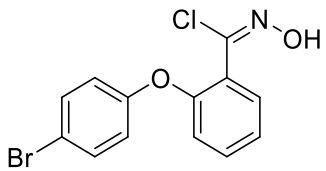
IX. Experimental data for the described substances

1. Experimental data for the described substrates



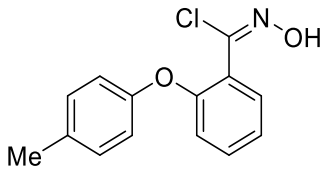
Methyl-4-(2-(chloro(hydroxyimino)methyl)phenoxy)benzoate (1b)

White solid, M.p.: 99-102 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.06 (brs, 1H), 8.00-7.96 (m, 2H), 7.63 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 7.47-7.42 (m, 1H), 7.29-7.23 (m, 1H), 7.04 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 6.98-6.93 (m, 2H), 3.88 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 166.8, 161.5, 153.3, 135.9, 132.1, 131.8, 131.3, 126.3, 124.9, 124.8, 121.3, 117.4, 52.3. HRMS (ESI$^-$): calcd for $C_{15}H_{12}{}^{35}Cl_2NO_4^-$ [M+^{35}Cl]$^-$ 340.0149, found 340.0144.



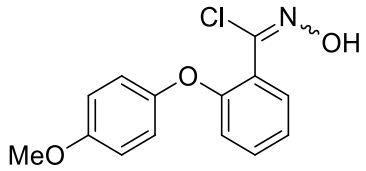
2-(4-Bromophenoxy)-*N*-hydroxybenzimidoyl chloride (1c)

White solid, M.p.: 80-83°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.63 (brs, 1H), 7.60 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.45-7.38 (m, 3H), 7.23-7.17 (m, 1H), 6.94 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 6.90-6.85 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 156.3, 154.4, 136.5, 132.9, 132.0, 131.2, 125.5, 124.1, 120.5, 119.9, 116.2. HRMS (ESI$^-$): calcd for $C_{13}H_9{}^{79}Br^{35}Cl_2NO_2^-$ [M+^{35}Cl]$^-$ 359.9199, found 359.9193; calcd for $C_{13}H_9{}^{81}Br^{35}Cl_2NO_2^-$ [M+^{35}Cl]$^-$ 361.9179, found 361.9169.



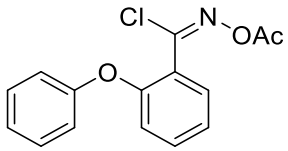
***N*-Hydroxy-2-(*p*-tolyloxy)benzimidoyl chloride (1d)**

White solid, M.p.: 75-78 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.05 (brs, 1H), 7.58 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.38-7.31 (m, 1H), 7.16-7.10 (m, 3H), 6.95-6.90 (m, 2H), 6.89 (d, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 155.7, 154.4, 136.8, 133.5, 131.8, 131.0, 130.4, 124.7, 123.0, 119.3, 118.9, 20.9. HRMS (ESI$^-$): calcd for $C_{14}H_{12}{}^{35}Cl_2NO_2^-$ [M+^{35}Cl]$^-$ 296.0251, found 296.0241.

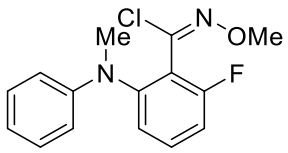


***N*-Hydroxy-2-(4-methoxyphenoxy)benzimidoyl chloride (1e)**

White solid (ratio of oxime isomers = 1:1), M.p.: 90-93 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.12 (brs, 1H for one isomer), 9.10 (s, 1H for one isomer), 7.60-7.55 (m, 2H for two isomers), 7.39-7.30 (m, 2H for two isomers), 7.18-6.93 (m, 6H for two isomers), 6.92-6.80 (m, 6H for two isomers), 3.88 (s, 3H for one isomer), 3.80 (s, 3H for one isomer). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) for two isomers, 156.3, 156.2, 155.5, 151.8, 150.0, 149.8, 136.9, 136.6, 131.9, 131.8, 131.2, 131.0, 124.6, 124.1, 123.4, 123.2, 122.6, 121.8, 121.0, 118.7, 118.5, 117.9, 115.0, 112.8, 56.7, 55.8. HRMS (ESI$^-$): calcd for $C_{14}H_{12}{}^{35}Cl_2NO_3^-$ [M+^{35}Cl]$^-$ 312.0200, found 312.0198.

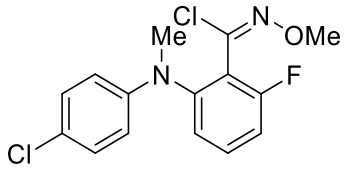


Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.57 (dd, *J* = 7.8 Hz, *J* = 1.8 Hz, 1H), 7.44-7.38 (m, 1H), 7.37-7.32 (m, 2H), 7.17-7.11 (m, 2H), 7.06-7.02 (m, 2H), 6.92 (dd, *J* = 7.8 Hz, *J* = 0.8 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 167.41, 156.59, 155.70, 144.79, 132.73, 131.16, 129.97, 124.41, 124.06, 123.22, 119.36, 119.00, 19.41. HRMS (ESI$^-$): calcd for $C_{15}H_{12}{}^{35}ClNNaO_3^+$ [M+Na]$^+$ 312.0398, found 312.0393.



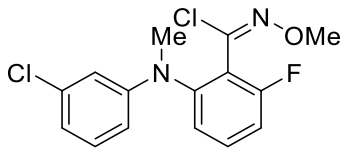
2-Fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride (4a)

White solid, M.p.: 65-67 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.44-7.38 (m, 1H), 7.23-7.17 (m, 2H), 7.06-7.03 (m, 1H), 7.01-6.96 (m, 1H), 6.86-6.81 (m, 1H), 6.75-6.72 (m, 2H), 3.92 (s, 3H), 3.25 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.1 (d, J = 251.5 Hz), 150.1 (d, J = 4.0 Hz), 148.8, 132.4 (d, J = 11.0 Hz), 129.0, 128.9, 123.4 (d, J= 4.0 Hz), 120.8 (d, J = 15.0 Hz), 119.5, 116.4, 112.6 (d, J = 22.0 Hz), 61.2, 40.7. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -112.2 (dd, J = 8.6 Hz, J = 6.4 Hz, 1F). HRMS (ESI^+): calcd for $C_{15}H_{15}{}^{35}ClFN_2O^+$ $[M+H]^+$ 293.0851, found 293.0851.



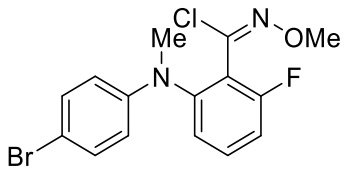
2-((4-Chlorophenyl)(methyl)amino)-6-fluoro-*N*-methoxybenzimidoyl chloride (4b)

White solid, M.p.: 64-65 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.46-7.39 (m, 1H), 7.16-7.11 (m, 2H), 7.05-6.99 (m, 2H), 6.65-6.61 (m, 2H), 3.93 (s, 3H), 3.22 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.1 (d, J = 252.0 Hz), 149.4 (d, J = 3.2 Hz), 147.4, 132.6 (d, J = 10.0 Hz), 128.8, 128.7, 124.2, 123.5 (d, J = 3.2 Hz), 121.1 (d, J = 14.6 Hz), 117.1, 113.2 (d, J = 21.3 Hz), 63.2, 40.7. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -111.8 (dd, J = 8.8 Hz, J = 6.4 Hz, 1F). HRMS (ESI^+): calcd for $C_{15}H_{14}{}^{35}Cl_2FN_2O^+$ $[M+H]^+$ 327.0462, found 327.0467.



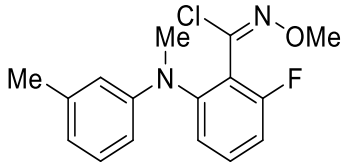
2-((3-Chlorophenyl)(methyl)amino)-6-fluoro-*N*-methoxybenzimidoyl chloride (4c)

White solid, M.p.: 62-64 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.48-7.41 (m, 1H), 7.10-7.03 (m, 3H), 6.78-6.74 (m, 1H), 6.65 (t, J= 2.4 Hz, 1H), 6.55-6.50 (m, 1H), 3.94 (s, 3H), 3.22 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.0 (d, J = 252.2 Hz), 149.7, 149.8 (d, J = 3.3 Hz), 134.7, 132.6 (d, J = 10.0 Hz), 129.8, 128.5, 124.1 (d, J = 3.3 Hz), 121.4, 118.8, 115.0, 113.7 (d, J = 21.4 Hz), 113.5, 63.3, 40.5. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -111.5 (dd, J = 8.3 Hz, J = 6.4 Hz, 1F). HRMS (ESI^+): calcd for $C_{15}H_{14}{}^{35}Cl_2FN_2O^+$ $[M+H]^+$ 327.0462, found 327.0464.



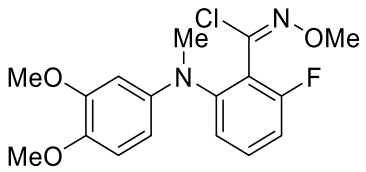
2-((4-Bromophenyl)(methyl)amino)-6-fluoro-*N*-methoxybenzimidoyl chloride (4d)

White solid, M.p.: 72-73 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.46-7.40 (m, 1H), 7.29-7.27 (m, 1H), 7.26-7.24 (m, 1H), 7.06-7.00 (m, 2H), 6.60-6.55 (m, 2H), 3.93 (s, 3H), 3.21 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.1 (d, J = 252.0 Hz), 149.2 (d, J = 3.3 Hz), 147.8, 132.6 (d, J = 10.0 Hz), 131.7, 128.6, 123.7 (d, J= 3.3 Hz), 121.2 (d, J = 14.4 Hz), 117.4, 113.3 (d, J = 21.4 Hz), 111.4, 63.3, 40.6. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -111.7 (dd, J = 8.6 Hz, J = 6.4 Hz, 1F). HRMS (ESI^+): calcd for $C_{15}H_{14}{}^{81}Br^{35}ClFN_2O^+$ $[M+H]^+$ 372.9936, found 372.9949.



2-Fluoro-*N*-methoxy-6-(methyl(*m*-tolyl)amino)benzimidoyl chloride (4e)

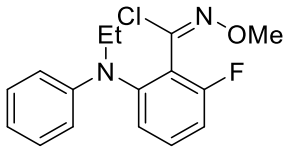
White solid, M.p.: 69-71 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.43-7.36 (m, 1H), 7.12-7.06 (m, 1H), 7.10-6.95 (m, 2H), 6.66 (d, J = 7.6 Hz, 1H), 6.57-6.53 (m, 2H), 3.93 (s, 3H), 3.23 (s, 3H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.1 (d, J = 251.1 Hz), 150.1 (d, J = 3.5 Hz), 148.8, 138.6, 132.3 (d, J = 10.2 Hz), 129.1, 128.8, 123.2 (d, J = 3.3 Hz), 120.5, 117.2, 113.7, 112.4 (d, J = 21.5 Hz), 63.1, 40.8, 21.8. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -112.2 (dd, J = 8.8 Hz, J = 6.4 Hz, 1F). HRMS (ESI^+): calcd for $C_{16}H_{17}{}^{35}ClFN_2O^+$ $[M+H]^+$ 307.1008, found 307.1009.



2-((3,4-Dimethoxyphenyl)(methyl)amino)-6-fluoro-*N*-methoxybenzimidoyl chloride (4f)

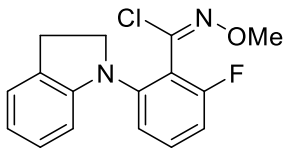
White solid, M.p.: 103-105 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.39-7.33 (m, 1H), 6.97-6.94 (m, 1H), 6.92-6.86 (m, 1H), 6.77-6.74 (m, 1H), 6.42-6.37 (m, 2H), 3.90 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H), 3.23 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.1 (d, J = 250.3 Hz), 150.7 (d, J = 3.7 Hz), 149.3, 144.1, 143.5, 132.1 (d, J = 10.3 Hz), 129.3, 120.5, 111.9, 111.0 (d, J = 21.6 Hz), 110.9, 104.8, 63.1, 56.4, 56.0, 41.8. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -112.6 (dd, J = 8.6 Hz, J

= 6.4 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{17}H_{19}{}^{35}ClFN_2O_3^+$ [M+H]$^+$ 353.1063, found 353.1045.



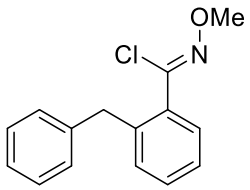
2-(Ethyl(phenyl)amino)-6-fluoro-*N*-methoxybenzimidoyl chloride (4g)

White solid, M.p.: 62-64 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.42-7.37 (m, 1H), 7.21-7.16 (m, 2H), 7.04-7.01 (m, 1H), 7.00-6.95 (m, 1H), 6.84-6.79 (m, 1H), 6.76-6.72 (m, 2H), 3.91 (s, 3H), 3.70 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* =7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.2 (d, *J* = 251.2 Hz), 149.0 (d, *J* = 3.6 Hz), 147.8, 132.1 (d, *J* = 10.1 Hz), 129.1, 128.9, 124.0 (d, *J* = 3.2 Hz), 121.0 (d, *J* = 7.6 Hz), 119.4, 117.4, 112.4 (d, *J* = 21.6 Hz), 63.1, 47.0, 12.8. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -112.0 (dd, *J* = 8.8 Hz, *J* = 6.4 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{16}H_{17}{}^{35}ClFN_2O^+$ [M+H]$^+$ 307.1008, found 307.1003.



2-Fluoro-6-(indolin-1-yl)-*N*-methoxybenzimidoyl chloride (4h)

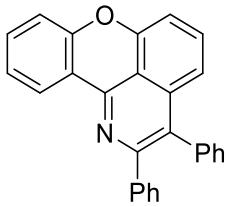
White solid, M.p.: 138-140 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.39-7.32 (m, 1H), 7.26-7.24 (m, 1H), 7.16 (d, *J* = 6.8 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.89 (t, *J* = 8.4 Hz, 1H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 4.04 (s, 3H), 3.86 (t, *J* = 8.4 Hz, 2H), 3.14 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 161.2 (d, *J* = 251.1 Hz), 148.5, 146.7, 132.0 (d, *J* = 10.2 Hz), 130.9, 129.6, 127.1, 125.0, 119.7, 118.7 (d, *J* = 13.3 Hz), 111.2 (d, *J* = 21.5 Hz), 110.1, 63.3, 55.0, 29.2. HRMS (ESI$^+$): calcd for $C_{16}H_{15}{}^{35}ClFN_2O^+$ [M+H]$^+$ 305.0851, found 305.0847.



2-Benzyl-*N*-methoxybenzimidoyl chloride (6)

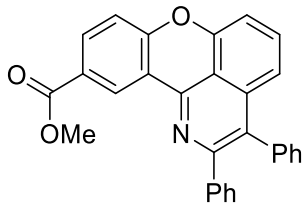
White solid, M.p.: 55-53 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.48 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.37-7.32 (m, 1H), 7.30-7.26 (m, 3H), 7.22-7.12 (m, 4H), 4.18 (s, 2H), 4.02 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 140.5, 140.0, 135.8, 133.3, 130.9, 130.3, 130.0, 129.2, 128.5, 126.6, 126.2, 63.1, 39.2. HRMS (ESI$^+$): calcd for $C_{15}H_{15}ClNO^+$ [M+H]$^+$ 260.0837, found 260.0840.

2. Experimental data for the described products



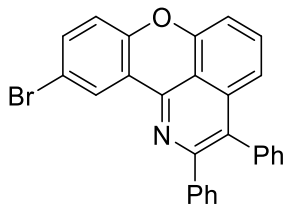
2,3-Diphenylchromeno[2,3,4-*ij*]isoquinoline (3a)

Following the general procedure I, *N*-hydroxy-2-phenoxybenzimidoyl chloride **1a** (37.1 mg, 0.15 mmol) and 1,2-diphenylethyne **2a** (32.3 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3a** as a yellow solid (27.0 mg, 87% yield). M.p.: 218-219 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.62 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.55-7.45 (m, 4H), 7.40-7.31 (m, 3H), 7.29-7.20 (m, 7H), 7.19-7.12 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.2, 152.5, 151.4, 147.3, 141.1, 137.8, 137.6, 131.9, 131.6, 131.2, 130.6, 128.7, 128.5, 127.6, 127.4, 127.3, 125.1, 124.0, 121.8, 117.5, 117.1, 116.4, 109.5. HRMS (ESI$^+$): calcd for $C_{27}H_{18}NO^+$ $[M+H]^+$ 372.1383, found 372.1383.



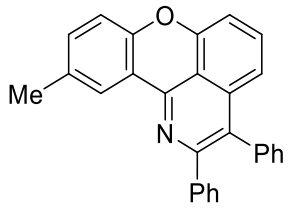
Methyl 2,3-diphenylchromeno[2,3,4-*ij*]isoquinoline-10-carboxylate (3b)

Following the general procedure I, methyl-4-(2-(chloro(hydroxyimino)methyl)phenoxy)benzoate **1b** (45.8 mg, 0.15 mmol) and 1,2-diphenylethyne **2a** (17.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3b** as a yellow solid (25.3 mg, 59% yield). M.p.: > 250 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.22 (d, J = 2.0 Hz, 1H), 8.14 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H), 7.53 (t, J = 8.4 Hz, 1H), 7.49-7.44 (m, 2H), 7.41-7.33 (m, 3H), 7.28 (d, J = 8.8 Hz, 1H), 7.25-7.20 (m, 6H), 7.14 (d, J = 7.6 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 166.5, 157.2, 151.9, 151.7, 146.4, 140.8, 137.54, 137.50, 133.1, 131.7, 131.09, 130.7, 129.0, 128.7, 127.7, 127.5, 127.5, 127.1, 126.1, 121.8, 118.3, 117.4, 116.3, 109.8, 52.3. HRMS (ESI$^+$): calcd for $C_{29}H_{20}NO_3^+$ $[M+H]^+$ 430.1438, found 430.1446.



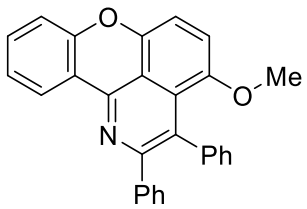
10-Bromo-2,3-diphenylchromeno[2,3,4-*ij*]isoquinoline (3c)

Following the general procedure I, 2-(4-bromophenoxy)-*N*-hydroxybenzimidoyl chloride **1c** (48.8 mg, 0.15 mmol) and 1,2-diphenylethyne **2a** (17.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3c** as a yellow solid (24.2 mg, 54% yield). M.p.: 215-216 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.71 (d, J = 2.4 Hz, 1H), 7.56-7.51 (m, 2H), 7.46-7.43 (m, 2H), 7.40-7.34 (m, 3H), 7.25-7.21 (m, 5H), 7.19 (d, J = 8.4 Hz, 1H), 7.14-7.10 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.1, 152.1, 151.6, 146.0, 140.8, 137.6, 137.5, 134.6, 131.8, 131.1, 130.6, 129.1, 128.7, 127.7, 127.6, 127.52, 127.49, 123.5, 119.0, 117.9, 117.1, 116.3, 109.7. HRMS (ESI$^+$): calcd for $C_{27}H_{17}{}^{79}BrNO^+$ $[M+H]^+$ 450.0488, found 450.0486.



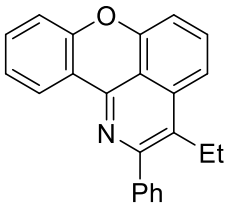
10-Methyl-2,3-diphenylchromeno[2,3,4-ij]isoquinoline (3d)

Following the general procedure I, *N*-hydroxy-2-(p-tolyloxy)benzimidoyl chloride **1d** (39.2 mg, 0.15 mmol) and 1,2-diphenylethyne **2a** (17.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3d** as a yellow solid (32.7 mg, 84% yield). M.p.: 211-212 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.41 (d, J = 1.6 Hz, 1H), 7.53 (t, J = 8.2 Hz, 1H), 7.49-7.43 (m, 2H), 7.40-7.32 (m, 3H), 7.31-7.27 (m, 2H), 7.25-7.19 (m, 4H), 7.19-7.11 (m, 3H), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 152.6, 152.3, 151.4, 147.5, 141.2, 137.8, 137.6, 133.6, 132.9, 131.6, 131.2, 130.6, 128.6, 128.4, 127.7, 127.3, 124.8, 121.2, 117.3, 116.8, 116.4, 109.4, 21.1. HRMS (ESI$^+$): calcd for $C_{28}H_{20}NO^+$ $[M+H]^+$ 386.1539, found 386.1547.



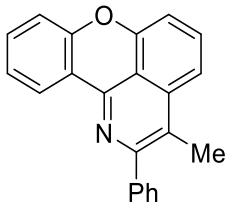
4-Methoxy-2,3-diphenylchromeno[2,3,4-*ij*]isoquinoline (3e)

Following the general procedure I, *N*-hydroxy-2-(4-methoxyphenoxy)benzimidoyl chloride **1e** (41.6 mg, 0.15 mmol) and 1,2-diphenylethyne **2a** (17.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3e** as a yellow solid (31.3 mg, 78% yield). M.p.: 219-220 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.07 (d, J = 2.8 Hz, 1H), 7.53 (t, J = 8.4 Hz, 1H), 7.48-7.44 (m, 2H), 7.38-7.32 (m, 3H), 7.27-7.26 (m, 1H), 7.25-7.20 (m, 5H), 7.17-7.12 (m, 2H), 7.10-7.06 (m, 1H), 3.92 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 156.3, 152.6, 151.4, 148.9, 147.4, 141.2, 137.9, 137.6, 131.6, 131.2, 130.7, 128.6, 127.6, 127.4, 127.3, 122.1, 120.2, 118.3, 117.1, 116.2, 110.2, 109.4, 106.7, 56.1. HRMS (ESI$^+$): calcd for $C_{28}H_{20}NO_2^+$ $[M+H]^+$ 402.1489, found 402.1493.



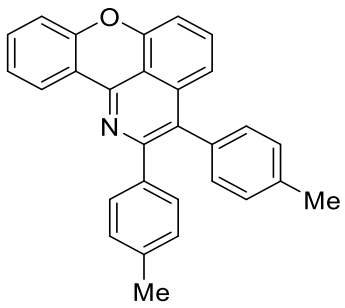
3-Ethyl-2-phenylchromeno[2,3,4-*ij*]isoquinoline (3f)

Following the general procedure I, *N*-hydroxy-2-phenoxybenzimidoyl chloride **1a** (37.1mg, 0.15 mmol) and but-1-yn-1-ylbenzene **2f** (13.0 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3f** as a yellow solid (23.9 mg, 74% yield). M.p.: 242-244 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.51 (d, J = 7.6 Hz, 1H), 7.71-7.66 (m, 1H), 7.63-7.59 (m, 2H), 7.55 (d, J = 8.4 Hz, 1H), 7.52-7.47 (m, 2H), 7.46-7.41 (m, 2H), 7.25-7.18 (m, 2H), 7.17-7.13 (m, 1H), 2.96 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.0, 153.0, 152.8, 145.6, 142.0, 136.7, 131.6, 131.59, 135.56, 129.5, 128.2, 127.7, 125.0, 123.9, 121.9, 116.9, 116.7, 115.7, 109.3, 22.3, 14.8. HRMS (ESI$^+$): calcd for $C_{23}H_{18}NO^+$ $[M+H]^+$ 324.1383, found 324.1386.



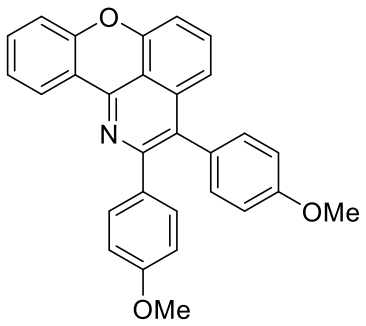
3-Methyl-2-phenylchromeno[2,3,4-*ij*]isoquinoline (3g)

Following the general procedure I, *N*-hydroxy-2-phenoxybenzimidoyl chloride **1a** (37.1mg, 0.15 mmol) and prop-1-yn-1-ylbenzene **2g** (11.6 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3g** as a yellow solid (21.0 mg, 68% yield). M.p.: 184-185 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.54 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.72-7.66 (m, 3H), 7.54-7.48 (m, 3H), 7.47-7.41 (m, 2H), 7.27-7.20 (m, 2H), 7.17 (d, J = 8.0 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.9, 152.8, 152.6, 145.6, 141.7, 137.7, 131.7, 131.5, 130.2, 128.1, 127.8, 124.9, 123.9, 122.0, 121.9, 117.0, 116.1, 115.7, 109.4, 16.1. HRMS (ESI$^+$): calcd for $C_{22}H_{16}NO^+$ $[M+H]^+$ 310.1226, found 310.1228.



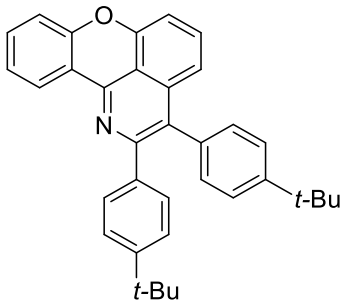
2,3-Di-*p*-tolylchromeno[2,3,4-*ij*]isoquinoline (3h)

Following the general procedure I, *N*-hydroxy-2-phenoxybenzimidoyl chloride **1a** (37.1mg, 0.15 mmol) and 1,2-di-p-tolylethyne **2h** (20.6 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3h** as a yellow solid (27.9 mg, 70% yield). M.p.: 240-241 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.62 (d, J = 8.0 Hz, 1H), 7.53-7.45 (m, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.29-7.27 (m, 1H), 7.25-7.23 (m, 1H), 7.21-7.10 (m, 6H), 7.05 (d, J = 7.6 Hz, 2H), 2.41 (s, 3H), 2.33 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.2, 152.5, 151.3, 147.0, 138.3, 137.8, 137.0, 136.97, 136.92, 134.9, 131.8, 131.4, 130.9, 130.5, 129.4, 128.4, 128.2, 125.0, 123.9, 121.8, 117.5, 117.0, 116.3, 109.2, 21.5, 21.4. HRMS (ESI$^+$): calcd for $C_{29}H_{22}NO^+$ $[M+H]^+$ 400.1696, found 400.1699.



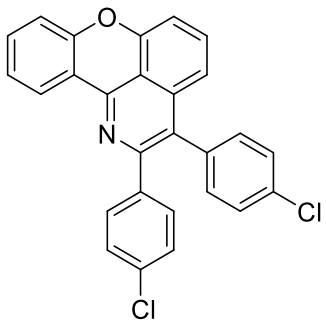
2,3-Bis(4-methoxyphenyl)chromeno[2,3,4-*ij*]isoquinoline (3i)

Following the general procedure I, *N*-hydroxy-2-phenoxybenzimidoyl chloride **1a** (37.1mg, 0.15 mmol) and 1,2-bis(4-methoxyphenyl)ethyne **2i** (23.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3i** as a yellow solid (20.3 mg, 47% yield). M.p.: 211-212 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.61 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.53-7.39 (m, 4H), 7.28-7.23 (m, 2H), 7.19-7.15 (m, 3H), 7.12-7.10 (m, 1H), 6.96-6.91 (m, 2H), 6.80-6.76 (m, 2H), 3.86 (s, 3H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 158.89, 158.84, 154.2, 152.5, 151.1, 147.0, 138.1, 133.8, 132.2, 131.9, 131.8, 131.5, 130.2, 127.6, 125.0, 124.0, 121.9, 117.4, 117.1, 116.2, 114.2, 113.2, 109.6, 55.4, 55.3. HRMS (ESI$^+$): calcd for $C_{29}H_{22}NO_3^+$ $[M+H]^+$ 432.1594, found 432.1597.



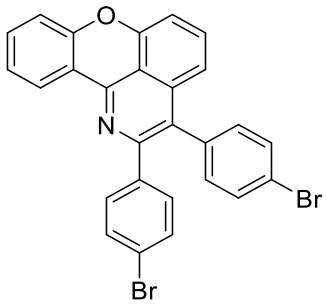
2,3-Bis(4-(tert-butyl)phenyl)chromeno[2,3,4-*ij*]isoquinoline (3j)

Following the general procedure I, *N*-hydroxy-2-phenoxybenzimidoyl chloride **1a** (37.1mg, 0.15 mmol) and 1,2-bis(4-(tert-butyl)phenyl)ethyne **2j** (29.0 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3j** as a yellow solid (36.7 mg, 76% yield). M.p.: > 250 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.36 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.54-7.45 (m, 2H), 7.42-7.36 (m, 4H), 7.30-7.17 (m, 7H), 7.11 (d, J = 7.6 Hz, 1H), 1.36 (s, 9H), 1.28 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.2, 152.5, 151.3, 150.3, 150.1, 147.0, 138.2, 137.8, 134.8, 131.8, 131.4, 130.7, 130.2, 128.4, 125.5, 125.1, 124.5, 123.9, 121.9, 117.7, 117.0, 116.3, 109.2, 34.7, 34.6, 31.5, 31.4. HRMS (ESI$^+$): calcd for $C_{35}H_{34}NO^+$ $[M+H]^+$ 484.2635, found 484.2638.



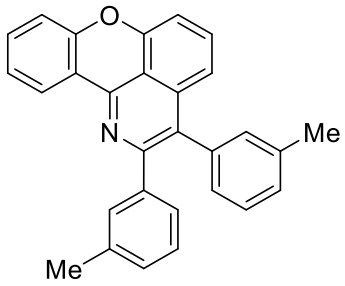
2,3-Bis(4-chlorophenyl)chromeno[2,3,4-*ij*]isoquinoline (3k)

Following the general procedure I, *N*-hydroxy-2-phenoxybenzimidoyl chloride **1a** (37.1mg, 0.15 mmol) and 1,2-bis(4-chlorophenyl)ethyne **2k** (24.6 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3k** as a yellow solid (30.3 mg, 69% yield). M.p.: 230-231 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.57 (dd, J = 8.2 Hz, J = 1.4 Hz, 1H), 7.56 (t, J = 8.2 Hz, 1H), 7.53-7.47 (m, 1H), 7.41-7.35 (m, 4H), 7.31-7.21 (m, 4H), 7.20-7.15 (m, 3H), 7.12 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.2, 152.6, 150.3, 147.8, 139.3, 137.3, 136.0, 133.7, 133.6, 132.5, 132.3, 132.0, 131.9, 129.2, 128.1, 127.3, 125.0, 124.2, 121.5, 117.2, 117.1, 116.4, 110.0. HRMS (ESI$^+$): calcd for $C_{27}H_{16}{}^{35}Cl_2NO^+$ $[M+H]^+$ 440.0603, found 440.0613.



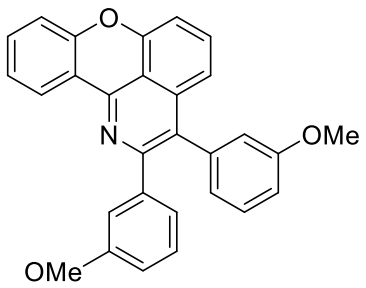
2,3-Bis(4-bromophenyl)chromeno[2,3,4-*ij*]isoquinoline (3l)

Following the general procedure I, *N*-hydroxy-2-phenoxybenzimidoyl chloride **1a** (37.1mg, 0.15 mmol) and 1,2-bis(4-bromophenyl)ethyne **2l** (33.4 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3l** as a yellow solid (35.8 mg, 68% yield). M.p.: > 250 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.58-8.55 (m, 1H), 7.58-7.48 (m, 4H), 7.40-7.36 (m, 2H), 7.33-7.27 (m, 4H), 7.19-7.16 (m, 1H), 7.14-7.10 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.2, 152.6, 150.3, 147.9, 139.7, 137.3, 136.5, 132.8, 132.3, 132.2, 132.2, 132.1, 131.0, 127.2, 125.0, 124.2, 122.0, 121.8, 121.4, 117.2, 117.1, 116.3, 110.0. HRMS (ESI$^+$): calcd for $C_{27}H_{16}{}^{79}Br_2NO^+$ $[M+H]^+$ 527.9593, found 527.9594; calcd for $C_{27}H_{16}{}^{79}Br^{81}BrNO^+$ $[M+H]^+$ 529.9573, found 529.9575; calcd for $C_{27}H_{16}{}^{81}Br_2NO^+$ $[M+H]^+$ 531.9552, found 531.9554.



2,3-Di-*m*-tolylchromeno[2,3,4-*ij*]isoquinoline (3m)

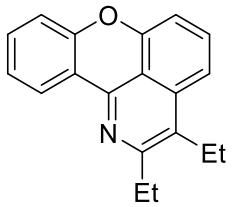
Following the general procedure I, *N*-hydroxy-2-phenoxybenzimidoyl chloride **1a** (37.1mg, 0.15 mmol) and 1,2-di-m-tolylethyne **2m** (20.6 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3m** as a yellow solid (31.9 mg, 80% yield). M.p.: > 250 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.63 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.55-7.46 (m, 2H), 7.36 (s, 1H), 7.29-7.27 (m, 2H), 7.25-7.23 (m, 1H), 7.21-7.16 (m, 2H), 7.15-7.12 (m, 2H), 7.10-7.06 (m, 2H), 7.04-7.00 (m, 2H), 2.34 (s, 3H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.2, 152.5, 151.4, 147.1, 141.0, 138.1, 137.7, 137.69, 137.1, 131.9, 131.7, 131.5, 131.4, 128.7, 128.5, 128.2, 128.07, 128.06, 127.7, 127.4, 125.1, 124.0, 121.8, 117.6, 117.1, 116.3, 109.4, 21.6. HRMS (ESI^+): calcd for $C_{29}H_{22}NO^+$ $[M+H]^+$ 400.1696, found 400.1698.



2,3-Bis(3-methoxyphenyl)chromeno[2,3,4-*ij*]isoquinoline (3n)

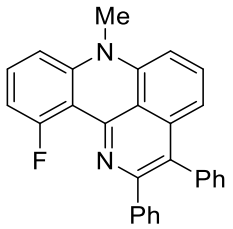
Following the general procedure I, *N*-hydroxy-2-phenoxybenzimidoyl chloride **1a** (37.1mg, 0.15 mmol) and 1,2-bis(3-methoxyphenyl)ethyne **2n** (23.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3n** as a yellow solid (34.0 mg, 79% yield). M.p.: 191-192 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.62 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.50-7.46 (m, 1H), 7.33-7.24 (m, 3H), 7.21 (d, J = 8.0 Hz, 1H), 7.18-7.10 (m, 3H), 7.04 (s, 1H), 6.91-6.85 (m, 2H), 6.81-6.74 (m, 2H), 3.72 (s, 3H), 3.64 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 159.9, 159.0, 154.2, 152.5, 151.0, 147.3, 142.4, 139.2, 137.5, 132.0, 131.7, 129.7, 128.7, 128.4, 125.1, 124.0, 123.6, 123.1, 121.7, 117.6, 117.1, 116.5, 116.4, 115.5, 113.9, 113.2, 109.6, 55.4, 55.3. HRMS (ESI^+): calcd for

$C_{29}H_{22}NO_3^+$ $[M+H]^+$ 432.1594, found 432.1597.



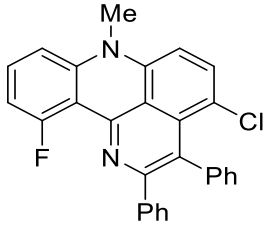
2,3-Diethylchromeno[2,3,4-*ij*]isoquinoline (3o)

Following the general procedure I, *N*-hydroxy-2-phenoxybenzimidoyl chloride **1a** (37.1mg, 0.15 mmol) and hex-3-yne **2o** (8.2 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **3o** as a yellow solid (17.3 mg, 63% yield). M.p.: 149-150 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.52 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.45-7.40 (m, 2H), 7.25-7.18 (m, 2H), 7.04 (d, J = 7.6 Hz, 1H), 3.02-2.94 (m, 4H), 1.41 (t, J = 7.6 Hz, 3H), 1.27 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.9, 153.9, 153.0, 145.4, 136.6, 131.3, 127.1, 124.5, 123.8, 122.2, 116.9, 116.3, 114.8, 108.2, 28.5, 21.2, 14.5, 14.3. HRMS (ESI$^+$): calcd for $C_{19}H_{18}NO^+$ $[M+H]^+$ 276.1383, found 276.1385.



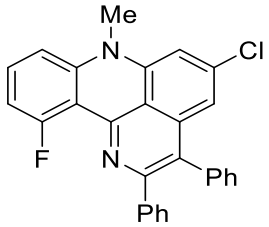
11-Fluoro-7-methyl-2,3-diphenyl-7*H*-pyrido[4,3,2-*kl*]acridine (5a)

Following the general procedure II, 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride **4a** (29.2 mg, 0.1 mmol) and 1,2-diphenylethyne **2a** (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5a** as a yellow solid (35.8 mg, 89% yield). M.p.: 234-236 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.57-7.52 (m, 2H), 7.45 (t, J = 8.0 Hz, 1H), 7.41-7.33 (m, 4H), 7.28-7.27 (m, 2H), 7.21-7.16 (m, 3H), 6.98 (t, J = 8.0 Hz, 2H), 6.88-6.81 (m, 1H), 6.75 (d, J = 8.0 Hz, 1H), 3.57 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.3 (d, J = 260.0 Hz), 151.0, 148.6 (d, J = 8.0 Hz), 144.2 (d, J = 4.0 Hz), 141.2, 138.5, 138.1, 131.29, 131.28 (d, J = 11.2 Hz), 131.2, 130.9 (d, J = 16.4 Hz), 130.8, 128.75, 128.70, 127.6, 127.5, 127.2 (d, J = 4.3 Hz), 119.1, 114.4, 109.5, 109.4 (d, J = 4.0Hz), 109.3, 105.0, 35.0. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -107.1 (dd, J = 11.6 Hz, J = 5.6 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{28}H_{20}FN_2^+$ $[M+H]^+$ 403.1605, found 403.1607.



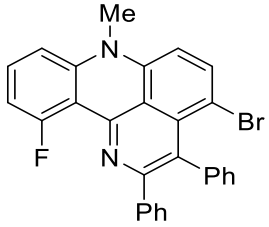
4-Chloro-11-fluoro-7-methyl-2,3-diphenyl-7*H*-pyrido[4,3,2-*kl*]acridine (5b)

Following the general procedure II, 2-((4-chlorophenyl)(methyl)amino)-6-fluoro-*N*-methoxybenzimidoyl chloride **4b** (32.6 mg, 0.1 mmol) and 1,2-diphenylethyne **2a** (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5b** as a yellow solid (17.4 mg, 40% yield). M.p.: > 250 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.53 (d, J = 8.8 Hz, 1H), 7.43-7.36 (m, 1H), 7.35-7.32 (m, 2H), 7.24-7.14 (m, 8H), 6.98 (d, J = 8.8 Hz, 1H), 6.86-6.81 (m, 1H), 6.71 (d, J = 8.8 Hz, 1H), 3.57 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.2 (d, J = 260.8 Hz), 154.4, 148.7 (d, J = 8.0 Hz), 143.6 (d, J = 4.0 Hz), 141.5, 140.6, 139.1, 134.6, 133.4, 132.3, 131.6 (d, J = 11.2 Hz), 130.6, 127.3, 127.2, 126.9 (d, J = 6.0 Hz), 125.7, 120.7, 118.7, 109.9, 109.7, 109.2 (d, J = 4.0 Hz), 106.7, 35.3. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -106.6 (dd, J = 11.6 Hz, J = 5.2 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{28}H_{19}ClFN_2^+$ $[M+H]^+$ 437.1215, found 437.1221.



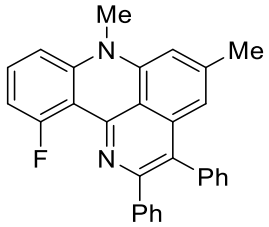
5-Chloro-11-fluoro-7-methyl-2,3-diphenyl-7*H*-pyrido[4,3,2-*kl*]acridine (5c)

Following the general procedure II, 2-((3-chlorophenyl)(methyl)amino)-6-fluoro-*N*-methoxybenzimidoyl chloride **4c** (32.6 mg, 0.1 mmol) and 1,2-diphenylethyne **2a** (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5c** as a yellow solid (15.3 mg, 35% yield). M.p.: 242-243 ℃. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) 7.50-7.35 (m, 6H), 7.28-7.18 (m, 5H), 7.07 (d, J = 9.3 Hz, 1H), 6.91-6.85 (m, 2H), 6.76 (s, 1H), 3.57 (s, 3H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ (ppm) 162.4 (d, J = 259.7 Hz), 160.2, 144.2 (d, J = 4.0 Hz), 142.8, 139.4, 138.1, 132.1 (d, J = 11.0 Hz), 131.5, 130.9, 129.3, 127.9, 127.6, 117.7, 113.5, 110.4 (d, J = 3.4 Hz), 110.3, 110.1, 106.1, 35.6. ^{19}F NMR (CD_2Cl_2, 376 MHz): δ (ppm) -107.7 (s, 1F). HRMS (ESI$^+$): calcd for $C_{28}H_{19}ClFN_2^+$ $[M+H]^+$ 437.1221, found 437.1223.



4-Bromo-11-fluoro-7-methyl-2,3-diphenyl-7*H*-pyrido[4,3,2-*kl*]acridine (5d)

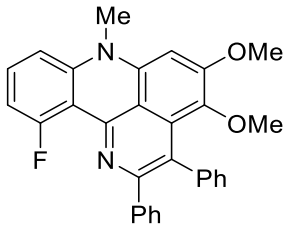
Following the general procedure II, 2-((4-bromophenyl)(methyl)amino)-6-fluoro-*N*-methoxybenzimidoyl chloride **4d** (37.0 mg, 0.1 mmol) and 1,2-diphenylethyne **2a** (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5d** as a yellow solid (18.2 mg, 38% yield). M.p.: >250 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.53 (d, J = 8.8 Hz, 1H), 7.42-7.32 (m, 3H), 7.25-7.13 (m, 8H), 6.97 (d, J = 8.8 Hz, 1H), 6.87-6.79 (m, 1H), 6.70 (d, J = 8.8 Hz, 1H), 3.65 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.2 (d, J = 260.0 Hz), 154.4, 148.6 (d, J = 8.0 Hz), 143.6, 141.5, 140.6, 139.1, 134.6, 133.4, 132.3, 131.6 (d, J = 11.2 Hz), 130.6, 127.3, 127.2, 126.9 (d, J = 5.7 Hz), 125.6, 120.7, 118.7, 109.9, 109.7, 109.2 (d, J = 4.0 Hz), 106.0, 35.3. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -106.6 (dd, J = 11.7 Hz, J = 5.4 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{28}H_{19}{}^{79}BrFN_2^+$ $[M+H]^+$ 481.0710, found 481.0714; calcd for $C_{28}H_{19}{}^{81}BrFN_2^+$ $[M+H]^+$ 483.0690, found 483.0695.



11-Fluoro-4,7-dimethyl-2,3-diphenyl-7*H*-pyrido[4,3,2-*kl*]acridine (5e)

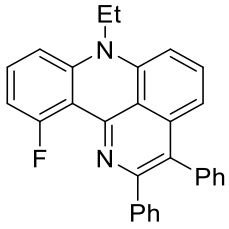
Following the general procedure II, 2-fluoro-*N*-methoxy-6-(methyl(*p*-tolyl)amino)benzimidoyl chloride **4e** (30.6 mg, 0.1 mmol) and 1,2-diphenylethyne **2a** (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5e** as a yellow solid (18.3 mg, 44% yield). M.p.: 242-243 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.55-7.50 (m, 2H), 7.42-7.33 (m, 4H), 7.29-7.25 (m, 2H), 7.21-7.15 (m, 3H), 6.96 (d, J = 8.4 Hz, 1H), 6.86-6.80 (m, 1H), 6.79 (s, 1H), 6.58 (s, 1H), 3.55 (s, 3H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.2 (d, J= 259.6 Hz), 151.2, 148.3 (d, J = 9.2 Hz), 144.2 (d, J = 4.8 Hz), 141.6, 141.3, 141.0, 138.6, 138.2, 131.3, 131.1 (d, J = 12.0 Hz), 130.8, 128.7, 127.5, 127.1 (d, J = 4.5 Hz), 126.3 (d, J = 1.9 Hz), 117.6, 114.0, 112.3 (d, J = 7.8 Hz), 109.43 (d, J = 3.0 Hz), 109.37, 109.2, 106.8, 34.9, 23.1. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -107.2 (dd, J = 11.6

Hz, J = 5.6 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{29}H_{22}FN_2^+$ $[M+H]^+$ 417.1762, found 417.1769.



11-Fluoro-4,5-dimethoxy-7-methyl-2,3-diphenyl-7*H*-pyrido[4,3,2-*kl*]acridine (5f)

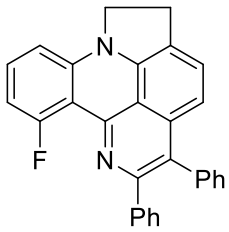
Following the general procedure II, 2-((3,4-dimethoxyphenyl)(methyl)amino)-6-fluoro-*N*-methoxybenzimidoyl chloride **4f** (35.2 mg, 0.1 mmol) and 1,2-diphenylethyne **2a** (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5f** as a yellow solid (33.7 mg,73% yield). M.p.: 211-212 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.41-7.37 (m, 2H), 7.36-7.29 (m, 1H), 7.27-7.22 (m, 2H), 7.21-7.08 (m, 6H), 6.92 (d, J = 8.4 Hz, 1H), 6.83-6.75 (m, 1H), 6.47 (s, 1H), 3.96 (s, 3H), 3.55 (s, 3H), 2.94 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.2 (d, J = 260.0 Hz), 154.6, 153.4, 148.3 (d, J = 8.0 Hz), 144.0 (d, J = 5.2 Hz), 141.9, 140.5, 138.9, 135.2, 131.9, 131.5, 131.1 (d, J = 11.2 Hz), 130.8, 127.2, 126.7 (d, J = 6.0 Hz), 126.0, 124.0 (d, J = 2.0 Hz), 115.7, 111.9 (d, J = 2.0 Hz), 110.1, 109.4 (d, J = 23.0 Hz), 109.2 (d, J = 4.0 Hz), 93.3, 60.6, 56.3, 35.3. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -106.7 (dd, J = 11.7 Hz, J = 5.3 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{30}H_{24}FN_2O_2^+$ $[M+H]^+$ 463.1816, found 463.1820.



7-Ethyl-11-fluoro-2,3-diphenyl-7*H*-pyrido[4,3,2-*kl*]acridine (5g)

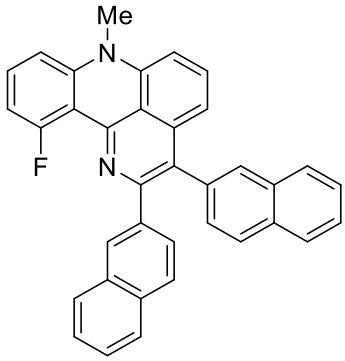
Following the general procedure II, 2-(ethyl(phenyl)amino)-6-fluoro-*N*-methoxybenzimidoyl chloride **4g** (30.6 mg, 0.1 mmol) and 1,2-diphenylethyne **2a** (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5g** as a yellow solid (39.5 mg, 95% yield). M.p.: 204-205 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.57-7.51 (m, 2H), 7.46 (t, J = 8.2 Hz, 1H), 7.42-7.33 (m, 4H), 7.30-7.24 (m, 2H), 7.22-7.16 (m, 3H), 7.02-6.97 (m, 2H), 6.87-6.81 (m, 1H), 6.79 (d, J = 8.0 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 1.48 (t, J =7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.4 (d, J = 260.0 Hz), 150.9, 148.7 (d, J = 8.0 Hz), 143.2 (d, J = 4.0 Hz), 141.2, 140.0, 138.5, 138.3, 131.34 (d, J =

12.0 Hz), 131.26, 130.8, 128.8, 127.5, 127.2 (d, J = 4.0 Hz), 126.7 (d, J = 2.0 Hz), 119.0, 114.2, 112.4 (d, J = 7.0 Hz), 109.4, 109.2, 108.9 (d, J = 4.0 Hz), 104.3, 42.1, 11.0. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -106.4 (dd, J = 11.7 Hz, J = 5.5 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{29}H_{22}FN_2^+$ $[M+H]^+$ 417.1762, found 417.1769.



12-Fluoro-2,3-diphenyl-6,7-dihydropyrido[2,3,4-*mn*]pyrrolo[3,2,1-*de*]acridine (5h)

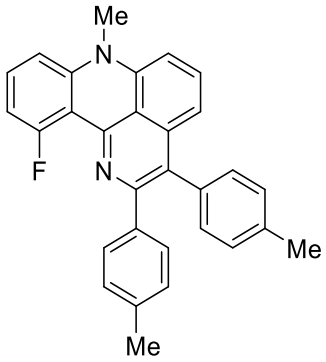
Following the general procedure II, 2-fluoro-6-(indolin-1-yl)-*N*-methoxybenzimidoyl chloride **4h** (30.4 mg, 0.1 mmol) and 1,2-diphenylethyne **2a** (26.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5h** as a yellow solid (23.2 mg, 56% yield). M.p.: > 250 ℃. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) 7.43-7.27 (m, 7H), 7.25-7.15 (m, 5H), 6.73-6.59 (m, 3H), 4.28 (t, J = 8.4 Hz, 2H), 3.44 (t, J = 8.4 Hz, 2H). The ^{13}C NMR data could not be recorded due to its poor solubility, but the X-ray single crystal diffraction of **5h** confirmed its structures. HRMS (ESI$^+$): calcd for $C_{29}H_{20}FN_2^+$ $[M+H]^+$ 415.1605, found 415.1609.



11-Fluoro-7-methyl-2,3-di(naphthalen-2-yl)-7*H*-pyrido[4,3,2-*kl*]acridine (5i)

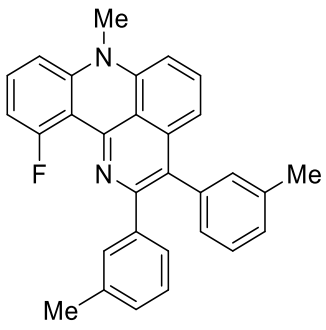
Following the general procedure II, 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride **4a** (29.2 mg, 0.1 mmol) and 1,2-di(naphthalen-2-yl)ethyne **2p** (41.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5i** as a yellow solid (42.6 mg, 85% yield). M.p.: > 185 ℃. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) 8.04 (s, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.82 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.68-7.56 (m, 3H), 7.54-7.32 (m, 7H), 7.09 (d, J = 8.0 Hz, 1H),

6.98 (d, J = 8.4 Hz, 1H), 6.93-6.84 (m, 2H), 3.62 (s, 3H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ (ppm) 162.5 (d, J = 258.0 Hz), 158.9, 153.5, 151.0, 149.1 (d, J = 7.9 Hz), 146.7, 144.8, 141.6, 138.6, 136.3, 134.1, 133.4, 133.0 (d, J = 8.5 Hz), 132.1, 132.0, 130.5 (d, J = 5.3 Hz), 129.9, 128.8, 128.4, 128.2, 127.8, 127.1, 126.6 (d, J = 4.2 Hz), 126.5, 126.2, 119.4, 114.7, 110.3 (d, J = 3.5 Hz), 109.6 (d, J = 22.6 Hz), 105.9, 35.5. ^{19}F NMR (CD_2Cl_2, 376 MHz): δ (ppm) -107.9–-108.0 (m, 1F). HRMS (ESI$^+$): calcd for $C_{36}H_{24}FN_2^+$ $[M+H]^+$ 503.1918, found 503.1921.



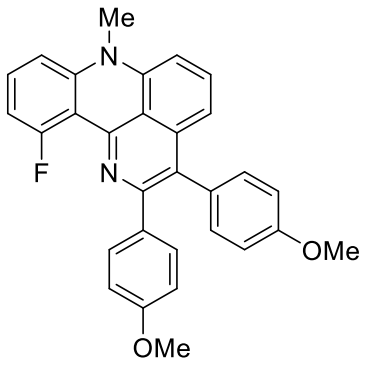
11-Fluoro-7-methyl-2,3-di-*p*-tolyl-7*H*-pyrido[4,3,2-*kl*]acridine (5j)

Following the general procedure II, 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride **4a** (29.2 mg, 0.1 mmol) and 1,2-di-*p*-tolylethyne **2h** (30.9 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5j** as a yellow solid (41.7 mg, 97% yield). M.p.: 237-238 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.47 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 1H), 7.38-7.32 (m, 1H), 7.22-7.15 (m, 4H), 7.02 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.86-6.79 (m, 1H), 6.70 (d, J = 7.6 Hz, 1H), 3.54 (s, 3H), 2.42 (s, 3H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.2 (d, J = 259.9 Hz), 150.9, 148.3 (d, J = 7.8 Hz), 144.2 (d, J = 4.4 Hz), 141.1, 138.3 (d, J = 8.6 Hz), 136.8 (d, J = 5.3 Hz), 135.5, 131.2 (d, J = 11.2 Hz), 131.1, 131.0, 130.7, 129.5, 128.3, 126.5 (d, J = 2.0 Hz), 118.9, 114.4, 112.5 (d, J = 7.8 Hz), 109.5, 109.3 (d, J = 3.8 Hz), 109.2, 104.8, 34.9, 21.5. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -107.2 (dd, J = 11.7, J = 5.4 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{30}H_{24}FN_2^+$ $[M+H]^+$ 431.1918, found 431.1925.



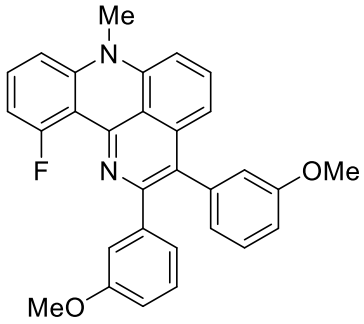
11-Fluoro-7-methyl-2,3-di-*m*-tolyl-7*H*-pyrido[4,3,2-*kl*]acridine (5k)

Following the general procedure II, 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride **4a** (29.2 mg, 0.1 mmol) and 1,2-di-*m*-tolylethyne **2m** (30.9 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5k** as a yellow solid (42.5 mg, 99% yield). M.p.: > 250 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.48-7.42 (m, 2H), 7.40-7.33 (m, 1H), 7.31-7.23 (m, 2H), 7.18-7.09 (m, 2H), 7.08-6.93 (m, 5H), 6.89-6.81 (m, 1H), 6.73 (d, J = 8.0 Hz, 1H), 3.56 (s, 3H), 2.35 (s, 3H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.2 (d, J = 259.6 Hz), 150.9, 148.3 (d, J = 7.9 Hz), 144.2 (d, J = 4.4 Hz), 141.0 (d, J = 12.6 Hz), 138.4, 138.2, 138.1, 136.9, 131.8, 131.6, 131.2 (d, J = 11.2 Hz), 131.1, 128.6, 128.3, 127.9 (d, J = 3.0 Hz), 127.8, 127.3, 126.9 (d, J = 2.1 Hz), 119.0, 114.5, 112.4 (d, J = 7.7 Hz), 109.5, 109.4 (d, J = 3.7 Hz), 109.3, 104.9, 35.0, 21.66, 21.64. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -107.1 (dd, J = 11.6 Hz, J = 5.6 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{30}H_{24}FN_2^+$ $[M+H]^+$ 431.1918, found 431.1925.



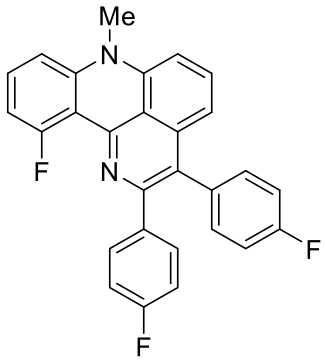
11-Fluoro-2,3-bis(4-methoxyphenyl)-7-methyl-7*H*-pyrido[4,3,2-*kl*]acridine (5l)

Following the general procedure II, 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride **4a** (29.2 mg, 0.1 mmol) and 1,2-bis(4-methoxyphenyl)ethyne **2i** (35.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5l** as a yellow solid (37.0 mg, 80% yield). M.p.: 242-243 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.54-7.51 (m, 2H), 7.43 (t, J = 8.2 Hz, 1H), 7.40-7.34 (m, 1H), 7.21-7.17 (m, 2H), 7.01-6.94 (m, 4H), 6.87-6.81 (m, 1H), 6.77-6.74 (m, 2H), 6.72 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 3.57 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.2 (d, J = 259.5 Hz), 150.8 (d, J = 9.5 Hz), 150.6, 144.2 (d, J = 4.5 Hz), 141.2, 138.5, 133.8, 132.3, 132.0, 131.2 (d, J = 11.3 Hz), 131.1, 130.8, 125.7, 118.9, 114.32, 114.29, 113.1, 112.5 (d, J = 7.7 Hz), 109.5, 109.4 (d, J = 3.7 Hz), 109.3, 104.7, 55.4, 55.3, 35.0. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -107.4 (dd, J = 11.6 Hz, J = 5.2 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{30}H_{24}FN_2O_2^+$ $[M+H]^+$ 463.1816, found 463.1822.



11-Fluoro-2,3-bis(3-methoxyphenyl)-7-methyl-7*H*-pyrido[4,3,2-*kl*]acridine (5m)

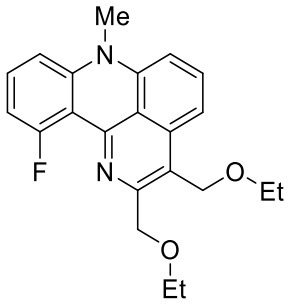
Following the general procedure II, 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride **4a** (29.2 mg, 0.1 mmol) and 1,2-bis(3-methoxyphenyl)ethyne **2n** (35.7 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5m** as a yellow solid (45.7 mg, 99% yield). M.p.: 207-208 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.46 (t, J = 8.2 Hz, 1H), 7.41-7.31 (m, 2H), 7.24 (s, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.92-6.81 (m, 4H), 6.77 (s, 1H), 6.75 (s, 1H), 3.74 (s, 3H), 3.66 (s, 3H), 3.57 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.3 (d, J = 259.9 Hz), 160.0, 158.9, 150.4 (d, J = 1.6 Hz), 148.5 (d, J = 8.1 Hz), 144.2 (d, J = 4.5 Hz), 142.3, 141.1, 139.9, 138.0, 131.3 (d, J = 11.3 Hz), 131.2, 129.9, 128.5, 126.5 (d, J = 1.9 Hz), 123.7, 123.3, 119.0, 116.5, 115.2, 114.4 (d, J = 10.0 Hz), 113.1, 109.5, 109.4 (d, J = 3.8 Hz), 109.3, 105.1, 55.4, 55.2, 35.0. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -107.2 (dd, J = 11.6 Hz, J = 5.3 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{30}H_{24}FN_2O_2^+$ $[M+H]^+$ 463.1816, found 463.1824.



11-Fluoro-2,3-bis(4-fluorophenyl)-7-methyl-7*H*-pyrido[4,3,2-*kl*]acridine (5n)

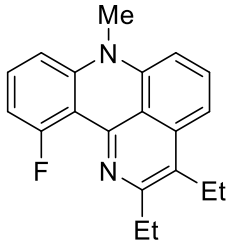
Following the general procedure II, 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride **4a** (29.2 mg, 0.1 mmol) and 1,2-bis(4-fluorophenyl)ethyne **2q** (32.1 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5n** as a yellow solid (41.2 mg, 94% yield). M.p.: 224-226 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.51-7.45 (m, 3H), 7.42-7.26 (m, 1H), 7.25-7.19 (m, 2H), 7.14-7.07

(m, 2H), 6.99 (d, J = 8.8 Hz, 1H), 6.95-6.82 (m, 4H), 6.77 (d, J = 8.0 Hz, 1H), 3.58 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.3 (d, J = 251.2 Hz), 162.2 (d, J = 253.9 Hz), 162.1 (d, J = 245.3 Hz), 150.2, 148.8 (d, J = 7.8 Hz), 144.2 (d, J = 4.5 Hz), 141.2, 138.1, 137.1 (d, J = 3.7 Hz), 134.1 (d, J = 3.6 Hz), 132.9 (d, J = 7.8 Hz), 132.5 (d, J = 8.1 Hz), 131.5 (d, J = 10.2 Hz), 125.4 (d, J = 1.8 Hz), 119.0, 116.0 (d, J = 21.2 Hz), 114.6 (d, J = 21.2 Hz), 114.0, 112.2 (d, J = 7.7 Hz), 109.6, 109.5 (d, J = 3.8 Hz), 109.4, 105.2, 35.0. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -107.2 (dd, J = 11.7 Hz, J = 5.5 Hz), -114.6 − -114.7 (m, 1F), -115.07 − -115.16 (m, 1F). HRMS (ESI$^+$): calcd for $C_{28}H_{18}F_3N_2^+$ $[M+H]^+$ 439.1417, found 439.1420.



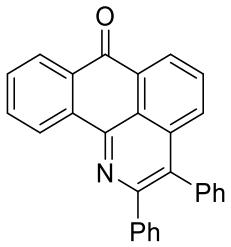
2,3-Bis(ethoxymethyl)-11-fluoro-7-methyl-7*H*-pyrido[4,3,2-*kl*]acridine (5o)

Following the general procedure II, 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride **4a** (29.2 mg, 0.1 mmol) and 1,4-diethoxybut-2-yne **2r** (21.3 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5o** as a yellow solid (24.2 mg, 66% yield). M.p.: 119-120 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.59 (t, J = 8.0 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.39-7.32 (m, 1H), 6.95 (d, J = 8.8 Hz, 1H), 6.84-6.78 (m, 1H), 6.76 (d, J = 8.0 Hz, 1H), 4.92 (s, 2H), 4.88 (s, 2H), 3.70 (q, J = 7.2 Hz, 2H), 3.64 (q, J = 7.2 Hz, 2H), 3.54 (s, 3H), 1.29-1.23 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.2 (d, J = 259.7 Hz), 151.1, 148.9 (d, J = 7.7 Hz), 144.0 (d, J = 4.5 Hz), 141.1, 138.0, 131.4, 131.3 (d, J = 11.1 Hz), 122.2 (d, J = 1.7 Hz), 120.0, 112.8, 109.4, 109.3 (d, J = 27.1 Hz), 105.0, 73.6, 66.2, 65.84, 65.79, 34.9, 15.5, 15.4. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -107.0 (dd, J = 12.0 Hz, J = 5.6 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{22}H_{24}FN_2O_2^+$ $[M+H]^+$ 367.1816, found 367.1815.



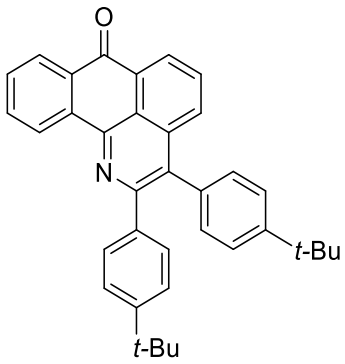
2,3-Diethyl-11-fluoro-7-methyl-7*H*-pyrido[4,3,2-*kl*]acridine (5p)

Following the general procedure II, 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride **4a** (29.2 mg, 0.1 mmol) and hex-3-yne **2o** (12.3 mg, 0.15 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 20:1, v/v) afforded **5p** as a yellow oil (29.7 mg, 97% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.53 (t, J = 8.2 Hz, 1H), 7.36-7.28 (m, 1H), 7.24 (d, J = 8.4 Hz, 1H), 6.92 (d, J = 8.8 Hz, 1H), 6.84-6.77 (m, 1H), 6.66 (d, J = 8.0 Hz, 1H), 3.52 (s, 3H), 3.01-2.91 (m, 4H), 1.43 (t, J = 7.6 Hz, 3H), 1.25 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 162.0 (d, J = 259.0 Hz), 154.7, 146.8 (d, J = 8.6 Hz), 144.0 (d, J = 4.6 Hz), 141.7, 136.8, 130.8, 130.6 (d, J = 11.3 Hz), 125.6, 119.1, 111.7, 109.4, 109.3 (d, J = 3.5 Hz), 109.2, 103.7, 34.9, 28.5, 21.2, 14.2, 13.9. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -108.1 (dd, J = 12.0 Hz, J = 5.6 Hz, 1F). HRMS (ESI$^+$): calcd for $C_{20}H_{20}FN_2$ $[M+H]^+$ 307.1605, found 307.1609.



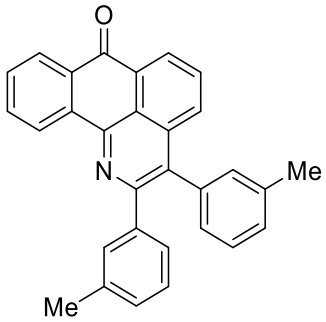
2,3-Diphenyl-7*H*-dibenzo[*de*,*h*]quinolin-7-one (7a)

Following the general procedure III, 2-benzyl-*N*-methoxybenzimidoyl chloride **6** (38.9mg, 0.15 mmol) and 1,2-diphenylethyne **2a** (17.8 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **7a** as a yellow solid (31.8 mg, 83% yield). M.p.: > 250 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) 9.03 (d, J = 7.6 Hz, 1H), 8.56 (d, J = 7.6 Hz, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.89-7.81 (m, 2H), 7.70 (t, J = 8.0 Hz, 1H), 7.56-7.49 (m, 2H), 7.46-7.39 (m, 3H), 7.35-7.31 (m, 2H), 7.30-7.24 (m, 3H). The ^{13}C NMR data could not be recorded due to its poor solubility. HRMS (ESI$^+$): calcd for $C_{28}H_{18}NO^+$ $[M+H]^+$ 384.1383, found 384.1383.



2,3-Bis(4-(tert-butyl)phenyl)-7*H*-dibenzo[*de*,*h*]quinolin-7-one (7b)

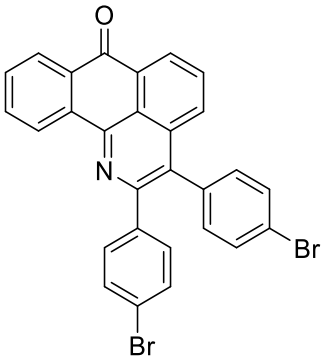
Following the general procedure III, 2-benzyl-*N*-methoxybenzimidoyl chloride **6** (38.9mg, 0.15 mmol) and 1,2-bis(4-(*tert*-butyl)phenyl)ethyne **2j** (29.0 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **7b** as a yellow solid (37.1 mg, 75% yield). M.p.: > 250 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.08-9.06 (m, 1H), 8.67-8.65 (m, 1H), 8.46-8.44 (m, 1H), 8.09 (dd, J = 8.4 Hz, J = 1.0 Hz, 1H), 7.84-7.78 (m, 2H), 7.68-7.64 (m, 1H), 7.47-7.41 (m, 4H), 7.29-7.27 (m, 1H), 7.25-7.20 (m, 3H), 1.39 (s, 9H), 1.31 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 184.0, 151.5, 150.9, 150.5, 147.3, 137.7, 137.2, 136.0, 134.0, 133.9, 133.1, 132.5, 131.4, 131.2, 130.32, 130.28, 129.3, 129.1, 127.5, 125.8, 125.4, 124.7, 121.6, 34.8, 34.7, 31.5, 31.4. HRMS (ESI$^+$): calcd for $C_{36}H_{34}NO^+$ $[M+H]^+$ 496.2635 found 496.2642.



2,3-Di-*m*-tolyl-7*H*-dibenzo[*de*,*h*]quinolin-7-one (7c)

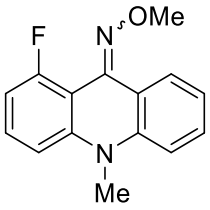
Following the general procedure III, 2-benzyl-*N*-methoxybenzimidoyl chloride **6** (38.9mg, 0.15 mmol) and 1,2-di-m-tolylethyne **2m** (20.6 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **7c** as a yellow solid (31.2 mg, 76% yield). M.p.: > 250 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.07 (d, J = 7.6 Hz, 1H), 8.67 (d, J = 7.2 Hz, 1H), 8.46 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.85-7.80 (m, 2H), 7.70-7.64 (m, 1H), 7.41 (s, 1H), 7.33-7.26 (m, 2H), 7.21 (d, J = 7.6 Hz, 1H), 7.17-7.11 (m, 2H), 7.10-7.05 (m, 2H), 2.37 (s, 3H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 184.0, 151.6, 147.4, 140.5, 138.1, 137.3, 137.1, 136.9, 135.8, 134.1, 133.1, 132.5, 132.1, 131.6,

131.4, 130.4, 130.3, 129.4, 129.1, 128.6, 128.5, 128.4, 128.3, 127.7, 127.6, 127.5, 125.8, 121.7, 21.7, 21.6. HRMS (ESI$^+$): calcd for $C_{30}H_{22}NO^+$ [M+H]$^+$ 412.1696, found 412.1686.



2,3-Bis(4-bromophenyl)-7*H*-dibenzo[*de,h*]quinolin-7-one (7d)

Following the general procedure III, 2-benzyl-*N*-methoxybenzimidoyl chloride **6** (38.9mg, 0.15 mmol) and 1,2-bis(4-bromophenyl)ethyne **2l**(33.4 mg, 0.1 mmol) were used. Purification via flash column chromatography on aluminum oxide (petroleum ether/ethyl acetate = 50:1, v/v) afforded **7d** as a yellow solid (51.2 mg, 95% yield). M.p.: > 250 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.01-8.98 (m, 1H), 8.68 (dd, J = 7.2 Hz, J = 0.8 Hz, 1H), 8.46-8.42 (m 1H), 7.98 (dd, J = 8.8 Hz, J = 1.2 Hz, 1H), 7.88-7.80 (m, 2H), 7.70-7.66 (m, 1H), 7.61-7.57 (m, 2H), 7.46-7.42 (m, 2H), 7.39-7.35 (m, 2H), 7.20-7.16 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 183.6, 150.3, 148.2, 139.3, 136.7, 135.6, 135.5, 134.2, 133.0, 132.5, 132.3, 132.2, 132.1, 131.3, 131.0, 130.8, 130.1, 129.8, 129.2, 127.7, 125.7, 122.5, 122.4, 121.8. HRMS (ESI$^+$): calcd for $C_{28}H_{16}{}^{79}Br_2NO^+$ [M+H]$^+$ 529.9593, found 539.9602; calcd for $C_{28}H_{16}{}^{79}Br^{81}BrNO^+$ [M+H]$^+$ 541.9573, found 541.9573; calcd for $C_{28}H_{16}{}^{81}Br_2NO^+$ [M+H]$^+$ 543.9552, found 543.9558.



1-Fluoro-10-methylacridin-9(10*H*)-one *O*-methyl oxime (8)

Following the general procedure II, reaction of 2-fluoro-*N*-methoxy-6-(methyl(phenyl)amino)benzimidoyl chloride **4a** (29.2 mg, 0.1 mmol) was conducted in the absence of an alkyne component. Purification via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) afforded **8** as a white solid (13.1 mg, 51% yield, major isomer: minor isomer = 1.7:1) M.p.: 119-121 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.41 (dd, J = 8.0 Hz, J =

1.6 Hz, 1H for major isomer), 7.85 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H for minor isomer), 7.45-7.26 (m, 2H for two isomers), 7.15-7.04 (m, 2H for two isomers), 6.90-6.76 (m, 2H for two isomers), 4.06 (s, 3H, for minor isomer), 4.05 (s, 3H, for major isomer), 3.53 (s, 3H for two isomers). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) for two isomers, 160.0 (d, J = 254.2 Hz), 159.7 (d, J = 251.3 Hz), 144.7 (d, J = 8.0 Hz), 144.0 (d, J = 4.8 Hz), 143.2 (d, J = 3.5 Hz), 142.8 (d, J = 6.0 Hz), 142.4, 141.1, 131.1 (d, J = 10.5 Hz), 130.9, 130.7, 129.8 (d, J = 11.0 Hz), 129.6, 124.8, 121.9, 120.0, 117.7, 113.5, 112.9, 109.7 (d, J = 14.7 Hz), 108.8, 108.7 (d, J = 3.5 Hz), 108.6 (d, J = 2.9 Hz), 108.6, 108.0, 107.8, 62.7, 62.6, 34.7, 34.4. ^{19}F NMR ($CDCl_3$, 376 MHz): δ (ppm) -96.1 (dd, J = 9.6, J = 6.1 Hz), -114.7 (dd, J = 10.4, J = 5.7 Hz). HRMS (ESI$^+$): calcd for $C_{15}H_{14}FN_2O^+$ $[M+H]^+$ 257.1085 found 257.1086.

X. Single crystal X-ray structures of 3b, 3d, 3e, 3f, 5g, 5h, 7d

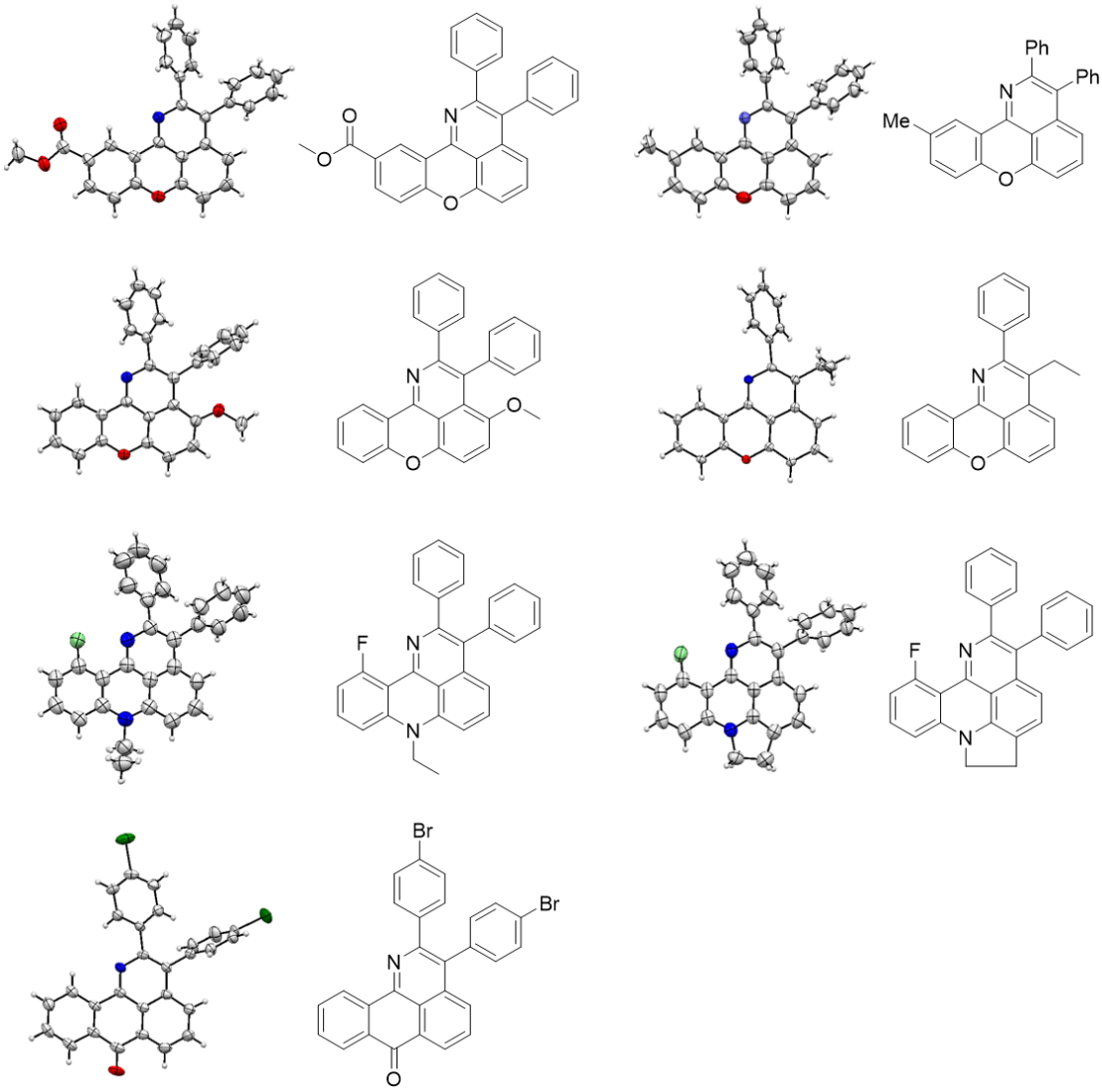


Figure S1. ORTEP diagrams of **3b, 3d, 3e, 3f, 5h, 5i** and **7d**. Thermal ellipsoids are shown at the 50% probability level. CCDC 1899576 (**3b**), CCDC 1913390 (**3d**), CCDC 1899575 (**3e**), CCDC

1899578 (**3f**), CCDC 1899572 (**5g**), CCDC 1899579 (**5h**), and CCDC 1899574 (**7d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

XI. References

(1) J. W. Kang, K. Moseley, P. M. Maitlis, *J. Am. Chem. Soc.* 1969, **91**, 5970.

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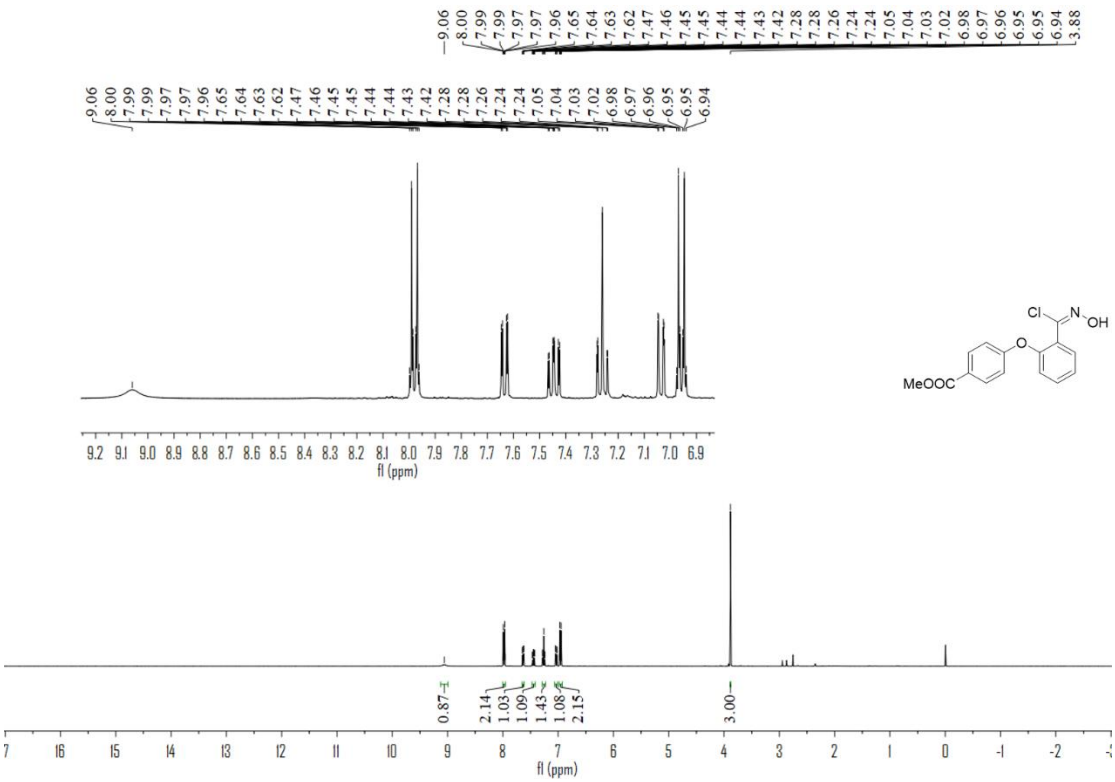
XII. Copies of NMR spectra:

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



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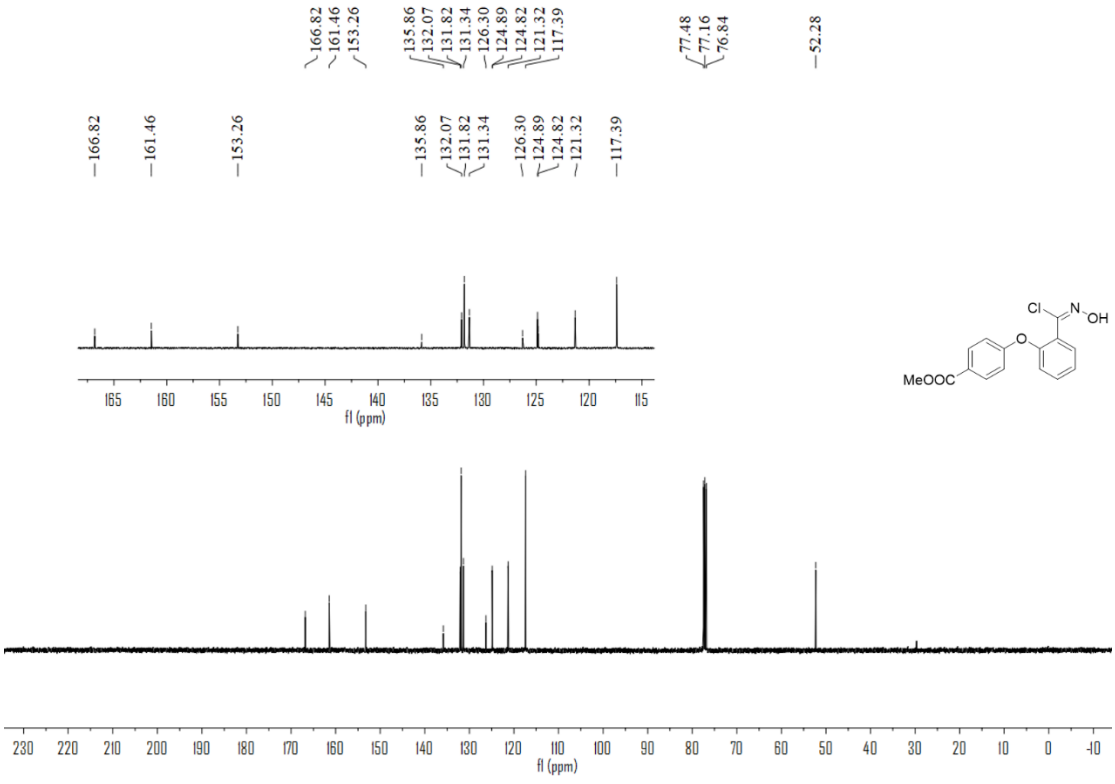

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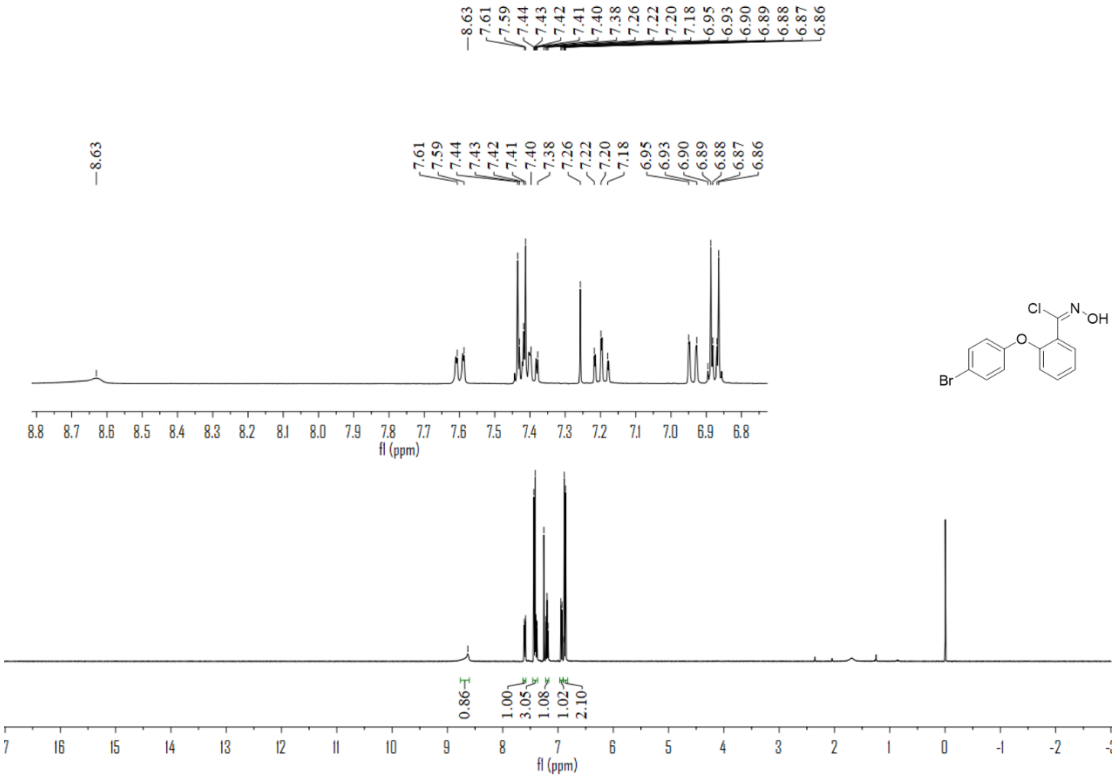

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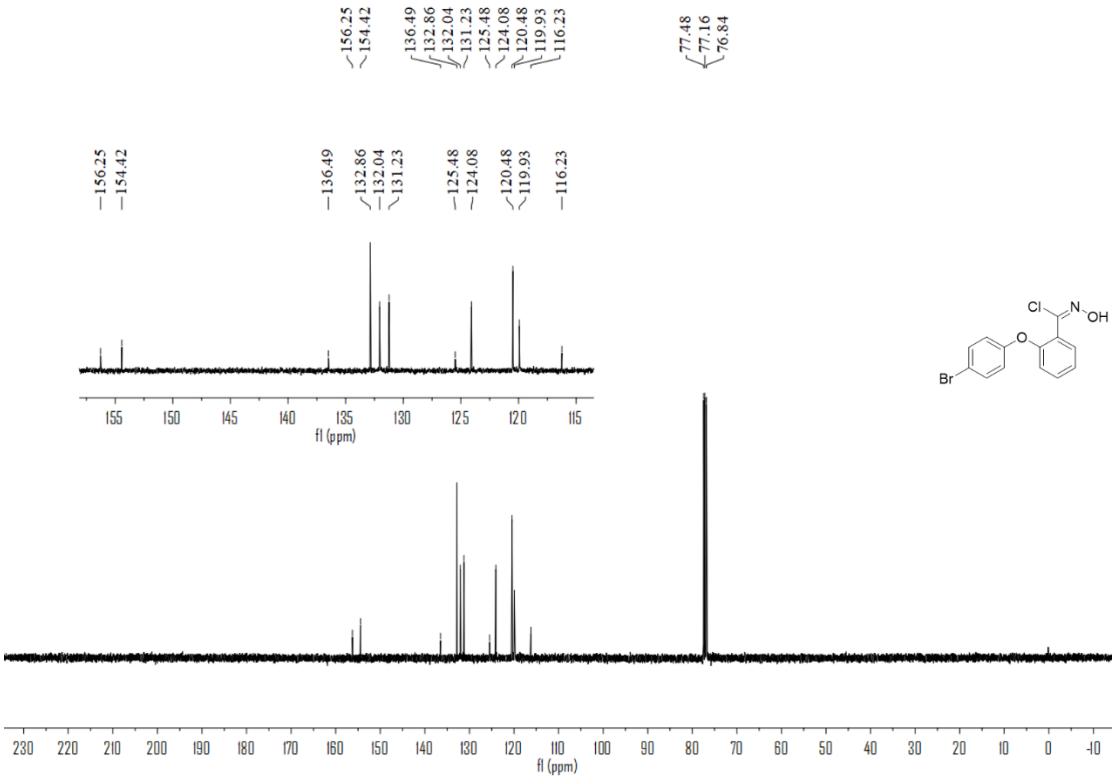

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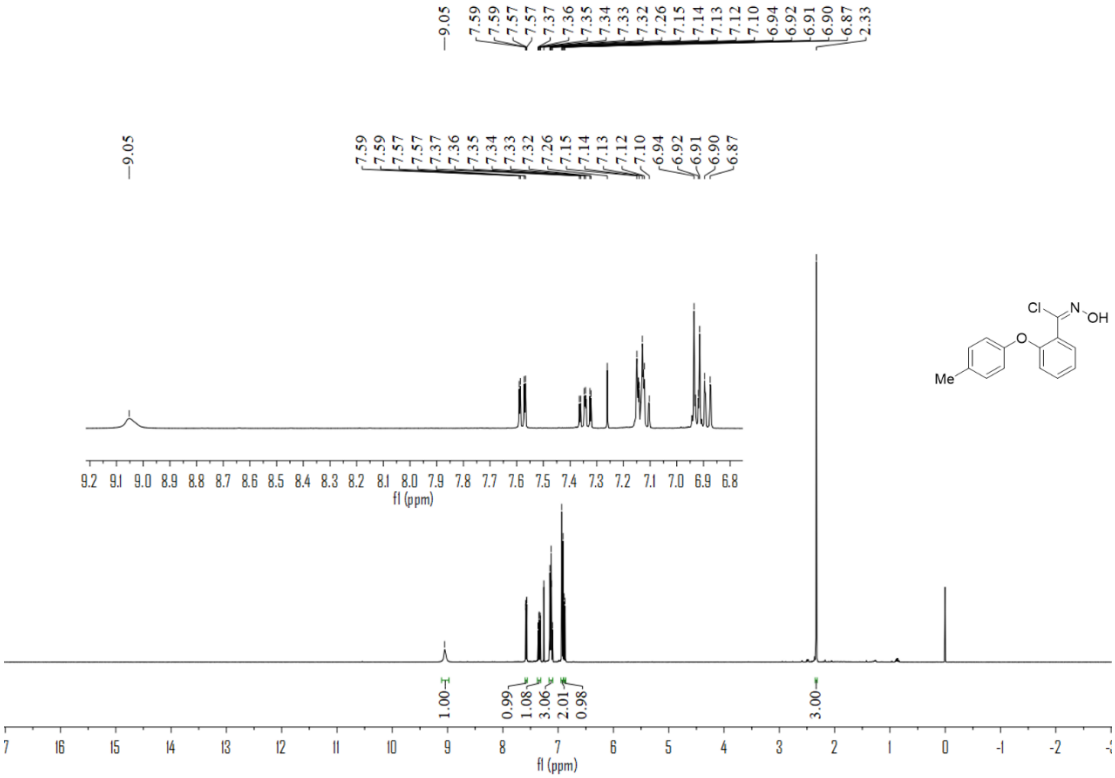

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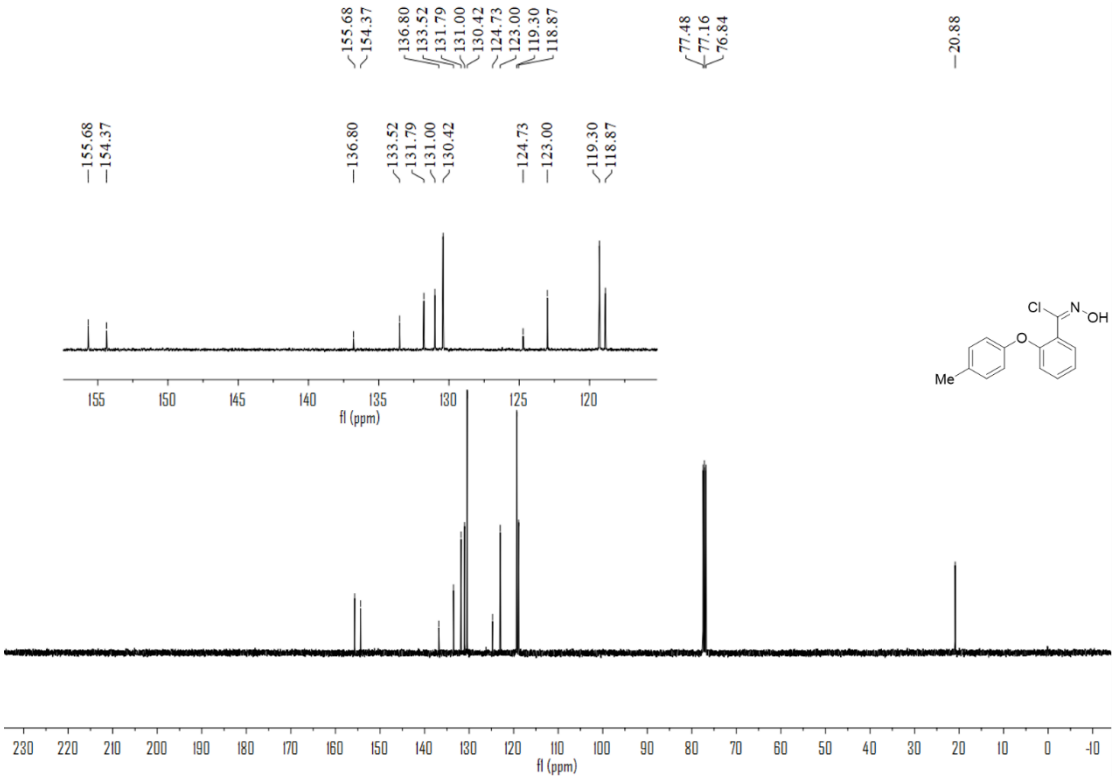

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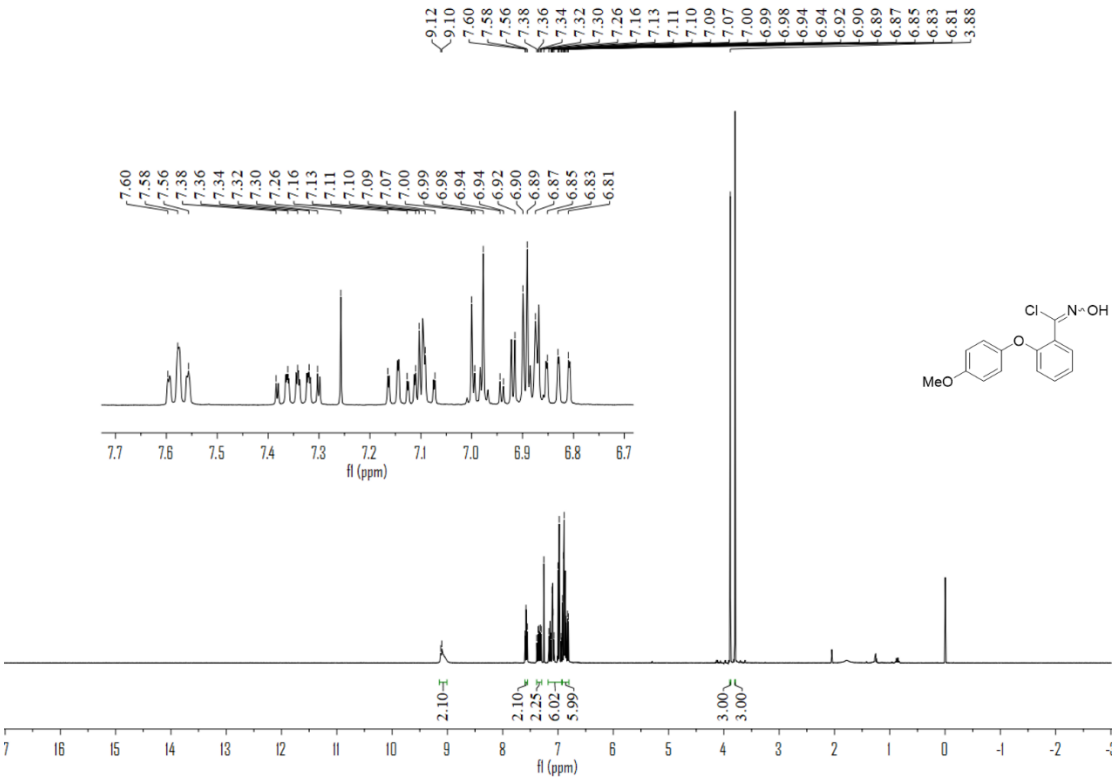

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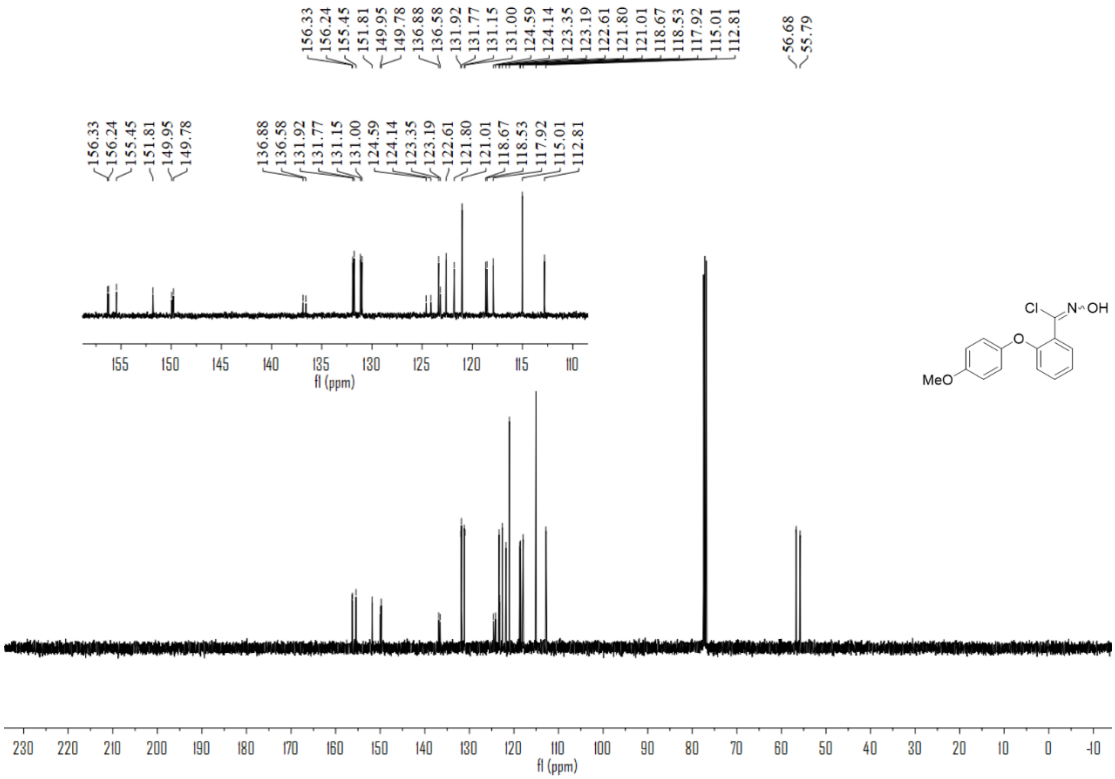

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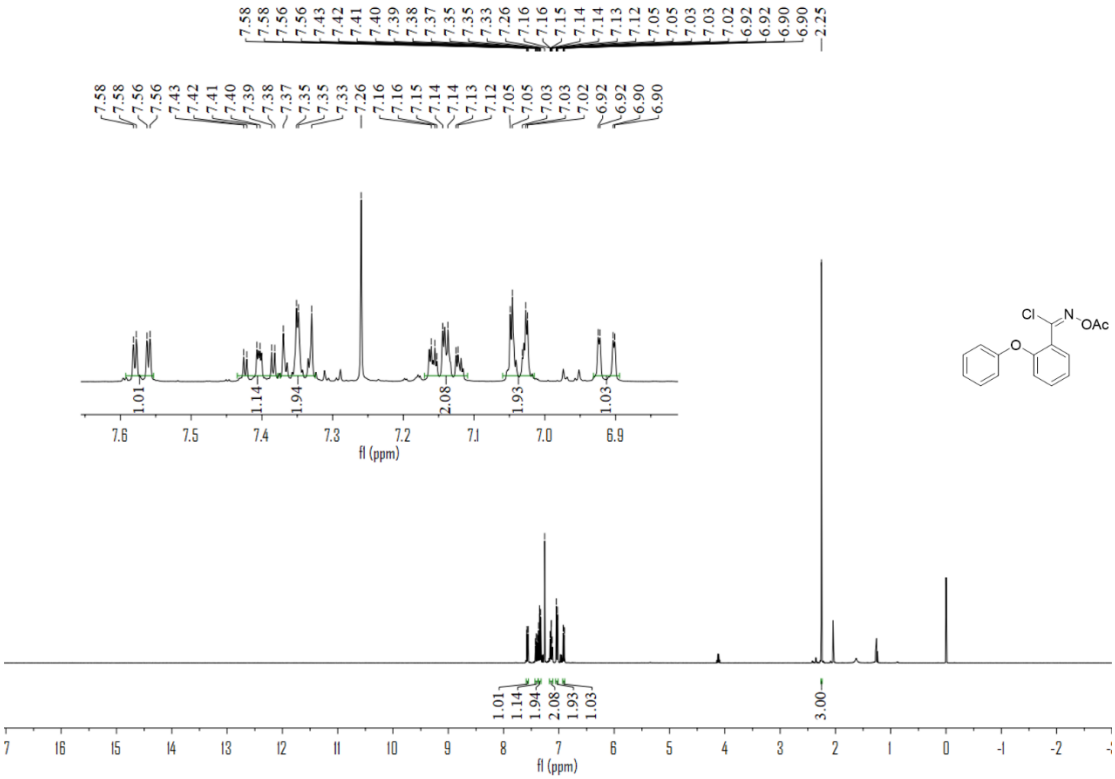

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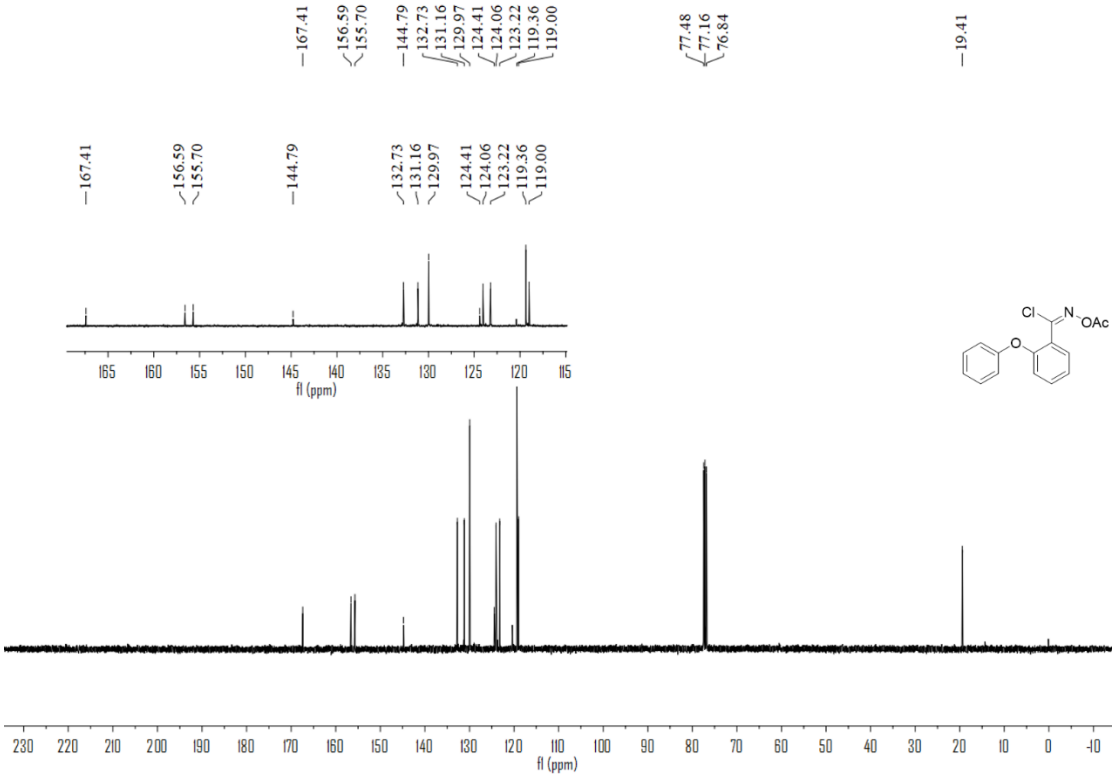

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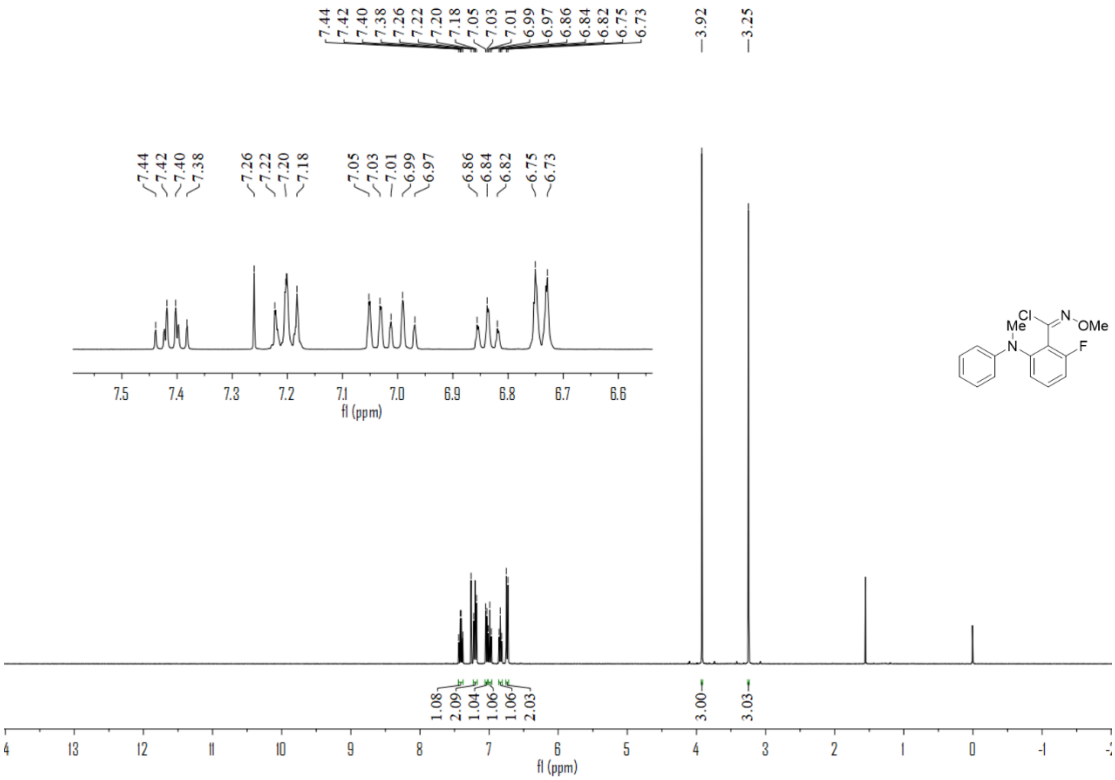

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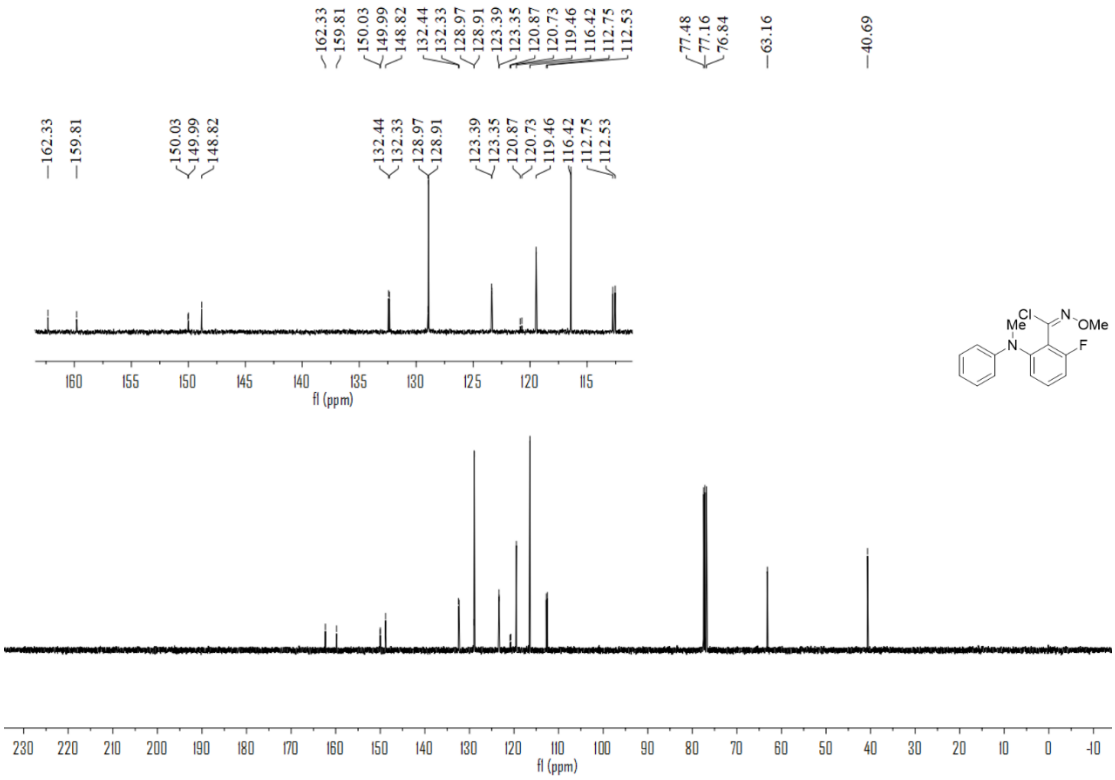
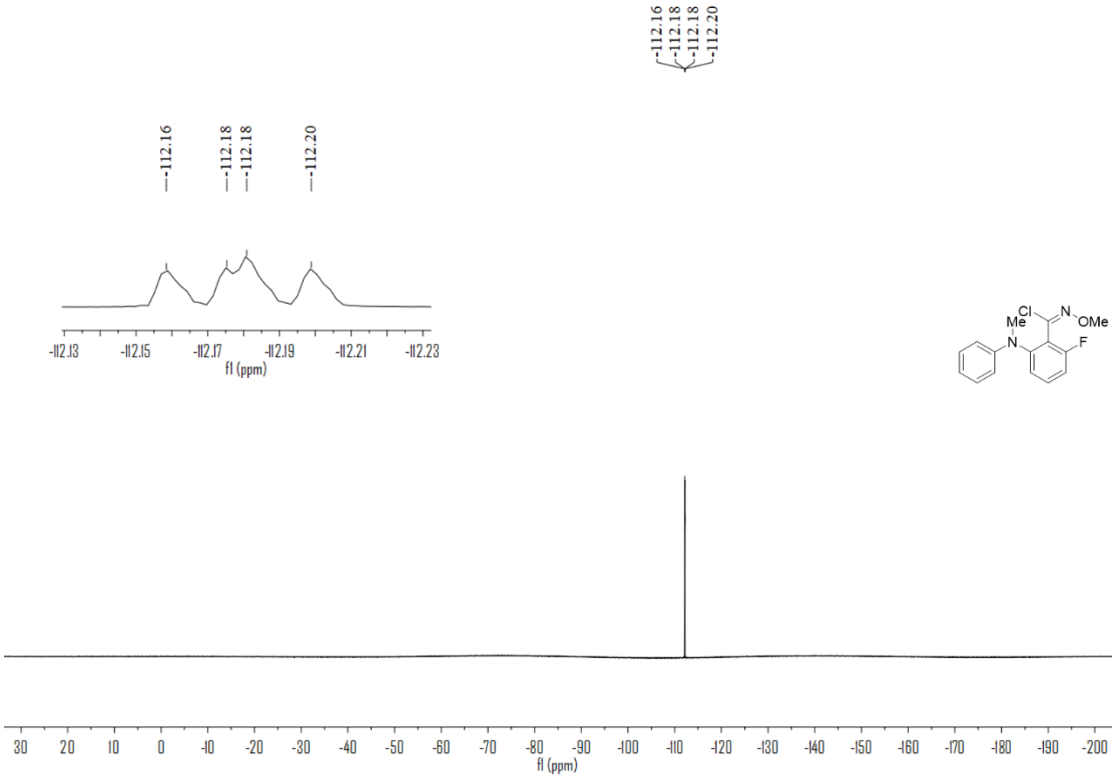


^{19}F NMR spectra of **4a** ($CDCl_3$)



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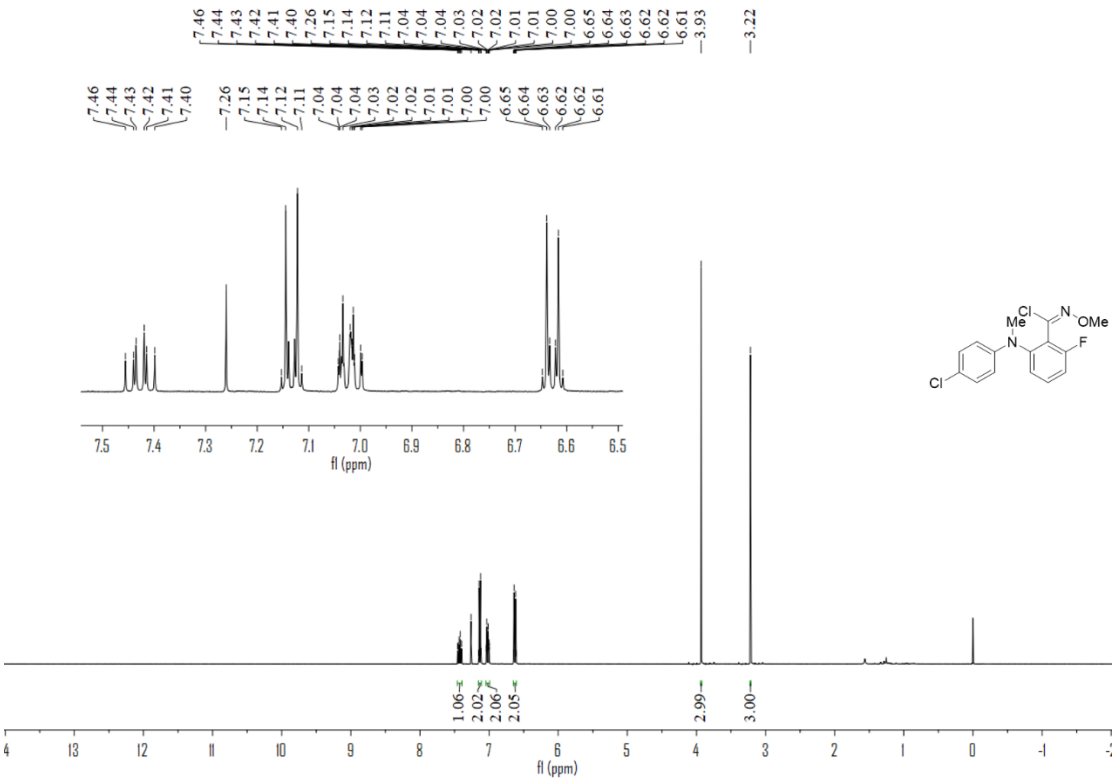

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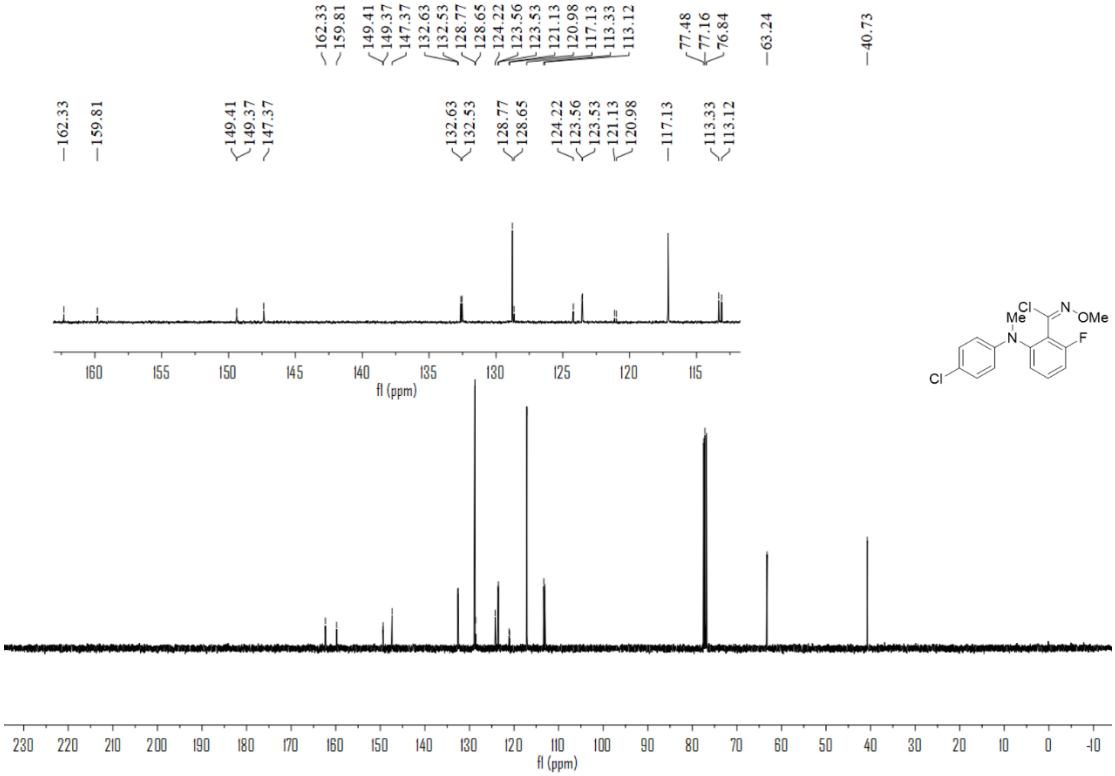

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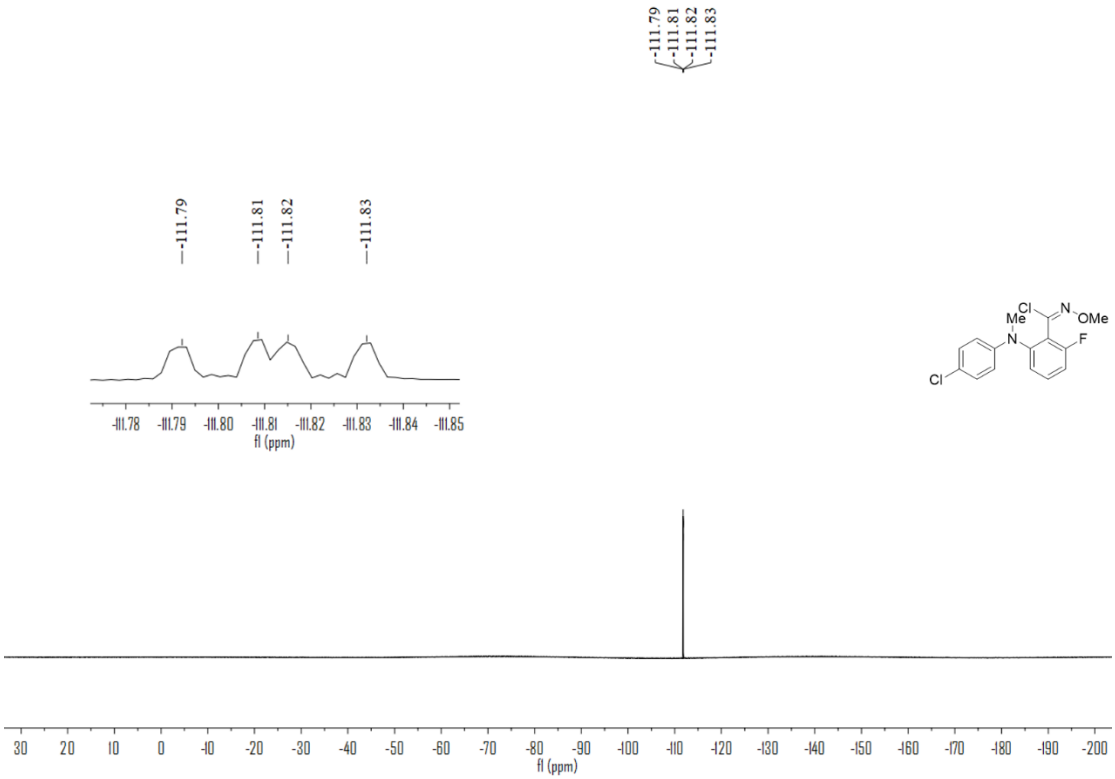

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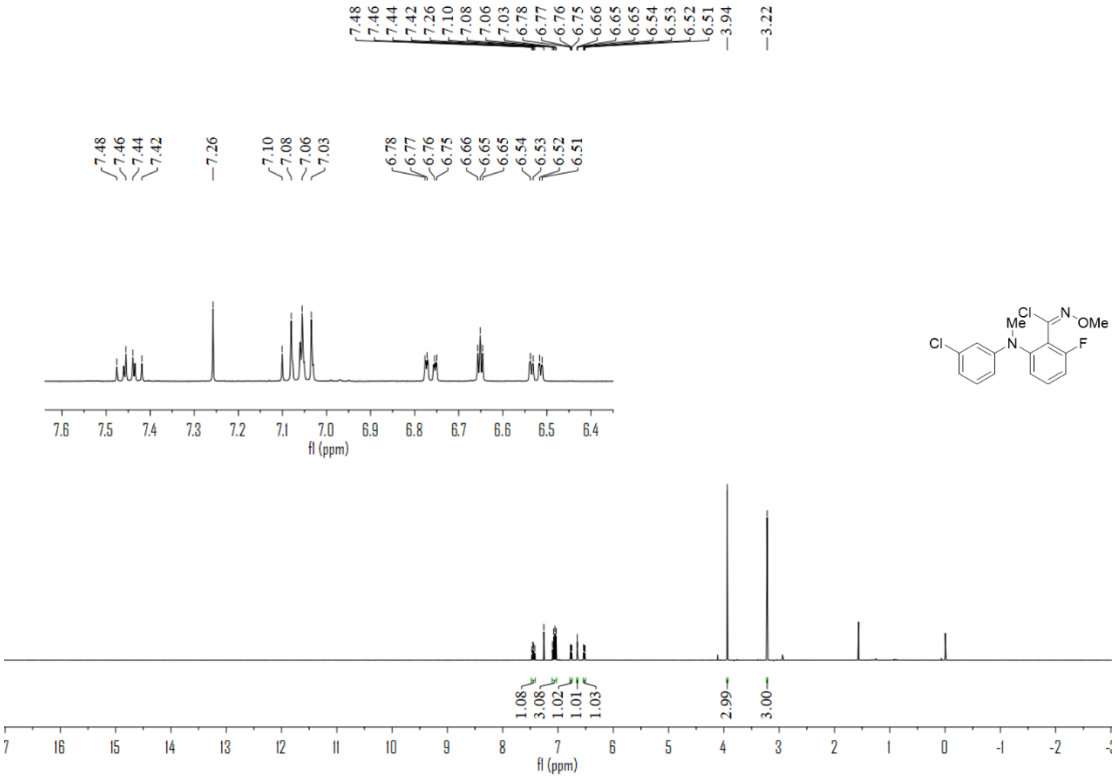

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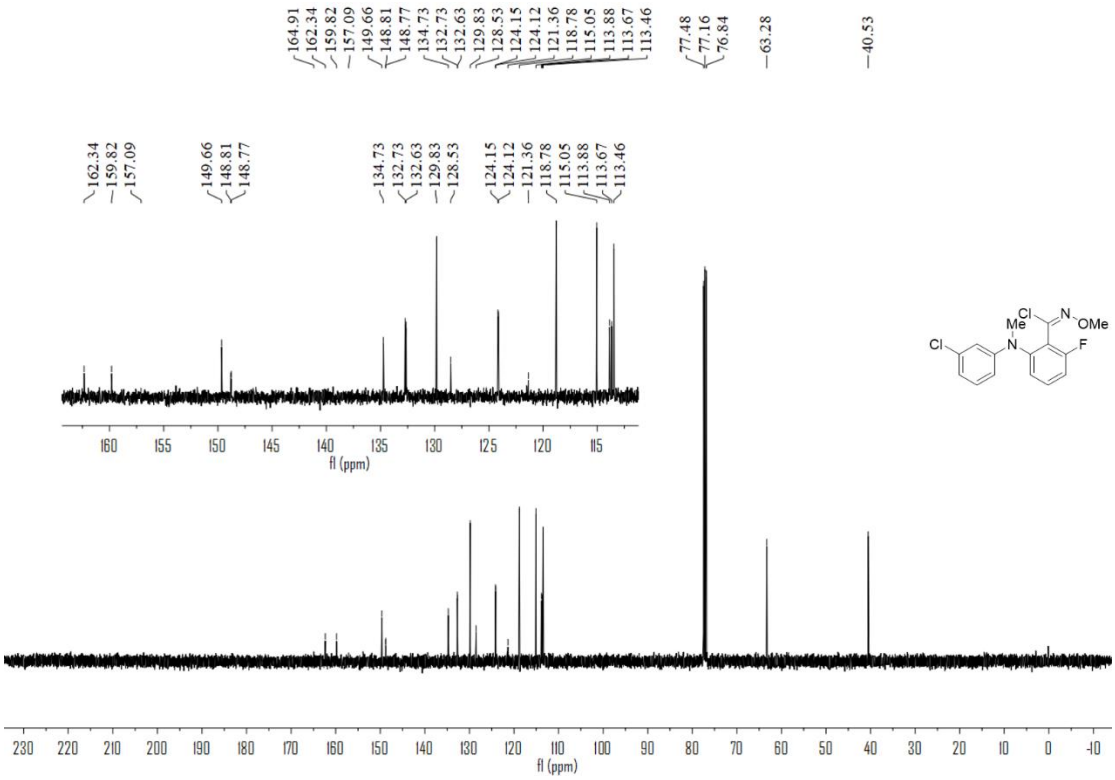

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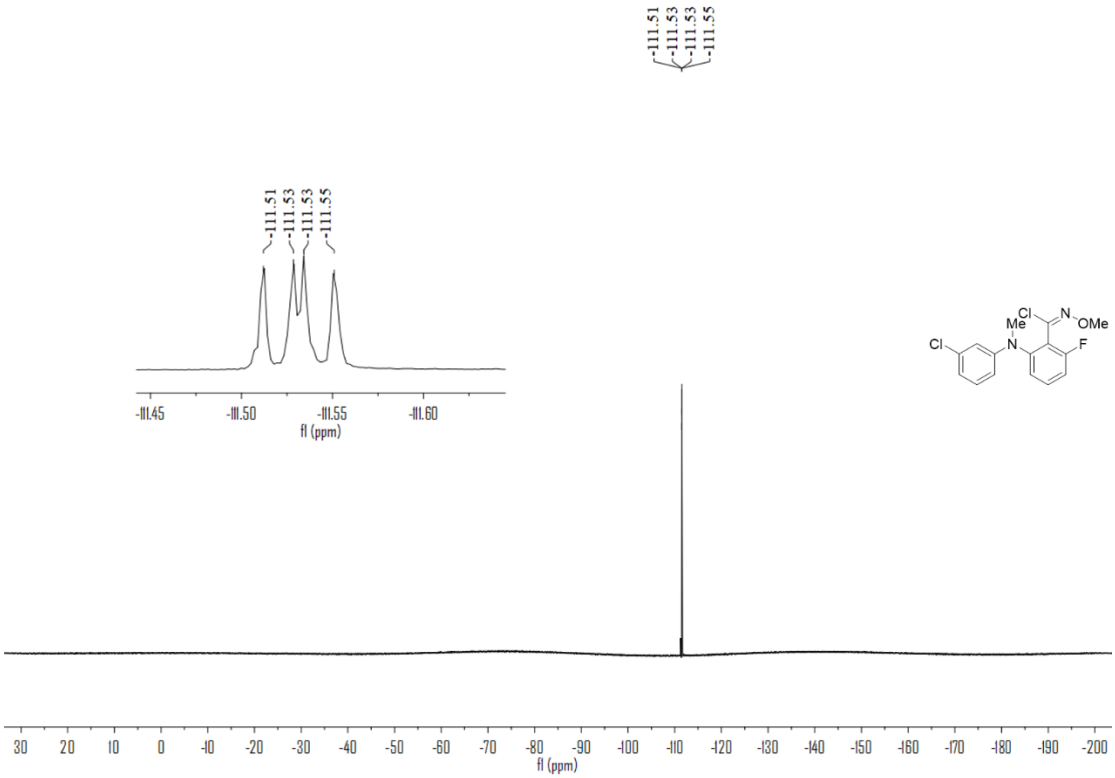

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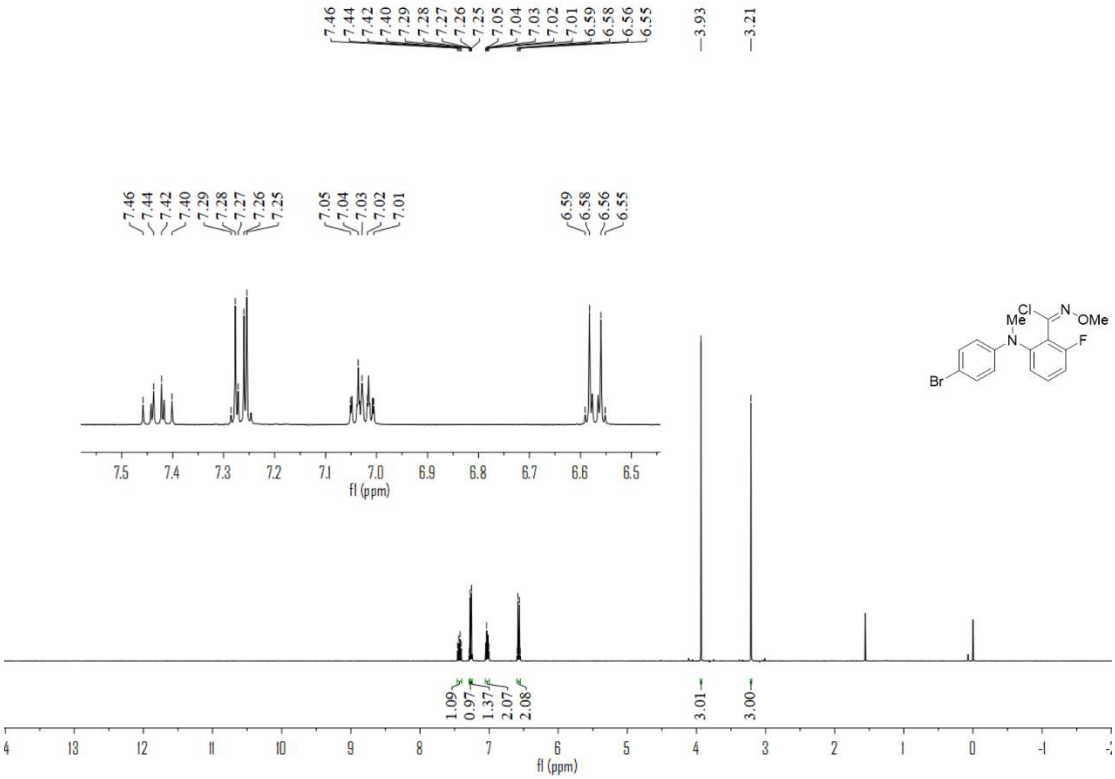

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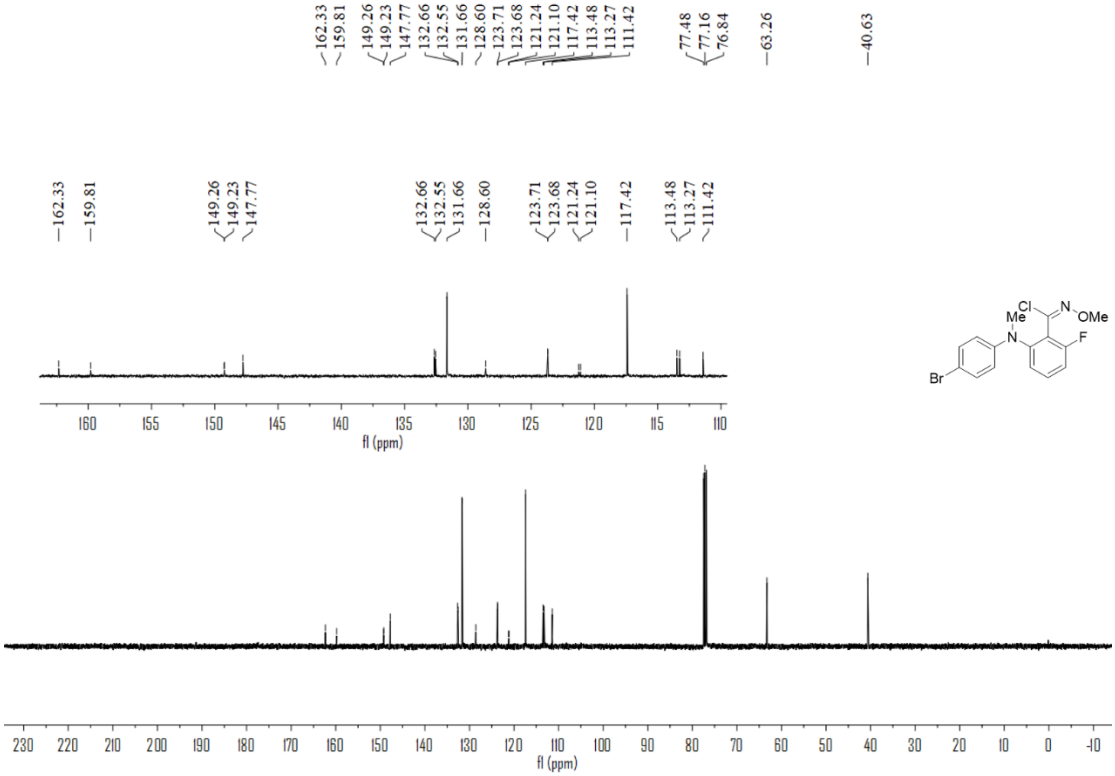

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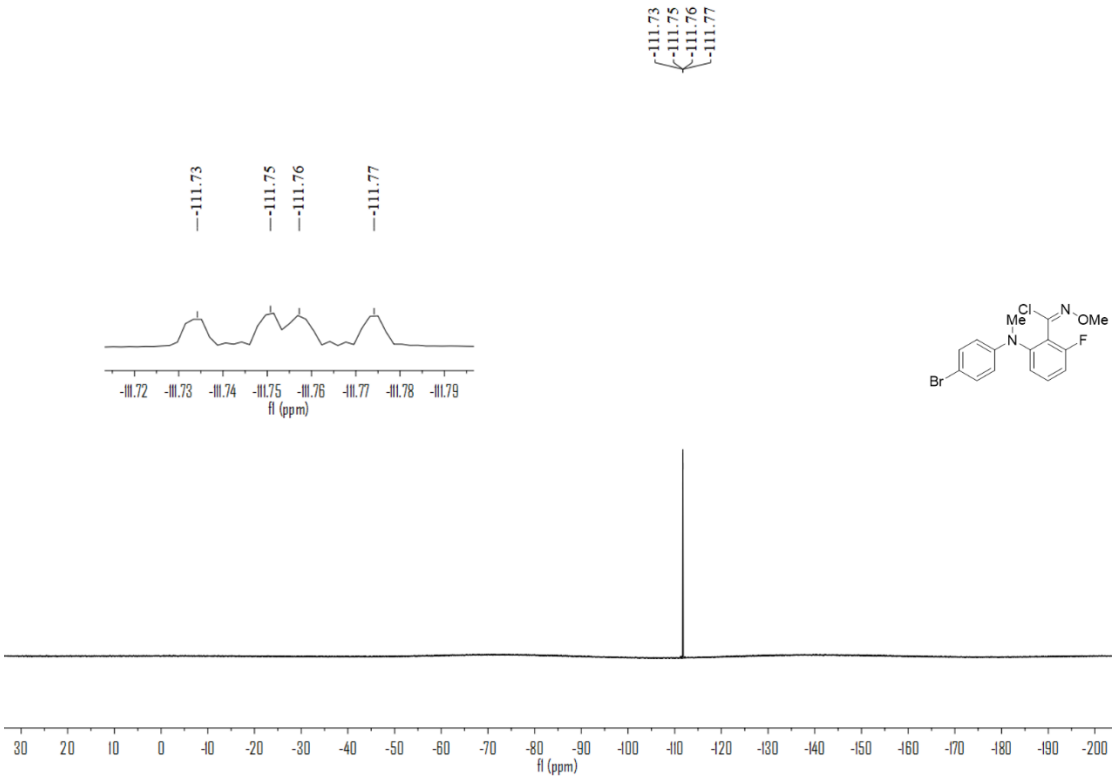

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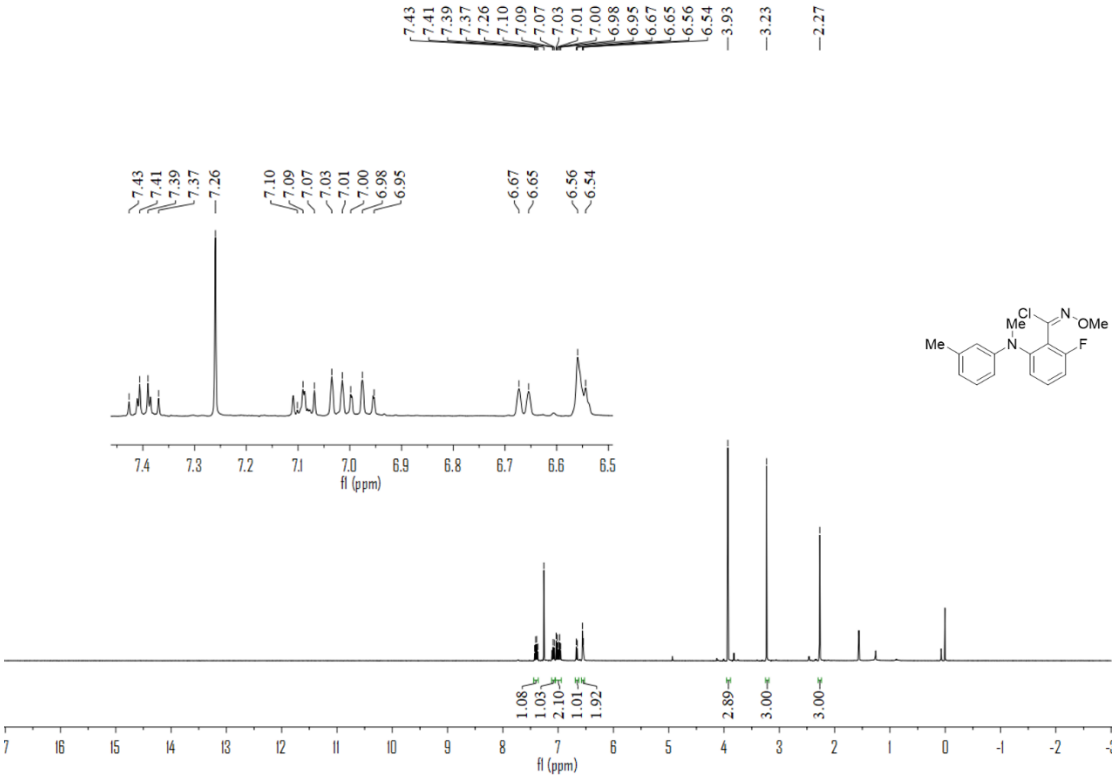

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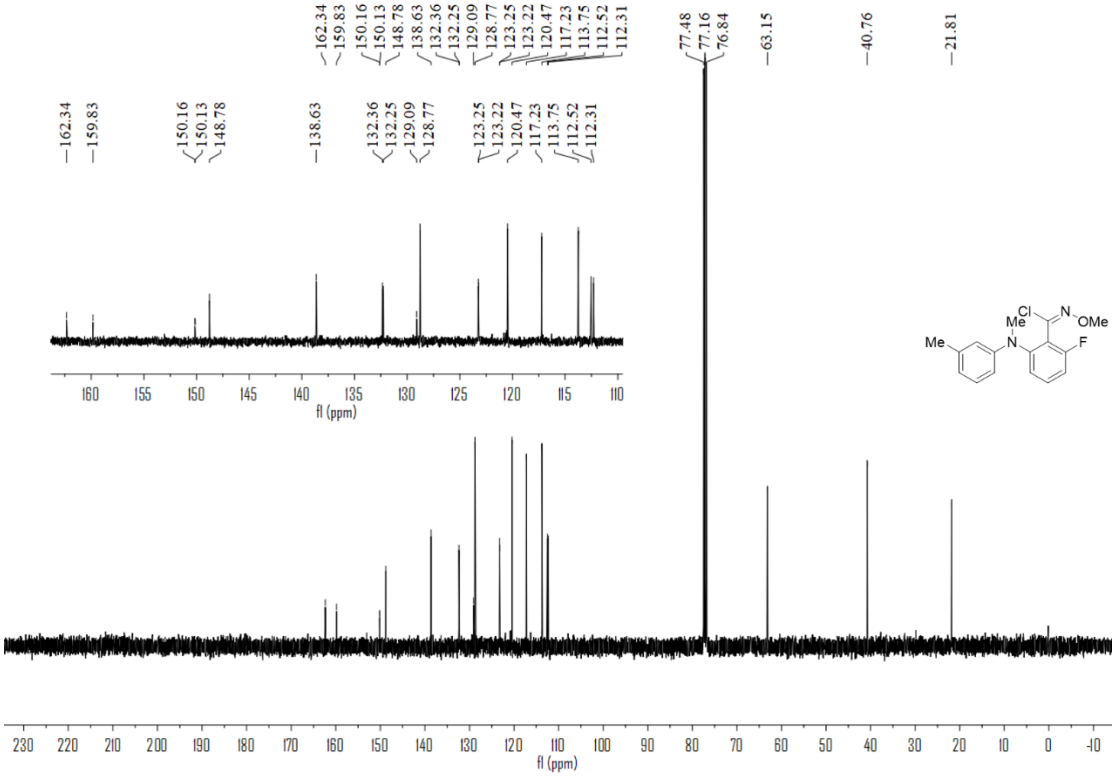

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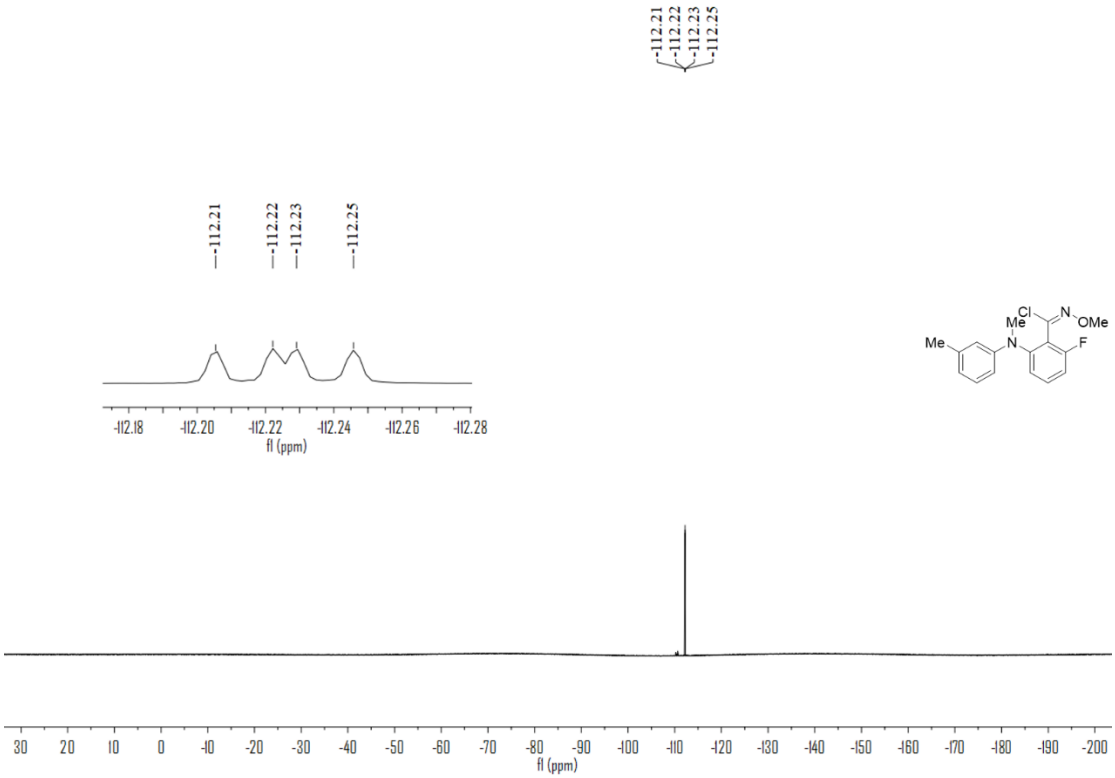

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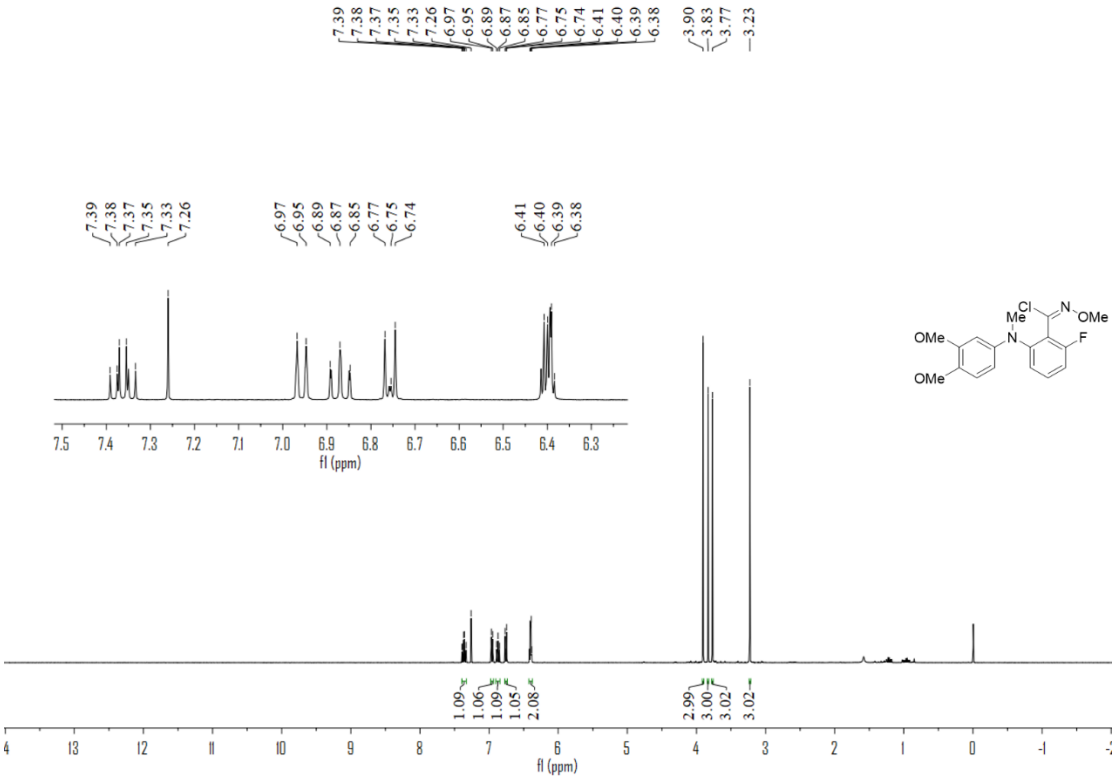

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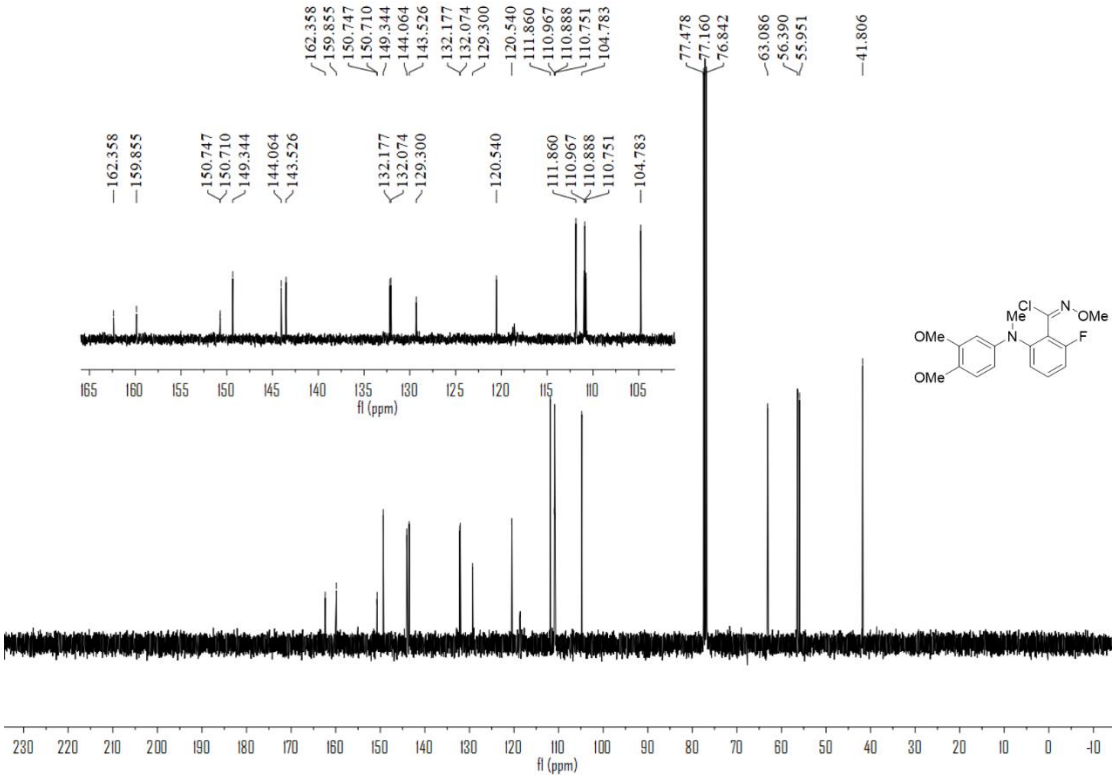

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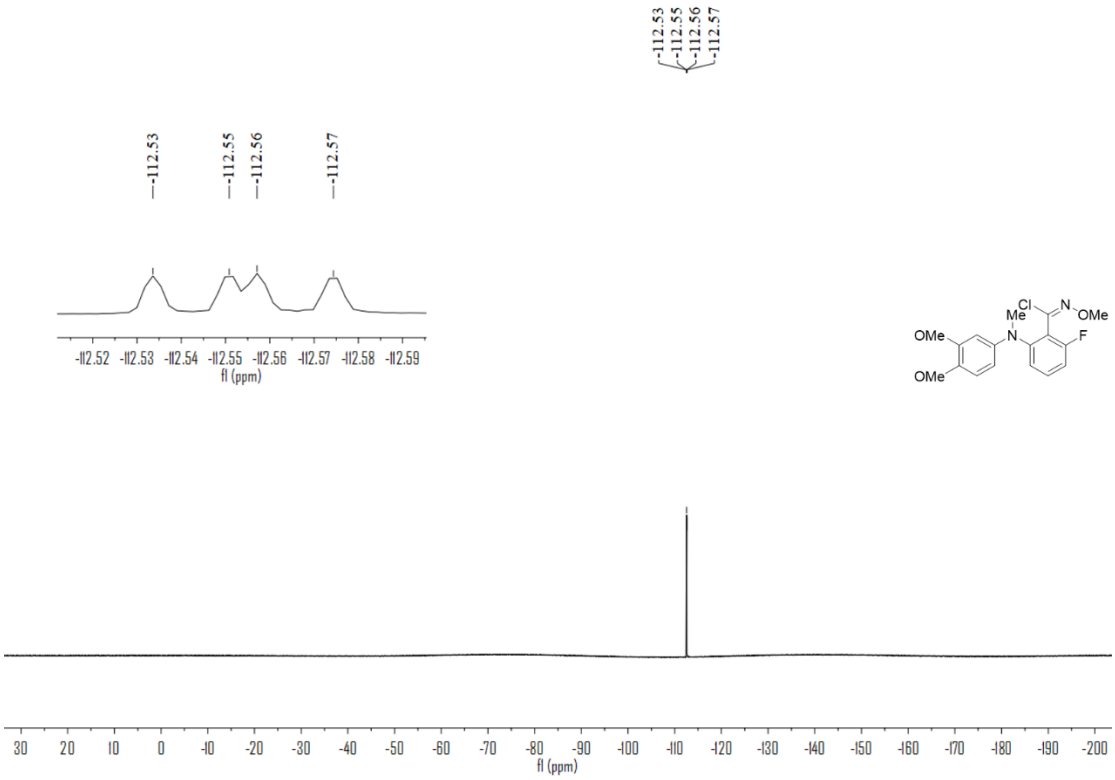
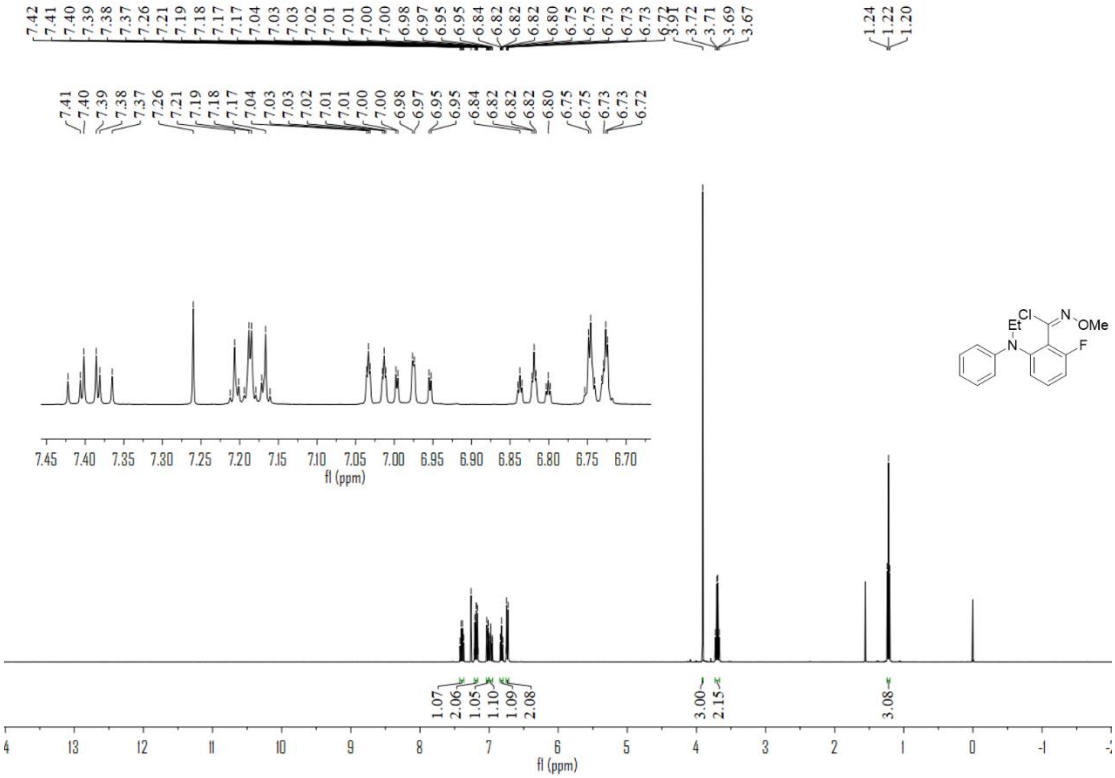
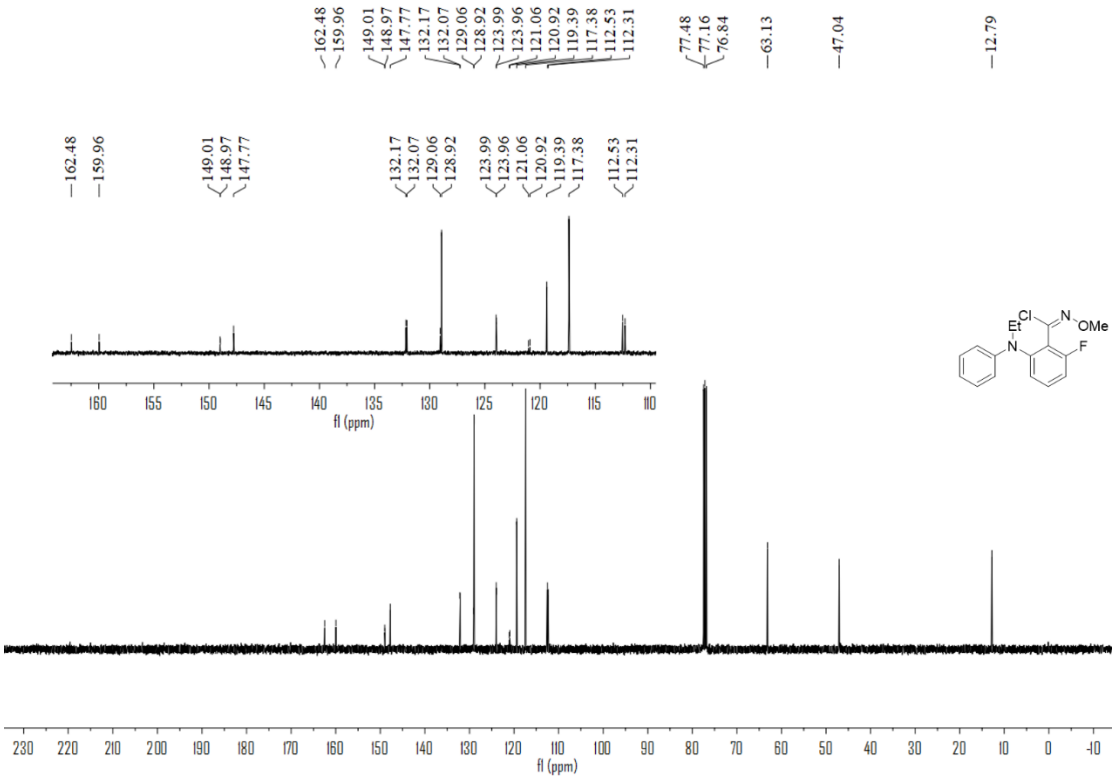


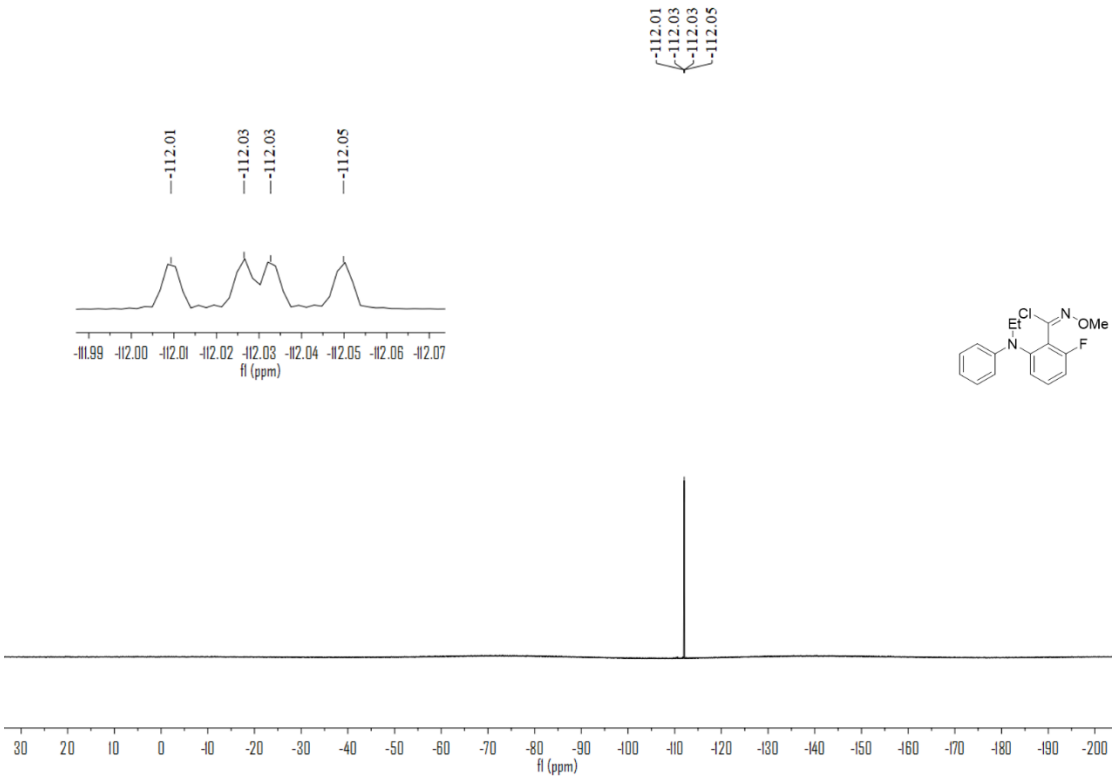
^{1}H NMR spectra of **4g** ($CDCl_3$)



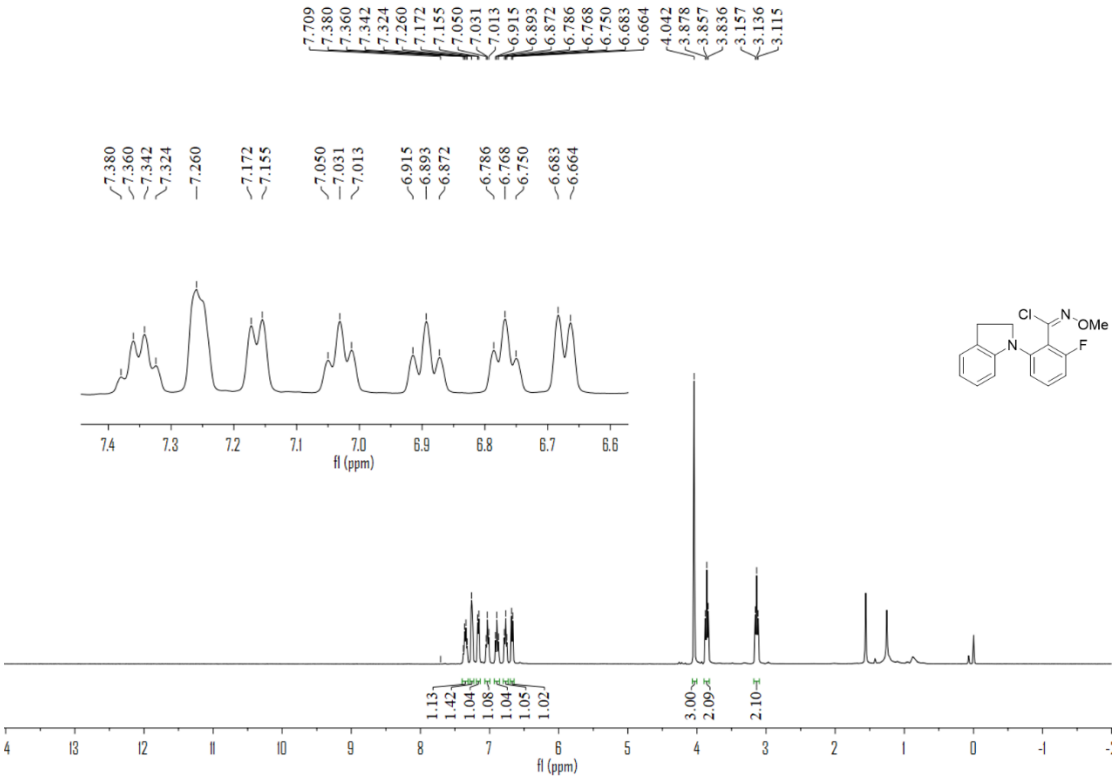
^{13}C NMR spectra of **4g** ($CDCl_3$)



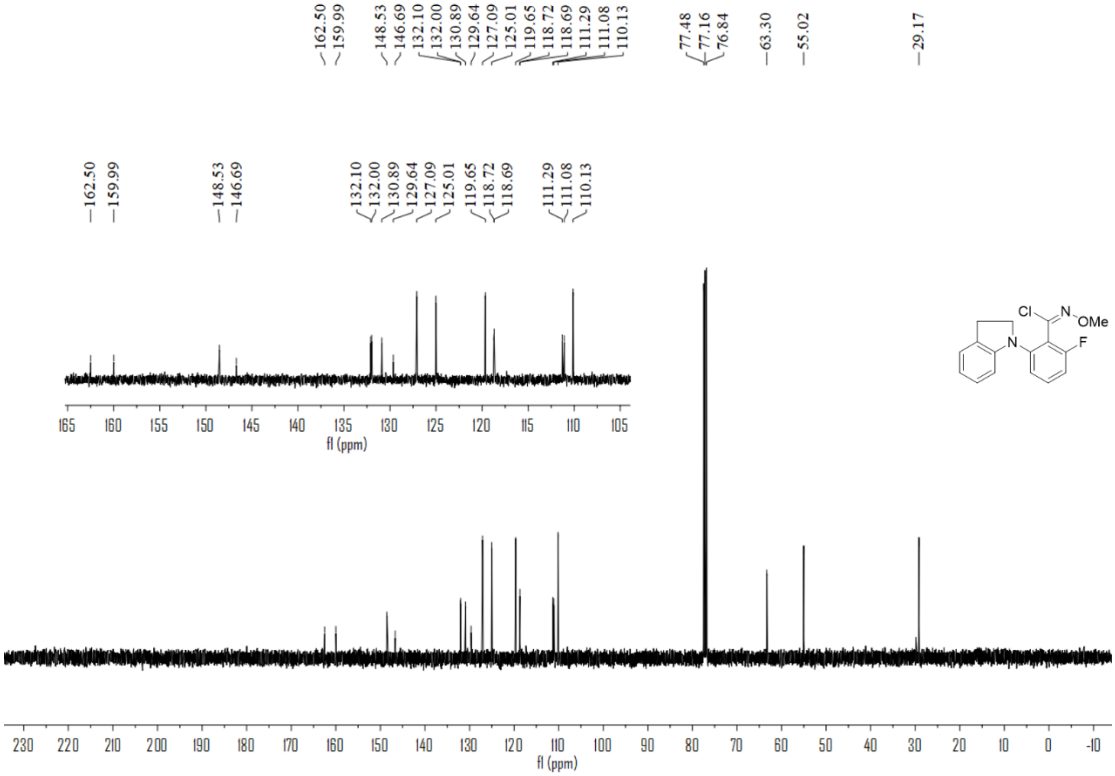
^{19}F NMR spectra of **4g** ($CDCl_3$)



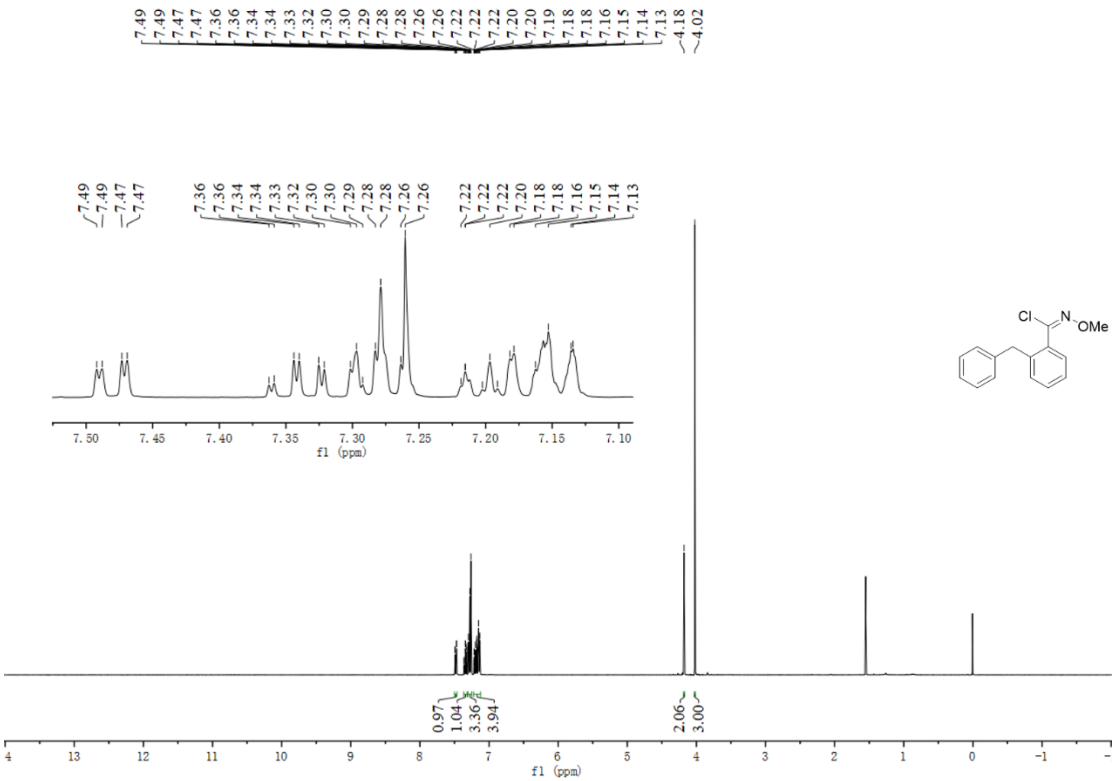
^{1}H NMR spectra of **4h** ($CDCl_3$)



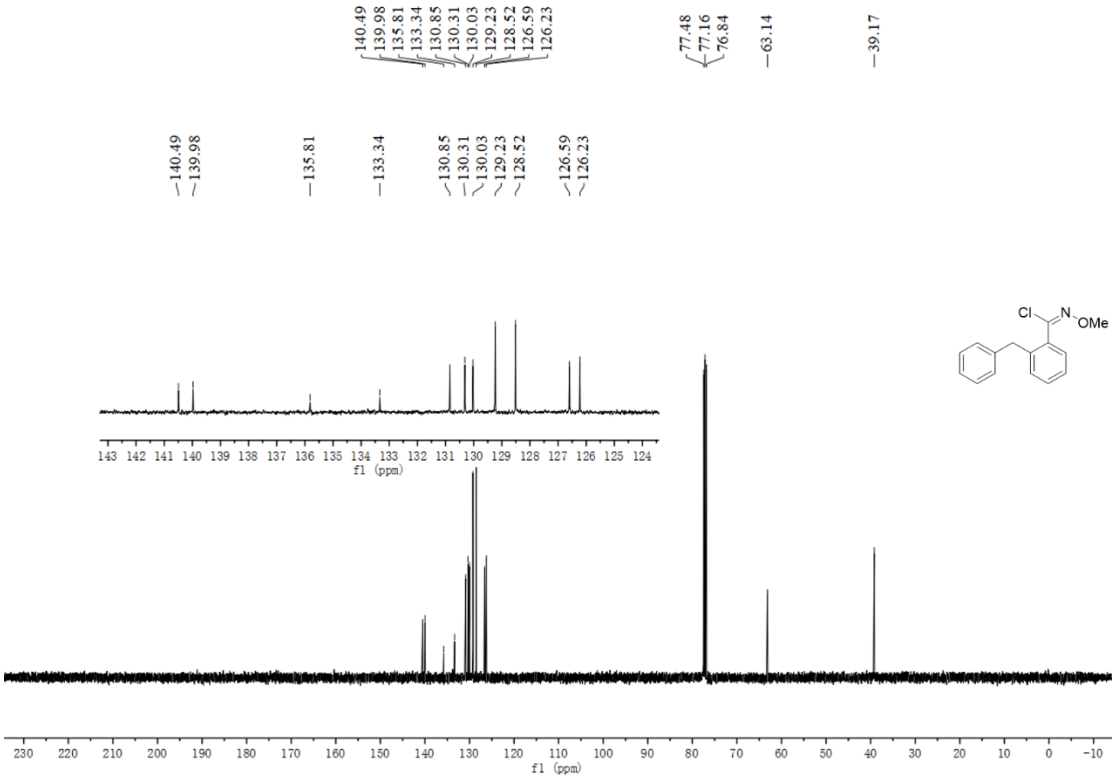
^{13}C NMR spectra of **4h** ($CDCl_3$)



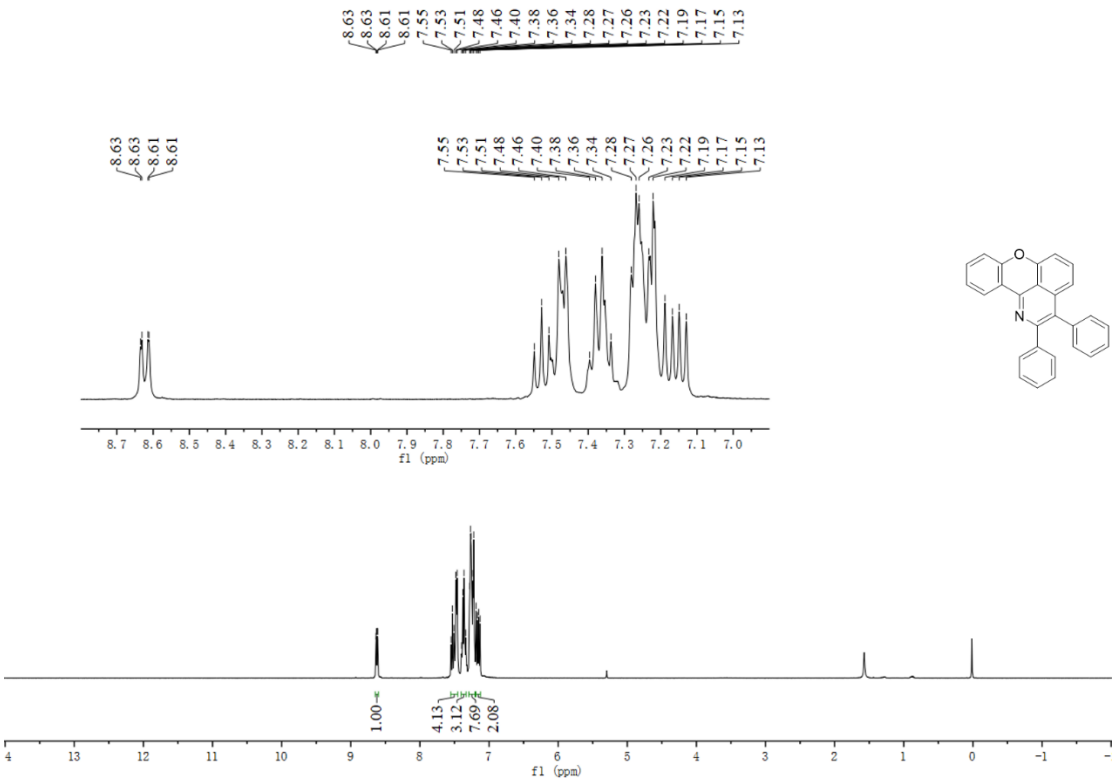
^{1}H NMR spectra of **6** ($CDCl_3$)



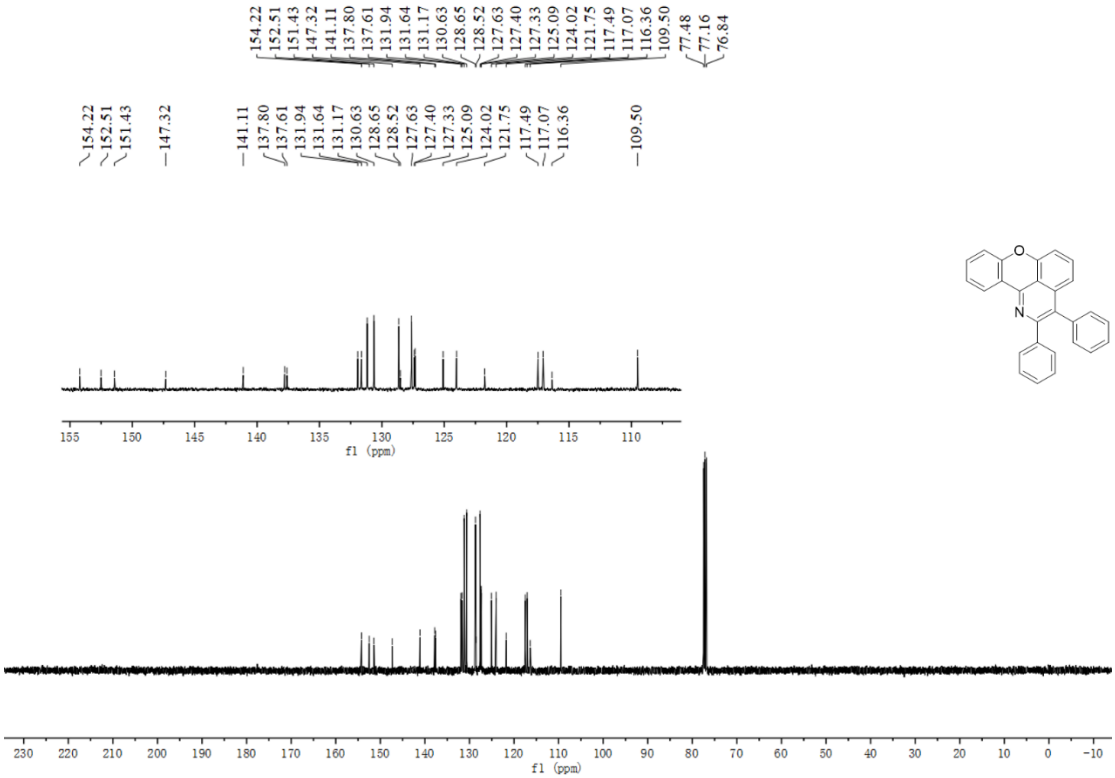
^{13}C NMR spectra of **6** ($CDCl_3$)



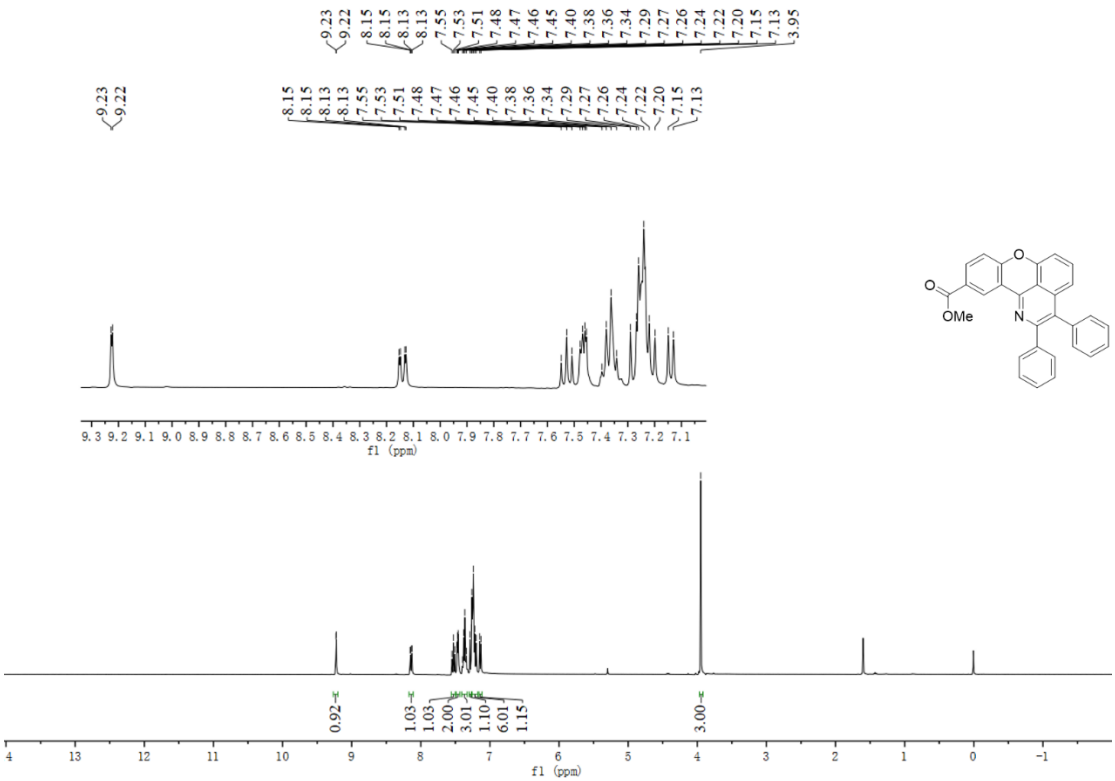
^{1}H NMR spectra of **3a** ($CDCl_3$)



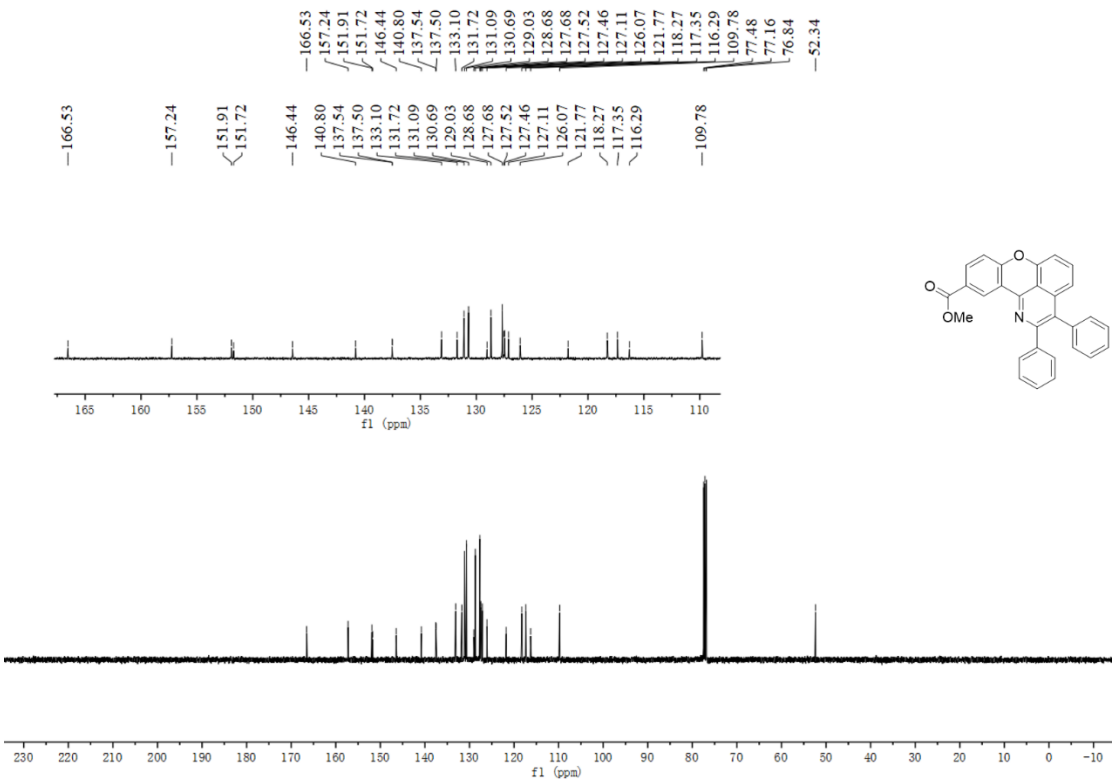
^{13}C NMR spectra of **3a** ($CDCl_3$)



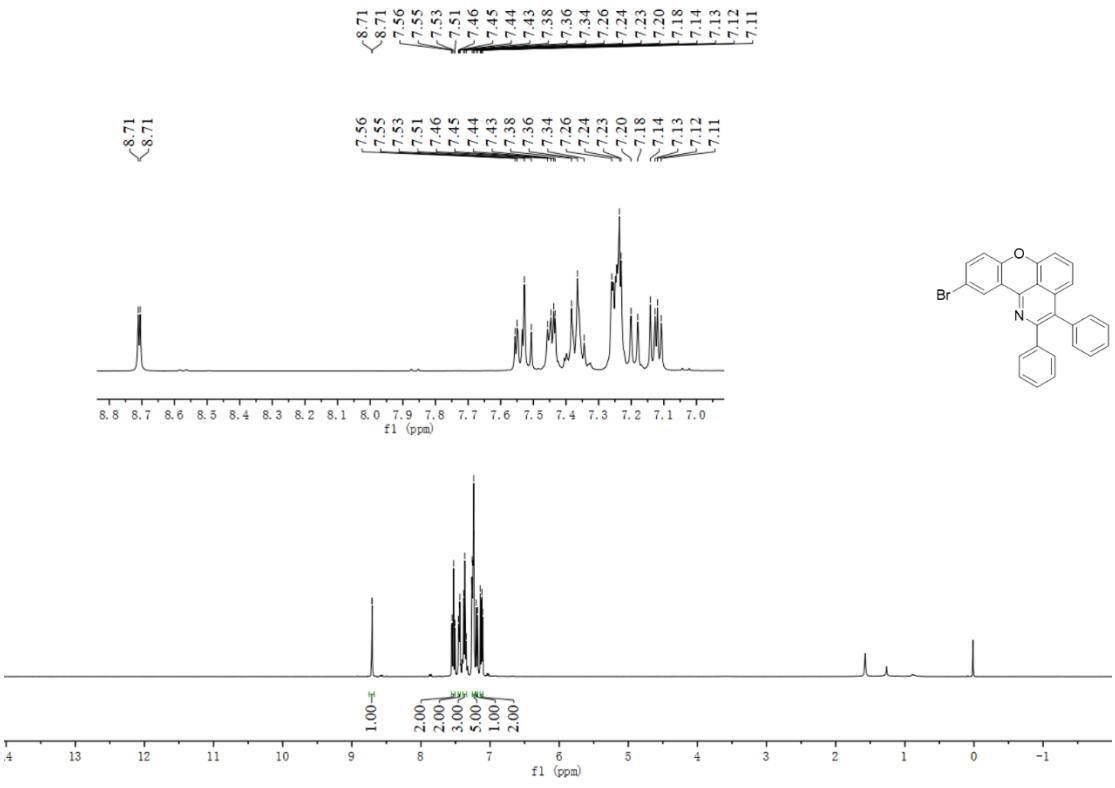
^{1}H NMR spectra of **3b** ($CDCl_3$)



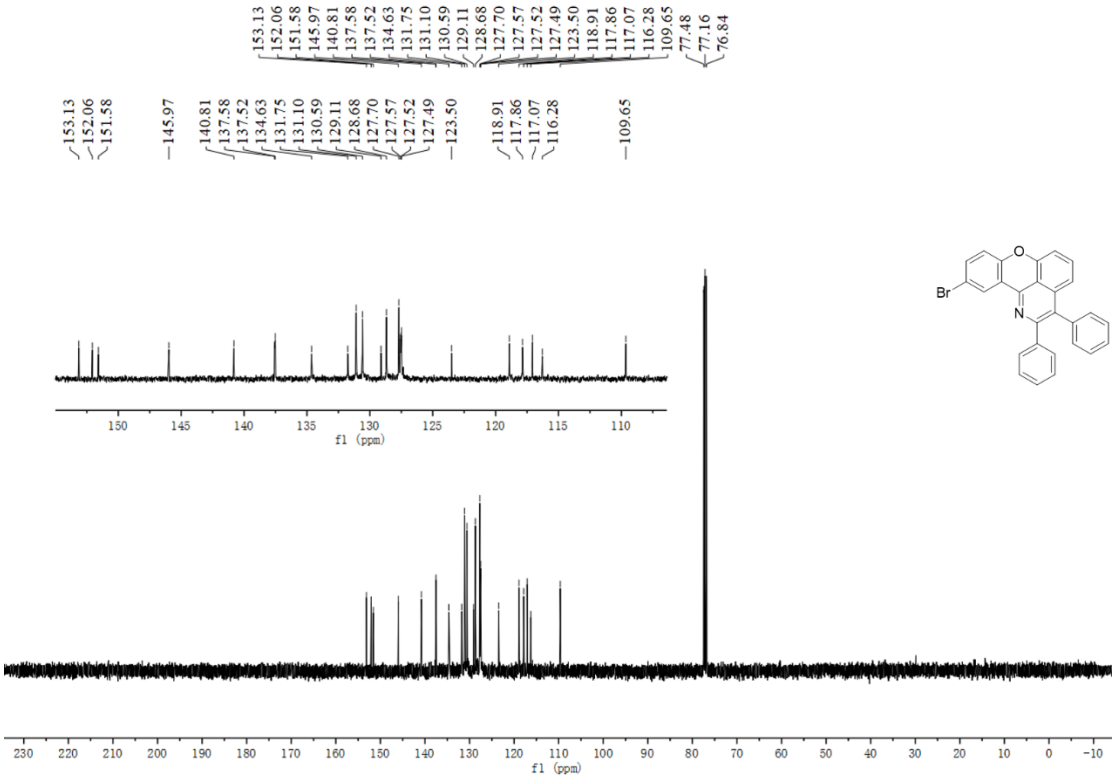
^{13}C NMR spectra of **3b** ($CDCl_3$)



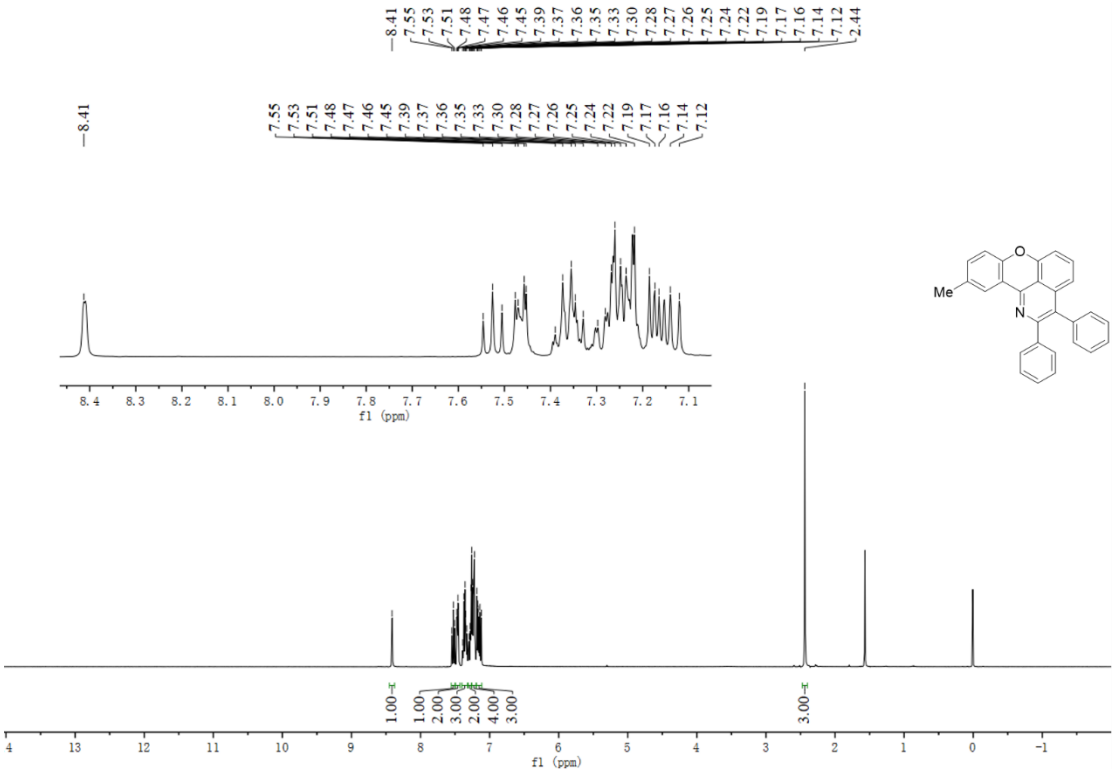
^{1}H NMR spectra of **3c** ($CDCl_3$)



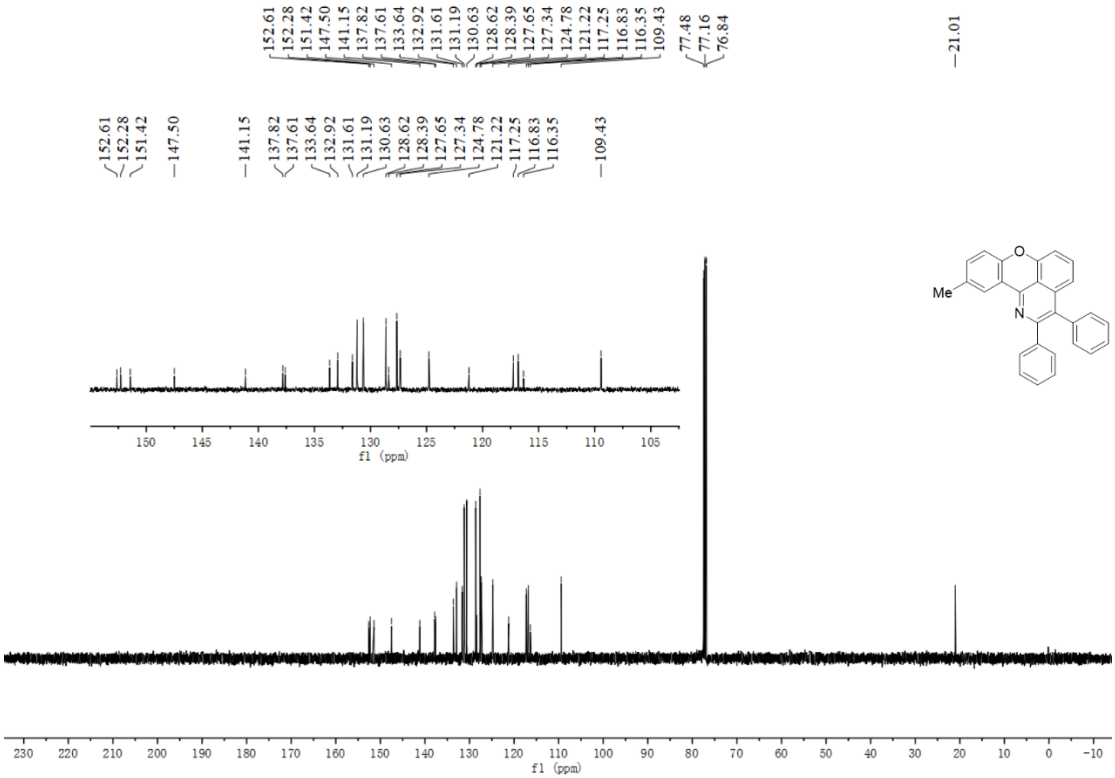
^{13}C NMR spectra of **3c** ($CDCl_3$)



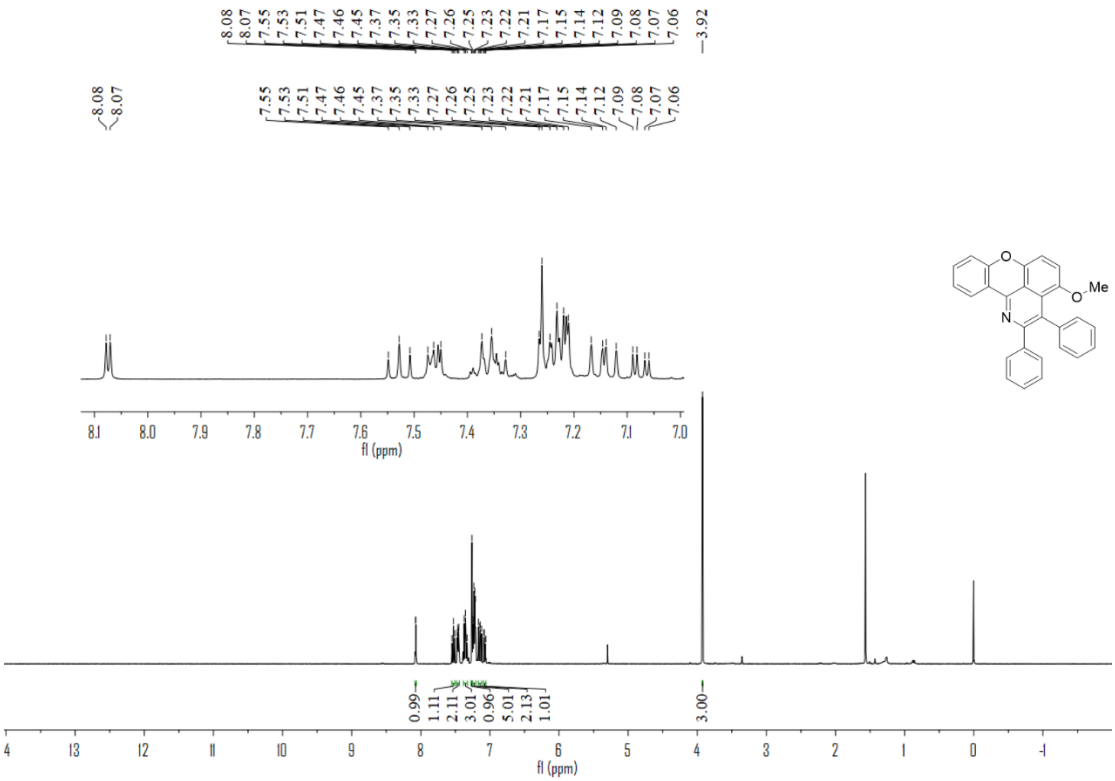
^{1}H NMR spectra of **3d** ($CDCl_3$)



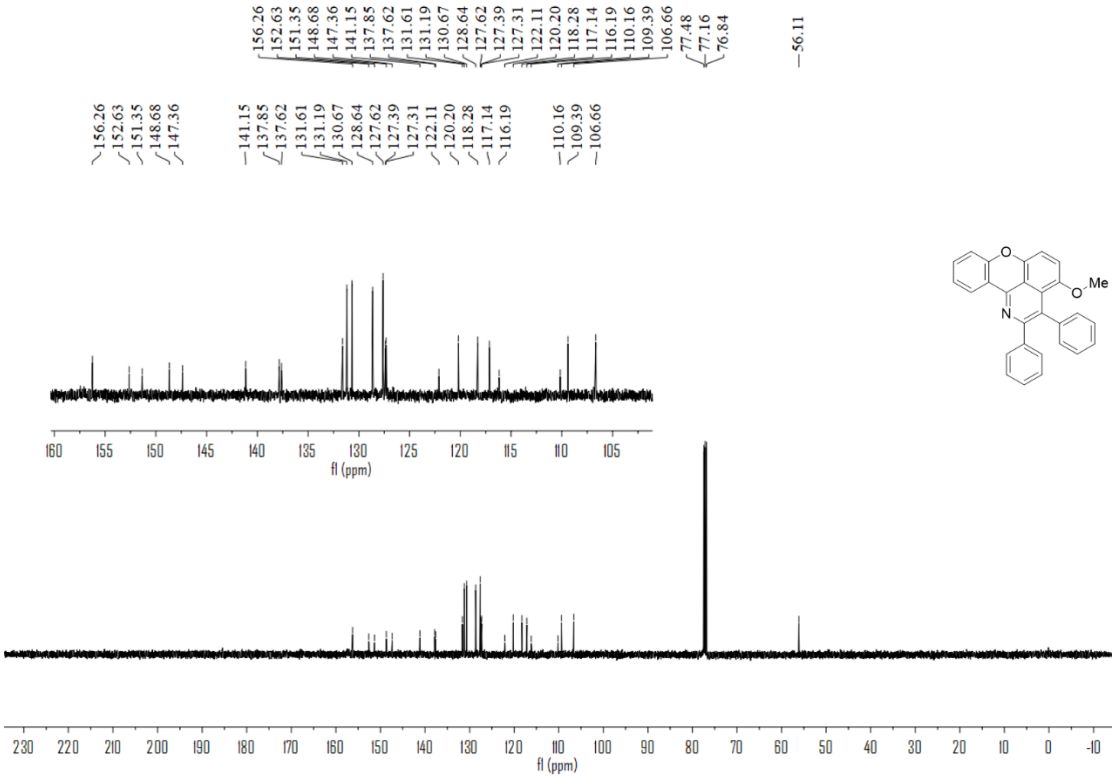
^{13}C NMR spectra of **3d** ($CDCl_3$)



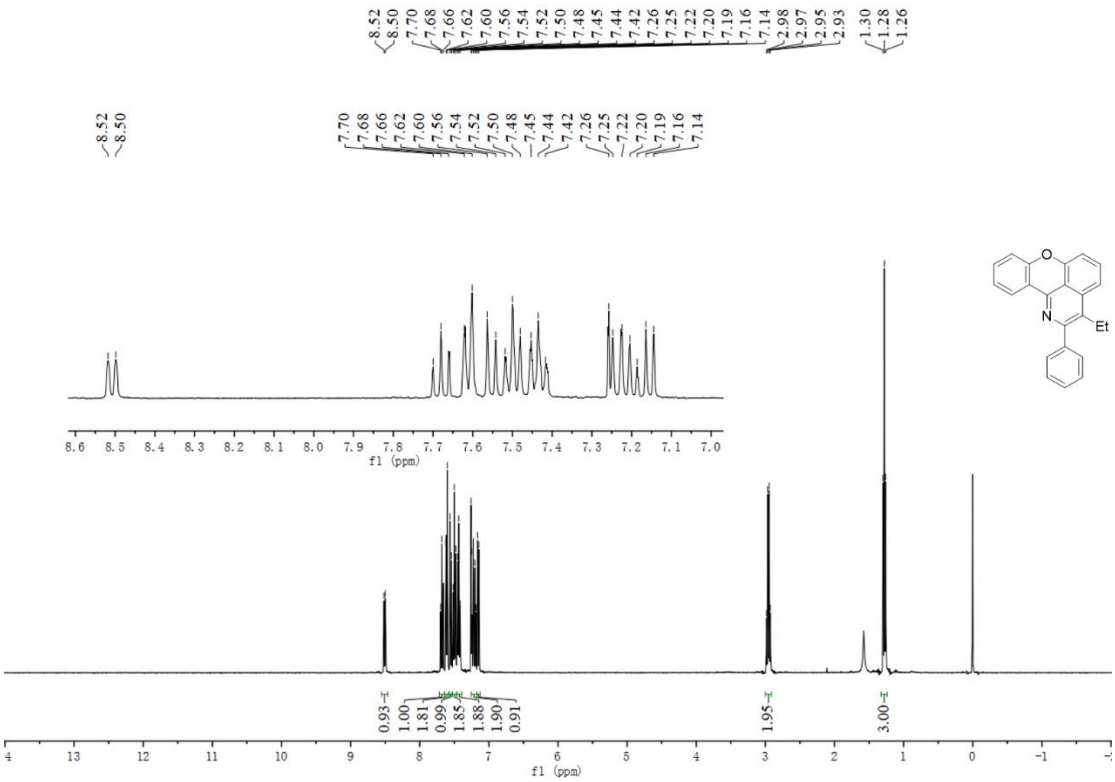
^{1}H NMR spectra of **3e** ($CDCl_3$)



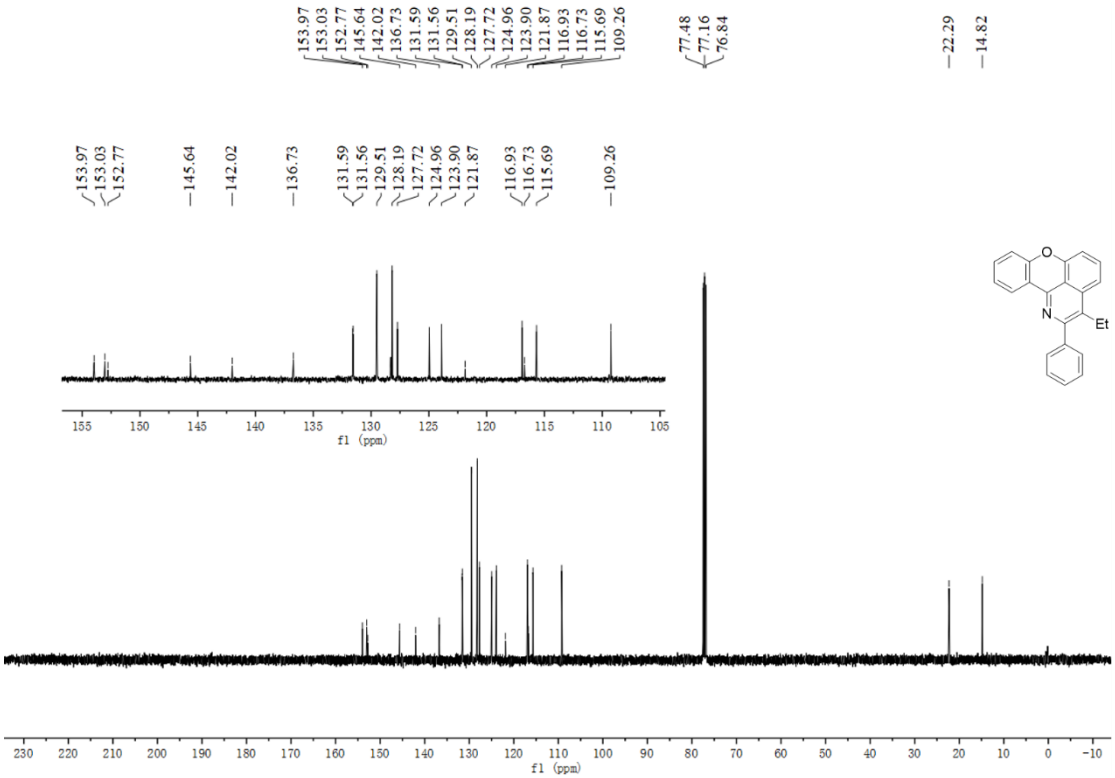
^{13}C NMR spectra of **3e** ($CDCl_3$)



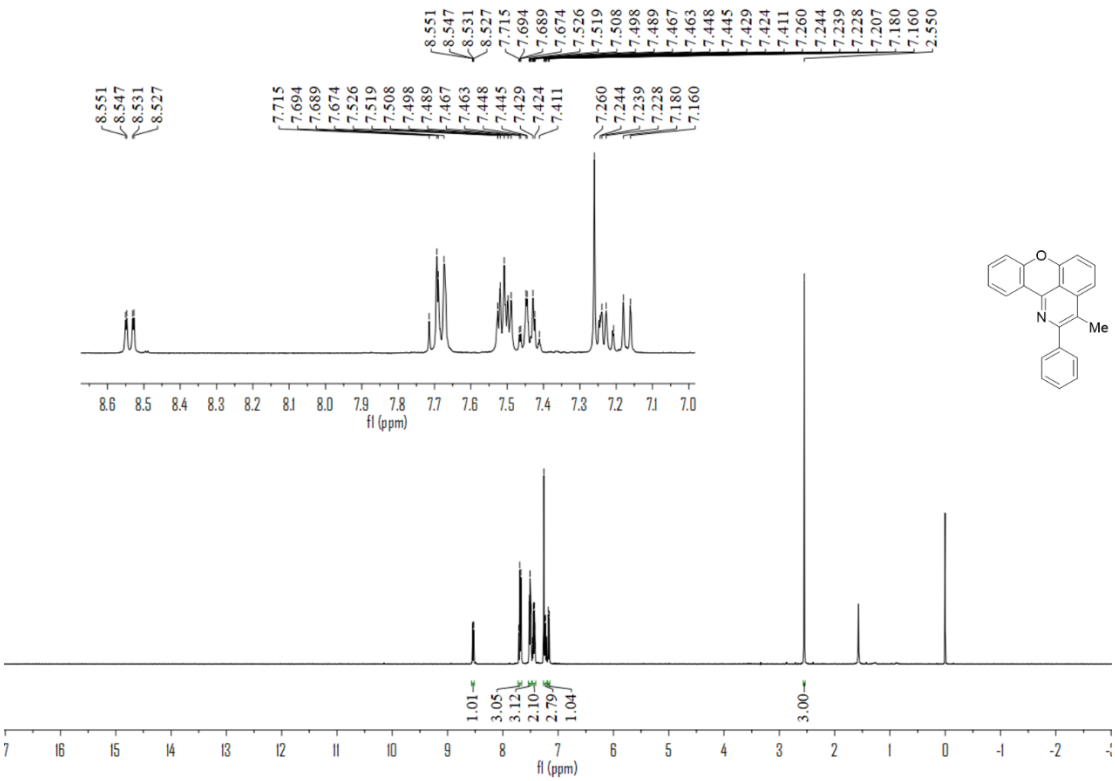
^{1}H NMR spectra of **3f** ($CDCl_3$)



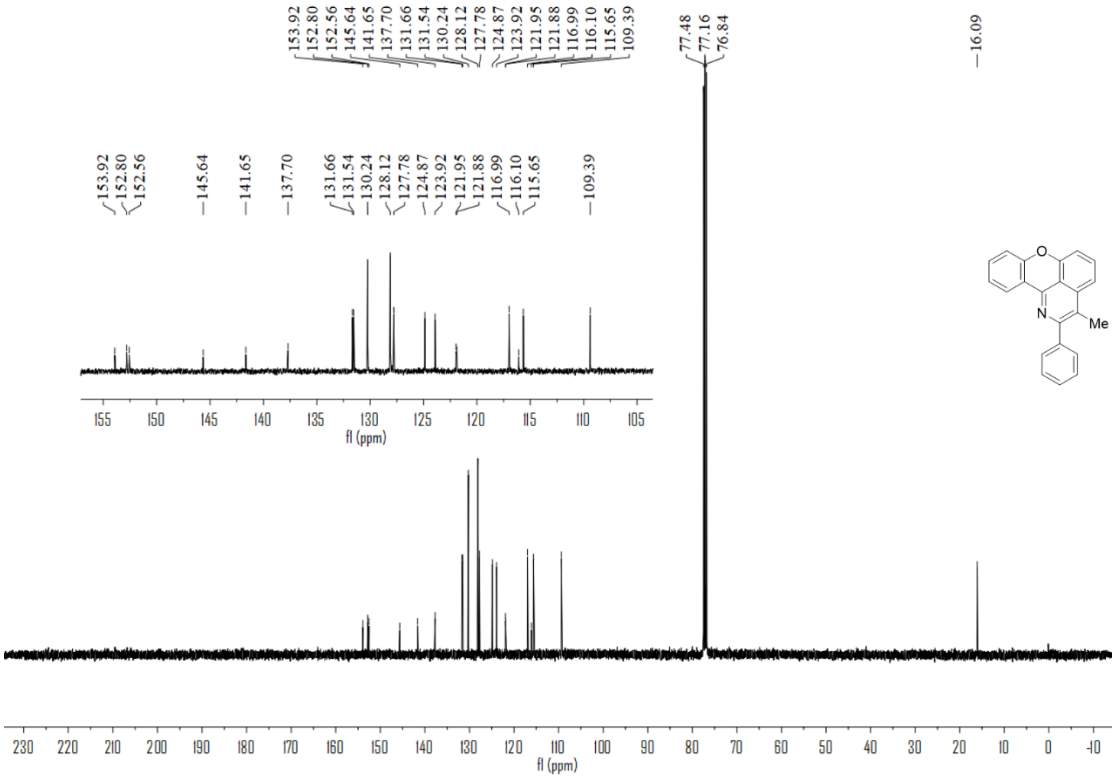
^{13}C NMR spectra of **3f** ($CDCl_3$)



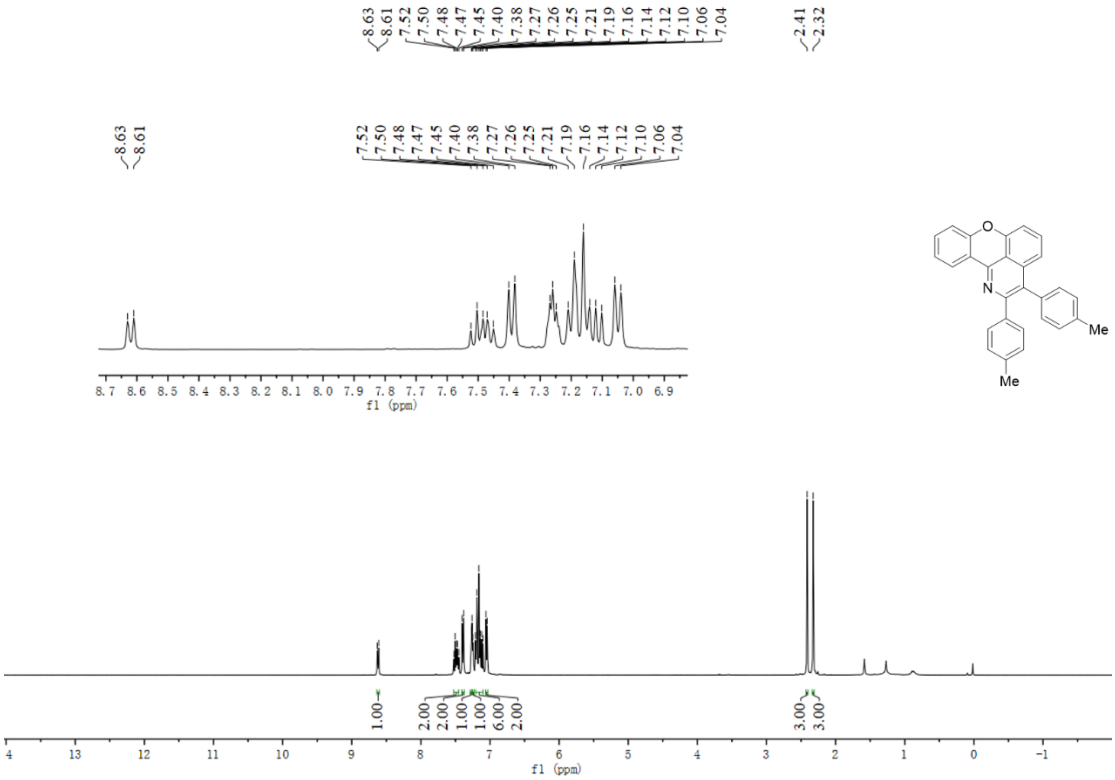
^{1}H NMR spectra of **3g** ($CDCl_3$)



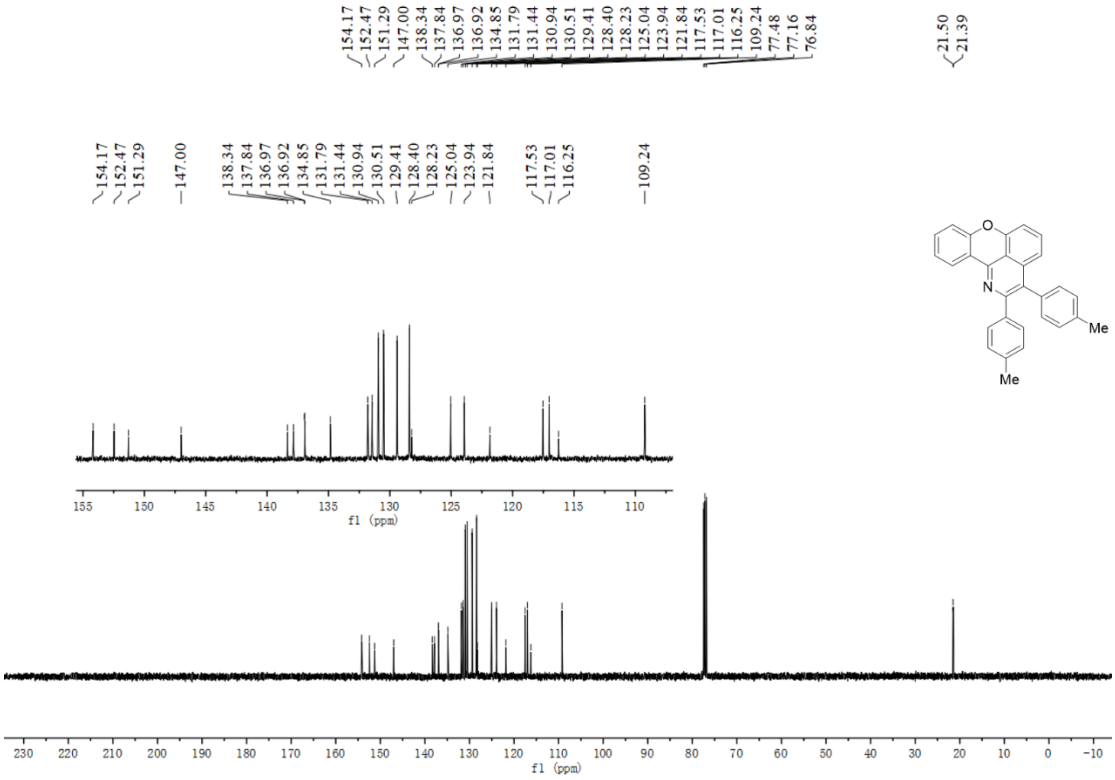
^{13}C NMR spectra of **3g** ($CDCl_3$)



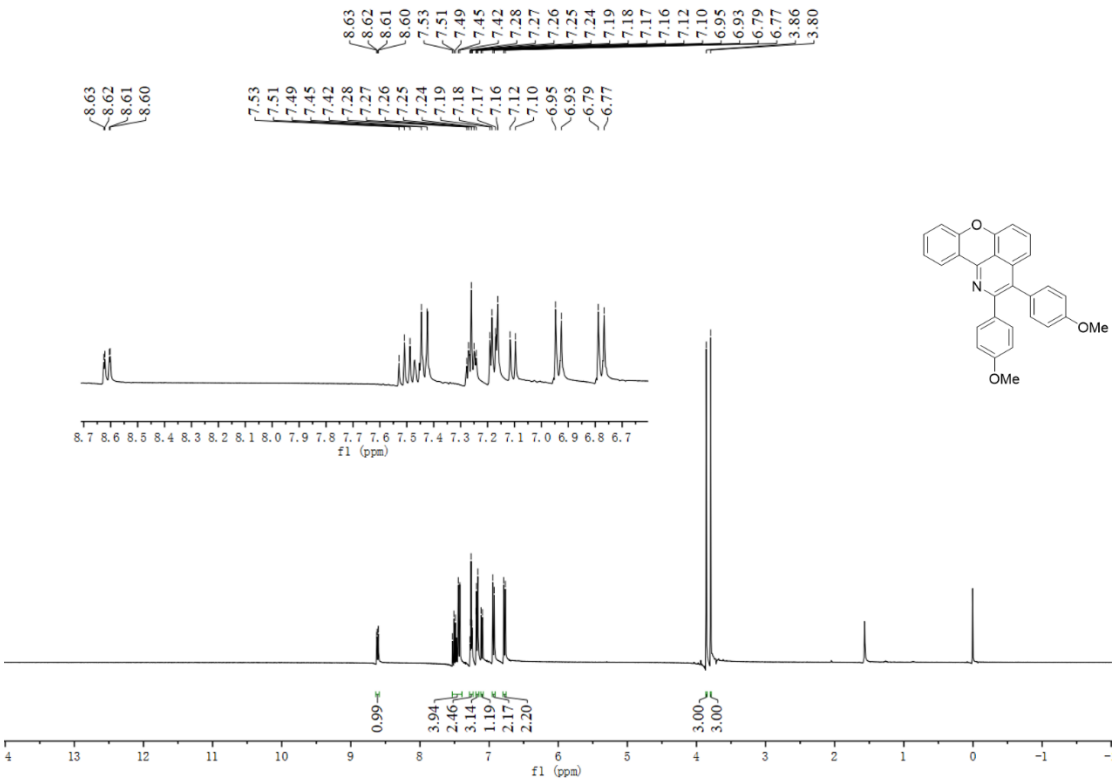
^{1}H NMR spectra of **3h** ($CDCl_3$)



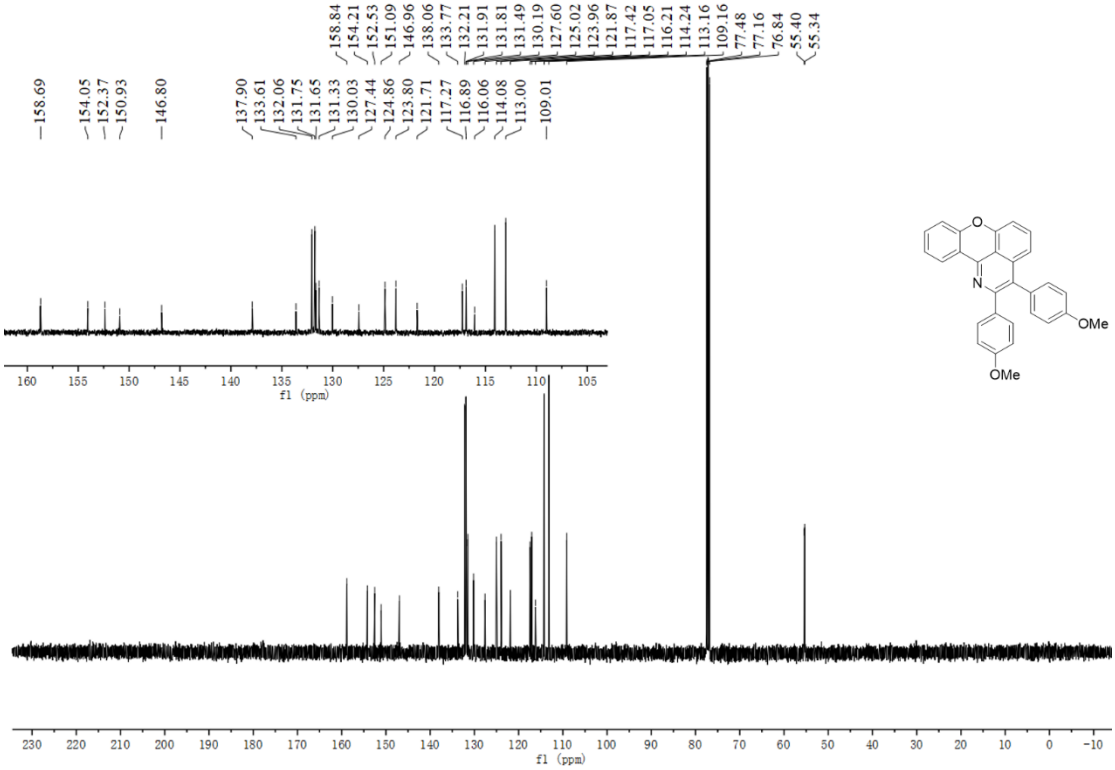
^{13}C NMR spectra of **3h** ($CDCl_3$)



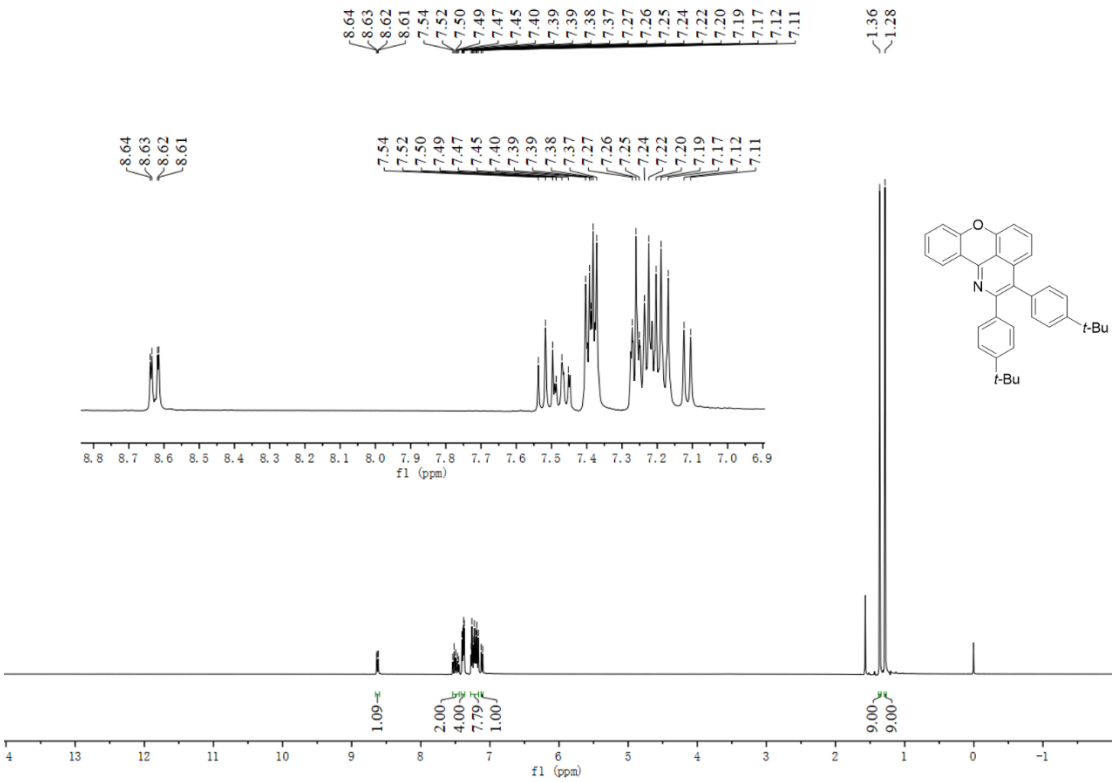
^{1}H NMR spectra of **3i** ($CDCl_3$)



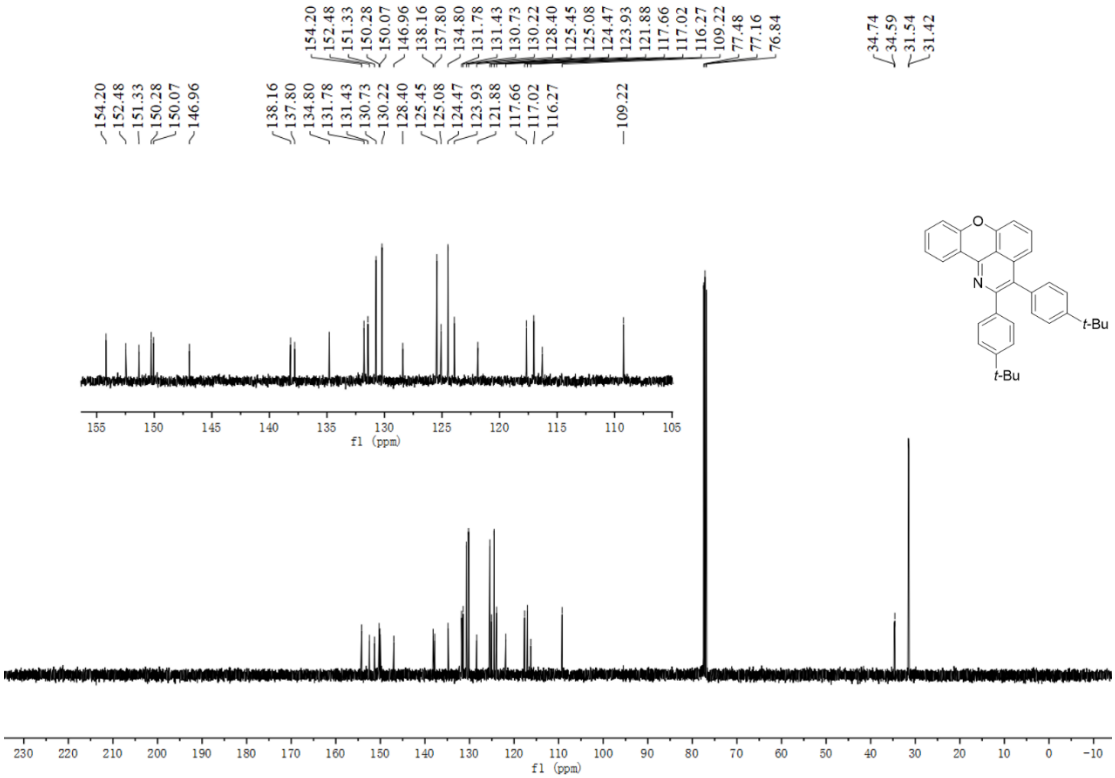
^{13}C NMR spectra of **3i** ($CDCl_3$)



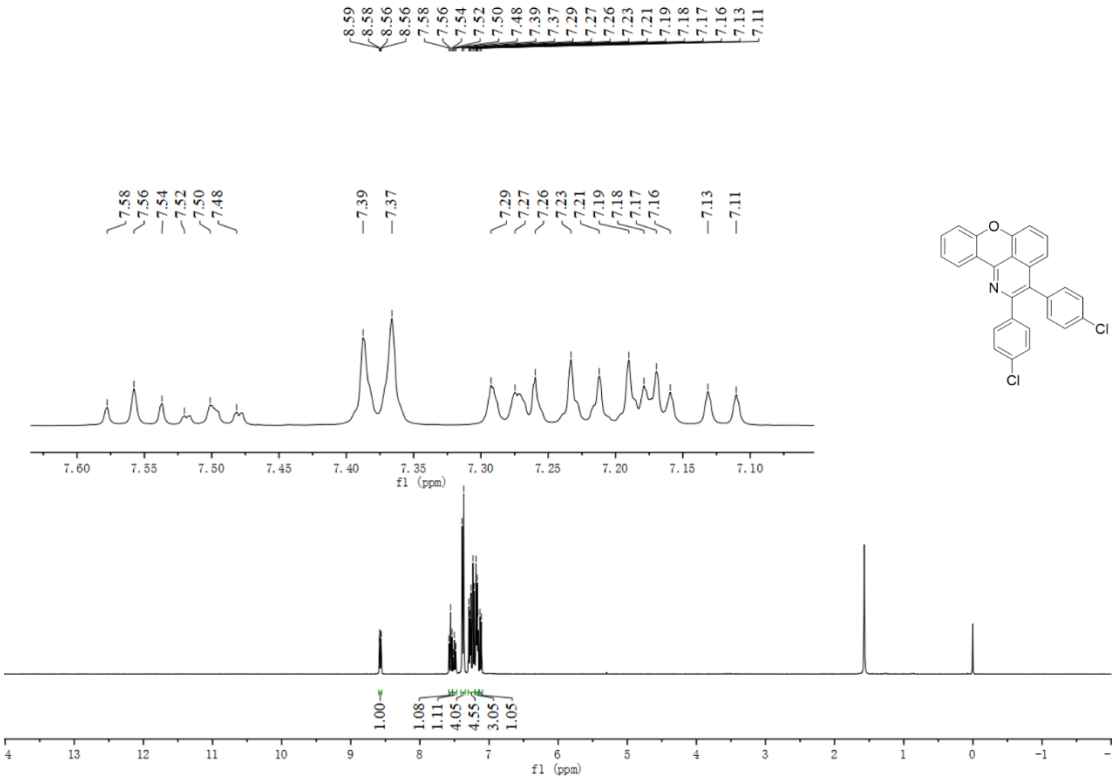
^{1}H NMR spectra of **3j** ($CDCl_3$)



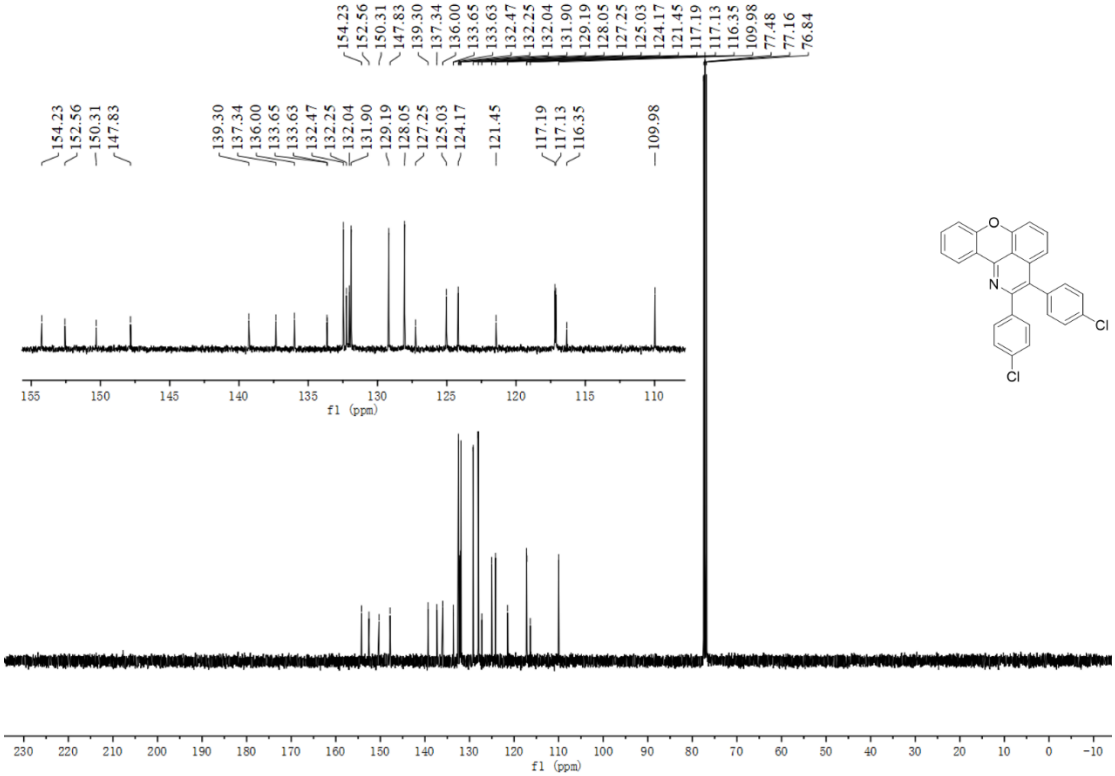
^{13}C NMR spectra of **3j** ($CDCl_3$)



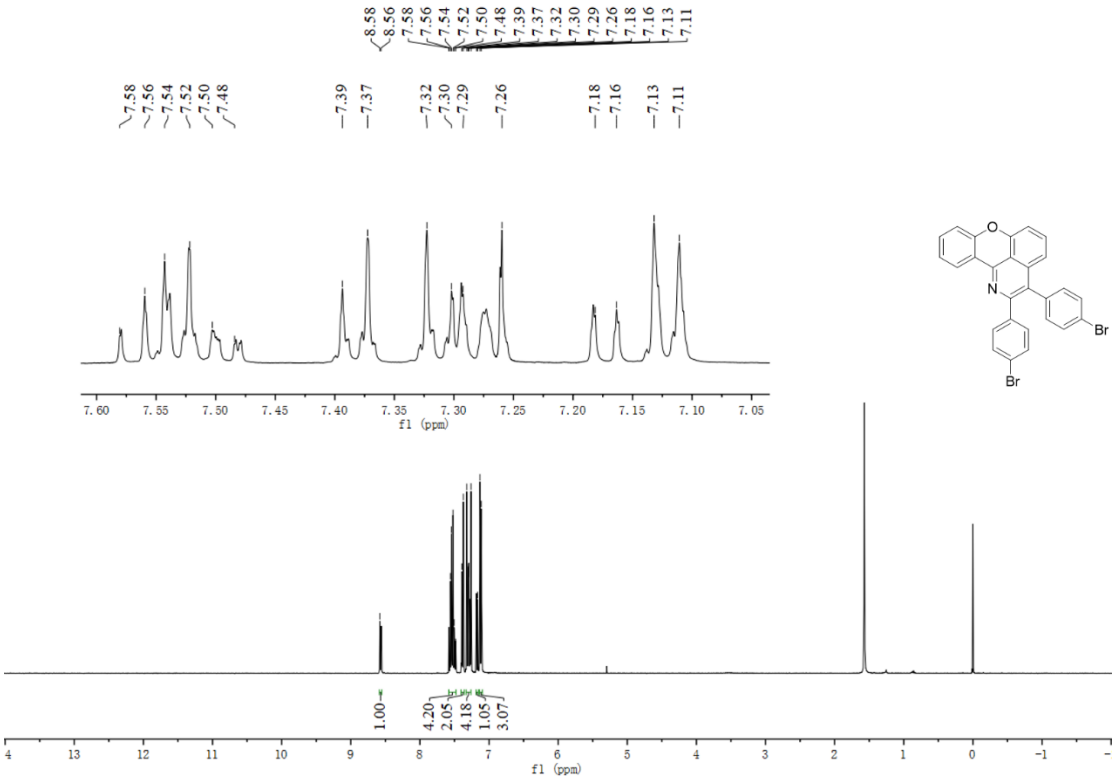
^{1}H NMR spectra of **3k** ($CDCl_3$)



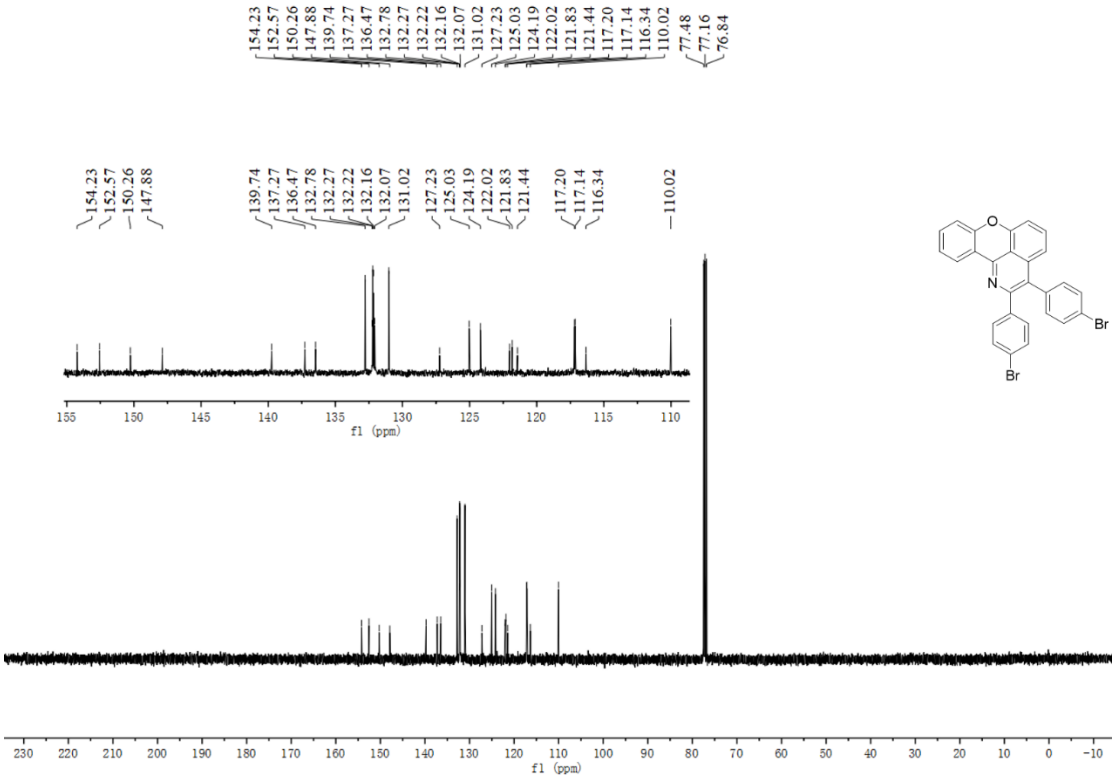
^{13}C NMR spectra of **3k** ($CDCl_3$)



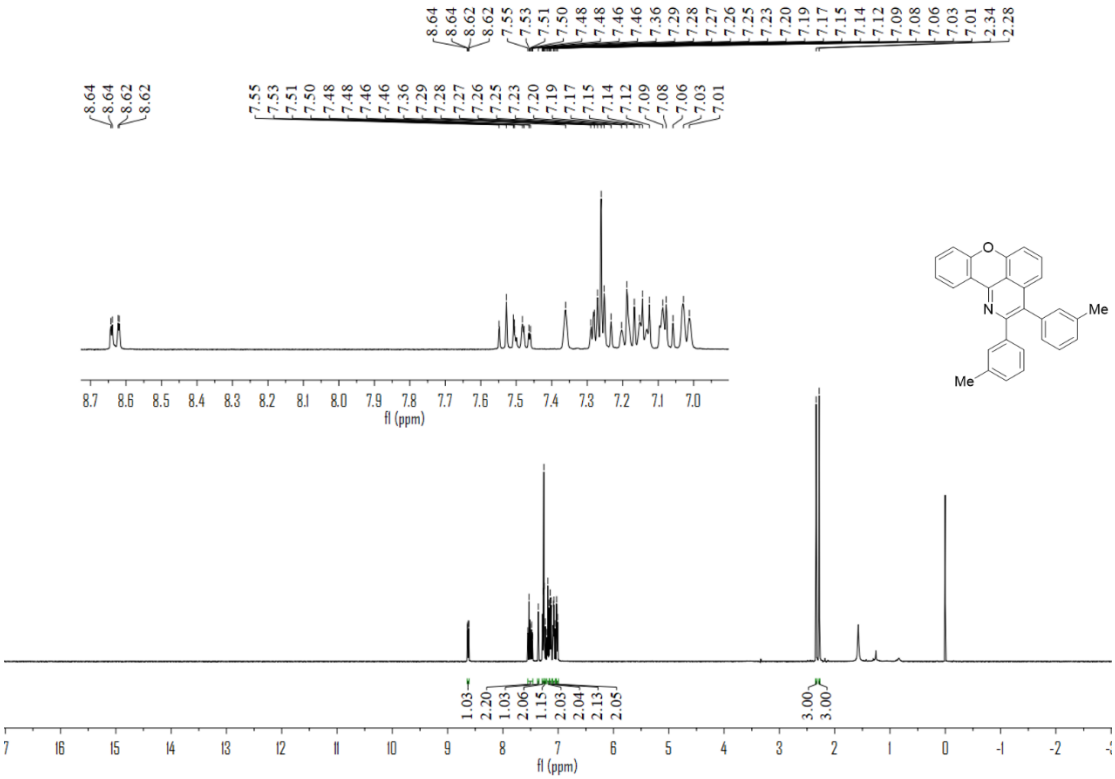
^{1}H NMR spectra of **3l** ($CDCl_3$)



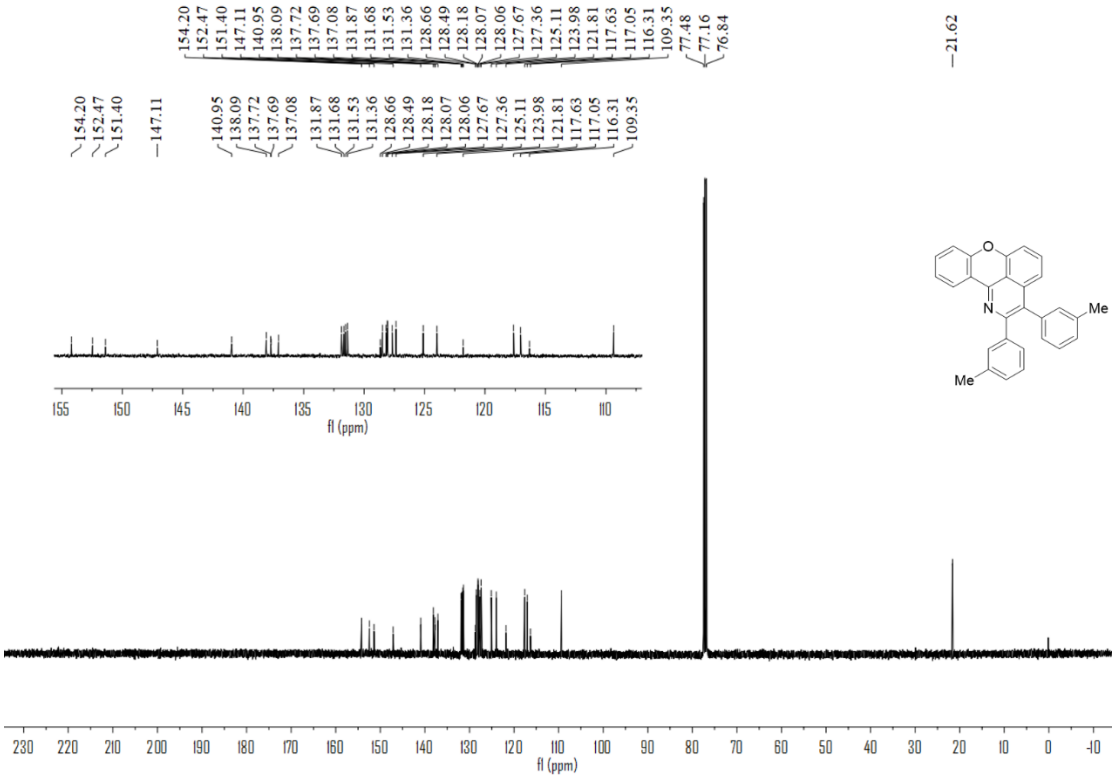
^{13}C NMR spectra of **3l** ($CDCl_3$)



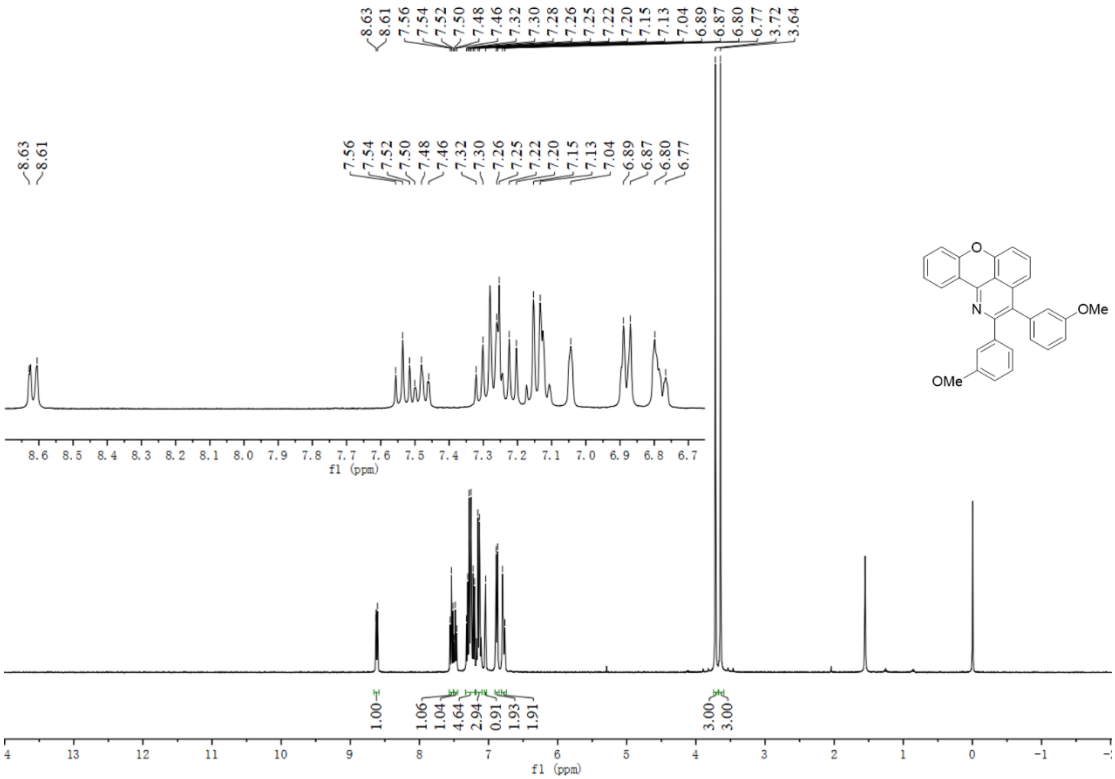
^{1}H NMR spectra of **3m** ($CDCl_3$)



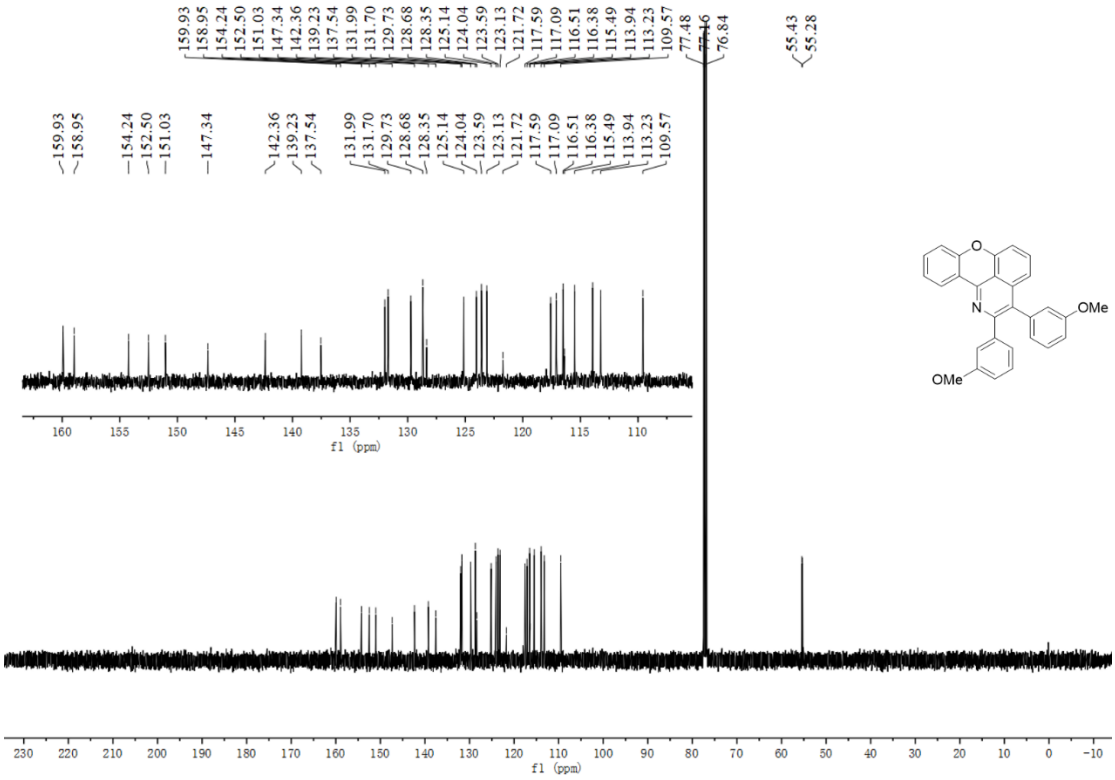
^{13}C NMR spectra of **3m** ($CDCl_3$)



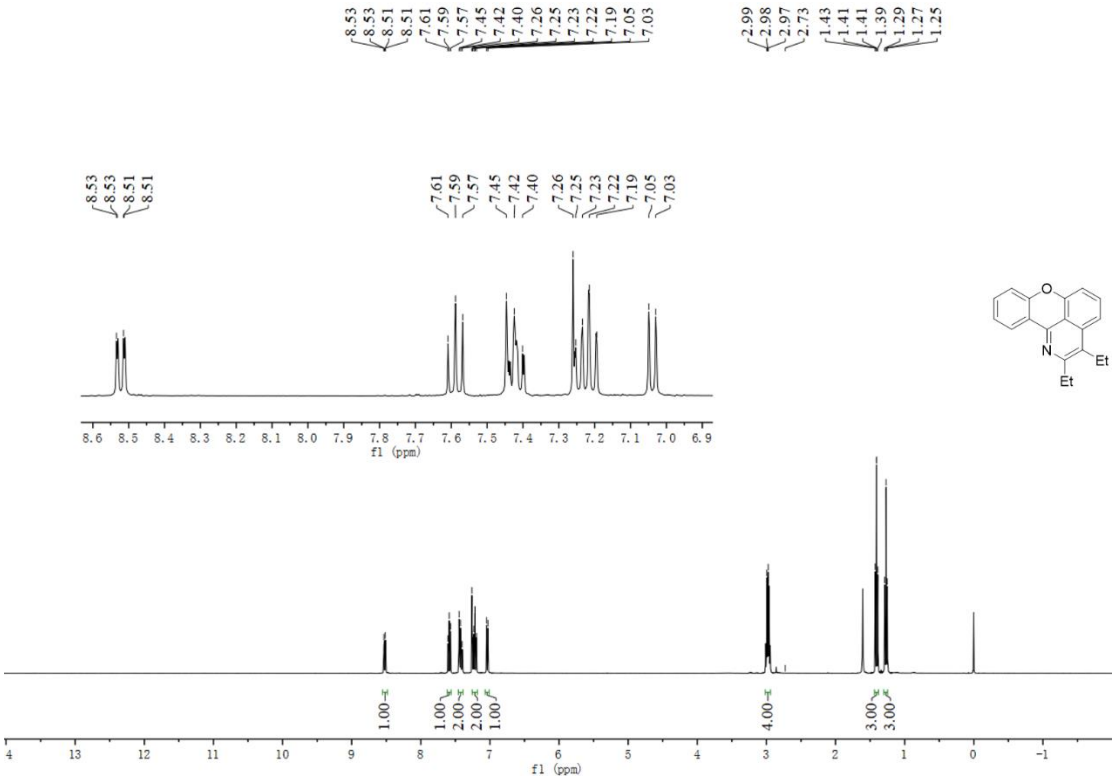
^{1}H NMR spectra of **3n** ($CDCl_3$)



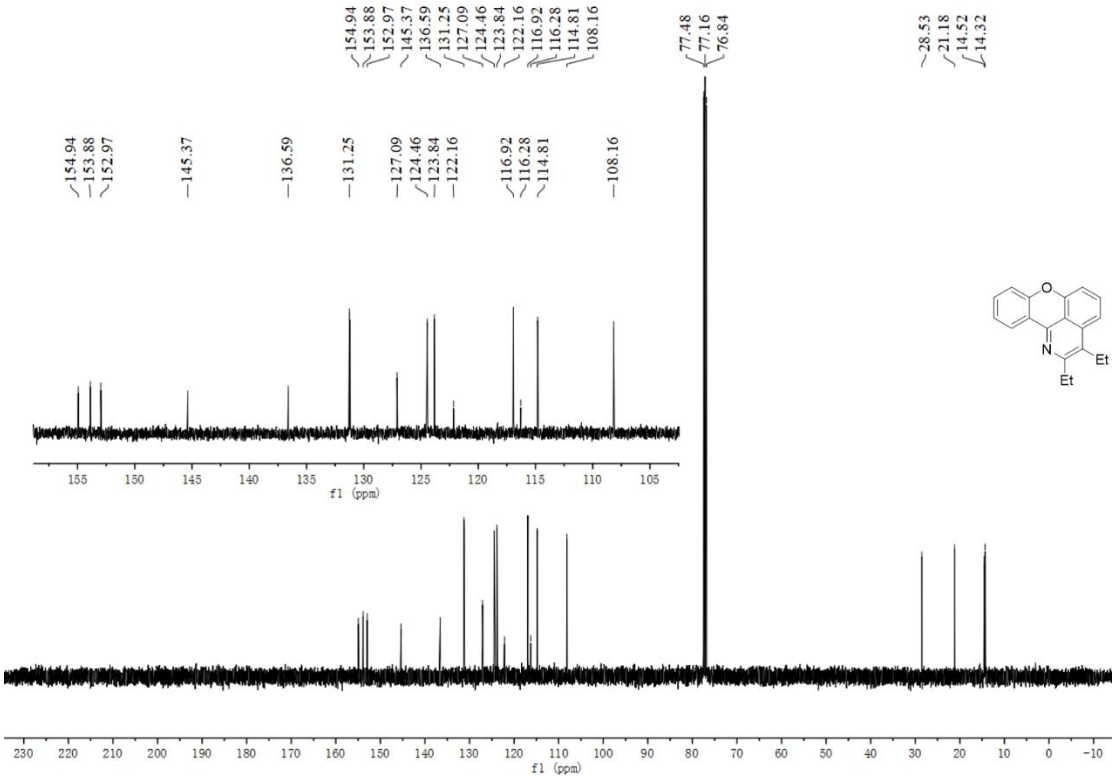
^{13}C NMR spectra of **3n** ($CDCl_3$)



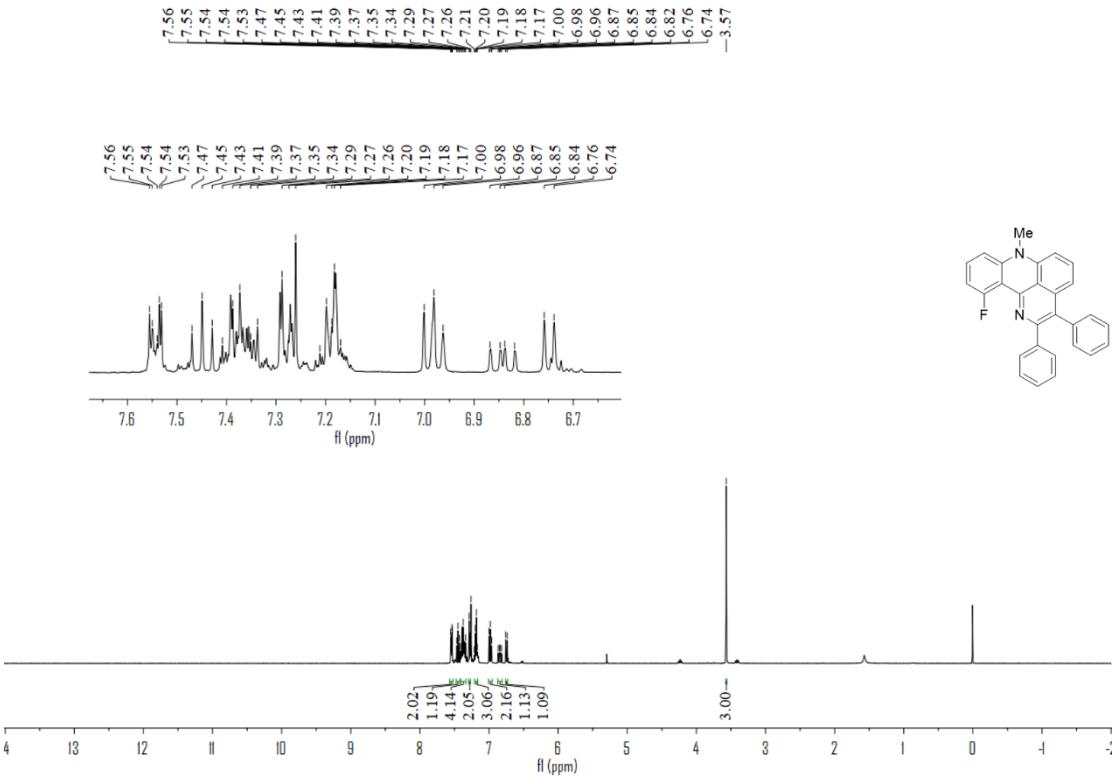
^{1}H NMR spectra of **3o** ($CDCl_3$)



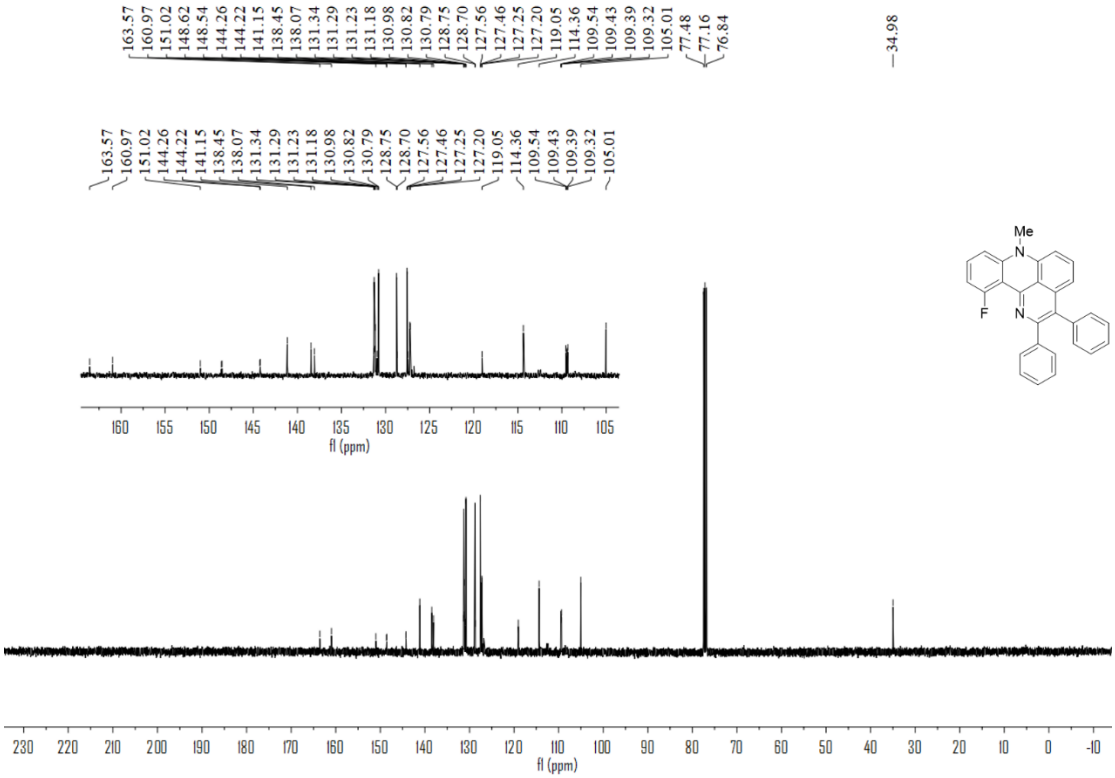
^{13}C NMR spectra of **3o** ($CDCl_3$)



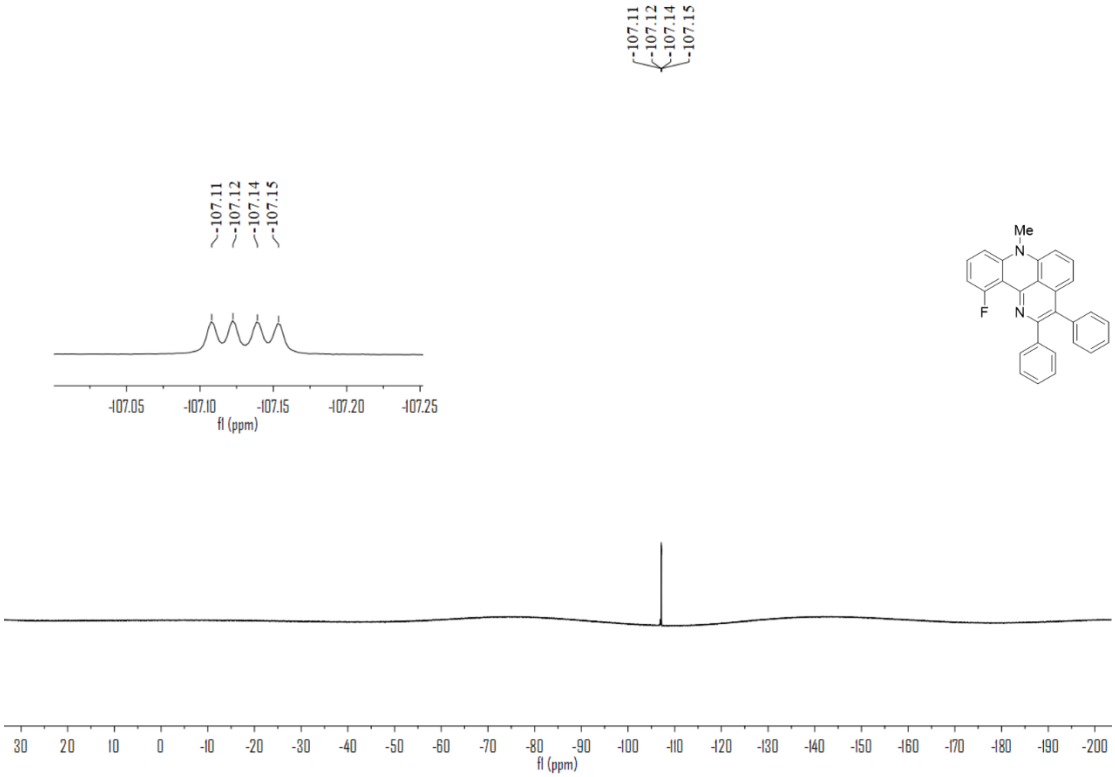
^{1}H NMR spectra of **5a** ($CDCl_3$)



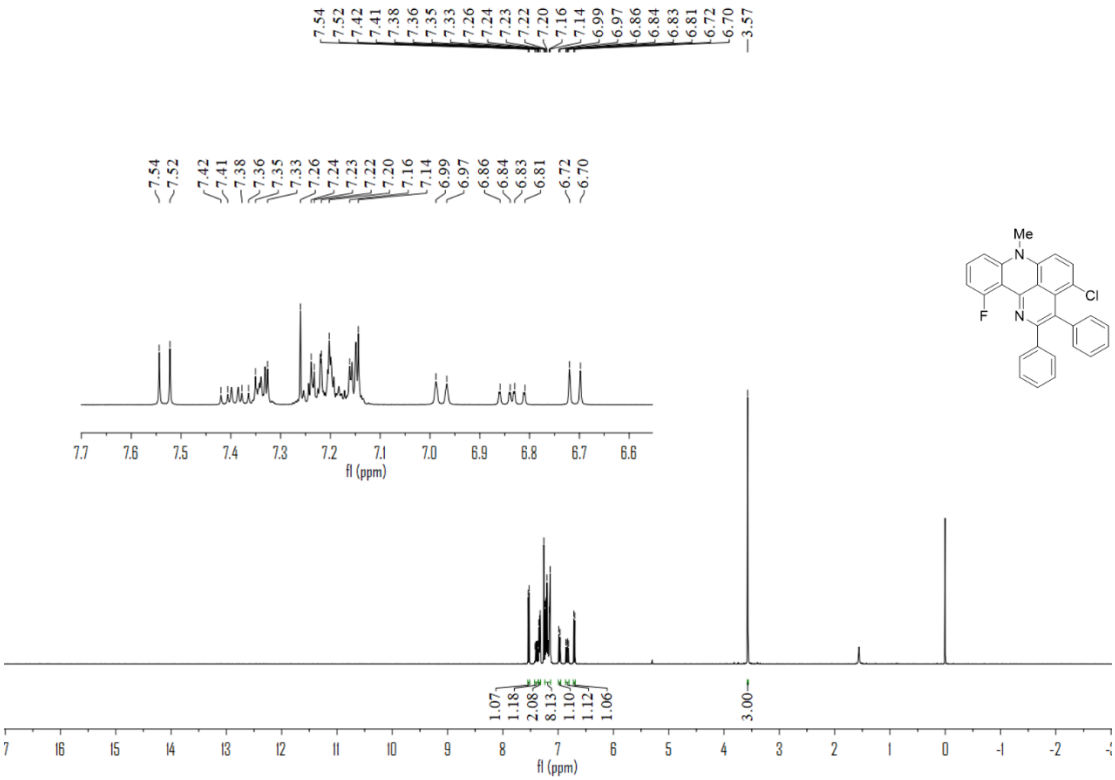
^{13}C NMR spectra of **5a** ($CDCl_3$)



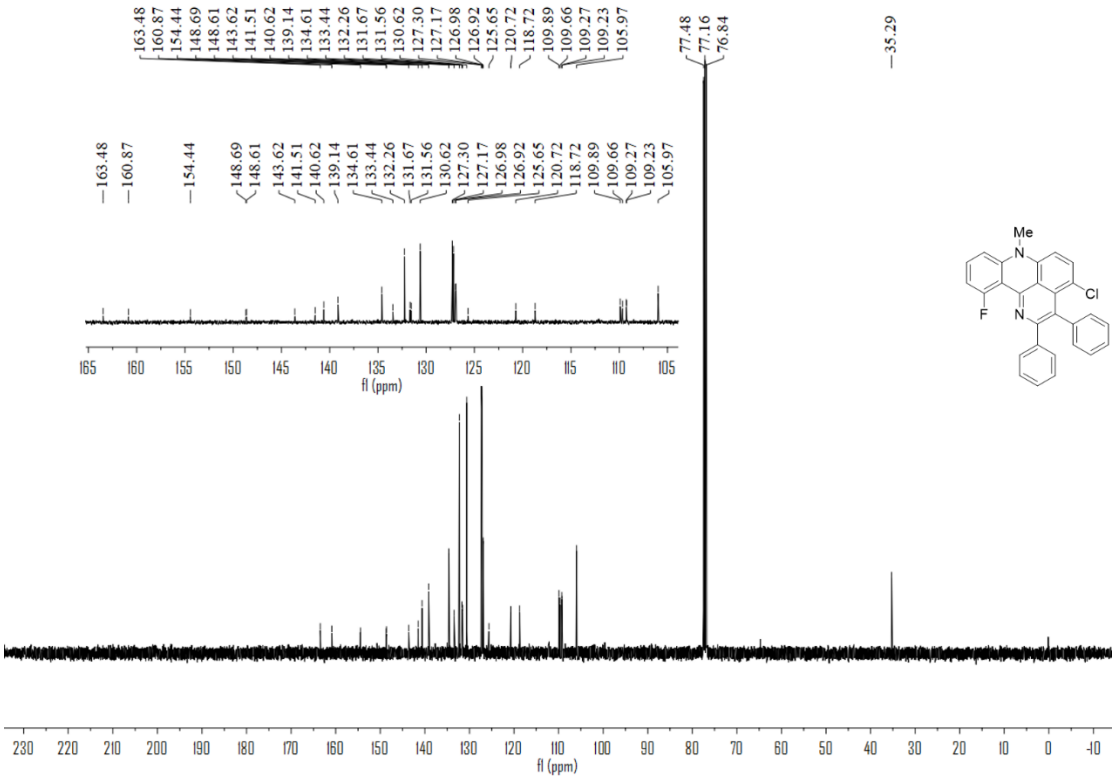
^{19}F NMR spectra of **5a** ($CDCl_3$)



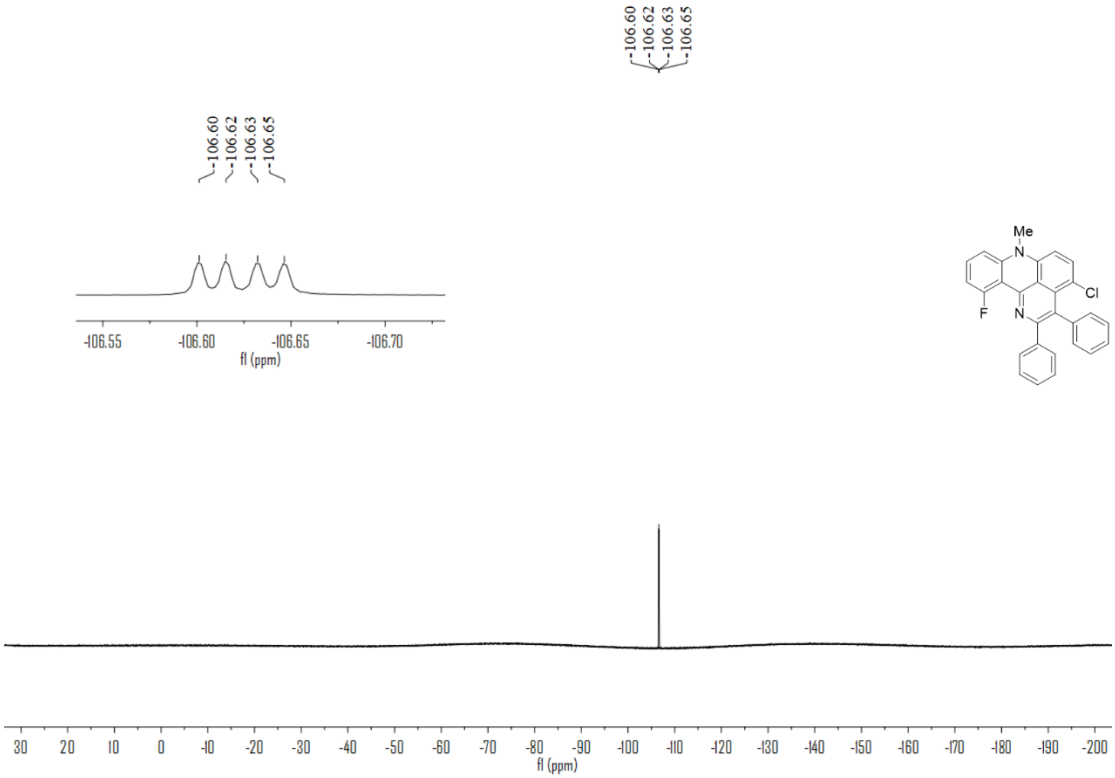
^{1}H NMR spectra of **5b** ($CDCl_3$)



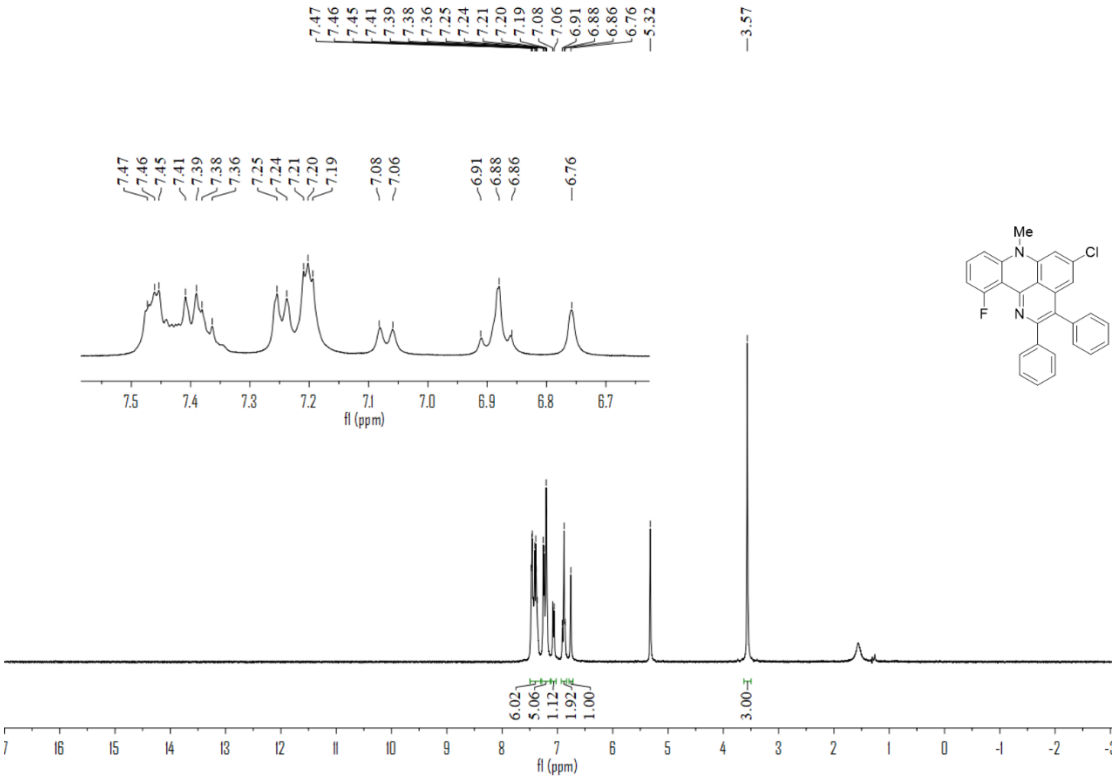
^{13}C NMR spectra of **5b** ($CDCl_3$)



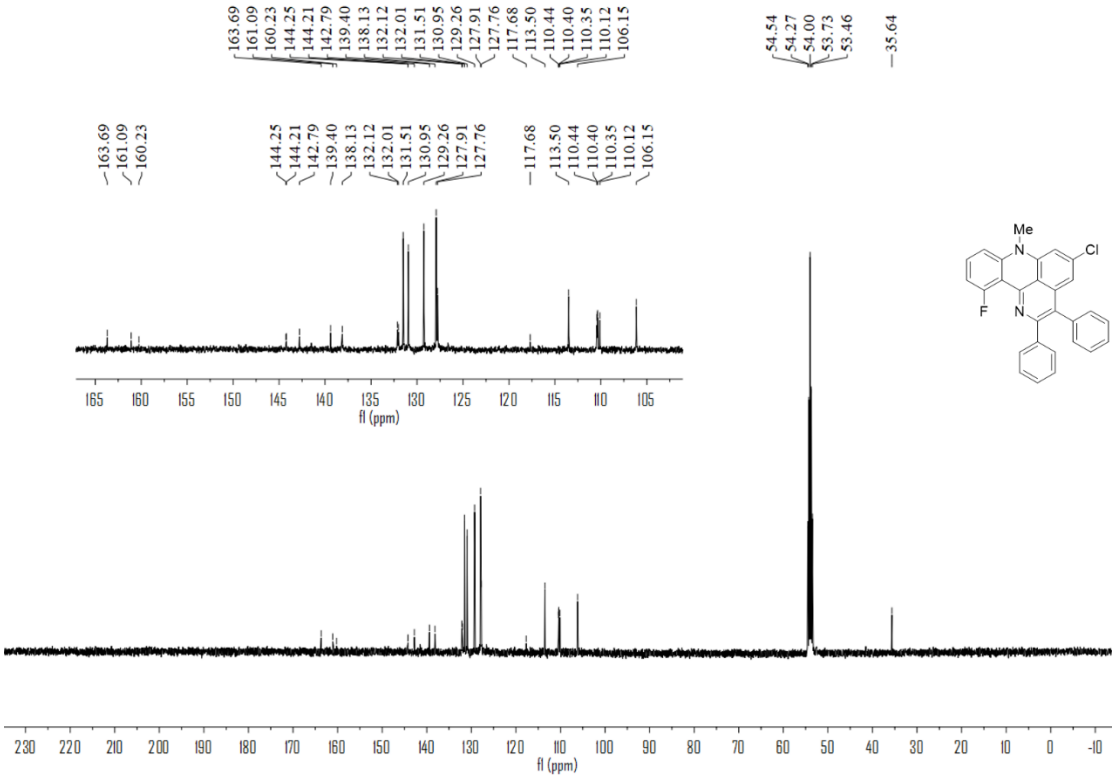
^{19}F NMR spectra of **5b** ($CDCl_3$)



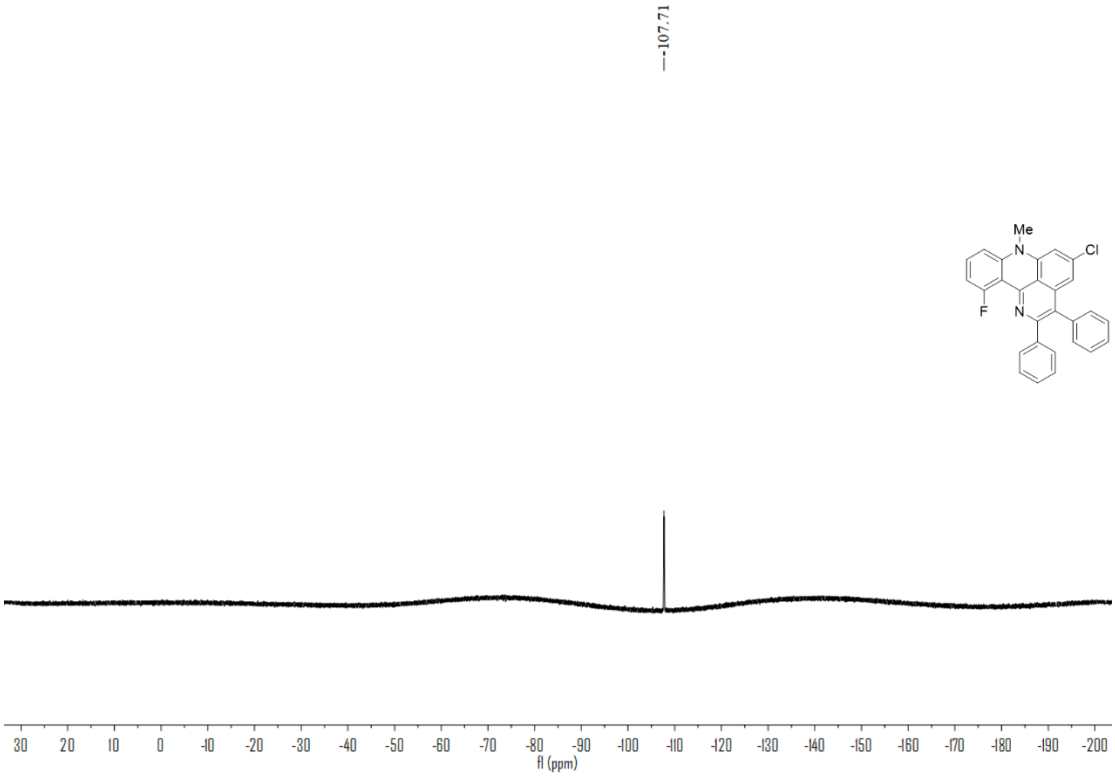
^{1}H NMR spectra of **5c** (CD_2Cl_2)



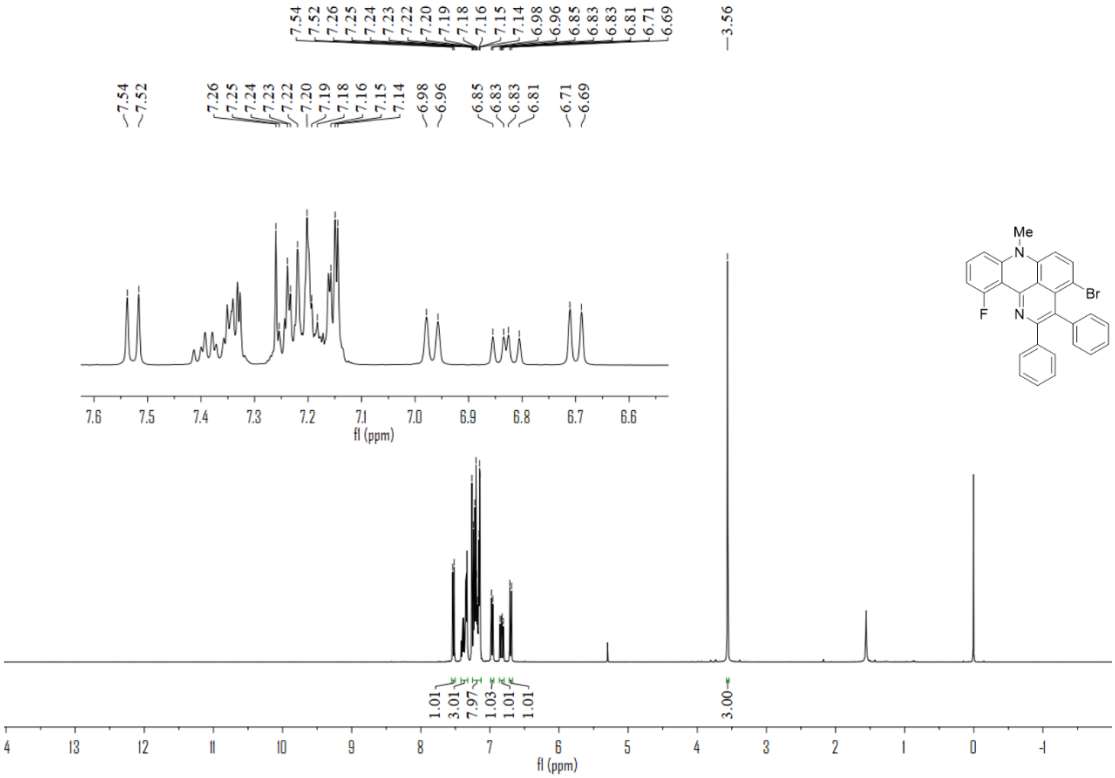
^{13}C NMR spectra of **5c** (CD_2Cl_2)



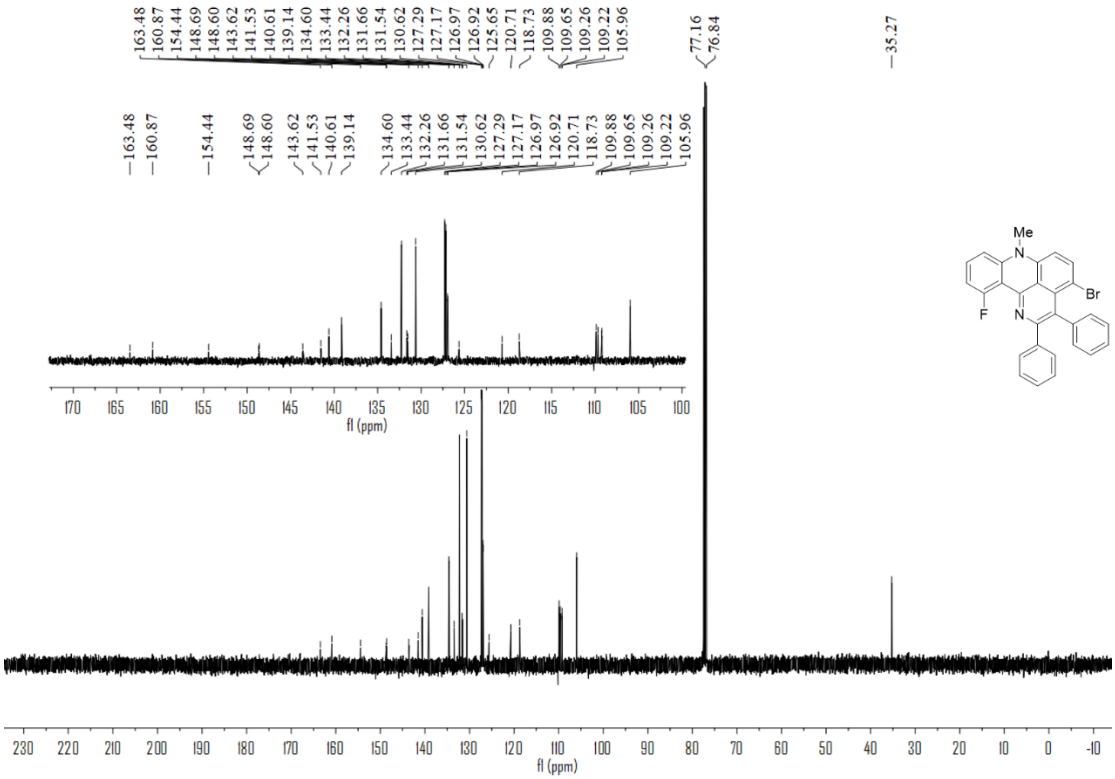
^{19}F NMR spectra of **5c** (CD_2Cl_2)



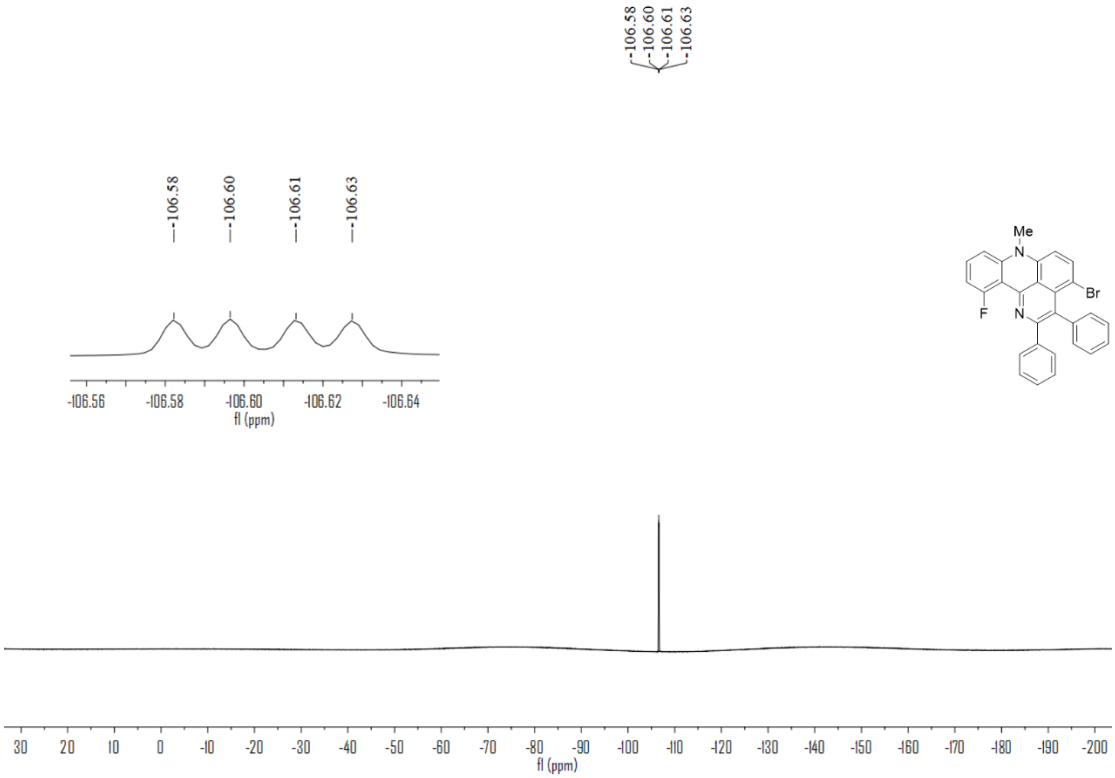
^{1}H NMR spectra of **5d** ($CDCl_3$)



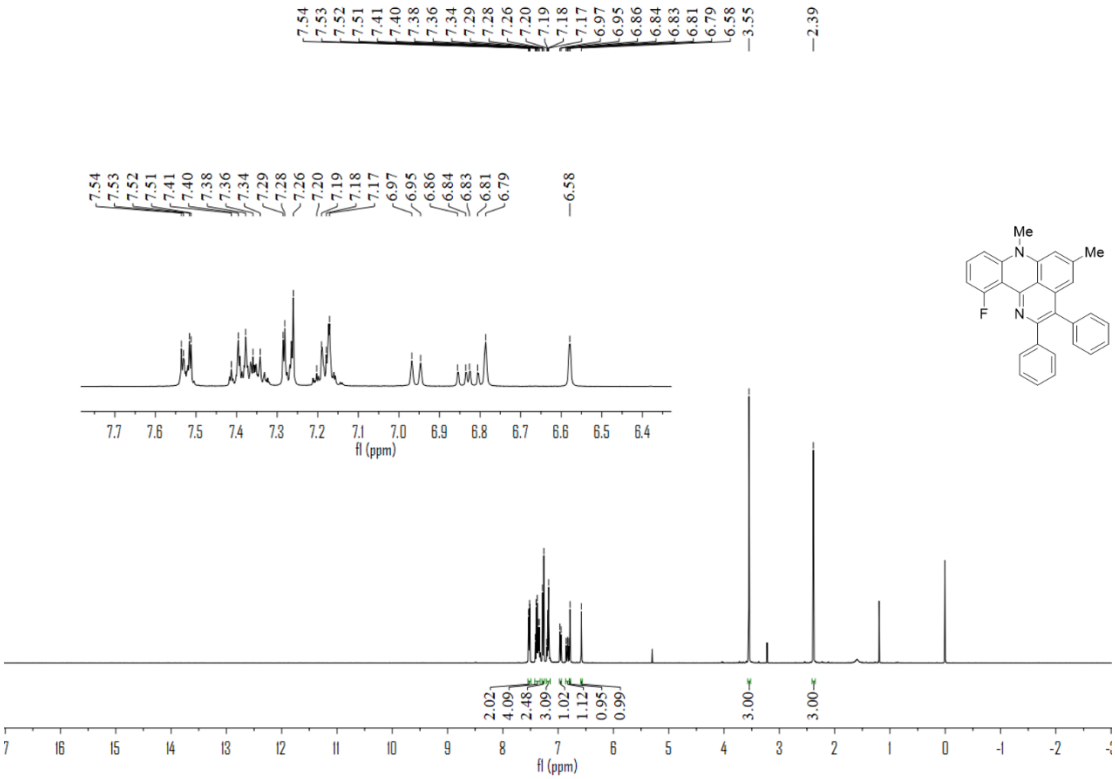
^{13}C NMR spectra of **5d** ($CDCl_3$)



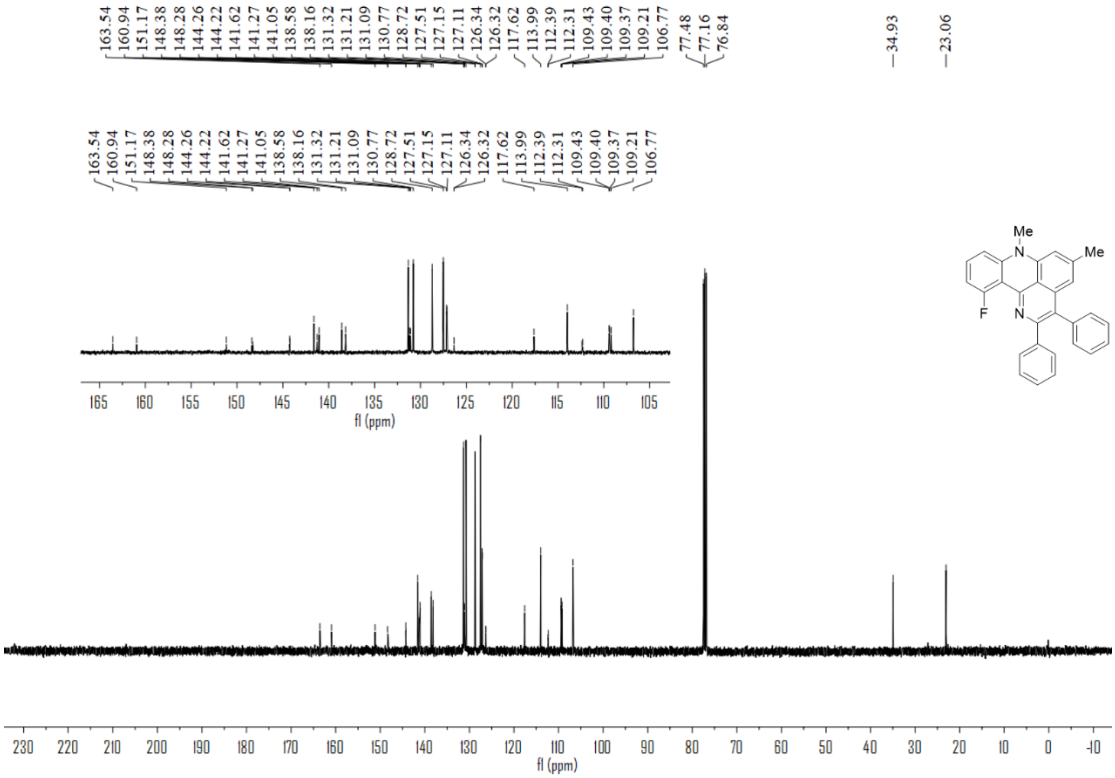
^{19}F NMR spectra of **5d** ($CDCl_3$)



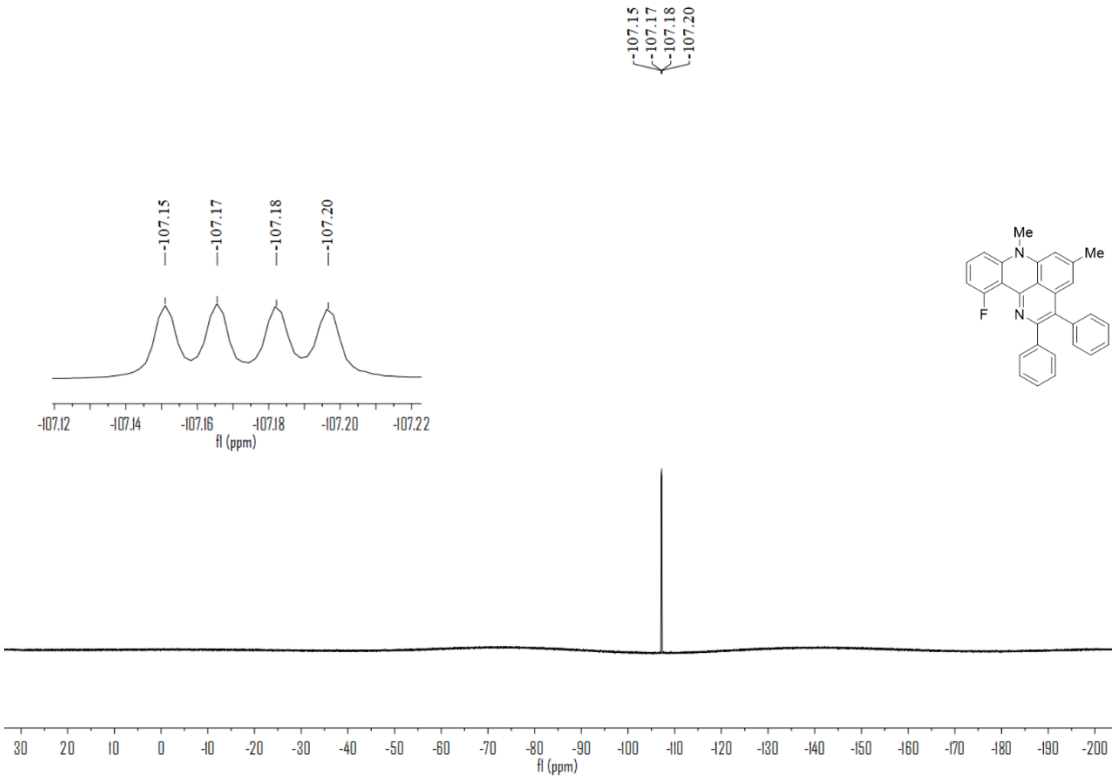
^{1}H NMR spectra of **5e** ($CDCl_3$)



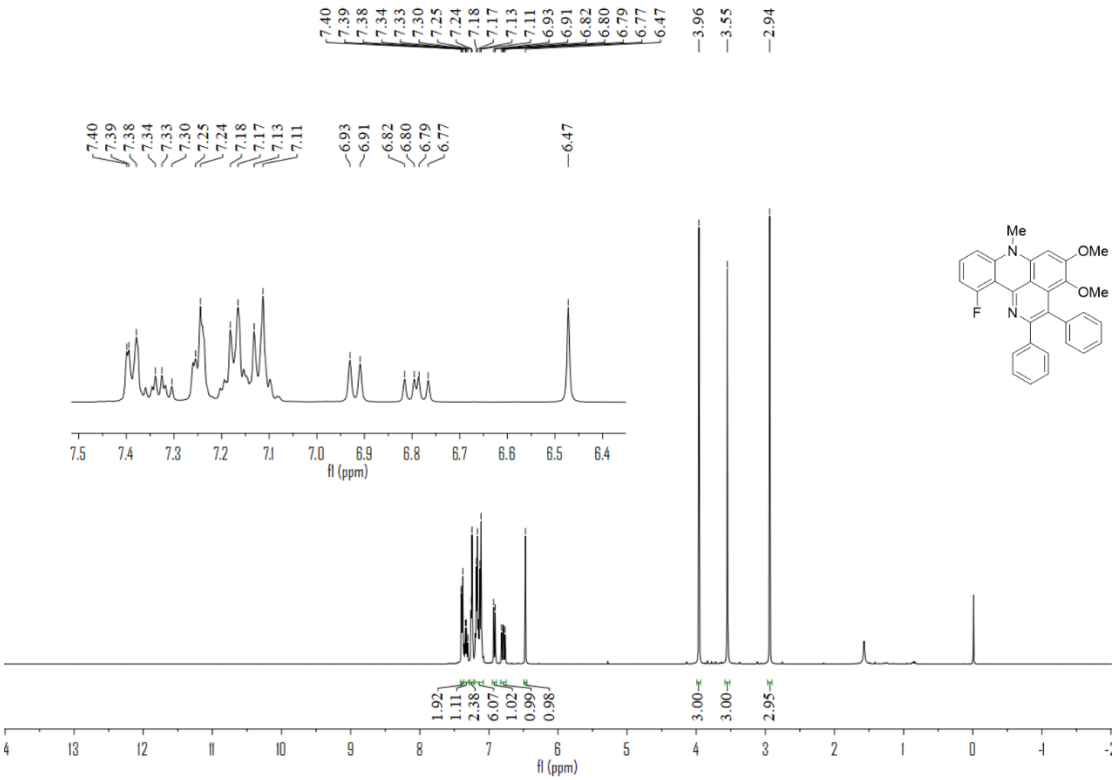
^{13}C NMR spectra of **5e** ($CDCl_3$)



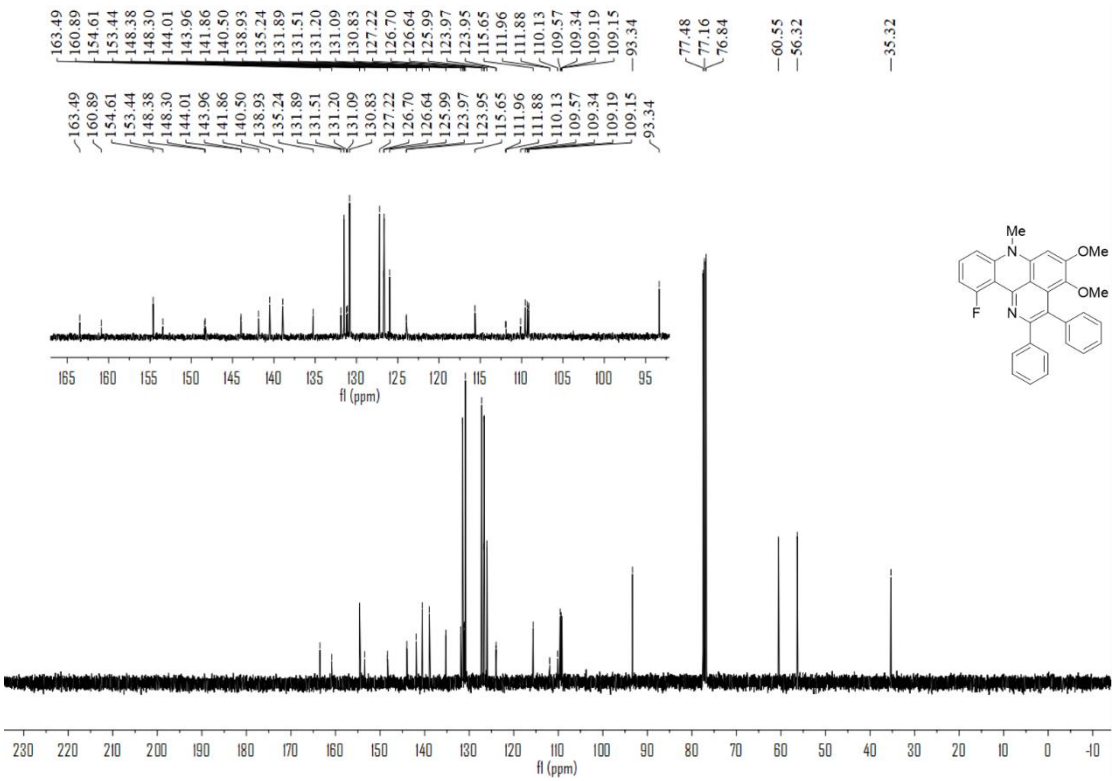
^{19}F NMR spectra of **5e** ($CDCl_3$)



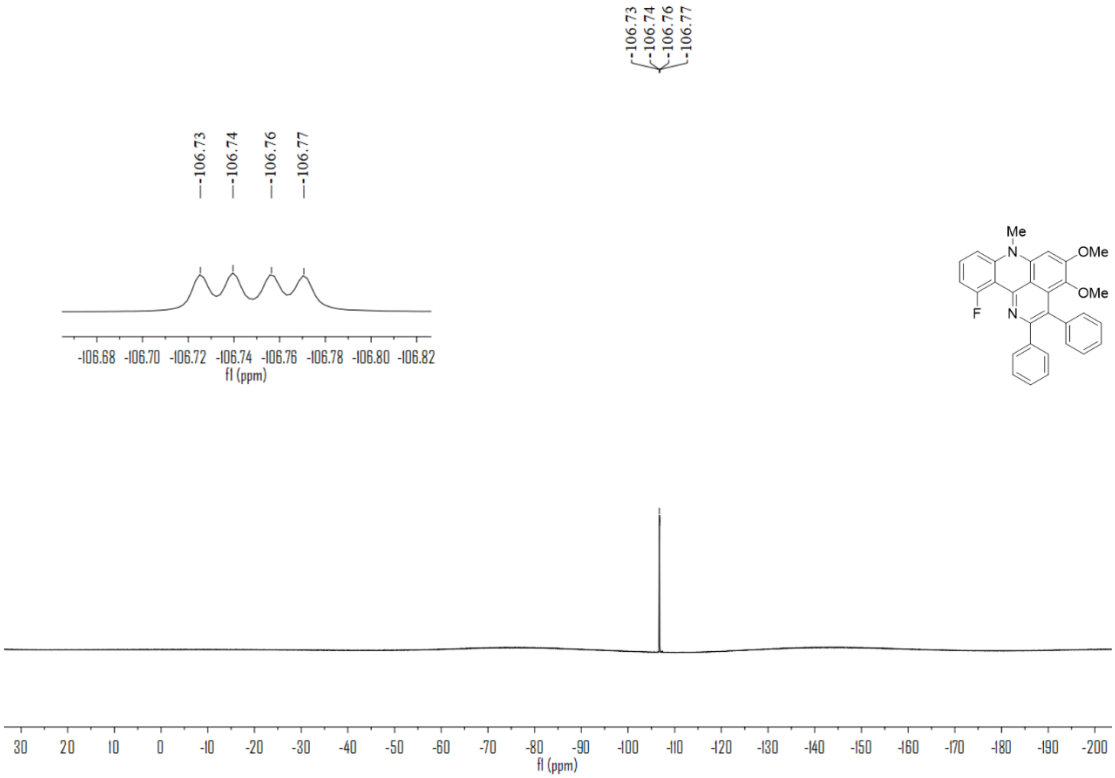
^{1}H NMR spectra of **5f** ($CDCl_3$)



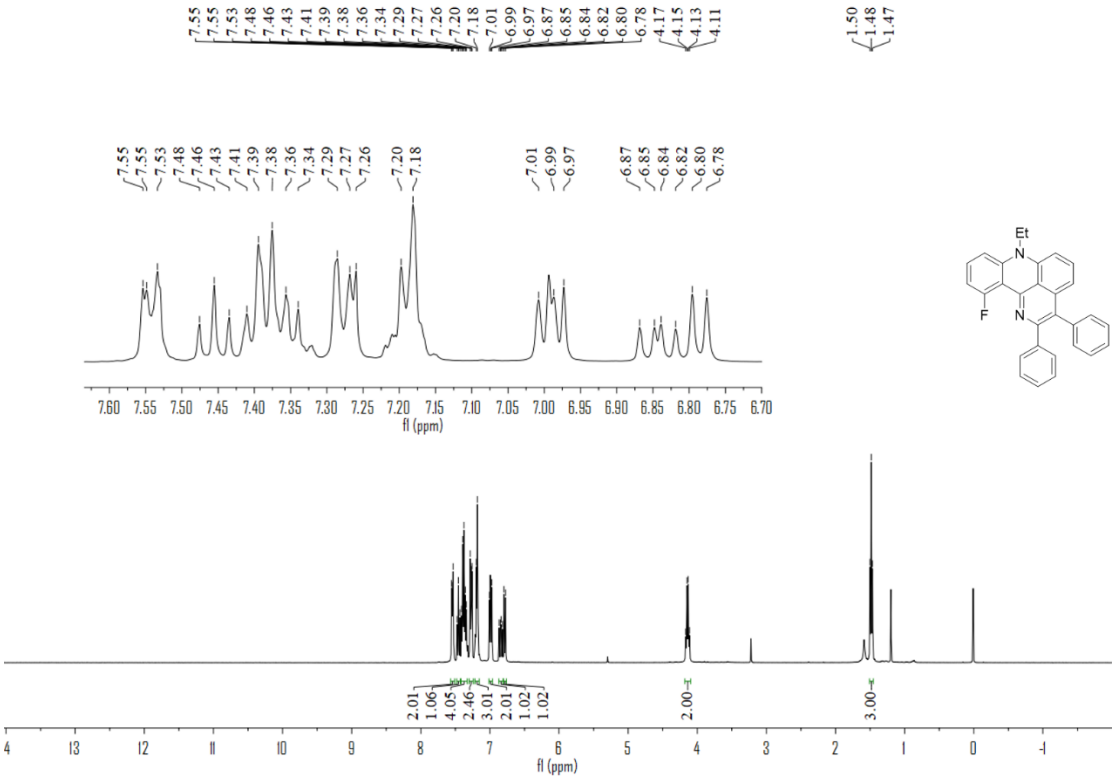
^{13}C NMR spectra of **5f** ($CDCl_3$)



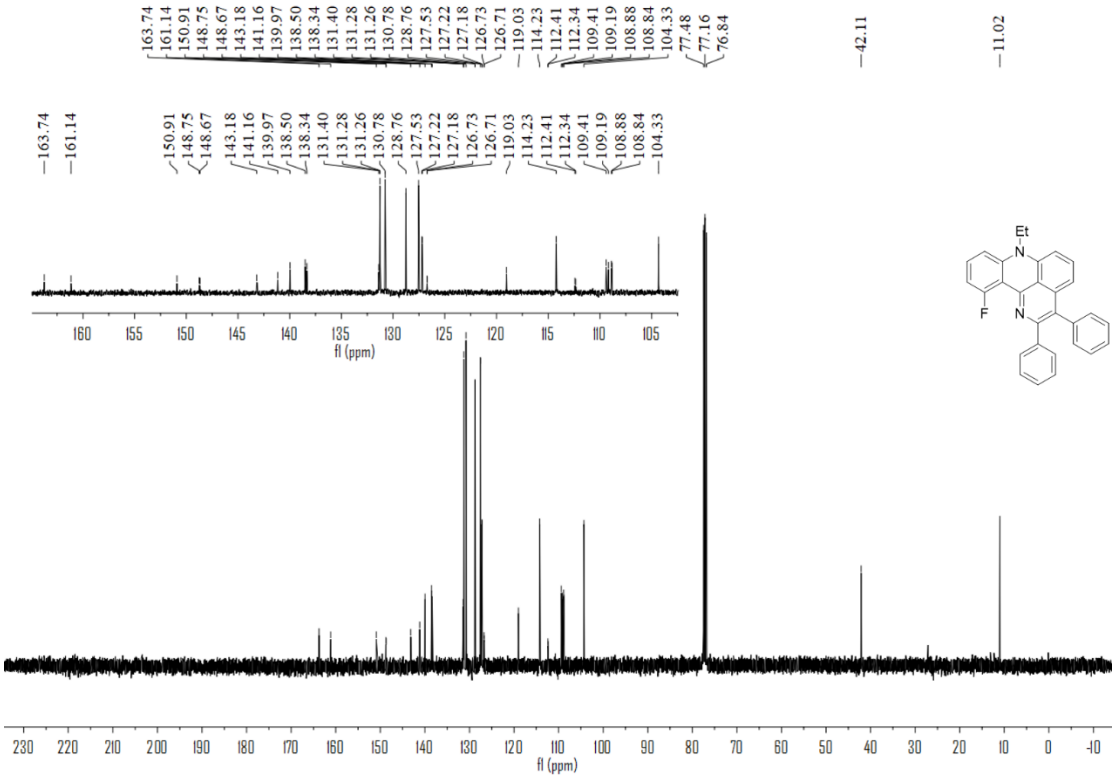
^{19}F NMR spectra of **5f** ($CDCl_3$)



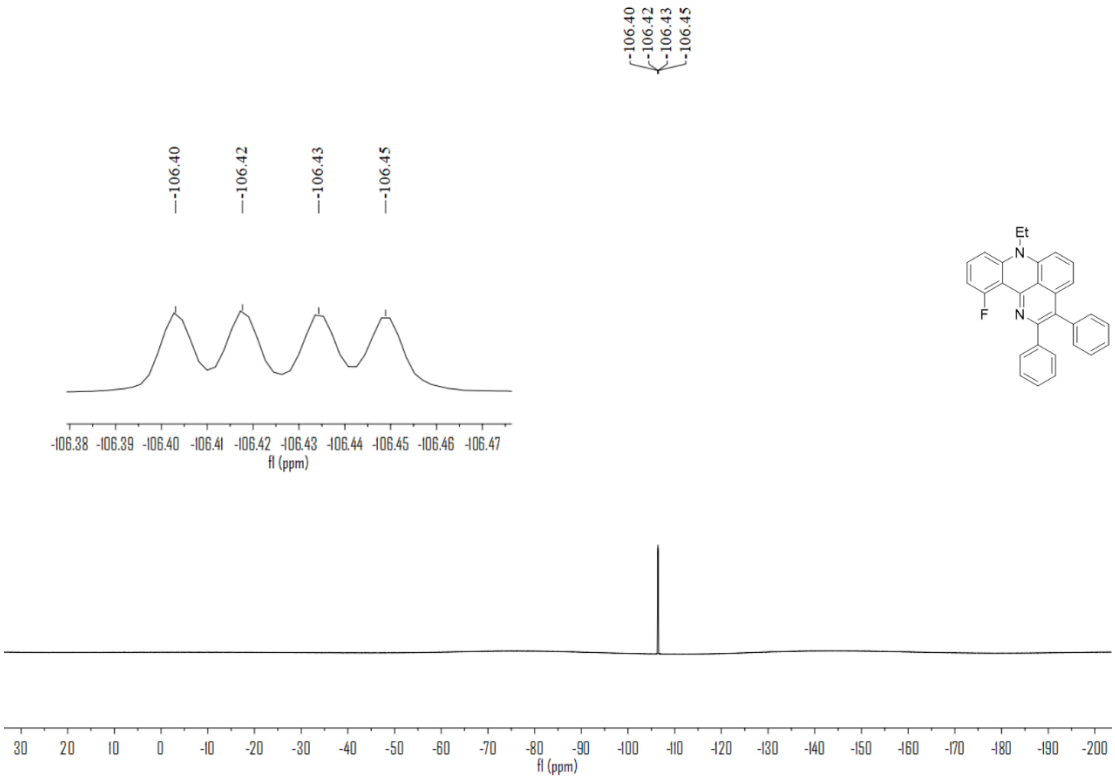
^{1}H NMR spectra of **5g** ($CDCl_3$)



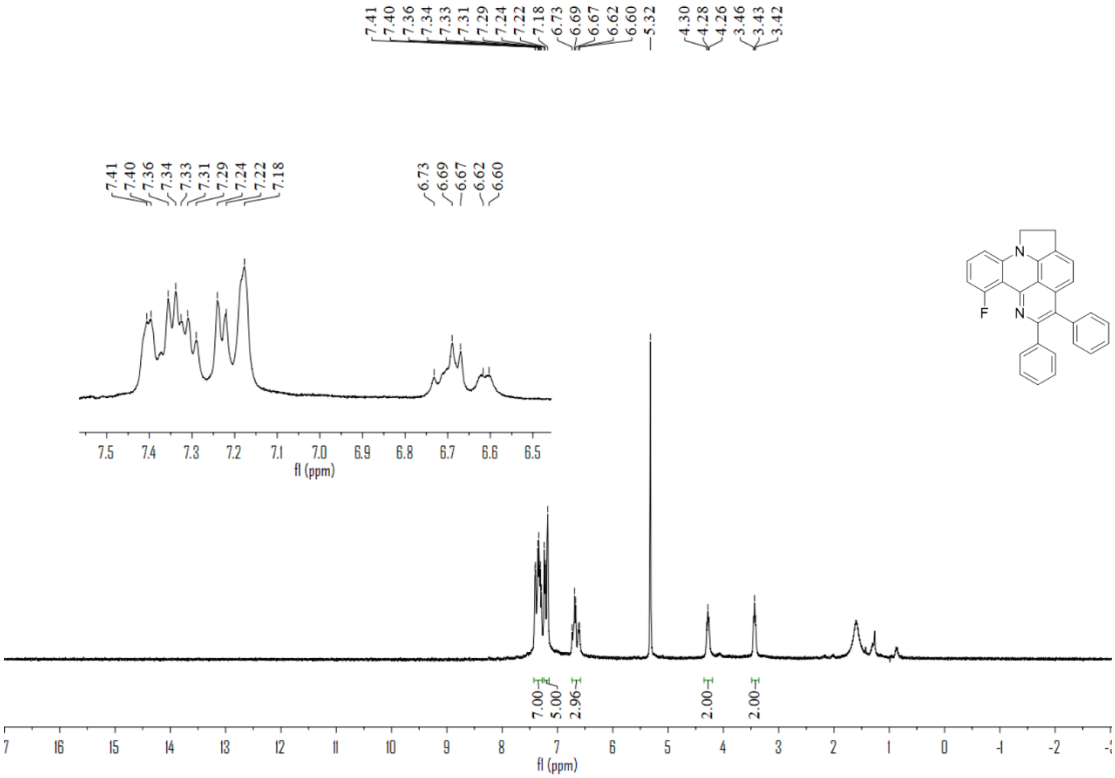
^{13}C NMR spectra of **5g** ($CDCl_3$)



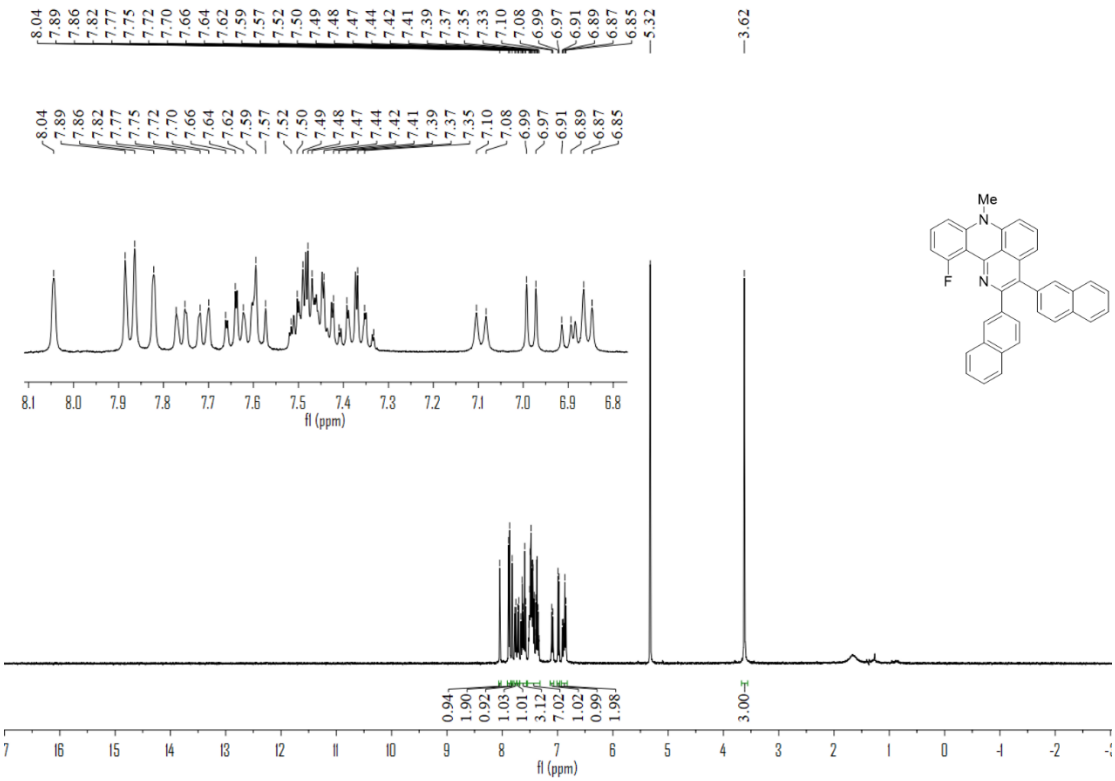
^{19}F NMR spectra of **5g** ($CDCl_3$)



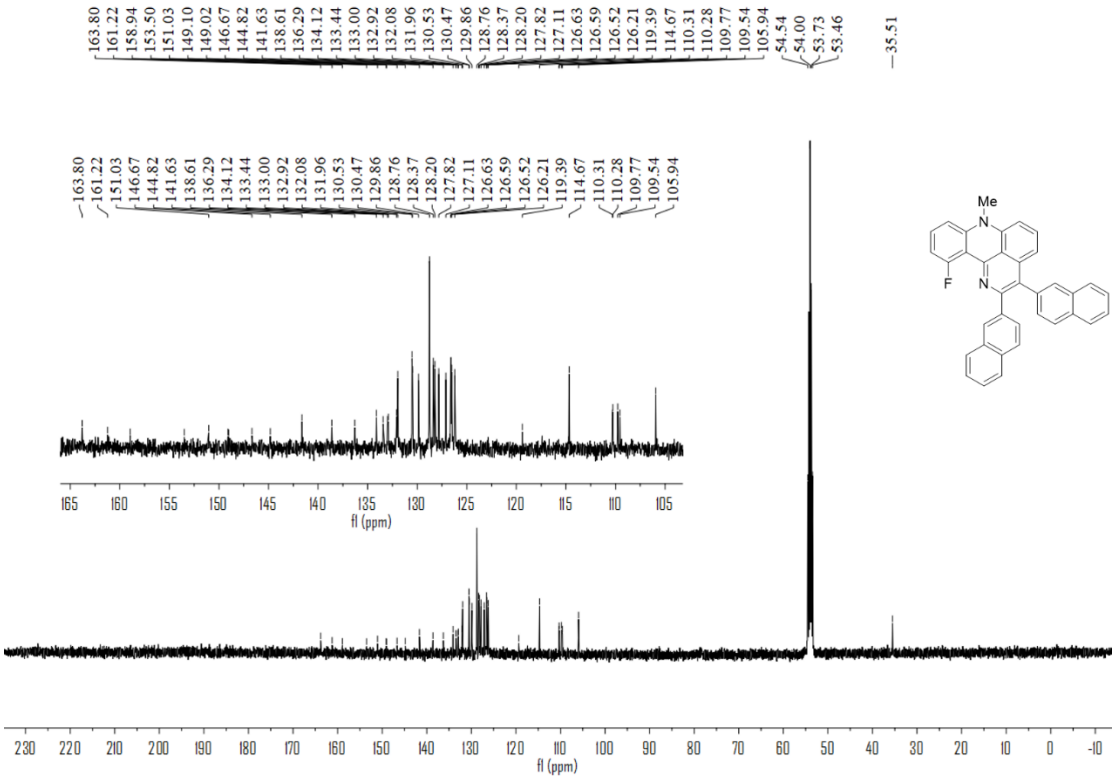
^{1}H NMR spectra of **5h** (CD_2Cl_2)



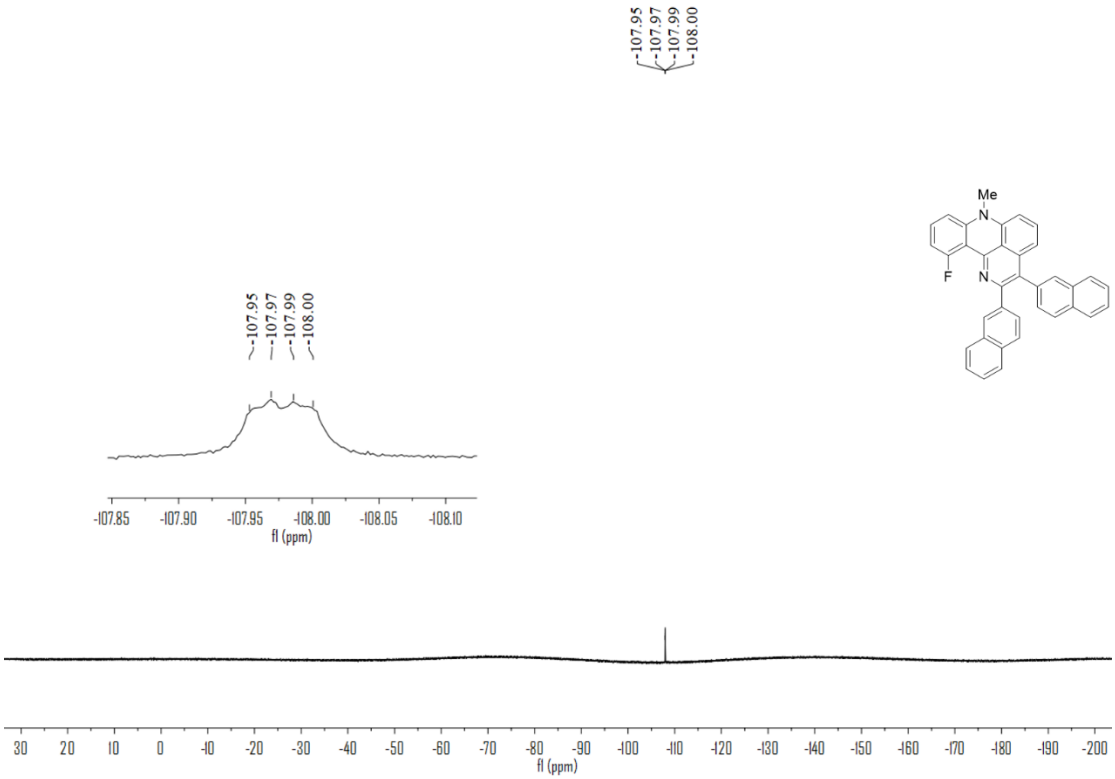
^{1}H NMR spectra of **5i** (CD_2Cl_2)



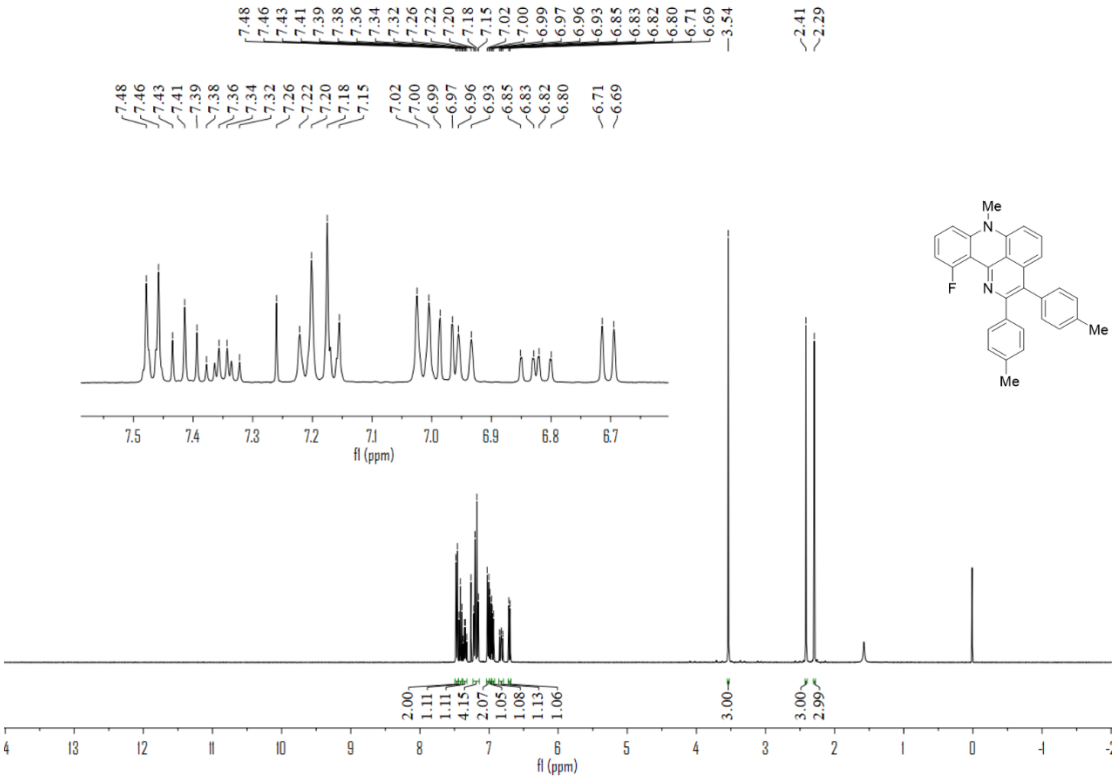
^{13}C NMR spectra of **5i** (CD_2Cl_2)



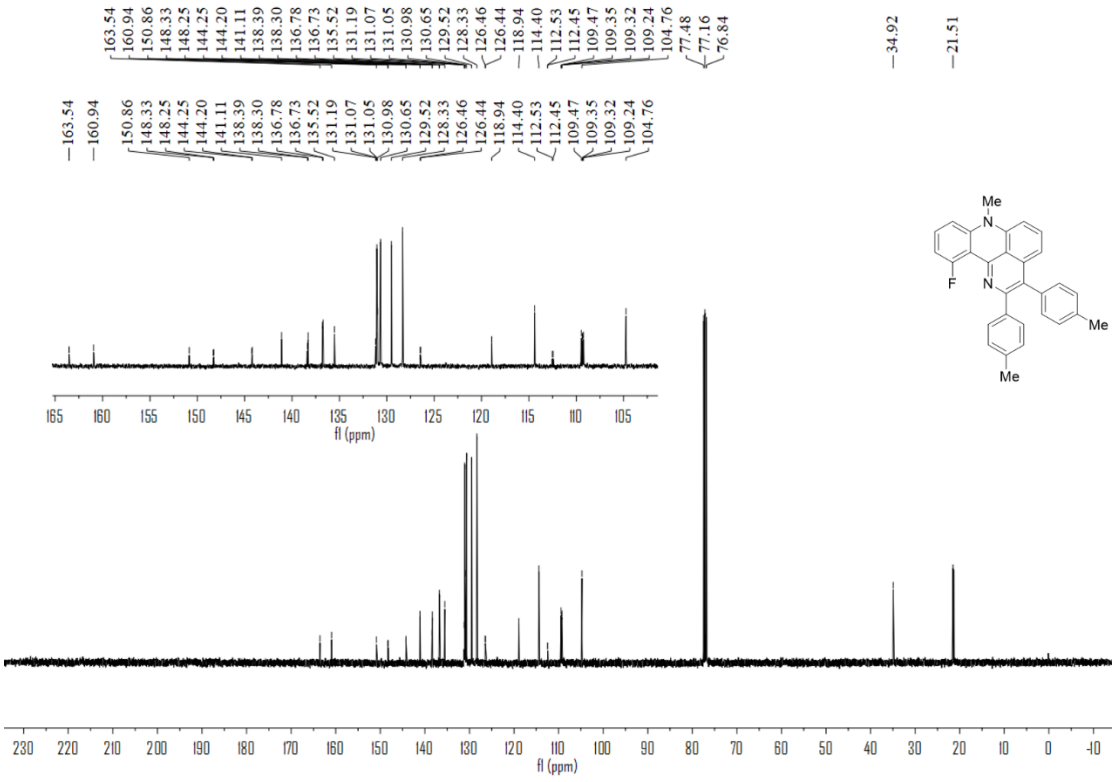
^{19}F NMR spectra of **5i** (CD_2Cl_2)



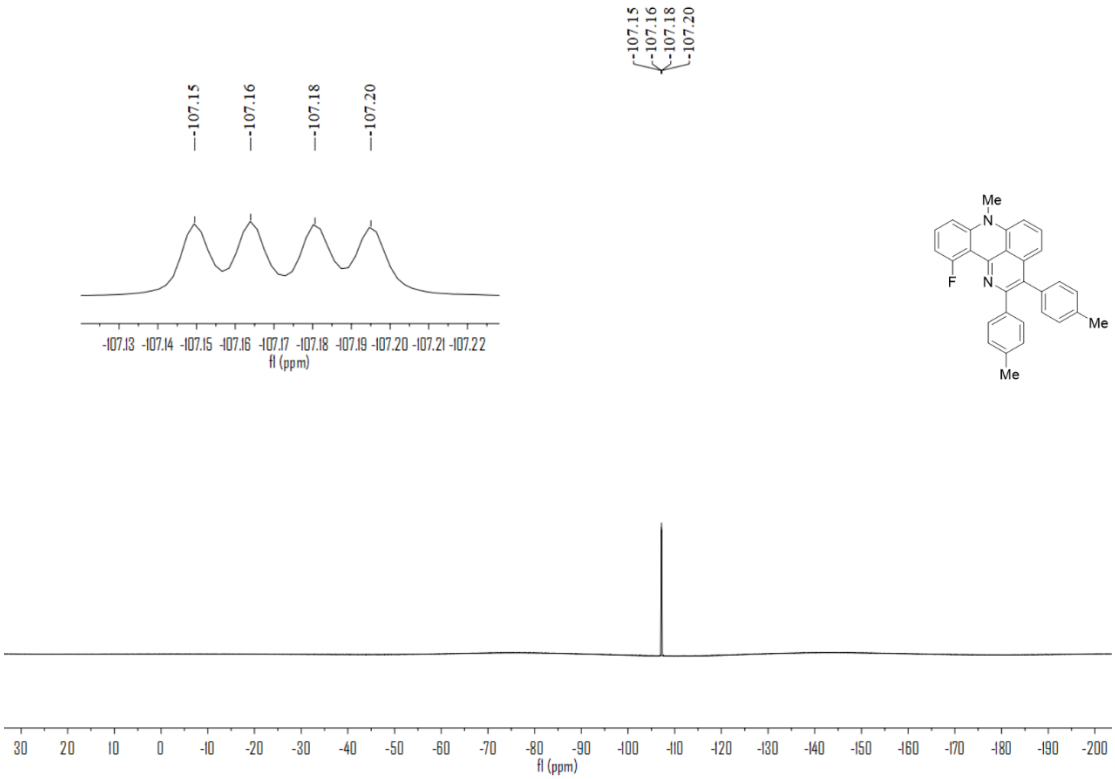
^{1}H NMR spectra of **5j** ($CDCl_3$)



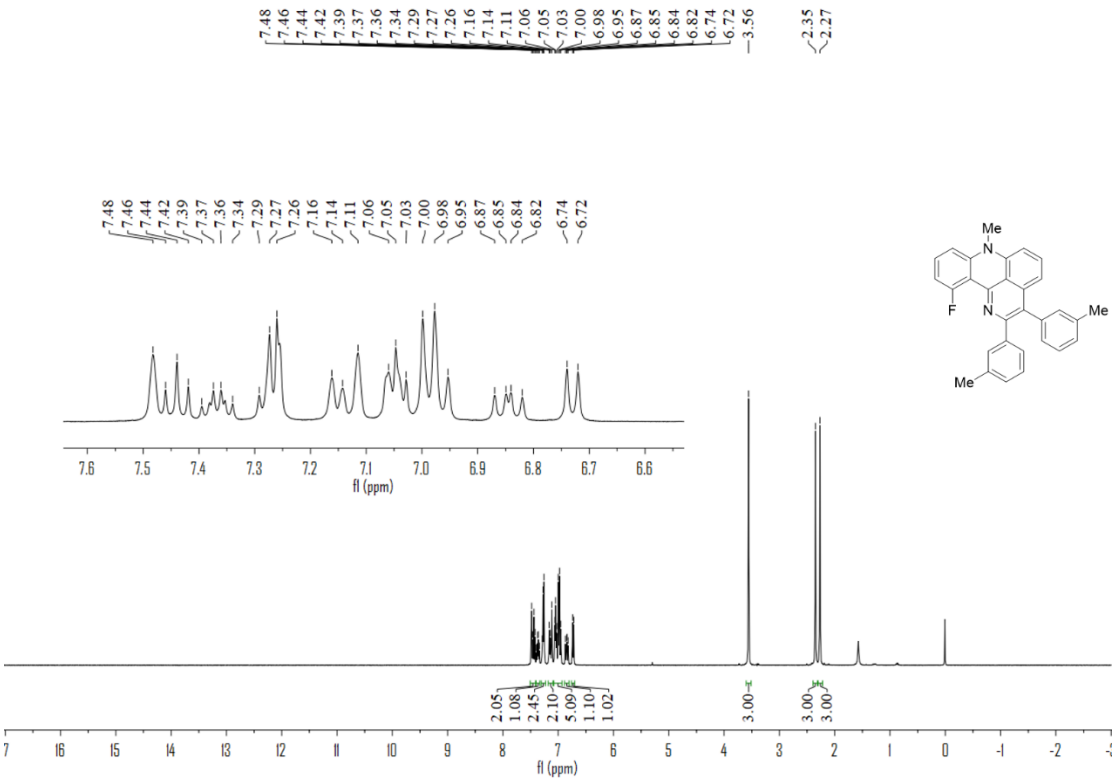
^{13}C NMR spectra of **5j** ($CDCl_3$)



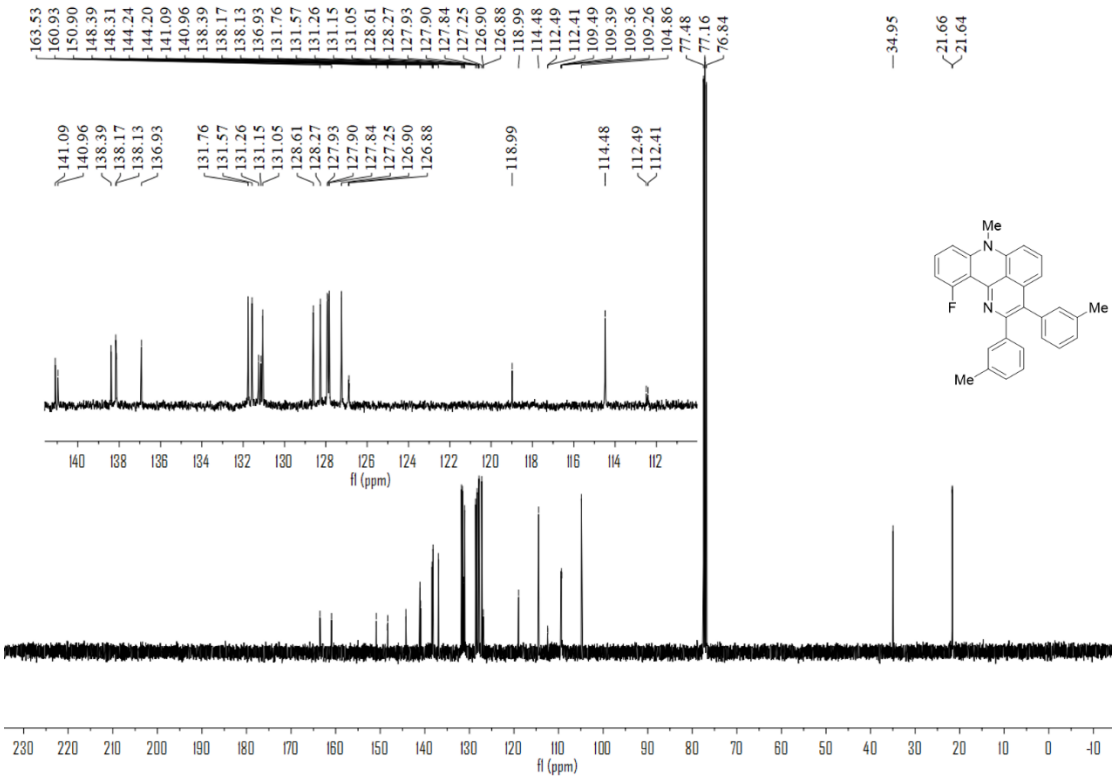
^{19}F NMR spectra of **5j** ($CDCl_3$)



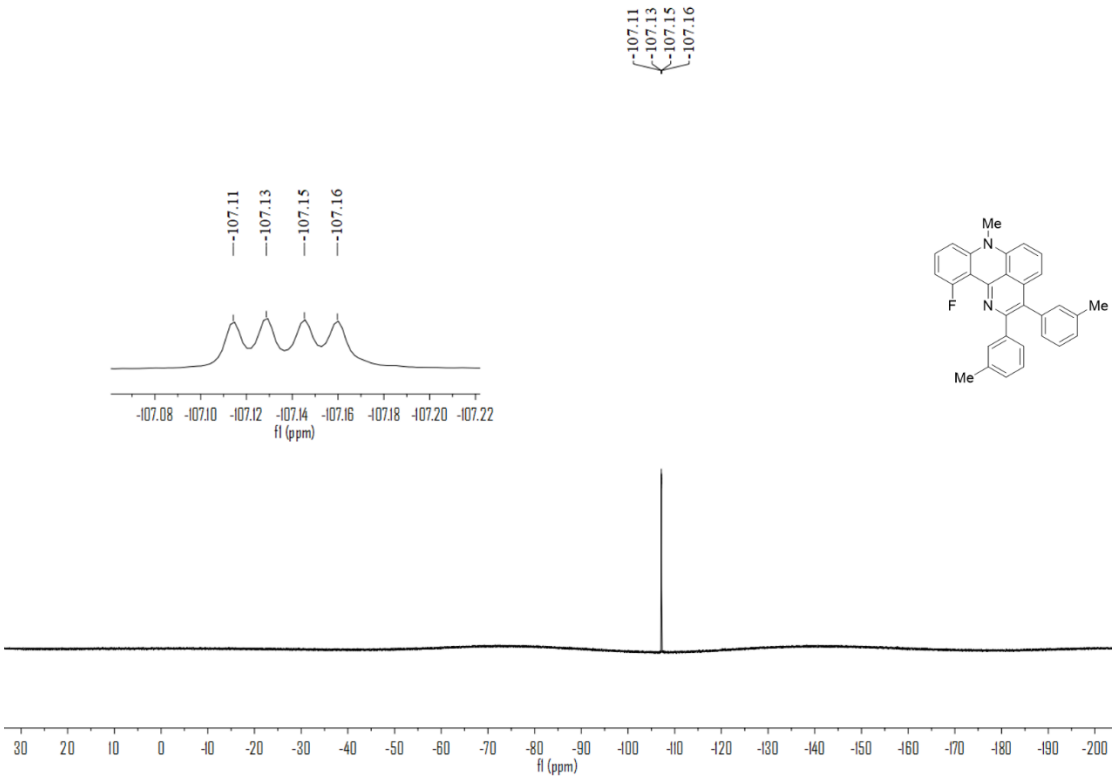
^{1}H NMR spectra of **5k** ($CDCl_3$)



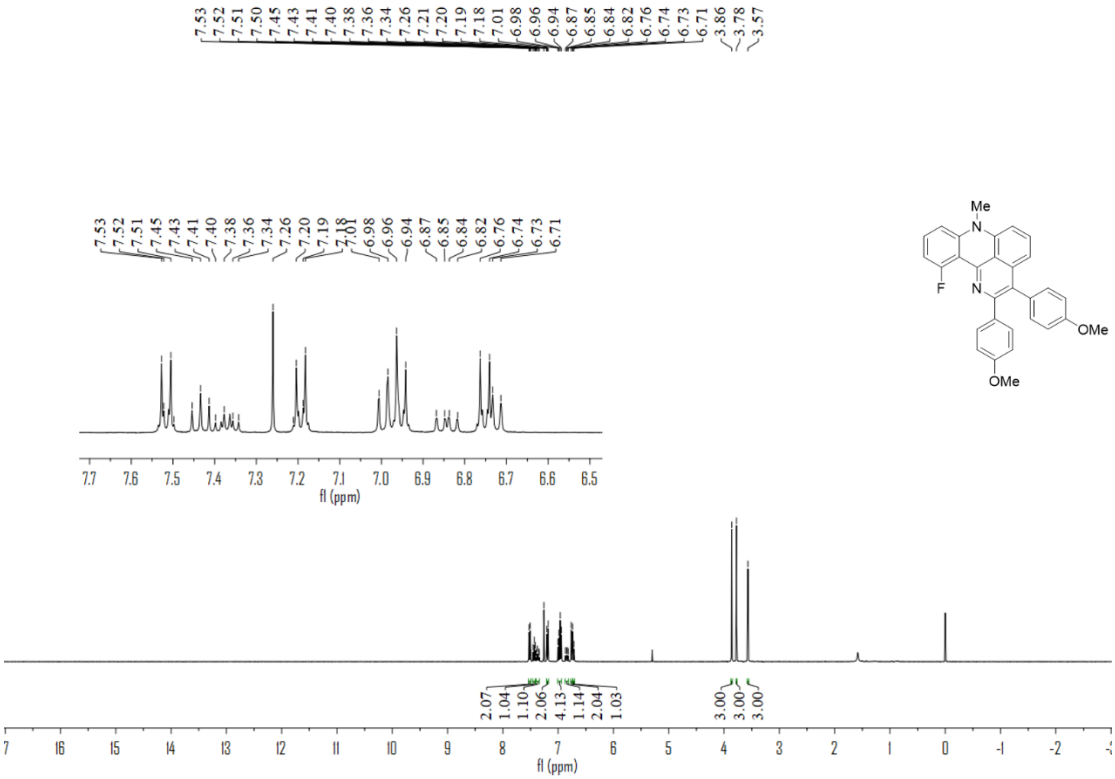
^{13}C NMR spectra of **5k** ($CDCl_3$)



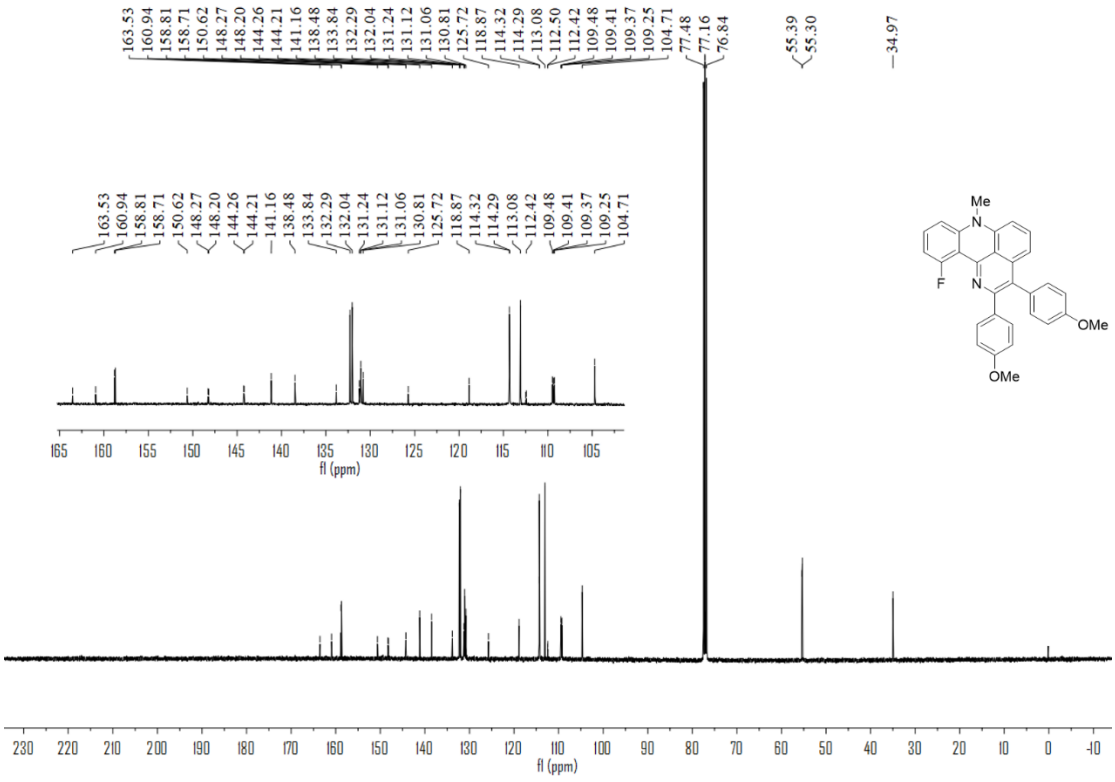
^{19}F NMR spectra of **5k** ($CDCl_3$)



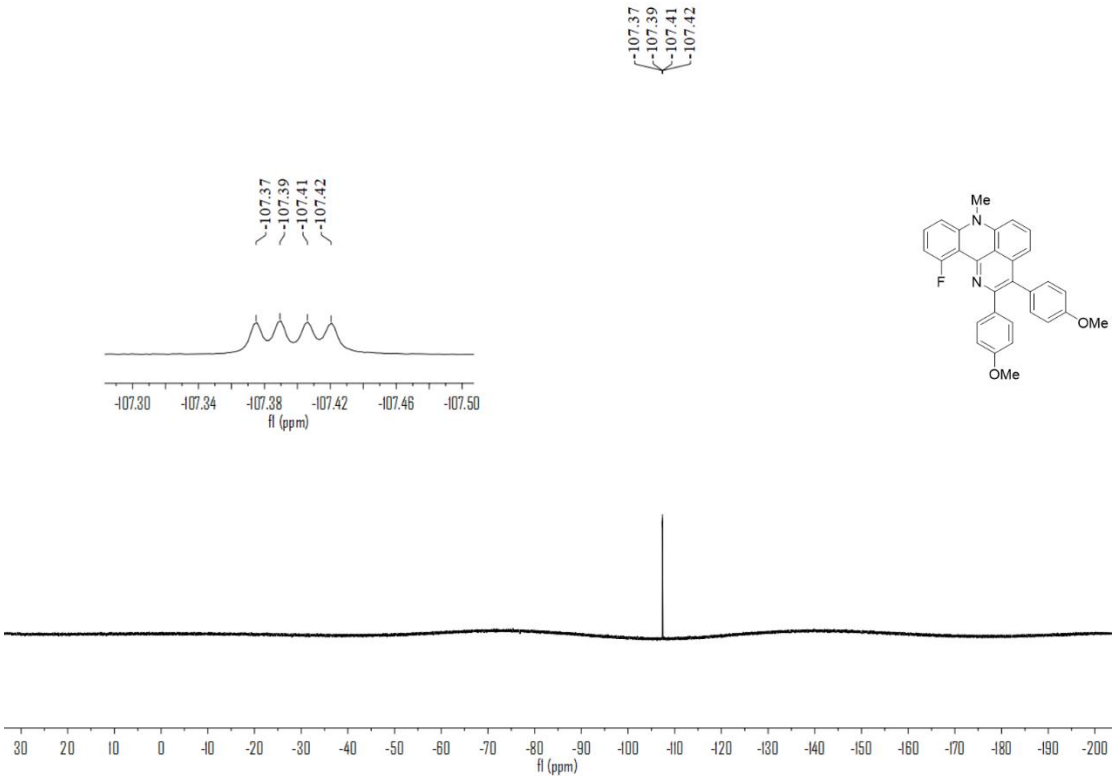
^{1}H NMR spectra of **5l** ($CDCl_3$)



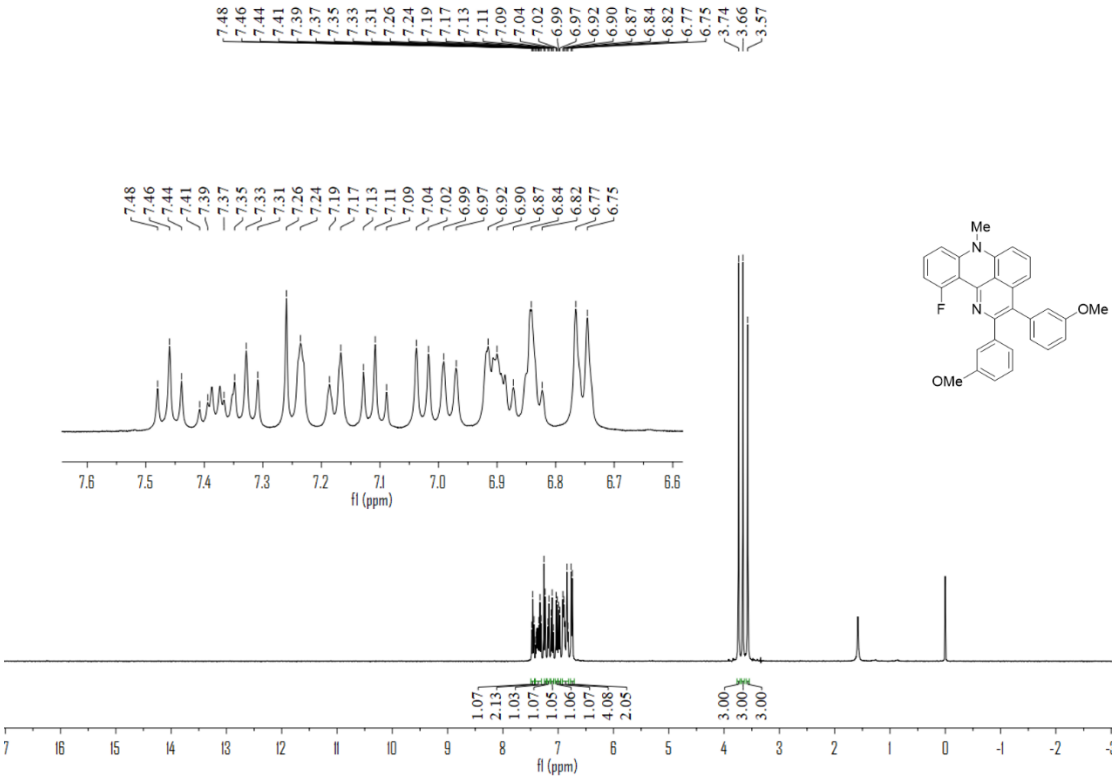
^{13}C NMR spectra of **5l** ($CDCl_3$)



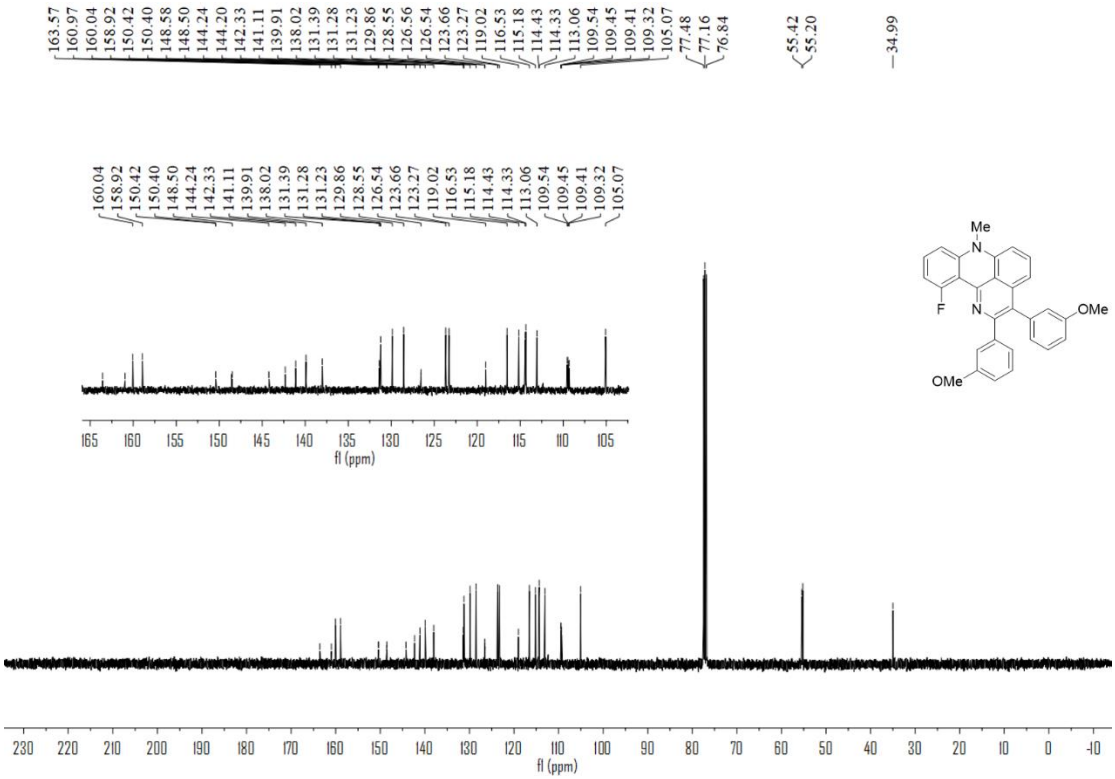
^{19}F NMR spectra of **5l** ($CDCl_3$)



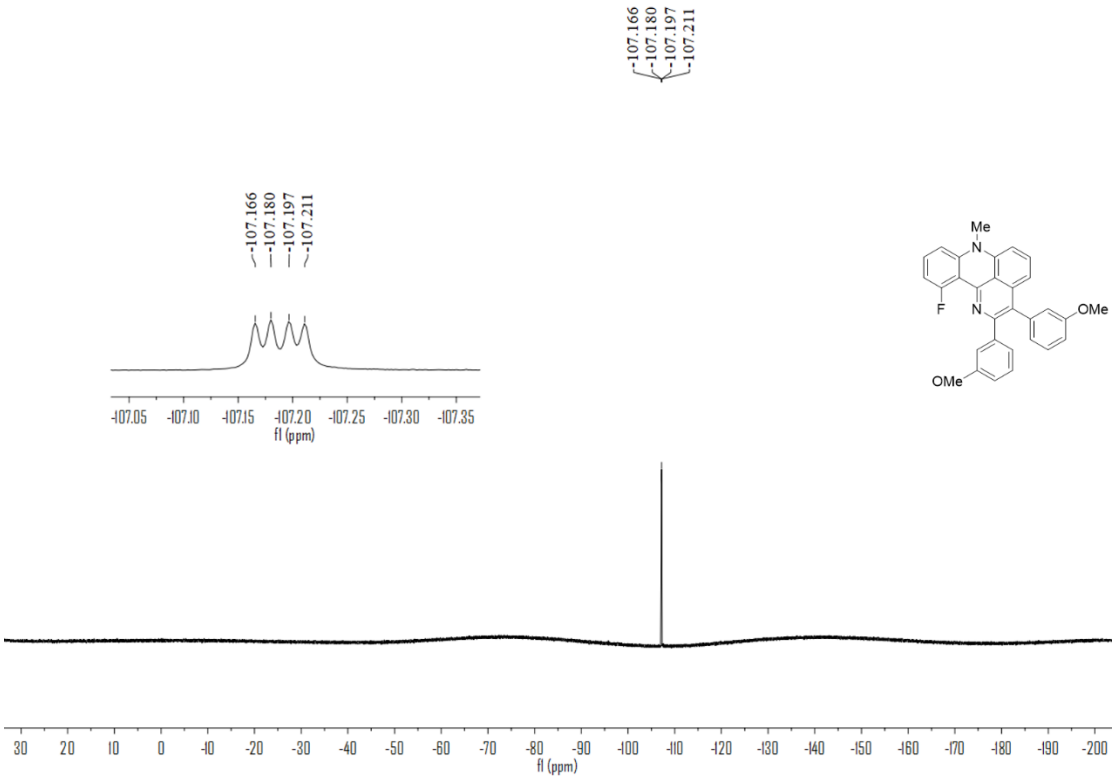
^{1}H NMR spectra of **5m** ($CDCl_3$)



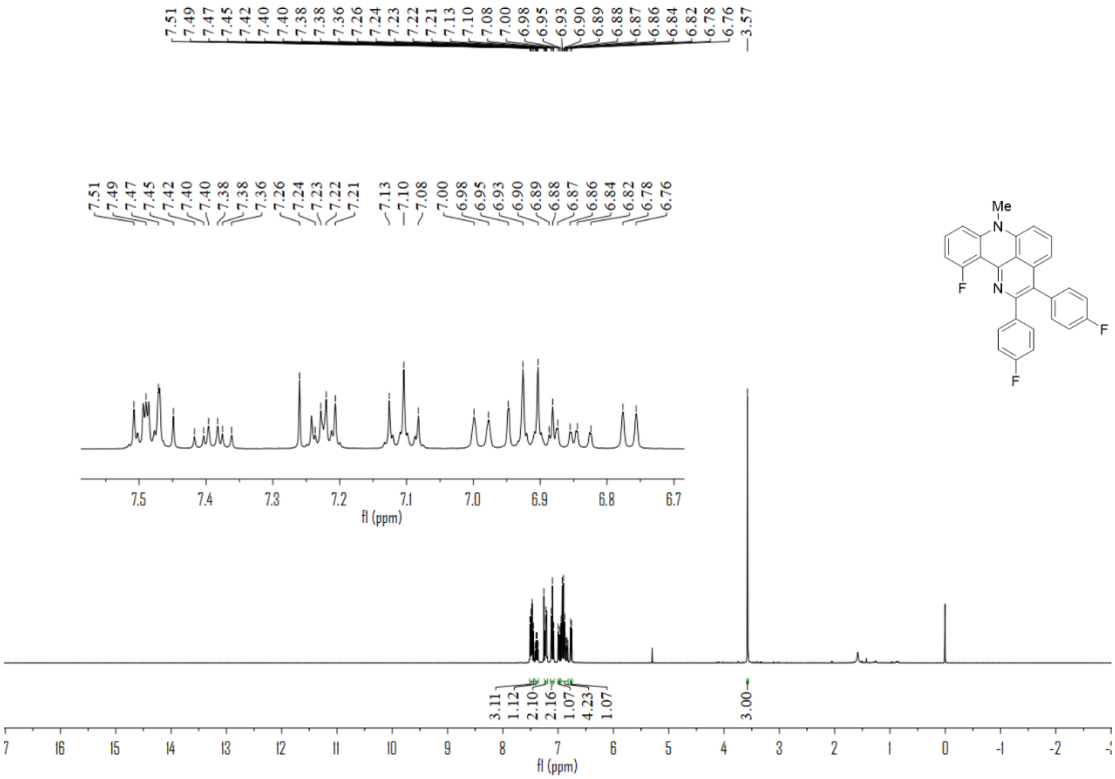
^{13}C NMR spectra of **5m** ($CDCl_3$)



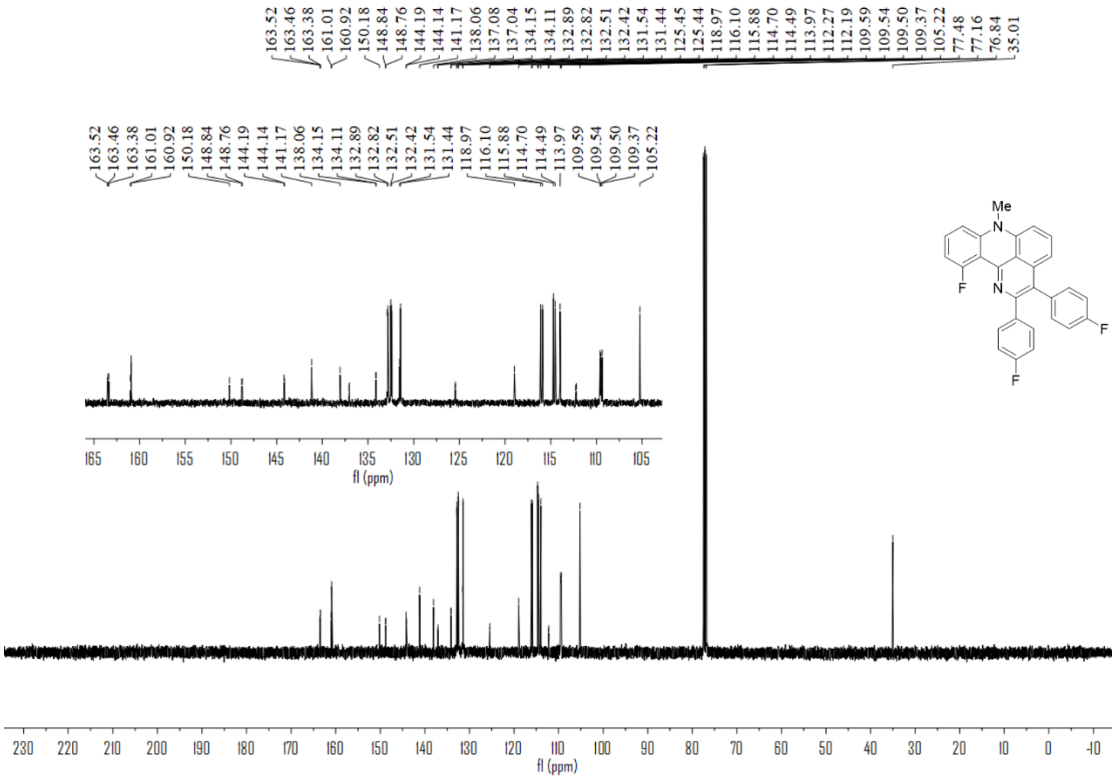
^{19}F NMR spectra of **5m** ($CDCl_3$)



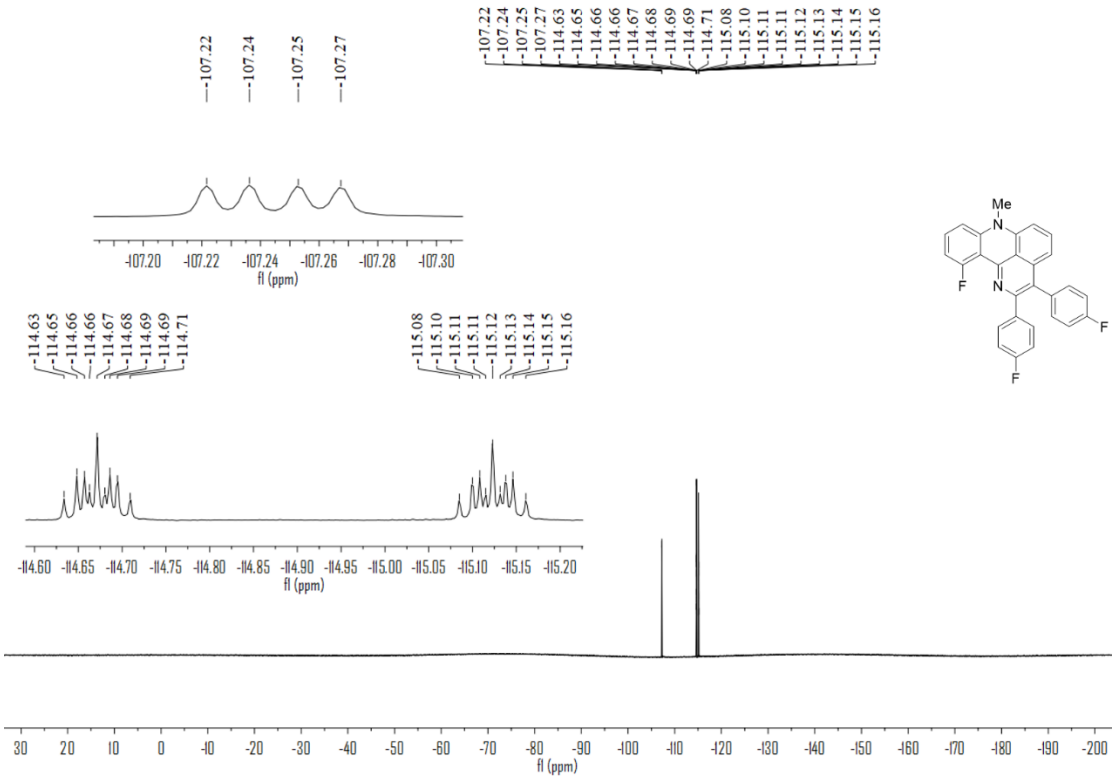
^{1}H NMR spectra of **5n** ($CDCl_3$)



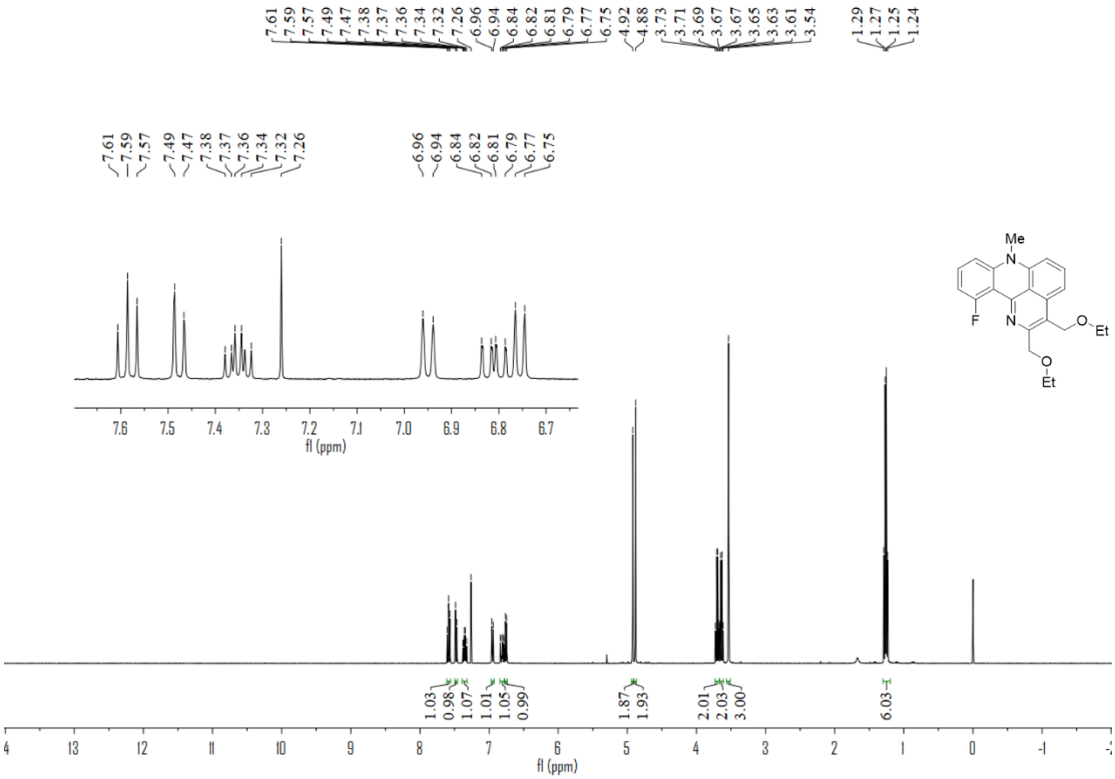
^{13}C NMR spectra of **5n** ($CDCl_3$)



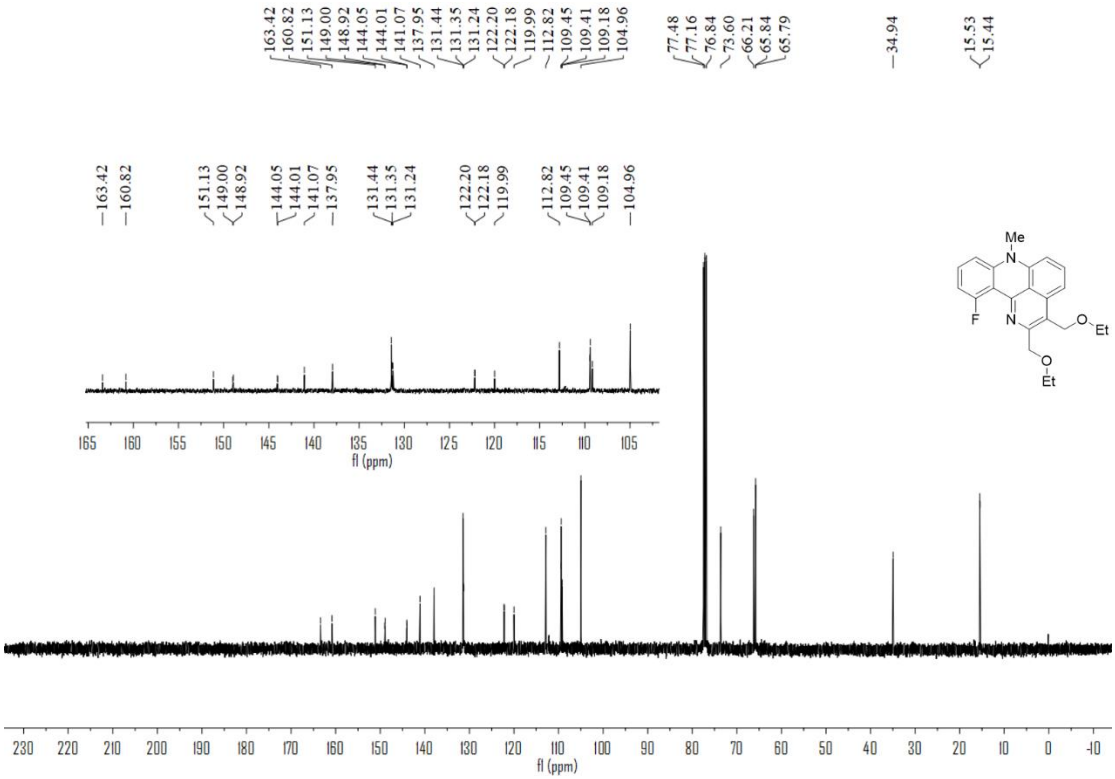
^{19}F NMR spectra of **5n** ($CDCl_3$)



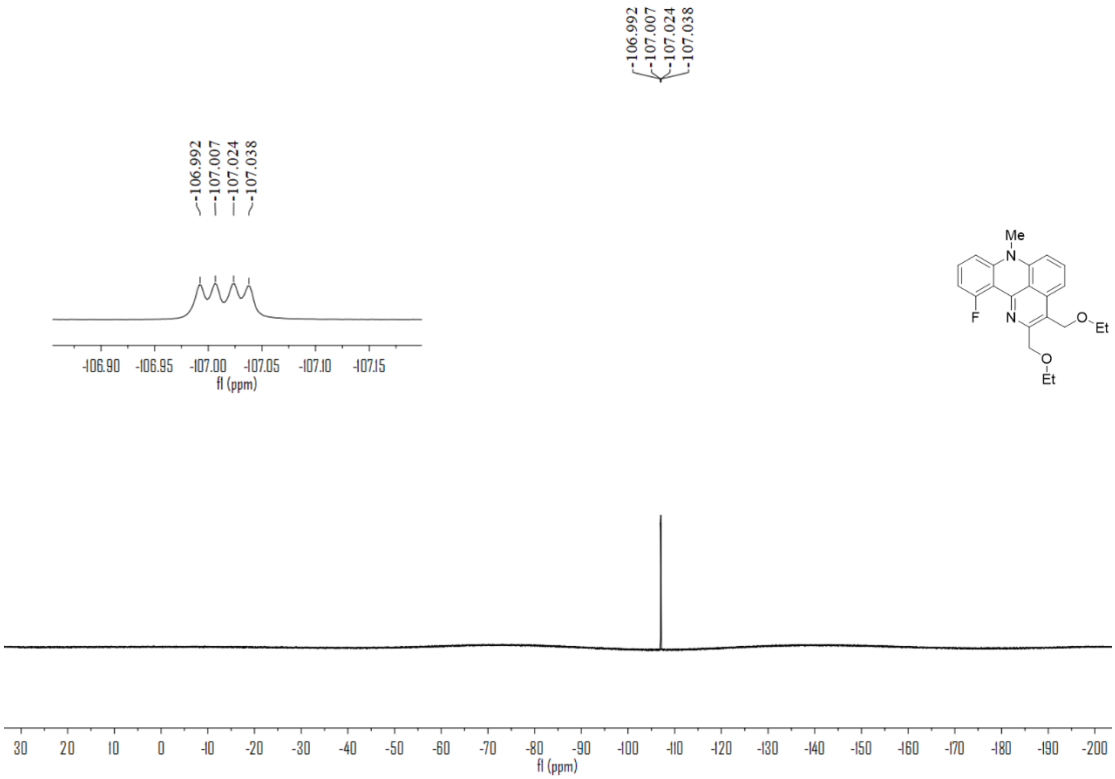
^{1}H NMR spectra of **5o** ($CDCl_3$)



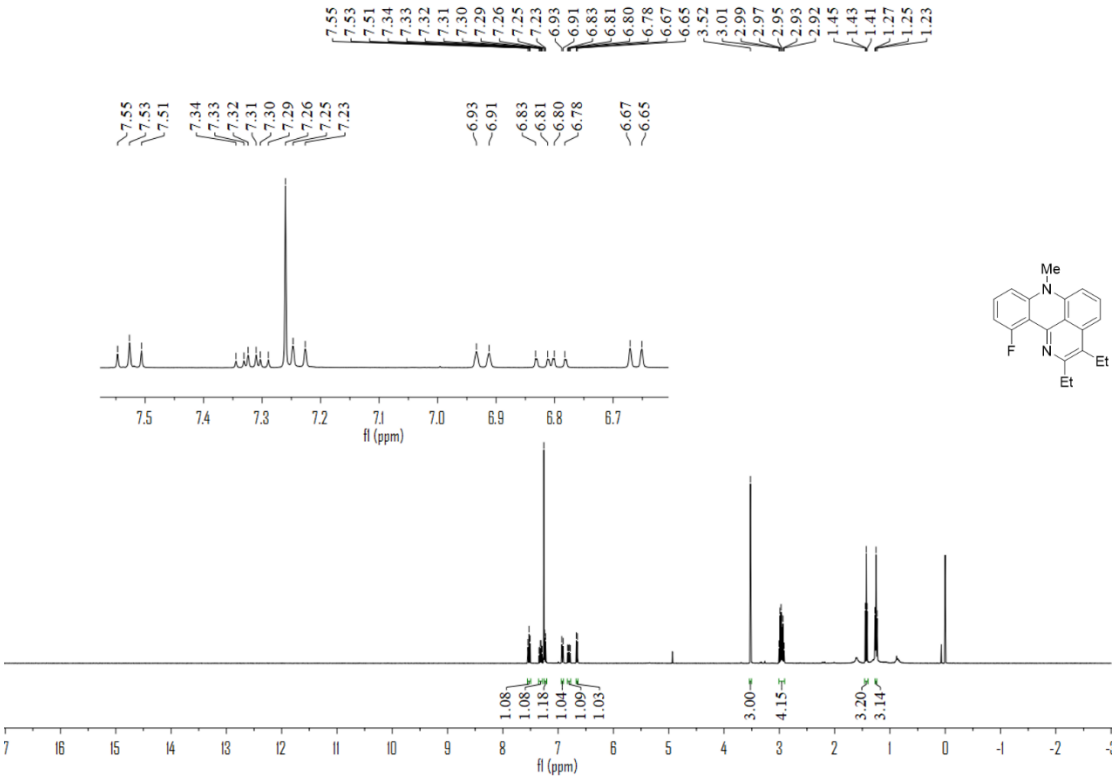
^{13}C NMR spectra of **5o** ($CDCl_3$)



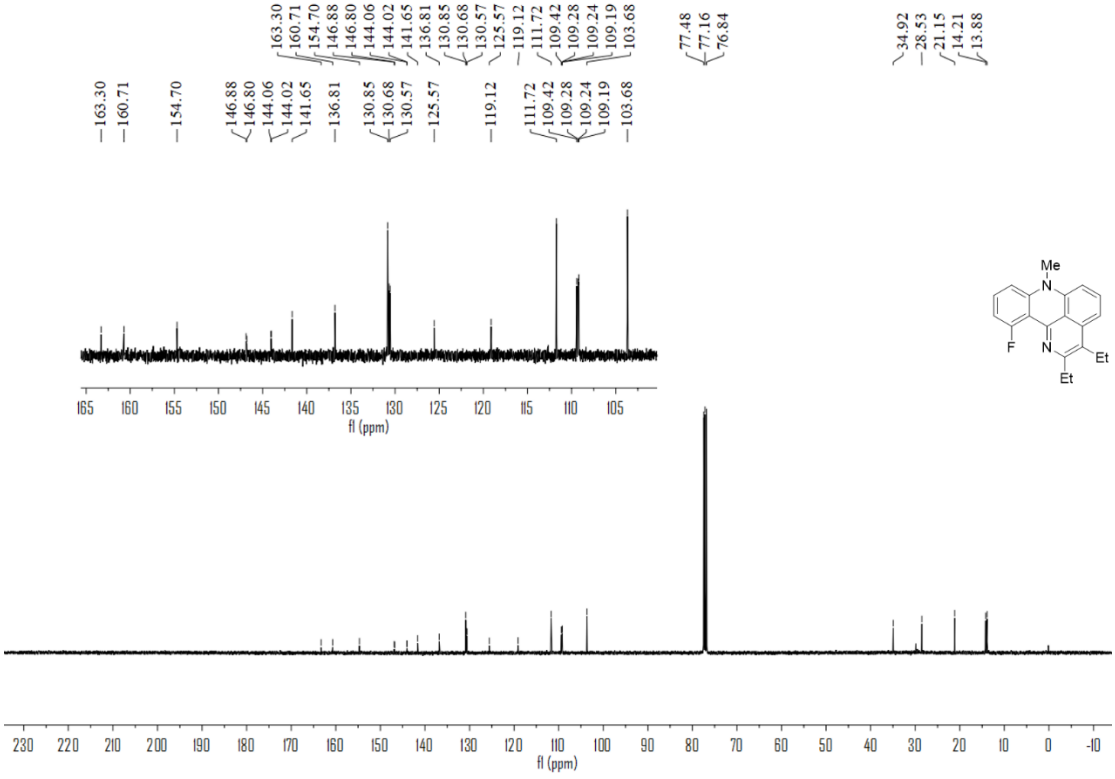
^{19}F NMR spectra of **5o** ($CDCl_3$)



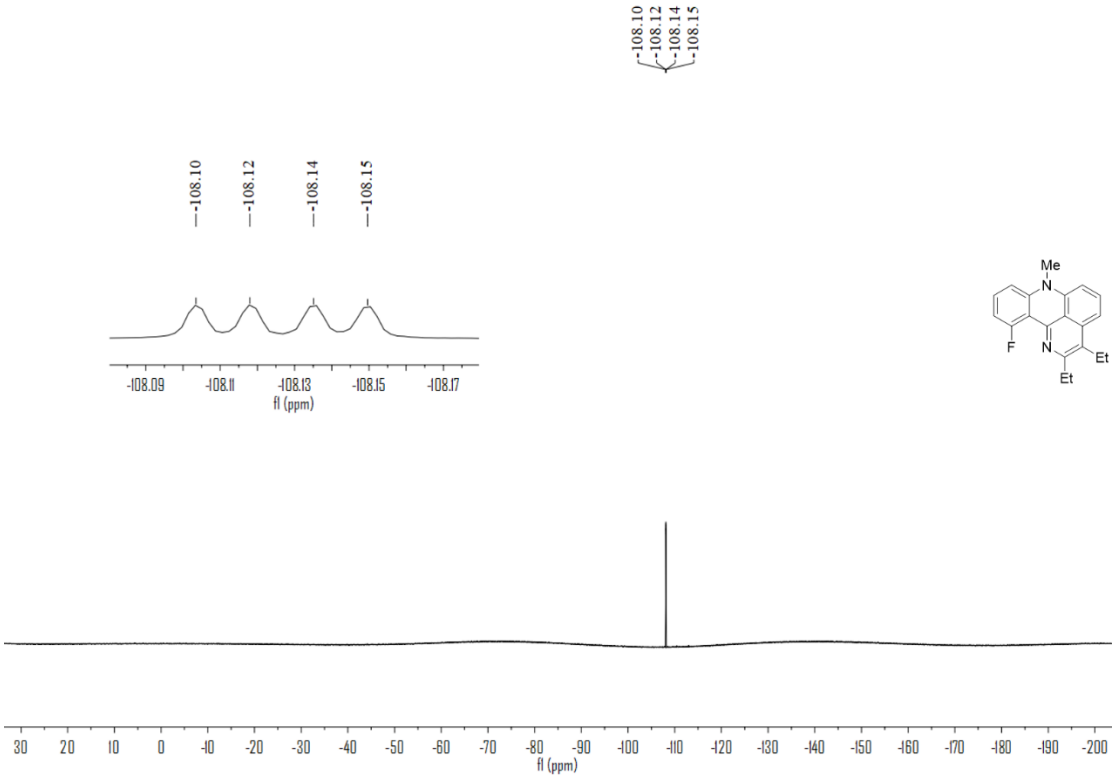
^{1}H NMR spectra of **5p** ($CDCl_3$)



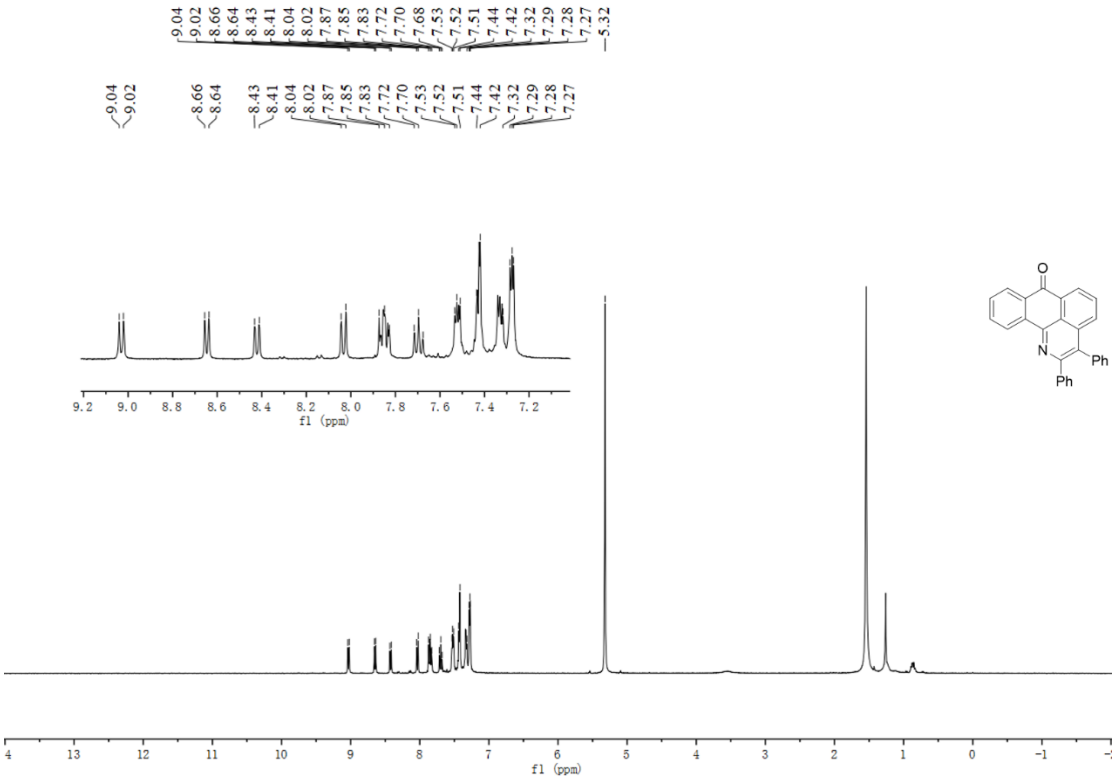
^{13}C NMR spectra of **5p** ($CDCl_3$)



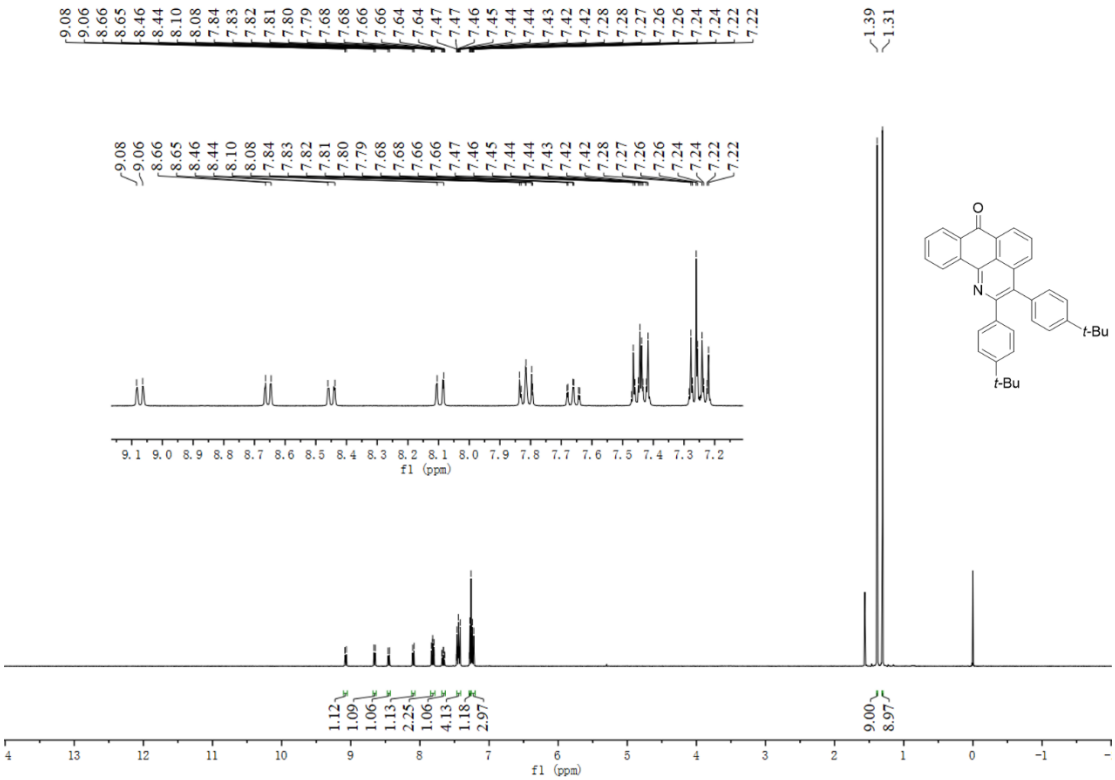
^{19}F NMR spectra of **5p** ($CDCl_3$)



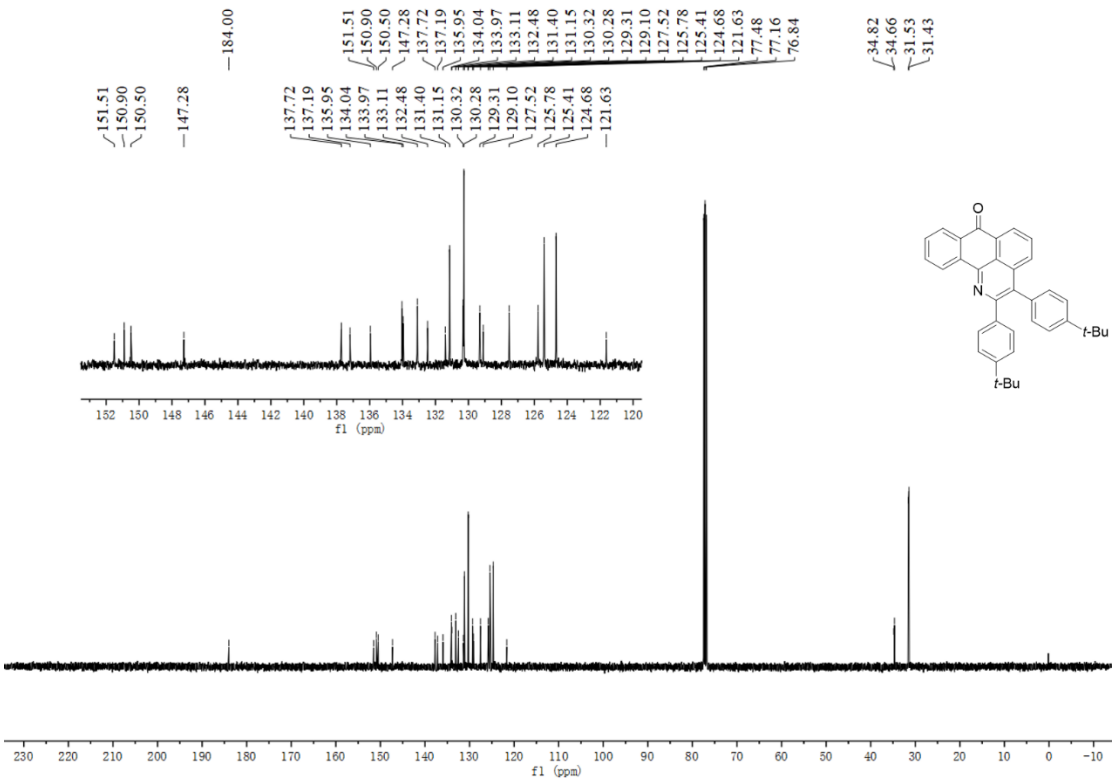
^{1}H NMR spectra of **7a** (CD_2Cl_2)



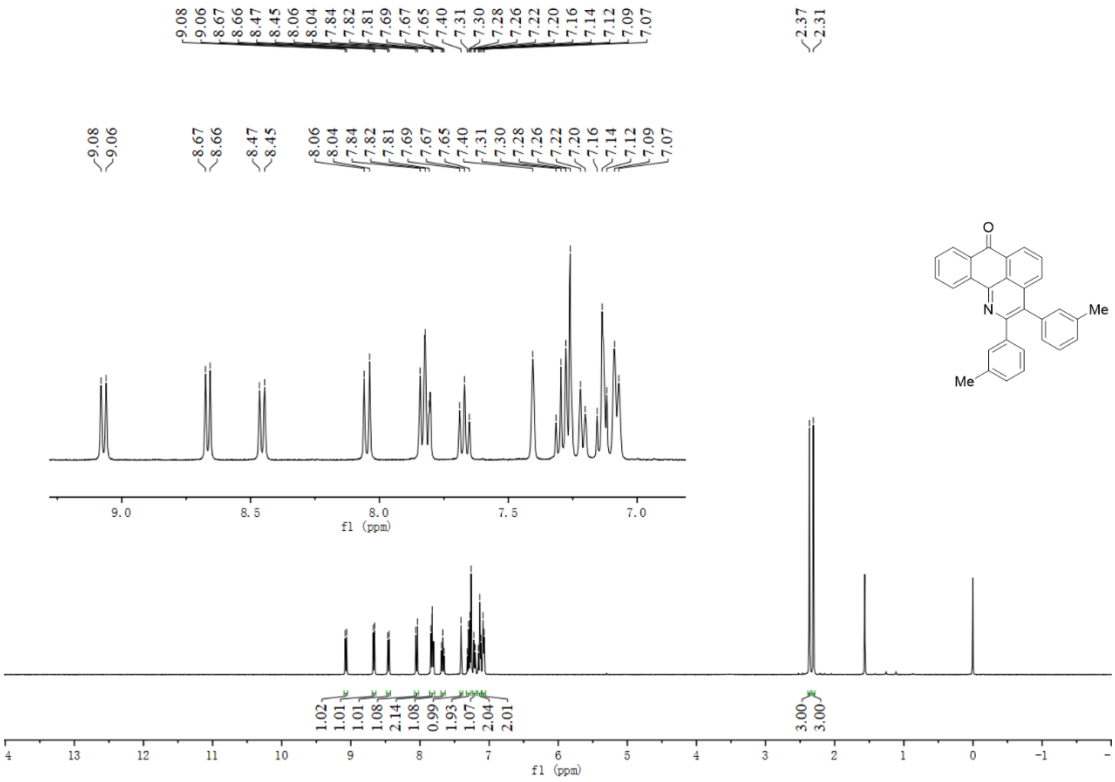
^{1}H NMR spectra of **7b** ($CDCl_3$)



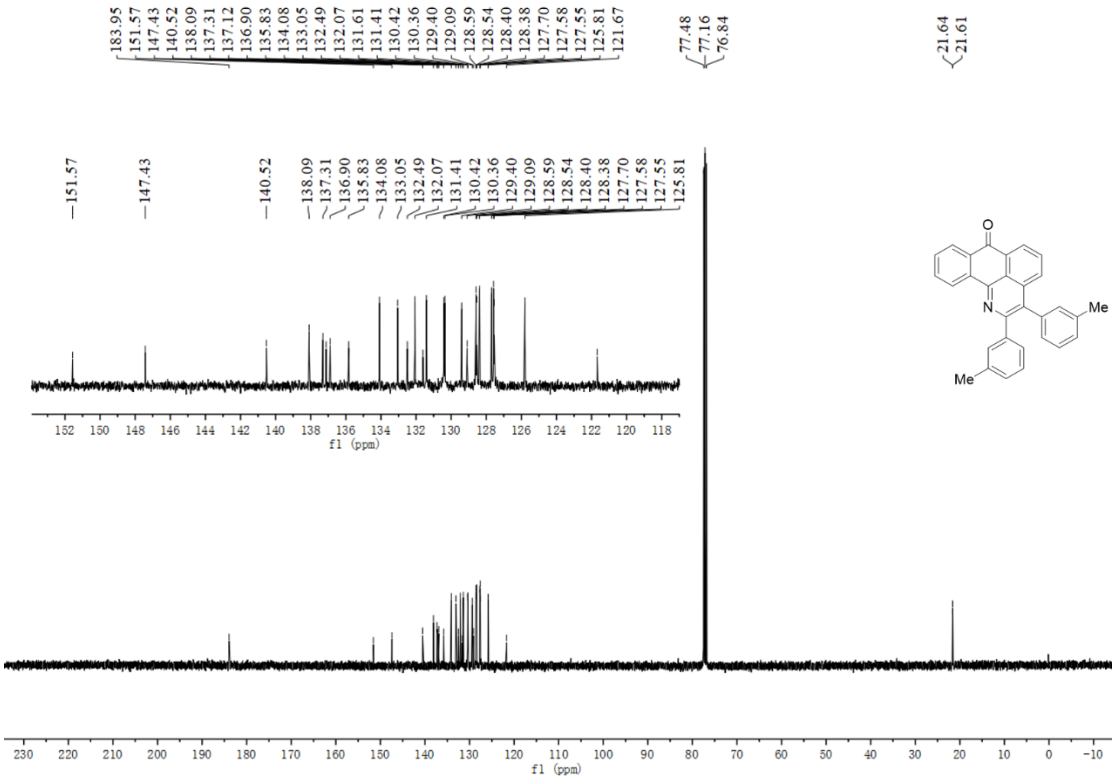
^{13}C NMR spectra of **7b** ($CDCl_3$)



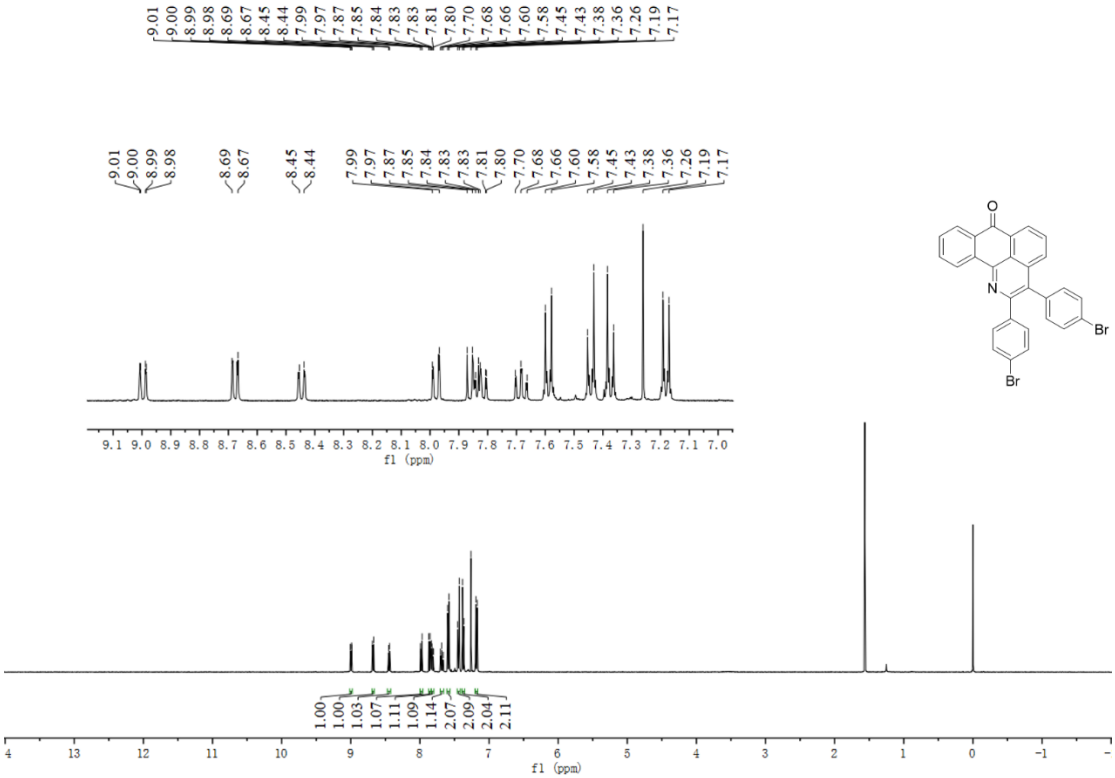
^{1}H NMR spectra of **7c** ($CDCl_3$)



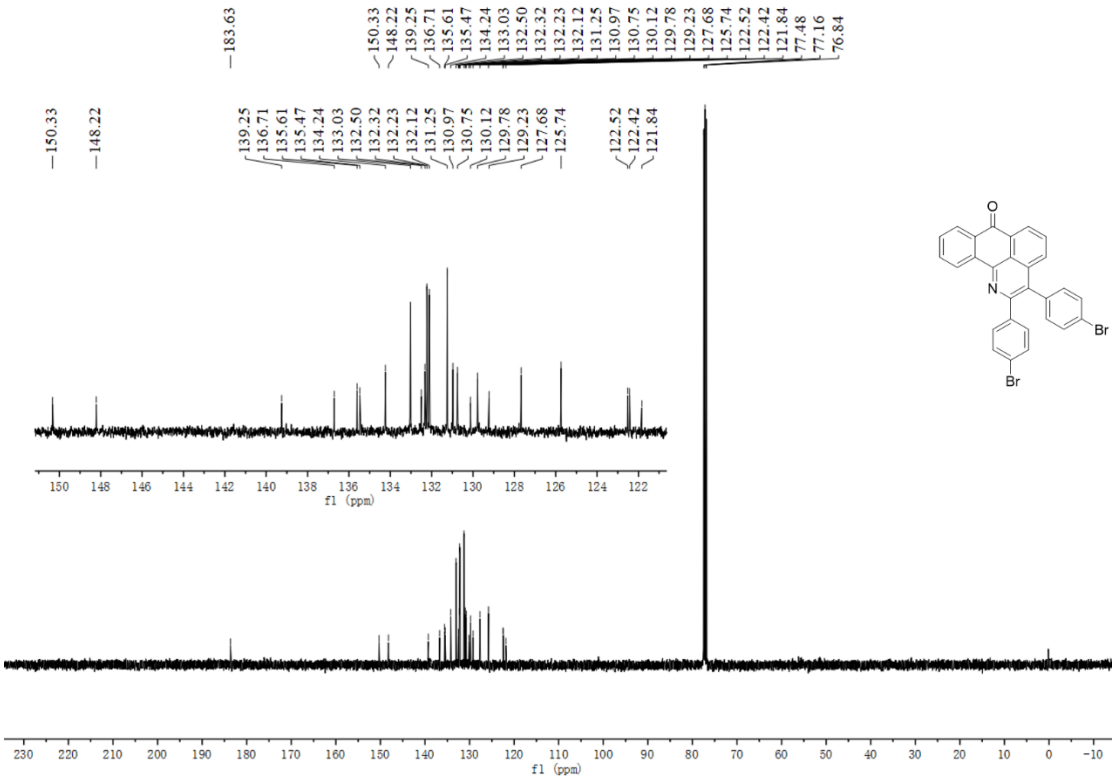
^{13}C NMR spectra of **7c** ($CDCl_3$)



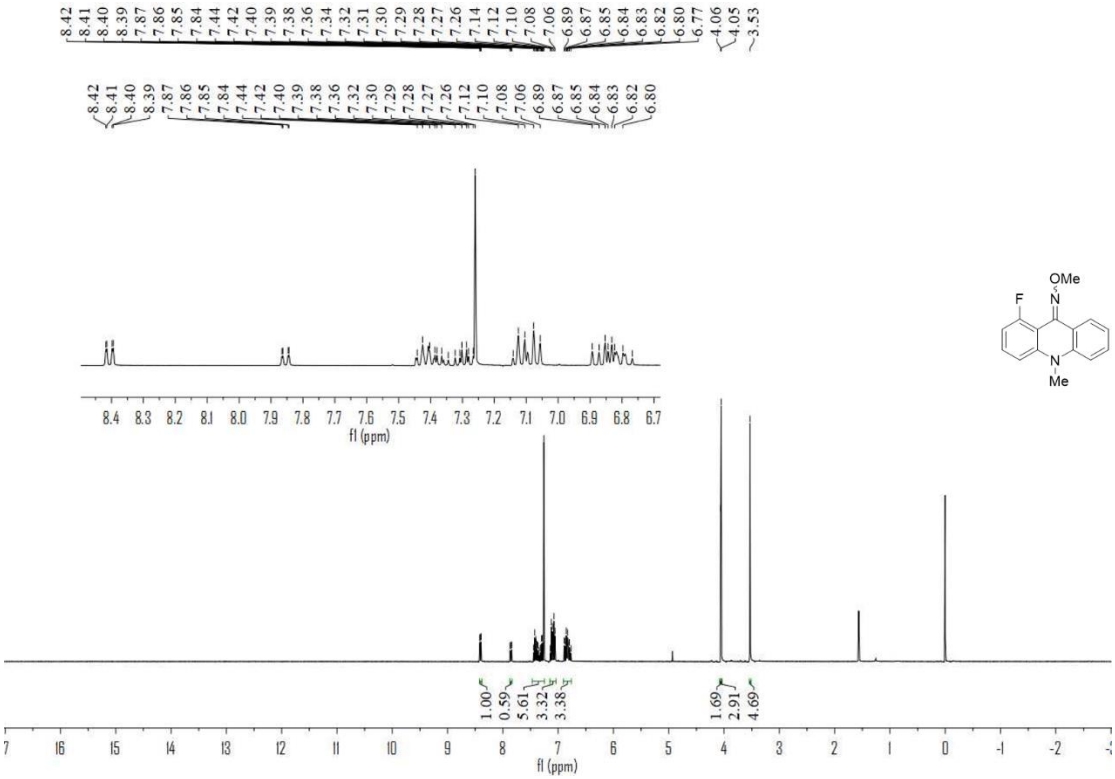
^{1}H NMR spectra of **7d** ($CDCl_3$)



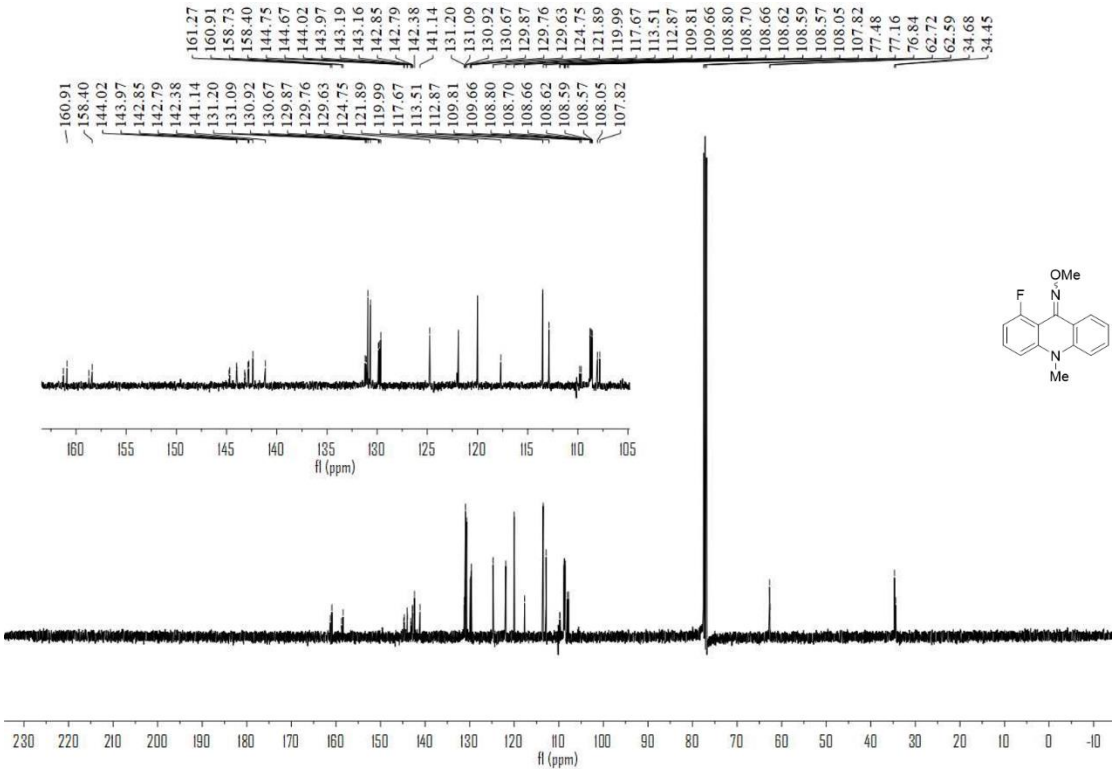
^{13}C NMR spectra of **7d** ($CDCl_3$)



^{1}H NMR spectra of **8** ($CDCl_3$)



^{13}C NMR spectra of **8** ($CDCl_3$)



^{19}F NMR spectra of **8** ($CDCl_3$)