Supporting Information

Rh(III)-Catalyzed domino annulation strategy to synthesize benzo[*c*]naphthyridinones from 3-diazooxindoles and isoxazolones

Man Miao,[a#] Zhenjie Qi,[c#] Fengkai Sun,[a] Hui Yuan,[a] Xiao-Bing Lan,[a] Ping Zheng,[a] Jian-Qiang Yu,[a] Xiaoli Guo,*[a] Jian Zhang,*[a,b] and Zhenyu An*[a]

[a] Key Laboratory of Protection, Development and Utilization of Medicinal Resources in Liupanshan Area, Ministry of Education, Peptide & Protein Drug Research Center, School of Pharmacy, Ningxia Medical University, Yinchuan 750004, China; E-mail: anzy@nxmu.edu.cn; gxl2018666@163.com

[b] Medicinal Chemistry and Bioinformatics Center, Shanghai Jiao Tong University School of Medicine, Shanghai 200025, China; E-mail: jian.zhang@sjtu.edu.cn

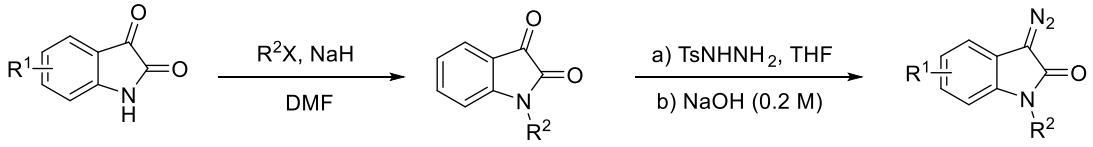
[c] School of Resource & Environment and Safety Engineering, Jining University, Qufu 273100, China

General Information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker 400M in $CDCl_3$. All ^{1}H NMR, ^{13}C NMR and ^{19}F NMR chemical shifts were given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; copies of their ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. All reagents were purchased commercially and used as received, unless otherwise noted.

Experimental Section

1. General procedure for the synthesis of diazooxindoles.[1]

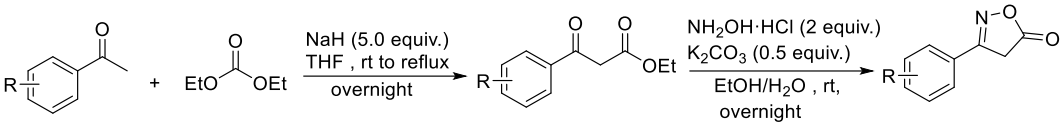


Step-I: NaH (60% dispersion in mineral oil, 12.0 mmol) was added to a solution of isatin (10.0 mmol) in DMF (55 mL) at 0 °C under Air. The mixture was stirred for 20 min at 0 °C and then a solution of halogenated reagents in DMF (15 mL) was added. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched by addition of water (5 mL) and solvent was evaporated. The crude product was suspended in sat. NH_4Cl solution (50 mL) and extracted with EtOAc. Combined organic layers were dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel with PE/EA (5:1) as eluent to provide the crude product as an orange solid.

Step-II: Alkyl protected isatin (10 mmol) and tosylhydrazine (12 mmol) were dissolved in THF (30 mL). The reaction mixture was refluxed for 2 h and then allowed to reach room temperature. A solution of the obtained tosylhydrazone was treated with 0.2 M NaOH water solution (0.2 M, 10 mL) at room temperature. The reaction mixture

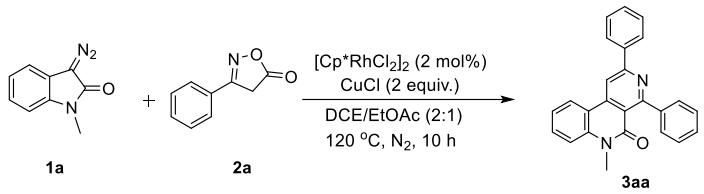
was stirred for approximately 2 h, then neutralized by addition of dry-ice, diluted with brine and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel with PE/EA (5:1) as eluent to provide diazooxindoles as an orange solid.

2. General procedure for the synthesis of 3-aryl-5-isoxazolones.[2]



To a suspension of sodium hydride (60% in mineral oil, 5 equiv.) and diethyl carbonate (10 mmol, 2.0 equiv.) in THF (10 mL) was added a solution of substituted acetophenone (5 mmol, 1.0 equiv.) in THF (10 mL) dropwise under reflux. The mixture was refluxed overnight then quenched with H_2O. The mixture was extracted with ethyl acetate for 3 times, and the combined organic phase was washed with brine, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified on a silica gel column to afford substituted ethyl benzoylacetate (petroleum ether/ethyl acetate, 20:1, v/v). To a mixture of ethyl benzoylacetate (3 mmol, 1.0 equiv.), hydroxylamine hydrochloride (6mmol, 2.0 equiv.) and potassium carbonate (1.5 mmol, 0.5 equiv.) in ethanol/water (10 mL, v/v = 1:1) was stirred at room temperature overnight. The solid was filtered, washed with water and extracted three times with ether. The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified on a silica gel column to afford substituted 3-arylisoxazol-5-ones (petroleum ether/ethyl acetate, 3:1, v/v).

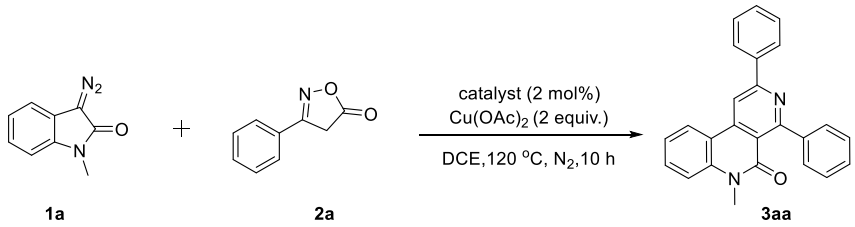
3. General procedure for the synthesis of 6-methyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one.



A mixture of 3-diazo-1-methylindolin-2-one **1a** (0.2 mmol, 1 equiv.), 3-phenylisoxazol-5(4*H*)-one **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under nitrogen atmosphere for 10 h (TLC monitored). Upon completion of the reaction, the reaction mixture was extracted with saturated brine (10 mL) and ethyl acetate (3×15 mL). The combined organic phase was dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo and the crude product was purified by column chromatography, eluting with petroleum ether/ethyl acetate (4 : 1) to afford the desired product **3aa**.

The process of optimizing reaction conditions

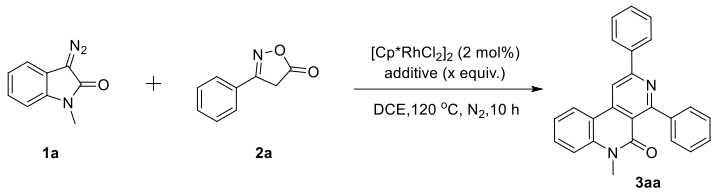
Table S1. Screening of the catalyst [a]



Entry	Catalyst	Yield[b] (%)
1	**$[Cp^*RhCl_2]_2$**	**71**
2	$[Cp^*NiCl_2]_2$	18
3	$[Cp^*RuCl_2]_2$	trace
4	$[Cp^*CoCl_2]_2$	33
5	$[Cp^*IrCl_2]_2$	38
6	$Rh_2(OAc)_4$	48
7	$[Cp^*Rh(MeCN)_3(SbF_6)_2]$	38
8	$PdCl_2$	trace
9	$Pd[(PPh_3)Cl]_2$	38
10	$Pd(OAc)_2$	67
11	$Zn(OAc)_2$	trace
12	$Ru(PPh_3)_3Cl_2$	50
13	$Ru_3(CO)_{12}$	trace
14	$AgSbF_6$	trace
15	AgOAc	trace
16	$Fe(OTf)_2$	28
17	$Fe(OTs)_3$	30

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), catalyst (2 mol%), $Cu(OAc)_2$ (2 equiv.), and DCE (3 mL) in sealed tube, N_2, 120 °C for 10 h. [b] Isolated yield. Entry in bold highlights optimized reaction conditions, and the reaction time was monitored by TLC.

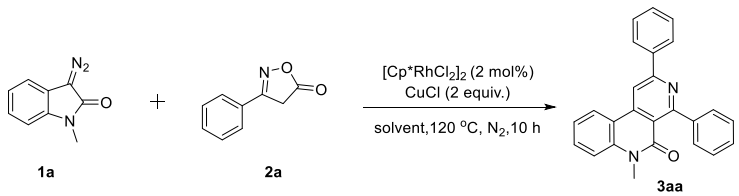
Table S2. Screening of the additive[a]



Entry	Additive	Equiv.	Yield[b] (%)
1	$Cu(OAc)_2$	2	71
2	$Cu(OAc)_2{\cdot}H_2O$	2	69
3	$CuCl_2$	2	64
4	$CuBr_2$	2	62
5	Cu_2O	2	63
6	CuBr	2	66
7	**CuCl**	**2**	**75**
8	CuI	2	67
9	$Cu(OTf)_2$	2	64
10	CuCl	1	70
11	CuCl	3	69
12	CuCl	1.5	73
13	CuCl	2.5	71

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), $[Cp^*RhCl_2]_2$ (2 mol%), additive (2 equiv.), and DCE (3 mL) in sealed tube, N_2, 120 °C for 10 h. [b] Isolated yield. Entry in bold highlights optimized reaction conditions, and the reaction time was monitored by TLC.

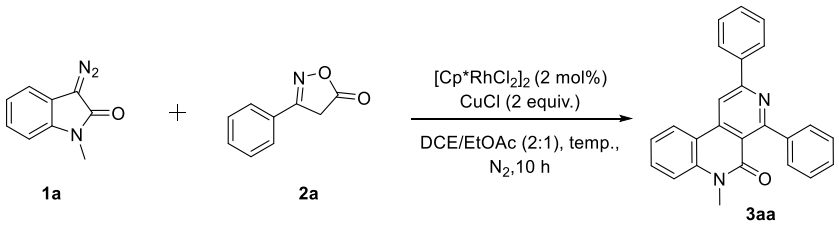
Table S3. Screening of the solvent [a]



Entry	Solvent	Yield[b] (%)
1	DCE	75
2	DCM	68
3	$CHCl_3$	66
4	HFIP	trace
5	PhCl	38
6	PhMe	40
7	NMP	28
8	DMSO	28
9	EtOAc	71
10	MeOH	trace
11	**DCE/EtOAc (2:1)**	80
12	DCE/EtOAc (1:1)	76

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), $[Cp^*RhCl_2]_2$ (2 mol%), CuCl (2 equiv.), and solvent (3 mL) in sealed tube, N_2, 120 °C for 10 h. [b] Isolated yield. Entry in bold highlights optimized reaction conditions, and the reaction time was monitored by TLC.

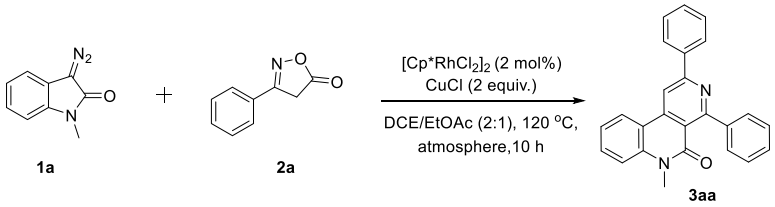
Table S4. Screening of the temperature [a]



Entry	Temperature	Yield[b] (%)
1	80 °C	52
2	100 °C	60
3	60 °C	43
4	110 °C	73
5	**120** °C	**80**
6	130 °C	74
7	140 °C	70
8	150 °C	65
9	rt	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), $[Cp^*RhCl_2]_2$ (2 mol%), CuCl (2 equiv.), and DCE/EtOAc (2:1) (3 mL) in sealed tube, N_2, 120 °C for 10 h. [b] Isolated yield. Entry in bold highlights optimized reaction conditions, and the reaction time was monitored by TLC.

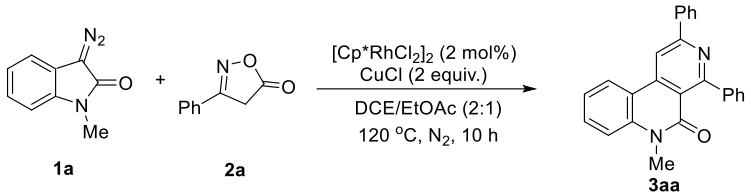
Table S5. Screening of the atmosphere [a]



Entry	Atmosphere	Yield[b] (%)
1	air	68
2	**N_2**	**80**
3	O_2	70

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), $[Cp^*RhCl_2]_2$ (2 mol%), CuCl (2 equiv.), and DCE/EtOAc (2:1) (3 mL) in sealed tube, atmosphere, 120 °C for 10 h. [b] Isolated yield. Entry in bold highlights optimized reaction conditions, and the reaction time was monitored by TLC.

Gram-scale synthesis



A mixture of 3-diazo-1-methylindolin-2-one **1a** (5.0 mmol 1 equiv.), 3-phenylisoxazol-5(4*H*)-one **2a** (12.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.1 mmol), CuCl (10 mmol 2.0 equiv.), DCE/EtOAc (15 mL) were stirred at 120 °C under nitrogen atmosphere for 10 h (TLC monitored). Upon completion of the reaction, the reaction mixture was extracted with saturated brine and ethyl acetate. The combined organic phase was dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo and the crude product was purified by column chromatography, eluting with petroleum ether/ethyl acetate (4 : 1) to afford the desired product **3aa**.When starting from **1a** (5.0 mmol), the desired product **3aa** was isolated in 70% yield without a significant decrease in reaction yield.

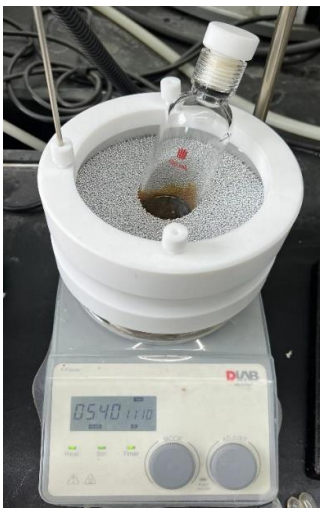


Figure S1. Gram-scale synthesis

The X-ray data of 3aa (CCDC 2381305)

An amount of 20 mg **3aa** were dissolved in dichloromethane/ethyl acetate (8:1) on the brown small reagent bottle (5 mL), which acted as good solvent, and a layer of ether was injected on the dichloromethane of tetrahydrofuran, and the cap is covered with a thin film, white crystals will be presented after seven days.

The crystal was kept at 273.15 K during data collection. Using Olex2[3], the structure was solved with the XT[4] structure solution program using Intrinsic Phasing and refined with the XL[5] refinement package using Least Squares minimisation. Nonhydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms were placed by geometrical considerations and were added to the structure factor calculations.

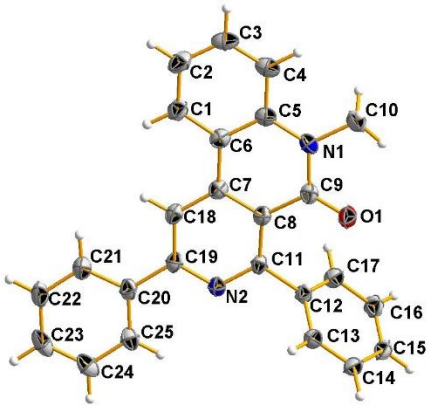


Figure S2. X-ray crystal structure of compound **3aa**, thermal ellipsoids are drawn at 30% probability level

Table S6. Crystal data and structure refinement for 3aa.

Identification code	3aa
Empirical formula	$C_{25}H_{18}N_2O$
Formula weight	362.41
Temperature/K	273.15
Crystal system	orthorhombic
Space group	P212121
a/Å	5.80080(10)
b/Å	12.5114(3)
c/Å	24.7796(5)
α /°	90
β /°	90
γ /°	90
Volume/Å3	1798.41(6)
Z	4
ρ calcg/cm3	1.339
μ /mm-1	0.647
F(000)	760.0
Crystal size/mm3	0.22 × 0.2 × 0.18
Radiation	CuK α (λ = 1.54178)
2Θ range for data collection/°	7.134 to 132.982

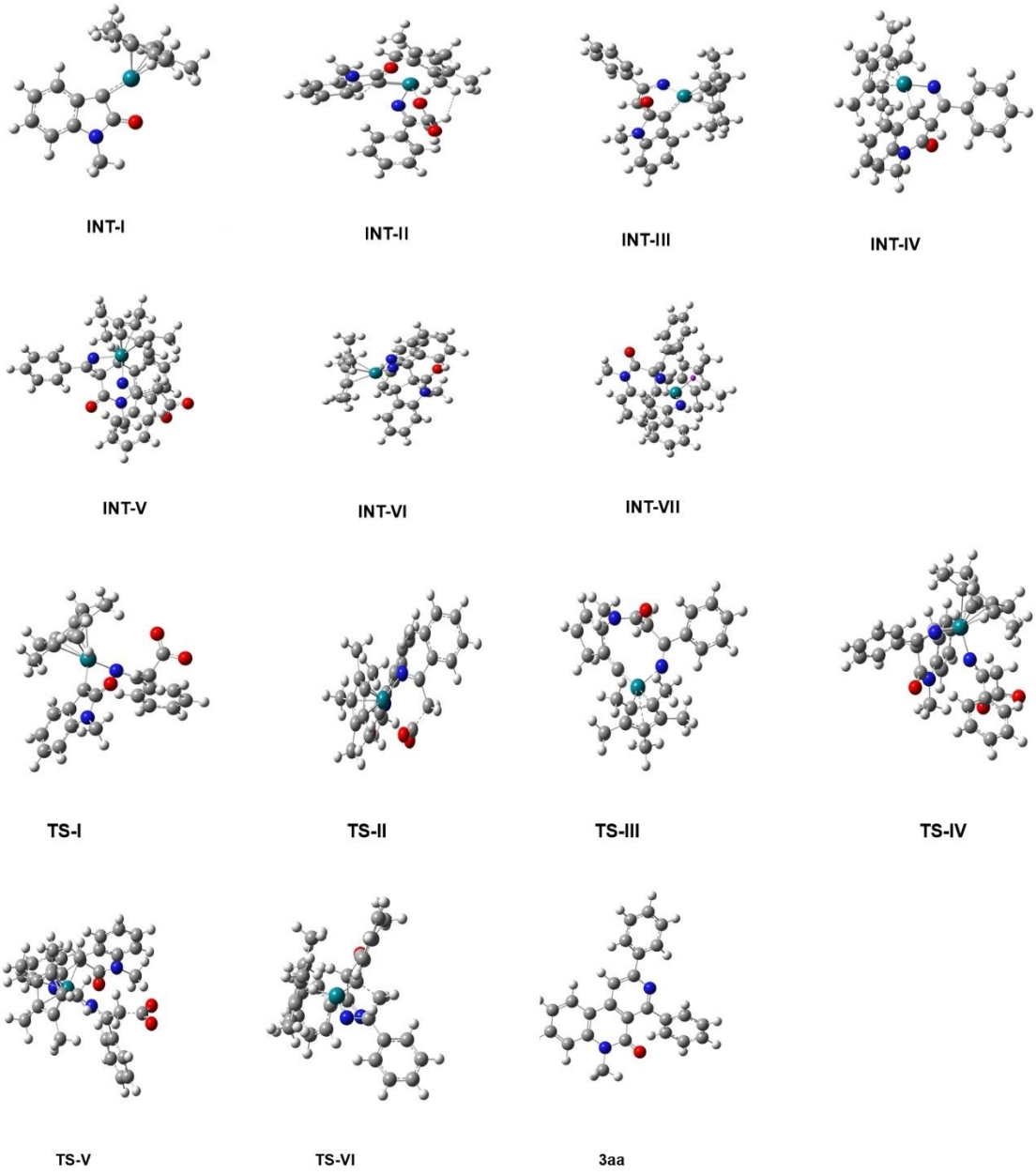
Index ranges	-4 ⩽ h ⩽ 6, -14 ⩽ k ⩽
Reflections collected	10687
Independent reflections	3078 [Rint = 0.0704, Rsigma =
Data/restraints/parameters	3078/0/25431|
Goodness-of-fit on F2	1.028
Final R indexes [I>=2 σ (I)]	R1 = 0.0471, wR2 = 0.1226
Final R indexes [all data]	R1 = 0.0538, wR2 = 0.1266
Largest diff. peak/hole / e Å-3	0.17/-0.28
Flack parameter	0.5(2)

DFT Calculations

Computational details

The theoretical calculations were performed using Gaussian 16 program.[6] The structures involved in this study were optimized, frequency calculations were conducted, and transition states were located at the B3LYP[7] level of theory with a hybrid basis set. The 6-31G(d) basis set was applied to all C, H, O, and N atoms, while the SDD basis set was used for the Rhodium (Rh) atoms. Dispersion corrections were included using DFT-D3 to ensure the accuracy of the calculations. To avoid the basis set superposition error, no geometric constraints were applied during the structure optimizations. Thermodynamic corrections for all structures involved in the reaction pathway were conducted at 393 K using the Shermo[8] program. All thermodynamic properties were computed under simulated conditions of 393 K and 101 kPa. For all transition state structures, Hessian analyses were performed, confirming that each transition state exhibited only one imaginary frequency. Intrinsic Reaction Coordinate (IRC) calculations were also carried out for all transition states to verify the validity of the transition structures.

Geometry of optimized compounds.



Cartesian coordinates of the computed structures:

INT-I

Zero-point correction=	0.363028
Thermal correction to Energy=	0.386738
Thermal correction to Enthalpy=	0.387682
Thermal correction to Gibbs Free Energy=	0.30801
Sum of electronic and zero-point Energies=	-977.474676
Sum of electronic and thermal Energies=	-977.450966
Sum of electronic and thermal Enthalpies=	-977.450022
Sum of electronic and thermal Free Energies=	-977.529694

C	-2.38401133	0.62742293	-0.00095585
C	-3.40545640	-0.37303797	-0.00056698
C	-4.75415937	-0.05108622	0.00024642
C	-5.10225400	1.30960392	0.00070954
C	-4.12256776	2.30739039	0.00032814
C	-2.76375570	1.97211449	-0.00049288
C	-1.11124473	-0.05604483	-0.00173930
H	-5.52181526	-0.81971427	0.00055829
H	-6.15304603	1.58663026	0.00136455
H	-4.42028255	3.35239777	0.00067671
H	-2.00334315	2.74886889	-0.00087088
C	-1.43609424	-1.47863467	-0.00180676
O	-0.56119874	-2.38532178	-0.00213172
C	-3.49351867	-2.92024667	-0.00054231
H	-4.12312128	-3.03022212	-0.89197683
H	-2.73127072	-3.70245529	-0.00098934
H	-4.12192765	-3.03009059	0.89175427
Rh	0.77140371	-0.27381571	-0.00094777
C	3.08058242	-0.58158587	-0.01619792
C	2.68122841	0.13012681	1.15950086
C	2.66799803	0.16059109	-1.16811613
C	1.99310011	1.33527945	0.74056388
C	1.98411666	1.35428080	-0.70954753
N	-2.80809599	-1.64712276	-0.00108930
C	3.80155382	-1.89988142	-0.03774414
H	3.54274438	-2.48458977	-0.92559835
H	4.89063630	-1.75475954	-0.04335795
H	3.55485076	-2.50689516	0.83848440
C	2.94529252	-0.19332139	-2.59994254
H	2.17047965	0.19640511	-3.26694075
H	3.90715475	0.22493792	-2.93100496
H	2.99271459	-1.27677630	-2.74529332
C	1.52782279	2.49119677	-1.57725515
H	0.72177132	3.05786435	-1.10356317
H	2.35668993	3.18696824	-1.77256083
H	1.15789864	2.13460833	-2.54280119
C	1.54446305	2.44778709	1.64309523
H	1.18589720	2.06489717	2.60283979
H	2.37423824	3.13980310	1.84767928
H	0.73217145	3.02507855	1.19354148

C	2.97292194	-0.26264615	2.57832263
H	3.01841491	-1.34973381	2.69423598
H	3.93956932	0.14379783	2.91008418
H	2.20656523	0.11126835	3.26391176

2a

Zero-point correction=	0.142307
Thermal correction to Energy=	0.151521
Thermal correction to Enthalpy=	0.152465
Thermal correction to Gibbs Free Energy=	0.136778
Sum of electronic and zero-point Energies=	-552.326507
Sum of electronic and thermal Energies=	-552.317294
Sum of electronic and thermal Enthalpies=	-552.316350
Sum of electronic and thermal Free Energies=	-552.362037

C	3.03778271	-1.09086460	0.00039446
C	1.65474431	-1.19855126	0.00035441
C	0.85556214	-0.04350792	0.00002170
C	1.47522086	1.21262512	-0.00031620
C	2.86390078	1.31532277	-0.00020647
C	3.64778039	0.16545554	0.00000296
H	3.64571533	-1.98822672	0.00056162
H	1.17564371	-2.16938485	0.00074352
H	0.87590532	2.11583299	-0.00041774
H	3.33089324	2.29334632	-0.00038278
H	4.72883403	0.24460083	-0.00009485
C	-0.60917367	-0.14733240	0.00002187
C	-1.57946160	0.99362171	0.00057813
H	-1.50266294	1.63333623	0.88339491
H	-1.50203517	1.63495645	-0.88096019
N	-1.19807029	-1.29175162	0.00003746
O	-2.60386279	-1.09485653	-0.00029750
C	-2.90413526	0.25186361	-0.00084605
O	-4.02352789	0.66060710	-0.00009444

TS-I

Zero-point correction=	0.506219
Thermal correction to Energy=	0.549891
Thermal correction to Enthalpy=	0.541834
Thermal correction to Gibbs Free Energy=	0.453763
Sum of electronic and zero-point Energies=	-1529.768412

Sum of electronic and thermal Energies= -1529.723745
Sum of electronic and thermal Enthalpies= -1529.722871
Sum of electronic and thermal Free Energies= -1529.811671

Rh	-0.52804988	-0.92255885	0.35368959
N	1.16360787	-0.13764730	0.43118426
C	2.22380369	0.36655640	-0.07275518
C	3.25837034	1.00270028	0.80018433
C	4.55799861	1.27948679	0.33206126
C	2.94612666	1.32889834	2.13699287
C	5.51397269	1.85910055	1.17494045
H	4.83006811	1.03534218	-0.68922000
C	3.89881314	1.91115789	2.97276175
H	1.94257151	1.12229915	2.49220943
C	5.19114779	2.17932415	2.49737877
H	6.51167300	2.06063424	0.79385382
H	3.63350777	2.16349121	3.99589113
H	5.93223624	2.63426362	3.14878517
C	-1.20148331	0.87267956	-0.34150766
C	-1.98184939	1.87493496	0.32021038
C	-2.27694381	2.91868995	-0.64160474
C	-2.48675764	2.03732278	1.62803324
C	-3.03305738	4.04117131	-0.31495029
C	-3.24922893	3.16810762	1.95386981
C	-3.52599079	4.16306532	0.99864149
H	-3.24016999	4.80972570	-1.05645859
H	-3.62904773	3.28159366	2.96789590
H	-4.11727301	5.03330810	1.27336670
C	-0.99805844	1.29235441	-1.67359287
O	-0.37166158	0.74557910	-2.67764234
N	-1.67997613	2.55298127	-1.83923152
C	-1.68726347	3.28609141	-3.08153973
H	-2.70611113	3.42342845	-3.47448444
H	-1.22624563	4.27959293	-2.97580837
H	-1.10488142	2.69214457	-3.79192710
H	-2.26776174	1.28706604	2.38493349
C	-0.68005731	-3.17143012	-0.26827242
C	-1.73250704	-2.31765706	-0.83877888
C	-0.82067764	-3.15914264	1.14045778
C	-2.58454932	-1.87735890	0.25951070
C	-1.98472799	-2.32611921	1.47079974
C	0.34518188	-3.90942348	-1.07677303

H	1.10621474	-4.36635103	-0.43777947
H	-0.12512506	-4.71178318	-1.66486436
H	0.87253348	-3.24378493	-1.76599450
C	-1.99318161	-2.12929550	-2.30893714
H	-3.06967210	-2.10476539	-2.51912343
H	-1.53974834	-1.19513607	-2.67551881
H	-1.55975023	-2.95552693	-2.88535183
C	-3.86683638	-1.11347142	0.10598686
H	-4.05782954	-0.46264817	0.96373645
H	-3.82425919	-0.46608305	-0.77304121
H	-4.72242639	-1.79742367	-0.00493253
C	0.02661513	-3.87946024	2.14940795
H	0.23220231	-3.24943092	3.02260439
H	-0.46625111	-4.79331250	2.51557294
H	0.99200925	-4.17046364	1.72487564
C	-2.51544814	-2.10643933	2.85704244
H	-3.10929142	-1.18960340	2.91271139
H	-3.15941801	-2.94204518	3.17305169
H	-1.70466299	-2.02338298	3.58884155
C	2.44217137	0.37223775	-1.59435864
H	1.43285700	0.35773805	-2.07391381
H	2.92933422	1.29848863	-1.90801101
C	3.23566741	-0.78642987	-2.09825507
O	3.07700658	-1.99012334	-1.85326722
O	4.26259824	-0.38933427	-2.96301434
H	4.72049349	-1.19444701	-3.29193463

INT-II

Zero-point correction=	0.505269
Thermal correction to Energy=	0.539893
Thermal correction to Enthalpy=	0.540837
Thermal correction to Gibbs Free Energy=	0.437716
Sum of electronic and zero-point Energies=	-1529.778418
Sum of electronic and thermal Energies=	-1529.743795
Sum of electronic and thermal Enthalpies=	-1529.742850
Sum of electronic and thermal Free Energies=	-1529.845971

Rh	-0.44797852	-0.85689575	0.04159566
N	1.30767220	0.14519206	0.25671705
C	2.27706238	-0.14960541	-0.51892597
C	3.60535917	0.52355936	-0.27055791

C	4.82884481	-0.11811703	-0.52560594
C	3.64342922	1.82371559	0.26311234
C	6.04555368	0.50824736	-0.24440690
H	4.83380972	-1.12398626	-0.93612167
C	4.85590015	2.45525412	0.53119228
H	2.70163748	2.32833081	0.44974161
C	6.06630505	1.79981489	0.28298909
H	6.97862985	-0.01601309	-0.44149428
H	4.85811754	3.46731065	0.93112486
H	7.01291255	2.29311062	0.49301301
C	2.22311623	-1.16513592	-1.66147562
H	3.10117332	-1.09853909	-2.30708490
H	2.21323283	-2.17810462	-1.22947220
C	0.98972065	-1.04949231	-2.58492890
O	1.16028188	-1.13921790	-3.80137023
O	-0.17291770	-0.90923145	-2.02490367
C	-1.40819990	0.88168349	-0.19425454
C	-1.14659670	2.21045030	0.25948115
C	-2.16162577	3.08862967	-0.25403879
C	-0.15136781	2.76064435	1.09259517
C	-2.17523888	4.45055966	0.02481674
C	-0.16733096	4.12628959	1.37987431
C	-1.16227370	4.96346071	0.84996195
H	-2.94846902	5.10075394	-0.37717470
H	0.60222644	4.55043353	2.02130251
H	-1.15420583	6.02642773	1.08243667
C	-2.66975948	0.96898948	-0.95830510
O	-3.37173094	0.08891490	-1.46858989
N	-3.05012748	2.33944865	-0.99900195
C	-4.23976408	2.81584272	-1.65320357
H	-4.93536107	3.28460732	-0.94161428
H	-4.00326883	3.54747633	-2.43822871
H	-4.72142688	1.94600876	-2.10613833
H	0.61911560	2.10216175	1.47620007
C	-0.49774101	-3.19142840	0.49377799
C	-1.86136176	-2.70100850	0.35045532
C	0.10109643	-2.52814608	1.59008329
C	-2.09074530	-1.75078606	1.37874348
C	-0.85612710	-1.57287937	2.11603885
C	0.11061806	-4.24707707	-0.38580095
H	1.17783684	-4.37928398	-0.18197551
H	-0.37714153	-5.22109326	-0.23597970

H	0.00435873	-3.98876280	-1.44588691
C	-2.85491086	-3.18322381	-0.66774734
H	-3.44824638	-4.03128616	-0.29106112
H	-3.53324010	-2.37683043	-0.95723237
H	-2.34688509	-3.51232791	-1.57995352
C	-3.40289192	-1.09200788	1.69479462
H	-3.25606468	-0.11451522	2.16462608
H	-3.99514269	-0.93952150	0.78934327
H	-3.98800658	-1.71093865	2.39164705
C	1.48438138	-2.72400846	2.14180324
H	2.01277416	-1.76762236	2.22422185
H	1.45078312	-3.17581011	3.14375027
H	2.08631372	-3.37957831	1.50480455
C	-0.66521310	-0.76311379	3.36707962
H	-1.34903737	0.09078261	3.39616052
H	-0.84025336	-1.36082122	4.27606261
H	0.35354844	-0.36493714	3.42279571

TS-II

Zero-point correction=	0.507259
Thermal correction to Energy=	0.541022
Thermal correction to Enthalpy=	0.541966
Thermal correction to Gibbs Free Energy=	0.460892
Sum of electronic and zero-point Energies=	-1529.392090
Sum of electronic and thermal Energies=	-1529.358327
Sum of electronic and thermal Enthalpies=	-1529.357382
Sum of electronic and thermal Free Energies=	-1529.458457

Rh	-0.69884287	-0.75372575	-0.04602984
N	1.29169237	-0.45854606	0.22850633
C	2.15057904	-0.38265451	-0.73083159
C	3.61135655	-0.27739487	-0.36805528
C	4.60206111	0.01540002	-1.32599543
C	4.02391648	-0.45446601	0.96939902
C	5.95014715	0.12449861	-0.96211358
H	4.32199736	0.16794414	-2.36162107
C	5.36662276	-0.35095473	1.33248296
H	3.25786985	-0.67151504	1.70499331
C	6.34189812	-0.06020588	0.36712805
H	6.69283112	0.35542435	-1.72151599
H	5.65697623	-0.49695262	2.37000835
H	7.38826438	0.02131356	0.64884951

C	1.81197968	-0.35714957	-2.22629187
H	1.92848609	0.66152846	-2.61866440
H	2.50718585	-1.01557573	-2.76265693
C	-1.06033410	1.19507714	-0.02851108
C	-0.30779238	2.34258609	0.40474186
C	-1.03233282	3.53519452	0.04918408
C	0.91906438	2.48543197	1.08327519
C	-0.55084774	4.81026446	0.33315554
C	1.40177949	3.76574669	1.37674988
C	0.68058115	4.91454167	1.00330015
H	-1.10670586	5.69905556	0.04994715
H	2.35097516	3.87480374	1.89368887
H	1.07757582	5.89944477	1.23533174
C	-2.30787428	1.73558900	-0.60662055
O	-3.33724473	1.15268553	-1.04625100
N	-2.21984278	3.15688174	-0.56610466
C	-3.23736136	4.03440396	-1.10094807
H	-3.65724903	4.68833712	-0.32389191
H	-2.84050008	4.66248412	-1.90935776
H	-4.02930856	3.39626792	-1.49971000
H	1.47447107	1.59520552	1.35223341
C	-1.53696444	-3.10935384	0.24200763
C	-2.65613616	-2.13903393	0.20080811
C	-0.68091870	-2.75954997	1.29264268
C	-2.51388843	-1.24908572	1.28542920
C	-1.19494450	-1.51100209	1.89149604
C	-1.37241471	-4.22044294	-0.74641855
H	-0.62522751	-4.94747394	-0.41312719
H	-2.31954881	-4.75142859	-0.90682158
H	-1.02842961	-3.79398839	-1.69776681
C	-3.78601130	-2.18263984	-0.78473393
H	-4.62533604	-2.79292182	-0.41581851
H	-4.14319970	-1.17078171	-0.99319944
H	-3.45059934	-2.61004992	-1.73426725
C	-3.52279198	-0.26007406	1.78532515
H	-3.03952028	0.59948700	2.26024528
H	-4.13940563	0.11977892	0.96819673
H	-4.17815100	-0.73032096	2.53471305
C	0.60416800	-3.41314353	1.70114127
H	1.44225064	-2.71690793	1.56944085
H	0.58116079	-3.71938722	2.75678652
H	0.81113792	-4.29926134	1.09438767

C	-0.66706428	-0.91028128	3.15991072
H	-1.06243736	0.09737411	3.31674321
H	-0.93630148	-1.52187876	4.03531756
H	0.42396983	-0.83531163	3.11805422
C	0.38052528	-0.84665690	-2.50215262
O	-0.48632062	0.00660899	-2.90089887
O	0.16228261	-2.10720096	-2.26397727

INT-III

Zero-point correction=	0.488279
Thermal correction to Energy=	0.520892
Thermal correction to Enthalpy=	0.521836
Thermal correction to Gibbs Free Energy=	0.452302
Sum of electronic and zero-point Energies=	-1341.164110
Sum of electronic and thermal Energies=	-1341.131497
Sum of electronic and thermal Enthalpies=	-1341.130553
Sum of electronic and thermal Free Energies=	-1341.230087

Rh	-1.00631731	-0.14835681	-0.30340729
C	2.46536933	-3.35693368	1.47262305
C	1.82835883	-2.42765070	0.64833105
C	1.96524736	-2.49918541	-0.74819298
C	2.73257714	-3.54504272	-1.28799341
C	3.36383104	-4.47751197	-0.46306043
C	3.23486023	-4.38685987	0.92462280
H	2.35909202	-3.27082682	2.55203053
H	1.23321641	-1.63227917	1.08517113
H	2.81881363	-3.62339686	-2.36820466
H	3.94947696	-5.28119780	-0.90636269
H	3.72348314	-5.11340141	1.57109528
C	1.30617576	-1.49342889	-1.65851860
C	2.00725415	-1.01472244	-2.72493017
H	3.04342705	-1.29414234	-2.88326335
H	1.56208609	-0.29946255	-3.40865187
N	-0.01280314	-1.24298220	-1.40971369
C	-2.52570580	-0.62950211	1.36075846
C	-3.03292951	-1.32753682	0.19122468
C	-2.60070395	0.77504719	1.09645592
C	-3.35149997	-0.36485983	-0.79140183
C	-3.05044991	0.94880403	-0.25068351
C	-2.15702038	-1.25391080	2.67700253
H	-2.99546551	-1.21723528	3.39149049

H	-1.88101593	-2.30620625	2.55149081
H	-1.29823189	-0.73956128	3.11691208
C	-3.16779764	-2.81781956	0.05945404
H	-4.13256522	-3.17725501	0.44901797
H	-3.09375221	-3.13425715	-0.98595386
H	-2.37620555	-3.33742580	0.60892029
C	-2.31519918	1.86799184	2.08773445
H	-1.99212558	2.78669843	1.58703372
H	-3.21191439	2.11080463	2.67873546
H	-1.52012110	1.57315742	2.77735087
C	-3.34829824	2.25880624	-0.92402244
H	-4.38685326	2.58329835	-0.74752808
H	-2.68916611	3.05211320	-0.55841943
H	-3.20734257	2.19359799	-2.00827049
C	-3.89687915	-0.63251435	-2.16529283
H	-3.59815945	-1.62117472	-2.52833857
H	-4.99700100	-0.59056064	-2.18462016
H	-3.52949447	0.10309446	-2.88901208
C	0.46756315	1.06314294	0.23526500
C	1.16044630	2.06624672	-0.52329034
C	2.09106214	2.74777328	0.32671784
C	1.06234512	2.48032564	-1.86234318
C	2.89264469	3.78781503	-0.12975126
C	1.86305563	3.52519914	-2.32881040
H	0.36572708	1.96816443	-2.52032932
C	2.76953971	4.17195797	-1.47486634
H	3.59355809	4.29279376	0.53121861
H	1.78893534	3.83916736	-3.36801304
H	3.38737310	4.98285417	-1.85565662
C	1.02210949	1.16035601	1.59319879
O	0.76722696	0.51902004	2.62813996
C	2.77776985	2.55786063	2.74466463
H	3.85402896	2.40818643	2.57547622
H	2.61764726	3.60910807	3.02681271
H	2.44966551	1.91209703	3.56292996
N	2.00237316	2.19213340	1.59053844

TS-III

Zero-point correction=	0.482938
Thermal correction to Energy=	0.514636
Thermal correction to Enthalpy=	0.515580
Thermal correction to Gibbs Free Energy=	0.46257

Sum of electronic and zero-point Energies= -1303.022657
Sum of electronic and thermal Energies= -1302.990959
Sum of electronic and thermal Enthalpies= -1302.990014
Sum of electronic and thermal Free Energies= -1303.087025

C	-2.94454956	4.04061180	-0.91201193
C	-1.95947600	3.91492295	0.06948867
C	-1.02686279	2.86895290	0.01297207
C	-1.08209838	1.92900759	-1.04352410
C	-2.07582280	2.08795693	-2.01969102
C	-3.00533340	3.12585220	-1.96318737
C	-0.05148348	0.78359782	-1.09251350
C	1.37017265	1.28475930	-0.48671345
C	2.22570579	-0.43457609	-0.30794629
N	-0.04167714	2.72041557	1.02247791
C	-0.15868894	3.49213220	2.25764914
H	0.01126582	4.56052670	2.07642486
H	-1.15585767	3.36305557	2.69128488
H	0.59945694	3.12506667	2.94667775
O	1.91337817	1.81463514	1.77371439
C	1.08385169	1.91861891	0.87746979
C	3.71415062	-0.44448220	-0.39371404
C	4.38118001	-1.65314413	-0.66349831
C	4.48040983	0.71937537	-0.22019672
C	5.76835473	-1.69399948	-0.76529209
H	3.78576158	-2.55138883	-0.79136681
C	5.87189366	0.67634106	-0.31849236
H	3.99334209	1.65477450	0.03087864
C	6.52098707	-0.52738111	-0.59532998
H	6.26638101	-2.63633179	-0.97996030
H	6.44872813	1.58604039	-0.17257746
H	7.60461963	-0.55863160	-0.67560543
N	1.36339561	-1.33266044	-0.17449627
Rh	-0.46723249	-0.99176909	-0.39938032
H	0.11259096	0.46257007	-2.13746609
H	1.95140486	1.97838228	-1.12093978
H	-2.10852788	1.37392665	-2.84034017
H	-3.76196535	3.22426197	-2.73679396
H	-3.65430392	4.86101150	-0.85267429
H	-1.91703702	4.64420977	0.87010073
C	-0.93076727	-2.59374680	1.16776972
C	-1.61899752	-2.98283672	0.00545674
C	-1.38058013	-1.24299217	1.50230714

C	-2.58317400	-1.93207621	-0.34615937
C	-2.48822963	-0.89802150	0.60705918
C	-0.99717884	-0.50456772	2.75003572
H	-1.19865777	0.56580878	2.66039098
H	-1.57139794	-0.88336577	3.60878290
H	0.06565201	-0.62857823	2.97499757
C	-3.38829106	0.29118902	0.75402918
H	-2.84565841	1.16801312	1.11687379
H	-3.85128053	0.57076777	-0.19577774
H	-4.19300586	0.07573985	1.47125252
C	-3.56176529	-2.02779623	-1.48066395
H	-4.40674906	-2.68013341	-1.21793509
H	-3.96968444	-1.04763657	-1.74262481
H	-3.09771758	-2.44846378	-2.37943846
C	-1.45364597	-4.26013865	-0.76523186
H	-0.54311362	-4.79080413	-0.47633546
H	-2.30577455	-4.93305297	-0.59645849
H	-1.39961606	-4.07299195	-1.84357628
C	0.15426437	-3.33135311	1.89488295
H	-0.06616478	-3.39842857	2.96722317
H	0.26949409	-4.35009381	1.51491289
H	1.11780181	-2.82027810	1.77347955

INT-IV

Zero-point correction=	0.495452
Thermal correction to Energy=	0.526103
Thermal correction to Enthalpy=	0.527048
Thermal correction to Gibbs Free Energy=	0.433729
Sum of electronic and zero-point Energies=	-1341.166686
Sum of electronic and thermal Energies=	-1341.136035
Sum of electronic and thermal Enthalpies=	-1341.135091
Sum of electronic and thermal Free Energies=	-1341.228409

C	-2.94454956	4.04061180	-0.91201193
C	-1.95947600	3.91492295	0.06948867
C	-1.02686279	2.86895290	0.01297207
C	-1.08209838	1.92900759	-1.04352410
C	-2.07582280	2.08795693	-2.01969102
C	-3.00533340	3.12585220	-1.96318737
C	-0.09443091	0.83132894	-1.09047203
C	1.25974040	1.22436827	-0.47613439
C	2.05624400	-0.06829022	-0.34642250

N	-0.04167714	2.72041557	1.02247791
C	-0.15868894	3.49213220	2.25764914
H	0.01126582	4.56052670	2.07642486
H	-1.15585767	3.36305557	2.69128488
H	0.59945694	3.12506667	2.94667775
O	1.91337817	1.81463514	1.77371439
C	1.08385169	1.91861891	0.87746979
C	3.54468883	-0.07819633	-0.43219026
C	4.21171823	-1.28685826	-0.70197452
C	4.31094804	1.08566125	-0.25867293
C	5.59889294	-1.32771361	-0.80376830
H	3.61629980	-2.18510296	-0.82984302
C	5.70243187	1.04262694	-0.35696857
H	3.82388031	2.02106037	-0.00759757
C	6.35152529	-0.16109523	-0.63380619
H	6.09691922	-2.27004592	-1.01843651
H	6.27926634	1.95232626	-0.21105367
H	7.43515784	-0.19234572	-0.71408164
N	1.38933918	-1.16143730	-0.24202469
Rh	-0.58381777	-1.06689740	-0.37480536
H	0.06964354	0.51030119	-2.13542462
H	1.79023183	1.95504075	-1.11322412
H	-2.10852788	1.37392665	-2.84034017
H	-3.76196535	3.22426197	-2.73679396
H	-3.65430392	4.86101150	-0.85267429
H	-1.91703702	4.64420977	0.87010073
C	-1.04735255	-2.66887511	1.19234468
C	-1.73558280	-3.05796504	0.03003170
C	-1.49716541	-1.31812048	1.52688210
C	-2.69975928	-2.00720452	-0.32158441
C	-2.60481491	-0.97314982	0.63163414
C	-1.11376412	-0.57969604	2.77461067
H	-1.31524305	0.49068047	2.68496594
H	-1.68798322	-0.95849409	3.63335786
H	-0.05093327	-0.70370654	2.99957253
C	-3.50487634	0.21606070	0.77860414
H	-2.96224369	1.09288481	1.14144875
H	-3.96786581	0.49563945	-0.17120278
H	-4.30959114	0.00061153	1.49582748
C	-3.67835057	-2.10292455	-1.45608899
H	-4.52333434	-2.75526172	-1.19336013
H	-4.08626972	-1.12276488	-1.71804985

H	-3.21430286	-2.52359209	-2.35486350
C	-1.57023124	-4.33526697	-0.74065690
H	-0.65969890	-4.86593245	-0.45176050
H	-2.42235983	-5.00818129	-0.57188354
H	-1.51620134	-4.14812027	-1.81900132
C	0.03767909	-3.40648143	1.91945791
H	-0.18275006	-3.47355689	2.99179813
H	0.15290881	-4.42522213	1.53948785
H	1.00121653	-2.89540642	1.79805451

TS-IV

Zero-point correction=	0.652197
Thermal correction to Energy=	0.694336
Thermal correction to Enthalpy=	0.695280
Thermal correction to Gibbs Free Energy=	0.574796
Sum of electronic and zero-point Energies=	-1893.964343
Sum of electronic and thermal Energies=	-1893.922205
Sum of electronic and thermal Enthalpies=	-1893.921260
Sum of electronic and thermal Free Energies=	-1894.041744

C	-2.46574421	0.48598410	4.32189579
C	-2.08395959	-0.67672070	3.65318833
C	-0.98364152	-0.67631534	2.78124462
C	-0.26367702	0.52475494	2.56030779
C	-0.65452518	1.66731179	3.27400027
C	-1.74429951	1.66594778	4.14247838
C	0.89001334	0.54761494	1.62543726
C	1.56640645	-0.82586180	1.51677462
C	2.47557202	-0.78497889	0.29886396
N	-0.60494738	-1.86561945	2.11738123
C	-1.48037834	-3.03978372	2.17693386
H	-1.51548055	-3.44048655	3.19749842
H	-2.48675215	-2.77355539	1.84894430
H	-1.05772825	-3.79102013	1.51350290
O	0.84961006	-3.00581435	0.77990401
C	0.57478305	-1.98715162	1.40767541
C	3.72662817	-1.60057593	0.22706368
C	4.69956485	-1.30065661	-0.74299437
C	3.97823693	-2.65674509	1.11728900
C	5.88445545	-2.02681943	-0.81643530
H	4.50567199	-0.48900505	-1.43615205

C	5.16713452	-3.38431571	1.04381345
H	3.22958150	-2.93937064	1.84796480
C	6.12624035	-3.07215435	0.08026078
H	6.62412587	-1.77627139	-1.57293563
H	5.33832522	-4.20201797	1.73926642
H	7.05248252	-3.63837688	0.02529632
N	2.16419778	0.01240606	-0.65109073
Rh	0.53890931	1.19840179	-0.37757914
N	-0.90622518	-0.07567735	-0.62135257
C	-2.09102336	-0.46460027	-0.82734522
C	-2.37131128	-1.61332262	-1.74421048
C	-1.38878716	-2.59786363	-1.94783045
C	-3.58729748	-1.70874655	-2.44003117
C	-1.62327290	-3.64973104	-2.83037318
H	-0.45720386	-2.54434062	-1.39373382
C	-3.81293380	-2.76033967	-3.32925280
H	-4.36240013	-0.95996440	-2.30145897
C	-2.83246068	-3.73364695	-3.52682537
H	-0.85951588	-4.40995794	-2.96948459
H	-4.75614043	-2.81723512	-3.86626014
H	-3.01113887	-4.55575432	-4.21480718
C	-0.06469342	2.73770599	-2.09968401
C	1.34334837	2.57000582	-2.09766978
C	-0.45498078	3.32332640	-0.83128165
C	1.83831274	3.00813441	-0.80520039
C	0.72692013	3.52989994	-0.06052113
H	1.62703745	1.28810208	1.95251475
H	2.13990537	-1.02989203	2.43862924
H	-0.07468448	2.57505517	3.14261332
H	-2.01768471	2.57005011	4.67966570
H	-3.31941047	0.45724518	4.99358733
H	-2.64966761	-1.58542585	3.81364715
C	-1.83258807	3.81118696	-0.48102308
H	-2.03753322	3.72005664	0.59038003
H	-1.95622940	4.87001845	-0.75100462
H	-2.60553542	3.25209440	-1.01606719
C	0.82285777	4.29820500	1.22431938
H	1.11496250	5.33841698	1.02195037
H	-0.13272642	4.32545210	1.75431042
H	1.57575963	3.88027775	1.90042290
C	3.29005001	3.09747430	-0.43386516
H	3.77374923	3.94810060	-0.93418342

H	3.42420075	3.23053495	0.64416540
H	3.82165890	2.18693681	-0.72701652
C	2.21270606	2.01548275	-3.18388257
H	2.96224435	2.75195826	-3.50168455
H	2.74027182	1.12533991	-2.81835235
H	1.63088769	1.72926767	-4.06440313
C	-1.00664715	2.43648162	-3.23035060
H	-0.54002608	1.79489261	-3.98202941
H	-1.90906335	1.92420753	-2.88041314
H	-1.32828233	3.36012786	-3.73072032
C	-3.26483705	0.30912785	-0.20253968
H	-2.86178663	0.90402355	0.62370417
H	-3.68629563	1.00697454	-0.93406465
C	-4.38390165	-0.54436509	0.35982008
O	-4.26046880	-1.54655211	1.02767267
O	-5.60088376	-0.02792674	0.05309277
H	-6.25735460	-0.61365587	0.47754642

INT-V

Zero-point correction=	0.649521
Thermal correction to Energy=	0.691716
Thermal correction to Enthalpy=	0.692660
Thermal correction to Gibbs Free Energy=	0.570373
Sum of electronic and zero-point Energies=	-1894.035351
Sum of electronic and thermal Energies=	-1893.993156
Sum of electronic and thermal Enthalpies=	-1893.992211
Sum of electronic and thermal Free Energies=	-1894.110931

C	-2.41857764	0.25299823	4.35895455
C	-2.02983104	-0.87438138	3.63427000
C	-0.95173383	-0.81898421	2.73726750
C	-0.25059457	0.39834920	2.55027501
C	-0.65090592	1.50575212	3.31496835
C	-1.72272725	1.45183168	4.20536138
C	0.88294291	0.47178803	1.59815594
C	1.59965438	-0.88227577	1.44515436
C	2.50416590	-0.76030950	0.21900019
N	-0.56032203	-1.97156765	2.01885654
C	-1.44299057	-3.13594769	2.00021661
H	-1.46902861	-3.62792913	2.98299046
H	-2.45048637	-2.82600480	1.71547672
H	-1.04209264	-3.83411700	1.26863990

O	0.97471356	-3.12214230	0.79064198
C	0.65059928	-2.07646084	1.34938418
C	3.77716163	-1.54461286	0.11644404
C	4.74263778	-1.18007253	-0.84082226
C	4.07020708	-2.62902160	0.96053437
C	5.95163048	-1.86153805	-0.94334177
H	4.51099071	-0.35017305	-1.50054643
C	5.28464232	-3.31202488	0.85987262
H	3.32629424	-2.96958870	1.67093676
C	6.23493706	-2.93217544	-0.08806610
H	6.68018934	-1.55597287	-1.69225909
H	5.48174284	-4.15246135	1.52269053
H	7.18055146	-3.46489181	-0.16549628
N	2.19808154	0.09789156	-0.67698620
Rh	0.55394107	1.21051557	-0.36139411
N	-0.53029492	-0.41709001	-0.92681169
C	-1.79225921	-0.57214496	-0.93838353
C	-2.35636830	-1.73383283	-1.71567173
C	-1.56855395	-2.88394663	-1.90889772
C	-3.62729268	-1.69475220	-2.31253128
C	-2.04355679	-3.95461474	-2.66139357
H	-0.58434773	-2.91178314	-1.45223689
C	-4.09774195	-2.76494509	-3.07927020
H	-4.25922868	-0.81799617	-2.19373033
C	-3.31027496	-3.90212952	-3.25539892
H	-1.42123497	-4.83842414	-2.78633567
H	-5.08214436	-2.70466089	-3.53997137
H	-3.67664505	-4.73868934	-3.84689339
C	-0.41767900	2.83221364	-1.85716932
C	0.96889248	2.68224104	-2.14775552
C	-0.55499960	3.35500323	-0.52423163
C	1.71068459	3.13066781	-0.99546948
C	0.77495511	3.54469745	-0.00445676
H	1.61187370	1.20632519	1.96486328
H	2.20648050	-1.09538336	2.34707305
H	-0.09334867	2.43081108	3.19746104
H	-2.00399922	2.33377857	4.77670172
H	-3.26001670	0.18326525	5.04438466
H	-2.57821544	-1.79889137	3.76540275
C	-1.81452997	3.85037609	0.13325593
H	-1.84359769	3.59984074	1.20054827
H	-1.91736501	4.94471062	0.05334168

H	-2.70897062	3.41160922	-0.31903806
C	1.11934663	4.22632458	1.29071874
H	1.38836921	5.28114870	1.12797378
H	0.27480766	4.21449170	1.98618537
H	1.96929159	3.75075128	1.79394424
C	3.20825263	3.20973276	-0.92118388
H	3.60428698	3.98899905	-1.58976013
H	3.54919125	3.44322161	0.09325386
H	3.65864294	2.25351595	-1.21139956
C	1.58192057	2.17774364	-3.42256972
H	2.09552701	2.97807434	-3.97777184
H	2.31536564	1.39040094	-3.21041498
H	0.82336072	1.74875376	-4.08538275
C	-1.52767700	2.54385432	-2.83340271
H	-1.59727017	1.47579925	-3.07127041
H	-2.49937507	2.86224064	-2.44314433
H	-1.36670865	3.08052080	-3.77811717
C	-2.80442259	0.39273922	-0.27156671
H	-2.25425550	0.90286158	0.52722854
H	-3.13726337	1.16262005	-0.97383557
C	-4.02557729	-0.23534157	0.34998736
O	-4.07947369	-1.22692373	1.04779917
O	-5.16529605	0.46882332	0.06352757
H	-5.87654267	-0.01347431	0.52665215

TS-V

Zero-point correction=	0.651513
Thermal correction to Energy=	0.697716
Thermal correction to Enthalpy=	0.695861
Thermal correction to Gibbs Free Energy=	0.592471
Sum of electronic and zero-point Energies=	-1894.125052
Sum of electronic and thermal Energies=	-1893.953652
Sum of electronic and thermal Enthalpies=	-1893.952161
Sum of electronic and thermal Free Energies=	-1894.201921

C	2.35563419	-0.18438298	4.61159418
C	1.83924792	0.91877974	3.92861442
C	0.86210055	0.75818903	2.93458126
C	0.39375539	-0.53843368	2.60641989
C	0.90991350	-1.62091366	3.33372576
C	1.88520870	-1.46345166	4.31931124
C	-0.62390246	-0.71457828	1.54395487

C	-1.55731649	0.50351509	1.42474656
C	-2.25143113	0.31084694	0.16172430
N	0.33720049	1.88191101	2.26131673
C	1.02824465	3.16037758	2.36242337
H	0.93250459	3.59326936	3.36818207
H	2.08865828	3.02690167	2.12765015
H	0.57112311	3.83661171	1.64320094
O	-1.29817665	2.87412357	1.02422339
C	-0.82876371	1.84454100	1.50262209
C	-3.63533343	0.88294759	0.10238549
C	-4.52905307	0.43745871	-0.88944116
C	-4.09829884	1.84201890	1.01892582
C	-5.83229764	0.92118151	-0.95663148
H	-4.16696270	-0.29513637	-1.60359849
C	-5.40681556	2.32679474	0.95270620
H	-3.41611102	2.24536343	1.75802148
C	-6.28371572	1.86809736	-0.03058782
H	-6.50291784	0.55657803	-1.73275732
H	-5.73680858	3.07496195	1.67096993
H	-7.30298108	2.24575628	-0.08036940
N	-1.82522311	-0.38700098	-0.86740719
Rh	0.03342737	-1.12953942	-0.45068132
N	0.74184253	0.72490081	-0.62580939
C	2.03350689	1.07833502	-0.59312629
C	2.36285113	2.34108123	-1.35682631
C	1.38062499	3.32860907	-1.54802381
C	3.63578968	2.55522747	-1.90960317
C	1.67556727	4.49946364	-2.24609037
H	0.39241519	3.15652994	-1.13346024
C	3.92882469	3.72508066	-2.61384735
H	4.39628796	1.78655125	-1.79926061
C	2.95025881	4.70661132	-2.78266423
H	0.90313859	5.25536498	-2.37335614
H	4.92139878	3.86468668	-3.03873419
H	3.17525758	5.61830493	-3.33263040
C	3.04094968	0.47729153	0.15360102
C	1.50538660	-2.33604580	-1.88699510
C	0.16404227	-2.46206526	-2.36387418
C	1.59363996	-2.97220522	-0.60355624
C	-0.58357576	-3.20347484	-1.37785313
C	0.28111639	-3.51444045	-0.25969206
H	-1.23267114	-1.60084769	1.76401407

H	-2.26282330	0.53049247	2.27814758
H	2.82634980	-0.40861931	0.73833008
H	0.52762721	-2.61256397	3.10753513
H	2.26534056	-2.33005718	4.85564506
H	3.11443131	-0.03314328	5.37594506
H	2.20012491	1.90944108	4.18045068
C	2.85378765	-3.22168177	0.17796050
H	2.69376976	-3.11928684	1.25794295
H	3.25380074	-4.23352598	0.00091175
H	3.63564352	-2.50860215	-0.09976755
C	-0.05698019	-4.37005852	0.92949726
H	-0.05261162	-5.43891964	0.666794532
H	0.66884352	-4.23526579	1.73696753
H	-1.04982186	-4.14155098	1.33340235
C	-2.02291456	-3.60646000	-1.52490725
H	-2.15615722	-4.34527703	-2.32042515
H	-2.41021626	-4.05232534	-0.60038713
H	-2.64560946	-2.73515691	-1.75675310
C	-0.40452033	-1.97234719	-3.66523468
H	-0.60158478	-2.79996364	-4.36439318
H	-1.34917269	-1.44233174	-3.49922792
H	0.27587326	-1.27480022	-4.16350800
C	2.65803689	-1.72094366	-2.62377211
H	2.31267365	-1.09467748	-3.45581360
H	3.25944356	-1.08538188	-1.96720176
H	3.31733113	-2.49513923	-3.04854748
C	4.38908914	1.18189275	0.39375949
O	5.37904109	0.80548427	1.01961837
O	4.44414199	2.40273633	-0.19612727

INT-VI

Zero-point correction=	0.621248
Thermal correction to Energy=	0.660347
Thermal correction to Enthalpy=	0.661291
Thermal correction to Gibbs Free Energy=	0.548957
Sum of electronic and zero-point Energies=	-1704.854255
Sum of electronic and thermal Energies=	-1704.815156
Sum of electronic and thermal Enthalpies=	-1704.814212
Sum of electronic and thermal Free Energies=	-1704.926545

C	2.35563419	-0.18438298	4.61159418
C	1.83924792	0.91877974	3.92861442

C	0.86210055	0.75818903	2.93458126
C	0.39375539	-0.53843368	2.60641989
C	0.90991350	-1.62091366	3.33372576
C	1.88520870	-1.46345166	4.31931124
C	-0.62390246	-0.71457828	1.54395487
C	-1.55731649	0.50351509	1.42474656
C	-2.32552964	0.32579848	0.11387739
N	0.33720049	1.88191101	2.26131673
C	1.02824465	3.16037758	2.36242337
H	0.93250459	3.59326936	3.36818207
H	2.08865828	3.02690167	2.12765015
H	0.57112311	3.83661171	1.64320094
O	-1.29817665	2.87412357	1.02422339
C	-0.82876371	1.84454100	1.50262209
C	-3.71811424	0.85760754	-0.04069645
C	-4.54151316	0.35999675	-1.06798072
C	-4.25770221	1.82885834	0.81937193
C	-5.85085624	0.80550178	-1.22320525
H	-4.12010357	-0.38206249	-1.73849375
C	-5.57239005	2.27529733	0.66478614
H	-3.62980054	2.27143516	1.58369821
C	-6.37915046	1.76519158	-0.35263907
H	-6.46609100	0.40091702	-2.02497570
H	-5.96240612	3.03391742	1.34075611
H	-7.40332735	2.11303855	-0.47125821
N	-1.79282440	-0.37684505	-0.81089974
Rh	0.02908098	-1.14651762	-0.42915075
N	0.73749615	0.70792261	-0.60427882
C	2.02916050	1.06135682	-0.57159572
C	2.35850475	2.32410303	-1.33529573
C	1.37627861	3.31163087	-1.52649324
C	3.63144329	2.53824927	-1.88807260
C	1.67122089	4.48248544	-2.22455980
H	0.38806881	3.13955174	-1.11192967
C	3.92447831	3.70810246	-2.59231677
H	4.39194158	1.76957305	-1.77773004
C	2.94591243	4.68963312	-2.76113366
H	0.89879221	5.23838678	-2.35182557
H	4.91705240	3.84770848	-3.01720362
H	3.17091120	5.60132673	-3.31109982
C	3.03660329	0.46031333	0.17513159
H	3.98813348	0.95762786	0.34460994

C	1.50538660	-2.33604580	-1.88699510
C	0.16404227	-2.46206526	-2.36387418
C	1.59363996	-2.97220522	-0.60355624
C	-0.58357576	-3.20347484	-1.37785313
C	0.29423013	-3.51569645	-0.30245533
H	-1.23267114	-1.60084769	1.76401407
H	-2.26282330	0.53049247	2.27814758
H	2.82200342	-0.42559751	0.75986066
H	0.52762721	-2.61256397	3.10753513
H	2.26534056	-2.33005718	4.85564406
H	3.11443131	-0.03314328	5.37594506
H	2.20012491	1.90944108	4.18045068
C	2.85378765	-3.22168177	0.17796050
H	2.69376976	-3.11928684	1.25794095
H	3.25380074	-4.23352598	0.00091975
H	3.63564352	-2.50860215	-0.09976055
C	-0.03649612	-4.39415609	0.87206229
H	-0.02699829	-5.45813428	0.59035996
H	0.69047125	-4.26982643	1.68018230
H	-1.02960536	-4.17826576	1.28318736
C	-2.02291456	-3.60646000	-1.52290725
H	-2.15615722	-4.34527703	-2.32742515
H	-2.41021626	-4.05232534	-0.60038713
H	-2.64560946	-2.73515691	-1.75775310
C	-0.40452033	-1.97234719	-3.66523468
H	-0.60158478	-2.79996364	-4.36439318
H	-1.34917269	-1.44233174	-3.49622792
H	0.27587326	-1.27480022	-4.16350800
C	2.65803689	-1.72094366	-2.62777211
H	2.31267365	-1.09467748	-3.45581360
H	3.25944356	-1.08538188	-1.96820176
H	3.31733113	-2.49513923	-3.04854748

TS-VI

Zero-point correction=	0.620151
Thermal correction to Energy=	0.661469
Thermal correction to Enthalpy=	0.661377
Thermal correction to Gibbs Free Energy=	0.589376
Sum of electronic and zero-point Energies=	-1704.861819
Sum of electronic and thermal Energies=	-1704.895563
Sum of electronic and thermal Enthalpies=	-1704.891959
Sum of electronic and thermal Free Energies=	-1704.928841

C	3.16495608	1.51833704	-3.61610571
C	2.67946908	0.24334304	-3.31945971
C	1.56011908	0.07403704	-2.48892171
C	0.91738808	1.20888904	-1.93713271
C	1.41723608	2.47560104	-2.27002271
C	2.53007008	2.64463904	-3.09362471
C	-1.04759492	-0.24301096	-1.31712371
C	-1.93877992	-0.45485296	-0.09102571
N	1.06773008	-1.21751596	-2.20591671
C	1.88518508	-2.37993296	-2.52759171
H	1.96266408	-2.53120196	-3.61346571
H	2.88919008	-2.25784096	-2.10969571
H	1.40379608	-3.24819196	-2.08245571
O	-0.60199892	-2.60589196	-1.51879071
C	-0.18208592	-1.45961996	-1.63852671
C	-3.27281792	-1.12601896	-0.20862071
C	-4.22043792	-0.96061996	0.81940929
C	-3.64020992	-1.89947896	-1.32243671
C	-5.48435392	-1.53675496	0.73385429
H	-3.93010692	-0.36935296	1.68206929
C	-4.90998092	-2.47581996	-1.40897771
H	-2.91127892	-2.09109696	-2.10105671
C	-5.84140892	-2.29624296	-0.38605071
H	-6.19878192	-1.39077296	1.54221929
H	-5.16608192	-3.07672096	-2.27960571
H	-6.83025292	-2.74515296	-0.45543571
N	-1.57254692	0.05462704	1.02315529
H	-1.67278492	-0.11473796	-2.22190071
H	0.91683308	3.34539304	-1.84886771
H	2.89363908	3.64323904	-3.32512271
H	4.03469508	1.62184704	-4.26096271
H	3.17537708	-0.62100296	-3.74610171
C	-0.24778492	1.04074704	-1.03842371
C	0.12817713	1.48830139	0.28664525
H	1.11724007	1.84597730	0.48342542
H	0.04906514	0.46806629	0.59931382
Rh	-1.64475362	2.41876986	-1.14586024
N	-1.52976241	3.20279917	0.04810964
C	-0.62568384	2.67710235	0.82696326
C	-0.30782523	3.19774862	2.24099769
C	-0.96242072	4.32788114	2.73168769

C	0.63437946	2.53946107	3.03122295
C	-0.67432164	4.79994546	4.01206885
H	-1.70462348	4.84708857	2.10814900
C	0.92196241	3.01096243	4.31239132
H	1.15026636	1.64862140	2.64470721
C	0.26790934	4.14109602	4.80284994
H	-1.18978274	5.69109036	4.39866573
H	1.66459615	2.49148592	4.93537890
H	0.49485722	4.51345237	5.81237545
C	-3.58666899	3.66183042	-2.23862658
C	-4.01233843	2.32084625	-2.09207658
C	-2.52872890	3.68451204	-3.17732687
C	-3.21747680	1.51475386	-2.94020378
C	-2.30055516	2.35754616	-3.61092573
C	-5.14267346	1.82548180	-1.17090516
H	-5.96145932	2.51323206	-1.20949639
H	-5.47148249	0.86083415	-1.49684922
H	-4.78044085	1.75819754	-0.16633542
C	-4.17221532	4.88271142	-1.50501559
H	-3.42925362	5.64998282	-1.44018888
H	-5.01914574	5.25106708	-2.04531456
H	-4.47508707	4.59535842	-0.51982680
C	-3.33051531	-0.01227889	-3.10450002
H	-4.32268288	-0.26509047	-3.41528906
H	-2.63017425	-0.34445493	-3.84211881
H	-3.11722851	-0.48828113	-2.17024598
C	-1.24008238	1.90915112	-4.63363750
H	-1.66429225	1.92124200	-5.61587973
H	-0.40493381	2.57707753	-4.59756550
H	-0.91419938	0.91758673	-4.39805242
C	-1.76028104	4.93442168	-3.64510223
H	-0.92373166	4.63620792	-4.24188836
H	-2.40951813	5.55558637	-4.22608899
H	-1.41367198	5.47991410	-2.79234190
H	0.11458403	3.33113271	0.41568748

INT-VII

Zero-point correction=	0.623354
Thermal correction to Energy=	0.662561
Thermal correction to Enthalpy=	0.663505
Thermal correction to Gibbs Free Energy=	0.547937
Sum of electronic and zero-point Energies=	-1704.862792

Sum of electronic and thermal Energies= -1704.823584
Sum of electronic and thermal Enthalpies= -1704.822640
Sum of electronic and thermal Free Energies= -1704.938208

C	2.84980500	1.82921400	-3.64034300
C	2.36431800	0.55422000	-3.34369700
C	1.24496800	0.38491400	-2.51315900
C	0.60223700	1.51976600	-1.96137000
C	1.10208500	2.78647800	-2.29426000
C	2.21491900	2.95551600	-3.11786200
C	-1.36274600	0.06786600	-1.34136100
C	-2.25393100	-0.14397600	-0.11526300
N	0.75257900	-0.90663900	-2.23015400
C	1.57003400	-2.06905600	-2.55182900
H	1.64751300	-2.22032500	-3.63770300
H	2.57403900	-1.94696400	-2.13393300
H	1.08864500	-2.93731500	-2.10669300
O	-0.91715000	-2.29501500	-1.54302800
C	-0.49723700	-1.14874300	-1.66276400
C	-3.58796900	-0.81514200	-0.23285800
C	-4.53558900	-0.64974300	0.79517200
C	-3.95536100	-1.58860200	-1.34667400
C	-5.79950500	-1.22587800	0.70961700
H	-4.24525800	-0.05847600	1.65783200
C	-5.22513200	-2.16494300	-1.43321500
H	-3.22643000	-1.78022000	-2.12529400
C	-6.15656000	-1.98536600	-0.41028800
H	-6.51393300	-1.07989600	1.51798200
H	-5.48123300	-2.76584400	-2.30384300
H	-7.14540400	-2.43427600	-0.47967300
N	-1.88769800	0.36550400	0.99891800
H	-1.98793600	0.19613900	-2.24613800
H	0.60168200	3.65627000	-1.87310500
H	2.57848800	3.95411600	-3.34936000
H	3.71954400	1.93272400	-4.28520000
H	2.86022600	-0.31012600	-3.77033900
C	-0.56293600	1.35162400	-1.06266100
C	0.12817713	1.48830139	0.28664525
H	1.11724007	1.84597730	0.48342542
H	0.04906514	0.46806629	0.59931382
Rh	-1.64475362	2.41876986	-1.14586024
N	-1.52976241	3.20279917	0.04810964

C	-0.62568384	2.67710235	0.82696326
C	-0.30782523	3.19774862	2.24099769
C	-0.96242072	4.32788114	2.73168769
C	0.63437946	2.53946107	3.03122295
C	-0.67432164	4.79994546	4.01206885
H	-1.70462348	4.84708857	2.10814900
C	0.92196241	3.01096243	4.31239132
H	1.15026636	1.64862140	2.64470721
C	0.26790934	4.14109602	4.80284994
H	-1.18978274	5.69109036	4.39866573
H	1.66459615	2.49148592	4.93537890
H	0.49485722	4.51345237	5.81237545
C	-3.58666899	3.66183042	-2.23862658
C	-4.01233843	2.32084625	-2.09207658
C	-2.52872890	3.68451204	-3.17732687
C	-3.21747680	1.51475386	-2.94020378
C	-2.30055516	2.35754616	-3.61092573
C	-5.14267346	1.82548180	-1.17090516
H	-5.96145932	2.51323206	-1.20949639
H	-5.47148249	0.86083415	-1.49684922
H	-4.78044085	1.75819754	-0.16633542
C	-4.17221532	4.88271142	-1.50501559
H	-3.42925362	5.64998282	-1.44018888
H	-5.01914574	5.25106708	-2.04531456
H	-4.47508707	4.59535842	-0.51982680
C	-3.33051531	-0.01227889	-3.10450002
H	-4.32268288	-0.26509047	-3.41528906
H	-2.63017425	-0.34445493	-3.84211881
H	-3.11722851	-0.48828113	-2.17024598
C	-1.24008238	1.90915112	-4.63363750
H	-1.66429225	1.92124200	-5.61587973
H	-0.40493381	2.57707753	-4.59756550
H	-0.91419938	0.91758673	-4.39805242
C	-1.76028104	4.93442168	-3.64510223
H	-0.92373166	4.63620792	-4.24188836
H	-2.40951813	5.55558637	-4.22608899
H	-1.41367198	5.47991410	-2.79234190
H	0.11458403	3.33113271	0.41568748

NH_3

Zero-point correction= 0.034550 (Hartree/Particle)

Thermal correction to Energy= 0.037411

Thermal correction to Enthalpy= 0.038355
Thermal correction to Gibbs Free Energy= 0.016511
Sum of electronic and zero-point Energies= -56.512768
Sum of electronic and thermal Energies= -56.509907
Sum of electronic and thermal Enthalpies= -56.508963
Sum of electronic and thermal Free Energies= -56.530807

N	-0.00000000	-0.00000000	0.11633156
H	0.00000000	0.94117953	-0.27144032
H	-0.81508538	-0.47058977	-0.27144032
H	0.81508538	-0.47058977	-0.27144032

CO_2

Zero-point correction= 0.011591 (Hartree/Particle)
Thermal correction to Energy= 0.014234
Thermal correction to Enthalpy= 0.015178
Thermal correction to Gibbs Free Energy= -0.009120
Sum of electronic and zero-point Energies= -188.572751
Sum of electronic and thermal Energies= -188.570109
Sum of electronic and thermal Enthalpies= -188.569165
Sum of electronic and thermal Free Energies= -188.593462

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16569984
O	0.00000000	0.00000000	-1.16569984

3aa

Zero-point correction= 0.36366
Thermal correction to Energy= 0.385067
Thermal correction to Enthalpy= 0.386011
Thermal correction to Gibbs Free Energy= 0.539451
Sum of electronic and zero-point Energies= -1148.181254
Sum of electronic and thermal Energies= -1148.159848
Sum of electronic and thermal Enthalpies= -1148.158903
Sum of electronic and thermal Free Energies= -1148.233059

C	4.40546642	-3.23053955	-0.33453107
C	4.42623285	-1.87344052	-0.05725570
C	3.22788774	-1.14182053	0.04270548
C	1.99343227	-1.80806975	-0.14028734
C	2.01045371	-3.18443327	-0.41997164
C	3.19315357	-3.89634304	-0.51872993
C	0.75447763	-1.03596979	-0.05643191
C	0.81871189	0.36457410	0.10282098
C	-0.39984799	1.10027448	0.04208449

C	-1.65285361	-0.85517839	-0.01457352
C	-0.50932643	-1.63626130	-0.12978086
H	5.34223885	-3.77096735	-0.40870270
H	5.37677391	-1.38025019	0.08052304
H	1.07583397	-3.70667135	-0.57460738
H	3.17452512	-4.95651556	-0.73972367
H	-0.60503777	-2.70265260	-0.26683948
N	3.25241412	0.21962357	0.33870589
C	2.10263262	1.02158566	0.43327085
O	2.19310409	2.18166921	0.79824567
N	-1.58054846	0.48770719	0.02329601
C	-3.01535175	-1.44597996	0.02425979
C	-4.12060979	-0.67016094	-0.35354375
C	-3.23402905	-2.76692472	0.44069827
C	-5.40267783	-1.20734769	-0.33318512
H	-3.95106334	0.35336901	-0.66083780
C	-4.51827323	-3.30150055	0.46461521
H	-2.40267956	-3.37521483	0.77740760
C	-5.60711858	-2.52513256	0.07325027
H	-6.24552981	-0.59606106	-0.63588426
H	-4.66971370	-4.32191054	0.79837664
H	-6.60778307	-2.94211280	0.09120157
C	-0.49572679	2.58550338	-0.05994245
C	-1.42093795	3.26824281	0.73588764
C	0.23212100	3.30085073	-1.01660722
C	-1.59029762	4.64317482	0.60229686
H	-2.00354353	2.71134187	1.45902384
C	0.04595775	4.66985480	-1.16624310
H	0.93882382	2.78262767	-1.65345292
C	-0.85917903	5.34795566	-0.35080256
H	-2.29870440	5.16234281	1.23829576
H	0.61033857	5.20982179	-1.91830189
H	-0.99611552	6.41790491	-0.46183024
C	4.53007768	0.87316335	0.63013247
H	5.02186624	0.39511095	1.48082862
H	5.19081718	0.83003209	-0.23925402
H	4.31480778	1.90867294	0.87298171

Reference

(1) (a) He, C.; Zhou, G.; Yang, G.; Wang, F.; Lu, C.; Nie, J.; Ma, C. Borane-Catalyzed Coupling of Diazooxindoles and Difluoroenoxysilanes to Tetrasubstituted Monofluoroalkenes. *Org. Lett.* **2024**, *26*, 5539-5543. (b) Qi, D.; Bai, J.; Song, Z.; Li, B.; Yang, C.; Guo, L.; Xia, W. Photoinduced synthesis of functionalized oxacyclic spirooxindoles via ring expansion. *Org. Lett.* **2023**, *25*, 506-511.

(2) (a) Jurberg, I. D. An aminocatalyzed stereoselective strategy for the formal α-propargylation of ketones. *Chem-Eur. J.* **2017**, *23*, 9716-9720. (b) Wan, T.; Pi, C.; Wu, Y.; Cui, X. Rh (III)-catalyzed [4+2] annulation of 3-aryl-5-isoxazolone with maleimides or maleic ester. *Org. Lett.* **2020**, *22*, 6484-6488.

(3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.

(4) Sheldrick, G. M. SHELXT–Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *71*, 3-8.

(5) Sheldrick, G. M. A short history of SHELX. *Acta Cryst.* **2008**, *64*, 112-122.

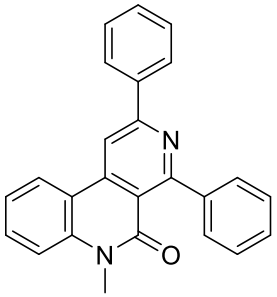
(6) Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. Uranyl extraction by N, N-dialkylamide ligands studied by static and dynamic DFT simulations. In *Gaussian 09*, Gaussian Inc Wallingford, 2009.

(7) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Phys. Chem.* **1994**, *98*, 11623-11627.

(8) Lu, T.; Chen, Q. Shermo: A general code for calculating molecular thermochemistry properties. *Comput. Theor. Chem.* **2021**, *1200*, 113249.

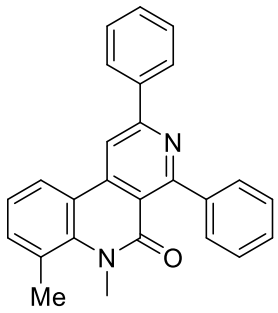
The data of product

6-Methyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3aa)



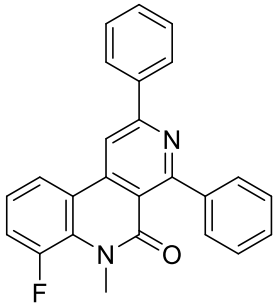
The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3aa** was obtained as a pale yellow solid (58.2 mg, 80% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 198-201 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.45 (s, 1 H), 8.40 (d, *J* = 8.0 Hz, 1 H), 8.21 (d, *J* = 7.6 Hz, 2 H), 7.65-7.58 (m, 3 H), 7.52-7.45 (m, 6 H), 7.40-7.33 (m, 2 H), 3.67 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.4, 160.3, 157.2, 143.1, 142.7, 139.9, 138.5, 131.9, 129.8, 128.9, 128.6, 127.9, 127.6, 124.2, 122.5, 117.6, 116.9, 115.2, 110.3, 30.0; **HRMS** (ESI) calcd for $C_{25}H_{19}N_2O$ $[M+H]^+$ 363.1492, found: 363.1489.

6,7-Dimethyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ba)



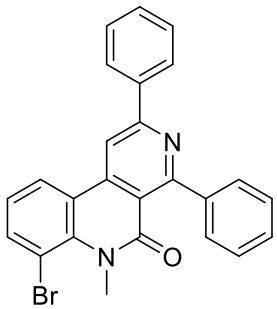
The reaction was performed with **1b** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ba** was obtained as a pale yellow solid (49.8 mg, 66% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 198-201 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.35 (s, 1 H), 8.20-8.15 (m, 3H), 7.71-7.68 (m, 2 H), 7.51-7.37 (m, 7 H), 7.26-7.22 (m, 1 H), 3.61 (s, 3 H), 2.60 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.9, 162.7, 157.5, 143.4, 142.5, 141.6, 138.6, 135.5, 129.8, 129.2, 128.9, 128.3, 127.8, 127.6, 126.9, 123.3, 121.8, 120.5, 117.1, 110.2, 38.3, 23.0; **HRMS** (ESI) calcd for $C_{26}H_{21}N_2O$ $[M+H]^+$ 377.1648; found: 377.1645.

7-Fluoro-6-methyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ca)



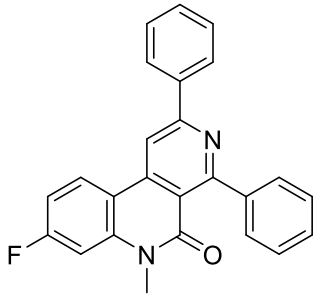
The reaction was performed with **1c** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 ^oC under N_2 for 10 h (TLC monitored). The product **3ca** was obtained as a pale yellow solid (40.4 mg, 53% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 248-251 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.40 (s, 1 H), 8.22-8.17 (m, 3H), 7.65-7.62 (m, 2 H), 7.53-7.47 (m, 6 H), 7.40-7.26 (m, 2 H), 3.82 (d, *J* = 8.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.3, 160.8, 157.6, 152.2, 149.8, 142.6, 142.4 (d, *J* = 2.5 Hz, 1 C), 138.3, 130.0, 129.4 (d, *J* = 6.9 Hz, 1 C), 128.9 (d, *J* = 9.9 Hz, 1 C), 128.3, 127.6 (d, *J* = 13.7 Hz, 1 C), 123.0 (d, *J* = 8.5 Hz, 1 C), 121.0 (d, *J* = 2.5 Hz, 1 C), 119.9 (d, *J* = 3.4 Hz, 1 C), 119.3, 119.1, 117.0, 110.4, 34.4 (d, *J* = 15.6 Hz, 1 C); **^{19}F NMR** (377 MHz, $CDCl_3$, ppm): δ = -119.0; **HRMS** (ESI) calcd for $C_{25}H_{18}FN_2O$ $[M+H]^+$ 381.1398; found: 381.1397.

7-Bromo-6-methyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3da)



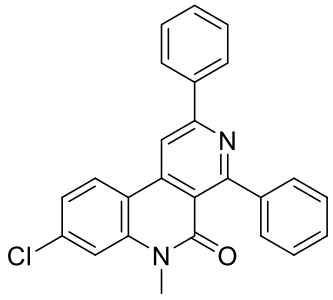
The reaction was performed with **1d** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 ^oC under N_2 for 10 h (TLC monitored). The product **3da** was obtained as a pale yellow solid (51.1 mg, 58% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 258-260 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.35 (s, 1 H), 8.23-8.17 (m, 3 H), 7.58-7.44 (m, 10 H), 3.61 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.4, 160.0, 157.5, 142.8, 142.0, 140.8, 138.3, 130.0, 128.9, 128.6, 128.1, 127.6, 127.6, 126.1, 125.6, 125.5, 118.2, 116.7, 116.6, 110.0, 30.1; **HRMS** (ESI) calcd for $C_{25}H_{18}BrN_2O$ $[M+H]^+$ 441.0597; found: 441.0593.

8-Fluoro-6-methyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ea)



The reaction was performed with **1e** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ea** was obtained as a pale yellow solid (43.4 mg, 57% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 255-258 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.43-8.38 (m, 2 H), 8.20 (d, *J* = 6.4 Hz, 2 H), 7.59-7.57 (m, 2 H), 7.54-7.46 (m, 6 H), 7.11-7.07 (m, 2 H), 3.64 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 166.0, 163.5 (d, *J* = 4.7 Hz, 1 C), 160.3, 157.4, 142.9, 142.2, 141.7 (d, *J* = 10.7 Hz, 1 C), 138.4, 129.9, 128.7 (d, *J* = 33.1 Hz, 1 C), 128.1, 127.6 (d, *J* = 4.0 Hz, 1 C), 126.5, 126.4, 116.3, 114.1 (d, *J* = 2.5 Hz, 1 C), 110.3, 110.1, 102.3 (d, *J* = 26.5 Hz, 1 C), 30.3; **^{19}F NMR** (377 MHz, $CDCl_3$, ppm): δ = -105.9; **HRMS** (ESI) calcd for $C_{25}H_{18}FN_2O$ $[M+H]^+$ 381.1398; found: 381.1397

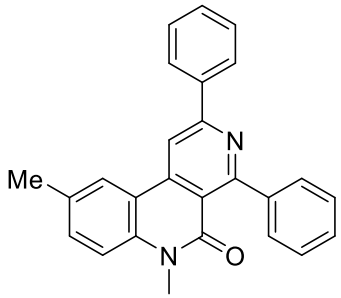
8-Chloro-6-methyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3fa)



The reaction was performed with **1f** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3fa** was obtained as a pale yellow solid (50.0 mg, 63% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 274-278 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.39 (s, 1 H), 8.33 (d, *J* = 8.8 Hz, 1 H), 8.20 (d, *J* = 6.4 Hz, 2 H), 7.59-7.57 (m, 2 H), 7.53-7.46 (m, 6 H), 7.40-7.39 (m, 1 H), 7.35-7.32 (m, 1 H), 3.65 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.5, 160.1, 157.5, 142.8, 142.0, 140.8, 138.3, 137.9, 130.0, 128.9, 128.6, 128.1, 127.6, 127.6,

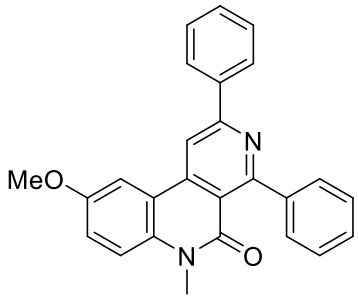
125.5, 122.8, 116.6, 116.2, 115.2, 110.1, 30.1; **HRMS** (ESI) calcd for $C_{25}H_{18}ClN_2O$ $[M+H]^+$ 397.1102; found: 397.1103.

6,9-Dimethyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ga)



The reaction was performed with **1g** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ga** was obtained as a pale yellow solid (52.8 mg, 70% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 204-208 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.42 (s, 1 H), 8.23-8.20 (m, 2 H), 8.15 (s, 1 H), 7.60-7.58 (m, 2 H), 7.52-7.41 (m, 7 H), 7.26-7.24 (m, 1 H), 3.62 (s, 3 H), 2.50 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.3, 160.1, 156.9, 143.2, 142.6, 138.6, 137.8, 132.9, 132.0, 129.8, 128.8, 128.7, 127.9, 127.6, 127.6, 124.2, 117.4, 117.1, 115.1, 110.2, 30.0, 20.9; **HRMS** (ESI) calcd for $C_{26}H_{21}N_2O$ $[M+H]^+$ 377.1648; found: 377.1645.

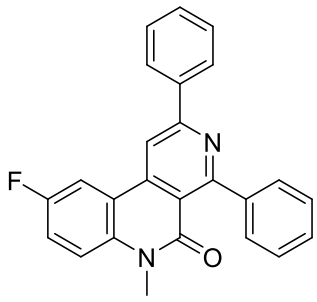
9-Methoxy-6-methyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ha)



The reaction was performed with **1h** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ha** was obtained as a pale yellow solid (55.8 mg, 71% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1),melting point: 256-259 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.37 (s, 1 H), 8.21-8.19 (m, 2 H), 7.83 (d, *J* = 2.8 Hz, 1 H), 7.59-7.57 (m, 2 H), 7.53-7.44 (m, 6 H), 7.33-7.31 (m, 1 H), 7.25-7.22 (m, 1 H), 3.95 (s, 3 H), 3.64 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.4, 159.8, 157.1, 155.1, 143.2, 142.3, 138.6, 134.3, 129.8, 128.8, 128.6, 127.9, 127.6,

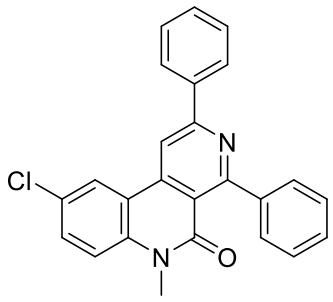
127.6, 118.8, 118.5, 117.2, 116.3, 110.3, 108.0, 55.9, 30.1; **HRMS** (ESI) calcd for $C_{26}H_{21}N_2O_2$ $[M+H]^+$ 393.1598; found: 393.1595.

9-Fluoro-6-methyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ia)



The reaction was performed with **1i** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ia** was obtained as a pale yellow solid (40.4 mg, 53% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 272-275 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.36 (s, 1 H), 8.23-8.21 (m, 2 H), 8.10-8.07 (m, 1 H), 7.60-7.58 (m, 2 H), 7.54-7.47 (m, 6 H), 7.40-7.38 (m, 2 H), 3.68 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.5, 159.9, 159.5, 157.4, 157.1, 142.8, 141.8 (d, *J* = 2.9 Hz, 1 C), 138.2, 136.4 (d, *J* = 1.8 Hz, 1 C), 130.0, 128.8 (d, *J* = 22.9 Hz, 1 C), 128.1, 127.6 (d, *J* = 2.1 Hz, 1 C), 119.3 (d, *J* = 23.1 Hz, 1C), 118.9 (d, *J* = 7.5 Hz, 1 C), 117.1, 116.8 (d, *J* = 7.9 Hz, 1 C), 110.3, 110.3, 110.0, 30.3; **^{19}F NMR** (377 MHz, $CDCl_3$, ppm): δ = -120.1； **HRMS** (ESI) calcd for $C_{25}H_{18}FN_2O$ $[M+H]^+$ 381.1398; found: 381.1397.

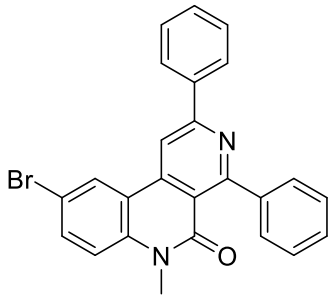
9-Chloro-6-methyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ja)



The reaction was performed with **1j** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ja** was obtained as a pale yellow solid (50.8 mg, 64% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 282-284 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.38-8.35 (m, 2 H), 8.22 (d, *J* = 6.4 Hz, 2 H), 7.61-7.46 (m, 9 H), 7.34 (d, *J* = 8.8 Hz, 1 H), 3.66 (s, 3 H); **^{13}C NMR** (100

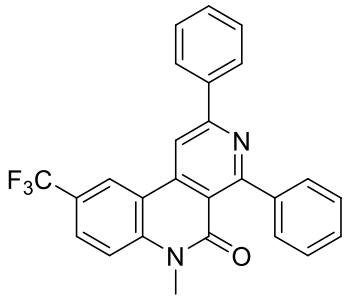
MHz, $CDCl_3$, ppm): δ 163.5, 159.9, 157.5, 142.8, 141.5, 138.4, 138.2, 131.7, 130.0, 128.9, 128.6, 128.2, 128.1, 127.6, 123.9, 119.0, 117.0, 116.6, 110.1, 30.2; **HRMS (ESI)** calcd for $C_{25}H_{18}ClN_2O$ $[M+H]^+$ 397.1102; found: 397.1103.

9-Bromo-6-methyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ka)



The reaction was performed with **1k** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ka** was obtained as a pale yellow solid (55.5 mg, 63% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 250-253 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.39 (s, 1 H), 8.26-8.19 (m, 3 H), 7.58-7.46 (m, 10 H), 3.64 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.5, 160.1, 157.5, 142.8, 142.0, 140.8, 138.3, 130.0, 128.9, 128.6, 128.1, 127.6, 127.6, 126.2, 125.6, 125.5, 118.2, 116.6, 110.0, 30.2; **HRMS** (ESI) calcd for $C_{25}H_{18}BrN_2O$ $[M+H]^+$441.0597; found: 441.0594.

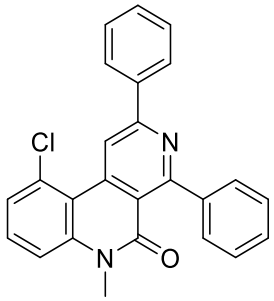
6-Methyl-2,4-diphenyl-9-(trifluoromethyl)benzo[*c*][2,7]naphthyridin-5(6*H*)-one (3la)



The reaction was performed with **1l** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3la** was obtained as a pale yellow solid (61.3 mg, 71% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 254-256 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.37 (s, 1 H), 8.24-8.22 (m, 3 H), 7.60-7.26 (m, 10 H), 3.69 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.6, 160.0, 157.6, 144.2, 144.2, 142.7, 141.6, 138.5, 138.2, 130.1, 128.9, 128.6, 128.1, 127.6, 124.7,

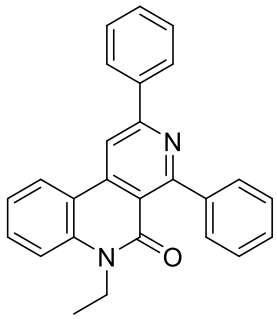
120.6 (q, *J* = 256.1 Hz, 1 C), 118.7, 117.0, 116.9, 116.6, 110.1, 30.3; **^{19}F NMR** (377 MHz, $CDCl_3$, ppm): δ = -58.0; **HRMS** (ESI) calcd for $C_{26}H_{18}F_3N_2O$ $[M+H]^+$ 431.1366; found: 431.1366.

10-Chloro-6-methyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3na)



The reaction was performed with **1n** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3na** was obtained as a pale yellow solid (49.3 mg, 62% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 278-281 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 9.54 (s, 1 H), 8.22 (d, *J* = 6.8 Hz, 2 H), 7.64-7.62 (m, 2 H), 7.54-7.44 (m, 8 H), 7.37-7.35 (m, 1 H), 3.66 (s, 3 H) ; **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.9, 159.8, 156.6, 143.2, 141.8, 141.7, 138.5, 133.3, 130.7, 129.9, 128.9, 128.9, 128.2, 127.6, 127.7, 126.5, 117.7, 116.1, 115.1, 114.0, 31.1; **HRMS** (ESI) calcd for $C_{25}H_{18}ClN_2O$ $[M+H]^+$ 397.1102; found: 397.1103.

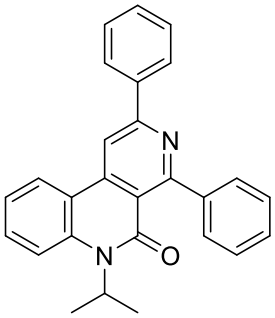
6-Ethyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3oa)



The reaction was performed with **1o** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3oa** was obtained as a pale yellow solid (52.7 mg, 70% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 207-210 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): 8.46 (d, *J* = 6.8 Hz, 2 H), 8.25-8.22 (m, 2 H), 7.68-7.62 (m, 3 H), 7.55-7.43 (m, 7 H), 7.38-7.34 (m, 1 H), 4.38-4.33 (m, 2 H), 1.35 (t, *J* = 4.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.2, 159.8, 157.1, 143.1, 142.7, 138.8, 138.6, 131.9,

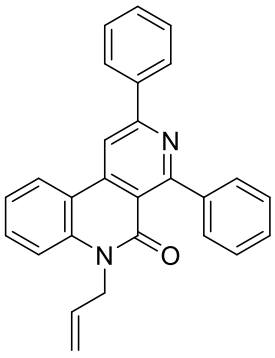
129.8, 128.9, 128.8, 128.0, 127.6, 124.5, 122.3, 117.9, 117.0, 115.1, 110.1, 37.7, 12.6; **HRMS** (ESI) calcd for $C_{26}H_{21}N_2O$ $[M+H]^+$ 377.1648; found: 377.1645.

6-Isopropyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3pa)



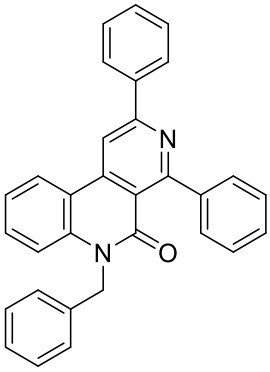
The reaction was performed with **1p** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3pa** was obtained as a pale yellow solid (56.3 mg, 72% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 182-186 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.42-8.40 (m, 2 H), 8.22-8.20 (m, 2 H), 7.64-7.59 (m, 4 H), 7.53-7.44 (m, 6 H), 7.34-7.29 (m, 1 H), 5.39 (br s, 1 H), 1.62 (d, *J* = 7.2 Hz, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.8, 161.0, 156.9, 142.8, 142.7, 139.2, 138.7, 131.2, 129.7, 128.9, 128.8, 128.1, 127.6, 127.6, 124.6, 122.0, 118.3, 118.0, 115.8, 109.9, 47.35, 19.8; **HRMS** (ESI) calcd for $C_{27}H_{23}N_2O$ $[M+H]^+$ 391.1805; found: 391.1800.

6-Allyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3qa)



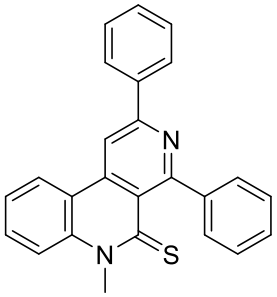
The reaction was performed with **1q** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3qa** was obtained as a pale yellow solid (56.0 mg, 72% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 221-224 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.50-8.44 (m, 2 H), 8.23 (d, *J* = 6.8 Hz, 2 H), 7.65-7.60 (m, 3 H), 7.55-7.35 (m, 8 H), 7.97-7.88 (m, 1 H), 5.22-5.12 (m, 2 H), 4.95 (s, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.4, 159.9, 157.3, 142.9, 142.8, 139.2, 138.5, 132.1, 131.7, 129.8, 128.9, 128.8, 128.1, 127.8, 127.6, 124.2, 122.5, 117.8, 116.9, 116.8, 115.9, 110.2, 45.0; **HRMS** (ESI) calcd for $C_{27}H_{21}N_2O$ $[M+H]^+$ 389.1648; found: 389.1639.

6-Benzyl-2,4-diphenylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ra)



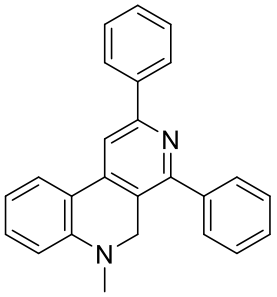
The reaction was performed with **1r** (0.2 mmol, 1 equiv.), **2a** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 ^oC under N_2 for 10 h (TLC monitored). The product **3ra** was obtained as a pale yellow solid (61.5 mg, 70% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 196-199 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.54 (s, 1 H), 8.47 (d, *J* = 8.0 Hz, 1 H), 8.28 (d, J = 7.2 Hz, 2 H), 7.68-7.67 (m, 2 H), 7.59-7.46 (m, 7 H), 7.37-7.22 (m, 7 H), 5.59-5.58 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.5, 160.5, 157.4, 143.1, 142.8, 139.2, 138.5, 136.4, 131.8, 130.1, 128.9, 128.6, 128.8, 128.1, 127.6, 127.2, 126.5, 124.2, 122.6, 117.9, 116.8, 116.2, 110.2, 46.2; **HRMS** (ESI) calcd for $C_{31}H_{23}N_2O$ $[M+H]^+$ 439.1805; found: 439.1802.

6-Methyl-2,4-diphenylbenzo[*c*][2,7]naphthyridine-5(6*H*)-thione (3ua)



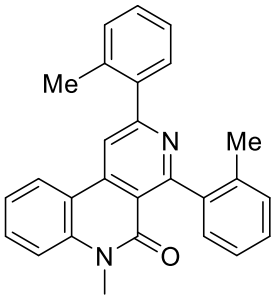
A mixture of compound **3aa** and P_2S_5 in toluene was stirred at 110 ^oC overnight, and then cooled to room temperature. The solvent was removed and the residue was diluted with EtOAc, washed with sat. NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo, and the residue was purified by prep-TLC to afford the desired compounds **3ua**. melting point: 216-219 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.50 (s, 1 H), 8.45 (d, *J* = 8.0 Hz, 1 H), 8.22 (d, *J* = 7.2 Hz, 2 H), 7.70-7.66 (m, 1 H), 7.60-7.58 (m, 2 H), 7.55-7.37 (m, 8 H), 3.70 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.3, 160.2, 157.1, 142.8, 139.9, 138.3, 132.0, 129.9, 128.9, 128.6, 128.0, 127.7, 127.6, 124.3, 122.6, 117.6, 117.0, 115.2, 110.5, 30.1; **HRMS** (ESI) calcd for $C_{25}H_{19}N_2S$ $[M+H]^+$ 379.1264; found: 379.1268.

6-Methyl-2,4-diphenyl-5,6-dihydrobenzo[*c*][2,7]naphthyridine (3va)



Add $LiAlH_4$ (0.2 mmol) to a solution of the reactant **3aa** (0.2 mmol, 1 equiv) in dried THF (2 mL) and stir the mixture at 60 °C for 2 hours. Once the conversion is complete, as indicated by TLC, add $NaHCO_3$ solution (2 mL) to the residue. Extract the mixture with ethyl acetate (15 mL), wash the collected organic layer with brine, dry it with $MgSO_4$, filter, and concentrate under vacuum. Finally, purify the product **3va** by flash column chromatography on silica gel using a mixture of acetone and petroleum ether. melting point: 189-192 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.12 (d, *J* = 7.6 Hz, 2 H), 8.00 (s, 1 H), 7.88 (d, *J* = 7.6 Hz, 1 H), 7.63 (d, *J* = 7.2 Hz, 2 H), 7.53-7.36 (m, 7 H), 6.98-6.94 (m, 1 H), 6.79 (d, *J* = 8.0 Hz, 1 H), 4.29 (s, 2 H), 2.87 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 154.9, 154.5, 147.1, 140.2, 138.7, 135.9, 135.8, 130.1, 128.1, 127.7, 127.6, 127.4, 127.2, 125.9, 123.6, 120.7, 117.8, 111.6, 111.5, 50.9, 37.5; **HRMS** (ESI) calcd for $C_{25}H_{21}N_2$ $[M+H]^+$ 349.1699; found: 349.1696.

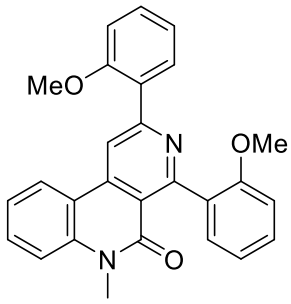
6-Methyl-2,4-di-o-tolylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ab)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2b** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ab** was obtained as a pale yellow solid (56.3 mg, 72% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 190-193 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.27-8.24 (m, 1 H), 8.13 (s, 1 H), 7.58-7.54 (m, 1 H), 7.46-7.44 (m, 1 H), 7.33-7.11 (m, 9 H), 3.58 (s, 3 H), 2.34 (s, 3 H), 2.06 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.0, 161.0, 156.0, 143.2, 141.9, 140.0, 139.9, 136.3, 134.5, 132.1, 131.0, 129.7, 129.6, 128.9, 127.5, 127.2, 126.0, 125.5, 124.3, 122.6, 117.4, 115.2, 114.5,

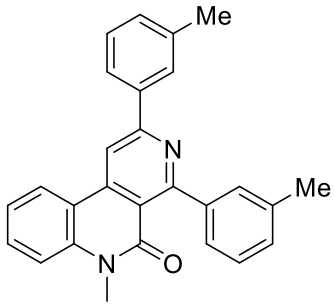
30.0, 20.5, 19.9; **HRMS** (ESI) calcd for $C_{27}H_{23}N_2O$ $[M+H]^+$ 391.1805; found: 391.1800.

2,4-Bis(2-methoxyphenyl)-6-methylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ac)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2c** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ac** was obtained as a pale yellow solid (64.1 mg, 71% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 208-211 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.66 (s, 1 H), 8.29-8.27 (m, 1 H), 7.97-7.95 (m, 1 H), 7.56-7.52 (m, 1 H), 7.37-7.25 (m, 5 H), 7.05-6.96 (m, 3 H), 6.90-6.88 (m, 1 H), 3.89 (s, 3 H), 3.60 (d, *J* = 14.4 Hz, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 160.3, 159.8, 157.4, 156.9, 156.0, 140.9, 139.9, 133.1, 131.9, 131.4, 130.5, 129.1, 129.0, 128.3, 124.3, 122.3, 121.3, 120.7, 118.2, 117.9, 115.5, 114.9, 111.6, 110.6, 55.9, 55.6, 29.9; **HRMS** (ESI) calcd for $C_{27}H_{23}N_2O_3$ $[M+H]^+$ 423.1703 found: 423.1698.

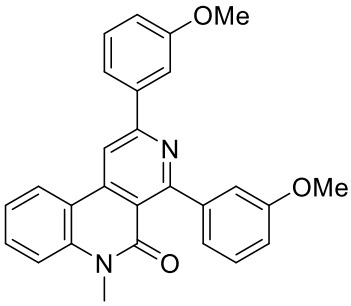
6-Methyl-2,4-di-m-tolylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ad)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2d** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ad** was obtained as a pale yellow solid (60.2 mg, 77% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 193-195 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.29-8.26 (m, 2 H), 8.01 (d, *J* = 6.4 Hz, 2 H), 7.53-7.49 (m, 1 H), 7.41-7.39 (m, 2 H), 7.27-7.14 (m, 6 H), 3.56 (s, 3 H), 2.35 (s, 3 H), 2.31 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.2, 160.3, 157.0, 142.6, 140.3, 140.1, 140.0, 137.6, 135.7, 131.7, 129.5, 128.7, 128.4, 127.5, 124.2, 122.4, 117.8,

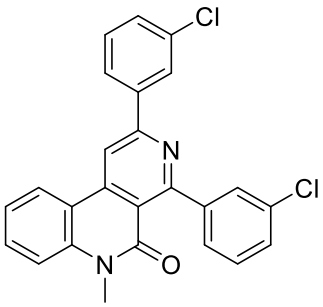
116.7, 115.1, 109.5, 30.0, 21.6, 21.4; **HRMS** (ESI) calcd for $C_{27}H_{23}N_2O$ $[M+H]^+$ 391.1805; found: 391.1800.

2,4-Bis(3-methoxyphenyl)-6-methylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ae)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2e** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ae** was obtained as a pale yellow solid (62.6 mg, 74% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 212-215 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.45-8.39 (m, 2 H), 7.79-7.76 (m, 2 H), 7.67-7.63 (m, 1 H), 7.44-7.34 (m, 4 H), 7.17-7.13 (m, 2 H), 7.03-7.00 (m, 2 H), 3.90 (s, 3 H), 3.87 (s, 3 H), 3.68 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.0, 160.1, 160.0, 159.0, 156.9, 144.4, 142.6, 140.0, 139.9, 131.9, 129.8, 128.5, 124.2, 122.5, 121.3, 120.0, 117.6, 117.1, 115.4, 115.1, 114.3, 113.4, 113.2, 110.5, 55.5, 55.3, 30.0; **HRMS** (ESI) calcd for $C_{27}H_{23}N_2O_3$ $[M+H]^+$ 423.1703; found: 423.1692.

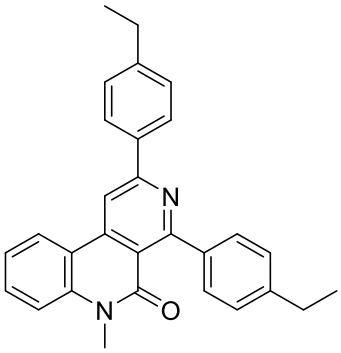
2,4-Bis(3-chlorophenyl)-6-methylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3af)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2f** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3af** was obtained as a pale yellow solid (52.6 mg, 61% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 294-296 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.43-8.41 (m, 2 H), 8.23-8.19 (m, 2 H), 7.70-7.66 (m, 1 H), 7.59-7.55 (m, 2 H), 7.44-7.37 (m, 2 H), 7.23-7.14 (m, 4 H), 3.70 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 165.3, 164.0, 162.9, 162.3, 161.6, 160.2, 156.1, 142.9, 139.9, 138.9, 134.5, 134.5, 132.1, 130.6, 130.5, 129.5, 129.4, 124.2, 122.7,

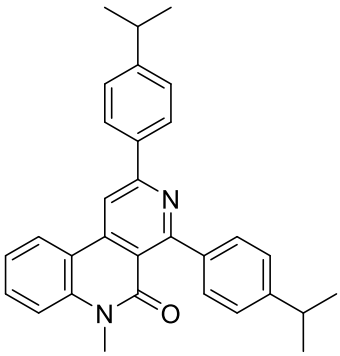
117.5, 116.8, 116.0, 115.8, 115.3, 114.7, 114.5, 110.0, 30.1; **HRMS** (ESI) calcd for $C_{25}H_{17}Cl_2N_2O$ $[M+H]^+$ 431.0712; found: 431.0705.

2,4-Bis(4-ethylphenyl)-6-methylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ah)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2h** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ah** was obtained as a pale yellow solid (58.7 mg, 70% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 206-209 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.40-8.37 (m, 2 H), 8.13 (d, *J* = 8.4 Hz, 2 H), 7.64-7.60 (m, 1 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.38-7.30 (m, 6 H), 3.67 (s, 3 H), 2.78-2.69 (m, 4 H), 1.33-1.26 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.3, 160.4, 157.2, 146.3, 143.8, 142.6, 140.5, 139.9, 136.1, 131.7, 128.8, 128.4, 127.6, 127.1, 124.2, 122.4, 117.8, 116.7, 115.1, 109.6, 30.0, 28.8, 28.8, 15.5, 15.3; **HRMS** (ESI) calcd for $C_{29}H_{27}N_2O$ $[M+H]^+$ 419.2118; found: 419.2118.

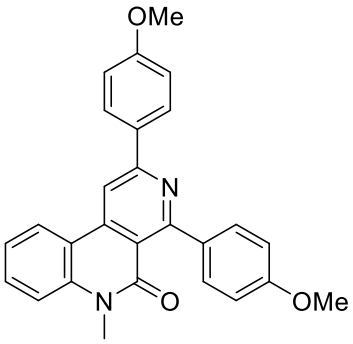
2,4-Bis(4-isopropylphenyl)-6-methylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ai)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2i** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ai** was obtained as a pale yellow solid (60.7 mg, 68% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 216-219 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.46-8.43 (m, 2 H), 8.14 (d, *J* = 8.4 Hz, 2 H), 7.70-8.66 (m, 1 H), 7.58 (d, *J* = 8 Hz, 2 H), 7.46-7.35 (m, 6 H), 3.73 (s, 3 H), 3.05-3.00 (m, 2 H), 1.36-1.32 (m, 12 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 164.4, 160.4, 157.3, 150.9, 148.4, 142.7, 140.4, 140.2, 136.2, 131.7, 128.9, 127.7, 126.9, 125.7,

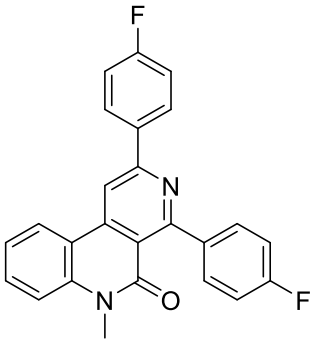
124.2, 122.5, 117.8, 116.5, 115.1, 109.7, 34.2, 33.9, 30.1, 24.0, 23.9; **HRMS** (ESI) calcd for $C_{31}H_{31}N_2O$ $[M+H]^+$ 447.2431; found: 447.2420.

2,4-Bis(4-methoxyphenyl)-6-methylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3aj)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2j** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3aj** was obtained as a pale yellow solid (64.3 mg, 76% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 218-221 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.40-8.35 (m, 2 H), 8.20 (d, *J* = 8.8 Hz, 2 H), 7.64-7.57 (m, 3 H), 7.41-7.35 (m, 2 H), 7.03-7.00 (m, 4 H), 3.88 (s, 6 H), 3.70 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.7, 161.2, 160.5, 159.6, 156.6, 142.7, 139.9, 135.5, 131.6, 131.1, 130.4, 129.1, 124.1, 122.4, 117.8, 116.1, 116.1, 114.2, 113.0, 108.7, 55.4, 55.3, 30.0; HRMS (ESI) calcd for $C_{27}H_{23}N_2O_3$ $[M+H]^+$ 423.1703 found: 423.1692.

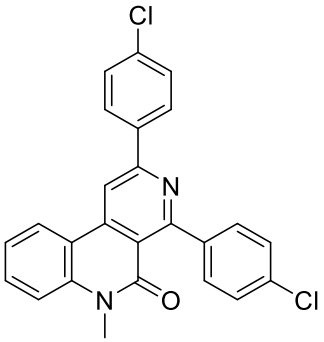
2,4-Bis(4-fluorophenyl)-6-methylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ak)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2k** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ak** was obtained as a pale yellow solid (44.7 mg, 56% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 254-258 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.41-8.39 (m, 2 H), 8.21-8.18 (m, 2 H), 7.69-7.65 (m, 1 H), 7.58-7.55 (m, 2 H), 7.43-7.36 (m, 2 H), 7.21-7.13 (m, 4 H), 3.68 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 164.1 (d, *J* = 248.5 Hz, 1 C), 162.8 (d, *J* = 245.4 Hz, 1 C), 162.3, 160.2, 156.1, 142.9, 139.9, 138.8 (d, *J* = 3.5 Hz, 1 C), 134.5

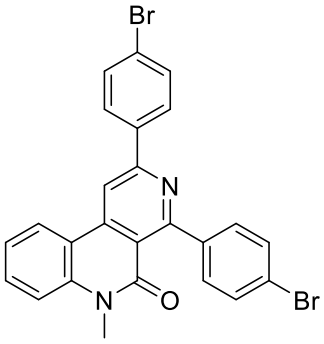
(d, *J* = 2.9 Hz, 1 C), 132.0, 130.6 (d, *J* = 8.0 Hz, 1 C), 129.5 (d, *J* = 8.4 Hz, 1 C), 124.2, 122.6, 117.5, 116.8, 115.9 (d, *J* = 21.4 Hz, 1 C), 115.2, 114.6 (d, *J* = 21.5 Hz, 1 C), 109.9, 30.0; **^{19}F NMR** (377 MHz, $CDCl_3$, ppm): δ = -111.3, -114.2; **HRMS** (ESI) calcd for $C_{25}H_{17}F_2N_2O$ $[M+H]^+$ 399.1303; found: 399.1297.

2,4-Bis(4-chlorophenyl)-6-methylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3al)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2l** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3al** was obtained as a pale yellow solid (54.3 mg, 63% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 283-286 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.39-8.34 (m, 2 H), 8.08 (d, J = 8.8 Hz, 2 H), 7.62-7.60 (m, 1 H), 7.46-7.31 (m, 8 H), 3.63 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.2, 160.1, 156.0, 142.9, 141.3, 139.8, 136.7, 136.2, 134.1, 132.2, 130.1, 129.1, 128.8, 127.9, 124.2, 122.7, 117.4, 117.1, 115.3, 110.3, 30.1; **HRMS** (ESI) calcd for $C_{25}H_{17}Cl_2N_2O$ $[M+H]^+$ 431.0712; found: 431.0705.

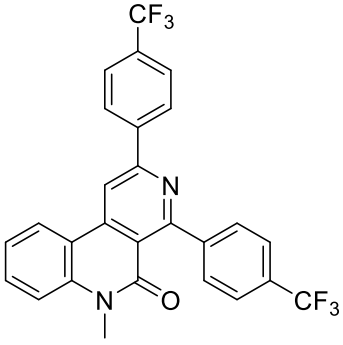
2,4-Bis(4-bromophenyl)-6-methylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3am)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2m** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3am** was obtained as a pale yellow solid (64.3 mg, 62% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 253-255 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.47-8.43 (m, 2 H), 8.33-8.32 (m, 1 H), 8.13 (d, *J* = 8.0 Hz, 1 H), 7.72-7.67 (m, 2 H), 7.62-7.57 (m, 2 H), 7.48-7.34 (m, 6 H), 3.70 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 161.9, 159.9, 155.8, 144.8,

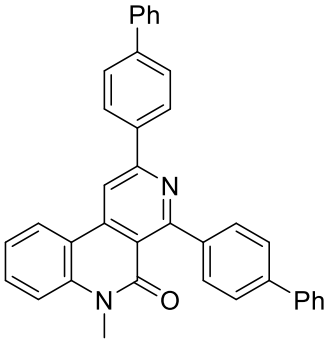
142.9, 140.4, 139.9, 132.8, 132.3, 131.4, 131.0, 130.5, 130.4, 129.0, 127.4, 126.2, 124.3, 123.2, 122.7, 121.7, 117.4, 117.3, 115.3, 110.9, 30.1; **HRMS** (ESI) calcd for $C_{25}H_{17}Br_2N_2O$ $[M+H]^+$ 518.9702; found: 518.9702.

6-Methyl-2,4-bis(4-(trifluoromethyl)phenyl)benzo[*c*][2,7]naphthyridin-5(6*H*)-one (3an)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2n** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3an** was obtained as a pale yellow solid (64.7 mg, 65% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 254-256 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.58 (s, 1 H), 8.48-8.46 (m, 1 H), 8.33-8.31 (m, 2 H), 7.80-7.67 (m, 7 H), 7.48-7.42 (m, 2 H), 3.72 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.2, 159.9, 155.9, 146.4, 143.1, 141.6, 139.9, 132.4, 131.9, 130.0, 129.8, 128.9, 127.9, 125.9 (q, *J* = 3.8 Hz, 1 C), 125.4, 124.6 (q, *J* = 3.9 Hz, 1 C), 124.3, 122.9, 117.6, 117.3, 115.4, 111.4, 30.1; **^{19}F NMR** (377 MHz, $CDCl_3$, ppm): δ = -62.4, -62.7; **HRMS** (ESI) calcd for $C_{27}H_{17}F_6N_2O$ $[M+H]^+$ 499.1240; found: 499.1243.

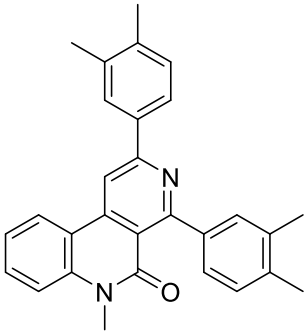
2,4-Di([1,1'-biphenyl]-4-yl)-6-methylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ao)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2o** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ao** was obtained as a pale yellow solid (70.1 mg, 68% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 192-195 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.54-8.46 (m, 2 H), 8.33 (d, *J* = 8.0 Hz, 2 H), 7.71-7.67 (m, 11 H), 7.51-7.35 (m, 9 H), 3.73 (s, 3 H); **^{13}C NMR** (100 MHz,

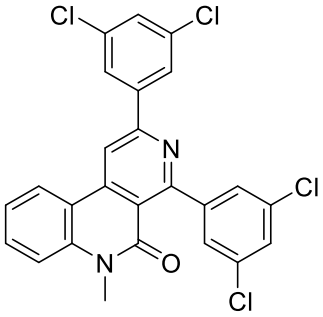
$CDCl_3$, ppm): δ 163.0, 160.4, 156.8, 142.8, 142.6, 142.1, 141.3, 140.7, 140.4, 139.9, 137.3, 131.9, 129.3, 128.9, 128.7, 128.0, 127.7, 127.6, 127.3, 127.2, 126.5, 124.3, 122.6, 117.7, 116.9, 115.2, 110.1, 30.1; **HRMS** (ESI) calcd for $C_{37}H_{27}N_2O$ $[M+H]^+$ 515.2118; found: 515.2120.

2,4-Bis(3,4-dimethylphenyl)-6-methylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3aq)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2q** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3aq** was obtained as a pale yellow solid (55.3 mg, 66% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 196-199 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.35-8.33 (m, 2 H), 7.93-7.85 (m, 2 H), 7.58-7.54 (m, 1 H), 7.32-7.26 (m, 3 H), 7.21-7.14 (m, 3 H), 3.60 (s, 3 H), 2.28-2.25 (m, 12 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 163.4, 160.4, 157.3, 142.5, 141.0, 140.0, 138.6, 137.1, 136.3, 136.2, 135.8, 131.7, 130.1, 129.6, 128.9, 128.7, 126.2, 125.1, 124.2, 122.4, 117.8, 116.7, 115.1, 109.6, 30.0, 20.1, 20.0, 19.9, 19.8; **HRMS** (ESI) calcd for $C_{29}H_{27}N_2O$ $[M+H]^+$ 419.2118; found: 419.2118.

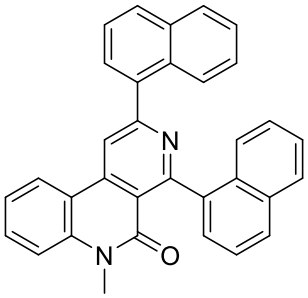
2,4-Bis(3,5-dichlorophenyl)-6-methylbenzo[*c*][2,7]naphthyridin-5(6*H*)-one (3ar)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2r** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3ar** was obtained as a pale yellow solid (63.7 mg, 64% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 215-218 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.39-8.34 (m, 2 H), 8.08 (d, *J* = 8.8 Hz, 2 H), 7.64-7.60 (m, 1 H), 7.46-7.37 (m, 6 H), 3.63 (s, 3 H); **^{13}C NMR** (100 MHz,

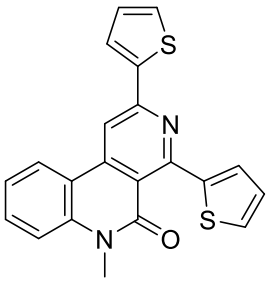
$CDCl_3$, ppm): δ 163.5, 159.9, 157.6, 142.8, 141.5, 138.9, 138.2, 134.5, 130.0, 128.9, 128.6, 128.1, 127.8, 127.6, 126.9, 119.4, 117.0, 116.9, 115.6, 110.1, 30.1; **HRMS** (ESI) calcd for $C_{25}H_{15}Cl_4N_2O$ $[M+H]^+$ 498.9933; found: 498.9921.

6-Methyl-2,4-di(naphthalen-1-yl)benzo[*c*][2,7]naphthyridin-5(6*H*)-one (3as)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2s** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3as** was obtained as a pale yellow solid (62.9 mg, 68% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 194-198 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.47 (s, 1 H), 8.36 (d, *J* = 6.8 Hz, 1 H), 8.22-8.19 (m, 1 H), 7.92-7.87 (m, 4 H), 7.80-7.78 (m, 1 H), 7.65-7.30 (m, 11 H), 3.57 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 162.5, 160.1, 159.7, 142.1, 141.3, 140.1, 137.9, 134.0, 133.4, 132.2, 131.9, 131.3, 129.6, 128.5, 128.2, 127.8, 126.9, 126.0, 125.9, 125.5, 125.4, 125.4, 125.2, 124.8, 124.4, 122.6, 118.7, 117.4, 115.9, 115.2, 30.0; **HRMS** (ESI) calcd for $C_{33}H_{23}N_2O$ $[M+H]^+$ 463.1805; found: 463.1804.

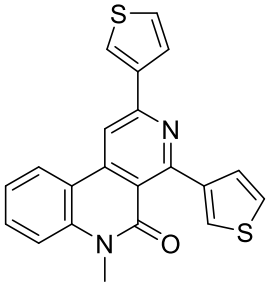
6-Methyl-2,4-di(thiophen-2-yl)benzo[*c*][2,7]naphthyridin-5(6*H*)-one (3at)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2t** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 °C under N_2 for 10 h (TLC monitored). The product **3at** was obtained as a pale yellow solid (47.2 mg, 63% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 191-194 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.16 (d, *J* = 6.8 Hz, 1 H), 8.05 (s, 1 H), 7.78-7.74 (m, 2 H), 7.57-7.53 (m, 1 H), 7.48-7.44 (m, 2 H), 7.29-7.23 (m, 2 H), 7.14-7.11 (m, 2 H), 3.63 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 159.9, 155.5, 151.9, 144.2, 143.9, 143.1, 139.6, 131.9, 130.5, 129.2, 128.4,

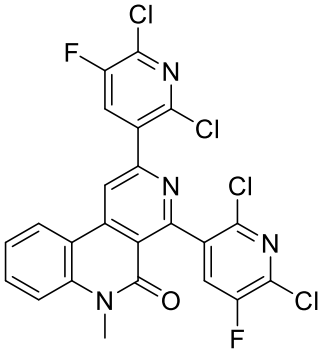
128.3, 127.0, 126.2, 124.1, 122.4, 117.3, 115.9, 114.9, 107.7, 30.0; **HRMS** (ESI) calcd for $C_{21}H_{15}N_2OS_2$ $[M+H]^+$ 375.0620; found: 375.0619.

6-Methyl-2,4-di(thiophen-3-yl)benzo[*c*][2,7]naphthyridin-5(6*H*)-one (3au)



The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2u** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 ^oC under N_2 for 10 h (TLC monitored). The product **3au** was obtained as a pale yellow solid (48.0 mg, 64% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 248-251 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.33 (d, *J* = 8.0 Hz, 1 H), 8.25 (s, 1 H), 8.16-8.15 (m, 1 H), 7.82-7.80 (m, 1 H), 7.71-7.70 (m, 1 H), 7.66-7.62 (m, 1 H), 7.44-7.33 (m, 5 H), 3.70 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 160.1, 158.1, 153.4, 143.4, 142.8, 141.5, 139.8, 131.9, 129.5, 126.6, 126.4, 125.8, 125.2, 124.2, 123.5, 122.5, 117.5, 116.7, 115.1, 109.7, 30.0; **HRMS** (ESI) calcd for $C_{21}H_{15}N_2OS_2$ $[M+H]^+$ 375.0620; found: 375.0619.

2,4-Bis(2,6-dichloro-5-fluoropyridin-3-yl)-6-methylbenzo[c][2,7]naphthyridin-5(6H)-one (3av)

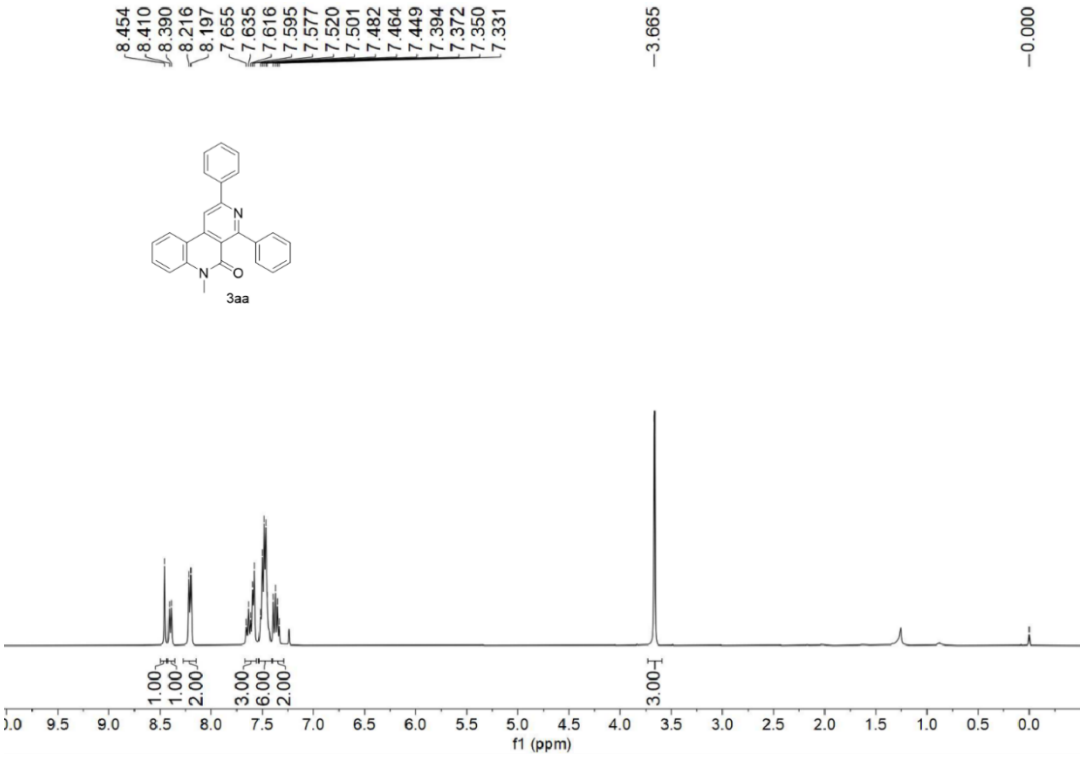


The reaction was performed with **1a** (0.2 mmol, 1 equiv.), **2v** (0.5 mmol 2.5 equiv.), $[Cp^*RhCl_2]_2$ (2 mol%, 0.004 mmol), CuCl (0.4 mmol, 2.0 equiv.), DCE/EtOAc (3 mL) were stirred at 120 ^oC under N_2 for 10 h (TLC monitored). The product **3av** was obtained as a pale yellow solid (66.4 mg, 62% yield) after purification by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1), melting point: 216-219 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.85 (s, 1 H), 8.40 (d, *J* = 7.6 Hz, 1 H), 8.08 (d, *J* = 7.6 Hz, 1 H), 7.79-7.75 (m, 1 H), 7.57 (d, *J* = 7.2 Hz, 1 H), 7.52-7.45 (m, 2 H), 3.74 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 159.4, 156.9, 154.6 (d, *J* = 249.4 Hz, 1 C), 154.1 (d, *J* = 259.2 Hz, 1 C), 153.3, 142.5, 142.0 (d, *J* = 3.4 Hz, 1 C),

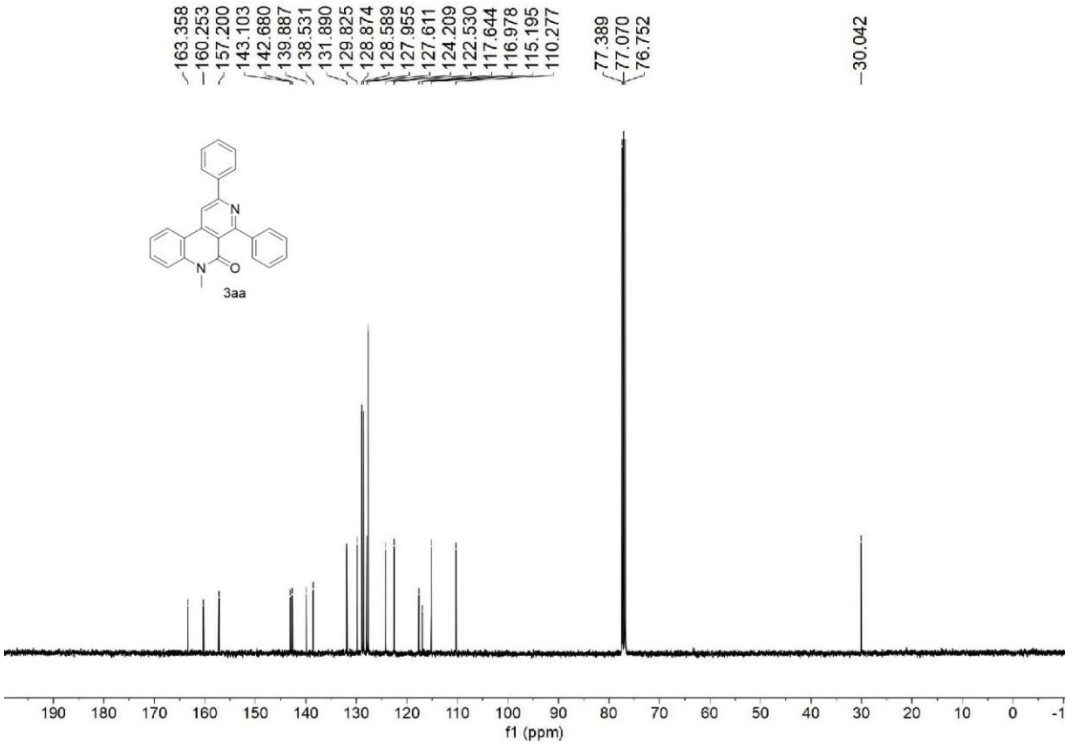
141.8 (d, *J* = 3.3 Hz, 1 C), 140.0, 138.6 (d, *J* = 21.1 Hz, 1 C), 138.5 (d, *J* = 3.2 Hz, 1 C), 136.5 (d, *J* = 21.1 Hz, 1 C), 134.7 (d, *J* = 3.1 Hz, 1 C), 133.3, 129.0 (d, *J* = 21.4 Hz, 1 C), 126.3 (d, *J* = 21.5 Hz, 1 C), 124.6, 123.6, 119.0, 117.3, 116.7, 115.7, 30.3; **^{19}F NMR** (377 MHz, $CDCl_3$, ppm): δ = -120.8, -122.2; **HRMS** (ESI) calcd for $C_{23}H_{11}Cl_4F_2N_4O$ $[M+H]^+$ 536.9650; found: 536.9658.

Copies of NMR spectra

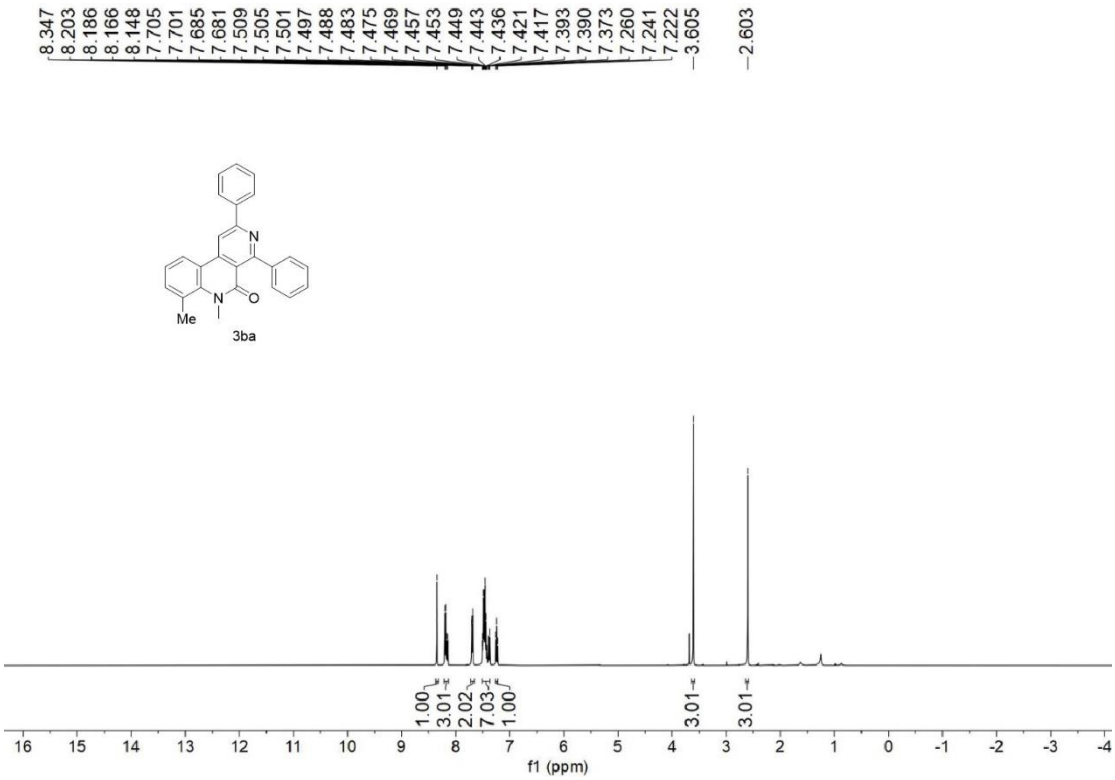
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3aa**



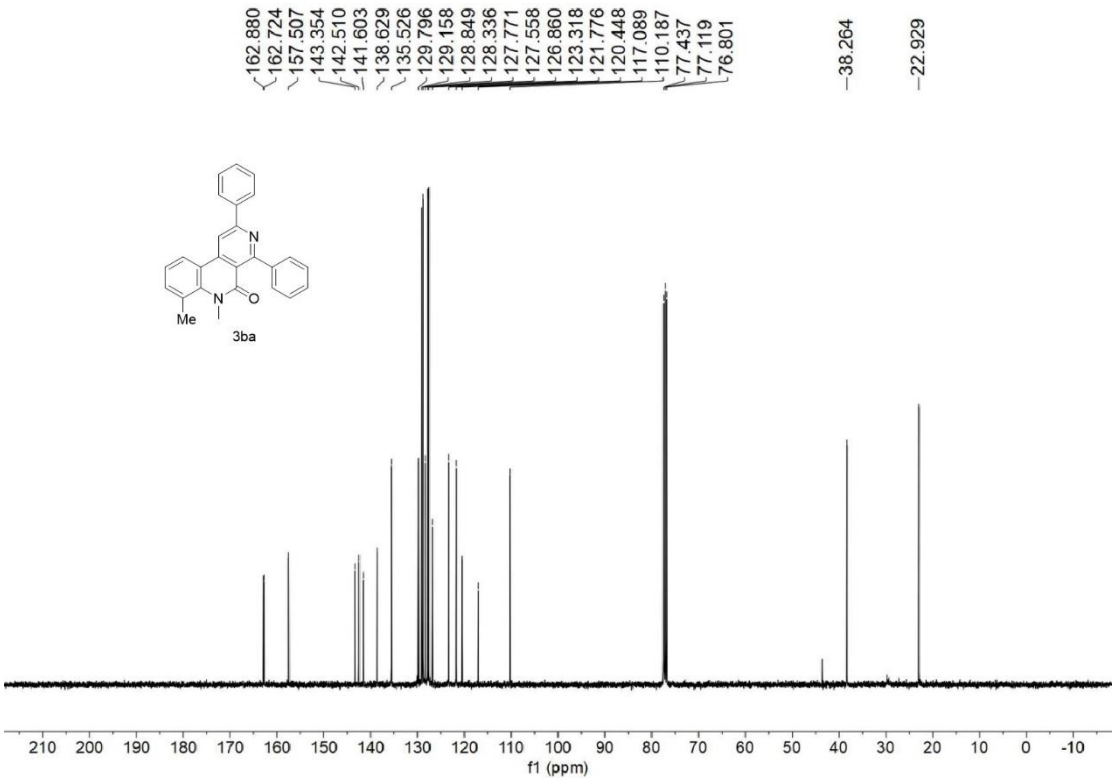
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3aa**



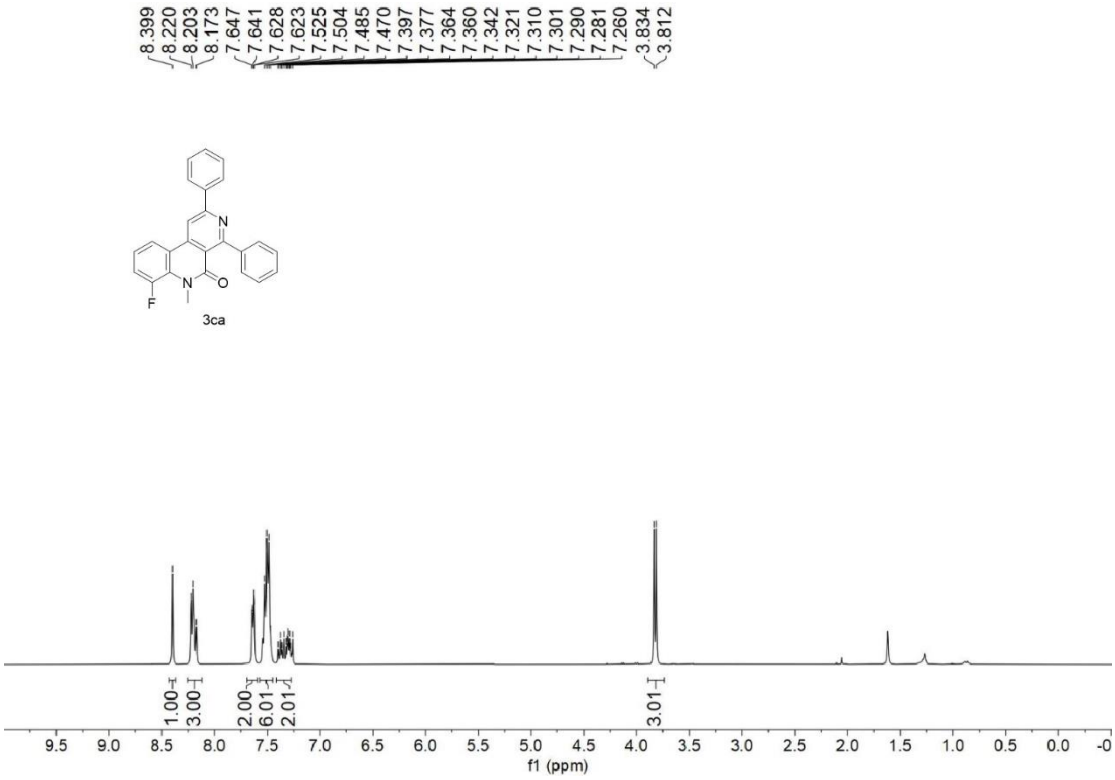
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ba**



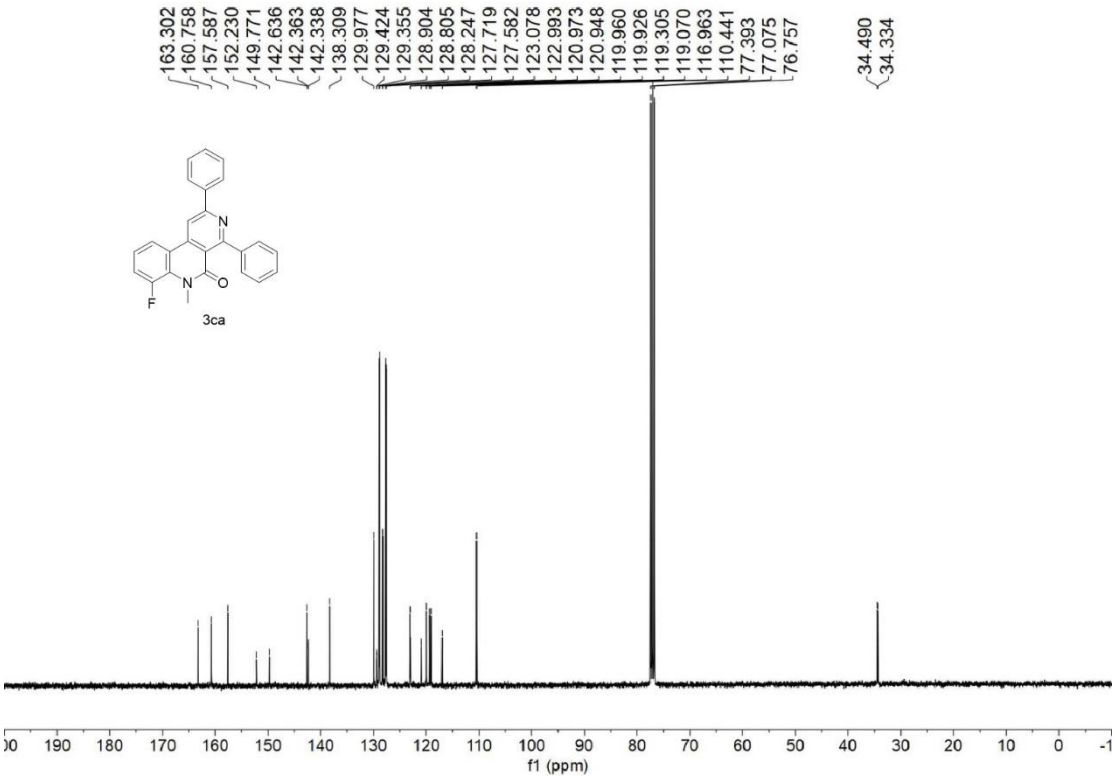
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ba**



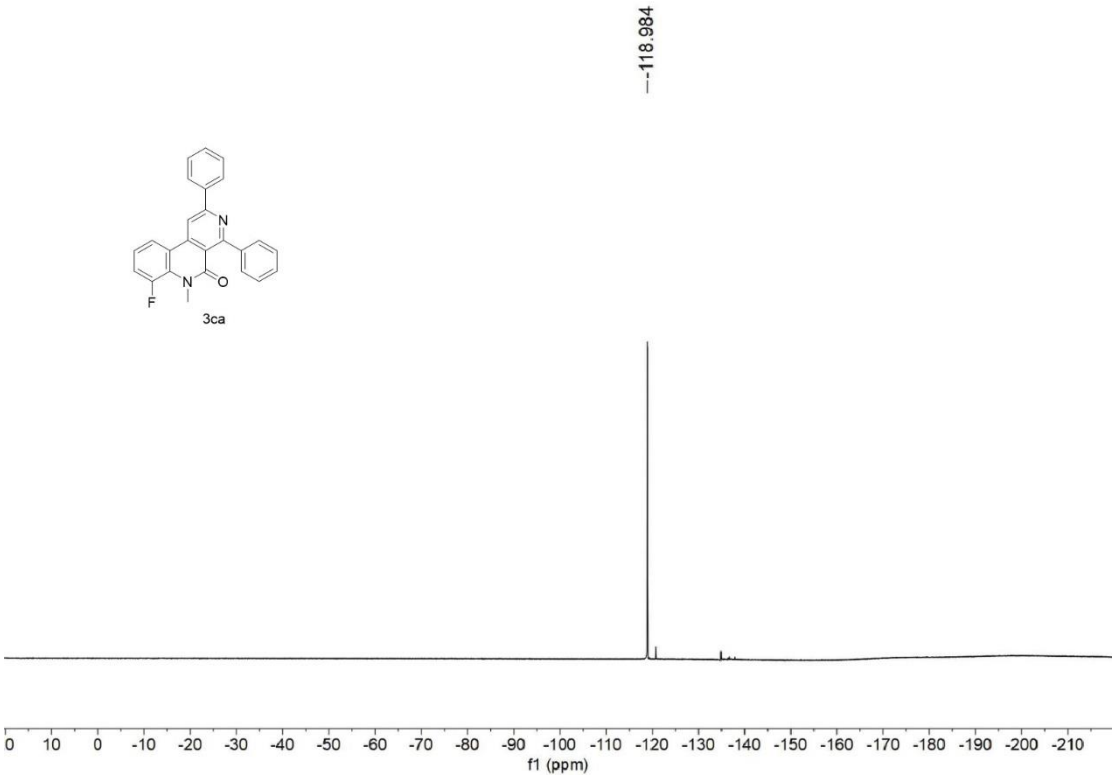
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ca**



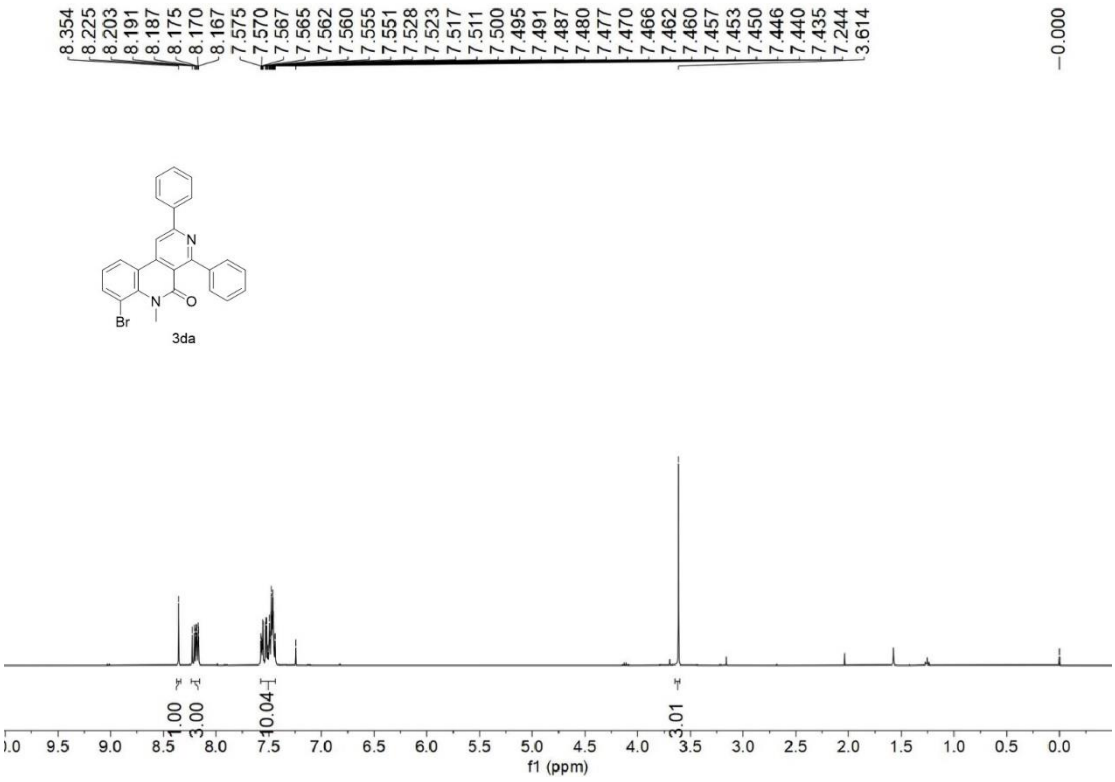
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ca**



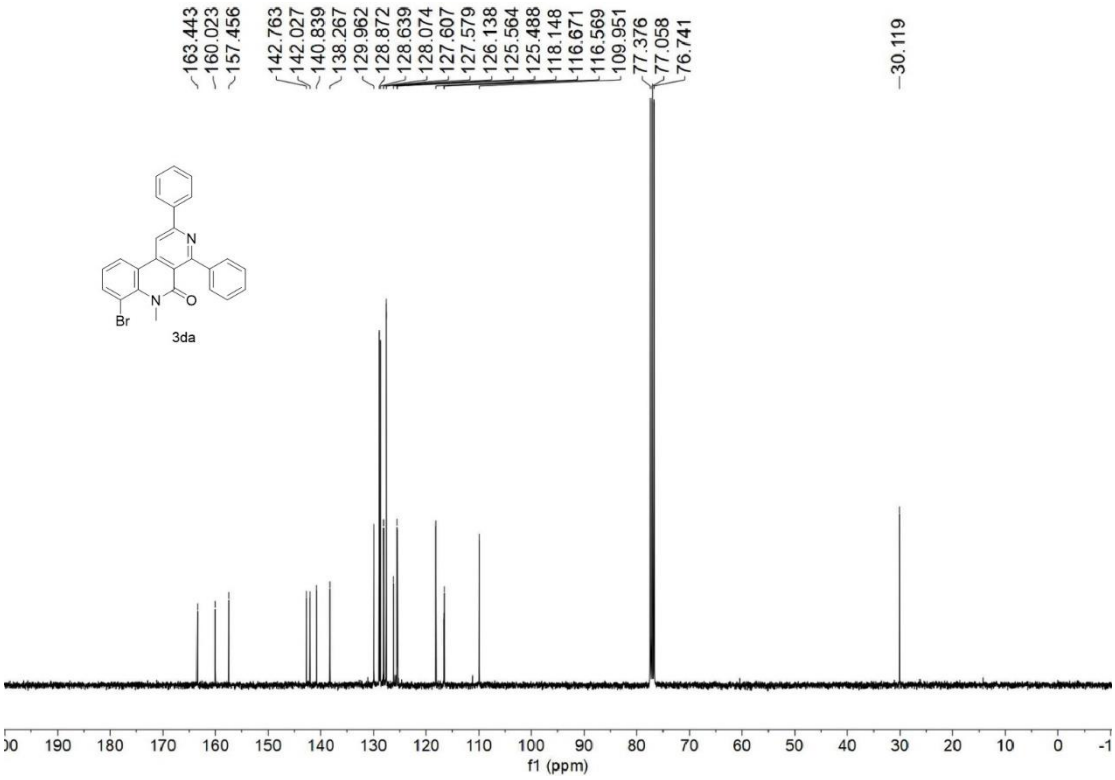
^{19}F-NMR spectrum ($CDCl_3$, 377 MHz) of **3ca**



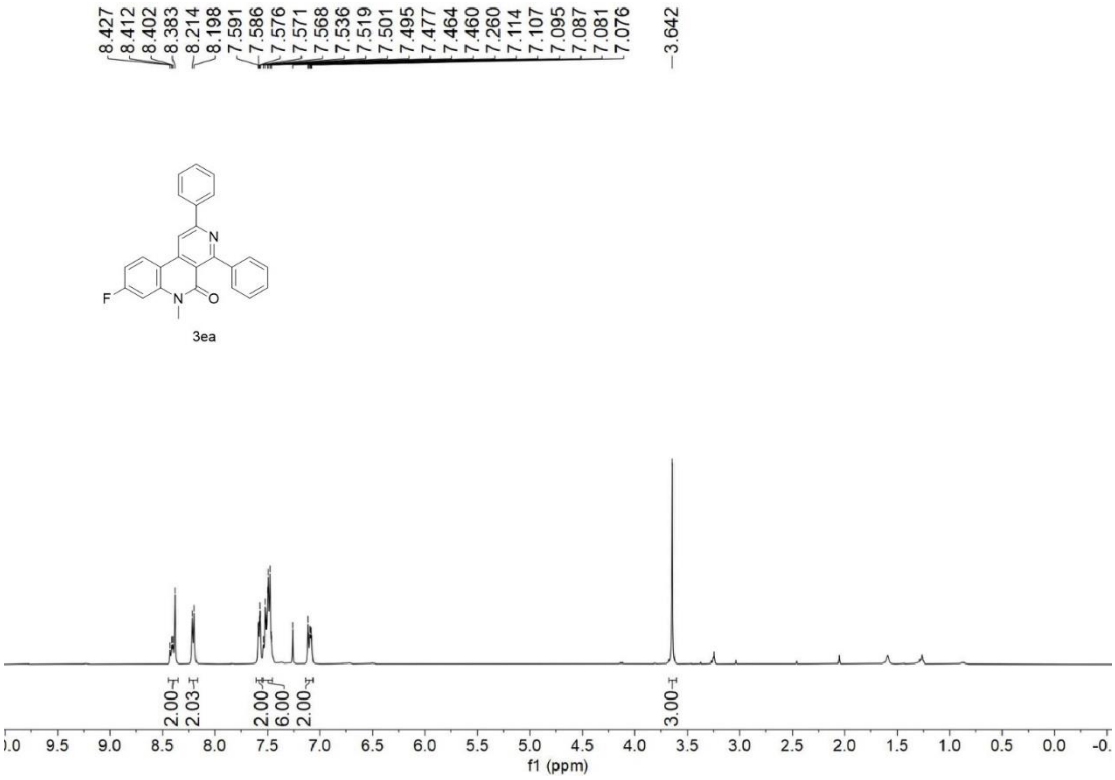
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3da**



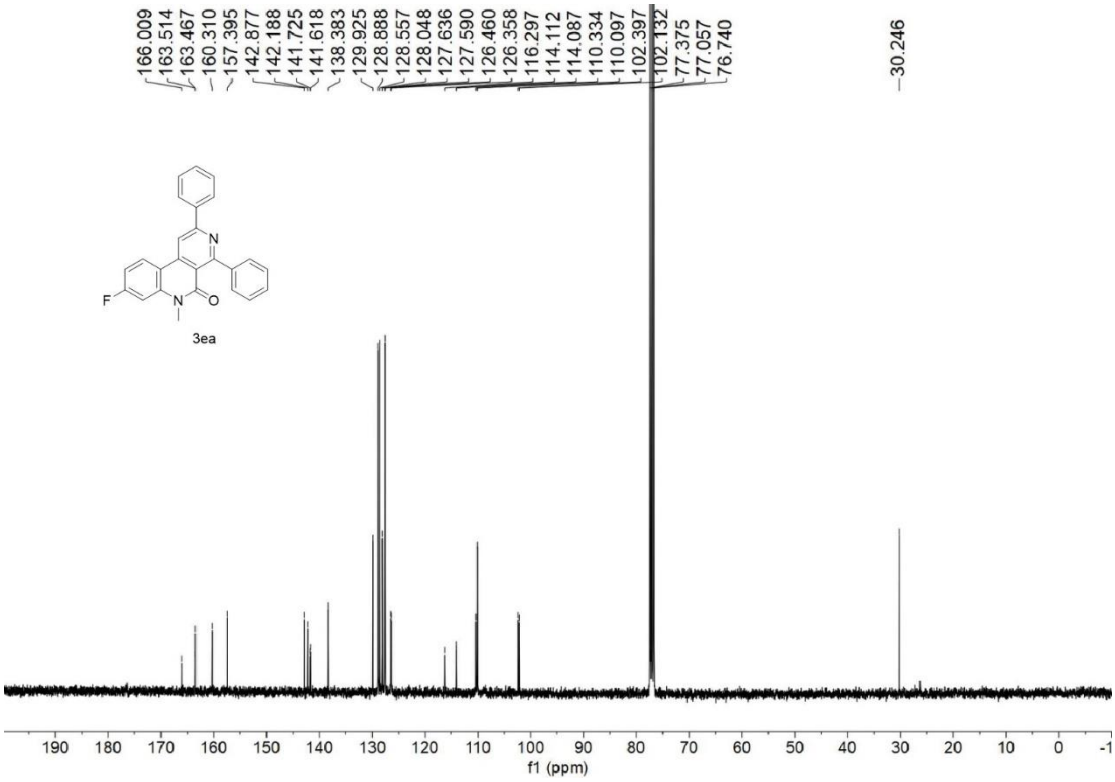
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3da**



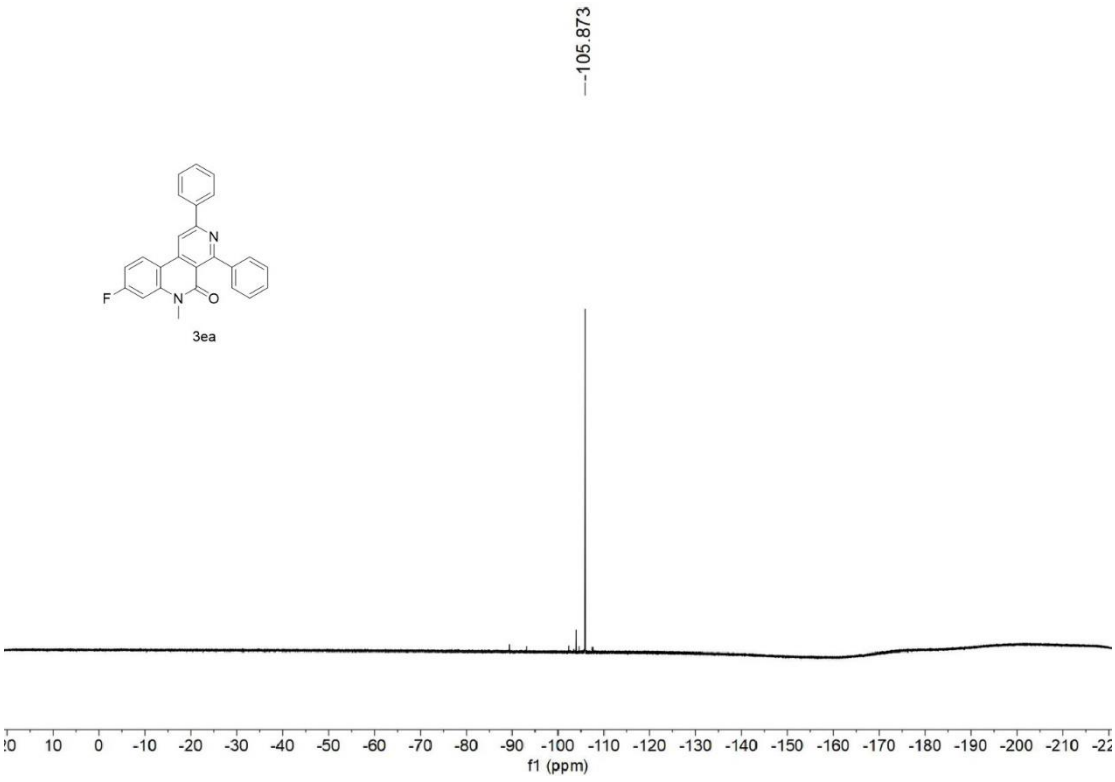
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ea**



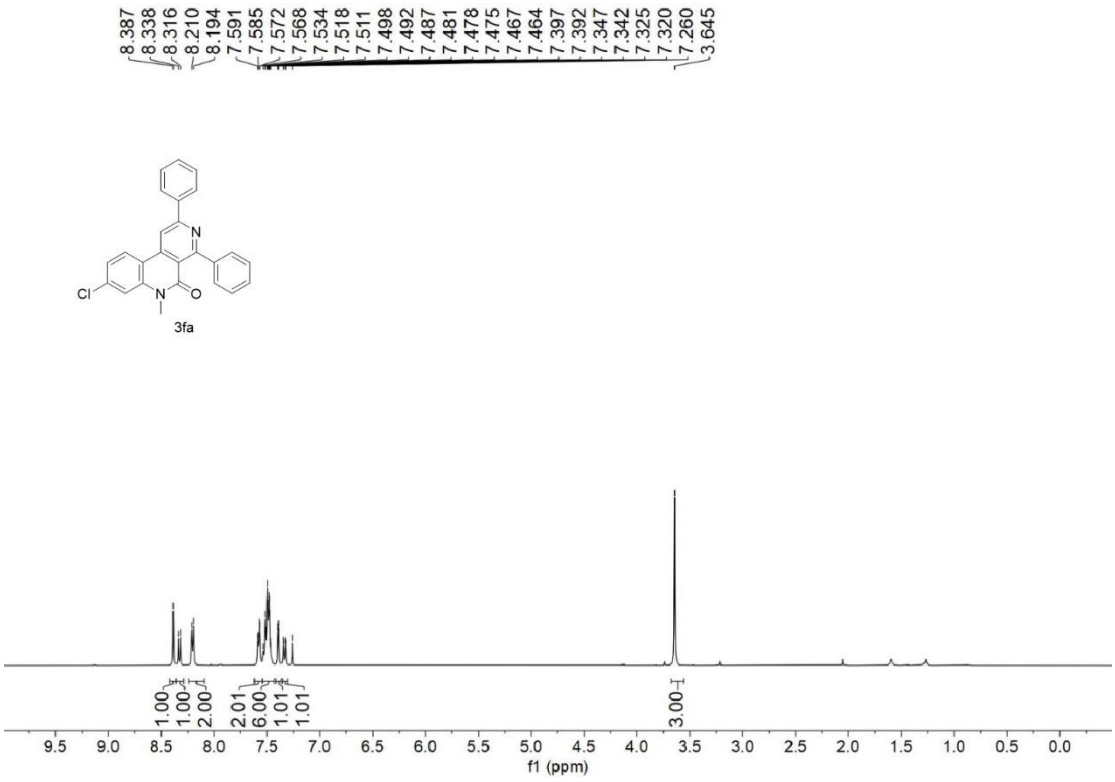
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ea**



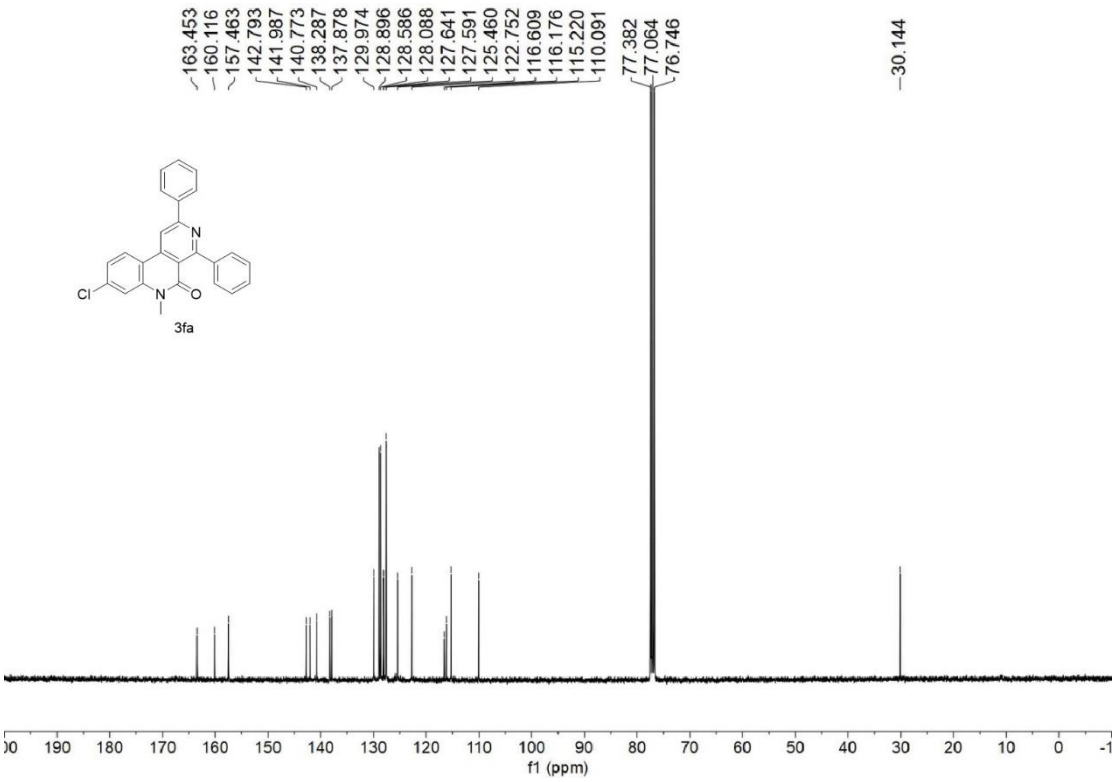
^{19}F-NMR spectrum ($CDCl_3$, 377 MHz) of **3ea**



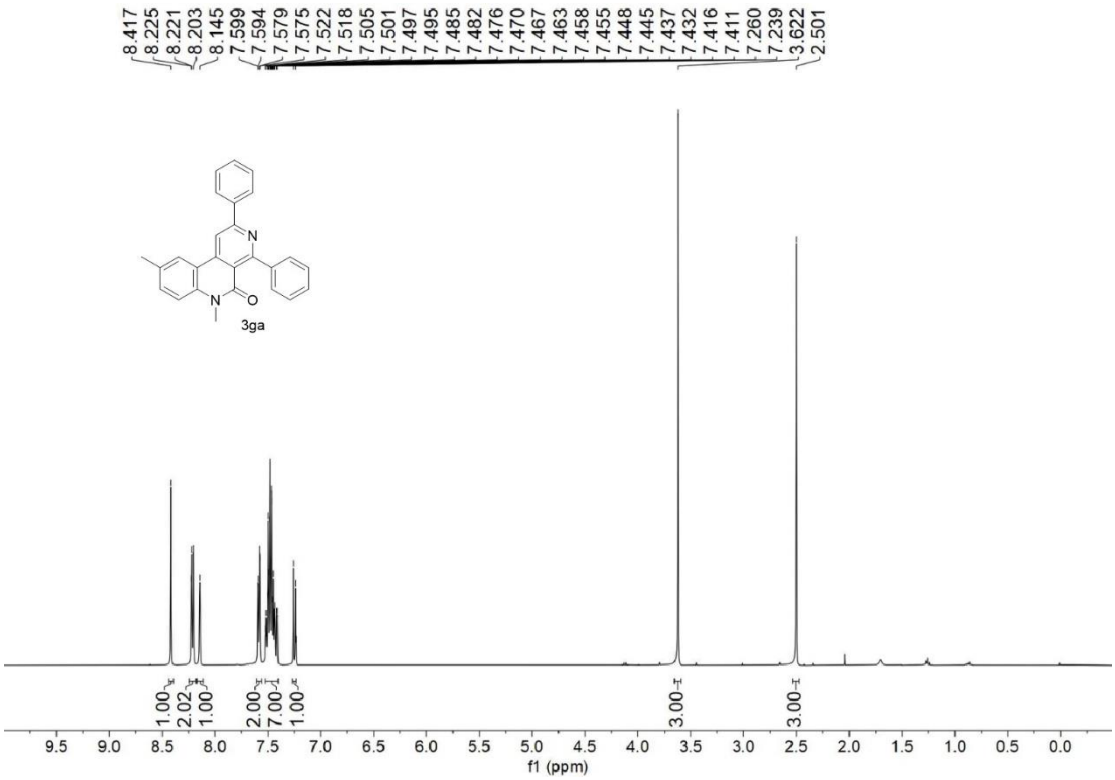
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3fa**



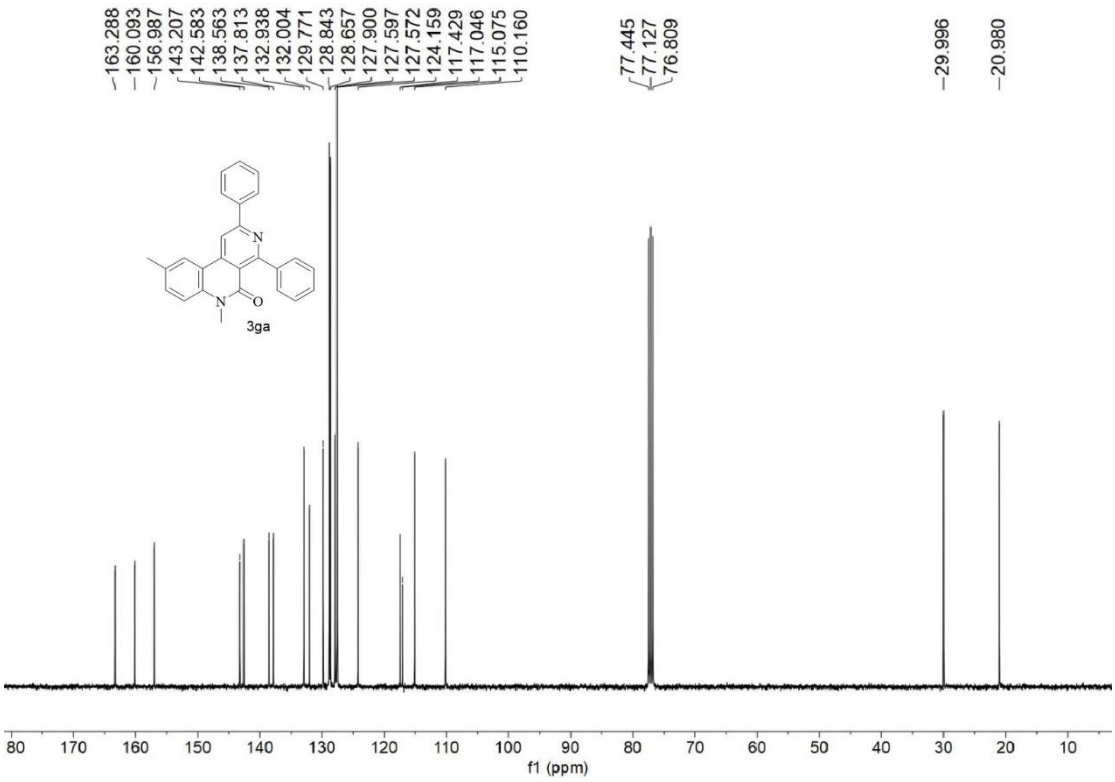
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3fa**



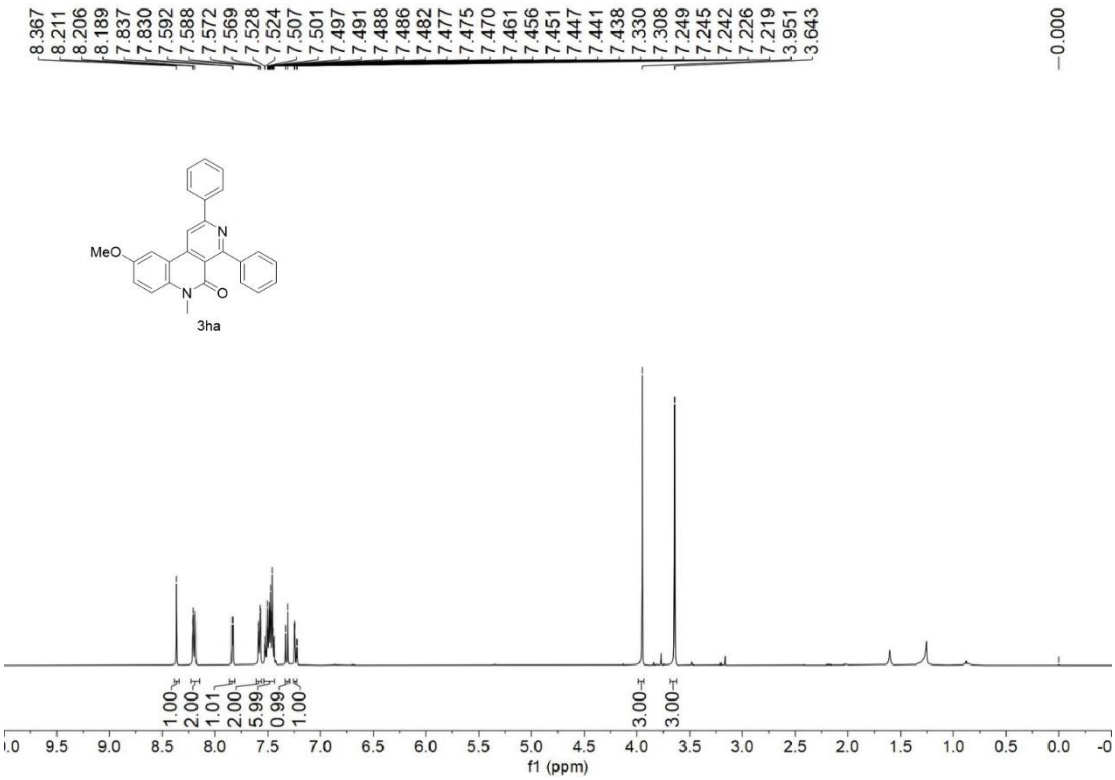
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ga**



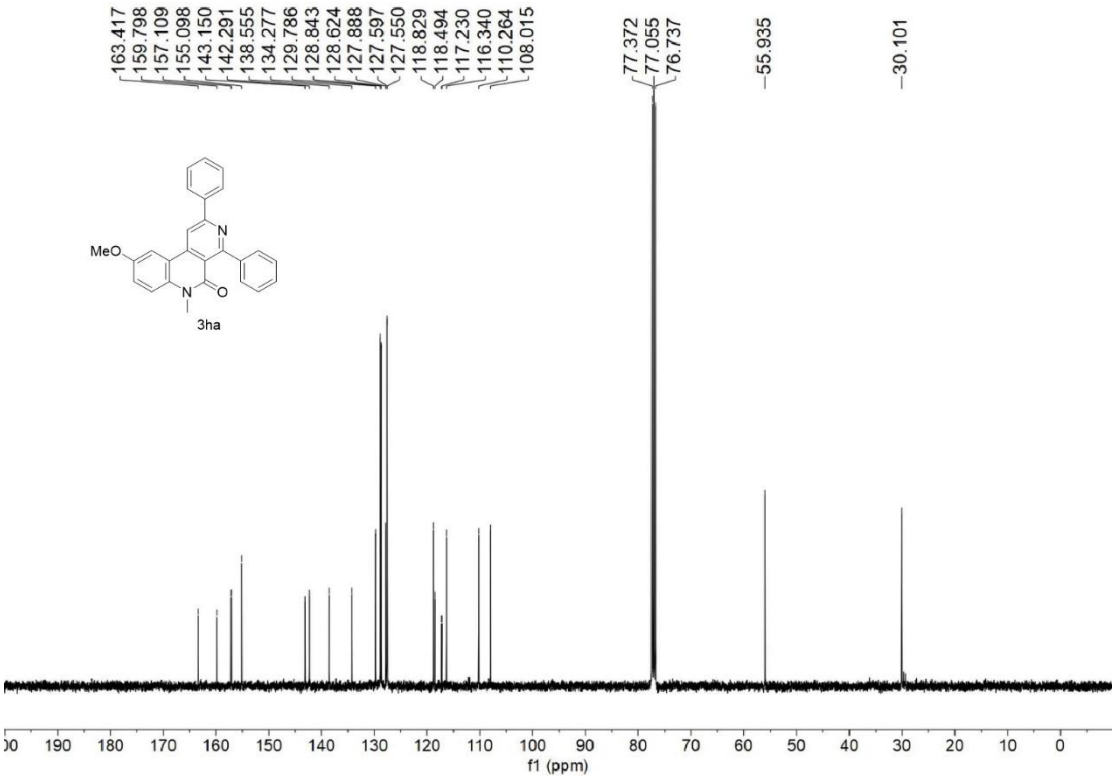
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ga**



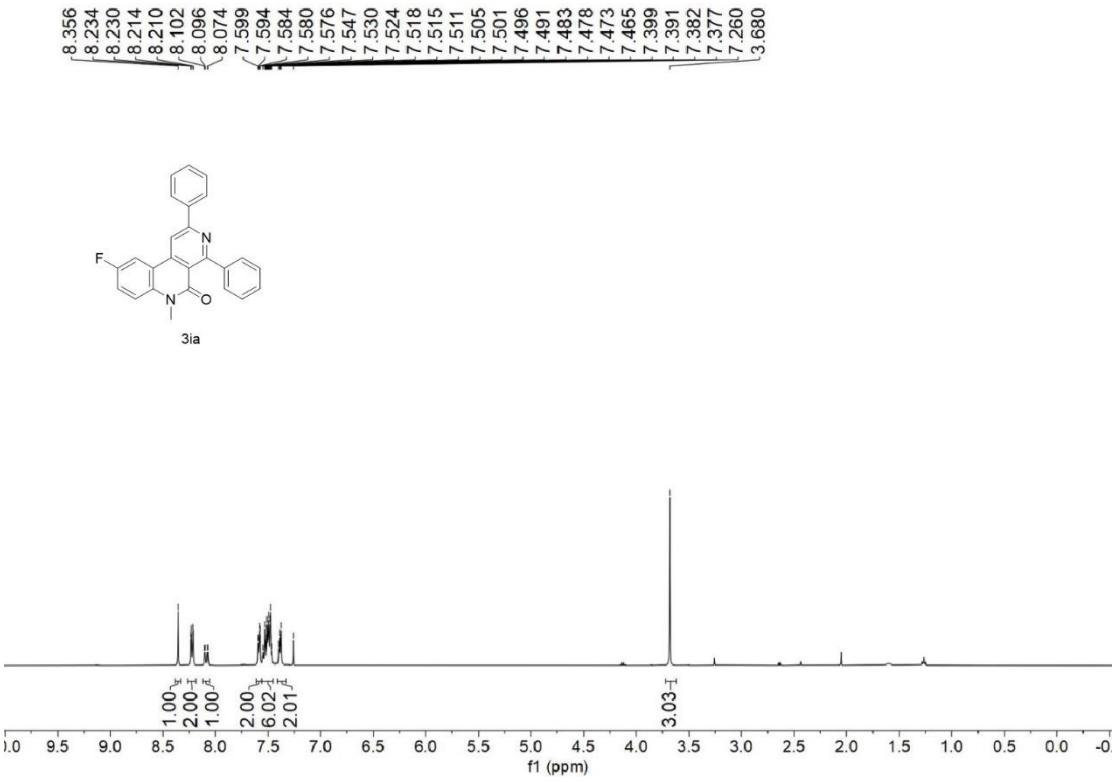
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ha**



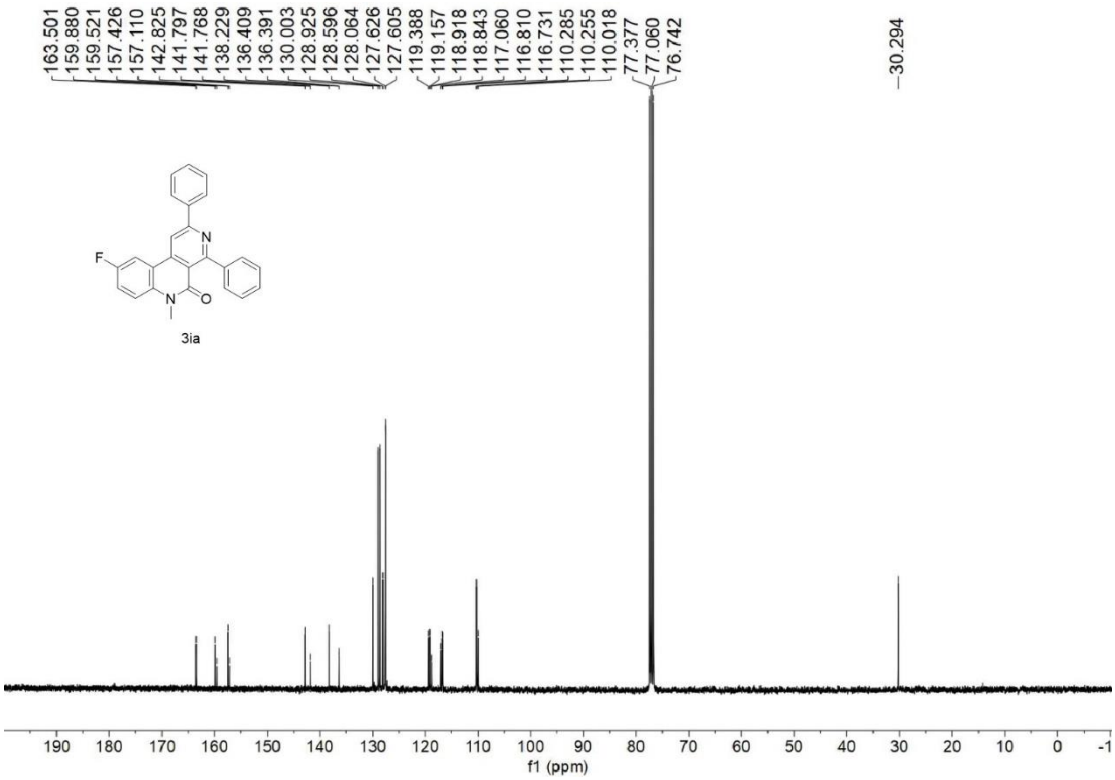
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ha**



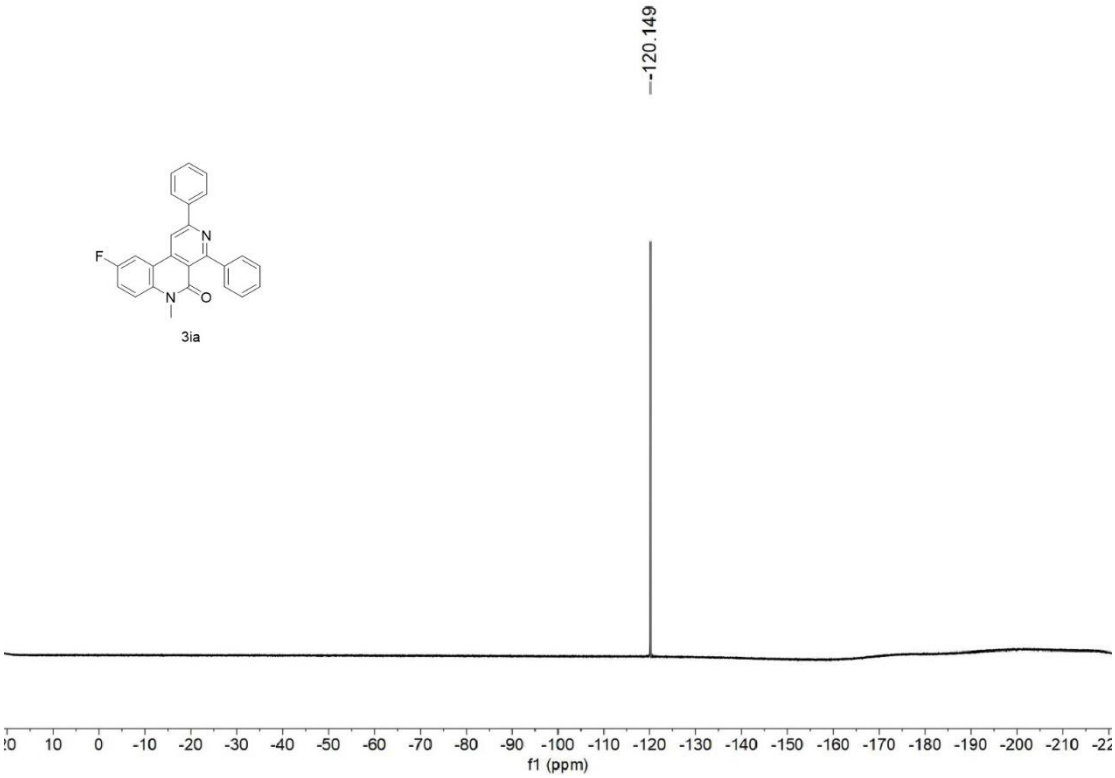
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ia**



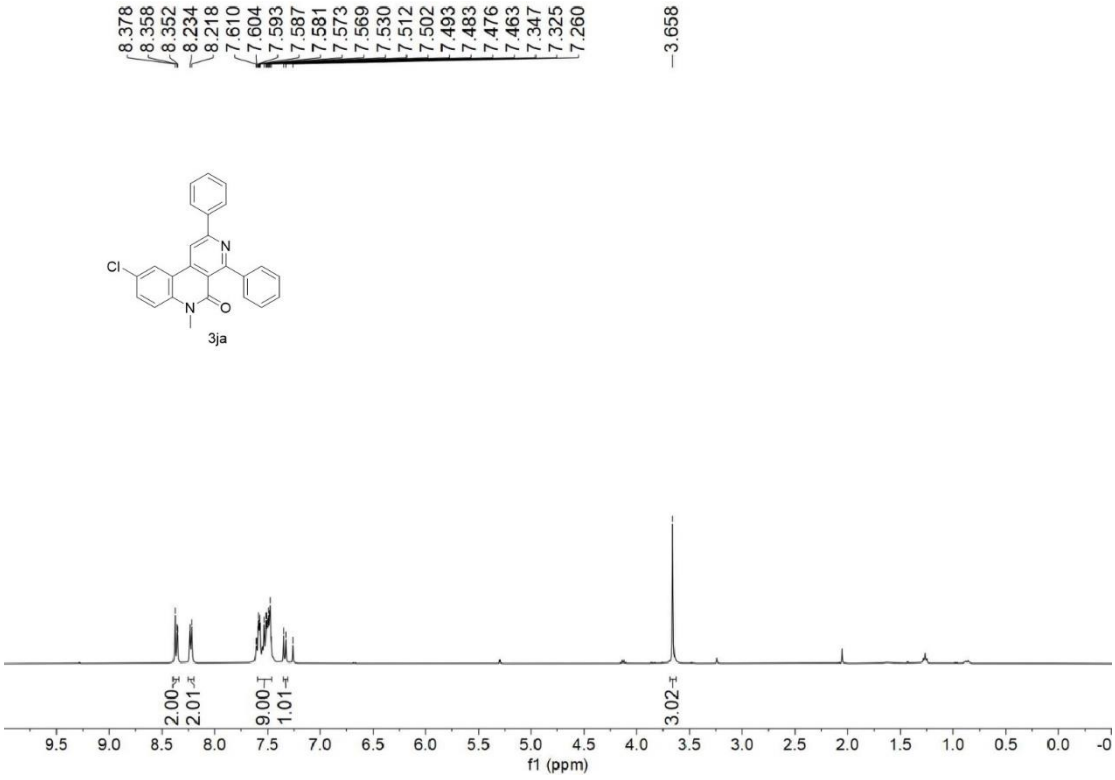
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ia**



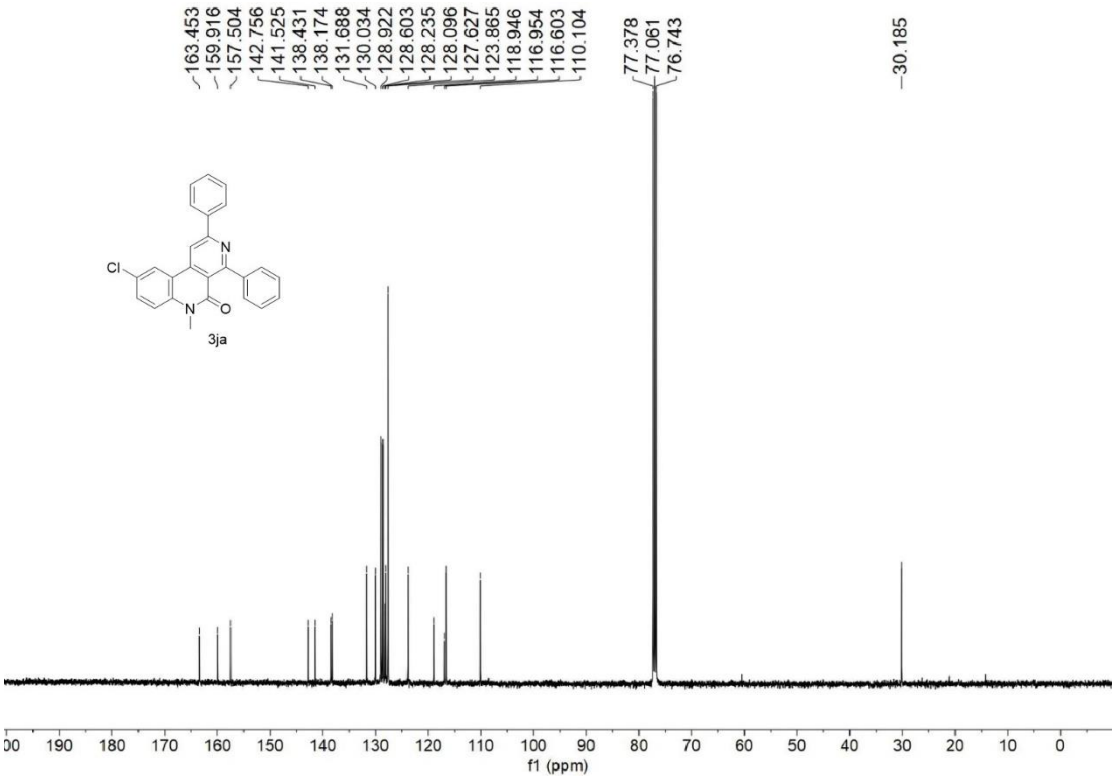
^{19}F-NMR spectrum ($CDCl_3$, 377 MHz) of **3ia**



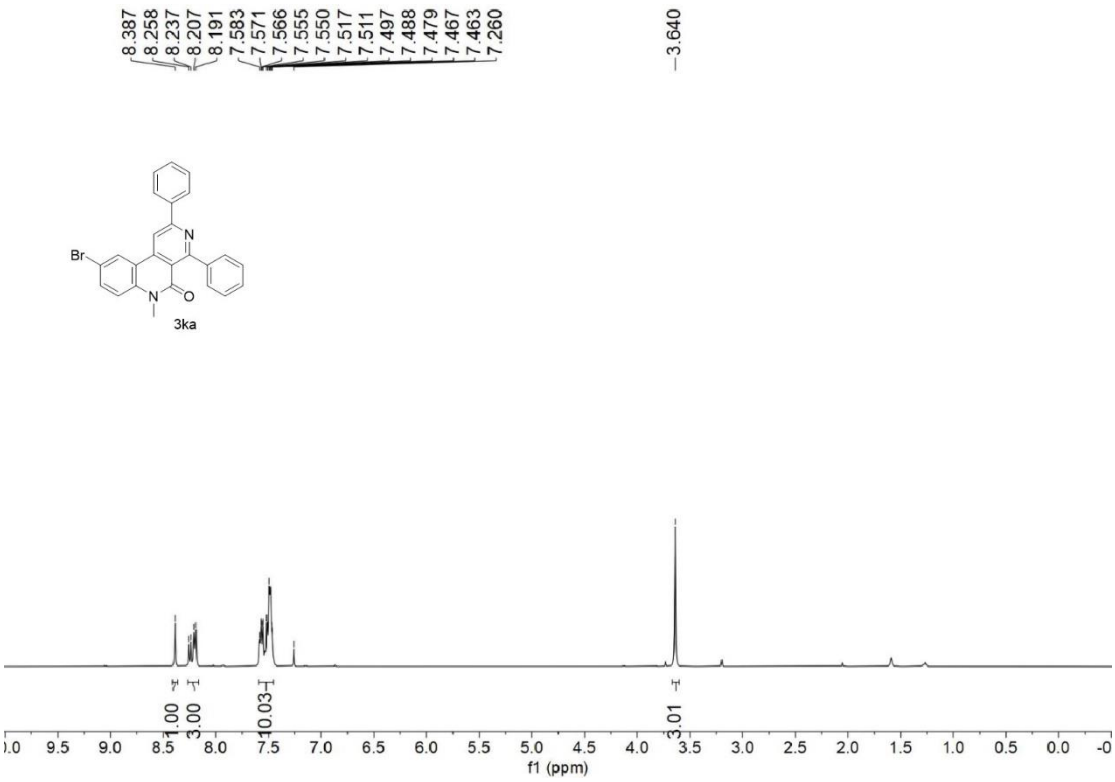
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ja**



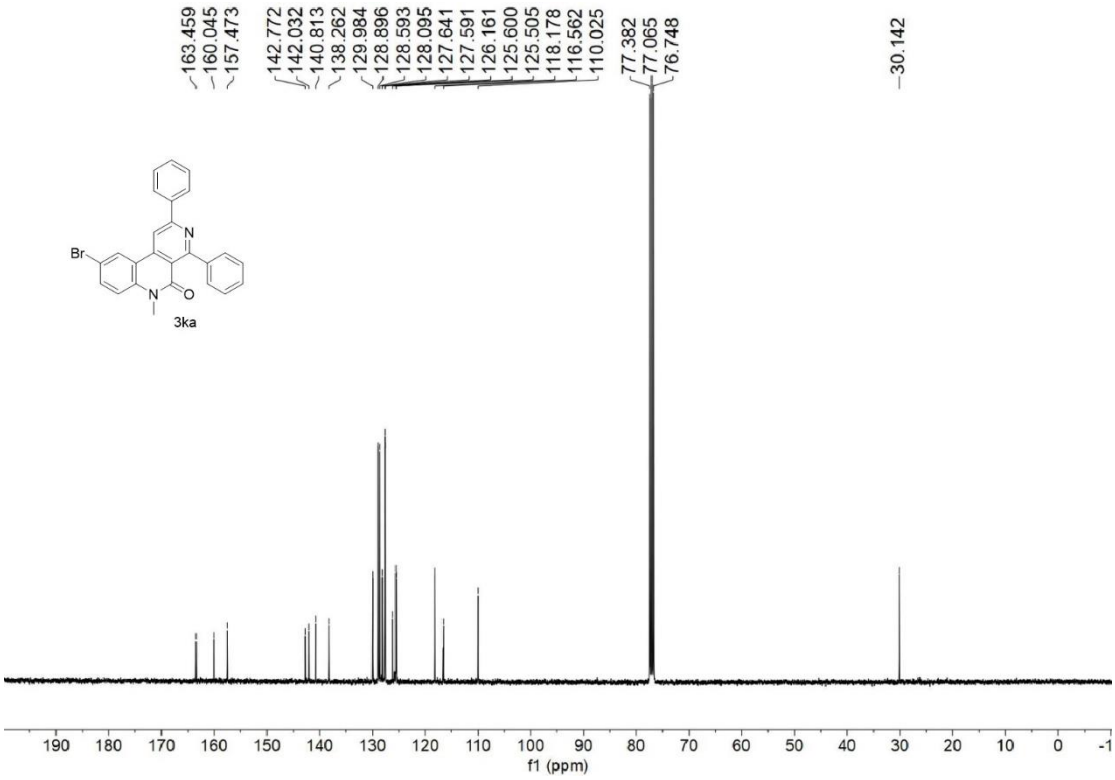
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ja**



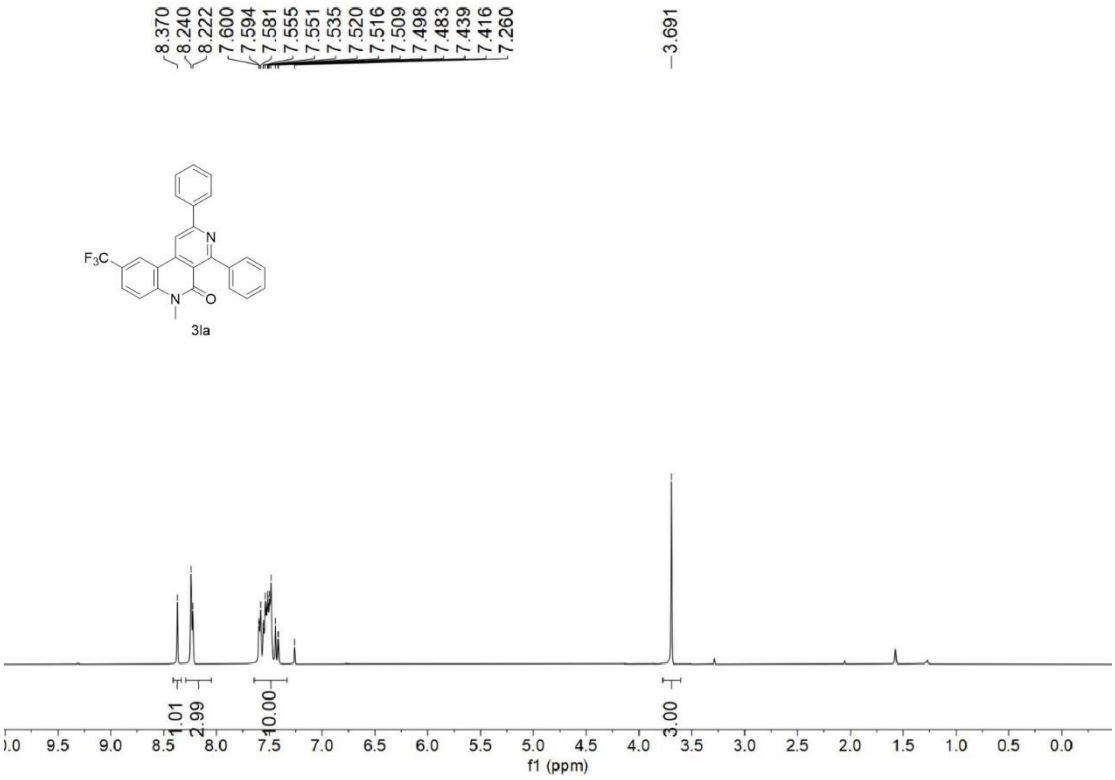
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ka**



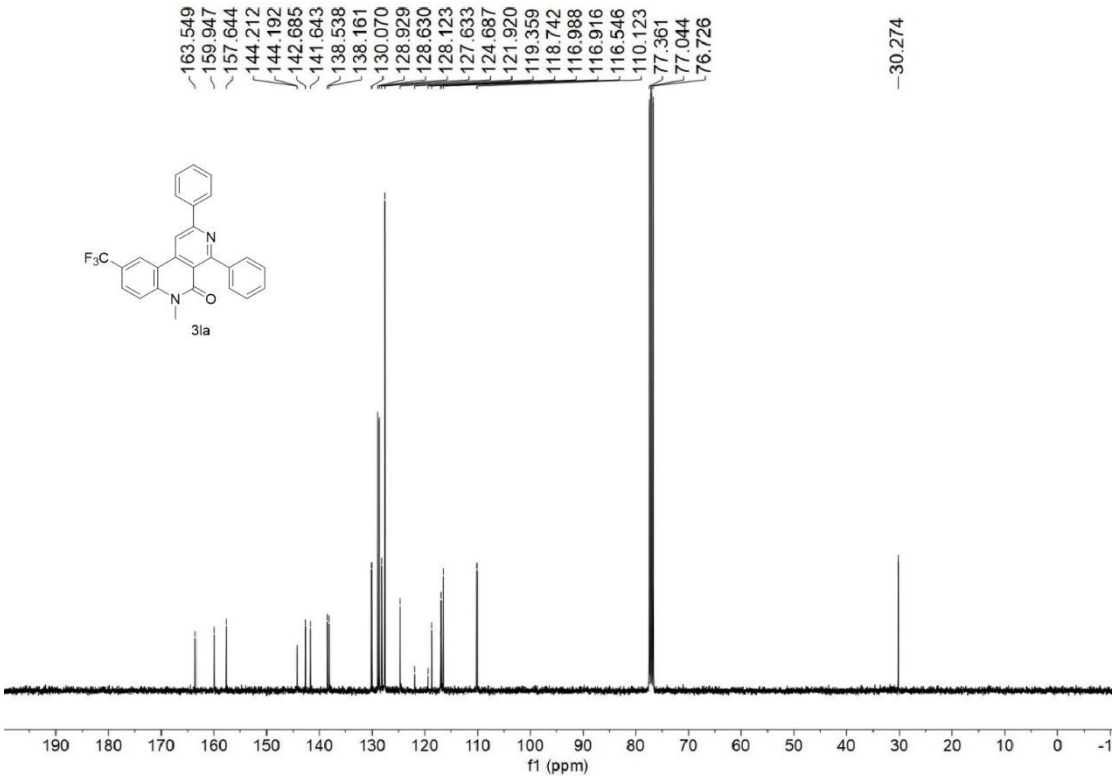
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ka**



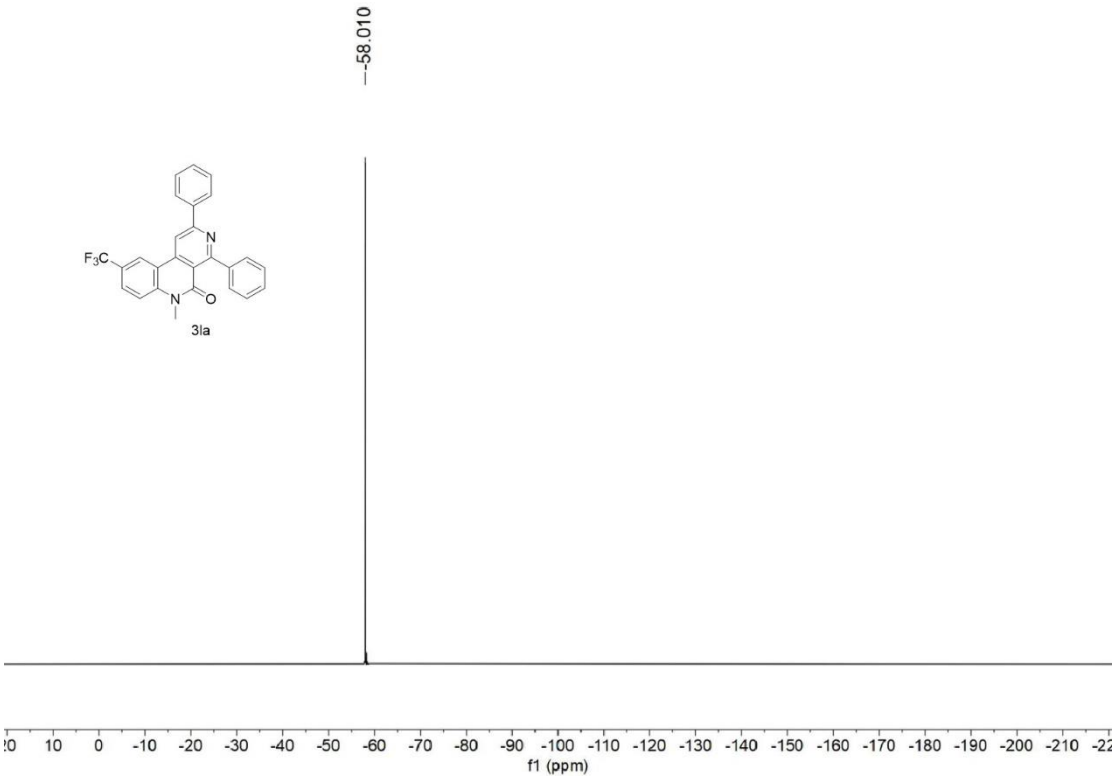
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3la**



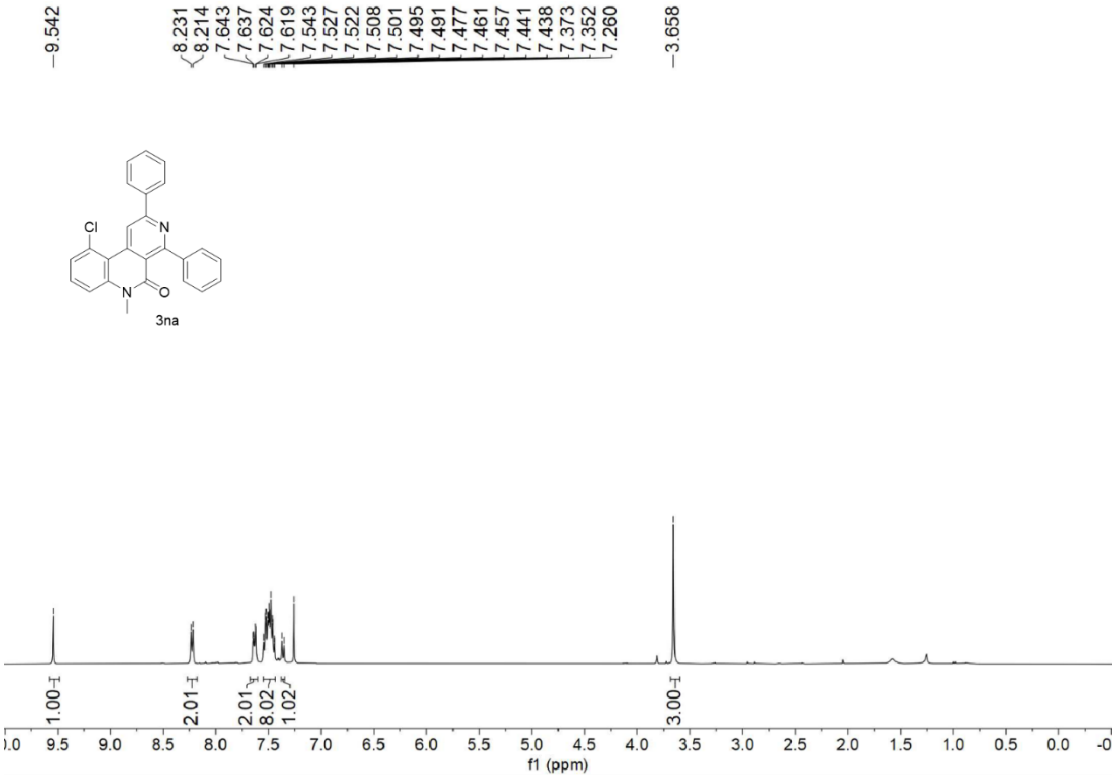
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3la**



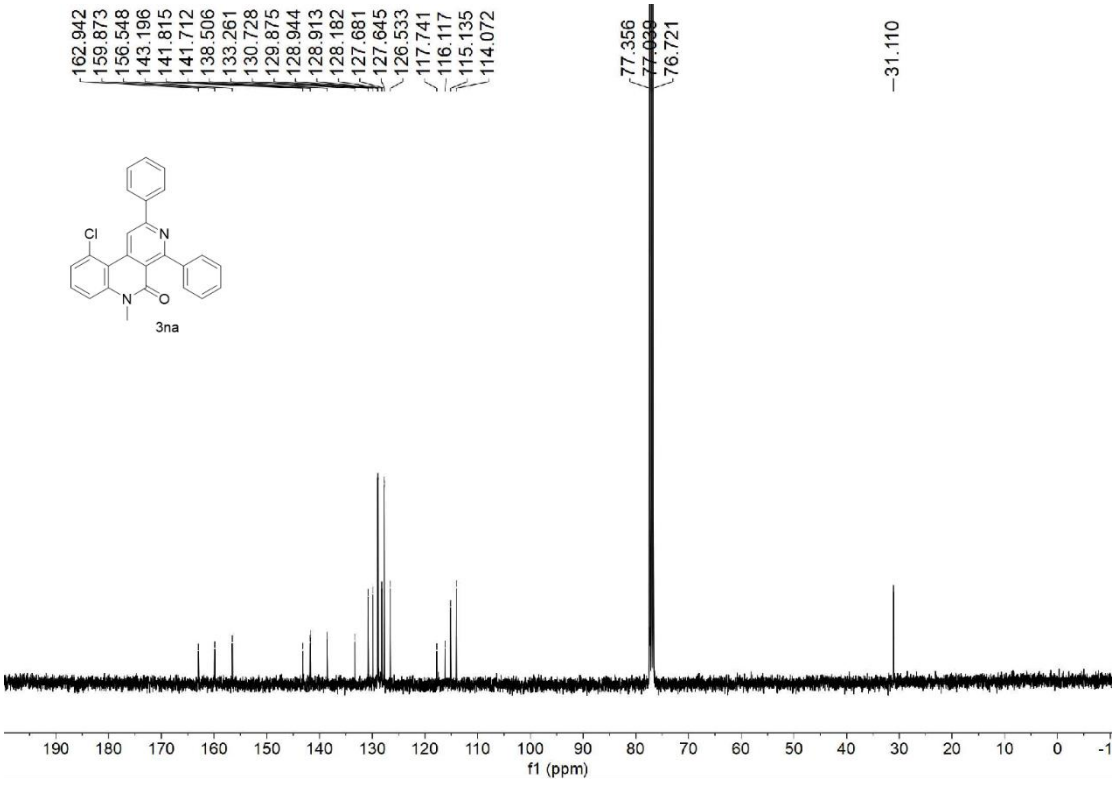
^{19}F-NMR spectrum ($CDCl_3$, 377 MHz) of **3la**



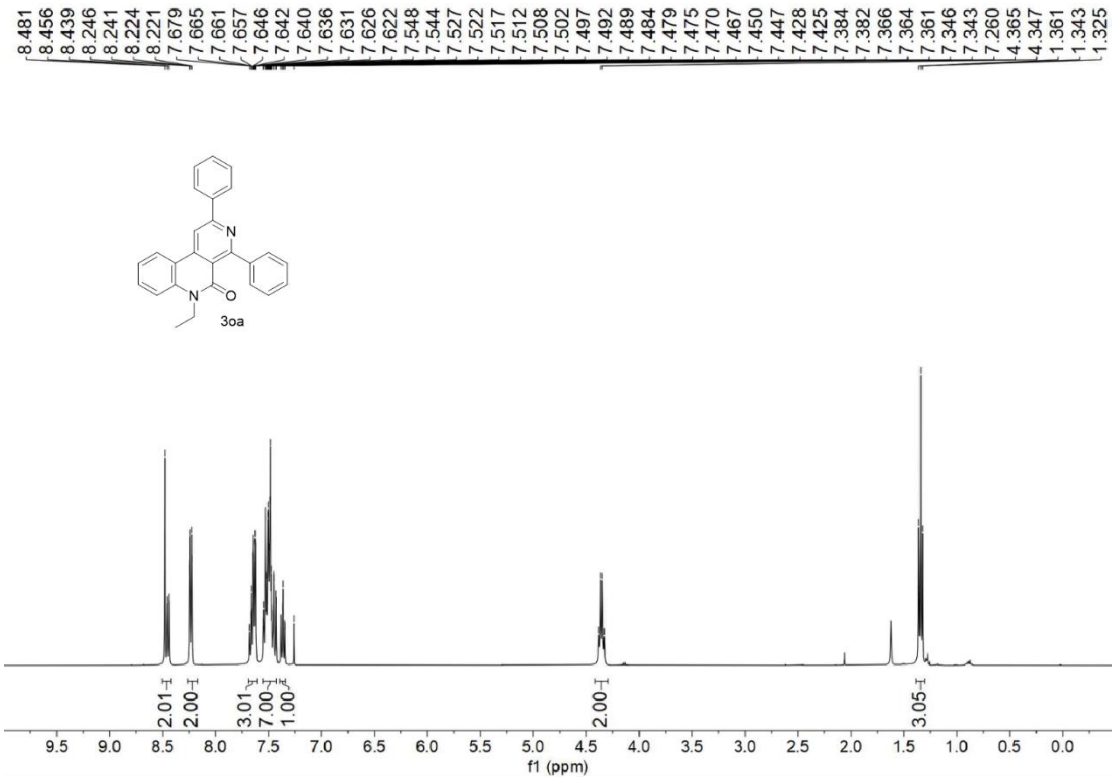
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3na**



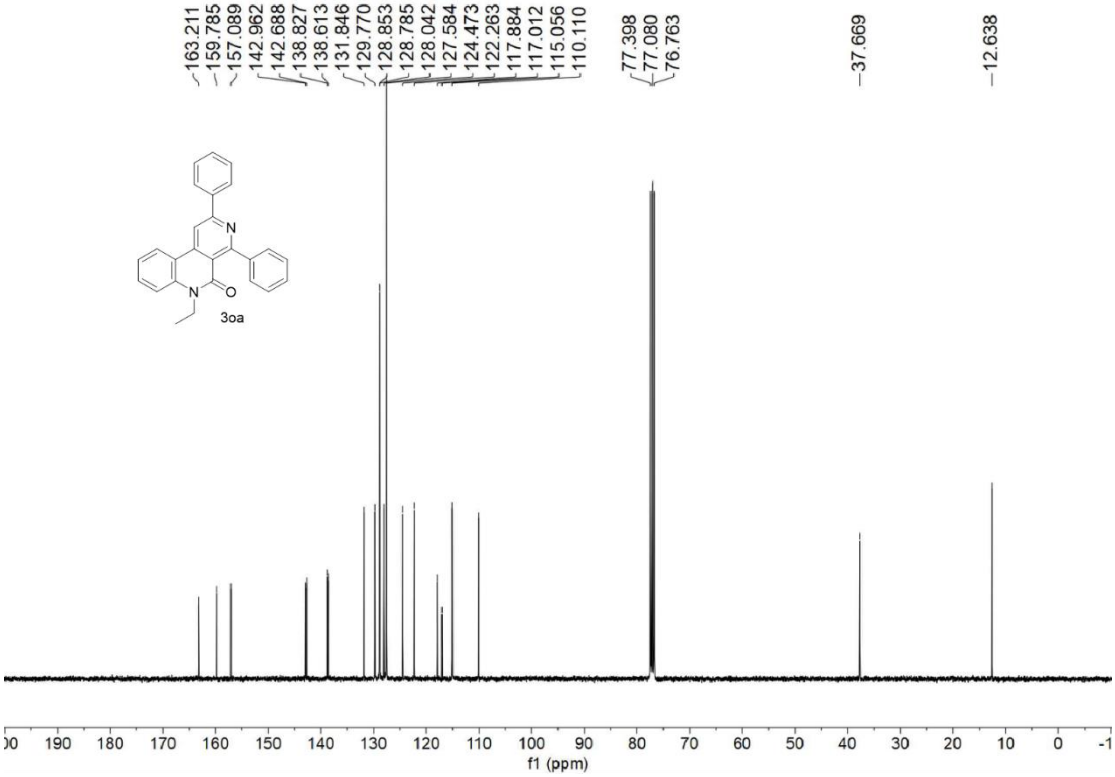
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3na**



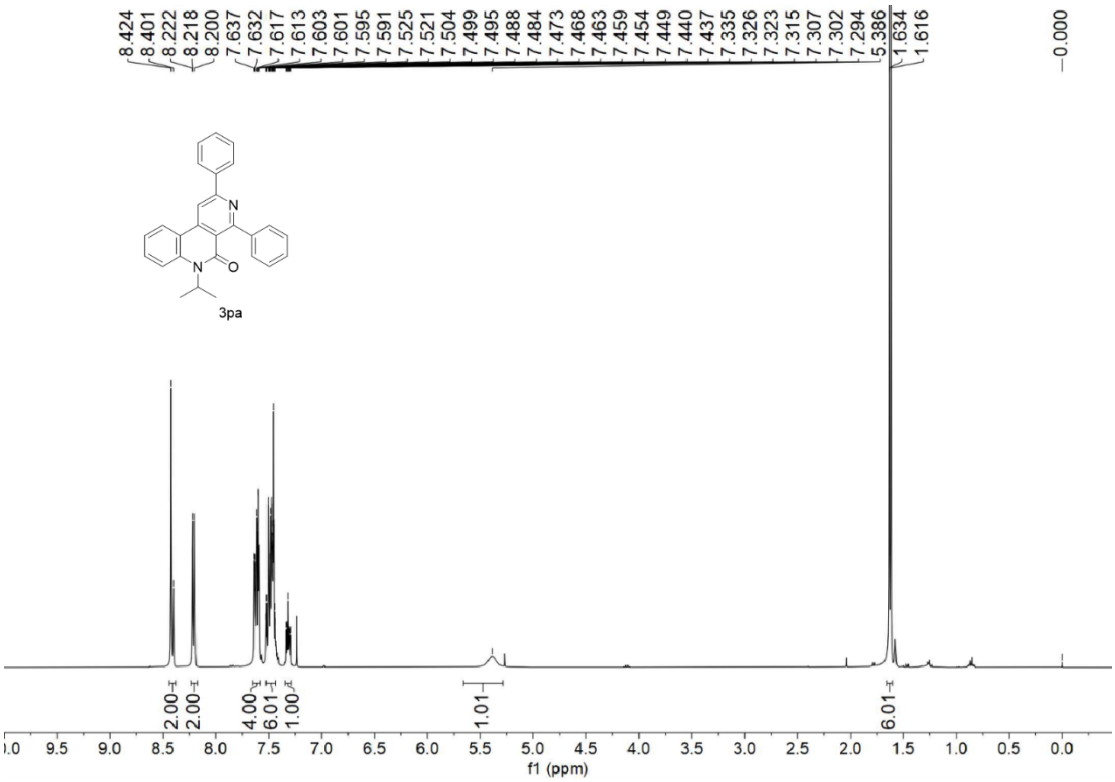
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3oa**



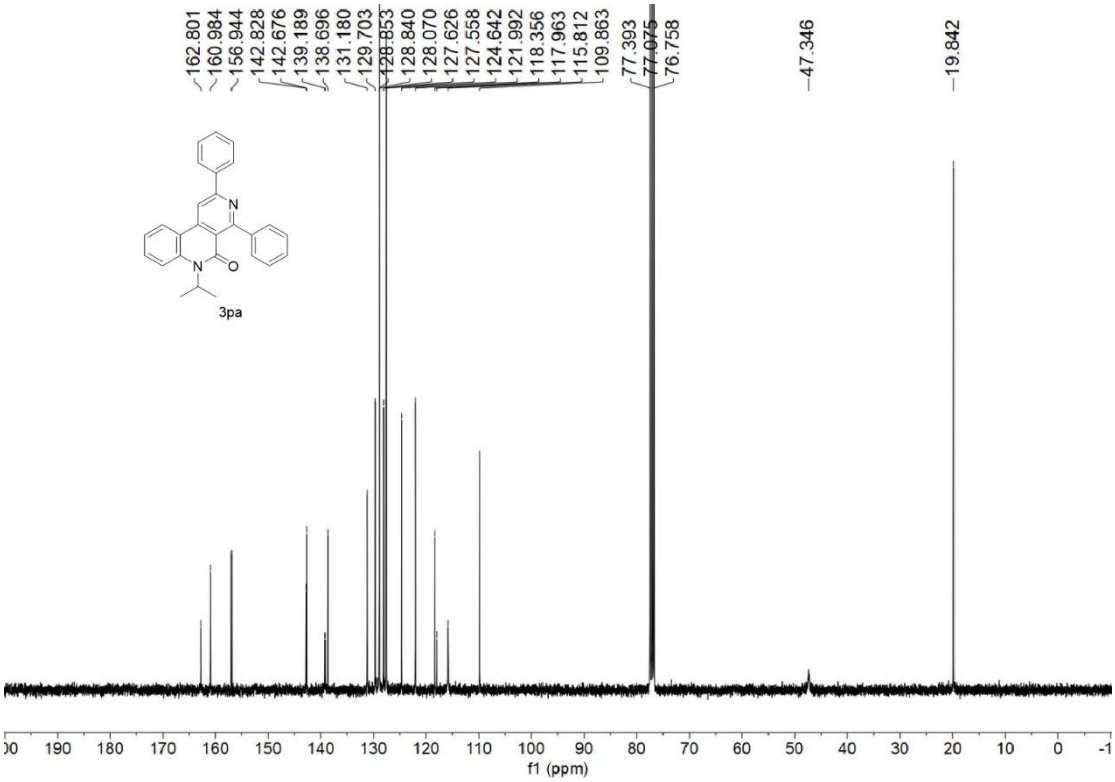
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3oa**



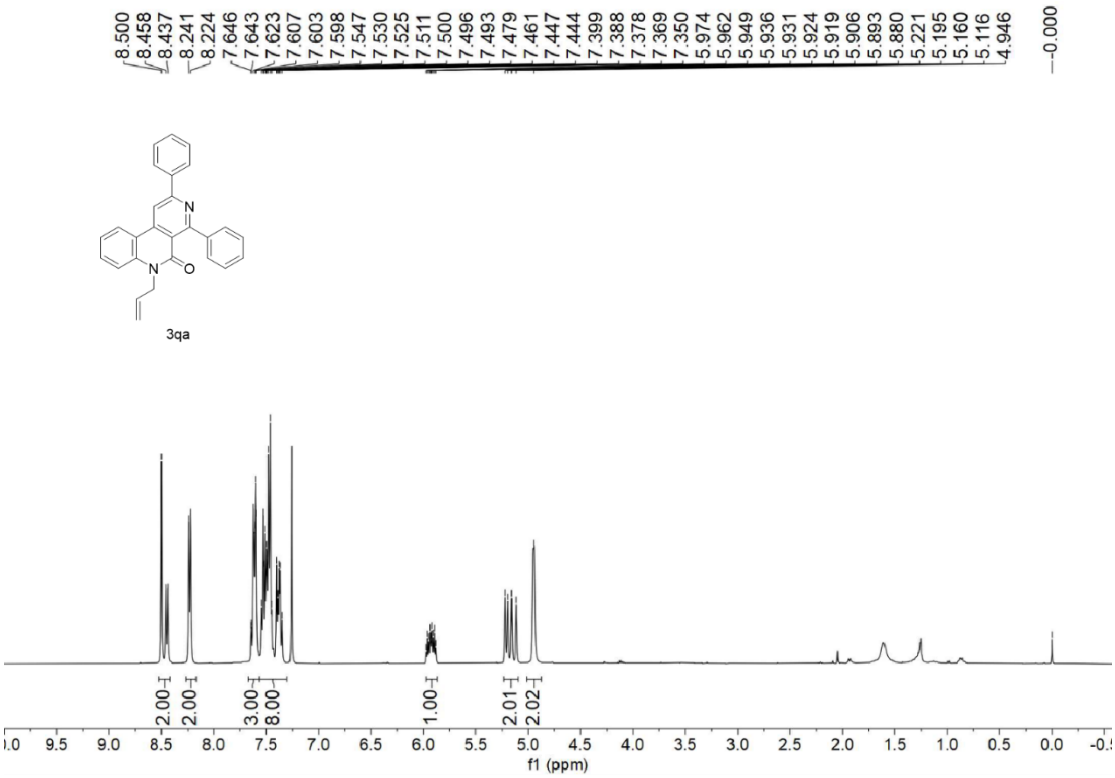
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3pa**



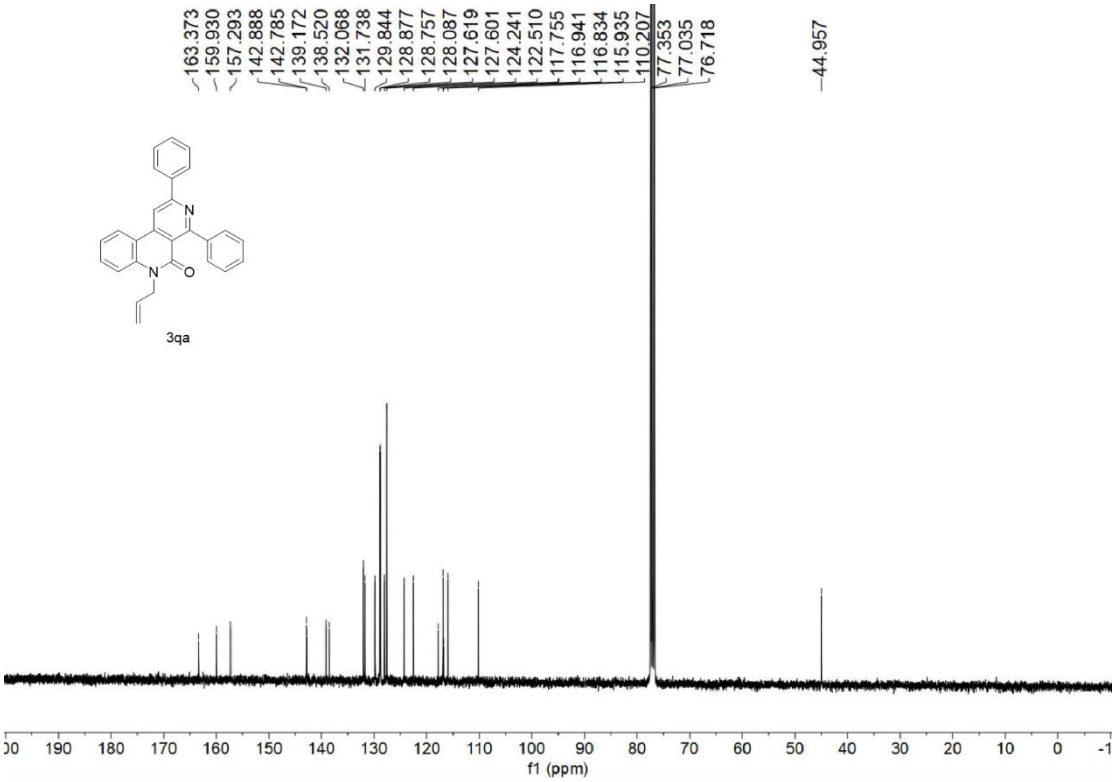
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3pa**



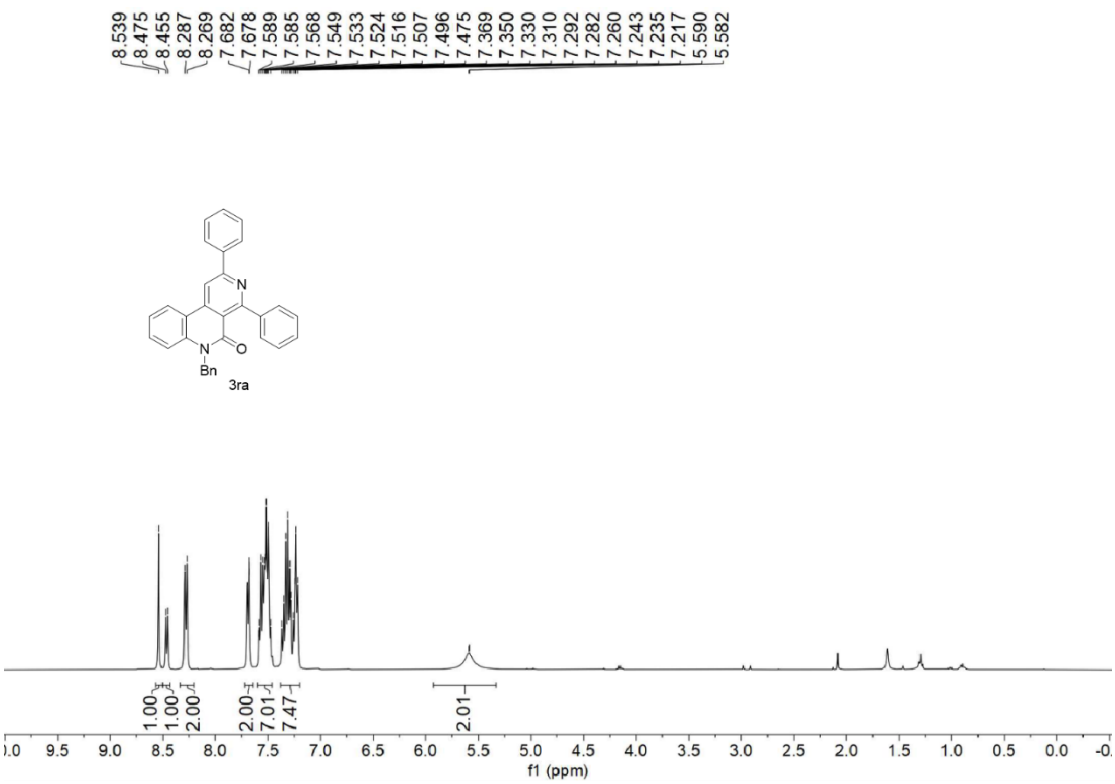
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3qa**



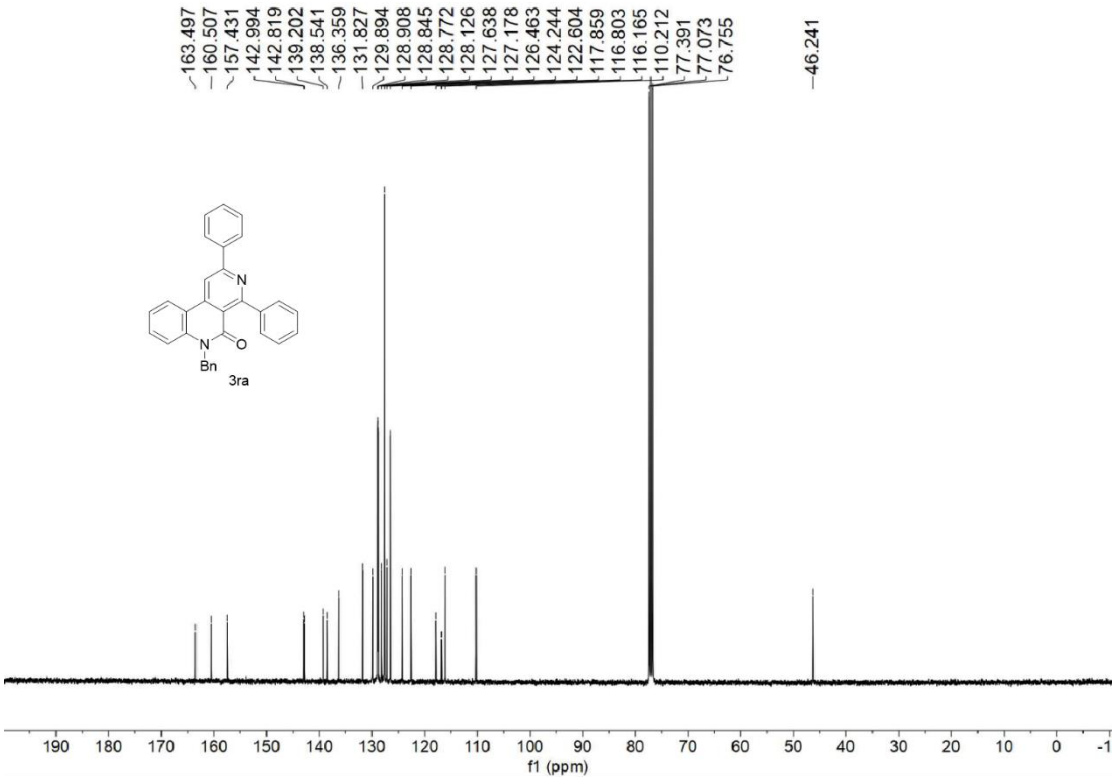
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3qa**



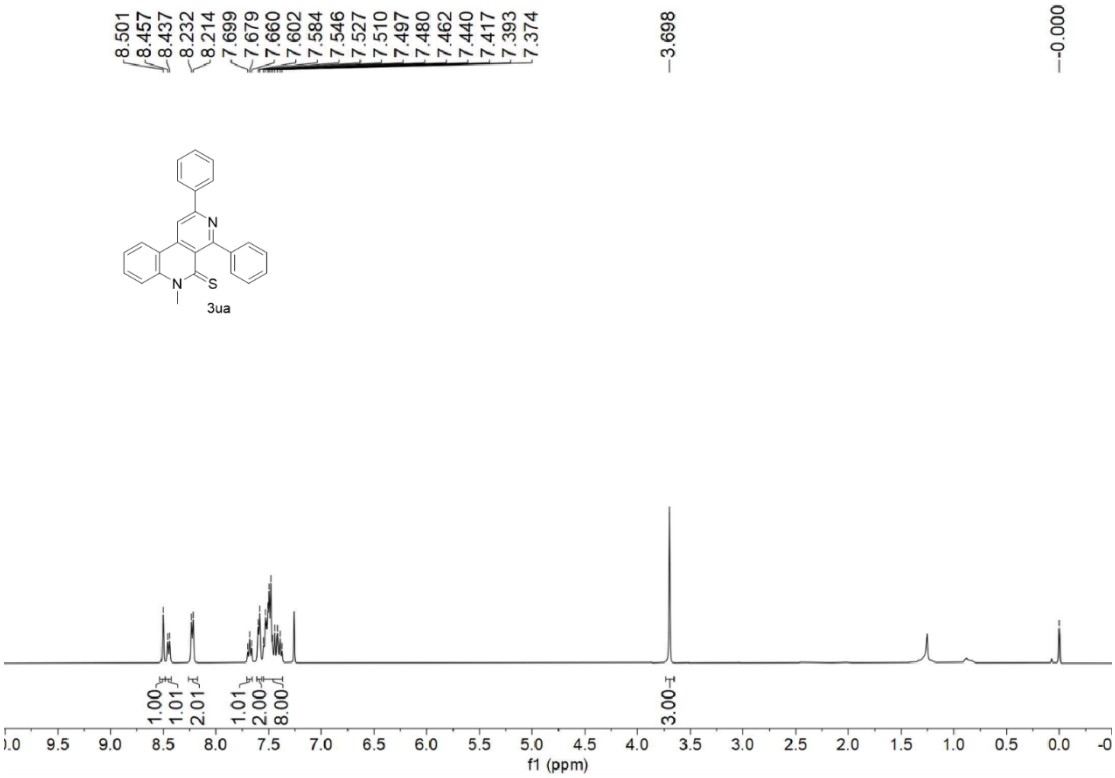
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ra**



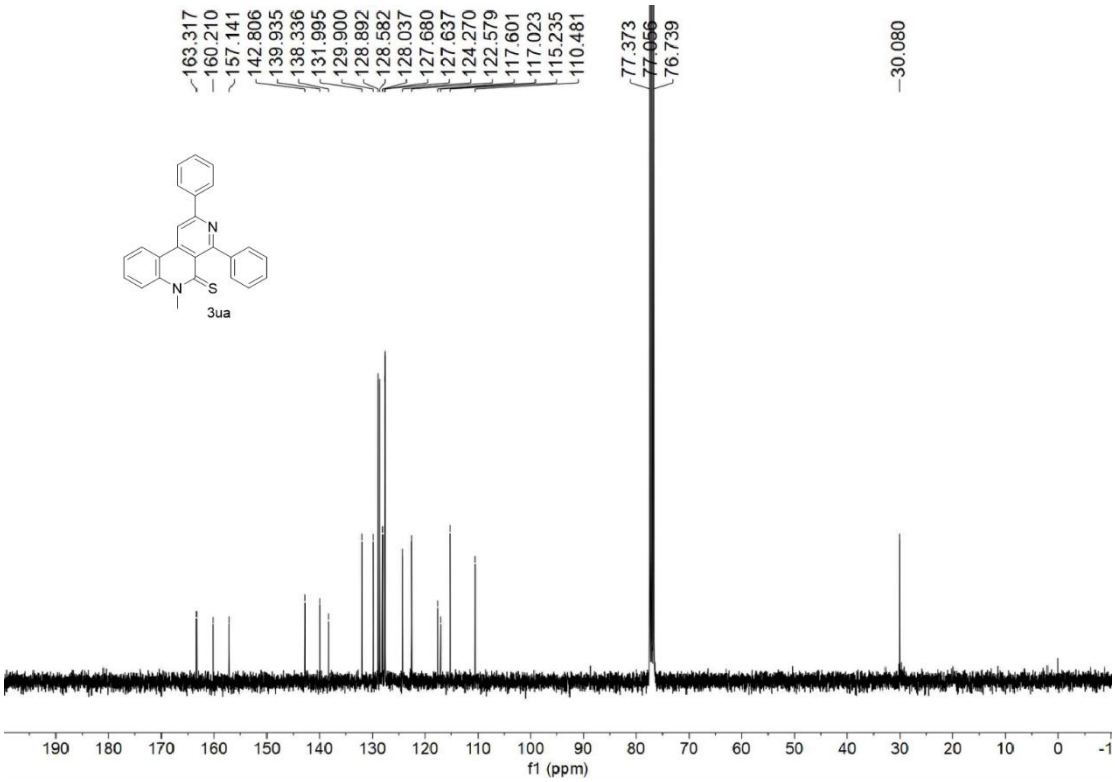
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ra**



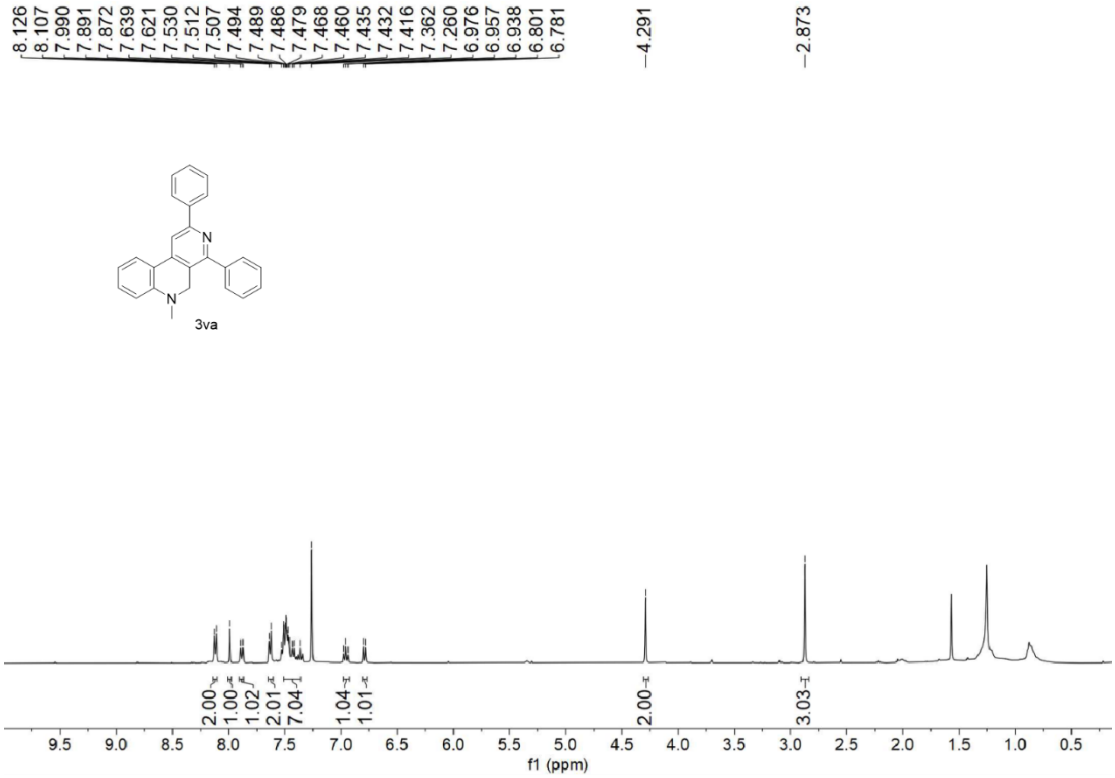
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ua**



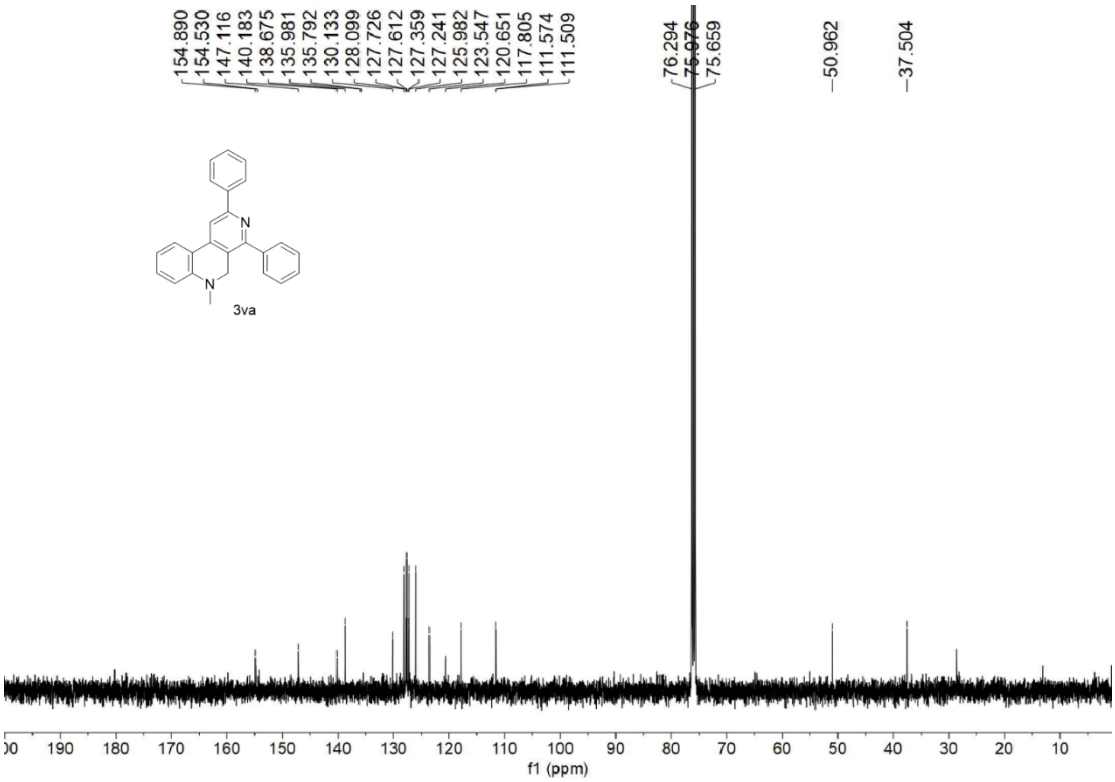
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ua**



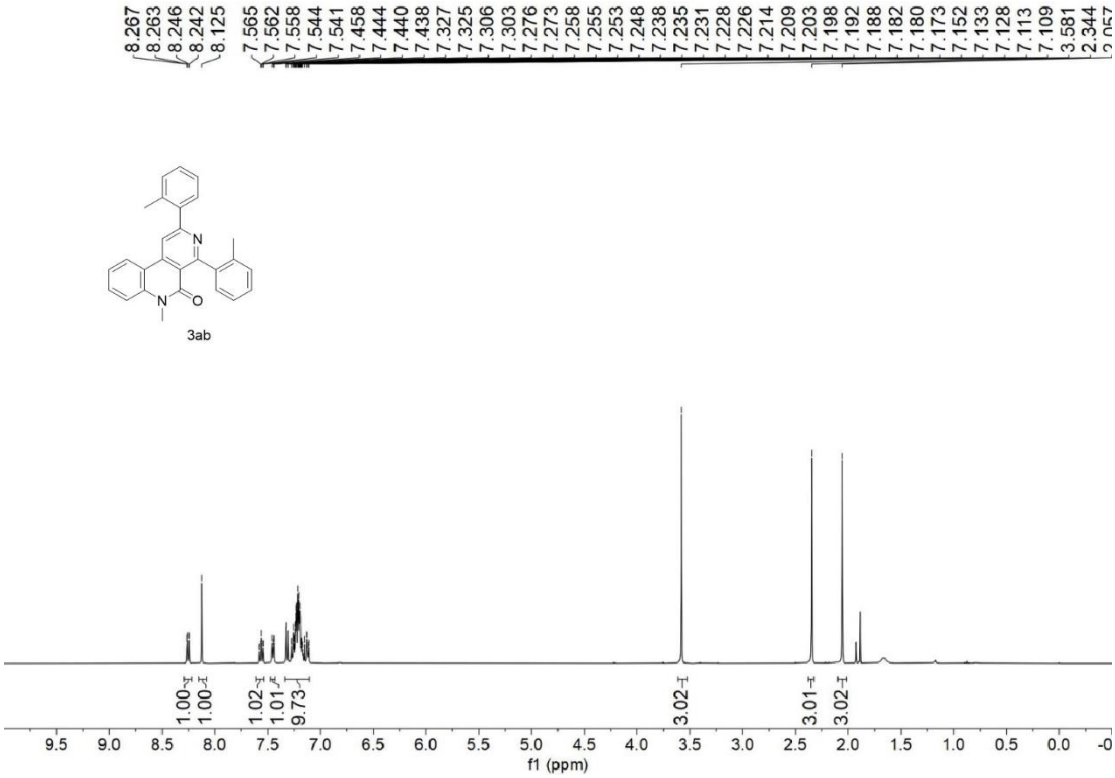
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3va**



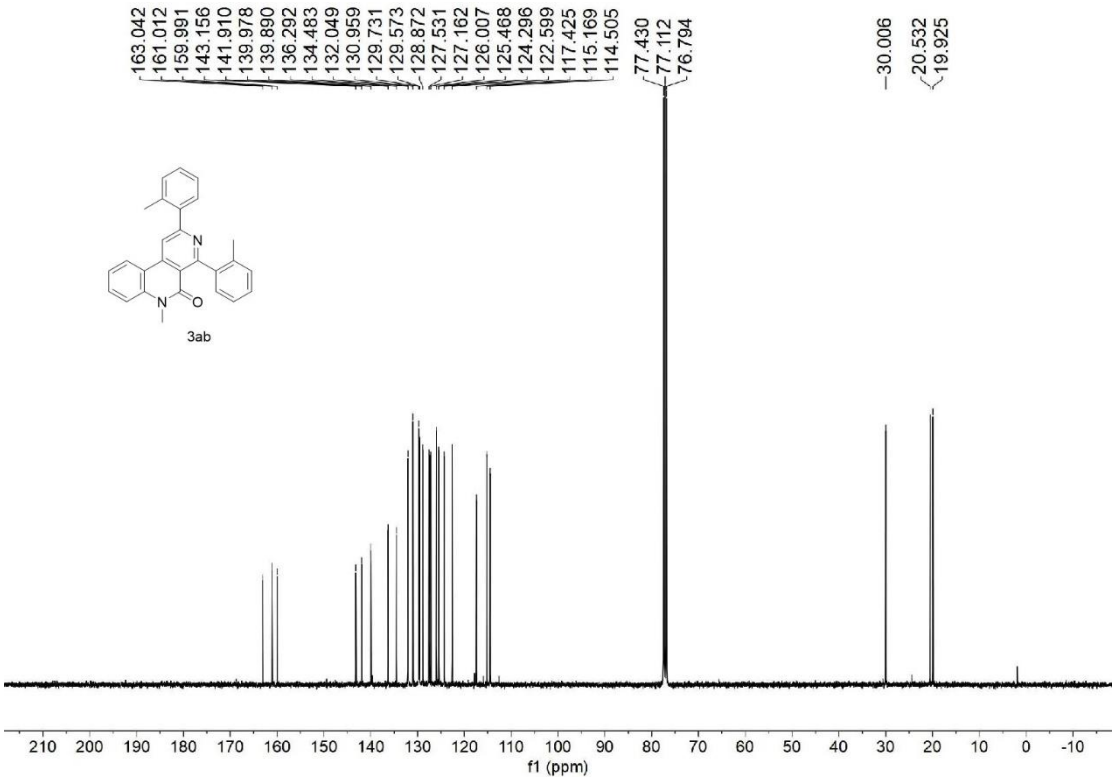
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3va**



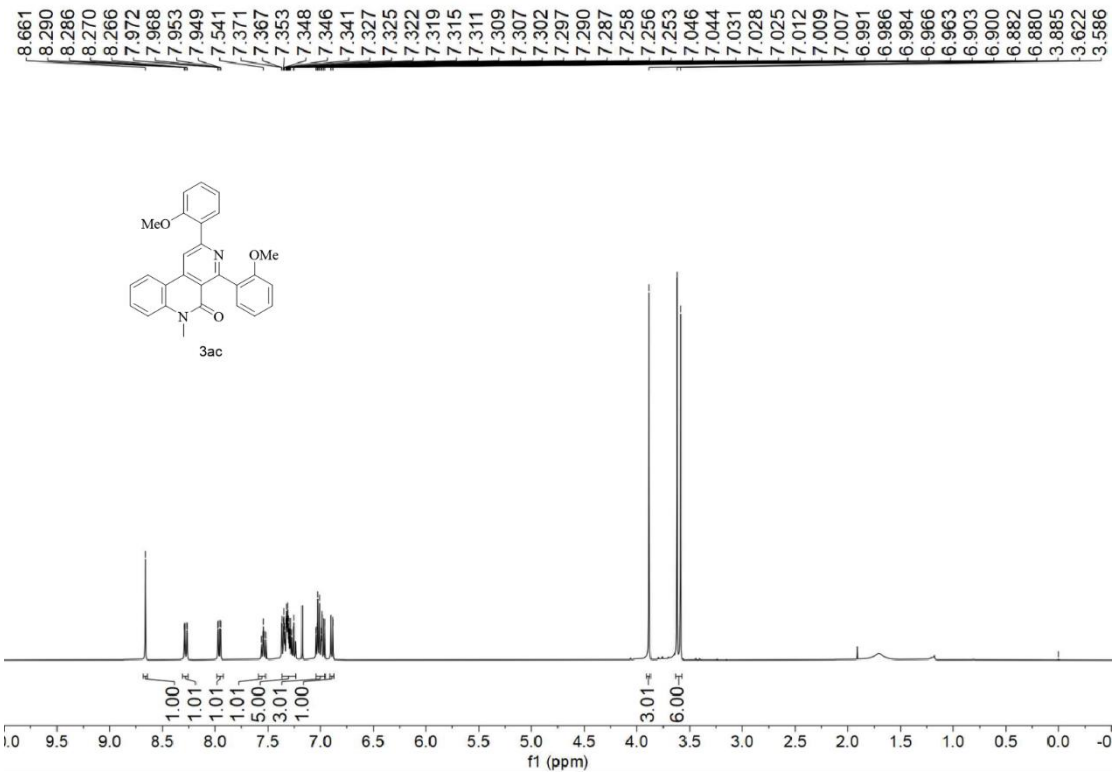
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ab**



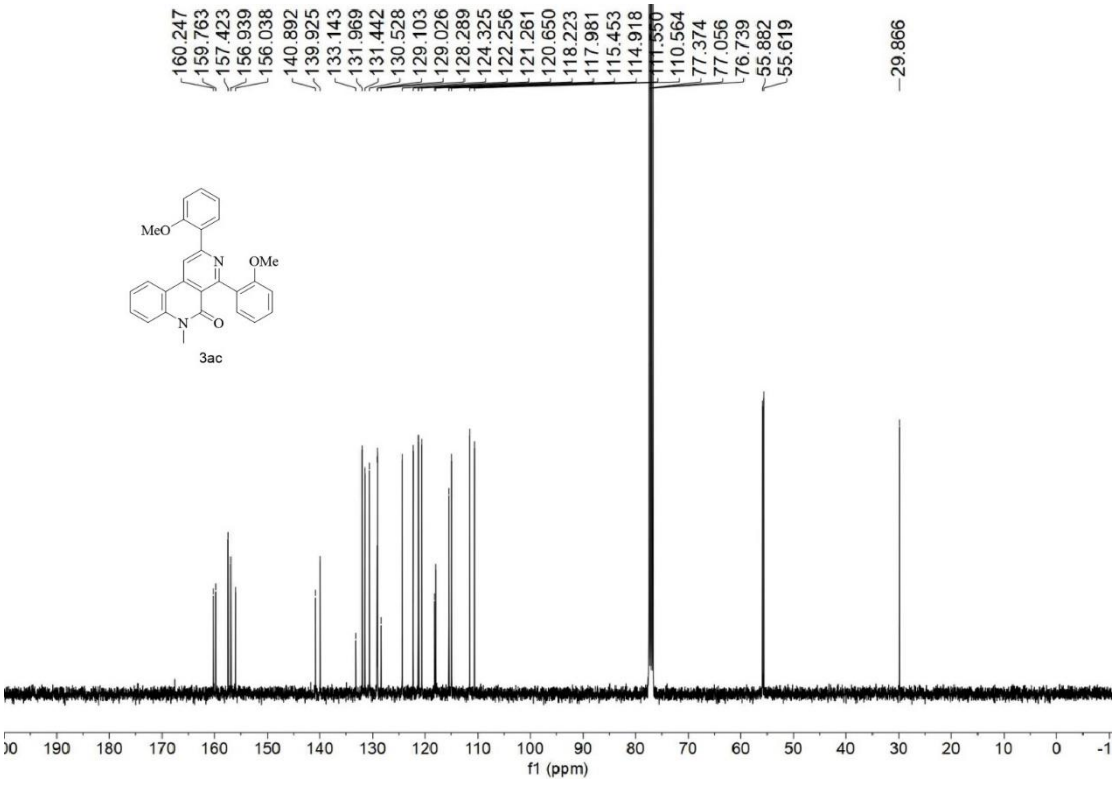
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ab**



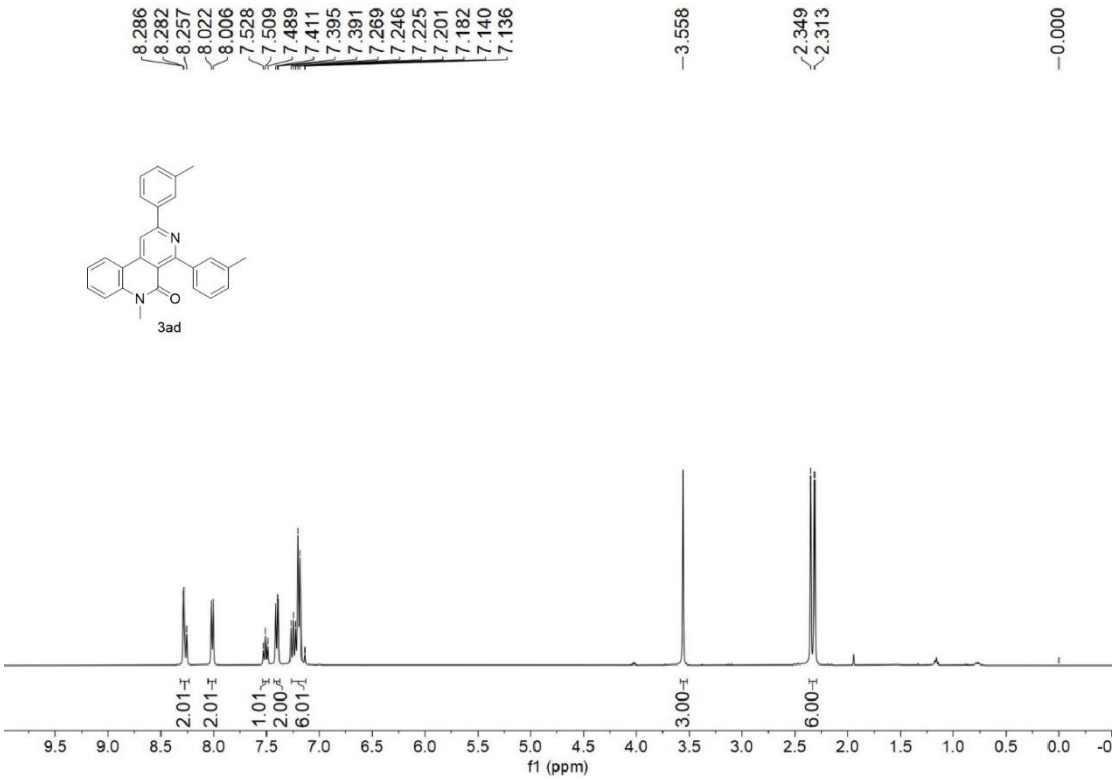
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ac**



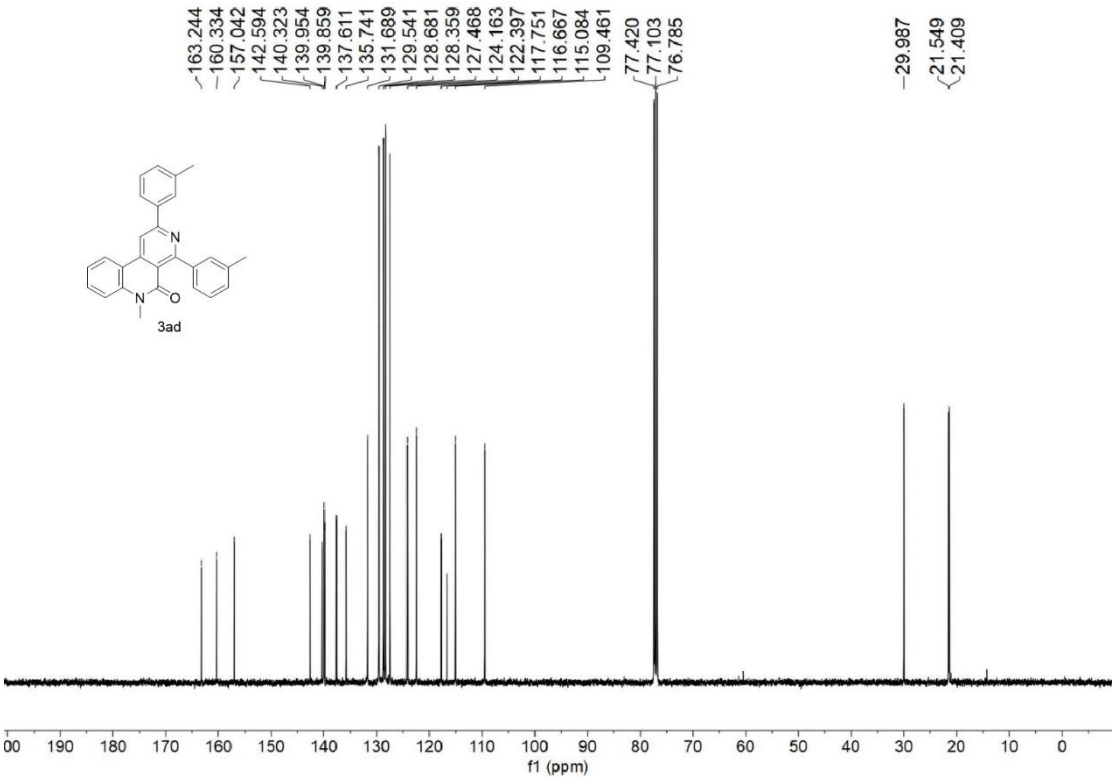
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ac**



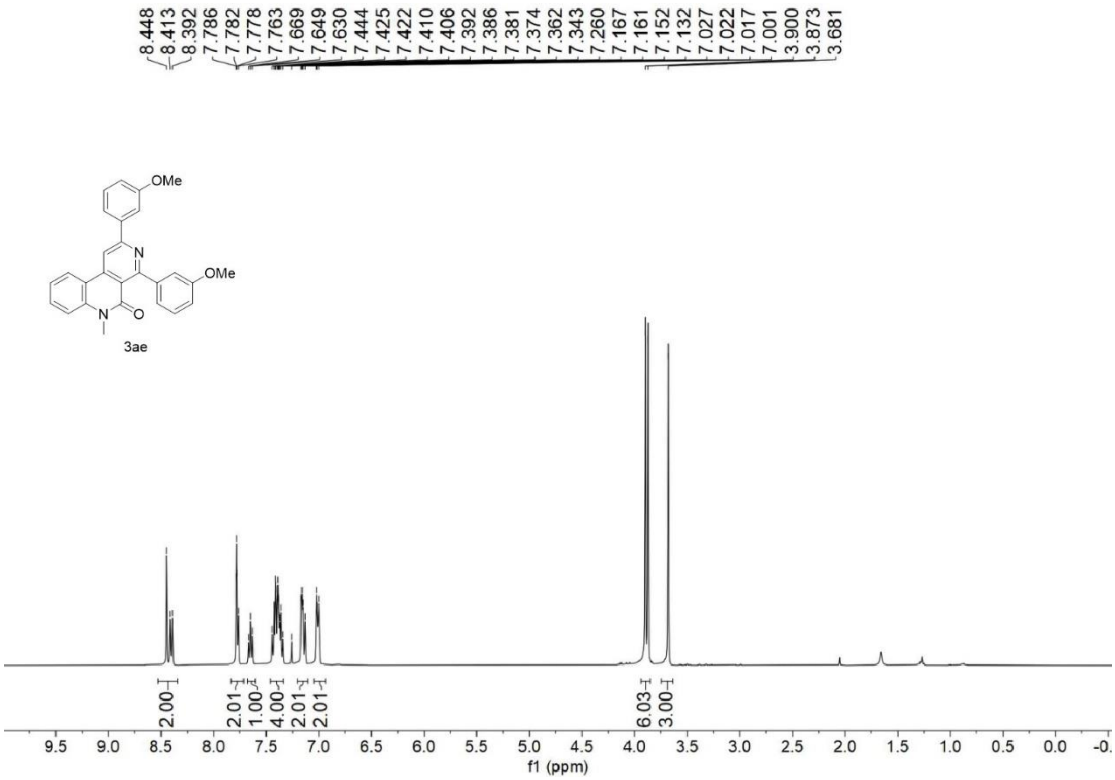
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ad**



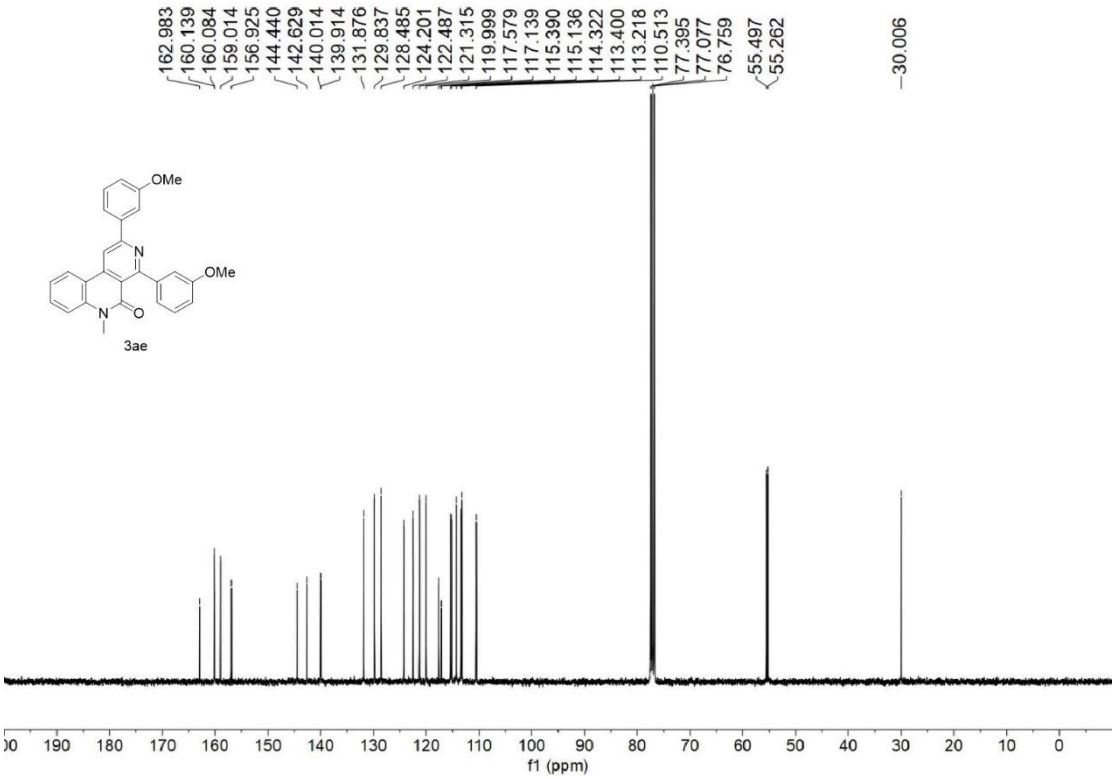
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ad**



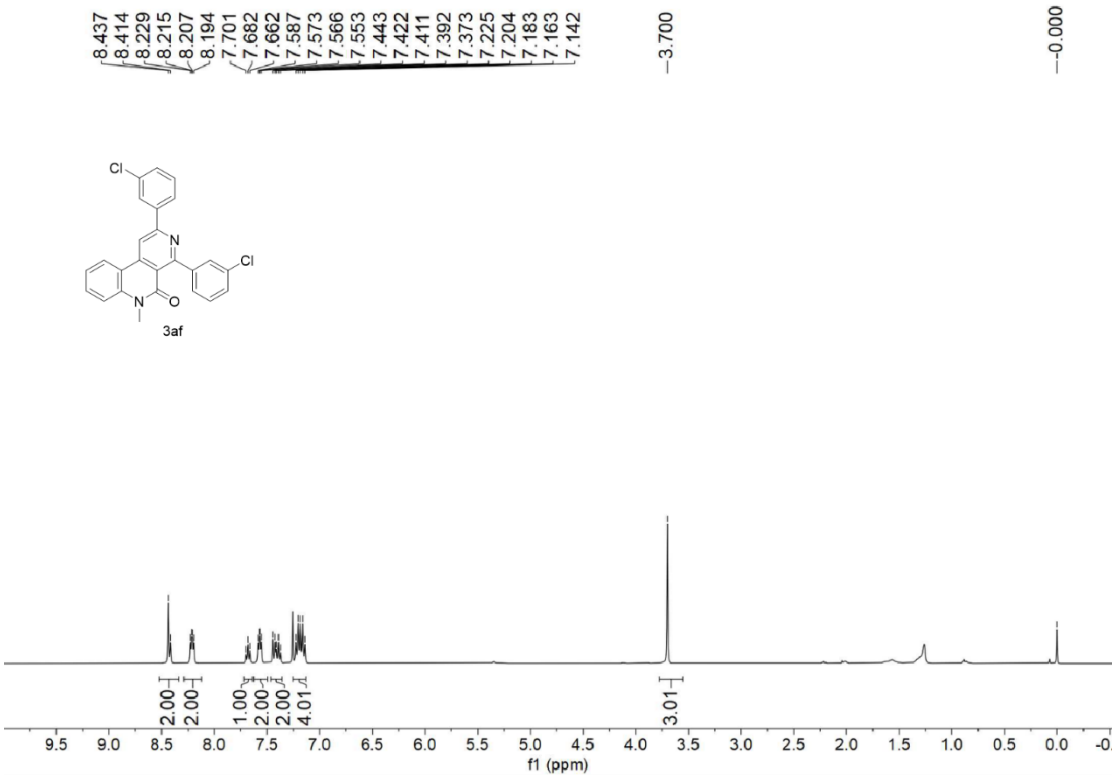
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ae**



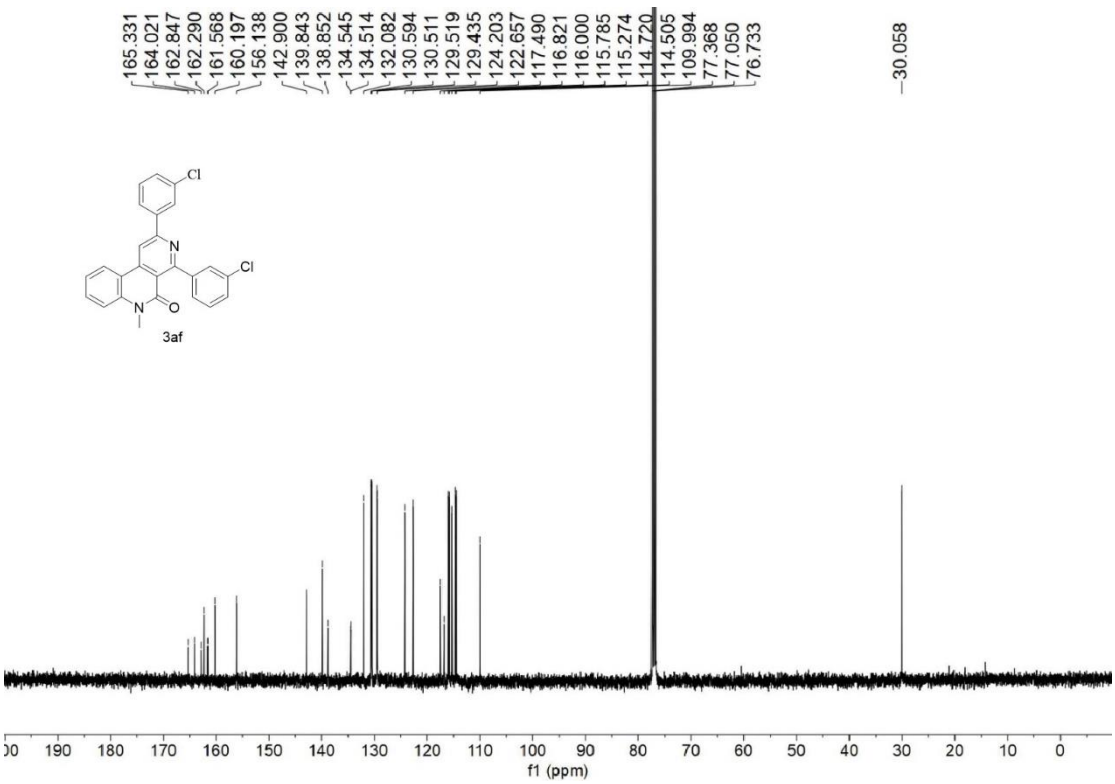
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ae**



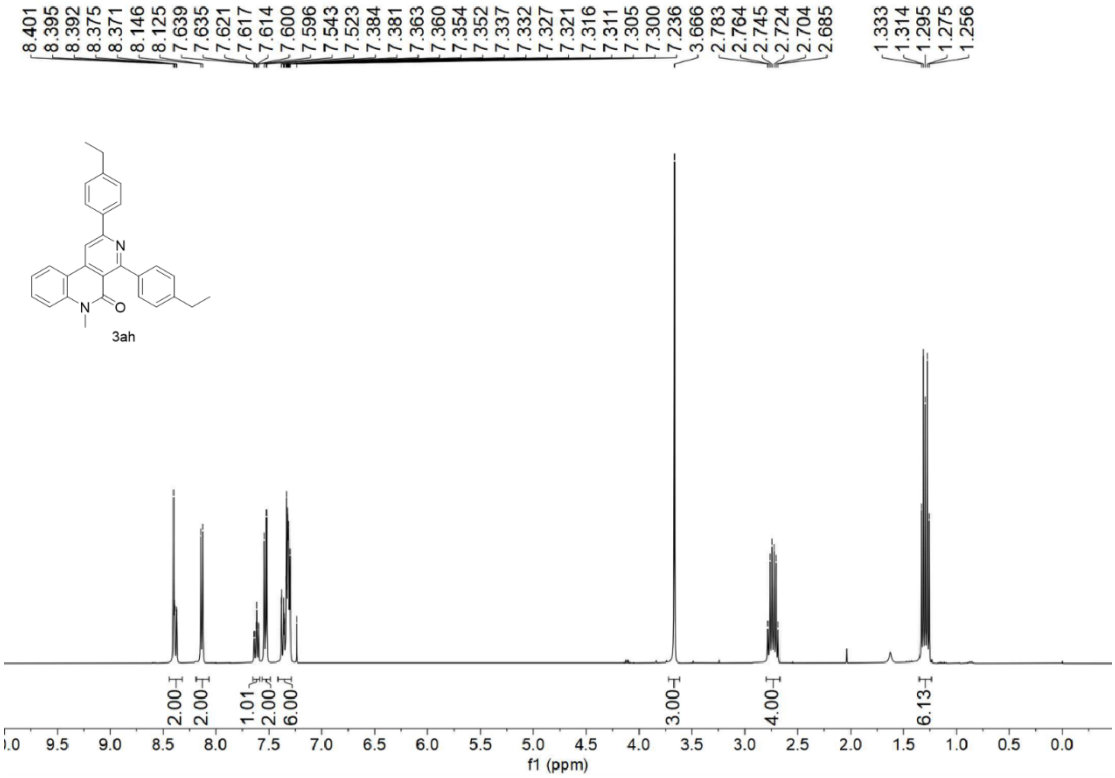
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3af**



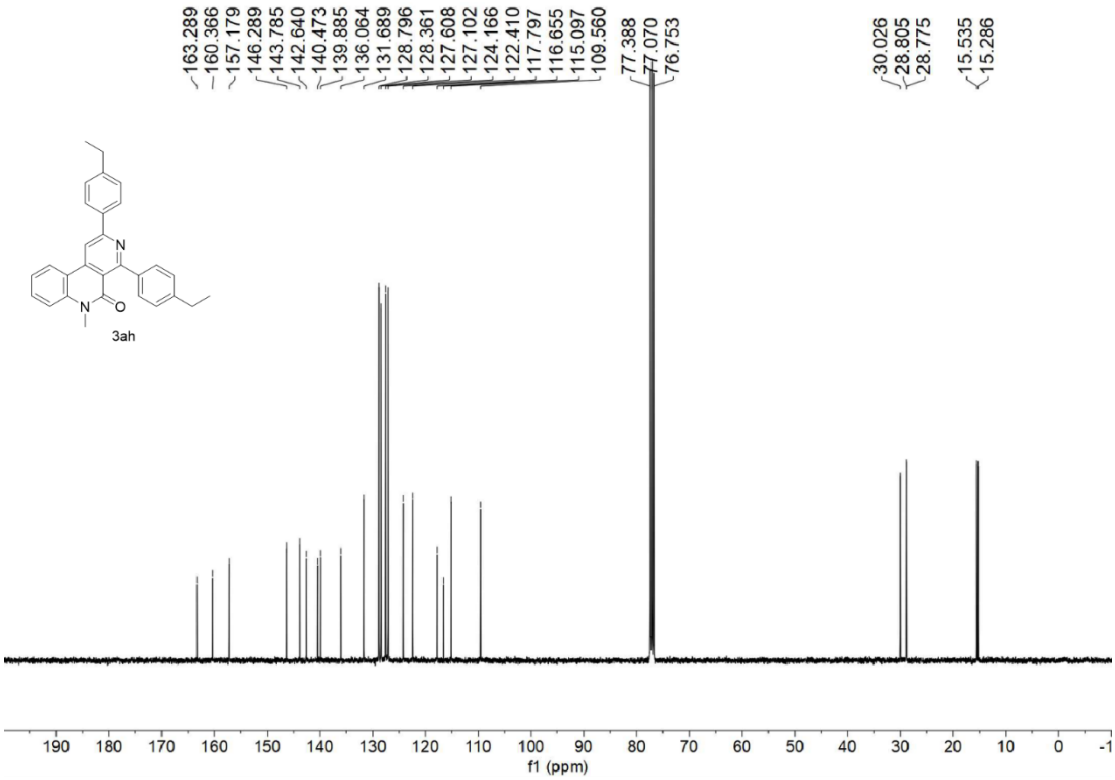
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3af**



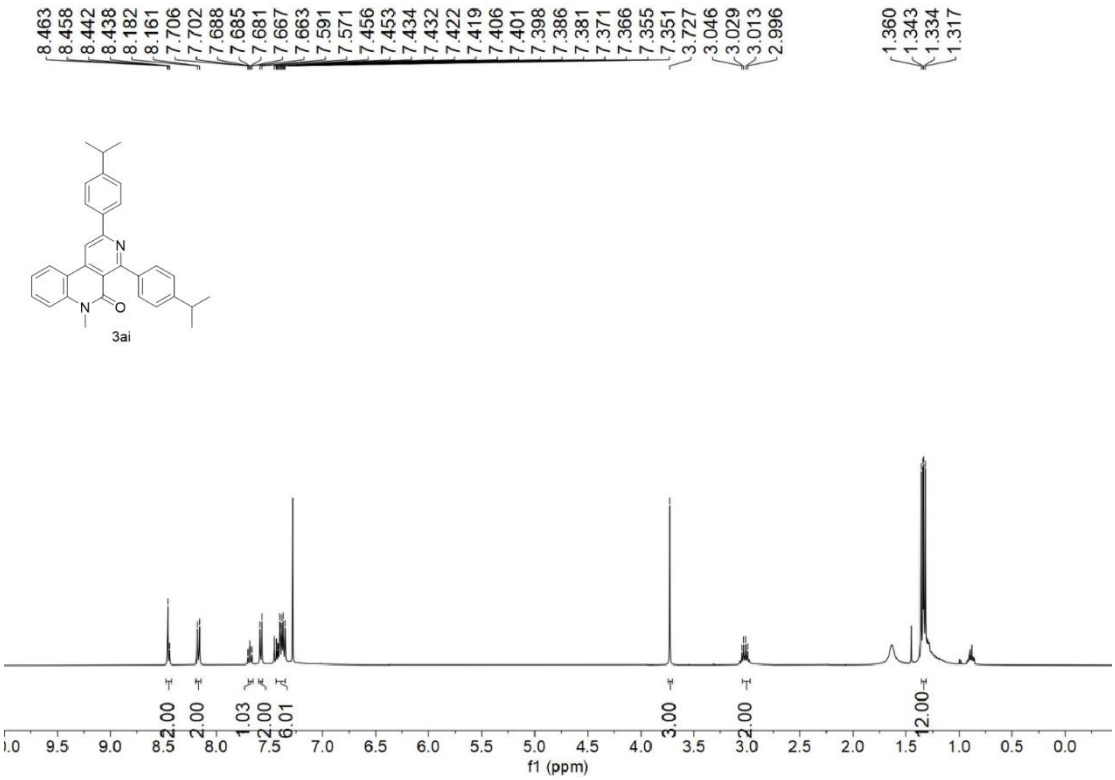
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ah**



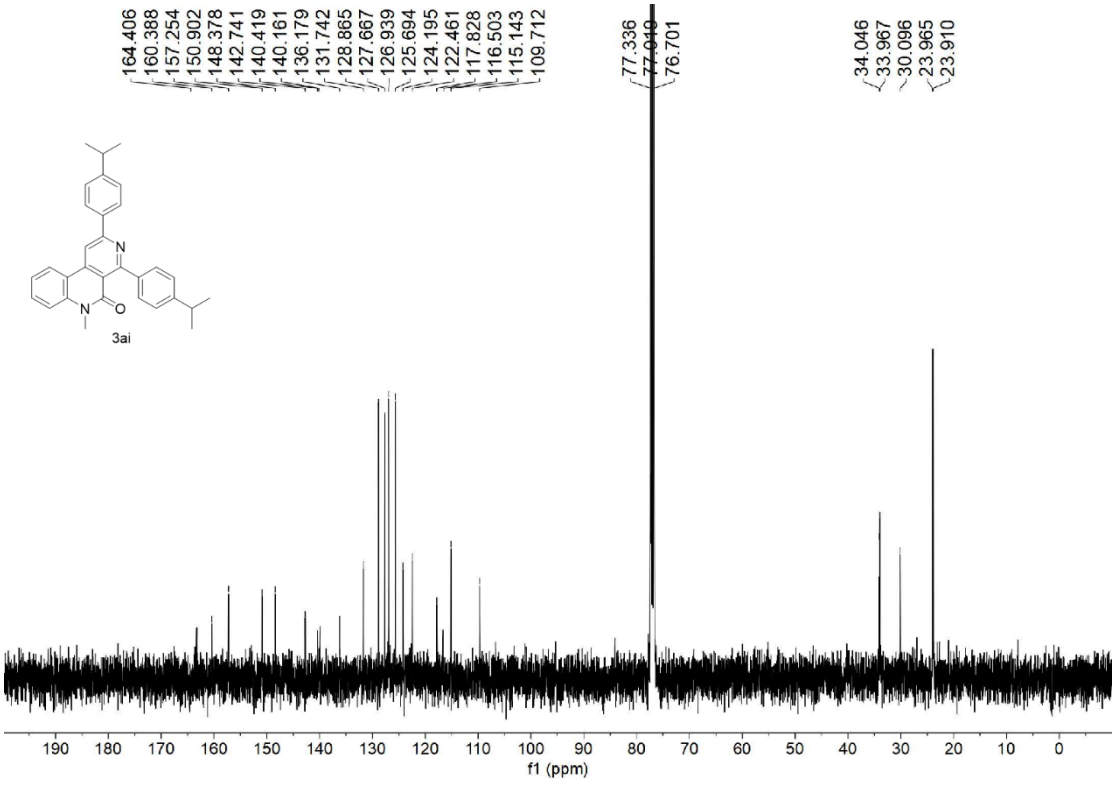
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ah**



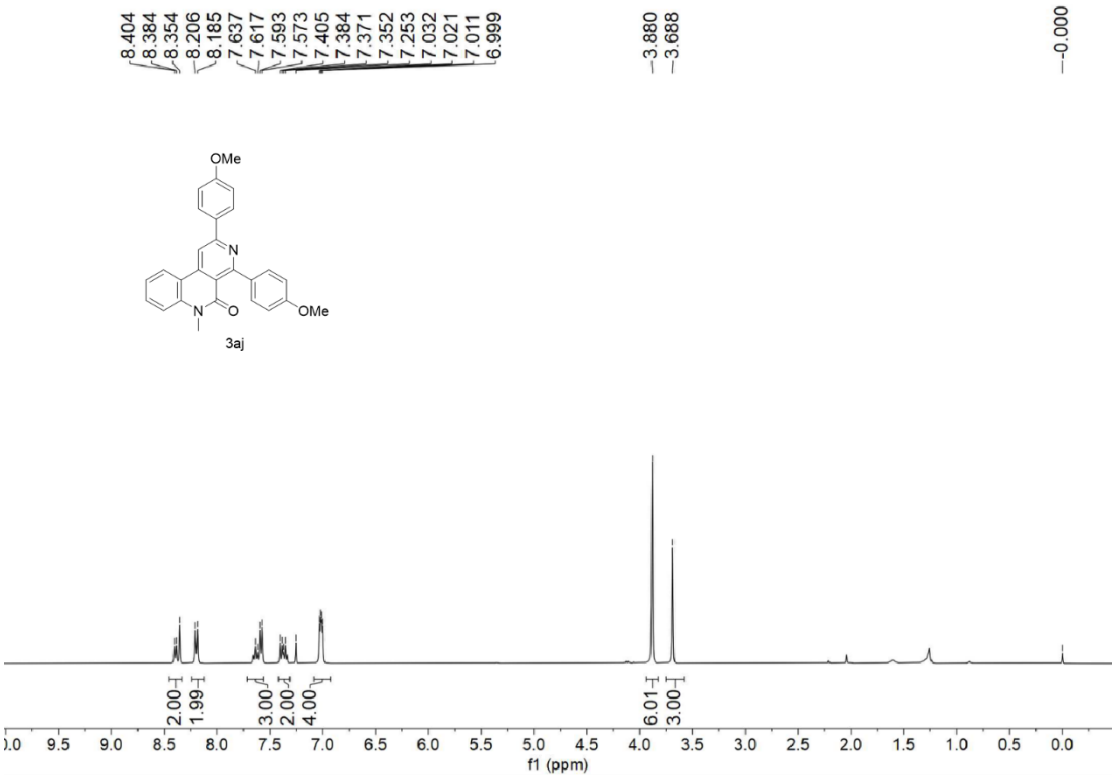
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ai**



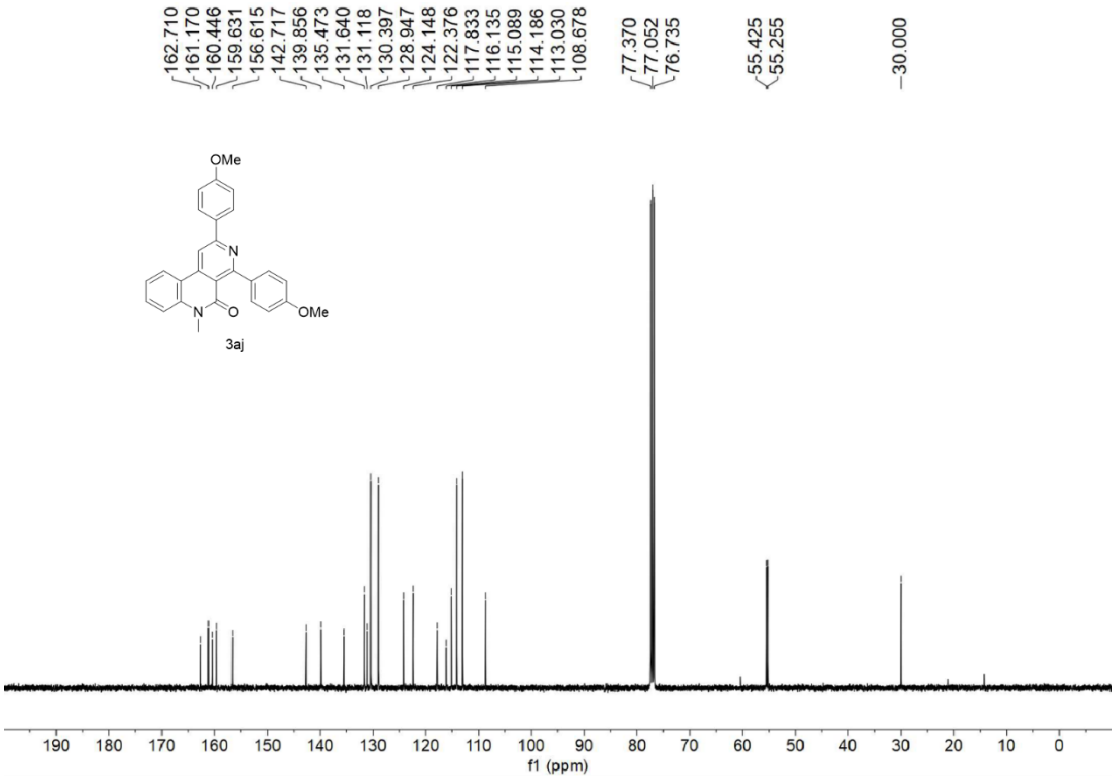
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ai**



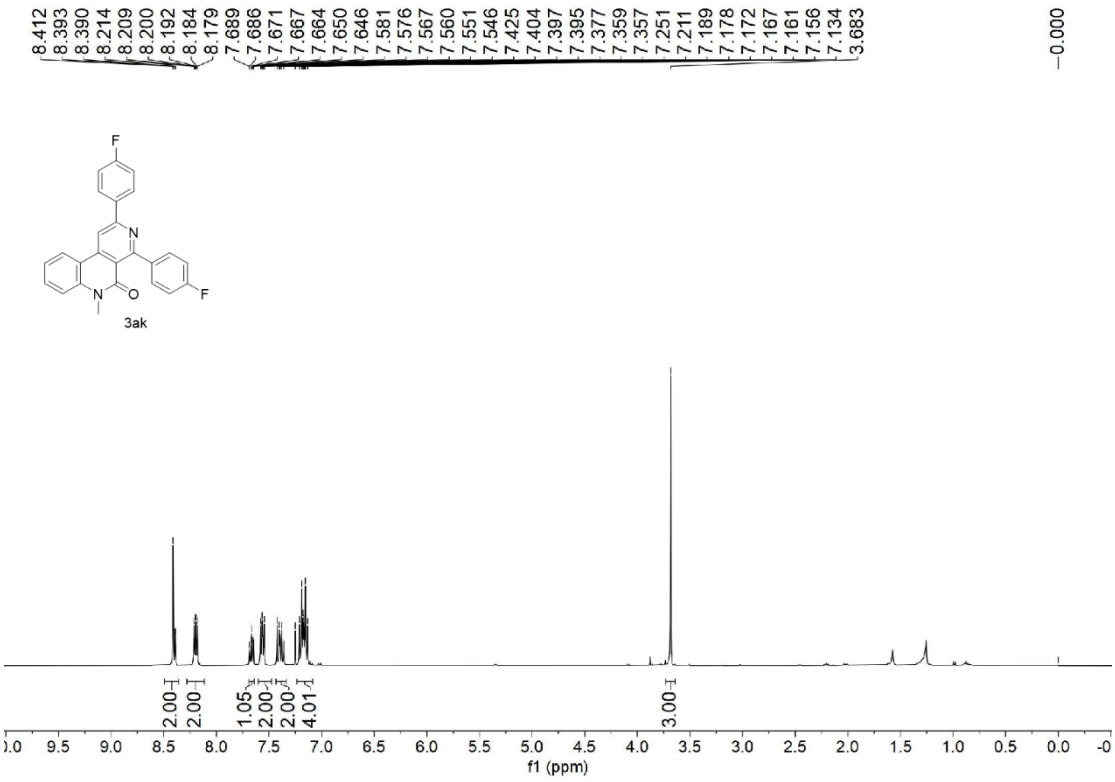
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3aj**



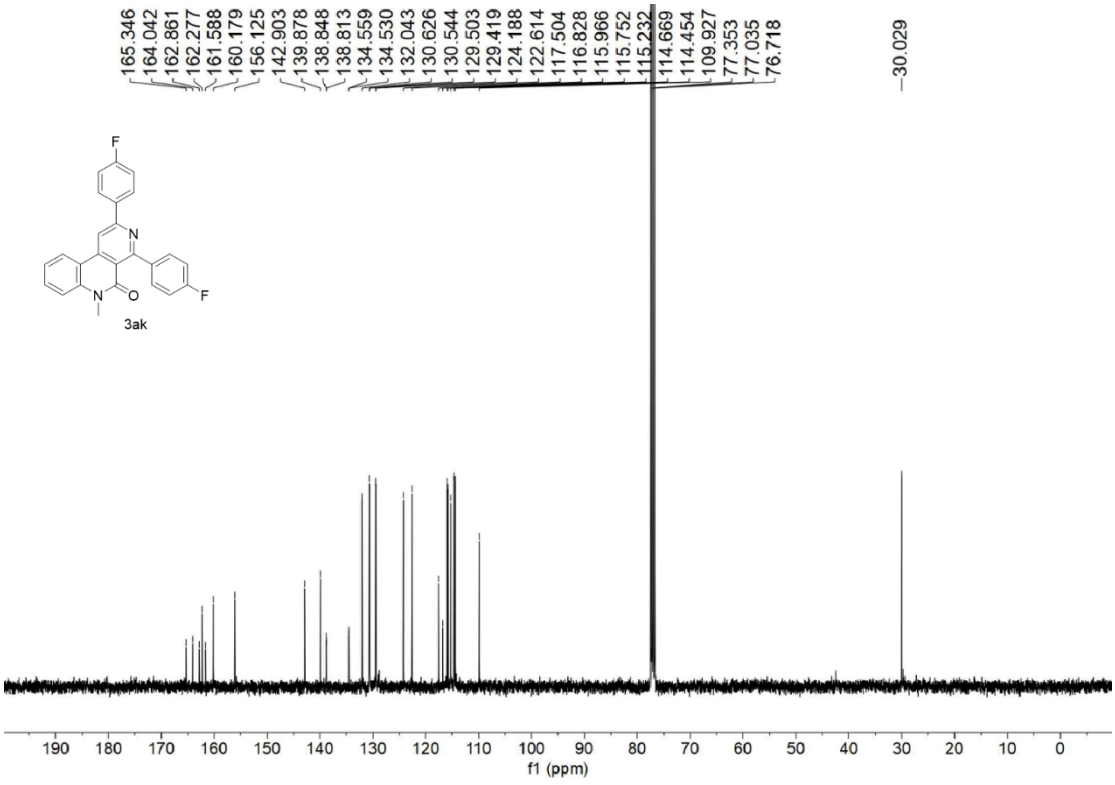
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3aj**



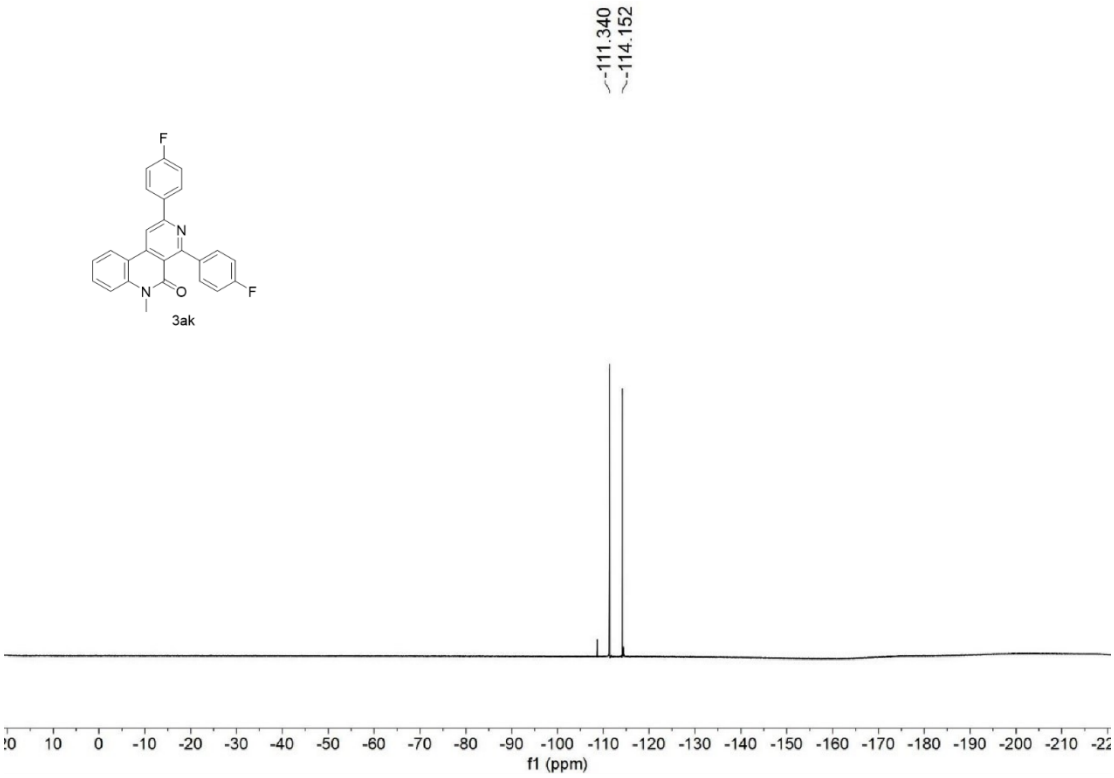
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ak**



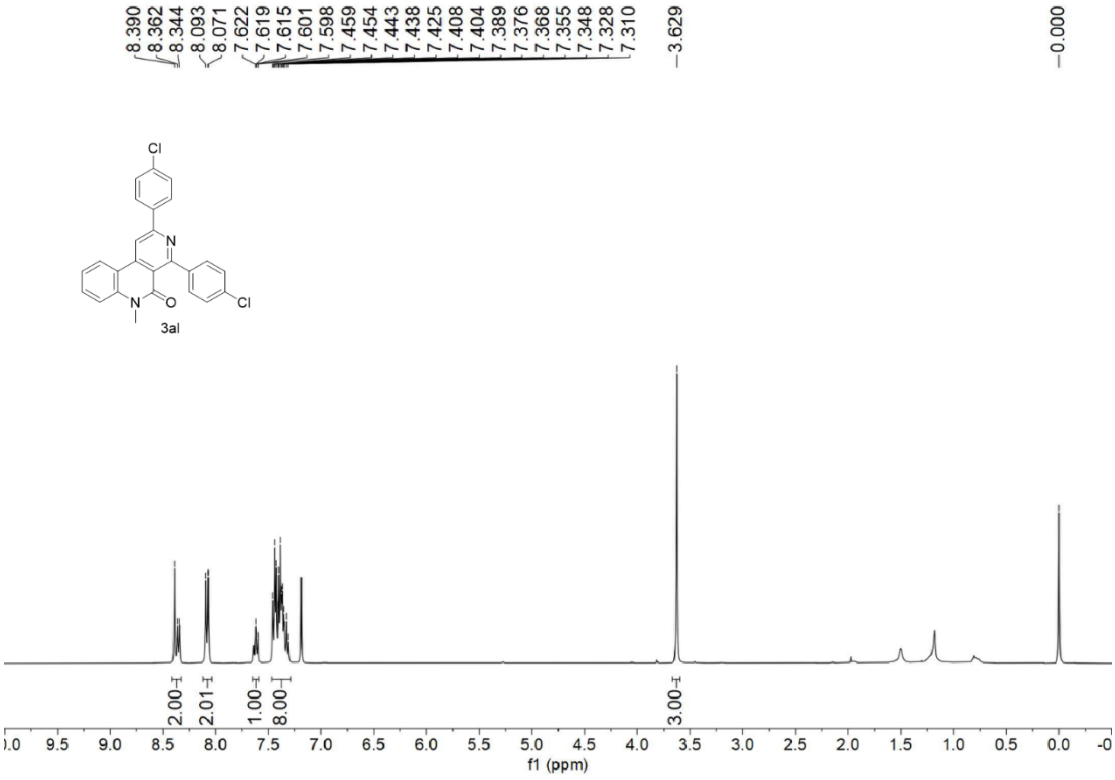
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ak**



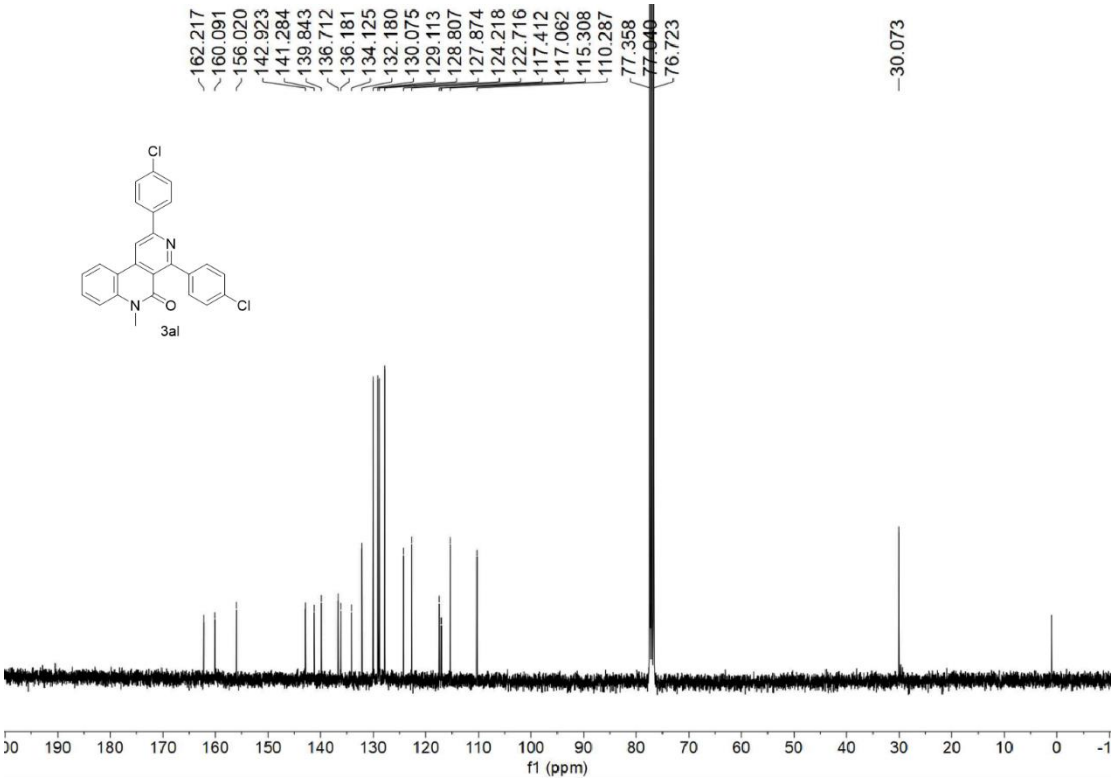
^{19}F-NMR spectrum ($CDCl_3$, 377 MHz) of **3ak**



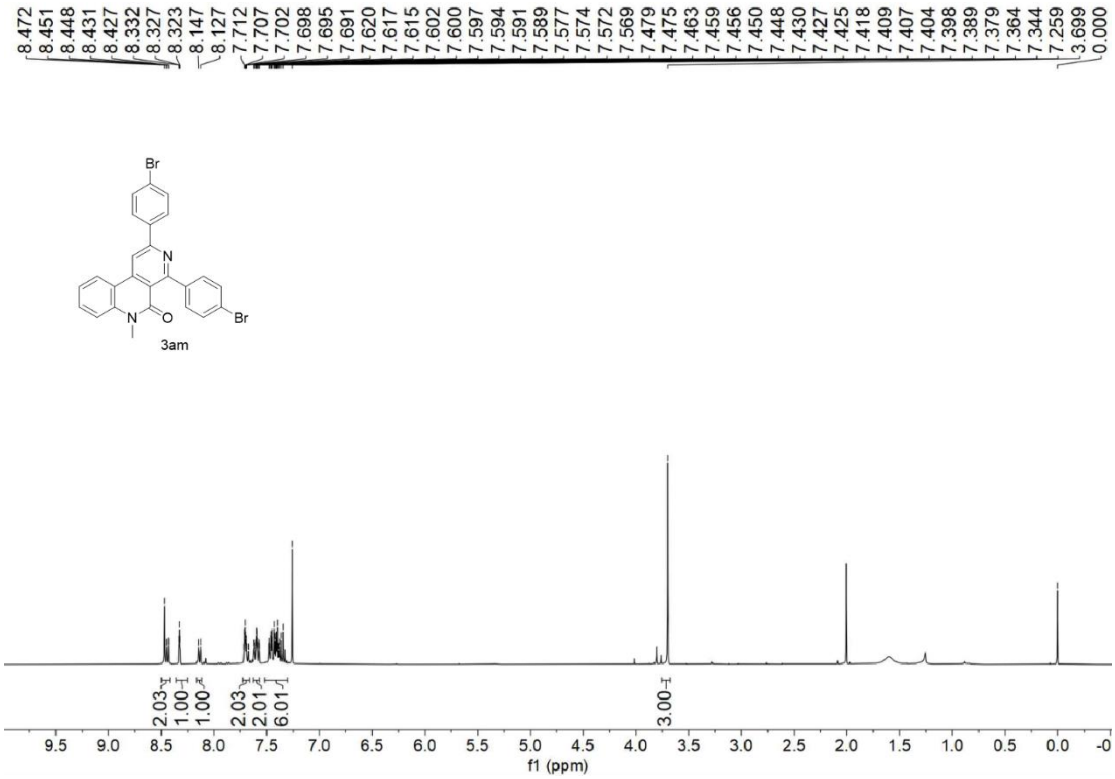
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3al**



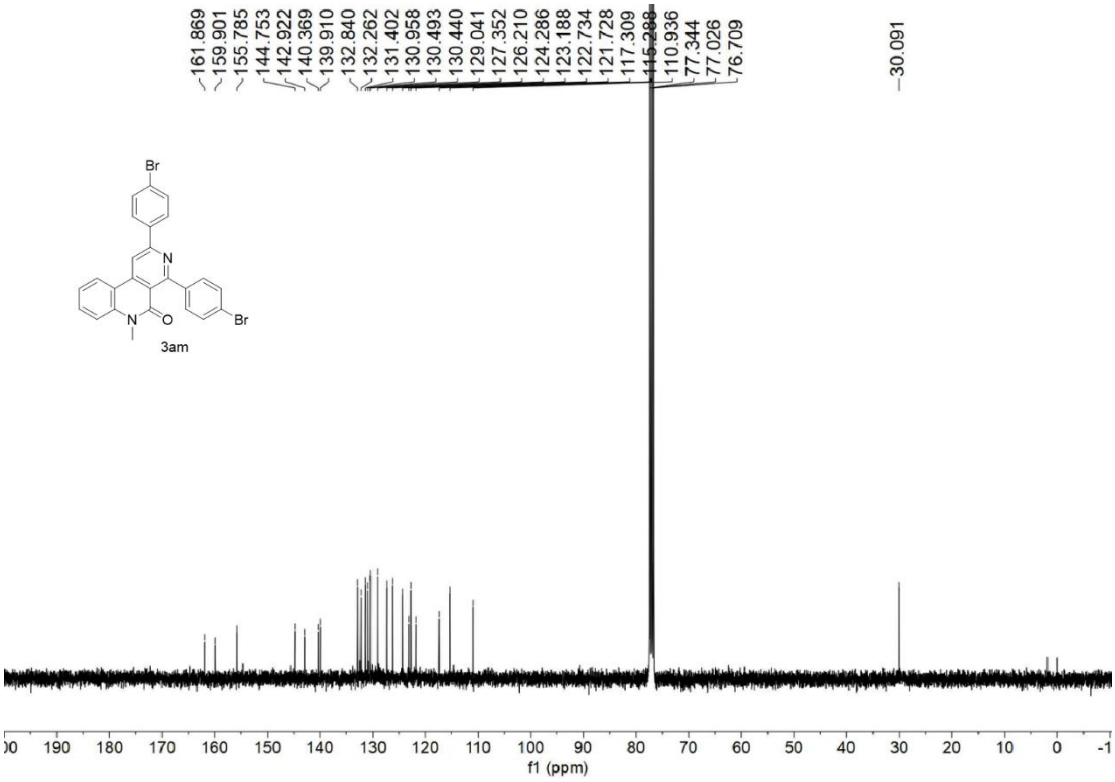
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3al**



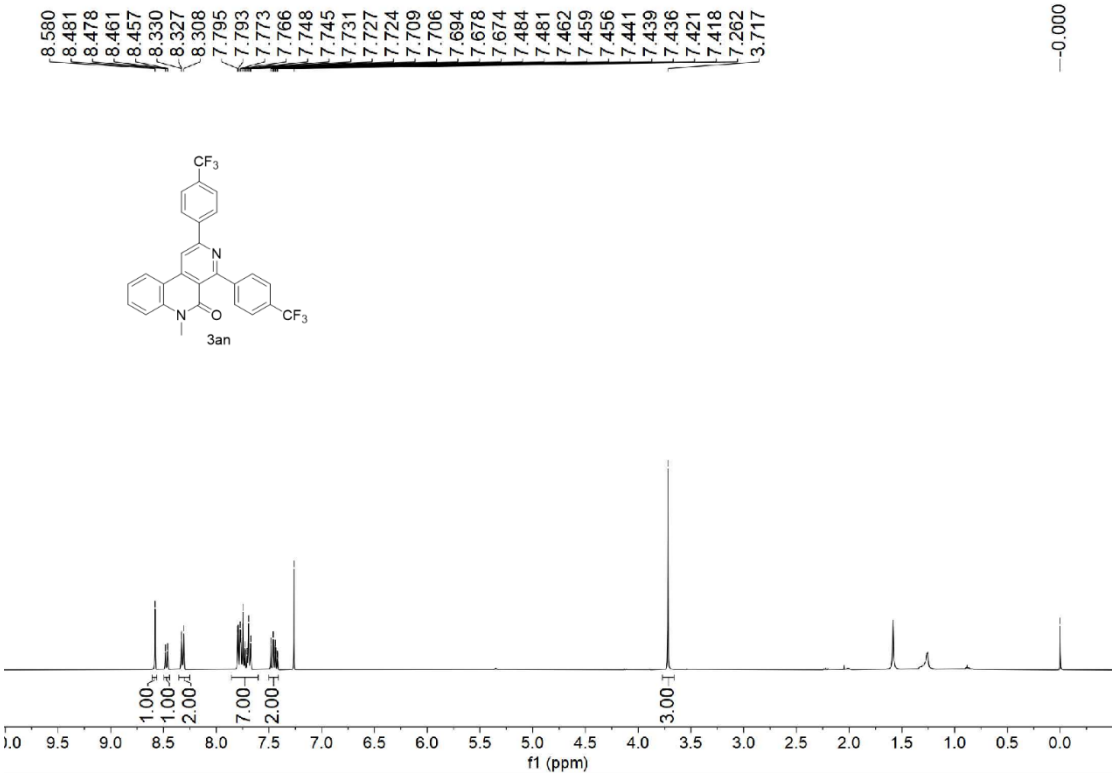
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3am**



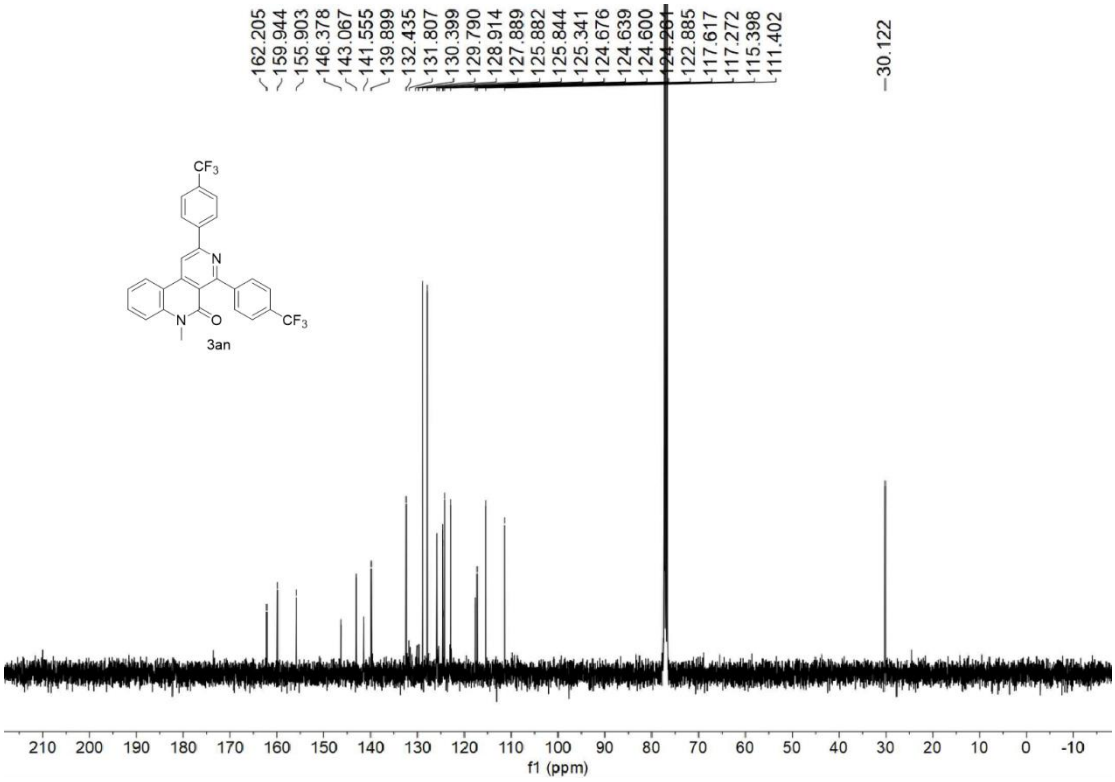
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3am**



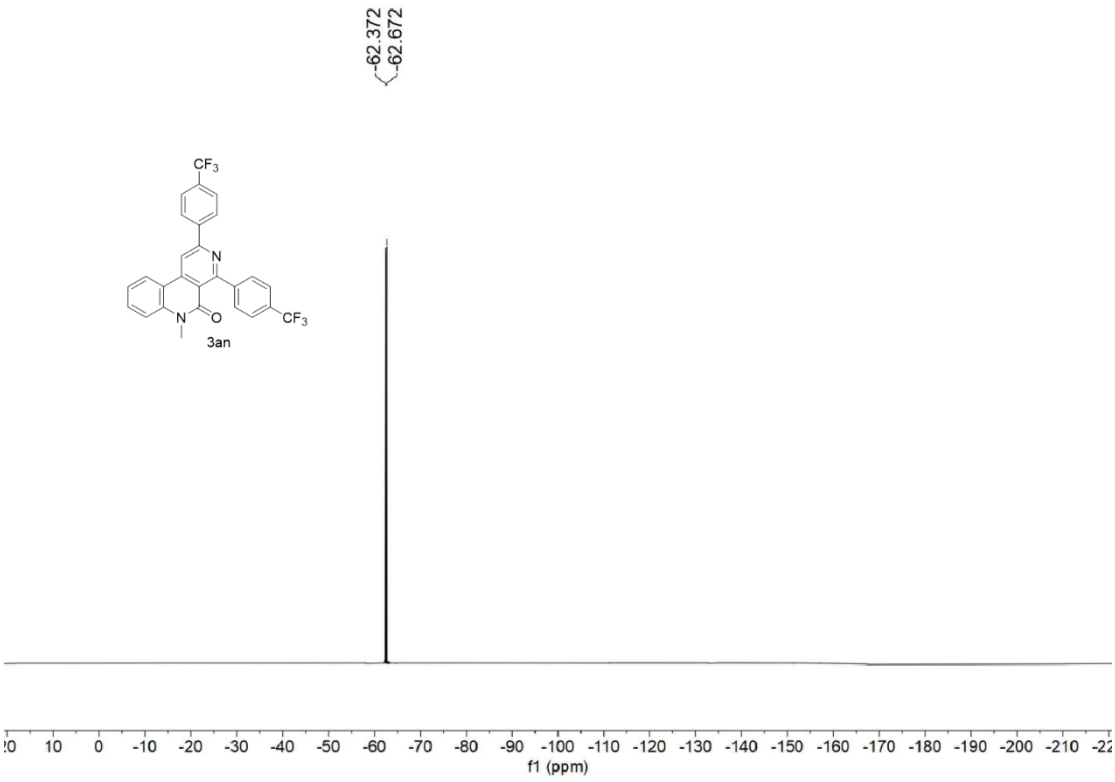
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3an**



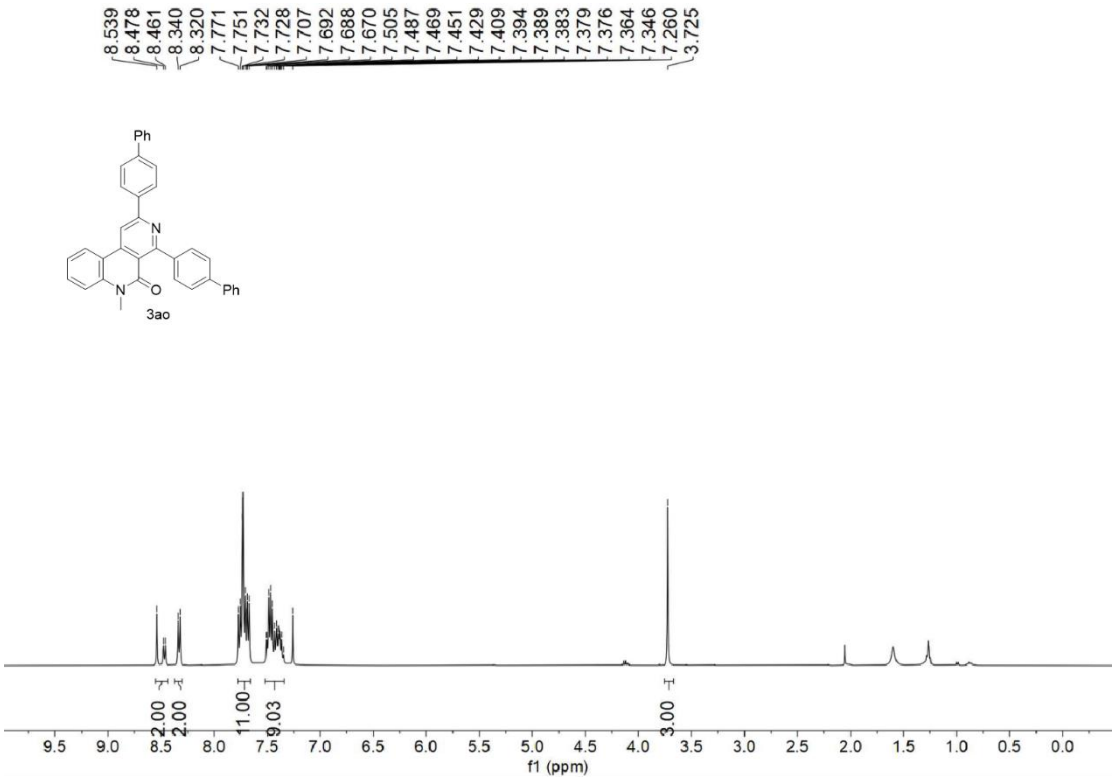
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3an**



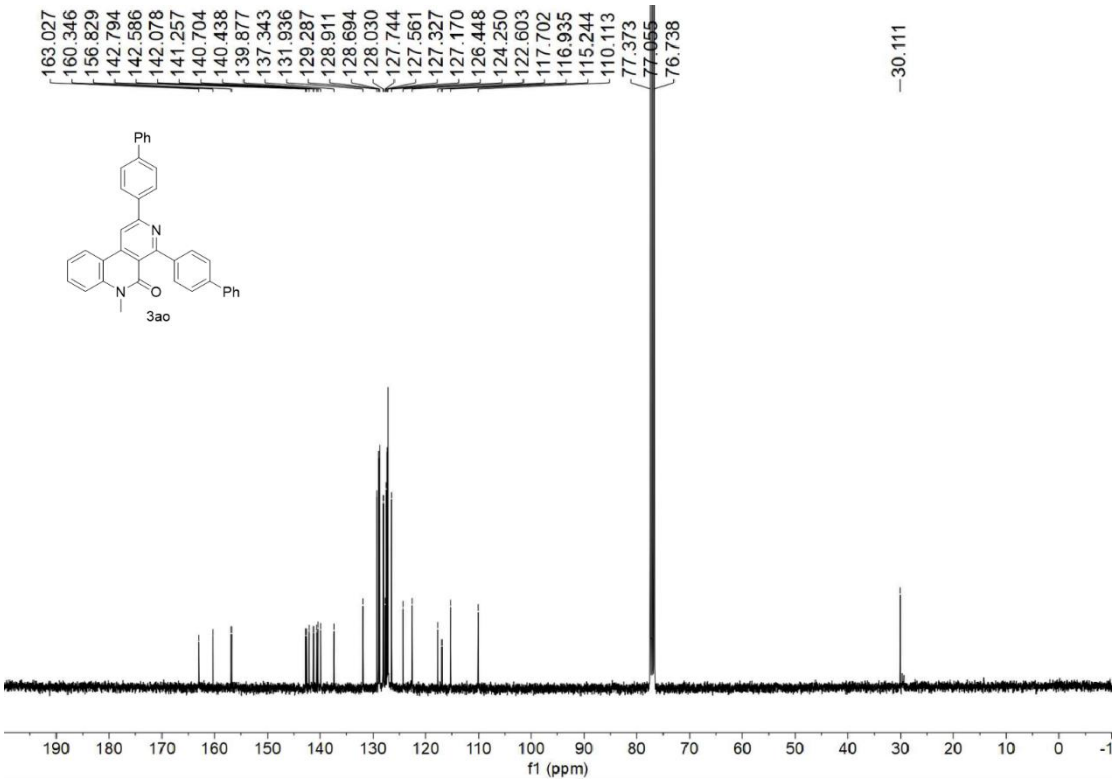
^{19}F-NMR spectrum ($CDCl_3$, 377 MHz) of **3an**



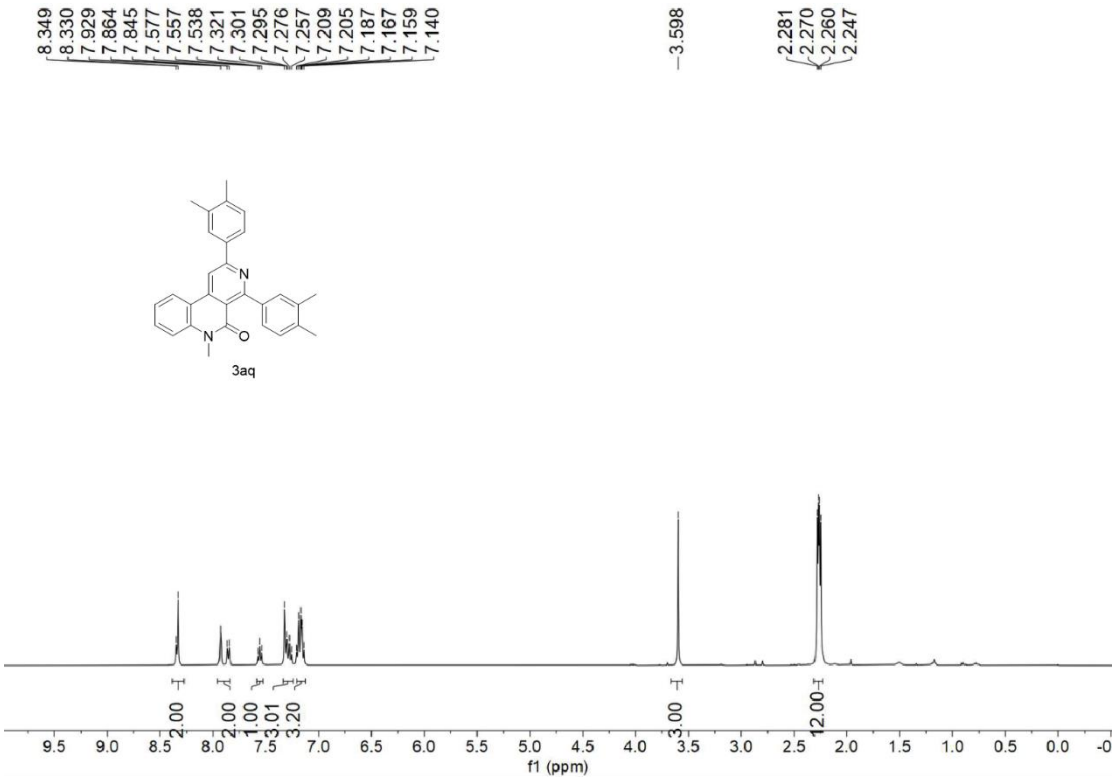
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ao**



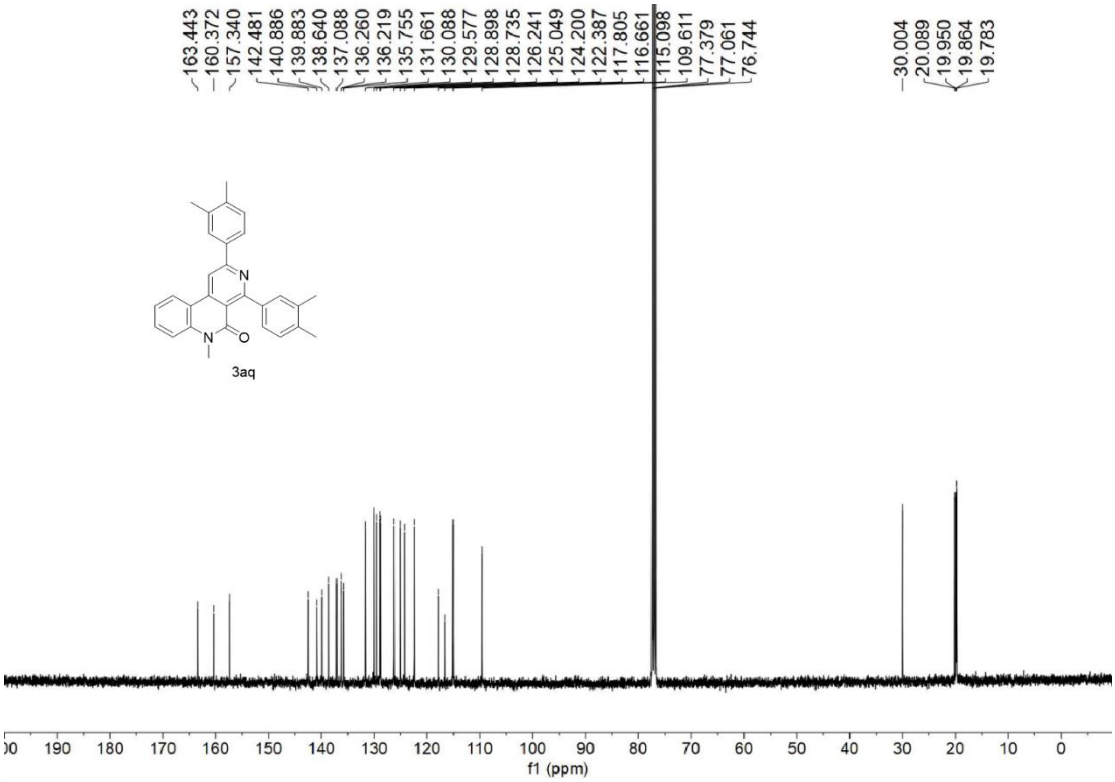
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ao**



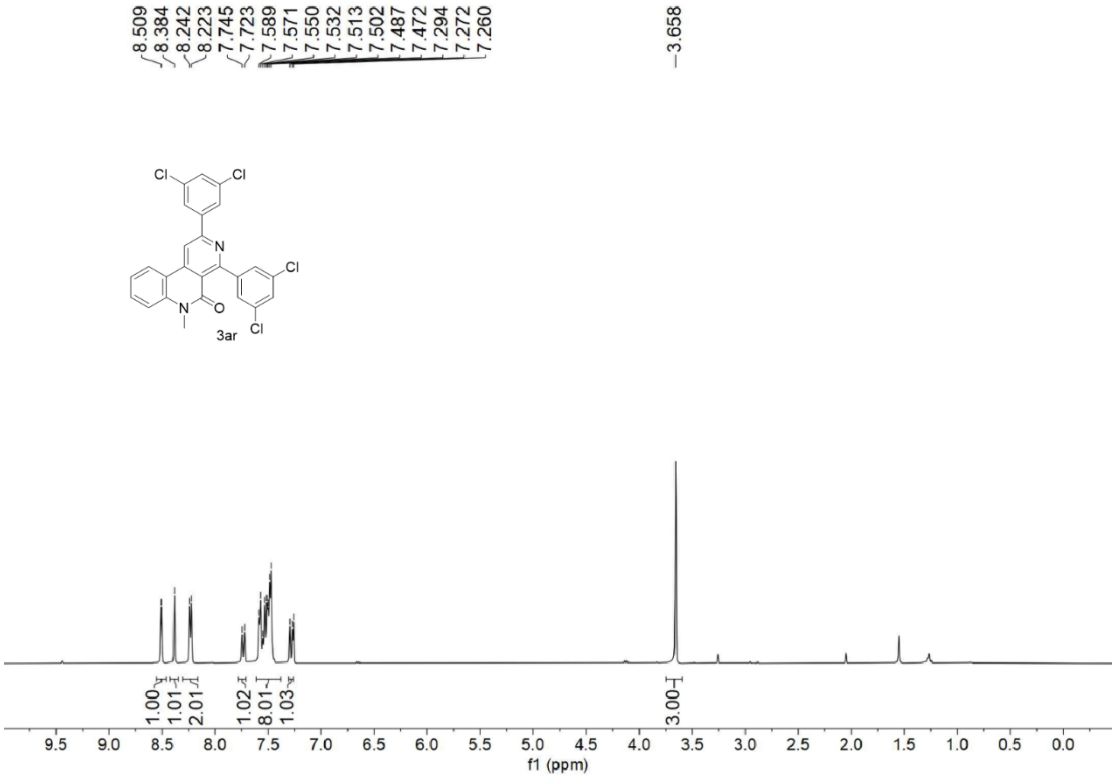
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3aq**



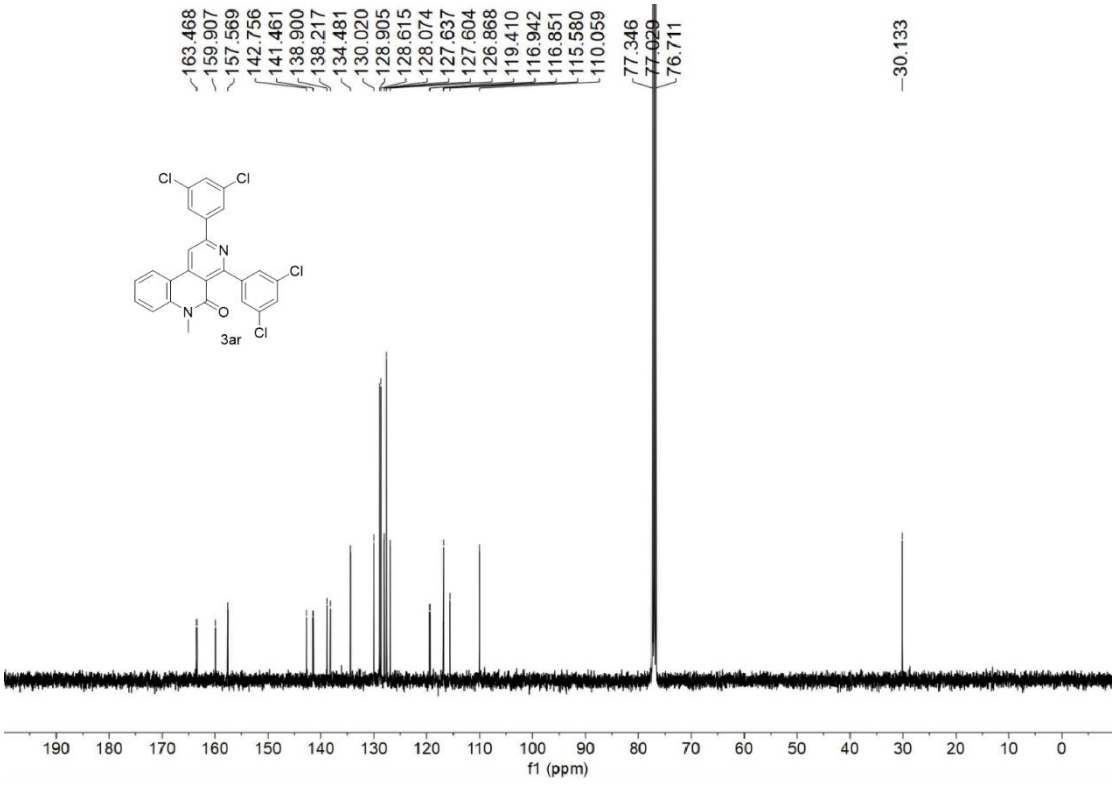
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3aq**



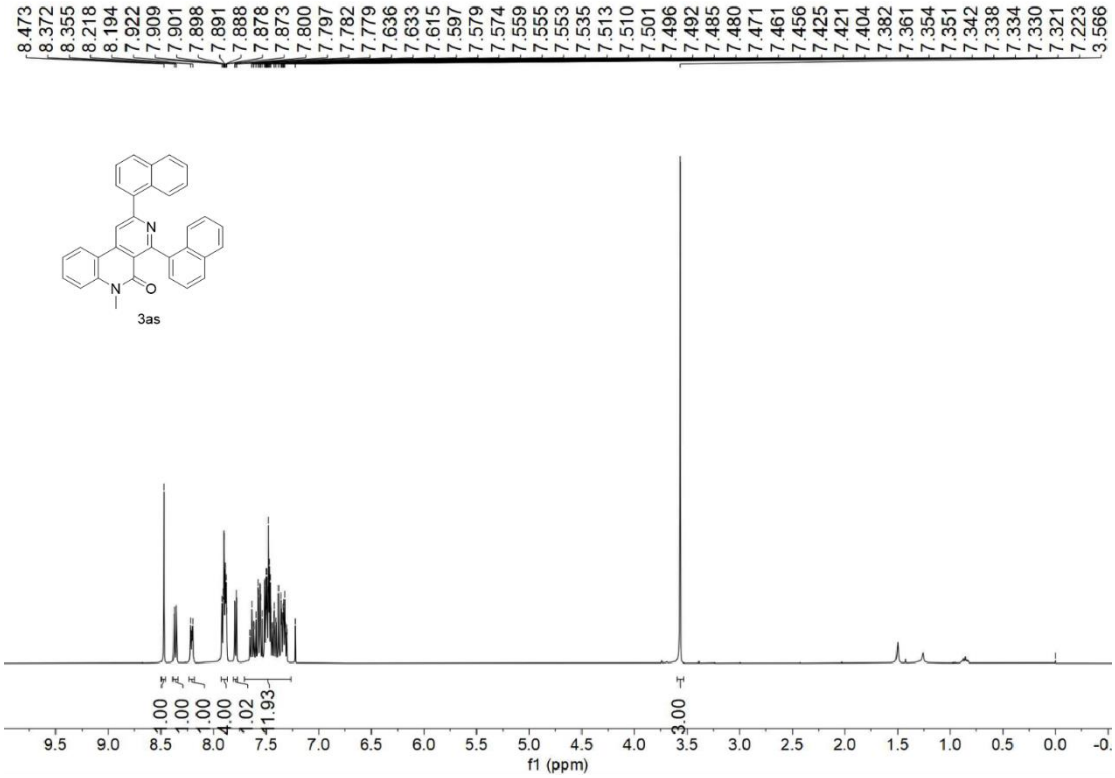
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3ar**



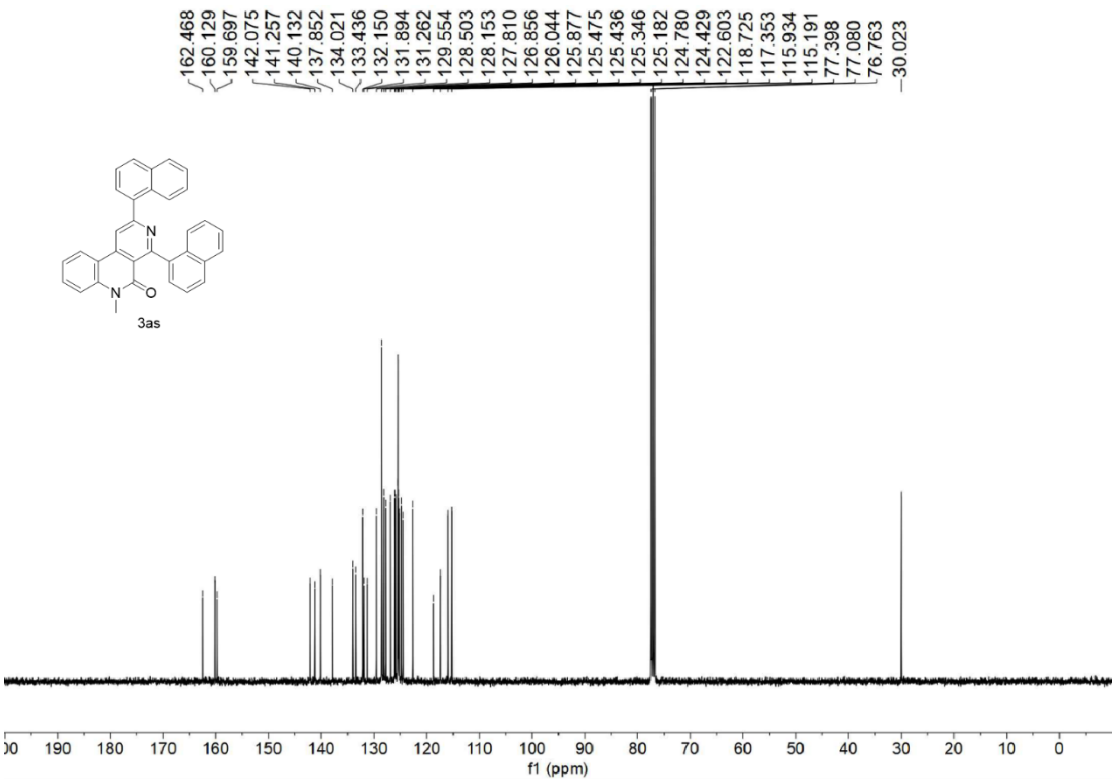
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3ar**



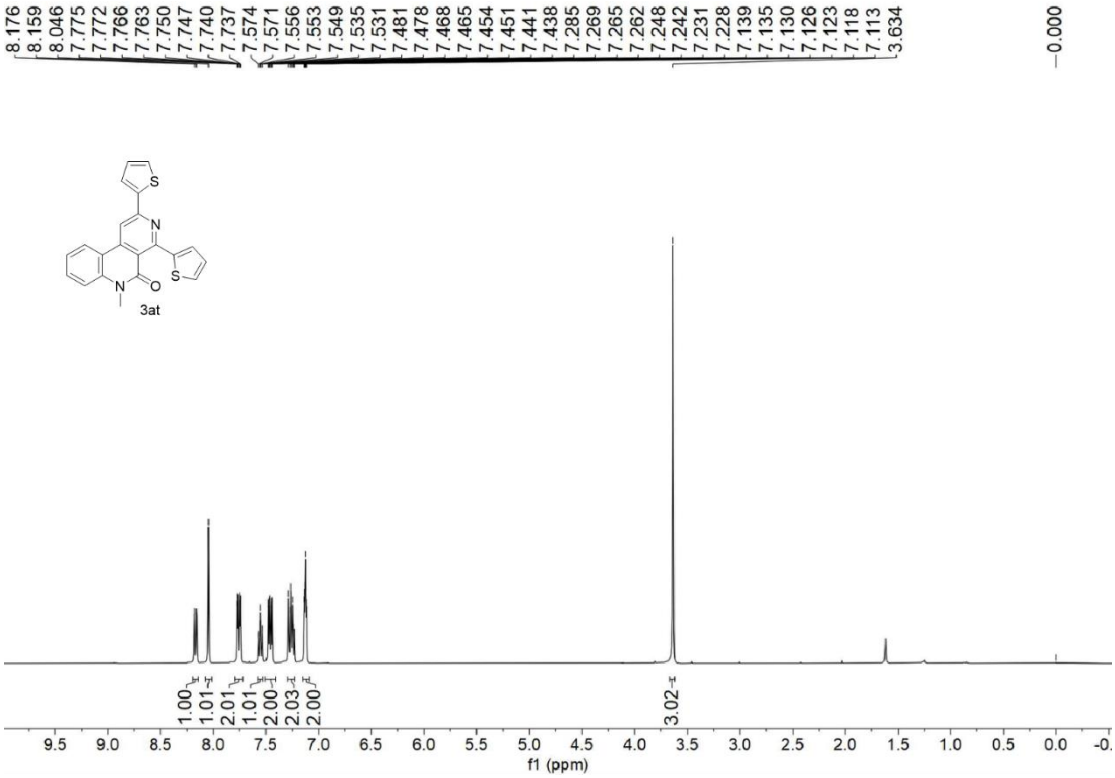
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3as**



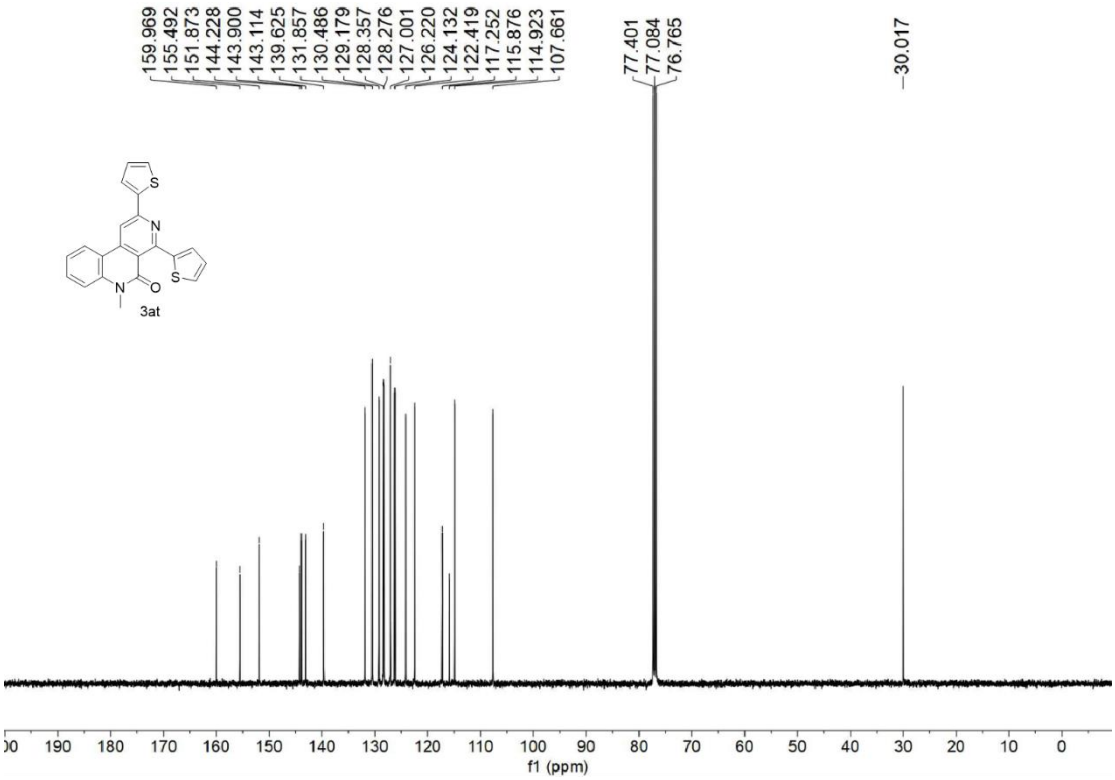
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3as**



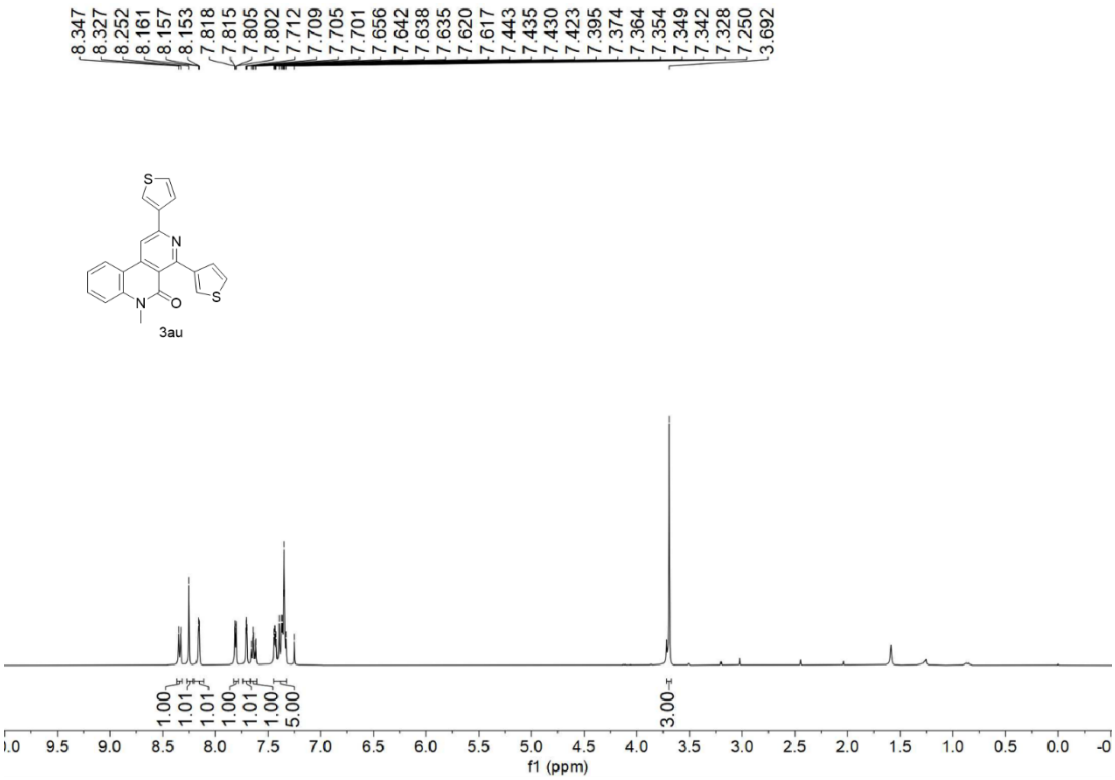
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3at**



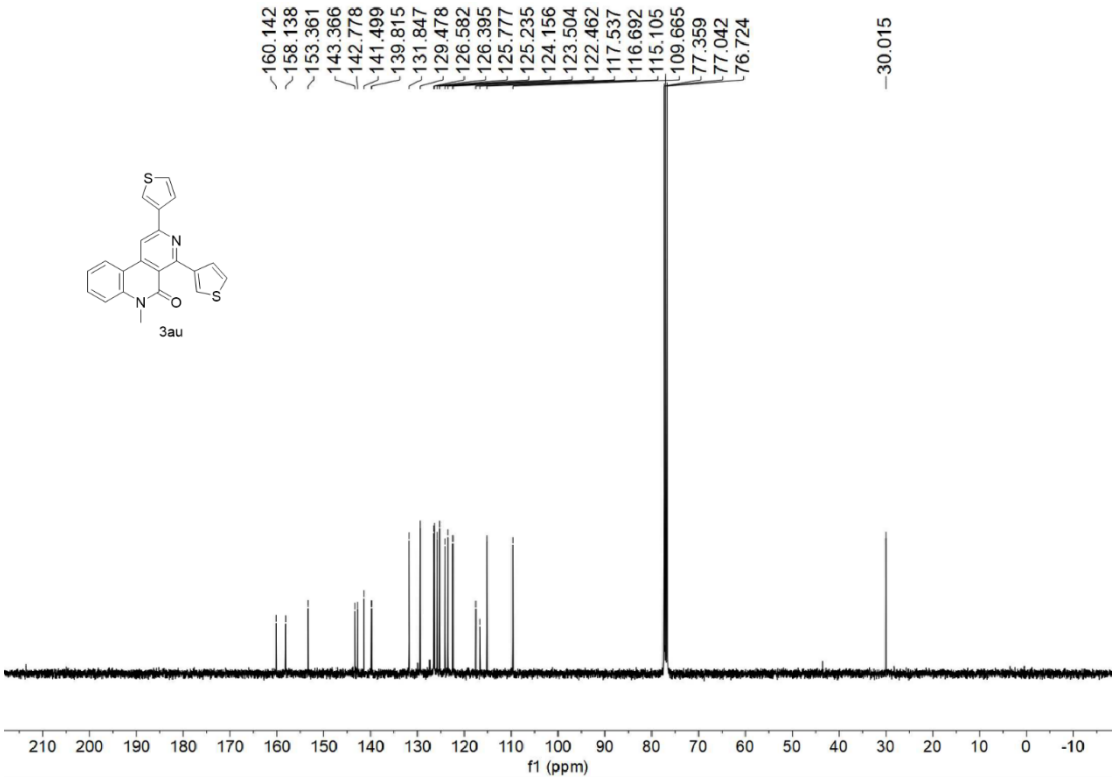
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3at**



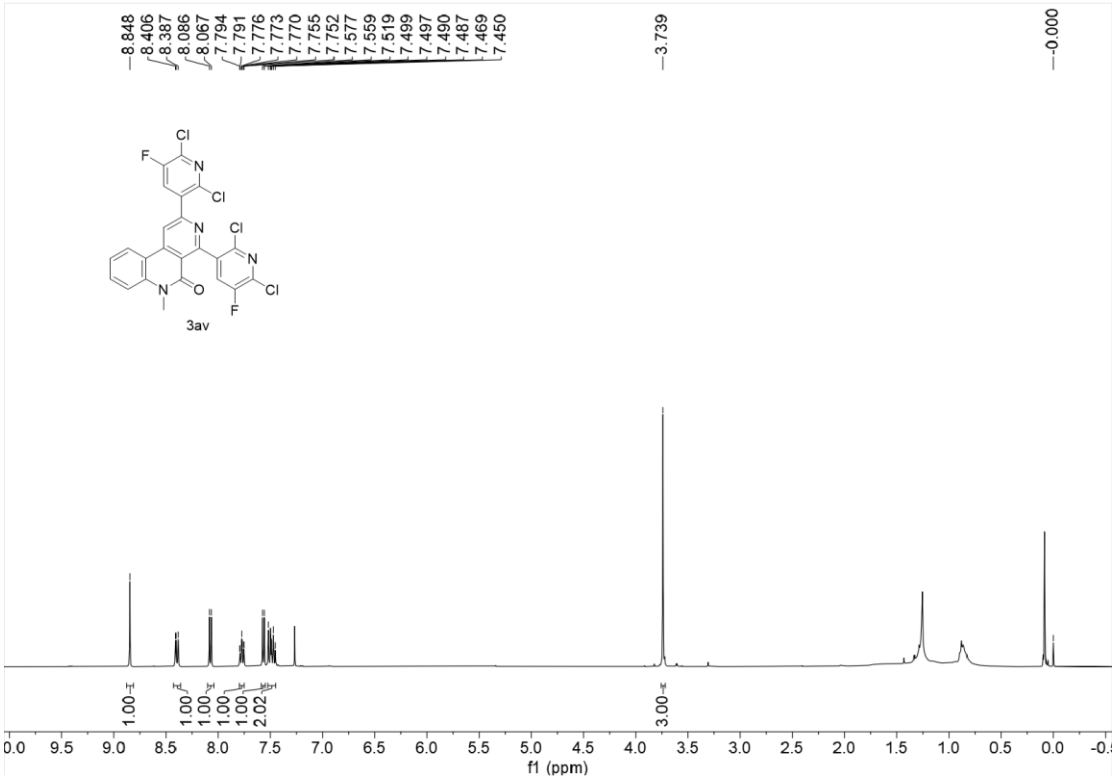
^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3au**



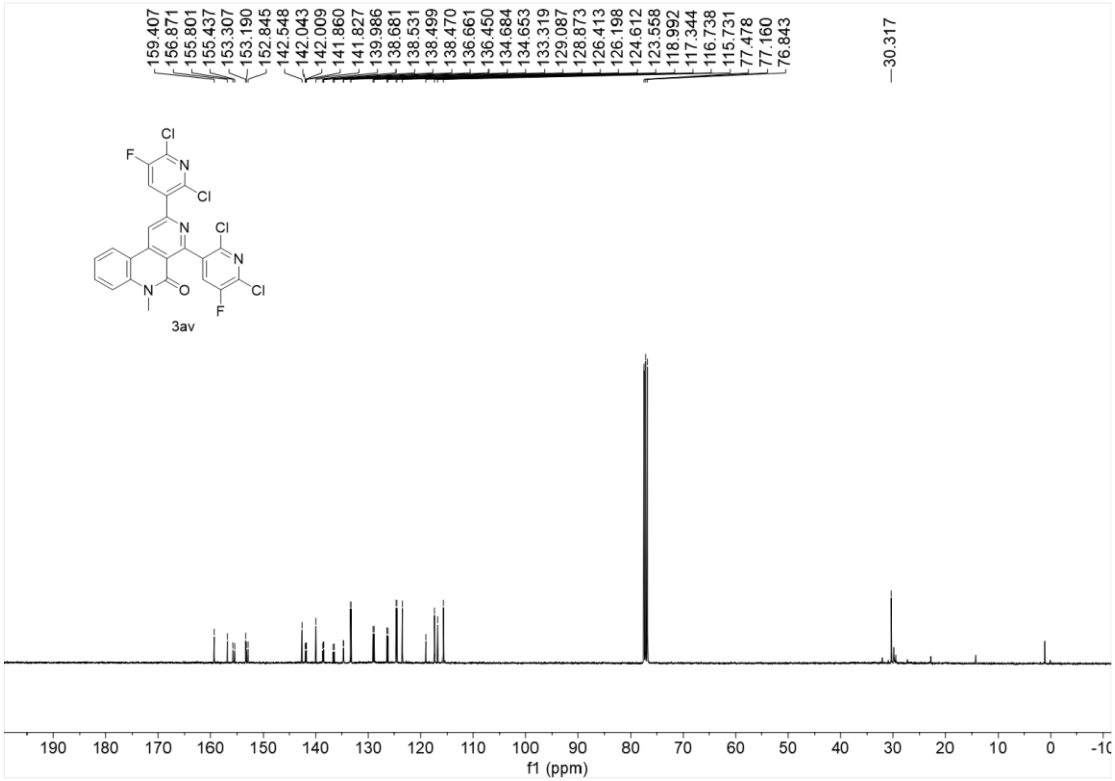
^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3au**



^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of **3av**



^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) of **3av**



^{19}F-NMR spectrum ($CDCl_3$, 377 MHz) of **3av**