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Co(III)-Catalyzed Regioselective Benzannulation of Substituted Pyridones with 1,6-Diynes *via* Dual C-H Bond Activation

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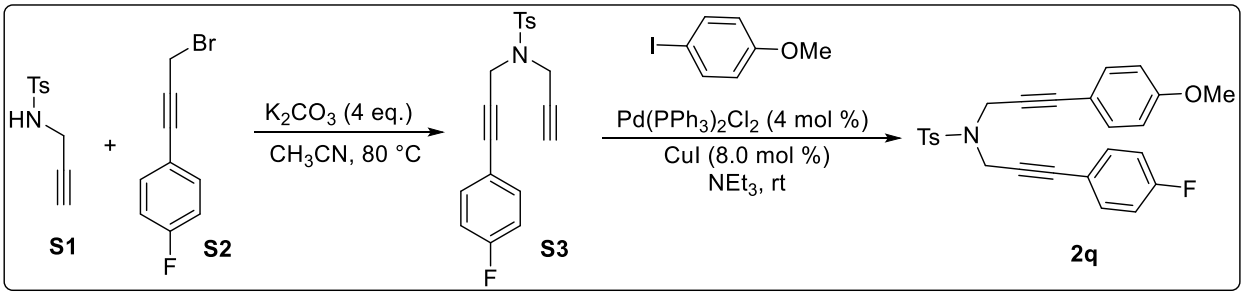
Electronic Supplementary Information (ESI)

Table of Contents

Experimental Section

General Information: All reactions were carried out under the N_2 atmosphere in flame-dried glassware. Syringes that were used to transfer anhydrous solvents or reagents were purged with nitrogen before use (three times). Dry solvents are used for the reaction. Column chromatographically purifications were performed using SiO_2 (120- 200 mesh ASTM) from Merck if not indicated otherwise. Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Starting Materials: Pyridones **1**[1], 1,6-diynes **2a-p**[2a-f], **2c**[2g] and $CoCp^*(CO)I_2$[3] were prepared according to literature procedures. Commercially available chemicals were purchased from Sigma-Aldrich and Spectrochem. Pvt. Ltd., India, and used without further purification.

General Procedure for the Synthesis of 2q



An oven-dried 100-mL two-neck round-bottom flask equipped with a magnetic stir bar was charged with a solution of alkyne **S1** (500 mg, 2.4 mmol, 1.0 equiv), anhydrous K_2CO_3 (1.3 g, 9.6 mmol, 4.0 equiv), alkyne **S2** and 15 mL acetonitrile solvent were added. The reaction mixture was allowed to stir at 80 °C on a preheated aluminum block for 12 hours. The mixture was allowed to cool to room temperature and was then filtered. The filtrate was concentrated under reduced pressure and purified through a silica gel column using hexane and ethyl acetate as the eluent to give the pure product S3 in 71% (819 mg).

An oven-dried Schlenk tube containing a Teflon-coated stirring bar was charged with $PdCl_2(PPh_3)_2$ (42 mg, 4 mol %) and CuI (23 mg, 8 mol %). The Schlenk tube was sealed, evacuated, and backfilled with N_2 (3 times). A solution of **S3** (500 mg, 1.5 mmol, 1.0 equiv) and 4-iodoanisole (421 mg, 1.2 mmol, 1 equiv) in 15 mL of Et_3N was injected. The reaction mixture

was stirred at room temperature for 6 hours. Then, the reaction mixture was diluted with EtOAc, filtered through Celite, and the filtrate was concentrated. The crude residue was purified through a silica gel column using hexane and ethyl acetate as the eluent to give the pure product **3q** in 58% (388 mg).

General Procedure for the Synthesis of 3

An oven-dried 15-mL pressure tube equipped with a magnetic stir bar was charged with the pyridone **1** (0.2 mmol, 1.0 equiv), 1,6-diyne **2** (0.24 mmol, 1.2 equiv), Cp*Co(CO)I_2 (0.02 mmol, 10 mol %), CuOAc(0.1 mmol, 50 mol %) and Ag_2CO_3 (0.24 mmol, 1.2 equiv). The sealed tube was high-vacuumed and refilled with N_2. Then $AgSbF_6$ (0.04 mmol, 20 mol %), and 2.0 ml TFE solvent were added to the reaction mixture after that screw cap was used to cover the pressure tube. The reaction mixture was allowed to stir at 110 °C on the preheated aluminum block for 24 h. Then the reaction mixture was diluted with CH_2Cl_2, filtered through celite, and the filtrate concentrated. The crude residue was purified through a silica gel column using hexane and ethyl acetate as eluent to give the pure product **3.**

General Procedure for the Synthesis of 3aa (1mmol scale).

An oven-dried 25-mL pressure tube equipped with a magnetic stir bar was charged with the pyridone **1a** (172 mg, 1.0 mmol, 1.0 equiv), 1,6-diyne **2a** (479 mg, 1.2 mmol, 1.2 equiv), Cp*Co(CO)I_2 (48 mg, 10 mol %, 0.1 mmol), CuOAc (62 mg, 0.5 mmol, 50 mol %) and Ag_2CO_3 (330 mg, 1.2 mmol, 1.2 equiv). The sealed tube was high-vacuumed and refilled with N_2. Then $AgSbF_6$ (69 mg, 0.2 mmol, 20 mol %), and 8.0 ml TFE solvent were added to the reaction mixture after that screw cap was used to cover the pressure tube. The reaction mixture was allowed to stir at 110 °C on the preheated aluminum block for 24 h. Then the reaction mixture was diluted with CH_2Cl_2, filtered through celite, and the filtrate concentrated. The crude residue was purified through a silica gel column using hexane and ethyl acetate as eluent to give the pure product **3aa** in 84% (478 mg).

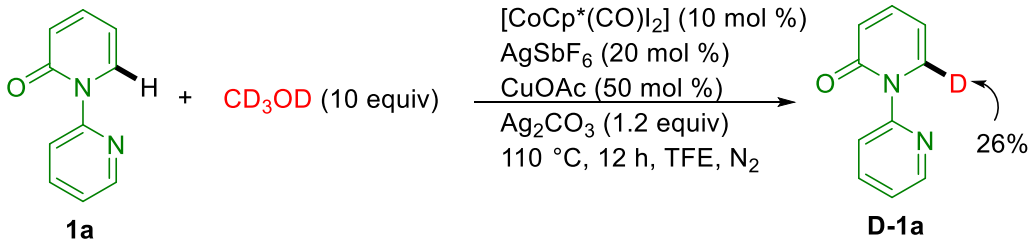
Table S1. Optimization of the Cyclization Reaction.[a]

Entry	catalyst	solvent	Additive-1 (20 mol %)	Additive-2 (50 mol %)	Oxidant	yield (%)[b]
1	Cp*Co(CO)I_2	TFE	$AgSbF_6$	-	CuOAc (2 equiv)	44
2	Cp*Co(CO)I_2	TFE	$AgSbF_6$	-	Ag_2CO_3 (1 equiv)	52
3	Cp*Co(CO)I_2	TFE	$AgSbF_6$	-	Ag_2O (1 equiv)	37
4	Cp*Co(CO)I_2	TFE	$AgSbF_6$	-	AgOAc (2 equiv)	28
5	Cp*Co(CO)I_2	TFE	$AgSbF_6$	-	$Cu(OAc)_2$ (2 equiv)	40
6	Cp*Co(CO)I_2	TFE	$AgSbF_6$	-	Ag_2CO_3 (1.2 equiv)	60
7	Cp*Co(CO)I_2	TFE	$AgSbF_6$	-	Ag_2CO_3 (1.5 equiv)	57
8	Cp*Co(CO)I_2	TFE	$AgSbF_6$	NaOAc (50 mol %)	Ag_2CO_3 (1.2 equiv)	55
9	Cp*Co(CO)I_2	TFE	$AgSbF_6$	$NaHCO_3$ (50 mol %)	Ag_2CO_3 (1.2 equiv)	62
10	**Cp*Co(CO)I_2**	**TFE**	**$AgSbF_6$**	**CuOAc (50 mol %)**	**Ag_2CO_3 (1.2 equiv)**	**96**
11	Cp*Co(CO)I_2	TFE	AgOTf	CuOAc (50 mol %)	Ag_2CO_3 (1.2 equiv)	81
12	Cp*Co(CO)I_2	TFE	$AgNTf_2$	CuOAc (50 mol %)	Ag_2CO_3 (1.2 equiv)	78
13	Cp*Co(CO)I_2	toluene	$AgSbF_6$	CuOAc (50 mol %)	Ag_2CO_3 (1.2 equiv)	trace
14	Cp*Co(CO)I_2	THF	$AgSbF_6$	CuOAc (50 mol %)	Ag_2CO_3 (1.2 equiv)	NR
15	Cp*Co(CO)I_2	HFIP	$AgSbF_6$	CuOAc (50 mol %)	Ag_2CO_3 (1.2 equiv)	78
16	Cp*Co(CO)I_2	MeOH	$AgSbF_6$	CuOAc (50 mol %)	Ag_2CO_3 (1.2 equiv)	NR
17	Cp*Co(CO)I_2	$ClCH_2CH_2Cl$	$AgSbF_6$	CuOAc (50 mol %)	Ag_2CO_3 (1.2 equiv)	40
18	-	TFE	$AgSbF_6$	CuOAc (50 mol %)	Ag_2CO_3 (1.2 equiv)	NR
19	Cp*Co(CO)I_2	TFE	$AgSbF_6$	CuOAc (50 mol %)	-	20

[a]All reactions were carried out using **1** (0.1 mmol, 1 equiv), **2** (0.12 mmol, 1.2 equiv), CoCp*COI_2 (0.01 mmol, 10 mol %), Additive-1 (20 mol %), Additive-2 (50 mol %), Oxidant in TFE (1 mL) under N_2 medium at 110 °C for 24 h. [b]Isolated yield of **3**.

Mechanistic Studies

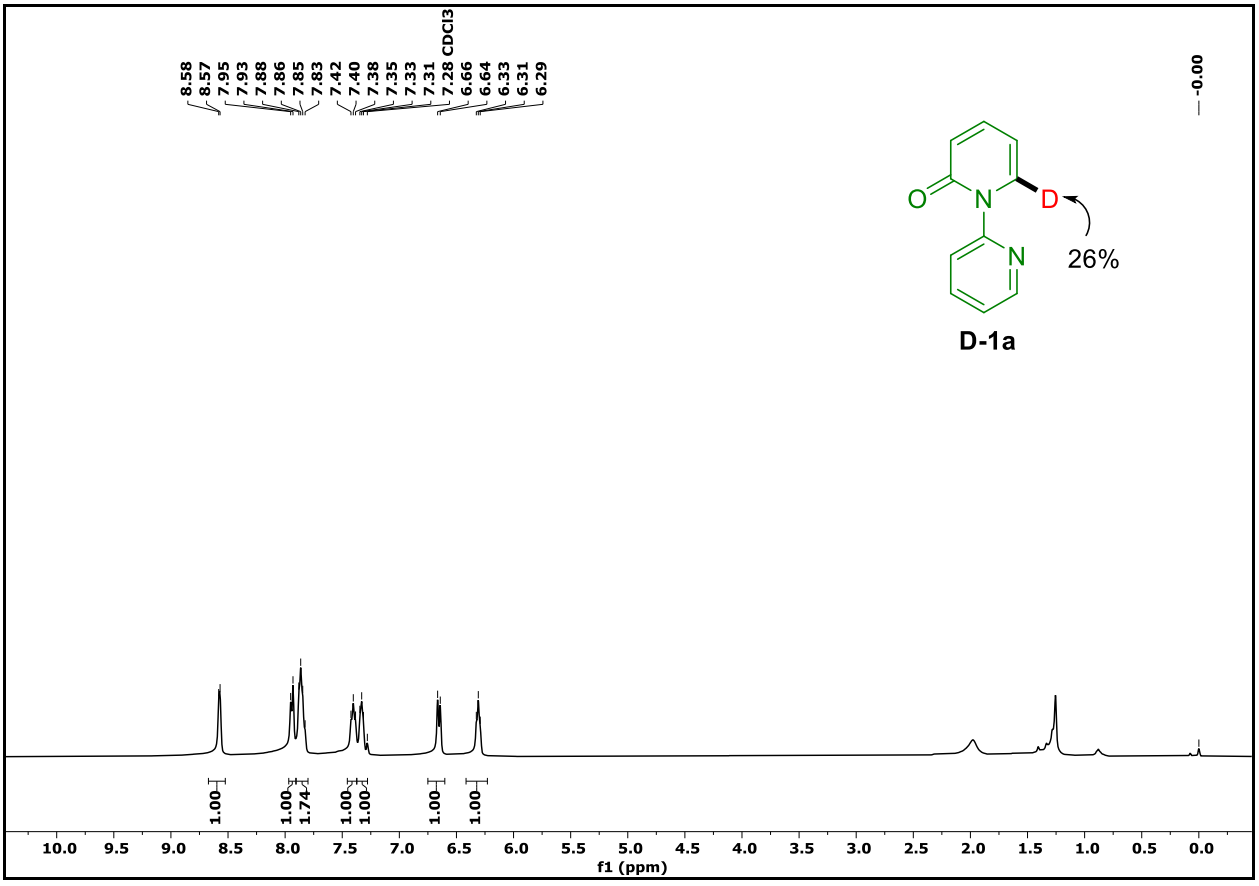
Deuterium Labelling Studies.



To an oven-dried sealed tube charged with a stirring bar under N_2 atmosphere, *2H*-[1,2'-bipyridin]-2-one **1a** (0.1 mmol), Cp*Co(CO)I_2 (10 mol %), $AgSbF_6$ (20 mol %), CuOAc (50 mol %), Ag_2CO_3 (1.2 equiv) were added and sealed. The sealed tube was high-vacuumed and

refilled with N_2. Then D_2O (10 equiv) was added to the reaction mixture followed by the addition of 1 ml TFE. The reaction mixture was vigorously stirred at 110 °C on a preheated aluminum block for 12 h. After 12 h, The reaction mixture was cooled to room temperature, diluted with ethyl acetate (EtOAc), and passed through a short celite pad. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography using 50% EtOAc/hexane mixture on silica gel (100-200 mesh) to give the deuterated product **D-1a** in 96% yield. The deuterium incorporation was calculated from ^{1}H NMR spectroscopy. In the reaction, 26% of deuterium incorporation was observed at C6 of *2H*-[1,2'- bipyridin]-2-one **1a**. This result reveals that the C-H bond activation is a reversible process.

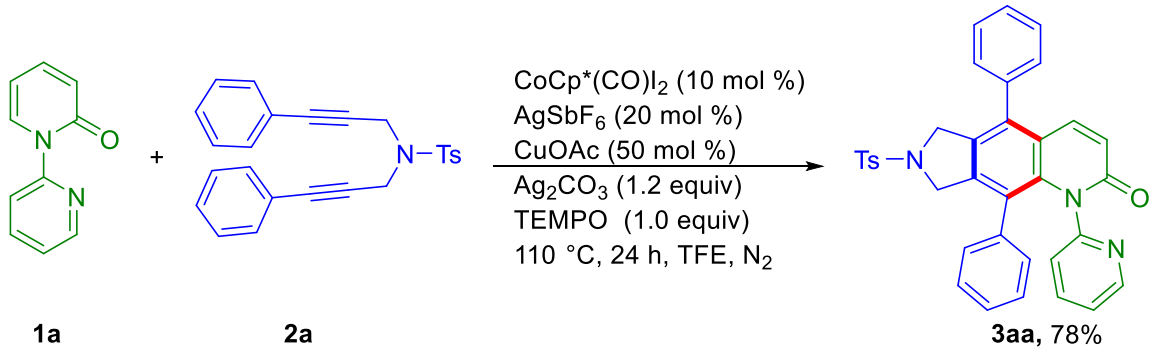
^{1}H NMR Spectra of Compound **D-1a.** (Solvent $CDCl_3$, 400 MHz)



Procedure for Radical Trapping Experiment.

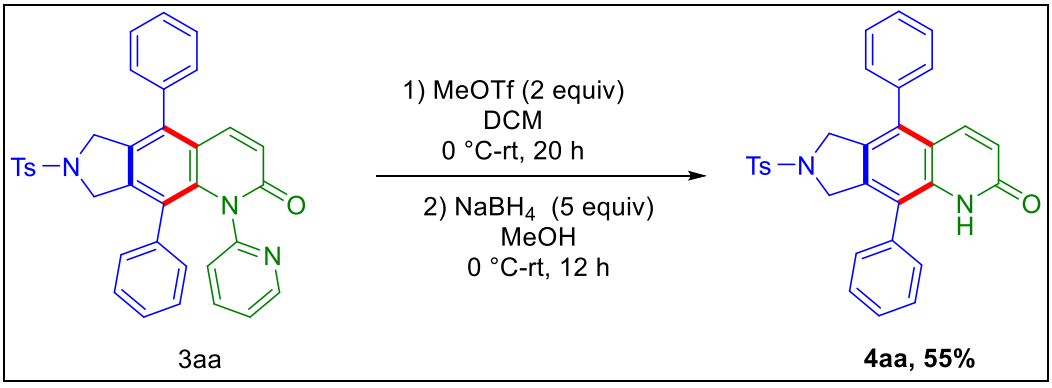
An oven-dried 15-mL pressure tube equipped with a magnetic stir bar was charged with the *2H*-[1,2'- bipyridin]-2-one **1a** (0.2 mmol, 1.0 equiv), 1,6 diyne **2a** (0.24 mmol, 1.2 equiv), Cp*Co(CO)I_2 (0.02 mmol, 10 mol %), CuOAc (0.1 mmol, 50 mol %), Ag_2CO_3 (0.24 mmol, 1.2 equiv) and TEMPO (0.2 mmol, 1.0 equiv). The sealed tube was high-vacuumed and refilled with

N_2. Then $AgSbF_6$ (0.04 mmol, 20 mol %), and 2.0 ml TFE solvent were added to the reaction mixture. a screw cap was used to cover the tube. Then, the reaction mixture was allowed to stir at 110 °C on the preheated aluminum block for 24 h. Then the reaction mixture was diluted with CH_2Cl_2, filtered through celite, and the filtrate concentrate. The crude residue was purified through a silica gel column using hexane and ethyl acetate (60%) as eluent to give products **3aa** in 78% yields.



Procedure for removal of directing group

An oven-dried 15-mL pressure tube equipped with a magnetic stir bar was charged with the **3aa** 57 mg (0.1 mmol, 1.0 equiv), CH_2Cl_2 (1 mL), and cooled to 0 °C. Then methyl trifluoromethanesulfonate, 33 mg (0.2 mmol, 2.0 equiv) was added dropwise to the solution. and the resulting solution was stirred for 20 h at room temperature under an N_2 atmosphere. Then, the solvent was removed under reduced pressure, the residue was dissolved in MeOH (1.0 mL), and $NaBH_4$ 19 mg (0.5 mmol, 5.0 equiv) was added in portions at 0 °C, and the solution was stirred at room temperature for 12 h. Then, the reaction mixture was diluted with CH_2Cl_2, filtered through celite, and the filtrate concentrate. The crude residue was purified through a silica gel column using hexane and ethyl acetate (50%) as eluent to give products **4aa** in 55% (27 mg) yields.

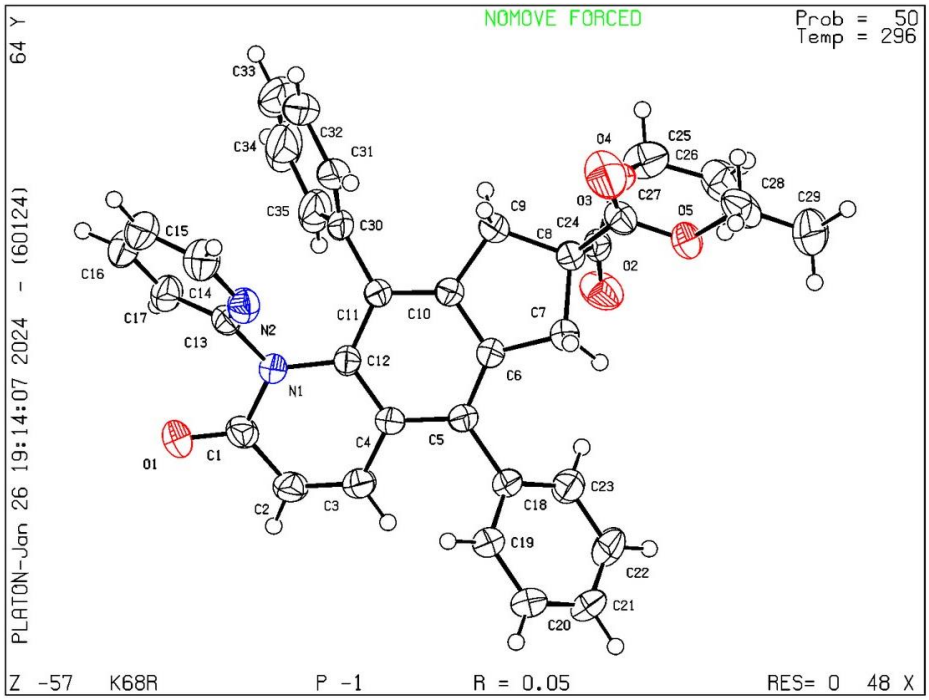


Sample Preparation for Crystal Growth of 3ab:

The compound **3ab** was dissolved in 1,2-dichloromethane (DCM) and methanol in a beaker and kept for slow evaporation at room temperature. The formation of crystals was observed after seven days. The single crystals were then subjected to X-ray diffraction analysis.

Single-crystal data were collected on a Bruker Axs Kappa Apex2 diffractometer, with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation at 293 K. The data was integrated using SAINT PLUS and absorption correction was done using the multi-scan absorption correction method (SADABS). The structure was solved by the direct method (SHELXS-97) as well as by using SHELXT-2014 and refined using the SHELXL-2018/3 program and WinGX v1.70.01 programs packages. All non-hydrogen atoms were refined anisotropically. These data were deposited with Cambridge Crystallographic Data Centre with the following numbers: **CCDC 2328534**

ORTEP Diagram of Compounds 3ab (CCDC No. 2328534).



Crystal data and structure refinement for **3ab**.

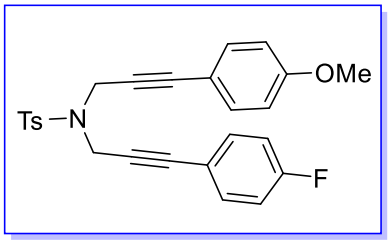
Identification code	3ab	
Empirical formula	$C_{35}H_{30}N_2O_5$	
Formula weight	558.61	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.1034(4) Å	a= 70.9583(19)°.
	b = 11.1882(5) Å	b= 87.9029(19)°.
	c = 12.5867(5) Å	g = 71.6281(18)°.
Volume	1398.89(10) $Å^3$	
Z	2	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	0.089 mm^{-1}	
F(000)	588	
Crystal size	0.230 x 0.150 x 0.120 mm^3	
Theta range for data collection	1.938 to 25.000°.	
Index ranges	-13<=h<=13, -13<=k<=13, -14<=l<=14	
Reflections collected	18573	
Independent reflections	4922 [R(int) = 0.0455]	
Completeness to theta	25.000° 99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4922 / 15 / 381	
Goodness-of-fit on F^2	1.136	
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.1074	
R indices (all data)	R1 = 0.0886, wR2 = 0.1245	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.257 and -0.290 $e.Å^{-3}$	

References

1. (a) Mohanty, S. R.; Prusty, N.; Gupta, L.; Biswal, P.; Ravikumar, P. C. Cobalt(III)-Catalyzed C-6 Alkenylation of 2-Pyridones by Using Terminal Alkyne with High Regioselectivity. *J. Org. Chem.* **2021**, *86*, *14*, 9444–9454.
2. (a) Bao, M.; Lu, W.; Su, H.; Qiu, L.; Xu, X. A convergent formal [4 + 2] cycloaddition of 1,6-diynes and benzyl azides: construction of spiro-polyheterocycles. *Org. Biomol. Chem.* **2018**, *16*, 3258– 3265. (b) Bai, L.; Yuan, Y.; Liu, J.; Wu, J.; Han, L.; Wang, H.; Wang, Y.; Luan, X. Palladium(0)-Catalyzed Intermolecular Carbocyclization of (1,*n*)-Diynes and Bromophenols: An Efficient Route to Tricyclic Scaffolds. *Angew. Chem., Int. Ed.* **2016**, *55*, 6946– 6950. (c) Richard, V.; Ipouck, M.; Mérel, D. S.; Gaillard, S.; Whitby, R. J.; Witulski, B.; Renaud, J. L. Iron(ii)-catalysed [2+2+2] cycloaddition for pyridine ring construction. *Chem. Commun.* **2014**, *50*, 593– 595. (d) Yamashita, K.; Yamamoto, Y.; Nishiyama, H. Ruthenium-Catalyzed Transfer Oxygenative Cyclization of α,ω-Diynes: Unprecedented [2 + 2 + 1] Route to Bicyclic Furans via Ruthenacyclopentatriene. *J. Am. Chem. Soc.* **2012**, *134*, 7660– 7663. (e) Wilking, M.; Mück-Lichtenfeld, C.; Daniliuc, C. G.; Hennecke, U. Enantioselective, Desymmetrizing Bromolactonization of Alkynes. *J. Am. Chem. Soc.* **2013**, *135*, 8133– 8136. (f) Hu, Y.; Yao, H.; Sun, Y.; Wan, J.; Lin, X.; Zhu, T. Efficient Activation of Aromatic C–H Bonds for Fused Polyaromatic Hydrocarbon Construction. *Chem. Eur. J.* **2010**, *16*, 7635– 7641. (g) Akhmetov, V.; Feofanov, M.; Sharapa, D. I.; Amsharov, K. Alumina-Mediated π-Activation of Alkynes. *J. Am. Chem. Soc.* **2021**, *143*, 15420– 15426.
3. Sun, B.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Adv. Synth. Catal*. **2014**, *356*, 1491.

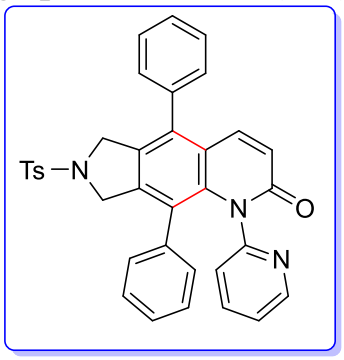
Spectral Data of all Compounds:

N-(3-(4-fluorophenyl)prop-2-yn-1-yl)-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamid (2q).



Brown semi-solid; eluent (10% ethyl acetate in hexane). The reaction scale is 1.5 mmol (**S3**), 388 mg was isolated and the yield is 58%.**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.09 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.85 (t, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 4.33 (s, 4H), 3.69 (s, 3H), 2.23 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 163.44, 161.45, 159.68, 143.68, 135.41, 133.55, 133.48, 133.05, 129.47, 127.91, 118.27, 118.24, 115.44, 115.27, 114.15, 113.73, 85.70, 84.53, 81.52, 80.08, 77.26, 77.00, 76.75, 55.19, 37.54, 37.31, 21.33.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}FNO_3SH$ 448.1377; Found 448.1391.

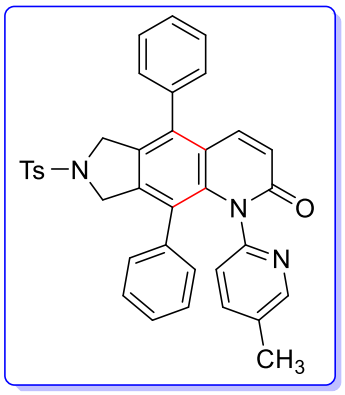
5,9-Diphenyl-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3aa).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 109 mg was isolated and the yield is 96%. Mp: 246–247 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 (d, *J* = 5.3 Hz, 1H), 7.51 (dd, *J* = 9.0, 6.1 Hz, 3H), 7.44 (p, 3H), 7.24 – 7.13 (m, 5H), 7.01 (dt, *J* = 20.0, 7.5 Hz, 2H), 6.93 – 6.82 (m, 2H), 6.75 (dd, *J* = 11.9, 6.8 Hz, 2H), 6.47 (d, *J* = 9.8 Hz, 2H), 4.44 – 4.22 (m, 3H), 3.91 (d, *J* = 15.0 Hz, 1H), 2.32 (s, 3H). **^{3}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 163.2, 152.8, 148.6, 143.8, 139.7, 139.2, 138.4, 137.3, 136.4, 136.0, 134.9, 133.2, 130.2, 129.8, 129.3, 128.9, 128.6, 128.4, 127.8, 127.3, 126.9, 125.9, 122.6, 121.3, 120.8, 54.3, 53.5, 21.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{27}N_3O_3SH$ 570.1807; Found 570.1832.

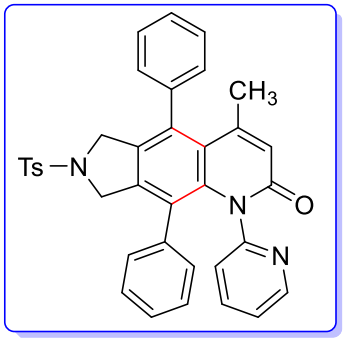
1-(5-Methylpyridin-2-yl)-5,9-diphenyl-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3ba).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1b**), 108 mg was isolated and the yield is 93%. Mp: 248–249 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (s, 1H), 7.64 – 7.47 (m, 6H), 7.28 (d, *J* = 8.3 Hz, 4H), 7.10 (d, *J* = 5.8 Hz, 2H), 6.99 (t, *J* = 7.6 Hz, 2H), 6.79 (d, *J* = 4.9 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.55 (t, *J* = 10.0 Hz, 2H), 4.47 (d, *J* = 13.6 Hz, 1H), 4.41 – 4.21 (m, 2H), 3.98 (d, *J* = 14.8 Hz, 1H), 2.41 (s, 3H), 2.18 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 163.3, 150.2, 148.6, 143.8, 139.8, 139.3, 138.4, 137.3, 137.1, 136.1, 135.0, 133.1, 132.5, 130.0, 129.8, 129.3, 129.0, 128.9, 128.8, 128.4, 128.1, 127.7, 127.3, 126.6, 125.6, 121.3, 120.8, 54.3, 53.5, 21.5, 17.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{29}N_3O_3SH$ 584.2002; Found 584.1990.

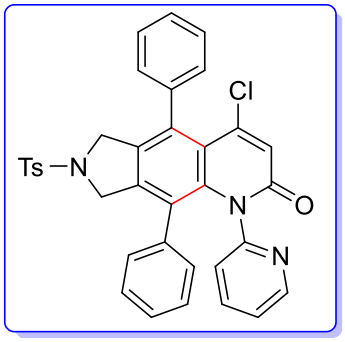
4-Methyl-5,9-diphenyl-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3ca).



Yellow semi-solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1c**), 103 mg was isolated and the yield is 88%. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (d, *J* = 4.8 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 4.5 Hz, 3H), 7.31 – 7.04 (m, 7H), 6.89 (dt, *J* = 26.0, 9.4 Hz, 3H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.44 (d, *J* = 14.8 Hz, 2H), 4.37 (dd, *J* = 30.8, 14.4 Hz, 2H), 4.14 (d, *J* = 14.0 Hz, 1H), 3.99 (d, *J* = 14.8 Hz, 1H), 2.41 (s, 3H), 1.77 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 162.5, 153.3, 149.7, 148.1, 143.7, 140.4, 140.0, 138.3, 137.9, 136.1, 134.9, 133.3, 132.0, 128.8, 128.6, 128.5, 128.2, 127.9, 127.4, 127.3, 126.9, 126.8, 123.4, 122.1, 122.0, 54.3, 54.0, 25.0, 21.4.

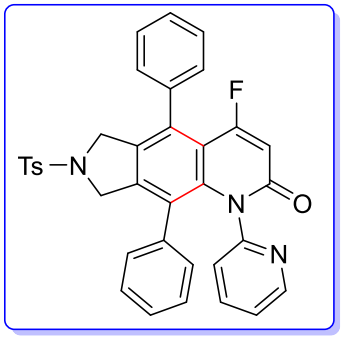
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{29}N_3O_3SH$ 584.2002; Found 584.2019.

4-Chloro-5,9-diphenyl-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3da).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1d**), 111 mg was isolated and the yield is 92%. Mp: 165–166 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (d, *J* = 5.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.44 (q, *J* = 3.0 Hz, 3H), 7.29 – 7.26 (m, 2H), 7.21 (tt, *J* = 4.5, 2.6 Hz, 3H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.98 – 6.90 (m, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 6.45 (d, *J* = 7.4 Hz, 1H), 4.47 – 4.30 (m, 2H), 4.18 (d, *J* = 14.1 Hz, 1H), 3.99 (d, *J* = 15.0 Hz, 1H), 2.41 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 161.2, 152.7, 148.2, 145.8, 143.8, 140.4, 140.0, 138.6, 137.3, 136.4, 134.9, 133.2, 133.1, 129.8, 128.8, 128.5, 128.3, 128.0, 127.35, 127.33, 127.1, 127.0, 123.5, 122.5, 119.3, 54.3, 54.0, 21.5.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{26}ClN_3O_3SH$ 604.1456; Found 604.1445.

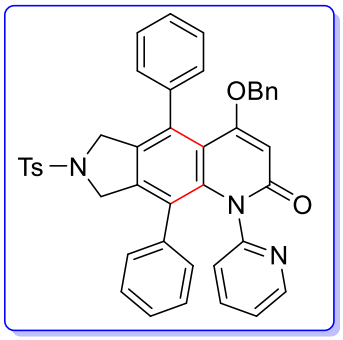
4-Fluoro-5,9-diphenyl-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3ea).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1e**), 105 mg was isolated and the yield is 89%. Mp: 169–170 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26 (d, *J* = 4.7 Hz, 1H), 7.56 (dd, *J* = 18.1, 8.2 Hz, 5H), 7.29 (dt, *J* = 16.6, 9.0 Hz, 6H), 7.10 (dt, *J* = 20.6, 7.8 Hz, 2H), 6.96 (q, *J* = 6.3 Hz, 2H), 6.84 (dd, *J* = 21.7, 7.7 Hz, 2H), 6.54 (d, *J* = 7.6 Hz, 1H), 4.41 (dt, *J* = 27.5, 14.1 Hz, 3H), 3.99 (d, *J* = 14.8 Hz, 1H), 2.41 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 157.4, 157.2, 151.9, 151.1, 148.6, 143.8, 138.9, 138.8, 136.9, 136.7, 136.3, 135.7, 134.7, 134.6, 133.0, 131.0, 129.8, 129.2, 129.1, 128.8, 128.7, 128.6, 127.9, 127.8, 127.3, 127.1, 127.0, 126.1, 123.0, 119.51, 119.45, 117.8, 117.6, 54.2, 53.5, 21.4. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -128.40 (s, 1F).

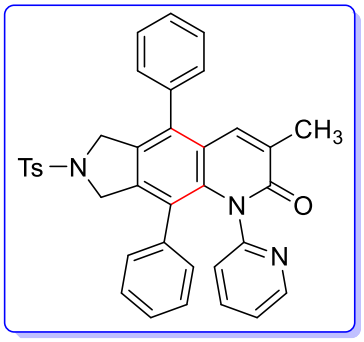
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{26}FN_3O_3SH$ 588.1752; Found 588.1730.

4-(Benzyloxy)-5,9-diphenyl-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3fa).



Yellow Semi-solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1f**), 116 mg was isolated, and the yield is 86%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.24 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.12 (m, 9H), 7.06 (q, *J* = 7.1, 6.7 Hz, 4H), 6.98 – 6.75 (m, 6H), 6.46 (s, 1H), 5.97 (s, 1H), 4.71 (s, 2H), 4.37 (d, *J* = 14.3 Hz, 1H), 4.25 (d, *J* = 12.5 Hz, 1H), 4.14 (d, *J* = 12.9 Hz, 1H), 3.97 (d, *J* = 14.8 Hz, 1H), 2.40 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 164.6, 164.4, 153.4, 143.7, 140.4, 140.3, 139.3, 137.7, 136.1, 134.1, 133.9, 133.4, 132.2, 129.8, 128.9, 128.6, 128.3, 128.1, 128.0, 127.8, 127.8, 127.3, 126.94, 126.90, 126.6, 117.1, 97.7, 71.0, 54.3, 54.0, 21.5.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{42}H_{33}N_3O_4SH$ 676.2265; Found 676.2272.

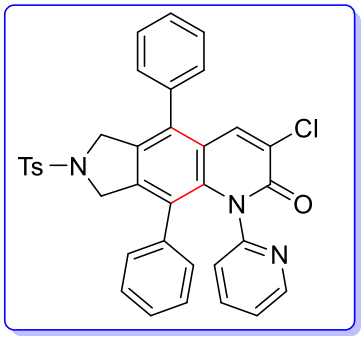
3-Methyl-5,9-diphenyl-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3ga).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1g**), 112 mg was isolated and the yield is 96%. Mp: 170–171 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.25 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.48 (m, 3H), 7.44 (d, *J* = 1.4 Hz, 1H), 7.30 – 7.26 (m, 4H), 7.25 – 7.21 (m, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.08 – 7.04 (m, 1H), 7.00 – 6.93 (m, 1H), 6.91 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.82 (d, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 1H), 4.46 (d, *J* = 13.5 Hz, 1H), 4.39 – 4.27 (m, 2H), 3.99 (d, *J* = 14.6 Hz, 1H),

2.41 (s, 3H), 2.09 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 163.9, 153.1, 148.5, 143.7, 138.3, 138.2, 137.4, 136.4, 136.3, 134.9, 134.0, 133.3, 130.0, 129.8, 129.7, 129.4, 129.0, 128.95, 128.94, 128.5, 128.3, 127.7, 127.3, 126.8, 125.5, 122.5, 120.9, 54.3, 53.6, 21.4, 17.2.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{29}N_3O_3SH$ 584.2002; Found 584.1999.

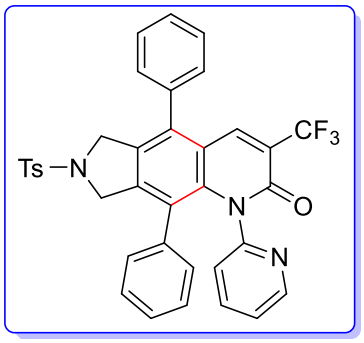
3-Chloro-5,9-diphenyl-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3ha).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1h**), 100 mg was isolated and the yield is 83%. Mp: 250–251 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (d, *J* = 4.7 Hz, 1H), 7.78 (s, 1H), 7.56 (q, *J* = 8.6 Hz, 5H), 7.31 – 7.23 (m, 5H), 7.09 (q, *J* = 9.8, 7.4 Hz, 2H), 6.95 (d, *J* = 6.8 Hz, 2H), 6.84 (dd, *J* = 20.0, 7.6 Hz, 2H), 6.53 (d, *J* = 7.7 Hz, 1H), 4.51 – 4.29 (m, 3H), 3.99 (d, *J* = 14.9 Hz, 1H), 2.41 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 159.3, 152.6, 148.5, 143.9, 139.9, 138.1, 136.9, 136.6, 135.8, 135.6, 134.4, 133.1, 130.9, 129.8, 129.3, 129.2, 129.1, 128.90, 128.86, 128.7, 127.9, 127.4, 127.2, 127.1, 126.6, 126.0, 122.9, 120.3, 54.3, 53.5, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{26}ClN_3O_3SH$ 604.1456; Found 604.1466.

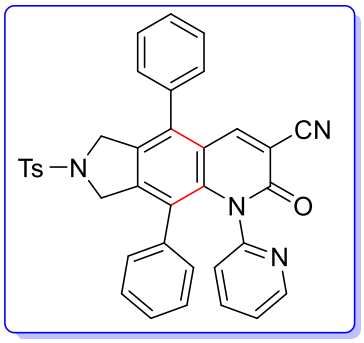
5,9-Diphenyl-1-(pyridin-2-yl)-7-tosyl-3-(trifluoromethyl)-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3ia).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1i**), 116 mg was isolated and the yield is 91%. Mp: 155–156 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 (d, *J* = 4.9 Hz, 1H), 7.94 (s, 1H), 7.58 – 7.41 (m, 5H), 7.18 (dt, *J* = 15.1, 7.8 Hz, 5H), 7.01 (dt, *J* = 14.6, 7.5 Hz, 2H), 6.93 – 6.83 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 6.46 (d, *J* =

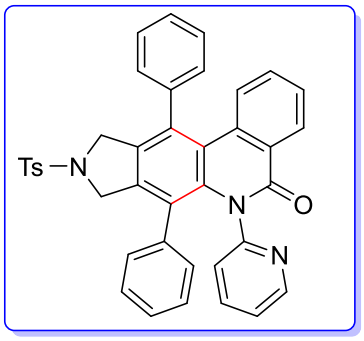
7.7 Hz, 1H), 4.57 – 4.24 (m, 3H), 3.93 (d, *J* = 15.3 Hz, 1H), 2.32 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 158.9, 151.9, 148.6, 143.9, 142.5, 140.3, 138.3, 138.2, 136.6, 136.5, 135.0, 133.1, 131.1, 129.8, 129.3, 129.2, 129.0, 128.83, 128.80, 128.7, 127.9, 127.4, 127.32, 127.27, 126.1, 123.0, 118.6, 54.3, 53.4, 21.4.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{26}F_3N_3O_3SH$ 638.1720; Found 638.1708.

2-Oxo-5,9-diphenyl-1-(pyridin-2-yl)-7-tosyl-2,6,7,8-tetrahydro-1*H*-pyrrolo[3,4-*g*]quinoline-3-carbonitrile (3ja).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1j**), 48 mg was isolated and the yield is 40%. Mp: 232–233 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.25 (d, *J* = 4.8 Hz, 1H), 8.11 (s, 1H), 7.58 (d, *J* = 6.9 Hz, 5H), 7.31 – 7.24 (m, 5H), 7.10 (dd, *J* = 11.1, 3.8 Hz, 2H), 6.97 (t, *J* = 6.4 Hz, 2H), 6.83 (dd, *J* = 15.5, 7.7 Hz, 2H), 6.52 (d, *J* = 7.7 Hz, 1H), 4.53 – 4.31 (m, 3H), 4.00 (d, *J* = 15.5 Hz, 1H), 2.41 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 159.5, 151.6, 148.7, 146.9, 144.0, 143.8, 140.4, 136.9, 136.4, 136.2, 134.6, 133.0, 131.6, 129.9, 129.4, 129.33, 129.32, 129.2, 128.8, 128.76, 128.72, 128.68, 128.1, 127.5, 127.4, 127.1, 126.5, 123.3, 119.5, 114.7, 106.8, 54.3, 53.3, 21.5.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{26}N_4O_3SH$ 595.1798; Found 595.1811.

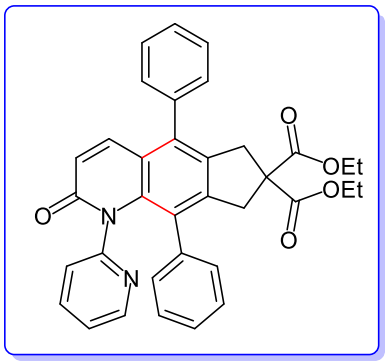
7,11-diphenyl-6-(pyridin-2-yl)-9-tosyl-6,8,9,10-tetrahydro-5*H*-pyrrolo[3,4-*b*]phenanthridin-5-one (3ka).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1k**), 117 mg was isolated and the yield is 94%. Mp: 247–248 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.40 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 4.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.57 – 7.48 (m, 3H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.16 (m, 7H), 7.09 (t, *J* = 7.1 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 3H), 6.49 (d, *J* =

12.2 Hz, 1H), 4.55 – 4.27 (m, 3H), 4.08 (d, *J* = 19.6 Hz, 1H), 2.40 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 162.8, 154.0, 147.9, 143.7, 140.3, 138.1, 138.0, 137.1, 136.1, 134.5, 134.2, 133.2, 132.4, 131.8, 129.83, 129.77, 128.6, 128.2, 127.60, 127.58, 127.4, 127.3, 127.1, 126.8, 126.7, 121.8, 120.7, 54.2, 21.4.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{29}N_3O_3SH$ 620.2002; Found 620.2025.

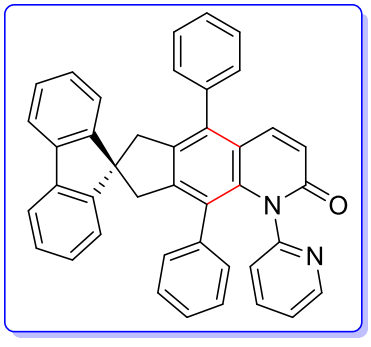
Diethyl 2-oxo-5,9-diphenyl-1-(pyridin-2-yl)-1,2,6,8-tetrahydro-7*H*-cyclopenta[*g*]quinoline-7,7-dicarboxylate (3ab).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 88 mg was isolated and the yield is 79%. Mp: 178–179 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.30 (s, 1H), 7.64 (d, *J* = 10.2 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 6.7 Hz, 2H), 7.24 (t, *J* = 9.0 Hz, 1H), 7.14 – 7.08 (m, 1H), 7.04 (d, *J* = 7.1 Hz, 1H), 6.90 (dt, *J* = 27.5, 8.8 Hz, 4H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 9.9 Hz, 1H), 4.09 (dd, *J* = 25.3, 8.2 Hz, 4H), 3.52 – 3.32 (m, 3H), 2.91 (d, *J* = 17.7 Hz, 1H), 1.15 (d, *J* = 24.9 Hz, 6H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 171.2, 170.9, 163.5, 153.0, 148.5, 143.9, 139.0, 138.8, 138.4, 137.2, 136.3, 135.9, 134.0, 129.9, 129.8, 129.3, 129.2, 128.7, 128.6, 128.3, 127.8, 127.5, 127.4, 127.1, 126.3, 122.4, 120.3, 120.3, 61.7, 61.6, 59.7, 41.0, 39.8, 13.8.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{30}N_2O_5H$ 559.2227; Found 559.2216.

5,9-Diphenyl-1-(pyridin-2-yl)-6,8-dihydrospiro[cyclopenta[*g*]quinoline-7,9'-fluoren]-2(1*H*)-one (3ac).

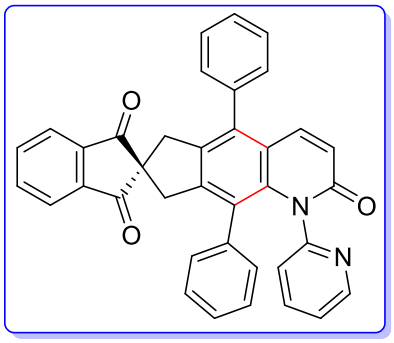


White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 98 mg was isolated and the yield is 87%. Mp: 266–167 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (d, *J* =

4.9 Hz, 1H), 7.67 (d, *J* = 9.8 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.29 (dd, *J* = 23.6, 7.4 Hz, 6H), 7.16 (dt, *J* = 15.5, 7.8 Hz, 4H), 7.08 – 6.97 (m, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.82 (td, *J* = 8.1, 3.7 Hz, 4H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.53 (d, *J* = 9.7 Hz, 2H), 3.19 (dt, *J* = 49.3, 16.2 Hz, 3H), 2.66 (d, *J* = 17.1 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 163.6, 161.7, 153.2, 152.2, 151.2, 148.6, 146.9, 139.5, 139.3, 139.0, 138.8, 137.4, 136.8, 136.3, 136.2, 129.9, 129.4, 129.2, 128.60, 128.56, 128.5, 128.1, 127.7, 127.6, 127.6, 127.5, 127.3, 126.1, 122.5, 122.3, 121.7, 120.4, 120.3, 119.7, 56.7, 45.9, 44.7.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{41}H_{28}N_2OH$ 565.2274; Found 565.2282.

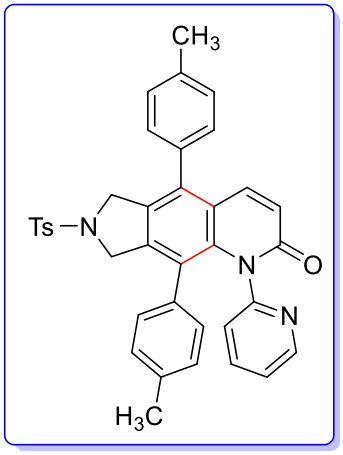
5,9-Diphenyl-1-(pyridin-2-yl)-6,8-dihydrospiro[cyclopenta[*g*]quinoline-7,2'-indene]-1',2,3'(1*H*)-trione (3ad).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 101 mg was isolated and the yield is 93%. Mp: 171–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 5.0 Hz, 1H), 7.79 (dd, *J* = 11.8, 6.0 Hz, 2H), 7.72 – 7.64 (m, 2H), 7.59 (d, *J* = 9.8 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.29 (q, *J* = 8.5, 8.0 Hz, 3H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.84 (dp, *J* = 21.2, 7.0 Hz, 5H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 9.8 Hz, 1H), 3.16 – 2.97 (m, 3H), 2.60 (d, *J* = 17.4 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 202.3, 202.2, 163.5, 152.6, 148.2, 144.6, 141.1, 141.0, 139.2, 138.8, 138.2, 137.1, 136.8, 135.9, 135.8, 134.5, 129.7, 129.6, 129.3, 129.2, 128.6, 128.5, 128.1, 127.9, 127.8, 127.6, 127.4, 126.9, 126.3, 123.4, 122.7, 120.5, 120.1, 57.9, 41.1, 40.2.

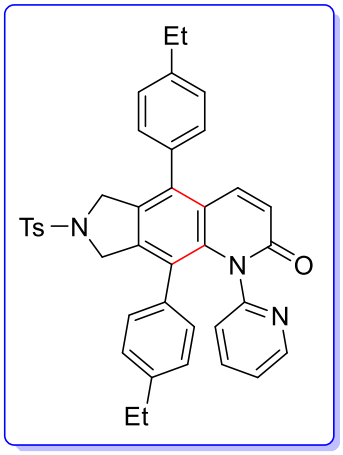
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{24}N_2O_3H$ 545.1860; Found 545.1859.

1-(Pyridin-2-yl)-5,9-di-p-tolyl-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3ae).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 100 mg was isolated and the yield is 84%. Mp: 181–182 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (d, *J* = 4.8 Hz, 1H), 7.63 (d, *J* = 10.0 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.25 (dd, *J* = 17.3, 8.1 Hz, 3H), 7.14 (d, *J* = 7.5 Hz, 2H), 6.92 (q, *J* = 5.6, 4.7 Hz, 2H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 9.8 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 1H), 4.51 – 4.29 (m, 3H), 4.00 (d, *J* = 14.8 Hz, 1H), 2.47 (s, 3H), 2.41 (s, 3H), 2.26 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 163.4, 152.9, 148.5, 143.7, 139.8, 139.4, 138.6, 138.2, 136.6, 136.2, 134.9, 134.3, 133.2, 133.0, 130.2, 129.8, 129.7, 129.5, 129.3, 129.2, 128.8, 128.8, 128.7, 128.4, 127.3, 125.8, 122.5, 121.1, 120.9, 54.3, 53.6, 21.5, 21.3, 21.0.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{31}N_3O_3SH$ 598.2159; Found 598.2130.

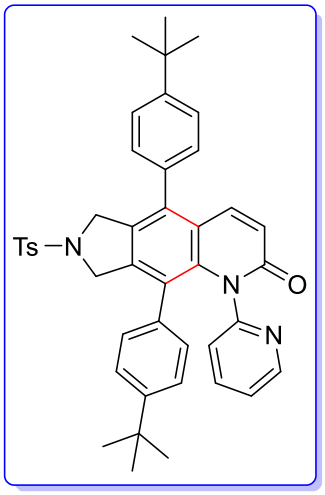
5,9-Bis(4-Ethylphenyl)-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3af).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 114 mg was isolated and the yield is 91%. Mp: 168–169 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (d, *J* = 4.9 Hz, 1H), 7.67 – 7.56 (m, 3H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.19 (dd, *J* = 18.3, 7.6 Hz, 3H), 6.96 – 6.88 (m, 2H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 9.8 Hz, 1H), 6.44 (d, *J* = 7.9 Hz, 1H), 4.53 – 4.30 (m, 3H), 4.02 (d, *J* = 14.8 Hz, 1H), 2.77 (q, *J* = 7.7 Hz, 2H), 2.55 (q, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.38 – 1.31 (m, 3H), 1.22 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 163.4, 152.9, 148.5,

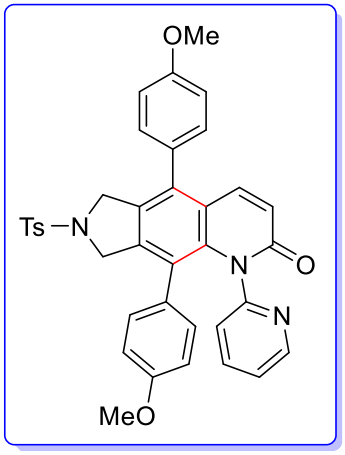
144.4, 143.7, 142.9, 139.8, 139.4, 138.6, 136.3, 134.9, 134.5, 133.25, 133.18, 130.2, 129.8, 129.3, 128.89, 128.87, 128.86, 128.4, 128.3, 128.1, 127.4, 127.35, 127.28, 125.8, 122.5, 121.1, 120.9, 54.4, 53.6, 28.6, 28.5, 21.5, 15.8, 15.4.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{35}N_3O_3SH$ 626.2472; Found 626.2499.

5,9-Bis(4-(*tert*-butyl)phenyl)-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3ag).



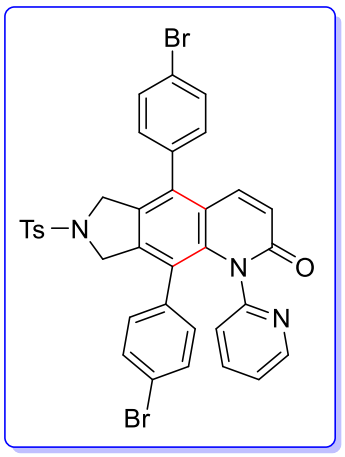
White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 113 mg was isolated and the yield is 83%. Mp: 174–175 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.23 (d, *J* = 4.9 Hz, 1H), 7.63 (ddd, *J* = 14.6, 9.0, 1.8 Hz, 3H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.19 (tt, *J* = 7.8, 3.7 Hz, 3H), 7.11 (d, *J* = 8.1 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.88 (t, *J* = 6.2 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.54 (dd, *J* = 9.9, 1.8 Hz, 1H), 6.46 (d, *J* = 8.2 Hz, 1H), 4.52 (d, *J* = 13.6 Hz, 1H), 4.43 – 4.25 (m, 2H), 4.06 (d, *J* = 14.8 Hz, 1H), 2.41 (s, 3H), 1.42 (s, 9H), 1.29 (s, 9H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 163.3, 152.8, 151.2, 149.5, 148.5, 143.7, 139.7, 139.3, 138.7, 136.2, 134.9, 134.1, 133.1, 132.9, 130.2, 129.7, 129.0, 128.6, 128.5, 127.4, 127.3, 125.8, 125.7, 125.6, 125.5, 124.5, 122.4, 121.0, 120.9, 54.4, 53.6, 34.7, 34.3, 31.3, 31.1, 21.4.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{43}H_{43}N_3O_3SH$ 682.3098; Found 682.3109.

5,9-Bis(4-methoxyphenyl)-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3ah).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 99 mg was isolated and the yield is 79%. Mp: 182–183 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.19 (d, *J* = 5.2 Hz, 1H), 7.62 – 7.50 (m, 3H), 7.31 – 7.16 (m, 4H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.87 (t, *J* = 6.3 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 8.8 Hz, 1H), 6.48 (d, *J* = 10.0 Hz, 1H), 6.40 (s, 1H), 4.45 – 4.23 (m, 3H), 3.94 (d, *J* = 15.0 Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H), 2.34 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 163.4, 159.6, 158.3, 153.0, 148.6, 143.8, 140.1, 139.6, 138.6, 136.4, 134.7, 133.3, 130.7, 130.5, 130.14, 130.07, 130.0, 129.6, 128.1, 127.4, 127.2, 125.4, 122.6, 121.1, 121.1, 114.4, 114.2, 113.3, 55.4, 55.3, 54.4, 53.6, 21.5.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{31}N_3O_5SH$ 630.2057; Found 630.2021.

5,9-Bis(4-bromophenyl)-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3ai).

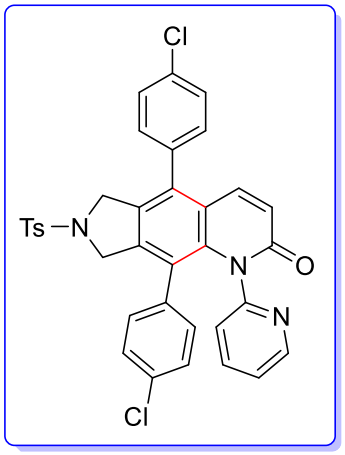


White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 82 mg was isolated and the yield is 57%. Mp: 190–191 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.27 (d, *J* = 4.2 Hz, 1H), 7.68 (d, *J* = 6.3 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 9.8 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.32 – 7.25 (m, 3H), 7.18 – 7.08 (m, 3H), 7.04 (t, *J* = 6.3 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 9.9 Hz, 1H), 6.44 (d, *J* = 8.2 Hz, 1H), 4.48 – 4.25 (m, 3H), 3.98 (d, *J* = 14.8 Hz, 1H), 2.42 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 163.0,

152.7, 148.8, 144.0, 139.6, 139.3, 138.0, 136.8, 135.9, 134.7, 134.1, 133.1, 132.4, 132.3, 132.3, 131.8, 131.7, 131.0, 130.7, 130.6, 130.5, 130.3, 129.9, 127.39, 127.37, 124.9, 123.0, 122.9, 121.8, 121.4, 120.7, 54.1, 53.3, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{25}Br_2N_3O_3SH$ 726.0056; Found 726.0082.

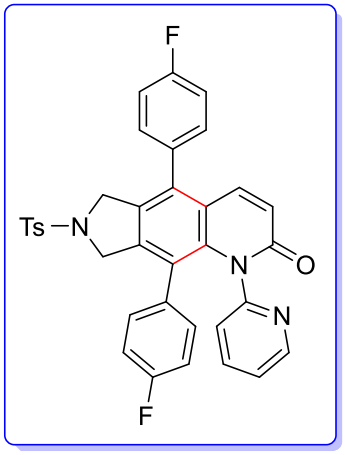
5,9-Bis(4-chlorophenyl)-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3aj).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 102 mg was isolated and the yield is 80%. Mp: 179–180 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.27 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.54 (dd, *J* = 12.7, 9.1 Hz, 3H), 7.37 (td, *J* = 7.7, 1.9 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.02 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 6.96 (s, 1H), 6.89 (d, *J* = 7.9 Hz, 1H), 6.77 (s, 1H), 6.58 (d, *J* = 9.9 Hz, 1H), 6.52 (s, 1H), 4.35 (dd, *J* = 41.8, 19.4 Hz, 3H), 3.98 (d, *J* = 14.9 Hz, 1H), 2.41 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 163.0, 152.7, 148.7, 143.9, 139.7, 139.3, 137.9, 136.7, 135.4, 134.8, 134.3, 134.0, 133.21, 133.16, 130.6, 130.3, 129.8, 129.4, 128.8, 127.35, 127.31, 124.9, 122.9, 121.7, 120.8, 54.1, 53.3, 21.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{25}Cl_2N_3O_3SH$ 638.1066; Found 638.1084.

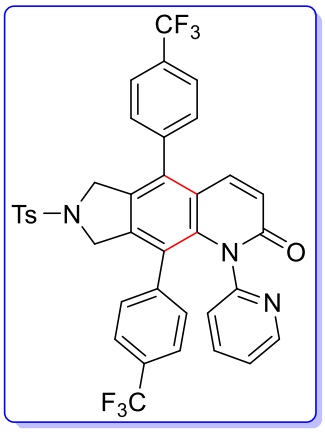
5,9-Bis(4-fluorophenyl)-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3ak).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 110 mg was isolated and the yield is 91%. Mp: 170–171 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26 (s, 1H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.29 (dt, *J* = 16.8, 9.2 Hz, 6H), 7.10 (dt, *J* = 16.6, 8.0 Hz, 2H), 6.96 (s, 2H), 6.83 (dd, *J* = 21.0, 8.0 Hz, 2H), 6.54 (d, *J* = 7.7 Hz, 1H), 4.41 (dt, *J* = 28.8, 14.0 Hz, 3H), 3.99 (d, *J* = 15.0 Hz, 1H), 2.40 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 157.4, 157.2, 151.9, 151.1, 148.6, 143.8, 138.9, 136.9, 136.7, 136.3, 135.7, 134.7, 134.6, 133.0, 131.0, 129.8, 129.2, 129.1, 128.9, 128.7, 128.6, 127.8, 127.3, 127.1, 127.0, 126.1, 123.0, 119.5, 119.4, 117.8, 117.6, 54.2, 53.5, 21.4. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -112.52 (s, 1F), -113.95 (s, 1F).

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{25}F_2N_3O_3SH$ 606.1657; Found 606.1647.

1-(Pyridin-2-yl)-7-tosyl-5,9-bis(4-(trifluoromethyl)phenyl)-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3al).

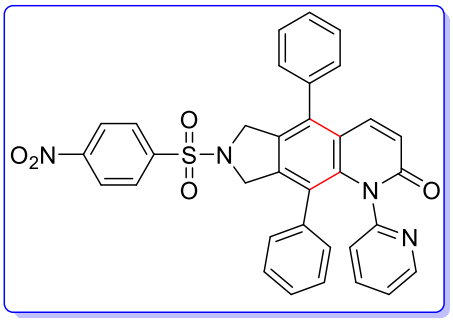


White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 59 mg was isolated and the yield is 42%. Mp: 245–246 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26 (d, *J* = 4.8 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 9.9 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 3H), 7.29 (dd, *J* = 14.6, 6.8 Hz, 4H), 7.06 – 6.91 (m, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.73 (s, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 4.35 (dd, *J* = 31.2, 15.9 Hz, 3H), 3.98 (d, *J* = 15.0 Hz,

1H), 2.42 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)** δ 162.9, 152.5, 148.8, 144.1, 140.7, 139.6, 139.5, 139.2, 137.7, 136.8, 134.0, 133.0, 131.1, 130.3, 129.9, 129.5, 129.2, 127.44, 127.39, 126.2, 125.5, 125.0, 124.9, 123.1, 122.3, 122.1, 120.7, 54.0, 53.2, 21.5. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.71 (s, 3F, CF_3), -62.97 (s, 3F, CF_3).

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{25}F_2N_3O_3SH$ 606.1657; Found 606.1647.

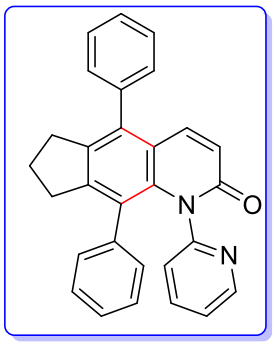
7-((4-nitrophenyl)sulfonyl)-5,9-diphenyl-1-(pyridin-2-yl)-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (3am).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 86 mg was isolated and the yield is 72%. Mp: 247–248 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.33 (d, *J* = 8.2 Hz, 2H), 8.25 (d, *J* = 4.8 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 9.8 Hz, 1H), 7.53 (dd, *J* = 12.3, 7.1 Hz, 3H), 7.27 (t, *J* = 8.5 Hz, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.95 – 6.91 (m, 1H), 6.84 (t, *J* = 9.8 Hz, 2H), 6.57 (d, *J* = 9.7 Hz, 2H), 4.44 (dd, *J* = 34.9, 17.1 Hz, 3H), 4.02 (d, *J* = 14.7 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)** δ 163.2, 152.7, 150.2, 148.6, 142.5, 139.5, 138.8, 138.3, 137.1, 136.5, 135.9, 135.2, 129.4, 129.3, 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 127.9, 127.3, 127.1, 126.0, 124.5, 122.7, 121.7, 121.1, 54.4, 53.7.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{34}H_{24}N_4O_5SH$ 601.1540; Found 601.1539.

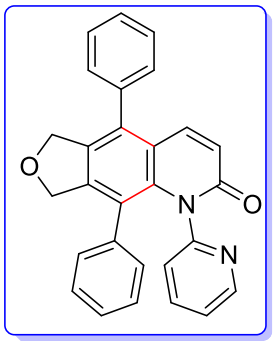
5,9-diphenyl-1-(pyridin-2-yl)-1,6,7,8-tetrahydro-2*H*-cyclopenta[*g*]quinolin-2-one (3an).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 20 mg was isolated and the yield is 24%. Mp: 172–173 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.29 (d, *J* = 4.9 Hz, 1H), 7.65 (dd, *J* = 9.9, 1.8 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.44 (dd, *J* = 8.3, 6.3 Hz, 1H), 7.36 (d, *J* = 7.1 Hz, 2H), 7.24 (t, *J* = 6.7 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.90 (dt, *J* = 21.7, 6.1 Hz, 4H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.52 (dd, *J* = 9.8, 1.8 Hz, 1H), 2.75 (td, *J* = 7.4, 1.8 Hz, 3H), 2.30 (dt, *J* = 16.8, 7.5 Hz, 1H), 1.89 (dt, *J* = 20.3, 7.6 Hz, 2H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 163.8, 153.4, 148.5, 148.3, 139.4, 138.5, 138.2, 138.1, 136.2, 135.7, 130.1, 129.5, 128.6, 128.4, 128.1, 127.6, 127.5, 127.4, 127.1, 126.1, 122.3, 119.8, 33.8, 32.5, 24.9.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{22}N_2OH$ 415.1805; Found 415.1825.

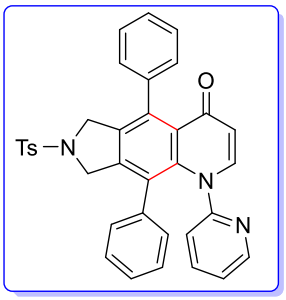
5,9-Diphenyl-1-(pyridin-2-yl)-6,8-dihydrofuro[3,4-*g*]quinolin-2(1*H*)-one (3ap).



Brown Semi-solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1a**), 72 mg was isolated, and the yield is 86%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.29 (dd, *J* = 5.3, 1.9 Hz, 1H), 7.72 (d, *J* = 9.9 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 1.7 Hz, 1H), 7.35 (d, *J* = 1.2 Hz, 1H), 7.26 (td, *J* = 7.5, 1.9 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 7.00 – 6.85 (m, 4H), 6.75 – 6.64 (m, 1H), 6.60 (d, *J* = 9.9 Hz, 1H), 4.97 (d, *J* = 4.5 Hz, 2H), 4.91 (d, *J* = 14.1 Hz, 1H), 4.45 (d, *J* = 13.7 Hz, 1H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 163.5, 152.9, 148.7, 143.2, 139.1, 138.7, 137.9, 136.7, 136.4, 133.5, 133.3, 129.6, 129.1, 129.0, 128.9, 128.8, 128.3, 128.2, 127.6, 127.4, 126.7, 124.6, 122.6, 120.9, 120.6, 74.2, 73.6.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{20}N_2O_2H$ 417.1598; Found 417. 1617.

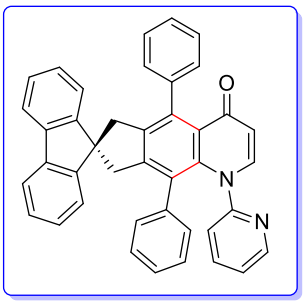
5,9-Diphenyl-1-(pyridin-2-yl)-7-tosyl-1,6,7,8-tetrahydro-4*H*-pyrrolo[3,4-*g*]quinolin-4-one (3la).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1l**), 74 mg was isolated and the yield is 65%. Mp: 172–173 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 4.8 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.32 – 7.25 (m, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 7.4 Hz, 2H), 7.00 (d, *J* = 5.9 Hz, 3H), 6.84 (t, *J* = 6.3 Hz, 1H), 6.75 (d, *J* = 6.7 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.06 (d, *J* = 7.8 Hz, 1H), 4.25 (d, *J* = 6.6 Hz, 4H), 2.32 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 178.5, 156.0, 148.9, 143.7, 143.5, 140.7, 140.3, 140.2, 138.5, 137.1, 136.8, 133.4, 133.1, 129.7, 129.3, 128.2, 128.1, 127.5, 127.3, 126.7, 126.7, 126.1, 122.2, 120.8, 112.5, 54.2, 53.6, 21.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{27}N_3O_3SH$ 570.1807; Found 570.1827.

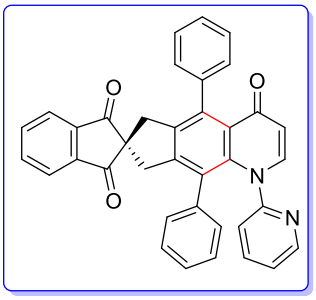
5,9-Diphenyl-1-(pyridin-2-yl)-6,8-dihydrospiro[cyclopenta[*g*]quinoline-7,9'-fluoren]-4(1*H*)-one (3lc).



White Solid; eluent (80% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1l**), 60 mg was isolated and the yield is 52%. Mp: 268–269 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.22 (d, *J* = 4.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.35 (dt, *J* = 20.4, 7.7 Hz, 3H), 7.28 – 7.17 (m, 9H), 6.99 – 6.89 (m, 6H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.24 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 2H), 3.19 (s, 2H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 179.1, 156.5, 151.5, 149.0, 147.5, 143.2, 141.8, 140.5, 140.3, 139.4, 138.3, 138.2, 138.1, 130.2, 128.8, 127.9, 127.8, 127.5, 127.4, 127.3, 126.6, 126.0, 125.9, 122.0, 121.0, 119.7, 112.6, 56.6, 46.0, 44.7.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{41}H_{28}N_2OH$ 565.2274; Found 565.2285.

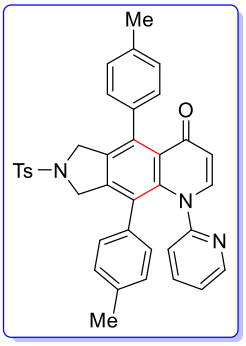
5,9-Diphenyl-1-(pyridin-2-yl)-6,8-dihydrospiro[cyclopenta[*g*]quinoline-7,2'-indene]-1',3',4(1*H*)-trione (3ld).



White Solid; eluent (80% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1l**), 36 mg was isolated and the yield is 33%. Mp: 224–225 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.20 (d, *J* = 5.0 Hz, 1H), 7.90 (dd, *J* = 5.7, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.7, 3.1 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.40 – 7.36 (m, 3H), 7.32 – 7.28 (m, 3H), 7.03 (t, *J* = 7.4 Hz, 2H), 6.98 (d, *J* = 7.3 Hz, 3H), 6.92 (dd, *J* = 7.4, 4.9 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.19 (d, *J* = 7.8 Hz, 1H), 3.10 (s, 2H), 3.09 (s, 2H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 202.4, 179.0, 156.3, 149.0, 145.2, 143.3, 141.7, 141.2, 140.7, 138.3, 138.0, 137.9, 137.7, 135.9, 132.0, 130.2, 128.4, 127.9, 127.3, 126.8, 126.2, 123.5, 122.0, 121.1, 112.5, 58.0, 41.1, 40.7.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{25}N_2O_3H$ 545.1860; Found 545.1872.

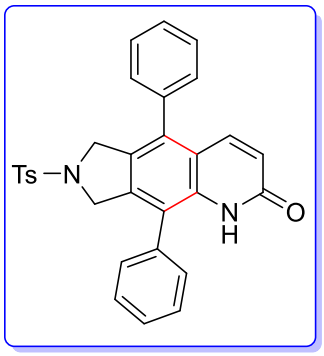
1-(Pyridin-2-yl)-5,9-di-p-tolyl-7-tosyl-1,6,7,8-tetrahydro-4H-pyrrolo[3,4-g]quinolin-4-one (3le).



White Solid; eluent (70% ethyl acetate in hexane). The reaction scale is 0.2 mmol (**1l**), 65 mg was isolated and the yield is 54%. Mp: 230–231 °C; **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.17 (d, *J* = 4.9 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.93 (dd, *J* = 7.5, 4.9 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 2H), 6.14 (d, *J* = 7.8 Hz, 1H), 4.36 (s, 2H), 4.33 (s, 2H), 2.44 (s, 3H), 2.40 (s, 3H), 2.24 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 178.7, 156.3, 148.9, 143.7, 143.4, 140.9, 140.4, 138.3, 137.24, 137.18, 137.0, 136.2, 133.9, 133.6, 133.3, 129.8, 129.3, 128.9, 127.4, 126.7, 126.3, 122.0, 120.8, 112.7, 54.4, 53.8, 21.5, 21.3, 21.0.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{31}N_3O_3SH$ 598.2159; Found 598.2167.

5,9-Diphenyl-7-tosyl-1,6,7,8-tetrahydro-2*H*-pyrrolo[3,4-*g*]quinolin-2-one (4aa).

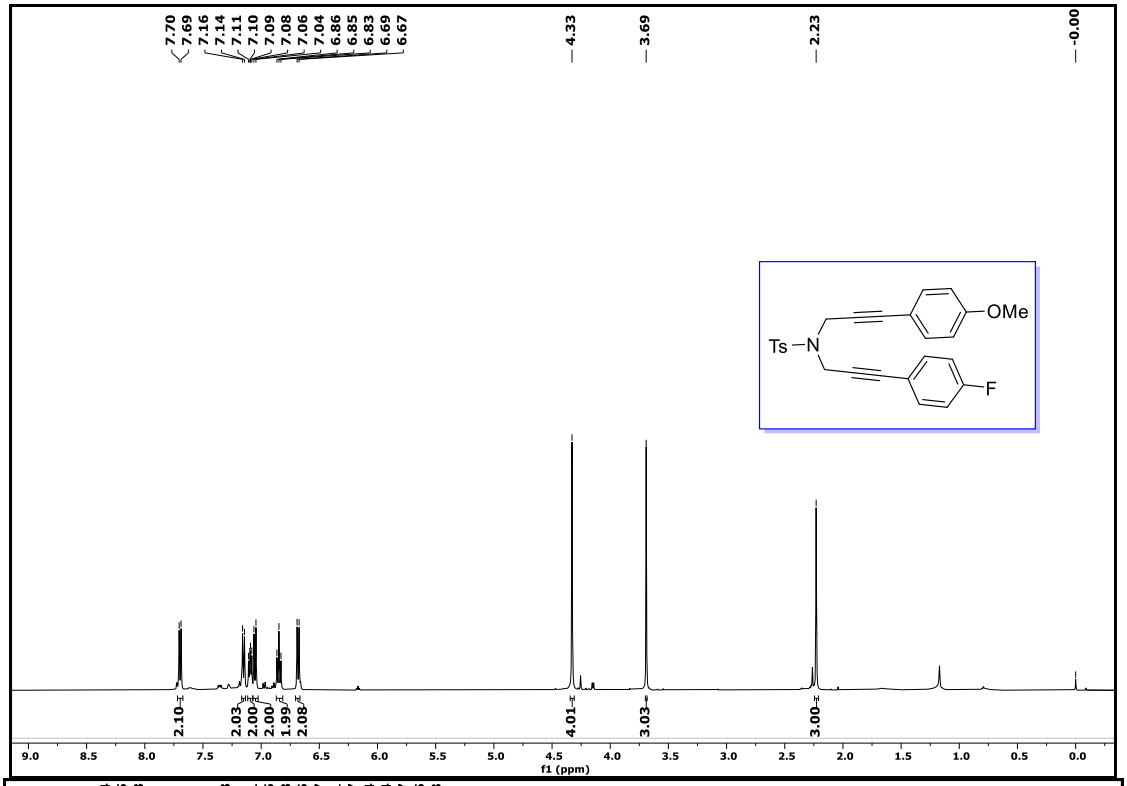


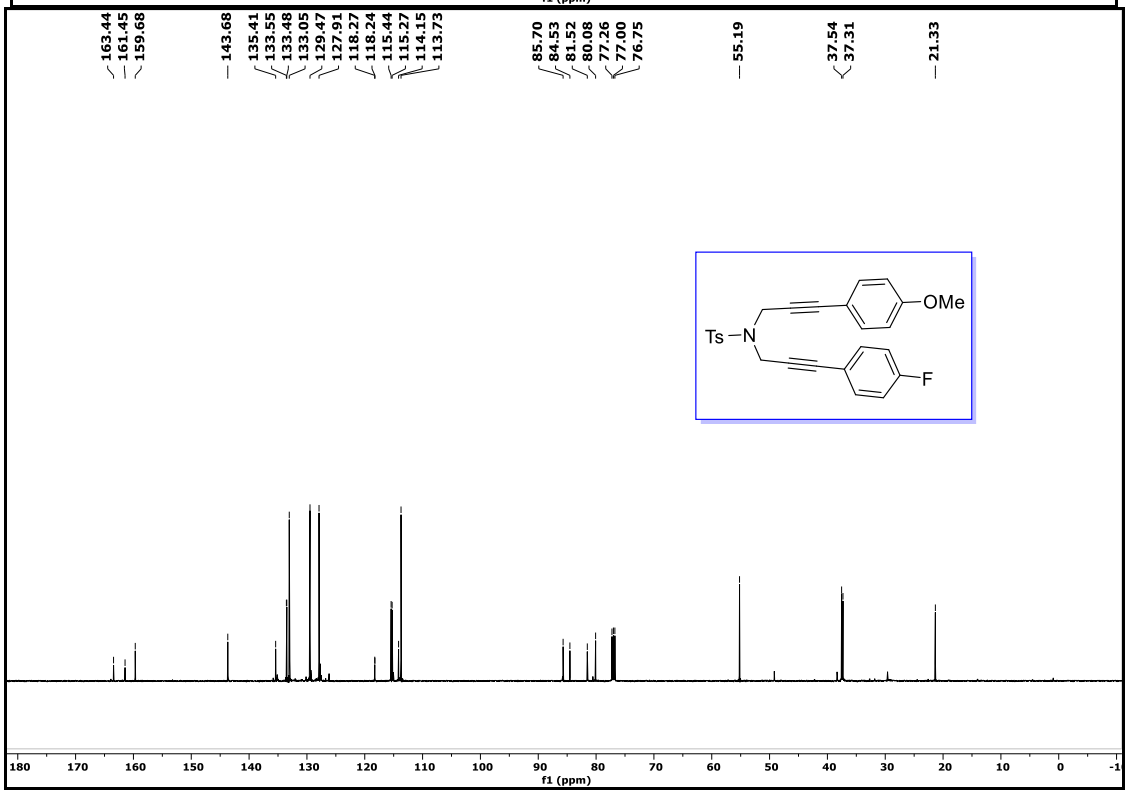
White Solid; eluent (50% ethyl acetate in hexane). The reaction scale is 0.1 mmol (**3aa**), 27 mg was isolated and the yield is 55%. Mp: 268–279 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.50 (s, 1H), 7.68 – 7.64 (m, 2H), 7.60 – 7.47 (m, 7H), 7.32 – 7.27 (m, 4H), 7.26 – 7.23 (m, 2H), 6.50 (d, *J* = 9.9 Hz, 1H), 4.49 – 4.45 (m, 4H), 2.41 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 161.9, 143.8, 138.5, 137.9, 136.1, 135.8, 135.0, 133.5, 132.6, 130.2, 129.9, 129.6, 129.5, 129.09, 129.07, 129.0, 128.6, 127.5, 122.5, 121.4, 118.4, 53.6, 53.3, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{24}N_2O_3SH$ 493.1580; Found 493.1586.

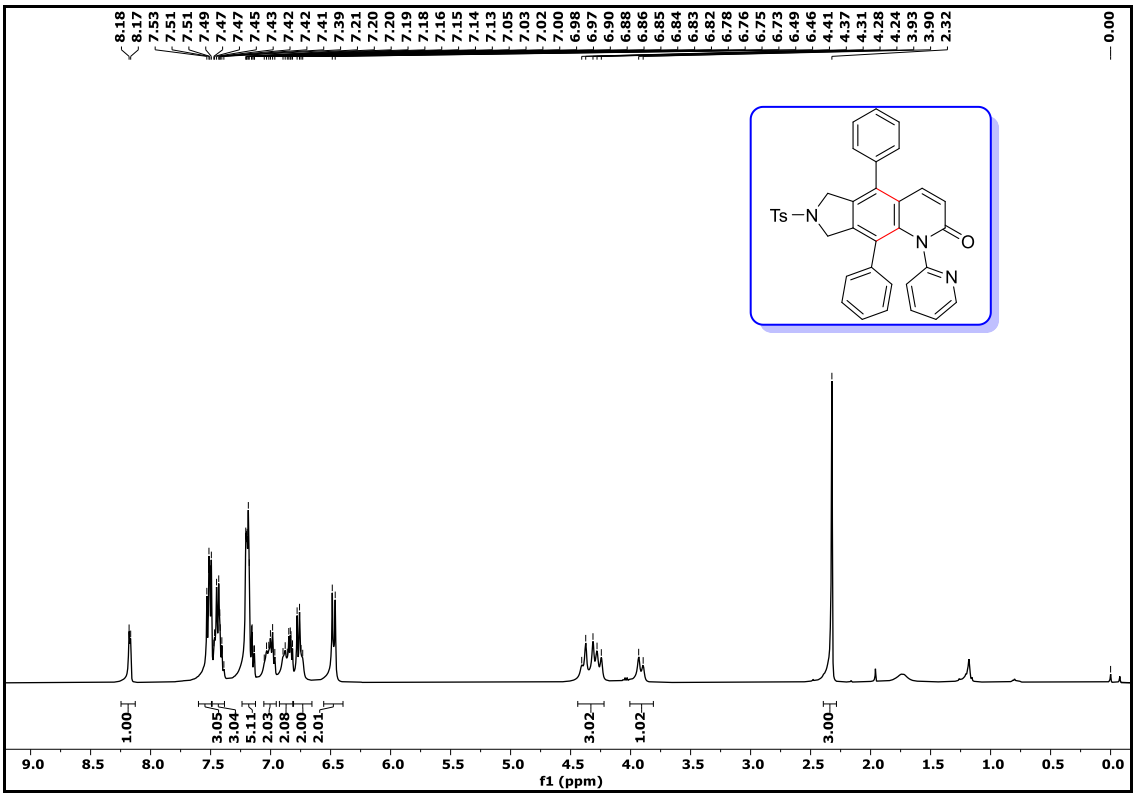
Spectral Data of all Compounds:

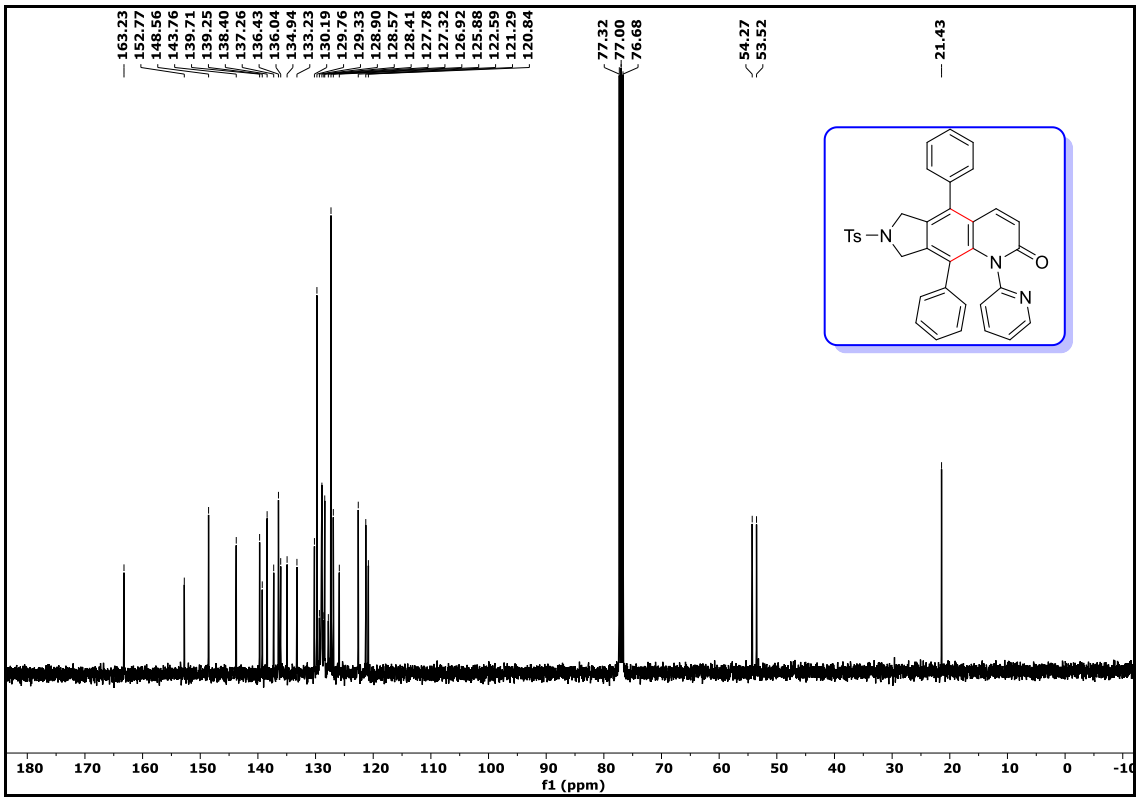
^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (126 MHz) NMR Spectra of Compound **2q.** Solvent $CDCl_3$



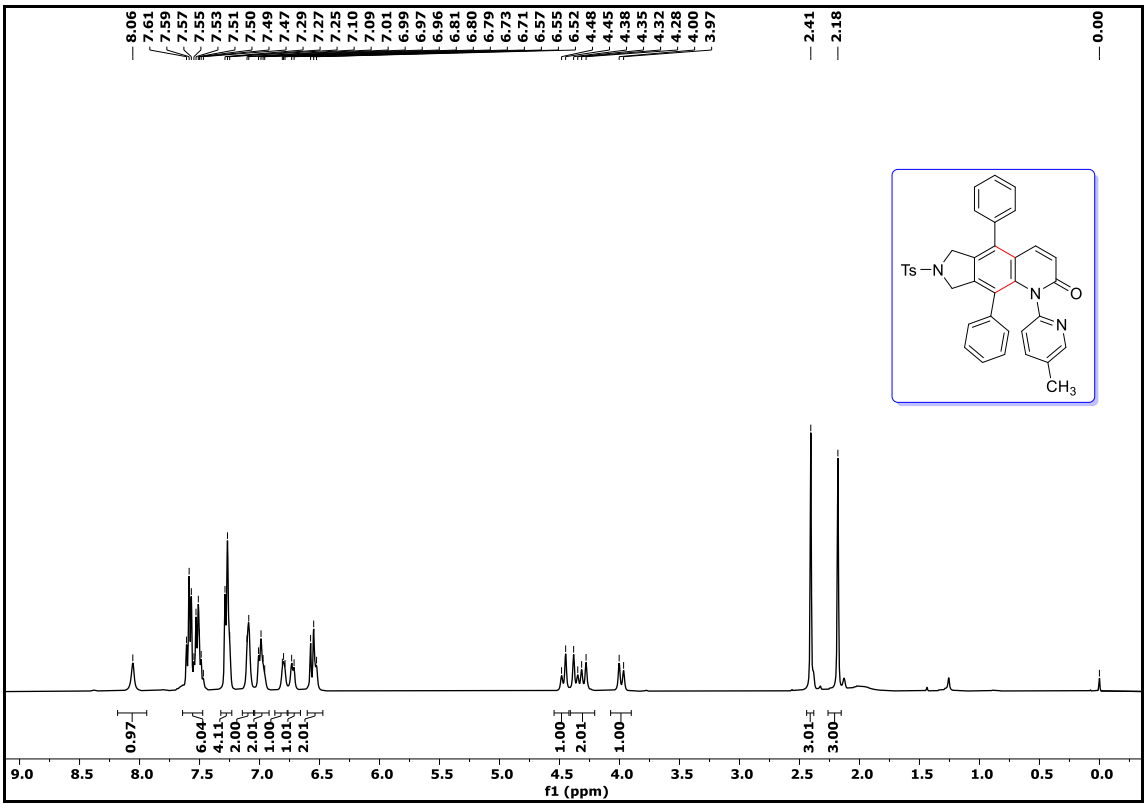


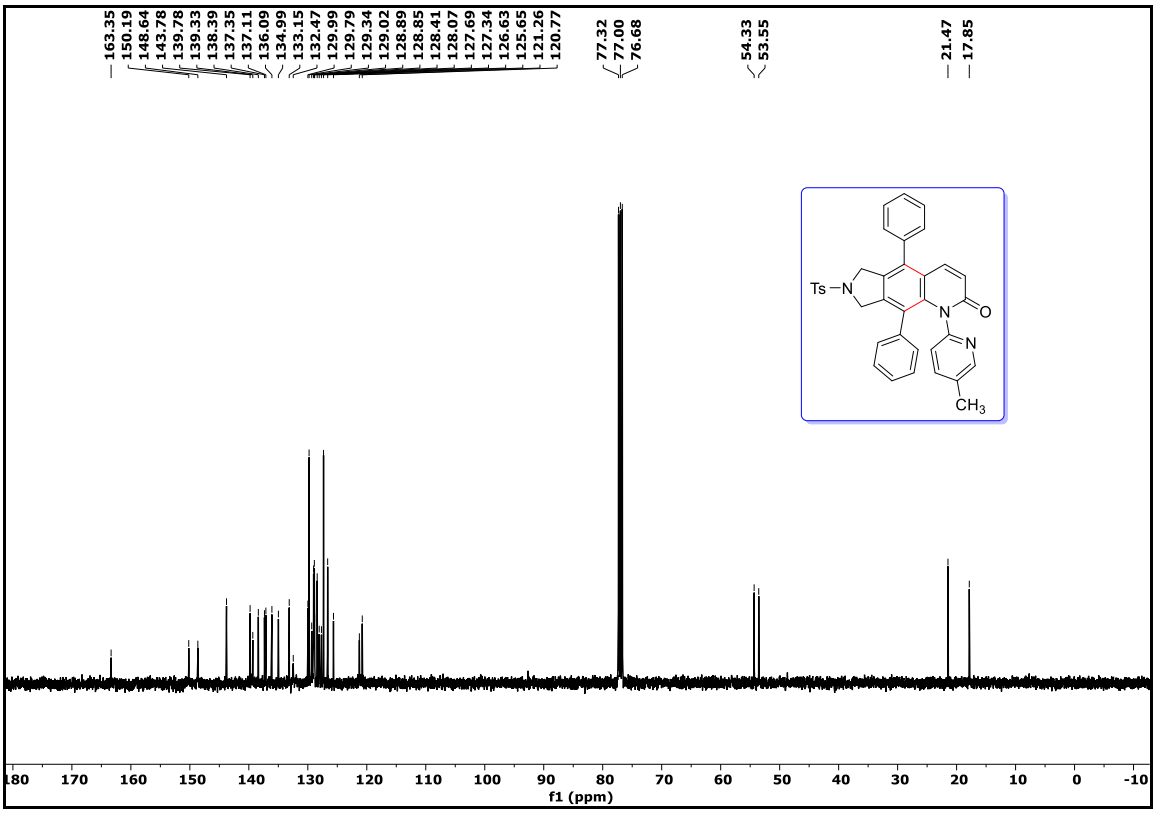
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3aa.** Solvent $CDCl_3$



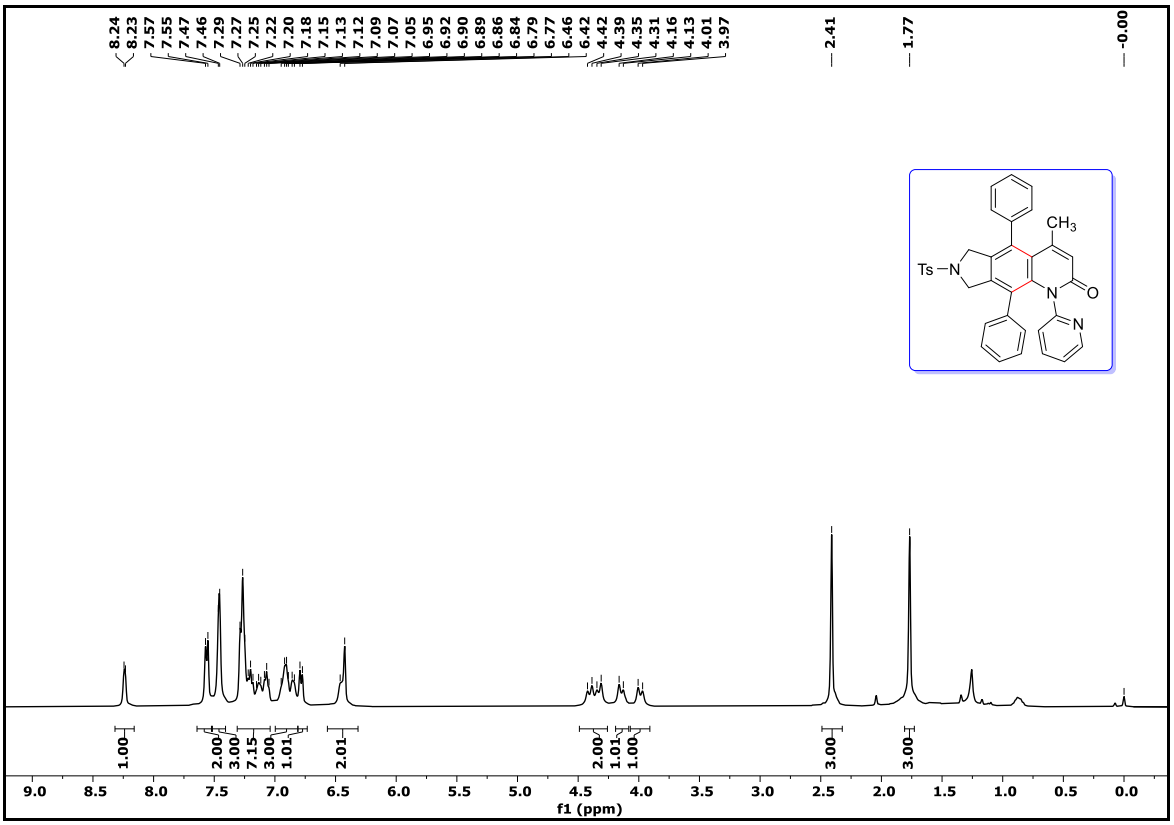


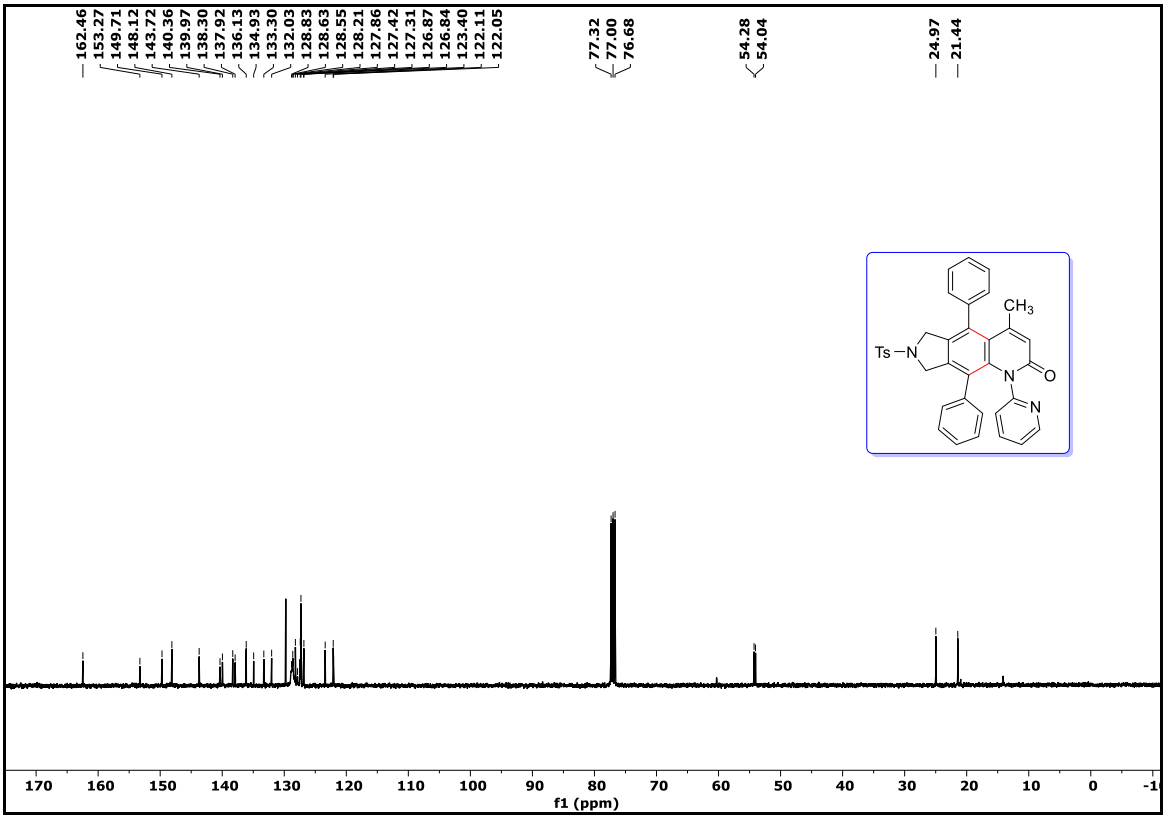
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ba.** Solvent $CDCl_3$**.**



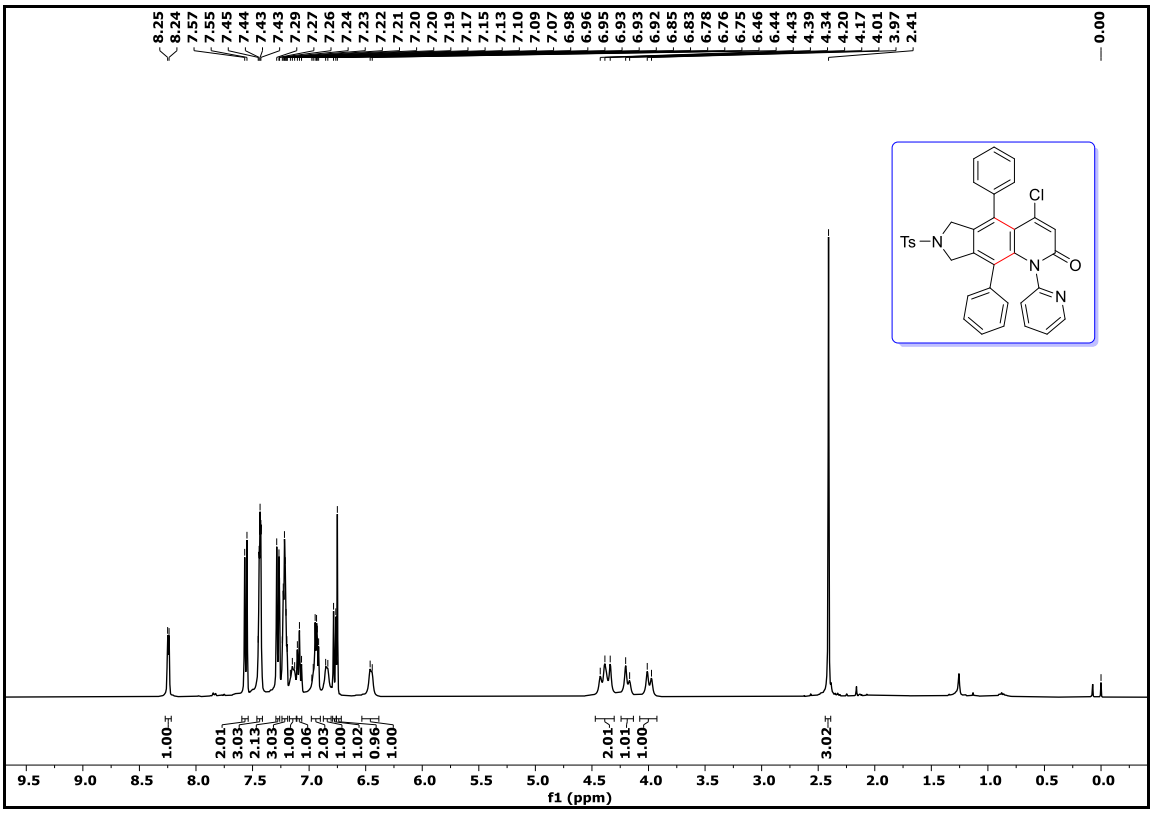


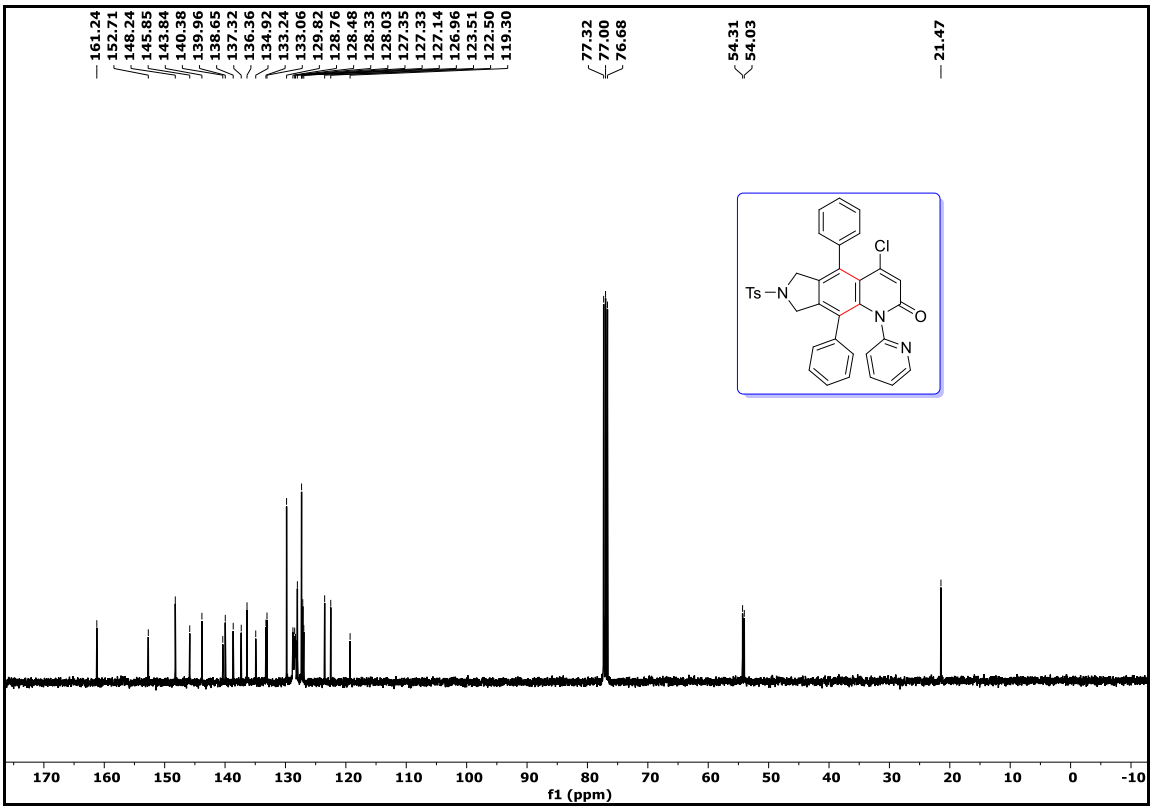
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ca.** Solvent $CDCl_3$



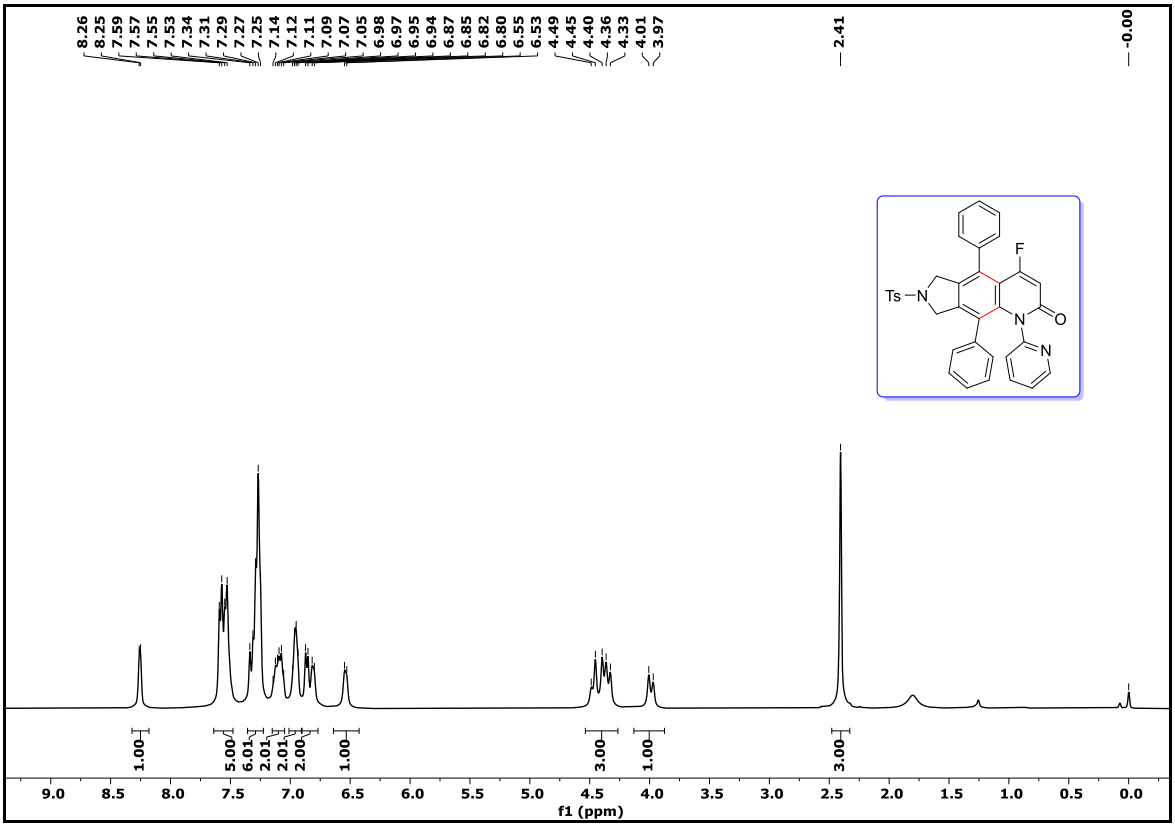


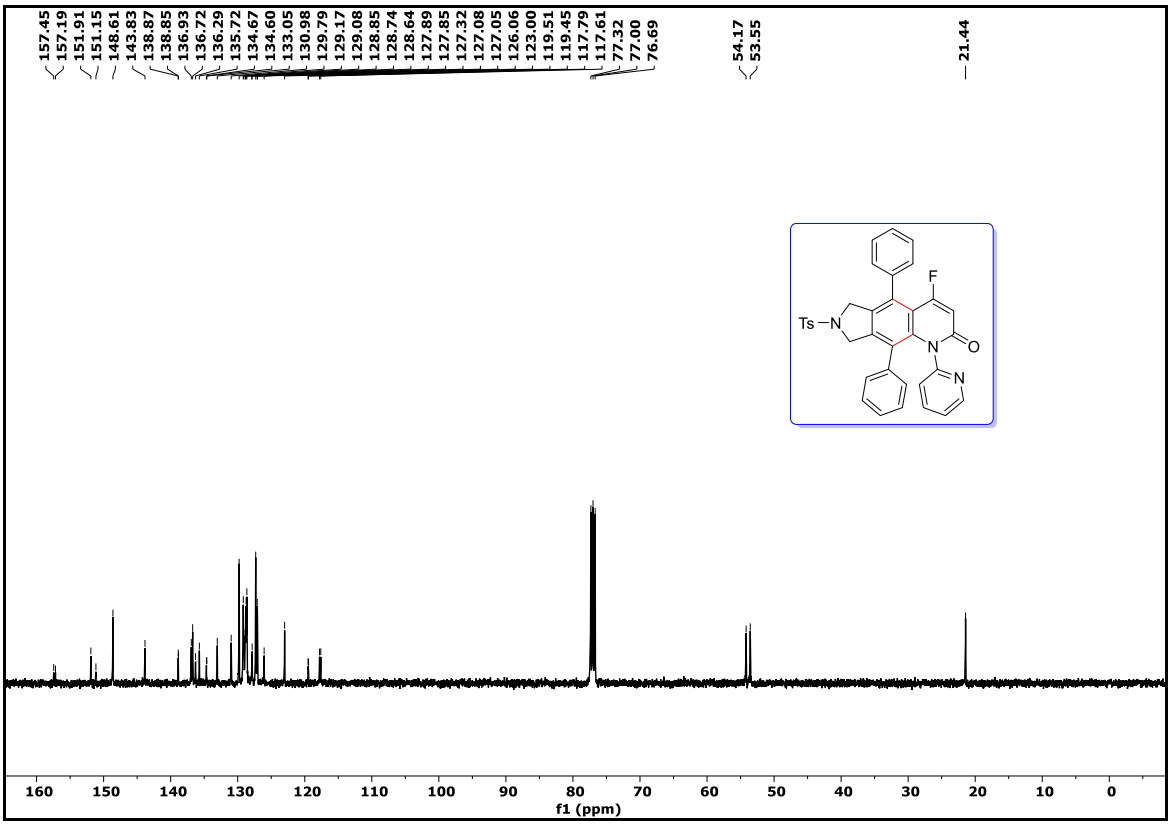
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3da.** Solvent $CDCl_3$



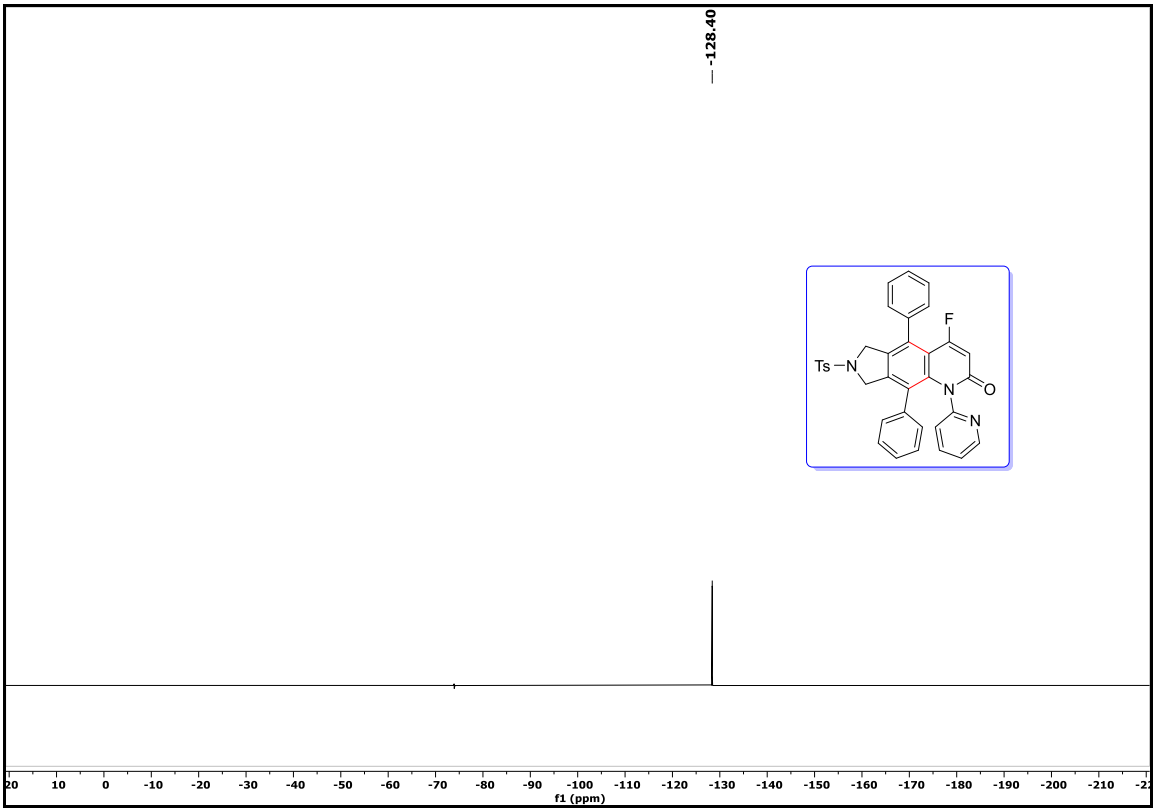


^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ea.** Solvent $CDCl_3$

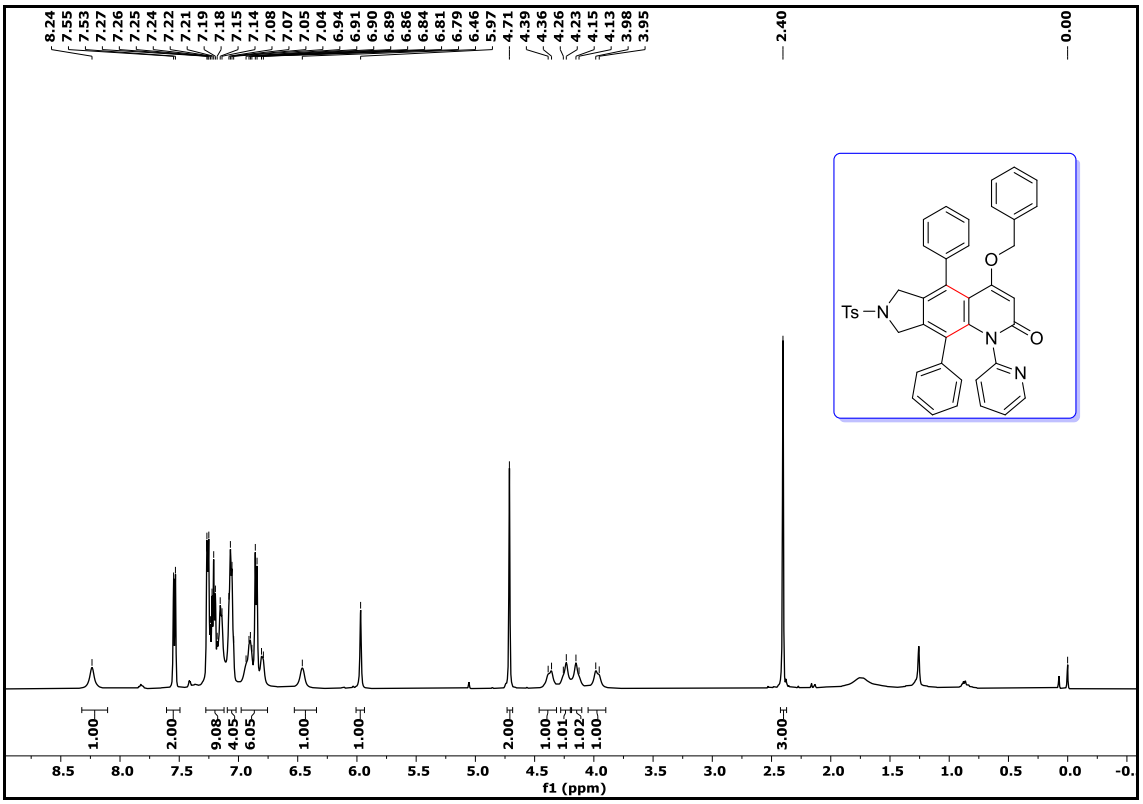


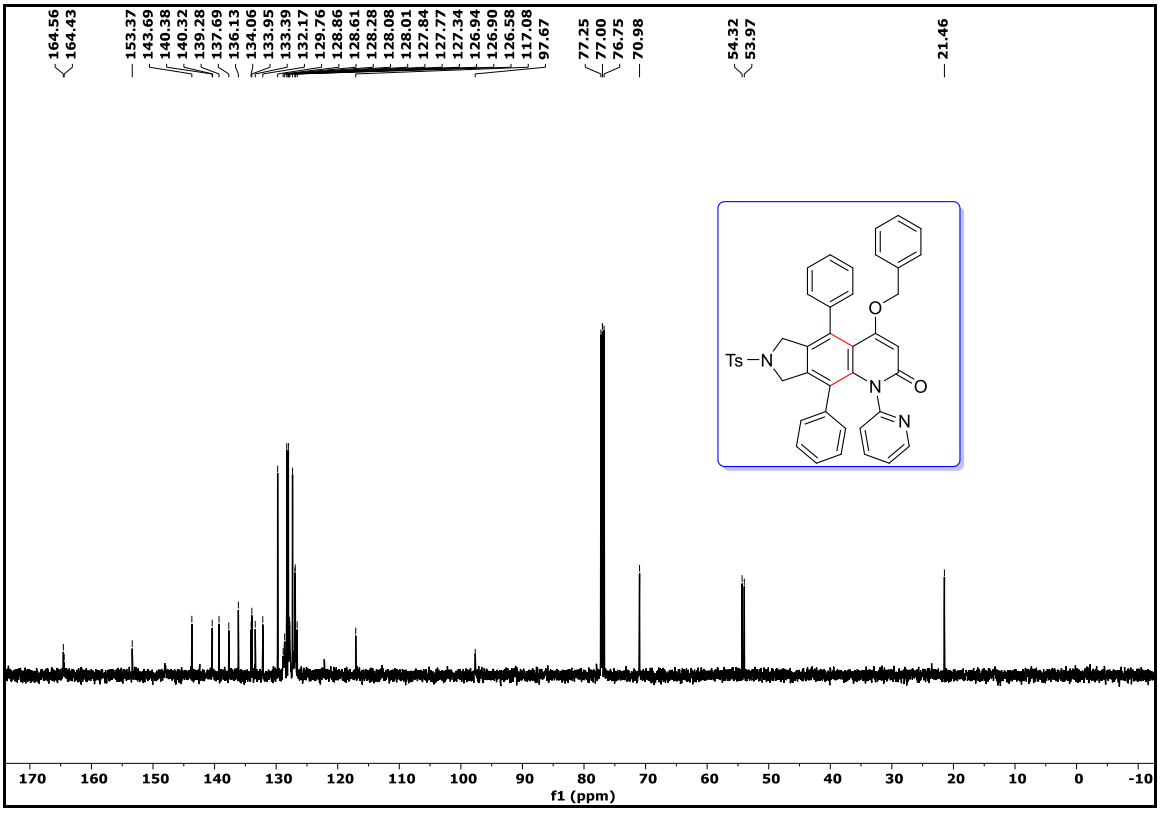


^{19}F NMR Spectra of Compound **3ea.** (Solvent $CDCl_3$, 471 MHz)

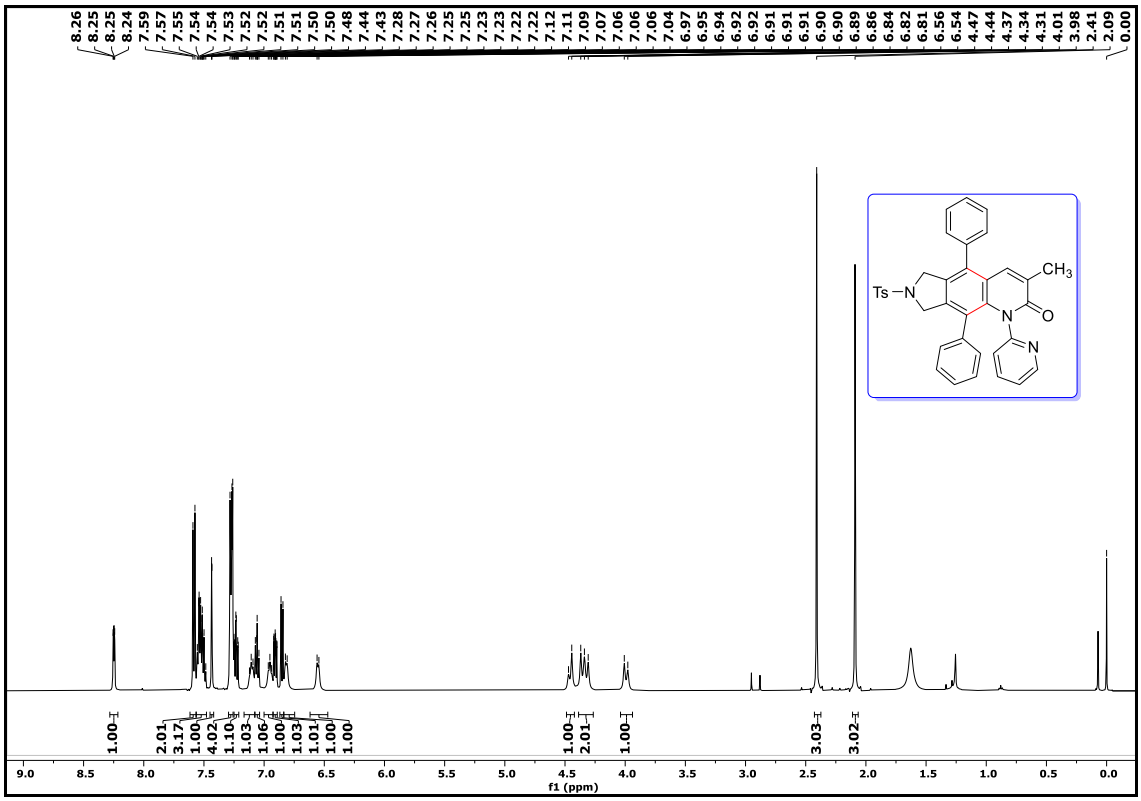


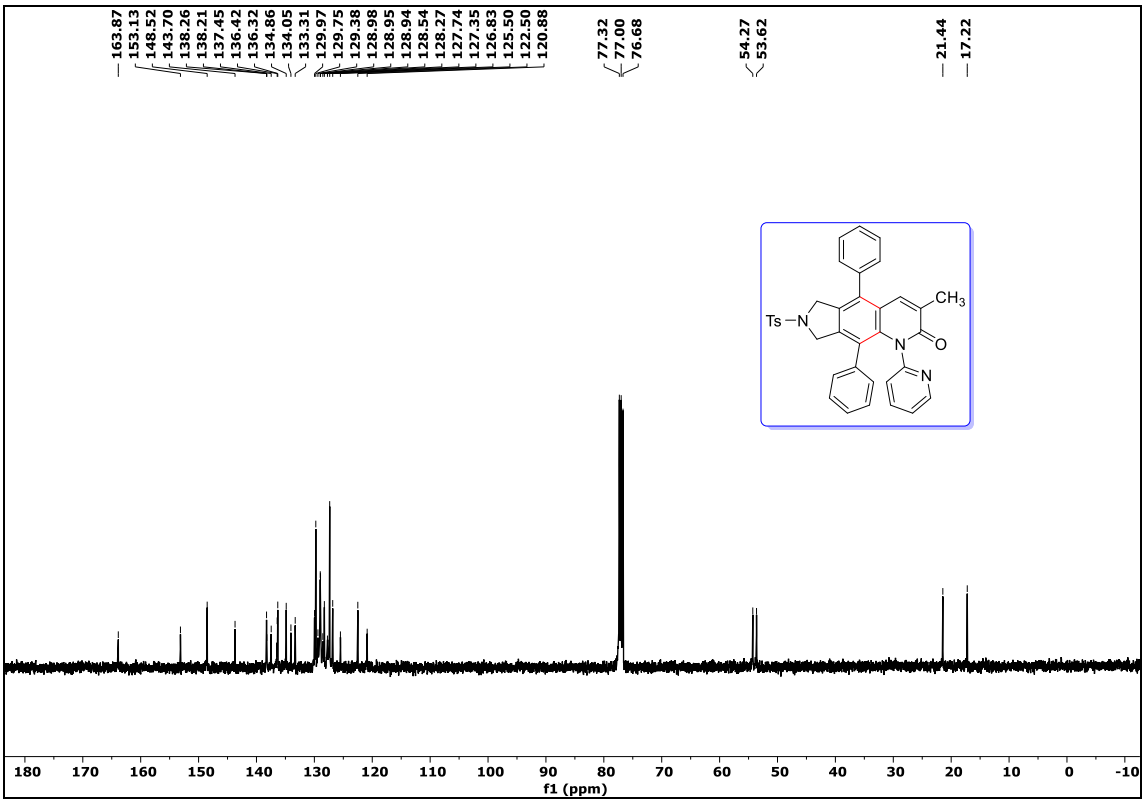
^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (126 MHz) NMR Spectra of Compound **3fa.** Solvent $CDCl_3$



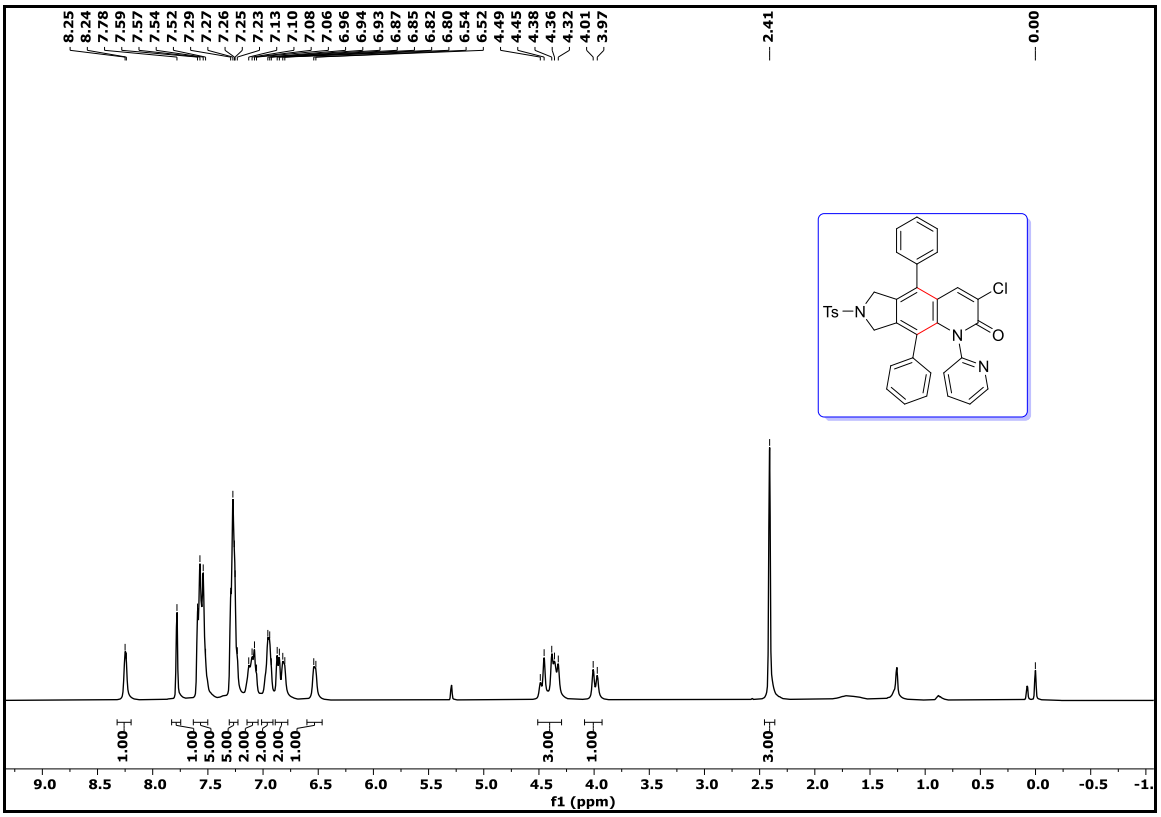


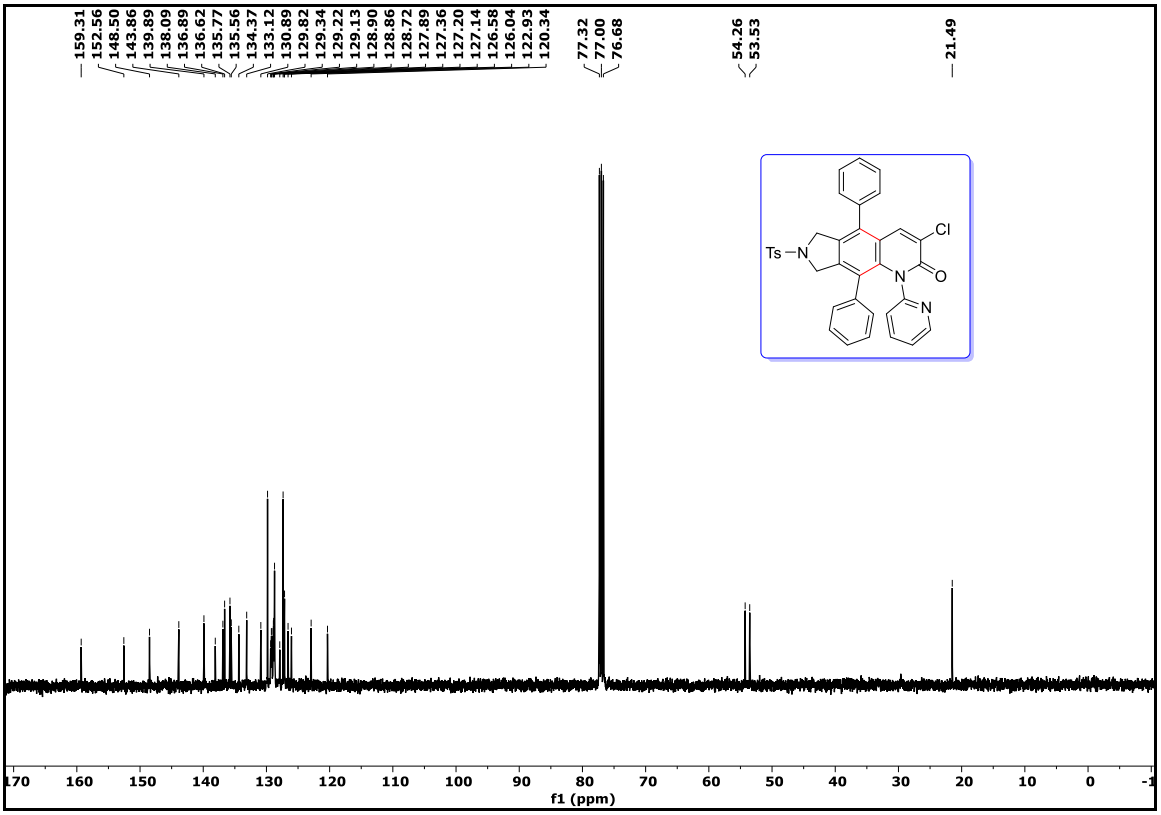
^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ga.** Solvent $CDCl_3$**.**



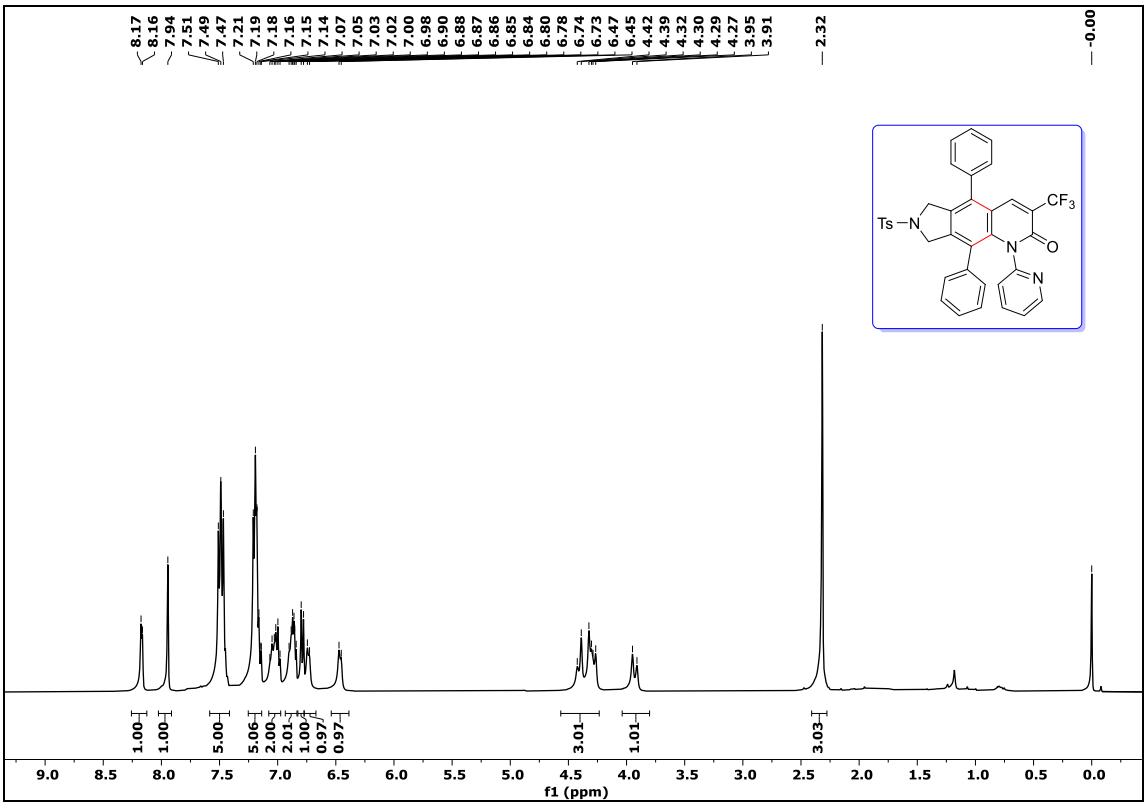


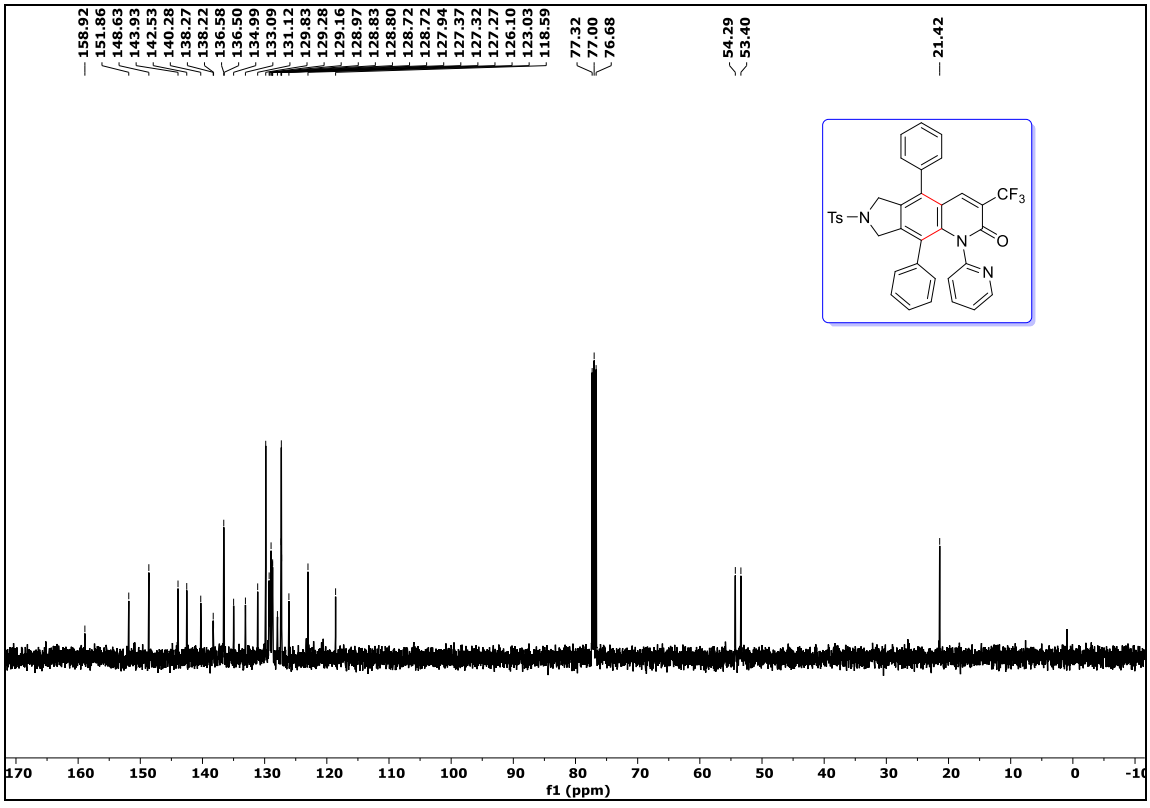
^{1}H (400 MHz) and ^{13}C{^{1}H} (101 MHz) NMR Spectra of Compound **3ha.** Solvent $CDCl_3$**.**



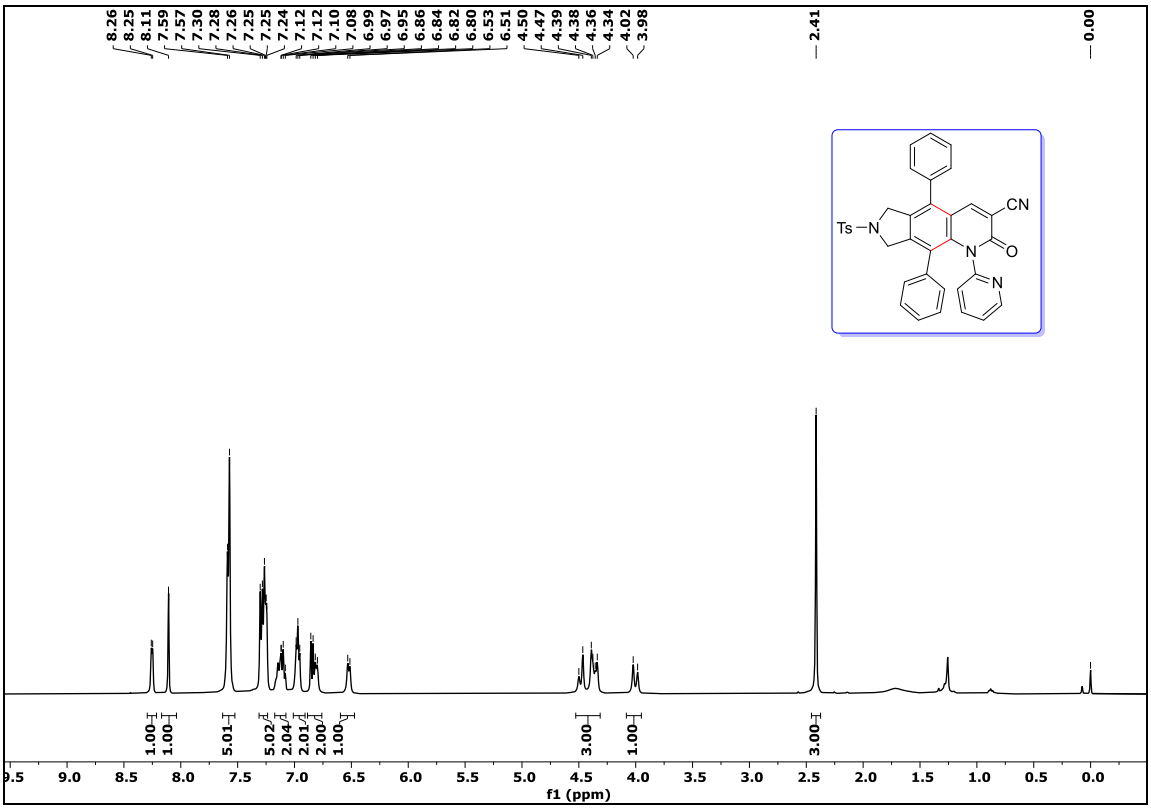


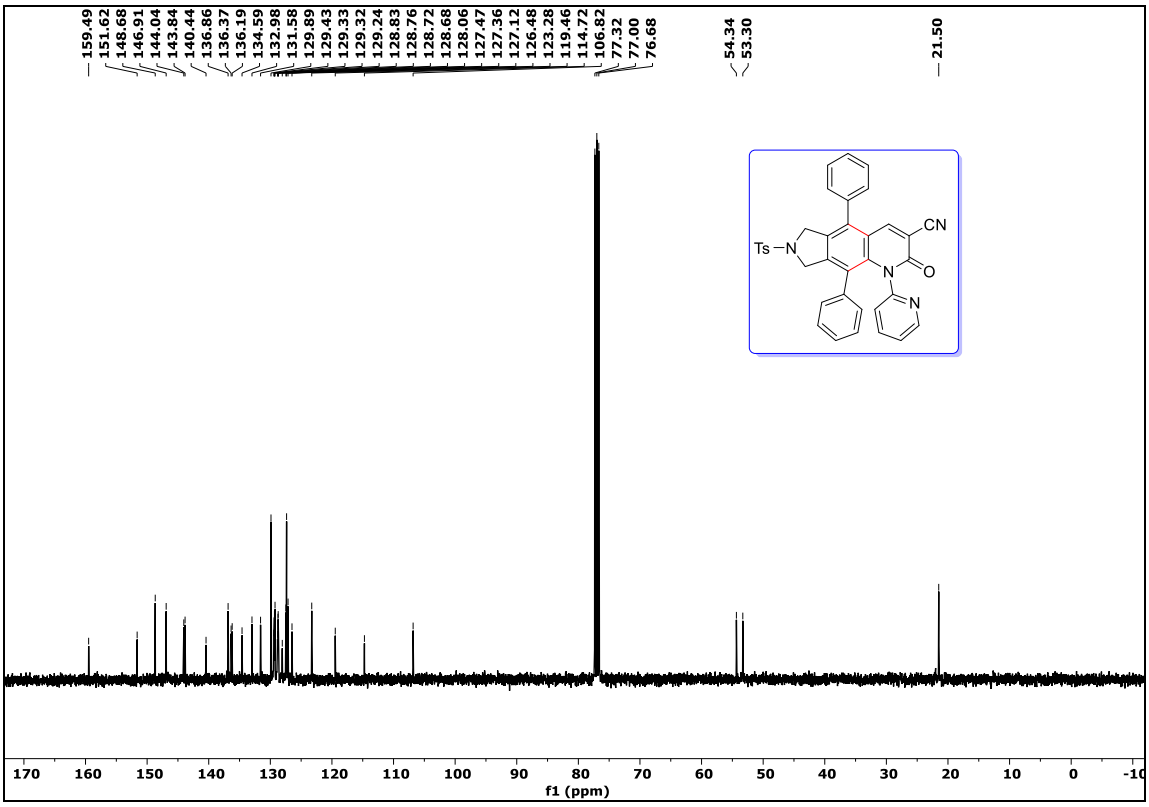
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ia.** Solvent $CDCl_3$



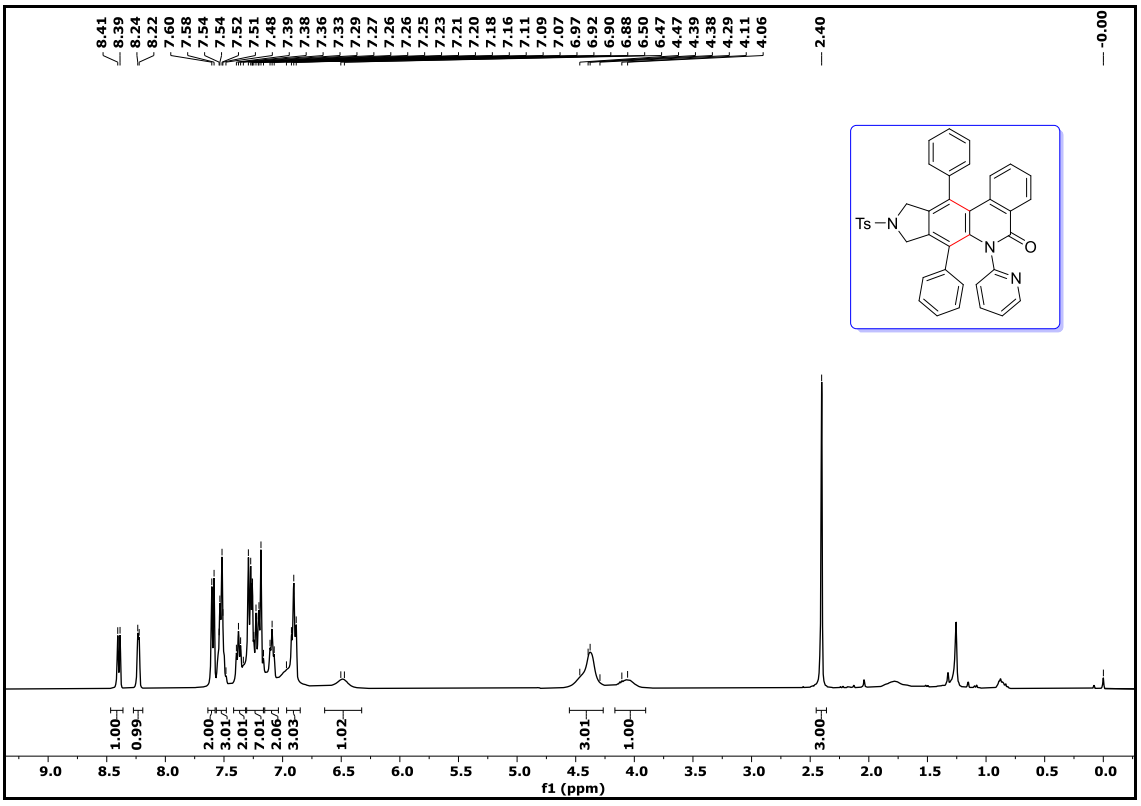


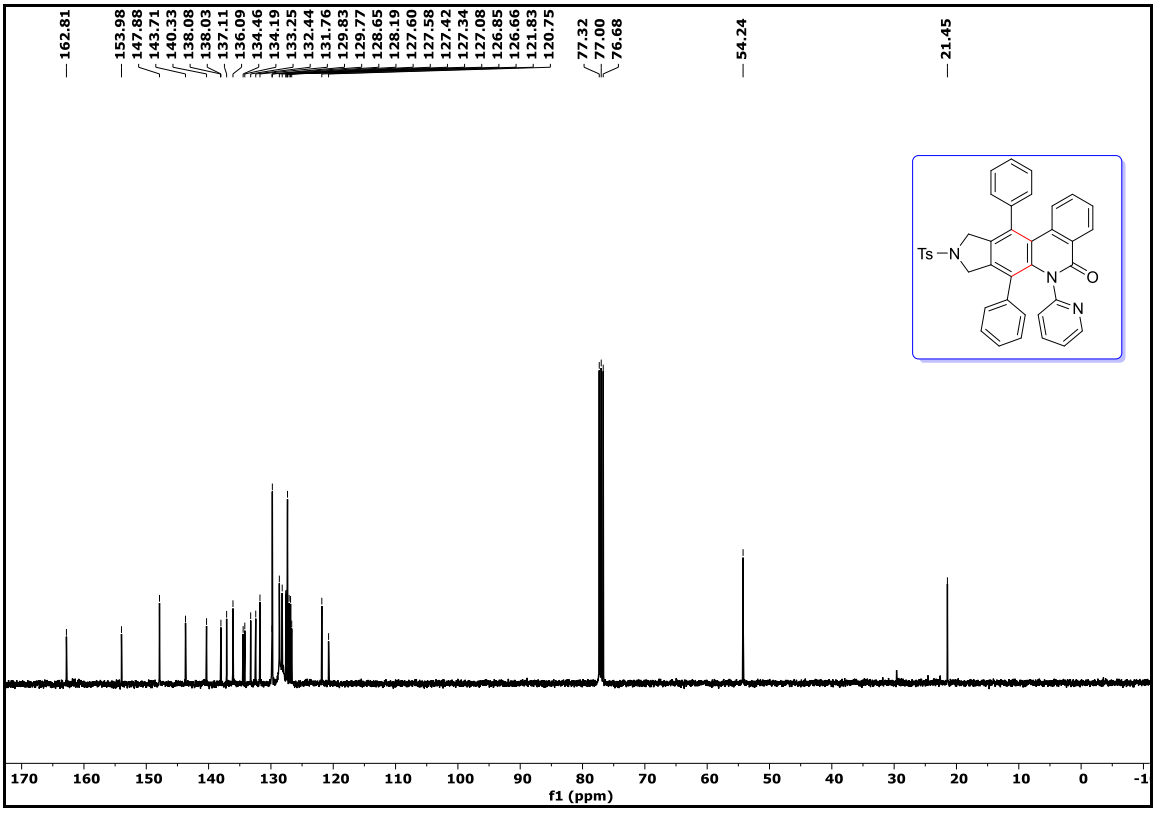
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ja.** Solvent $CDCl_3$



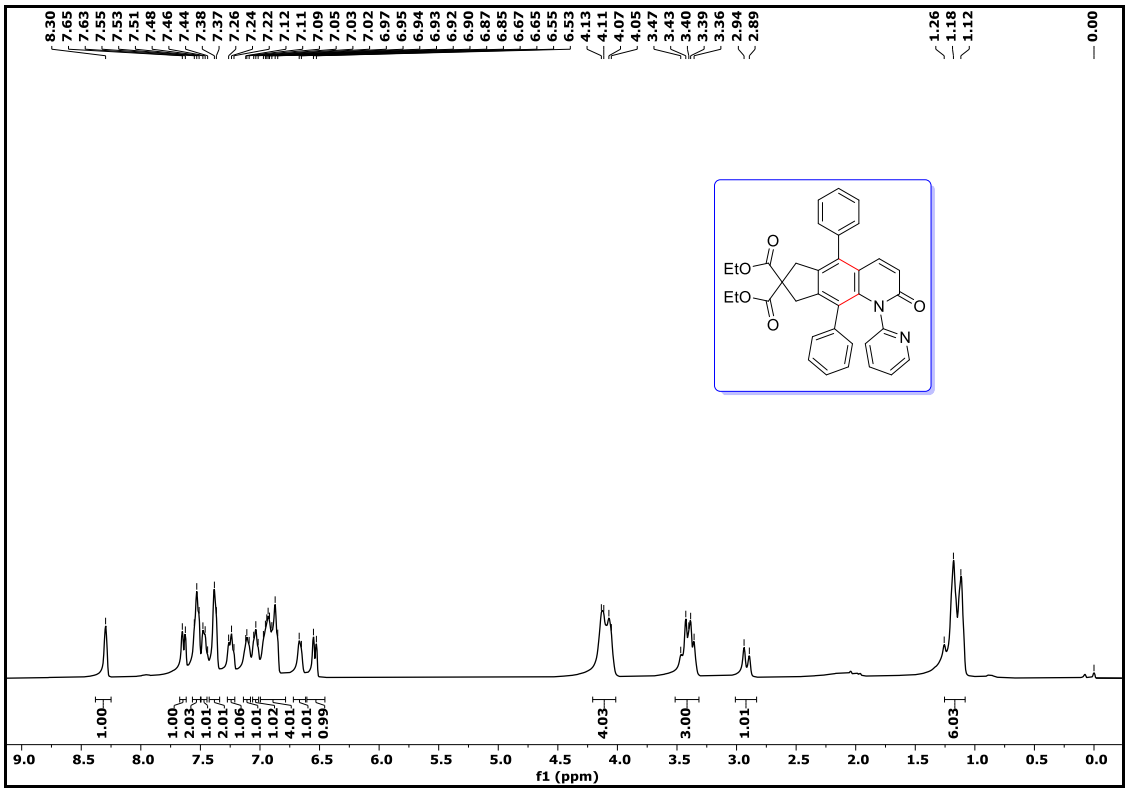


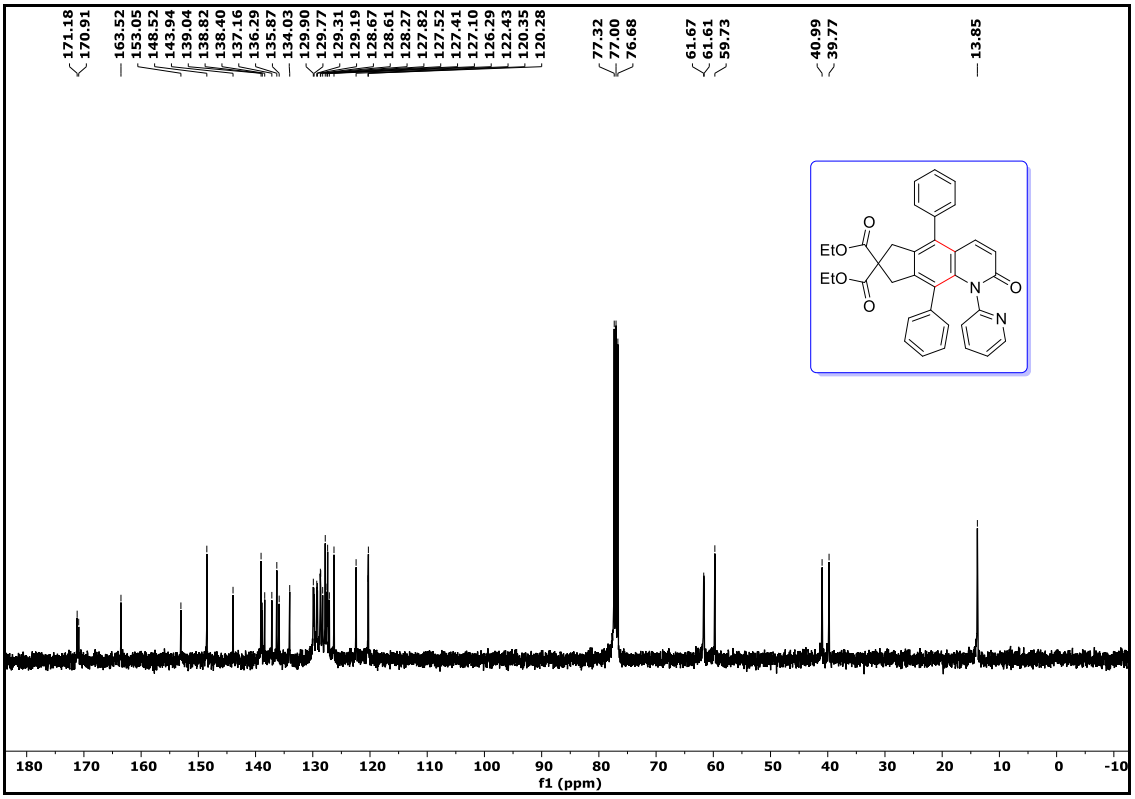
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ka.** Solvent $CDCl_3$



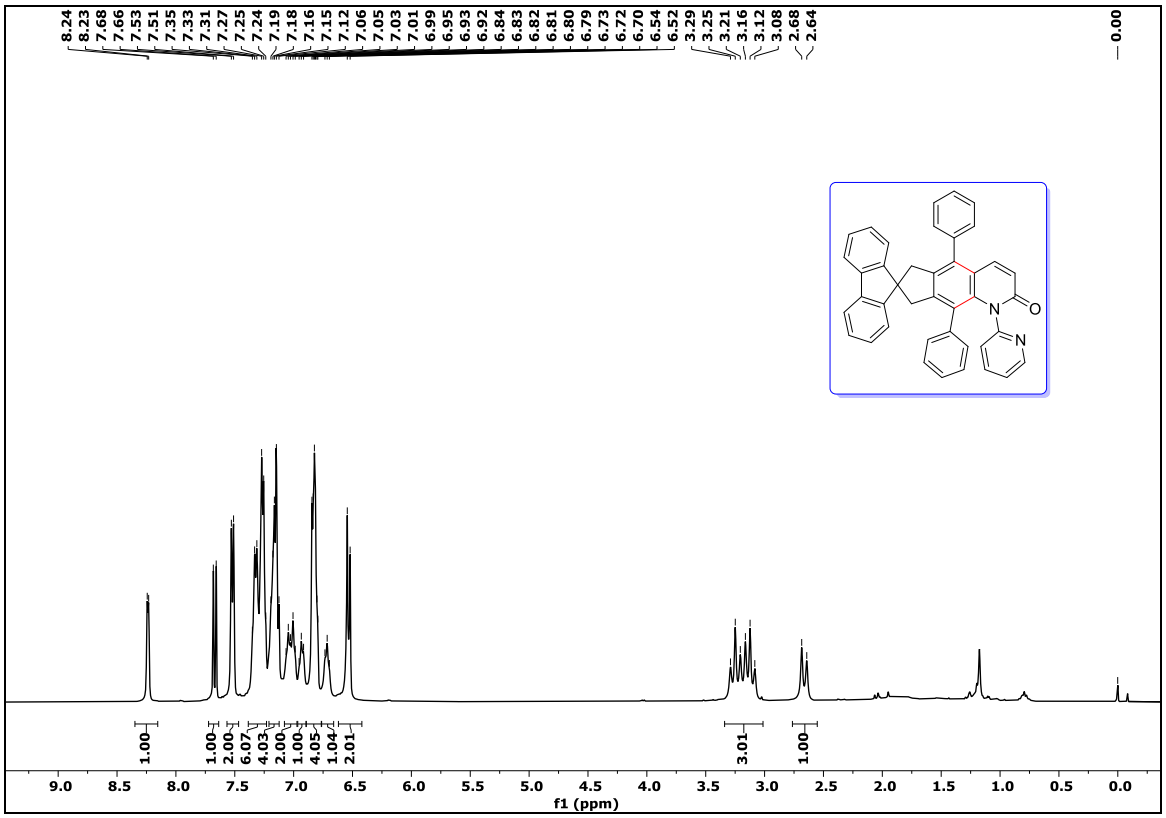


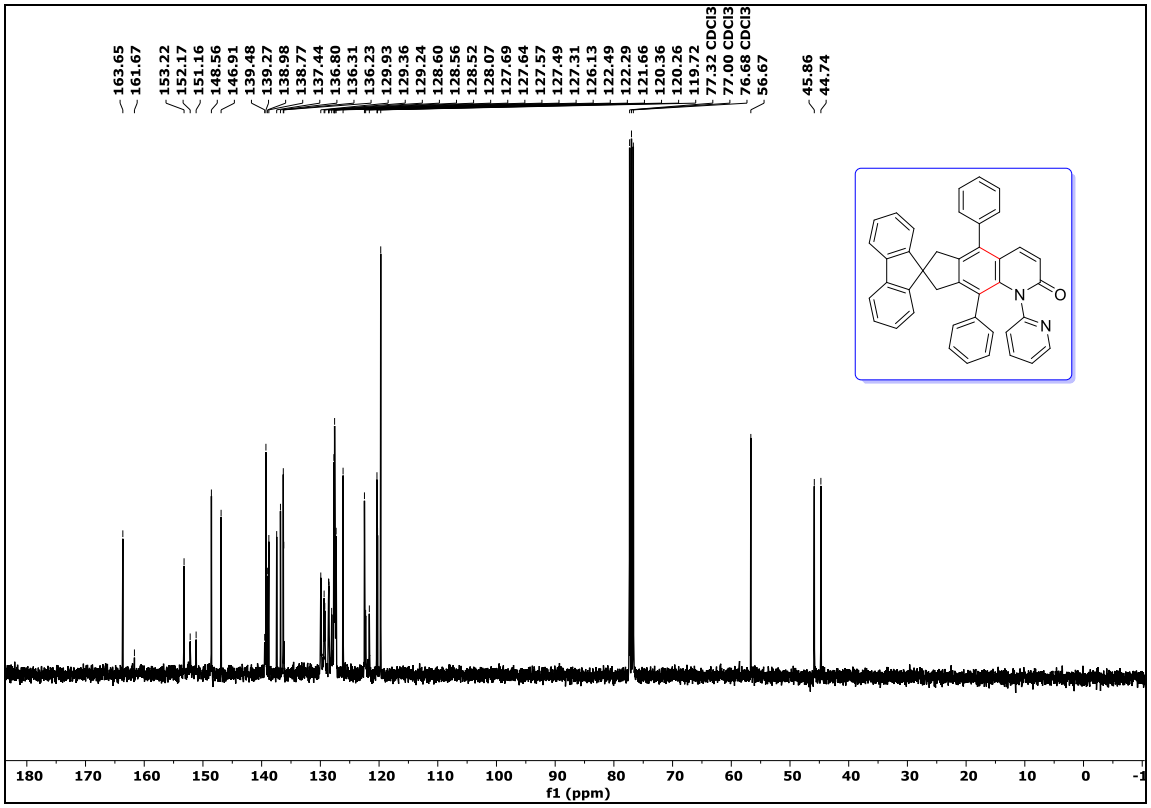
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ab.** Solvent $CDCl_3$



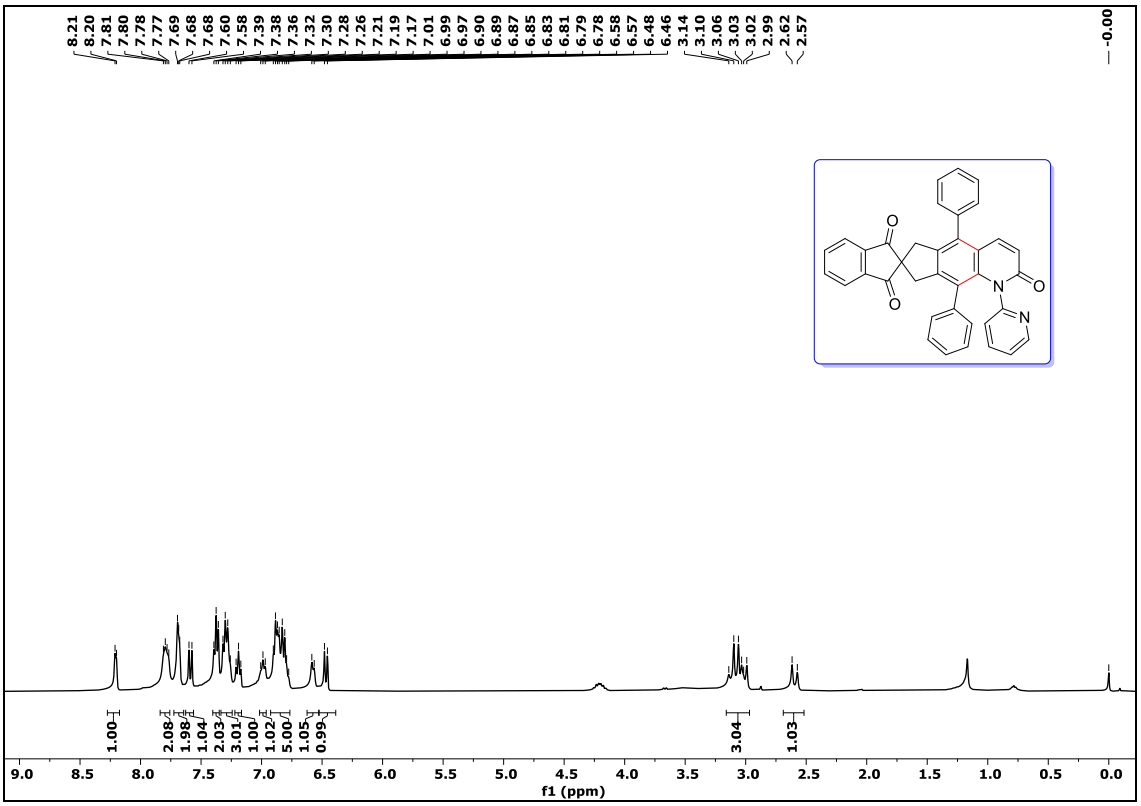


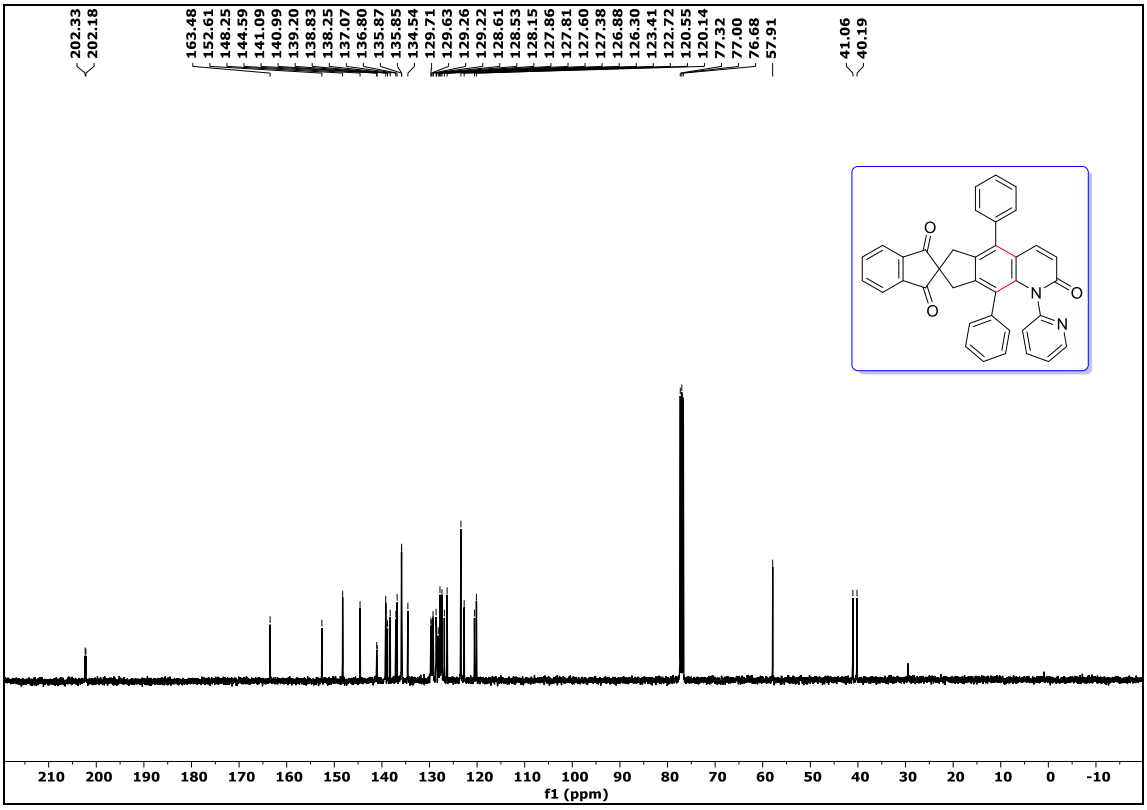
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ac.** Solvent $CDCl_3$



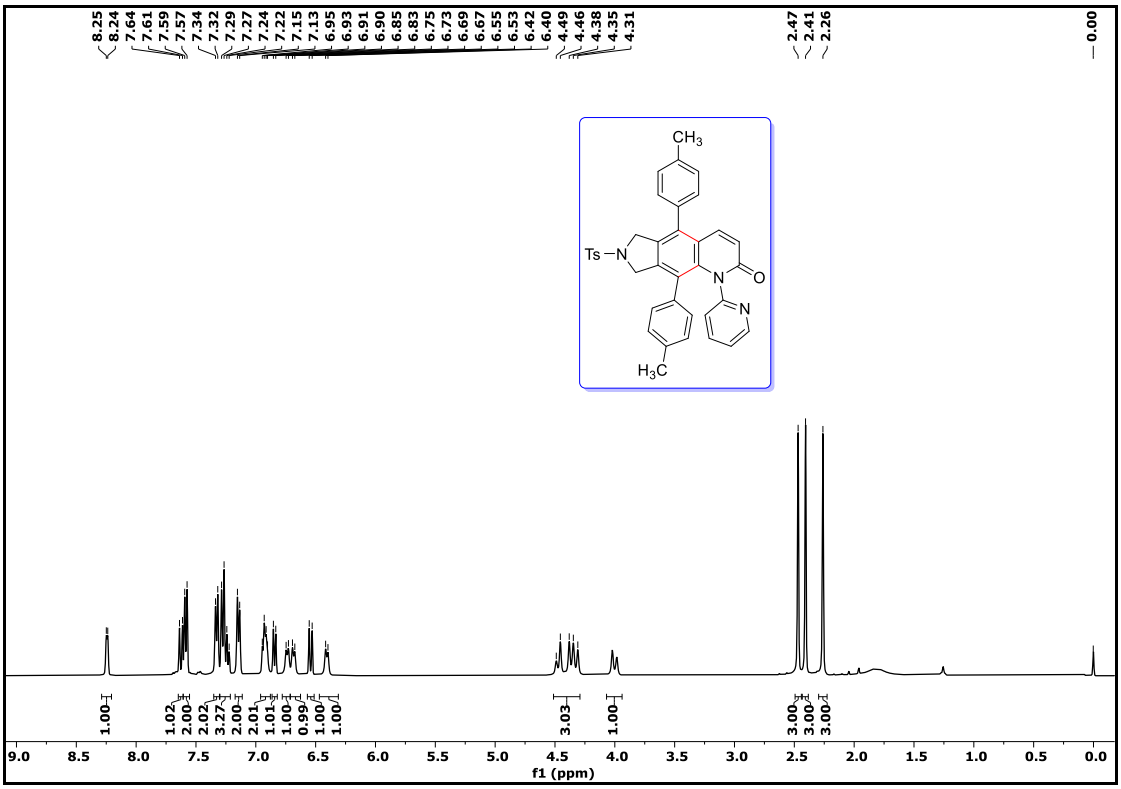


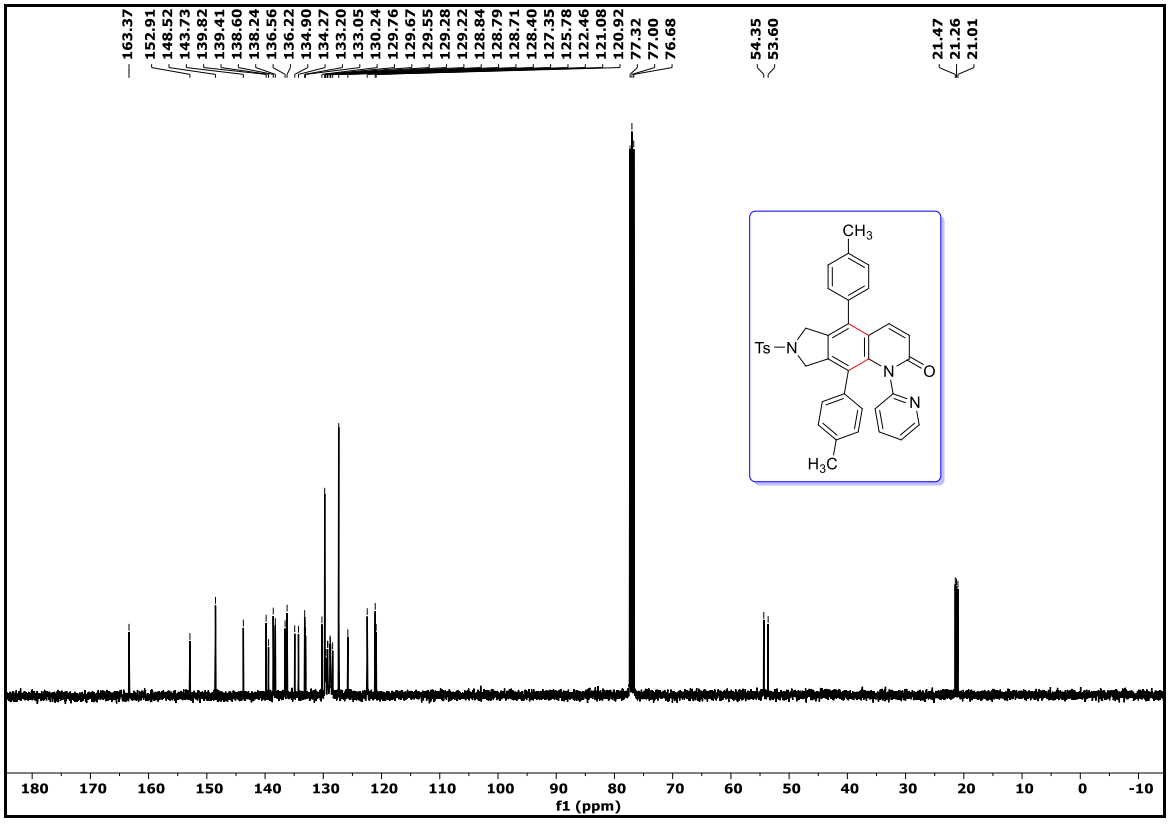
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ad.** Solvent $CDCl_3$



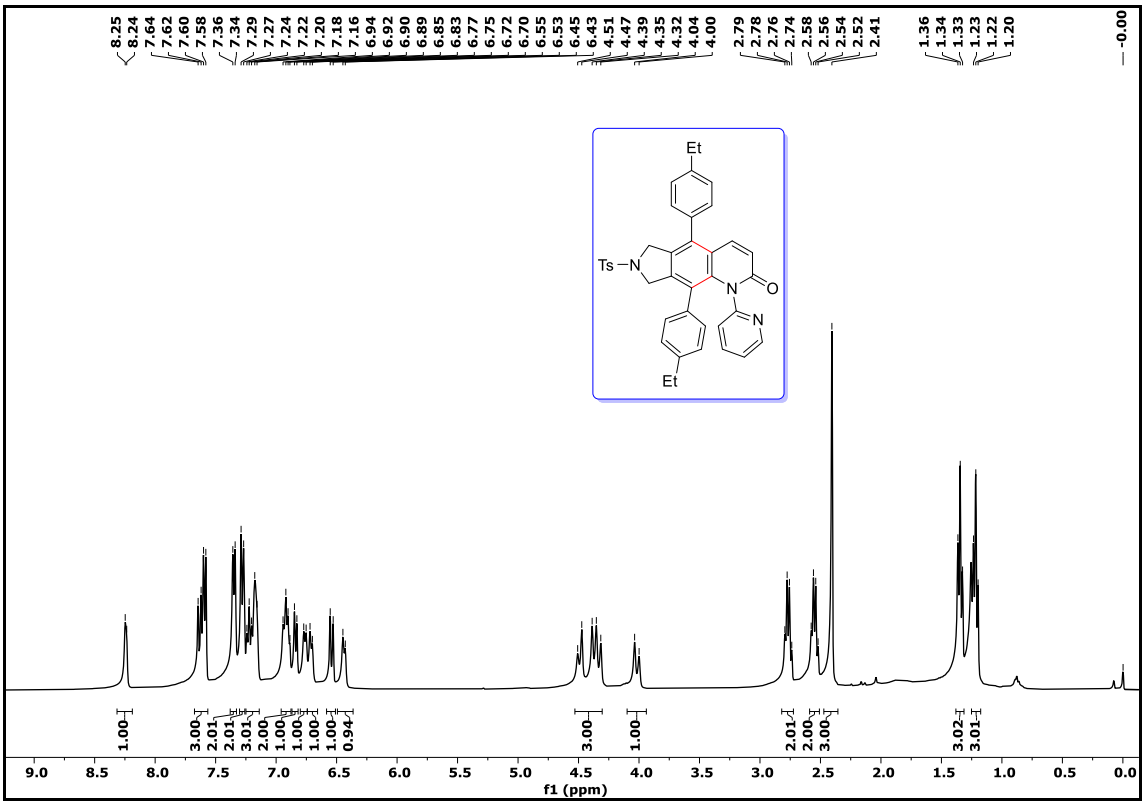


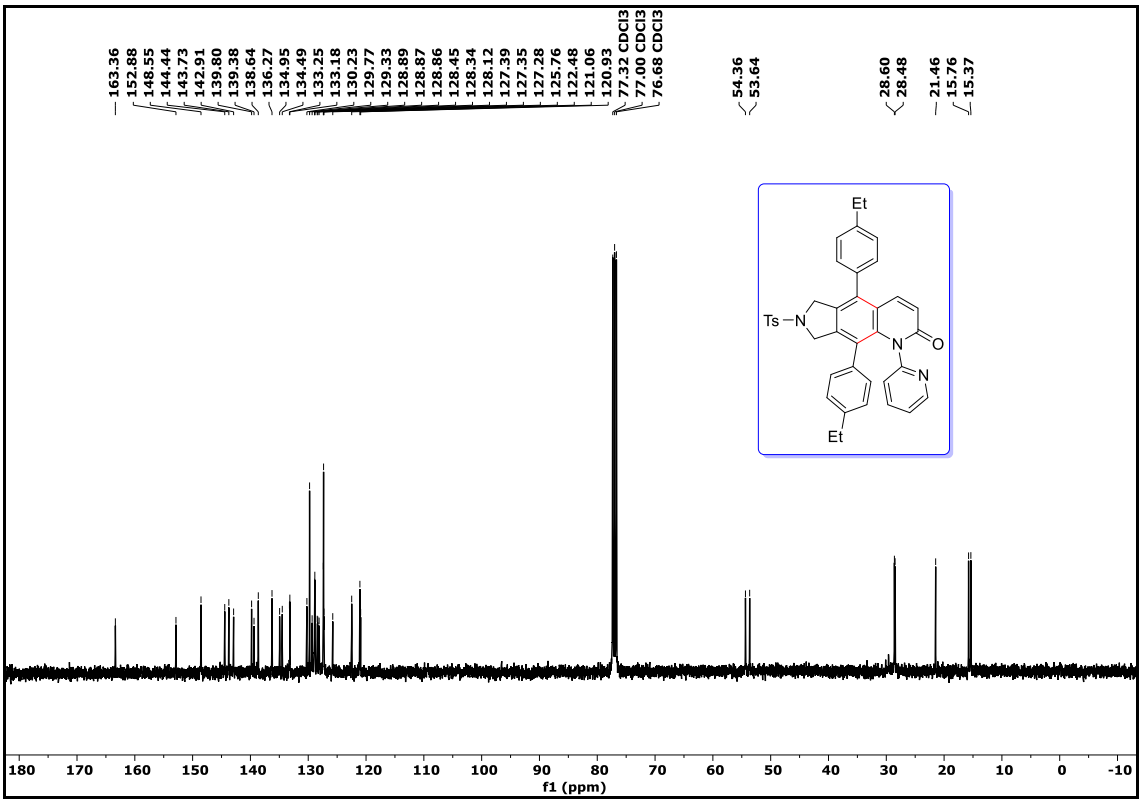
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ae.** Solvent $CDCl_3$



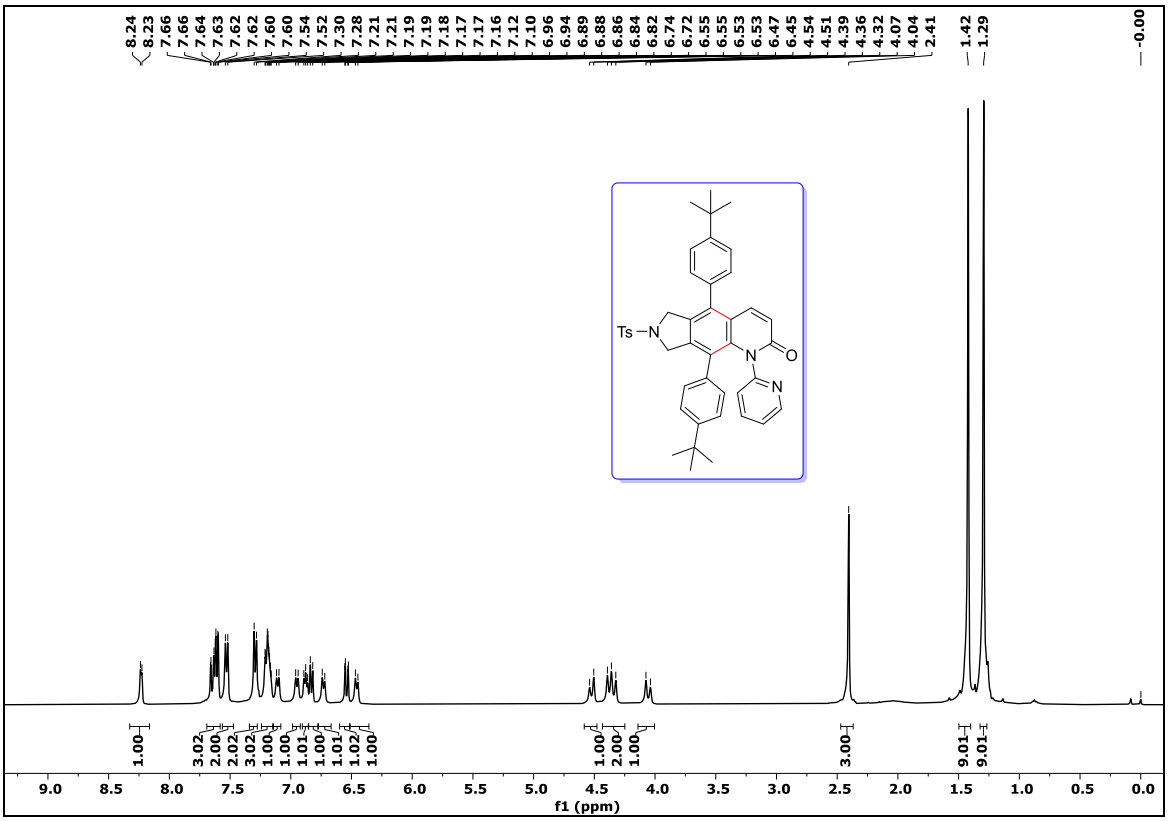


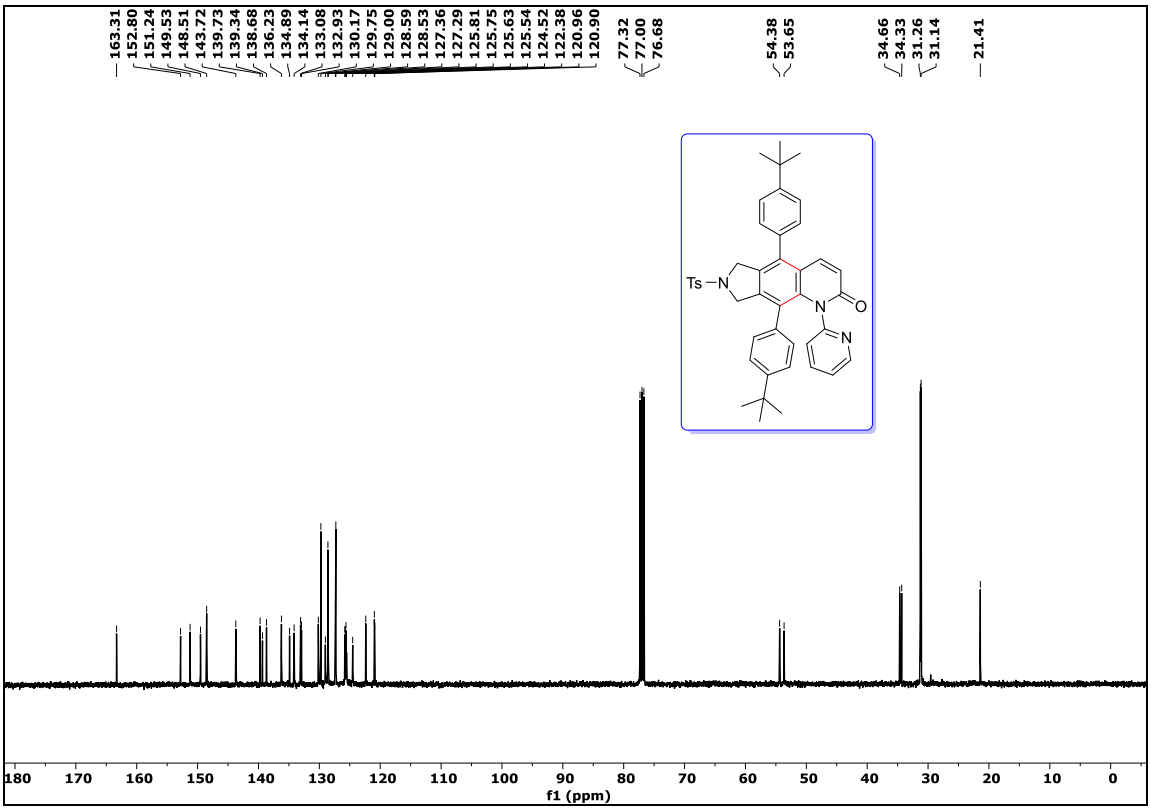
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3af.** Solvent $CDCl_3$



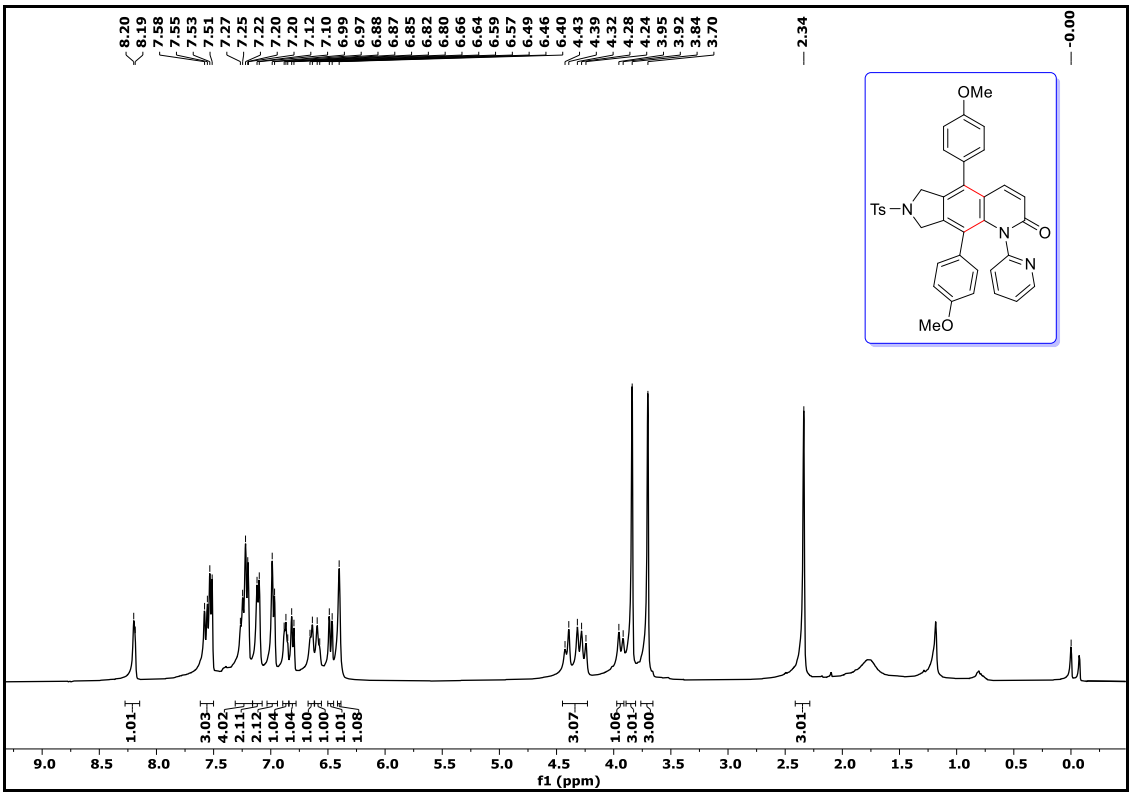


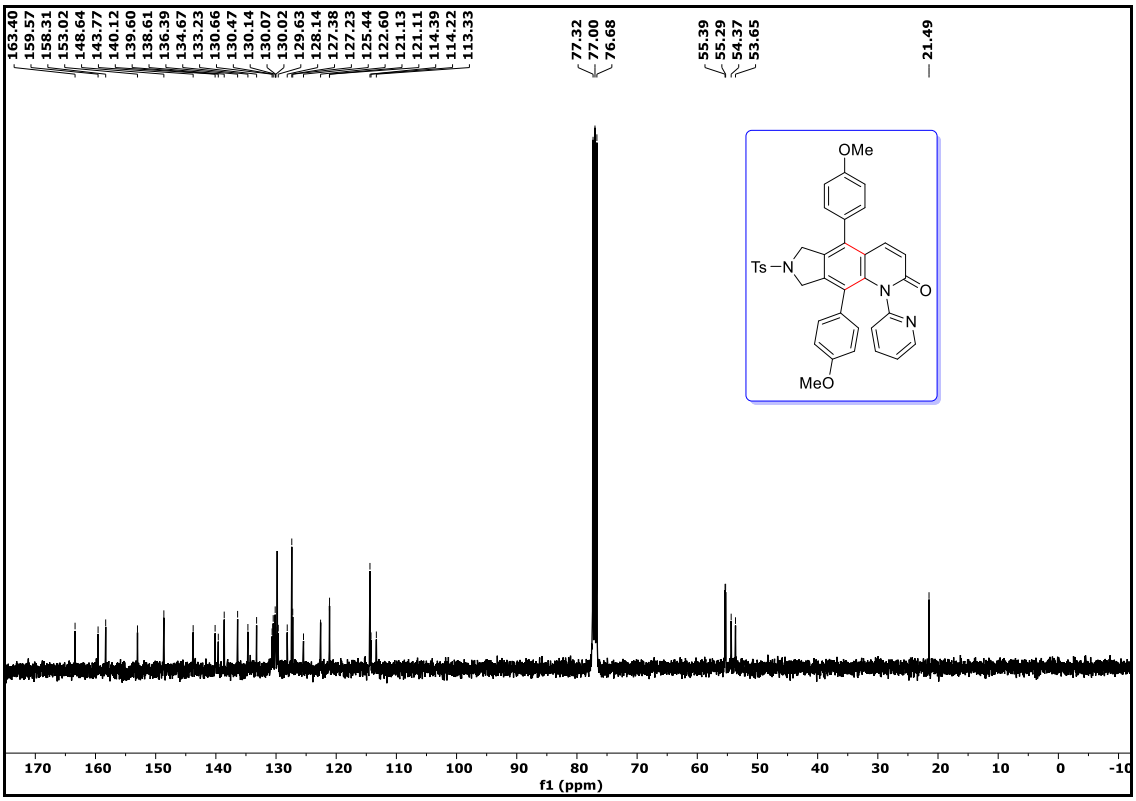
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ag.** Solvent $CDCl_3$



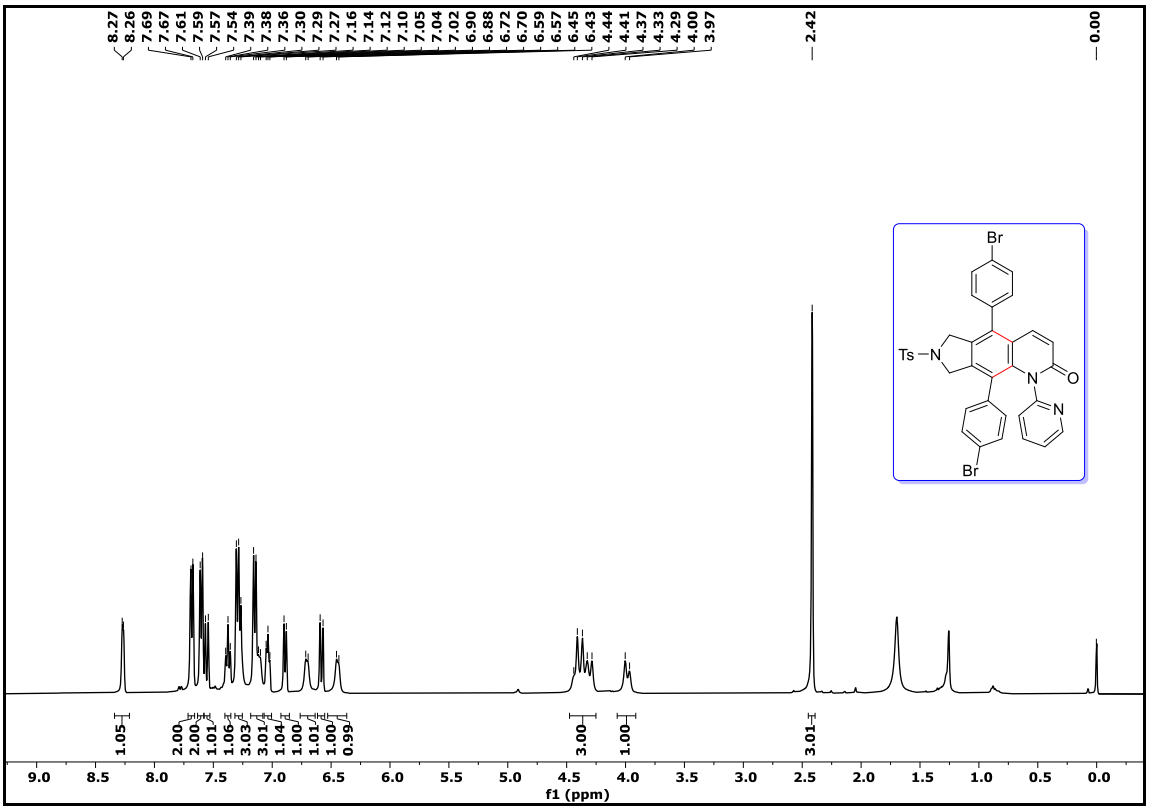


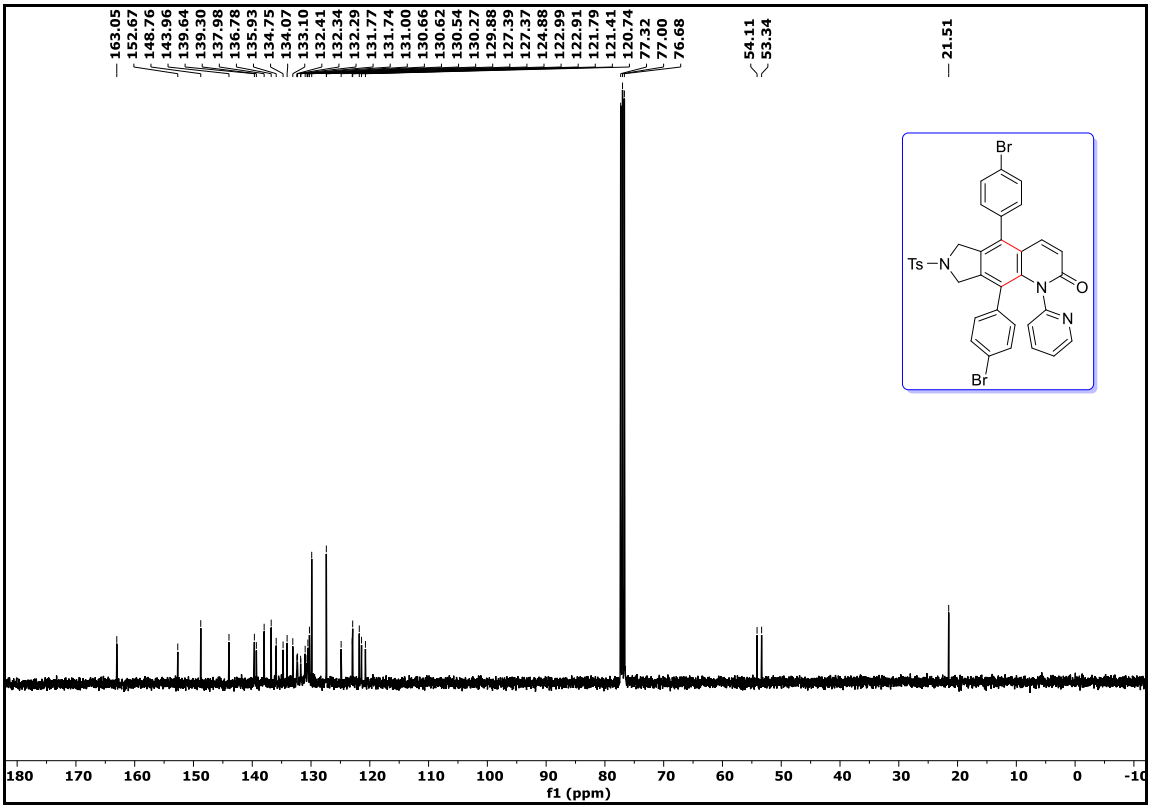
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ah.** Solvent $CDCl_3$



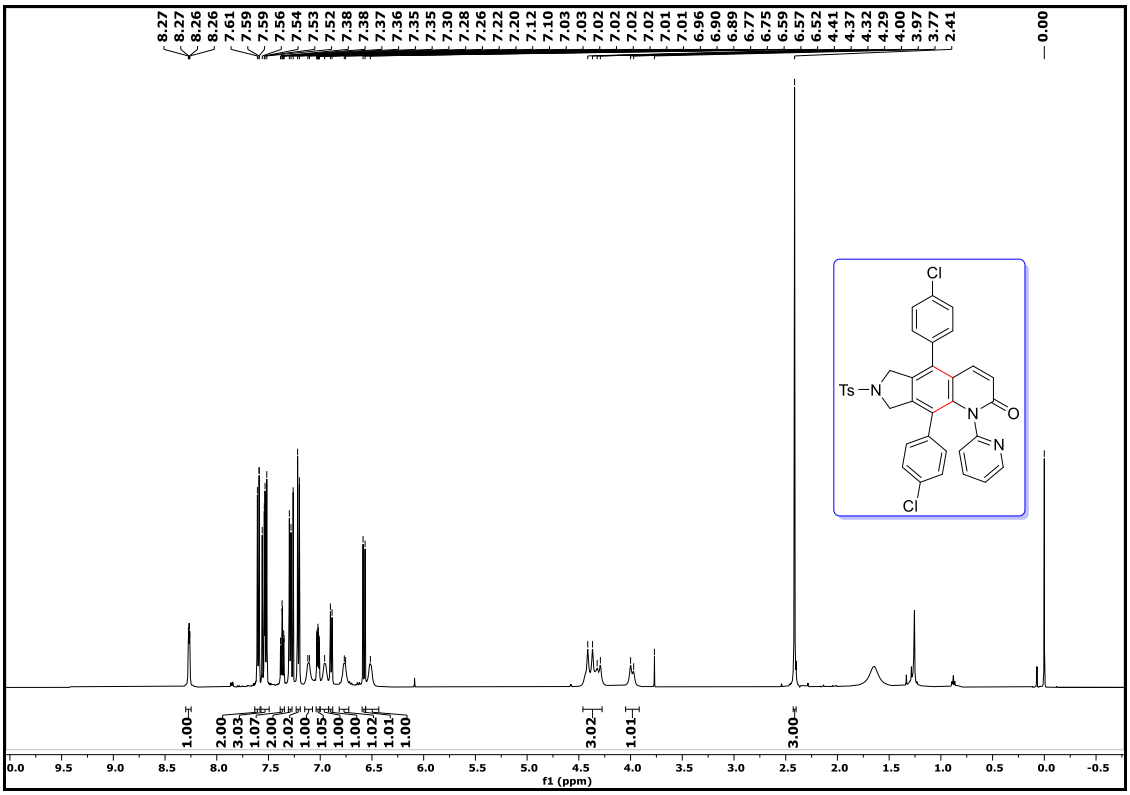


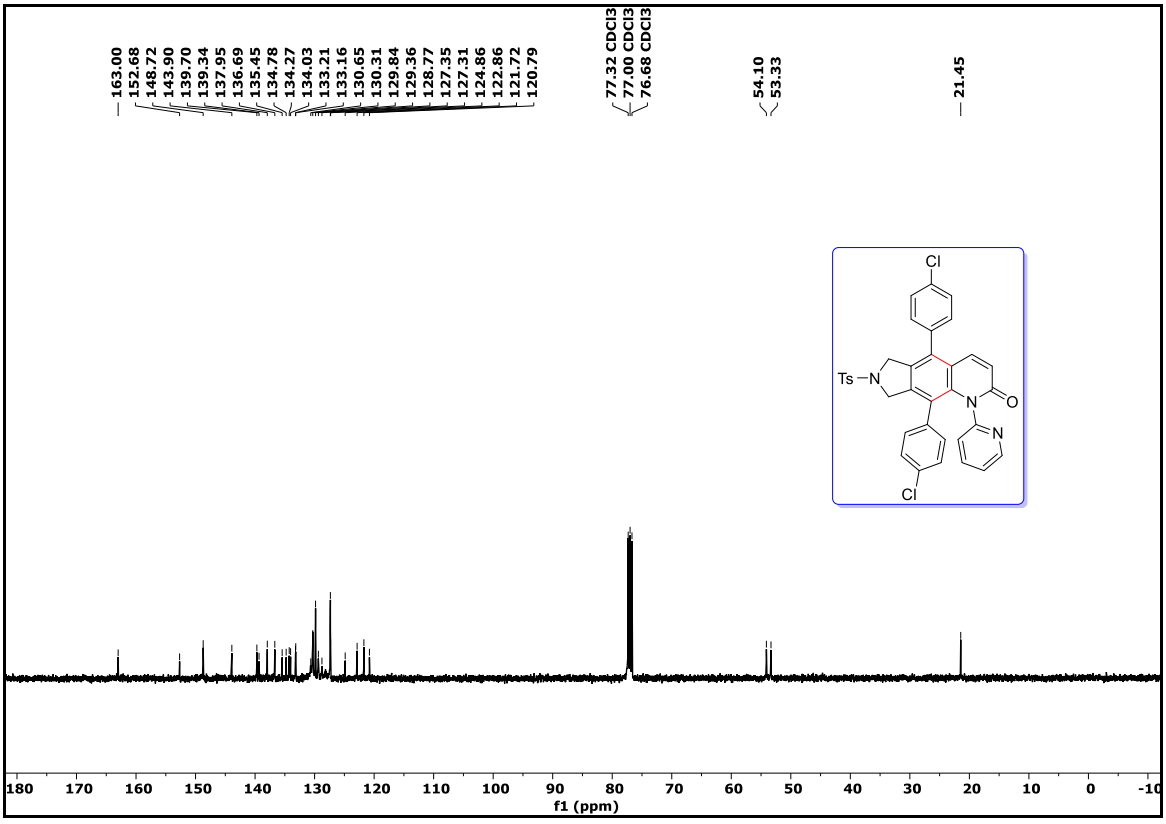
^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ai.** Solvent $CDCl_3$



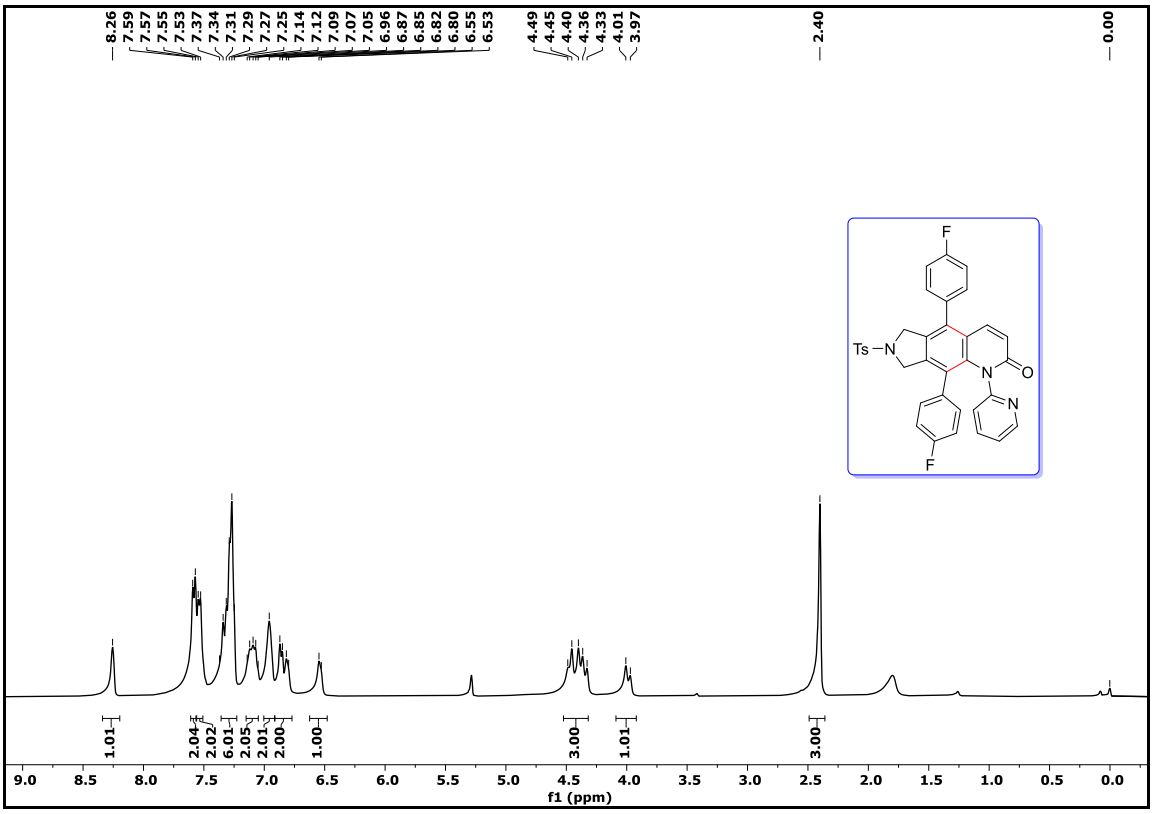


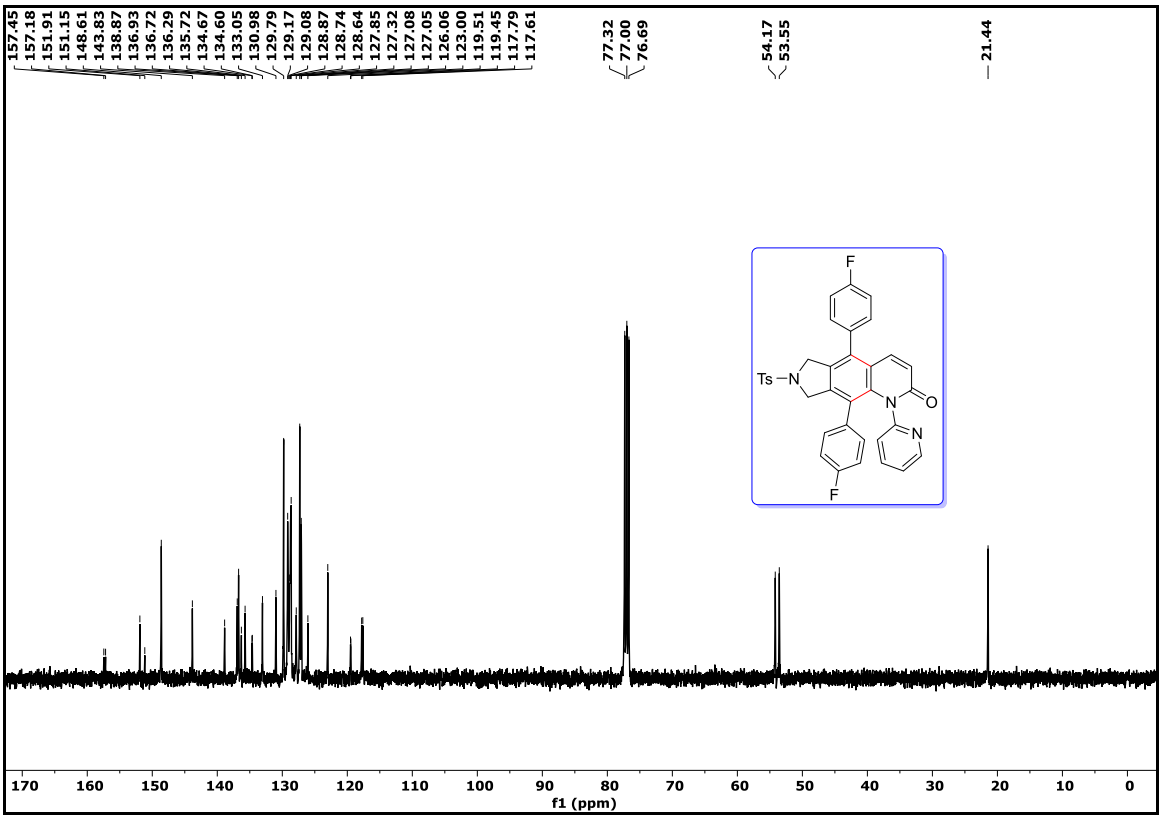
^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3aj.** Solvent $CDCl_3$



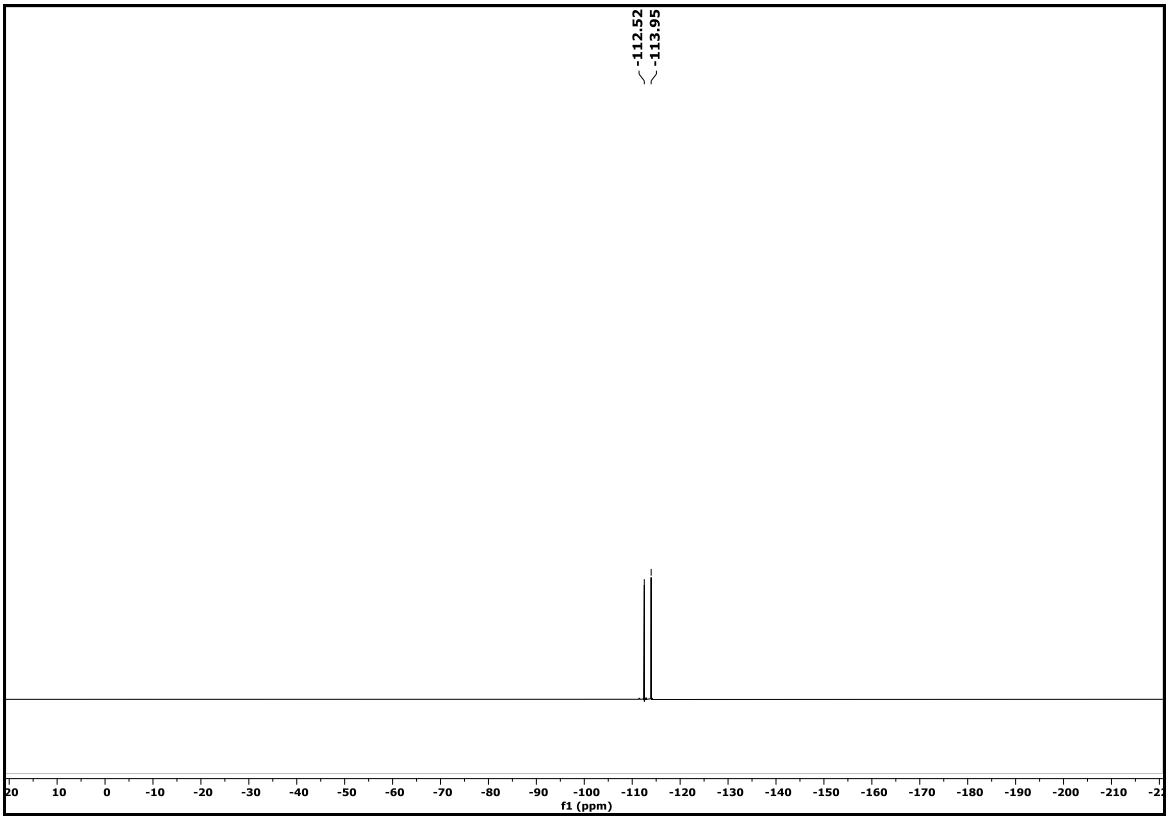


^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound **3ak.** Solvent $CDCl_3$

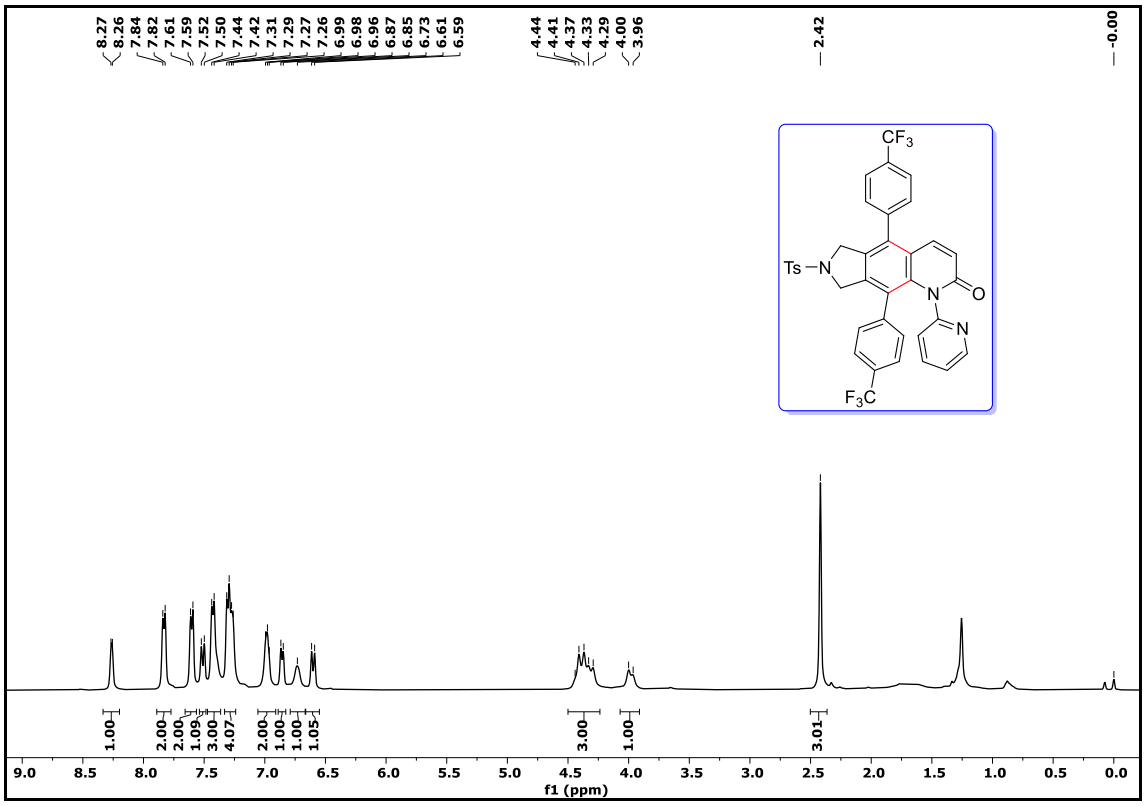


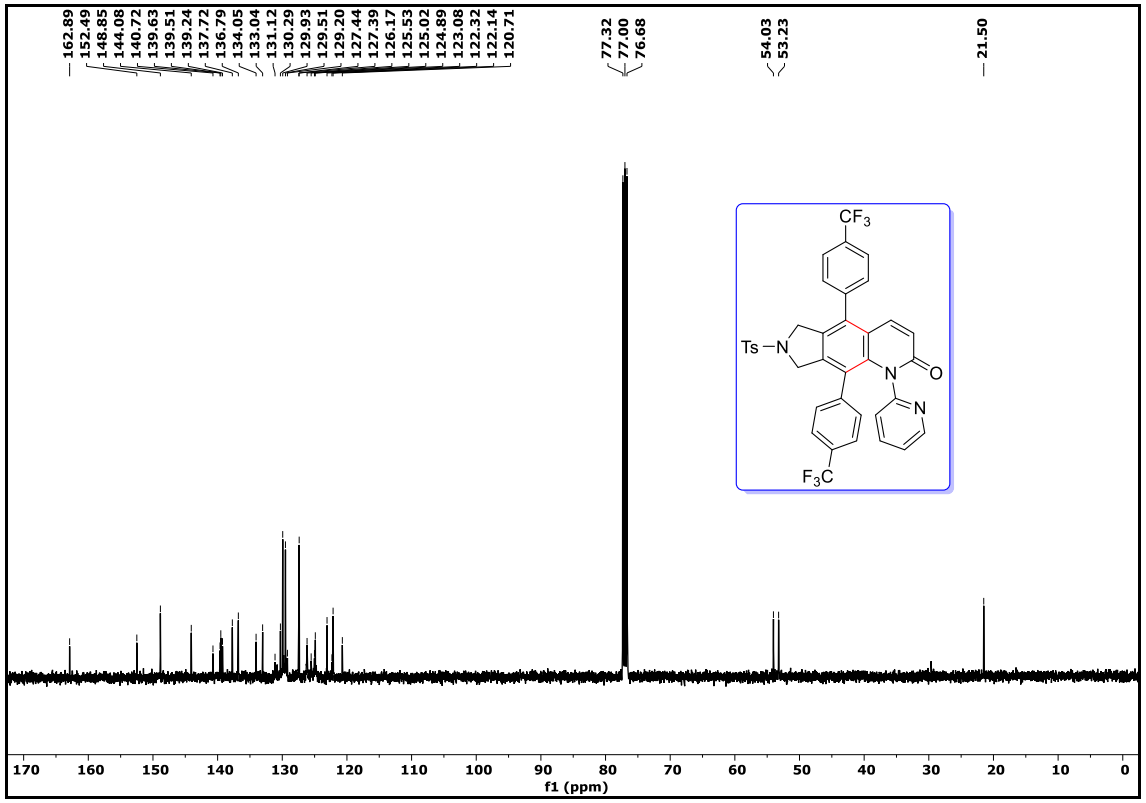


^{19}F NMR Spectra of Compound 3ak. (Solvent $CDCl_3$, 471 MHz)

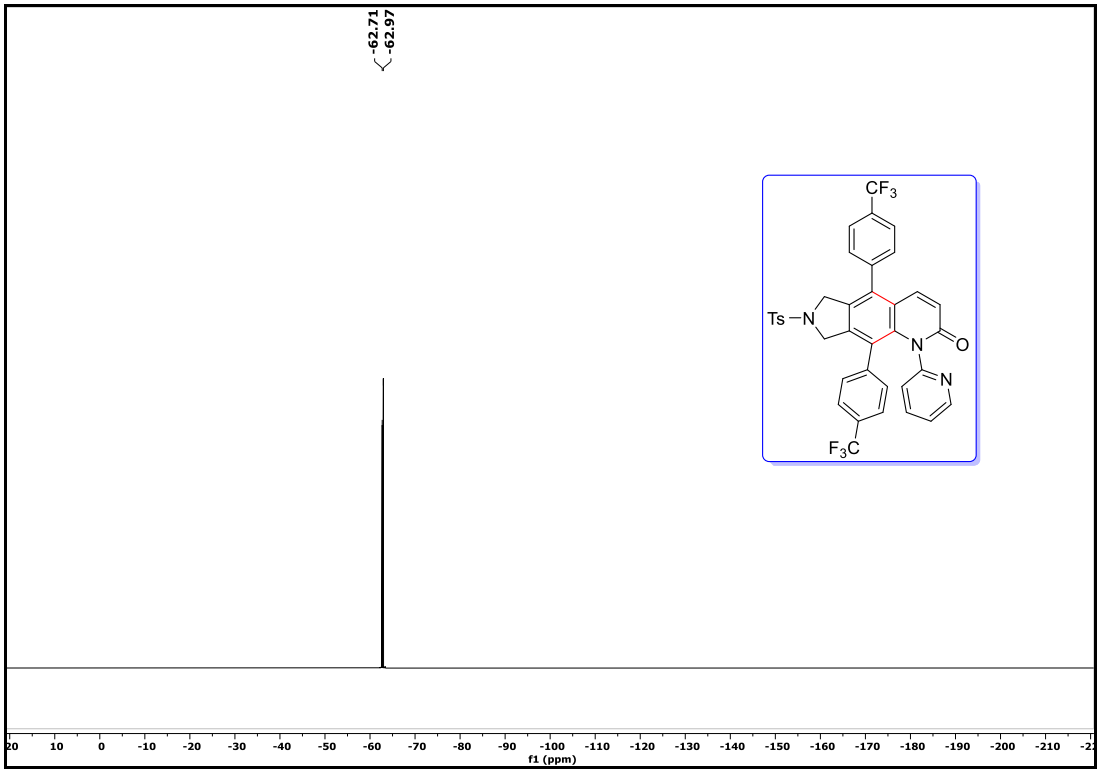


^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (101 MHz) NMR Spectra of Compound 3al. Solvent $CDCl_3$

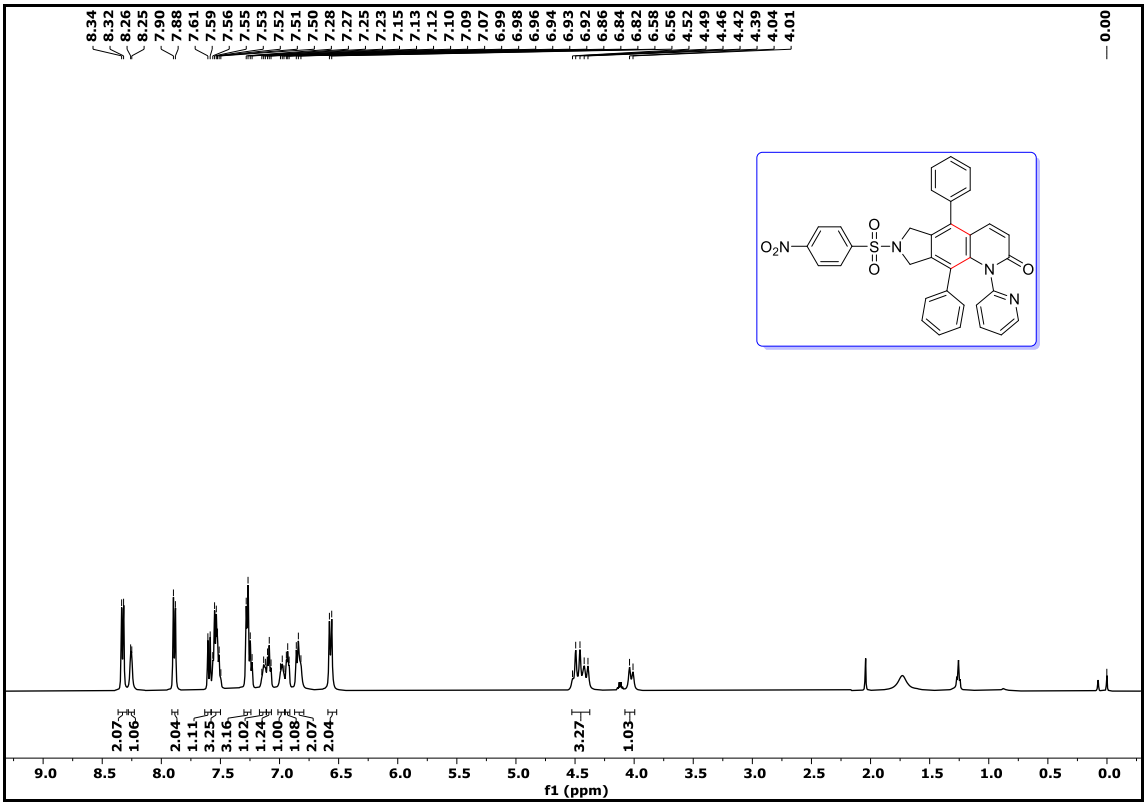


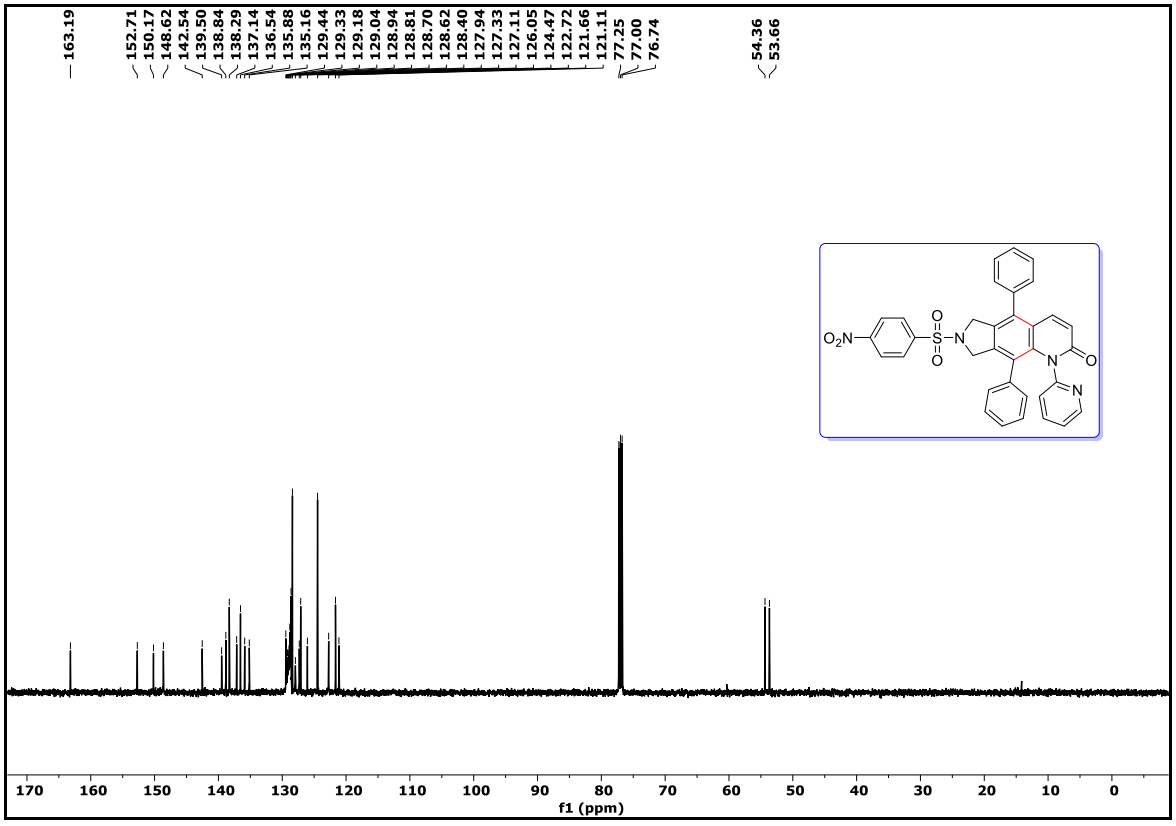


^{19}F NMR Spectra of Compound 3al. (Solvent $CDCl_3$, 471 MHz)

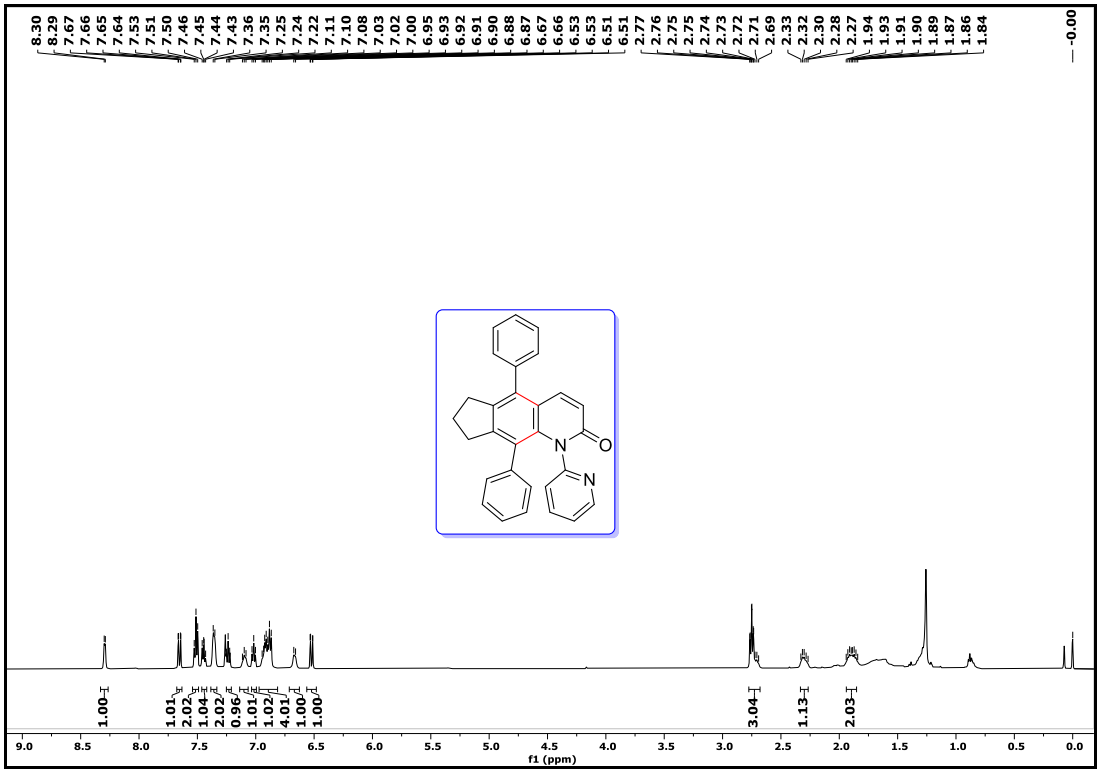


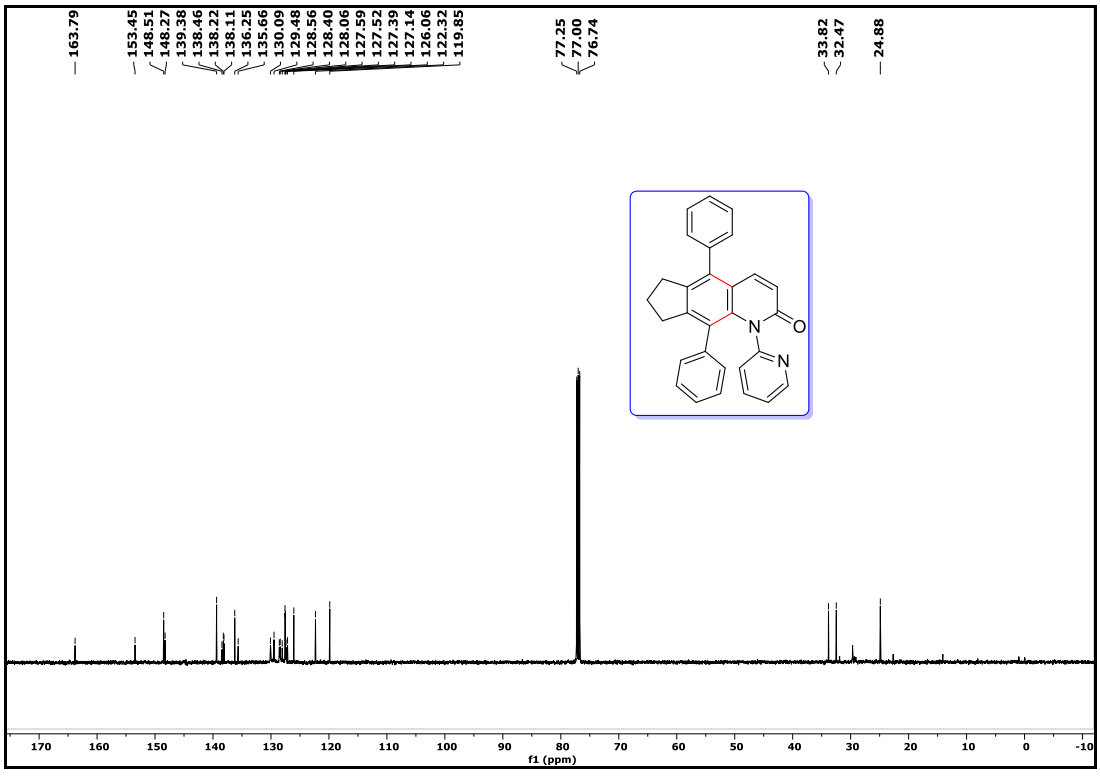
^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (126 MHz) NMR Spectra of Compound 3am. Solvent $CDCl_3$



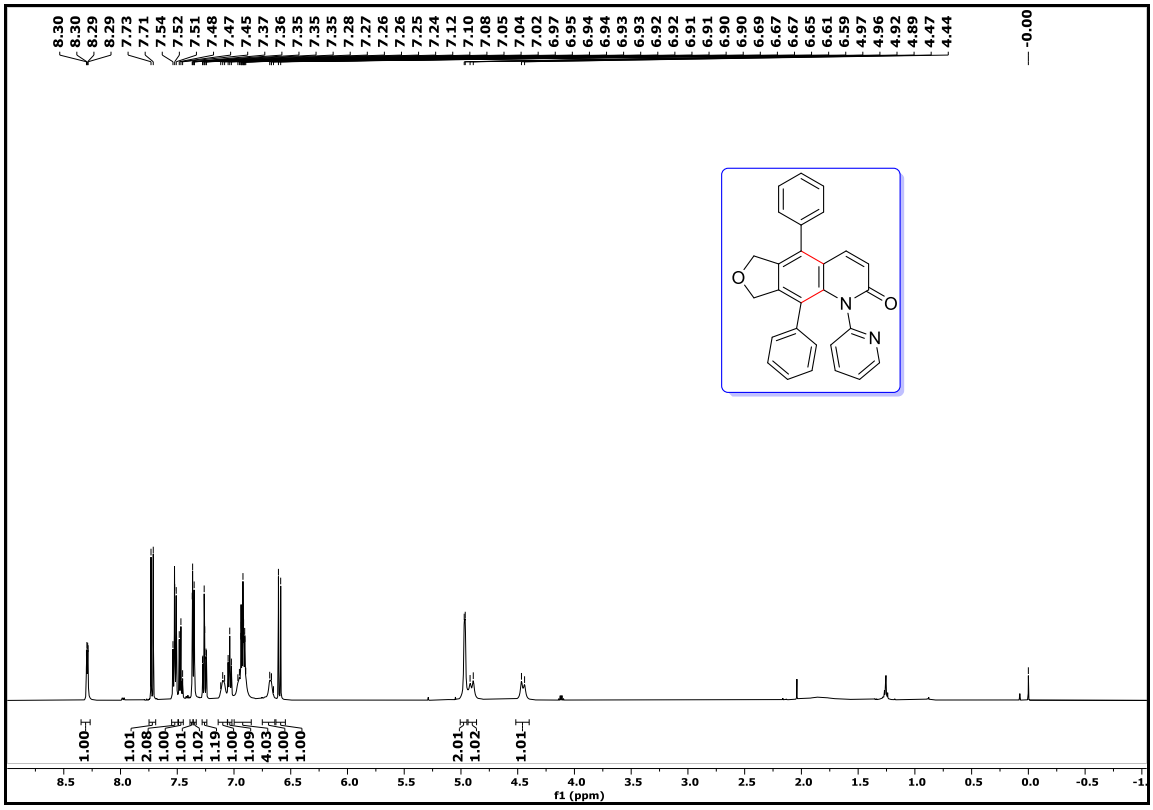


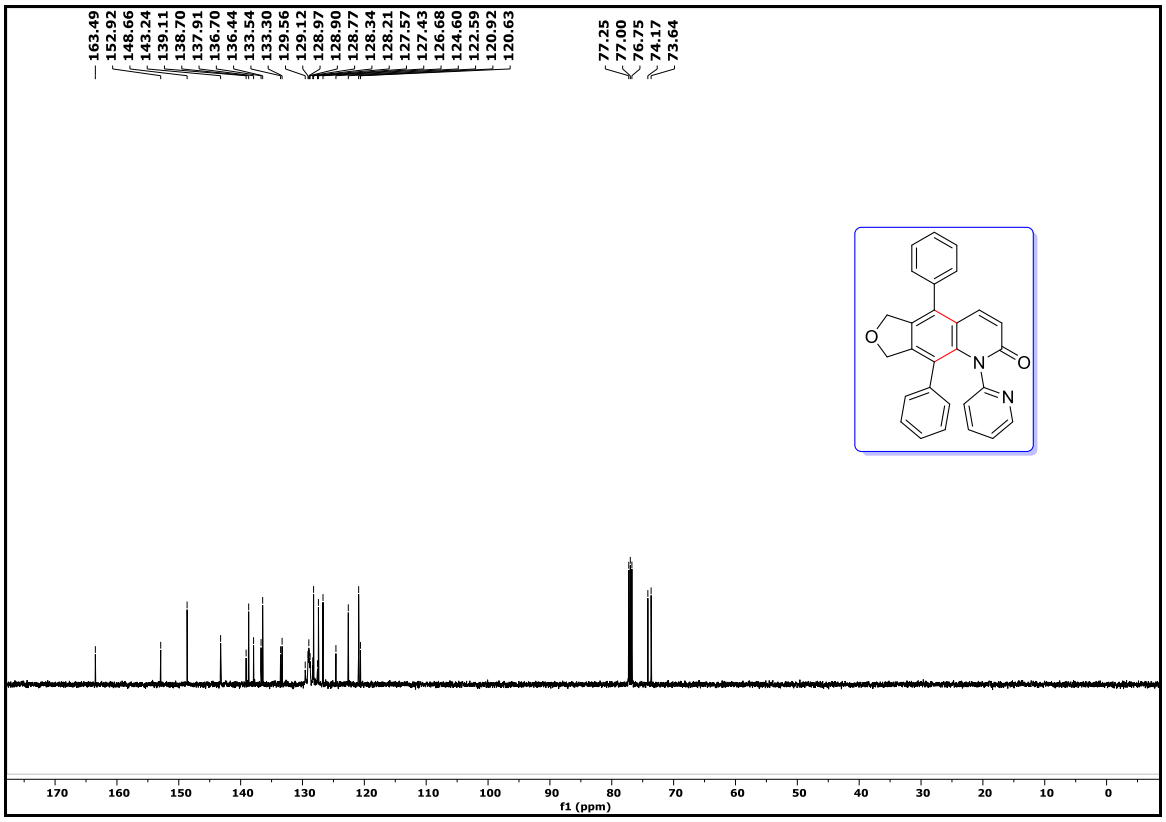
^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (126 MHz) NMR Spectra of Compound 3an. Solvent $CDCl_3$



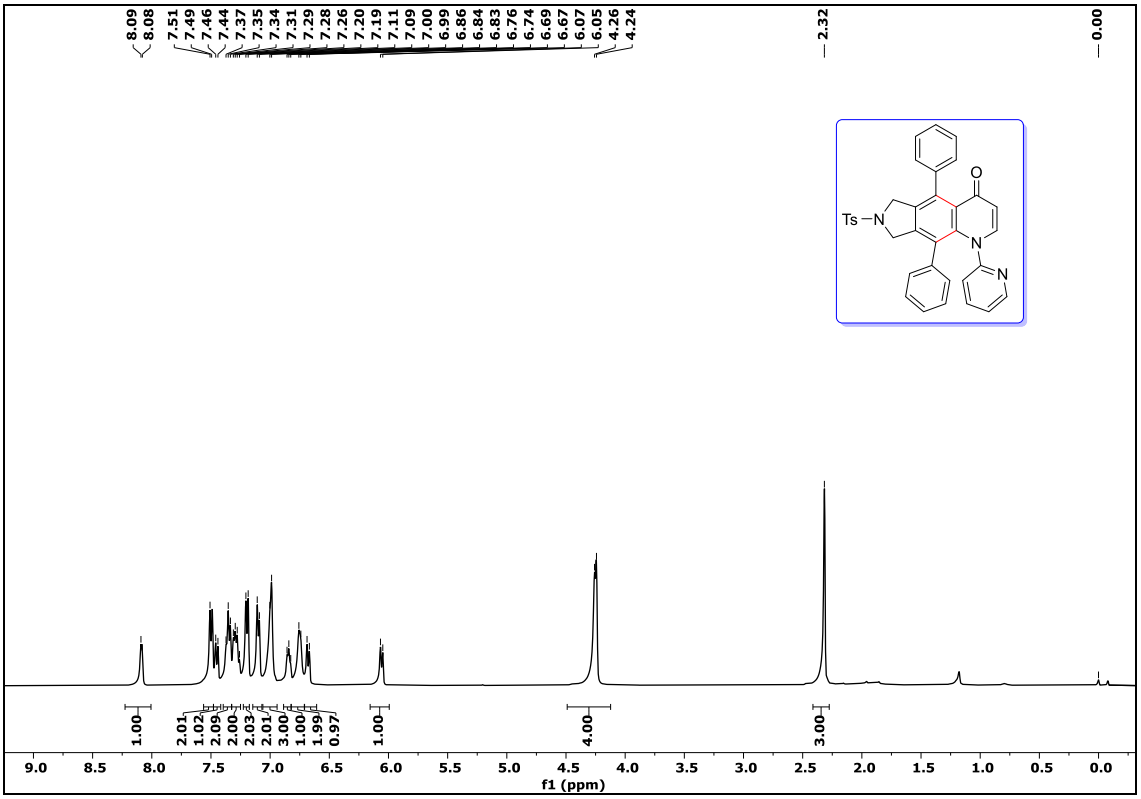


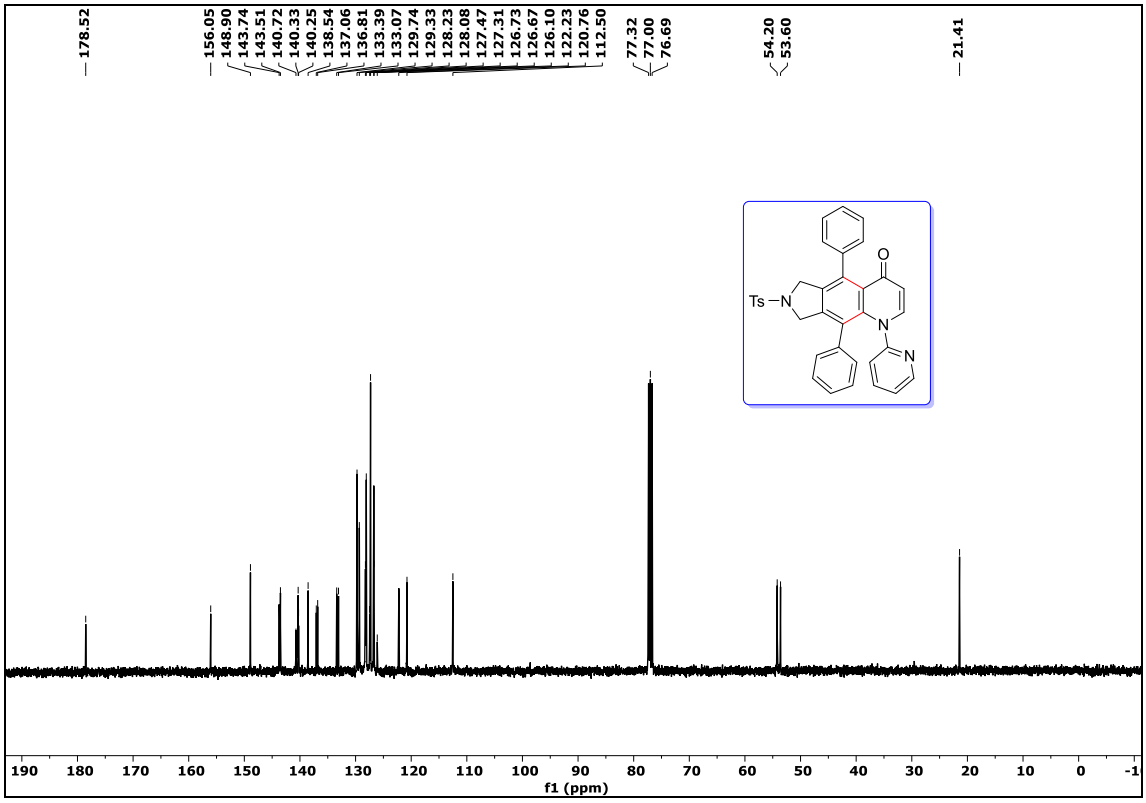
^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (126 MHz) NMR Spectra of Compound 3ap. Solvent $CDCl_3$



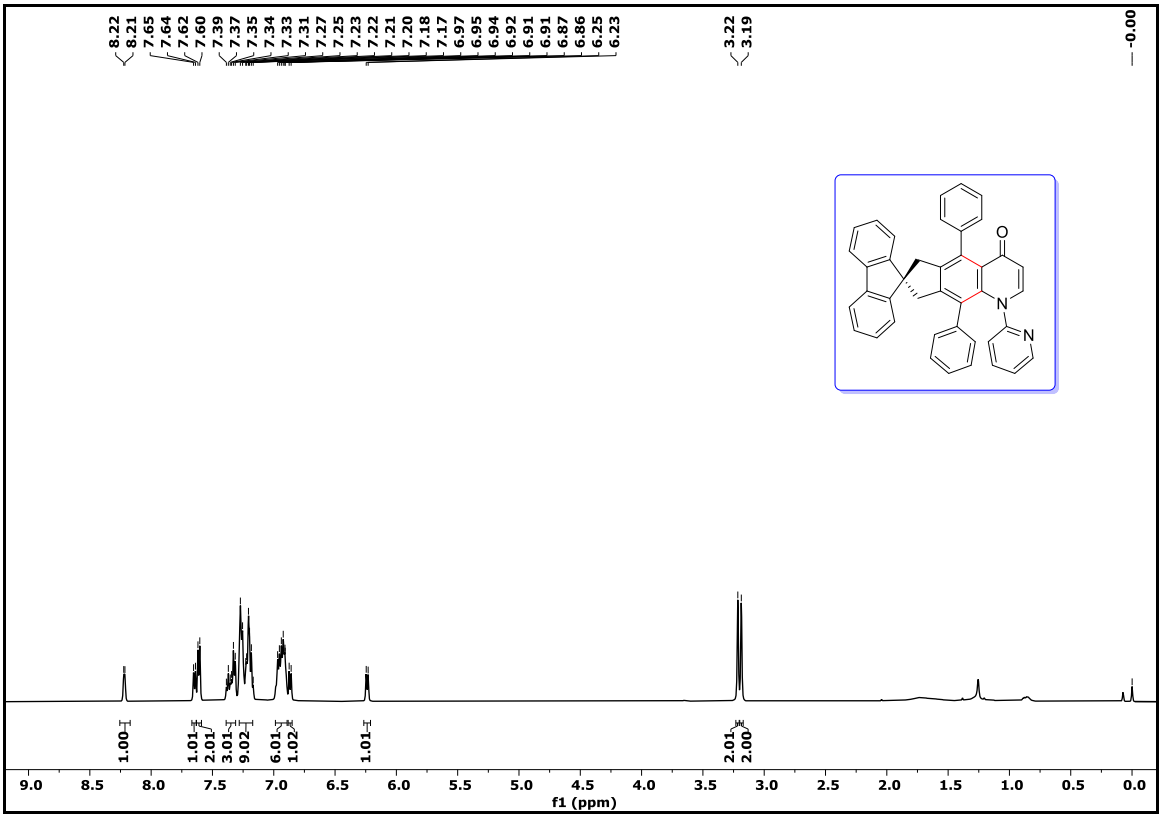


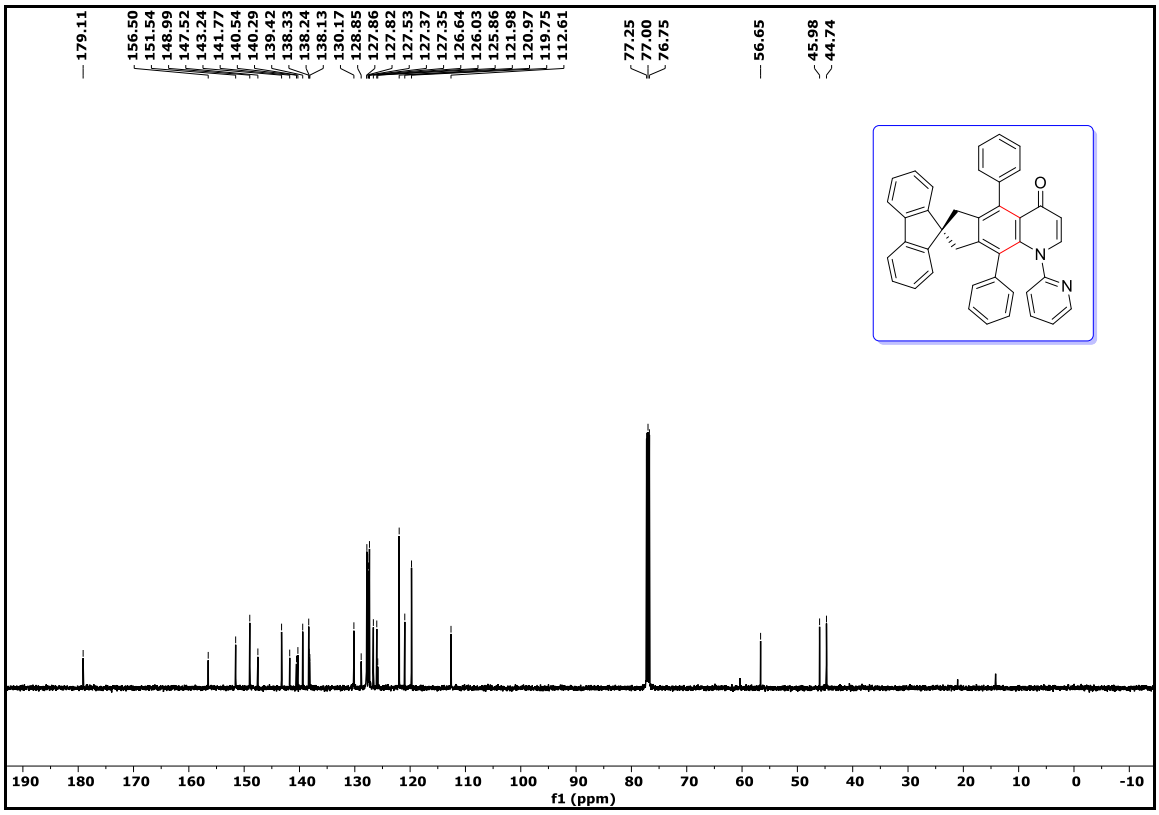
^{1}H (400 MHz) and ^{13}C{^{1}H} (101 MHz) NMR Spectra of Compound 3la. Solvent $CDCl_3$



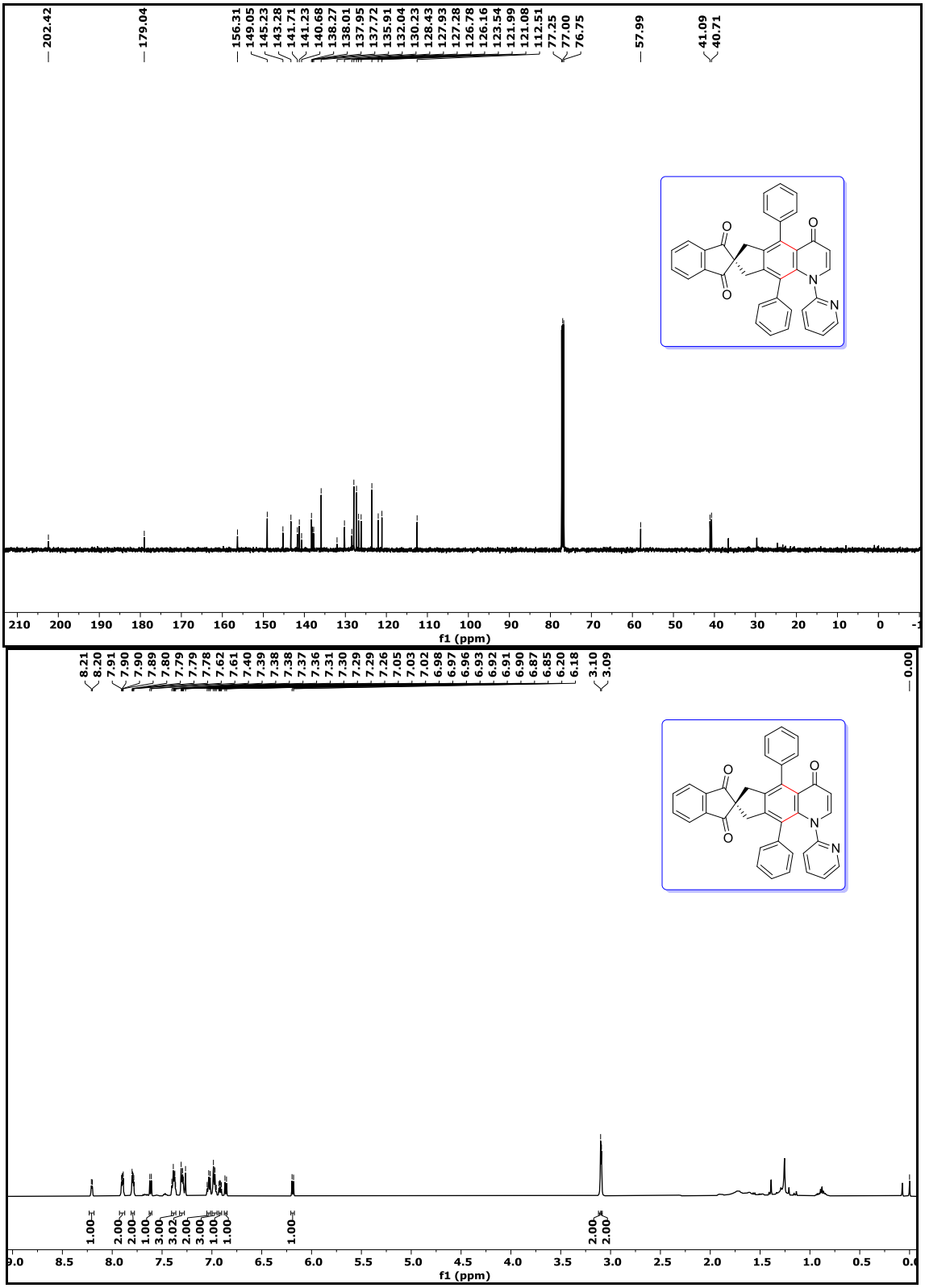


^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (126 MHz) NMR Spectra of Compound 3lc. Solvent $CDCl_3$

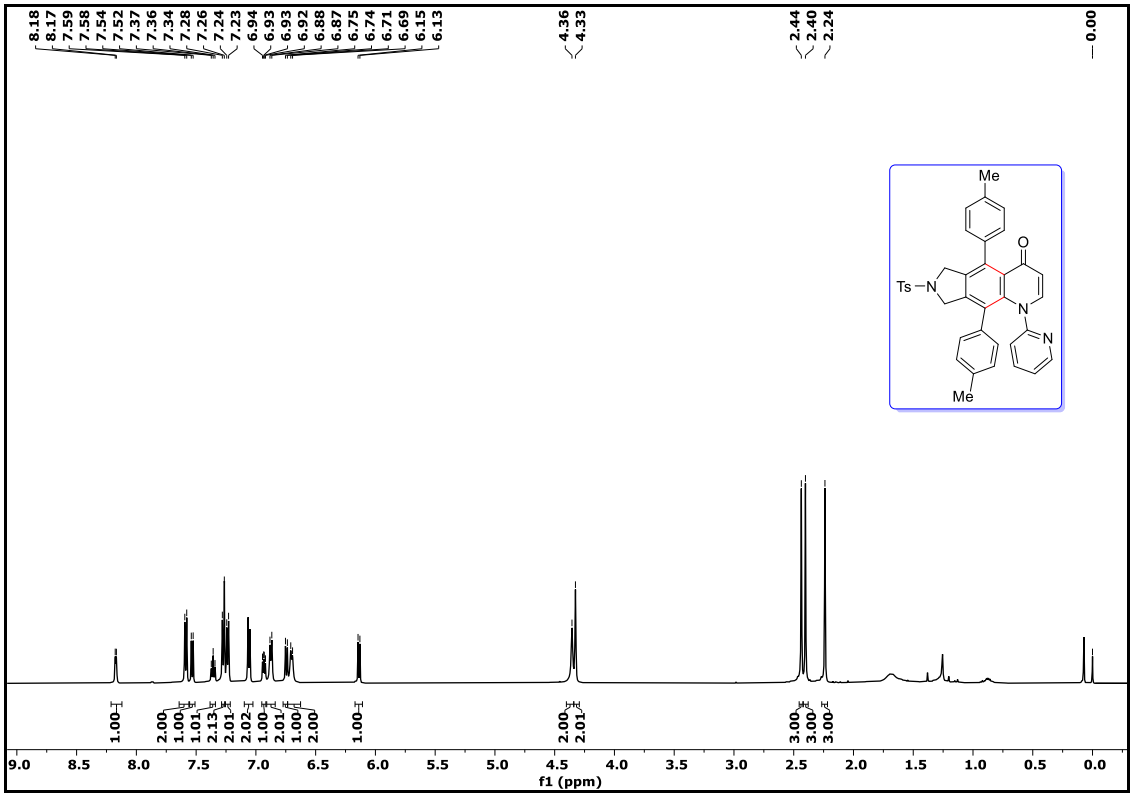


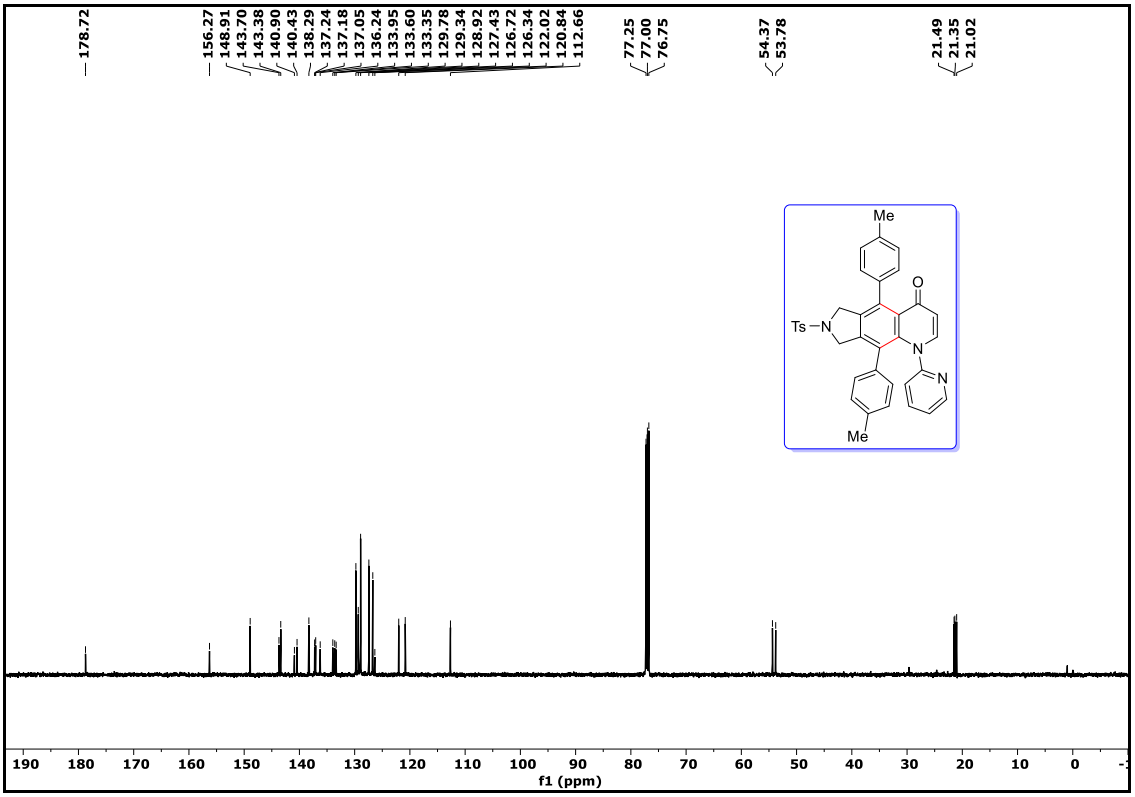


^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (126 MHz) NMR Spectra of Compound 3ld. Solvent $CDCl_3$



^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (126 MHz) NMR Spectra of Compound 3le. Solvent $CDCl_3$





^{1}H (500 MHz) and $^{13}C\{^{1}H\}$ (126 MHz) NMR Spectra of Compound 4aa. Solvent $CDCl_3$