Supporting Information

Harnessing the benzyne insertion consequence to enable π-extended pyrido-acridine and quinazolino-phenanthridine

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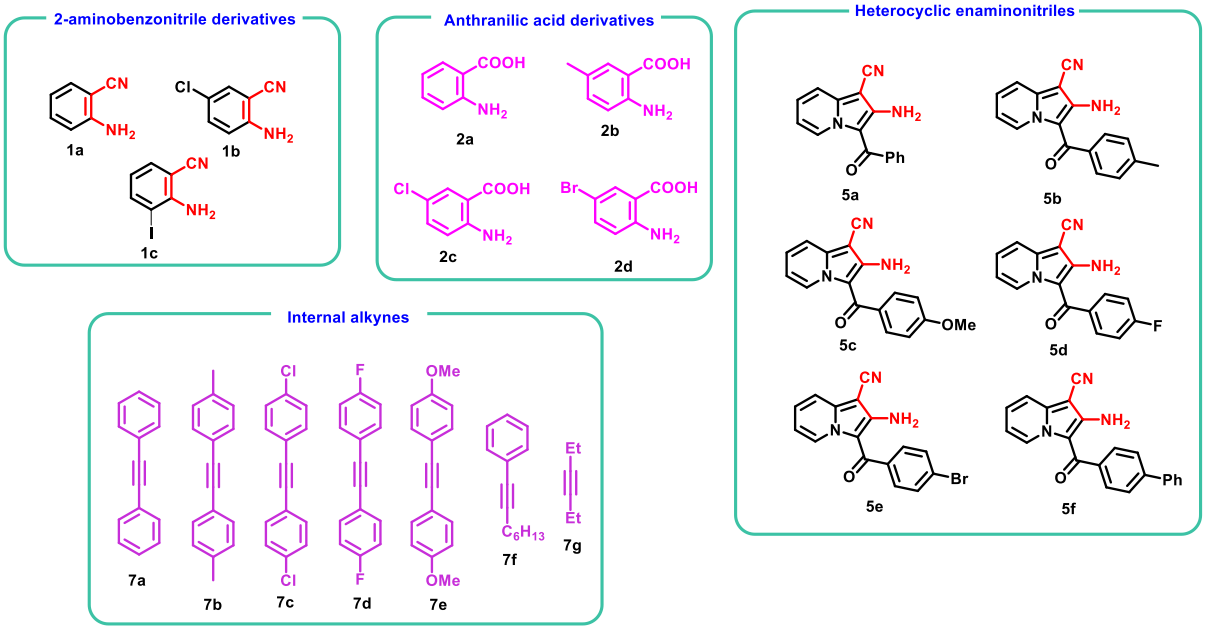
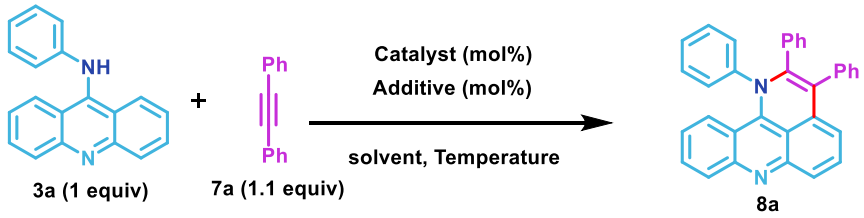
1. List of starting materials:



2. Optimization Studies

Table S1. Optimization study for the π-extension reaction leading to pyrido-acridine scaffold (8)[a]

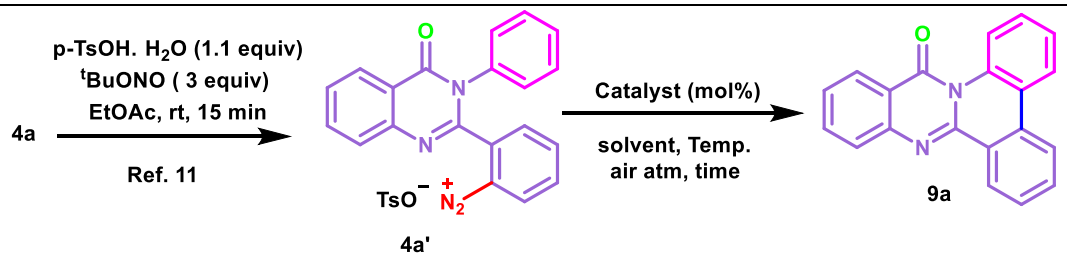


Entry	Catalyst (mol%)	Additive (mol%)	Solvent	Temp. (°C)	Yield (%)[b]
1	$[RuCl_2(p\text{-cymene})]_2$ (5)	$AgSbF_6$ (20)	DCE	90	*nd*
2	$[RuCl_2(p\text{-cymene})]_2$ (5)	$Cu(OAc)_2 \cdot H_2O$ (20)	DCE	90	40
3	$[RuCl_2(p\text{-cymene})]_2$ (5)	$Cu(OAc)_2 \cdot H_2O$ (20)	DCE	120	52
4	$[RuCl_2(p\text{-cymene})]_2$ (5)	$Cu(OAc)_2 \cdot H_2O$ (20)	DMF	120	*nd*
5	$[Cp^*RhCl_2]_2$ (2)	$Cu(OAc)_2 \cdot H_2O$ (20)	DCE	120	60
6	$[Cp^*RhCl_2]_2$ (2)	$Cu(OAc)_2 \cdot H_2O$ (20)	o-xylene	120	70
7	**$[Cp^*RhCl_2]_2$ (2)**	**$Cu(OAc)_2 \cdot H_2O$ (20)**	**o-xylene**	**100**	**76**
8	$[Cp^*RhCl_2]_2$ (5)	$Cu(OAc)_2 \cdot H_2O$ (20)	o-xylene	100	77
9	$[Cp^*RhCl_2]_2$ (2)	AgOAc (20)	o-xylene	100	55
10	$[Cp^*RhCl_2]_2$ (2)	NaOAc (20)	o-xylene	100	*nd*
11[c]	$[Cp^*RhCl_2]_2$ (2)	$Cu(OAc)_2 \cdot H_2O$ (20)	o-xylene	100	15
12	$[Cp^*RhCl_2]_2$ (2)	-	o-xylene	100	*nd*
13	$[Cp^*Co(CO)I_2]$ (5)	$Cu(OAc)_2 \cdot H_2O$ (20)	o-xylene	100	27

14	$Pd(OAc)_2$ (10)	$Cu(OAc)_2 \cdot H_2O$ (20)	o-xylene	100	*nd*

[a]Reaction Conditions: All the reactions were carried out with 0.1 mmol of **3a** and 0.11 mmol of **7a** in 1 mL of solvent for 24h under air atmosphere. [b]isolated yield. [c]Argon atmosphere.

Table S2. Optimization study for the deaminative coupling reaction enabling quinazolinone fused phenanthridine (**9**)[a]



Entry	Catalyst (mol%)	Solvent	Temp. (°C)	Time (h)	Yield(%)[b]
1	$Pd(OAc)_2$ (5 mol%)	CH_3CN	90	24	14
2	$Pd(OAc)_2$ (10 mol%)	CH_3CN	90	24	20
3	$Pd(OAc)_2$ (10 mol%)	1,4-dioxane	100	24	29
4	$Pd(OAc)_2$ (10 mol%)	DMF	100	18	47
5	$Pd(OAc)_2$ (10 mol%)	DMF	100	12	58
6	$Pd(OAc)_2$ (10 mol%)	DMF	90	12	70
7	$Pd(OAc)_2$ (10 mol%)	DMSO	90	12	81
8	**$Pd(OAc)_2$ (5 mol%)**	**DMSO**	**90**	**12**	**80**
9	$Pd(TFA)_2$ (5 mol%)	DMSO	90	12	78
10	$Cu(OTf)_2$ (10 mol%)	DMSO	90	24	nd
11	$Fe(OTf)_3$ (10 mol%)	DMSO	90	24	nd

[a]Reaction Condition: Step 1. The reaction was carried out with 0.1 mmol of 4a in 1.5 mL of EtOAc at rt. Step 2. After evaporation of EtOAc, 1mL solvent was added and the reaction was continued under air atmosphere. [b]isolated yield.

3. Materials and Methods

All reactions were carried out in an oven dried sealed tube. Unless otherwise stated, all solvents were dried by standard procedure: THF and o-xylene were distilled over sodium metal, and DMSO was distilled over calcium hydride. Acetonitrile and ethylene glycol were used as received from commercial sources. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F254 plates. Visualization of the compounds on TLC was

achieved under UV light (254 nm), exposure to iodine vapour or treatment with $KMnO_4$ solution followed by heating. Column chromatography was performed through silica gel (100-200 mesh or 230-400 mesh) using a proper solvent system. The ^1H NMR spectroscopic data were recorded with a Bruker 300 or 400 MHz NMR instruments. ^{13}C NMR spectra were similarly recorded by using 75 or 101 MHz NMR instruments applying a broadband decoupled mode. Proton and carbon NMR chemical shifts (δ) are reported in parts per million (ppm) relative to residual proton or carbon signals in $CDCl_3$ (δ = 7.26, 77.16) and DMSO-*d*$_6$ (δ= 2.50, 39.52). Coupling constants (*J*) are reported in Hertz (Hz) and refer to apparent multiplicities. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, dd: doublet of doublets, dt: doublet of triplets, ddd: doublet of doublet of doublets, tt: triplet of triplets, td: triplet of doublets, m: multiplet, br: broad. High resolution mass spectra (HRMS) were recorded in ESI (+Ve) method using a time-of-flight (TOF) mass analyzer. Other chemicals were obtained from commercial sources and used without further purification.

4. General Procedures

4.1. General Procedure for the Synthesis of Acridine derivatives 3 (GP I):

The reactions to prepare the acridines were carried out according to the following procedure unless otherwise stated. Initially, an oven dried sealed tube was charged with anthranilic acid **2** (1.1 mmol, 2.2 equiv.) and dissolved in 2mL of THF. Then it was placed at -10 ℃ bath under a continuous stream of argon gas and *tert*-butyl nitrite (1.1 mmol, 2.2 equiv, 114.0 mg) was introduced to this solution. The tube was sealed using a PTFE cap and the mixture was stirred for additional 5 minutes. Then, a solution of 2-aminobenzonitrile **1** (0.5 mmol, 1 equiv.) in 1 mL of THF and $Yb(OTf)_3$ (0.1 mmol, 62.0 mg) was inserted gradually in the sealed tube keeping the temperature constant. The tube was flashed by argon gas and sealed. The resulting mixture was then applied stirring at room temperature for a period of 10 minutes and following that subjected to transfer in an oil bath, pre-heated at 60 ℃. After completion of the reaction (monitored by TLC), the reaction mixture was diluted through 5 mL of ethyl acetate and 20 mL saturated aqueous sodium bicarbonate solution was added to the mixture. The aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Finally, the concentrated reaction mixture was purified by column chromatography using the petroleum ether and ethyl acetate mixture as eluent.

4.2. General Procedure for the Synthesis of quinazolimine derivatives 4 (GP II):

The reactions to prepare the quinazolimines were carried out according to the following procedure unless otherwise stated. Initially, an oven dried sealed tube was charged with anthranilic acid **2** (0.26 mmol, 1.0 equiv.) and dissolved in 1mL of THF. Then it was placed in -10 ℃ bath under a continuous stream of argon gas and *tert*-butyl nitrite (0.26 mmol, 1.0 equiv, 30.0 mg) was added in this solution. The tube was sealed using a PTFE cap and the mixture was stirred for additional 5 minutes. Then, a solution of 2-aminobenzonitrile **1** (0.5 mmol, 2.0 equiv.) in 1 mL of THF and $Yb(OTf)_3$ (0.15 mmol, 93.0 mg) was gradually added in the sealed tube maintaining the temperature constant. The tube was flashed by argon and sealed. Then, the reaction mixture was stirred at room temperature for a period of 10 minutes and following that it was subjected to transfer in an oil bath, pre-heated at 100 ℃. After completion of the reaction (monitored by TLC), the reaction mixture was diluted by adding 5 mL of ethyl acetate and then 20 mL saturated aqueous sodium bicarbonate solution was added. The aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. Finally, the concentrated reaction mixture was purified by column chromatography using the petroleum ether and ethyl acetate mixture as eluent.

4.3. General Procedure for the Synthesis of Indolizine fused quinoline derivatives 6 (GP III):

The reactions to prepare the acridines were carried out according to the following procedure unless otherwise stated. Initially, an oven dried sealed tube was charged with anthranilic acid **2** (1.65 mmol, 3.3 equiv.) and dissolved in 2mL of THF. Then it was placed in -10 ℃ bath under a continuous stream of argon gas and *tert*-butyl nitrite (1.65 mmol, 3.3 equiv, 170.0 mg) was added in this solution. The tube was sealed using a PTFE cap and the mixture was stirred for 5 minutes. Then, a solution of indolizine derivatives **5** (0.5 mmol, 1 equiv.) in 1 mL of THF and $Yb(OTf)_3$ (0.1 mmol, 62.0 mg) was added in the sealed tube maintaining the same temperature. The tube was flashed by argon and sealed. Then, the reaction mixture was stirred at room temperature for 10 minutes and transferred to an oil bath, pre-heated at 60 ℃. After completion of the reaction (monitored by TLC), the reaction mixture was diluted by adding 5 mL of ethyl acetate and then 20 mL saturated aqueous sodium bicarbonate solution was added. The aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. Then the concentrated reaction mixture

was purified by column chromatography using the petroleum ether and ethyl acetate mixture as eluent.

4.4. General Procedure for the Synthesis of π- extended pyrido-acridine derivatives 7 (GP IV):

The reactions to prepare the π- extended pyrido-acridines were carried out according to the following procedure unless otherwise stated. To an oven dried 10 mL RB flask equipped with a magnetic stirrer, acridine derivatives **3** (0.2 mmol, 1 equiv), internal alkynes **7** (0.22 mmol, 1.1 equiv), $[(Cp^*RhCl_2)_2]$ (2.5 mg, 2 mol%), $Cu(OAc)_2 \cdot H_2O$ (8.0 mg, 20 mol%), and 2 mL o-xylene were added sequentially. The RB flask was immersed in an oil bath, pre-heated at 100 °C and heated under air atmosphere for 24 h. After completion of the reaction (monitored by TLC), the reaction mixture was diluted by adding 5 mL of ethyl acetate and filtered through a short celite pad. Then, the celite pad was washed with ethyl acetate (2×5 mL). The combined organic layers were concentrated under vaccum and purified by column chromatography using the ethyl acetate and methanol mixture as eluent.

4.5. General Procedure for the Synthesis of quinazolinone fused phenanthridine derivatives 9 (GP V):

The reactions to prepare the quinazolinone fused phenathidine derivatives were carried out according to the following procedure unless otherwise stated. To an oven dried 10 mL RB flask equipped with a magnetic stirrer, quinazolimine derivatives **4** (0.2 mmol, 1 equiv) and p-$TsOH \cdot H_2O$ (0.22 mmol, 1.1 equiv, 42 mg) were dissolved in 3 mL ethyl acetate. Then, ^{t}BuONO (0.6 mmol, 3.0 equiv, 62 mg) was added dropwise in this solution and stirred for 15 minutes till a gummy solid was precipitated. Next, the solvents and other volatile substances were removed under vaccum. The residue was dissolved in dry DMSO (1.5 mL). Then, $Pd(OAc)_2$ (2.3 mg, 5 mol%) was added in the RB flask. Next, the flask was transferred to an oil bath preheated at 90°C. After completion of the reaction (monitored by TLC), the reaction mixture was diluted by adding 5 mL of ethyl acetate and then 20 mL saturated aqueous NH_4Cl solution was added. The aqueous layer was extracted with ethyl acetate (2×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. Then the concentrated reaction mixture was purified by column chromatography using the petroleum ether and ethyl acetate mixture as eluent.

5. Single crystal X-ray data analysis of compound 4f and 9b

Crystals for X-ray diffraction study of **4f** were grown from a mixture of cyclohexane and ethyl acetate (1:4) and crystal of **9b** were grown from a mixture of cyclohexane and ethyl acetate (1:1). The crystals suitable for SC-XRD analysis were carefully chosen using a stereo zoom microscope supported by a rotatable polarizing stage. The data were processed using the package SAINT[1]. Structures were solved by direct and Fourier methods and further refined by Olex2 package.[2]

Compound	**4f**	**9b**
Empirical formula	C_{20} H_{14} Cl_2 N_4	C_{21} H_{14} N_2 O
Formula weight	381.25	310.34
Crystal system	monoclinic	monoclinic
Space group	C 1 2/c 1	C 1 2/c 1
***a* (Å)**	26.70(4)	35.11(4)
***b*(Å)**	6.71(2)	5.380(6)
***c* (Å)**	22.55(4)	15.739(18)
α (°)	90	90
β (°)	92.50(9)	94.649(16)
γ (°)	90	90
***V* (Å^3)**	4036(16)	2963(6)
Z	8	8
***T*, K**	295.00	296.15
Wavelength (Å)	1.54178	0.71073
2θ (°)	3.91-66.47	2.328- 27.627
μ (mm^{-1})	2.969	0.087
ρ_{calcd} (g cm^{-3})	1.255	1.391
***F* (000)**	1568	1296
Absorption correction	multi-scan	multi-scan
Index ranges	–31≤h≤31	–44≤h≤44

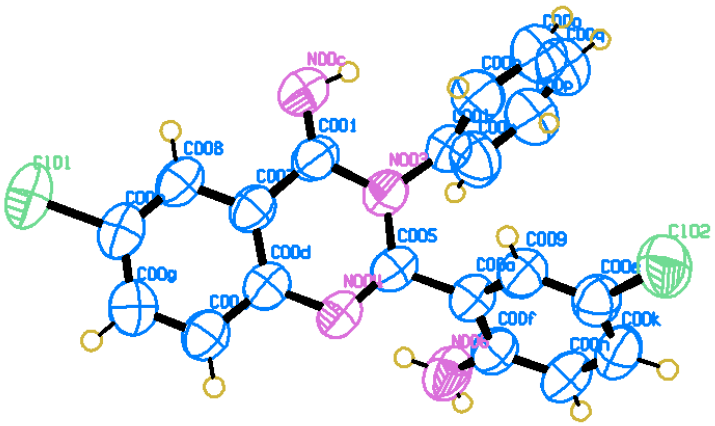
	–8≤k≤8	–6≤k≤6
	–26≤ l≤ 26	–20≤ l≤18
Reflections collected	3542	14911
Independent reflections (R_{int})	9838 (0.1397)	2799 (0.0587)
Goodness-of-fit on F^2	1.038	1.017
R_1^a /wR_2^b (I> 2σ(I))	0.0978/ 0.2548	0.0498/ 0.1252
R_1^a/wR_2^b (for all data)	0.1630/ 0.2683	0.0795/ 0.1433
Largest diff. peak/hole /eÅ^{-3}	0.733/ -0.493	0.141/ -0.202

[a] $R_1 = [\sum||F_o| - |F_c||/\sum|F_o|]$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$

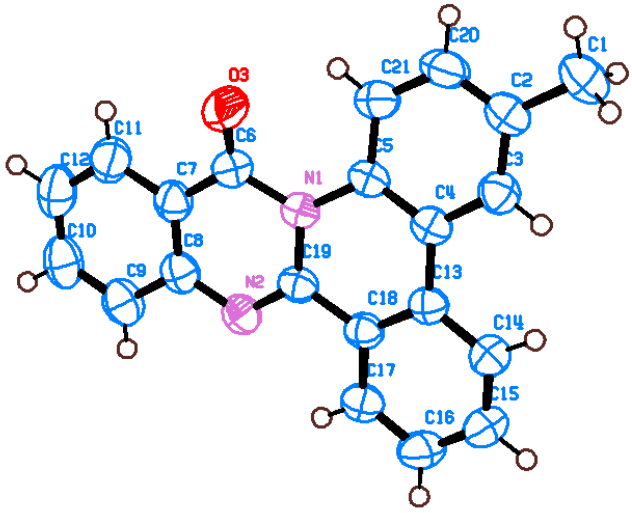
References:

1. APEX-II, SAINT-Plus, and *TWINABS*; Bruker-Nonius AXS Inc.: Madison, WI, 2004.

2.a) Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H, *Acta Cryst. A*, 2015, **71**, 59-75. b) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H, *J. Appl. Cryst.*, 2009, **42**, 339-341.



(A)

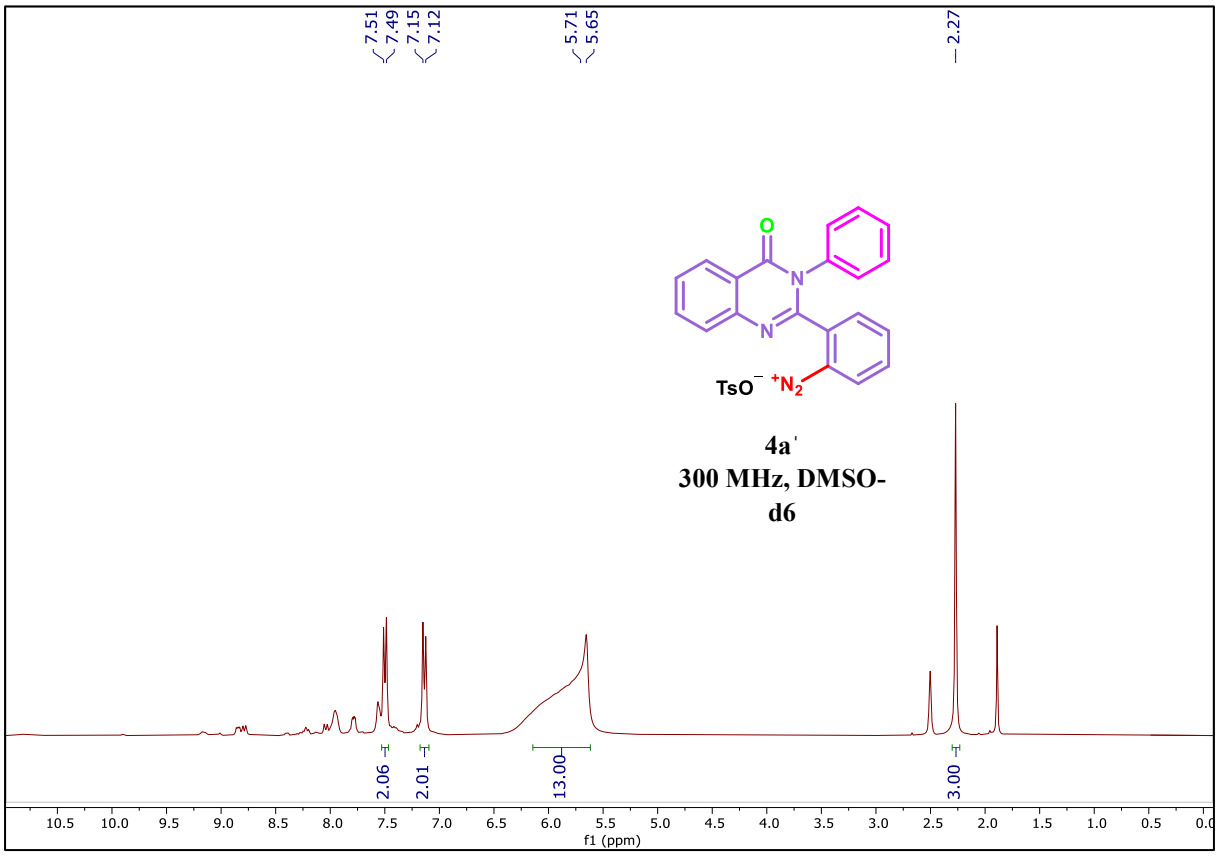


(B)

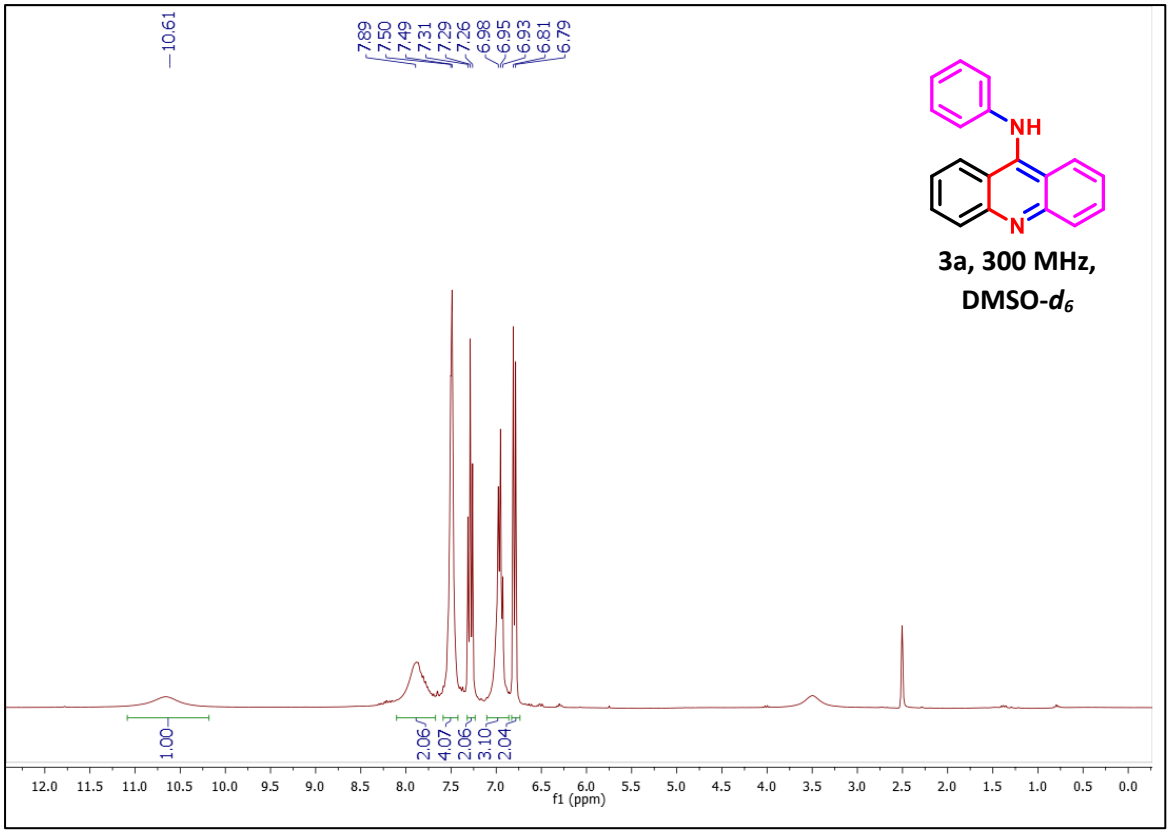
Figure S1: (A) ORTEP diagram of **4f** at 60% probability (CCDC 2292766) **(B)** ORTEP diagram of **9b** at 60% probability (CCDC 2292647)

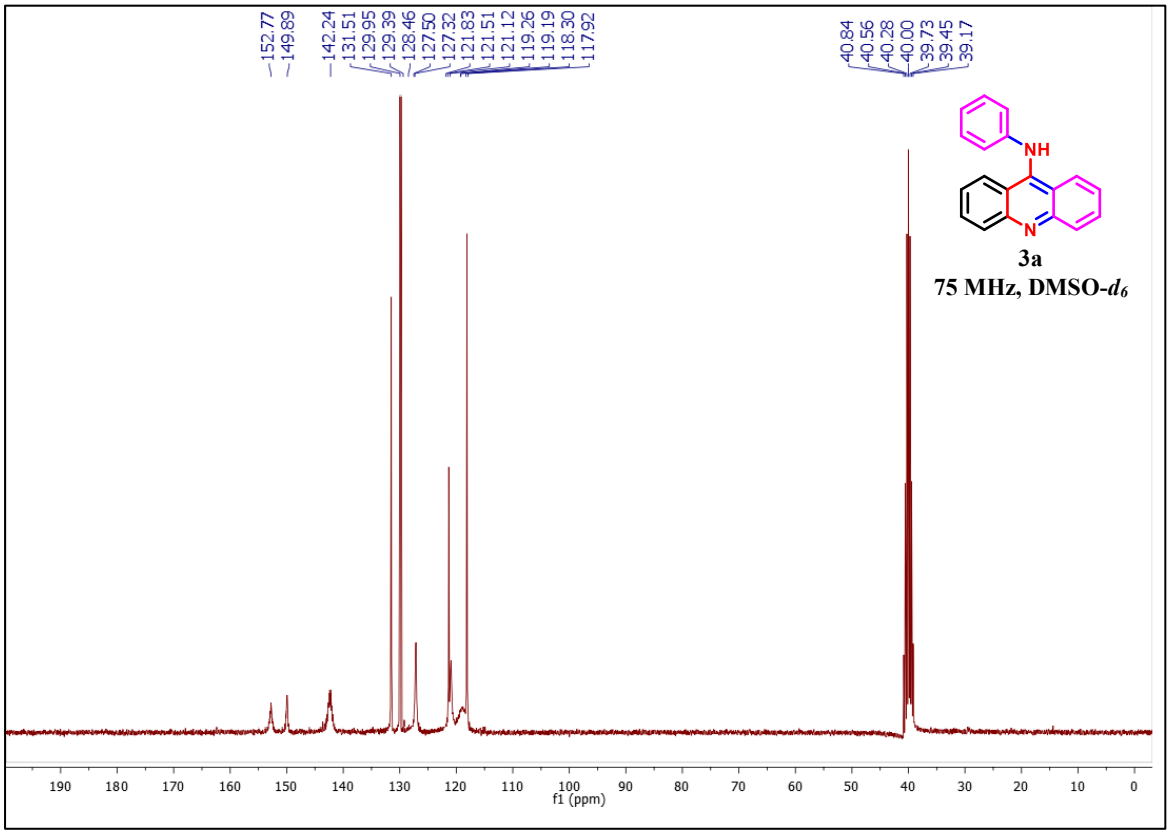
6. ^{1}H-NMR of reaction mixture for the identification of intermediate 4a'

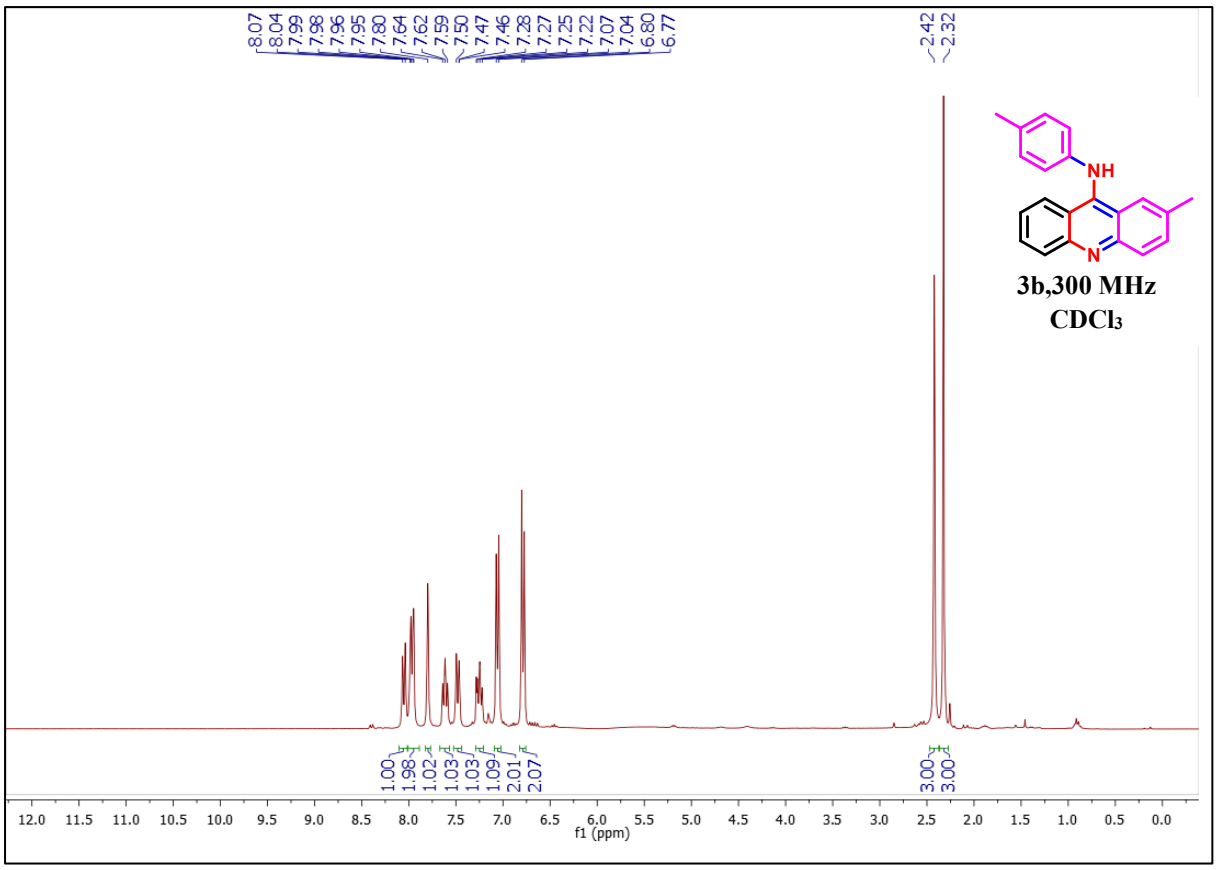
^{1}H NMR (300 MHz, DMSO-d6) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 6.14 – 5.62 (m, 13H), 2.27 (s, 3H).



7. Copies of ^{1}H and ^{13}C NMR spectra for the products **3a-j**, **4a-h, 6a-f, 8a-h, 9a-f** and ^{19}F NMR of **6d** and **8d:**



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7.28
7.27
7.25
7.22
7.07
7.04
6.80
6.77
2.42
2.32
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N
3b,300 MHz
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1.03
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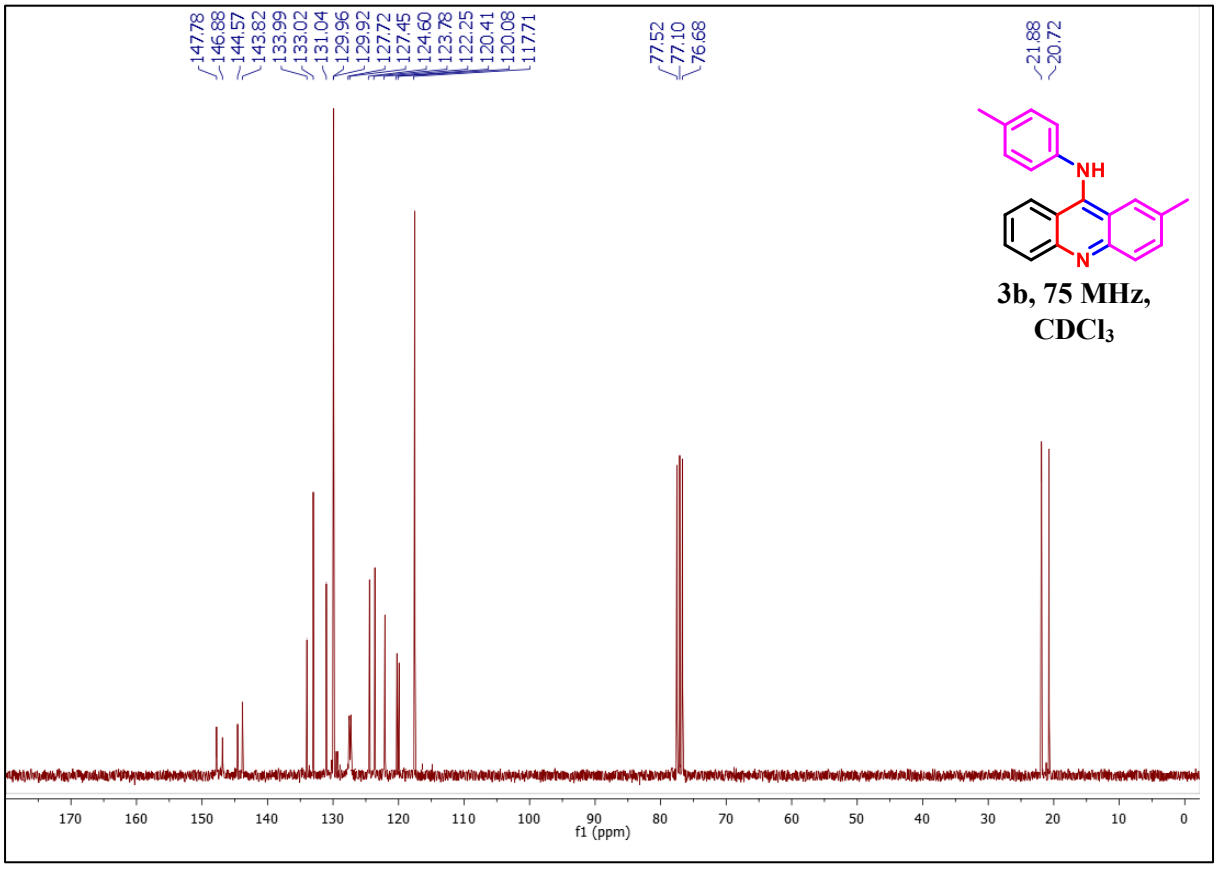
2.07
3.00
3.00
f1 (ppm)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122.25
120.41
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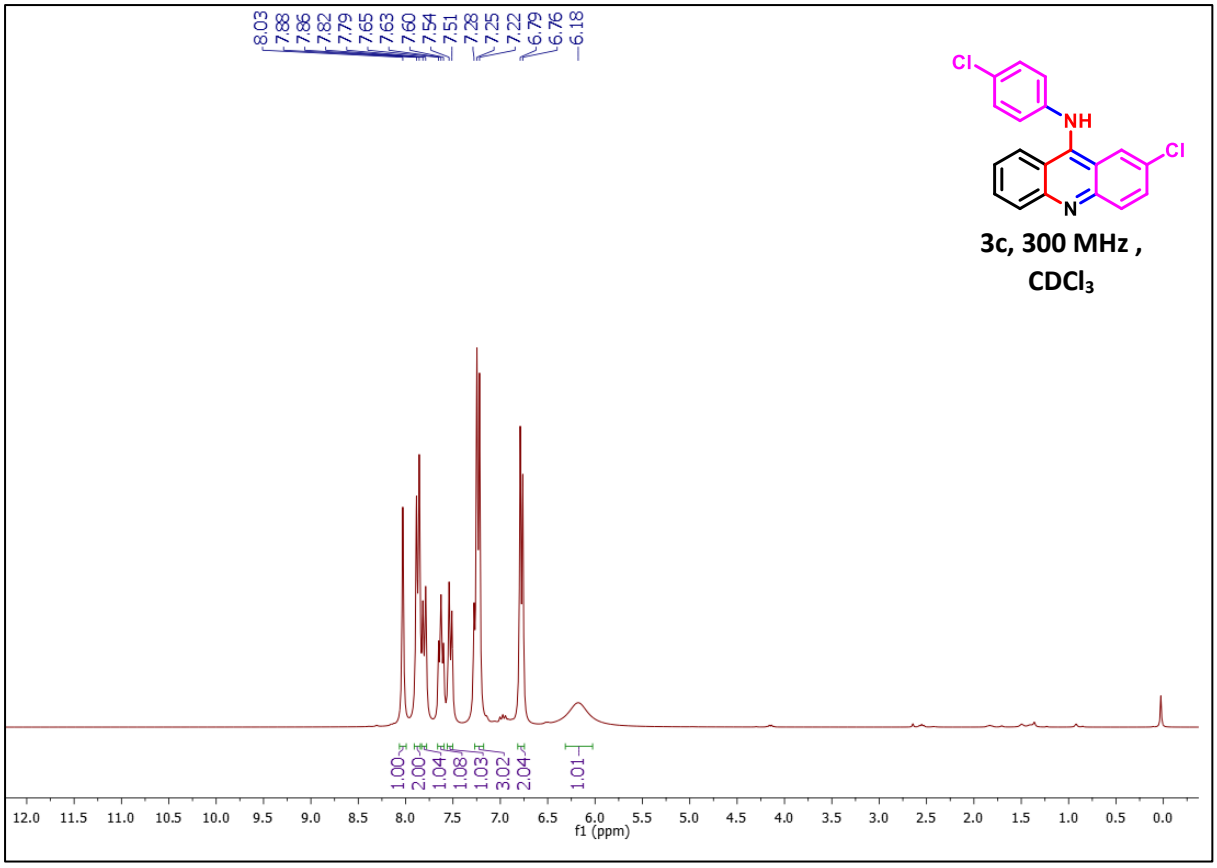
CDCl3
f1 (ppm)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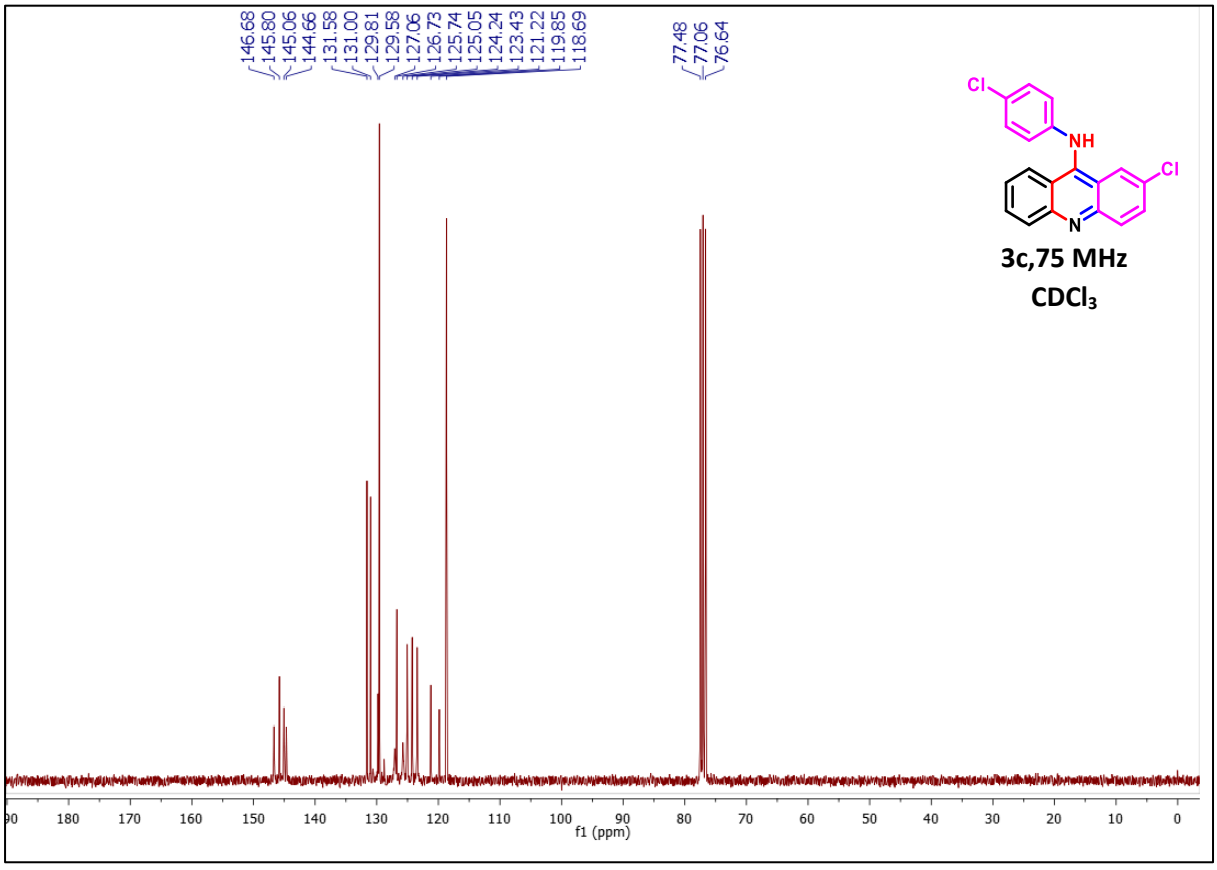
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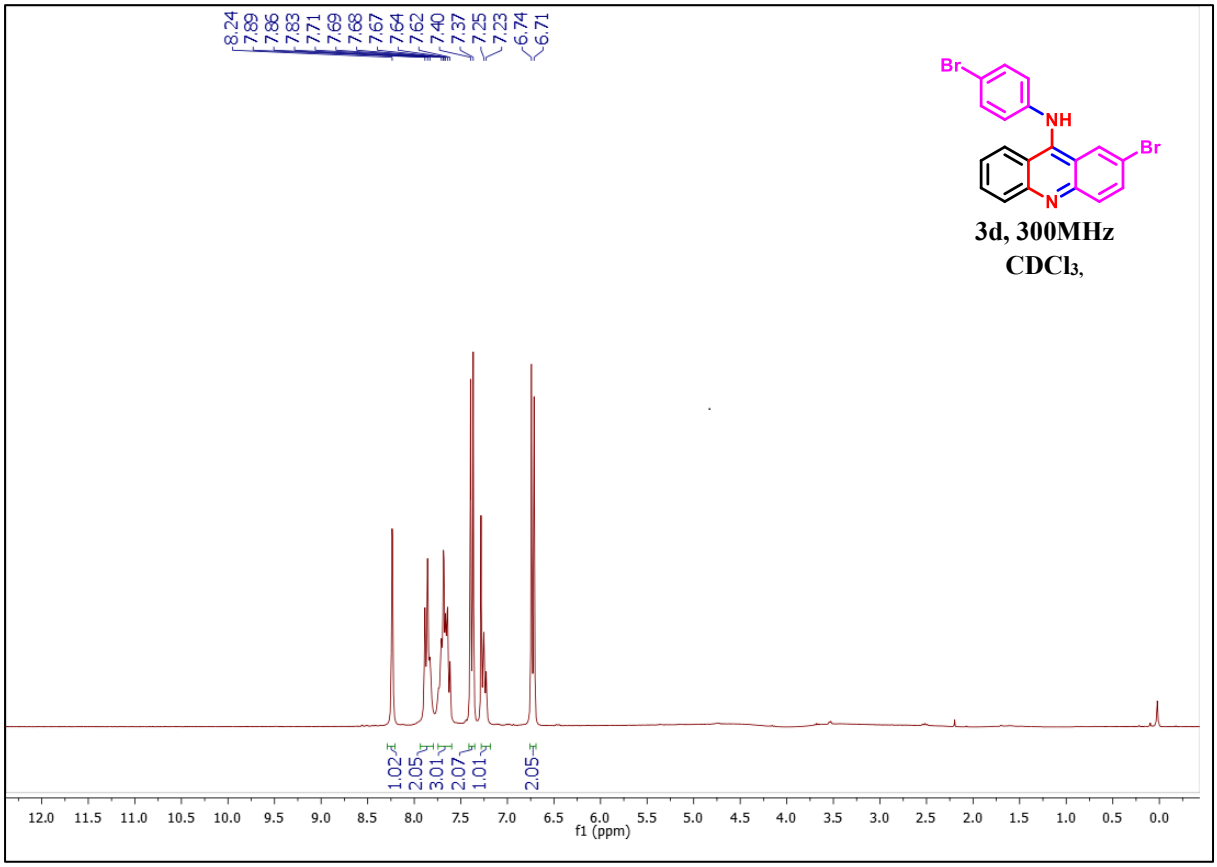
CDCl3
f1 (ppm)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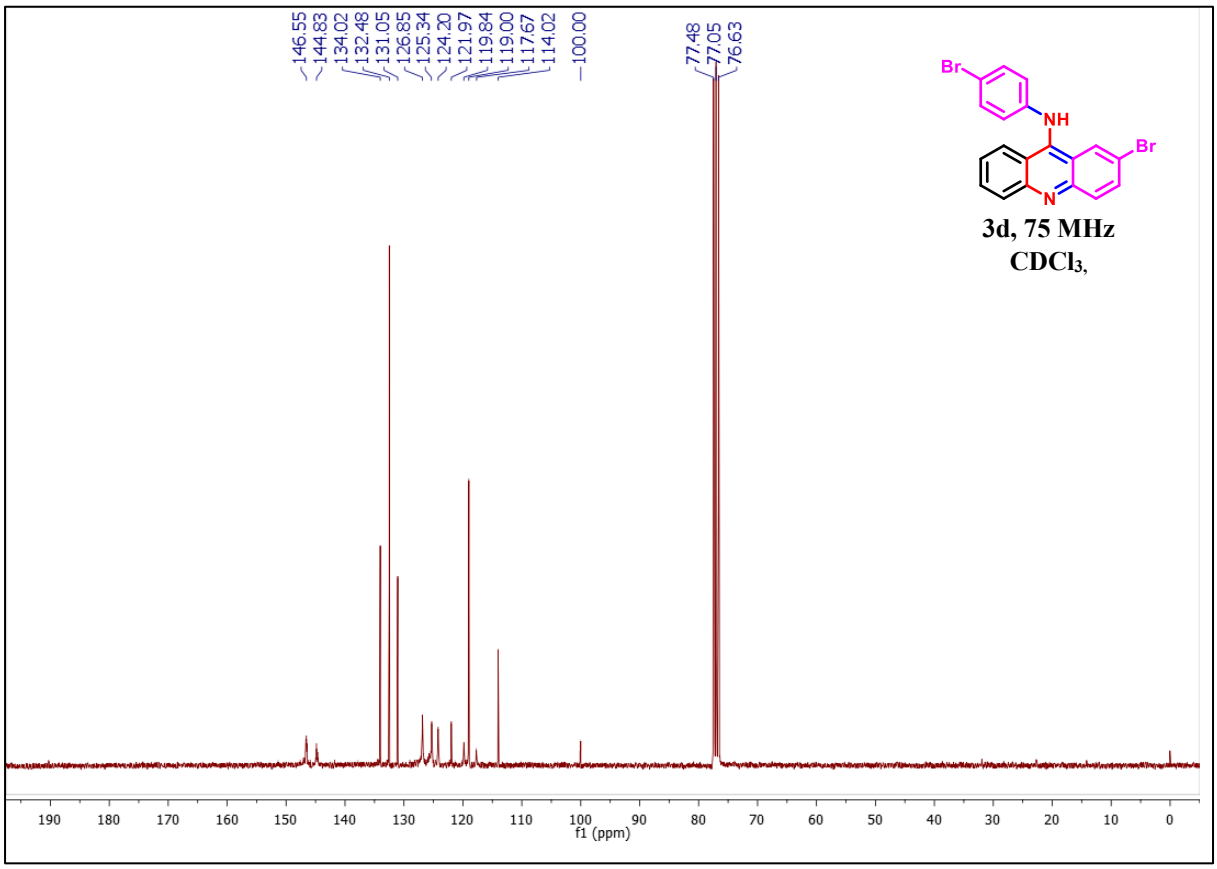
2.05
f1 (ppm)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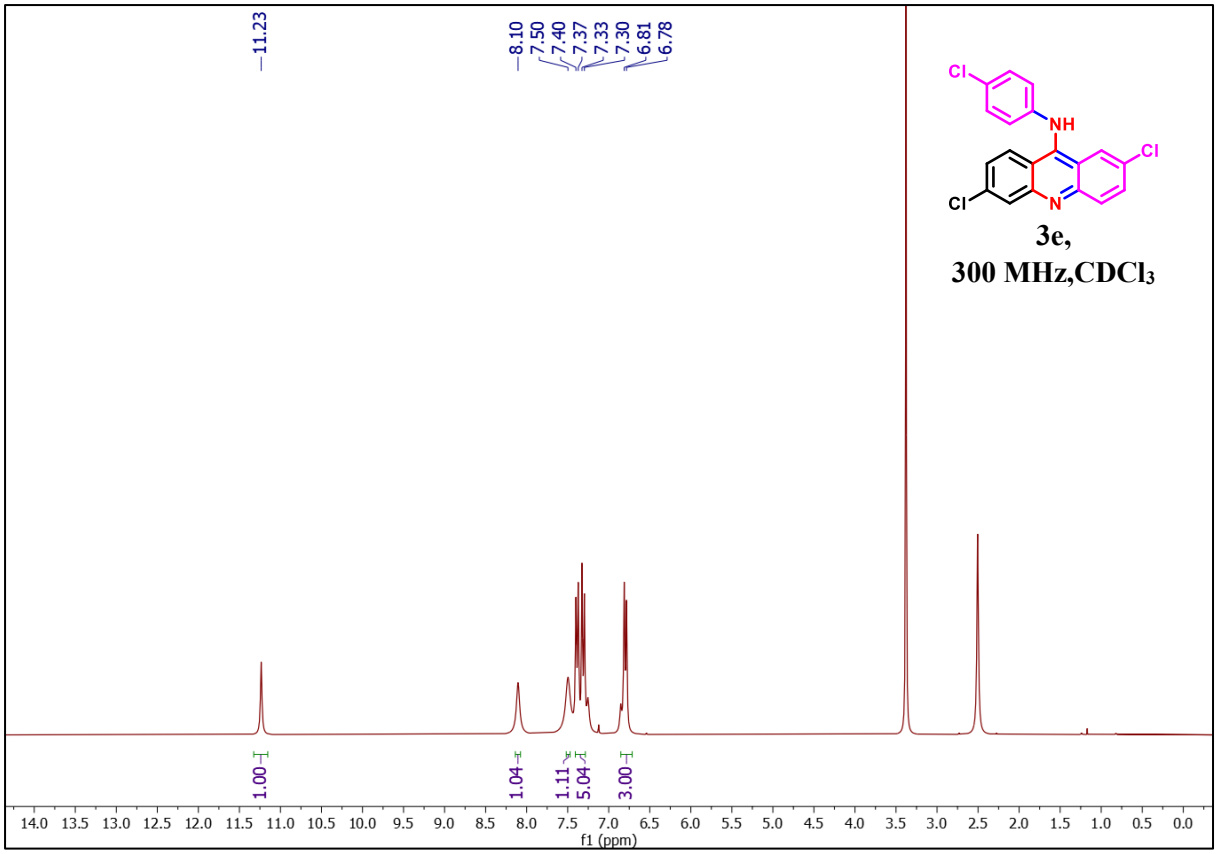
f1 (ppm)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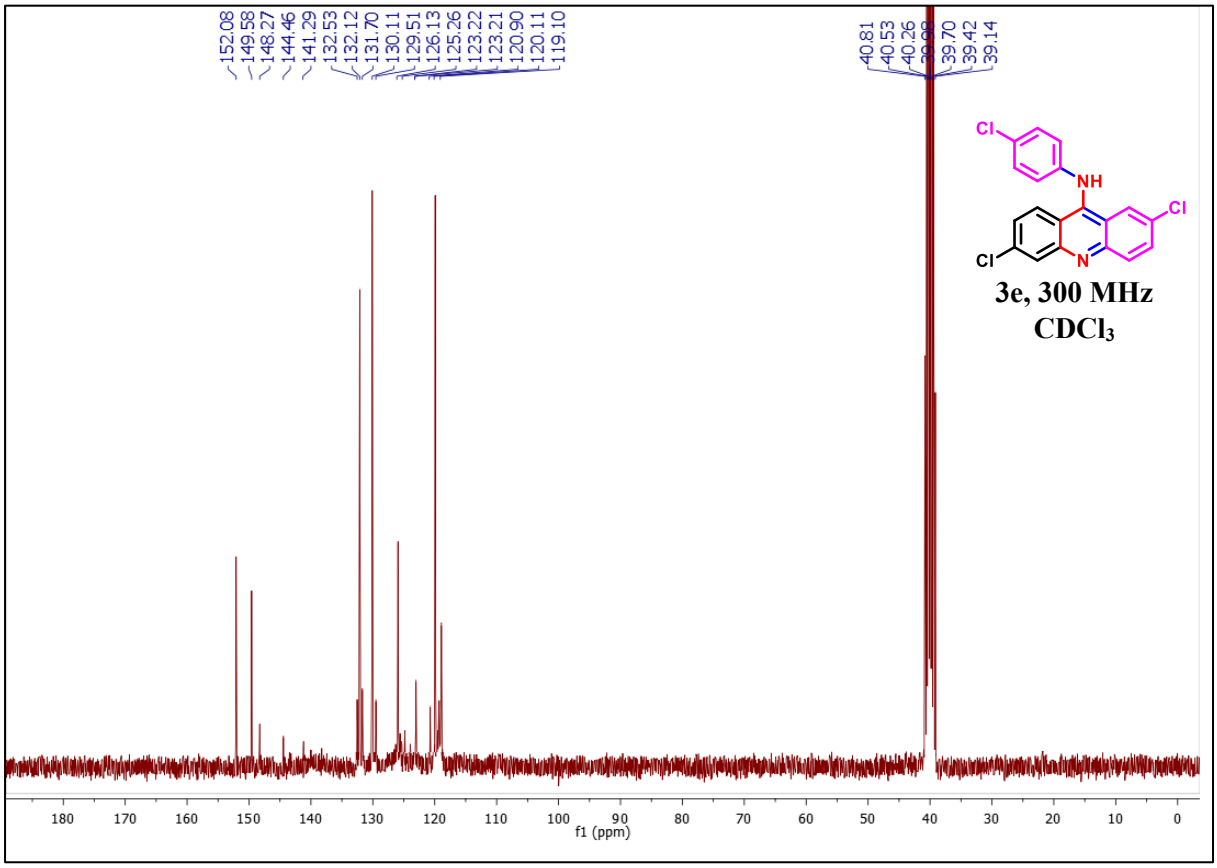
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119.10
40.81
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f1 (ppm)
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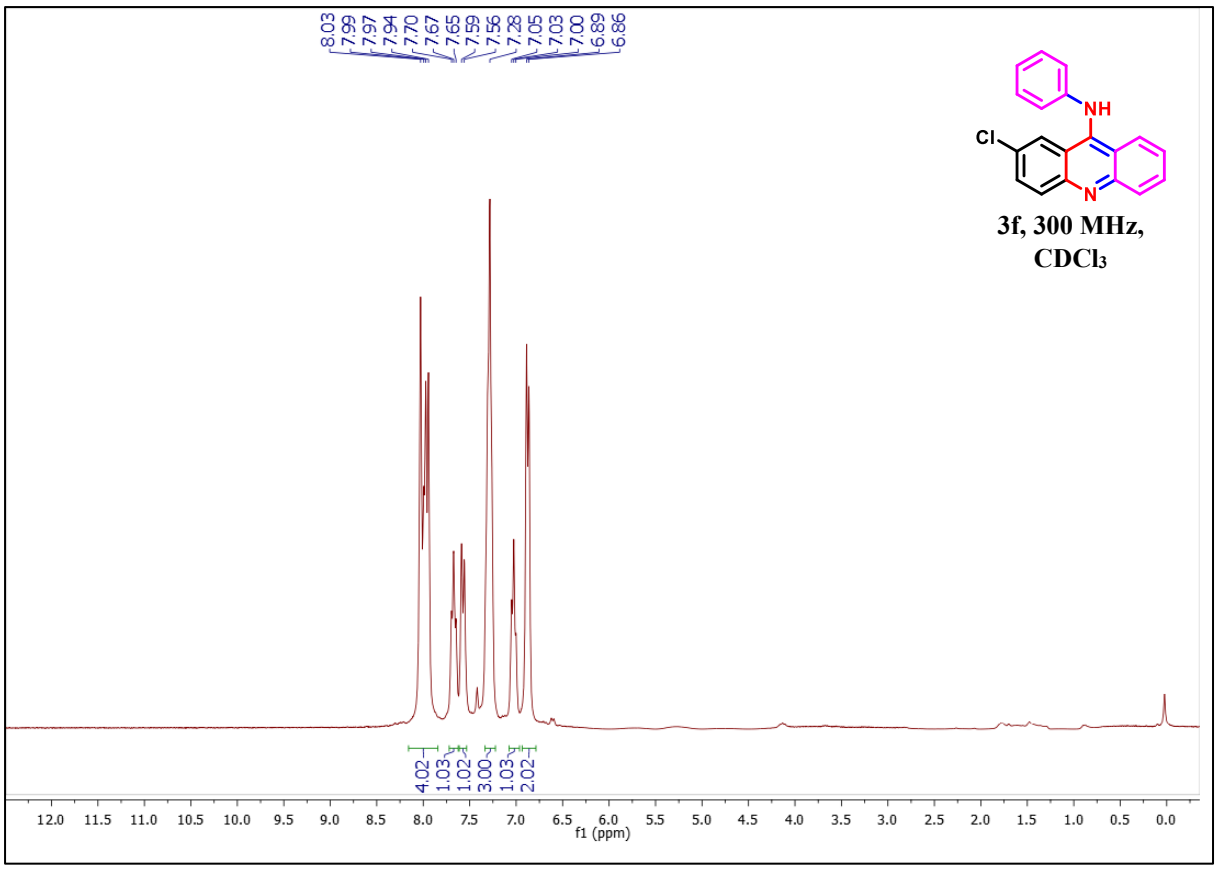
NH
Cl
Cl
N
3e, 300 MHz
CDCl3



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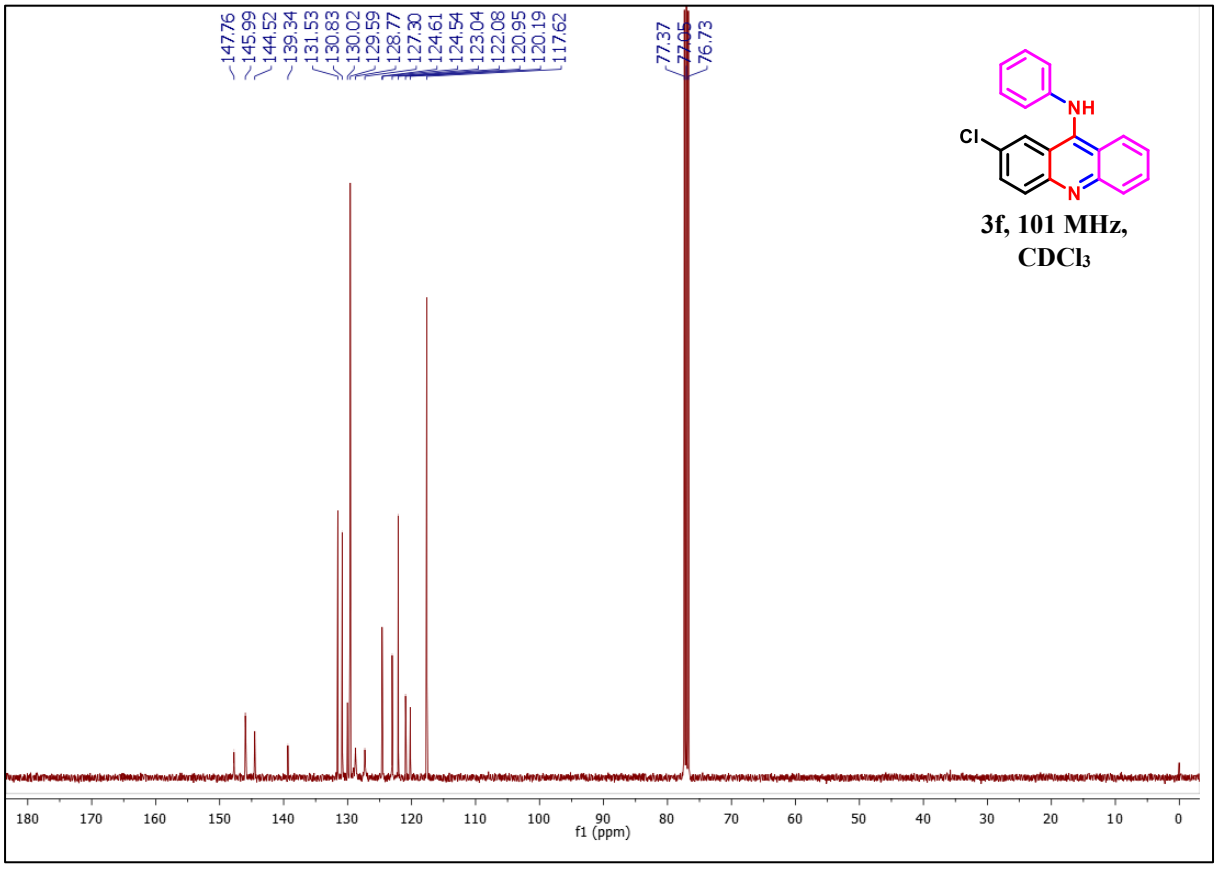
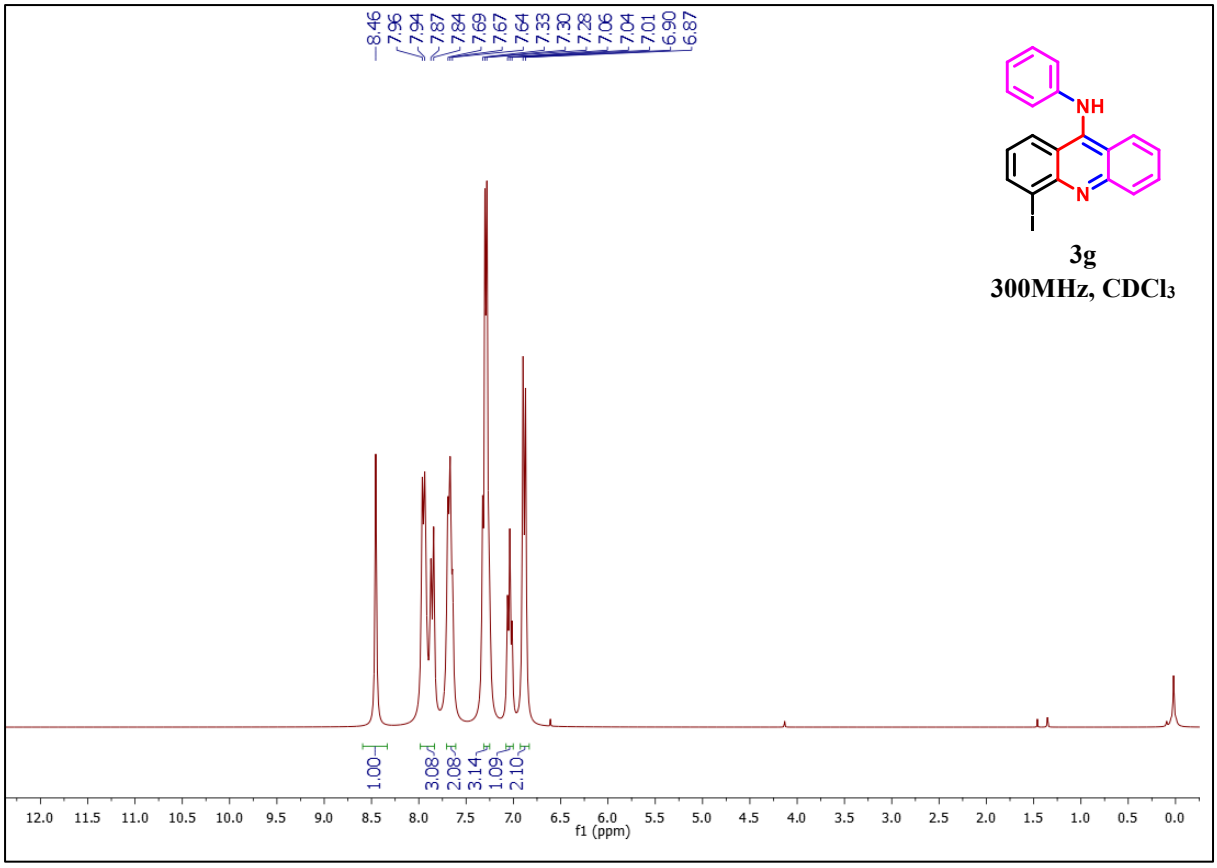
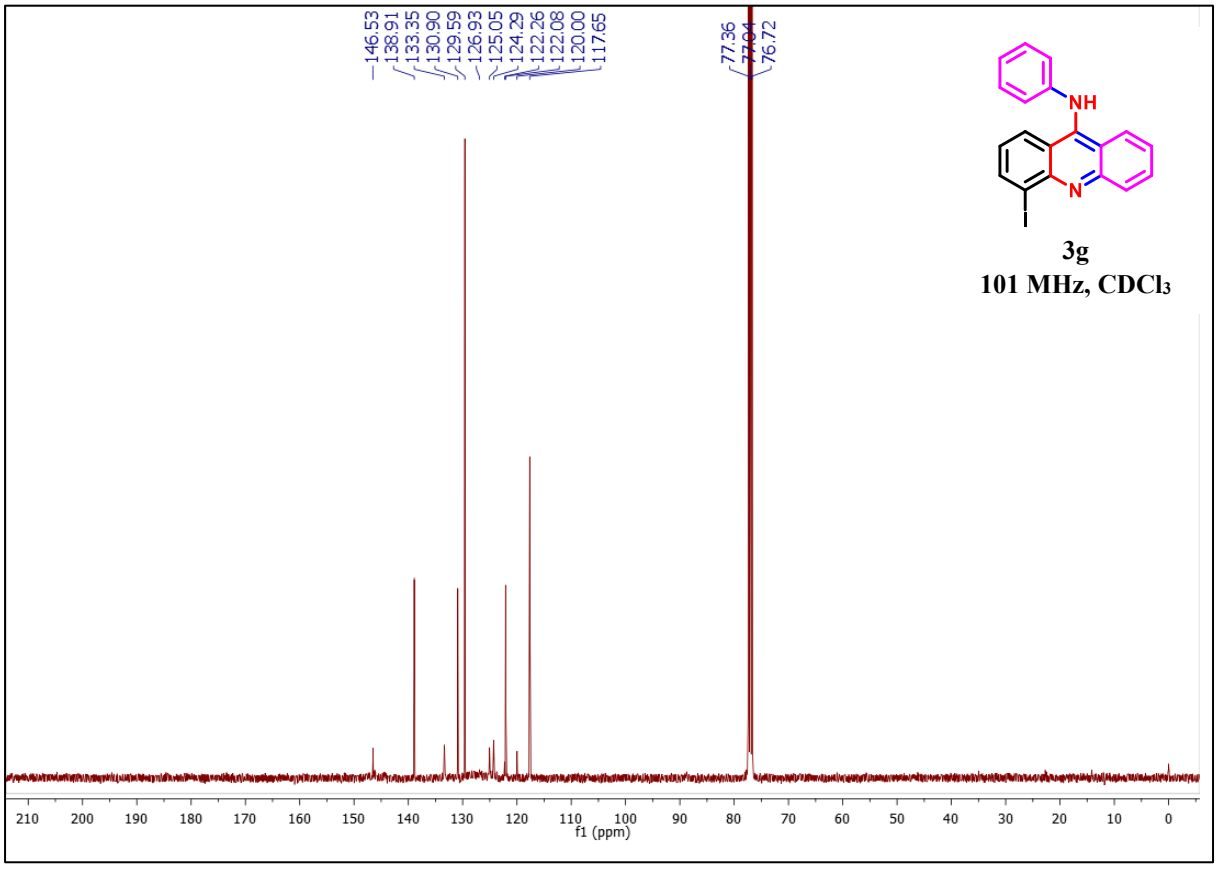


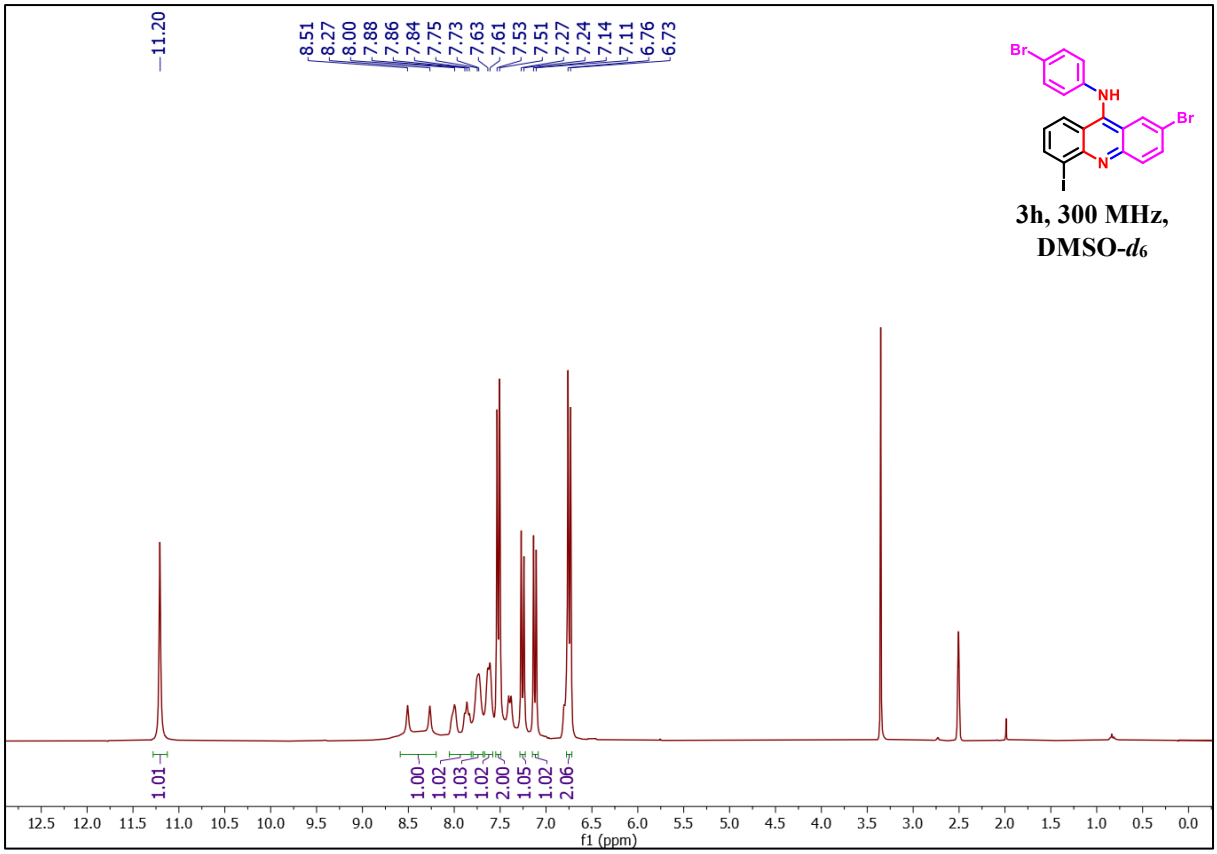
3f, 101 MHz, $CDCl_3$



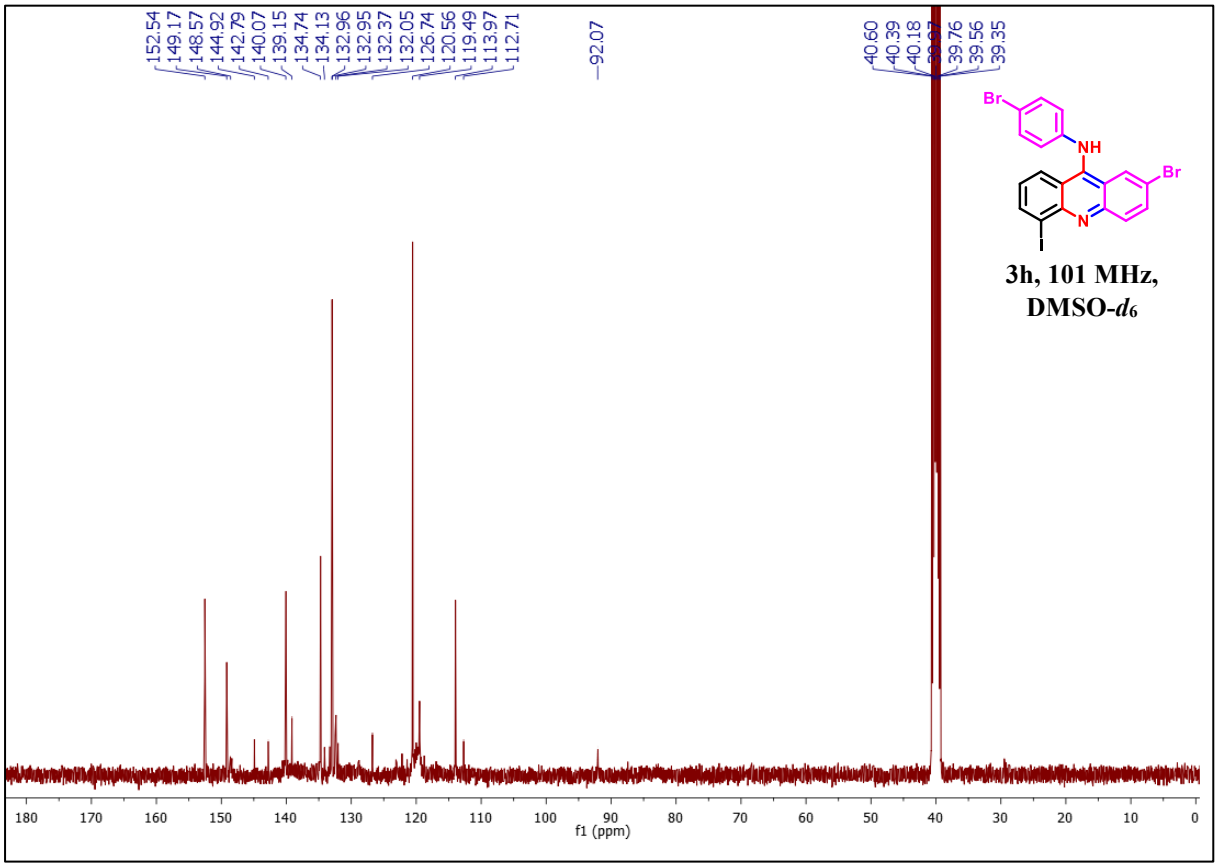
3g
300MHz, $CDCl_3$



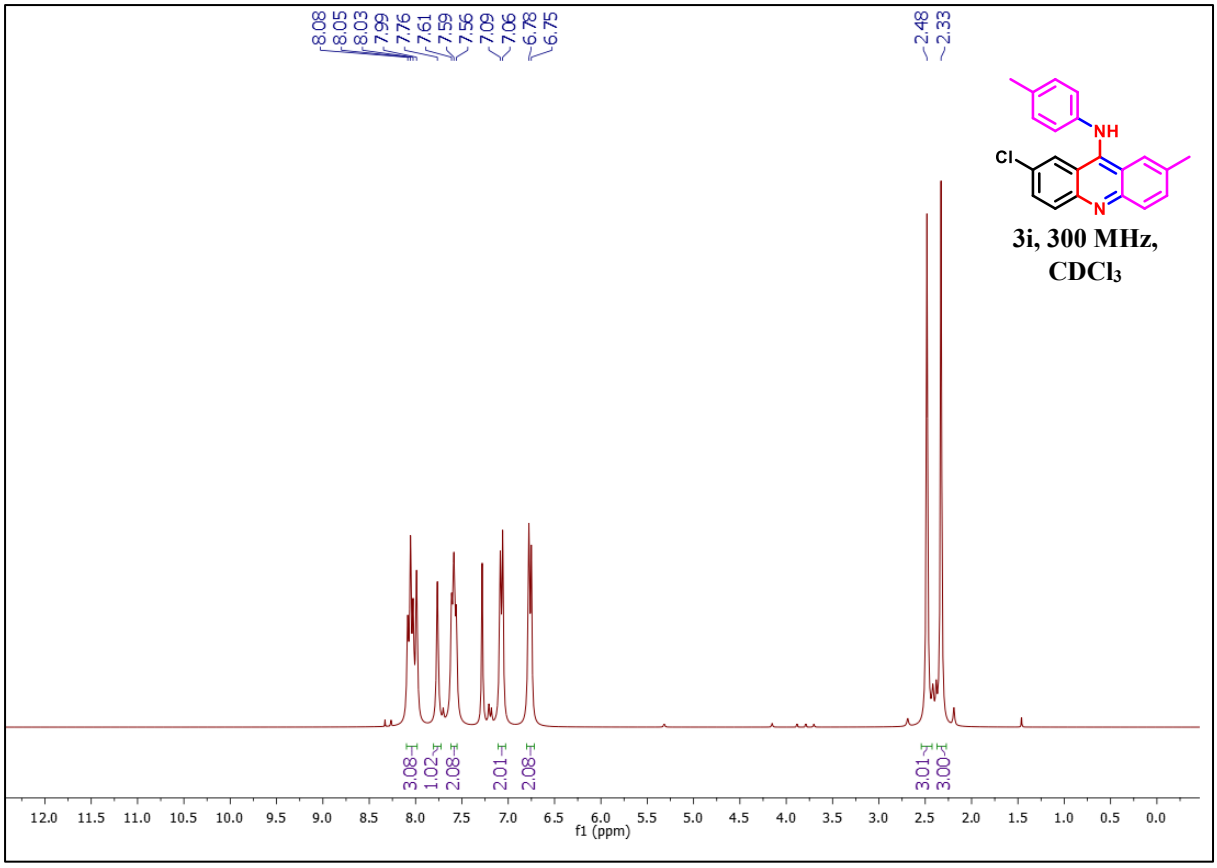
3g
101 MHz, $CDCl_3$

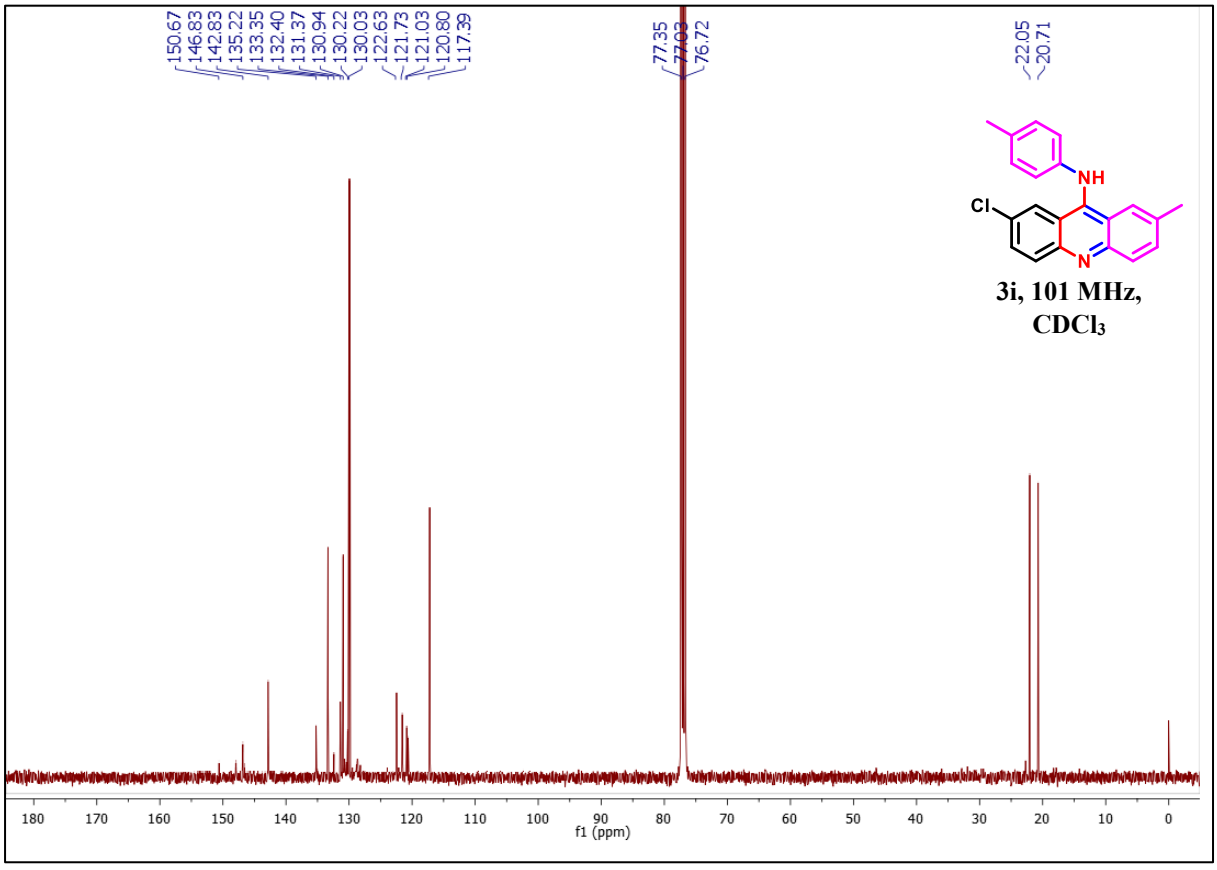


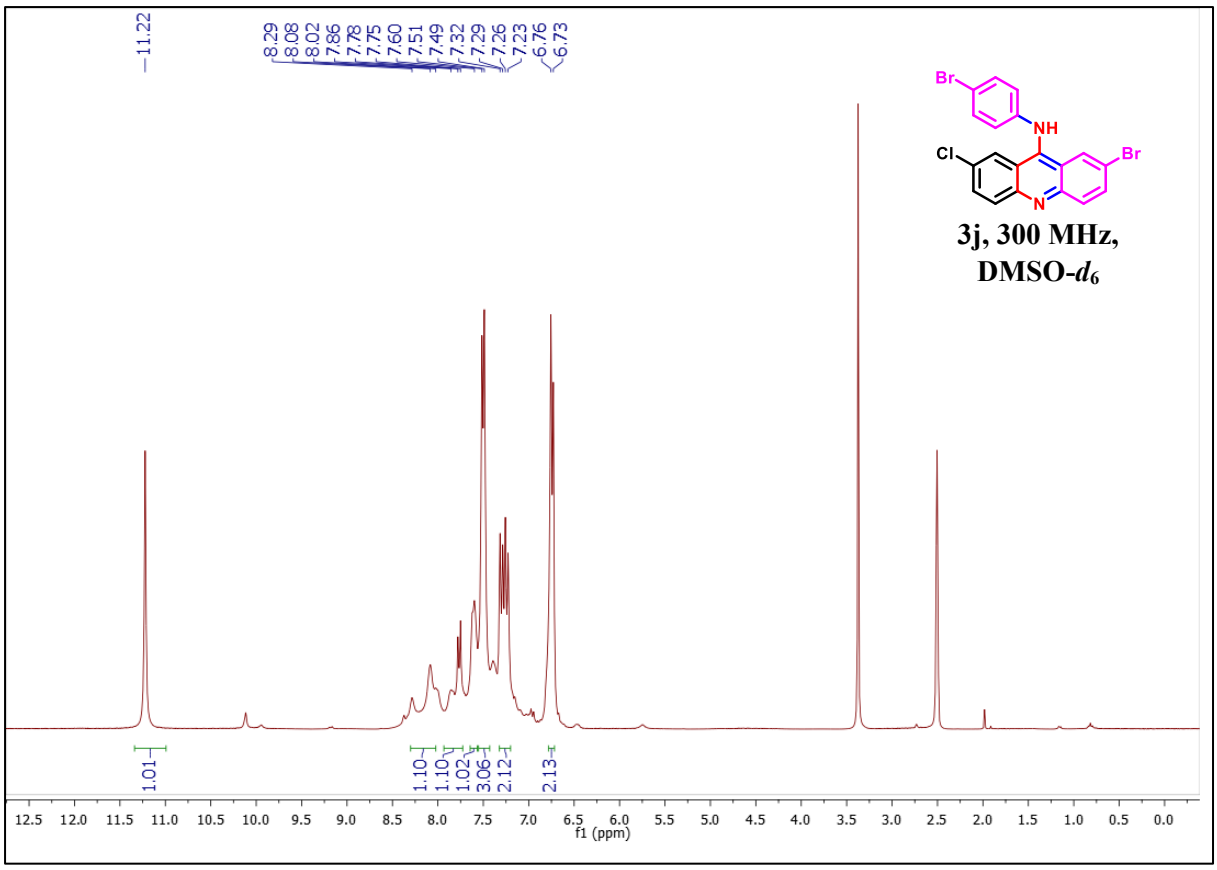
3h, 300 MHz, DMSO-*d*$_6$



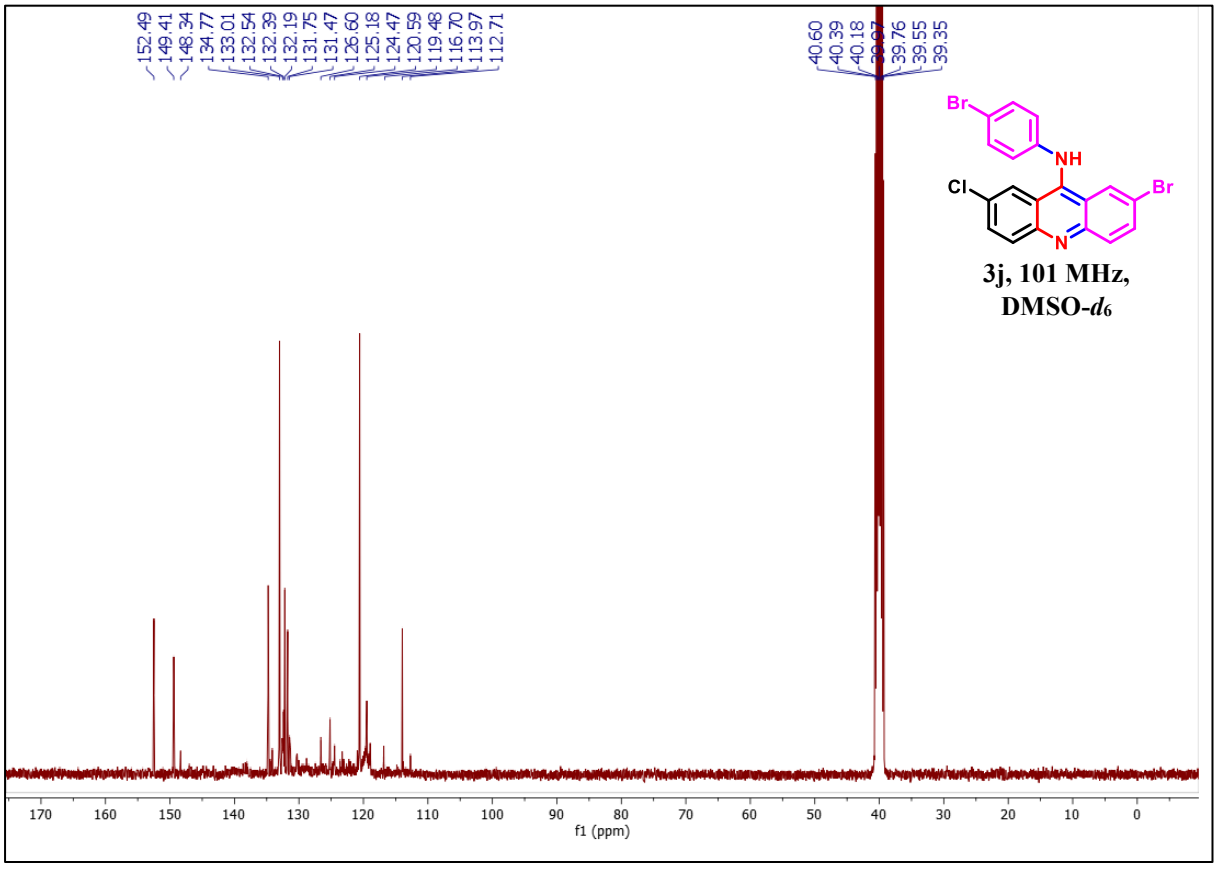
3h, 101 MHz, DMSO-*d*$_6$


8.08
8.05
8.03
7.99
7.76
7.61
7.59
7.55
7.09
7.06
6.78
6.75
2.48
2.33
NH
Cl
N
3i, 300 MHz,
CDCl3
3.08
1.02
2.08
2.01
2.08
3.01
3.00
f1 (ppm)

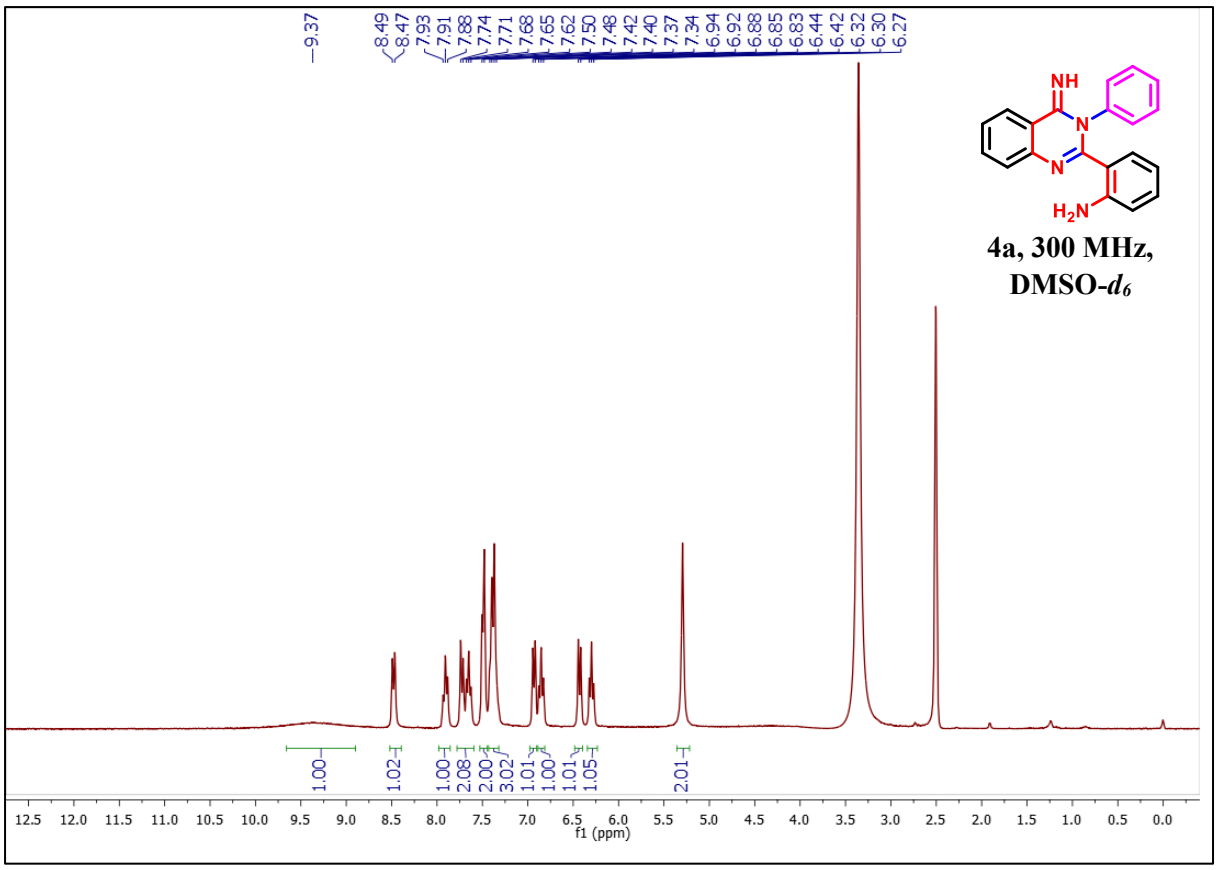

150.67
146.83
142.83
135.22
133.35
132.40
131.37
130.94
130.22
130.03
122.63
121.73
121.03
120.80
117.39
77.35
77.03
76.72
22.05
20.71
NH
Cl
N
3i, 101 MHz,
CDCl3
f1 (ppm)

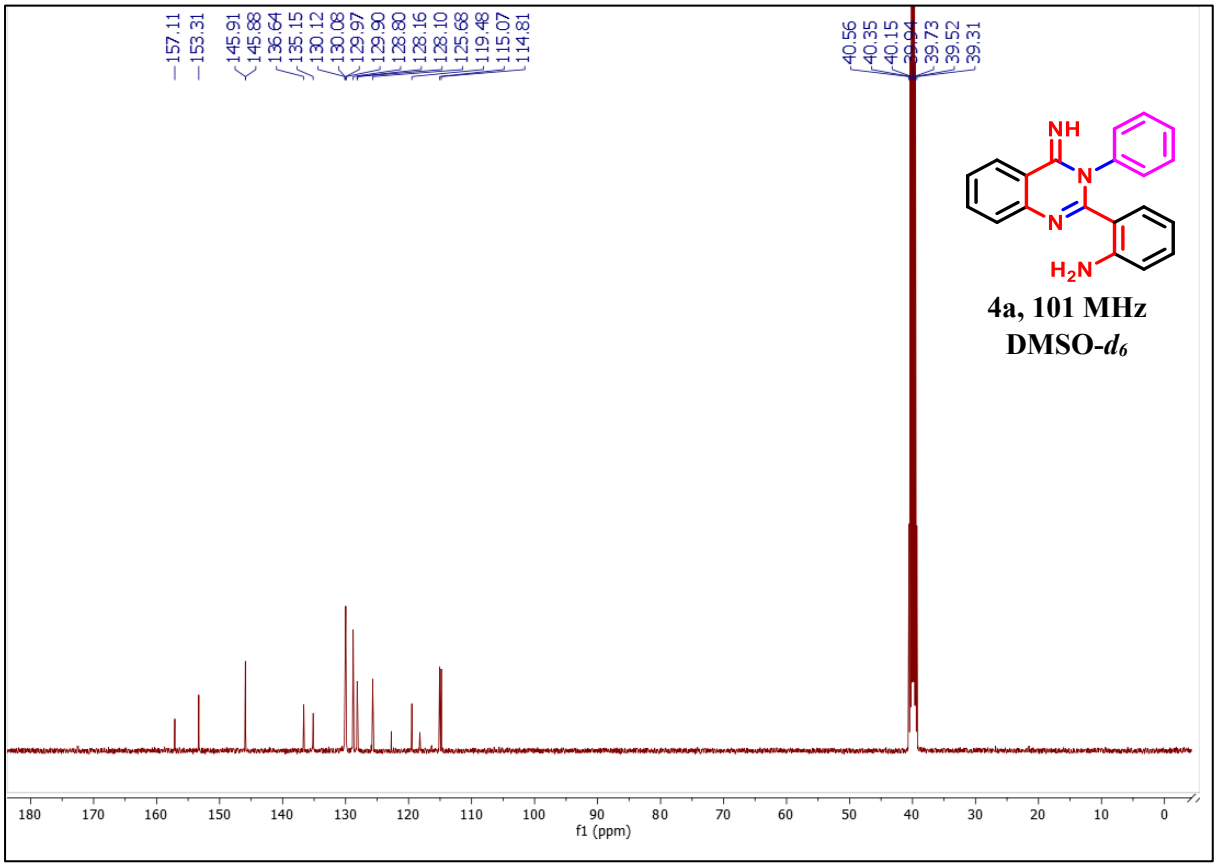


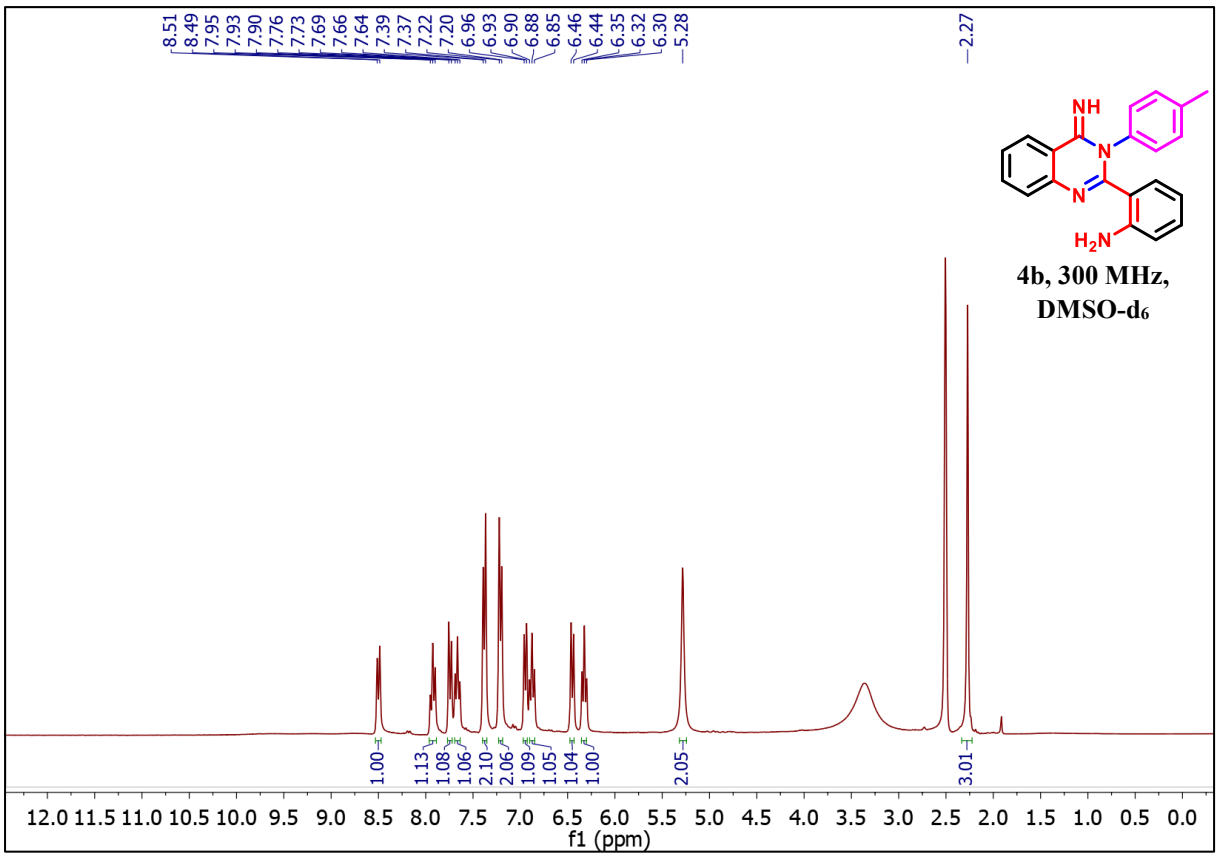
3j, 300 MHz, DMSO-d_6

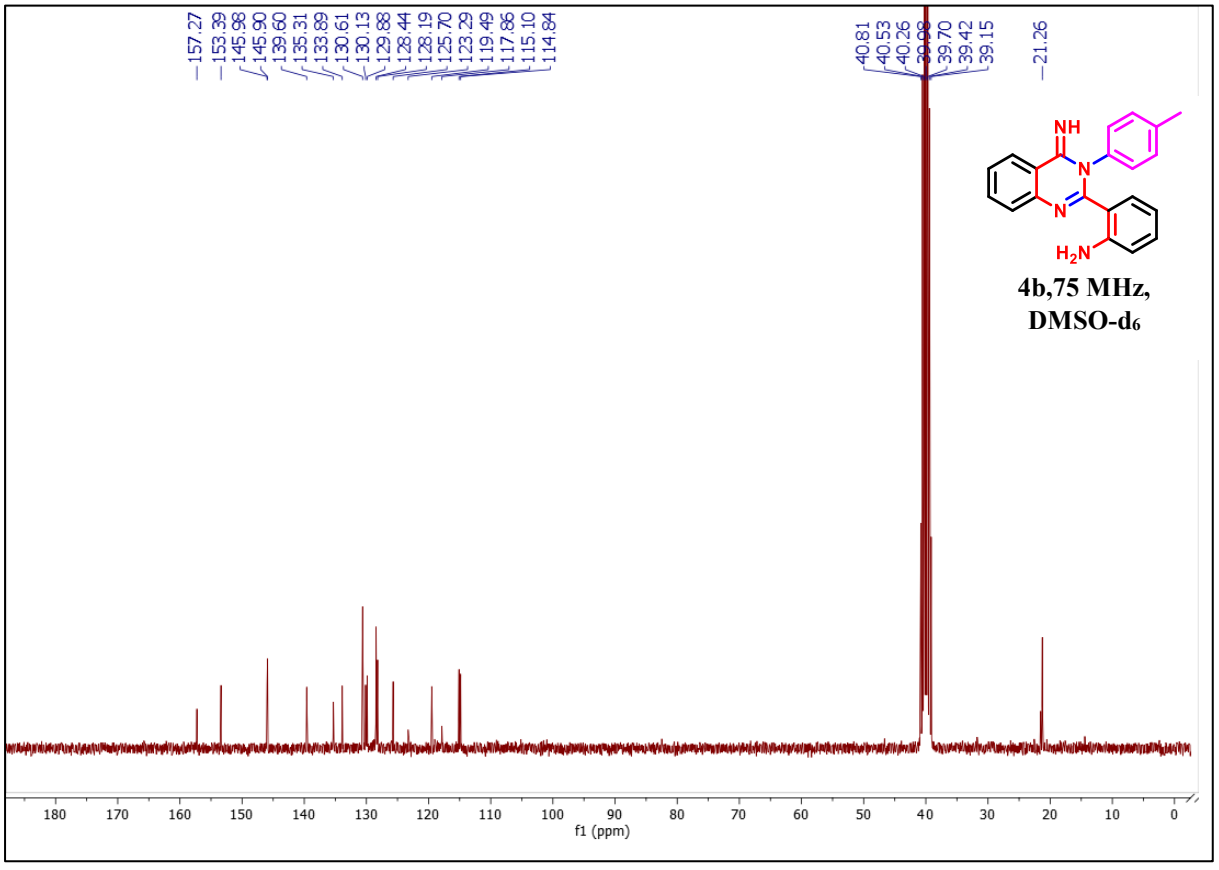


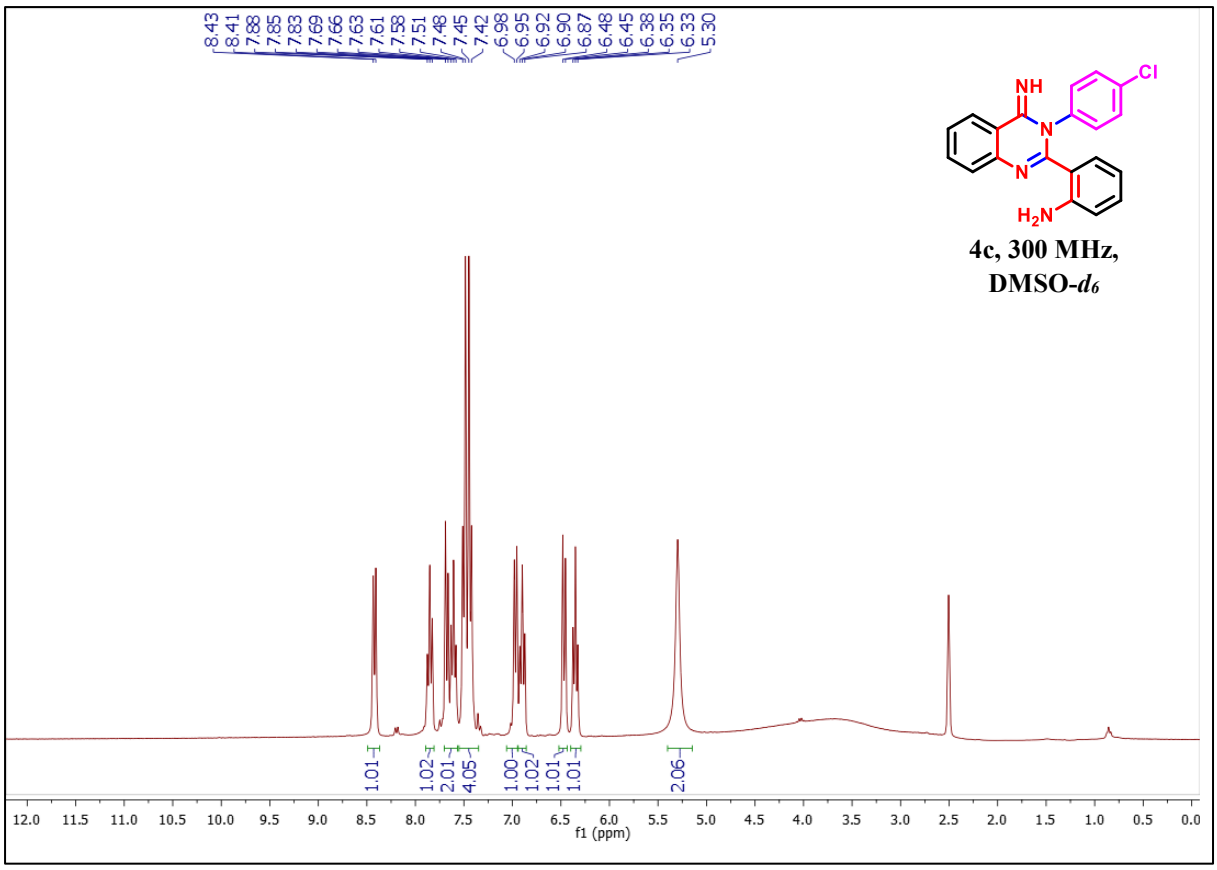
3j, 101 MHz, DMSO-d_6


9.37
8.49
8.47
7.93
7.91
7.88
7.74
7.71
7.68
7.65
7.62
7.50
7.48
7.42
7.40
7.37
7.34
6.94
6.92
6.88
6.85
6.83
6.44
6.42
6.32
6.30
6.27
NH
N
N
H2N
4a, 300 MHz,
DMSO-d6
1.00
1.02
1.00
2.08
2.00
3.02
1.01
1.00
1.01
1.05
2.01
f1 (ppm)

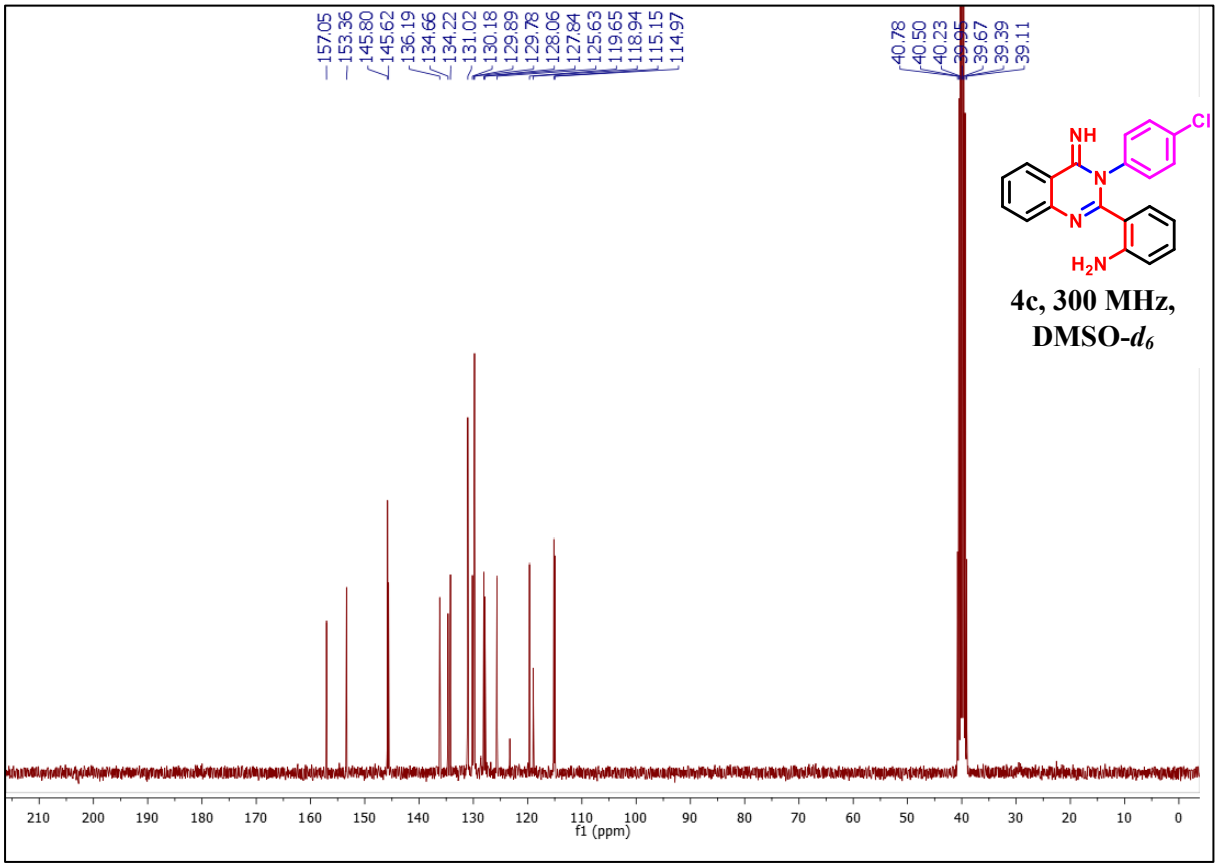

157.11
153.31
145.91
145.88
136.64
135.15
130.12
130.08
129.97
129.90
128.80
128.16
128.10
125.68
119.48
115.07
114.81
40.56
40.35
40.15
39.94
39.73
39.52
39.31
NH
N
N
H2N
4a, 101 MHz
DMSO-d6
f1 (ppm)


8.51
8.49
7.95
7.93
7.90
7.76
7.73
7.69
7.66
7.64
7.39
7.37
7.22
7.20
6.96
6.93
6.90
6.88
6.85
6.46
6.44
6.35
6.32
6.30
5.28
2.27
NH
N
N
H2N
4b, 300 MHz,
DMSO-d6
1.00
1.13
1.08
1.06
2.10
2.06
1.09
1.05
1.04
1.00
2.05
3.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

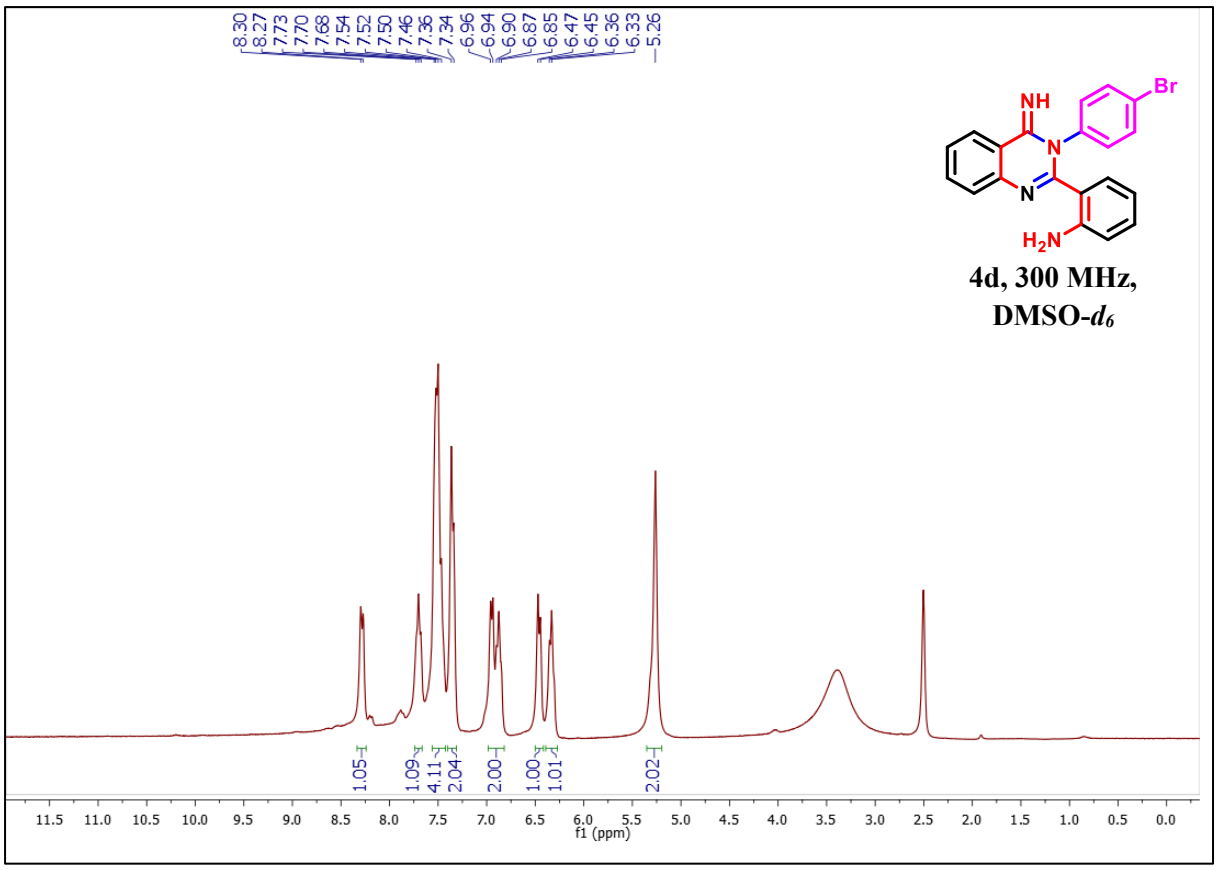

157.27
153.39
145.98
145.90
139.60
135.31
133.89
130.61
130.13
129.88
128.44
128.19
125.70
123.29
119.49
117.86
115.10
114.84
40.81
40.53
40.26
39.98
39.70
39.42
39.15
21.26
NH
N
N
H2N
4b,75 MHz,
DMSO-d6
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



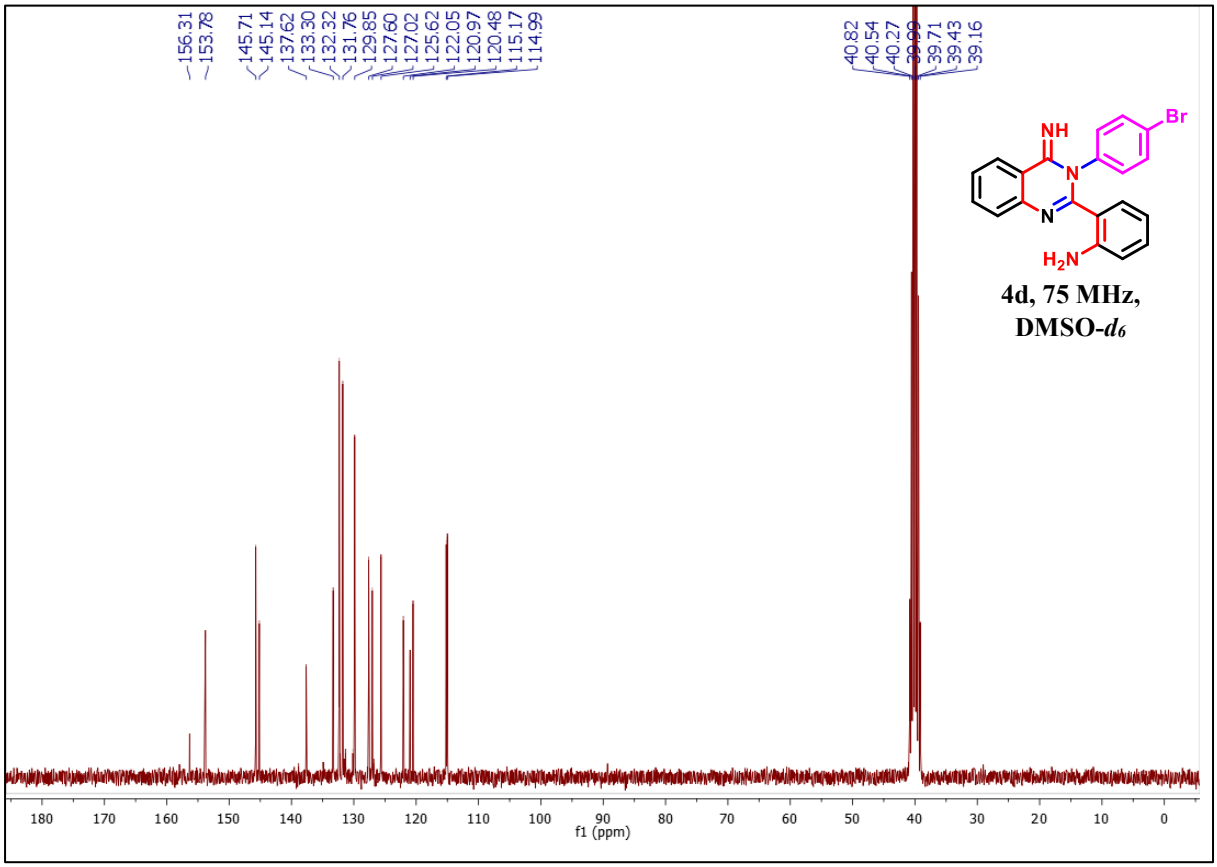
4c, 300 MHz, DMSO-*d*$_6$



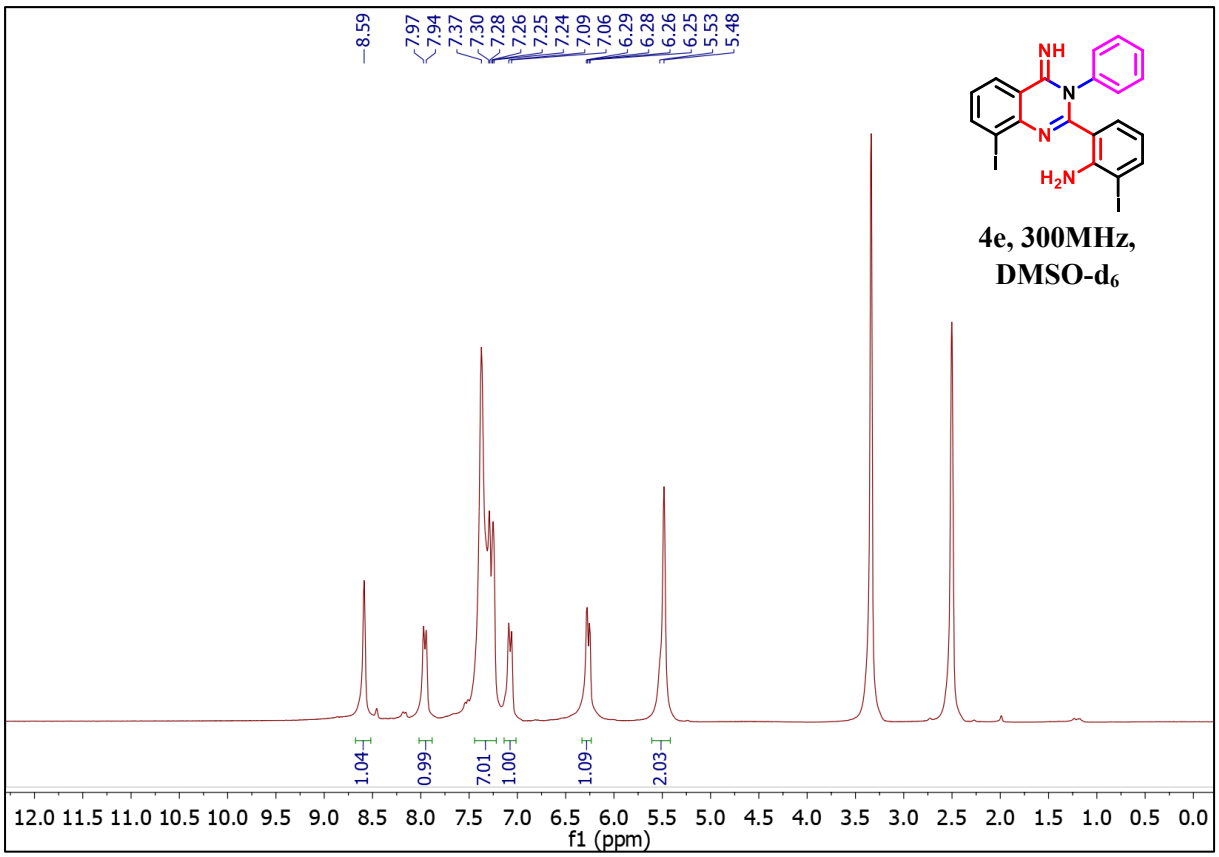
4c, 300 MHz, DMSO-*d*$_6$

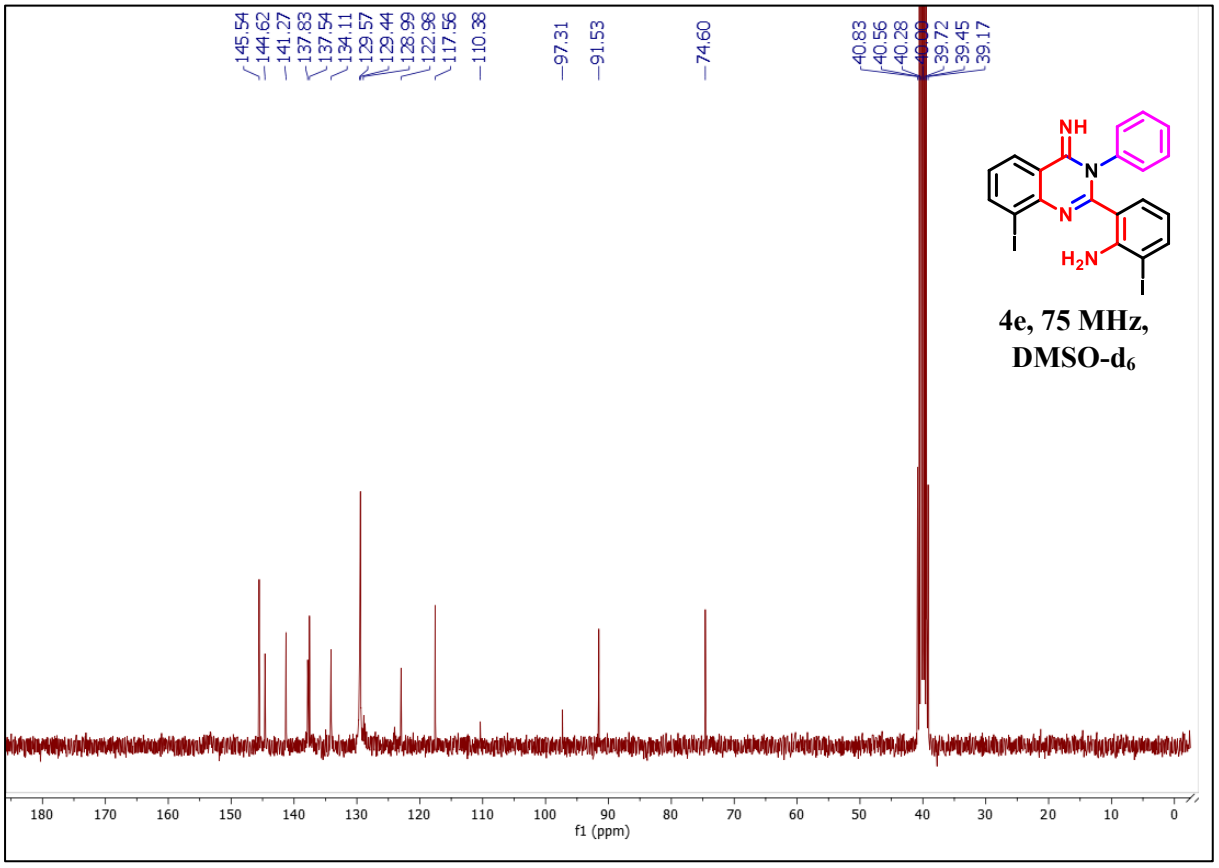


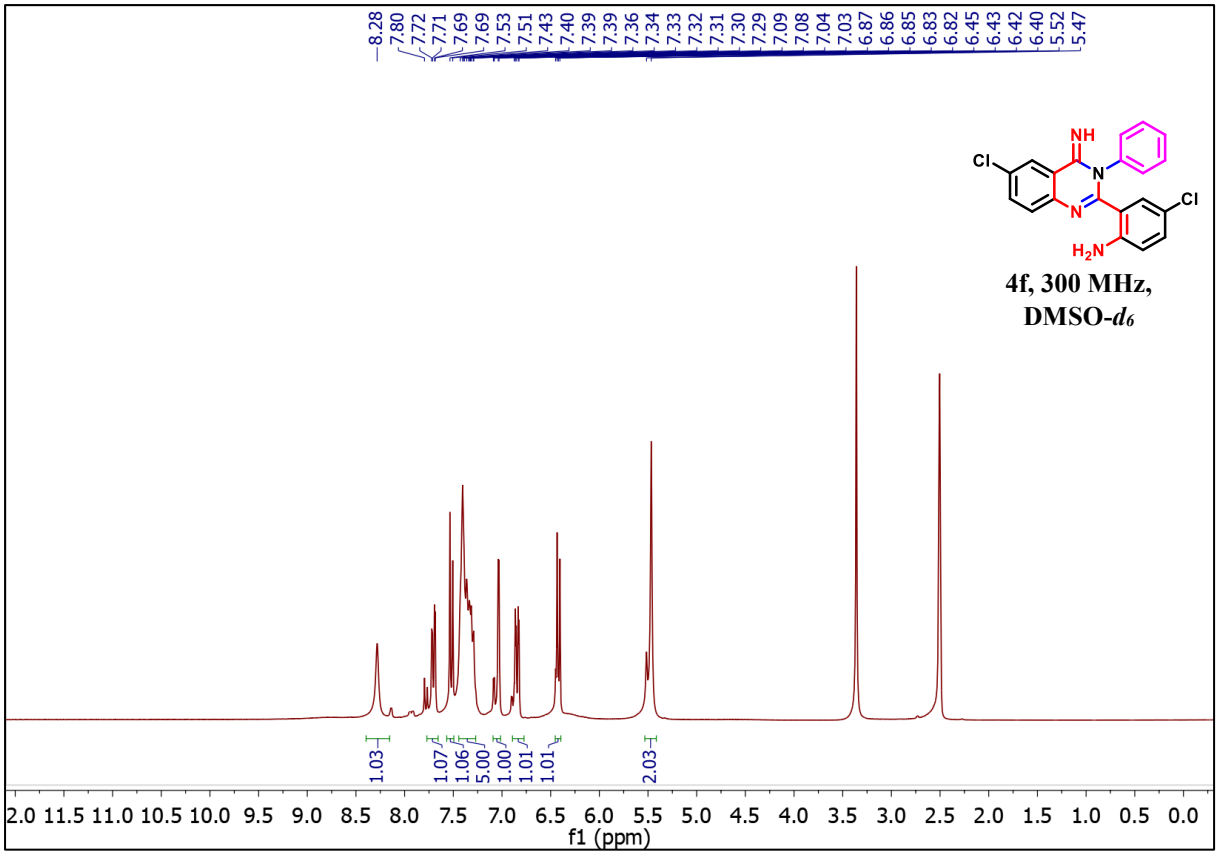
4d, 300 MHz, DMSO-*d*$_6$



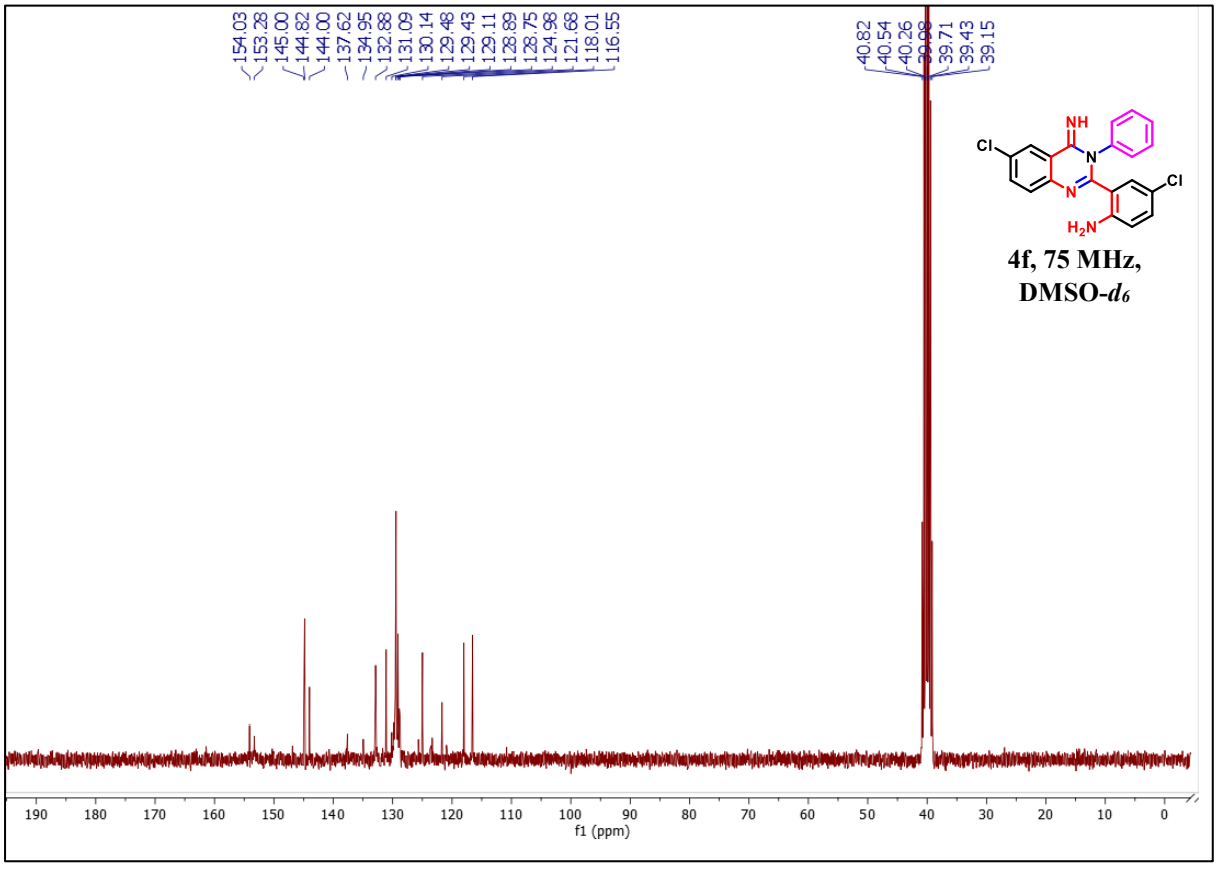
4d, 75 MHz, DMSO-*d*$_6$


8.59
7.97
7.94
7.37
7.30
7.28
7.26
7.25
7.24
7.09
7.06
6.29
6.28
6.26
6.25
5.53
5.48
NH
N
N
H2N
4e, 300MHz,
DMSO-d6
1.04
0.99
7.01
1.00
1.09
2.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

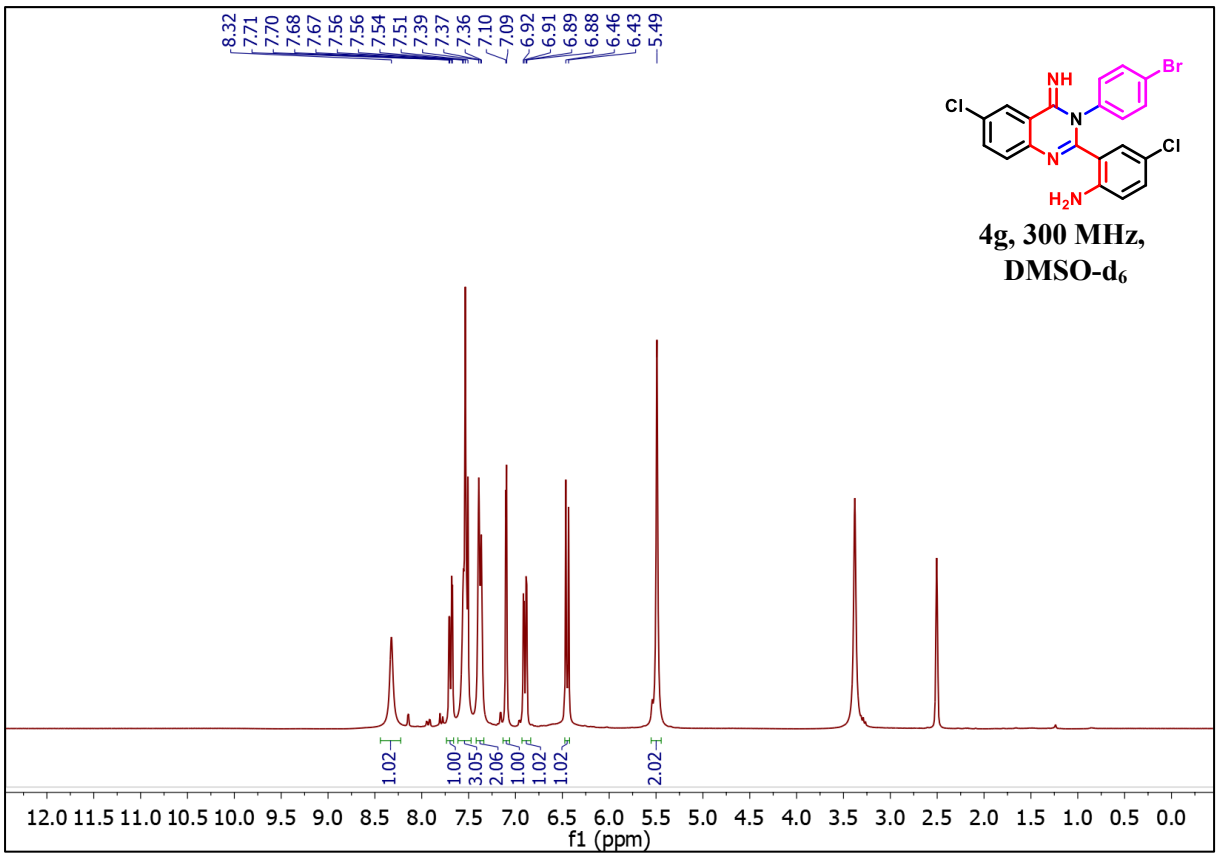

145.54
144.62
141.27
137.83
137.54
134.11
129.57
129.44
128.99
122.98
117.56
110.38
97.31
91.53
74.60
40.83
40.56
40.28
40.00
39.72
39.45
39.17
NH
N
N
H2N
4e, 75 MHz,
DMSO-d6
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



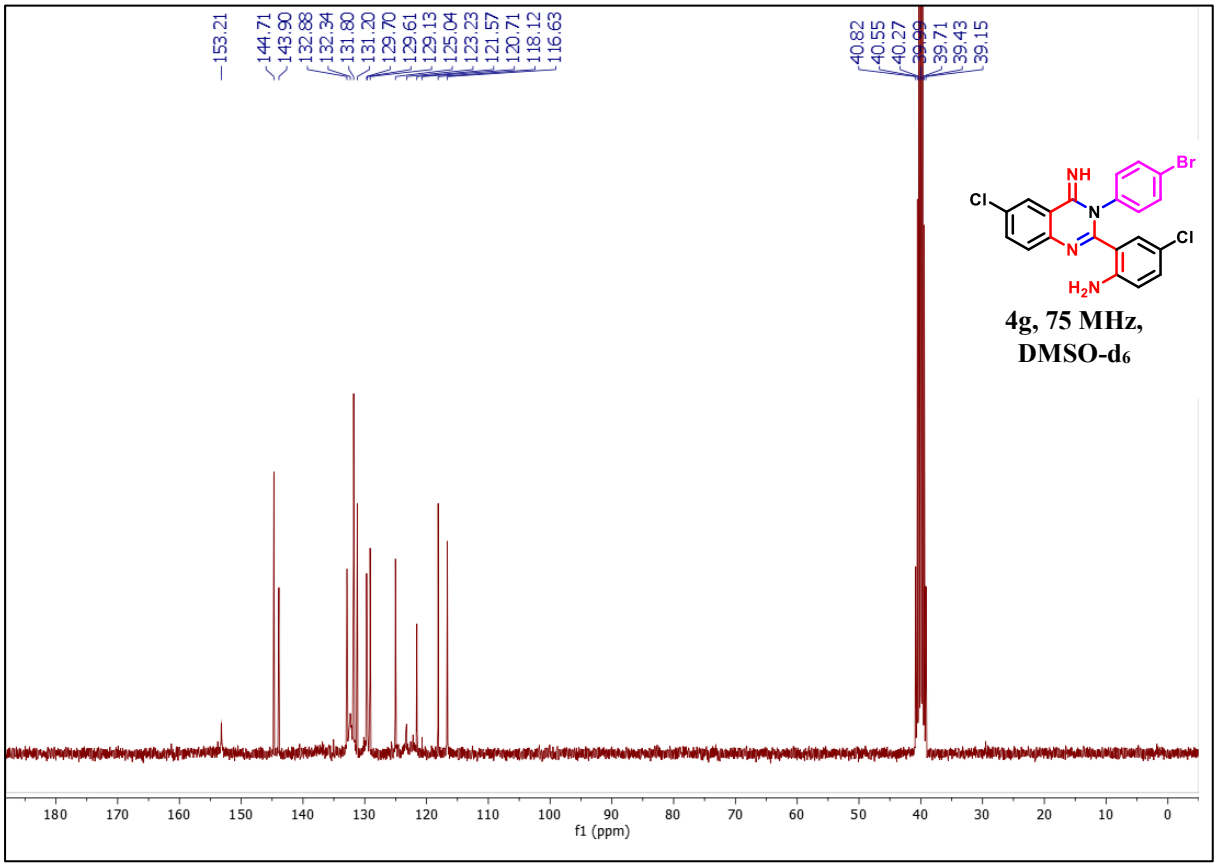
4f, 300 MHz, DMSO-*d*6



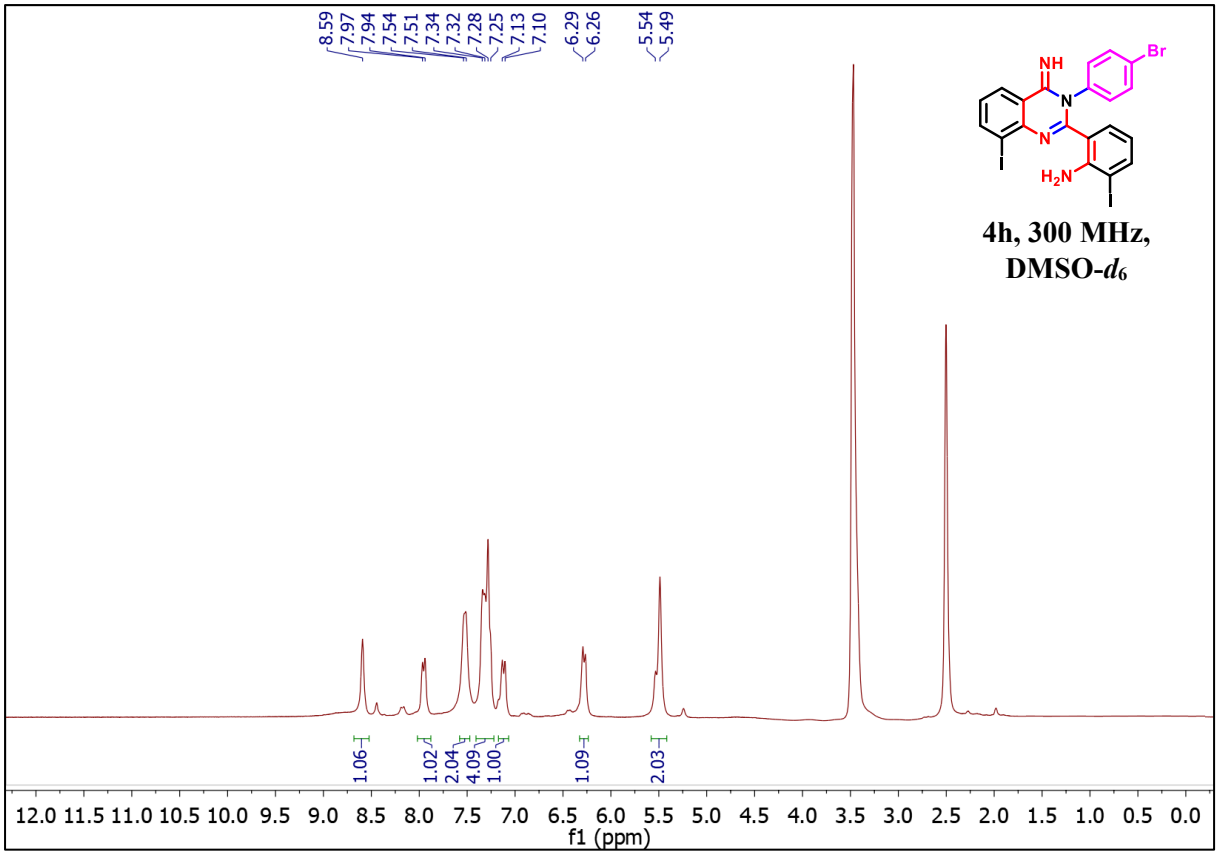
4f, 75 MHz, DMSO-*d*6



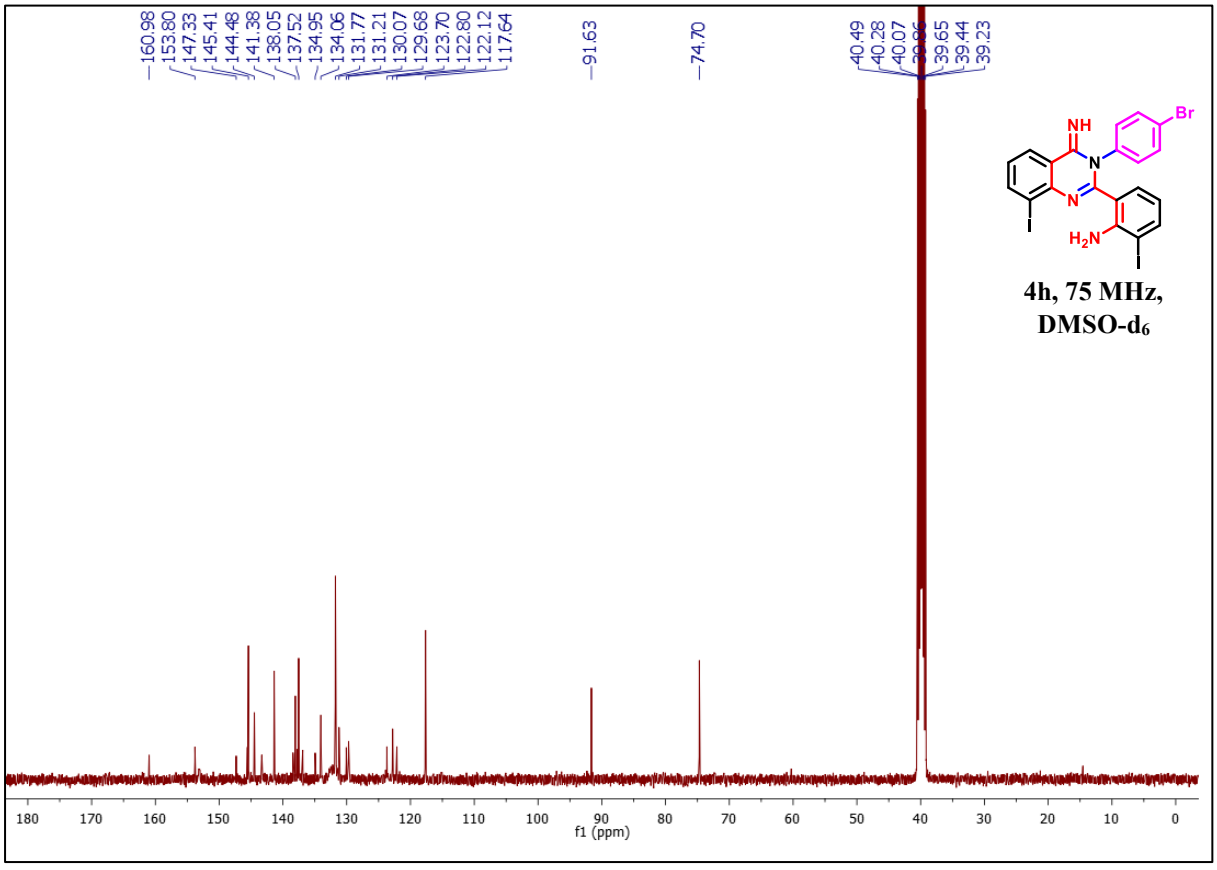
4g, 300 MHz, DMSO-d$_6$



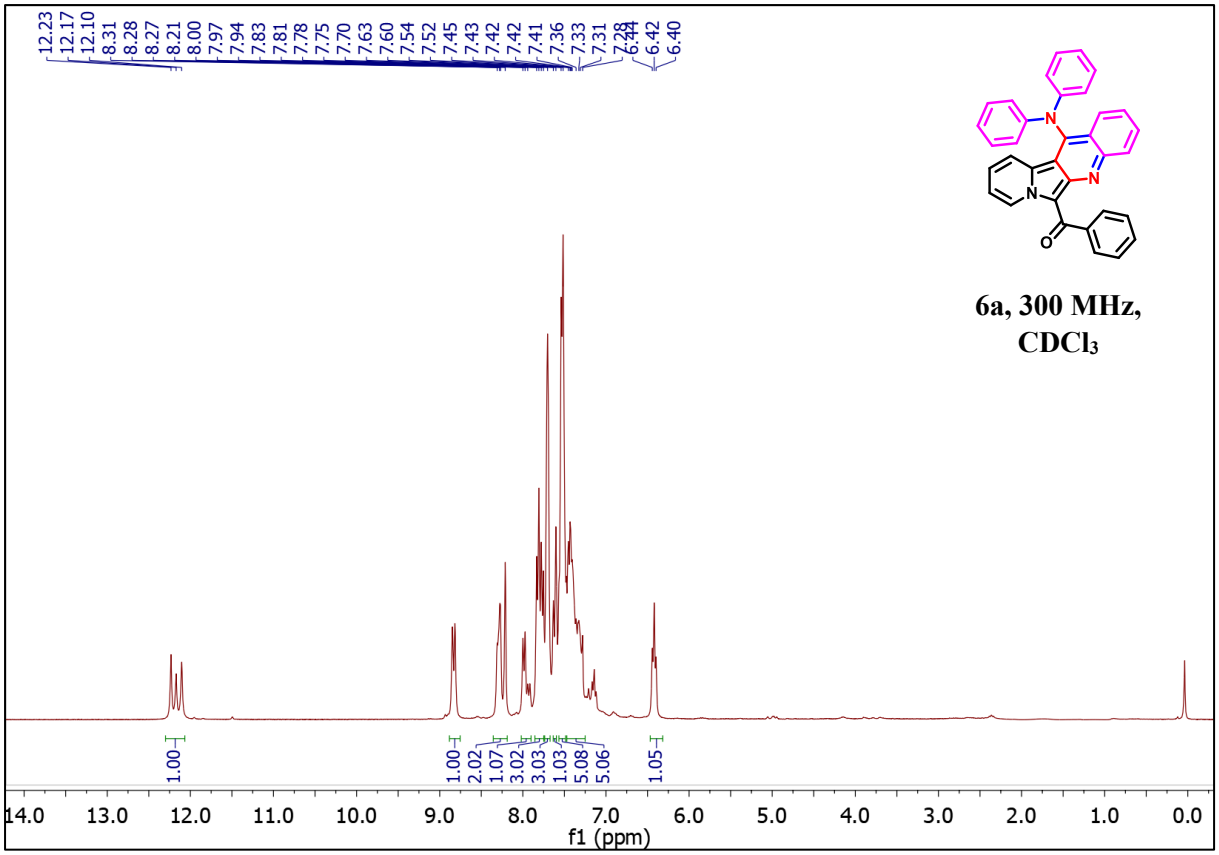
4g, 75 MHz, DMSO-d$_6$



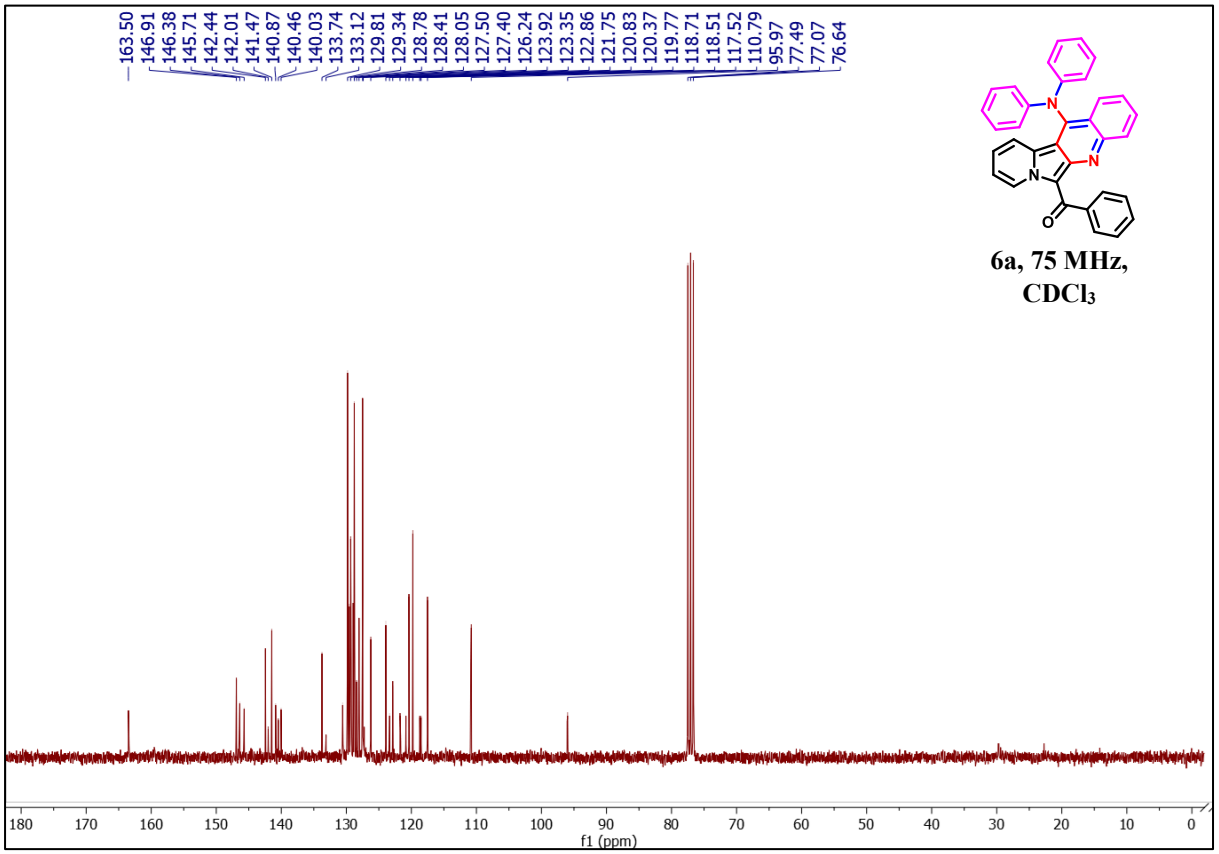
4h, 300 MHz, DMSO-d_6



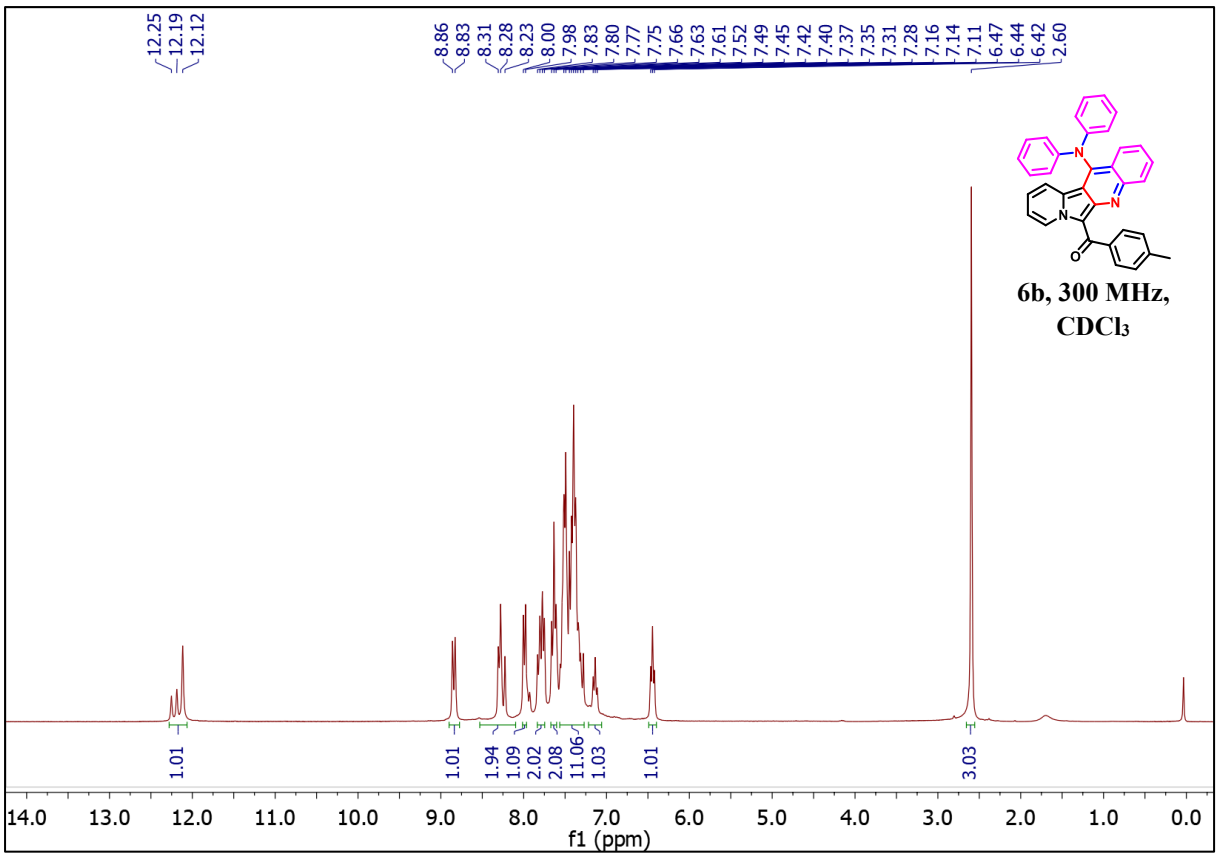
4h, 75 MHz, DMSO-d_6



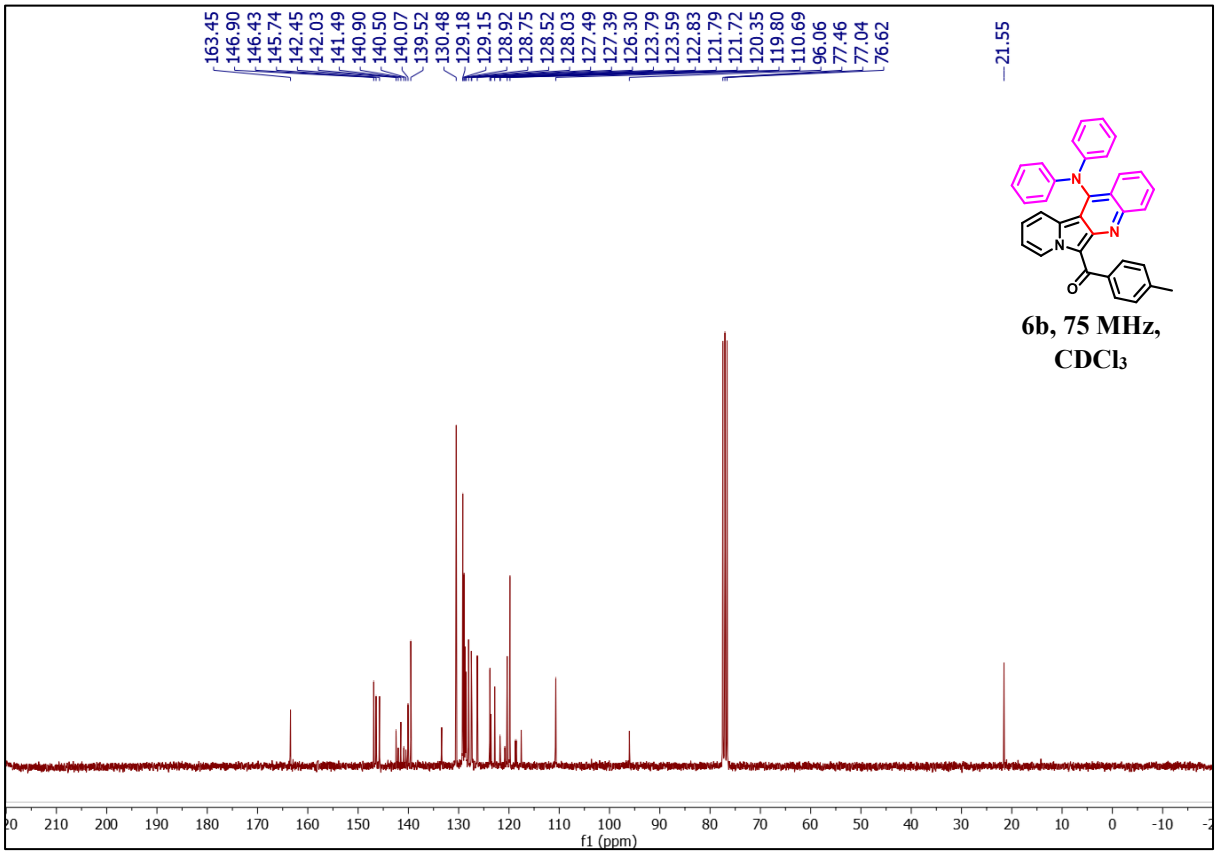
6a, 300 MHz, $CDCl_3$



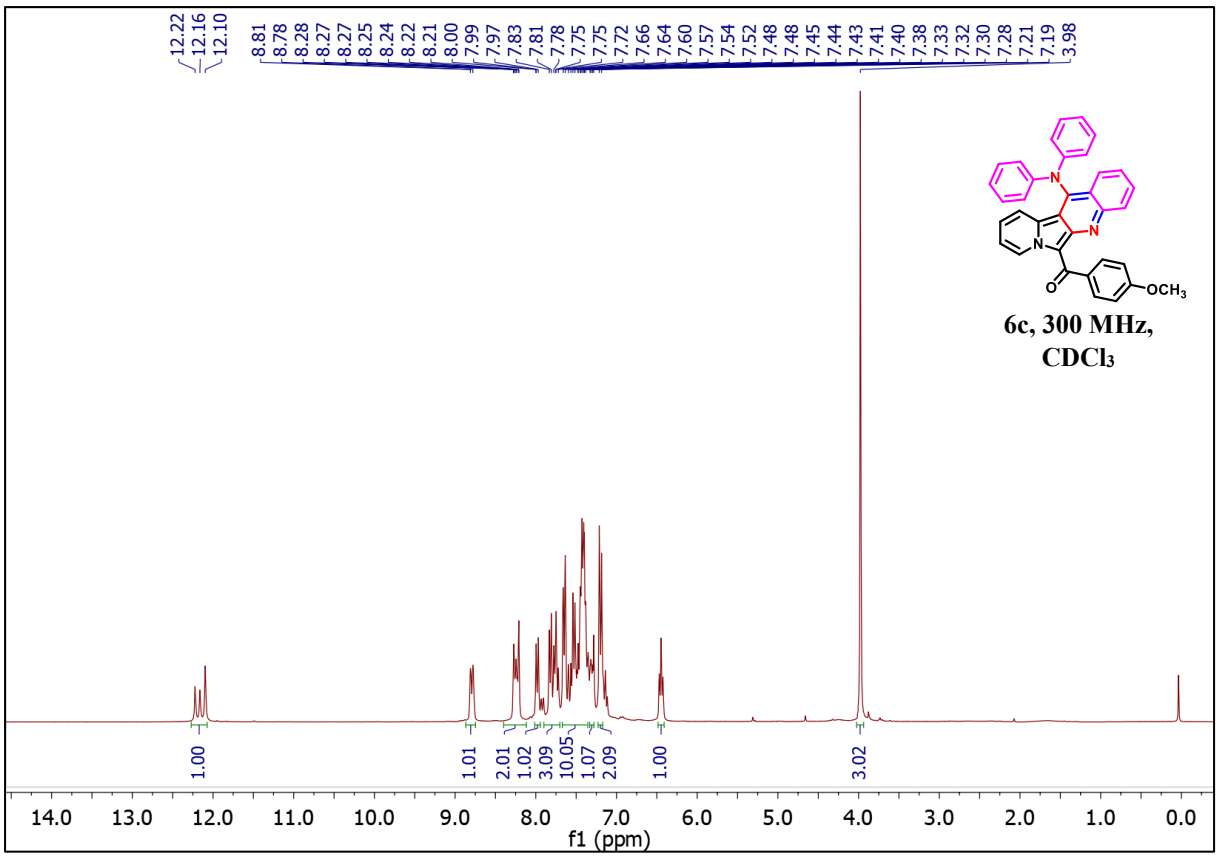
6a, 75 MHz, $CDCl_3$



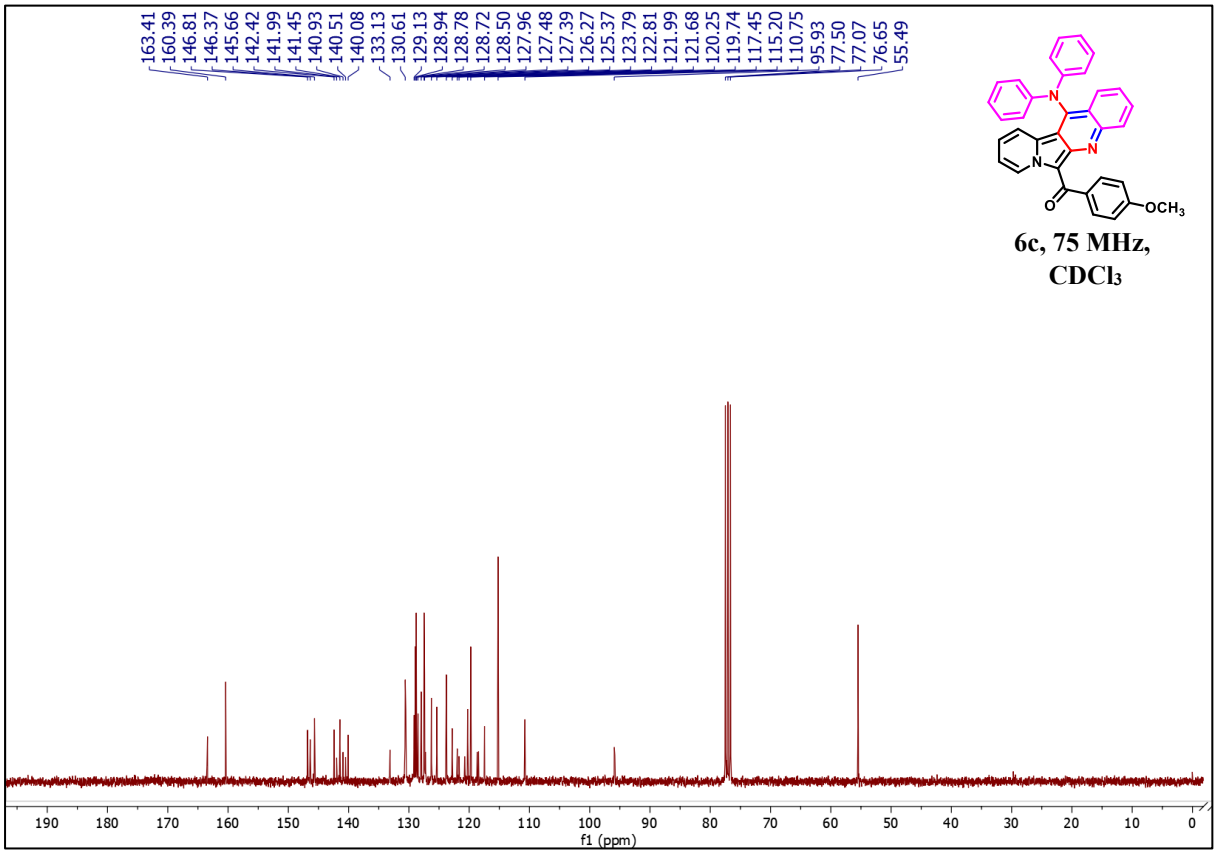
6b, 300 MHz, $CDCl_3$



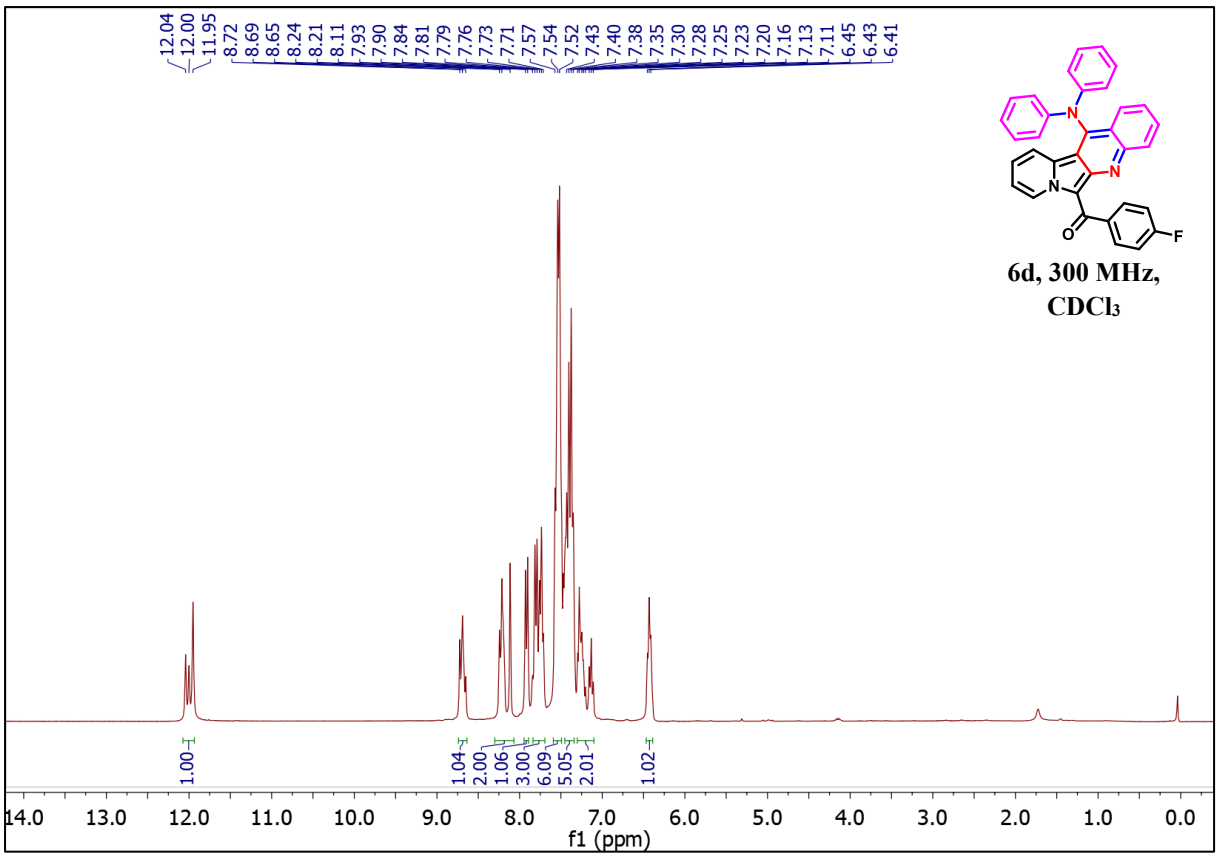
6b, 75 MHz, $CDCl_3$

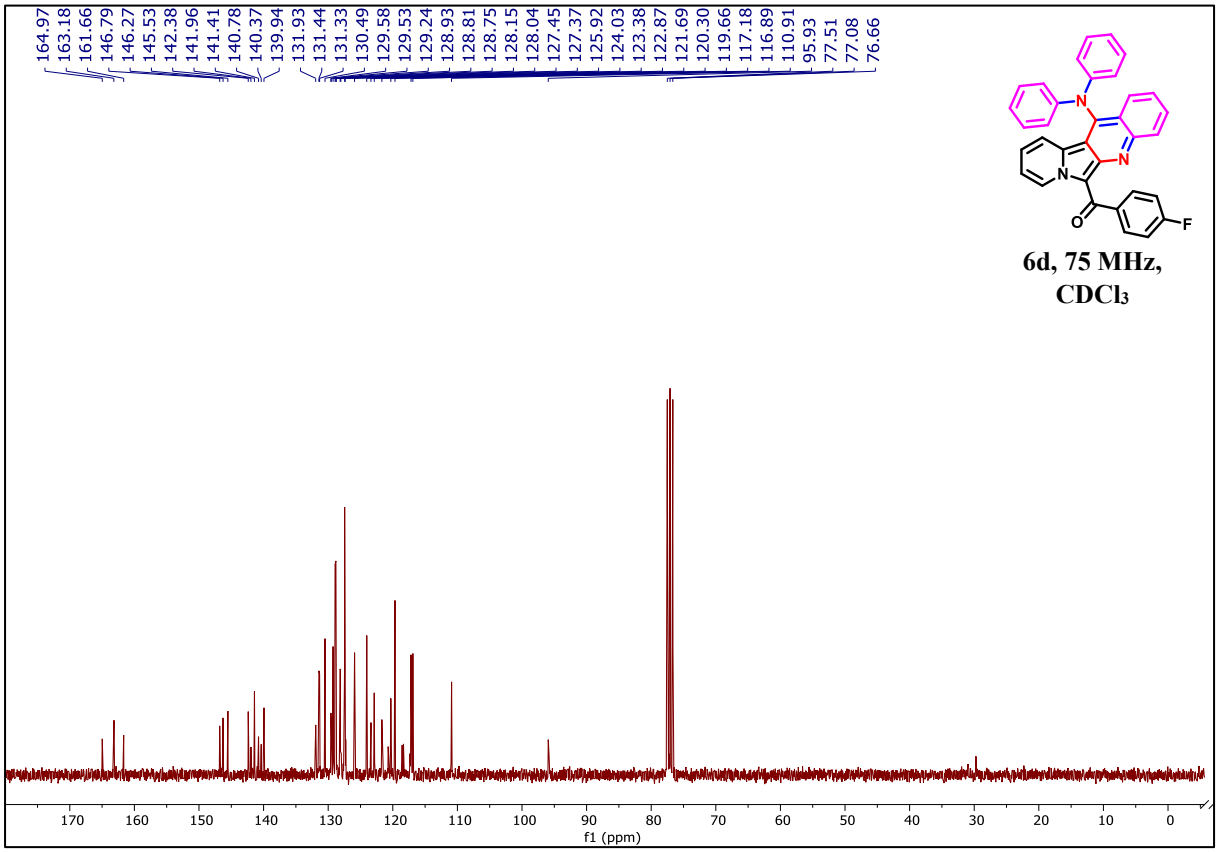


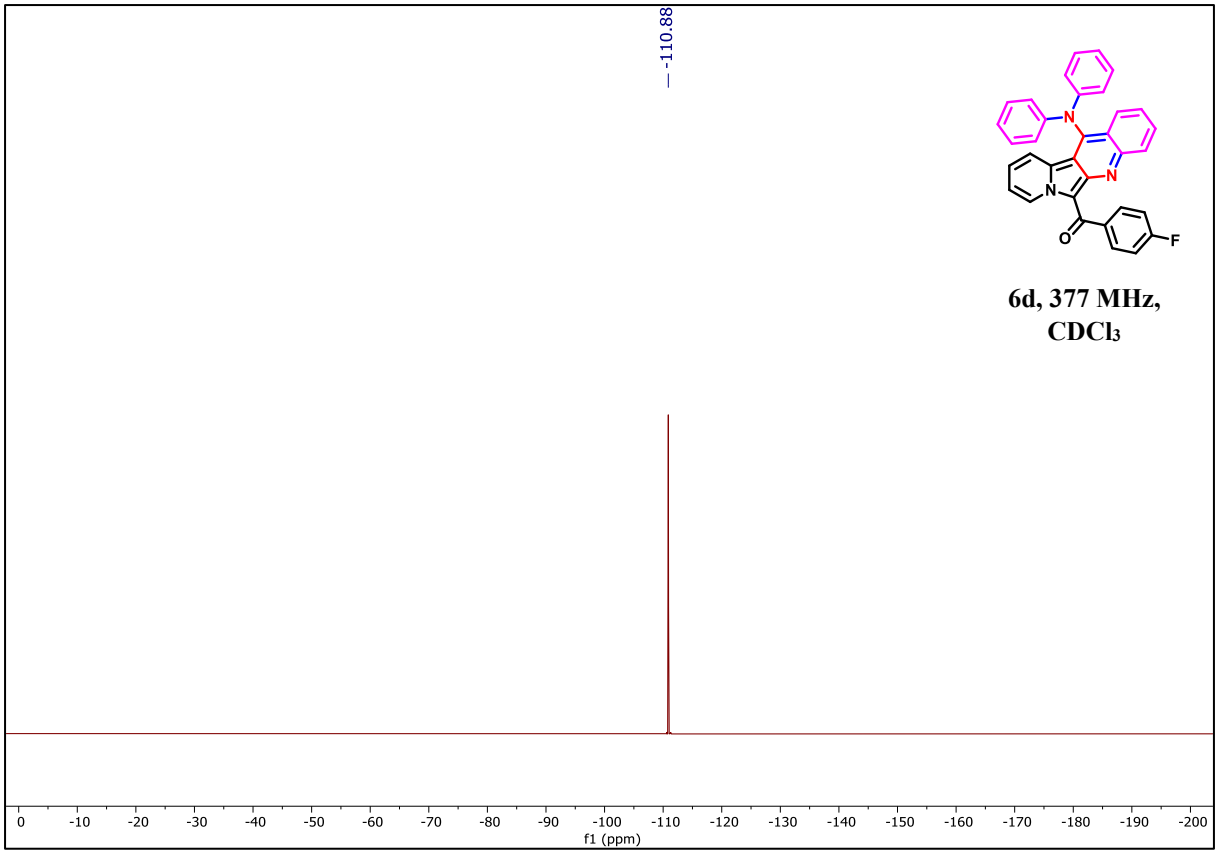
6c, 300 MHz, $CDCl_3$

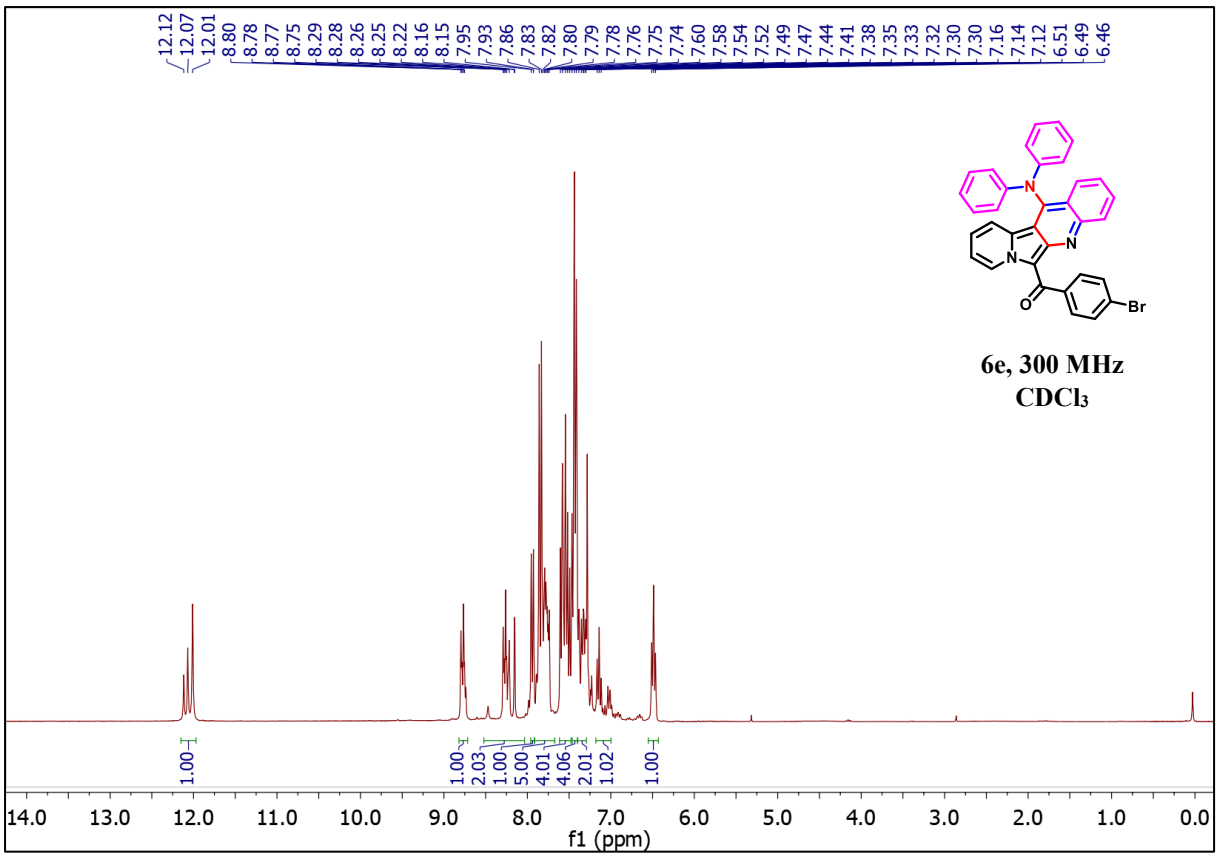


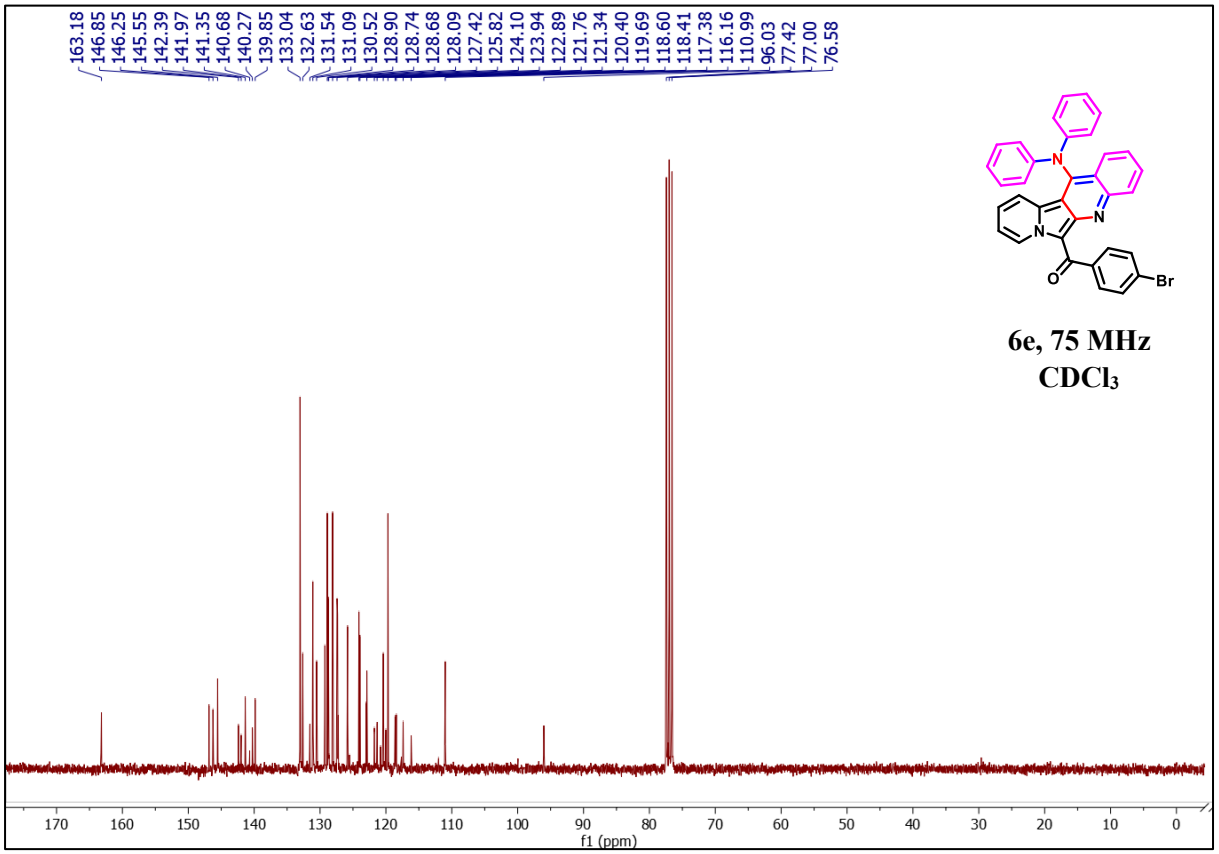
6c, 75 MHz, $CDCl_3$

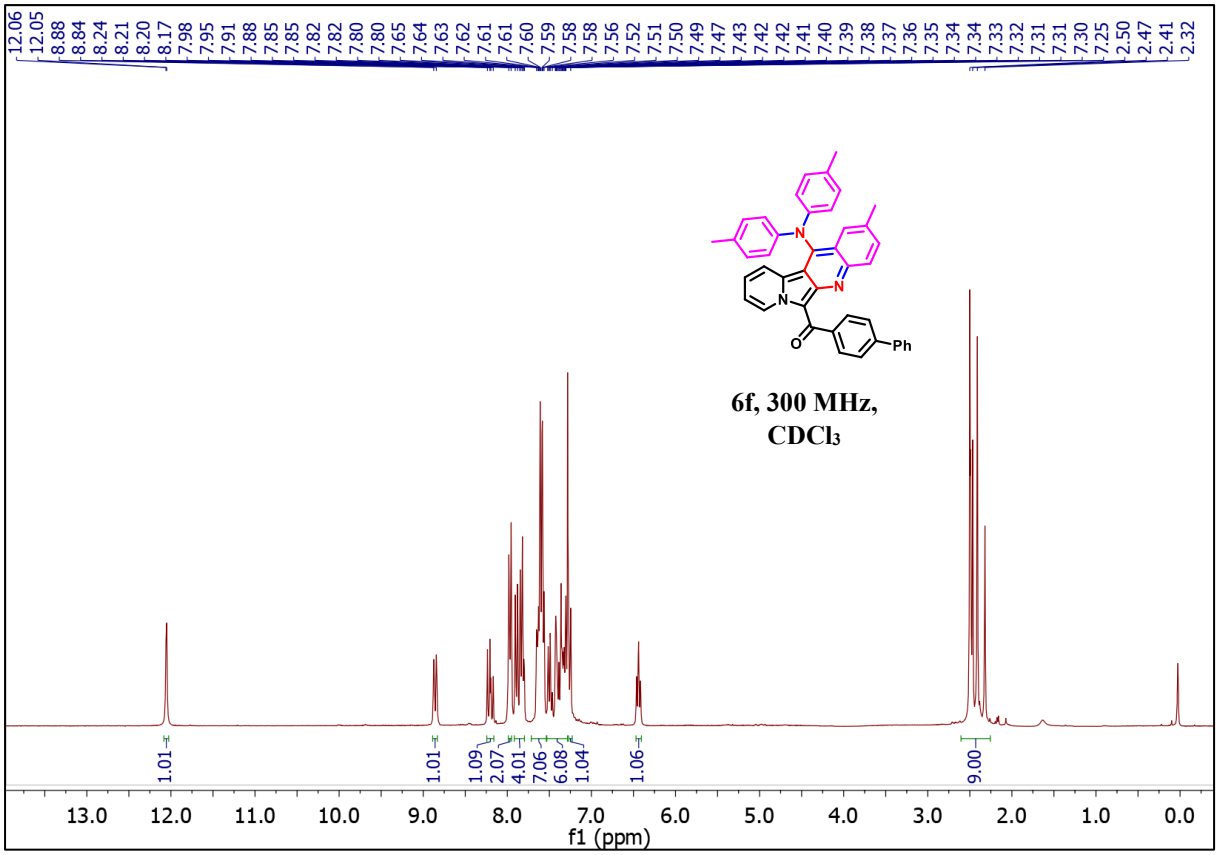

12.04
12.00
11.95
8.72
8.69
8.65
8.24
8.21
8.11
7.93
7.90
7.84
7.81
7.79
7.76
7.73
7.71
7.57
7.54
7.52
7.43
7.40
7.38
7.35
7.30
7.28
7.25
7.23
7.20
7.16
7.13
7.11
6.45
6.43
6.41
1.00
1.04
2.00
1.06
3.00
6.09
5.05
2.01
1.02
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
6d, 300 MHz,
CDCl3

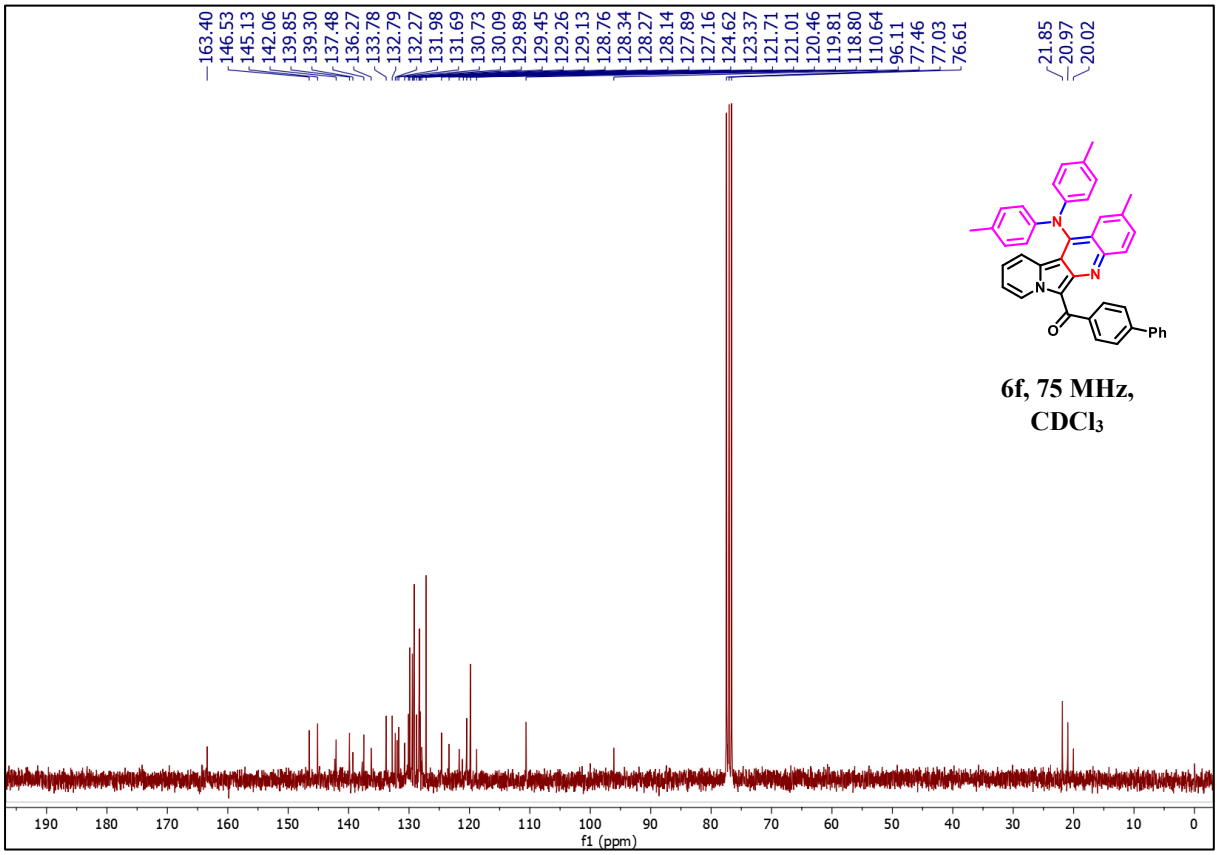

164.97
163.18
161.66
146.79
146.27
145.53
142.38
141.96
141.41
140.78
140.37
139.94
131.93
131.44
131.33
130.49
129.58
129.53
129.24
128.93
128.81
128.75
128.15
128.04
127.45
127.37
125.92
124.03
123.38
122.87
121.69
120.30
119.66
117.18
116.89
110.91
95.93
77.51
77.08
76.66
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
6d, 75 MHz,
CDCl3

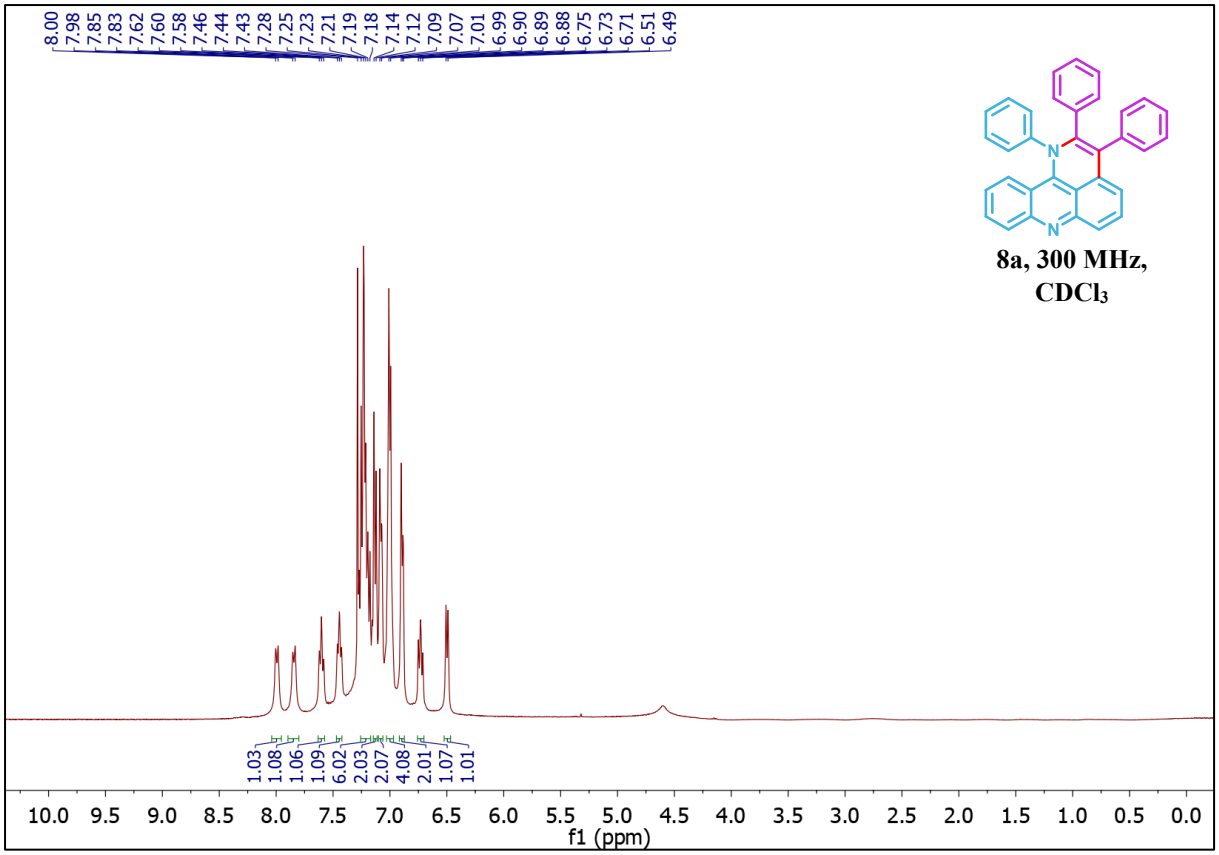

-110.88
N
N
N
O
F
6d, 377 MHz,
CDCl3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


12.12
12.07
12.01
8.80
8.78
8.77
8.75
8.29
8.28
8.26
8.25
8.22
8.16
8.15
7.95
7.93
7.86
7.83
7.82
7.80
7.79
7.78
7.76
7.75
7.74
7.60
7.58
7.54
7.52
7.49
7.47
7.44
7.41
7.38
7.35
7.33
7.32
7.30
7.30
7.16
7.14
7.12
6.51
6.49
6.46
1.00
1.00
2.03
1.00
5.00
4.01
4.06
2.01
1.02
1.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
N
N
N
O
Br
6e, 300 MHz
CDCl3

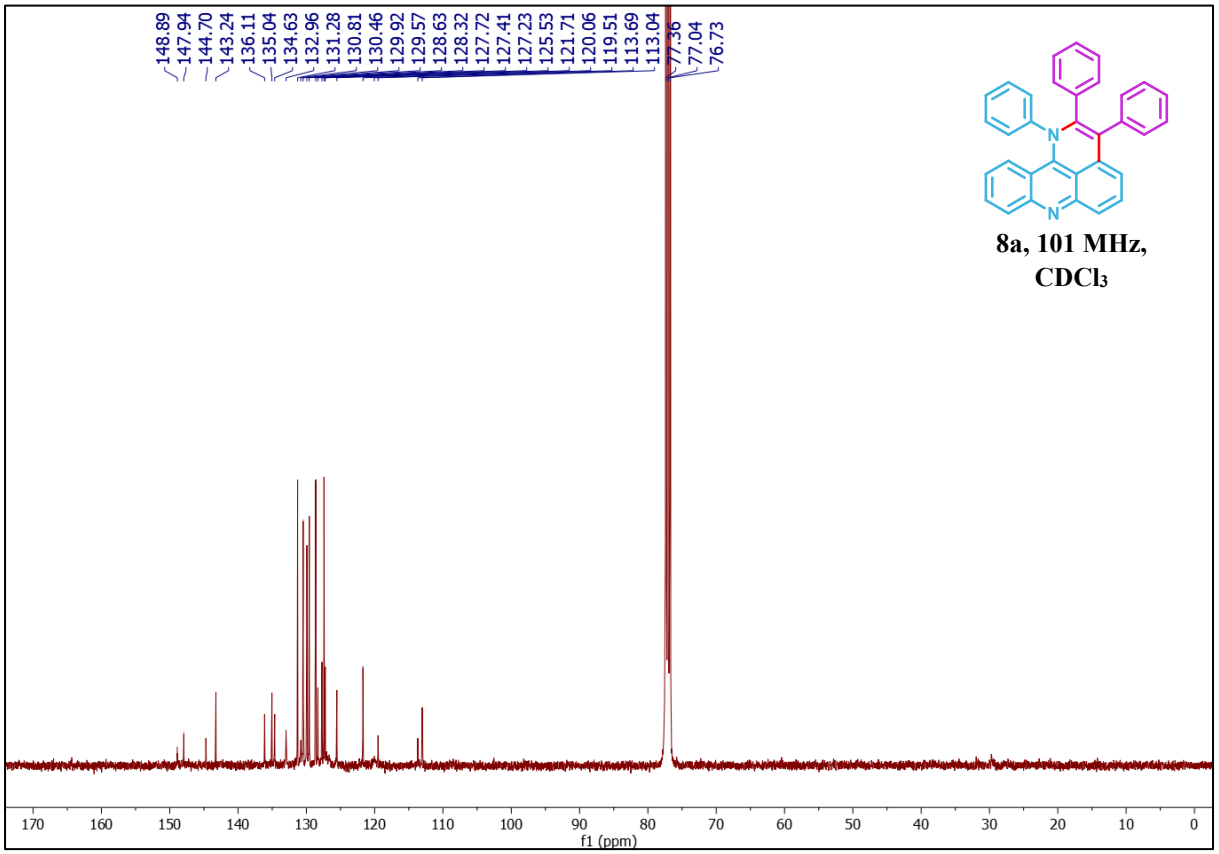

163.18
146.85
146.25
145.55
142.39
141.97
141.35
140.68
140.27
139.85
133.04
132.63
131.54
131.09
130.52
128.90
128.74
128.68
128.09
127.42
125.82
124.10
123.94
122.89
121.76
121.34
120.40
119.69
118.60
118.41
117.38
116.16
110.99
96.03
77.42
77.00
76.58
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
N
N
N
O
Br
6e, 75 MHz
CDCl3


12.06 12.05 8.88 8.84 8.24 8.21 8.20 8.17 7.98 7.95 7.91 7.88 7.85 7.85 7.82 7.82 7.80 7.80 7.65 7.64 7.63 7.62 7.61 7.61 7.60 7.59 7.58 7.58 7.56 7.52 7.51 7.50 7.49 7.47 7.43 7.42 7.42 7.41 7.40 7.39 7.38 7.37 7.36 7.35 7.34 7.34 7.33 7.32 7.31 7.31 7.30 7.25 2.50 2.47 2.41 2.32
1.01 1.01 1.09 2.07 4.01 7.06 6.08 1.04 1.06 9.00
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)
Ph
6f, 300 MHz,
CDCl3

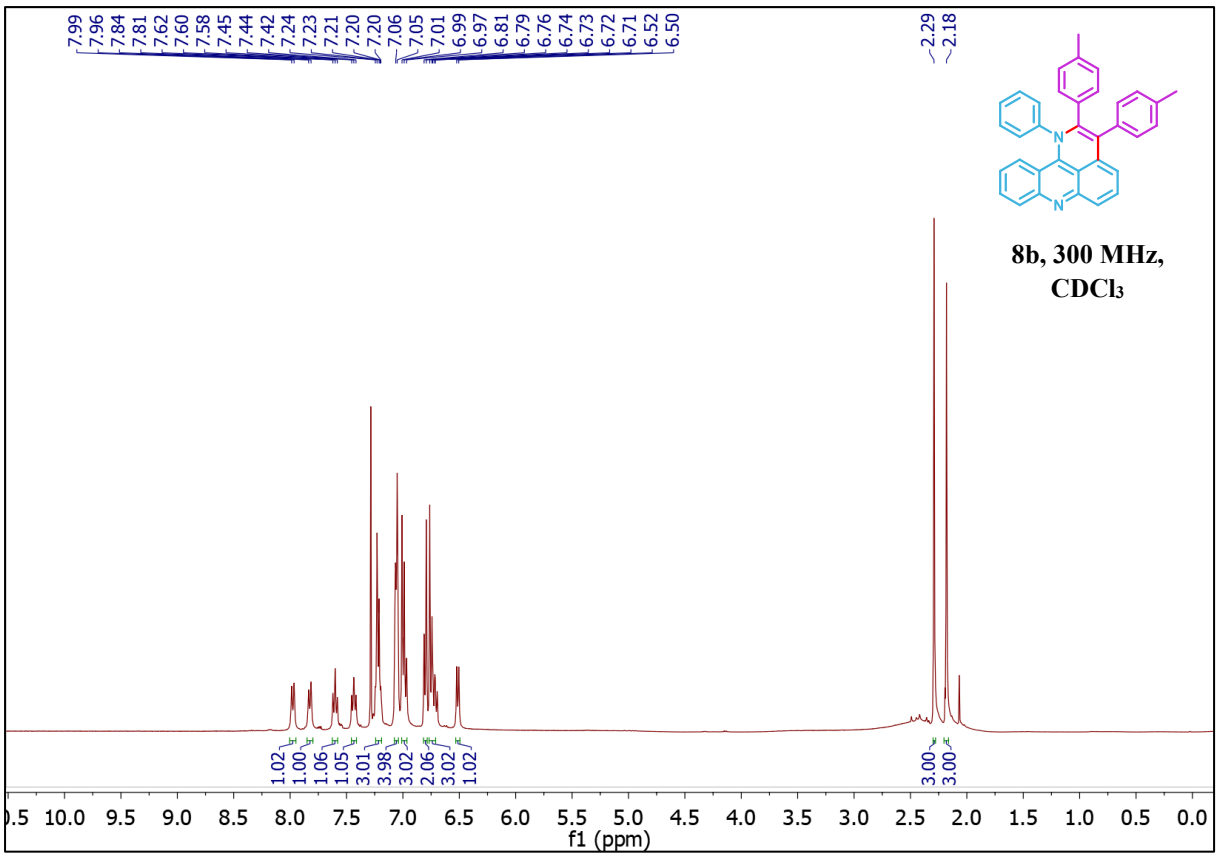

163.40 146.53 145.13 142.06 139.85 139.30 137.48 136.27 133.78 132.79 132.27 131.98 131.69 130.73 130.09 129.89 129.45 129.26 129.13 128.76 128.34 128.27 128.14 127.89 127.16 124.62 123.37 121.71 121.01 120.46 119.81 118.80 110.64 96.11 77.46 77.03 76.61
21.85 20.97 20.02
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Ph
6f, 75 MHz,
CDCl3



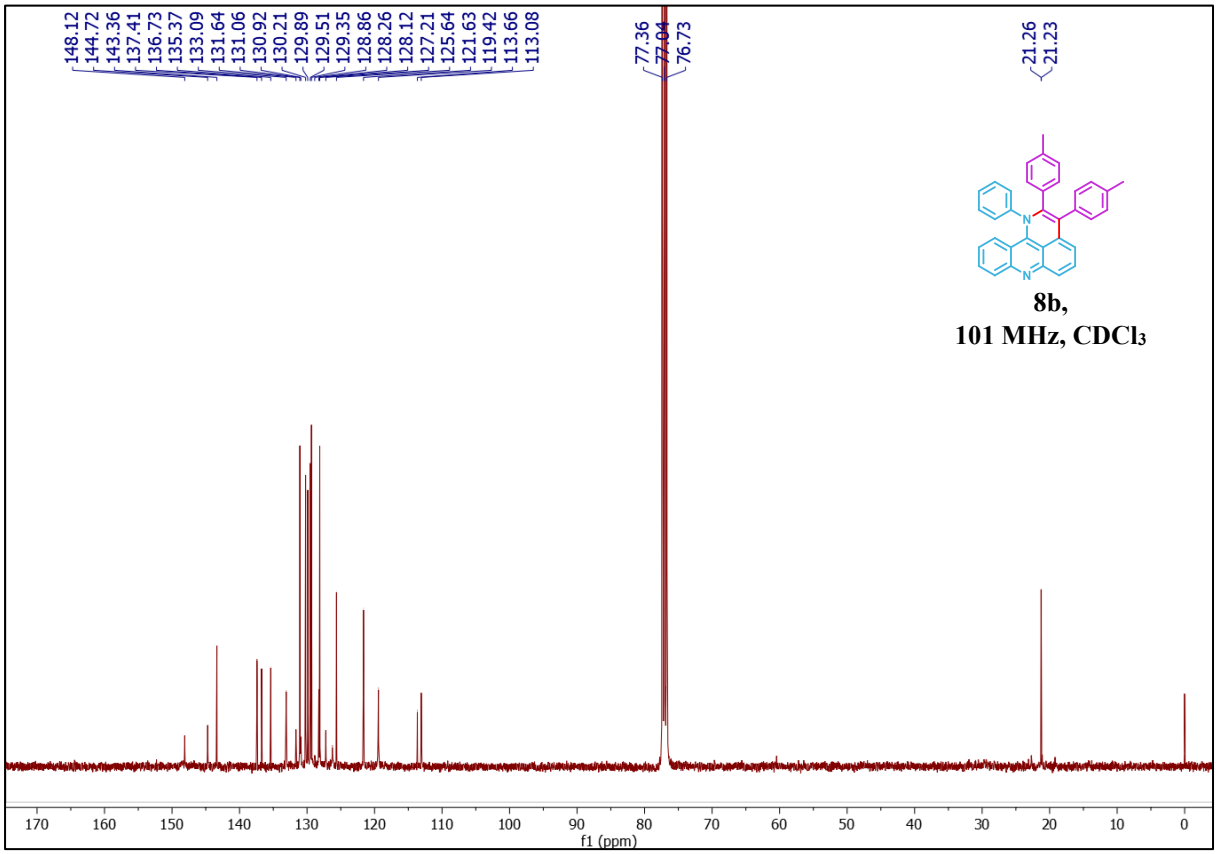
8a, 300 MHz, $CDCl_3$



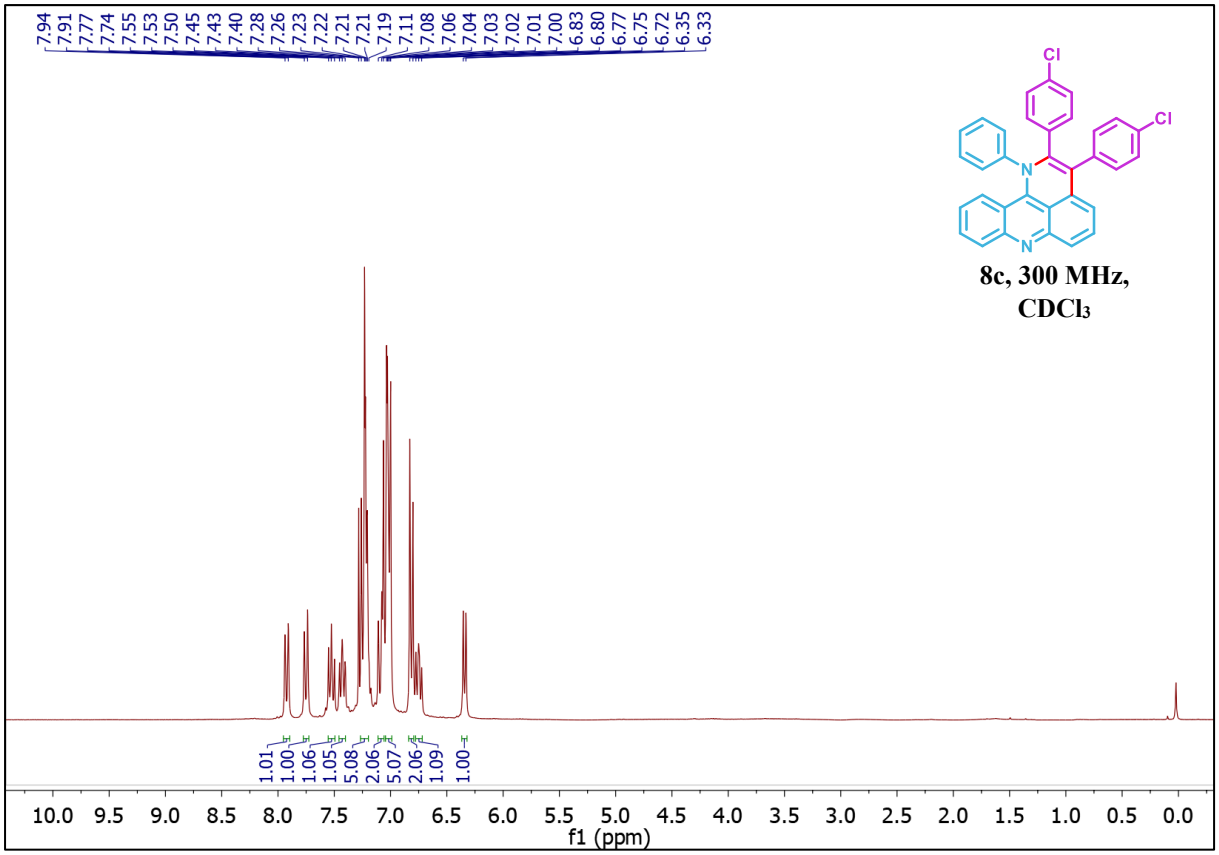
8a, 101 MHz, $CDCl_3$



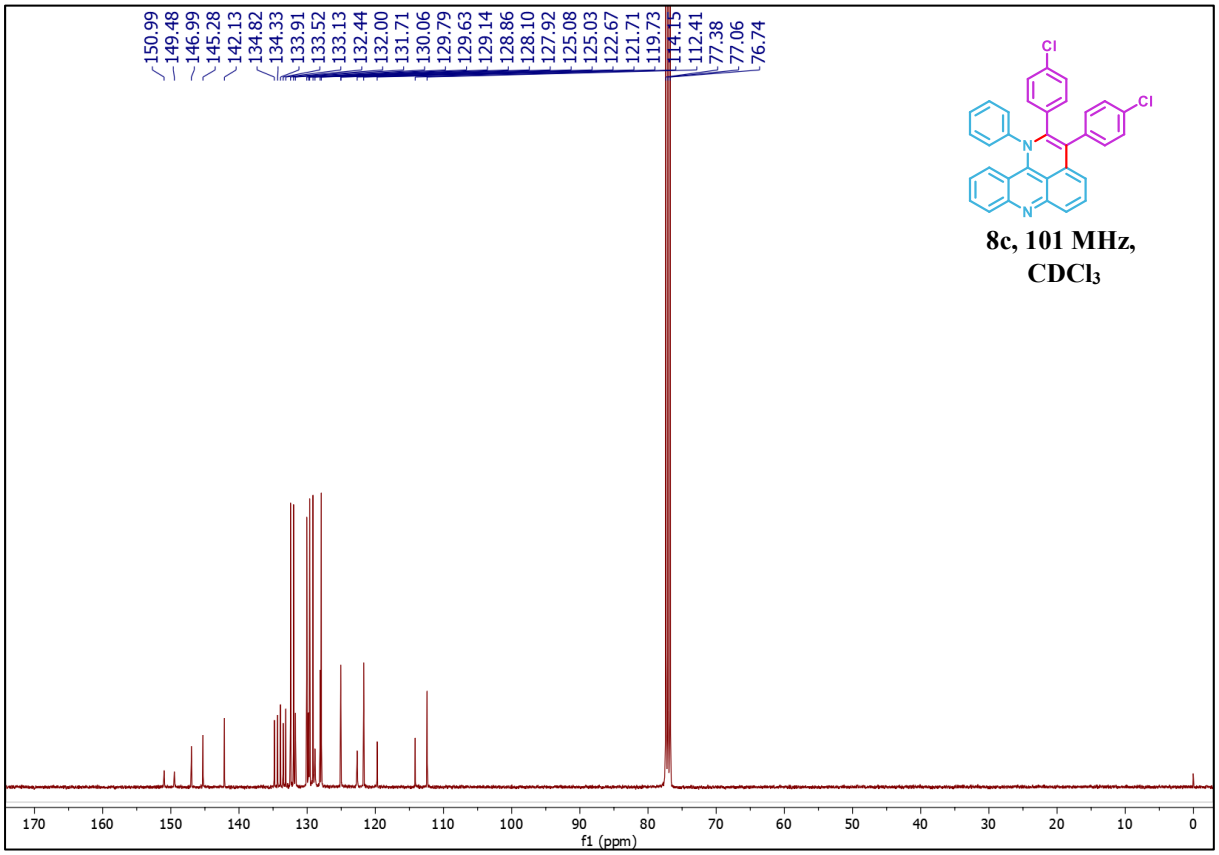
8b, 300 MHz, $CDCl_3$



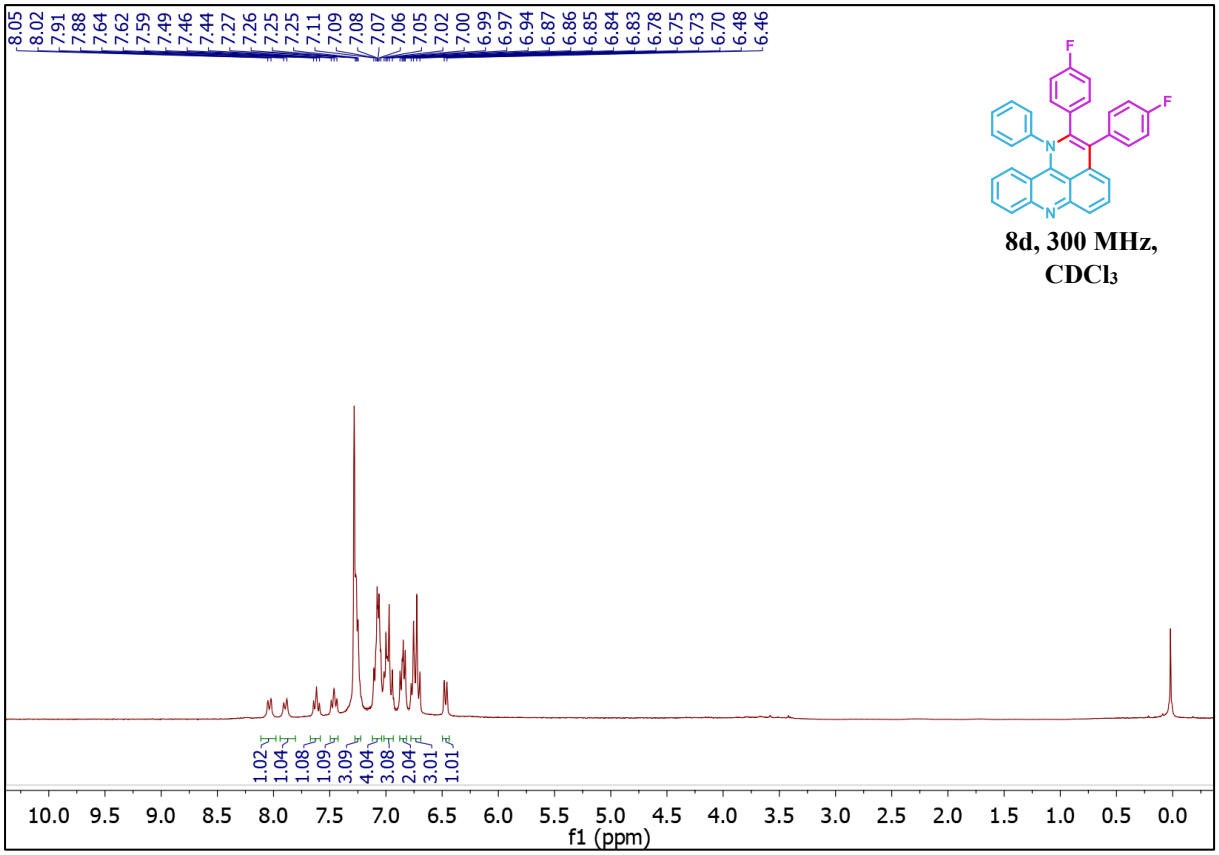
8b, 101 MHz, $CDCl_3$

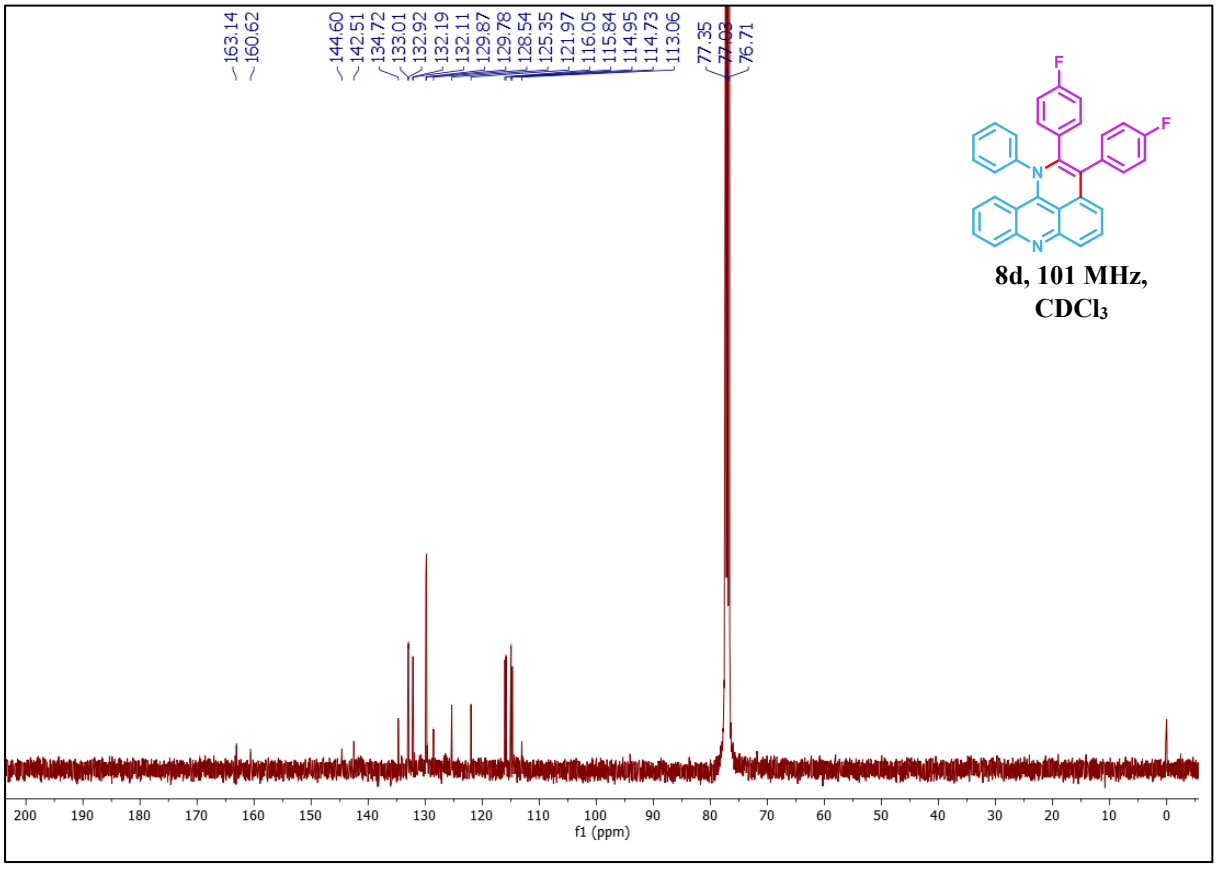


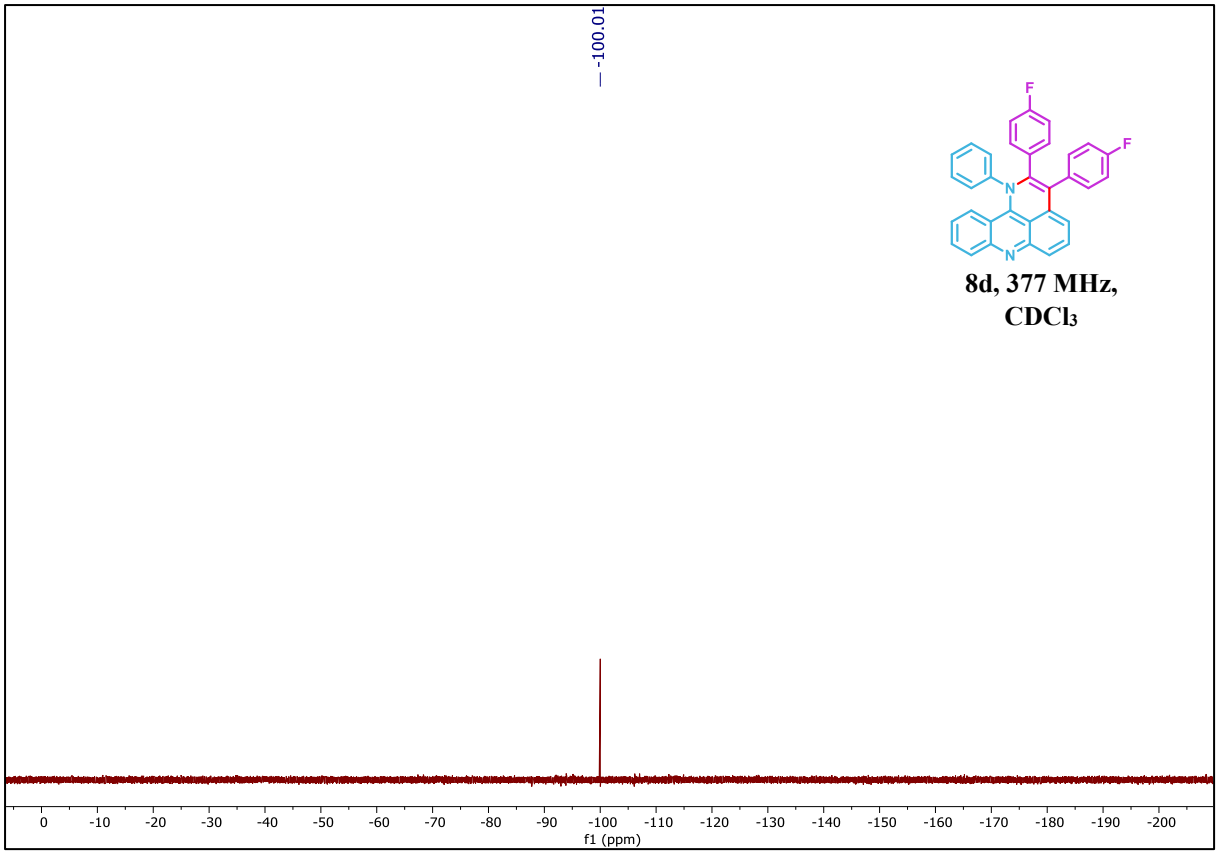
8c, 300 MHz, $CDCl_3$



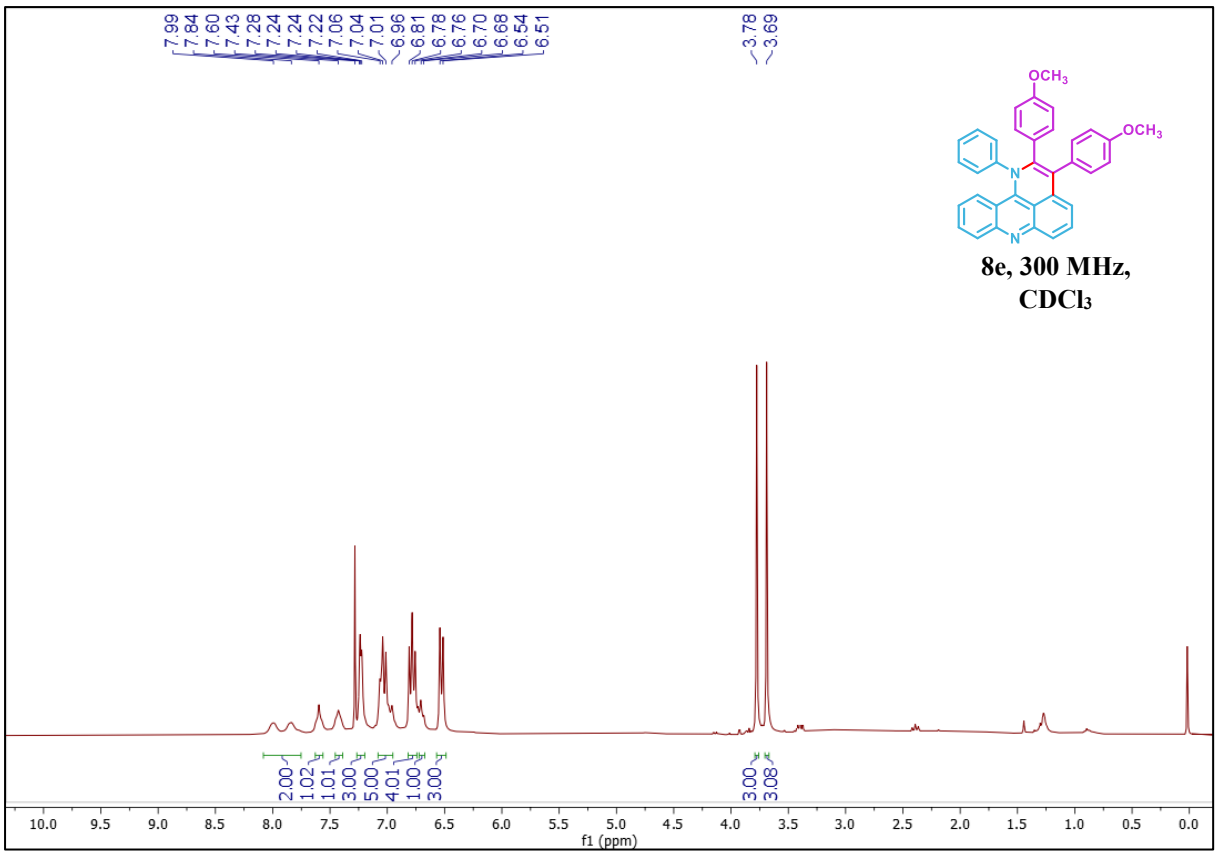
8c, 101 MHz, $CDCl_3$


8.05
8.02
7.91
7.88
7.64
7.62
7.59
7.49
7.46
7.44
7.27
7.26
7.25
7.11
7.09
7.08
7.07
7.06
7.05
7.02
7.00
6.99
6.97
6.94
6.87
6.86
6.85
6.84
6.83
6.78
6.75
6.73
6.70
6.48
6.46
F
F
N
N
8d, 300 MHz,
CDCl3
1.02
1.04
1.08
1.09
3.09
4.04
3.08
2.04
3.01
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

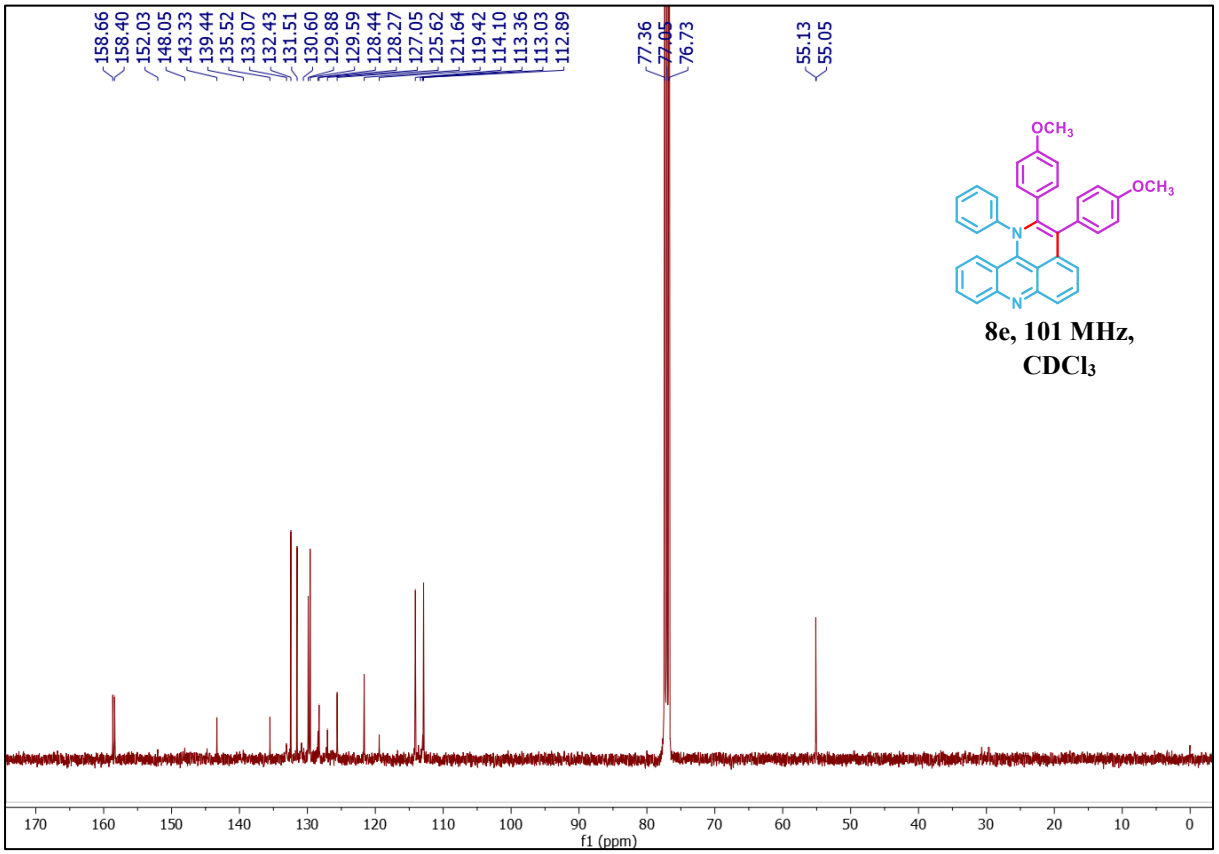

163.14
160.62
144.60
142.51
134.72
133.01
132.92
132.19
132.11
129.87
129.78
128.54
125.35
121.97
116.05
115.84
114.95
114.73
113.06
77.35
77.03
76.71
F
F
N
N
8d, 101 MHz,
CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



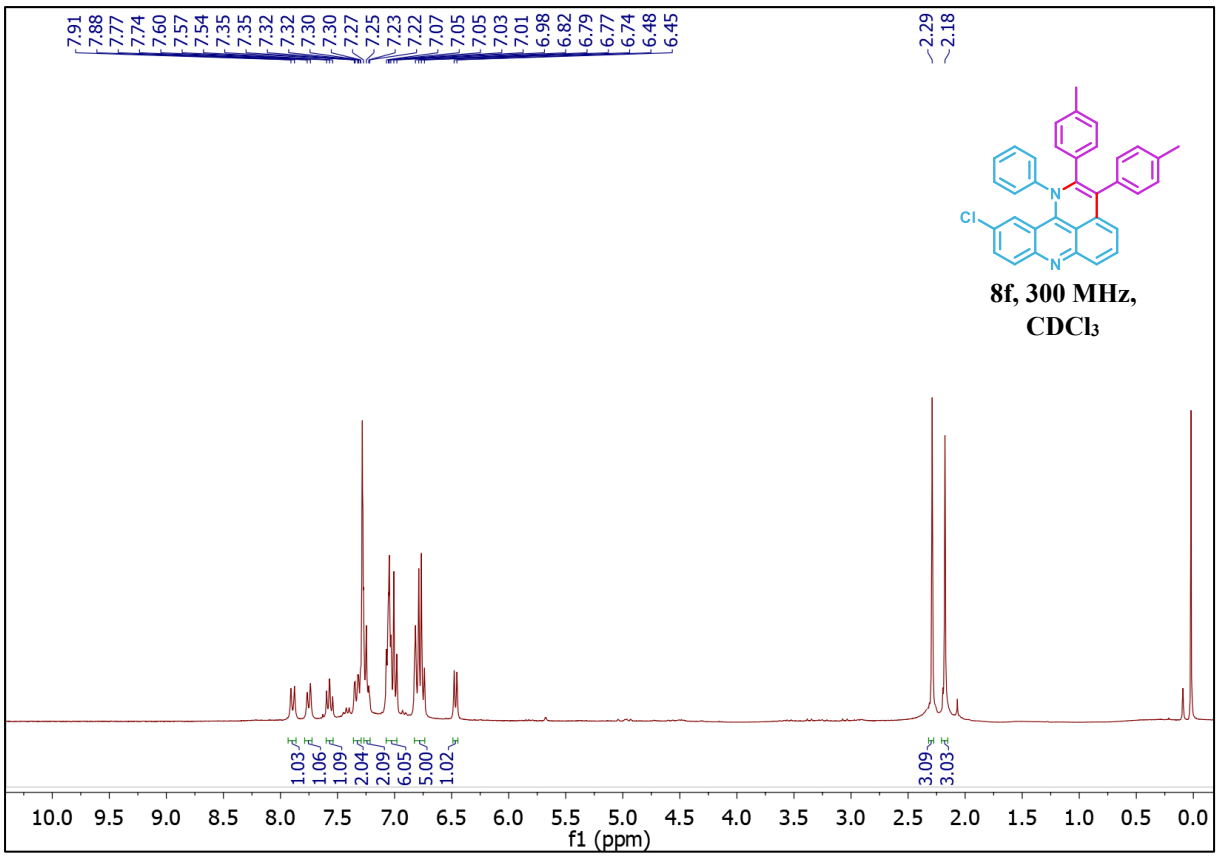
8d, 377 MHz, $CDCl_3$

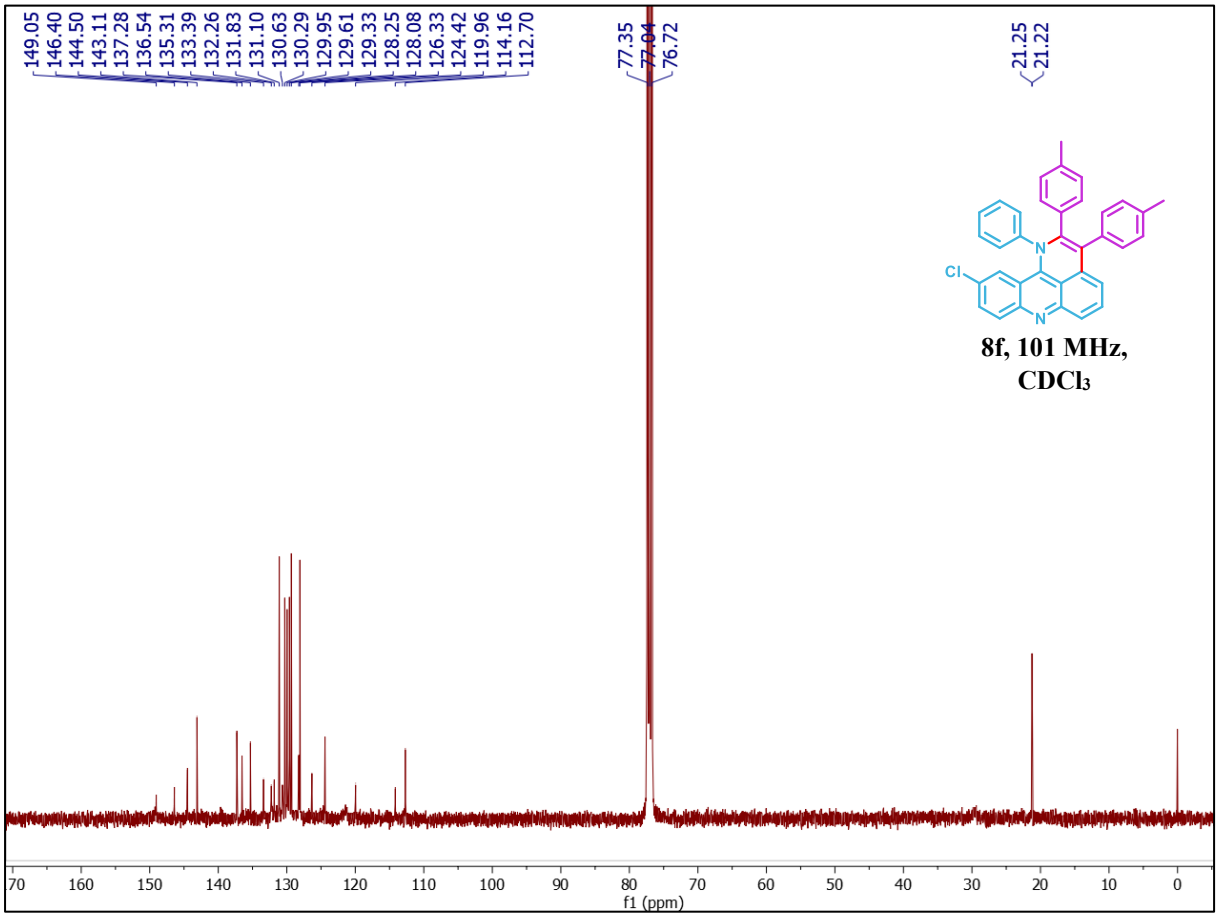


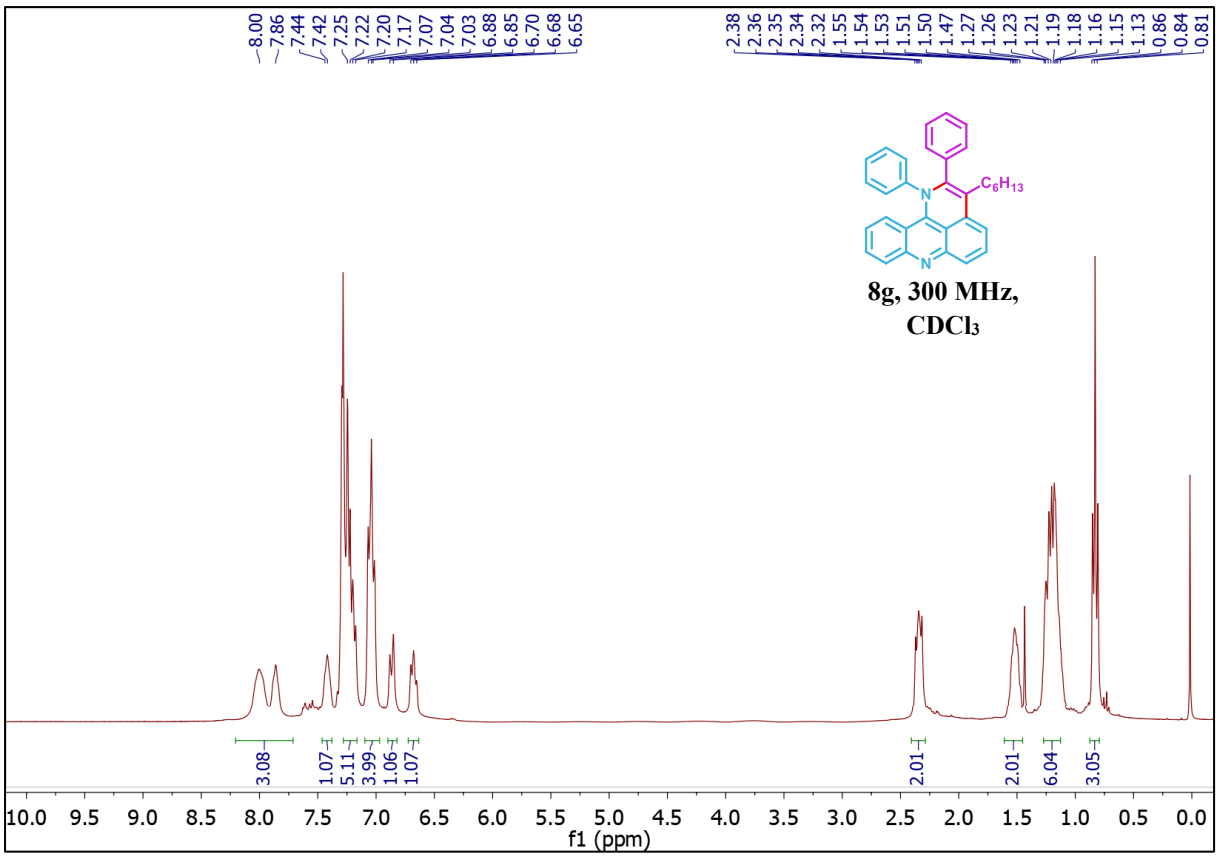
8e, 300 MHz, $CDCl_3$



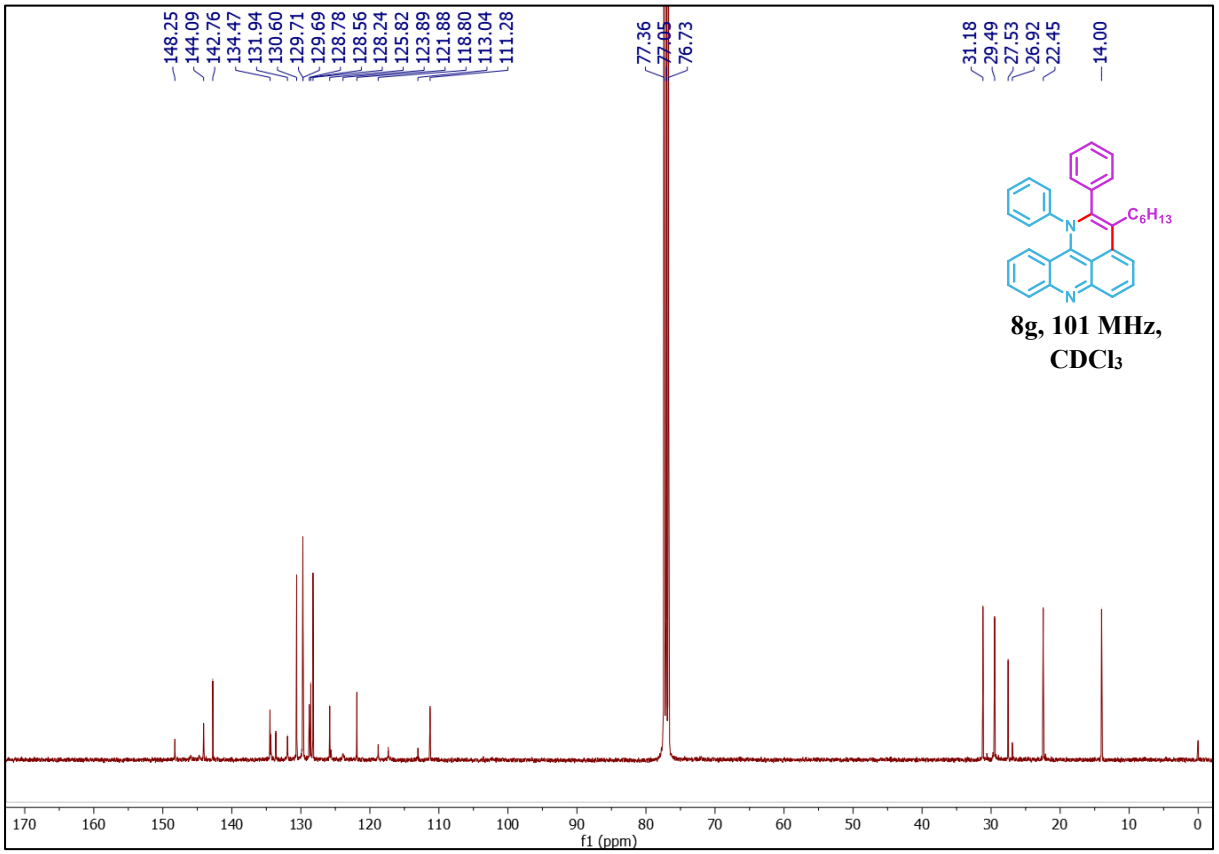
8e, 101 MHz, $CDCl_3$


7.91
7.88
7.77
7.74
7.60
7.57
7.54
7.35
7.35
7.32
7.32
7.30
7.30
7.27
7.25
7.23
7.22
7.07
7.05
7.05
7.03
7.01
6.98
6.82
6.79
6.77
6.74
6.48
6.45
2.29
2.18
Cl
N
N
8f, 300 MHz,
CDCl3
1.03
1.06
1.09
2.04
2.09
6.05
5.00
1.02
3.09
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

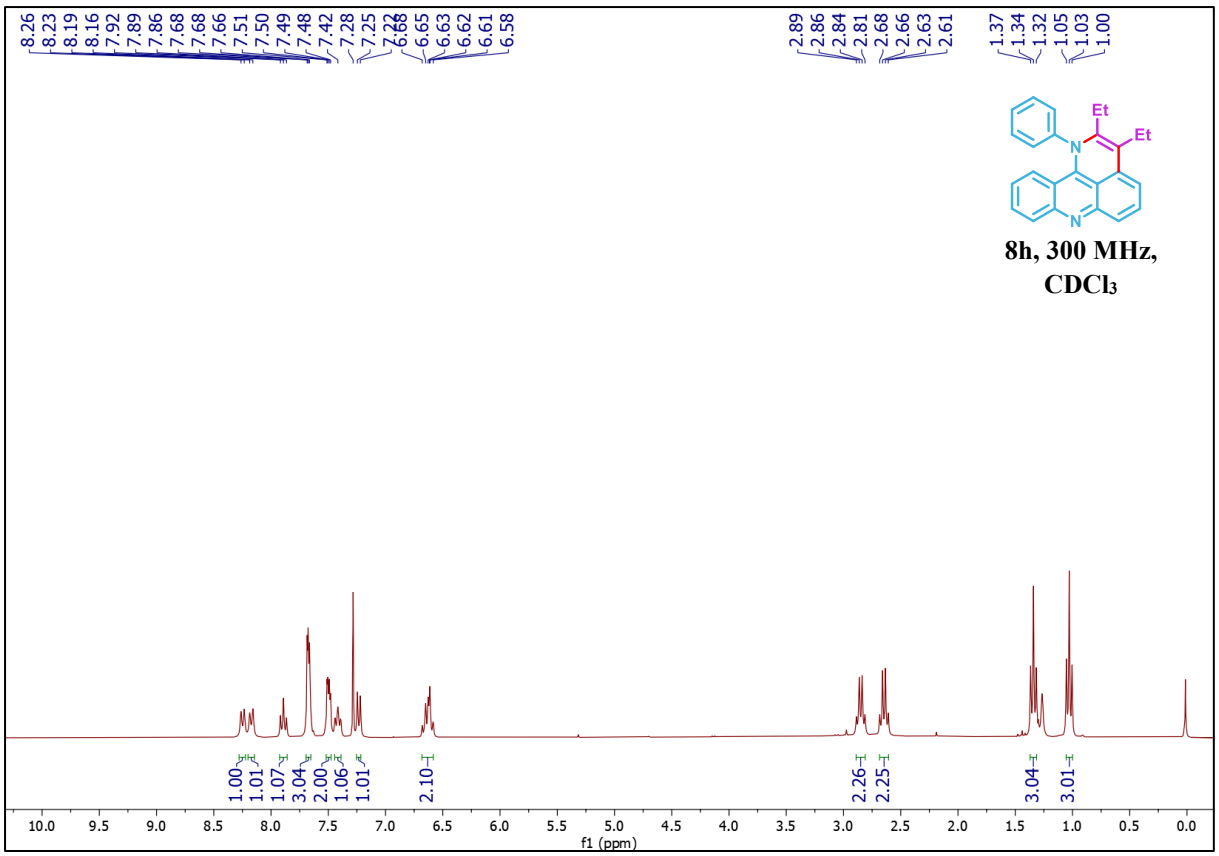

149.05
146.40
144.50
143.11
137.28
136.54
135.31
133.39
132.26
131.83
131.10
130.63
130.29
129.95
129.61
129.33
128.25
128.08
126.33
124.42
119.96
114.16
112.70
77.35
77.04
76.72
21.25
21.22
Cl
N
N
8f, 101 MHz,
CDCl3
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



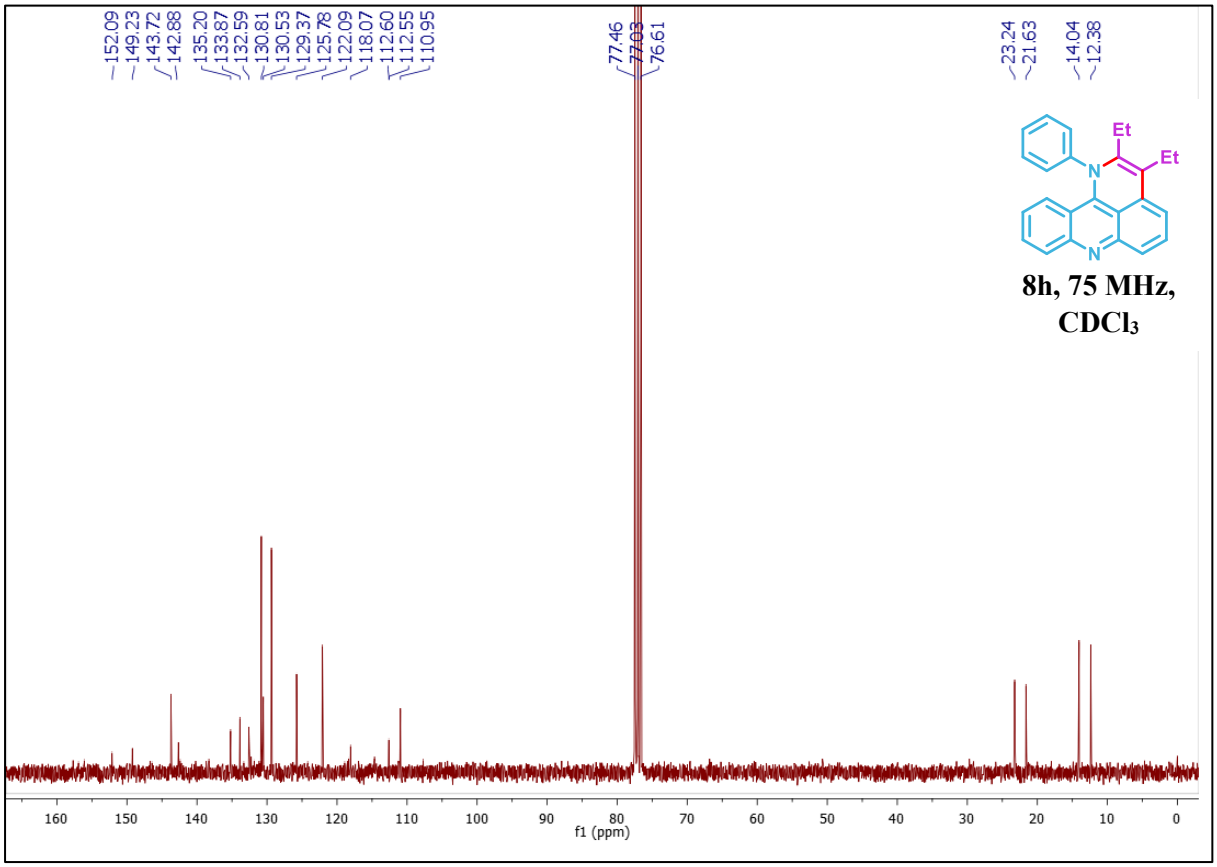
8g, 300 MHz, $CDCl_3$



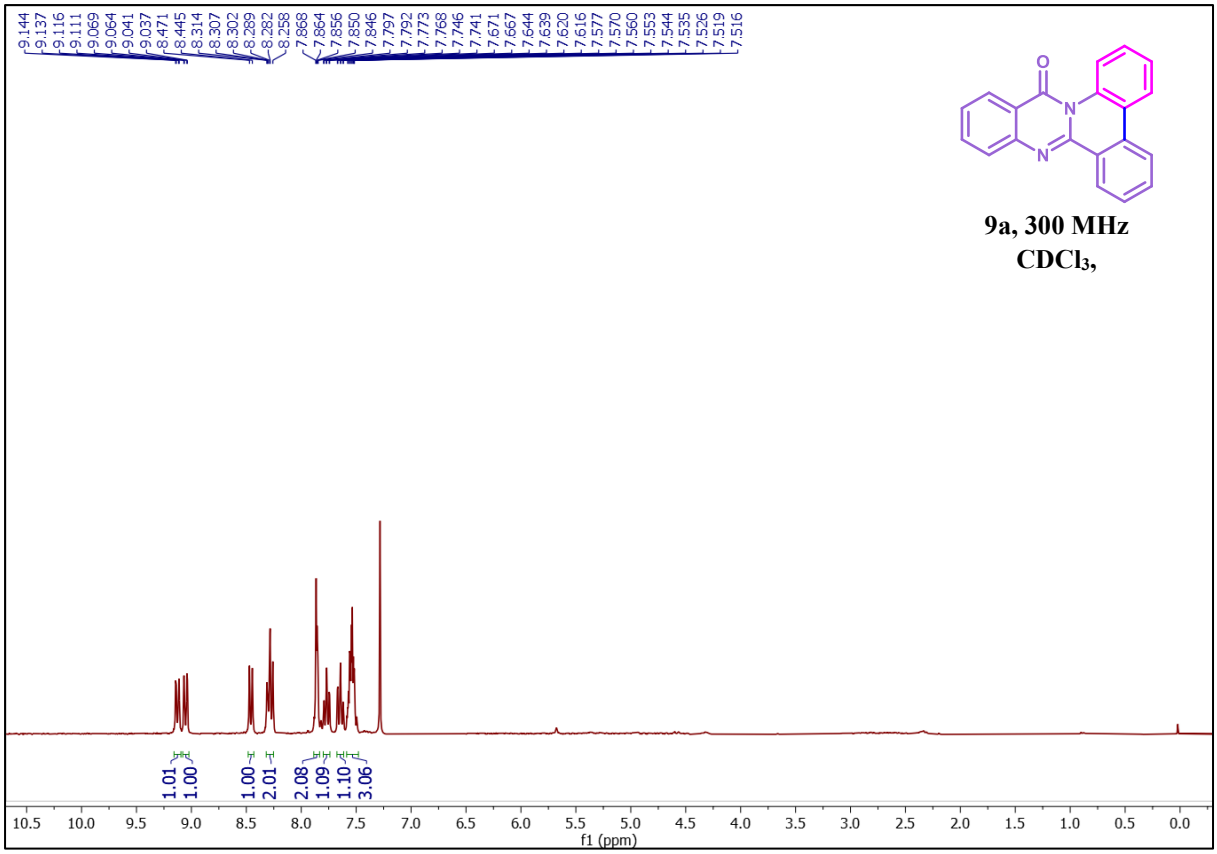
8g, 101 MHz, $CDCl_3$



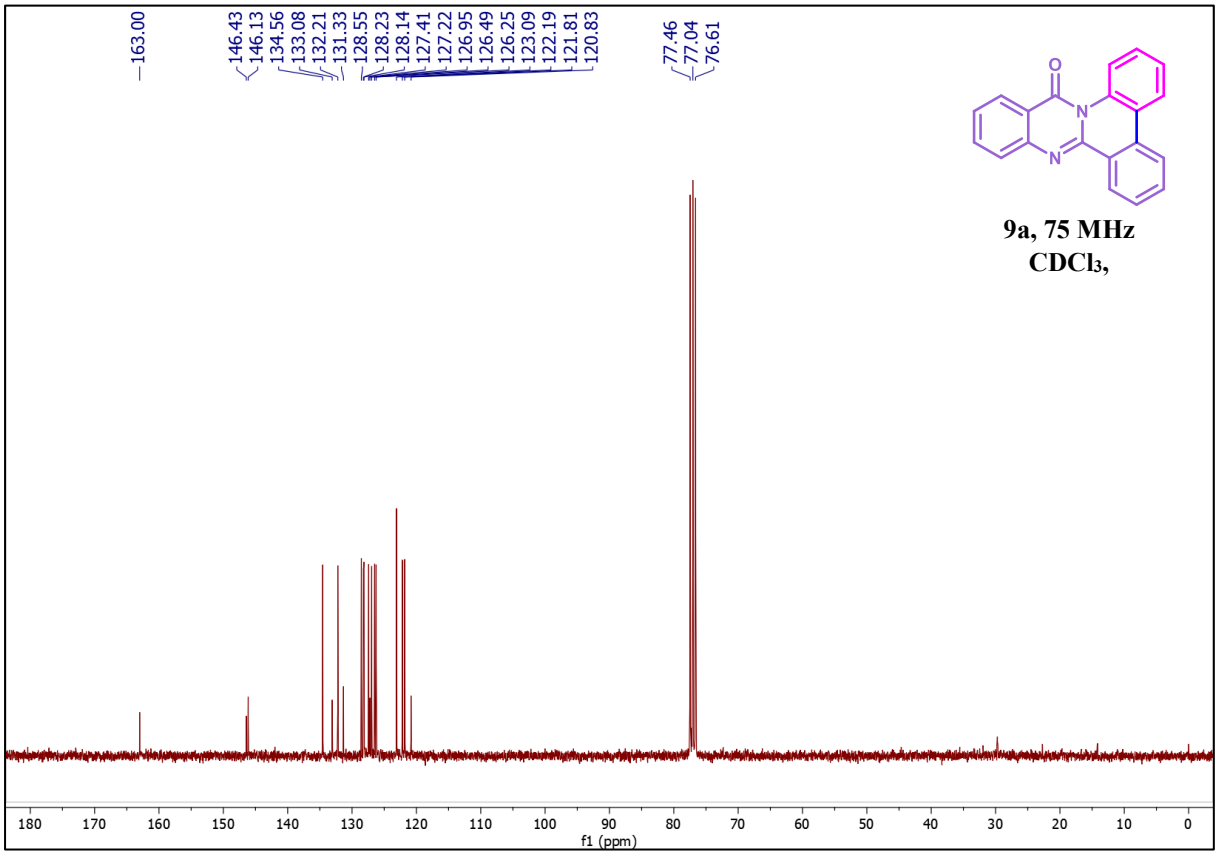
8h, 300 MHz, $CDCl_3$



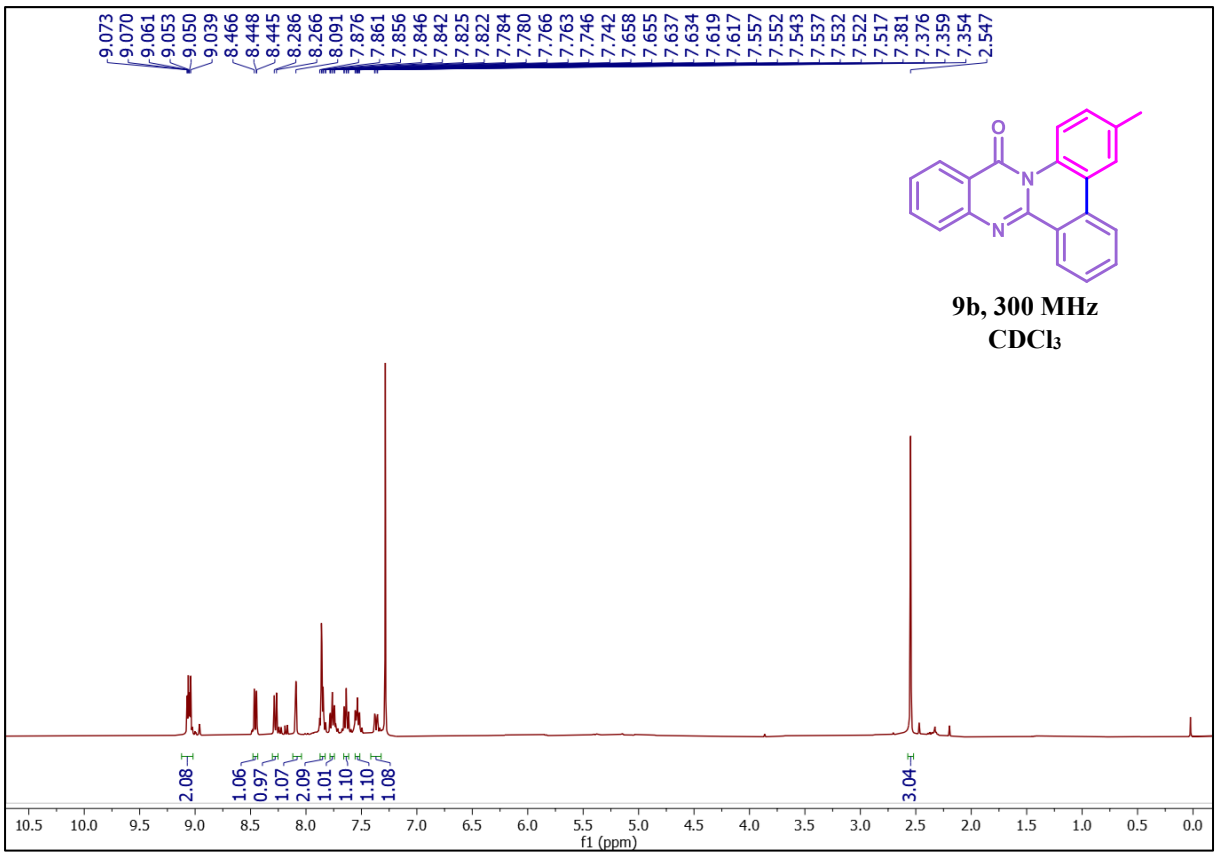
8h, 75 MHz, $CDCl_3$

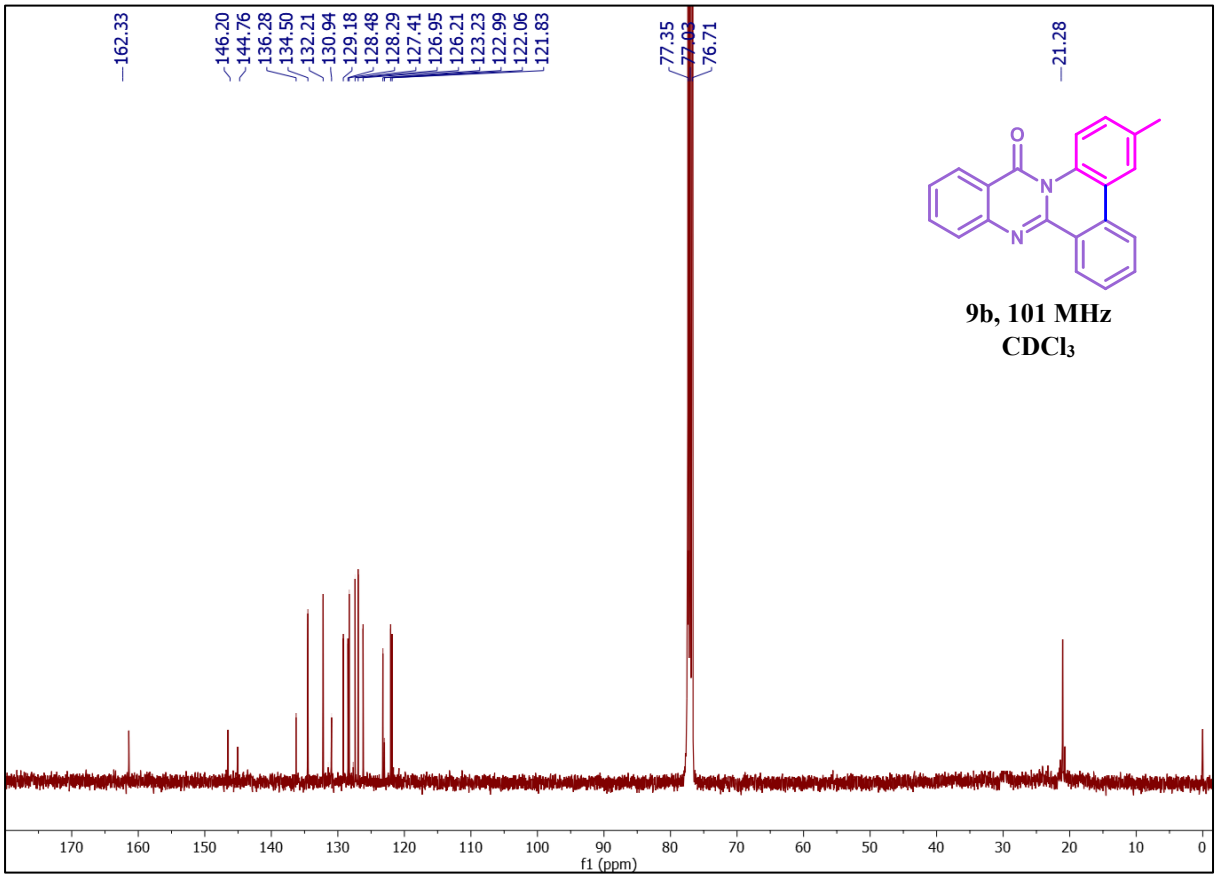


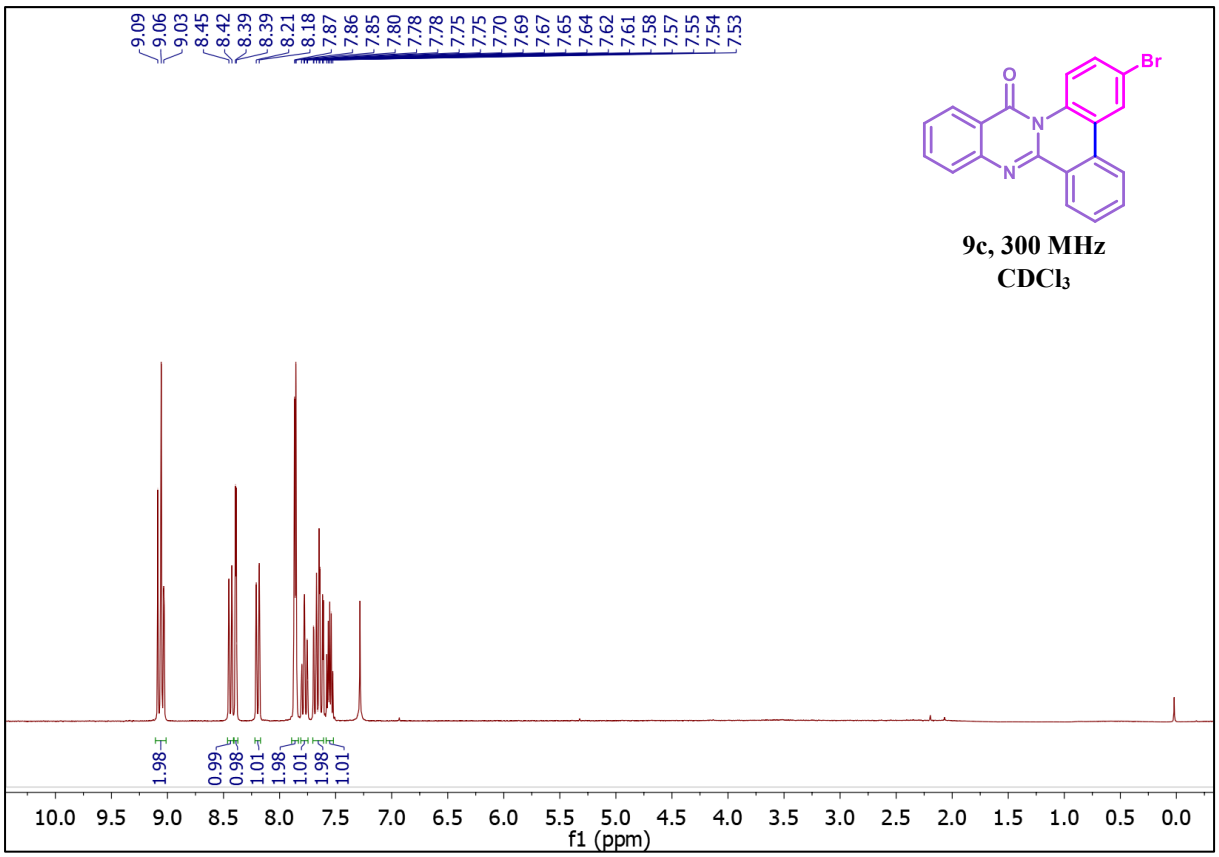
9a, 300 MHz
$CDCl_3$,

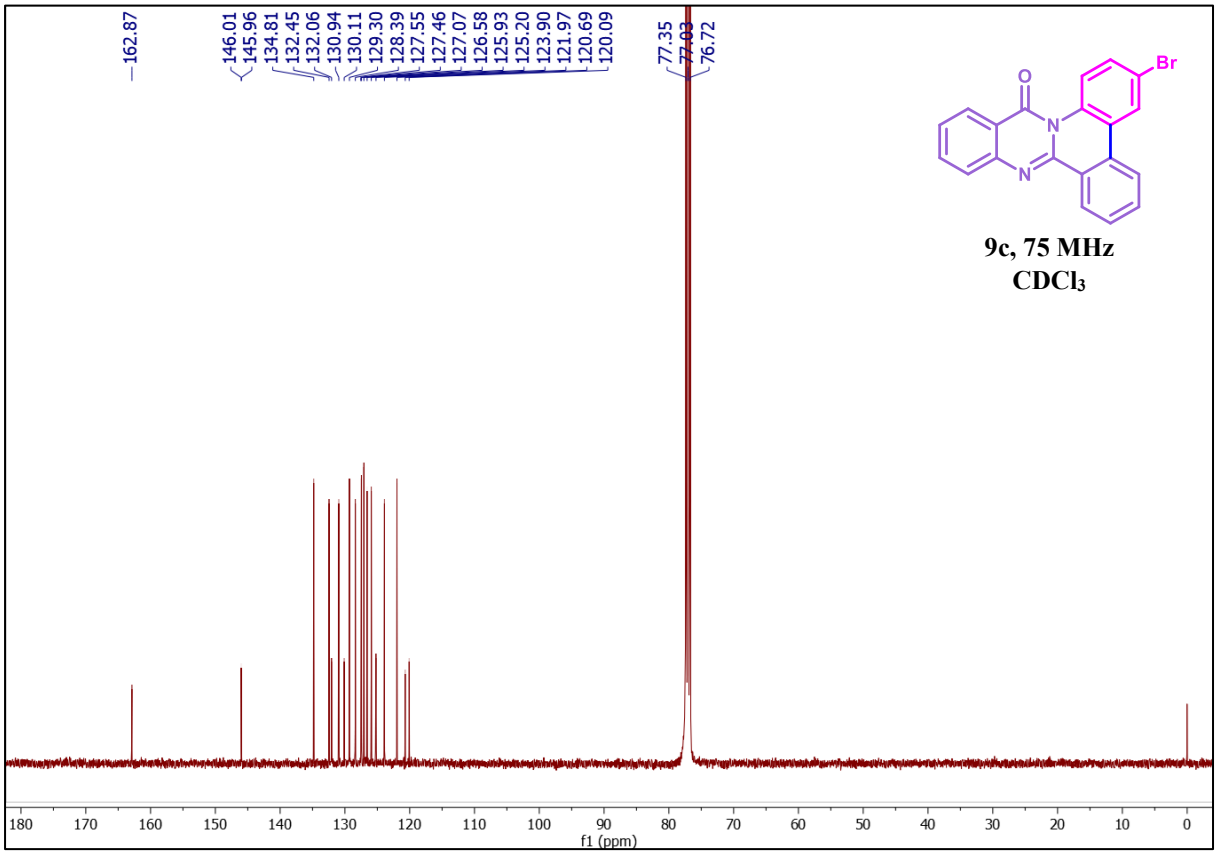


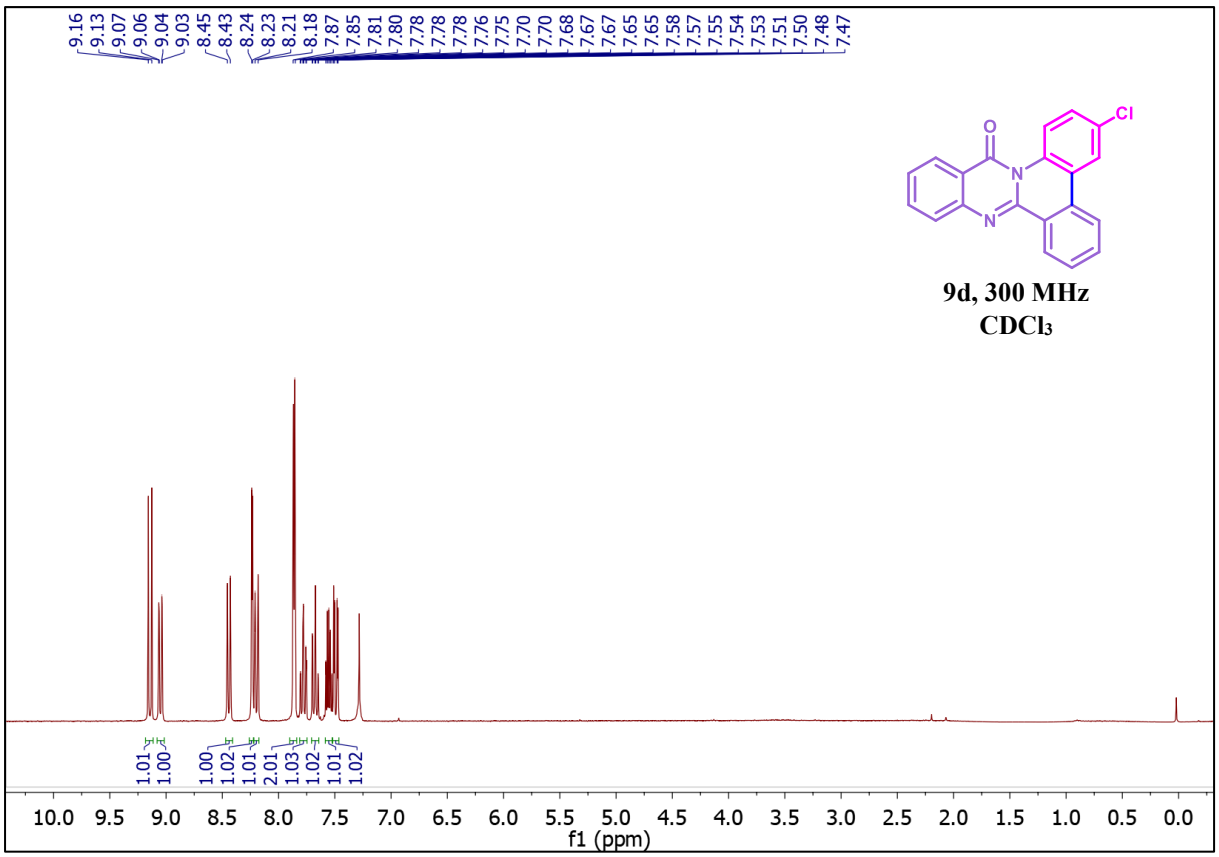
9a, 75 MHz
$CDCl_3$,

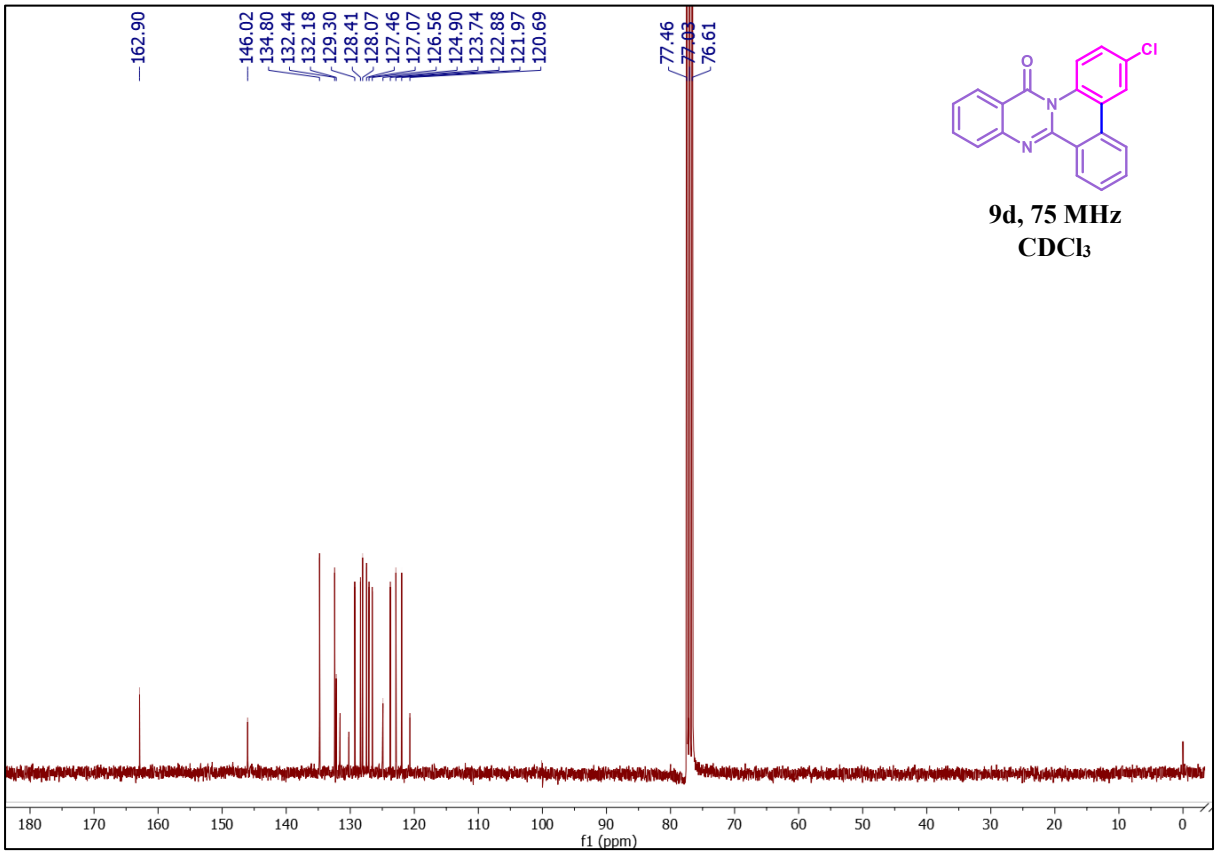

9.073
9.070
9.061
9.053
9.050
9.039
8.466
8.448
8.445
8.286
8.266
8.091
7.876
7.861
7.856
7.846
7.842
7.825
7.822
7.784
7.780
7.766
7.763
7.746
7.742
7.658
7.655
7.637
7.634
7.619
7.617
7.557
7.552
7.543
7.537
7.532
7.522
7.517
7.381
7.376
7.359
7.354
2.547
O
N
N
9b, 300 MHz
CDCl3
2.08
1.06
0.97
1.07
2.09
1.01
1.10
1.10
1.08
3.04
f1 (ppm)

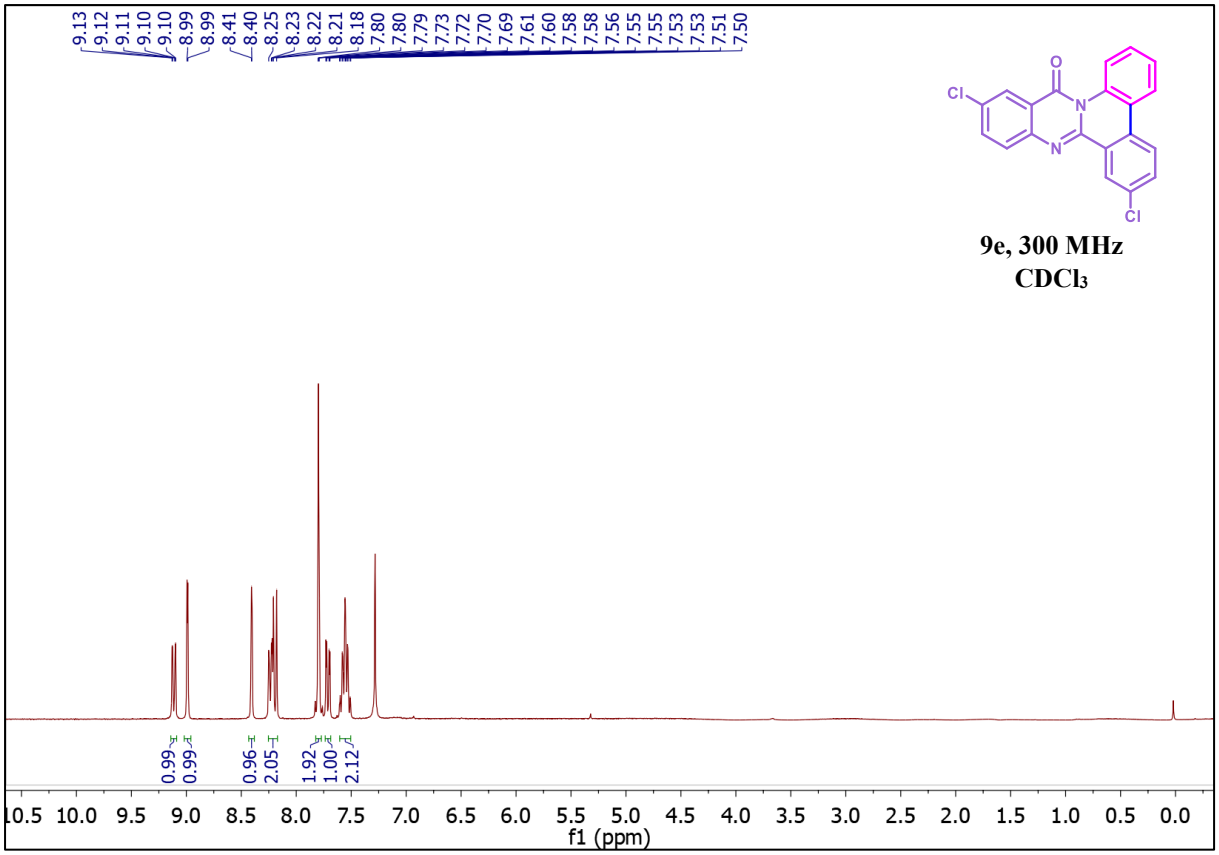

162.33
146.20
144.76
136.28
134.50
132.21
130.94
129.18
128.48
128.29
127.41
126.95
126.21
123.23
122.99
122.06
121.83
77.35
77.03
76.71
21.28
O
N
N
9b, 101 MHz
CDCl3
f1 (ppm)


9.09
9.06
9.03
8.45
8.42
8.39
8.39
8.21
8.18
7.87
7.86
7.85
7.80
7.78
7.78
7.75
7.75
7.70
7.69
7.67
7.65
7.64
7.62
7.61
7.58
7.57
7.55
7.54
7.53
Br
O
N
N
9c, 300 MHz
CDCl3
1.98
0.99
0.98
1.01
1.98
1.01
1.98
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

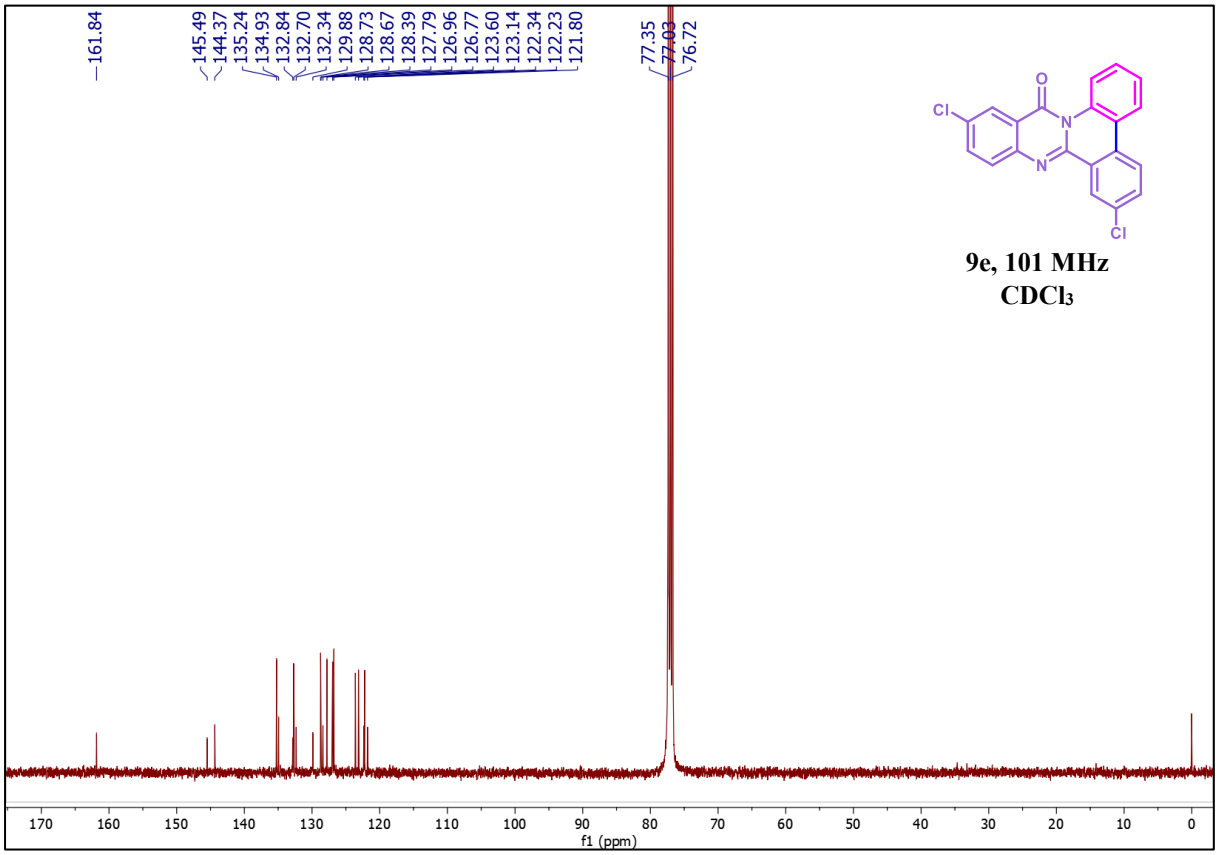

162.87
146.01
145.96
134.81
132.45
132.06
130.94
130.11
129.30
128.39
127.55
127.46
127.07
126.58
125.93
125.20
123.90
121.97
120.69
120.09
77.35
77.03
76.72
Br
O
N
N
9c, 75 MHz
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.16
9.13
9.07
9.06
9.04
9.03
8.45
8.43
8.24
8.23
8.21
8.18
7.87
7.85
7.81
7.80
7.78
7.78
7.78
7.76
7.75
7.70
7.70
7.68
7.67
7.67
7.65
7.65
7.58
7.57
7.55
7.54
7.53
7.51
7.50
7.48
7.47
O
N
N
Cl
9d, 300 MHz
CDCl3
1.01
1.00
1.00
1.02
1.01
2.01
1.03
1.02
1.01
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

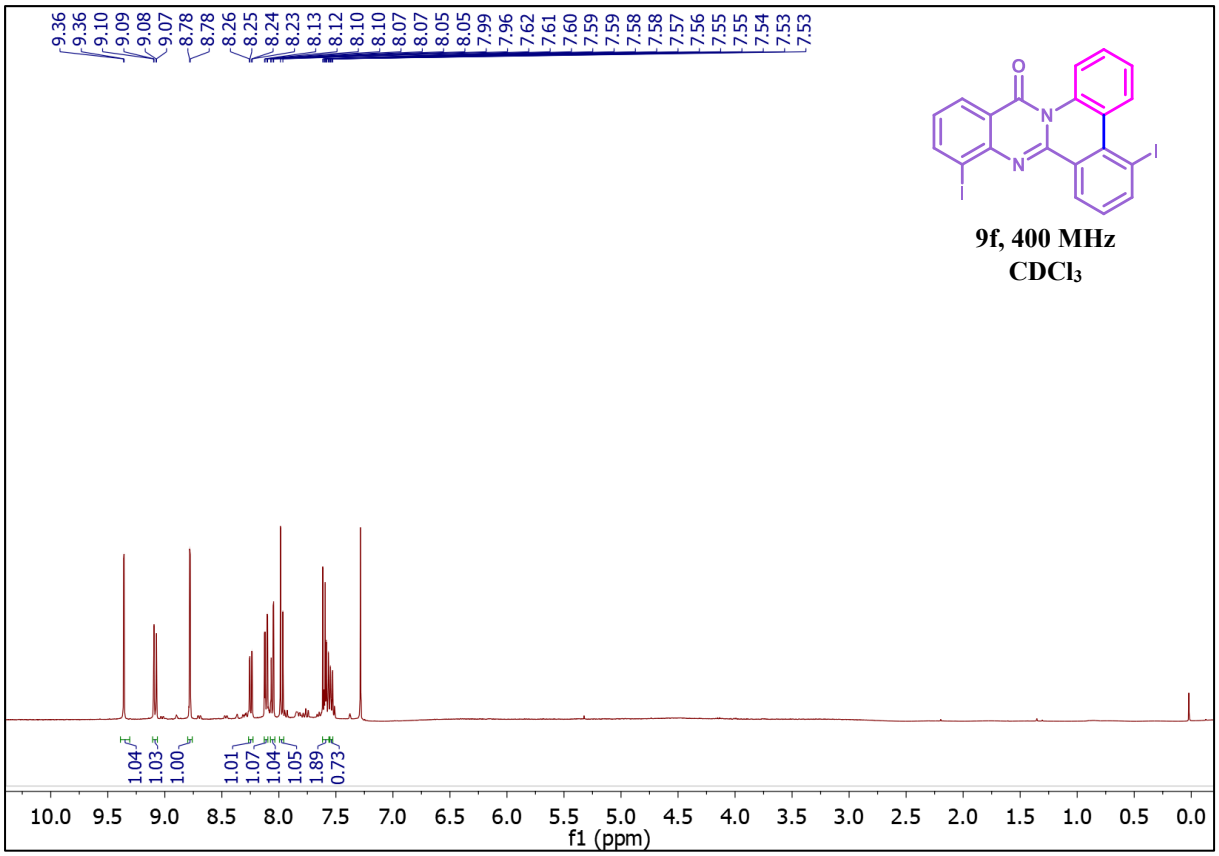

162.90
146.02
134.80
132.44
132.18
129.30
128.41
128.07
127.46
127.07
126.56
124.90
123.74
122.88
121.97
120.69
77.46
77.03
76.61
O
N
N
Cl
9d, 75 MHz
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



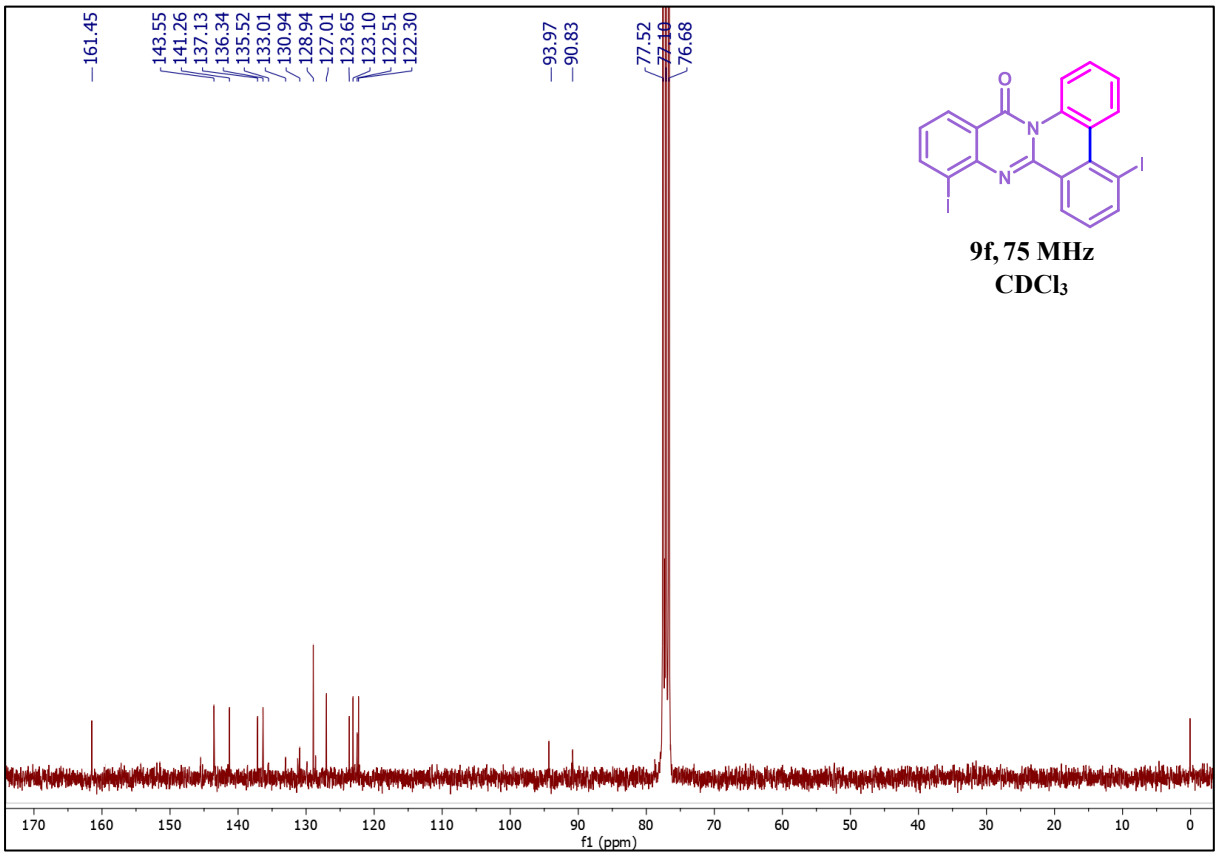
9e, 300 MHz
$CDCl_3$



9e, 101 MHz
$CDCl_3$



9f, 400 MHz
$CDCl_3$



9f, 75 MHz
$CDCl_3$