Donor-acceptor 1,2,4,5-Tetrazines Prepared by Buchwald-Hartwig Cross-Coupling Reaction and Their Photoluminescence Turn-on Property by Inverse Electron Demand Diels-Alder Reaction

Yangyang Qu,[a] Piotr Pander,[b] Oleh Vybornyi,[c] Marharyta Vasylieva,[d] Régis Guillot,[e] Fabien Miomandre,[a] Fernando B. Dias,[b] Peter Skabara,[c] Przemyslaw Data,[d] Gilles Clavier[a] and Pierre Audebert*[a]

[a] PPSM, CNRS, ENS Paris-Saclay, 61 Avenue Président Wilson, 94235 Cachan, France

[b] Physics Department, Durham University, South Road, Durham DH1 3LE, UK

[c] WestCHEM, School of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK

[d] Faculty of Chemistry, Silesian University of Technology, M. Stzody 9, 44-100 Gliwice, Poland

[e] Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO), Université Paris-Sud 11, Université Paris-Saclay, UMR CNRS 8182, Rue du doyen Georges Poitou, 91405 Orsay cedex, France

* E-mail: audebert@ppsm.ens-cachan.fr

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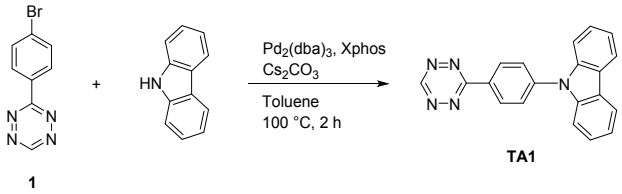
1. Supporting data for optimization of reaction conditions

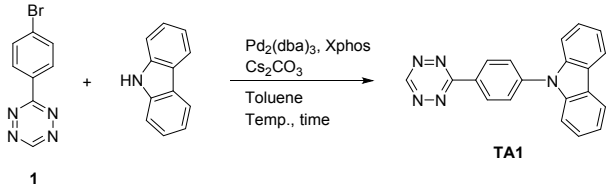
Table S1: Optimization of the palladium catalyst and ligand loading[(a)].



Entry	$Pd_2(dba)_3$ (%)[(b)]	Xphos (%)[(b)]	Yield (%)[(c)]
1	10	0	0
2	10	20	51
3	10	40	71
4	5	20	69
5	3	12	72
6	1	4	40

(a) All reactions were carried out on a 0.2 mmol scale in 10 ml of toluene. (b) Percentage amount relative to the tetrazine precursor **1**. (c) Yields (isolated) based on the tetrazine precursor **1**.

Table S2: Optimization of the reaction temperature and time[(a)].



Entry	Temp. (°C)	Time (h)	Yield (%)[(b)]
1	110	1	62
2	100	2	72
3	90	3	70
4	80	4	59
5	70	6	55

(a) All reactions were carried out on a 0.2 mmol scale in 10 ml of toluene. Temp. = temperature. (b) Yields (isolated) based on the tetrazine precursor **1**.

2. Supporting photophysical and electrochemical data

Table S3: Photophysical and electrochemical properties of **TA1-TA7**.

	λ_{Abs} (nm)[(a)]	E_{ox} vs Fc/Fc^+ (V)[(b)]	E_{red} vs Fc/Fc^+ (V)[(b)]	HOMO (eV)[(c)]	LUMO (eV)[(d)]
TA1	256, 310, 360, 561	0.86	-1.17	-5.96	-3.93
TA2	241, 261, 323, 413, 541	0.29	-1.17	-5.39	-3.93
TA3	276, 370, 561	0.24	-1.24	-5.34	-3.86
TA4	270, 369, 542	0.40	-1.21	-5.50	-3.89
TA5	240, 303, 546	0.27	-1.22	-5.37	-3.88
TA6	257, 302, 547	0.21	-1.2	-5.31	-3.90
TA7	291, 547	0.45	-1.14	-5.55	-3.96

(a) Absorption maxima measured in DCM (1×10^{-5} M) at room temperature. (b) *Onset* oxidation potential recorded in DCM / 0.1 M Bu_4NPF_6 supporting electrolyte at room temperature by cyclic voltammetry. (c) Highest occupied molecular orbital energy estimated from the *onset* oxidation potential, $E_{HOMO} = -(E_{ox} + 5.1)$. (d) Lowest unoccupied molecular orbital energy estimated from the *onset* reduction potential, $E_{LUMO} = -(E_{red} + 5.1)$.

3. Crystallographic data of TA2, TA3, DA2 and DA3

Table S4: Crystallographic data and structure refinement details.

Compound	**TA2**	**TA3**	**DA2**	**DA3**
CCDC	1937098	1937101	1937099	1937100
Empirical Formula	$C_{20}H_{13}N_5O$	$C_{20}H_{13}N_5S$	$C_{28}H_{25}N_3O$	$C_{28}H_{25}N_3S$
M_r	339.35	355.41	419.51	435.57
Crystal color	dark red	red	colorless	colorless
Crystal size, mm^3	0.13 x 0.11 x 0.035	0.14 x 0.09 x 0.025	0.12 x 0.10 x 0.08	0.13 x 0.06 x 0.0015
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	*P* -1	$P\,2_1/c$	*C 2/c*	$P\,2_1/n$
a, Å	7.8191(7)	9.7253(6)	29.091(9)	14.502(5)
b, Å	8.2110(8)	7.5932(5)	8.713(3)	11.158(4)
c, Å	13.3817(13)	21.9133(11)	17.546(6)	15.629(6)
α, °	80.524(3)	90	90	90
β, °	73.188(3)	92.088(2)	102.525(12)	116.616(9)
γ, °	67.372(3)	90	90	90

Cell volume, $Å^3$	757.73(13)	1617.14(17)	4342(2)	2261.0(14)
Z ; Z'	2 ; 1	4 ; 1	8 ; 1	4 ; 1
T, K	100(1)	100(1)	100(1)	250(1)
Radiation type ; wavelength Å	MoKα ; 0.71073	MoKα ; 0.71073	MoKα ; 0.71073	MoKα ; 0.71073
F_{000}	352	736	1776	920
μ, mm^{-1}	0.097	0.215	0.079	0.162
θ range, °	2.692 - 31.116	2.751 - 31.568	2.378 - 31.044	2.336 - 30.840
Reflection collected	49 942	76 057	78 219	158 600
Reflections unique	4 861	5 414	6 909	7 032
R_{int}	0.0465	0.0869	0.1216	0.2082
GOF	1.083	1.050	1.013	0.897
Refl. obs. (I>2σ(I))	4 185	4 134	4 353	2 732
Parameters	235	235	344	289
wR_2 (all data)	0.1234	0.0975	0.1305	0.1180
R value (I>2σ(I))	0.0423	0.0391	0.0588	0.0534
Largest diff. peak and hole (e-.$Å^{-3}$)	0.555 ; -0.261	0.383 ; -0.466	0.282 ; -0.271	0.479 ; -0.290

4. Supporting photophysical and electrochemical spectra

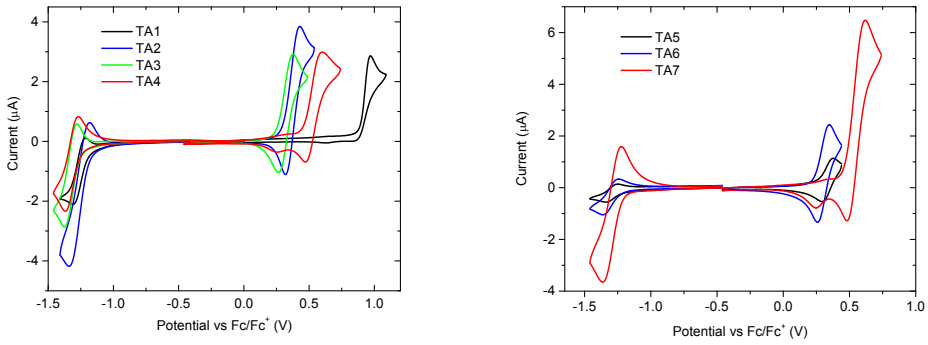


Figure S1: Cyclic voltammetry of **TA1-TA7** in DCM / 0.1 M Bu_4NPF_6 supporting electrolyte at room temperature.

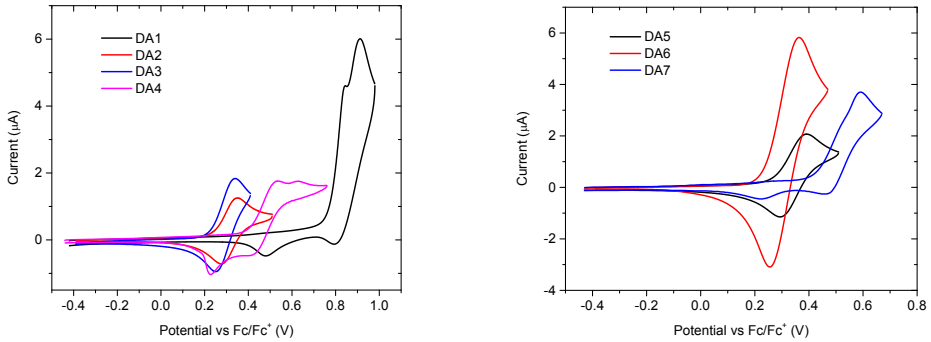


Figure S2: Cyclic voltammetry of **DA1-DA7** in DCM / 0.1 M Bu_4NPF_6 supporting electrolyte at room temperature.

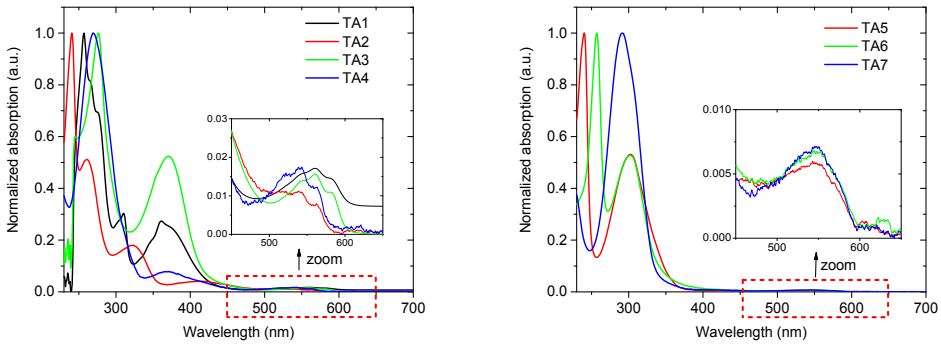


Figure S3: Absorption spectra of **TA1-TA7** in DCM at room temperature.

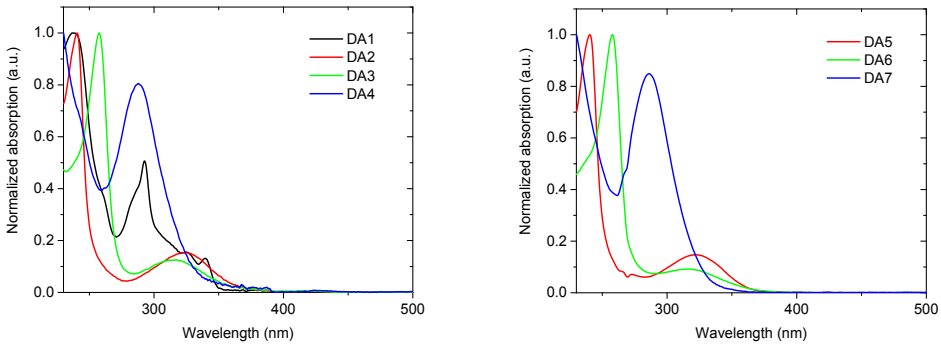


Figure S4: Absorption spectra of **DA1-DA7** in DCM at room temperature.

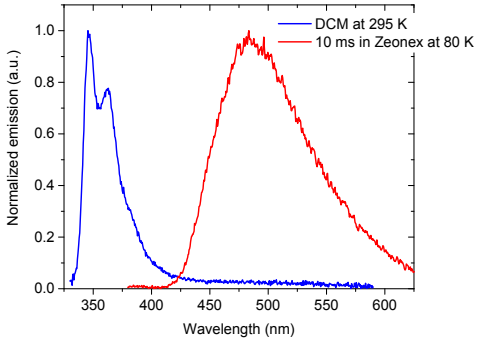


Figure S5: Normalized fluorescence spectrum of **DA1** in DCM at room temperature (blue) and normalized phosphorescence spectrum of **DA1** in Zeonex at 80 K (red).

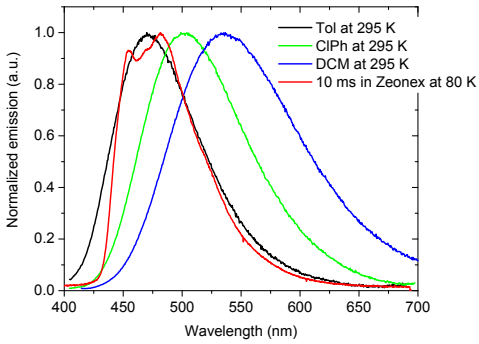


Figure S6: Normalized fluorescence spectra of **DA2** in toluene (black), chlorobenzene (green) and DCM (blue) at room temperature and normalized phosphorescence spectrum of **DA2** in Zeonex at 80 K (red).

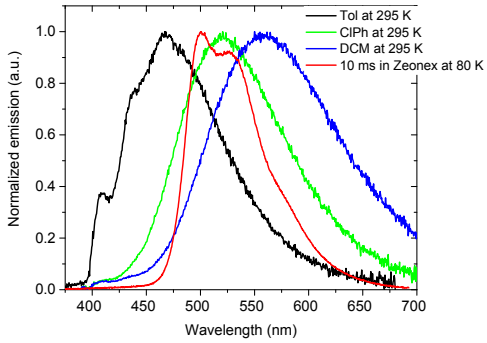


Figure S7: Normalized fluorescence spectra of **DA3** in toluene (black), chlorobenzene (green) and DCM (blue) at room temperature and normalized phosphorescence spectrum of **DA3** in Zeonex at 80 K (red).

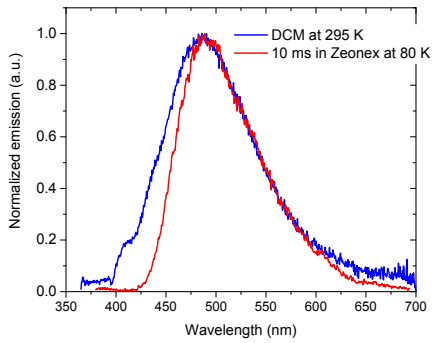


Figure S8: Normalized fluorescence spectrum of **DA4** in DCM at room temperature (blue) and normalized phosphorescence spectrum of **DA4** in Zeonex at 80 K (red).

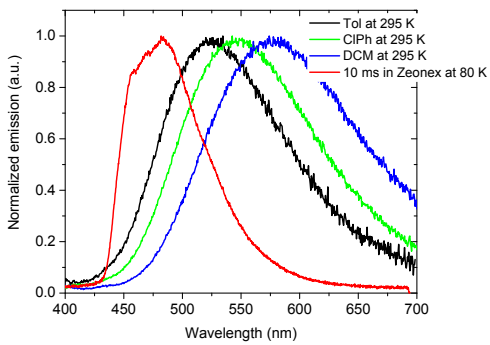


Figure S9: Normalized fluorescence spectra of **DA5** in toluene (black), chlorobenzene (green) and DCM (blue) at room temperature and normalized phosphorescence spectrum of **DA5** in Zeonex at 80 K (red).

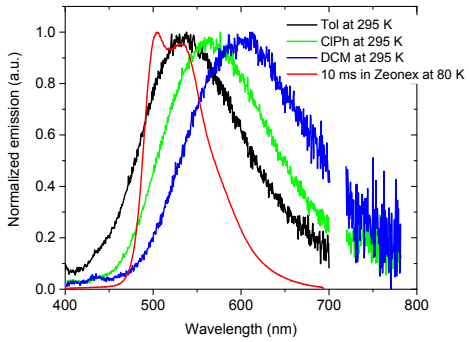


Figure S10: Normalized fluorescence spectra of **DA6** in toluene (black), chlorobenzene (green) and DCM (blue) at room temperature and normalized phosphorescence spectrum of **DA6** in Zeonex at 80 K (red).

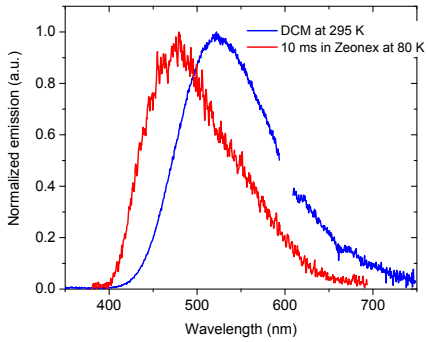
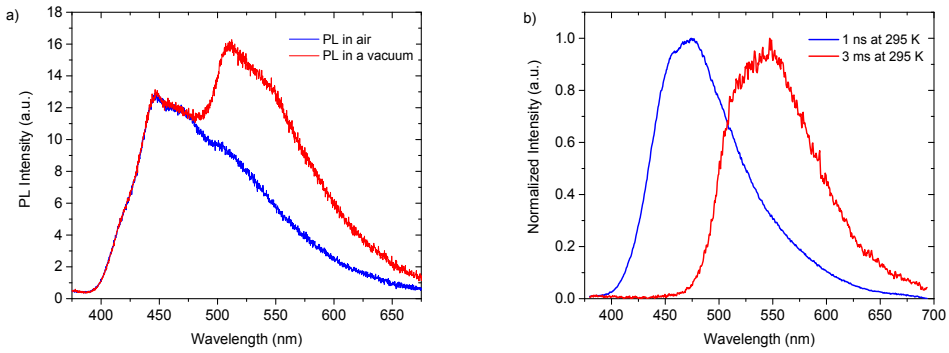


Figure S11: Normalized fluorescence spectra of **DA7** in DCM at room temperature (blue) and normalized phosphorescence spectrum of **DA7** in Zeonex at 80 K (red).



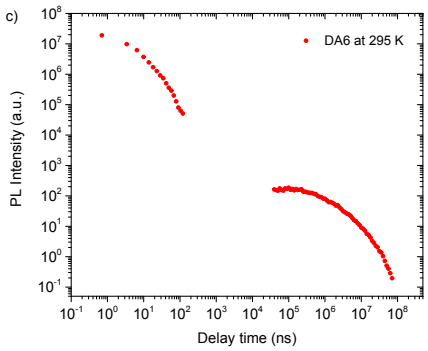


Figure S12: (a) Photoluminescence spectra of **DA6** in Zeonex 1% (w/w) in a vacuum (red) and air-equilibrated (blue) condition at room temperature, the ratio of the RTP component to the fluorescence one was determined to be 0.48. (b) Time-resolved spectra of **DA6** in Zeonex 1% (w/w) at room temperature in a vacuum: prompt fluorescence (blue), phosphorescence (red), the singlet and triplet energy levels were estimated to be 3.06 eV and 2.61 eV respectively. (c) PL decays of **DA6** in Zeonex 1% (w/w) at room temperature in a vacuum.

5. ORTEP drawings of TA2, TA3, DA2 and DA3

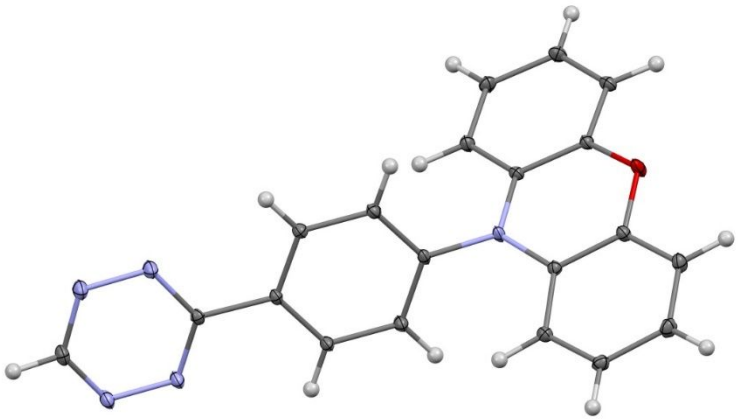


Figure S13. An ORTEP drawing of compound **TA2** at 100K. Thermal ellipsoids are shown at the 30% level. The single crystal sample of **TA2** was grown from slow evaporation of petroleum ether/CH_2Cl_2 (3:1) mixture.

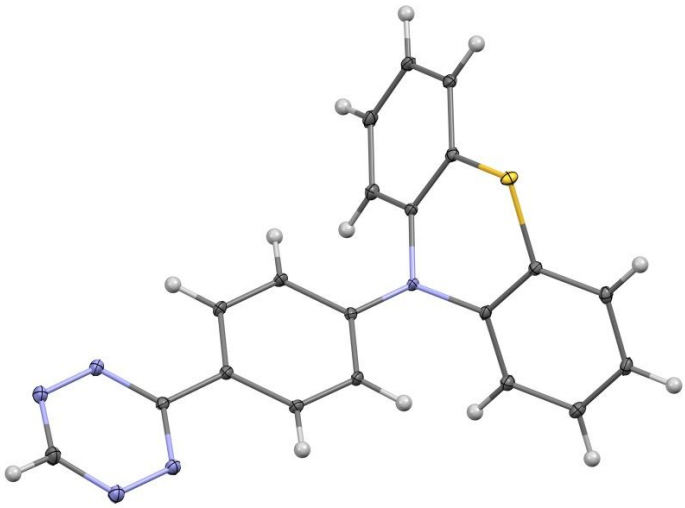


Figure S14. An ORTEP drawing of compound **TA3** at 100K. Thermal ellipsoids are shown at the 30% level. The single crystal sample of **TA3** was grown from slow evaporation of petroleum ether/CH_2Cl_2 (3:1) mixture.

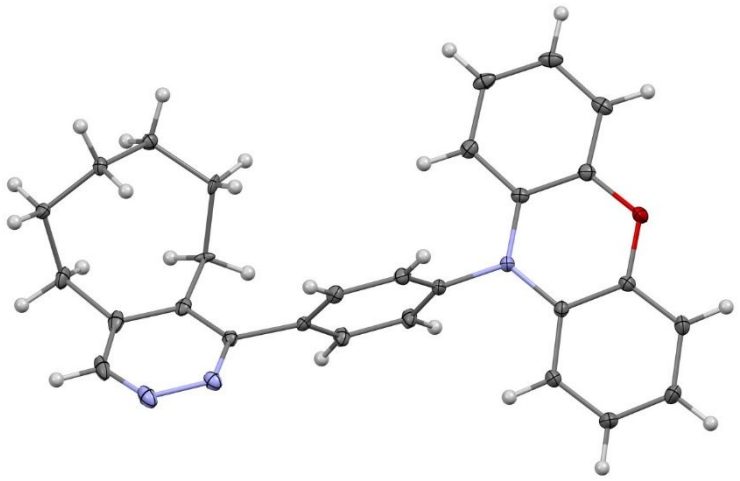


Figure 15. An ORTEP drawing of compound **DA2** at 100K. Only one position of the disordered is shown. Thermal ellipsoids are shown at the 30% level. The single crystal sample of **DA2** was grown from slow evaporation of petroleum ether/EtOAc (2:3) mixture.

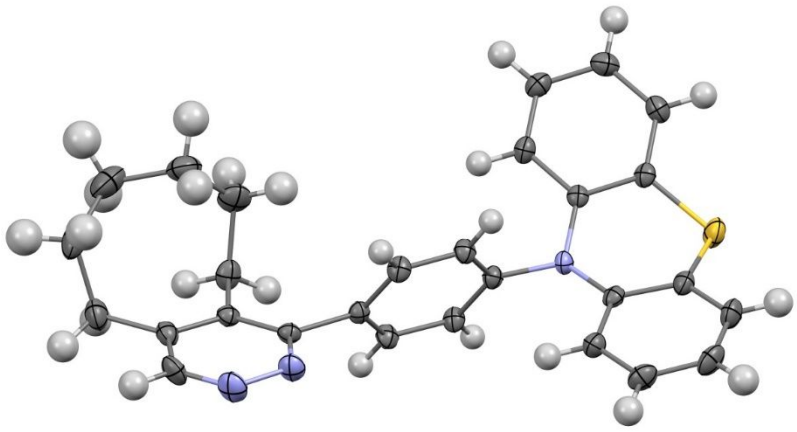
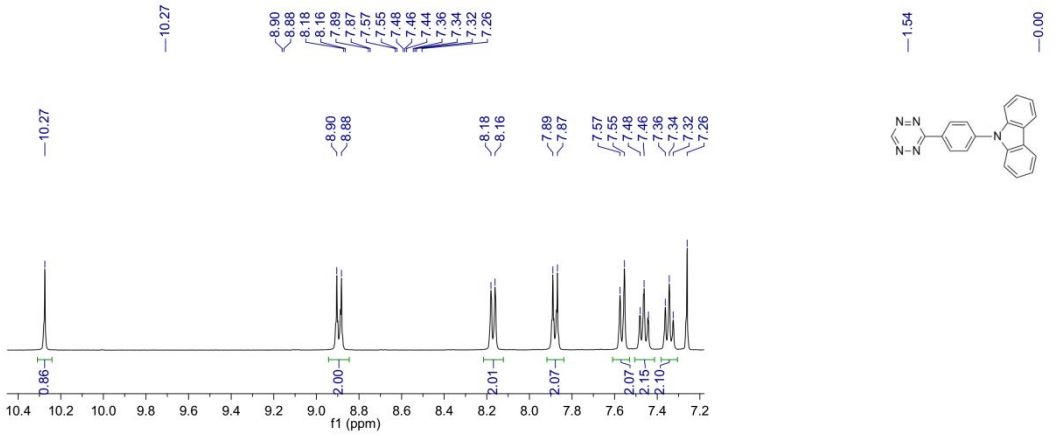
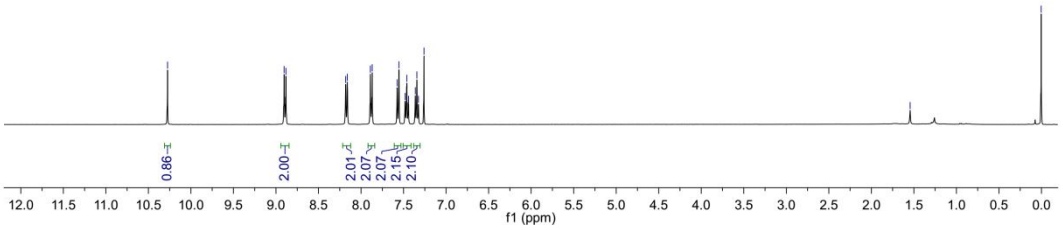
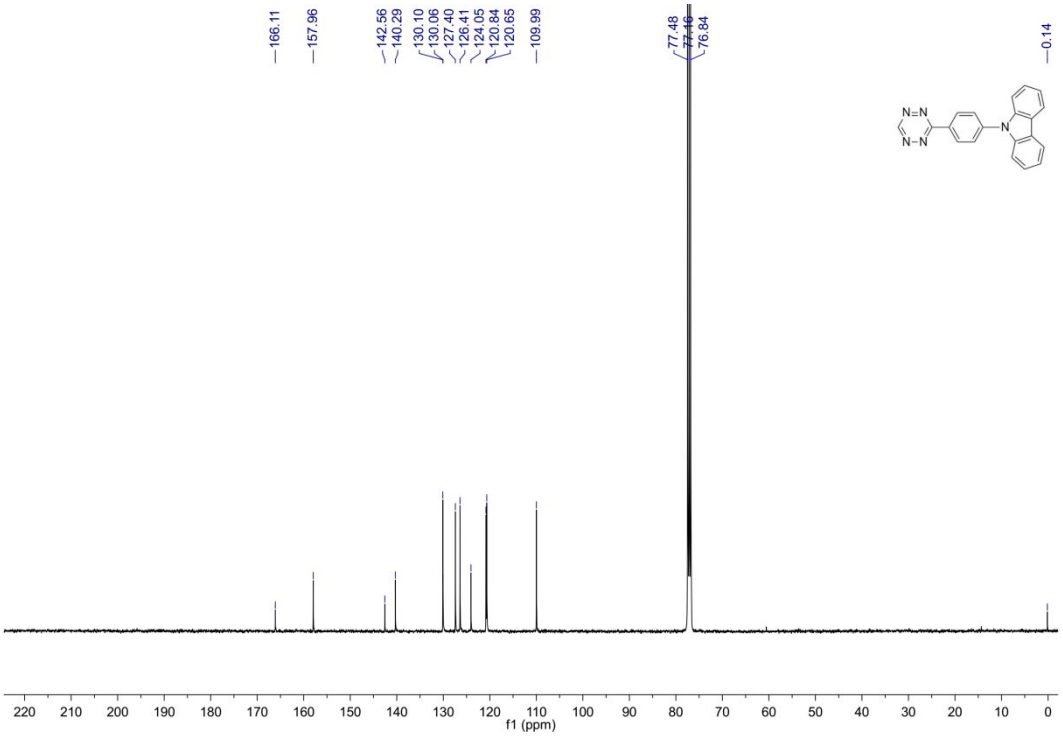


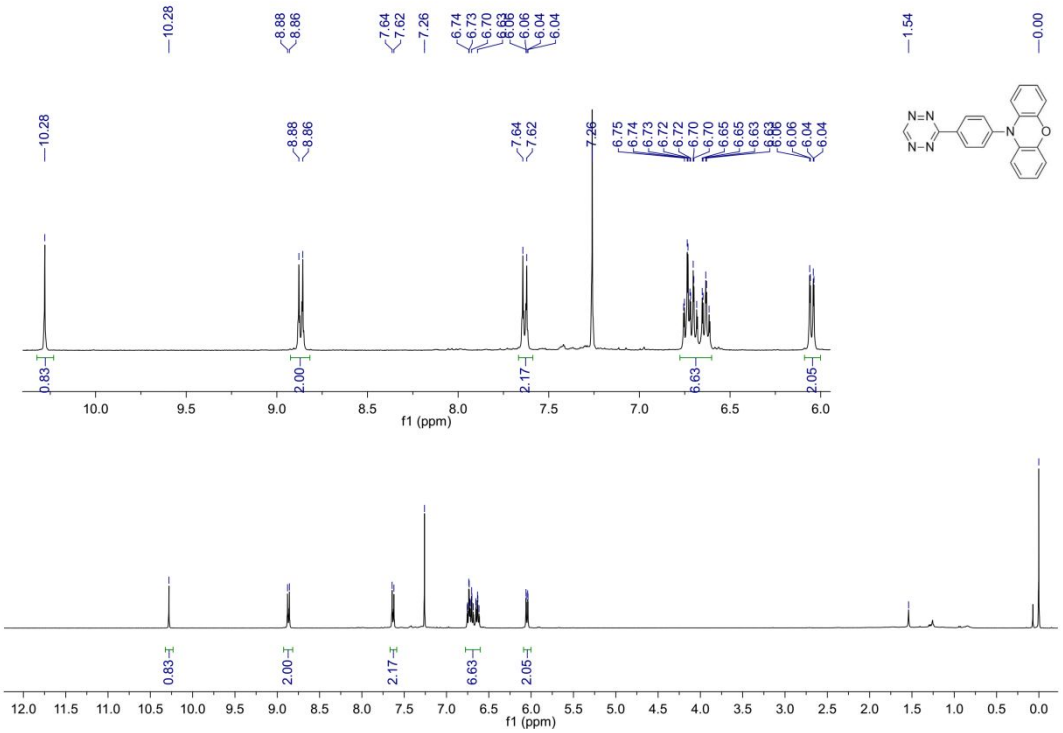
Figure 16. An ORTEP drawing of compound **DA3** at 250K. Thermal ellipsoids are shown at the 30% level. The single crystal sample of **DA3** was grown from slow evaporation of petroleum ether/EtOAc (2:3) mixture.

6. ^{1}H and ^{13}C NMR spectra of compounds





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7.62
7.26
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6.74
6.73
6.72
6.70
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6.06
6.04
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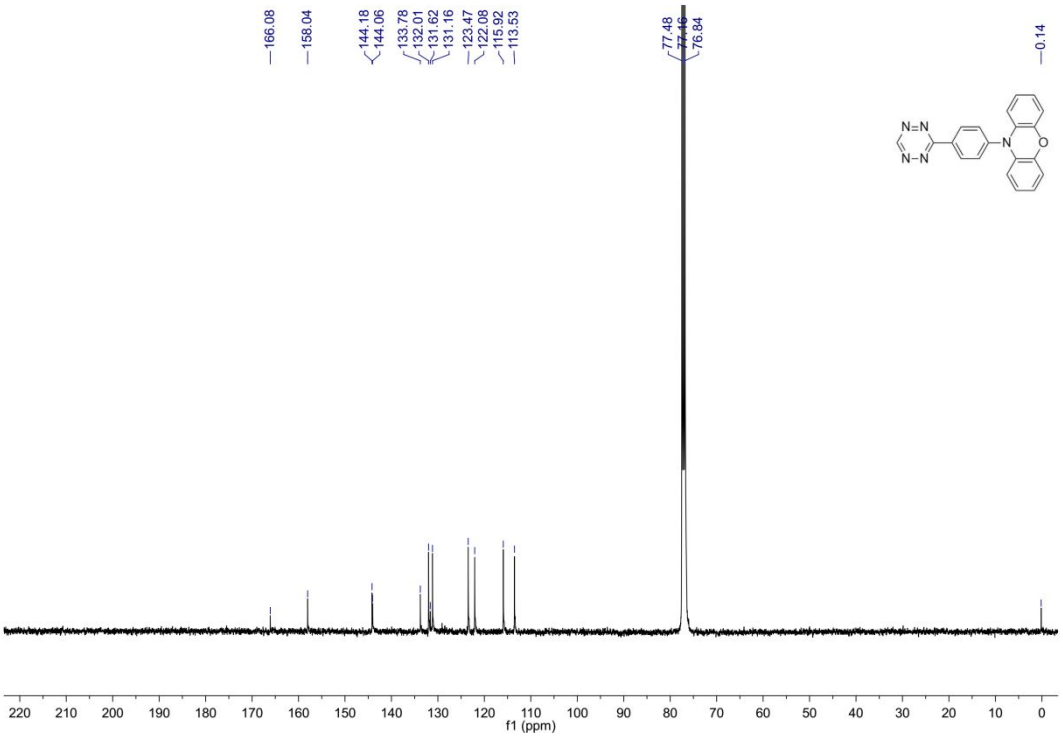
2.17
6.63
2.05
f1 (ppm)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144.06
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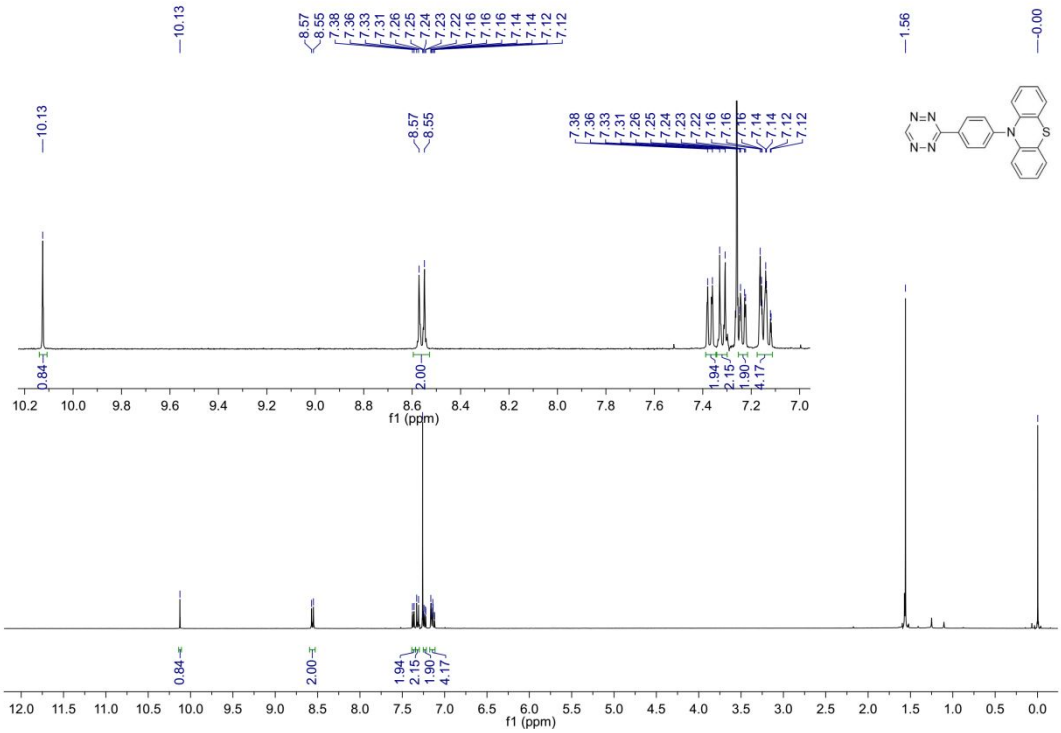
76.84
0.14
f1 (ppm)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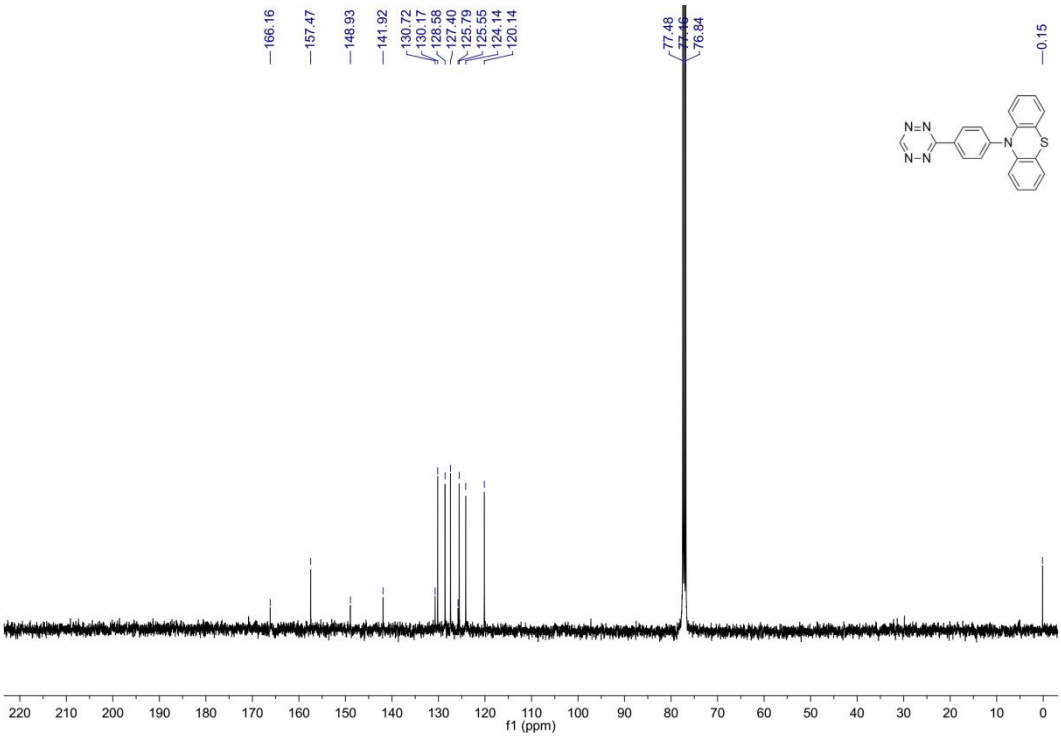
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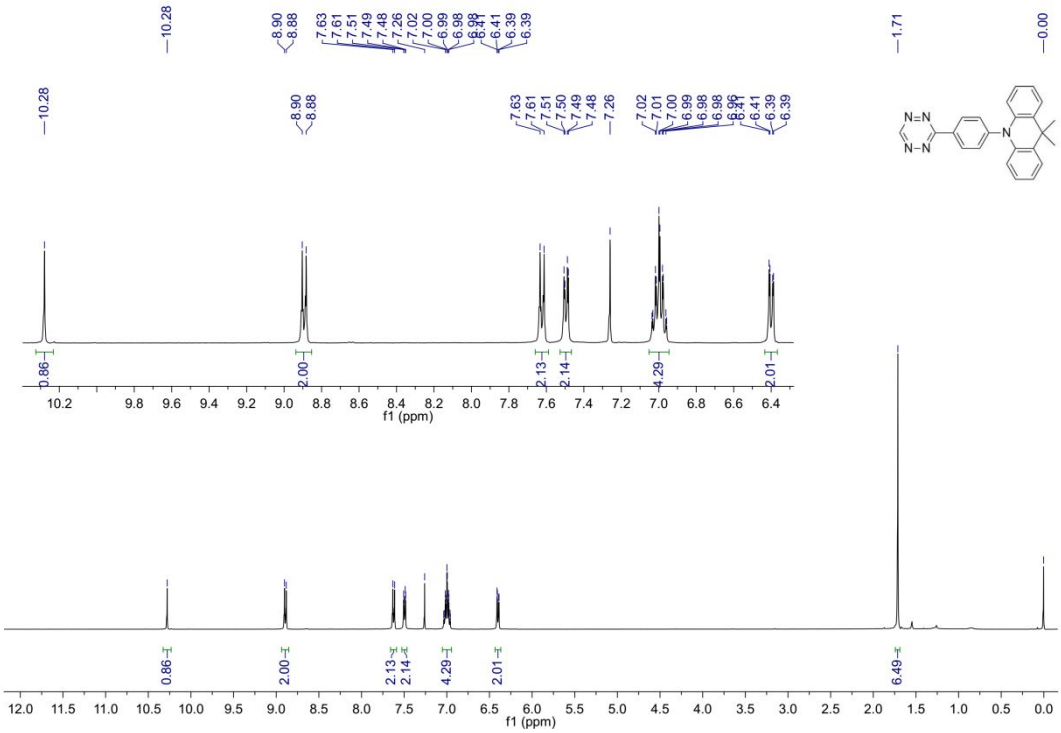
0.15
f1 (ppm)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6.99
6.98
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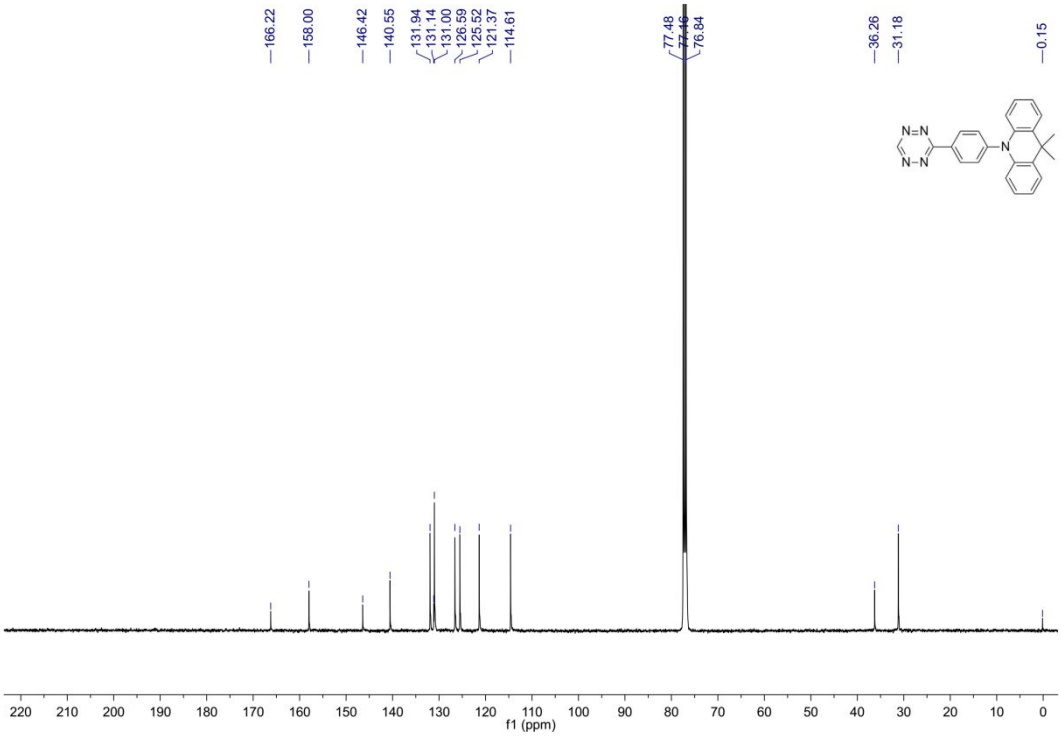
6.49
f1 (ppm)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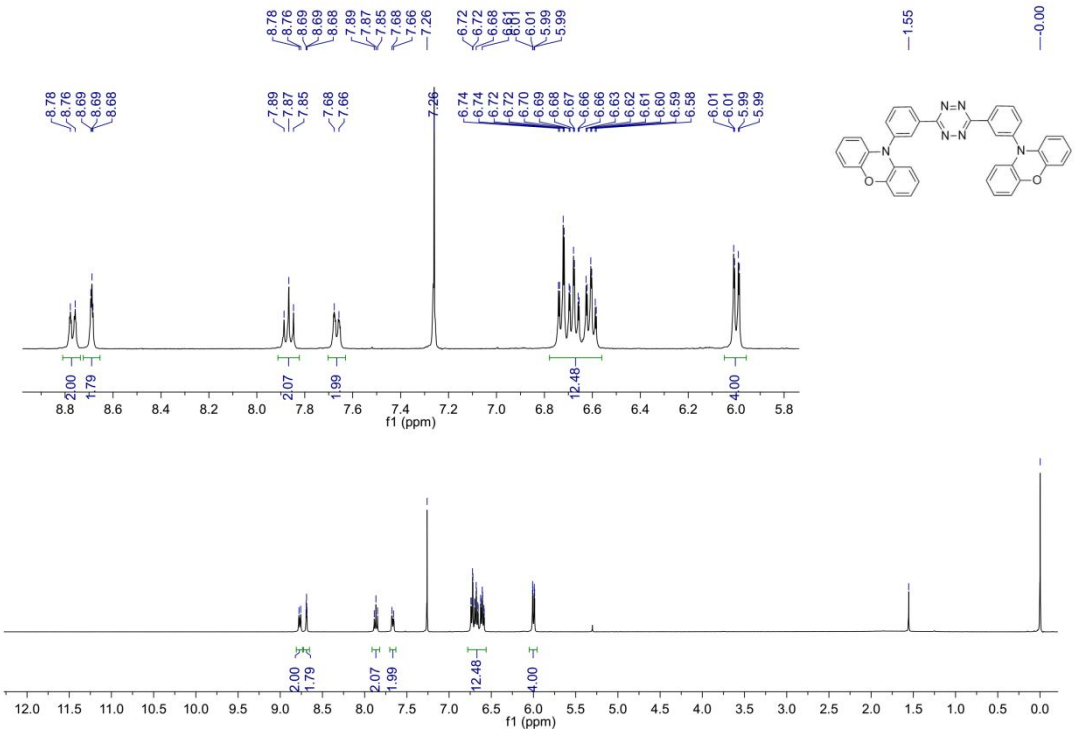
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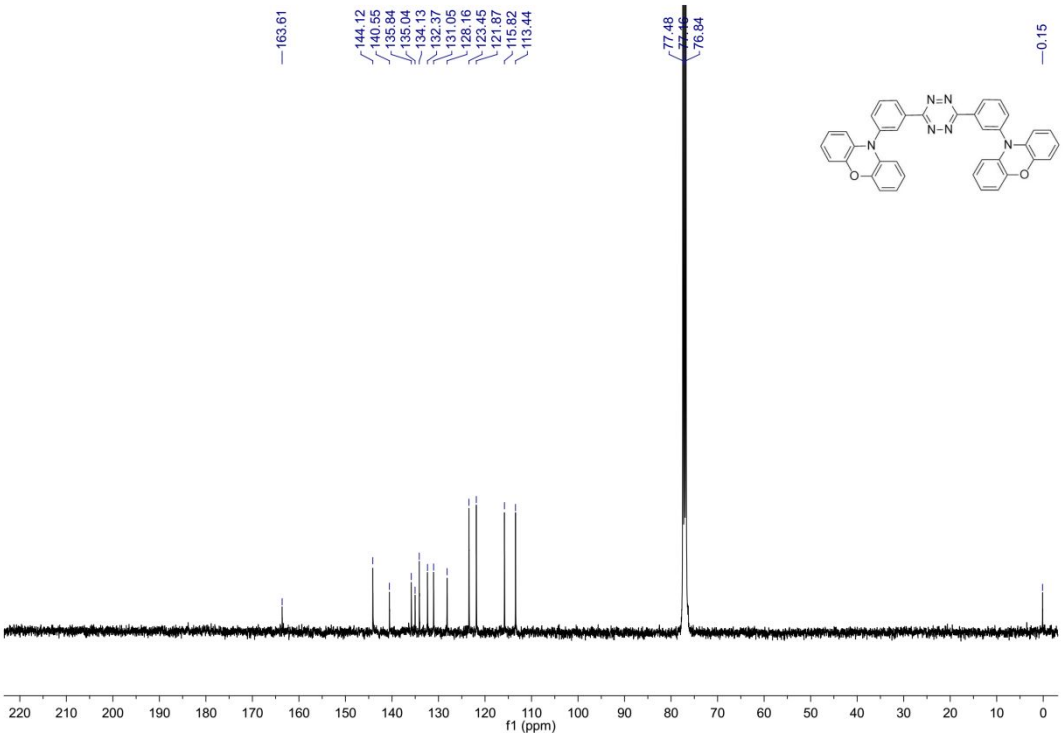
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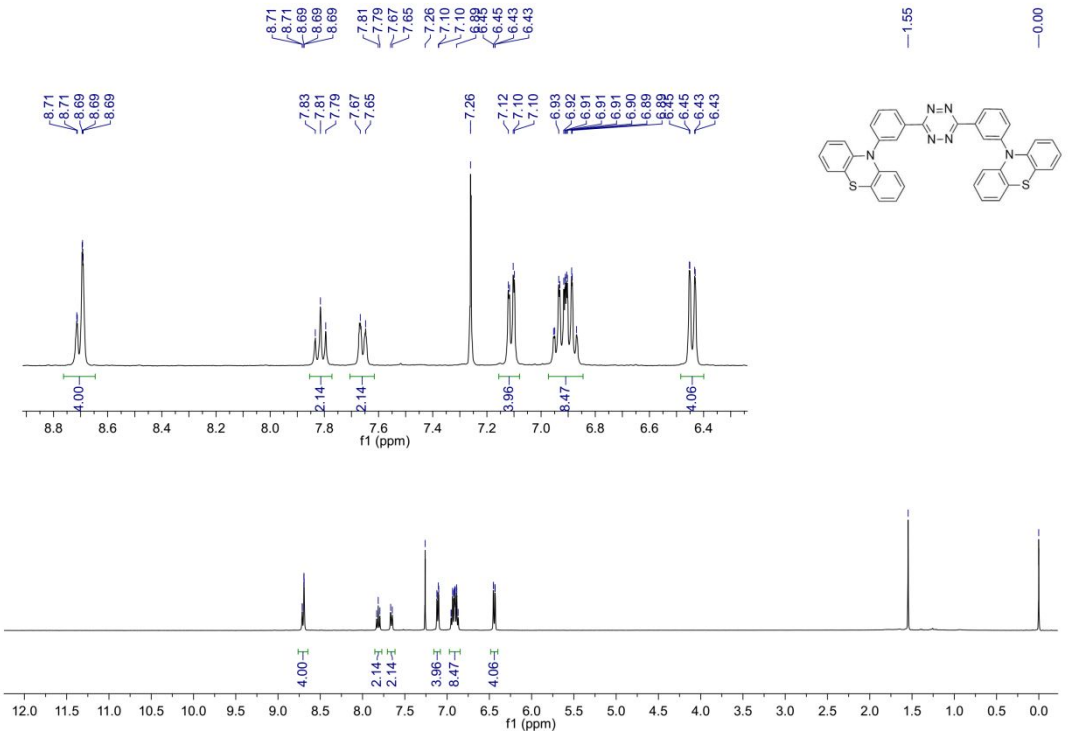
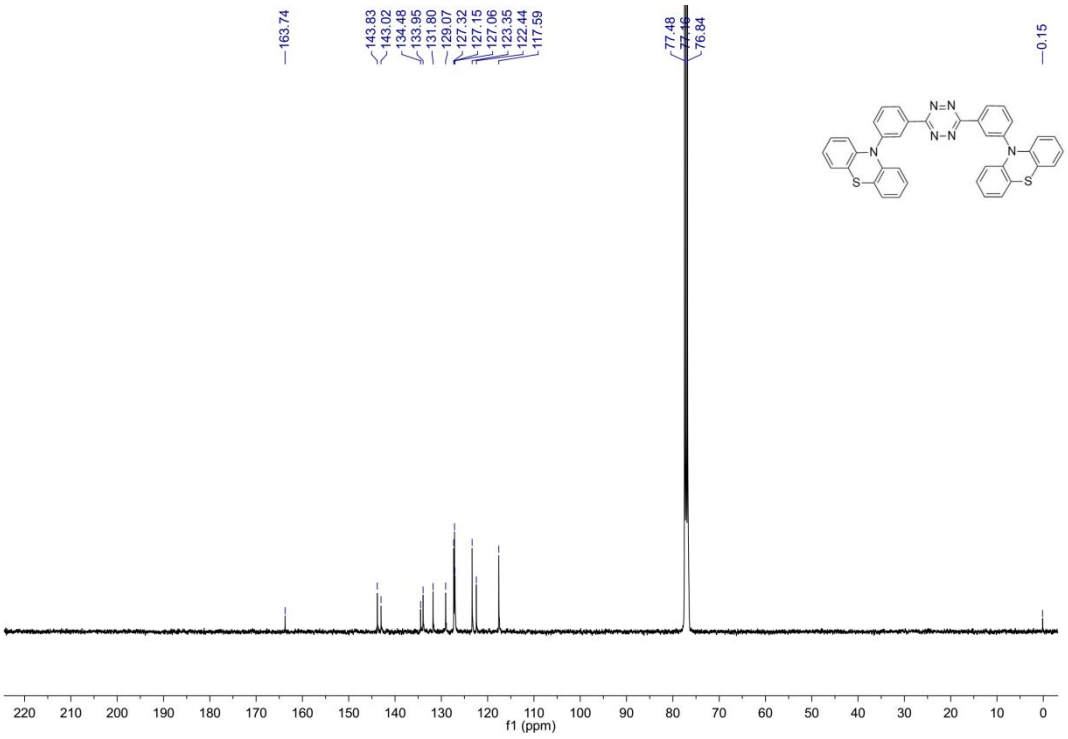
77.48
77.16
76.84
0.15
f1 (ppm)


8.71
8.71
8.69
8.69
8.69
7.83
7.81
7.79
7.67
7.65
7.26
7.12
7.10
7.10
6.93
6.92
6.91
6.91
6.90
6.89
6.45
6.43
6.43
1.55
0.00
4.00
2.14
2.14
3.96
8.47
4.06
f1 (ppm)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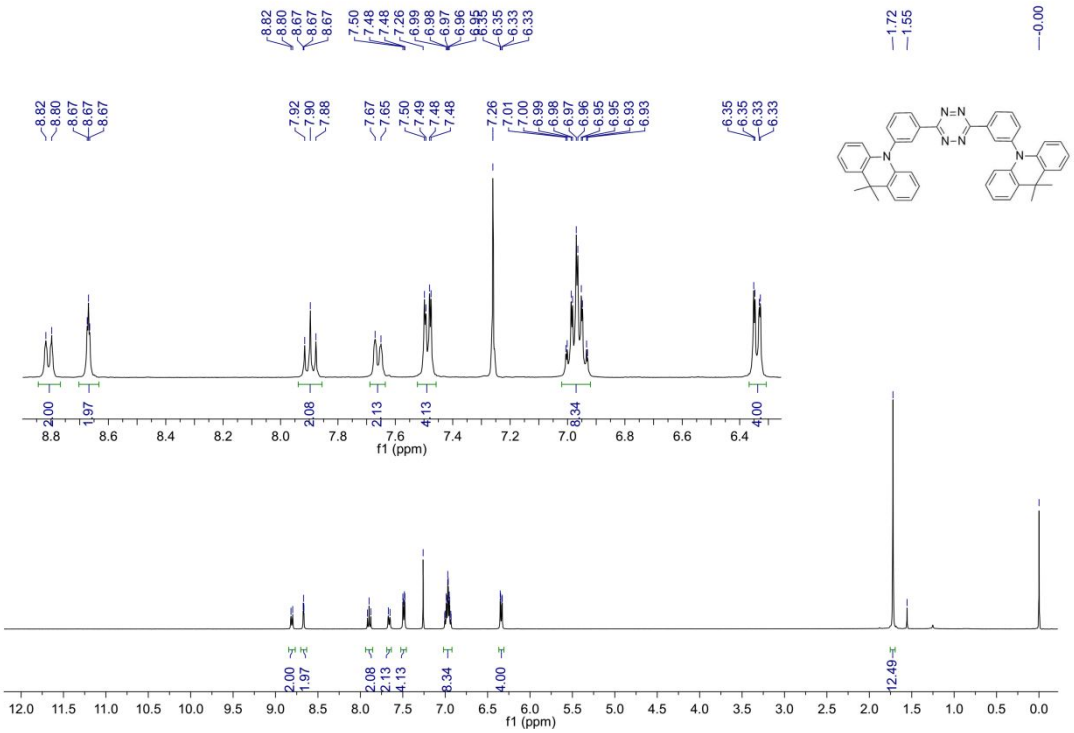
143.02
134.48
133.95
131.80
129.07
127.32
127.15
127.06
123.35
122.44
117.59
77.48
76.84
0.15
f1 (ppm)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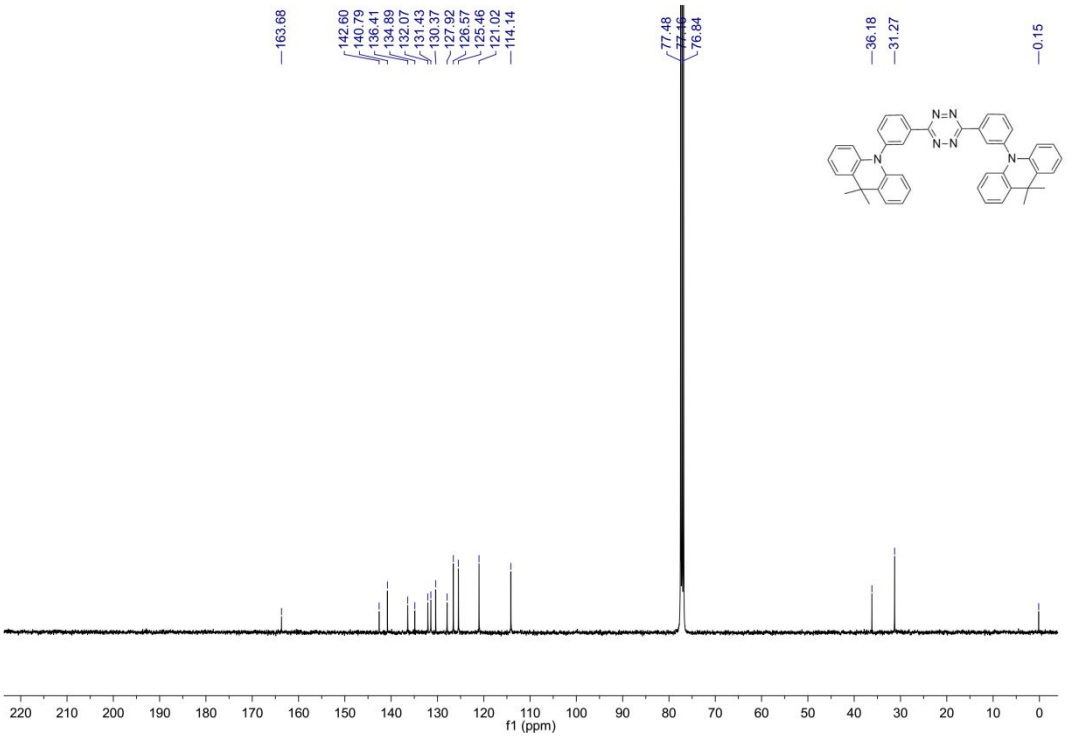
8.80
8.67
8.67
8.67
7.50
7.48
7.48
7.26
6.99
6.98
6.97
6.96
6.95
6.35
6.33
6.33
1.72
1.55
0.00
7.92
7.90
7.88
7.67
7.65
7.50
7.49
7.48
7.48
7.26
7.01
7.00
6.99
6.98
6.97
6.96
6.95
6.95
6.93
6.93
6.35
6.35
6.33
6.33
N=N
N-N
N
N
2.00
1.97
2.08
2.13
4.13
8.34
4.00
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
f1 (ppm)
2.00
1.97
2.08
2.13
4.13
8.34
4.00
12.49
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)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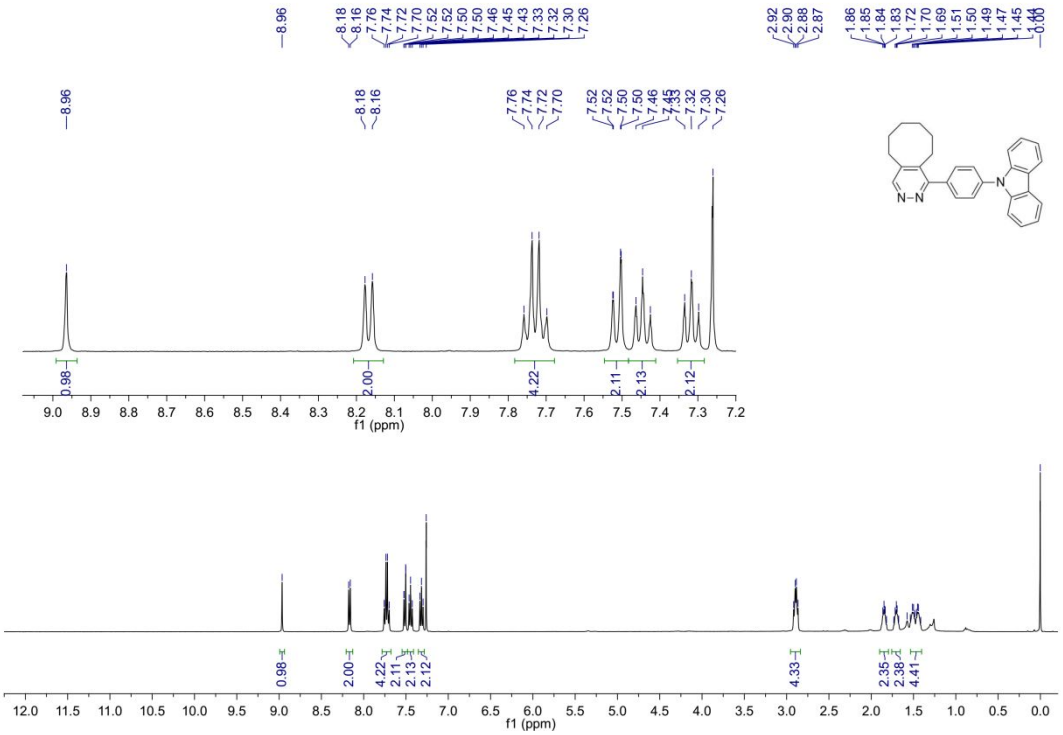
134.89
132.07
131.43
130.37
127.92
126.57
125.46
121.02
114.14
77.48
77.16
76.84
36.18
31.27
0.15
N=N
N-N
N
N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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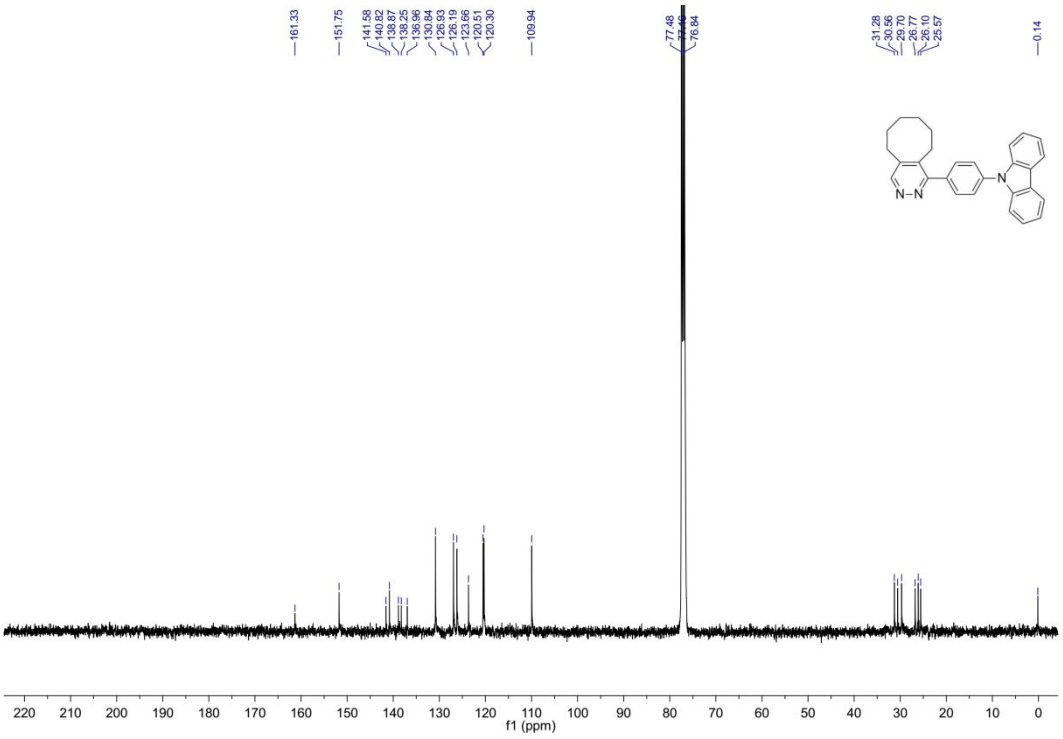
8.18
8.16
7.76
7.74
7.72
7.70
7.52
7.50
7.46
7.43
7.33
7.32
7.30
7.26
2.92
2.90
2.88
2.87
1.86
1.85
1.84
1.83
1.72
1.70
1.69
1.51
1.50
1.49
1.47
1.45
0.00
0.98
2.00
4.22
2.11
2.13
2.12
4.33
2.35
2.38
4.41
f1 (ppm)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141.58
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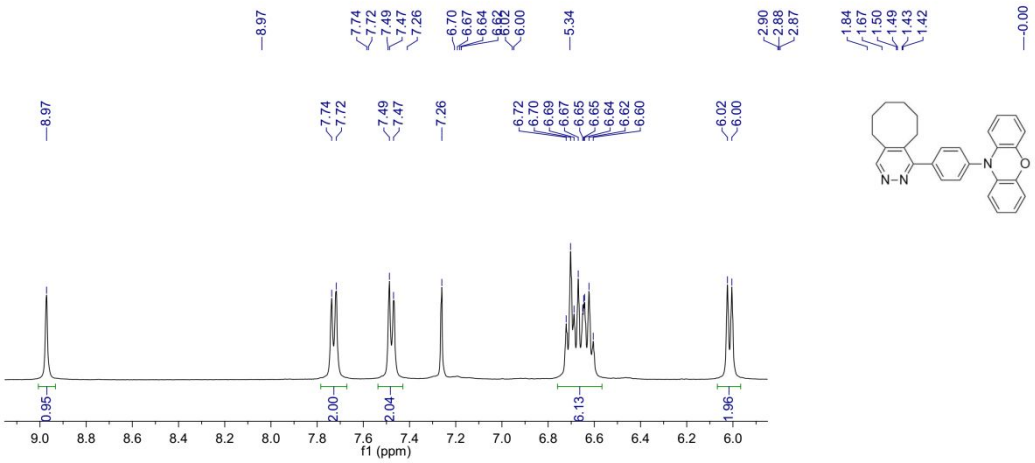
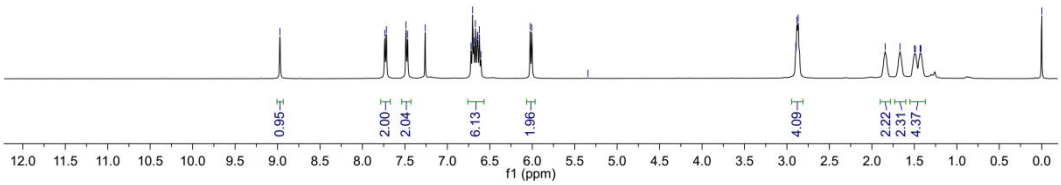
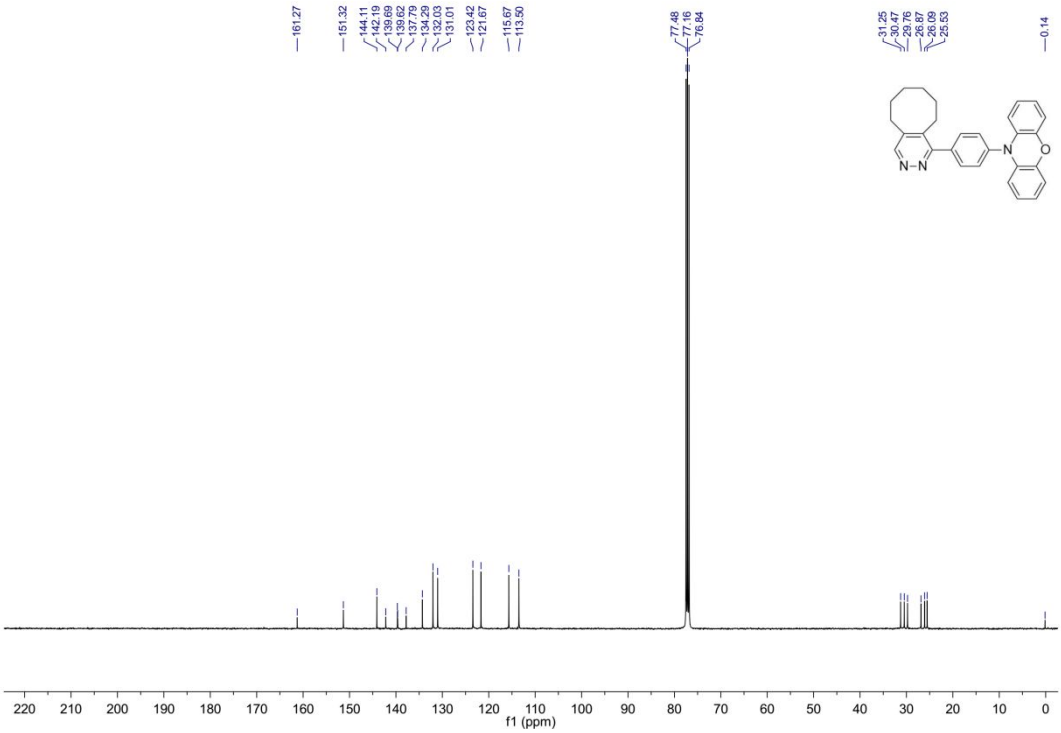
138.87
138.25
136.96
130.84
126.93
126.19
123.66
123.51
120.30
109.94
77.48
77.16
76.84
31.28
30.56
29.70
28.77
26.10
25.57
0.14
f1 (ppm)


8.97
7.74
7.72
7.49
7.47
7.26
6.72
6.70
6.69
6.67
6.65
6.65
6.64
6.62
6.60
6.02
6.00
0.95
2.00
2.04
6.13
1.96
f1 (ppm)


8.97
7.74
7.72
7.49
7.47
7.26
6.70
6.67
6.64
6.62
6.00
5.34
2.90
2.88
2.87
1.84
1.67
1.50
1.49
1.43
1.42
0.00
0.95
2.00
2.04
6.13
1.96
4.09
2.22
2.31
4.37
f1 (ppm)


161.27
151.32
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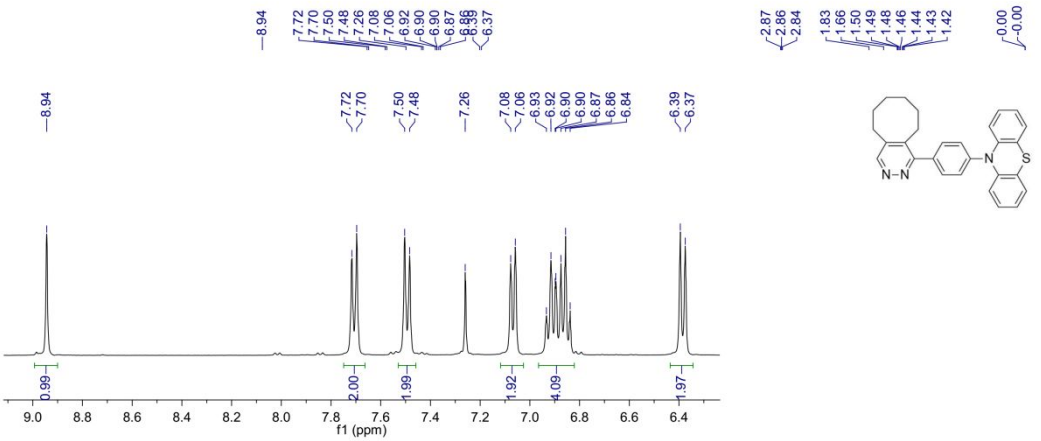
142.19
139.69
139.62
137.79
134.29
132.03
131.01
123.42
121.67
115.67
113.50
77.48
77.16
76.84
31.25
30.47
29.76
26.87
26.09
25.53
0.14
f1 (ppm)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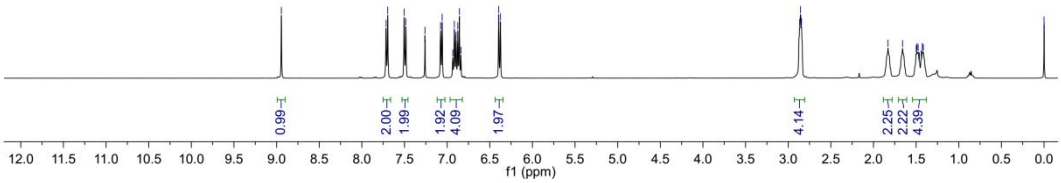
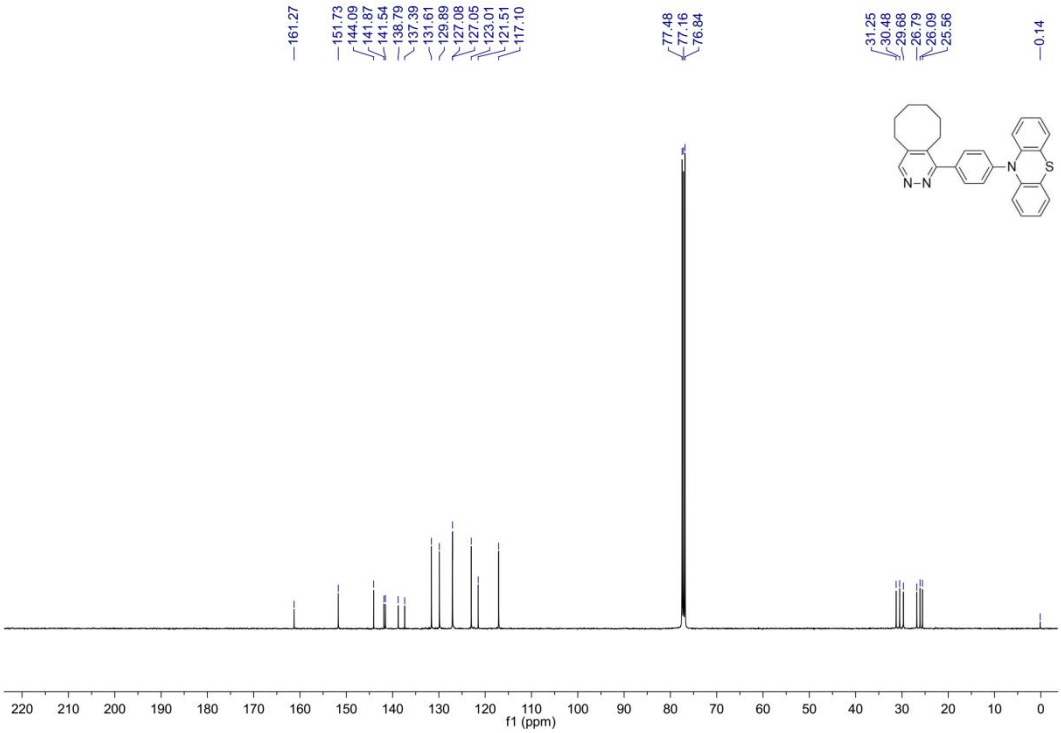
7.72
7.70
7.50
7.48
7.26
7.08
7.06
6.93
6.92
6.90
6.87
6.86
6.84
6.39
6.37
0.99
2.00
1.99
1.92
4.09
1.97
f1 (ppm)


0.99
2.00
1.99
1.92
4.09
1.97
4.14
2.25
2.22
4.39
f1 (ppm)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151.73
144.09
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141.54
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137.39
131.61
129.89
127.08
127.05
123.01
121.51
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76.84
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29.68
26.79
26.09
25.56
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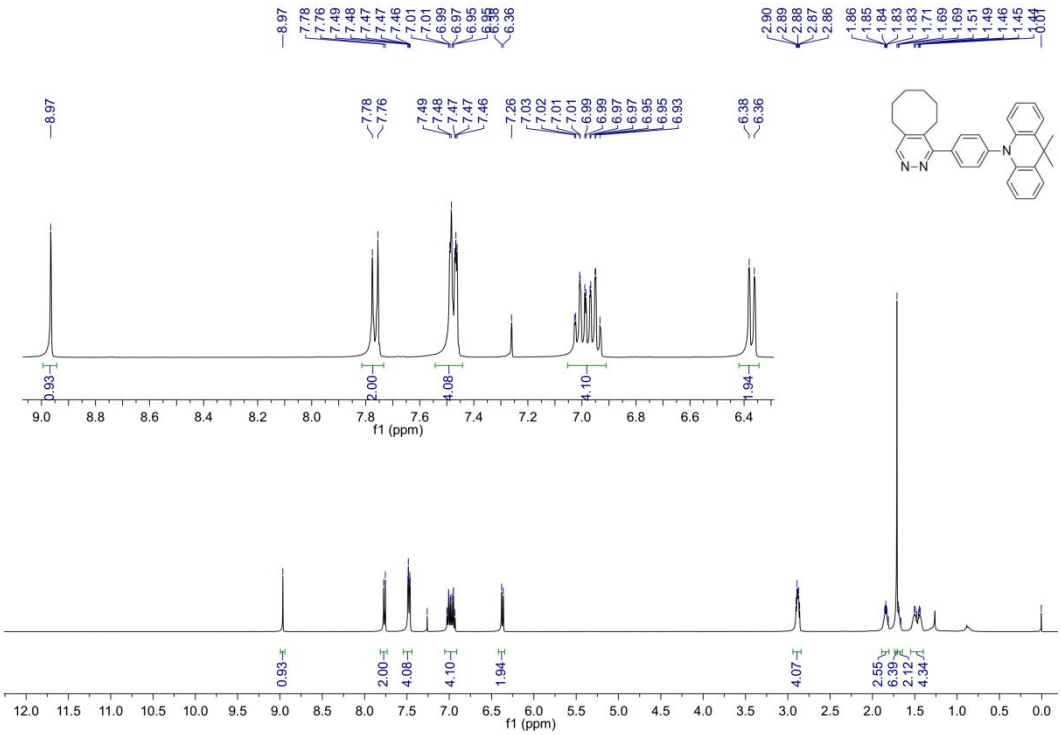
f1 (ppm)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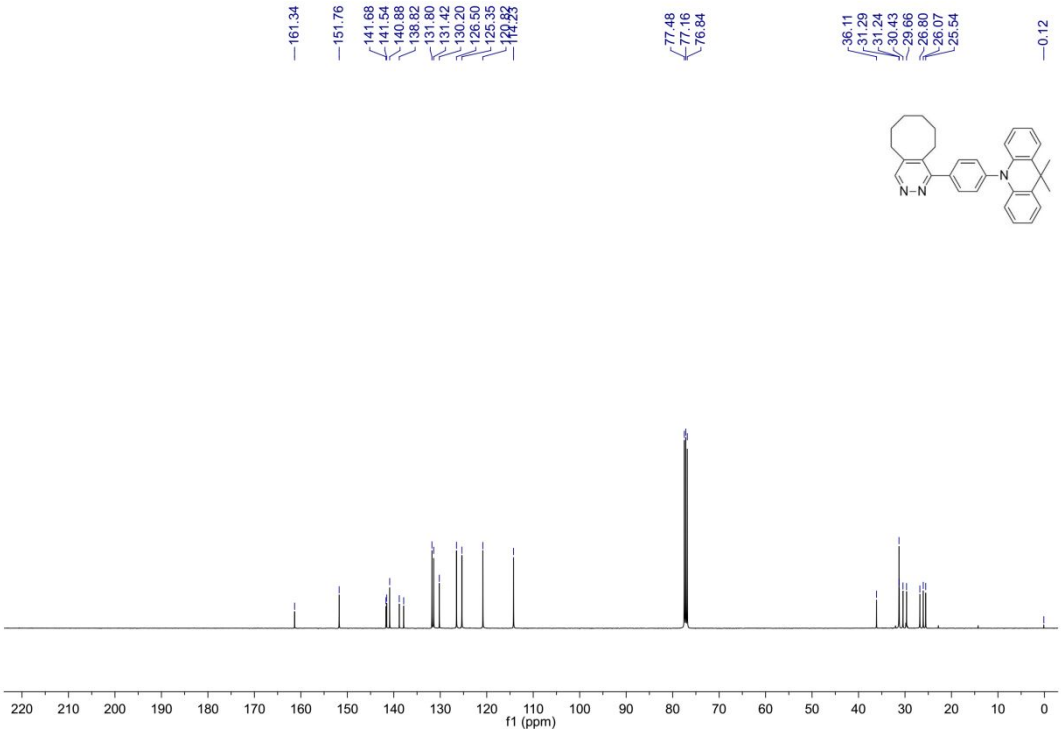
7.48
7.47
7.47
7.46
7.26
7.03
7.02
7.01
7.01
6.99
6.99
6.97
6.97
6.95
6.95
6.93
6.38
6.36
2.90
2.89
2.88
2.87
2.86
1.86
1.85
1.84
1.83
1.83
1.71
1.69
1.69
1.51
1.49
1.46
1.45
0.01
0.93
2.00
4.08
4.10
1.94
4.07
2.55
6.39
2.12
4.34
f1 (ppm)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151.76
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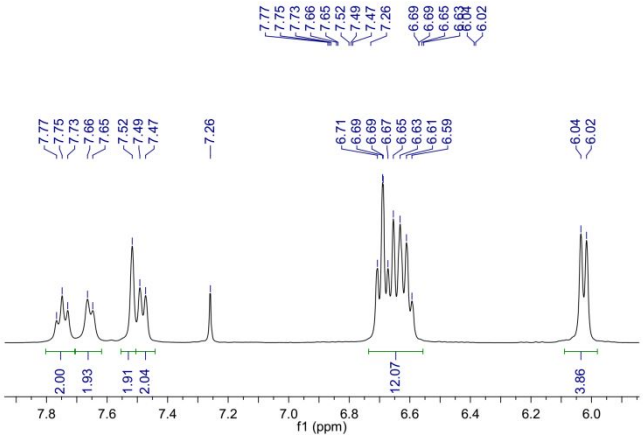
140.88
138.82
131.80
131.42
130.20
126.50
125.35
77.48
77.16
76.84
36.11
31.29
31.24
30.43
29.66
26.80
26.07
25.54
0.12
f1 (ppm)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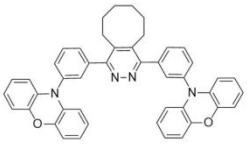
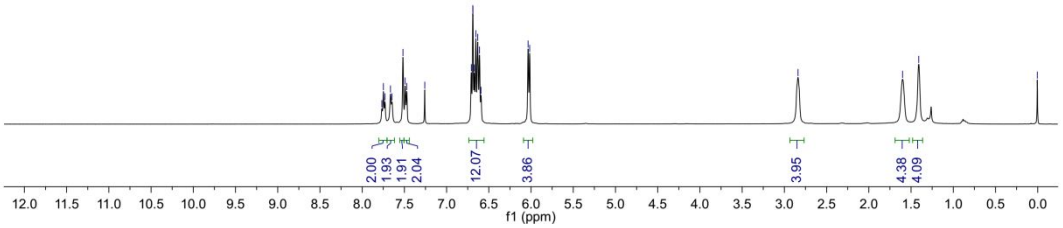
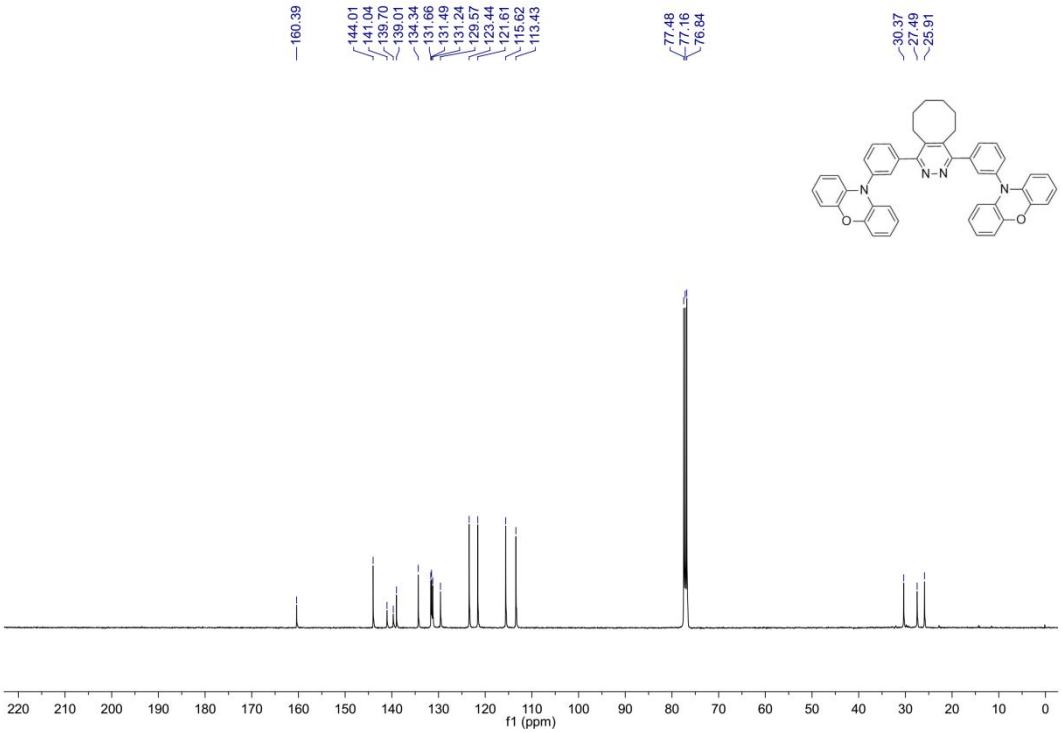
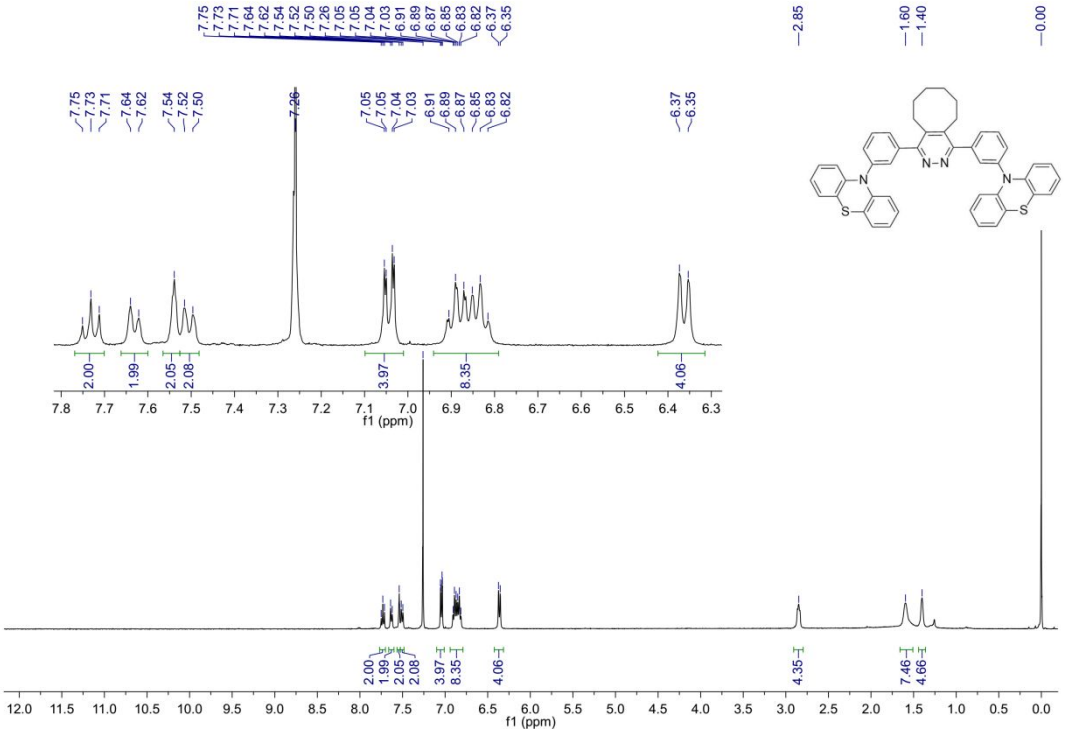
7.52
7.49
7.47
7.26
6.71
6.69
6.69
6.67
6.65
6.63
6.61
6.59
6.04
6.02
2.00
1.93
1.91
2.04
12.07
3.86
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0
f1 (ppm)


N-N
N
O
N
O


2.84
1.60
1.41
0.00
2.00
1.93
1.91
2.04
12.07
3.86
3.95
4.38
4.09
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)


160.39
144.01
141.04
139.70
139.01
134.34
131.66
131.49
131.24
129.57
123.44
121.61
115.62
113.43
77.48
77.16
76.84
30.37
27.49
25.91
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

N-N
N
O
N
O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7.71
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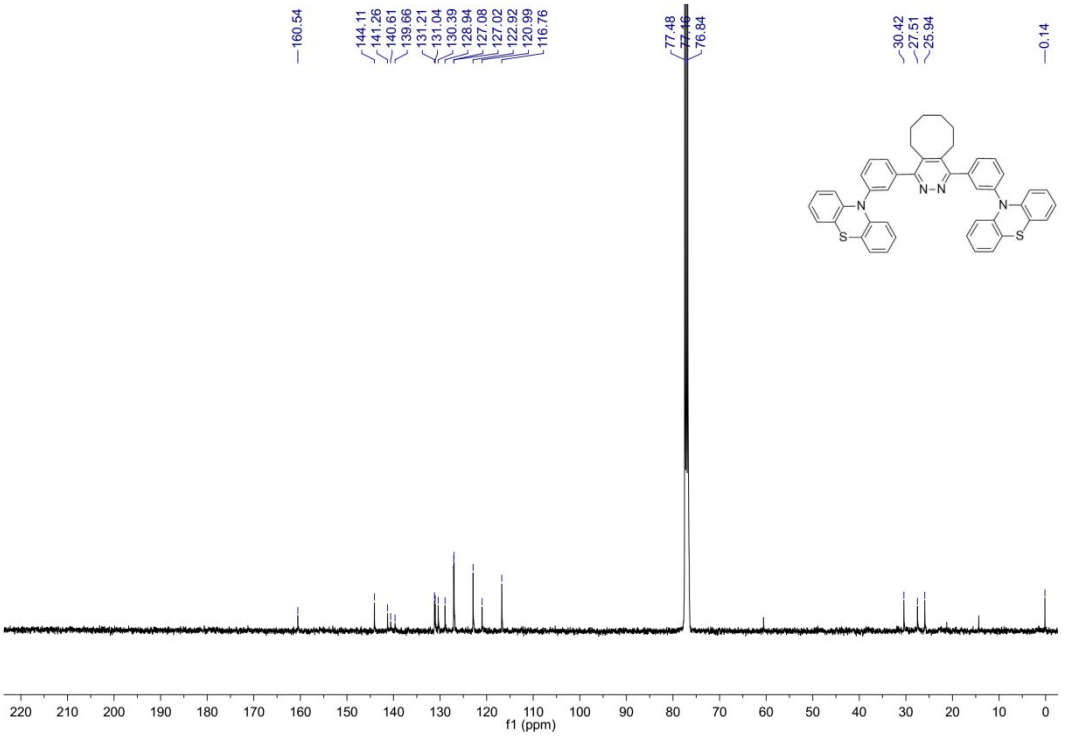
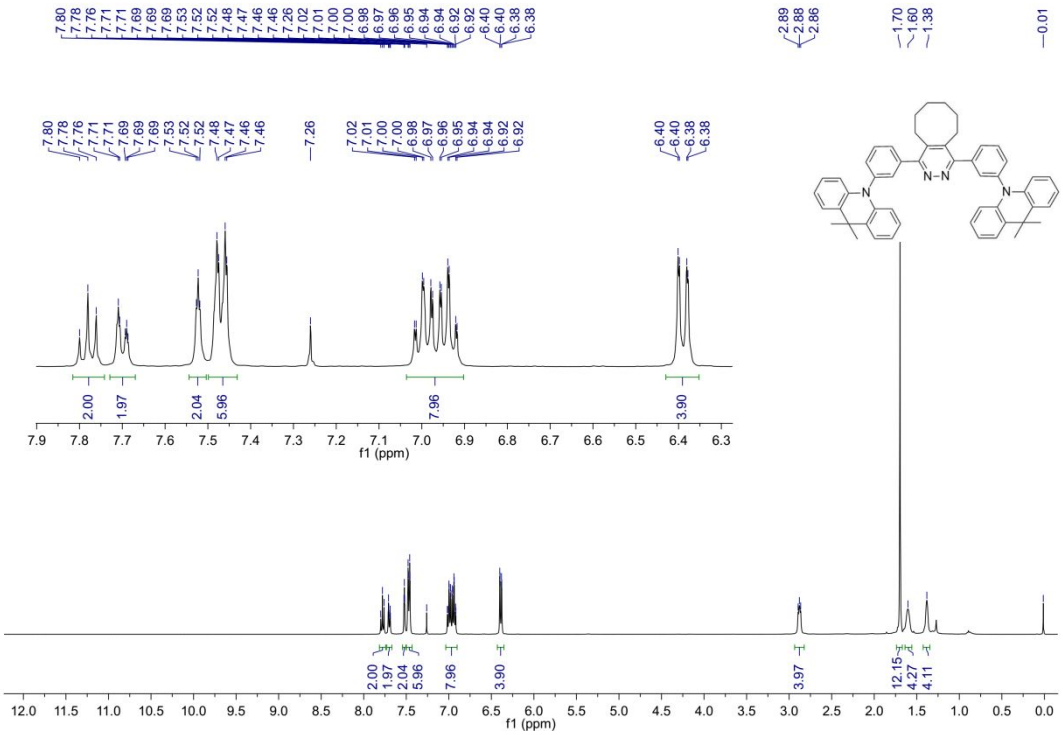
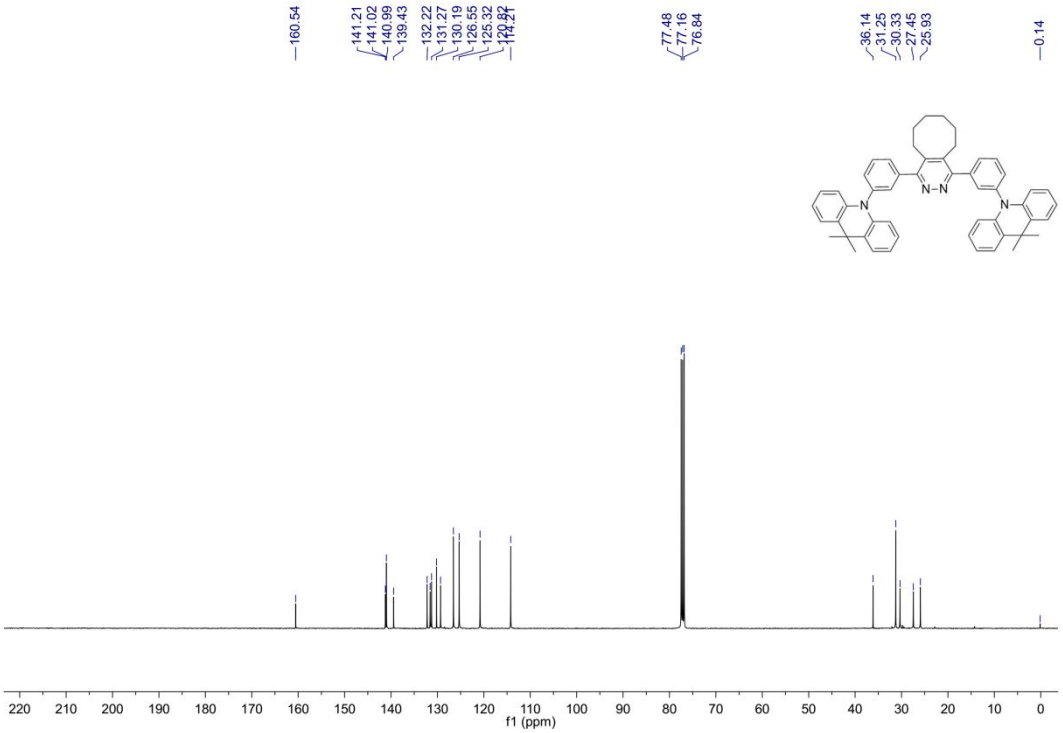
7.62
7.54
7.52
7.50
7.26
7.05
7.05
7.04
7.03
6.91
6.89
6.87
6.85
6.83
6.82
6.37
6.35
2.85
1.60
1.40
0.00
2.00
1.99
2.05
2.08
3.97
8.35
4.06
f1 (ppm)
4.35
7.46
4.66
N-N
N
S


160.54
144.11
141.26
140.61
139.66
131.21
131.04
130.39
128.94
127.08
127.02
122.92
120.99
116.76
77.48
77.16
76.84
30.42
27.51
25.94
0.14
f1 (ppm)
N-N
N
S


7.80 7.78 7.76 7.71 7.71 7.69 7.69 7.69 7.53 7.52 7.52 7.48 7.47 7.46 7.46 7.26 7.02 7.01 7.00 7.00 7.00 6.98 6.97 6.96 6.95 6.94 6.94 6.92 6.92 6.40 6.40 6.38 6.38
2.89 2.88 2.86
1.70 1.60 1.38
0.01
N-N
2.00 1.97 2.04 5.96 7.96 3.90
f1 (ppm)
3.97
12.15 4.27 4.11


160.54
141.21 141.02 140.99 139.43
132.22 131.27 130.19 126.55 125.32 120.82 114.21
77.48 77.16 76.84
36.14 31.25 30.33 27.45 25.93
0.14
N-N
f1 (ppm)