Supporting Information

Successive C-C/C-H Activation towards Cyano Substituted Carbazoles

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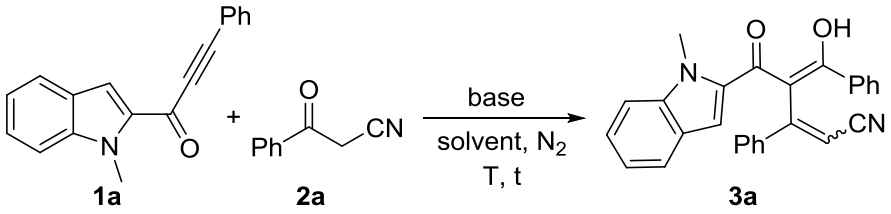
Table of Contents

1. Optimization of 3a Conditions

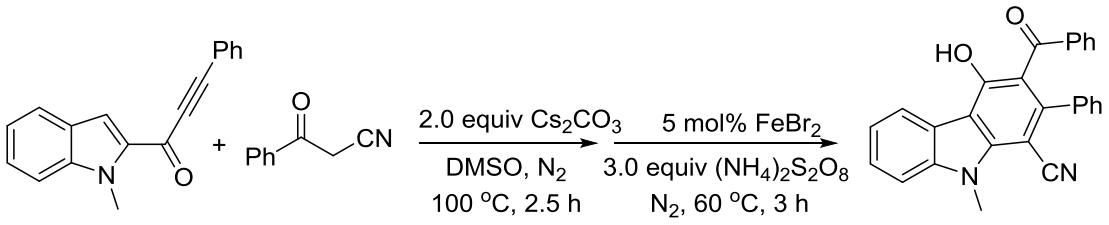
Table S1 Optimization of reaction conditions for the synthesis of **3a**



entry	solvent	base (equiv)	T	t	yield[a]
1	DMSO	3.0 Cs_2CO_3	100 °C	2.5 h	77 %
2	DMSO	1.5 Cs_2CO_3	100 °C	2.5 h	74 %
3	**DMSO**	**2.0 Cs_2CO_3**	**100 °C**	**2.5 h**	**90 %**
4	DMSO	2.0 Cs_2CO_3	80 °C	2.0 h	75 %
5	DMSO	2.0 K_2CO_3	100 °C	2.5 h	73 %
6	DMSO	2.0 DABCO	100 °C	2.5 h	--
7	DMAc	2.0 Cs_2CO_3	100 °C	2.5 h	79 %
8	DMF	2.0 Cs_2CO_3	100 °C	2.5 h	72 %
9	tol	2.0 Cs_2CO_3	100 °C	2.5 h	70 %

[a] **1a** : **2a** = 1.0 : 1.1, 0.2 mmol scale in 2 mL solvent

2. Gram Scale



Scales: 4.0 mmol

In a Schlenk tube, indolyl alkynyl ketones **1a** (4.0 mmol, 1.04 g), benzoyl acetonitrile **2a** (4.4 mmol, 0.64 g), Cs_2CO_3 (8.0 mmol, 2.61 g) and DMSO (40 mL) were stirred at 100 ^oC under N_2. After 2.5 h, $FeBr_2$ (0.2 mmol, 43.13 mg) and $(NH_4)_2S_2O_8$ (12.0 mmol, 2.74 g) were added to the reaction mixture. After the completion of the addition, the reaction mixture was allowed to react at 60 ℃ for 3 h. Then, the reaction mixture was cooled to room temperature and was treated with H_2O, then extracted with EA and dried over anhydrous Na_2SO_4. After removal of the EA, the residue was purified by chromatography on basic silica gel (PE:EA = 10:1) to afford **4a** (yellow solid, 0.97 g, 60%).

3. Copies of Spectra of New Products

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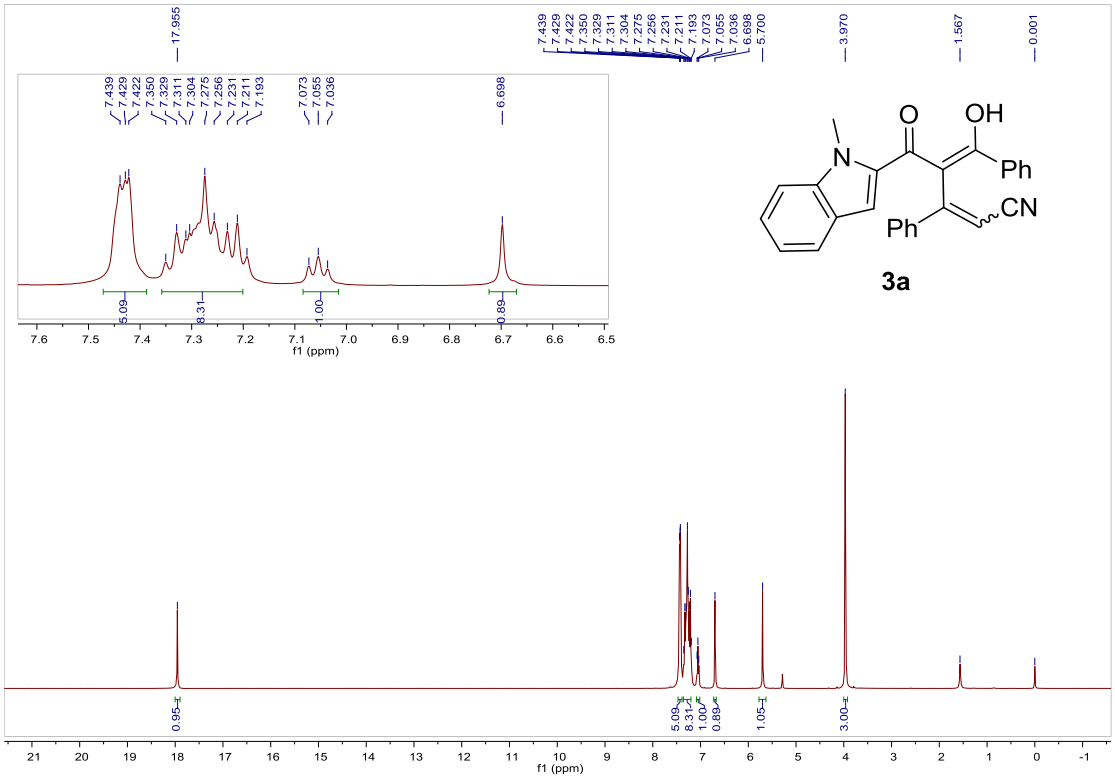

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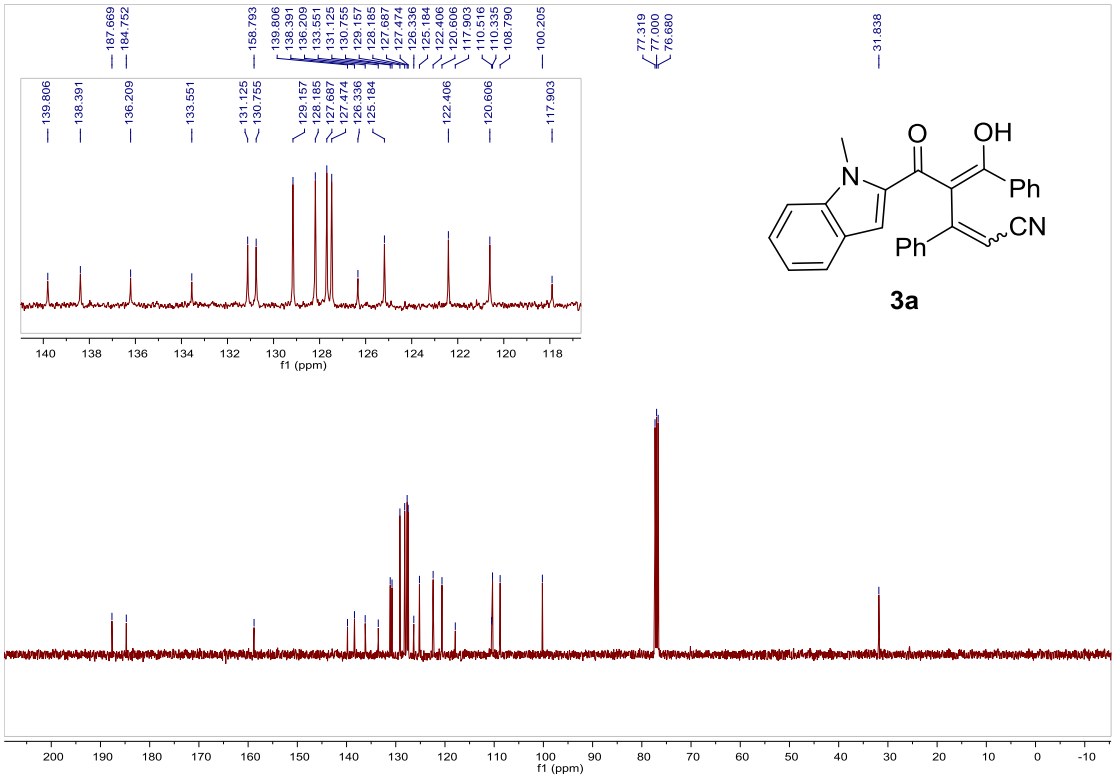

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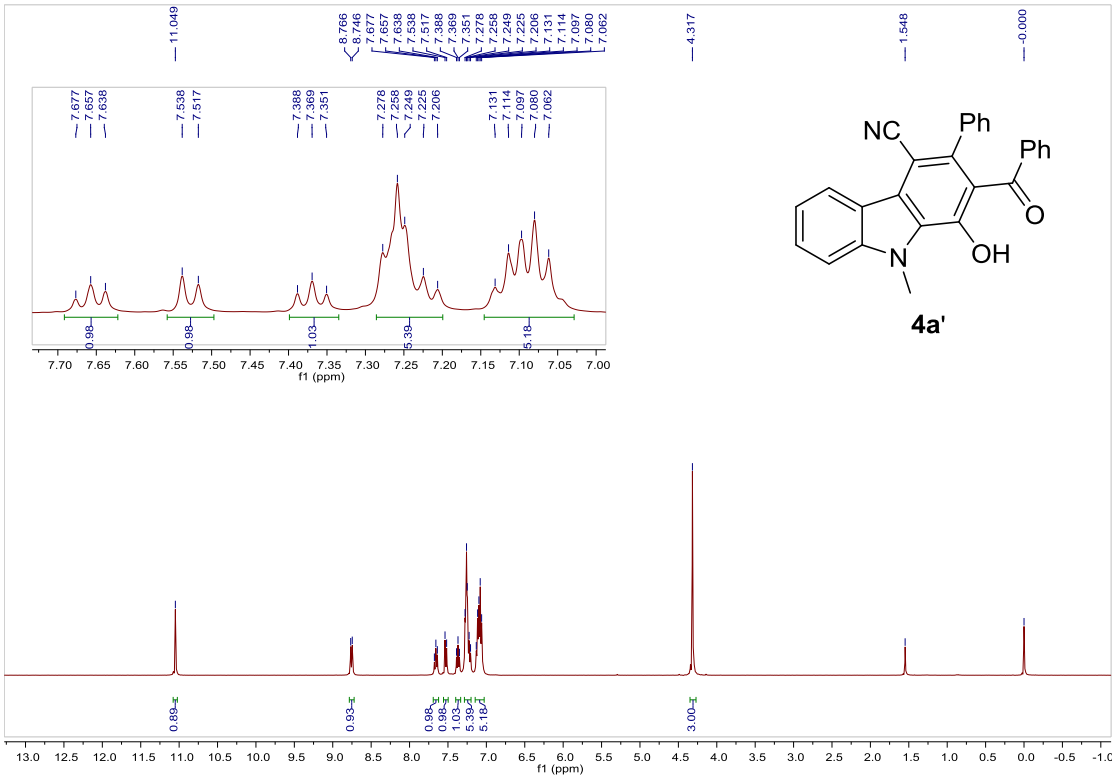

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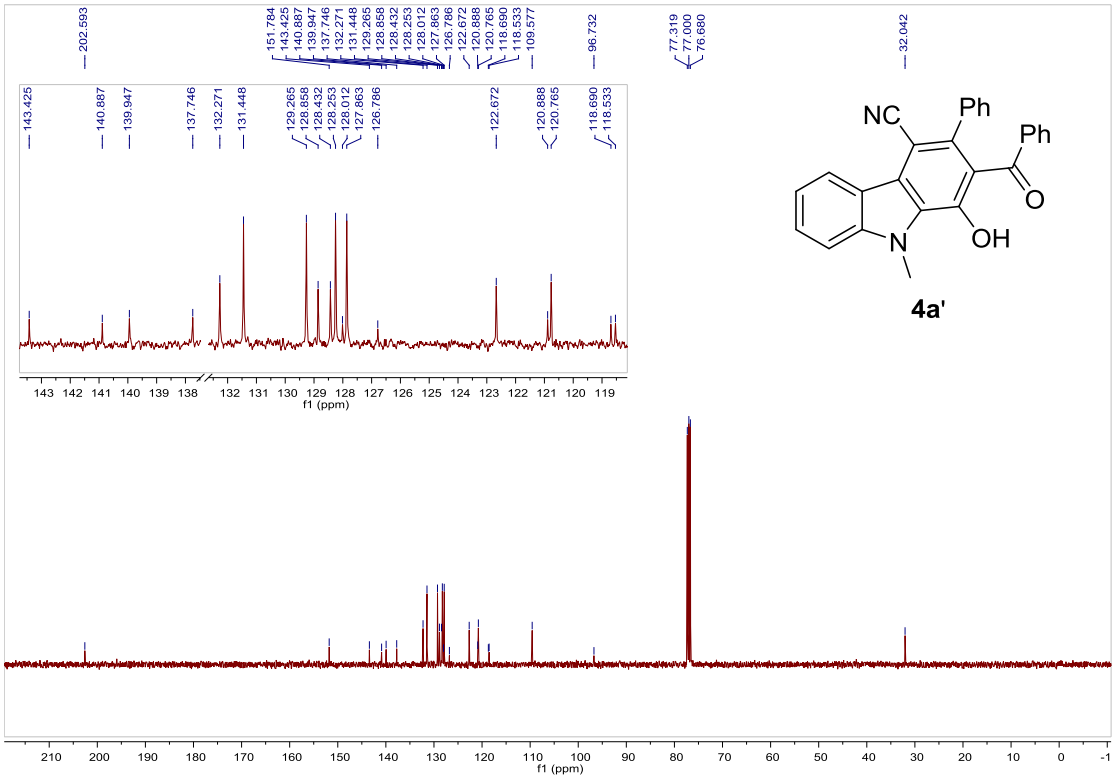

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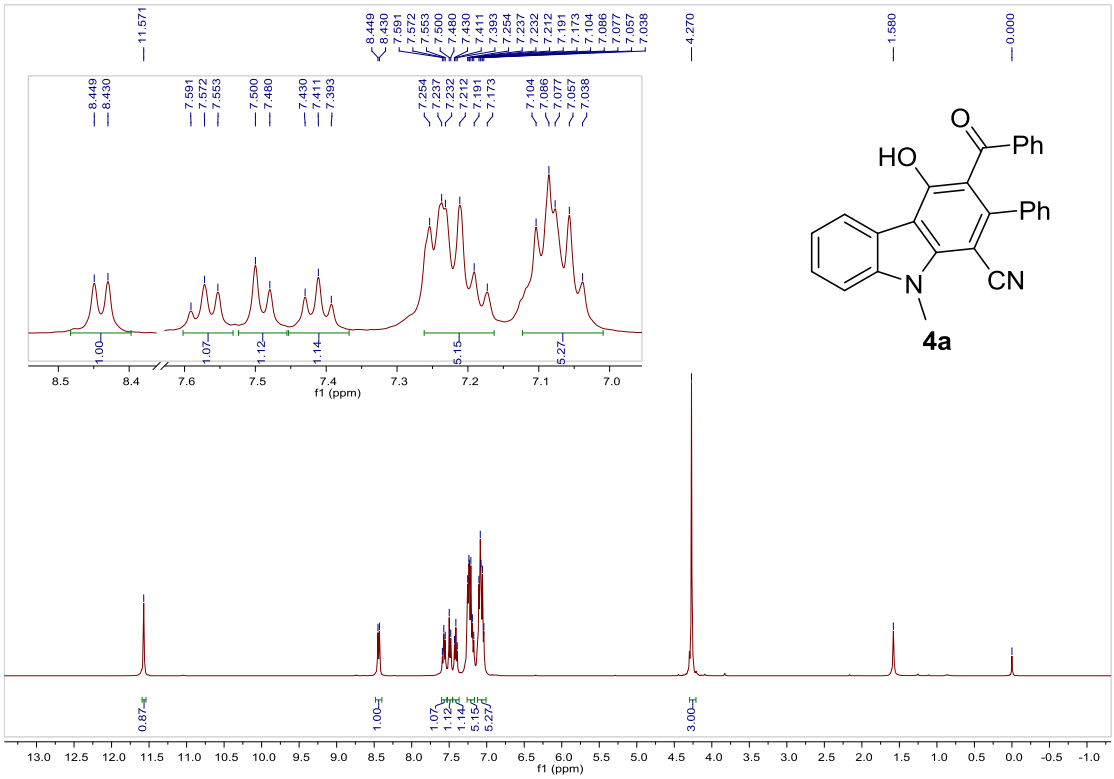

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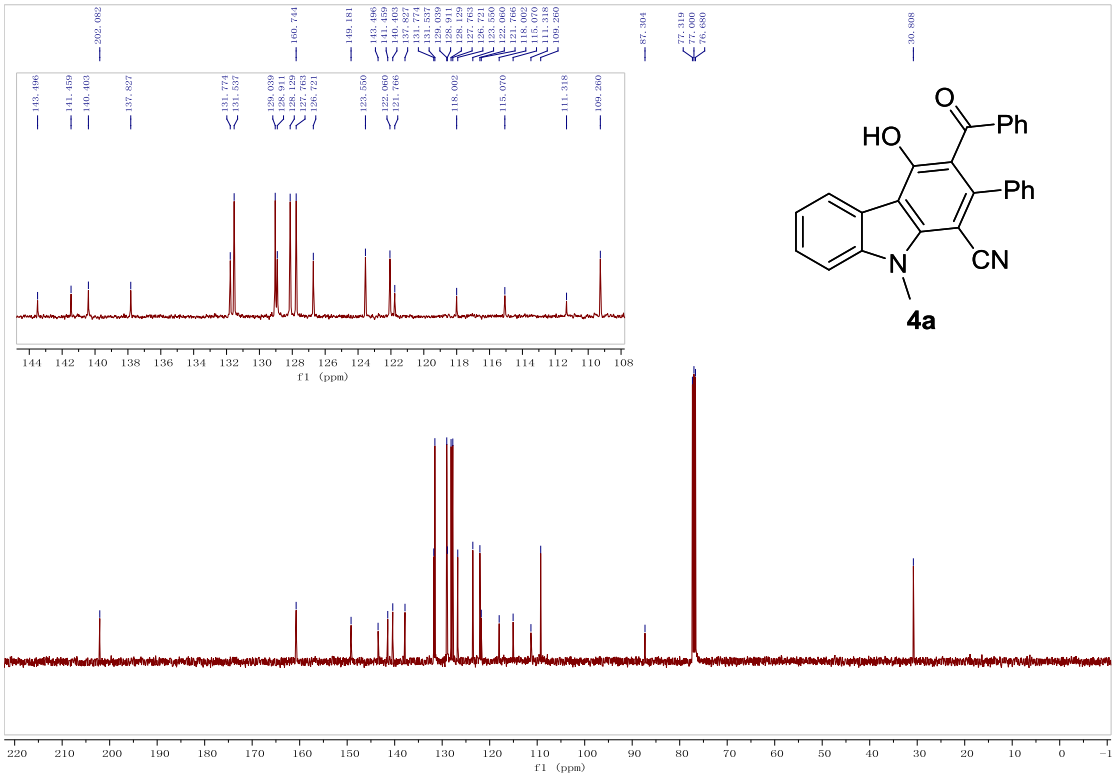

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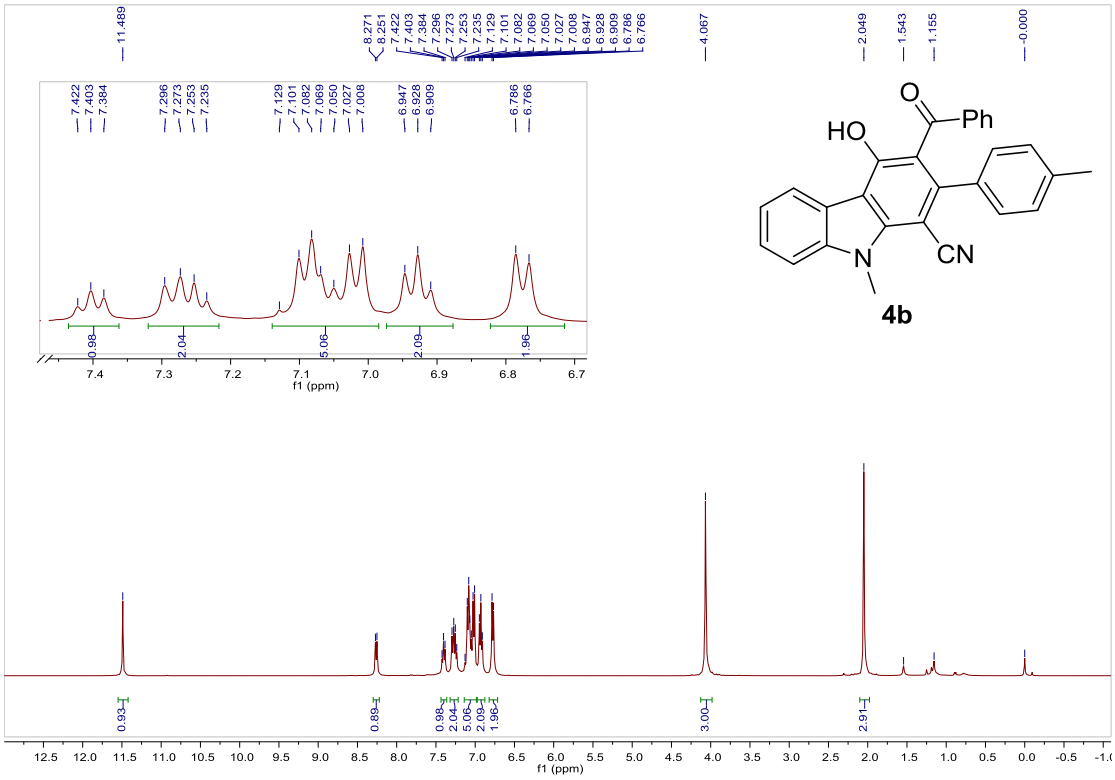

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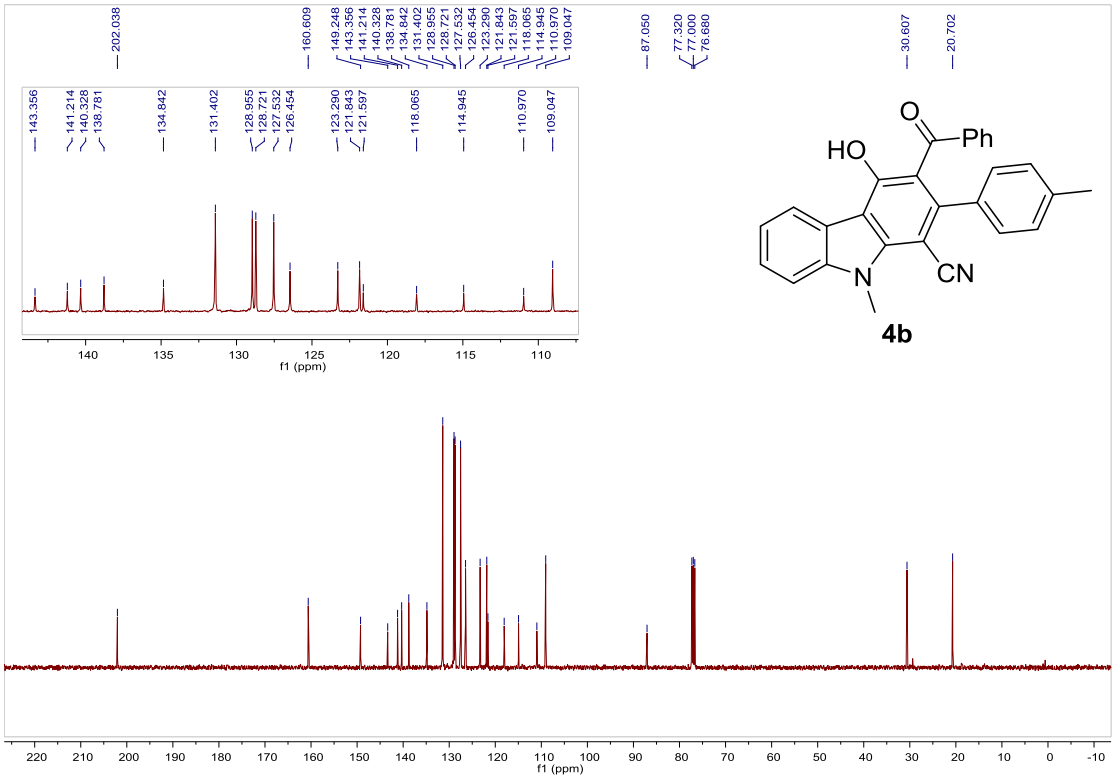

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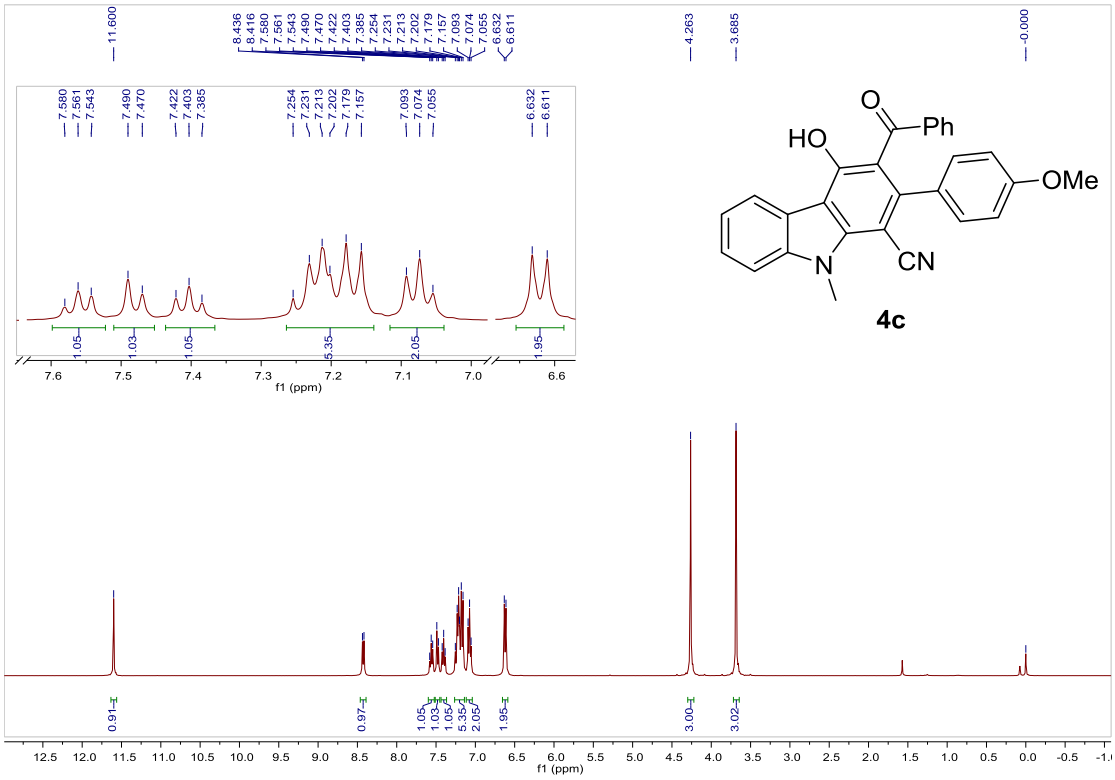

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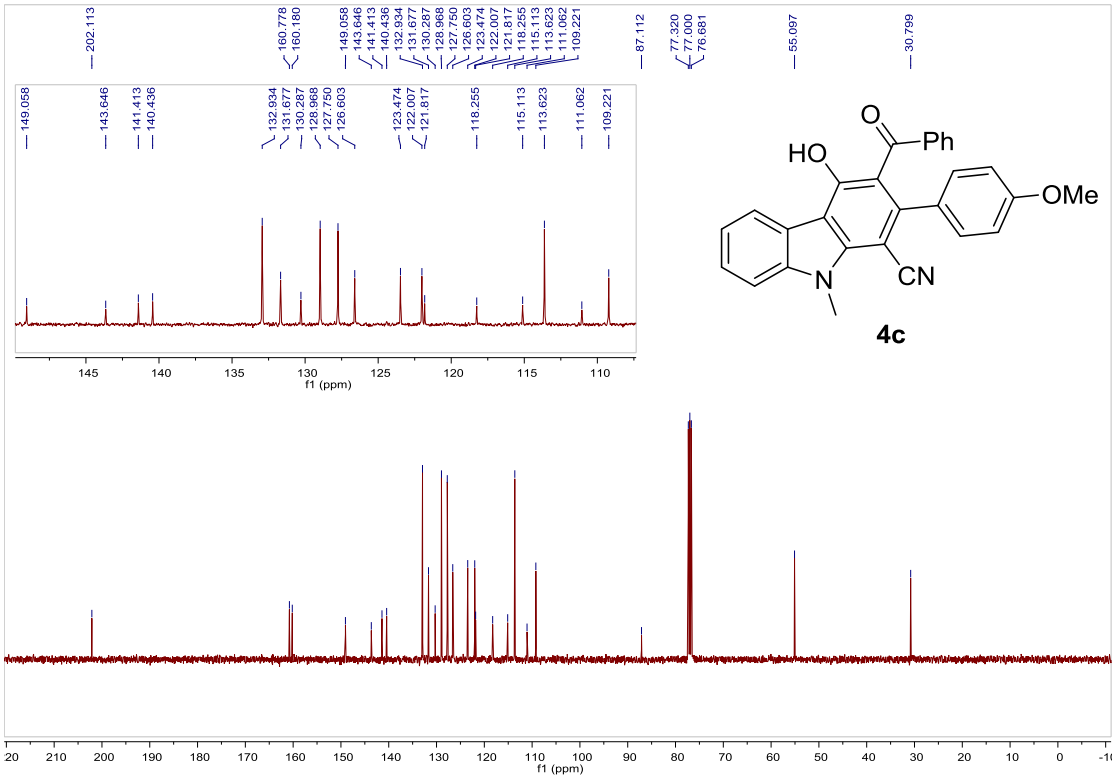

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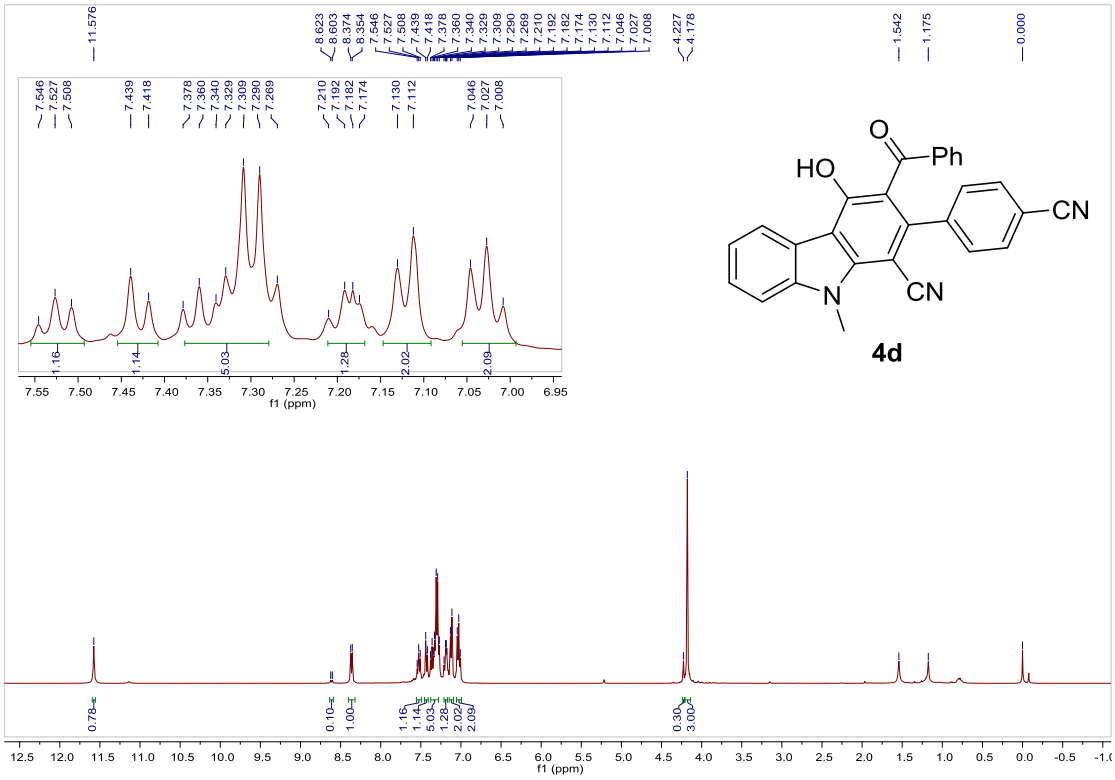

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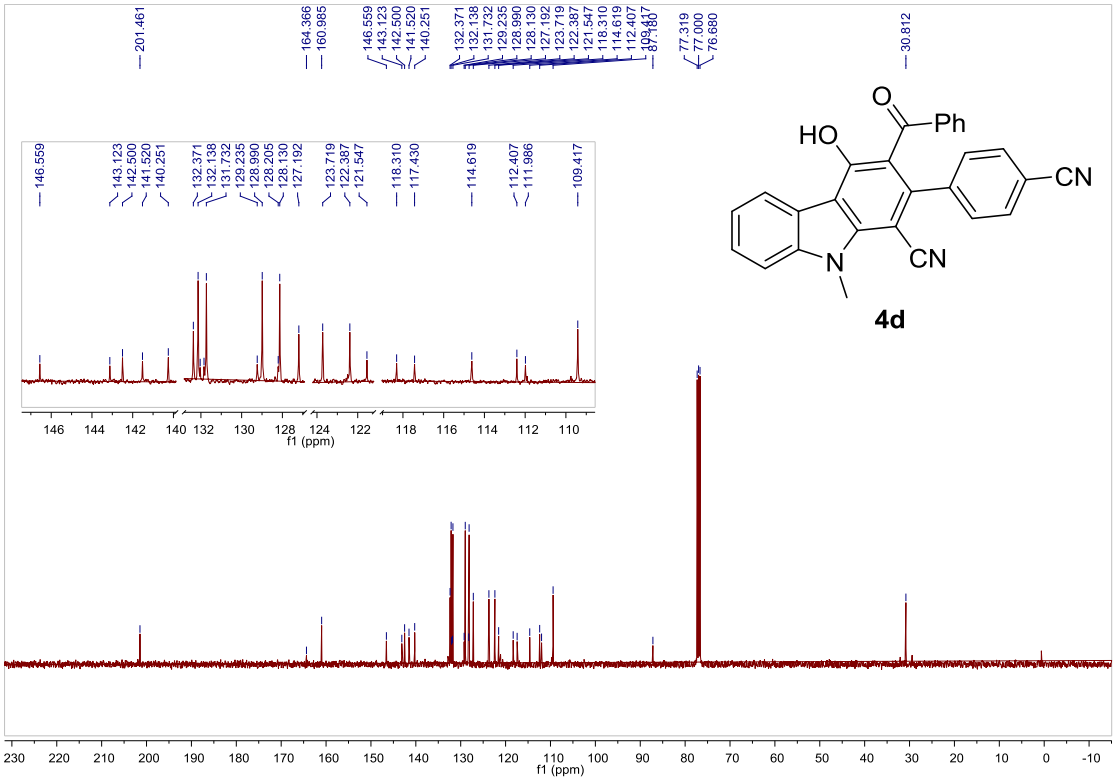

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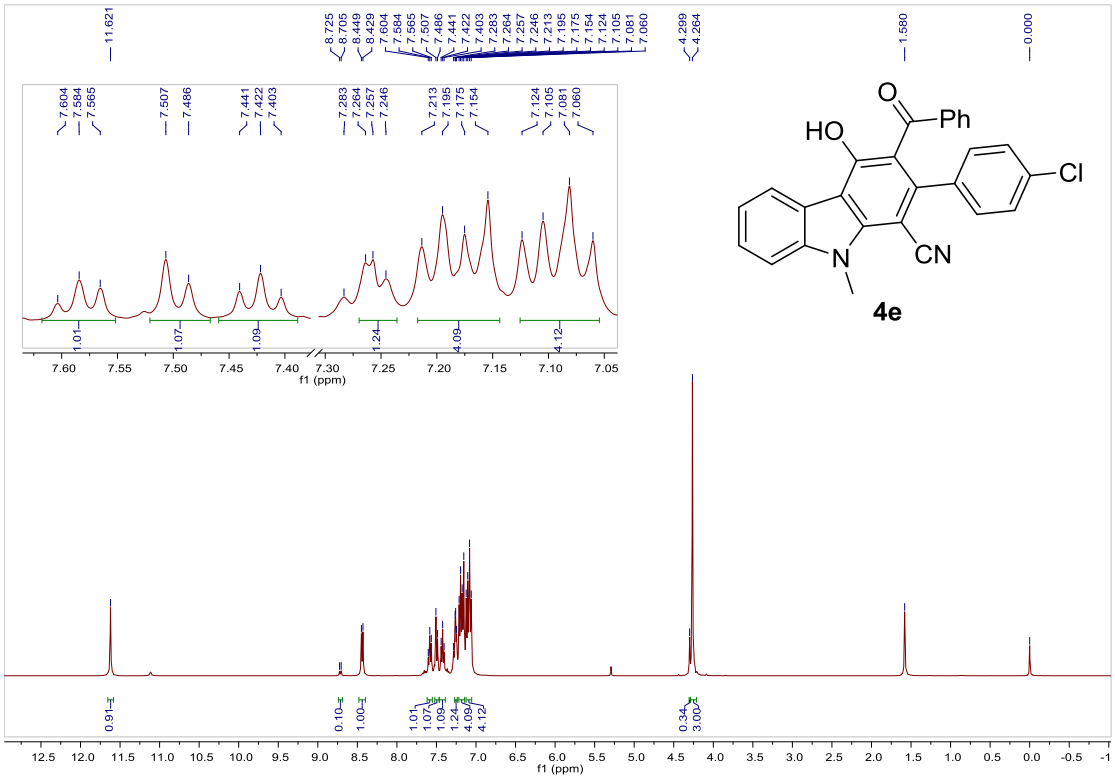

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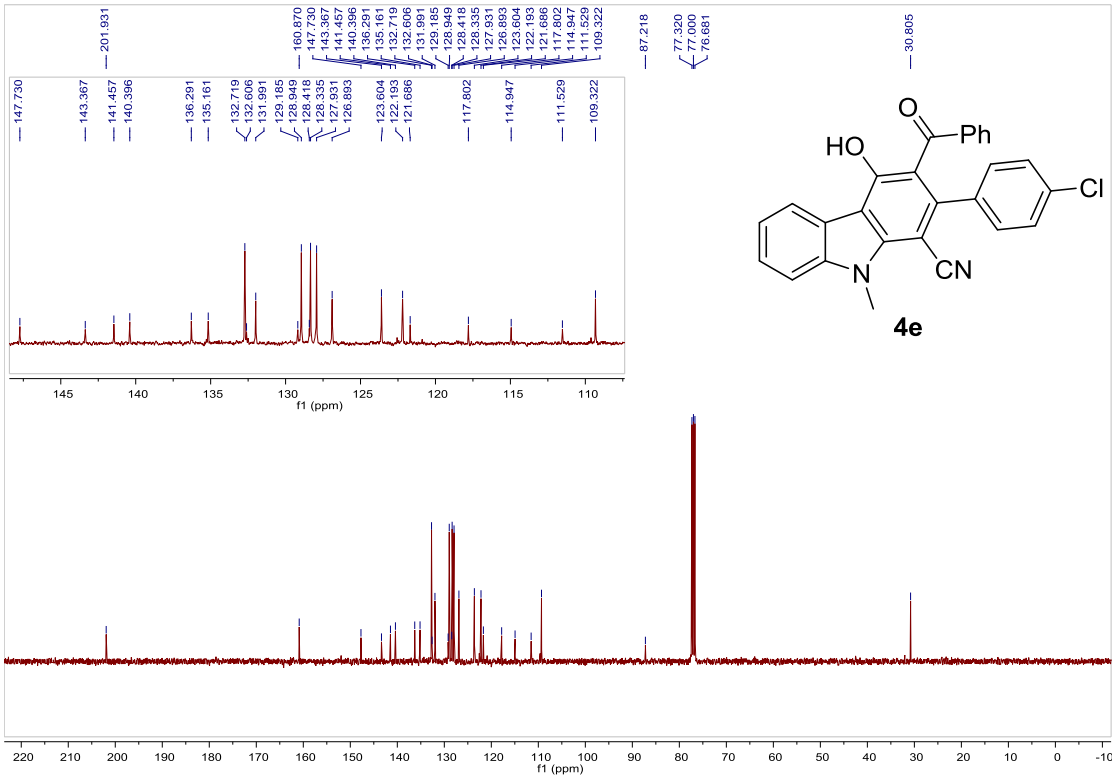

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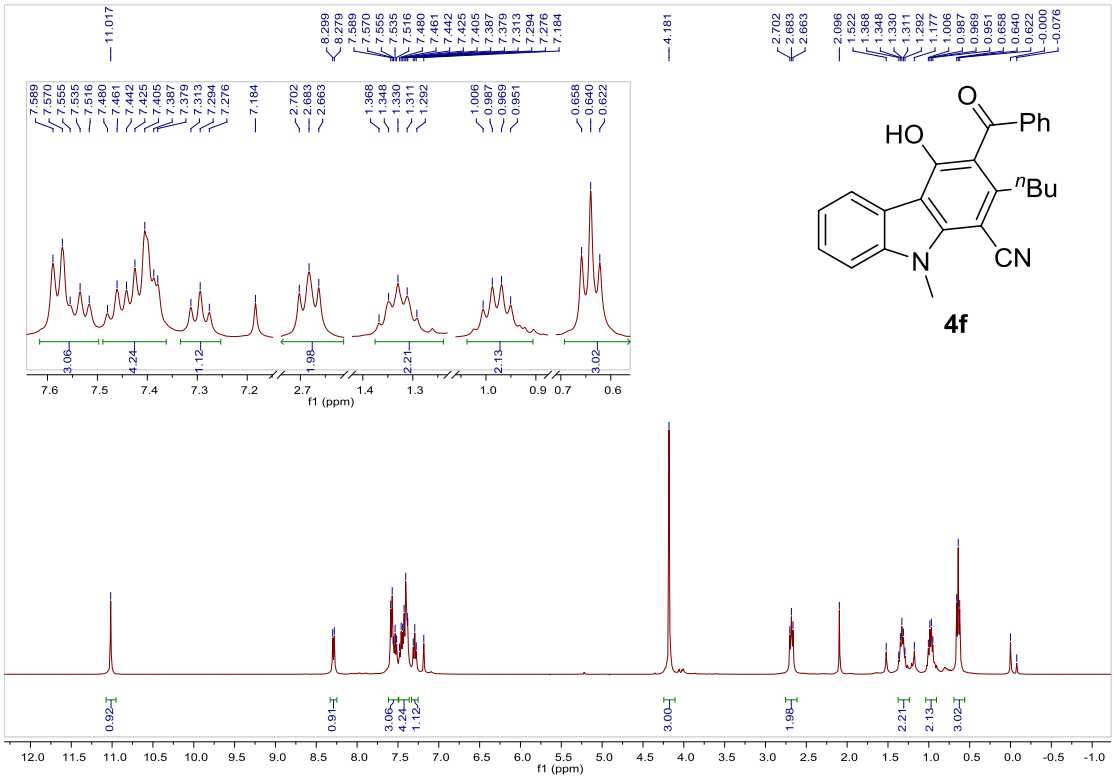

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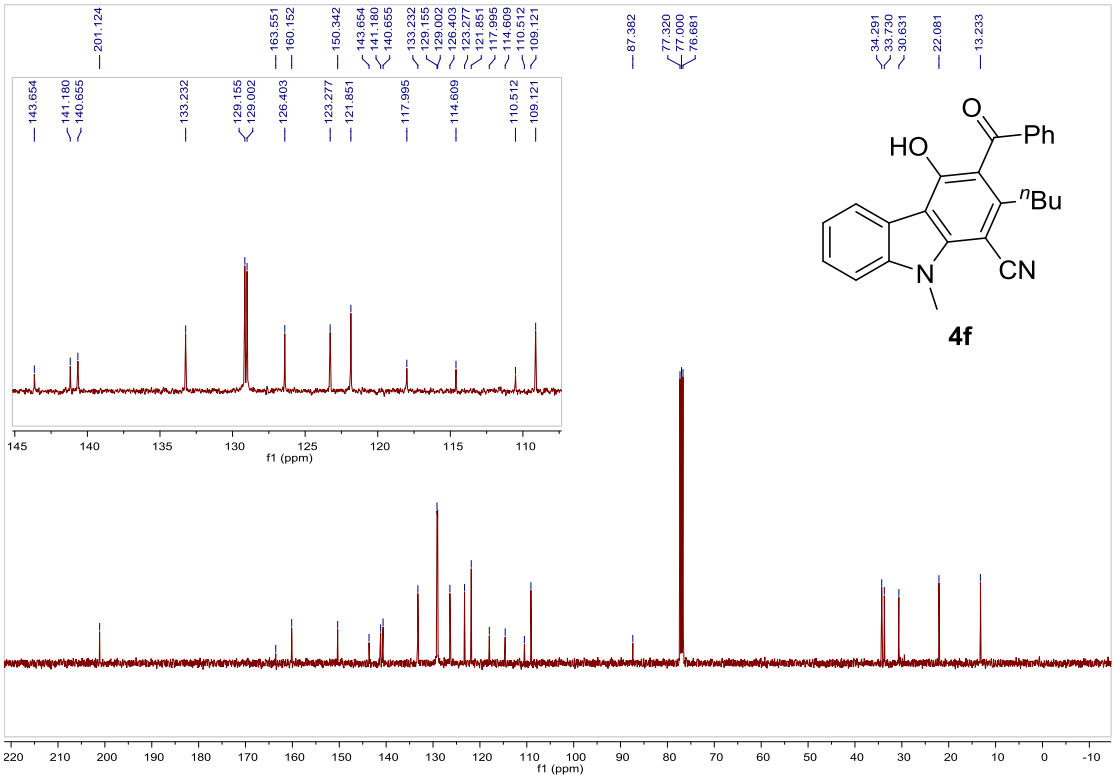

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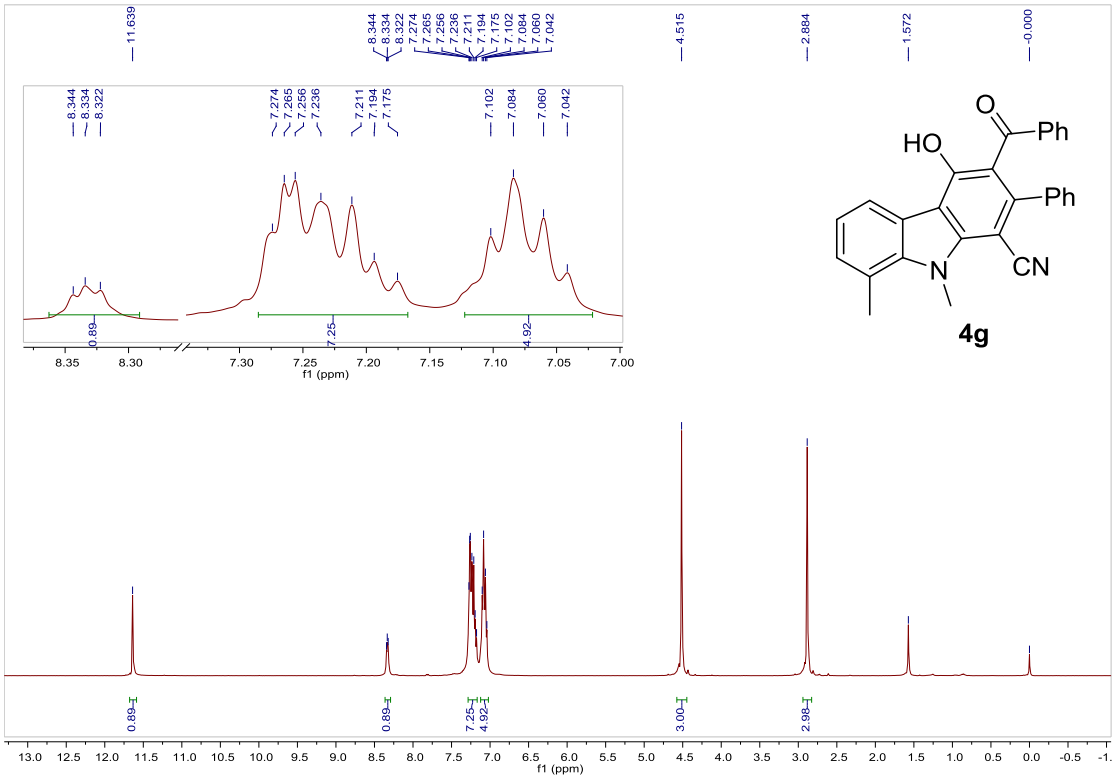

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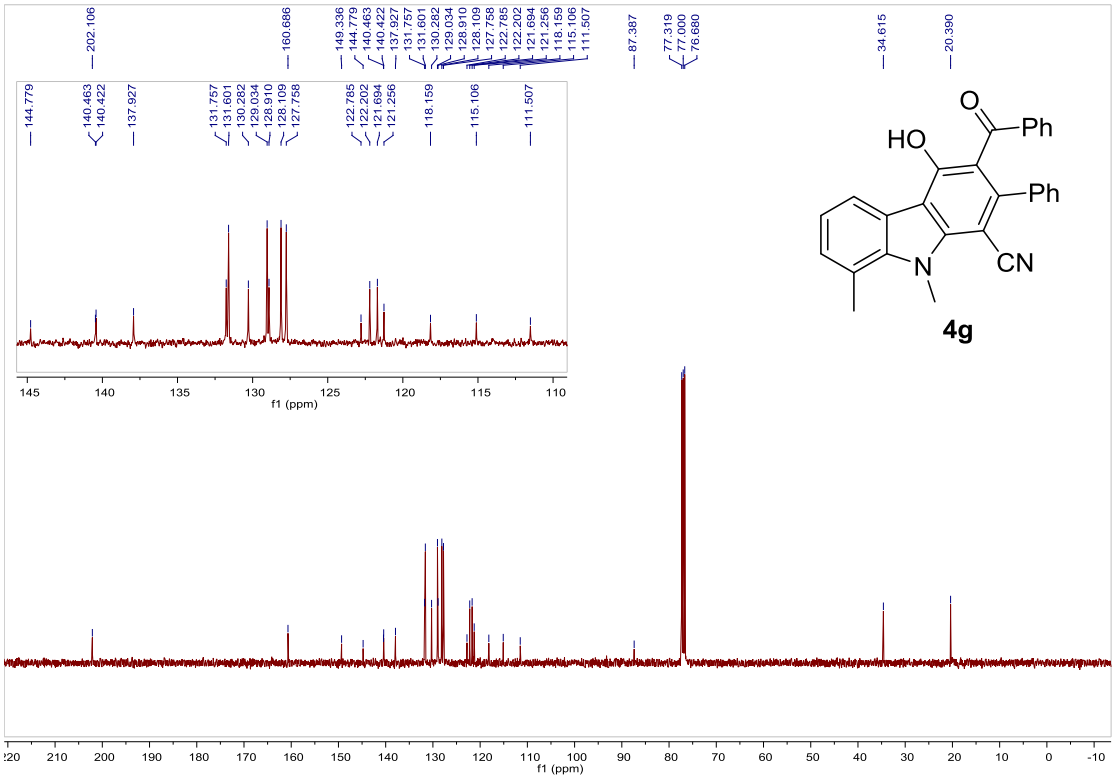

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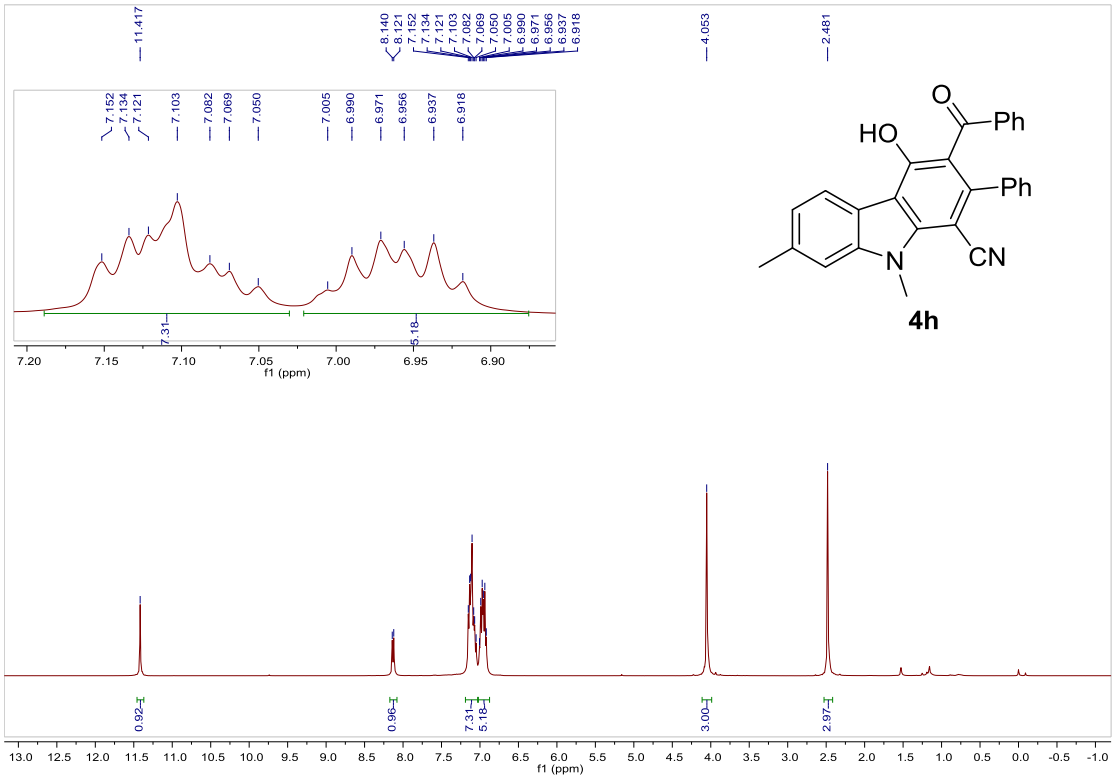

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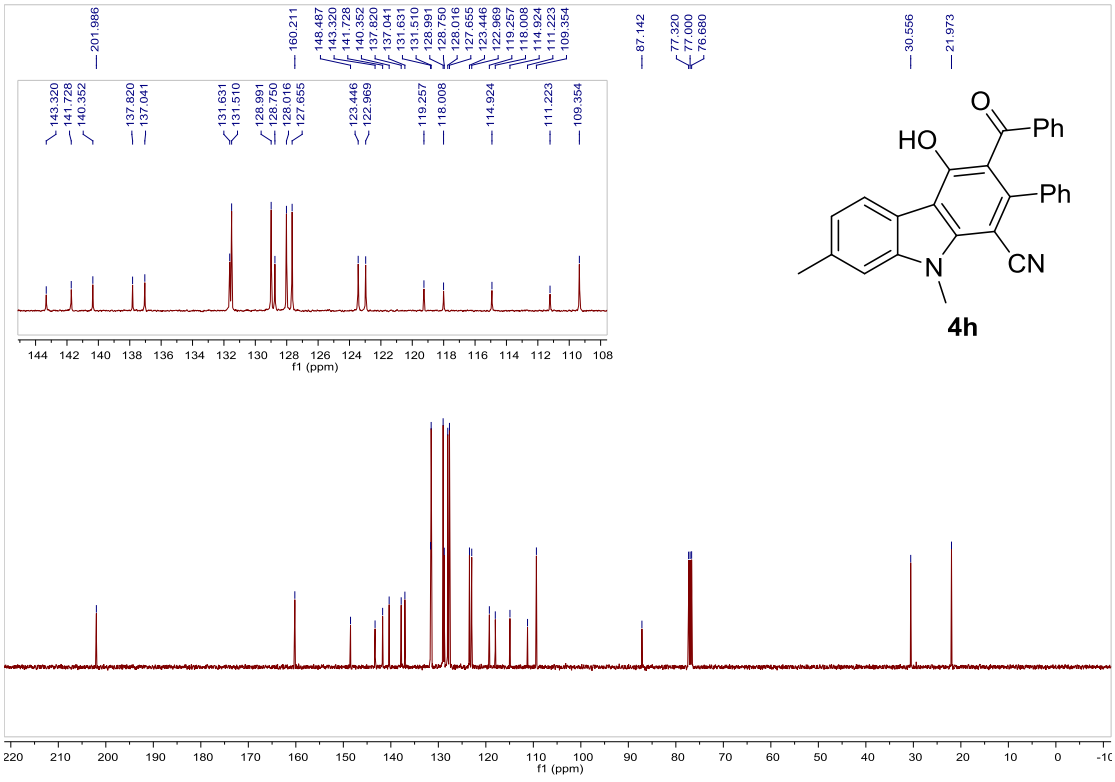

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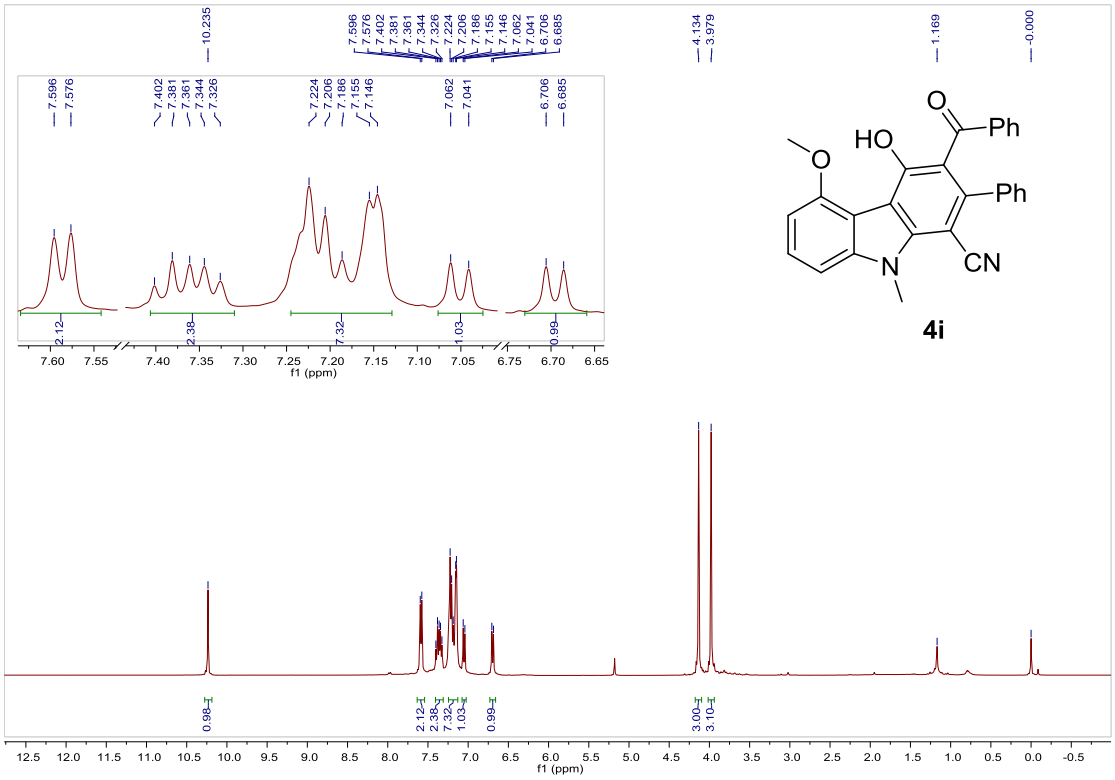

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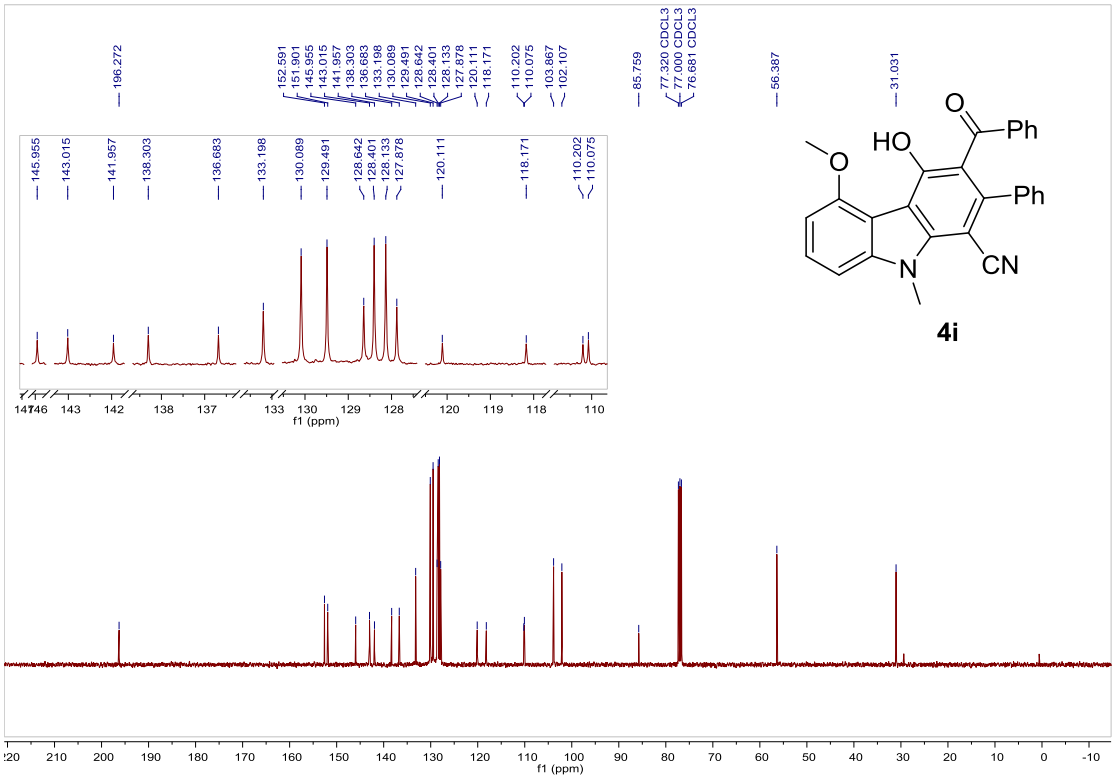

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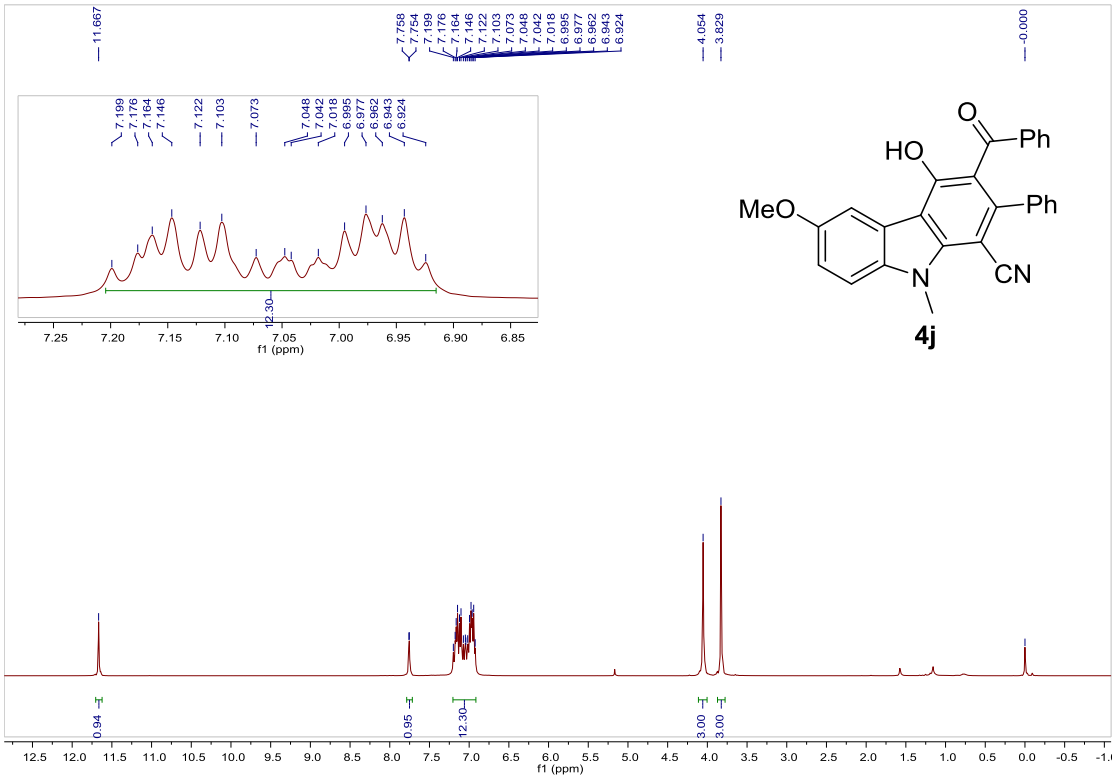

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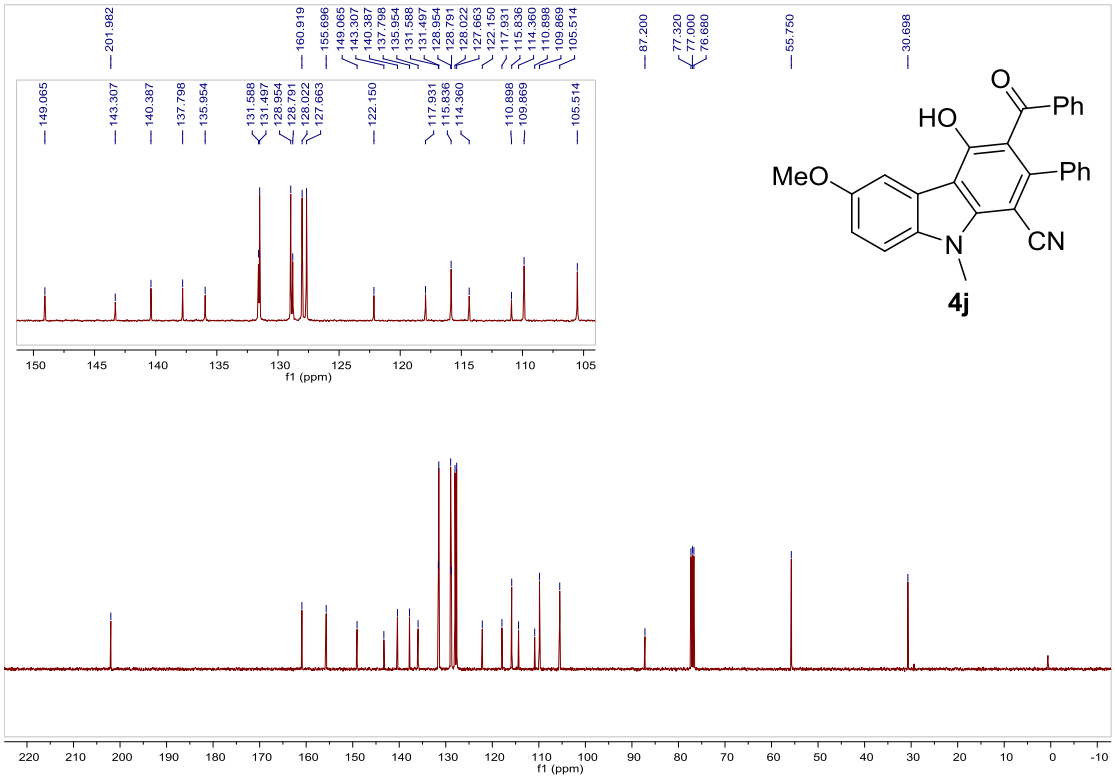

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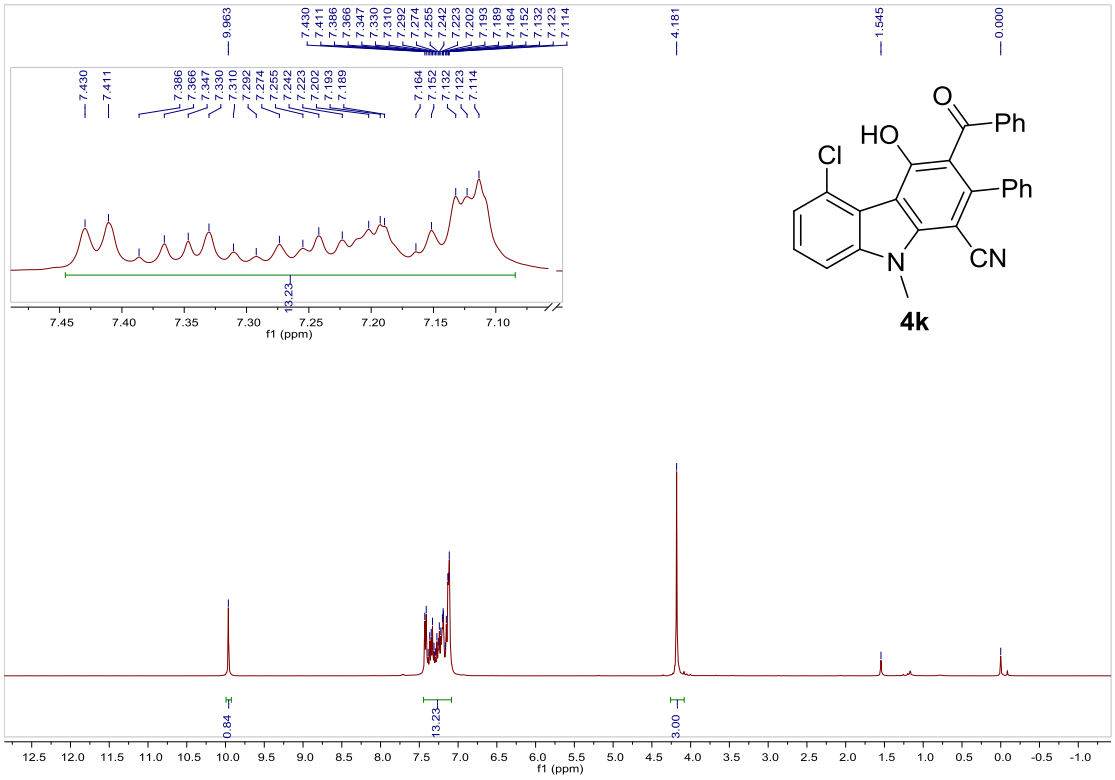

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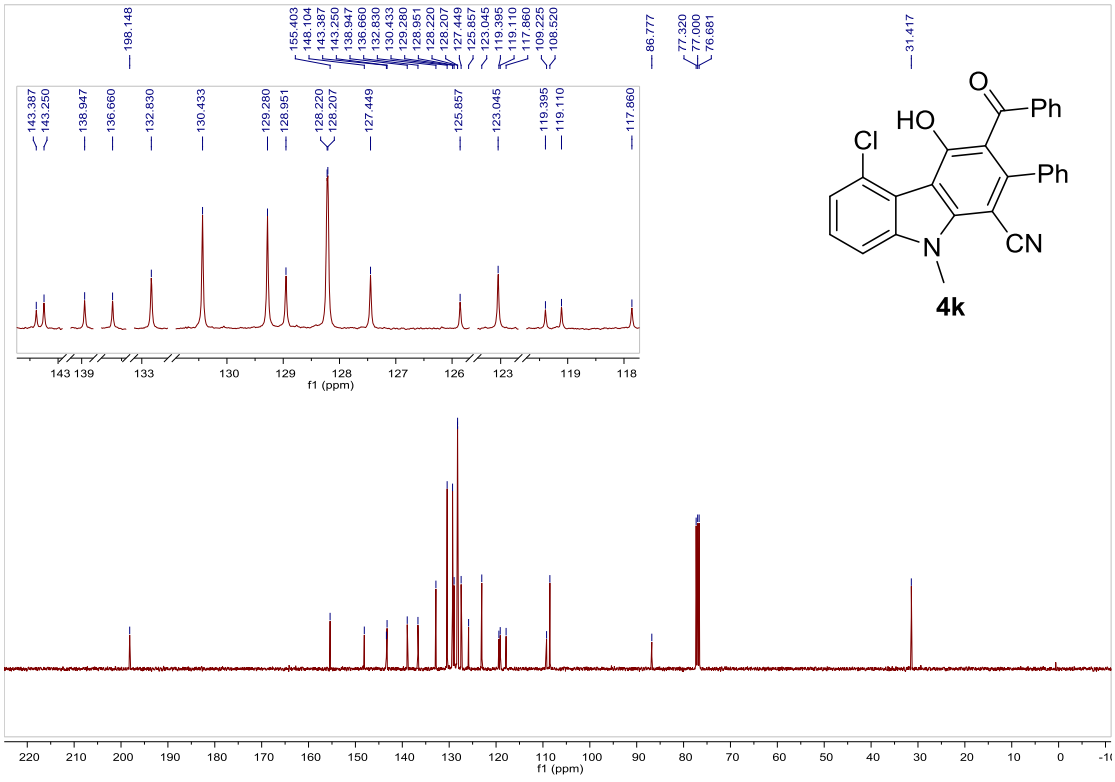

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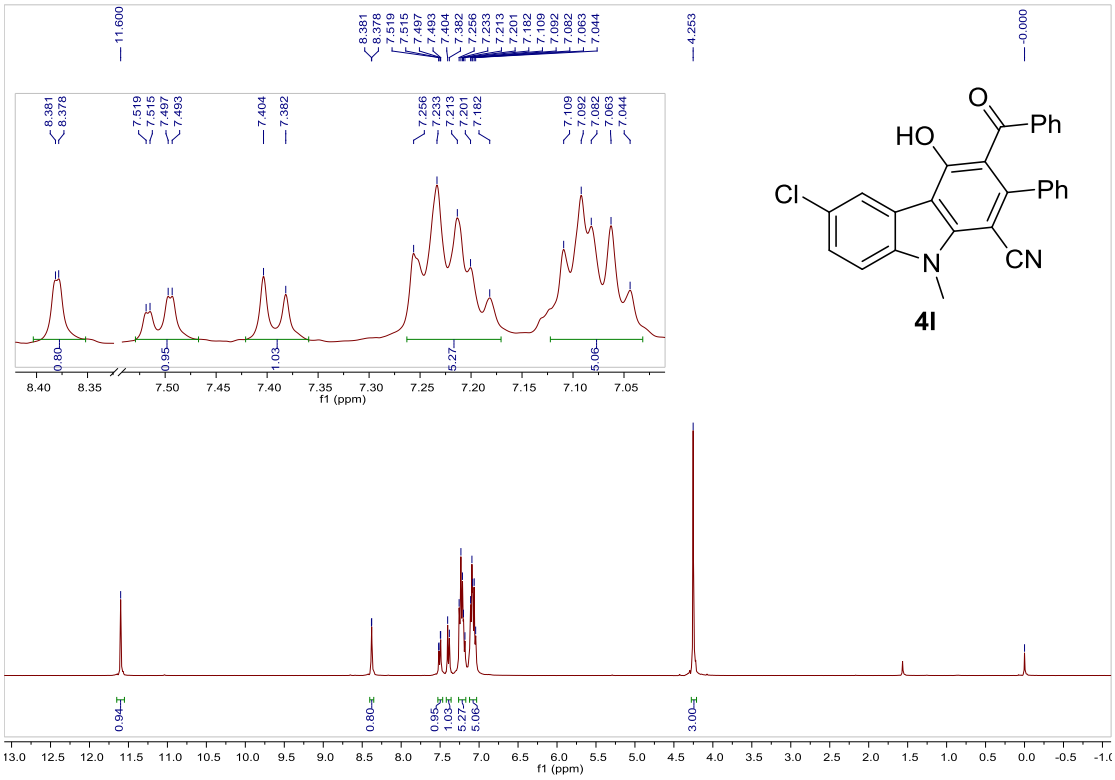

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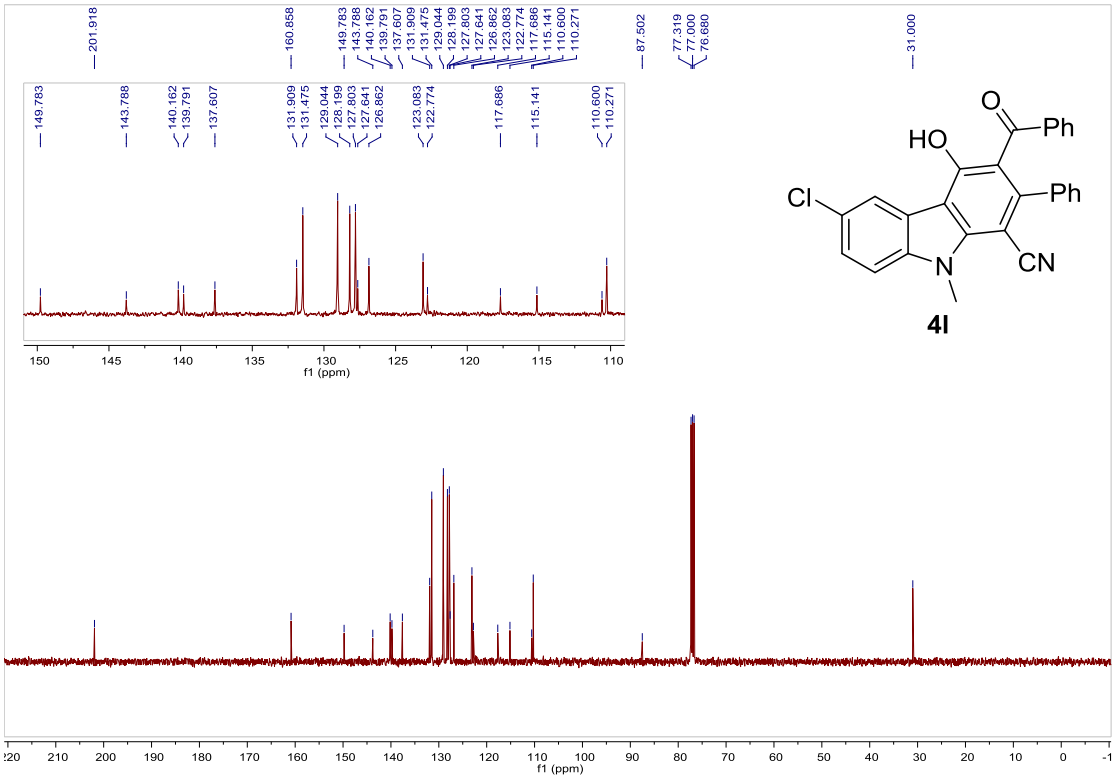

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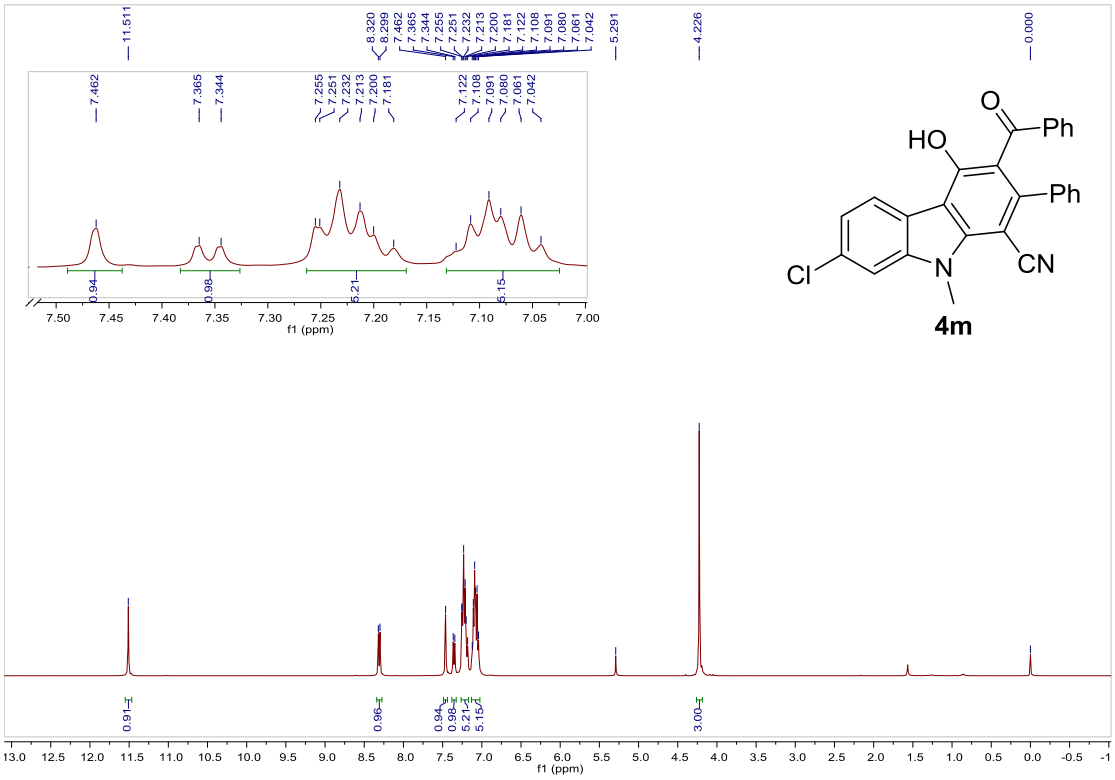

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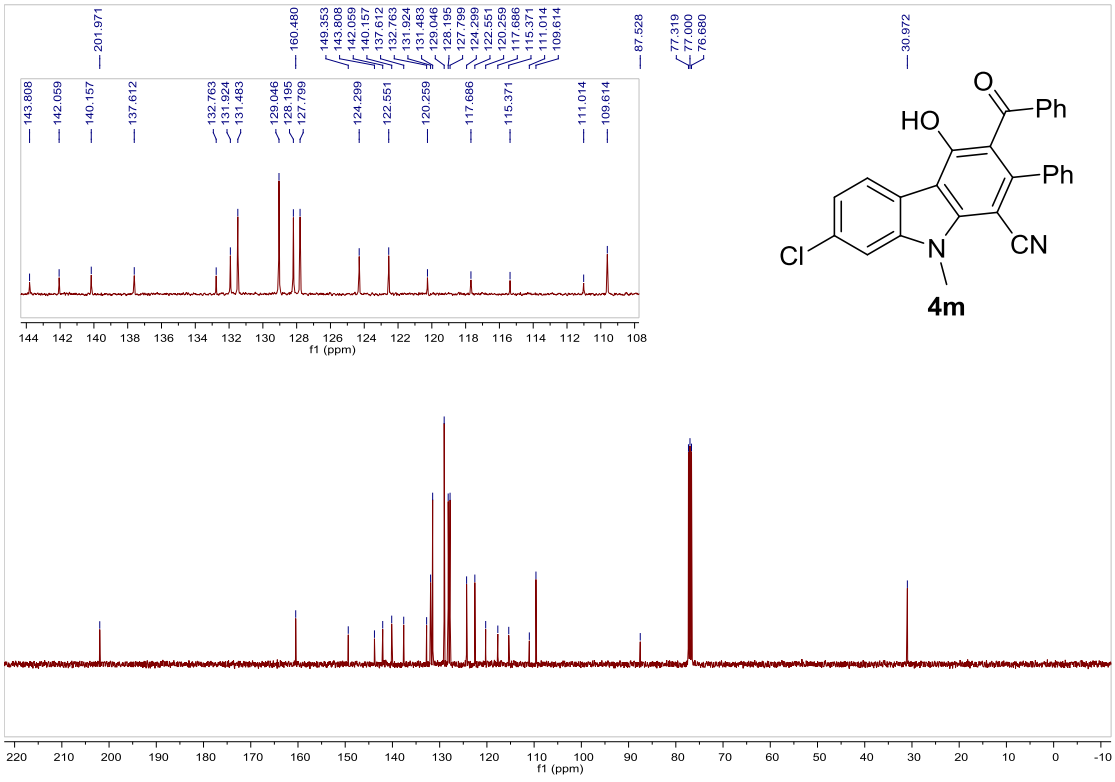

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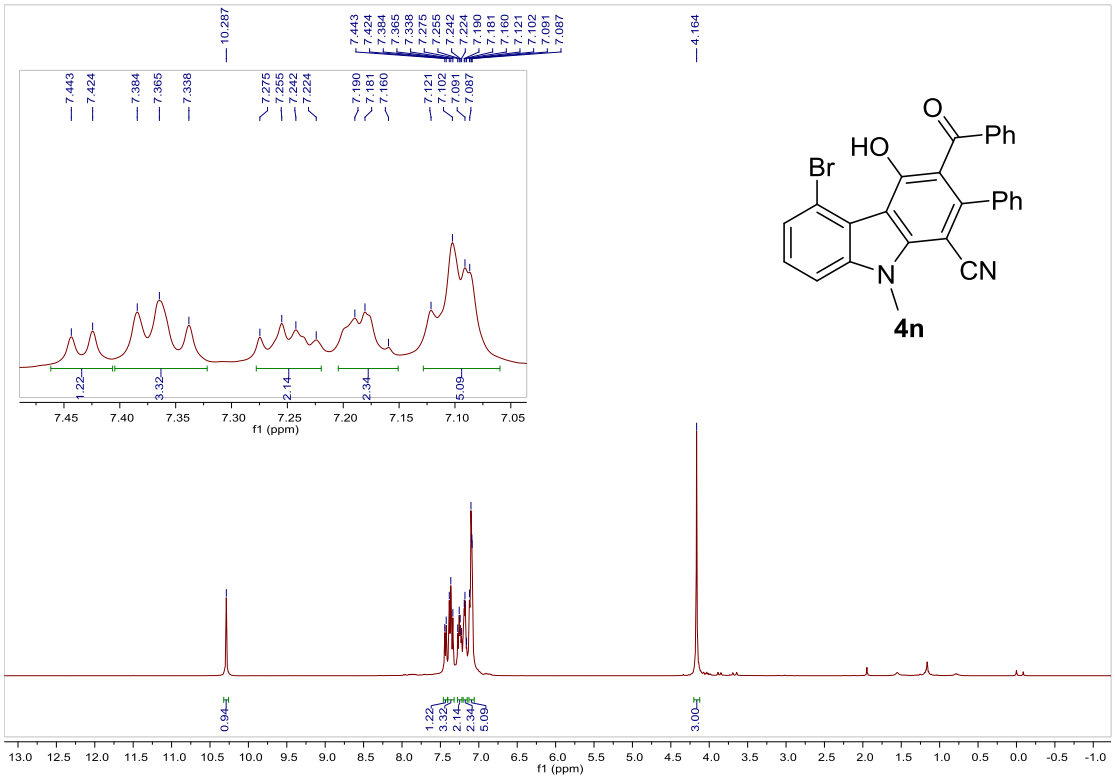

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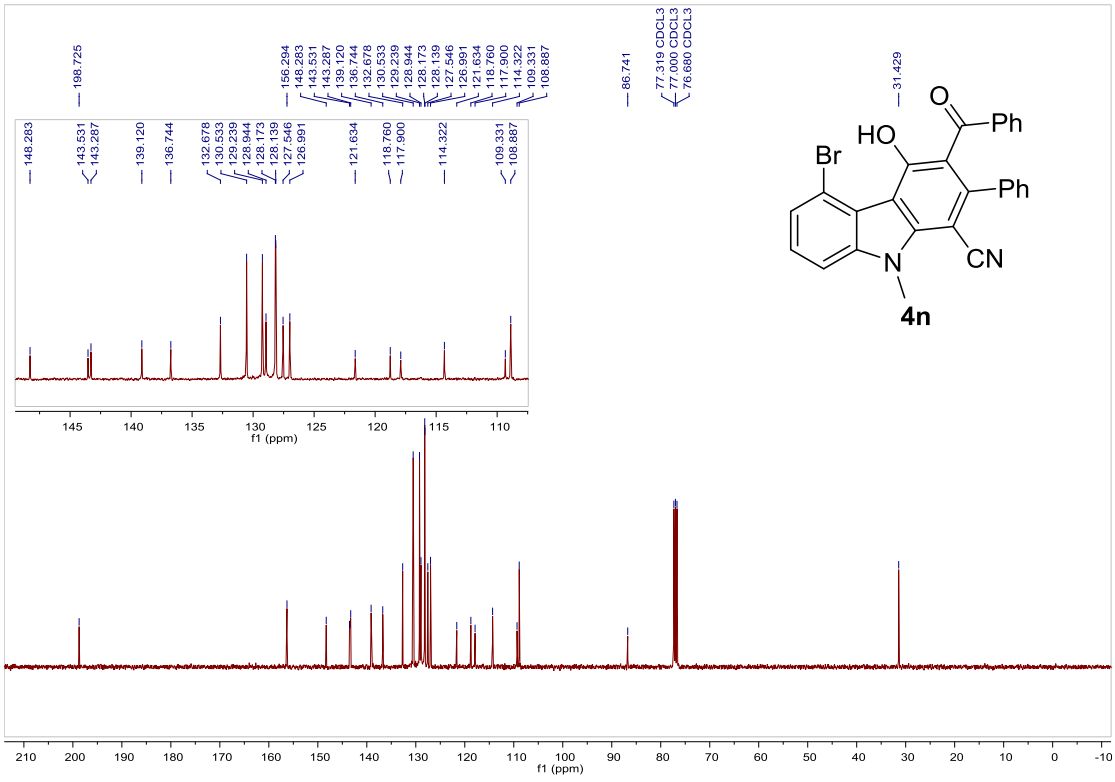

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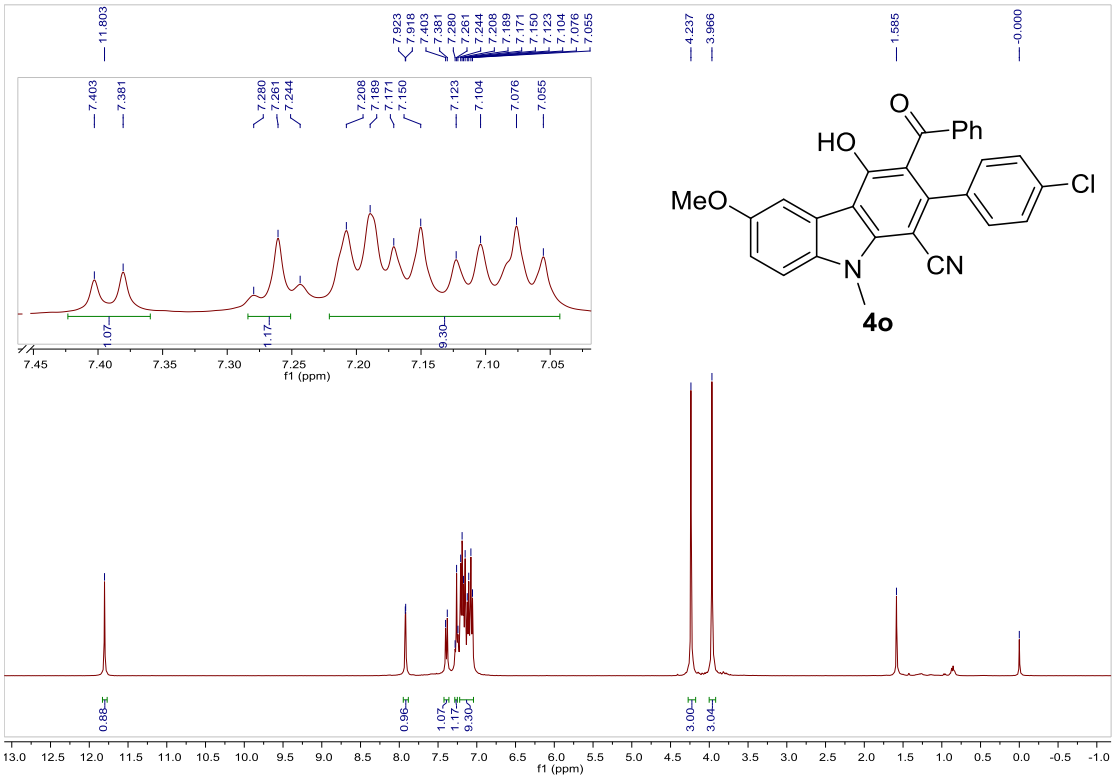

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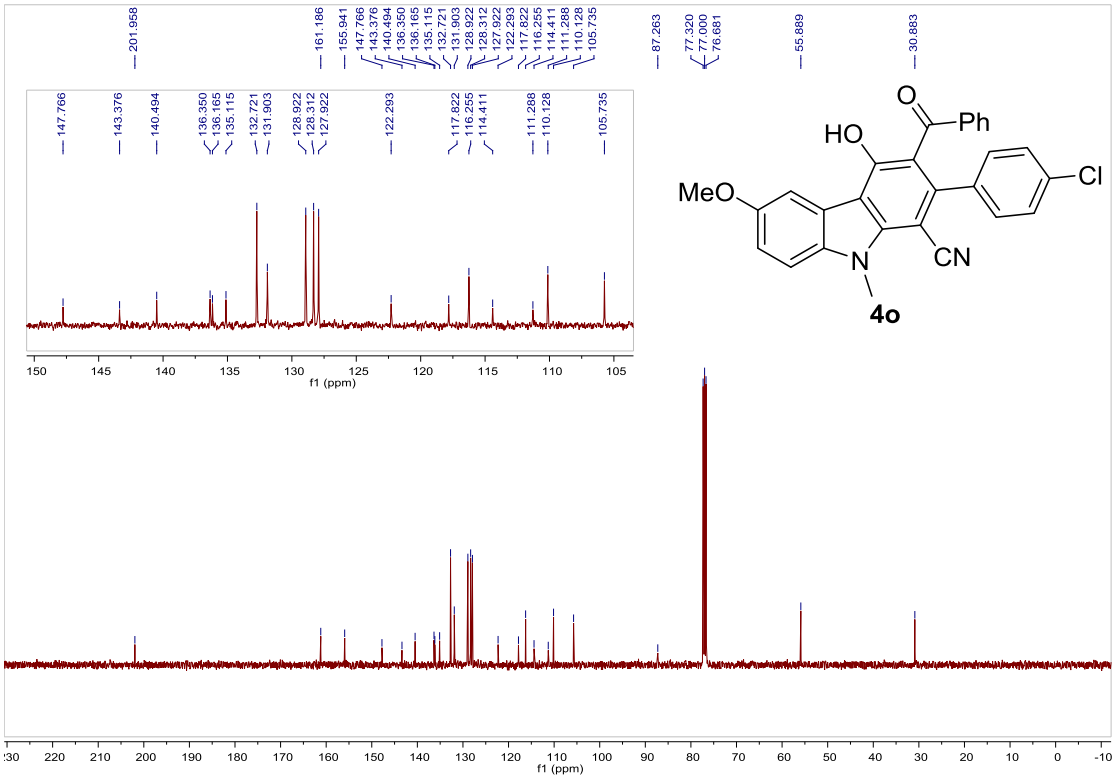

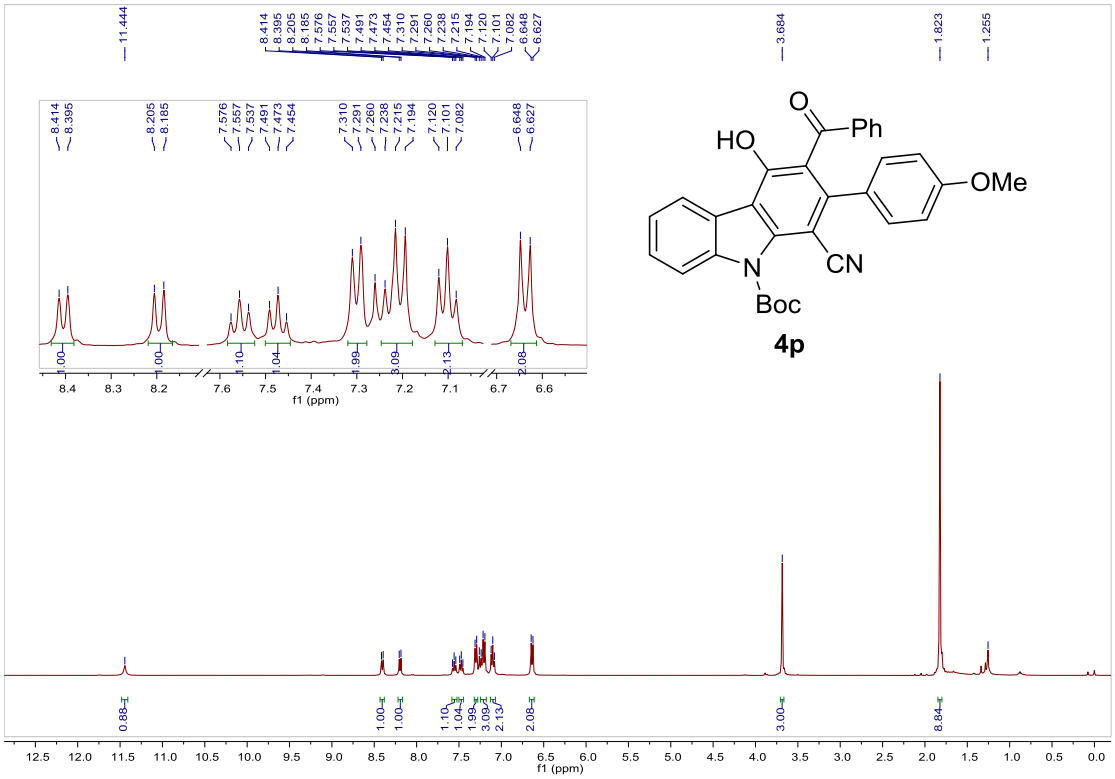
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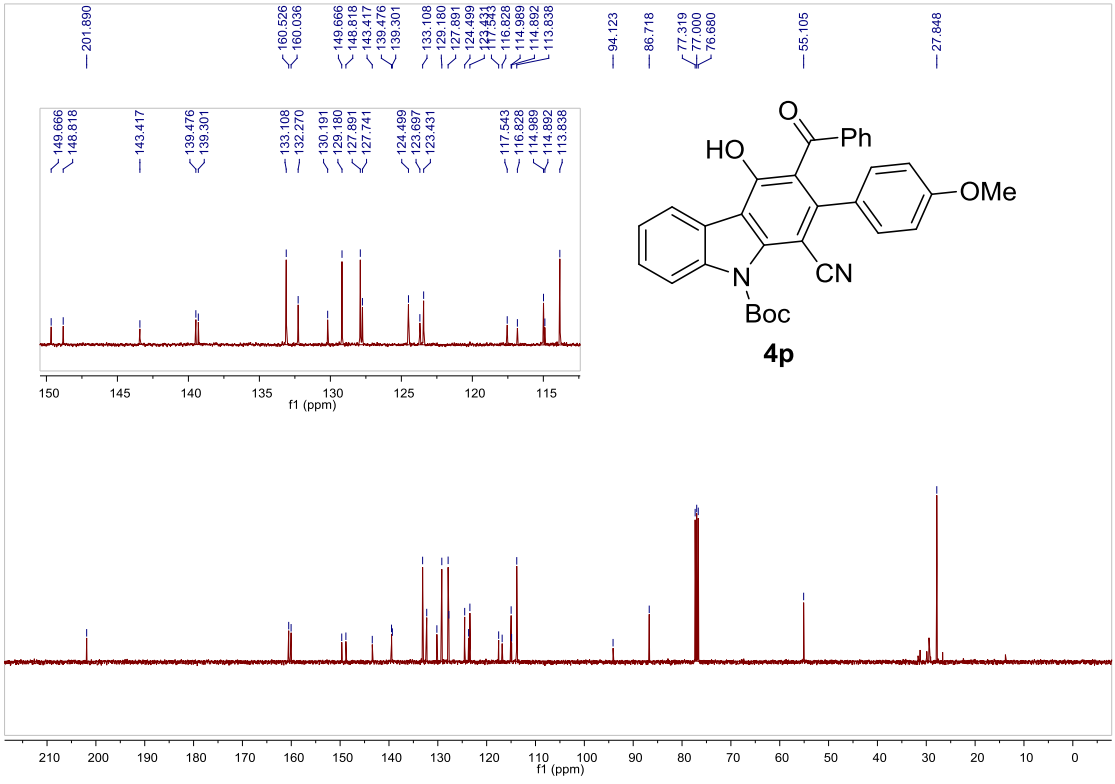
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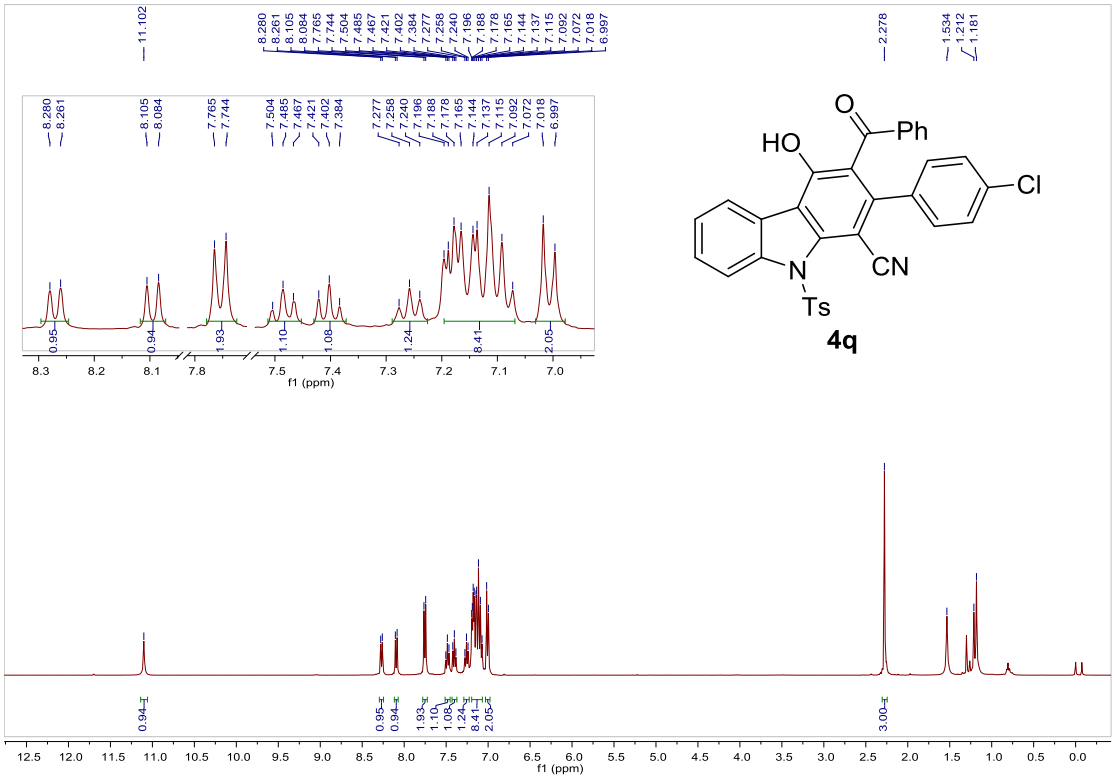
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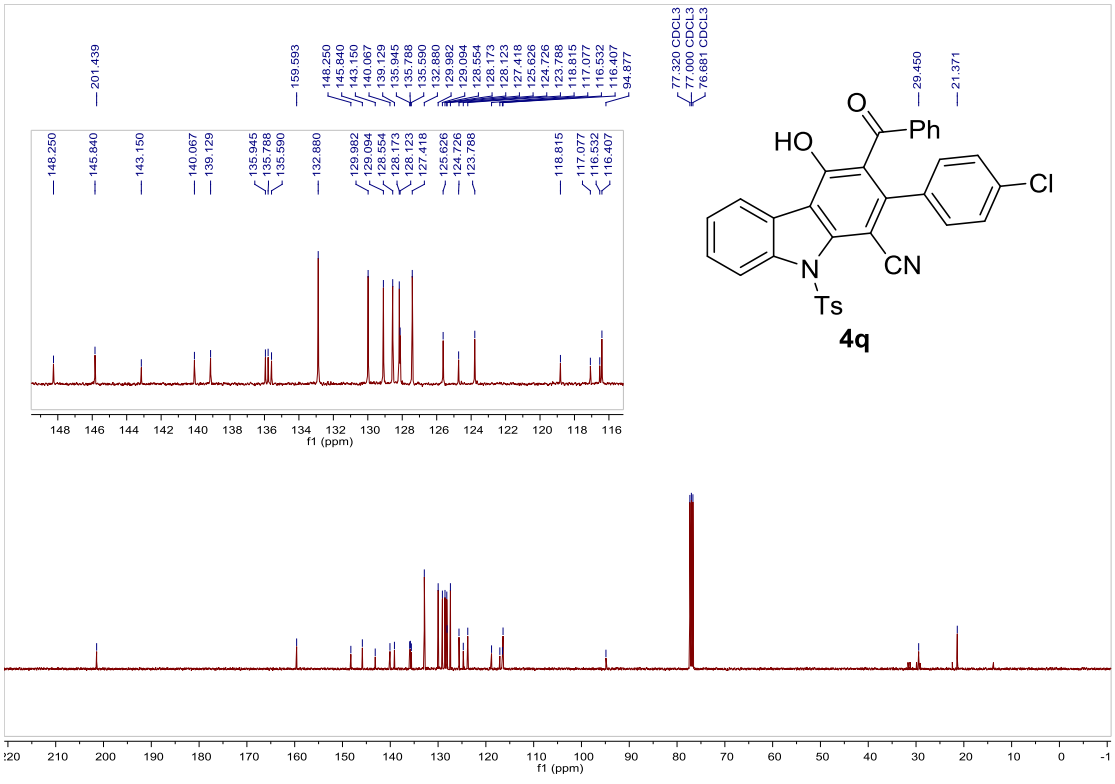
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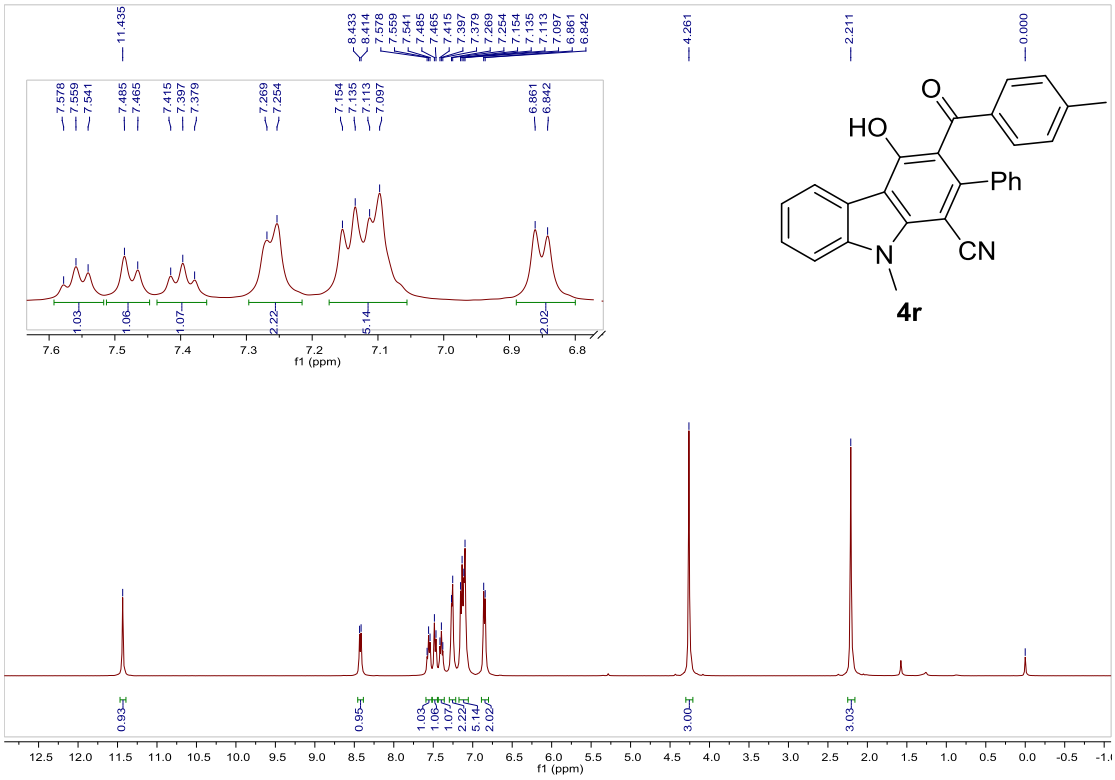
^{1}H NMR (400 MHz, $CDCl_3$)



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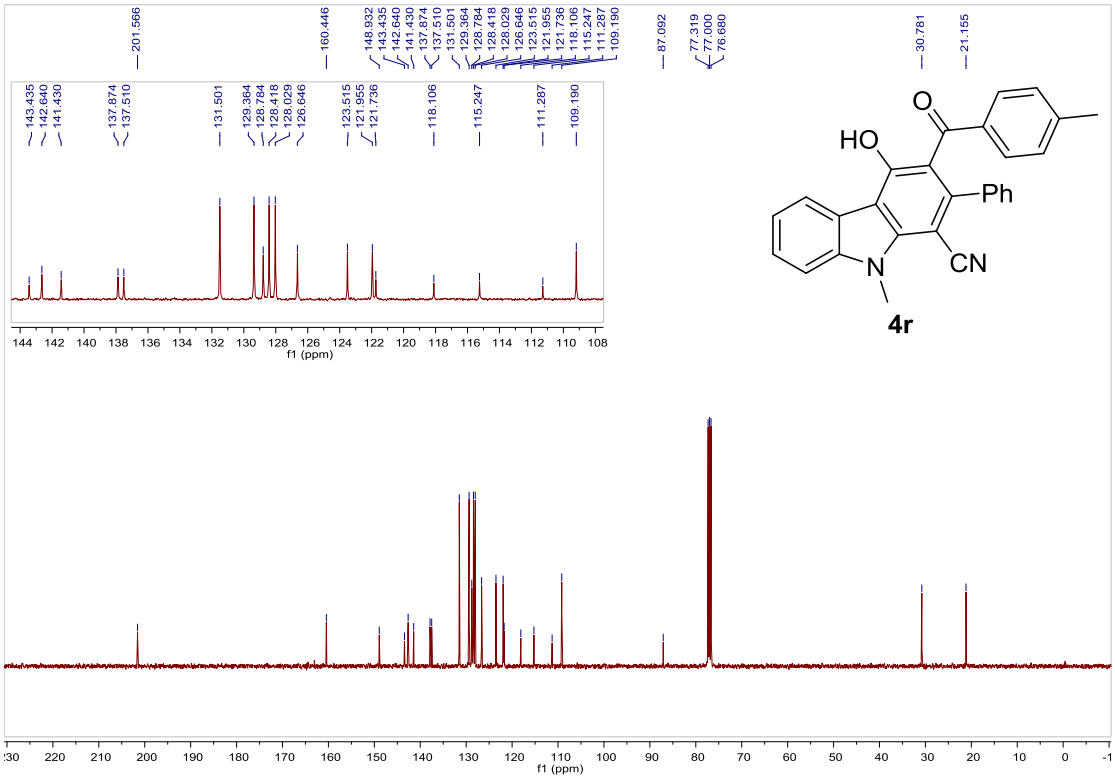

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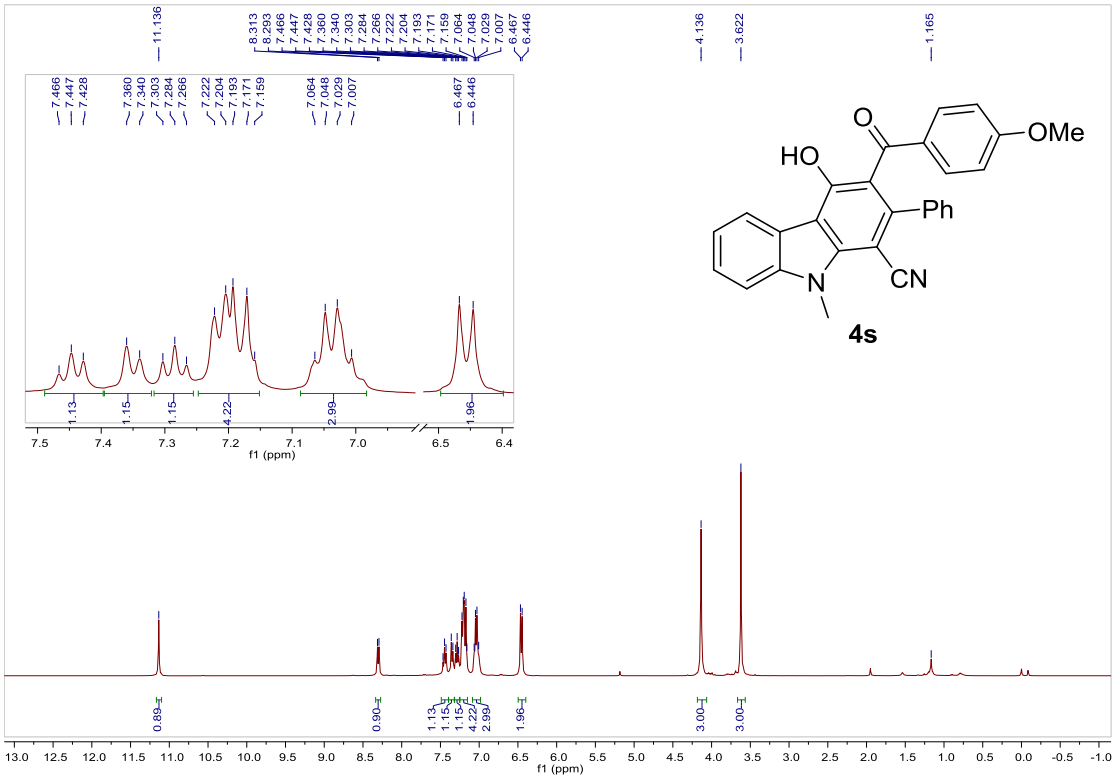

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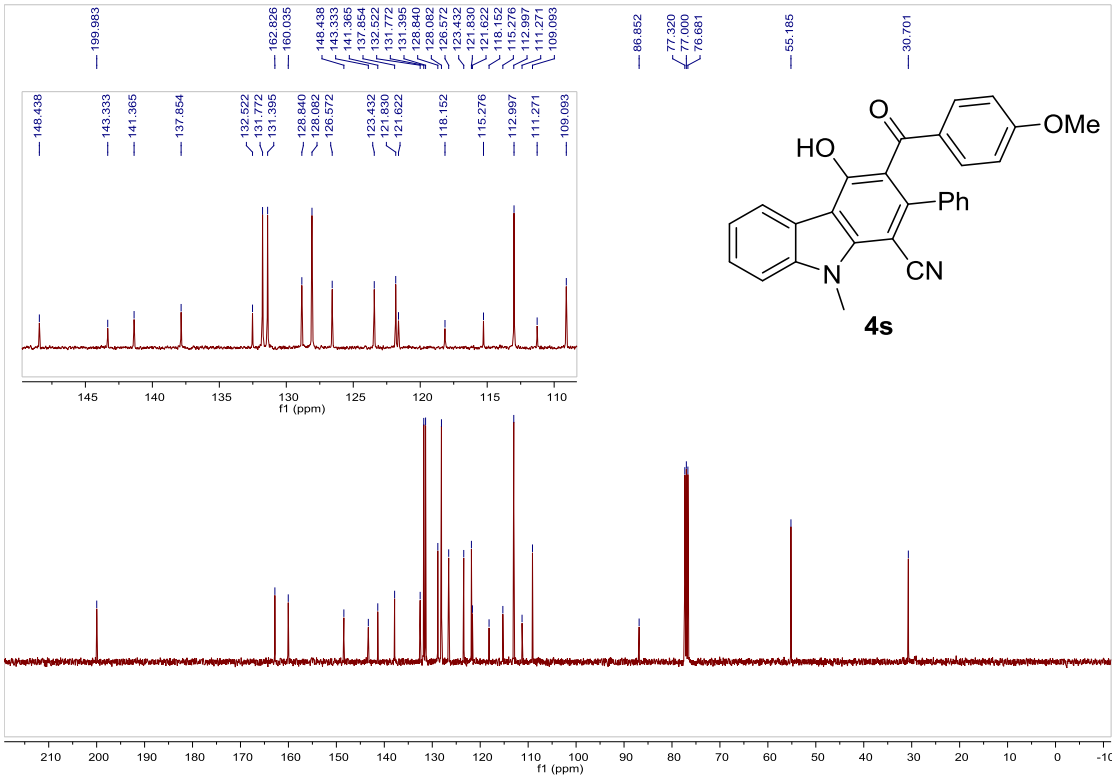

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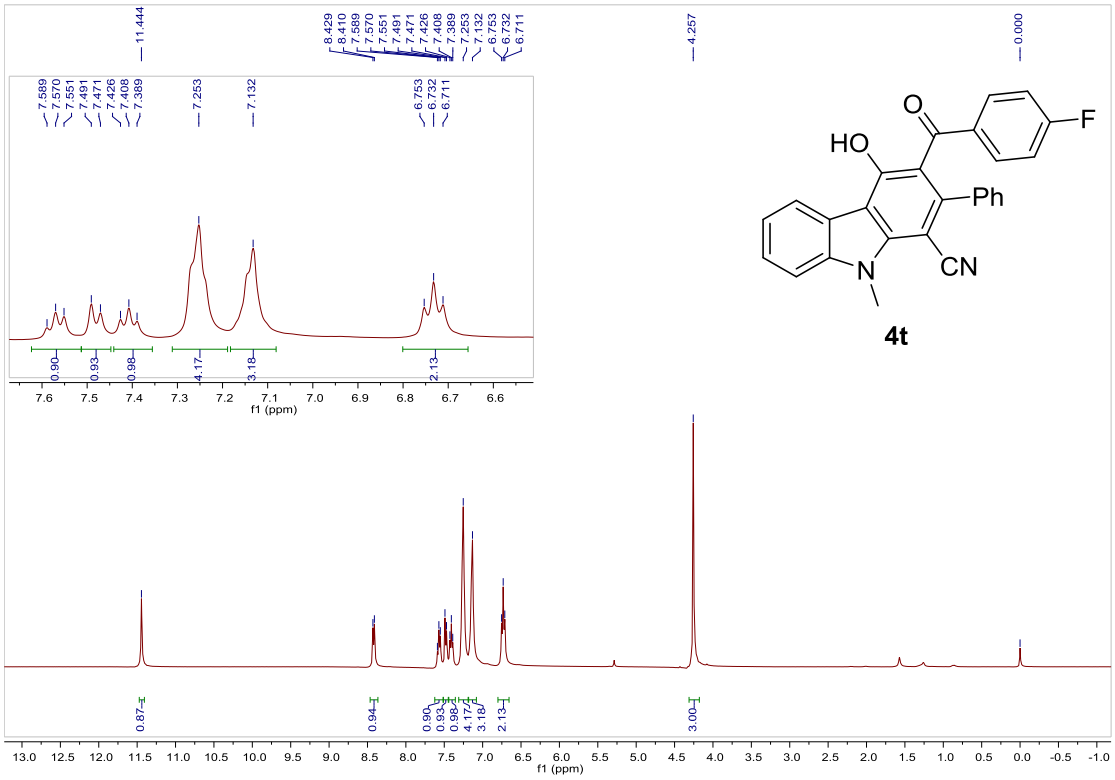

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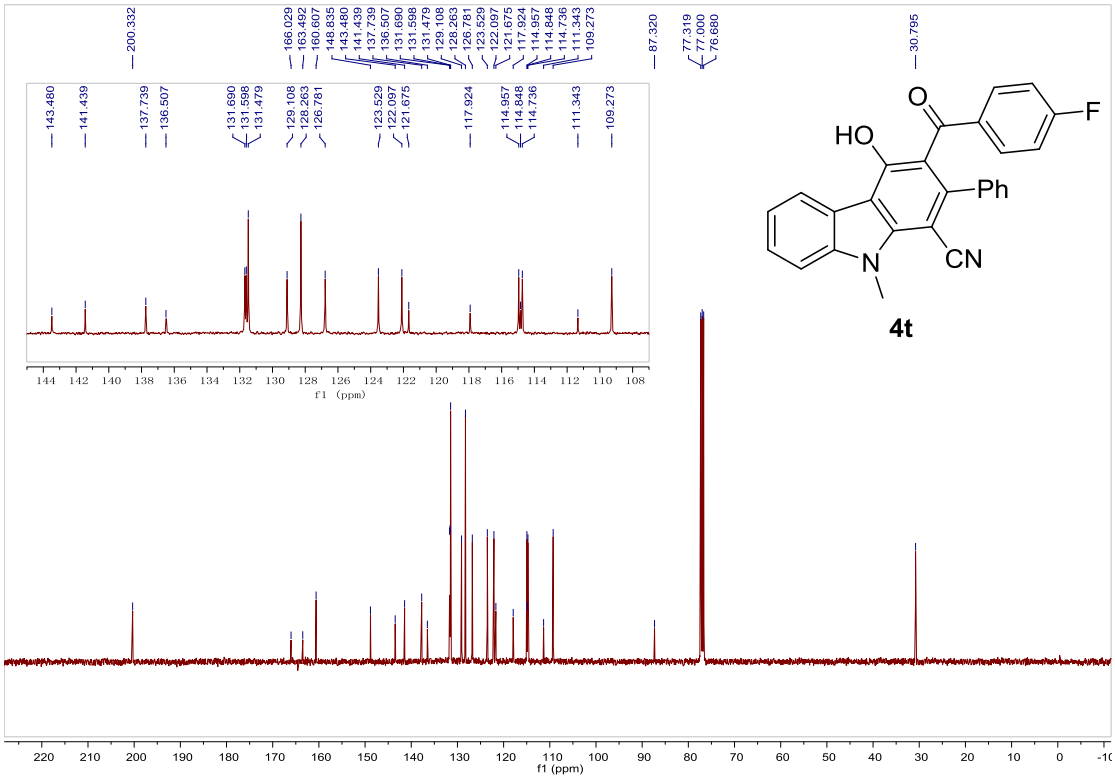
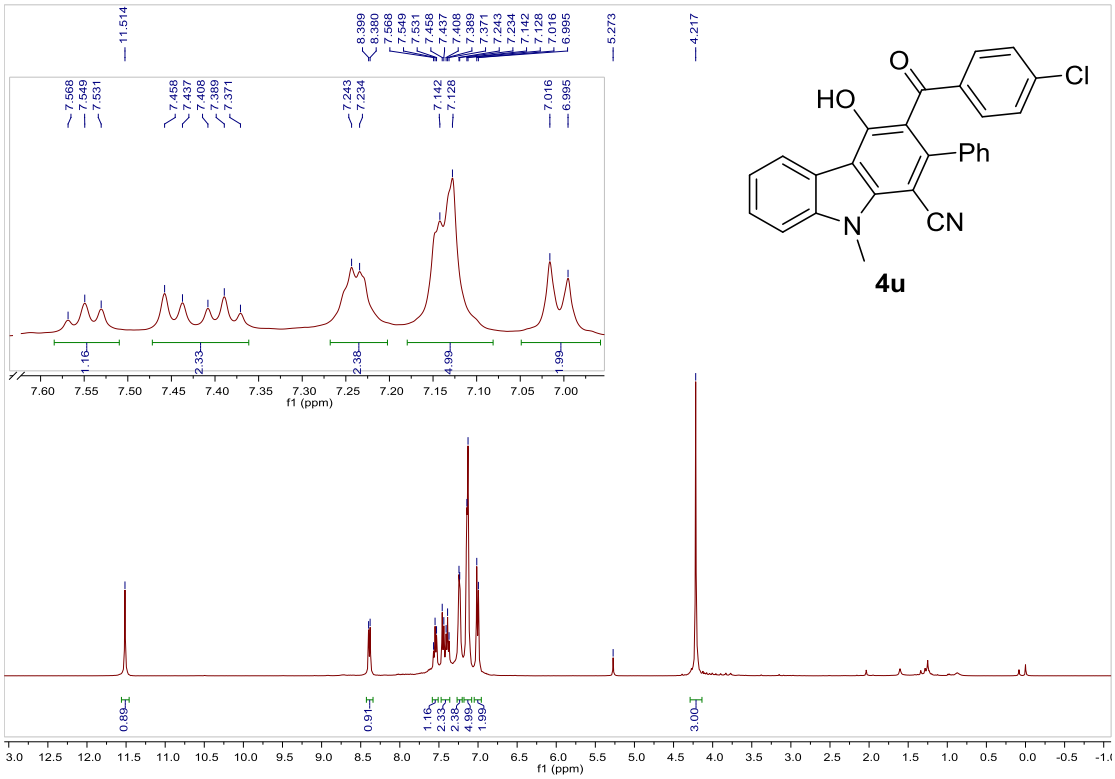
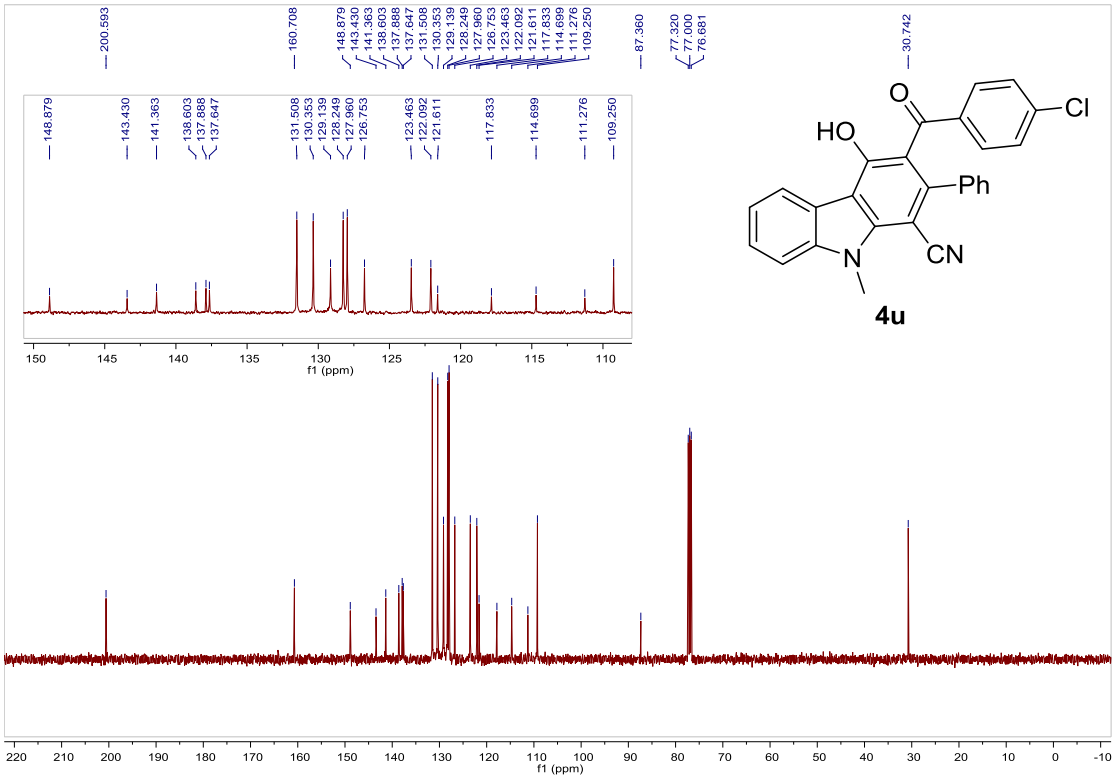


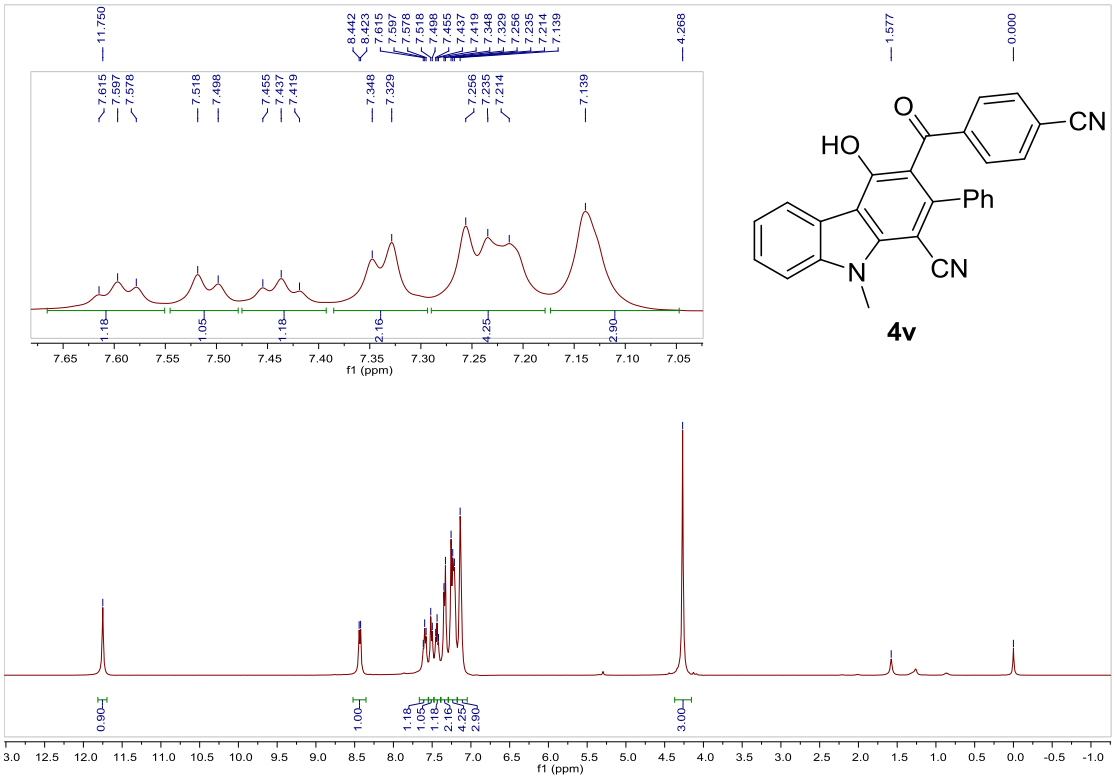
^{1}H NMR (400 MHz, $CDCl_3$)



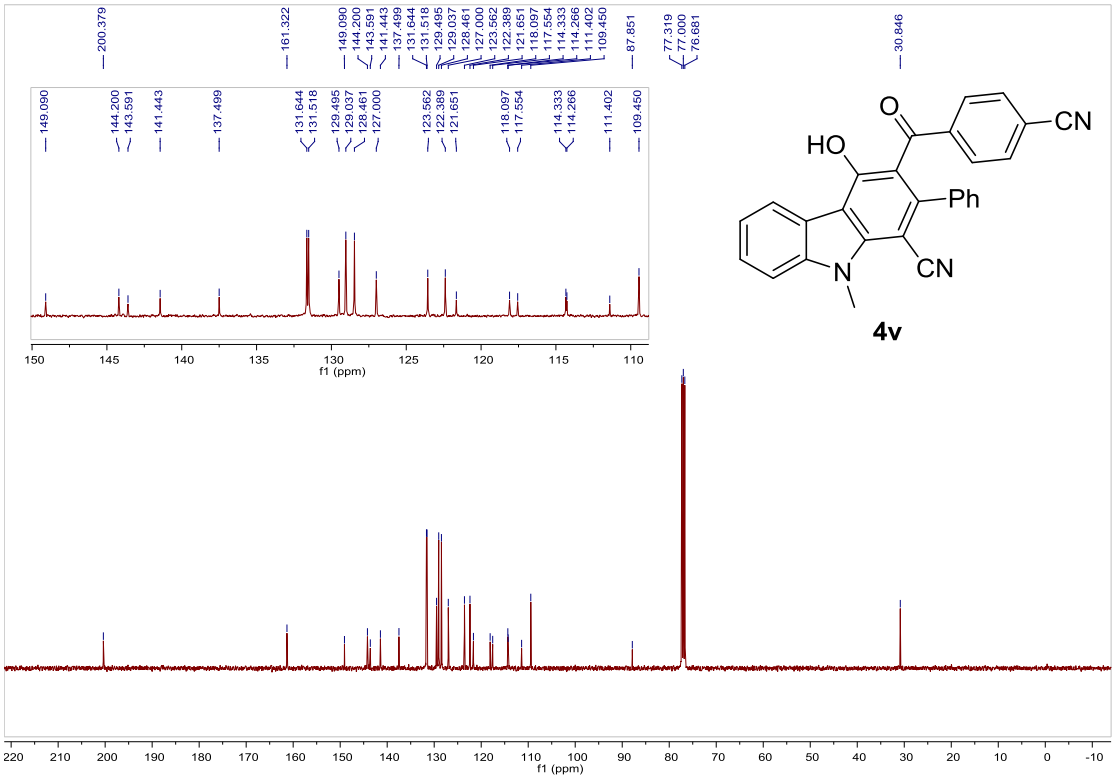
^{13}C NMR (100 MHz, $CDCl_3$)



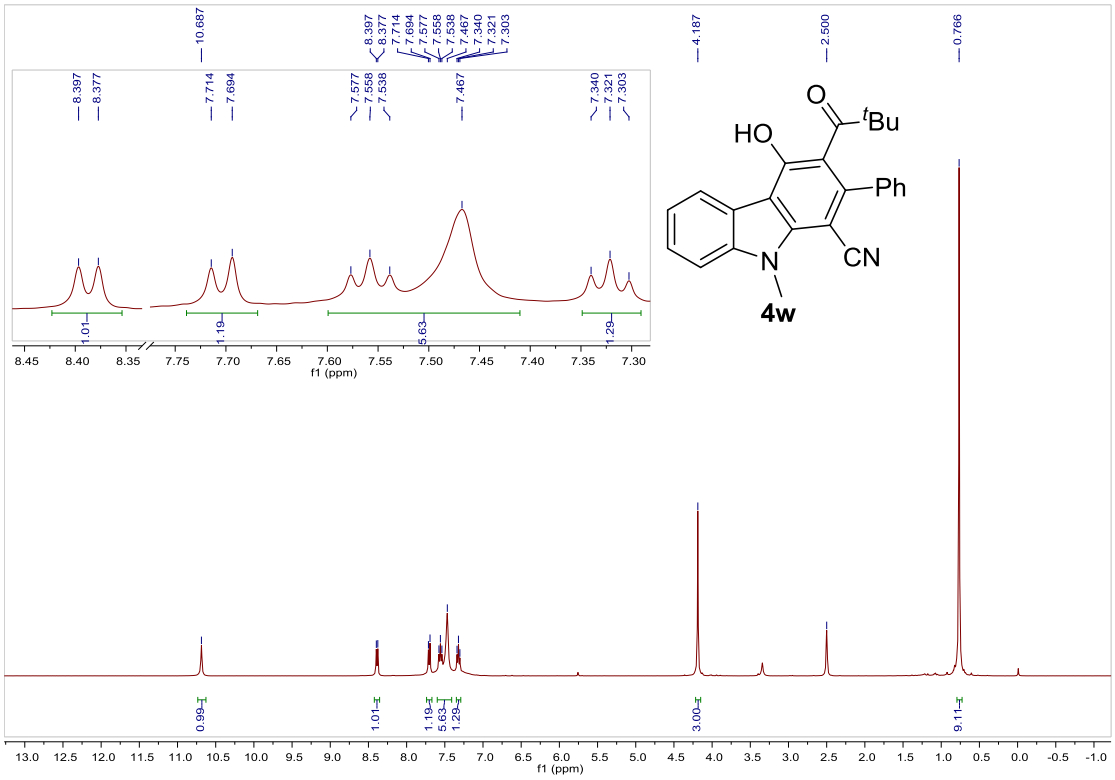
^{1}H NMR (400 MHz, $CDCl_3$)



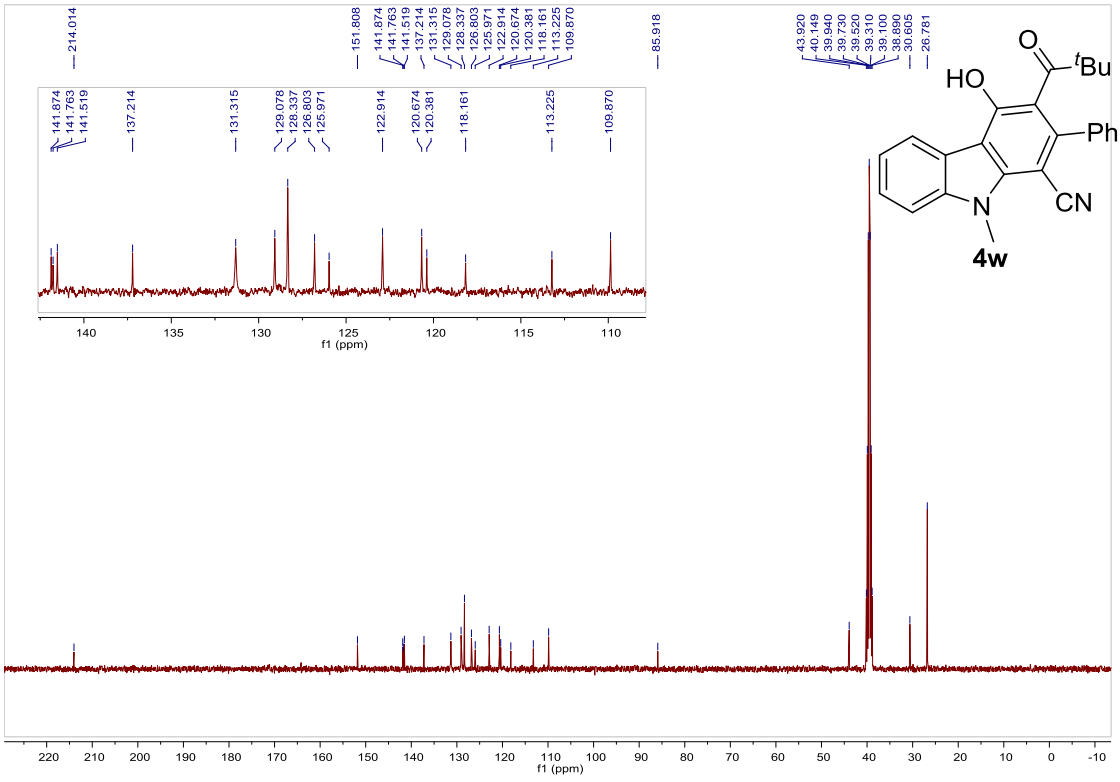
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, d^{6}-DMSO)



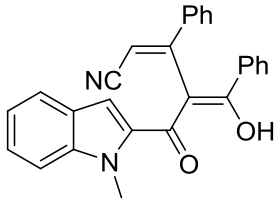
^{13}C NMR (100 MHz, d^{6}-DMSO)



4. X-ray crystallography of compounds 3a

(*4Z*)-5-Hydroxy-4-(1-methyl-1*H*-indole-2-carbonyl)-3,5-diphenylpenta-2,4-dienenitrile (3a, mo-d8v17800-0m)

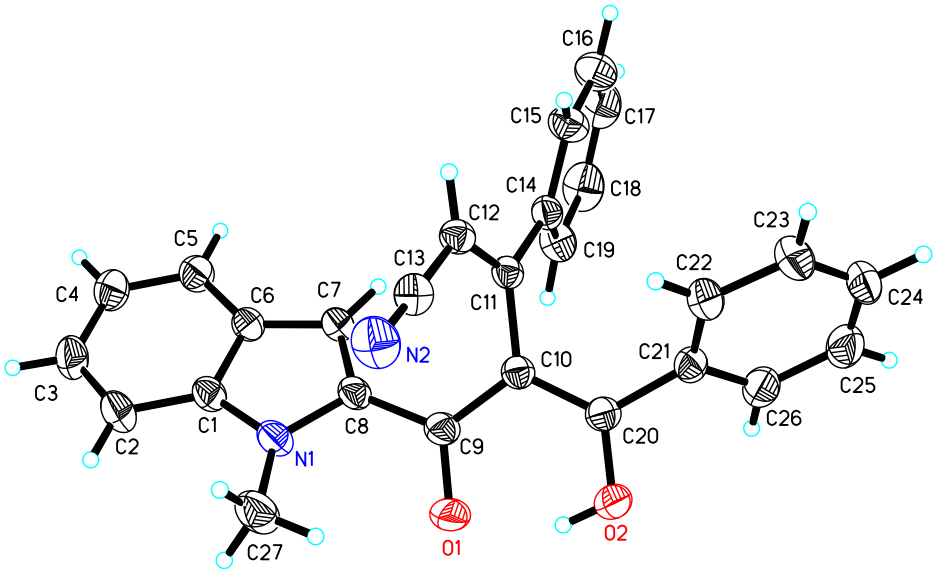
(Ortep ellipsoids are depicted at the 50% level)

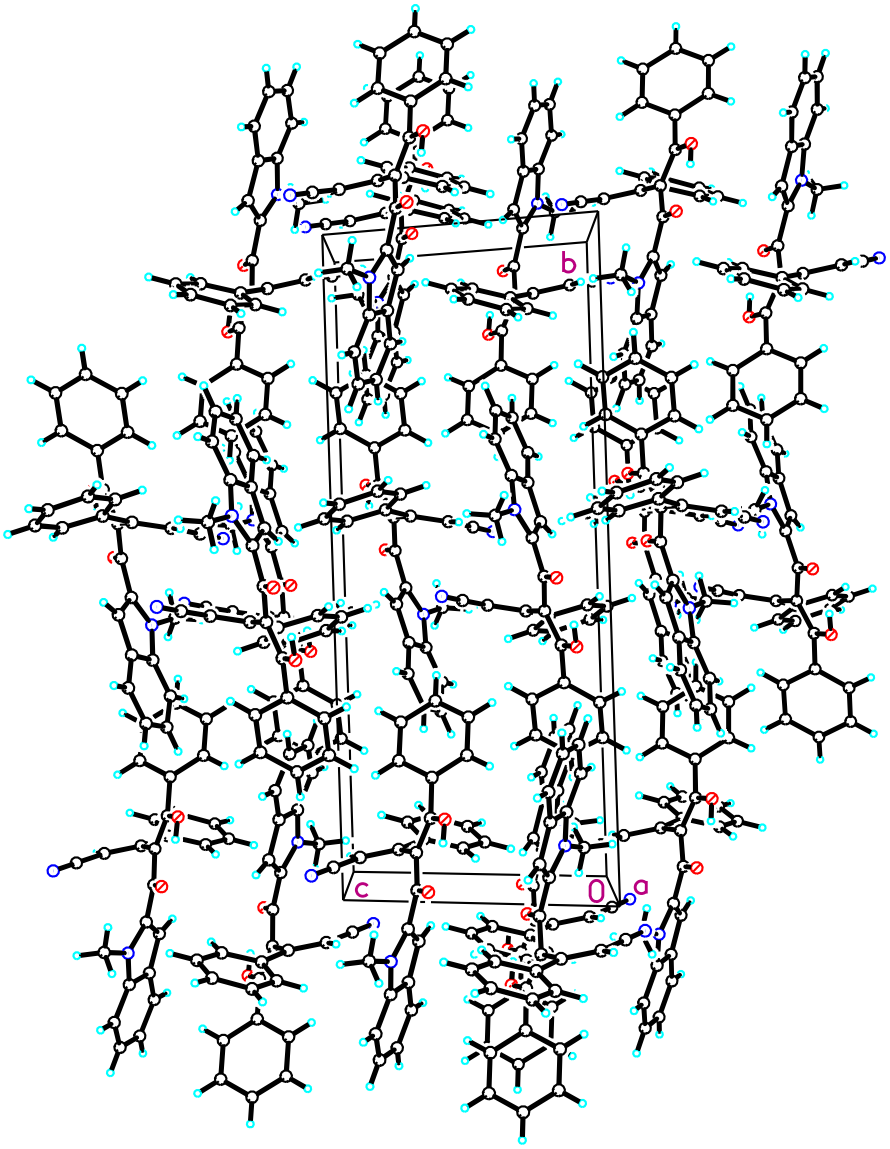


3a

Table S2. Crystal data and structure refinement for **3a**

Identification code	**3a**
Empirical formula	$C_{27}H_{20}N_2O_2$
Formula weight	404.45
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 10.2176(5) Å α= 90 °. b = 22.5674(12) Å β= 117.4990(10) °. c = 10.3343(5) Å γ = 90 °.
Volume	2113.70 (18) $Å^3$
Z, Calculated density	4, 1.271 Mg/m^3
Absorption coefficient	0.081mm^{-1}
F(000)	848
Crystal size	0.160 x 0.120 x 0.100 mm^3
Theta range for data collection	2.863 to 25.999 °.
Index ranges	-12<=h<=12, -27<=k<=27, -12<=l<=12
Reflections collected / Independent reflections	49545/4142 [R(int) = 0.0477]
Completeness to theta = 25.242 °	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6979
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4142 / 0 / 283
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.1097
R indices (all data)	R1 = 0.0576, wR2 = 0.1214
Extinction coefficient	0.019(3)
Largest diff. peak and hole	0.204 and -0.181 e.$Å^{-3}$

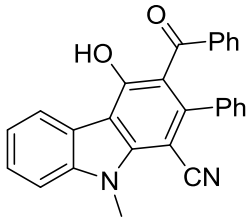

C16
C15
C17
C14
C18
C12
C23
C5
C13
C19
C22
C4
C6
C7
C11
C24
N2
C10
C21
C3
C1
C8
C9
C20
C25
C2
N1
C26
C27
01
02


b
c
0
a

5. X-ray crystallography of compounds 4a

3-benzoyl-4-hydroxy-9-methyl-2-phenyl-9H-carbazole-1-carbonitrile (4a, d8v17495)

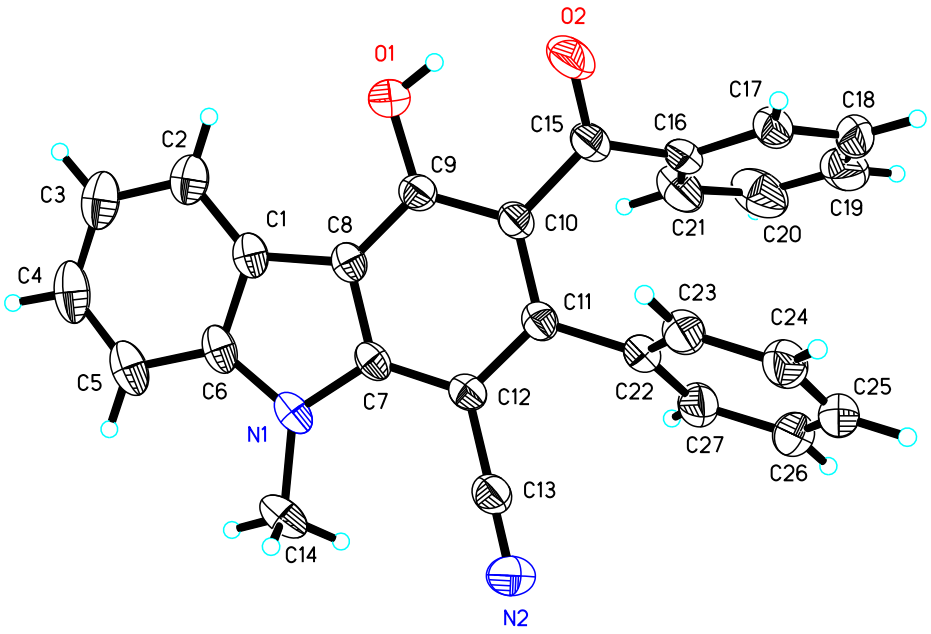
(Ortep ellipsoids are depicted at the 50% level)

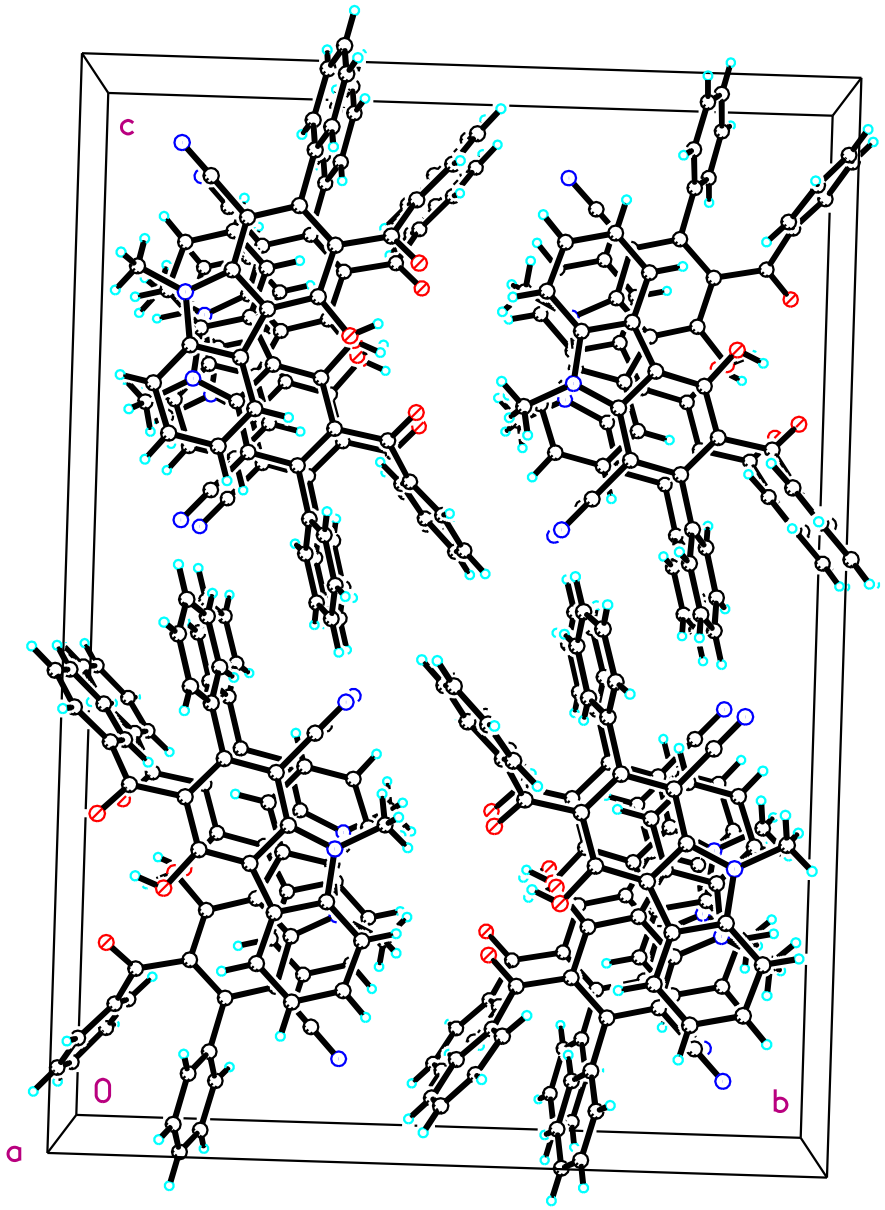


4a

Table S3. Crystal data and structure refinement for **4a**

Identification code	**4a**
Empirical formula	$C_{27}H_{18}N_2O_2$
Formula weight	402.43
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P b c a
Unit cell dimensions	a = 6.9632(9) Å α= 90 °. b = 20.434(3) Å β= 90 °. c = 28.769(3) Å γ = 90 °.
Volume	4093.5(9) $Å^3$
Z, Calculated density	8, 1.306 Mg/m^3
Absorption coefficient	0.083 mm^{-1}
F(000)	1680
Crystal size	0.20 x 0.14 x 0.08 mm^3
Theta range for data collection	2.832 to 25.499 °.
Index ranges	-8<=h<=8, -24<=k<=24, -34<=l<=34
Reflections collected / Independent reflections	82706/3805 [R(int) = 0.0904]
Completeness to theta = 25.242 °	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5620
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3805 / 0 / 283
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.1130
R indices (all data)	R1 = 0.0605, wR2 = 0.1283
Extinction coefficient	0.0074(10)
Largest diff. peak and hole	0.181 and -0.147 e.$Å^{-3}$

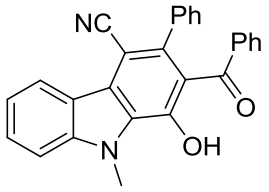

O2
O1
C17
C18
C15
C16
C2
C9
C3
C1
C8
C10
C21
C20
C19
C4
C11
C23
C24
C5
C6
C7
C12
C22
C25
N1
C27
C26
C13
C14
N2


c
0
a
b

6. X-ray crystallography of compounds 4a’

2-benzoyl-1-hydroxy-9-methyl-3-phenyl-9H-carbazole-4-carbonitrile (4a’, d8v18043)

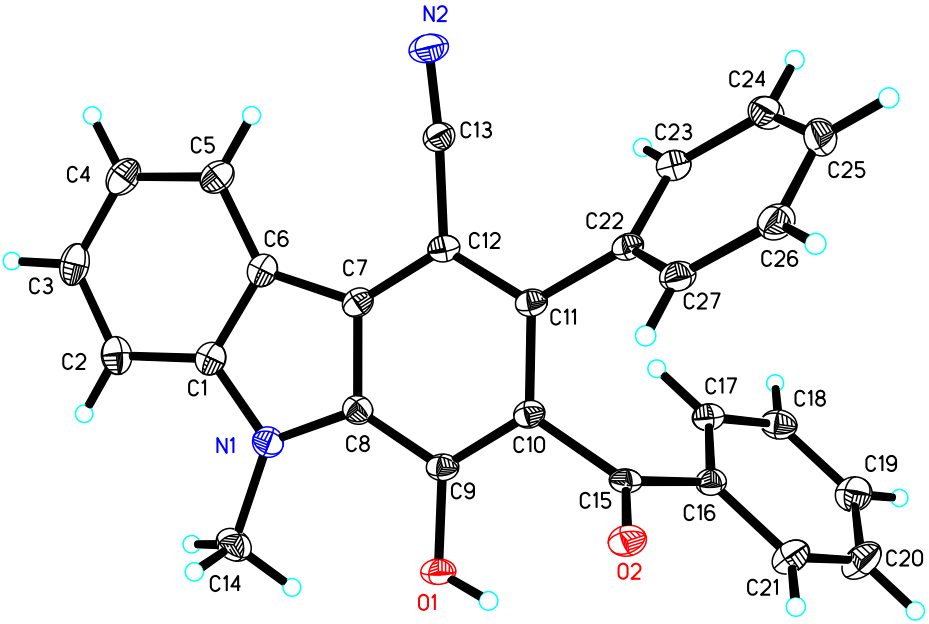
(Ortep ellipsoids are depicted at the 50% level)

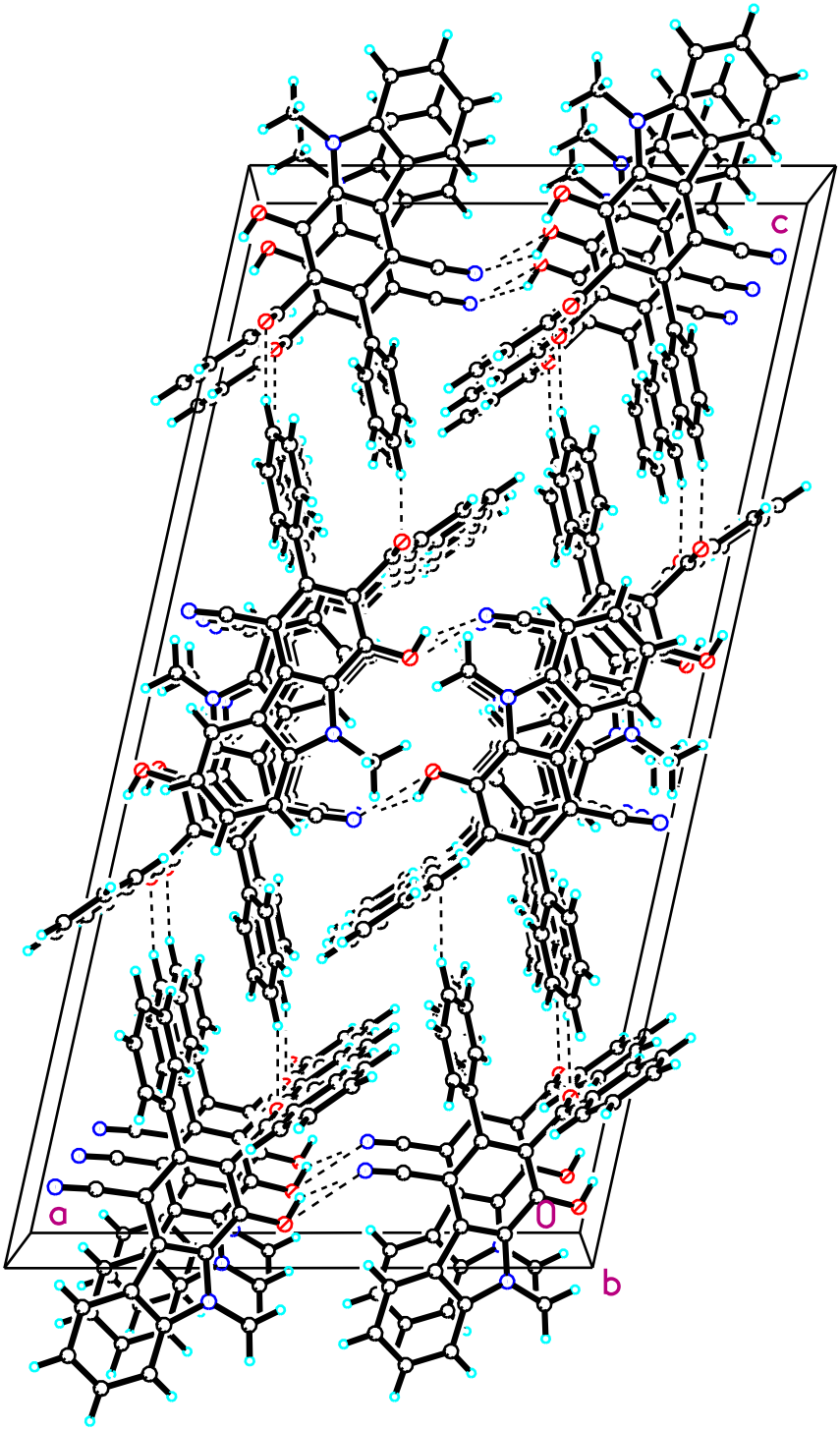


4a'

Table S4. Crystal data and structure refinement for **4a’**

Identification code	**4a’**
Empirical formula	$C_{27}H_{18}N_2O_2$
Formula weight	402.43
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 16.4009(8) Å α= 90 °. b = 7.8236(4) Å β= 102.498(3) °. c = 31.4855(17) Å γ = 90 °.
Volume	3944.3(4) $Å^3$
Z, Calculated density	8, 1.355 Mg/m^3
Absorption coefficient	0.086 mm^{-1}
F(000)	1680
Crystal size	0.200 x 0.170 x 0.130 mm^3
Theta range for data collection	2.602 to 26.000 °.
Index ranges	-19<=h<=20, -9<=k<=9, -38<=l<=38
Reflections collected / Independent reflections	73827/3876[R(int) = 0.0567]
Completeness to theta = 25.242 °	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6668
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3876 / 0 / 283
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1154
R indices (all data)	R1 = 0.0497, wR2 = 0.1199
Extinction coefficient	0.0028(5)
Largest diff. peak and hole	0.248 and -0.240 e.$Å^{-3}$


N2
C13
C24
C23
C25
C5
C4
C22
C12
C6
C7
C26
C3
C27
C11
C2
C1
C17
C18
N1
C8
C10
C19
C9
C15
C16
C14
O2
C20
O1
C21


c
a
0
b