

Supporting Information

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

Yajie Yang, Lingkai Kong, Mengdan Wang, Yang Yuan, Qihai Tao and Yanzhong Li*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, 500 Dongchuan Road, Shanghai, 200241, China

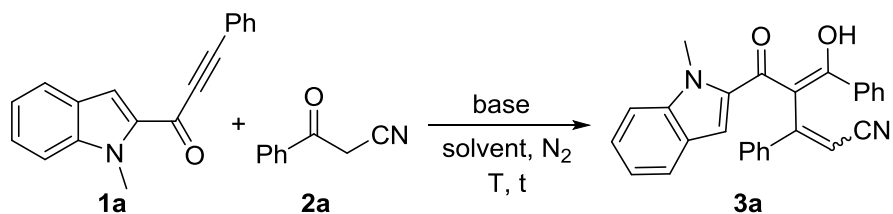
Fax: (+86) 021-54340096, E-mail: yzli@chem.ecnu.edu.cn

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1. Optimization of 3a Conditions

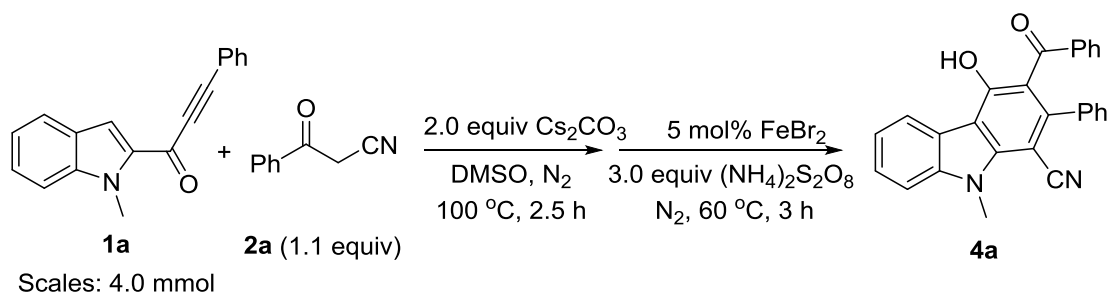
Table S1 Optimization of reaction conditions for the synthesis of **3a**



entry	solvent	base (equiv)	T	t	yield ^a
1	DMSO	3.0 Cs ₂ CO ₃	100 °C	2.5 h	77 %
2	DMSO	1.5 Cs ₂ CO ₃	100 °C	2.5 h	74 %
3	DMSO	2.0 Cs₂CO₃	100 °C	2.5 h	90 %
4	DMSO	2.0 Cs ₂ CO ₃	80 °C	2.0 h	75 %
5	DMSO	2.0 K ₂ CO ₃	100 °C	2.5 h	73 %
6	DMSO	2.0 DABCO	100 °C	2.5 h	--
7	DMAc	2.0 Cs ₂ CO ₃	100 °C	2.5 h	79 %
8	DMF	2.0 Cs ₂ CO ₃	100 °C	2.5 h	72 %
9	tol	2.0 Cs ₂ CO ₃	100 °C	2.5 h	70 %

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

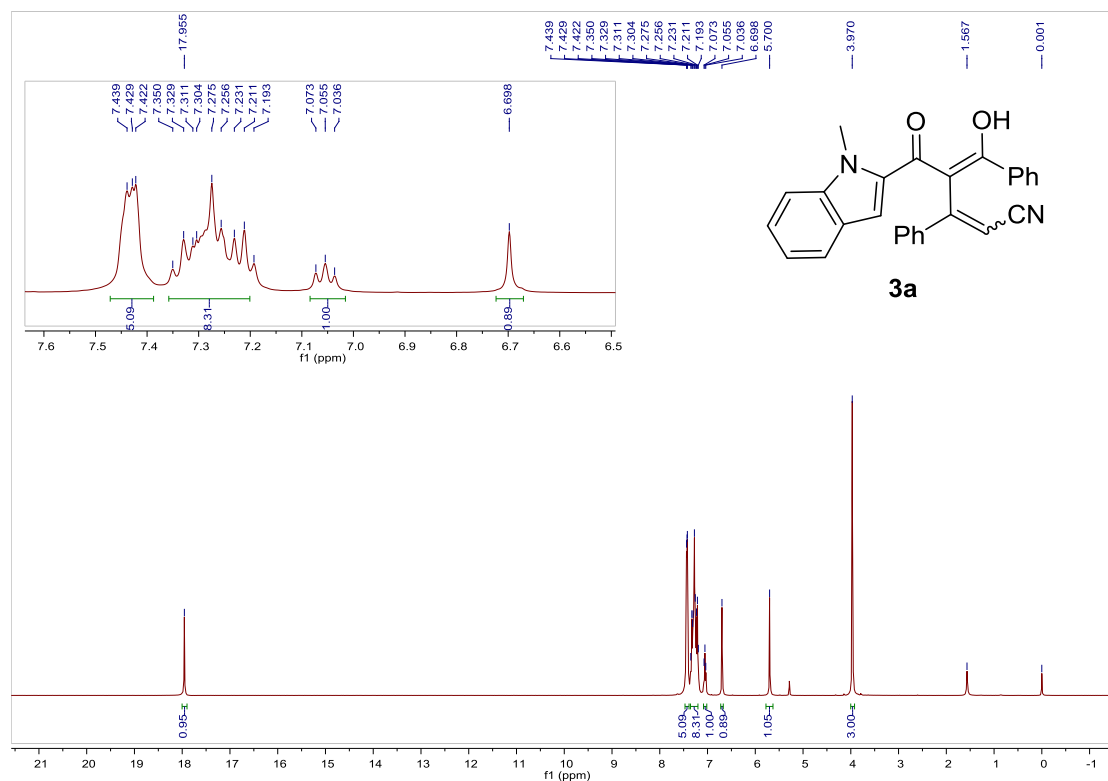
2. Gram Scale



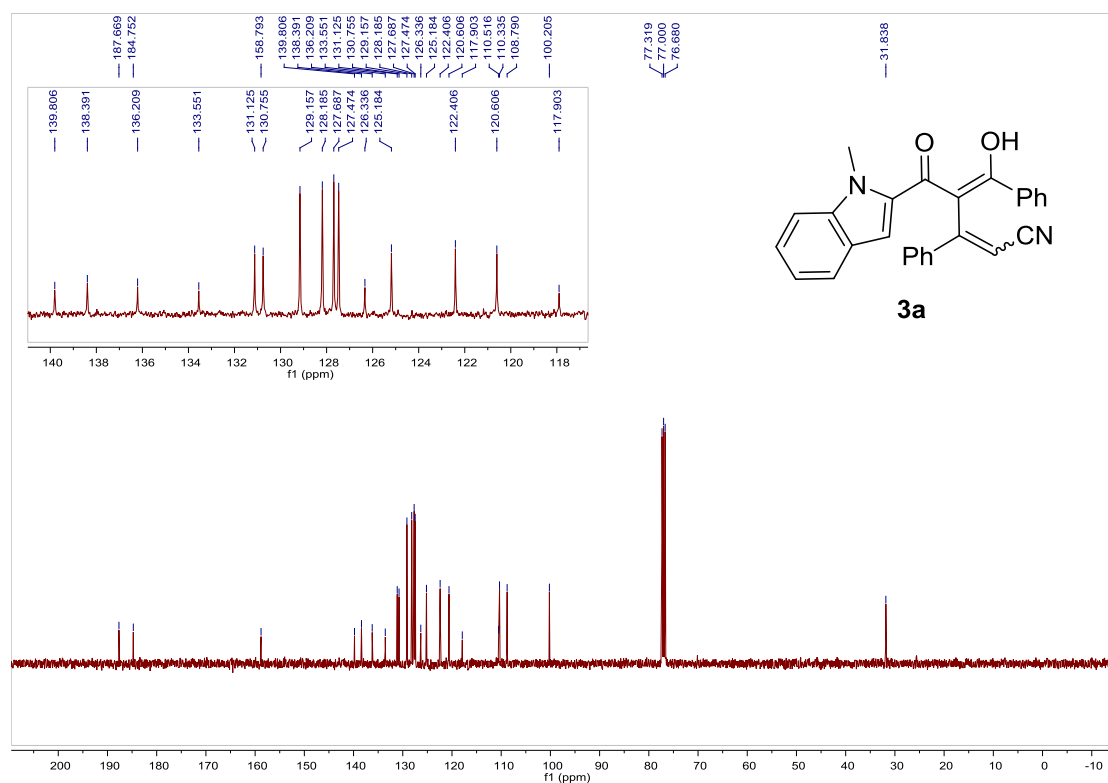
In a Schlenk tube, indolyl alkynyl ketones **1a** (4.0 mmol, 1.04 g), benzoyl acetonitrile **2a** (4.4 mmol, 0.64 g), Cs_2CO_3 (8.0 mmol, 2.61 g) and DMSO (40 mL) were stirred at 100 °C under N_2 . After 2.5 h, FeBr_2 (0.2 mmol, 43.13 mg) and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (12.0 mmol, 2.74 g) were added to the reaction mixture. After the completion of the addition, the reaction mixture was allowed to react at 60 °C 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

^1H NMR (400 MHz, CDCl_3)



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



Chemical structure of 4a': Nc1ccc2c(c1)c(c3ccccc3c2C(=O)O)c4ccccc4

¹H NMR spectrum (CDCl₃):

Chemical Shift (ppm)	Integration
~11.049	0.85
~8.766, 8.746, 8.717, 8.657, 8.638	0.93
~7.278, 7.268, 7.248, 7.238, 7.225, 7.206	0.98, 1.03, 5.39, 5.18
~7.131, 7.128, 7.114, 7.097, 7.080, 7.062	5.18
~4.317	3.00
0.000	-

Figure 1 displays the ^{13}C NMR spectra of compound **4a'**. The chemical structure of **4a'** is shown on the right. The figure includes two spectra: a top spectrum (119–143 ppm) and a bottom spectrum (–1–210 ppm). The chemical structure of **4a'** is shown on the right.

¹H NMR spectrum of compound 4a in CDCl₃.

Chemical structure of 4a: CN1c2cc(C#N)c(C(=O)c3ccccc3)c(O)c2c3ccccc13

Peak list (ppm): 11.571, 8.449, 8.430, 7.591, 7.572, 7.552, 7.500, 7.480, 7.430, 7.411, 7.393, 7.383, 7.364, 7.254, 7.237, 7.232, 7.212, 7.211, 7.181, 7.104, 7.086, 7.077, 7.058, 4.270, 1.580, 0.000.

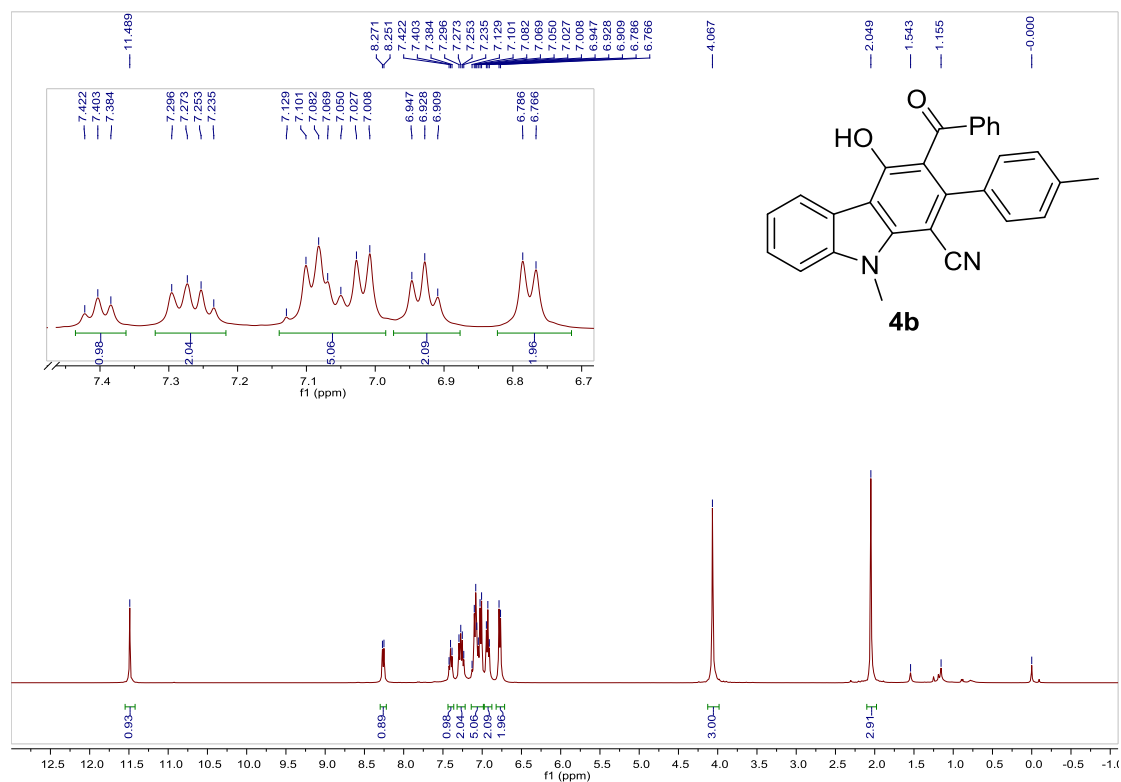
Integration values: 0.87, 1.00, 1.07, 1.12, 1.14, 5.15, 5.27, 3.00.

Chemical structure of **4a** is shown on the right. The structure is a benzimidazole derivative with a phenyl group (Ph) and a cyano group (CN) on the benzimidazole ring, and a phenyl group (Ph) and a hydroxyl group (HO) on the benzimidazole ring.

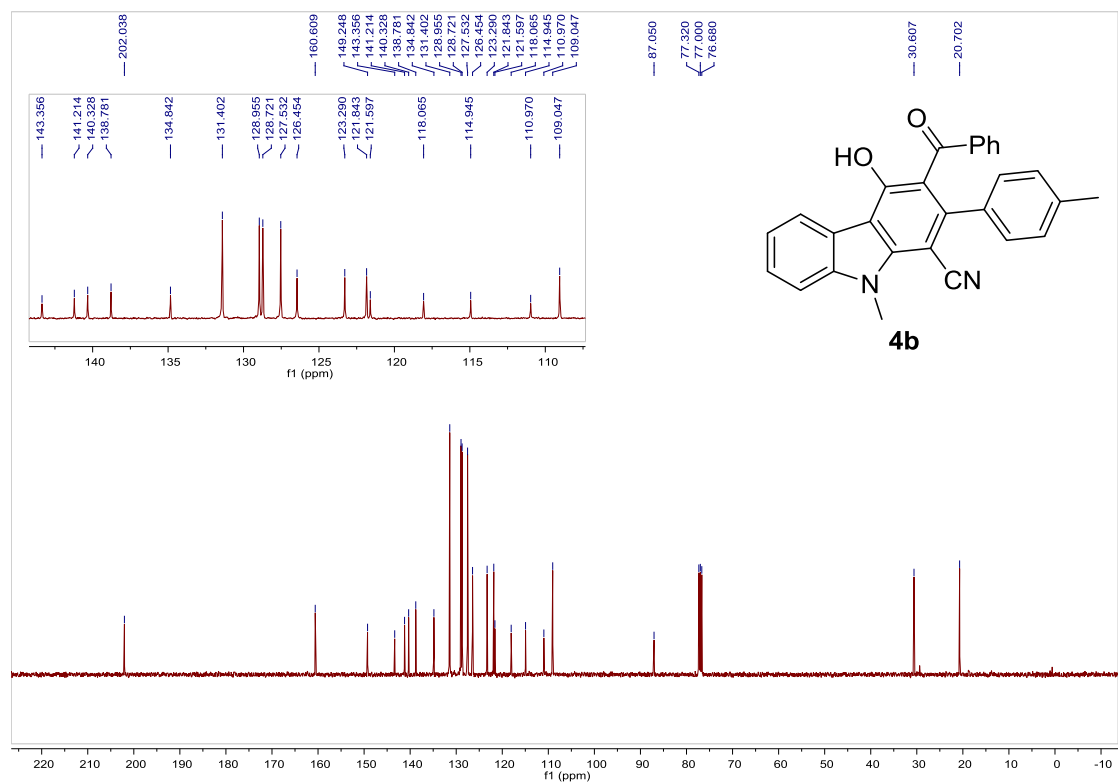
The ^{13}C NMR spectrum (top) shows peaks at the following chemical shifts (ppm): 143.486, 141.459, 140.403, 137.827, 131.774, 131.537, 129.039, 128.721, 127.763, 125.550, 122.060, 121.766, 118.002, 115.070, 111.318, and 109.260.

The ^{13}C NMR spectrum (bottom) shows peaks at the following chemical shifts (ppm): 220.000, 217.519, 217.000, 216.680, 197.304, 143.486, 141.459, 140.403, 137.827, 131.774, 131.537, 129.039, 128.721, 127.763, 125.550, 122.060, 121.766, 118.002, 115.070, 111.318, 109.260, and 30.808.

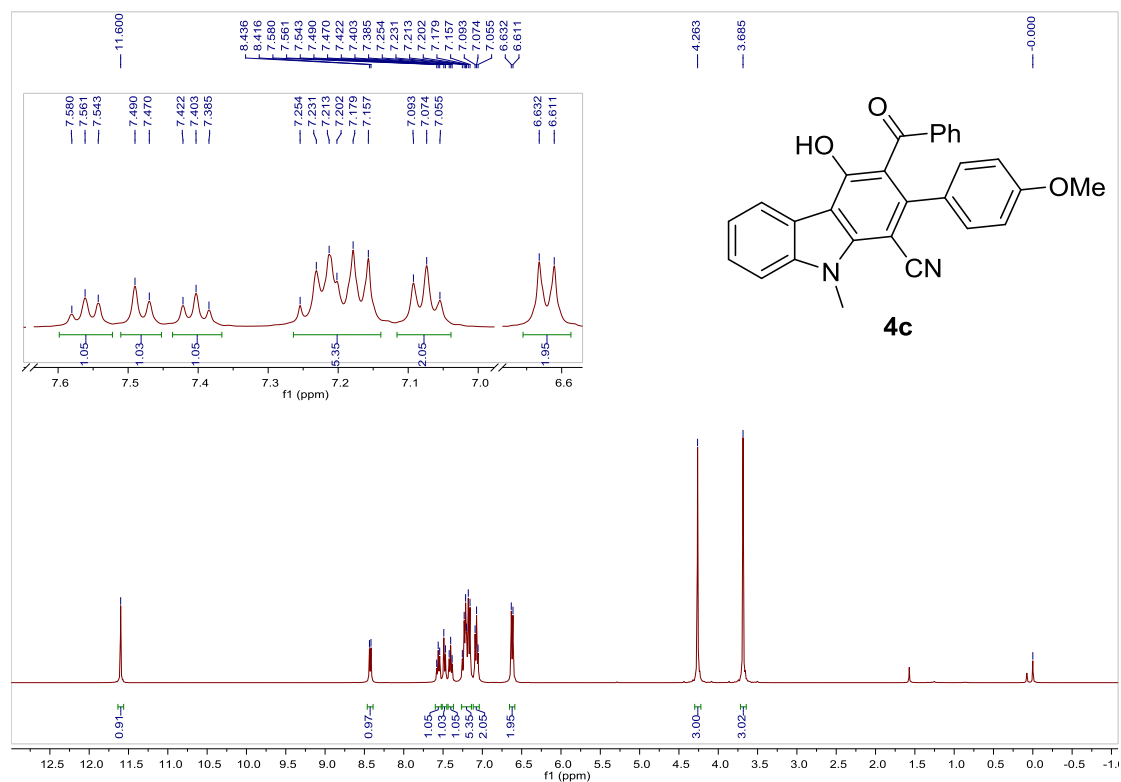
^1H NMR (400 MHz, CDCl_3)



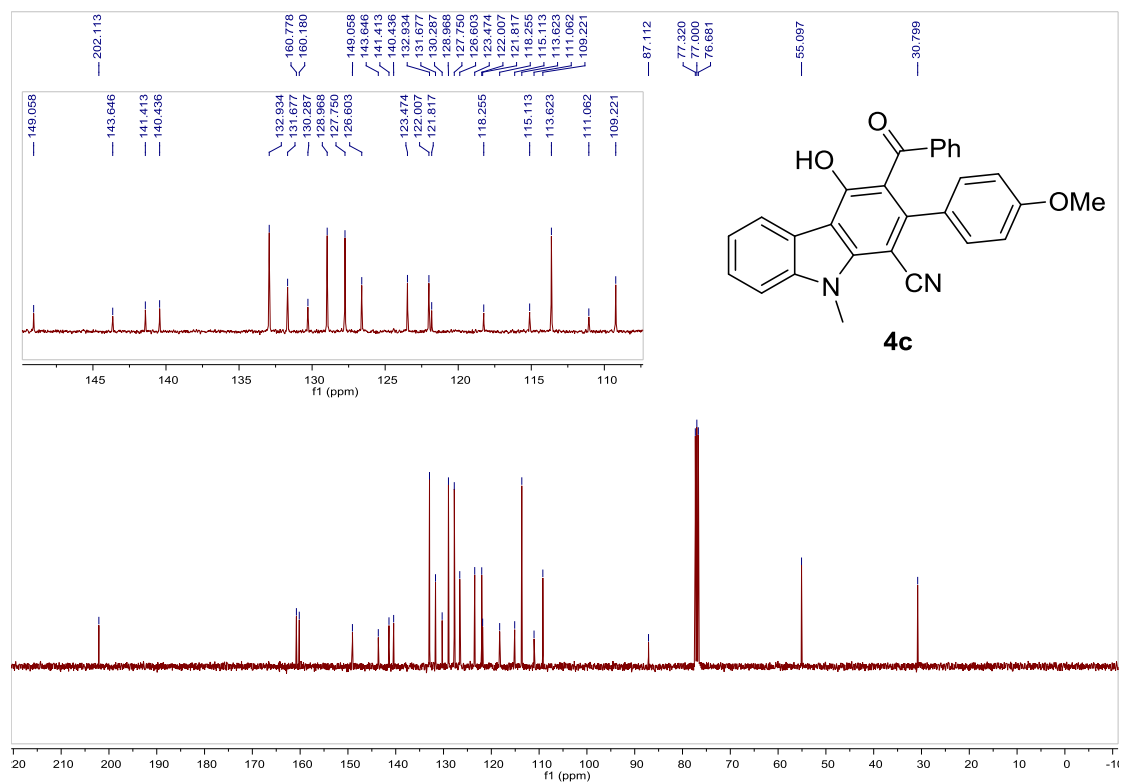
^{13}C NMR (100 MHz, CDCl_3)



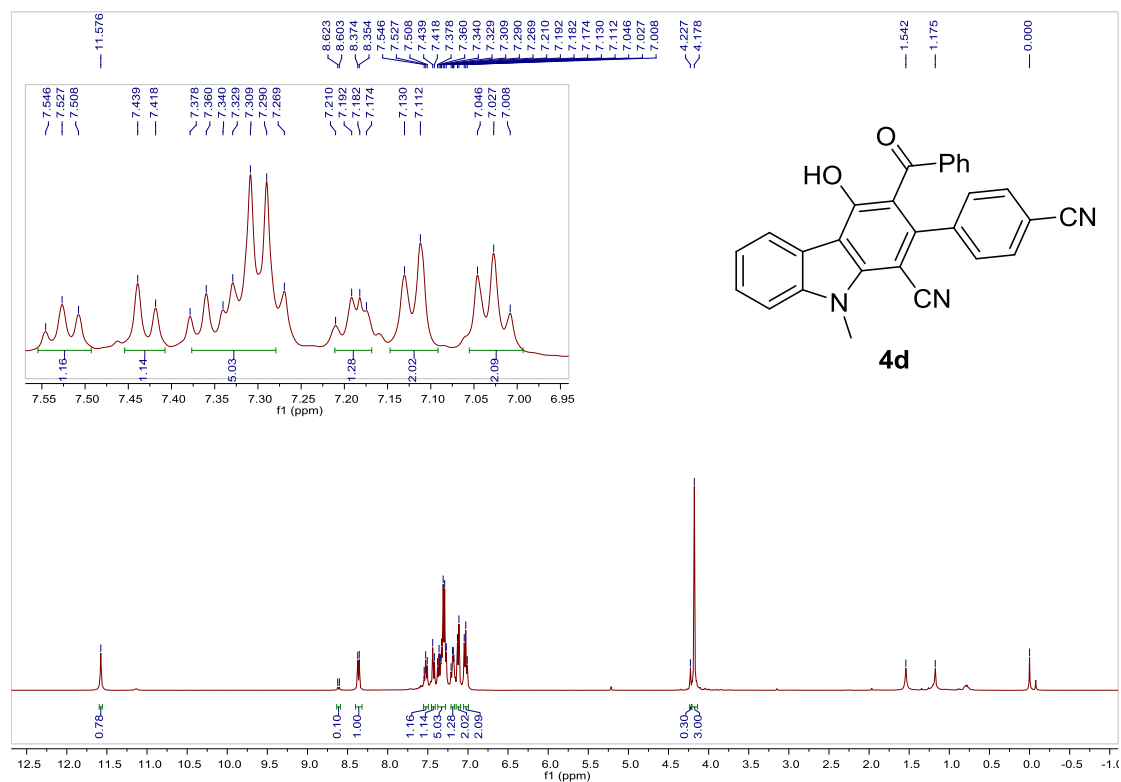
¹H NMR (400 MHz, CDCl₃)



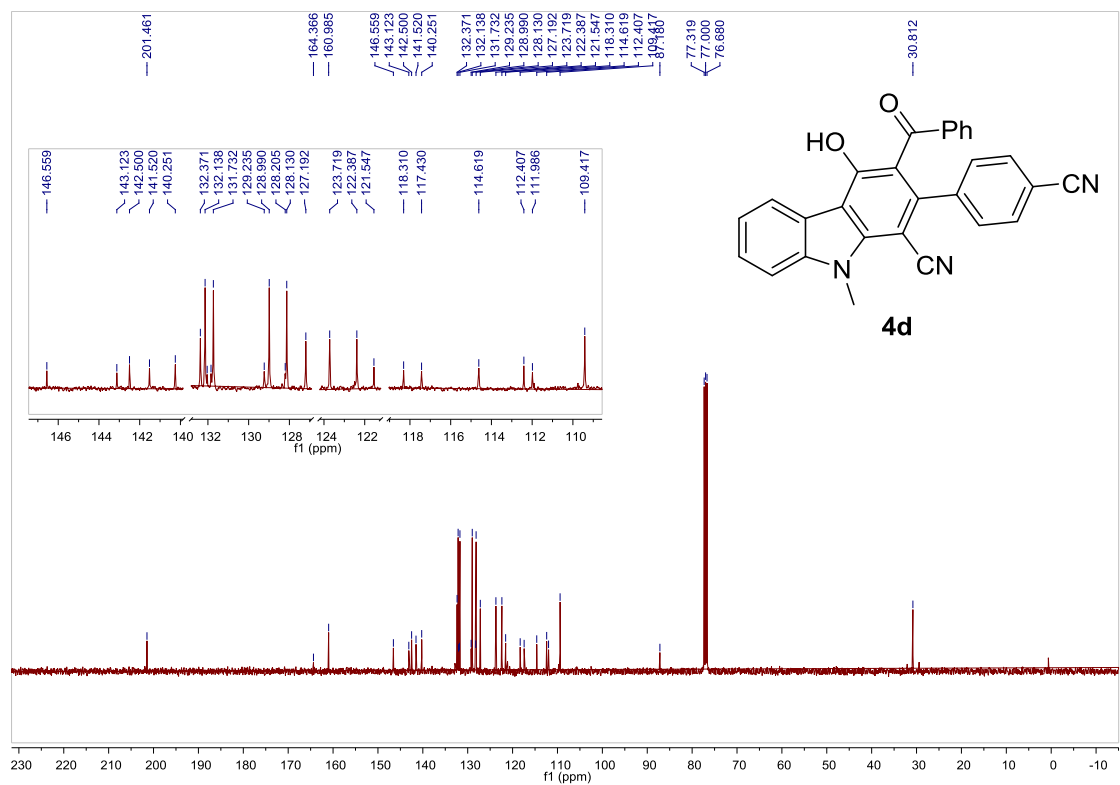
¹³C NMR (100 MHz, CDCl₃)



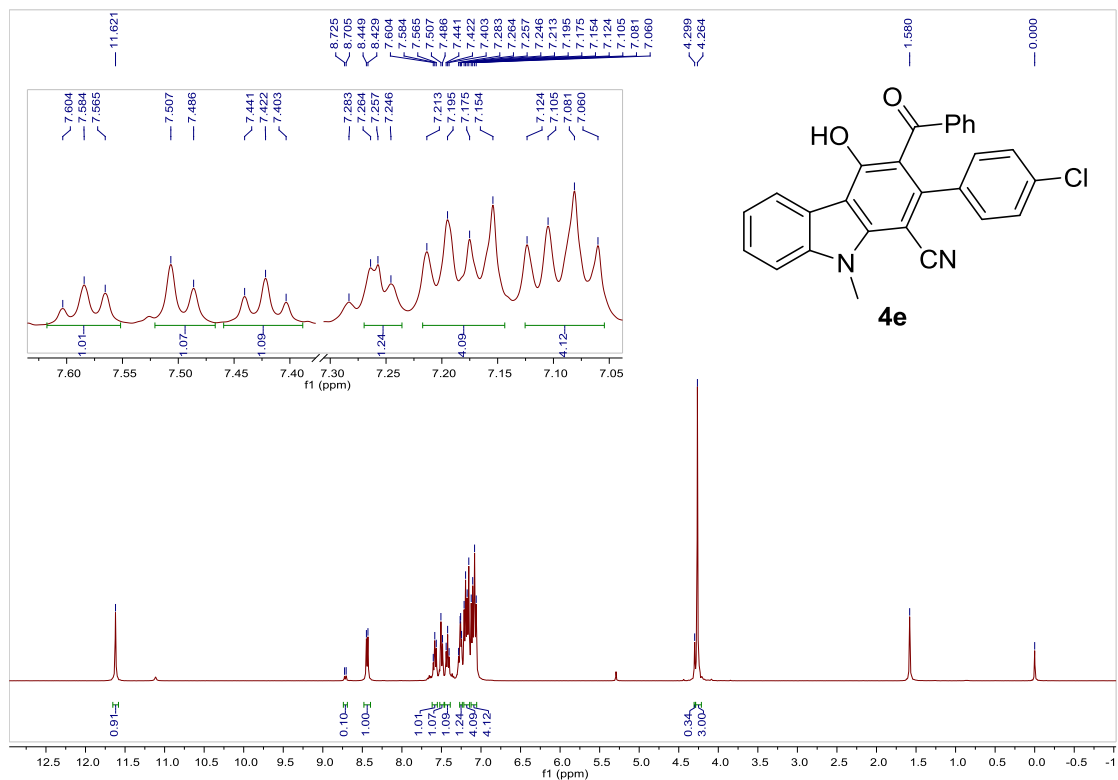
^1H NMR (400 MHz, CDCl_3)



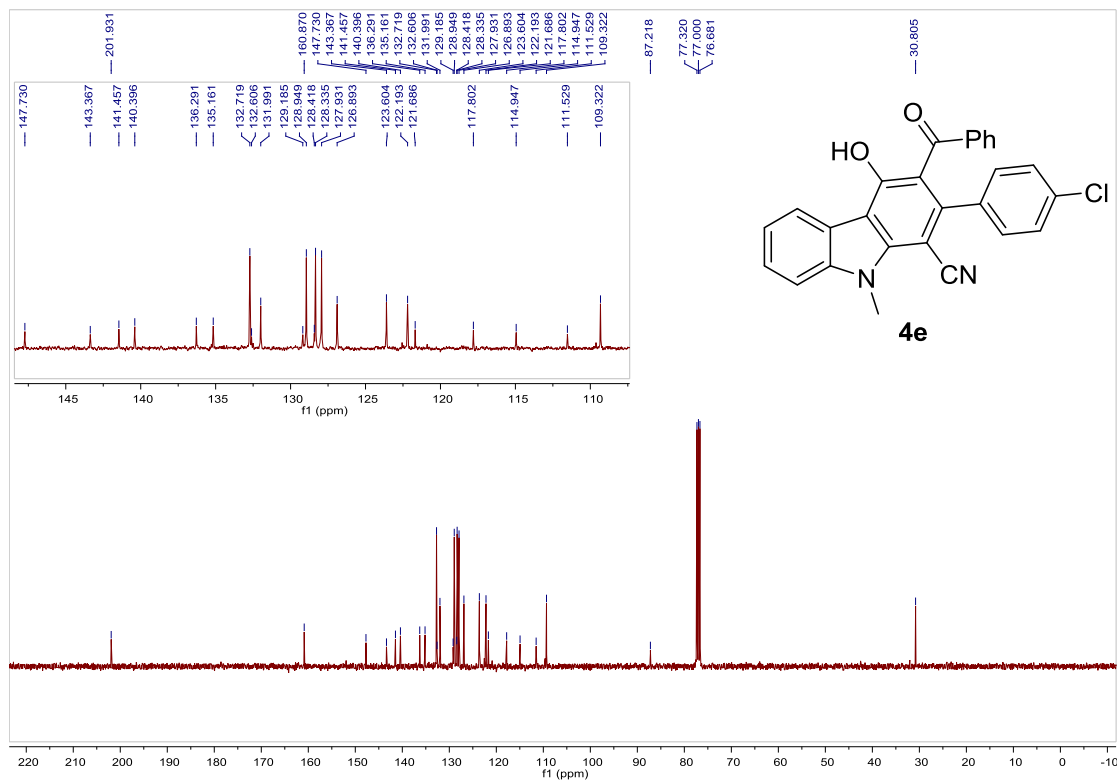
^{13}C NMR (100 MHz, CDCl_3)



¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)



Chemical structure of 4f: CCCC1=C(C#N)C(=C(C(=O)c2ccccc2)C(O)c3ccccc3N1C)C

¹H NMR spectrum (CDCl₃):

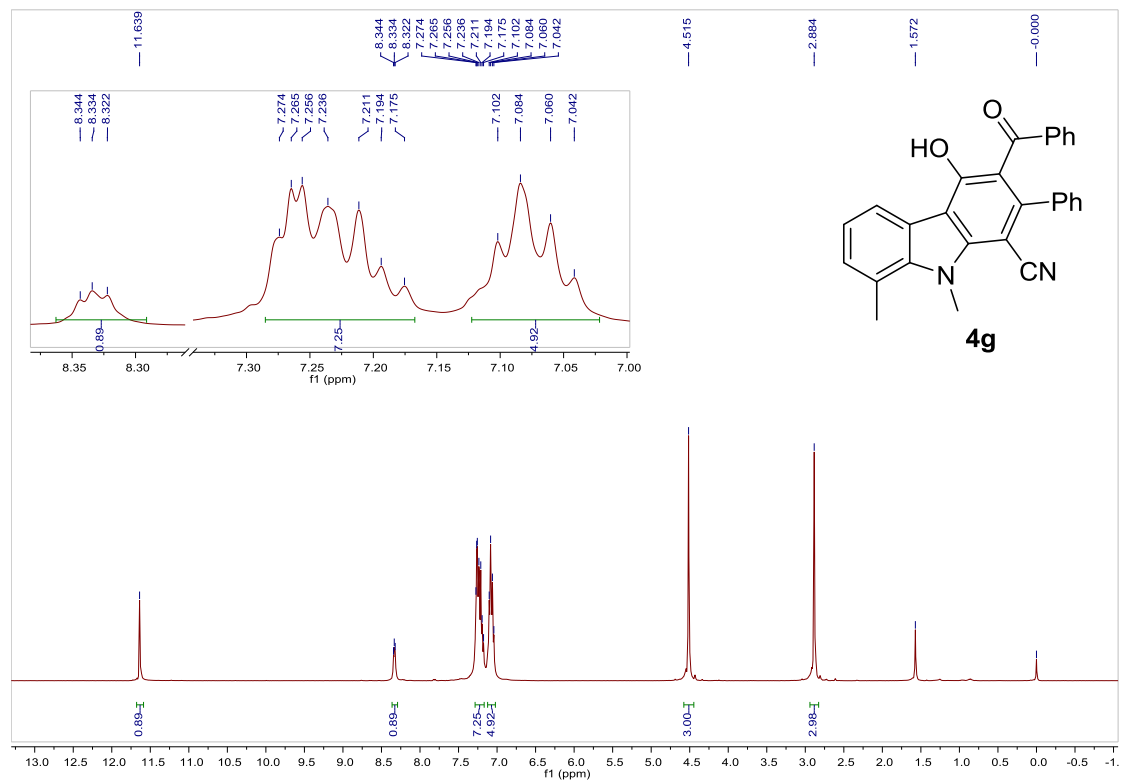
Chemical Shift (ppm)	Integration
7.589, 7.570, 7.555, 7.535, 7.516, 7.481, 7.442, 7.425, 7.405, 7.379, 7.313, 7.294, 7.276	0.92
7.184	0.91
2.702, 2.683, 2.663	3.06, 4.24, 1.12
1.368, 1.348, 1.330, 1.311, 1.292	3.06, 4.24, 1.12
1.006, 0.989, 0.969, 0.951	2.21
0.658, 0.640, 0.622	2.13
0.6	3.02

Chemical structure of **4f** is shown as an inset. The structure is 1-methyl-2-cyano-3-(n-butyl)-4-hydroxy-5-phenyl-1H-indole.

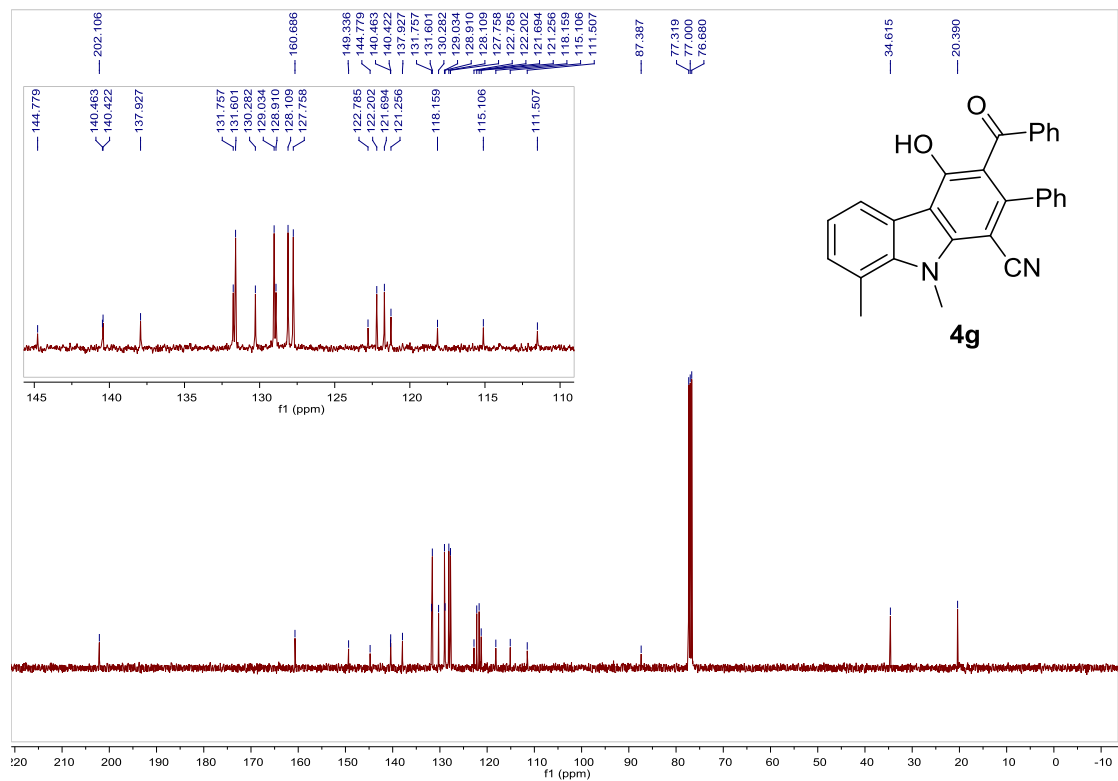
¹³C NMR spectrum (CDCl₃) peaks (ppm):

- 143.654
- 141.180
- 140.655
- 133.232
- 129.155
- 129.002
- 126.403
- 125.277
- 121.851
- 117.995
- 114.609
- 110.512
- 109.121
- 87.382
- 77.320
- 77.063
- 76.681
- 34.291
- 33.730
- 30.651
- 22.081
- 13.233

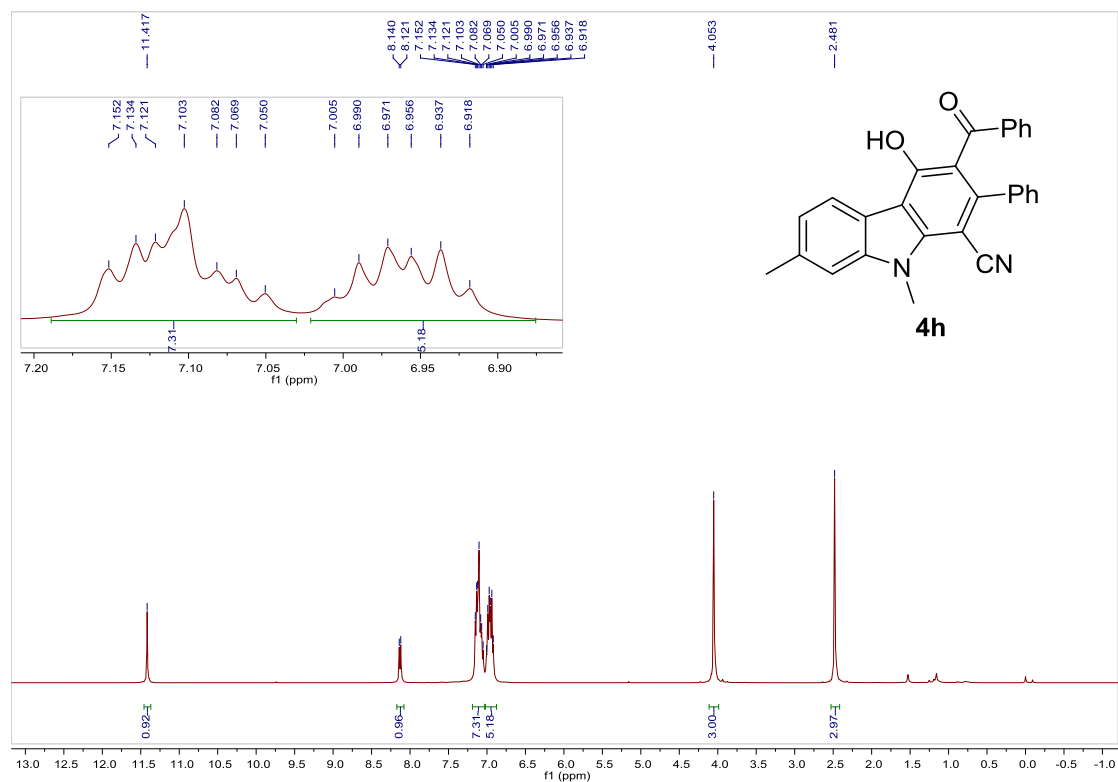
^1H NMR (400 MHz, CDCl_3)



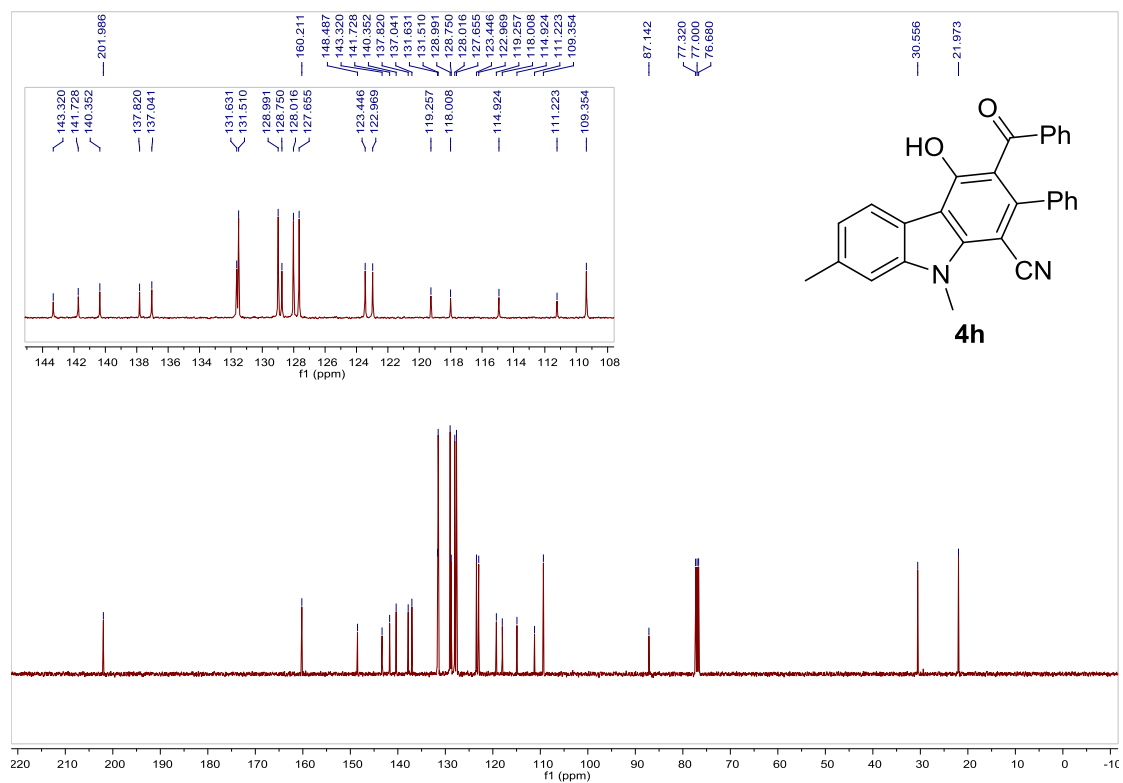
^{13}C NMR (100 MHz, CDCl_3)



^1H NMR (400 MHz, CDCl_3)



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



Chemical structure of 4i: COc1ccc2c(c1)c(c3cc(C#N)c(C(=O)c4ccccc4)c(Cc5ccccc5)c32)O

¹H NMR spectrum (CDCl₃):

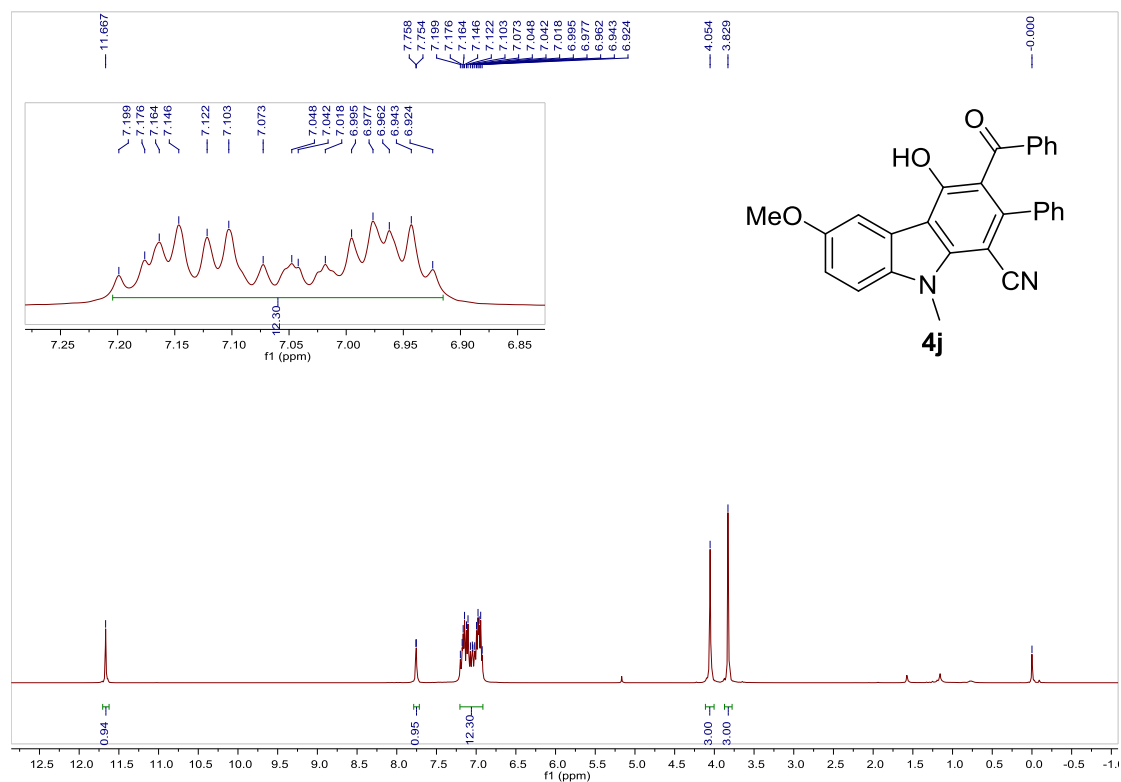
- Chemical shift range: 0.00 to 12.50 ppm.
- Integration values (from left to right): 0.98, 2.12, 2.38, 7.32, 1.03, 0.98, 3.00, 3.10.
- Peak list (ppm): 7.596, 7.576, 7.402, 7.381, 7.361, 7.344, 7.326, 7.294, 7.266, 7.186, 7.155, 7.146, 7.062, 7.041, 7.004, 6.706, 6.685, 4.154, 3.979, 1.169, -0.000.

Figure S10 displays the ^{13}C NMR spectrum of compound **4i**. The spectrum shows peaks corresponding to the chemical structure of **4i**, which is a benzimidazole derivative with a methoxy group, a hydroxyl group, and two phenyl groups.

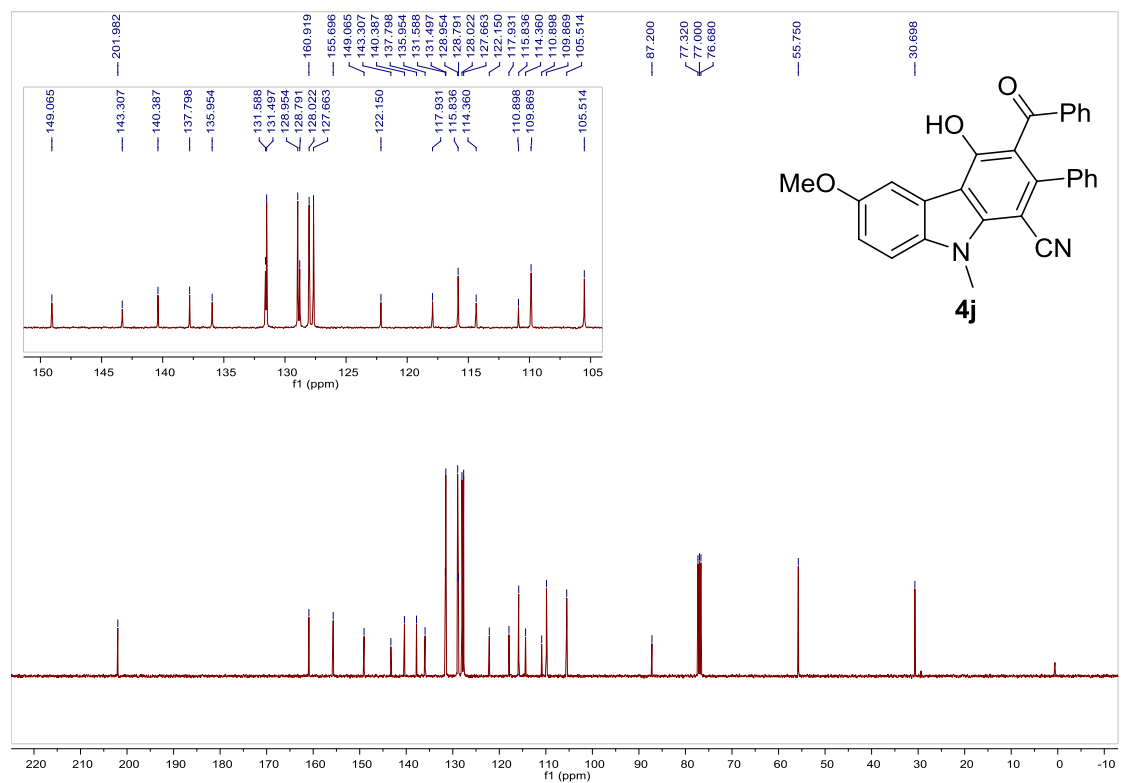
The chemical structure of **4i** is shown on the right. The structure is a benzimidazole derivative with a methoxy group at position 2, a hydroxyl group at position 4, a phenyl group at position 5, a cyano group at position 6, and a phenyl group at position 7.

The ^{13}C NMR spectrum (top) shows peaks at the following chemical shifts (ppm): 145.955, 143.015, 141.957, 138.303, 136.683, 133.198, 130.089, 129.491, 128.642, 128.401, 128.133, 127.878, 120.111, 118.171, 110.202, 110.075, 85.759, 77.320, 77.000, 76.681, 56.387, and 31.031. The spectrum is recorded in CDCl_3 .

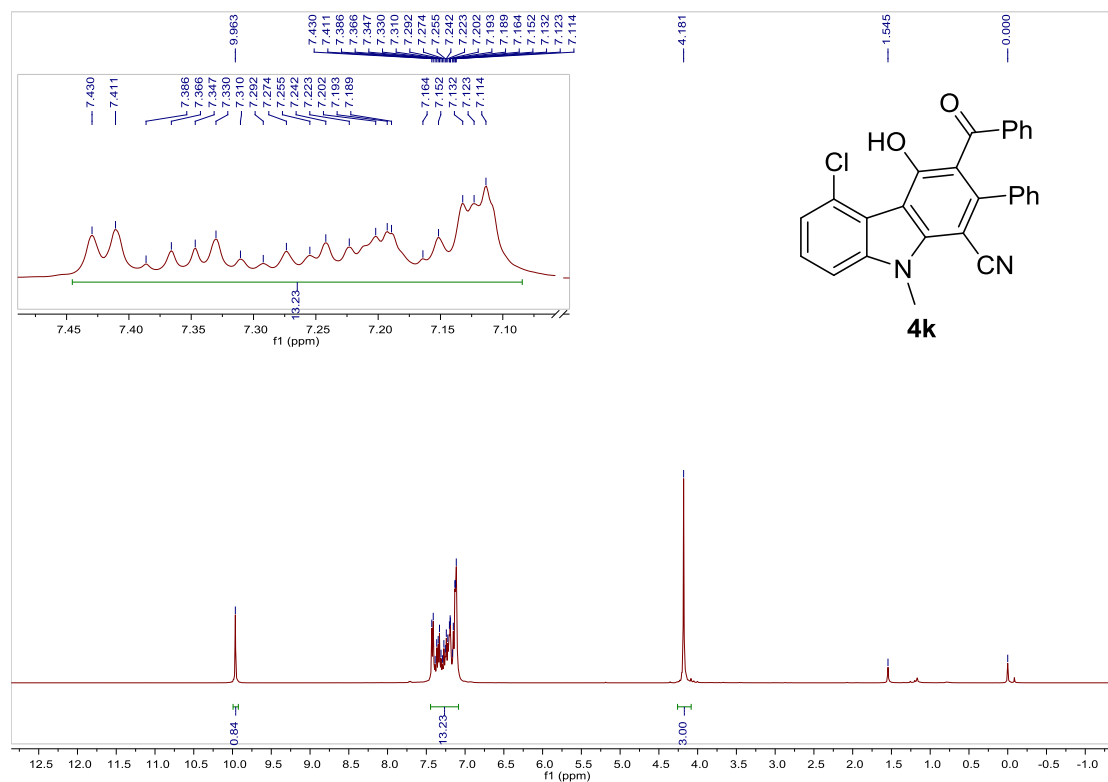
¹H NMR (400 MHz, CDCl₃)



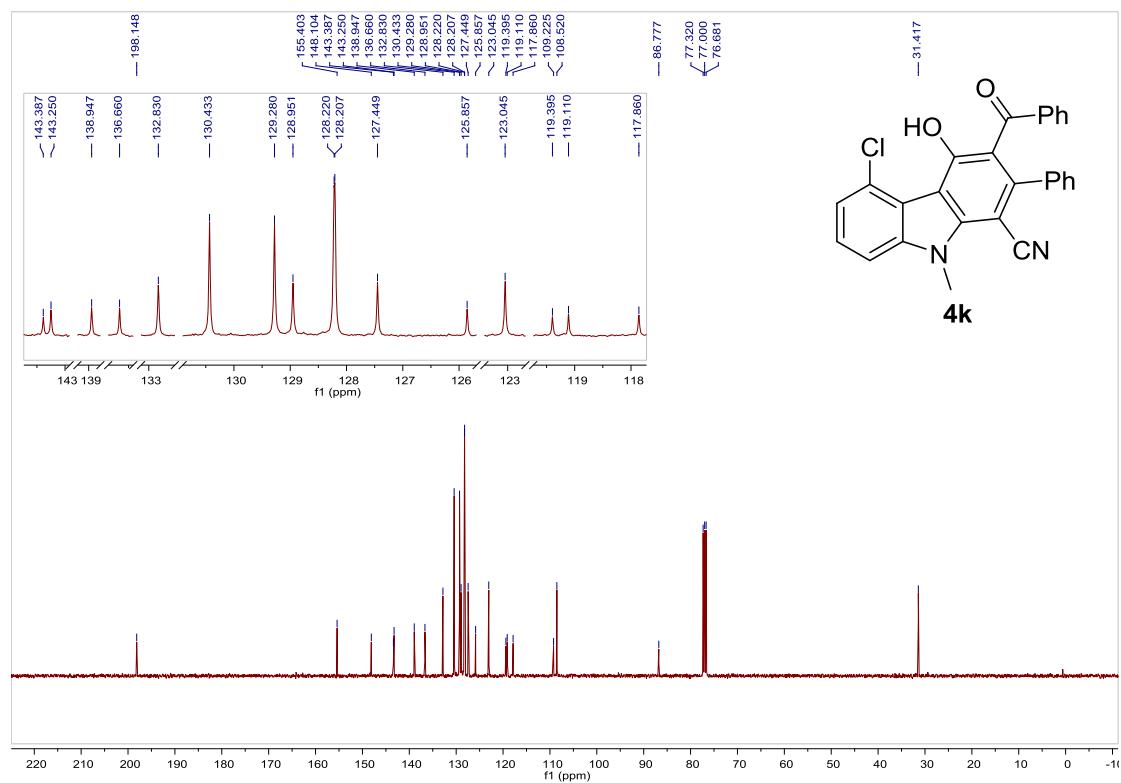
¹³C NMR (100 MHz, CDCl₃)



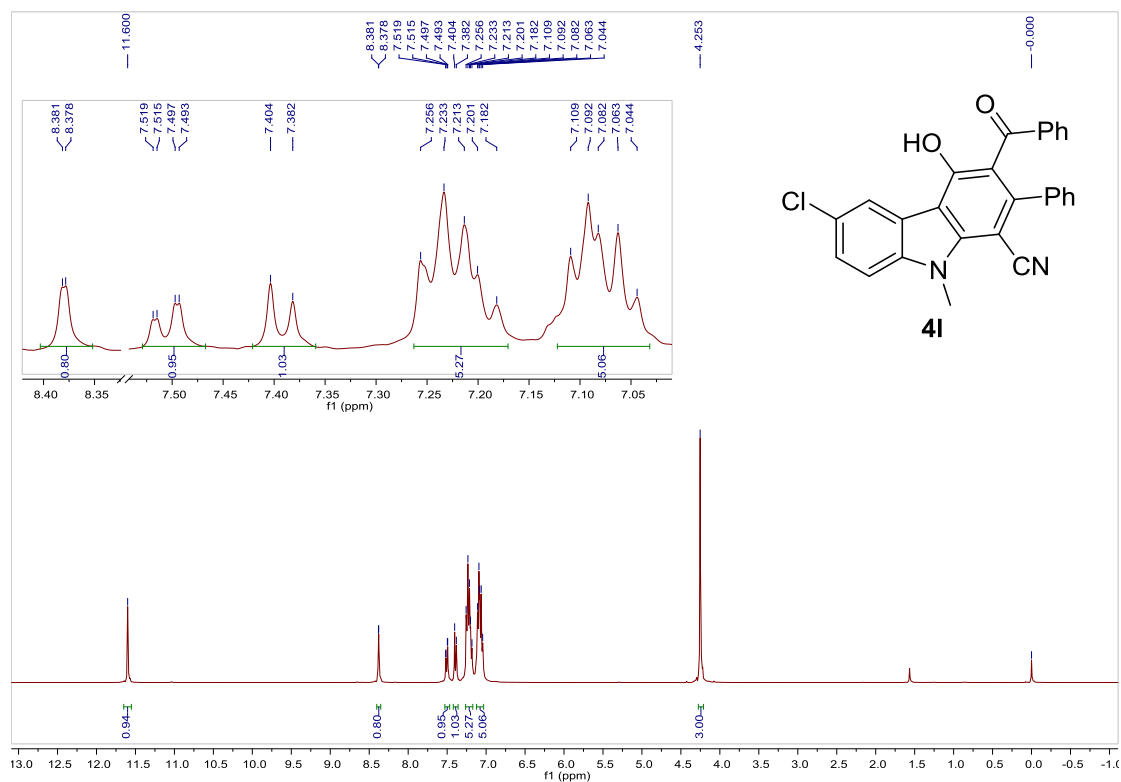
^1H NMR (400 MHz, CDCl_3)



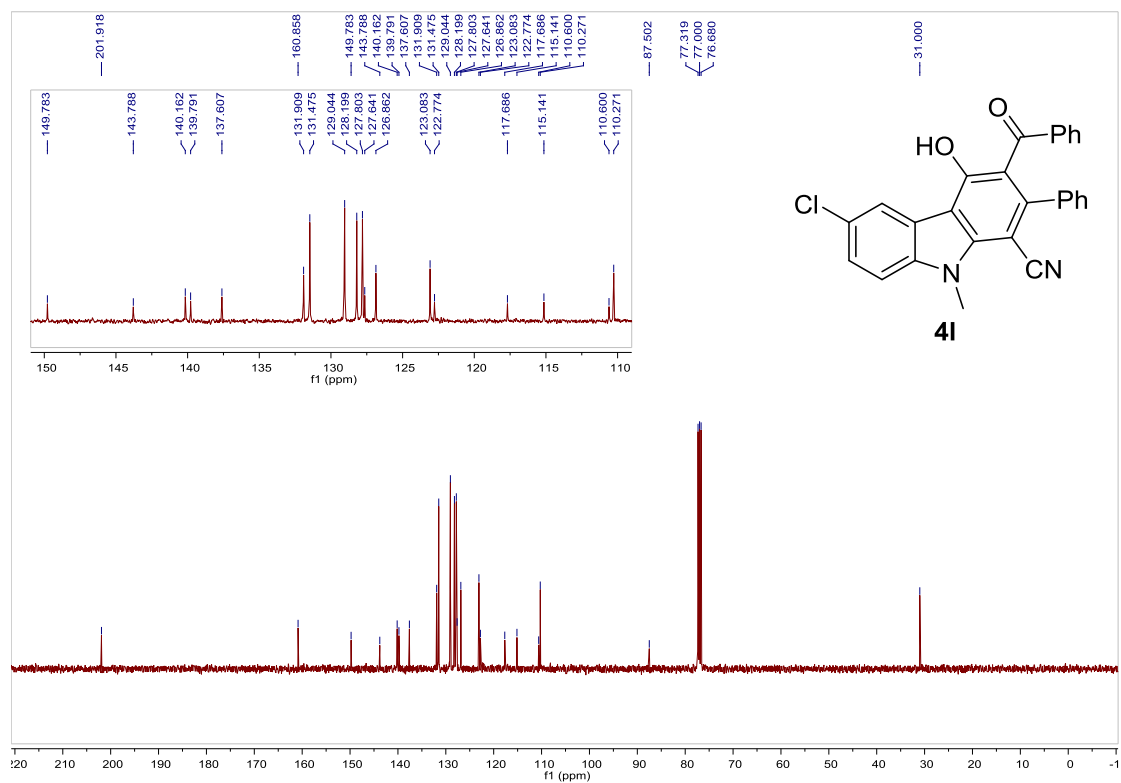
^{13}C NMR (100 MHz, CDCl_3)



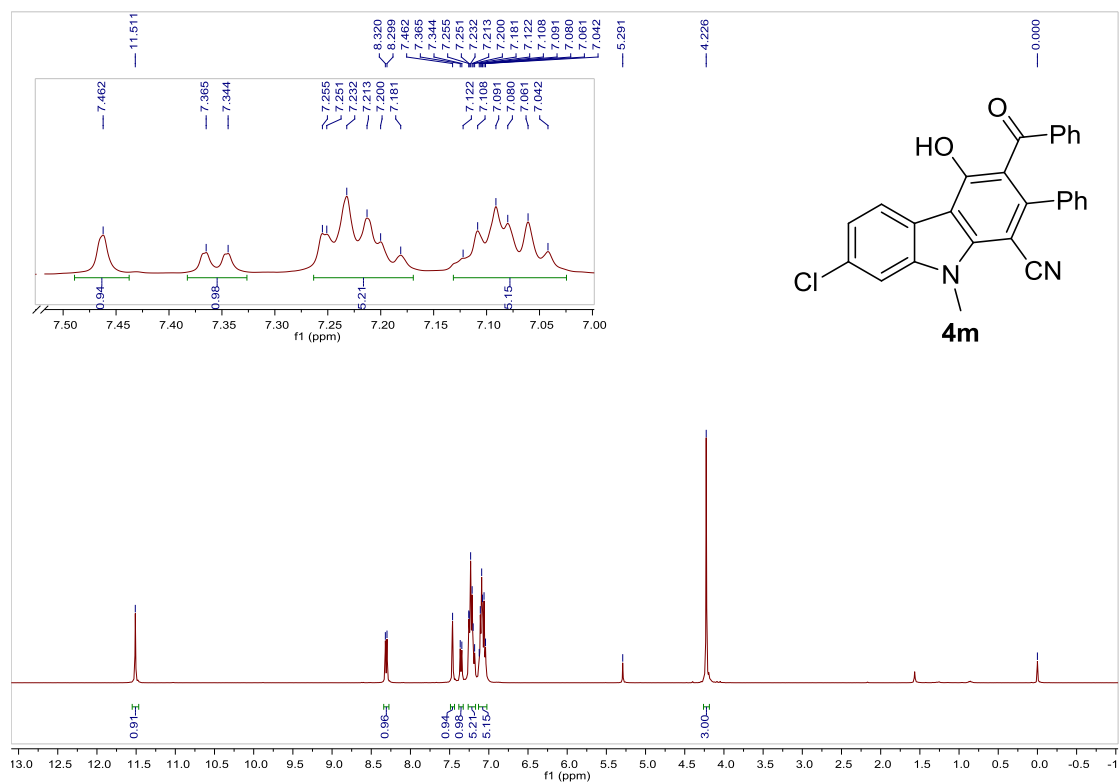
^1H NMR (400 MHz, CDCl_3)



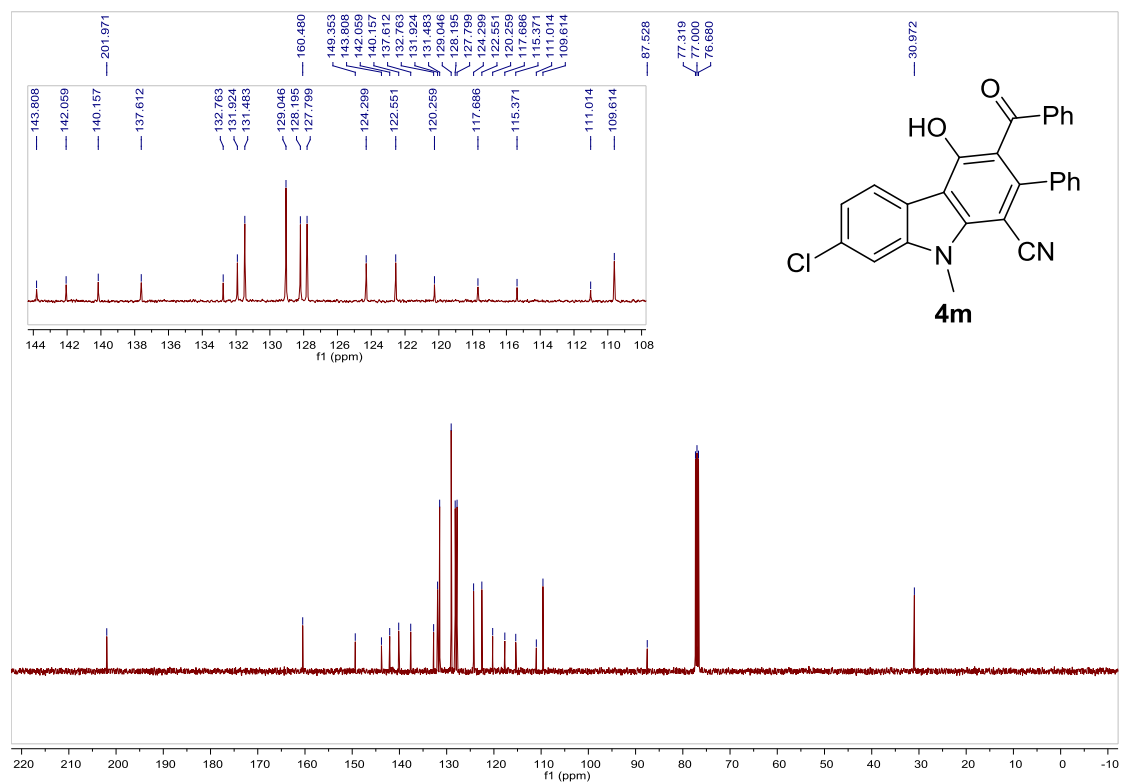
^{13}C NMR (100 MHz, CDCl_3)



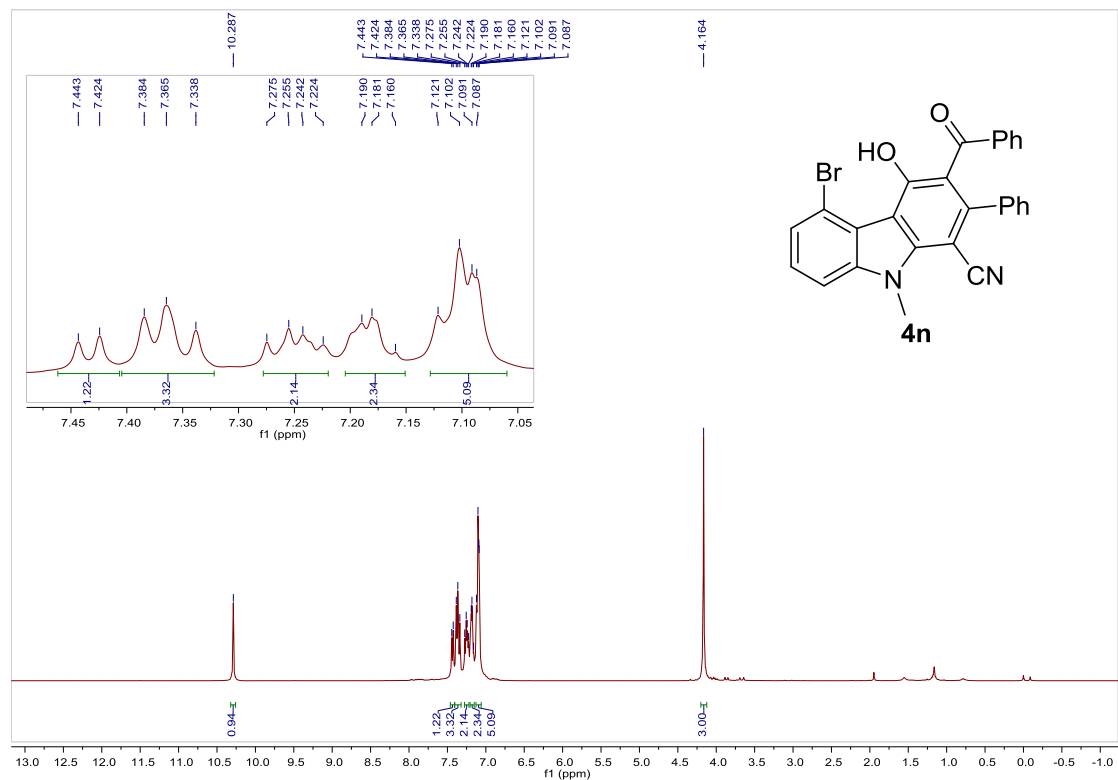
^1H NMR (400 MHz, CDCl_3)



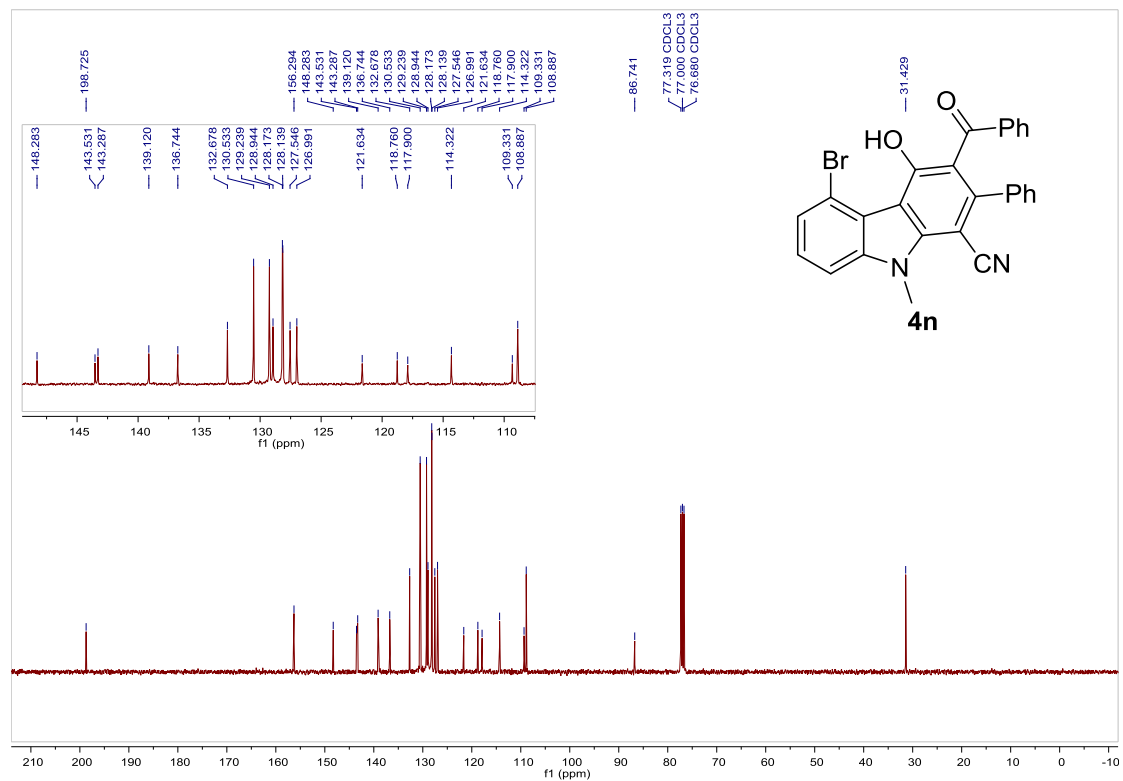
^{13}C NMR (100 MHz, CDCl_3)



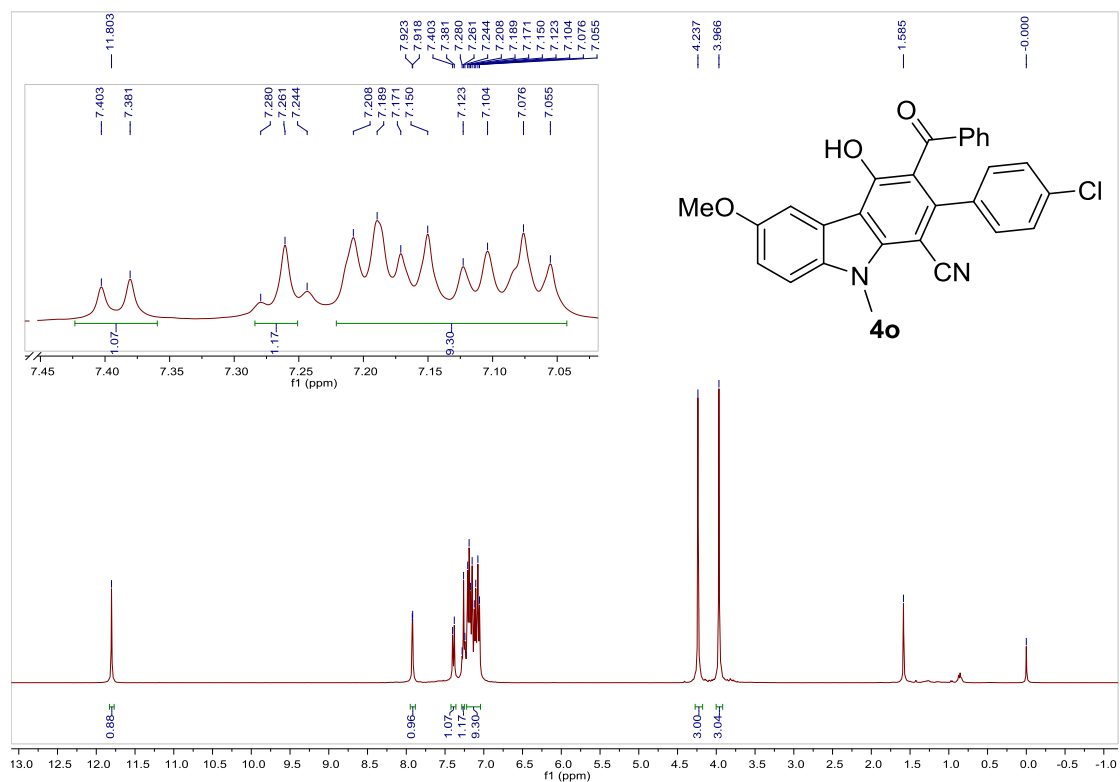
^1H NMR (400 MHz, CDCl_3)



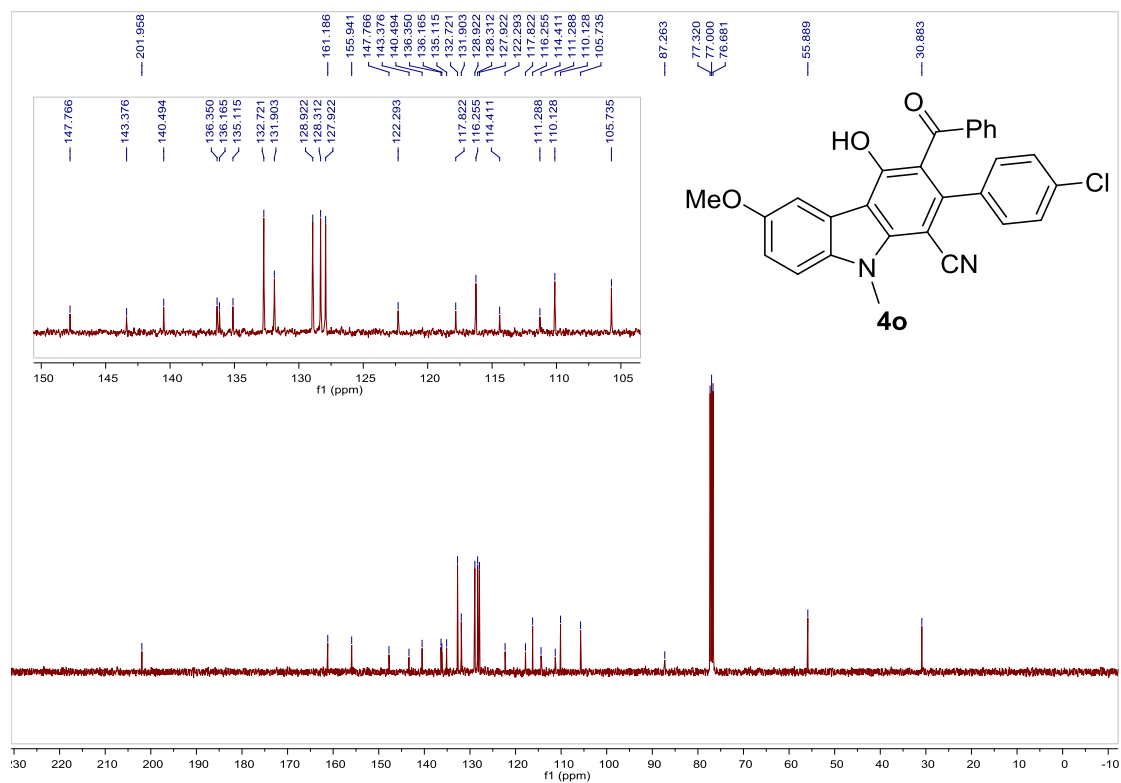
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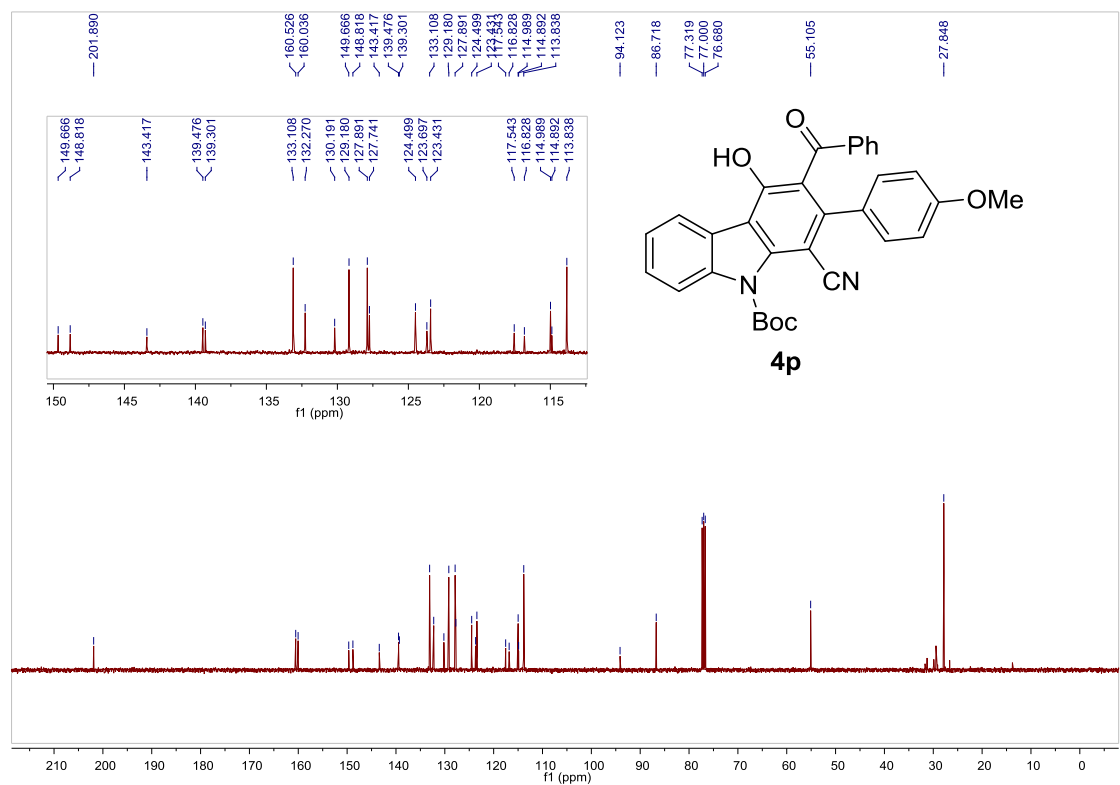
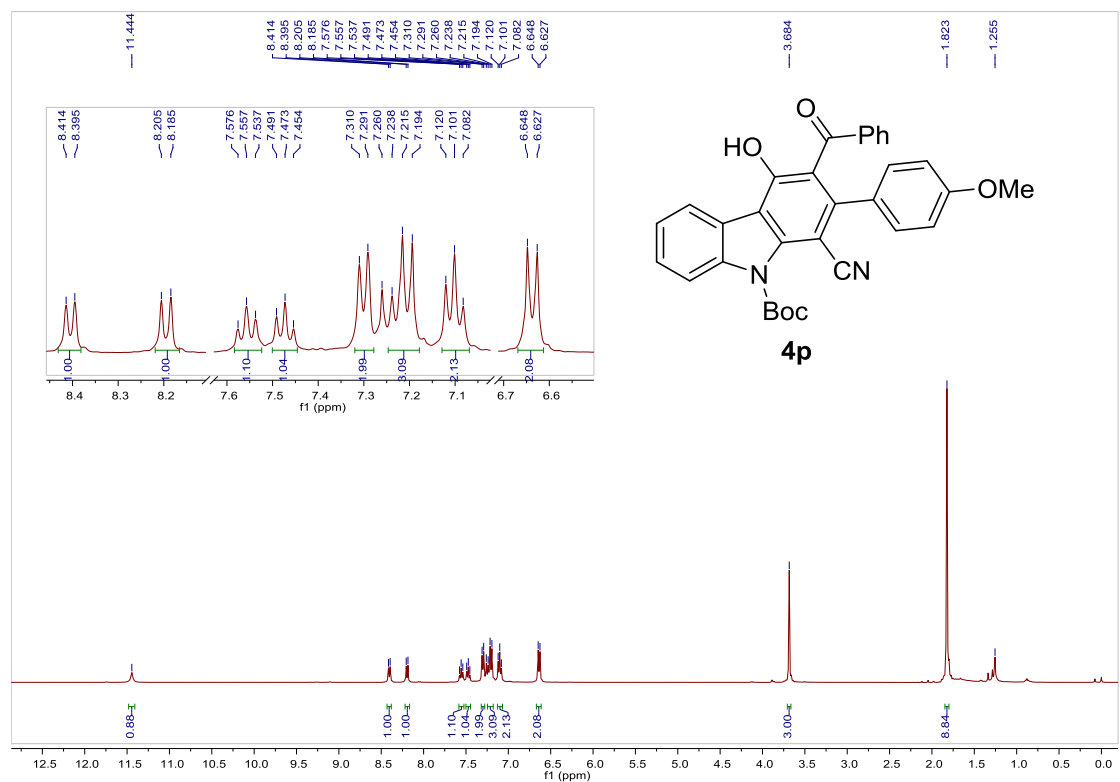


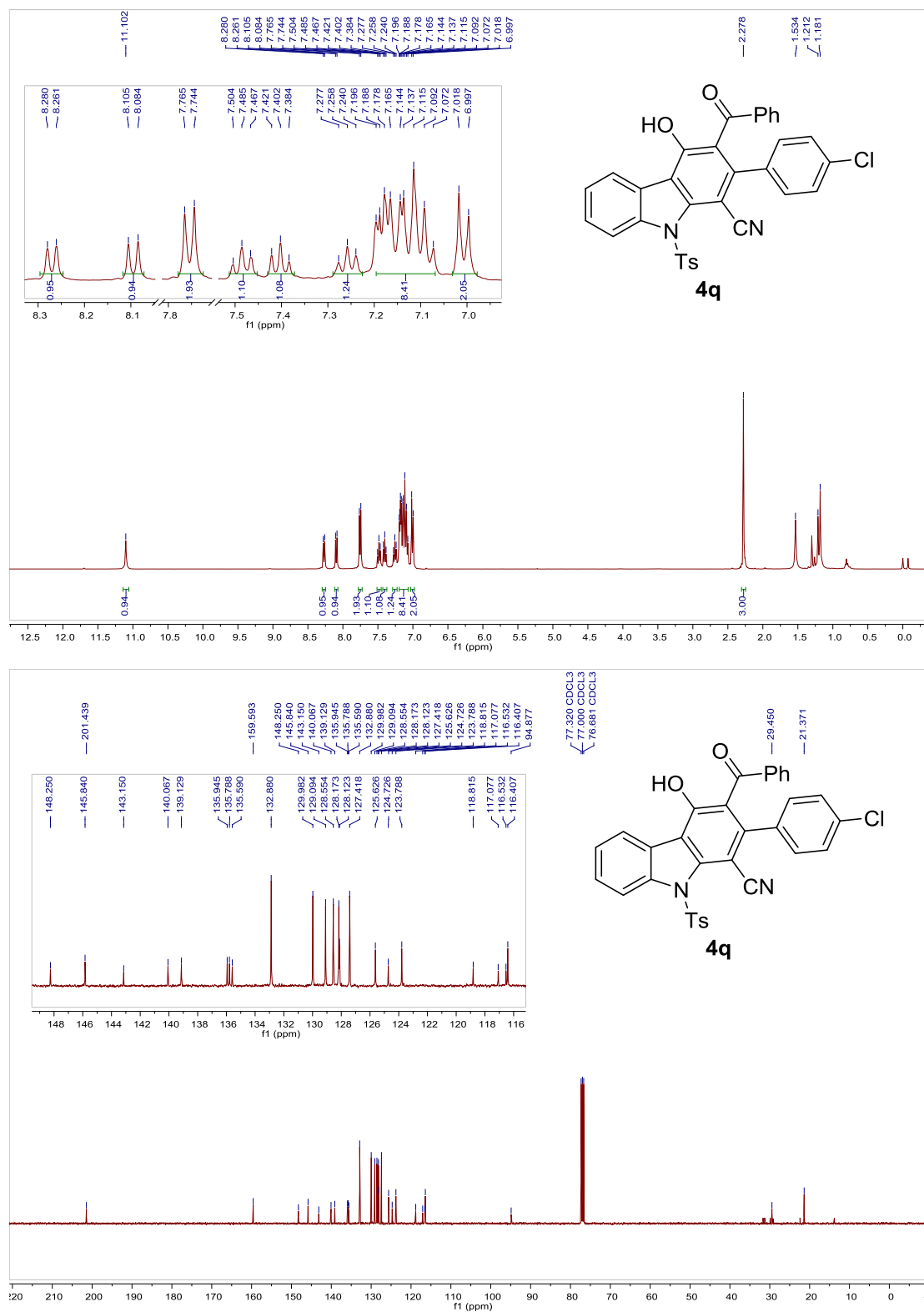
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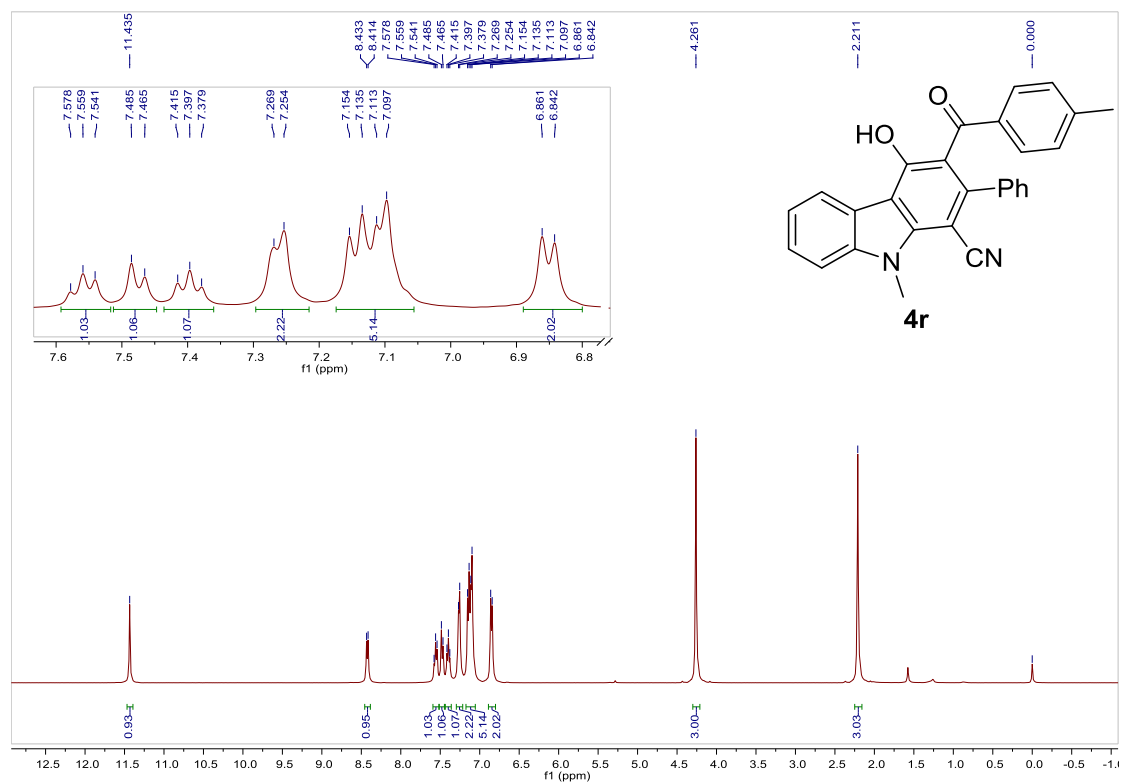
^{13}C NMR (100 MHz, CDCl_3)



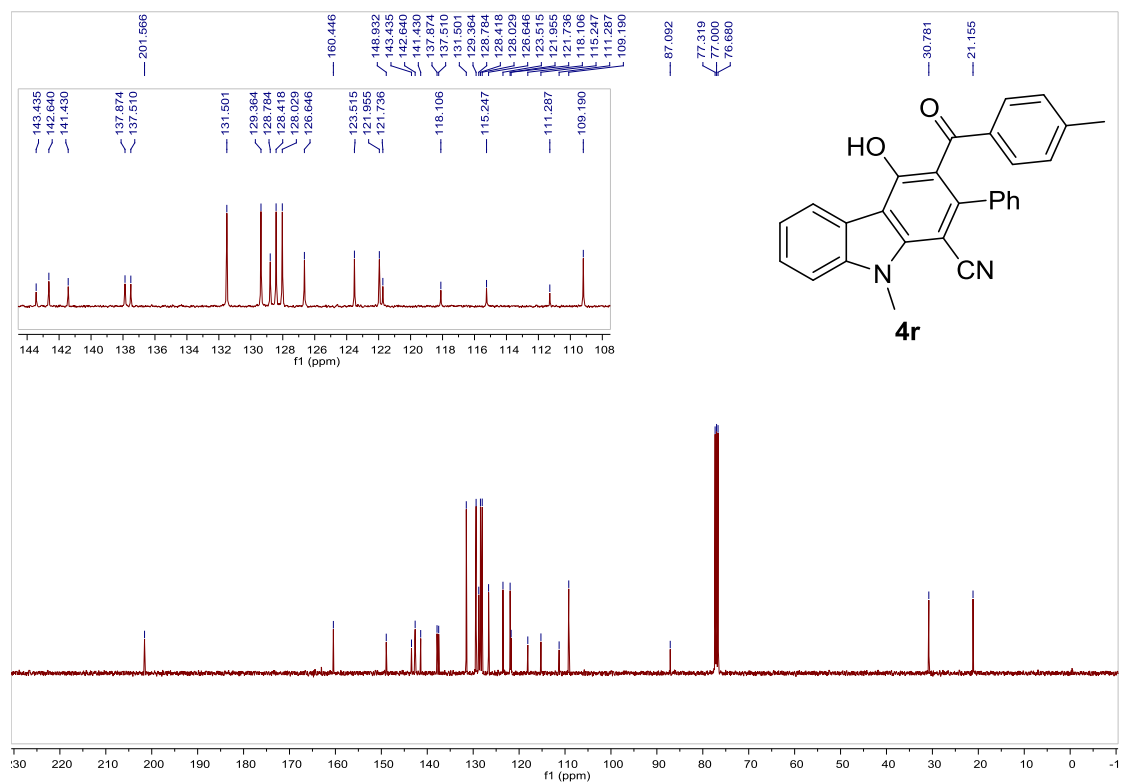




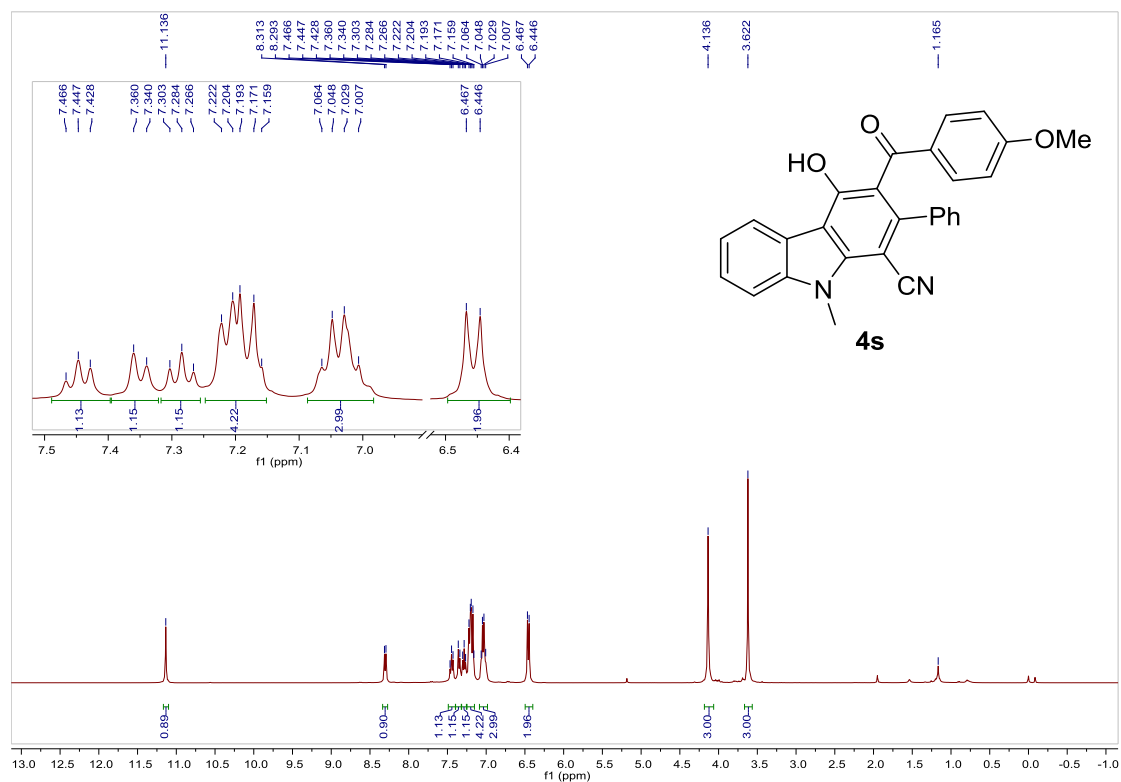
^1H NMR (400 MHz, CDCl_3)



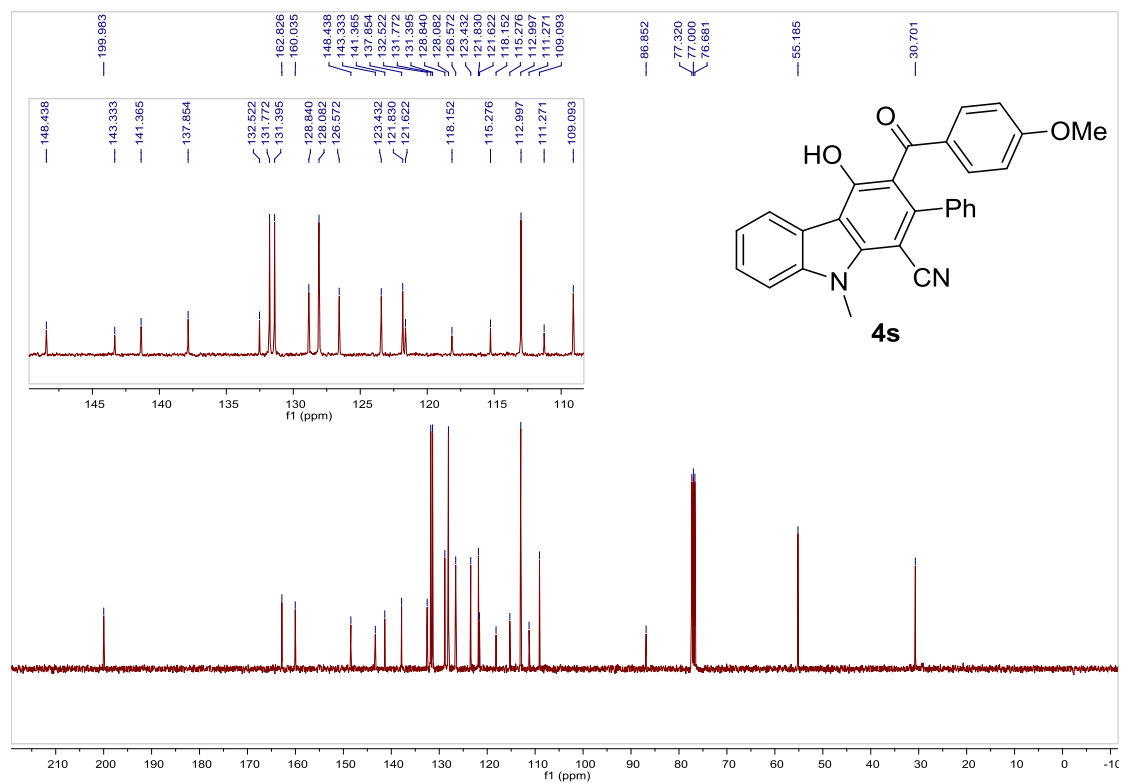
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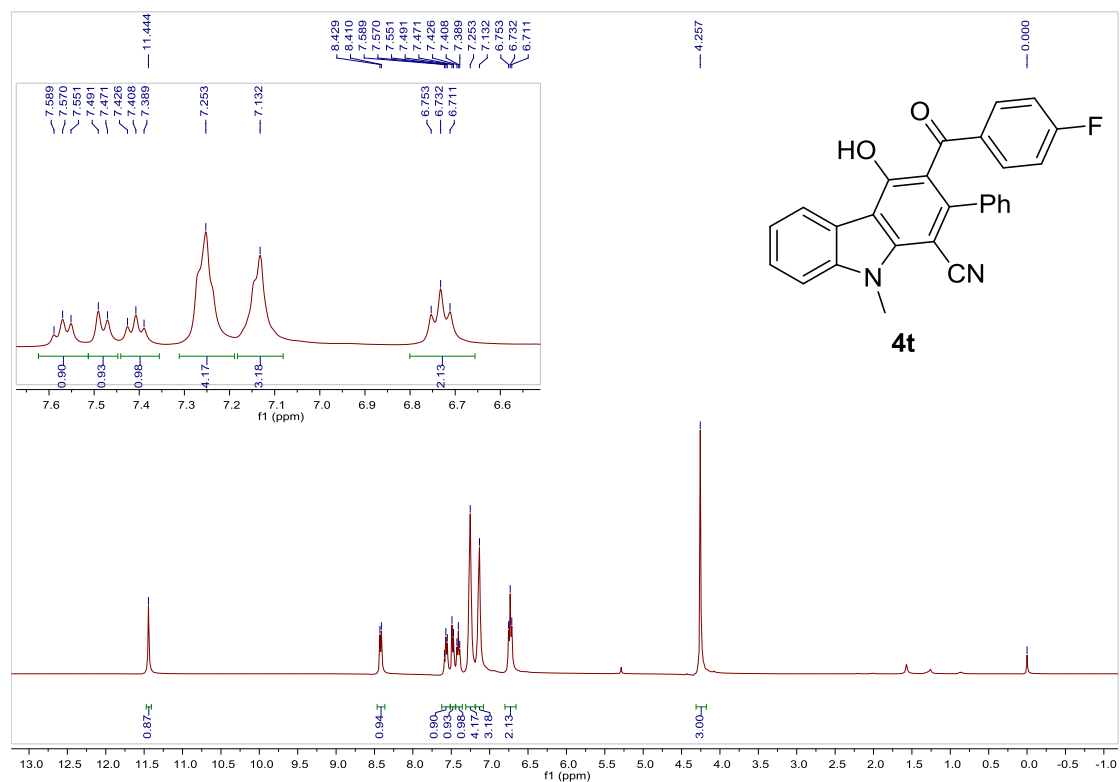
^1H NMR (400 MHz, CDCl_3)



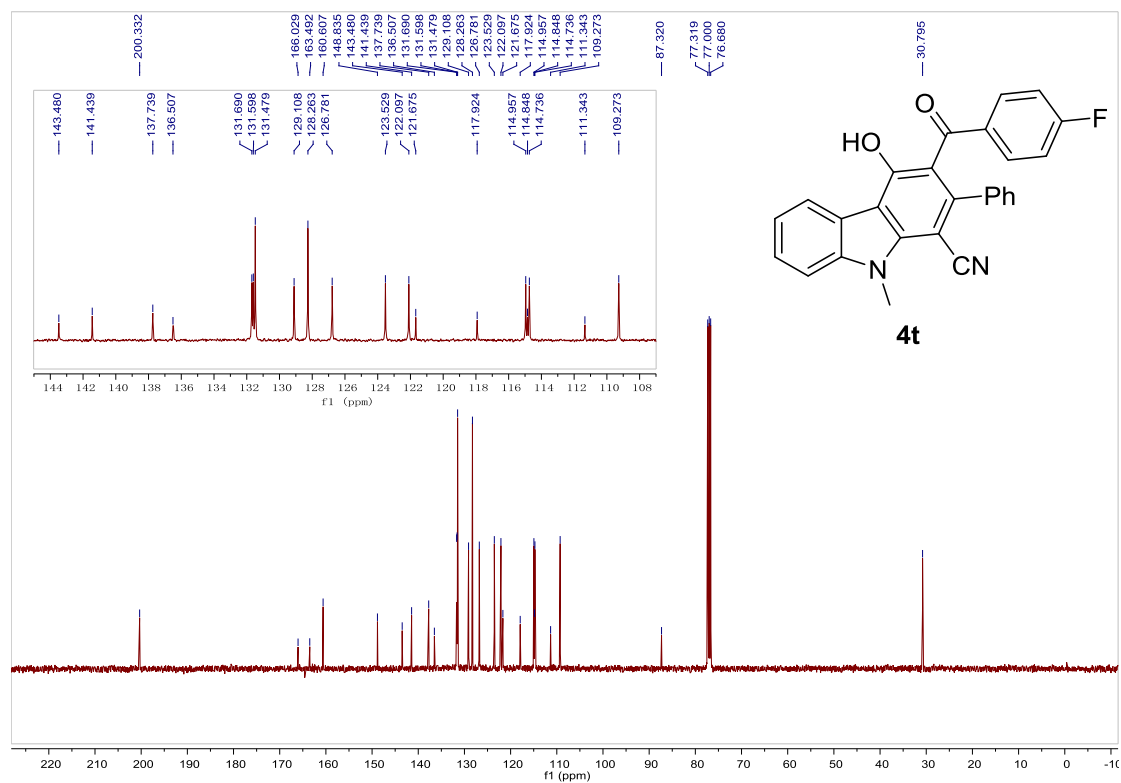
^{13}C NMR (100 MHz, CDCl_3)



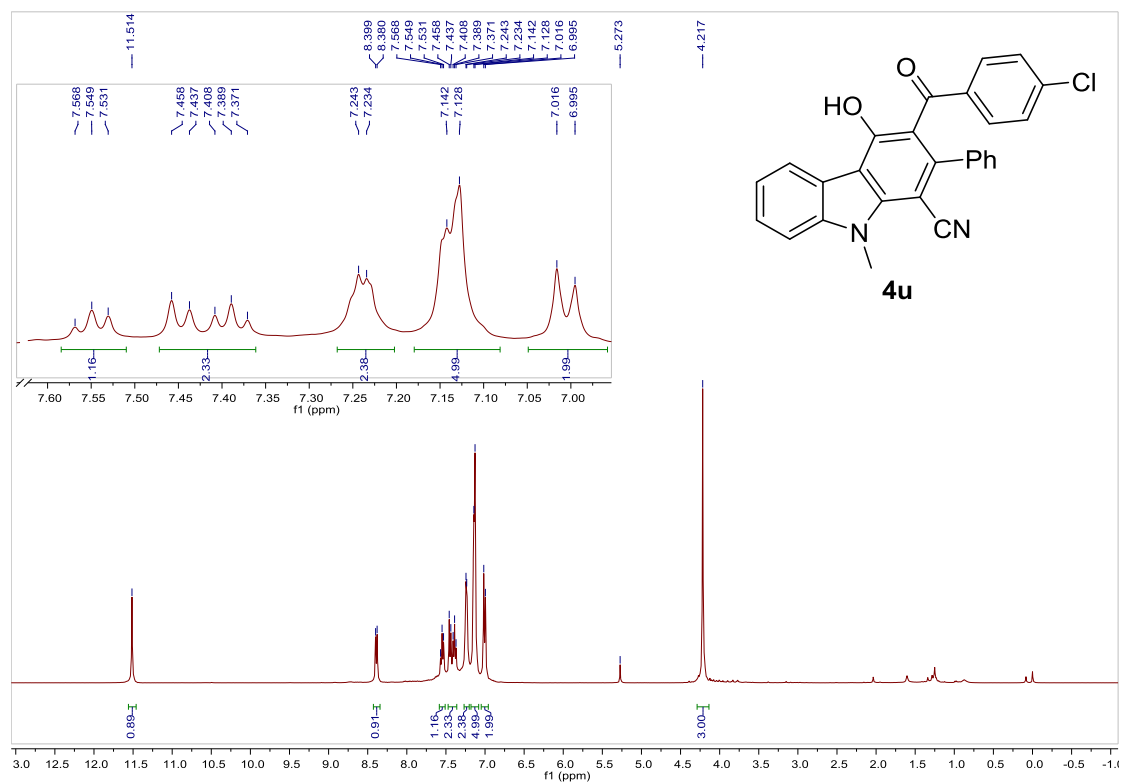
^1H NMR (400 MHz, CDCl_3)



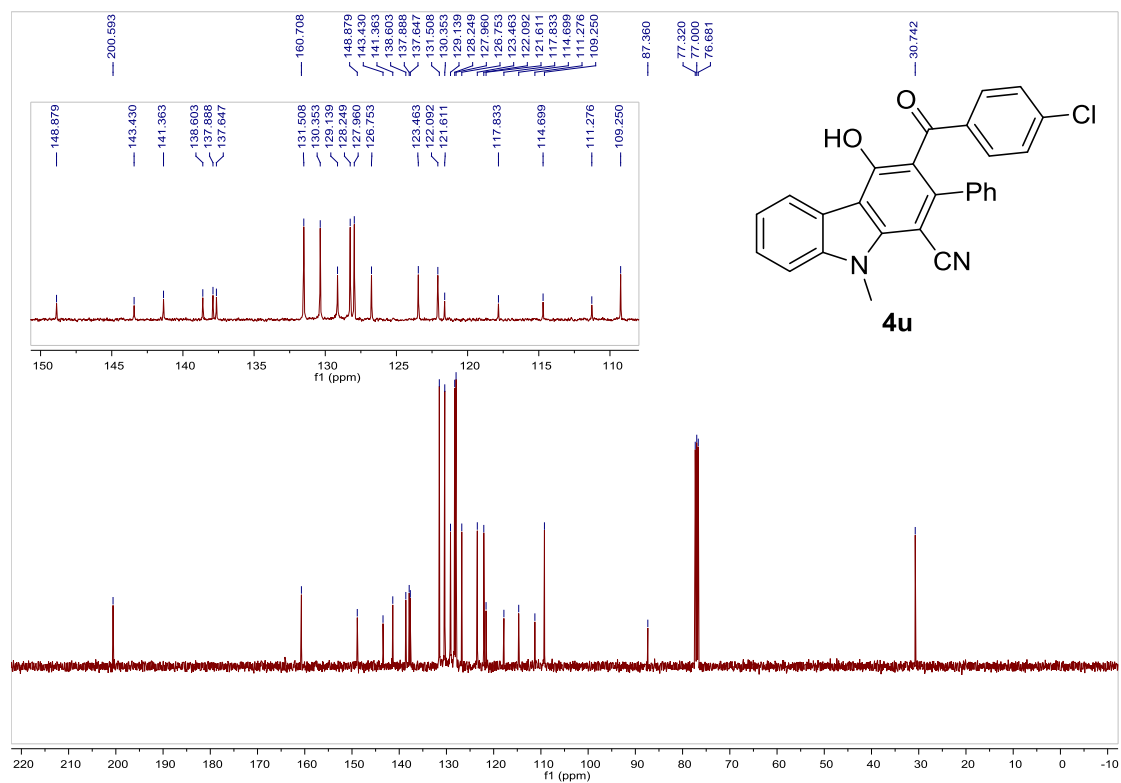
^{13}C NMR (100 MHz, CDCl_3)



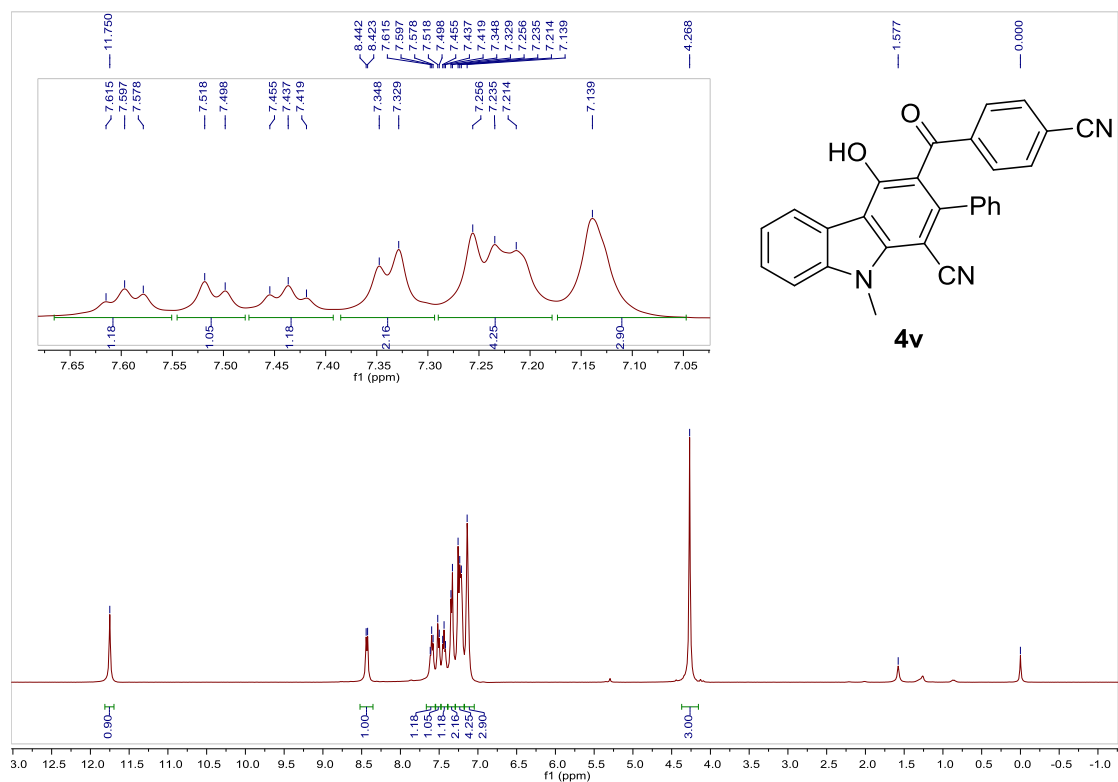
^1H NMR (400 MHz, CDCl_3)



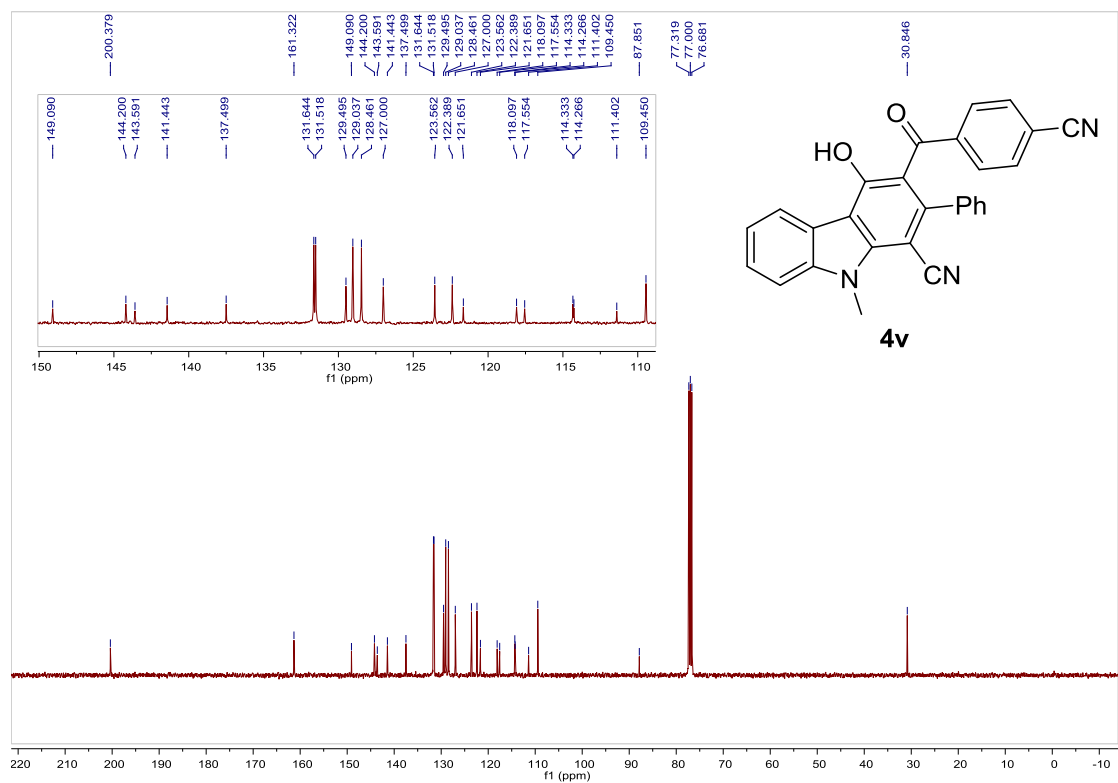
^{13}C NMR (100 MHz, CDCl_3)



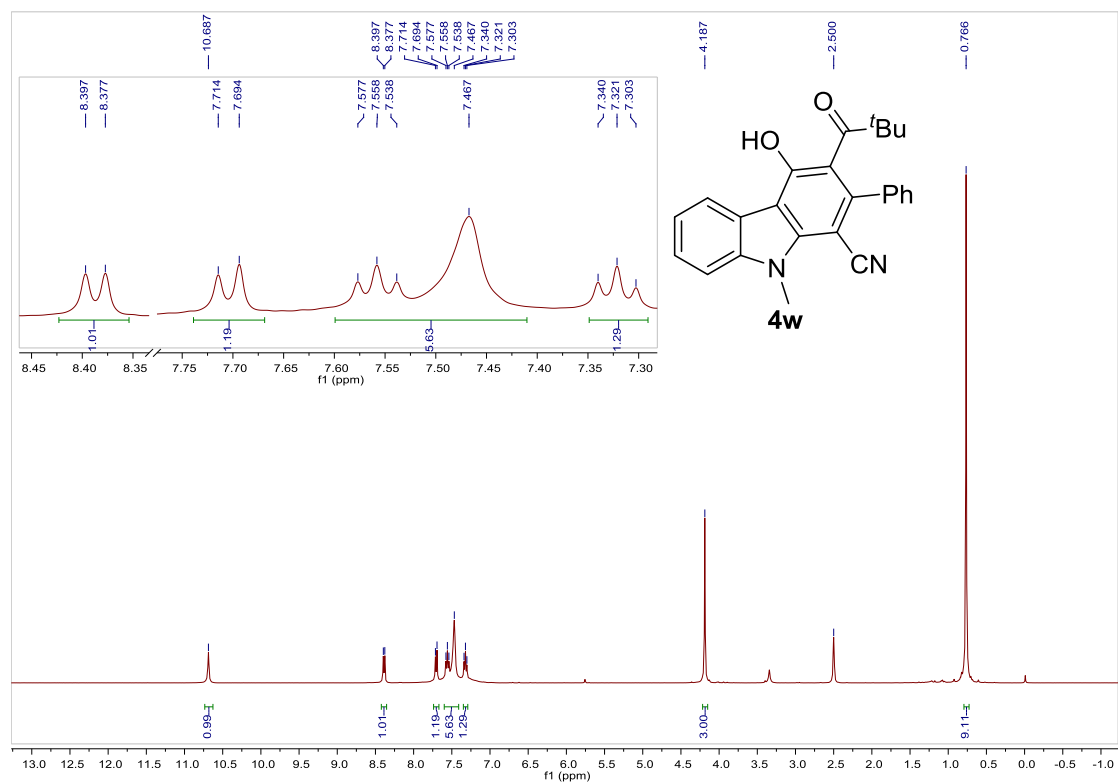
^1H NMR (400 MHz, CDCl_3)



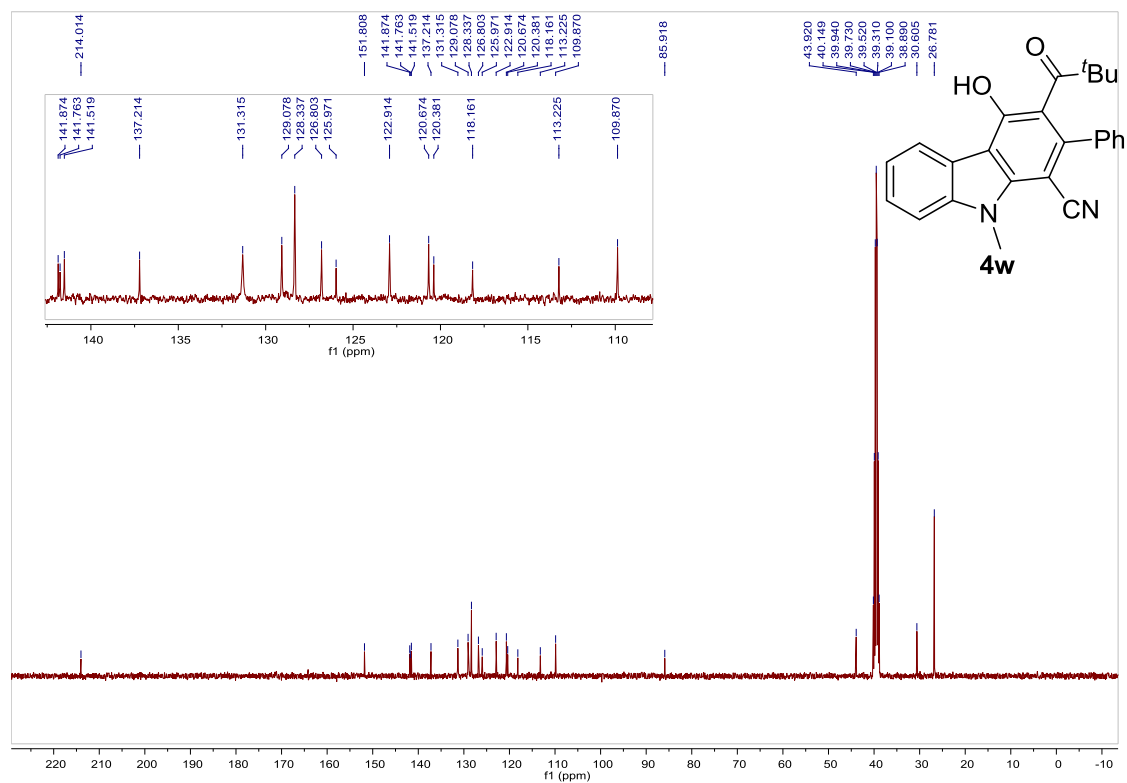
^{13}C NMR (100 MHz, CDCl_3)



^1H 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-1H-indole-2-carbonyl)-3,5-diphenylpenta-2,4-dienitrile (3a, mo-d8v17800-0m)

(Ortep ellipsoids are depicted at the 50% level)

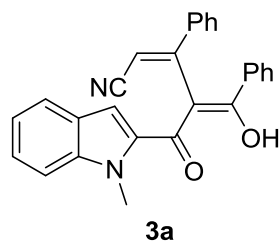
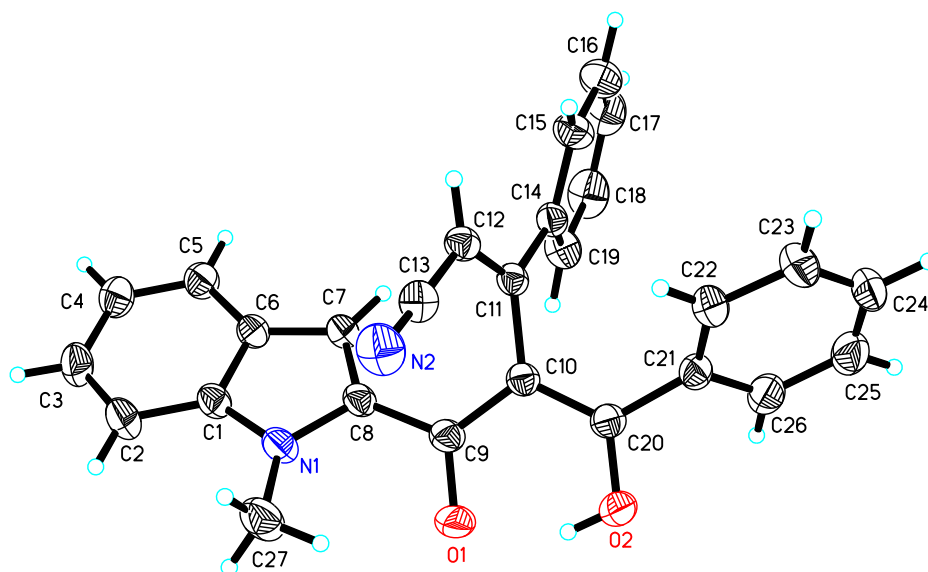
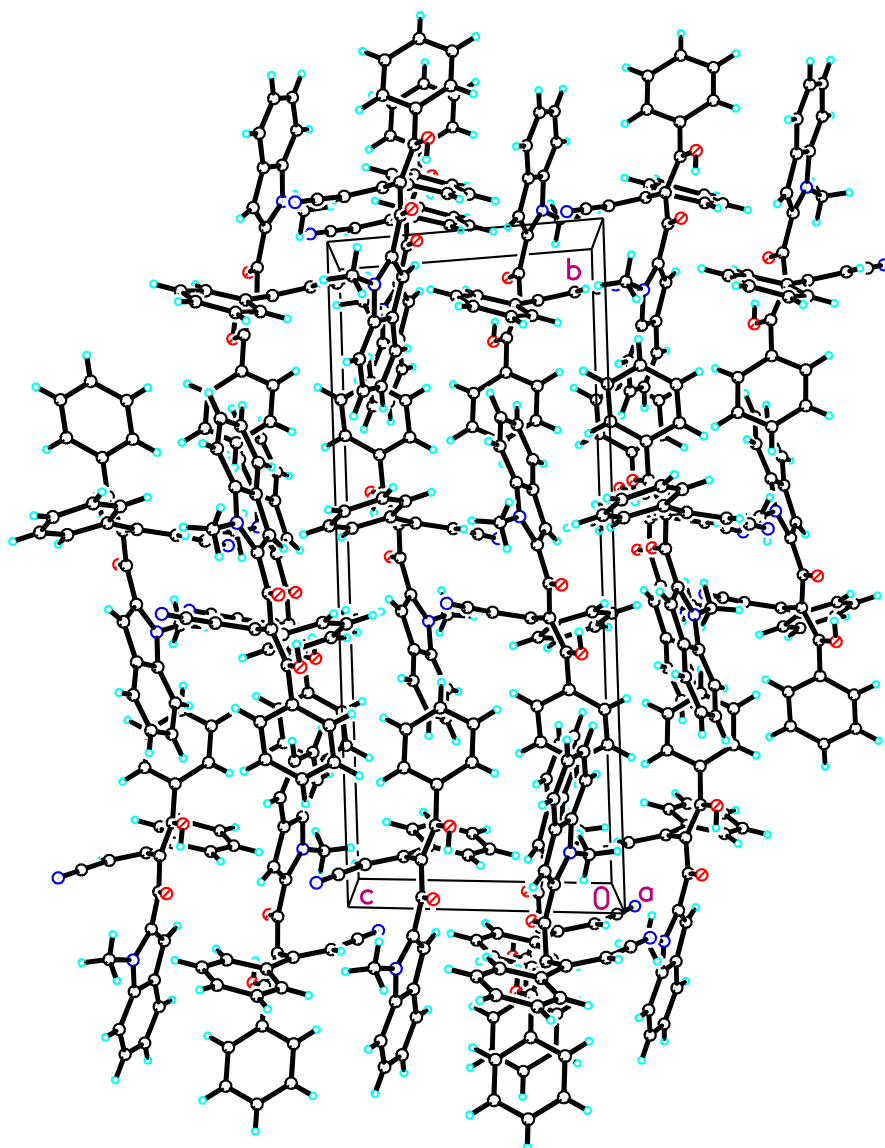


Table S2. Crystal data and structure refinement for **3a**

Identification code	3a
Empirical formula	C ₂₇ H ₂₀ N ₂ O ₂
Formula weight	404.45
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 2 ₁ /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 > 2σ(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





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)

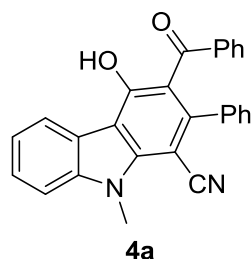
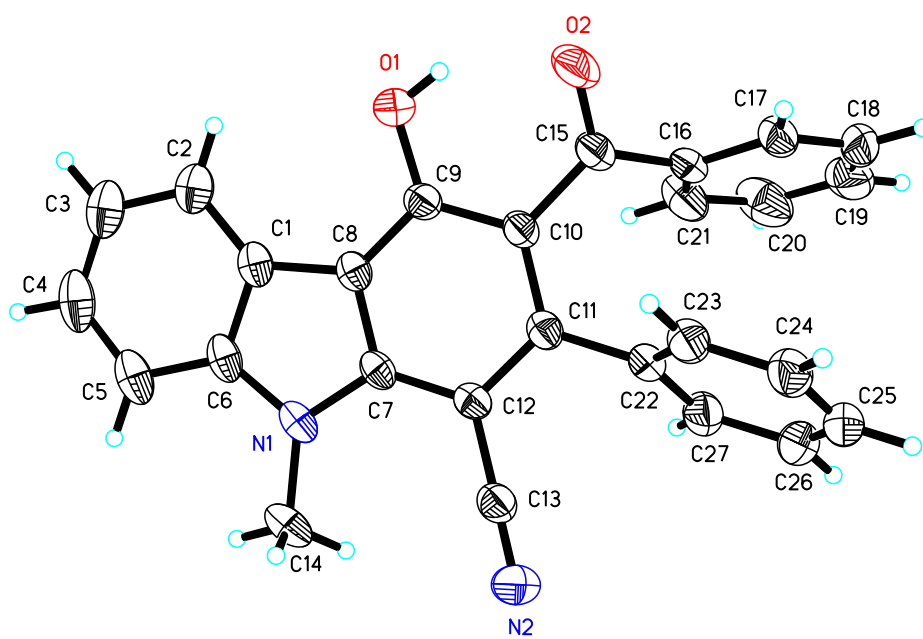
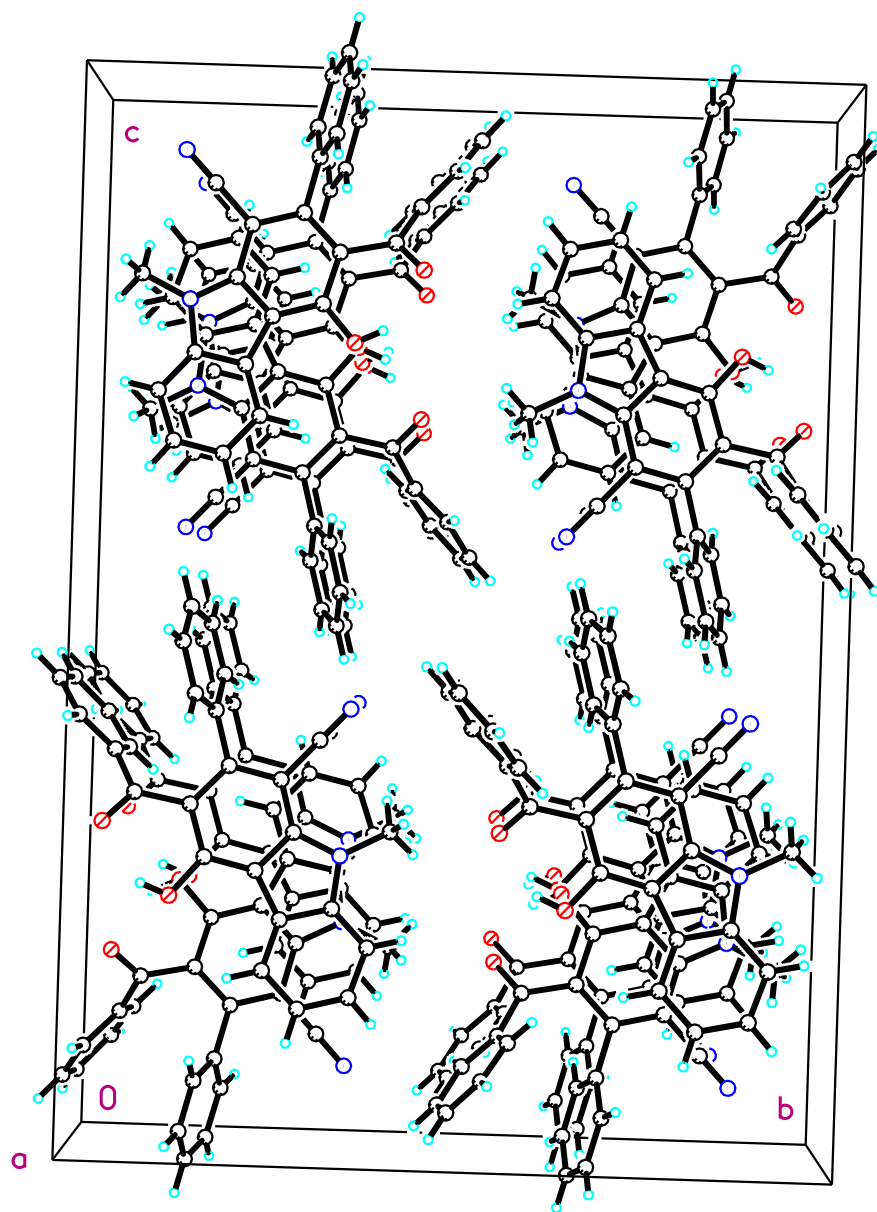


Table S3. Crystal data and structure refinement for 4a

Identification code	4a
Empirical formula	C ₂₇ H ₁₈ N ₂ O 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 > 2σ(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





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)

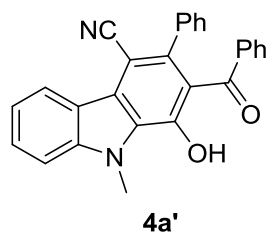


Table S4. Crystal data and structure refinement for **4a'**

Identification code	4a'
Empirical formula	C ₂₇ H ₁₈ N ₂ O 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 > 2σ(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

