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Rh(III)-Catalyzed Tandem Indole C4-Arylamination/Annulation with Anthranils: Access to Indoloquinolines and its Application in Photophysical Studies

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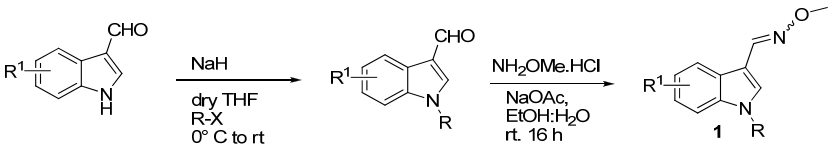
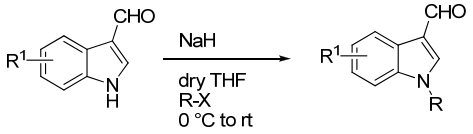
General introduction:

All commercially available compounds were used without further purification. Solvents for elution in column were distilled. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F254. Visualization on TLC was achieved by the use of UV light (254 nm). Column chromatography was undertaken on silica gel (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on BRUKER ULTRA SHIELD and BRUKER ASCEND (400 MHz, 500 MHz and 600 MHz) instruments. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br= broad, s= singlet, d= doublet, t= triplet, q= quartet, dd= doublet of doublet, td= triplet of doublet, ddd= doublet of doublet of doublet, m= multiplet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR spectra were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the centre of a triplet at 77.16 ppm of $CDCl_3$. Infrared (IR) spectra were recorded using Spectrum BX FT-IR instrument from Perkin Elmer. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance peaks are reported. High resolution mass spectra were obtained from waters XEVO-G2QTOF by using TOF MS ES+ method. LC-MS were obtained from Agilent Technologies A6120BW (single quadruple mass analyzer). Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted.

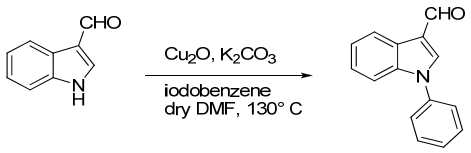
1. General procedure for the synthesis of starting materials:



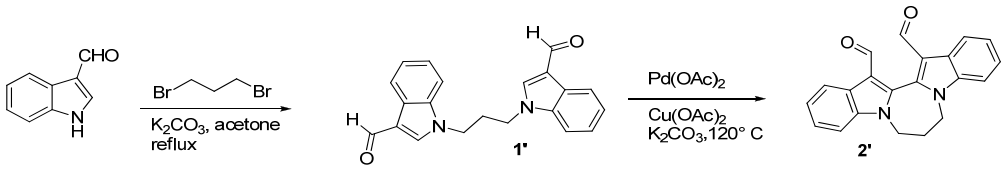
1.1 Synthesis of *N*-protected indole derivatives[1a, b]:



To a stirred suspension of NaH (60 wt% in mineral oil, 1.5 equiv) in dry THF, solution of 3-formyl indole derivative (1 equiv.) was added at 0 °C and stirred for 15 min. Then corresponding alkyl halide (1.1 equiv.) was added drop wise to the reaction mixture and stirred overnight at the room temperature. After completion of the reaction (as monitored by TLC), it was cooled to 0 °C and quenched by addition of saturated NH_4Cl solution and extracted with ethyl acetate. Combined organic layers were washed with water, brine, and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to obtain desired *N*-alkylated 3-formyl indole derivatives.



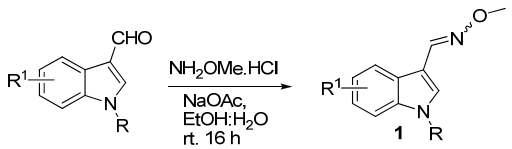
A suspension of indole-3-carbaldehyde (290 mg, 2 mmol), Cu_2O (85 mg, 0.6 mmol), anhydrous K_2CO_3 (553 mg, 4 mmol) and iodobenzene (8.16 g, 40 mmol) in anhydrous DMF (50 mL) was heated to 130 °C for 40 h. After cooling to room temperature, the reaction mixture was filtered through a celite pad eluting with EtOAc to remove any solid residue. Solvent was removed under reduced pressure and the residue was dissolved in EtOAc (20 mL) and washed by saturated brine solution. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1) to furnish the desired compound *N*-phenyl indole-3- aldehyde[1a] with 80% of isolated yield.



Indole-3-carboxyaldehyde (600 mg, 4.13 mmol, 2.2 equiv.) was taken in 40 mL acetone, K_2CO_3 (656 mg, 4.74 mmol, 2.5 equiv.), 1,3-dibromopropane (222 uL, 1.9 mmol, 1.0 equiv.), a catalytic amount of NaI (29 mg, 10 mol%) was added to the solution sequentially at room temperature. The reaction mixture was refluxed for 16 h and cooled to room temperature. The inorganic salts were removed by filtration and the resulting filtrate was concentrated under vacuo. The crude mixture was purified by silica gel column chromatography (70-100% ethyl acetate) and the final product **1´** was isolated in 70% yield as a white solid.

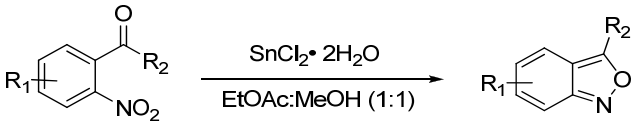
Finely crushed compound **1´** (210 mg, 0.8 mmol), anhydrous K_2CO_3 (112.0 mg, 0.8 mmol), $Pd(OAc)_2$ (18 mg, 0.08 mmol) and anhydrous $Cu(OAc)_2$ (436.0 mg, 2.4 mmol) were taken in 5 ml DMA in a seal tube and was flushed with nitrogen before being sealed. The reaction mixture was allowed to stir at room temperature until the starting material completely dissolved before being placed into a pre-heated oil bath at 120 °C for 16 h. The mixture was allowed to cool to rt, excess solvent was removed under reduced pressure, and directly purified by silica gel column chromatography. The product was eluted with a mixture of hexane/EtOAc. Pure product **2´** was obtained in 63% yield as a white solid.[1b]

1.2 General procedure for preparation of aldoximes: [2]



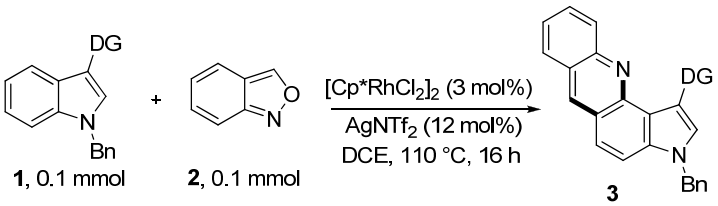
Indole-3-aldehyde derivative (1 equiv) was taken in a 50 mL round bottom flask equipped with a stirring bar, $MeONH_2 \cdot HCl$ (3.0 equiv), NaOAc (5.0 equiv), and EtOH:H_2O (1:3) were added to the flask. The reaction mixture was allowed to stir for 16 to 24 h. After completion of reaction (as monitored by TLC), EtOH was removed under vacuum. The mixture was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to yield the desired aldoxime **1** in good to moderate yield.

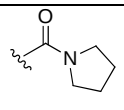
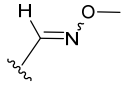
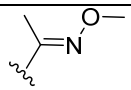
1.3 General procedure for synthesis of substituted anthranils:[3]



2-Nitroacyl benzene (1.0 mmol) was taken in a round-bottom flask equipped with a magnetic stirring bar in EtOAc/ MeOH (1:1; 5 mL). Next $SnCl_2 \cdot 2H_2O$ (3.0 mmol) was added to the reaction mixture and the resulting mixture was stirred overnight at room temperature. The reaction was partitioned between CH_2Cl_2 (30 mL) and saturated $NaHCO_3$ solution (20 mL). The aqueous phase was extracted with CH_2Cl_2 (10 mL × 3), and the combined organic layers were washed with H_2O (10 mL), saturated brine solution (10 mL) and dried over anhydrous Na_2SO_4. The organic layer was filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using 15-30% ethyl acetate in hexane as the eluent.

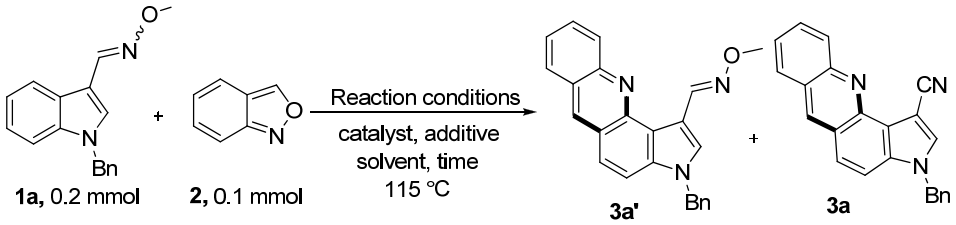
Tabel S1: Optimization for directing group



Entry	Directing group (DG)	Yield (%)
1	-CHO	nr
2	$-COCH_3$	nr
3	$-CO(CH_3)_3$	nr
3	$-CO_2Me$	nr
4	-CN	nr
5	-COOH	decomposition
6		nr
7		10
8		nr

Reaction conditions: All the reactions were performed with 0.1 mmol indole substrate (**1**) 0.1 mmol anthranil (**2a**) under air.

Table S2: Detailed optimization table for synthesis of 3-benzyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile:

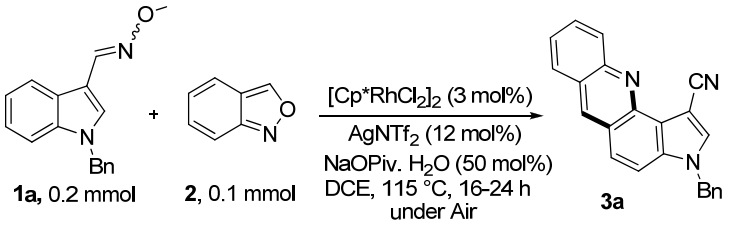


Entry	Catalyst (3 mol%)	Additive 1 (12 mol%)	Additive 2 (x mol%)	Solvent	Time h	yield % **3a´**	yield % **3a**
1[a]	Ir(III)	$AgSbF_6$	-	DCE	12	-	-
2[b]	Co(III)	$AgSbF_6$	NaOAc (50)	DCE	12	-	-
3[c]	Ru(II)	$AgNTf_2$	NaOAc (50)	DCE	12	-	-
4[d]	Rh(III)	Ag NTf_2	-	DCE	12	10	-
5	Rh(III)	Ag NTf_2	PivOH(100)	DCE	16	-	-
6	Rh(III)	Ag NTf_2	AgOAc (10)	DCE	16	22	-
7	Rh(III)	-	AgOAc (20)	DCE	16	-	-
8	Rh(III)	Ag NTf_2	$Zn(OAc)_2.2H_2O$ (20)	DCE	16	-	-
9	Rh(III)	Ag NTf_2	LiOAc. $2H_2O$ (20)	DCE	16	15	-
10	Rh(III)	Ag NTf_2	$Cu(OAc)_2$(20)	DCE	16	-	-
11	Rh(III)	Ag NTf_2	CsOAc(20)	DCE	16	-	-
12	Rh(III)	Ag NTf_2	NaOAc (10)	DCE	16	15	<5
13	Rh(III)	Ag NTf_2	NaOAc (30)	DCE	16	25	<10
14	Rh(III)	Ag NTf_2	NaOAc (50)	DCE	24	<5	31
15	Rh(III)	Ag NTf_2	NaOAc (100)	DCE	24	-	30
16	Rh(III)	Ag NTf_2	NaOTFA (50)	DCE	24	trace	-
17	Rh(III)	Ag NTf_2	NaOPiv. H_2O (20)	DCE	16	<10	65
18	Rh(III)	-	NaOPiv. H_2O (20)	DCE	16	-	-
19	**Rh(III)**	**Ag NTf_2**	**NaOPiv. H_2O (50)**	**DCE**	**16**	**trace**	**75**
20	Rh(III)	Ag SbF_6	NaOPiv. H_2O (50)	DCE	24	trace	69

21	Rh(III)	$AgPF_6$	NaOPiv. H_2O (50)	DCE	24	-	15
22	Rh(III)	$AgBF_4$	NaOPiv. H_2O (50)	DCE	16	-	-
23	Rh(III)	$AgClO_4$	NaOPiv. H_2O (50)	DCE	16	-	-
24	Rh(III)	Ag_2CO_3	NaOPiv. H_2O (50)	DCE	16	-	-
25	Rh(III)	Ag NTf_2	NaOPiv. H_2O (100)	DCE	24	-	68
26	Rh(III)	Ag NTf_2	NaOPiv. H_2O (50)	MeOH	24	-	-
27	Rh(III)	Ag NTf_2	NaOPiv. H_2O (50)	dioxane	24	-	37
28	Rh(III)	Ag NTf_2	NaOPiv. H_2O (50)	toluene	24	-	22
29	Rh(III)	Ag NTf_2	NaOPiv. H_2O (50)	DMF	24	-	-
30	Rh(III)	Ag NTf_2	NaOPiv. H_2O (50)	DMSO	24	<10	-

Reaction conditions: All the reactions were performed with indole 3-aldoxime (0.2 mmol) and anthranil (0.1 mmol). (yields were reported with respect to anthranil) [a][Cp*$IrCl_2$]$_2$, [b][Cp*Co(CO)I_2]$_2$, [c][Ru(*p*-cymene)Cl_2]$_2$, [d][Cp* $RhCl_2$]$_2$, Reaction temperature 115 °C, under air.

3. General procedure for the synthesis of 3-benzyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile:



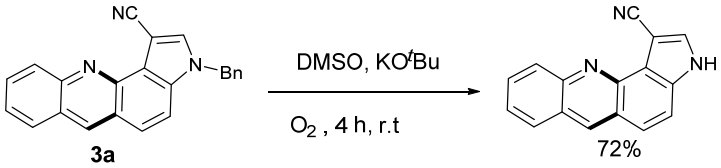
In a 10 mL screw-cap vial, [Cp*$RhCl_2$]$_2$ (3 mol%, 1.82 mg) was dissolved in 1 mL of dry DCE, followed by the addition of $AgNTf_2$ (12 mol%, 4.65 mg) and NaOPiv·H_2O (50 mol%, 6.2 mg). Next indole 3-aldoxime (0.2 mmol, 52 mg) was added to the reaction mixture and was allowed to stir for 1 min under ambient temperature. Anthranil **2** (0.1 mmol, 12 mg) was added to the reaction mixture at room temperature. Then it was heated to 115−130 °C (depending on substrate) and allowed to stir for 16−24 h. After the completion of the reaction, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and the solution was filtered through celite, and washed with CH_2Cl_2. The filtrate was concentrated and purified by flash column chromatography using a 30−70% EtOAc in hexane solvent mixture as the eluent.

Note: For (**3x**, **3y**) isolated compounds were dissolved in 3 mL 1:1 mixture of 1,4- dioxane and 6N HCl and stirred at room temperature (for **3x**)/ heated at 80 °C (for **3y**) for 4 hrs. Next reaction was diluted with water, neutralized with saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 (2x10 mL). The organic

layer was concentrated and purified by flash column chromatography using 30−50% EtOAc in hexane solvent mixture as the eluent.

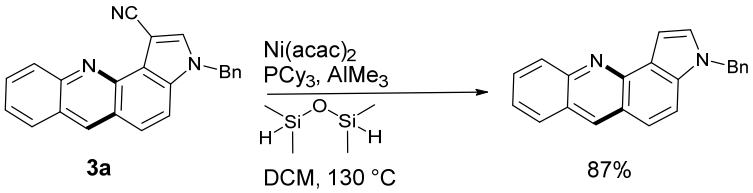
4. Product modifications:

4.1. Deprotection of benzyl group:[4]



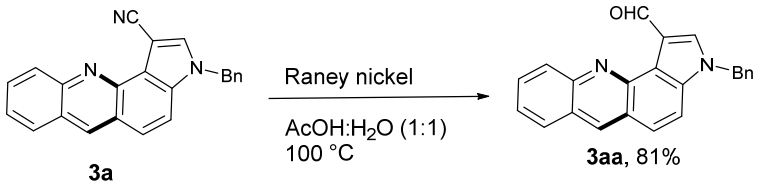
To a stirred solution of compound **3a** (33.3 mg, 0.1 mmol) dissolved in dry DMSO (1.5 mL), KO^{t}Bu (90 mg, 0.8 mmol) was added. Oxygen was then bubbled into the solution until complete consumption of starting material (as monitored by TLC). After completion, the reaction mixture was quenched by saturated solution of ammonium chloride and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to obtain pure product **7** (17.5 mg, 72%) as yellow amorphous solid. The product was further characterized by analytical data.

4.2 Deprotection of nitrile group:[5]



An oven dried reaction tube containing a magnetic stirring bar was charged with compound **3a** (67 mg, 0.2 mmol), $Ni(acac)_2$ (15.36 mg, 30 mol%, 0.06 mmol), PCy_3 (50.4 mg, 90 mol%, 0.18 mmol). The tube was then evacuated and back-filled with argon. The evacuation/backfill sequence was repeated two additional times. Under a counter flow of argon, 1,1,3,3-Tetramethyldisiloxane (35.3 µL, 0.2 mmol), $AlMe_3$ in toluene solution (115.2 µL, 0.6 mmol) and toluene (1.5 mL) were added by syringe. The tube was placed in a pre-heated oil bath at 130 °C and the reaction mixture was stirred for 24 h. The reaction mixture was cooled to room temperature, diluted with 3 mL ethyl acetate and filtered through celite, eluting with additional 10 mL of ethyl acetate. The filtrate was concentrated and the resulting residue was purified by column chromatography to obtain the desired indole derivative **8** with 87% isolated yield.

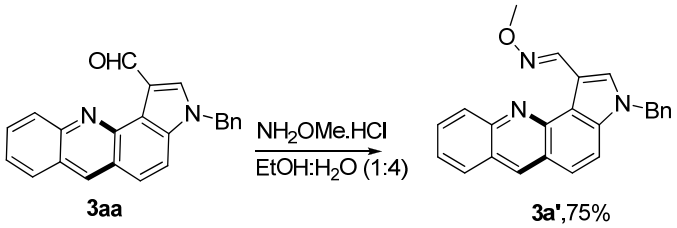
4.3 Reduction of nitrile group to aldehyde:[6]



3a **3aa**, 81%

To a solution of compound **3a** (67 mg, 0.2 mmol) in 2 mL of 50% AcOH in water, nickel- aluminium alloy (50 mg wt) was added and the reaction tube was placed in an oil bath with a temperature of 100 °C. Stirring at this temperature was continued for 2 h until no more starting material could be detected by TLC. Water(10 mL) was added, the reaction mixture was filtered over celite, and the resulting solution was extracted with dichloromethane (3 X 10 mL).The combined extracts were washed with a $NaHCO_3$ solution twice and water (10 mL) and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography to obtain compound **3aa** with 81% isolated yield. The product was further characterized by analytical data.

4.4 Synthsis of aldoxime from compound 3a´:

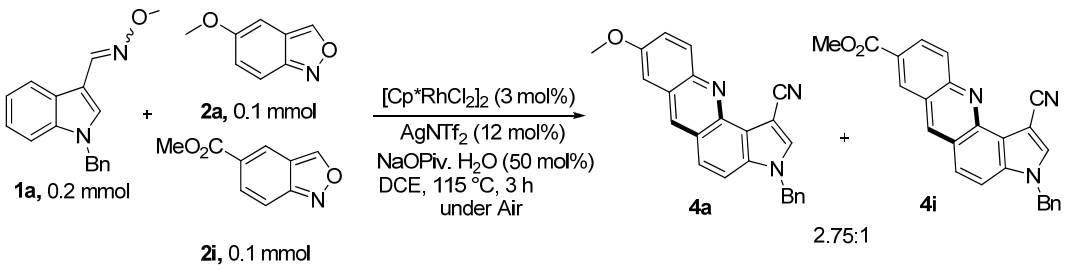


3aa **3a'**,75%

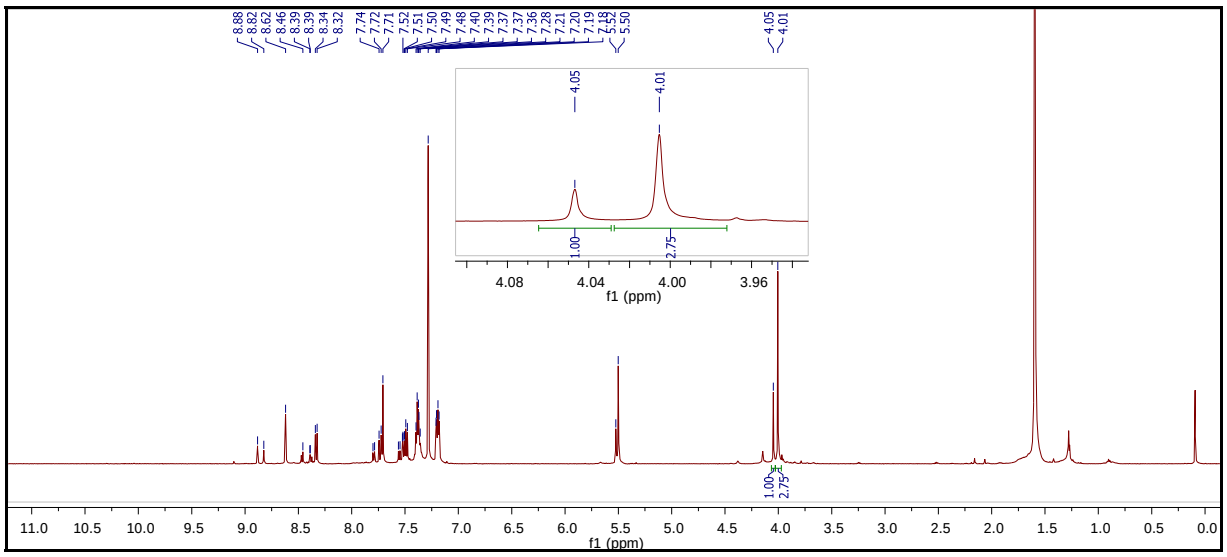
Compound **3aa** can be converted to corresponding aldoxime **3a´** following the standard procedure **1.2**, with an isolated yield of 75%

5. Control experiments and mechanistic studies:

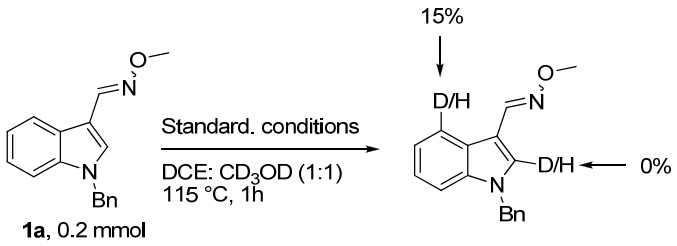
5.1 Reaction rate experiments with electronically variable anthranils:



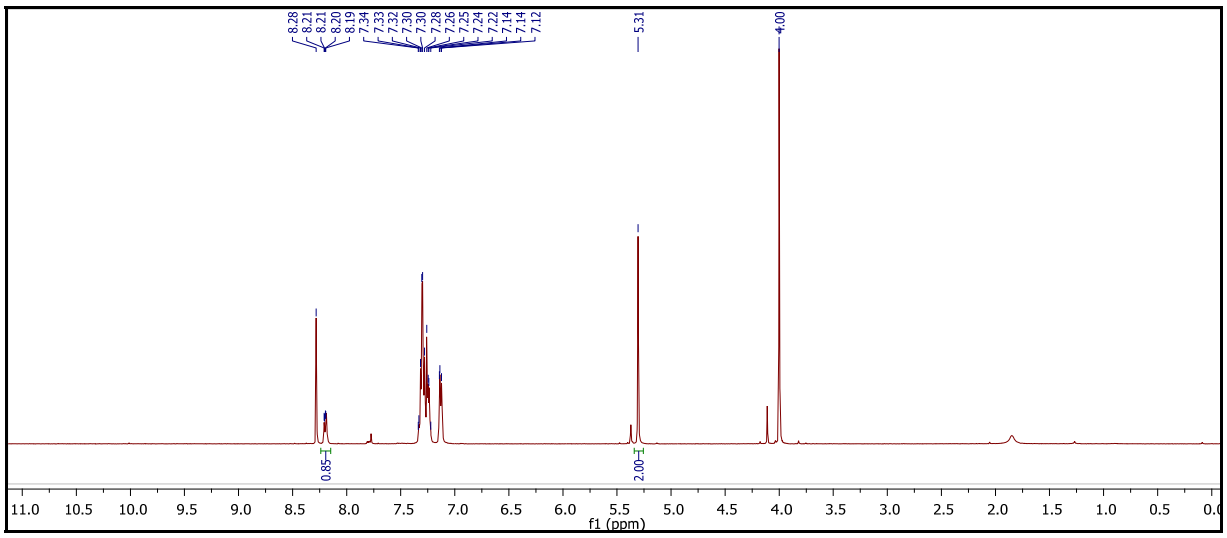
In a 10 mL screw-cap vial $[Cp^*RhCl_2]_2$ (3 mol%, 1.82 mg) was dissolved in 1 mL of dry DCE, followed by $AgNTf_2$ (12 mol%, 4.65 mg), NaOPiv. H_2O (50 mol%, 6.2 mg) were added to the reaction mixture. Next indole 3-aldoxime (0.2 mmol, 52 mg) was added to the reaction mixture and stirred for 1 min at room temperature. To this solution, anthranil **2a** (14.9 mg, 0.1 mmol) and anthranil **2i** (17.7 mg, 0.1 mmol) were added. Then it was heated to 115 °C and allowed to stir for 3 h. Next, the solvent was removed under reduced pressure and the mixture of product was filtered by flash column chromatography. The product ratio was identified by ^{1}H NMR to be 2.75:1(**4a**:**4i**).



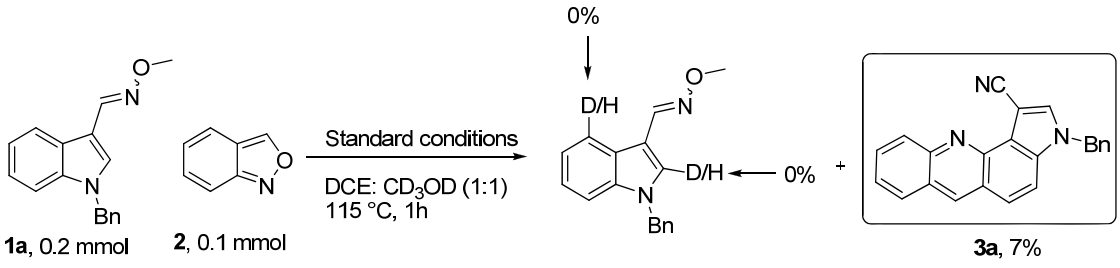
5.2 H/D scrambling experiment in the absence of anthranil:



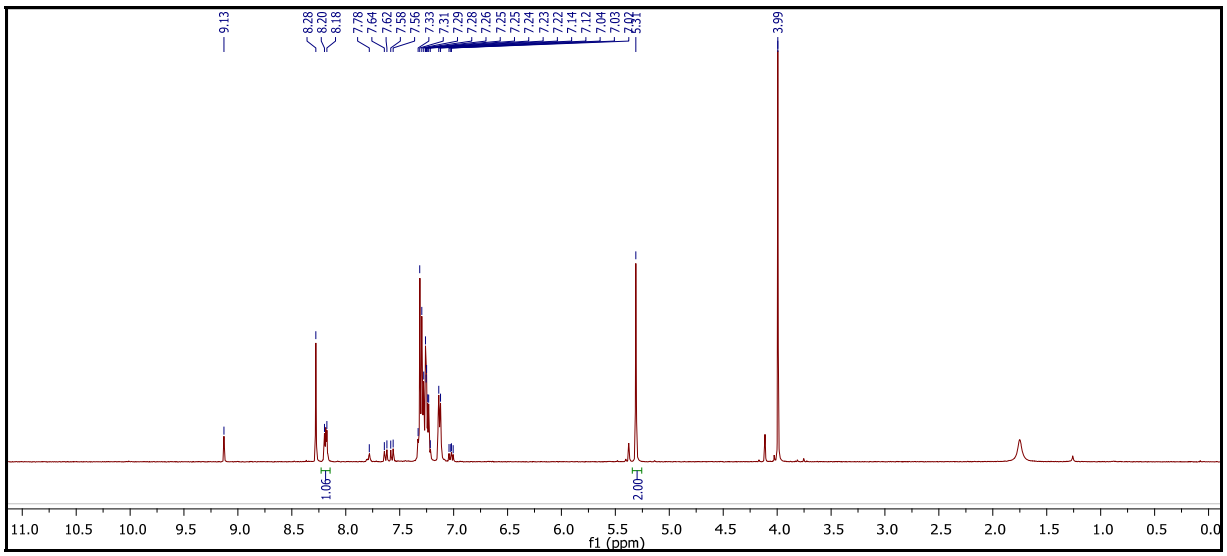
Indole-3-aldoxime **1a** (0.2 mmol, 52 mg) was taken in a 10 mL screw cap vial equipped with magnetic stirring bar and dissolved in mixture of 0.5 mL dry DCE and 0.5 mL of CD_3OD. Then $[Cp^*RhCl_2]_2$ (3 mol%, 1.8 mg), followed by $AgNTf_2$ (12 mol%, 4.65 mg), NaOPiv. H_2O (50 mol%, 6.2 mg) were added to the reaction mixture. Next, it was stirred for 60 min at 115 °C under air. Afterwards the reaction mixture was rapidly filtered through a silica gel column. 15% Deuterium incorporation was observed at the C4 position of recovered indole 3-aldoxime **1a** via ^1H NMR measurement.



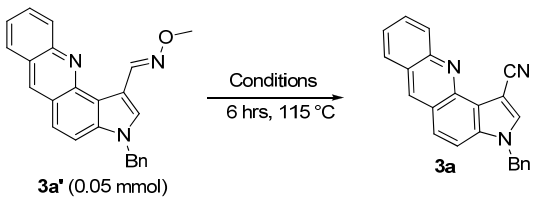
5.3 H/D scrambling experiment in the presence of anthranil:



Indole-3-aldoxime **1a** (0.2 mmol, 52 mg) was taken in a 10 mL screw cap vial equipped with magnetic stirring bar and dissolved in mixture of 0.5 mL dry DCE and 0.5 mL of CD_3OD. Then $[Cp^*RhCl_2]_2$ (3 mol%, 1.8 mg), $AgNTf_2$ (12 mol%, 4.65 mg), $NaOPiv{\cdot}H_2O$ (50 mol%, 6.2 mg) were added to the reaction mixture. Next anthranil **2**(12 mg, 0.1 mmol) was added to the reaction mixture and it was stirred for 60 min at 115 °C. After wards it was cooled to rt and rapidly filtered through silica gel column. No deuterium incorporation was observed at C4/ C2-position of recovered indole 3-aldoxime **1a** via ^1H NMR measurement.



5.4 Mechanistic investigation for oxime to nitrile formation:



3a' (0.05 mmol) **3a**

To understand the condition for the formation of nitrile, oxime **3a´** was allowed to react under different catalytic conditions and product **3a** was isolated by flash column chromatography.

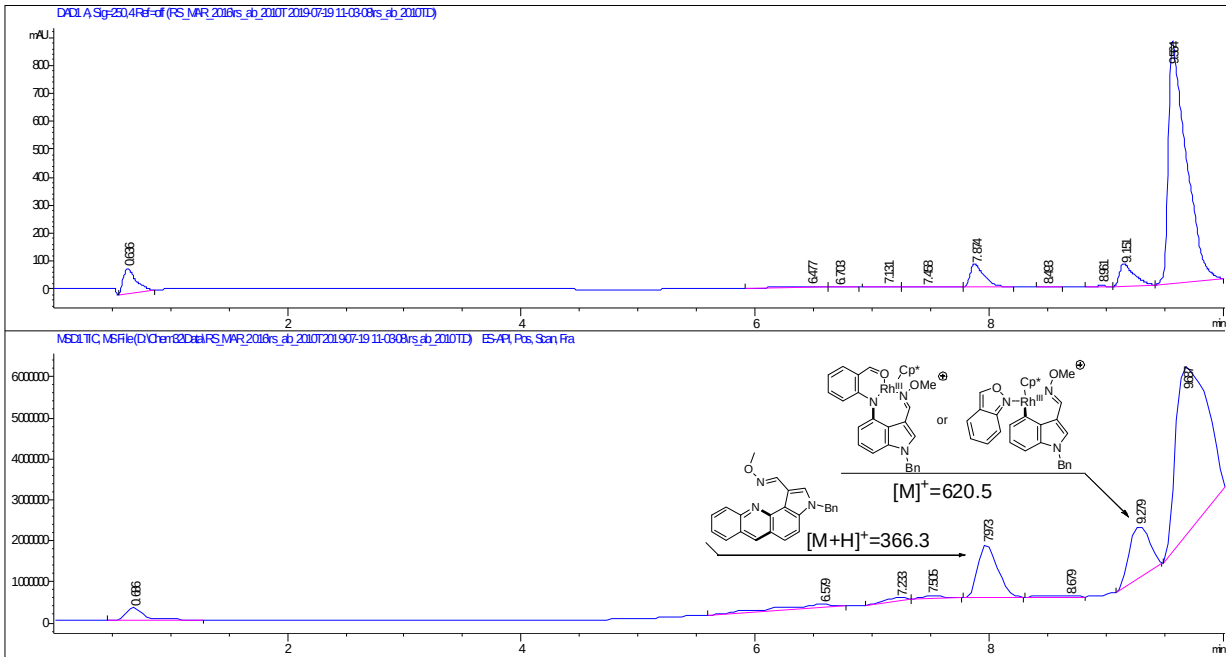
Table S3:

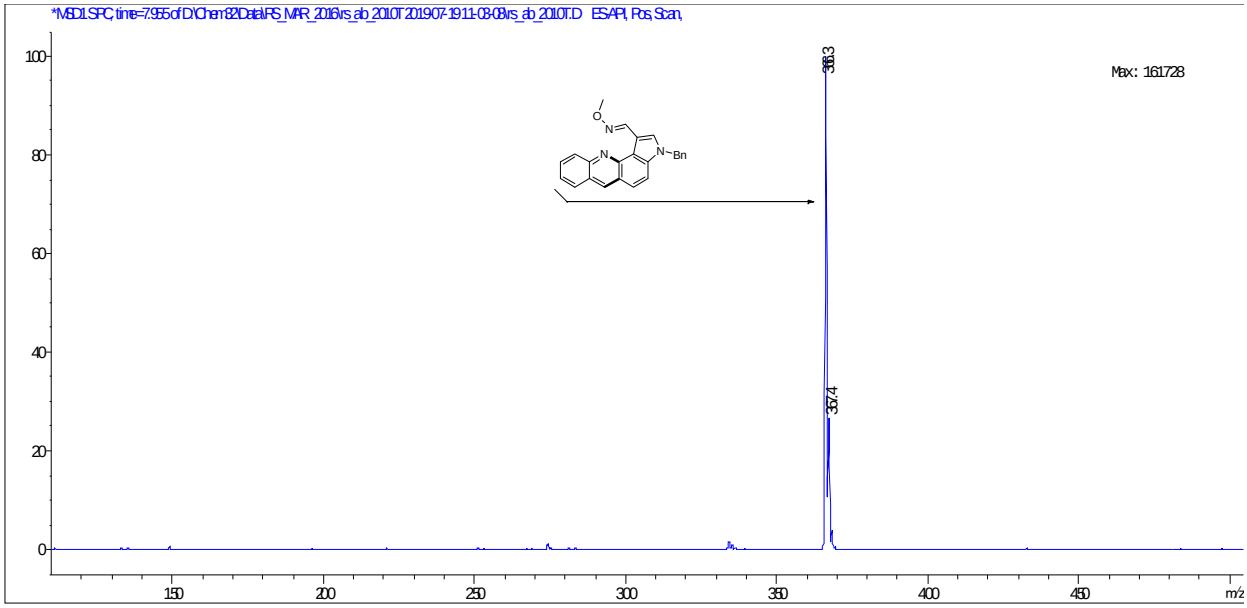
Catalyst (3 mol%)	**Additive 1** (12 mol%)	**Additive 2** (50 mol%)	**Yield % (3a)**
$[Cp^*RhCl_2]_2$	-	-	Trace

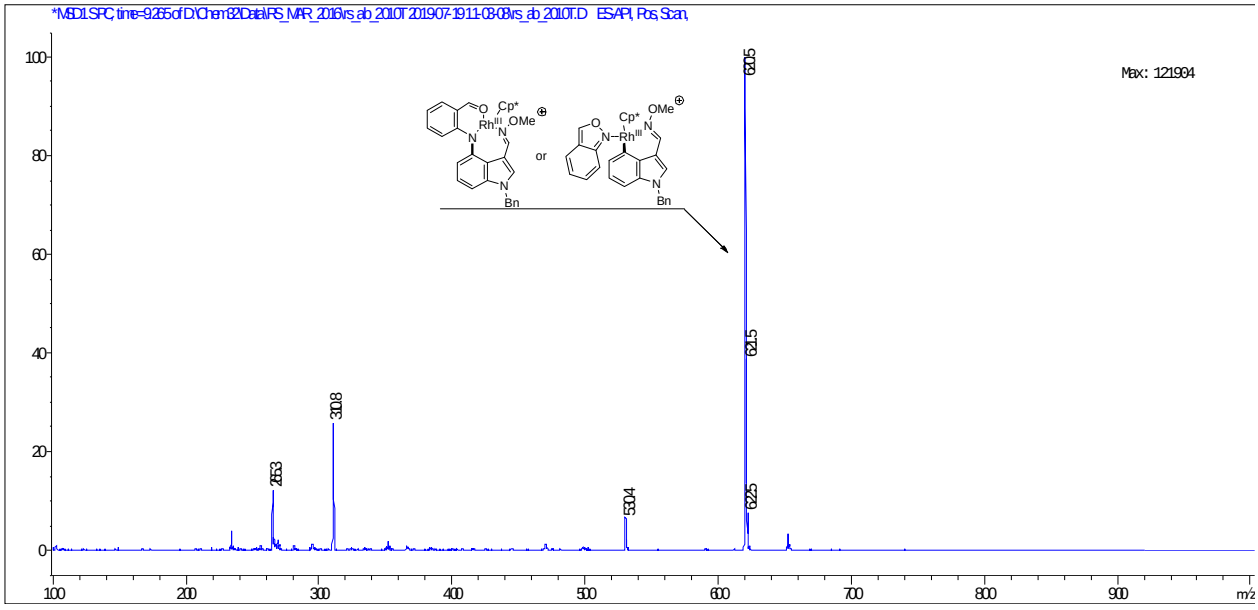
$[Cp^*RhCl_2]_2$	$AgNTf_2$	-	45
$[Cp^*RhCl_2]_2$	-	$NaOPiv.H_2O$	93 (100% conv.)
-	$AgNTf_2$	-	NR
-	-	$NaOPiv.H_2O$	NR
-	$AgNTf_2$	$NaOPiv.H_2O$	NR
$[Cp^*RhCl_2]_2$	$AgNTf_2$	$NaOPiv.H_2O$	91

5.5 Identification of intermediates through LCMS analysis:

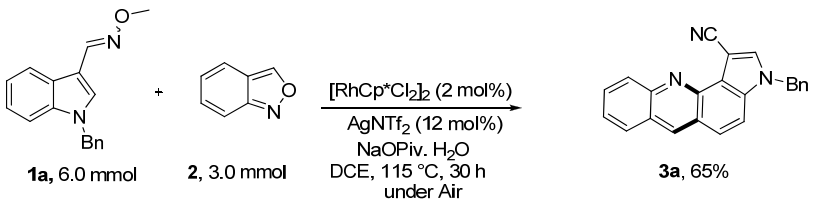
In order to identify the possible intermediates involved in the optimized reaction a standard reaction was stopped at 1h of reaction time. Next, 0.1 mL of reaction mixture was taken out and diluted to 0.5 mL with $CHCl_3$ and filtered through a 0.2 µm filter to remove any solid residue, further the solvent was removed and LCMS analysis was carried out.







6. Large-scale experiment:



In a 50 mL screw-cap seal tube $[Cp^*RhCl_2]_2$ (2 mol%, 36 mg) was dissolved in 12 mL of dry DCE, followed by $AgNTf_2$ (12 mol%, 137.0 mg), NaOPiv. H_2O (50 mol%, 186 mg) were added to the solution. Next, indole-3-aldoxime (**1a**, 6.0 mmol, 1.4 g) was added to the solution and mixture was stirred for 1 min at room temperature. Then anthranil (**2aa**) (3.0 mmol, 360 mg) were added to the reaction mixture at the room temperature, and solution was heated to 115 °C and allowed to stir for 30 h. After the completion of the reaction, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and the solution was filtered through celite, and washed with CH_2Cl_2. The filtrate was concentrated and purified by flash column chromatography using a 30−70% EtOAc in hexane solvent mixture as the eluent. Isolated yield of product **3a** was 65%.

Analytical Data:

Table S4. Crystal data and structure refinement for 3-Benzyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (3a, CCDC 1944062):

Datablock: A

Bond precision: C-C = 0.0045 A Wavelength=0.71073

Cell: a=9.549(2) b=21.299(4) c=9.583(2)
alpha=90 beta=111.20(3) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1817.1(7)	1817.1(7)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C23 H15 N3	?
Sum formula	C23 H15 N3	C23 H15 N3
Mr	333.38	333.38
Dx,g cm-3	1.219	1.219
Z	4	4
Mu (mm-1)	0.073	0.073
F000	696.0	696.0
F000'	696.24	
h,k,lmax	10,23,10	10,23,10
Nref	2600	2581
Tmin,Tmax	0.992,0.995	0.632,0.795
Tmin'	0.989	

Correction method= # Reported T Limits: Tmin=0.632 Tmax=0.795
AbsCorr = EMPIRICAL

Data completeness= 0.993 Theta(max)= 23.259

R(reflections)= 0.0495(1506) wR2(reflections)= 0.1548(2581)

S = 1.031 Npar= 236

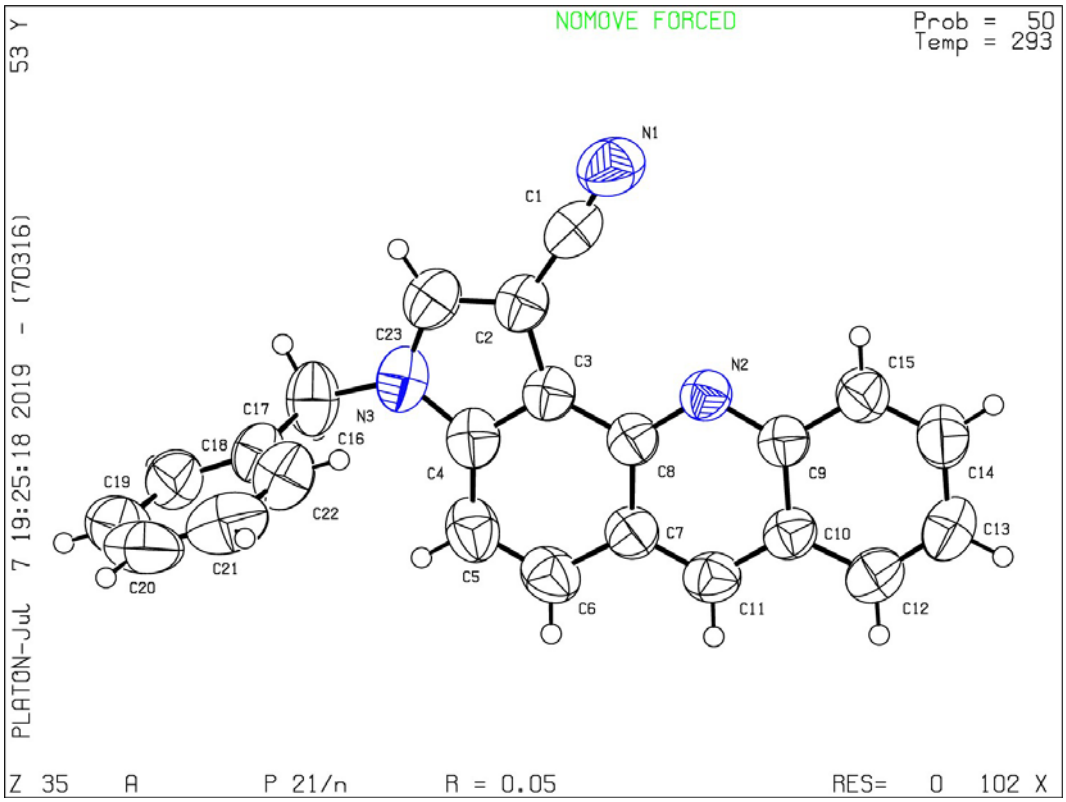


Figure 1: ORTEP presentation of 3a (drawn at 50% probability)

Experimental section for photo-physical studies:

Absorbance (A) measurement and determination of molar absorption coefficient(ε): All the UV−Vis absorption spectra were recorded using a Shimadzu UV−Vis spectrophotometer (model UV 2450) in dicholoromethane. Molar absorption coefficient (ε)was calculated by using Beer-Lambert's law (A= εcl); path length (l) was kept as 1cm and the concentration (c) of the samples was around 10^{-6} M. For determining ε, the absorbance (A) values of the solutions were kept below 0.1.

Fluorescence measurement and determination of fluorescence Quantum yield (Φ): Steady-state fluorescence emission spectra were recorded using a Shimadzu RF-6000 fluorimeter. For the detection of emission spectra the excitation and emission slits were adjusted to 5 nm. For calculating quantum yield, all the measurement was done by maintaining the concentration of the samples and reference at a low value of5×10^{-6}M to minimize error due or self-aggregation or self-quenching. The absorbance (A) values of the solutions were kept below 0.1.A secondary standard quinine sulphate (λ_{abs}= 350 nm) in 0.1 M H_2SO_4 (Φ = 0.54 at 298 K) was used for measuring fluorescence quantum yields. The quantum yield was calculated by using these following equation:[7]

$$\frac{\Phi_S}{\Phi_R} = \frac{(Abs)_R}{(Abs)_S}\frac{A_S}{A_R}\frac{\eta_S^2}{\eta_R^2}$$

Here Φ denotes the quantum yield, (Abs) denotes the absorbance, A_S and A_R denotes the area under the fluorescence emission curve and η is the refractive index of the medium. The subscript S and R represent the corresponding parameters for the samples and reference respectively.

Result and Discussion:

UV Absorption Spectroscopy: The absorption properties of the compounds were investigated in dicholoromethane. All the samples were completely soluble in this solvent at the concentration range that was used. All the molecules studied in this paper have generally two absorption bands. An intense absorption band below 325 nm corresponding to $\pi\rightarrow\pi^*$ transition was observed. A comparatively weak absorption band above 325 nm correspond to $n\rightarrow\pi^*$transition. In dicholoromethane the compounds do not form hydrogen bond with the solvent, as a result the fine structures of the absorption band were observed. In Table S5, we have presented the values of λ_{max}(wavelength corresponding to the maximum of the absorption) and molar absorption coefficients, ε (at the λ_{max}) for the absorption band of lower energy.

Although the nature of the UV-vis spectra for all the compounds was similar in nature, the presence of different substituents in the base structure influenced the spectra to some extent. For example, as shown in Fig 1, electron donating group at C2 position (e.g. **3h**, **3g**) of **3a**caused significant red-shift of the absorption band along with reduction in ε (at the λ_{max}). Different alkyl and aryl substitution on indole

nitrogen (e.g. **3a**, **3b**, **3c**,**3d**,**3e**) gives similar absorbance spectra which are slightly red shifted with respect to the unsubstituted **3f** (Fig S2). However, the red-shift in this case of N-substituted molecules was less compared to the molecules with electron donating group at C2 position as presented in Fig 1. Next, we compare the absorption spectra of compounds with substitution at C7 position of indole moiety. Strong electron donating groups like cyclopropyl (**3l**) and methoxy (**3m**) caused red-shift of the absorption spectra, whereas other weakly electron donating/withdrawing groups (**3k**, **3n**, **3p**, **3q**) do not have significant effect on unsubstituted counterpart, **3a** (Fig S3). Substitution of the acridine ring have practically no significant effect on the absorption band as shown in Fig S4 for compounds **3j**, **3p**, **3q**, **4e**, **4f**, **4g**,**4h**, **4j**, **4k**. Presence of strong electron donating OMe group in the acridine ring red-shifted the absorption band in **4a** compared to **3a**. (Fig S5). Absorption spectra of 4b and 4c are slightly different than **4a**. Absorption spectra of rest of the compounds (viz. **3s**, **4l**, **4d**, **3t**) are presented in Fig S6.

Table S5: Spectroscopic data for all the samples studied in this work.

Molecules	**Absorption**		**Emission**	
	λ_{max}/ nm	**ε /(10^4L $mol^{-1}cm^{-1}$)**	**$\lambda_{emission}$ / nm**	**Q.Y.**
3a	368.0	2.7	433.0	0.25
3b	368.7	2.0	423.0	0.32
3c	370.0	4.1	429.0	0.19
3d	370.0	2.9	437.0	0.31
3e	368.0	4.3	433.0	0.24
3f	361.0	1.3	389.0	0.32
3g	388.0	2.1	449.0	0.31
3h	370.0	1.6	452.0	0.49
3i	359.8	2.6	408.0	0.07
3j	370.0	3.2	446.0	0.16
3k	372.0	2.8	423.0	0.05
3l	372.2	2.5	437.0	0.30
3m	396.0	4.7	441.0	0.17
3n	372.0	3.0	429.0	0.25
3o	359.0	2.3	454.0	0.64
3p	375.0	2.0	429.0	0.02
3q	374.0	2.5	442.0	0.29
3r	363.7	1.4	458.0	0.75
3s	368.0	2.0	421.0	0.10
3t	347.0	3.8	446.0	0.15
4a	400.5	3.1	428.6	0.21
4b	381.0	3.9	409.0	0.27
4c	380.0	3.7	419.0	0.27
4d	368.7	1.9	504.0	0.50
4e	376.0	2.8	450.0	0.46
4f	373.0	4.3	437.4	0.10

4g	393.0	3.4	437.4	0.44
4h	372.5	2.3	442.0	0.44
4i	376.9	3.6	441.0	0.25
4j	367.6	2.5	433.0	0.45
4k	368.0	3.0	442.8	0.41

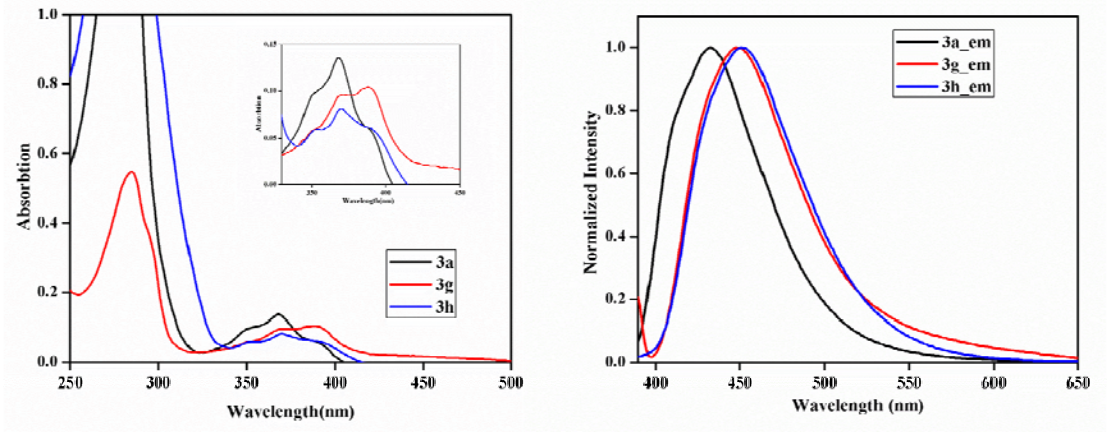


Figure S1: (Left) Absorption spectra and (right) fluorescence spectra of **3a, 3g and 3h** having electron donating group at C2 position.

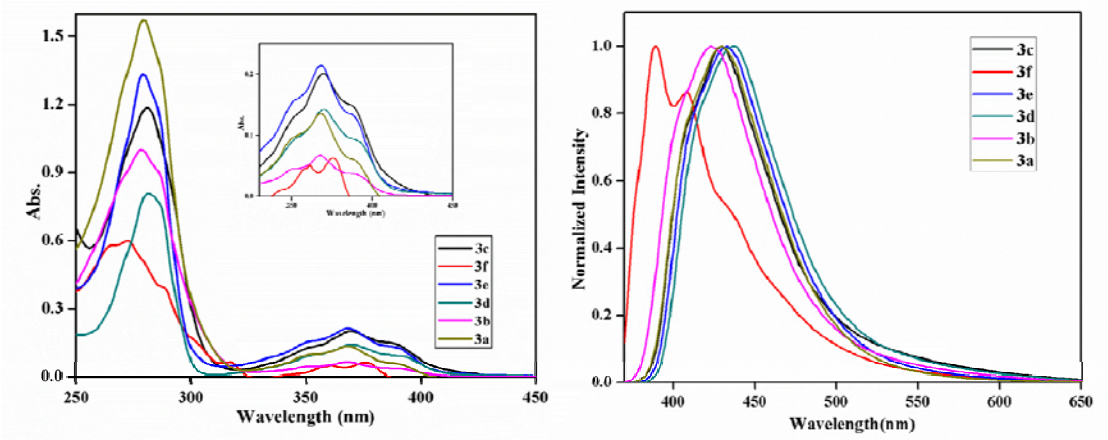


Figure S2: (Left) Absorption spectra and (right) fluorescence spectra of **3b**, **3c**, **3d**, **3e** and **3f** having different alkyl and aryl substitution on indole nitrogen.

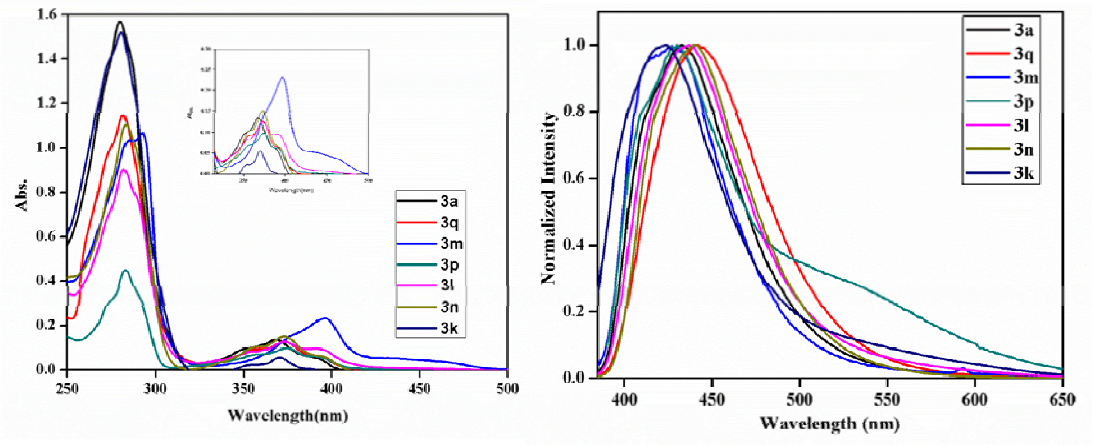


Figure S3: (Left) Absorption spectra and (right) fluorescence spectra of compounds having substitution at C7 position of indole moiety.

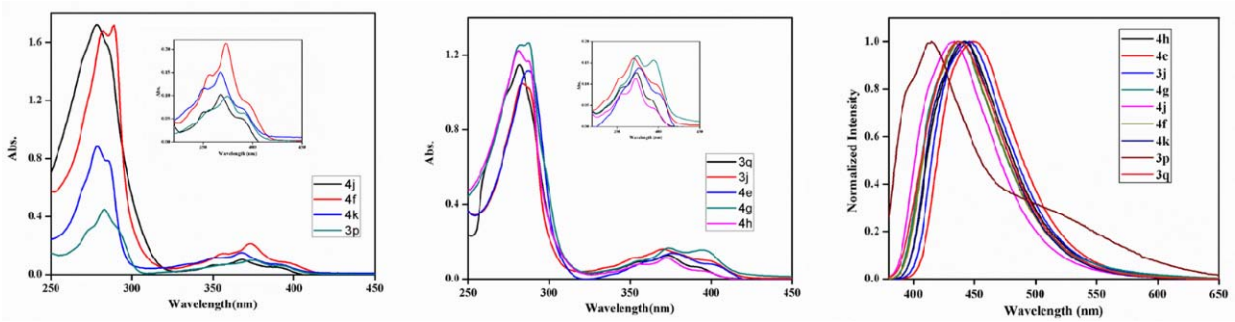


Figure S4: (Left, middle) Absorption spectra and (right) fluorescence spectra of compounds **3j**, **3p**, **3q**, **4e**, **4f**, **4g**, **4h**, **4j**, **4k** having substitution at various positions of acridine ring.

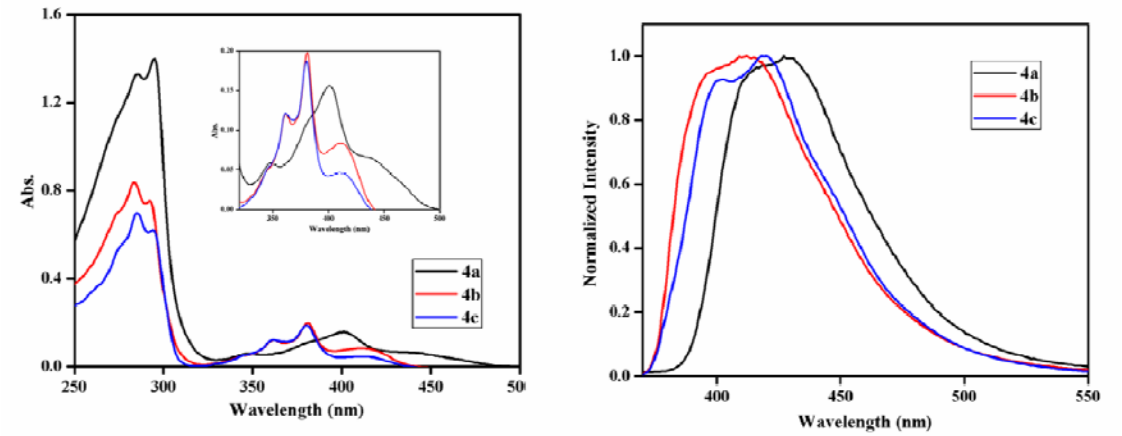


Figure S5: (Left) Absorption spectra and (right) fluorescence spectra of compounds **4a**, **4b**, **4c**.

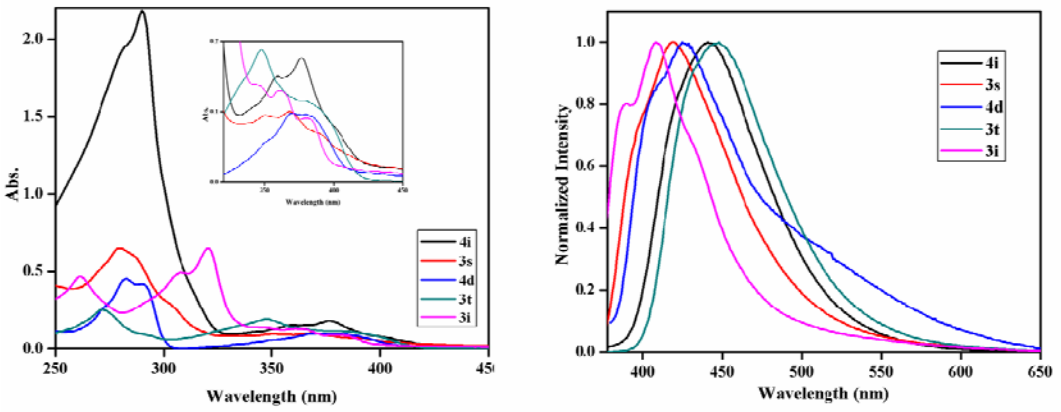


Fig S6: (Left) Absorption spectra and (right) fluorescence spectra of **3s**, **4l**, **4d**, **3t**

Fluorescence Spectroscopy

Along with being UV active, all the molecules studies in this work was also found to be fluorescent, As representative examples, the fluorescence excitation and emission spectra of compound 3r and 3o are shown in Fig 7. These molecules were highly fluorescent with quantum yield values of 0.75 and 0.64 respectively. Fig. 6 also provides a picture of fluorescence behavior of these two compounds. It can also be seen that fluorescence excitation spectra match exactly with corresponding absorption spectra confirming the purity of the compound. It may be also noted that we obtained similar fluorescence spectra for these compounds irrespective of the excitation wavelength including the wavelength those belong to the other absorption band of lower wavelengths. These results implied that these two compounds may be employed as emitting materials in OLED device and as biosensor (i.e. acting as a probe in biological studies).

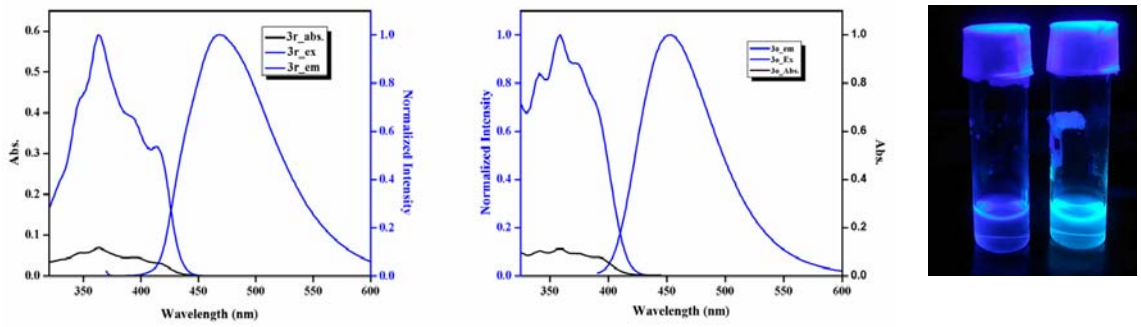


Figure S7: Absorption, fluorescence excitation and emission spectra of compound **3r** (top left) and **3o** (top right). A picture showing their fluorescent behavior is given at the bottom.

3-Benzyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3a**) showed highly fluorescence character. Substituents at different position affect the emission properties as well. Electron donating group at C2 position (e.g. **3h**, **3g**) increases the quantum yield along with red shift of fluorescence spectra (Figure S1). Different alkyl and aryl substitution on indole nitrogen produced similar fluorescence spectra with red shift with respect to **3f** (where free N-H is present) that generated a different type of emission spectra (Figure S3). Presence of –OMe or acetal group in acridine moiety resulted in similar characteristics bimodal emission spectra (Figure S4). Electron donating alkyl, aryl and methoxy group at C7 position of indole gives different emission spectra (**3k**-**3n**), halogen substituents such as –Br, -Cl at C7 found to provide similar emission spectra with different quantum yield (**3n**-**3o**) (Figure S5). The emission spectra of rest of the molecules are shown in Figure S 6. Among all the substituents **3r** and **3o** emitted intense bluish green fluorescence colour with highest quantum yield

References:

1 (a) C. Sagnes, G. Fournet, G. Satala, A. J. Bojarski and B. Josepha, *Eur. J. Med. Chem.* 2014, ***75***, 159. (b) D. G. Pintori and M. F. Greaney, *J. Am. Chem. Soc.* 2011, **133**, 1209.

2. A. Biswas and R. Samanta, *Eur. J. Org. Chem.* 2018, 1426.

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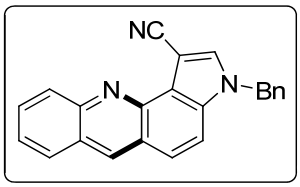
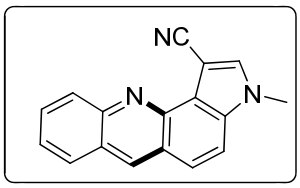
7. (a) J. R. Lakowicz, Principles of Fluorescence Spectroscopy; Plenum: New York, **1999**; 3rd edition. (b) A. Chakraborty, D. Chakrabarty, P. Hazra, D. Seth, N. Sarkar, *Chem. Phys. Lett.* 2003, **382**, 508.

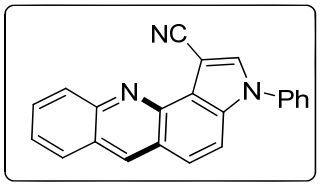
Analytical Data:



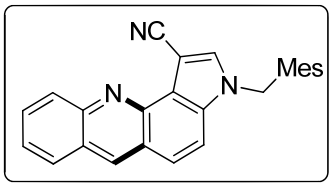
3-Benzyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3a**); yellow solid (75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.42 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.77 (m, 1H), 7.68 (d, *J* = 9.1 Hz, 1H), 7.65 (s, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 9.1 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.19 – 7.10 (m, 2H), 5.45 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.66, 144.49, 136.24, 135.44, 134.68, 133.48, 130.19, 129.93, 129.38, 128.69, 128.11, 127.09, 126.07, 125.60, 125.37, 123.66, 122.67, 116.61, 112.61, 89.13, 51.48; FT-IR: $\tilde{\nu}$ =2921, 2222, 1611, 1532, 1440, 1356, 1182 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{23}H_{16}N_3$: 334.1339; found: 334.1341



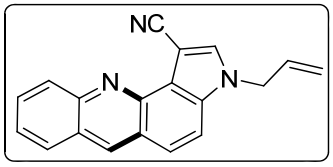
3-Methyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3b**); green amorphous solid (73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.41 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.82 (t, *J* = 7.1 Hz, 1H), 7.77 (d, *J* = 9.1 Hz, 1H), 7.62 (s, 1H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.51 (d, *J* = 9.1 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.74, 144.55, 136.25, 135.01, 133.83, 130.15, 130.00, 128.10, 126.08, 125.59, 125.25, 123.64, 122.52, 116.64, 112.24, 88.70, 34.24; FT-IR: $\tilde{\nu}$ = 2940, 2221, 1610, 1529, 1444, 1396, 1166 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{17}H_{12}N_3$: 258.1026; found: 258.1026



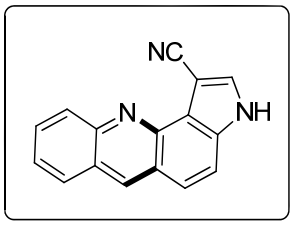
3-Phenyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3c**); light yellow amorphous solid (80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.44 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.88 (s, 1H), 7.82 (m, 1H), 7.77 (d, *J* = 9.2 Hz, 1H), 7.70 – 7.60 (m, 2H), 7.60 – 7.52 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.78, 144.51, 137.78, 136.21, 134.72, 133.31, 130.26, 130.23, 130.03, 129.05, 128.13, 126.20, 125.72, 125.71, 125.56, 123.84, 122.73, 116.41, 113.30, 90.61; FT-IR: $\tilde{\nu}$ = 2938, 2221, 1595, 1525, 1495, 1369, 1166 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{22}H_{14}N_3$: 320.1182; found: 320.1188



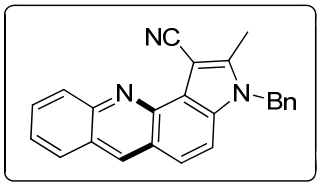
3-(2,4,6-Trimethylbenzyl)-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3d**); yellow amorphous solid (77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.41 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.81 (m, 2H), 7.71 (d, *J* = 9.1 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.15 (s, 1H), 6.99 (s, 2H), 5.37 (s, 2H), 2.35 (s, 3H), 2.24 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.69, 144.59, 139.40, 138.10, 136.26, 134.68, 131.73, 130.12, 129.97, 129.95, 128.09, 127.03, 126.01, 125.54, 125.15, 123.80, 122.70, 116.90, 112.32, 88.42, 45.07, 21.21, 19.72; FT-IR: $\tilde{\nu}$ = 2929, 2220, 1612, 1523, 1459, 1348, 1173 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{26}H_{22}N_3$: 376.1808; found: 376.1805



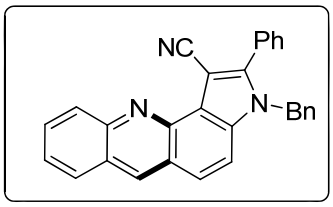
3-Allyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3e**); yellow amorphous solid (66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.40 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 9.1 Hz, 1H), 7.66 (s, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 9.1 Hz, 1H), 6.06 (m, 1H), 5.34 (d, *J* = 10.2 Hz, 1H), 5.14 (d, *J* = 17.1 Hz, 1H), 4.89 (d, *J* = 5.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.60, 144.49, 136.25, 134.50, 133.10, 131.95, 130.17, 129.90, 128.11, 126.03, 125.58, 125.21, 123.63, 122.50, 119.17, 116.67, 112.58, 88.87, 50.02; FT-IR: $\tilde{\nu}$ = 2928, 2222, 1608, 1530, 1411, 1305, 1169 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{19}H_{14}N_3$: 284.1182; found: 284.1182



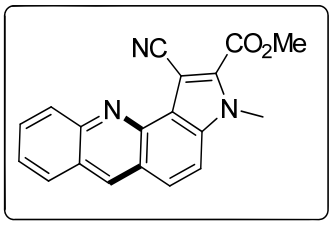
3*H*-Pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3f**); light yellow amorphous solid (53%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.75 (s, 1H), 9.12 (s, 1H), 8.32 (s, 1H), 8.17 (dd, *J* = 13.1, 8.5 Hz, 2H), 7.89 (dd, *J* = 16.5, 8.8 Hz, 2H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.63 (m, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 147.25, 144.05, 136.51, 134.54, 132.58, 130.20, 128.53, 128.49, 125.34, 125.16, 124.56, 123.34, 120.27, 117.01, 115.37, 87.23; FT-IR: $\tilde{\nu}$ = 3403, 2920, 2211, 1624, 1564, 1439, 1326, 1177 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{16}H_{10}N_3$: 244.0869; found: 244.0875



3-Benzyl-2-methyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3g**); light yellow amorphous solid (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.43 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.81 (t, *J* = 7.3 Hz, 1H), 7.68 (d, *J* = 9.1 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 9.1 Hz, 1H), 7.36 – 7.28 (m, 3H), 6.98 (d, *J* = 6.4 Hz, 2H), 5.47 (s, 2H), 2.64 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.62, 144.04, 143.81, 136.23, 135.75, 134.82, 130.08, 129.94, 129.36, 128.28, 128.11, 126.01, 125.98, 125.45, 124.41, 123.78, 121.62, 117.15, 112.52, 88.57, 47.90, 12.03; FT-IR: $\tilde{\nu}$ = 2918, 2216, 1713, 1609, 1530, 1438, 1356, 1255 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{24}H_{18}N_3$: 348.1495; found: 348,1501

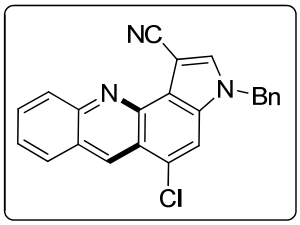


3-Benzyl-2-phenyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3h**); yellow amorphous solid (79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.47 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 9.1 Hz, 1H), 7.57 (dd, *J* = 8.8, 6.2 Hz, 3H), 7.54 – 7.46 (m, 3H), 7.39 (d, *J* = 9.1 Hz, 1H), 7.31 (d, *J* = 6.9 Hz, 3H), 6.99 (d, *J* = 6.8 Hz, 2H), 5.51 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.65, 146.84, 144.33, 136.58, 136.38, 135.34, 130.21, 130.17, 130.06, 130.02, 129.30, 129.26, 128.85, 128.11, 126.11, 125.93, 125.64, 125.26, 123.94, 122.47, 117.08, 113.30, 89.12, 48.82; FT-IR: $\tilde{\nu}$ = 2926, 2219, 1614, 1530, 1451, 1402, 1350, 1130 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{29}H_{20}N_3$: 410.1652; found: 410.1652

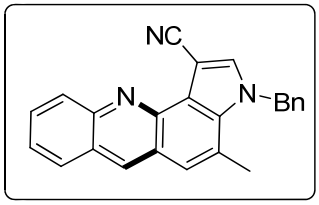


Methyl 1-cyano-3-methyl-3*H*-pyrrolo[2,3-*c*]acridine-2-carboxylate (**3i**); white amorphous solid (61%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.15 (s, 1H), 8.27 – 8.15 (m, 2H), 8.10 (d, *J* = 9.3 Hz, 1H), 7.99 (d, *J* = 9.3 Hz, 1H), 7.92 (t, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 4.24 (s, 3H), 4.00 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 159.58, 147.41, 143.75, 137.62, 136.95, 130.74, 130.72, 128.60, 127.85, 125.84,

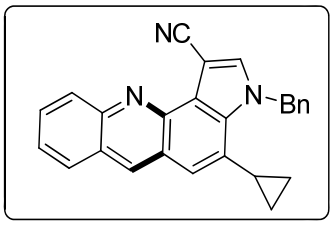
125.77, 123.50, 120.55, 114.93, 113.65, 92.70, 52.48, 33.54; FT-IR: $\tilde{\nu}$ = 2936, 2229, 1645, 1614, 1531, 1459, 1301, 1166 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{19}H_{14}N_3O_2$: 316.1081; found: 316.1087



3-Benzyl-5-chloro-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3j**); yellow amorphous solid (69%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.43 (d, *J* = 8.7 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.89 8 (m, 1H), 7.67 (s, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.57 (s, 1H), 7.44 – 7.32 (m, 3H), 7.20 – 7.15 (m, 2H), 5.45 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.62, 143.60, 134.94, 134.51, 133.86, 133.51, 131.22, 129.52, 128.92, 128.65, 128.56, 127.12, 126.32, 126.03, 121.85, 121.77, 121.69, 116.13, 112.67, 89.56, 51.55; FT-IR: $\tilde{\nu}$ =2916, 2229, 1602, 1534, 1436, 1254, 1165 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{23}H_{15}{}^{35}ClN_3$: 368.0949; found: 368.0943

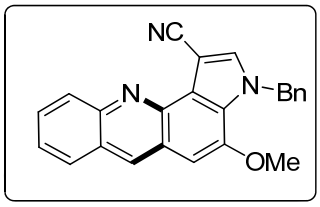


3-Benzyl-4-methyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3k**); yellow amorphous solid (80%)**;** ^1H NMR (400 MHz, DMSO-d_6) δ 8.95 (s, 1H), 8.45 (s, 1H), 8.23 – 8.09 (m, 2H), 7.86 (t, *J* = 7.4 Hz, 1H), 7.73 – 7.52 (m, 2H), 7.46 – 7.19 (m, 3H), 6.97 (d, *J* = 7.1 Hz, 2H), 5.88 (s, 2H), 2.60 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 147.01, 143.35, 138.32, 137.68, 134.83, 133.98, 129.88, 128.94, 128.47, 128.36, 127.51, 125.73, 125.23, 125.19, 124.91, 124.83, 123.28, 122.26, 116.41, 87.09, 52.41, 19.35; FT-IR: $\tilde{\nu}$ = 2924, 2223, 1614, 1537, 1455, 1375, 1171 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{24}H_{18}N_3$: 348.1495; found: 348.1499

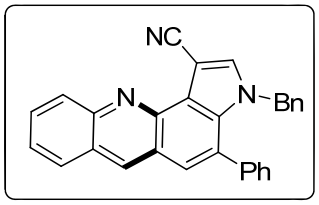


3-Benzyl-4-cyclopropyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3l**); light yellow amorphous solid (72%); ^1H NMR (400 MHz, DMSO-d_6) δ 8.98 (s, 1H), 8.44 (s, 1H), 8.15 (d, *J* = 8.5 Hz, 2H), 7.86 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.72 – 7.53 (m, 2H), 7.31 (m, 3H), 7.00 (d, *J* = 7.7 Hz, 2H), 6.08 (s, 2H), 2.10 (m, 1H),

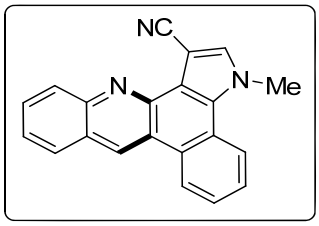
1.03 – 0.92 (m, 2H), 0.93 – 0.81 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.17, 143.41, 138.52, 137.70, 135.44, 134.41, 130.05, 129.58, 128.92, 128.53, 128.44, 127.50, 125.73, 125.32, 125.25, 123.24, 122.67, 122.09, 116.47, 87.27, 52.59, 13.16, 7.46; FT-IR: $\tilde{\nu}$ = 2945, 2849, 2224, 1615, 1529, 1451, 1385, 1161 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{26}H_{20}N_3$: 374.1652; found: 374.1655



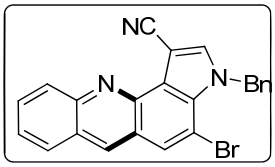
3-Benzyl-4-methoxy-3H-pyrrolo[2,3-c]acridine-1-carbonitrile (**3m**); light yellow amorphous solid (67%); ^{1}H NMR (400 MHz, DMSO) δ 8.87 (s, 1H), 8.50 (s, 1H), 8.11 (d, *J* = 8.7 Hz, 2H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.26 (m, 4H), 5.77 (s, 2H), 4.01 (s, 3H). ^{13}C NMR (150 MHz, DMSO) δ 148.02, 145.90, 141.29, 138.08, 137.17, 133.68, 129.20, 128.71, 128.57, 127.99, 127.69, 126.93, 126.88, 125.96, 125.46, 124.65, 123.36, 116.31, 100.21, 87.47, 55.95, 53.03; FT-IR: $\tilde{\nu}$ = 2931, 2223, 1607, 1542, 1437, 1388, 1181 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{24}H_{18}N_3O$: 364.1444; found: 364.1449



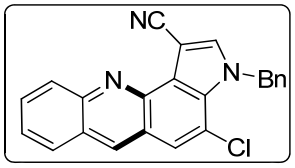
3-Benzyl-4-phenyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3n**); light yellow amorphous solid (83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.44 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.76 (m, 1H), 7.59 (s, 1H), 7.58 – 7.50 (m, 1H), 7.48 (s, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.24 – 7.08 (m, 3H), 6.53 (d, *J* = 7.2 Hz, 2H), 4.99 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.53, 143.99, 138.30, 136.31, 135.77, 135.73, 132.84, 130.11, 129.89, 129.77, 129.63, 128.81, 128.34, 128.32, 128.04, 128.01, 126.69, 126.39, 126.23, 125.65, 123.67, 123.22, 116.62, 89.47, 53.18; FT-IR: $\tilde{\nu}$ =3029, 2227, 1611, 1537, 1439, 1375, 1169 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{29}H_{20}N_3$: 410.1652; found: 410.1655



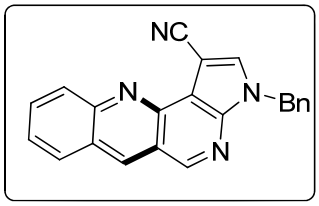
3-Methyl-3*H*-benzo[*a*]pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3o**); white amorphous solid (63%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.85 (s, 1H), 9.05 (d, *J* = 7.6 Hz, 1H), 8.58 (d, *J* = 7.4 Hz, 1H), 8.25 (d, *J* = 3.7 Hz, 2H), 8.13 (d, *J* = 8.6 Hz, 1H), 7.90 (t, *J* = 7.5 Hz, 1H), 7.77 (dd, *J* = 12.9, 6.6 Hz, 2H), 7.68 (t, *J* = 7.3 Hz, 1H), 4.37 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 147.09, 144.37, 137.92, 131.82, 130.90, 130.47, 128.83, 128.60, 128.34, 128.03, 126.37, 125.88, 125.70, 124.99, 123.66, 122.28, 121.64, 121.01, 116.59, 86.87, 27.02; FT-IR: $\tilde{\nu}$ =3051, 2929, 2226, 1612, 1525, 1433, 1391, 1189 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{21}H_{14}N_3$: 308.1182; found: 308.1187



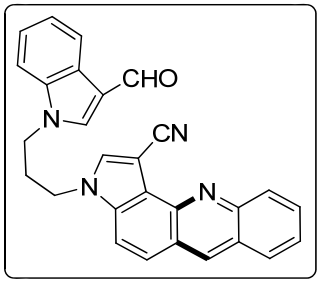
3-Benzyl-4-bromo-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3p**); light yellow amorphous solid (51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.41 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.83 (t, *J* = 7.6 Hz, 1H), 7.66 (s, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.41 – 7.29 (m, 3H), 7.07 (d, *J* = 6.5 Hz, 2H), 5.98 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.79, 143.40, 136.60, 136.33, 134.94, 130.60, 130.59, 130.00, 129.29, 129.15, 128.43, 128.10, 126.64, 126.44, 126.23, 125.55, 124.07, 115.88, 106.11, 89.68, 53.07; FT-IR: $\tilde{\nu}$ =2925, 2219, 1615, 1540, 1438, 1387, 1158 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{23}H_{15}{}^{79}BrN_3$: 412.0444; found: 412.0439



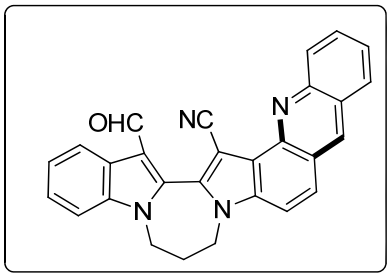
3-Benzyl-4-chloro-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3q**); light yellow amorphous solid (46%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 1H), 8.61 (s, 1H), 8.18 (t, *J* = 7.8 Hz, 2H), 8.06 (s, 1H), 8.00 – 7.82 (m, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.31 – 7.22 (m, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 5.99 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 147.58, 142.49, 138.76, 137.87, 135.78, 130.85, 129.12, 128.77, 128.60, 128.57, 127.54, 125.98, 125.83, 125.80, 124.74, 124.30, 123.19, 118.48, 115.78, 87.77, 52.36; FT-IR: $\tilde{\nu}$ = 2956, 2217, 1606, 1535, 1444, 1378, 1277, 1169 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{23}H_{15}{}^{35}Cl\ N_3$: 368.0949; found: 368.0938



3-Benzyl-3*H*-benzo[*b*]pyrrolo[2,3-*h*][1,6]naphthyridine-1-carbonitrile (**3r**); light yellow amorphous solid (37%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.49 (s, 1H), 9.40 (s, 1H), 8.61 (s, 1H), 8.32 (d, *J* = 8.1 Hz, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 8.03 (t, *J* = 7.7 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.22 (m, 5H), 5.73 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 151.80, 150.10, 144.53, 143.36, 139.73, 137.05, 134.18, 132.87, 129.66, 128.72, 128.56, 127.82, 127.47, 126.00, 125.65, 119.21, 116.08, 111.77, 85.05, 48.64; FT-IR: $\widetilde{\nu}$ = 2925, 2225, 1618, 1561, 1501, 1434, 1378, 1188 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{22}H_{15}N_4$: 335.1291; found: 335.1297

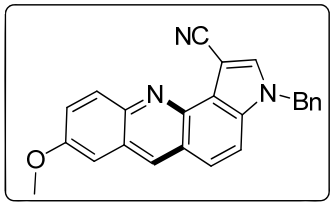


3-(3-(3-Formyl-1*H*-indol-1-yl)propyl)-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**3s**); bright yellow amorphous solid (51%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.89 (s, 1H), 9.14 (s, 1H), 8.41 (s, 1H), 8.35 (s, 1H), 8.18 (dd, *J* = 13.8, 8.6 Hz, 2H), 8.11 (d, *J* = 7.0 Hz, 1H), 8.00 – 7.80 (m, 3H), 7.63 (dd, *J* = 18.2, 7.5 Hz, 2H), 7.35 – 7.19 (m, 2H), 4.53 (t, *J* = 7.2 Hz, 2H), 4.39 (t, *J* = 7.3 Hz, 2H), 2.50 – 2.43 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 184.49, 147.39, 143.87, 140.61, 136.95, 136.62, 135.07, 134.47, 130.39, 128.59, 128.53, 125.48, 125.32, 124.72, 124.67, 123.55, 123.29, 122.55, 121.10, 120.90, 117.31, 116.64, 113.61, 110.91, 86.80, 44.39, 43.77, 30.18; FT-IR: $\widetilde{\nu}$ = 2926, 2229, 1642, 1611, 1532, 1401, 1186 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{28}H_{21}N_4O$: 429.1710; found: 429.1709

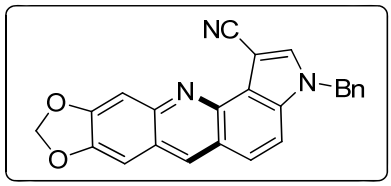


19-Formyl-7,8-dihydro-6*H*-indolo[2'',1'':3',4'][1,4]diazepino[1',2':1,5]pyrrolo[2,3-*c*]acridine-18-carbonitrile (**3t**); dark yellow amorphous solid (43%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.22 (s, 1H),

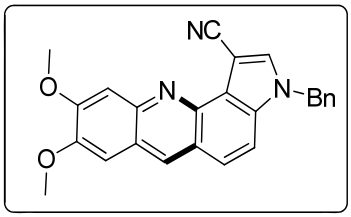
9.21 (s, 1H), 8.34 (d, *J* = 7.9 Hz, 1H), 8.27 – 8.16 (m, 3H), 8.13 (d, *J* = 9.2 Hz, 1H), 7.92 (dd, *J* = 17.6, 8.1 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 5.11 (d, *J* = 14.0 Hz, 1H), 4.90 (d, *J* = 14.0 Hz, 1H), 4.14 (dd, *J* = 22.3, 10.5 Hz, 1H), 3.97 (dd, *J* = 22.3, 10.5 Hz, 1H), 2.65 – 2.56 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 184.91, 147.50, 143.55, 137.17, 136.95, 136.87, 136.04, 133.49, 130.69, 128.67, 128.54, 126.44, 125.68, 125.64, 124.83, 124.58, 123.41, 123.27, 121.52, 121.11, 116.37, 115.10, 113.49, 110.87, 90.53, 41.92, 40.58, 29.52; FT-IR: $\tilde{\nu}$ =2941, 2223, 1676, 1607, 1537, 1456, 1381, 1242, 1183 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{28}H_{19}N_4O$: 427.1553; found: 427.1558



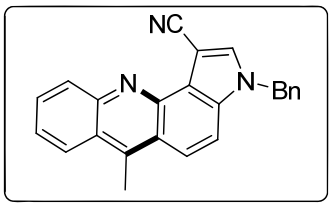
3-Benzyl-8-methoxy-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**4a**); yellow amorphous solid (78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.31 (d, *J* = 9.4 Hz, 1H), 7.69 (d, *J* = 9.3 Hz, 2H), 7.49 (dd, *J* = 9.4, 2.4 Hz, 1H), 7.45 (d, *J* = 9.0 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.17 (dd, *J* = 10.2, 4.9 Hz, 3H), 5.47 (s, 2H), 3.98 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.19, 145.58, 142.79, 135.52, 134.26, 134.22, 133.44, 131.48, 129.38, 128.68, 127.09, 126.96, 125.03, 124.77, 123.96, 122.97, 116.71, 112.63, 103.80, 88.84, 55.74, 51.52; FT-IR: $\tilde{\nu}$ =2853, 2218, 1608, 1505, 1440, 1359, 1179 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{24}H_{18}N_3O$: 364.1444; found: 364.1445



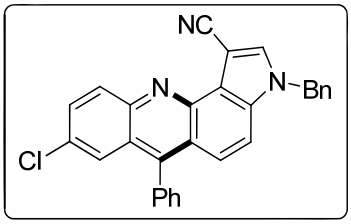
3-Benzyl-3*H*-[1,3]dioxolo[4,5-*b*]pyrrolo[3,2-*h*]acridine-1-carbonitrile (**4b**); light yellow amorphous solid (72%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.79 (s, 1H), 8.47 (s, 1H), 7.80 (s, 2H), 7.46 (s, 1H), 7.40 – 7.11 (m, 6H), 6.25 (s, 2H), 5.65 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 151.98, 147.29, 146.43, 141.94, 136.86, 135.48, 134.58, 134.15, 128.77, 127.85, 127.17, 124.25, 122.96, 121.88, 121.02, 116.65, 112.70, 103.34, 102.17, 101.94, 86.30, 50.15; FT-IR: $\tilde{\nu}$ = 2938, 2218, 1609, 1534, 1455, 1378, 1182 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{24}H_{16}N_3O_2$: 378.1237; found: 378.1241



3-Benzyl-8,9-dimethoxy-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**4c**); bright yellow amorphous solid (75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.67 (m, 3H), 7.41 (d, *J* = 9.1 Hz, 1H), 7.34 (t, *J* = 6.1 Hz, 3H), 7.16 (d, *J* = 5.6 Hz, 3H), 5.46 (s, 2H), 4.13 (s, 3H), 4.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.03, 149.95, 146.72, 142.96, 135.53, 134.40, 133.68, 133.46, 129.34, 128.63, 127.06, 125.02, 122.65, 122.59, 122.41, 116.98, 111.33, 107.46, 104.25, 88.41, 56.63, 56.17, 51.41; FT-IR: $\tilde{\nu}$ = 2929, 2223, 1601, 1531, 1447, 1381, 1225, 1161 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{25}H_{20}N_3O_2$: 394.1550; found: 394. 1557

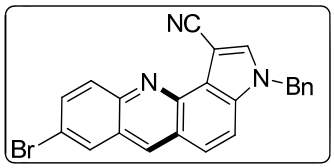


3-Benzyl-6-methyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**4d**); white amorphous solid (61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.6 Hz, 1H), 8.25 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 9.4 Hz, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.68 (s, 1H), 7.59 (m, 1H), 7.47 (d, *J* = 9.4 Hz, 1H), 7.35 (d, *J* = 6.7 Hz, 3H), 7.16 (d, *J* = 6.5 Hz, 2H), 5.48 (s, 2H), 3.11 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.95, 143.97, 142.51, 135.54, 134.43, 133.60, 130.73, 129.70, 129.38, 128.69, 127.10, 125.40, 125.24, 124.43, 123.18, 122.33, 121.86, 116.74, 112.15, 89.45, 51.50, 14.33; FT-IR: $\tilde{\nu}$ = 2937, 2227, 1615, 1536, 1447, 1389, 1231, 1175 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{24}H_{18}N_3$: 348.1495; found: 348.1501

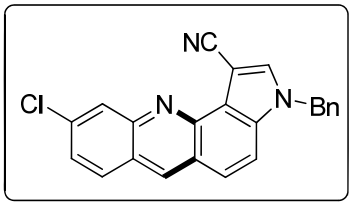


3-Benzyl-8-chloro-6-phenyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**4e**); light yellow amorphous solid (74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 9.2 Hz, 1H), 7.71 (s, 1H), 7.68 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.59 (dd, *J* = 7.1, 1.8 Hz, 4H), 7.39 (dd, *J* = 6.1, 3.3 Hz, 3H), 7.36 – 7.29 (m, 4H), 7.17 – 7.10 (m, 2H), 5.45 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.73, 146.48, 144.26, 135.82, 135.36, 134.58,

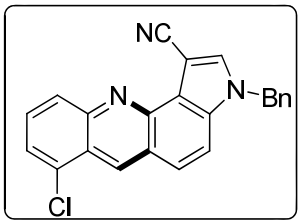
133.85, 131.73, 131.30, 130.93, 130.47, 129.37, 128.77, 128.75, 128.72, 127.08, 125.21, 125.16, 123.87, 122.70, 122.32, 116.55, 112.97, 89.36, 51.56; FT-IR: $\tilde{\nu}$ = 2916, 2225, 1714, 1613, 1524, 1435, 1253, 1176 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{29}H_{19}ClN_3$: 444.1262; found: 444.1262



3-Benzyl-8-bromo-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**4f**); yellow amorphous solid (71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.58 (s, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.66 (t, *J* = 4.5 Hz, 2H), 7.58 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.45 (d, *J* = 9.1 Hz, 1H), 7.41 – 7.31 (m, 3H), 7.16 (d, *J* = 5.9 Hz, 2H), 5.46 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.69, 144.89, 136.29, 135.29, 134.91, 133.62, 131.92, 129.41, 129.29, 129.17, 128.76, 127.09, 125.29, 124.62, 124.42, 123.66, 122.48, 116.43, 112.99, 89.18, 51.52; FT-IR: $\tilde{\nu}$ = 2950, 2222, 1604, 1531, 1431, 1385, 1160 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{23}H_{15}{}^{79}BrN_3$: 412.0444; found: 412.0441

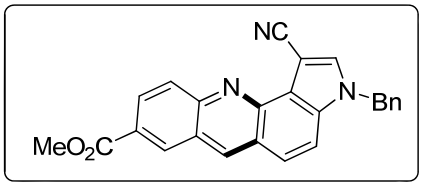


3-Benzyl-9-chloro-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**4g**); light yellow amorphous solid (78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.40 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.42 (m, 2H), 7.41 – 7.29 (m, 3H), 7.16 (d, *J* = 6.1 Hz, 2H), 5.47 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.79, 143.40, 136.60, 136.33, 134.94, 130.60, 130.59, 130.00, 129.29, 129.15, 128.43, 128.10, 126.64, 126.44, 126.23, 125.55, 124.07, 115.88, 106.11, 89.68, 53.07; FT-IR: $\tilde{\nu}$ =2939, 2229, 1614, 1531, 1459, 1402, 1166 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{23}H_{15}{}^{35}ClN_3$: 368.0949; found: 368.0943

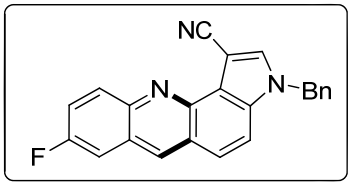


3-Benzyl-7-chloro-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**4h**); light yellow amorphous solid (63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.36 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 9.1 Hz, 1H), 7.72 (dd, *J* = 9.4, 6.5 Hz, 2H), 7.65 (d, *J* = 7.1 Hz, 1H), 7.53 (d, *J* = 9.2 Hz, 1H), 7.43 – 7.30 (m, 3H), 7.21 – 7.10 (m,

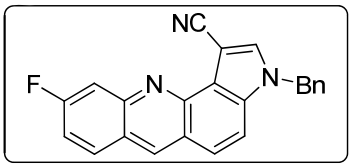
2H), 5.49 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.88, 144.78, 135.25, 135.05, 133.76, 133.63, 131.33, 129.58, 129.45, 129.25, 128.81, 127.13, 125.67, 125.42, 124.16, 123.99, 122.40, 116.41, 113.37, 89.33, 51.60; FT-IR: $\tilde{\nu}$ = 2927, 2225, 1606, 1527, 1433, 1386, 1162 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{23}H_{15}{}^{35}ClN_3$: 368.0949; found: 368.0955



Methyl 3-benzyl-1-cyano-3*H*-pyrrolo[2,3-*c*]acridine-8-carboxylate (**4i**); light yellow amorphous solid (56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.81 (s, 1H), 8.48 (d, *J* = 9.1 Hz, 1H), 8.37 (d, *J* = 9.1 Hz, 1H), 7.79 (d, *J* = 9.1 Hz, 1H), 7.74 (s, 1H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.44 – 7.32 (m, 3H), 7.17 (d, *J* = 6.0 Hz, 2H), 5.51 (s, 2H), 4.02 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.94, 149.63, 145.70, 138.52, 135.36, 135.19, 133.95, 132.07, 129.99, 129.46, 129.32, 128.84, 127.16, 127.10, 125.55, 124.88, 124.04, 122.41, 116.30, 113.34, 89.57, 52.59, 51.63; FT-IR: $\tilde{\nu}$ = 2927, 2216, 1671, 1621, 1573, 1529, 1437, 1387, 1179 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{25}H_{18}N_3O_2$: 392.1394; found: 392.1387

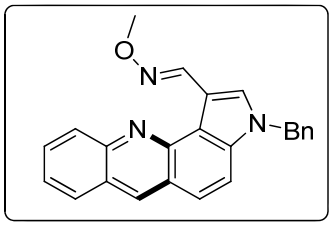


3-Benzyl-8-fluoro-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**4j**); yellow amorphous solid (74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.06 – 7.93 (m, 2H), 7.79 – 7.67 (m, 2H), 7.47 (d, *J* = 9.2 Hz, 1H), 7.41 – 7.30 (m, 4H), 7.16 (d, *J* = 5.9 Hz, 2H), 5.48 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.70 (d, *J* = 252.3 Hz), 149.36 (d, *J* = 13.5 Hz), 145.05, 136.49, 135.33, 135.01, 133.67, 130.39 (d, *J* = 10.3 Hz), 129.41, 128.75, 127.08, 125.43, 123.27, 123.05 (d, *J* = 1.8 Hz), 122.33, 117.28 (d, *J* = 27.1 Hz), 116.47, 112.55, 112.42, 89.19, 51.52; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.50; FT-IR: $\tilde{\nu}$ = 2935, 2217, 1619, 1509, 1436, 1381, 1176 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{23}H_{15}FN_3$: 352.1245; found : 352.1249

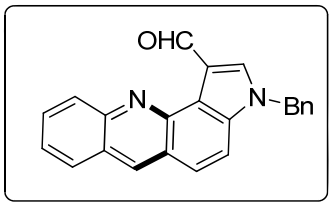


3-Benzyl-9-fluoro-3*H*-pyrrolo[2,3-*c*]acridine-1-carbonitrile (**4k**); white amorphous solid (81%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.17 (s, 1H), 8.54 (s, 1H), 8.30 (dd, *J* = 11.1, 4.4 Hz, 1H), 7.93 (s, 2H),

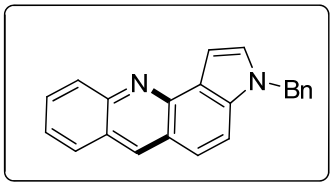
7.77 (d, *J* = 10.7 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.43 – 7.22 (m, 5H), 5.69 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 163.04 (d, *J* = 250.3 Hz), 147.98 (d, *J* = 13.3 Hz), 144.40, 137.20, 136.76, 135.76, 134.87, 131.64 (d, *J* = 10.6 Hz), 128.81, 127.91, 127.21, 124.93, 122.87, 122.71 (d, *J* = 1.7 Hz), 120.65, 116.60 (d, *J* = 26.7 Hz), 116.39, 113.81, 110.84 (d, *J* = 19.7 Hz), 86.96, 50.23; ^{19}F NMR (376 MHz, DMSO-d_6) δ -107.45; FT-IR: $\tilde{\nu}$ = 2950, 2218, 1612, 1538, 1438, 1401, 1186 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{23}H_{15}FN_3$: 352.1245; found: 352.1245



(*E*)-3-benzyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbaldehyde *O*-methyl oxime (**3a'**); yellow amorphous solid (75%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.77 (s, 1H), 9.05 (s, 1H), 8.15 (d, *J* = 8.6 Hz, 2H), 8.05 (s, 1H), 7.89 (d, *J* = 9.1 Hz, 1H), 7.84 (m, 1H), 7.80 (d, *J* = 9.1 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.25 (m, 5H), 5.66 (s, 2H), 3.93 (s, 3H); ^{13}C NMR (150 MHz, DMSO) δ 147.26, 145.95, 145.32, 137.53, 136.26, 134.80, 130.03, 128.73, 128.46, 127.71, 127.29, 126.93, 124.89, 124.86, 124.54, 123.55, 122.87, 119.30, 114.19, 111.64, 61.11, 49.76; FT-IR: $\tilde{\nu}$ = 2929, 1630, 1601, 1567, 1493, 1427, 1387, 1255 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{24}H_{20}N_3O$: 366.1601; found: 366.1595

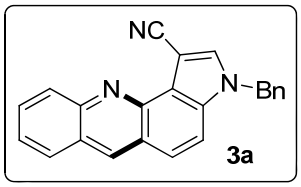


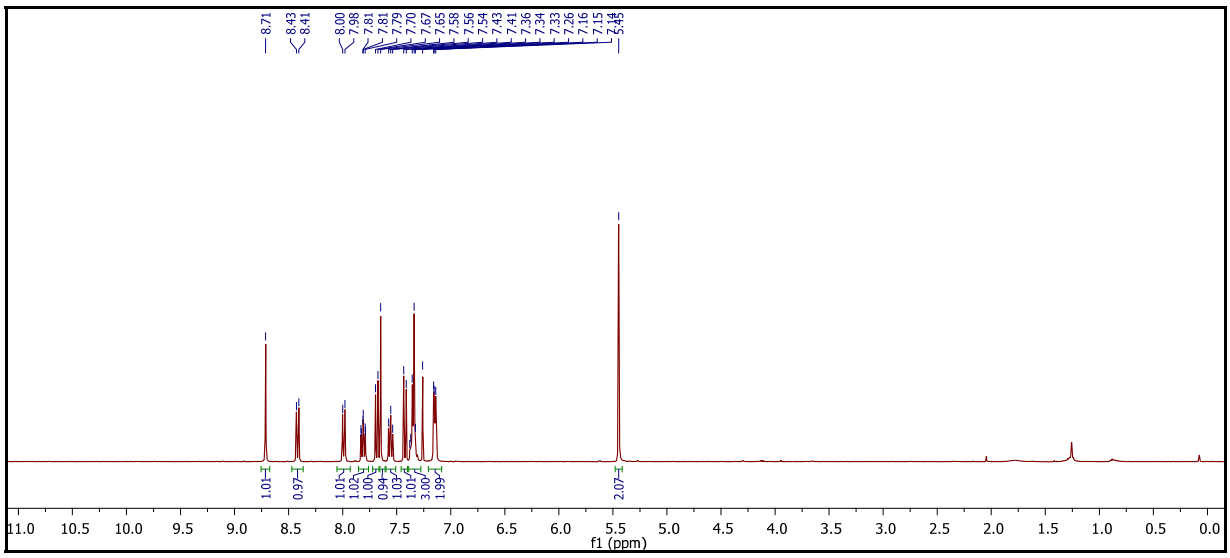
3-Benzyl-3*H*-pyrrolo[2,3-*c*]acridine-1-carbaldehyde (**3aa**); yellow amorphous solid (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.65 (s, 1H), 8.74 (s, 1H), 8.24 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.96 (s, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 9.1 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 9.1 Hz, 1H), 7.34 (t, *J* = 7.0 Hz, 3H), 7.20 (d, *J* = 7.0 Hz, 2H), 5.49 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.74, 148.68, 146.14, 136.32, 135.76, 135.62, 130.13, 129.66, 129.55, 129.33, 128.60, 128.27, 127.26, 125.86, 125.37, 124.29, 122.43, 122.42, 113.14, 51.59; FT-IR: $\tilde{\nu}$ = 2931, 2787, 1731, 1621, 1536, 1502, 1442, 1388, 1187 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{23}H_{17}N_2O$: 337.1335; found: 337.1336



3-Benzyl-3*H*-pyrrolo[2,3-*c*]acridine (**5**); yellow green gel (87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.38 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.71 – 7.56 (m, 2H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.37 – 7.26 (m, 4H), 7.12 (d, *J* = 7.0 Hz, 2H), 5.49 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.43, 136.59, 135.15, 129.89, 129.85, 129.05, 128.80, 128.29, 127.98, 126.76, 126.46, 125.60, 124.64, 123.73, 122.67, 113.62, 104.12, 50.79; FT-IR: $\widetilde{\nu}$ = 2945, 1602, 1545, 1465, 1339, 1251, 1178 cm^{-1}; HRMS: Calculated for $[M+H]^+$: $C_{22}H_{17}N_2$: 309.1386; found: 309.1386

NMR spectra:


NC
N
N–Bn
3a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7.54
7.43
7.41
7.36
7.34
7.33
7.26
7.16
7.15
5.45
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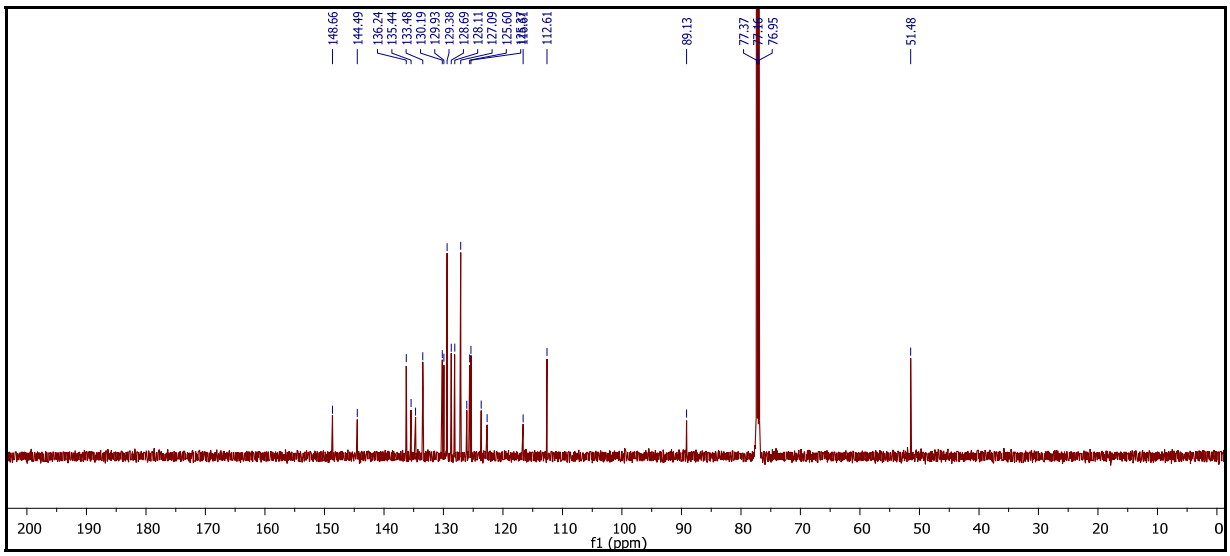
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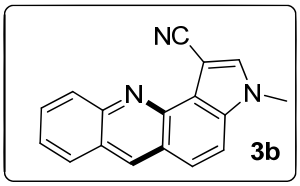
f1 (ppm)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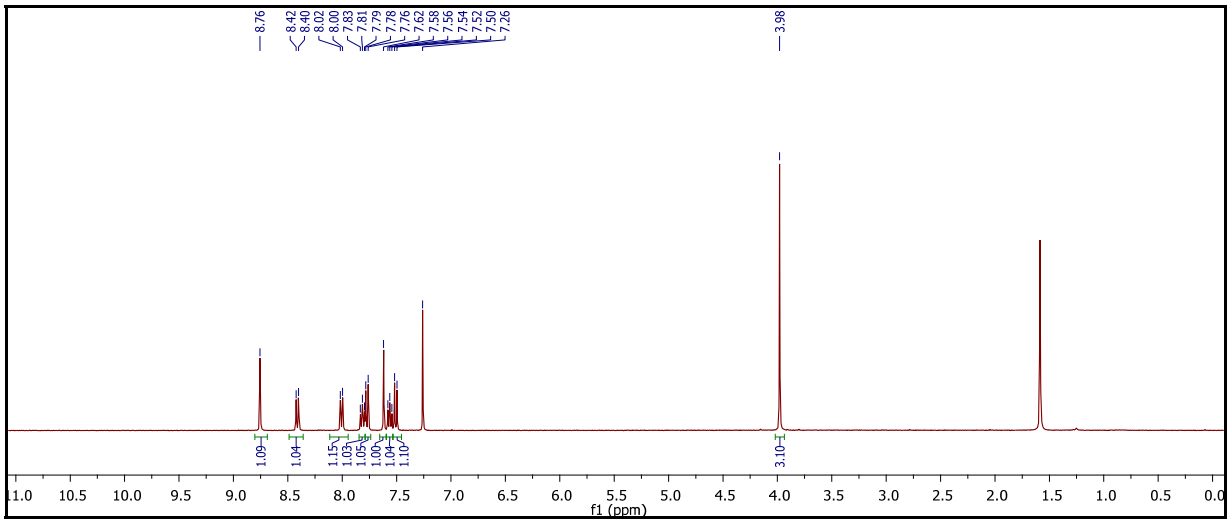
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7.52
7.50
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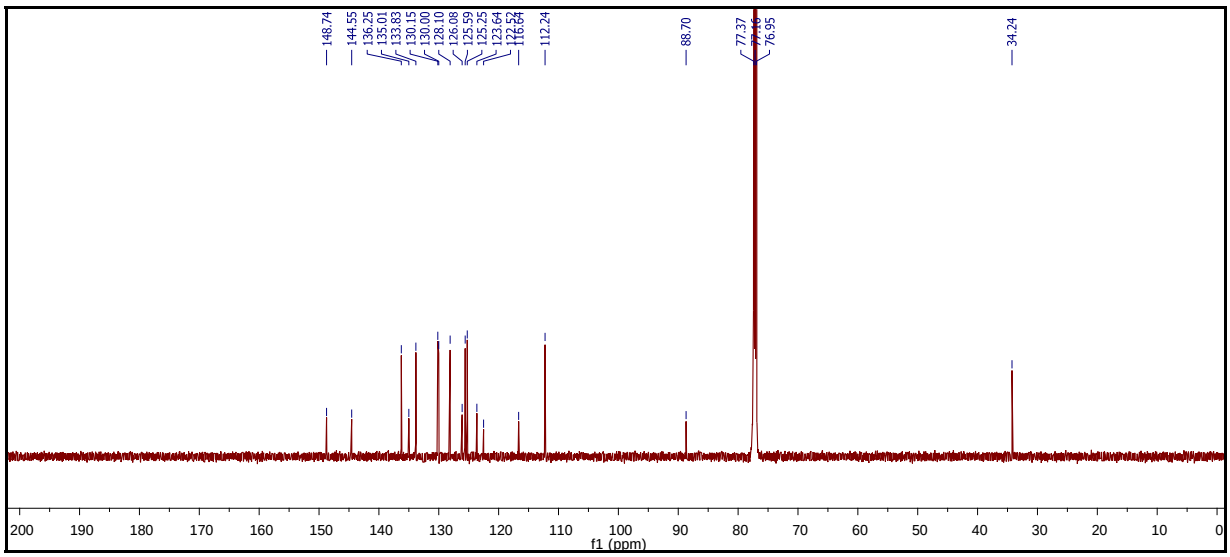
1.03
1.05
1.00
1.04
1.10
3.10
f1 (ppm)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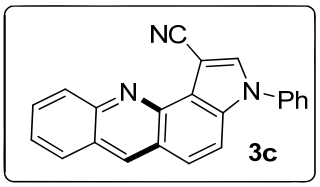
77.16
76.95
34.24
f1 (ppm)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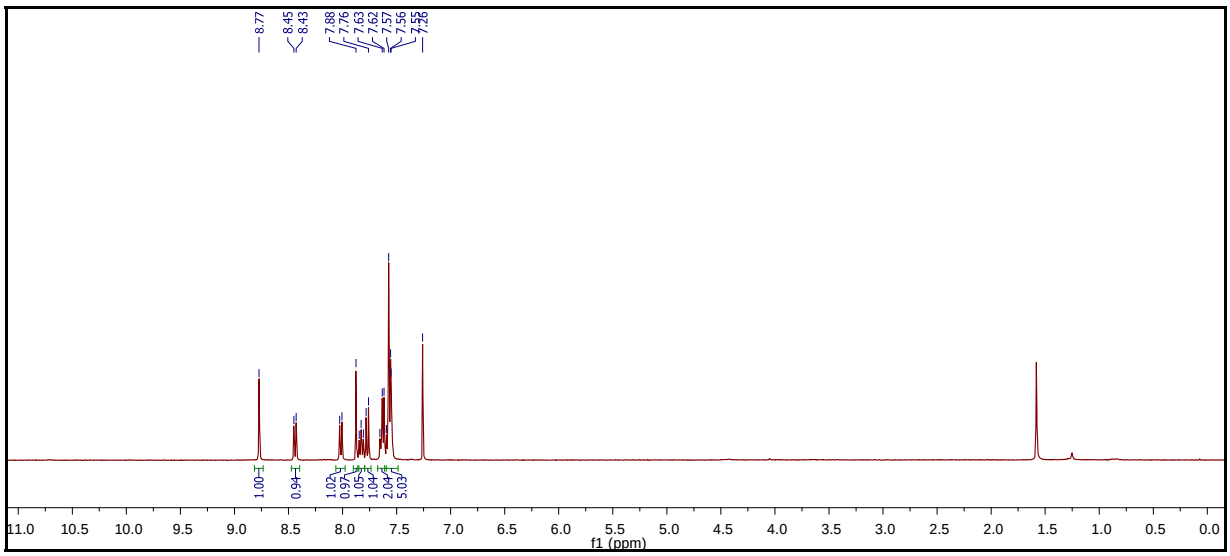
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1.02
0.97
1.05
1.04
2.04
5.03
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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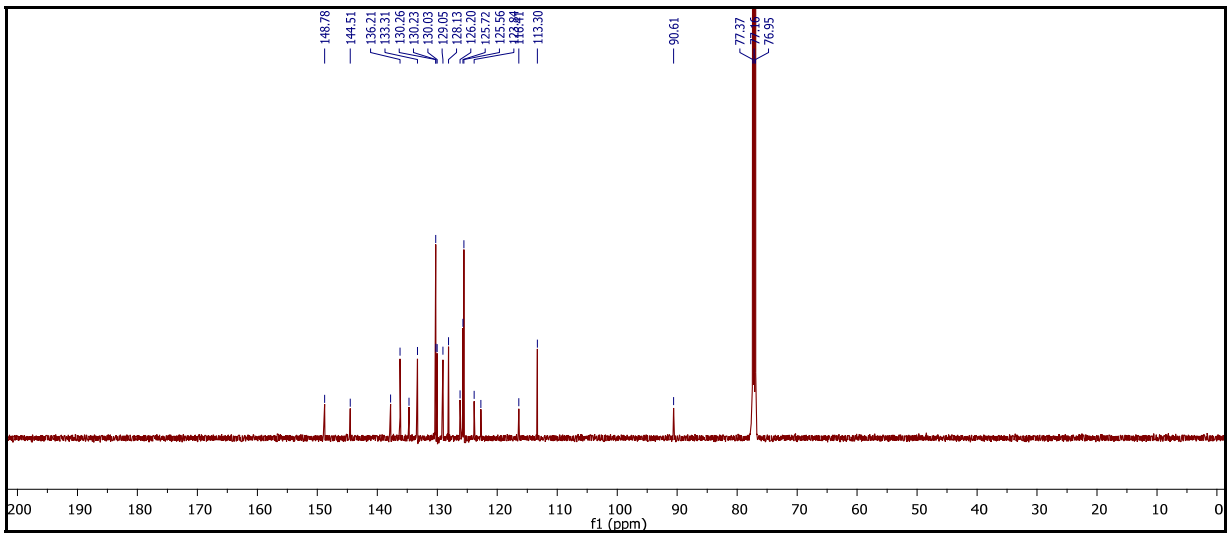
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77.37
76.95
200
190
180
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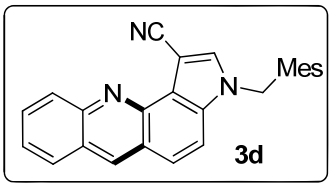
f1 (ppm)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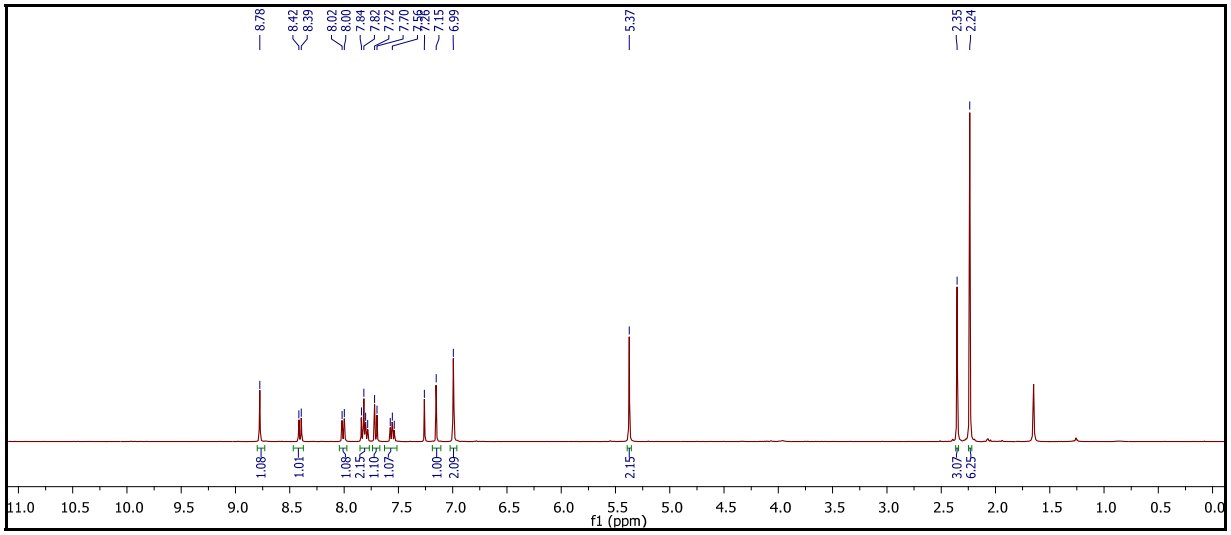
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7.15
6.99
5.37
2.35
2.24
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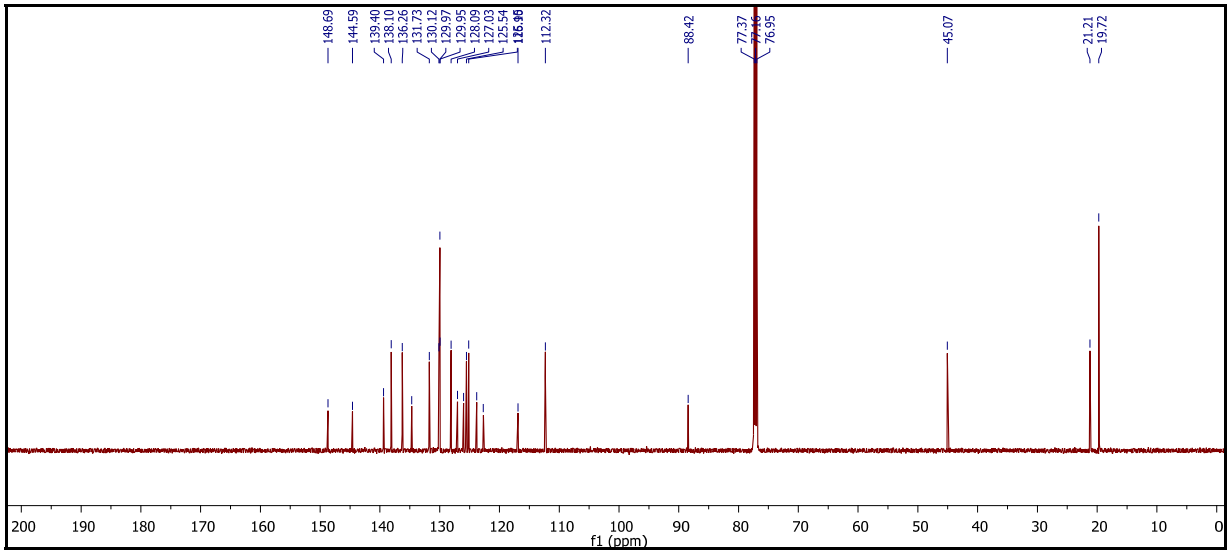
1.07
1.00
2.09
2.15
3.07
6.25
f1 (ppm)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129.97
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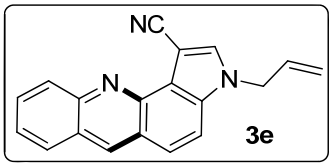
76.95
45.07
21.21
19.72
f1 (ppm)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N
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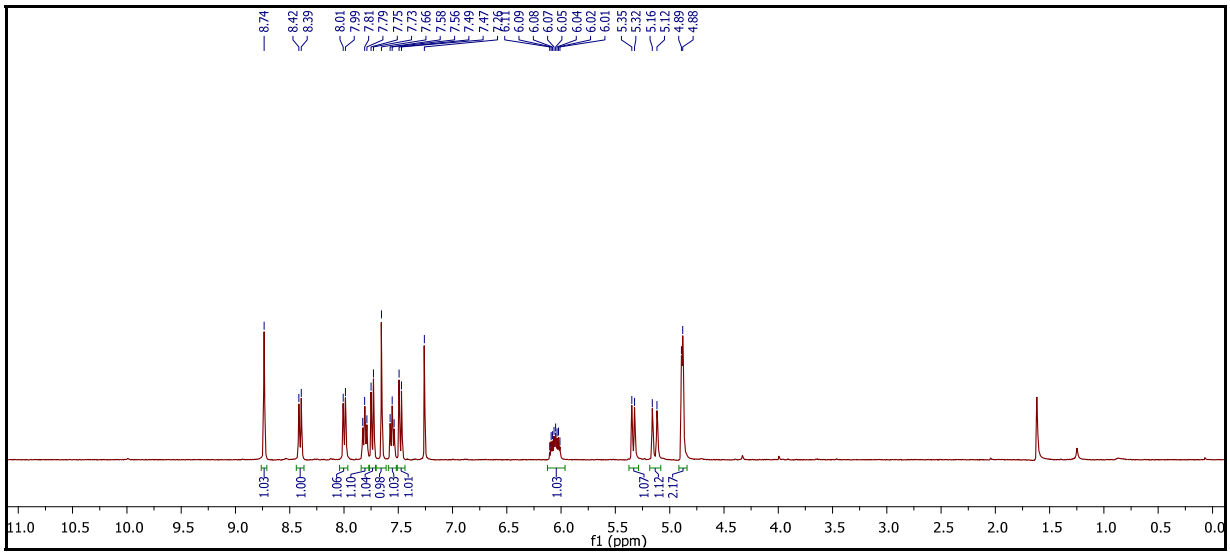
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6.09
6.08
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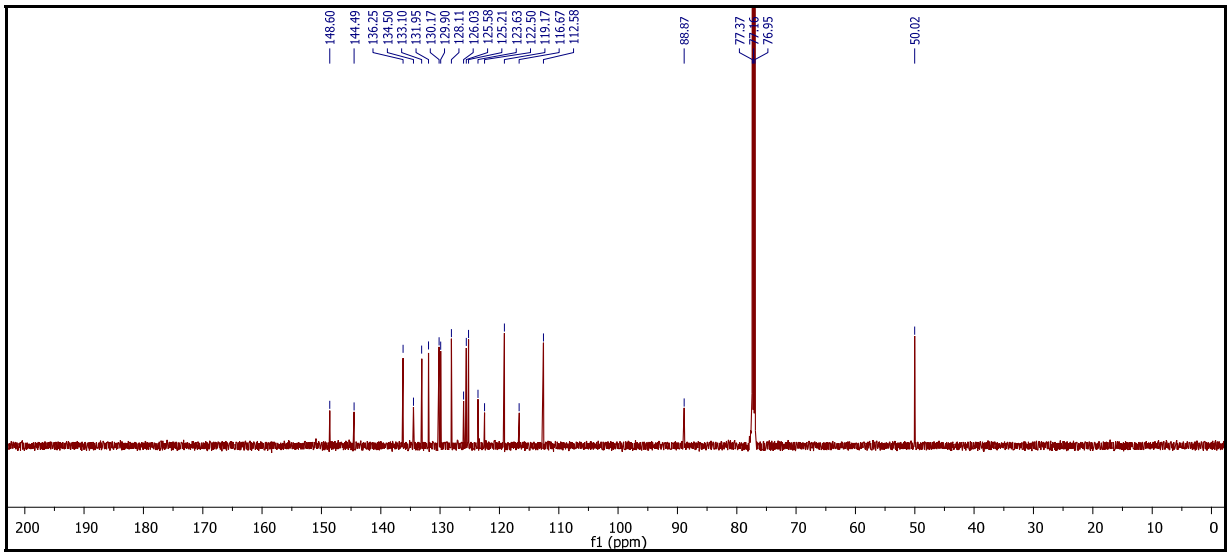
6.05
6.04
6.02
6.01
5.35
5.32
5.16
5.12
4.89
4.88
1.03
1.00
1.06
1.10
1.04
0.98
1.03
1.01
1.03
1.07
1.12
2.17
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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122.50
119.17
116.67
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77.16
76.95
50.02
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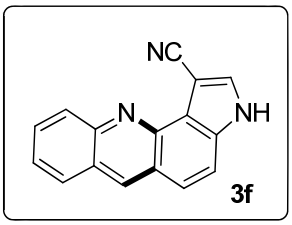
f1 (ppm)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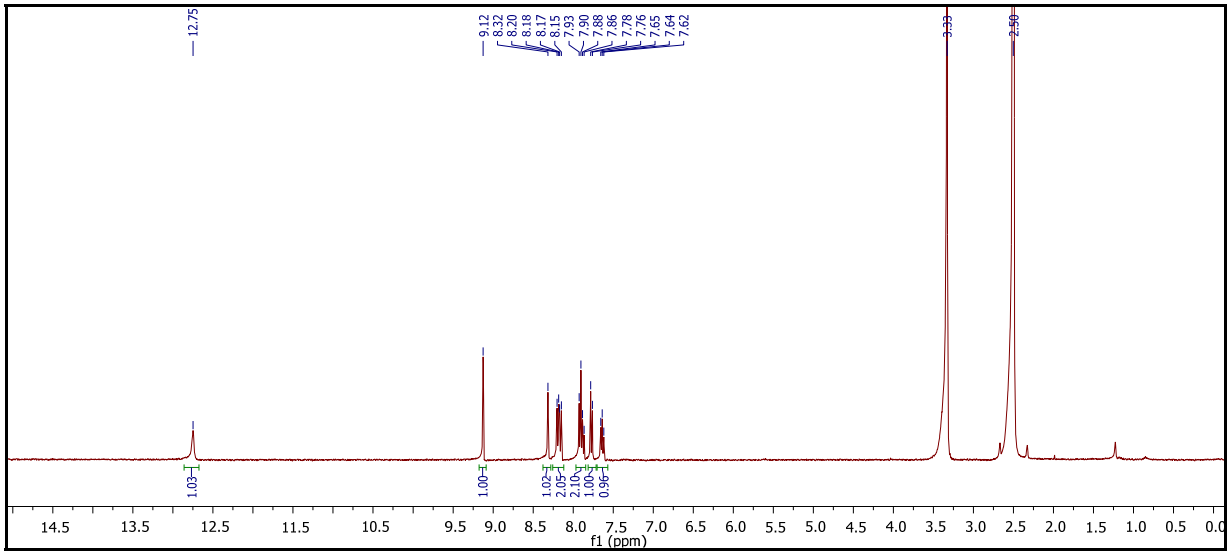
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7.88
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7.78
7.76
7.65
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1.00
1.02
2.05
2.10
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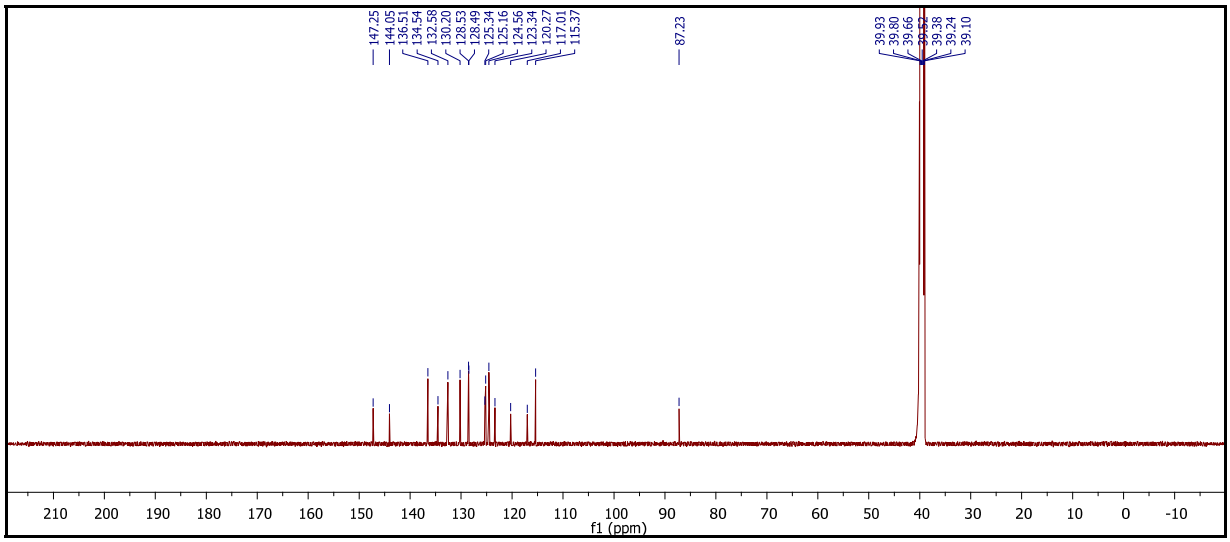
0.96
f1 (ppm)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125.16
124.56
123.34
120.27
117.01
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87.23
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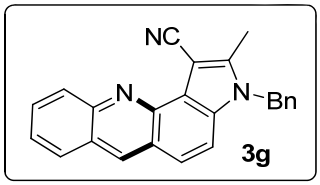
39.80
39.66
39.52
39.38
39.24
39.10
f1 (ppm)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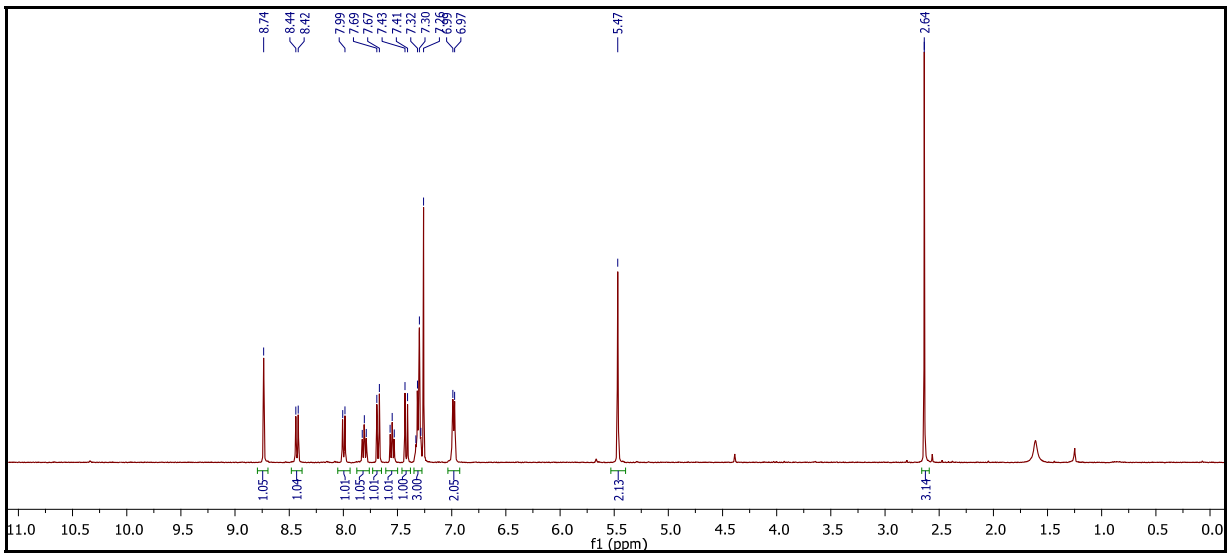
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5.47
2.64
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1.05
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2.05
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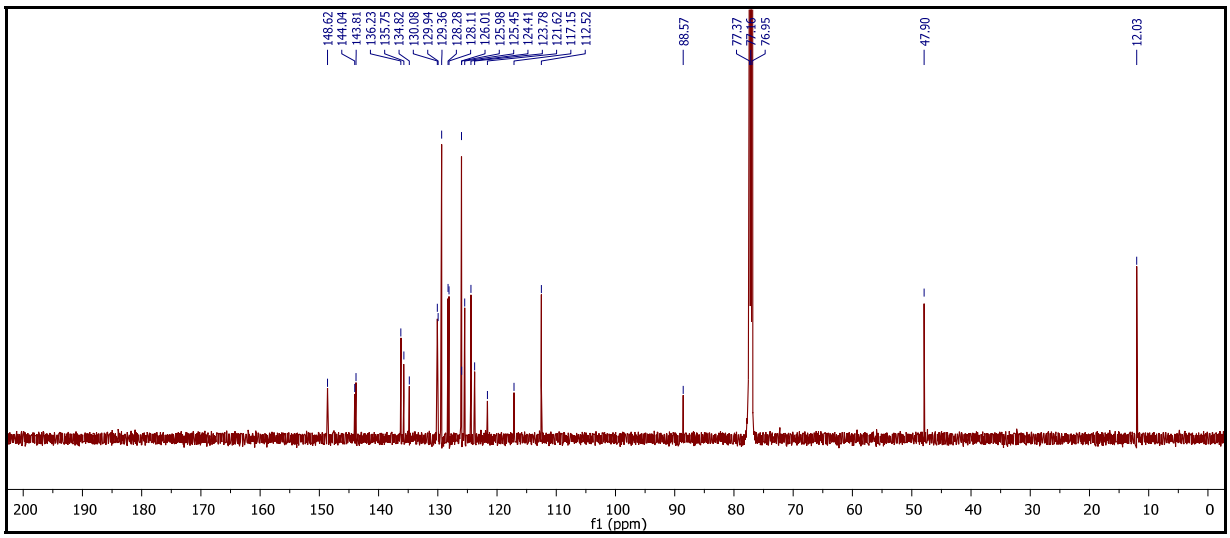
3.14
f1 (ppm)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125.98
125.45
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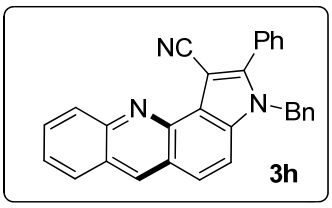
112.52
88.57
77.37
77.16
76.95
47.90
12.03
f1 (ppm)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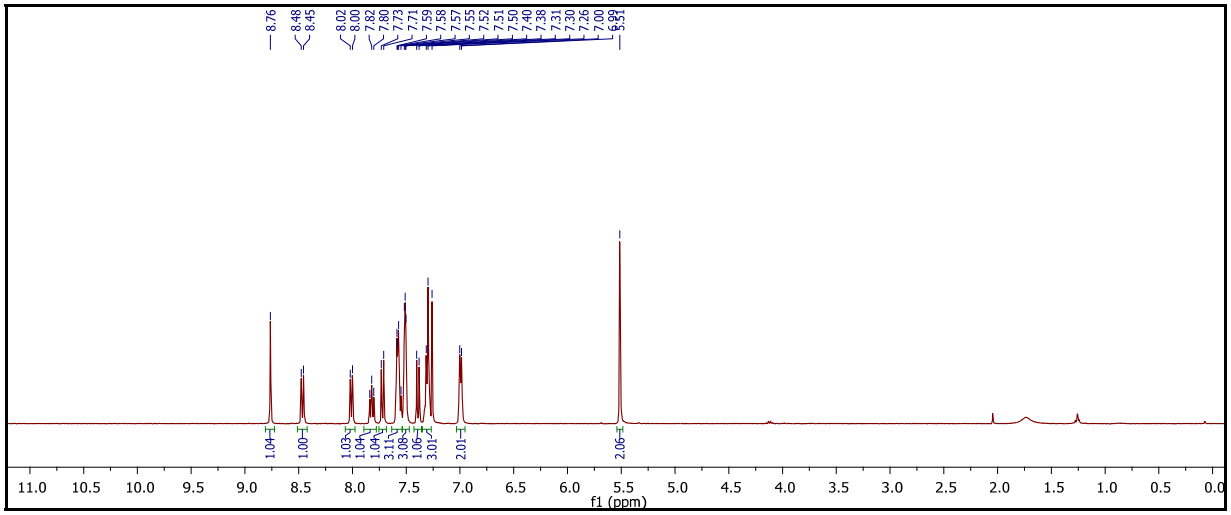
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7.38
7.31
7.30
7.26
7.00
6.99
5.51
1.04
1.00
1.03
1.04
1.04
3.11
3.08
1.06
3.01
2.01
2.06
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10.5
10.0
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8.0
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7.0
6.5
6.0
5.5
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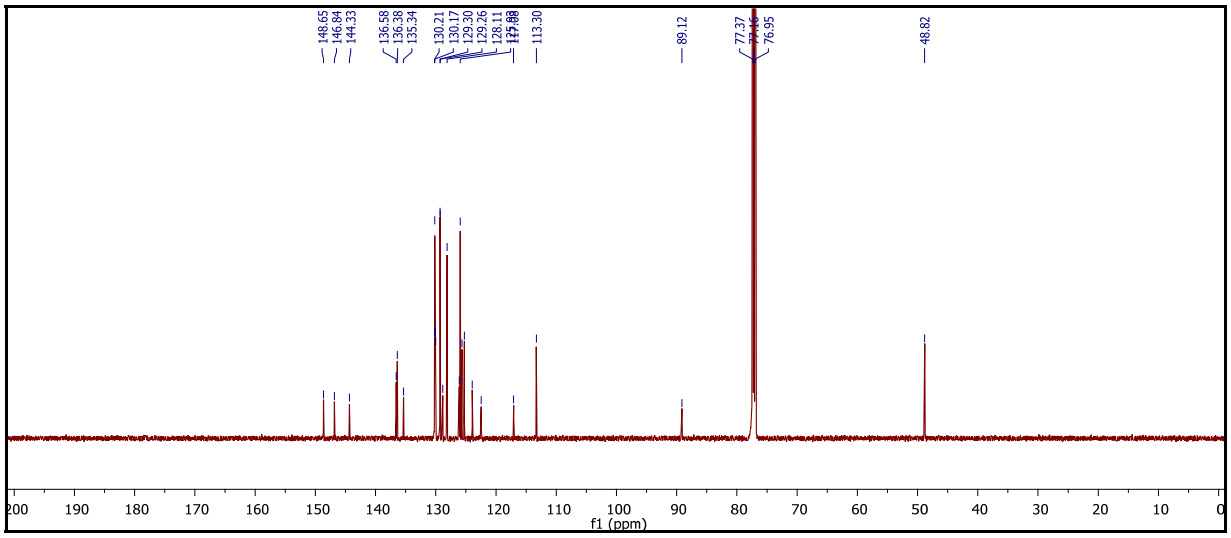
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130.17
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129.26
128.11
113.30
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77.37
76.95
48.82
200
190
180
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110
100
90
80
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50
40
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10
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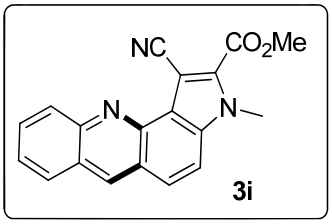
f1 (ppm)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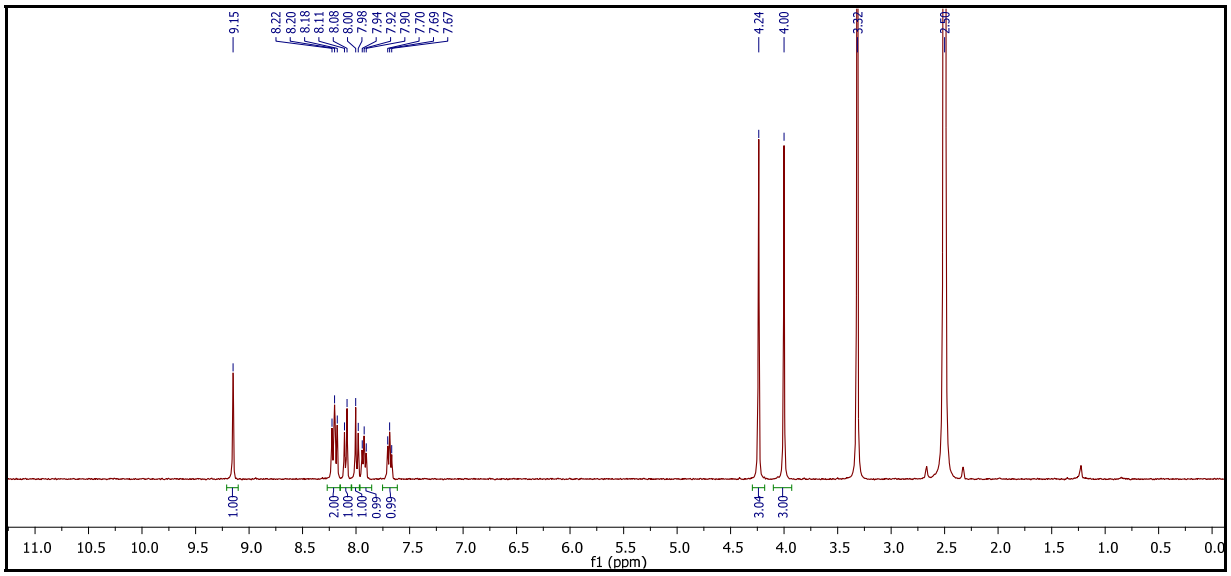
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7.98
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7.92
7.90
7.70
7.69
7.67
4.24
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1.00
1.00
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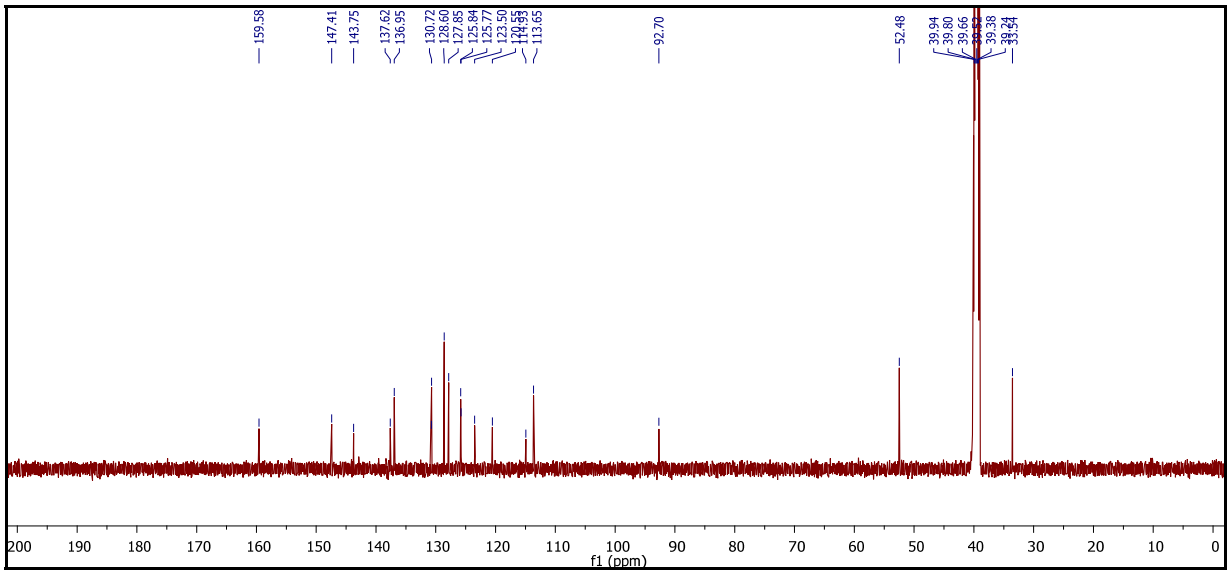
3.00
f1 (ppm)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39.94
39.80
39.66
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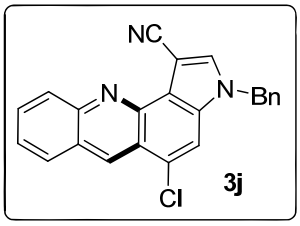
39.24
f1 (ppm)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Cl
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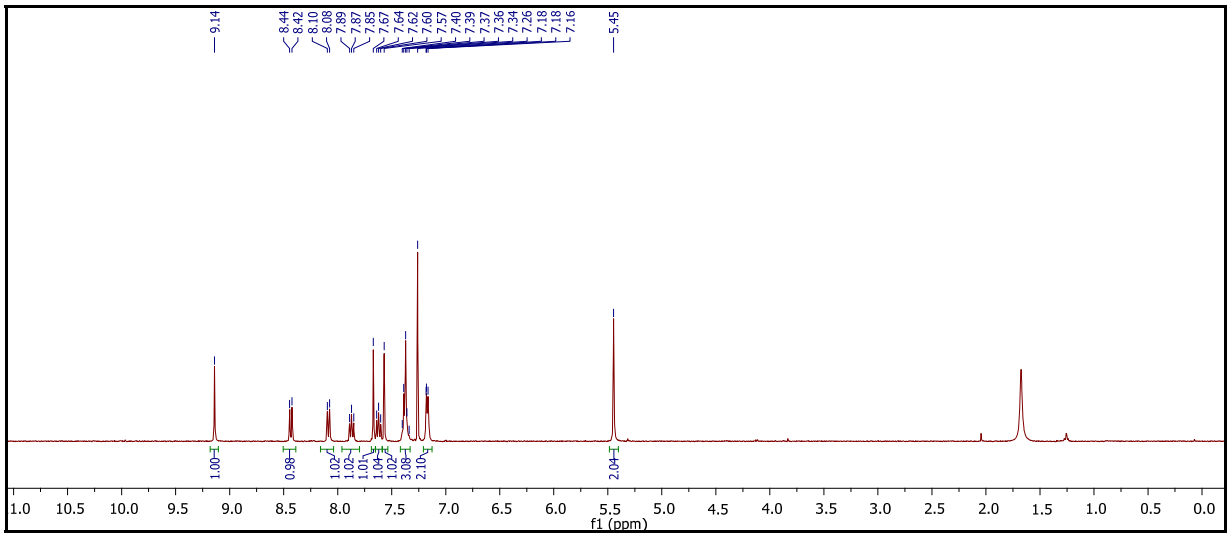
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7.39
7.37
7.36
7.34
7.26
7.18
7.18
7.16
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1.01
1.04
1.02
3.08
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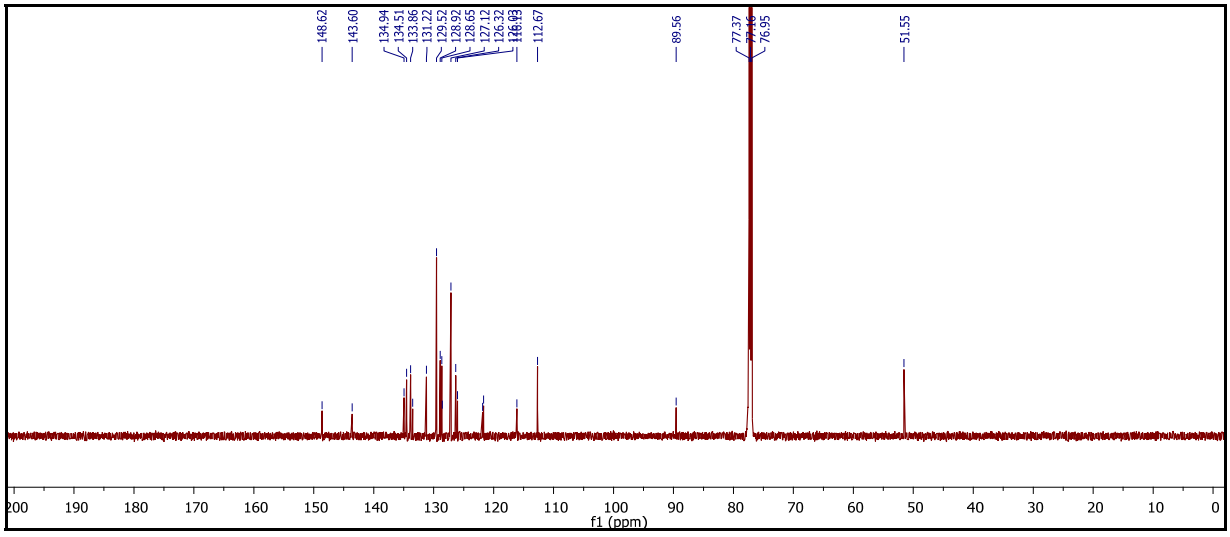
2.04
f1 (ppm)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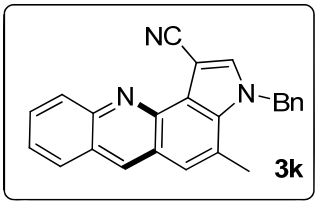
77.16
76.95
51.55
f1 (ppm)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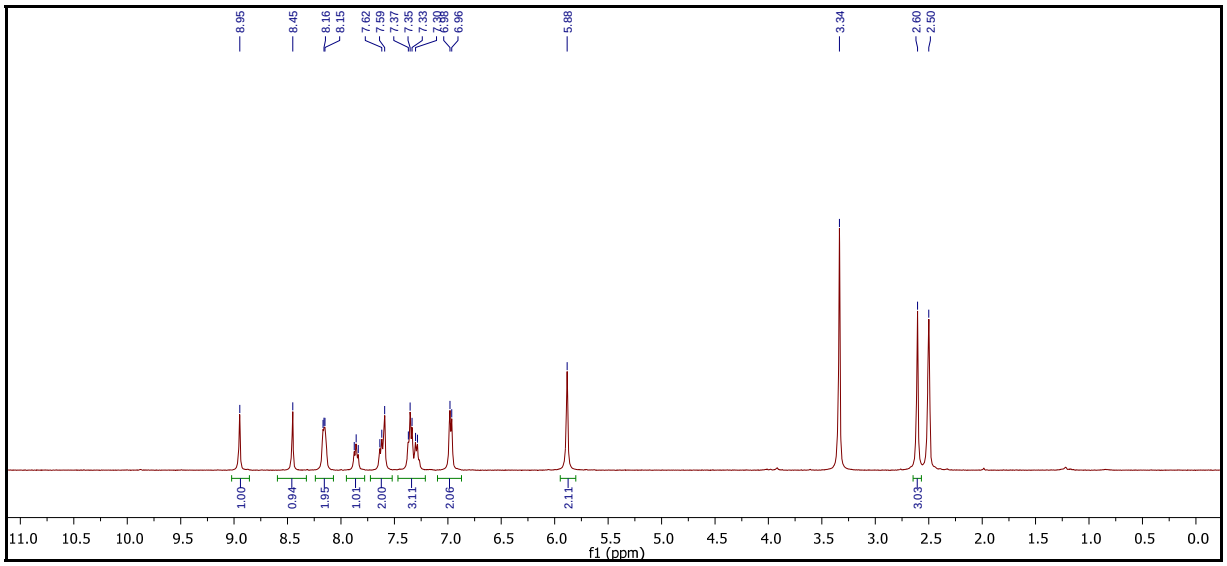
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3.34
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1.95
1.01
2.00
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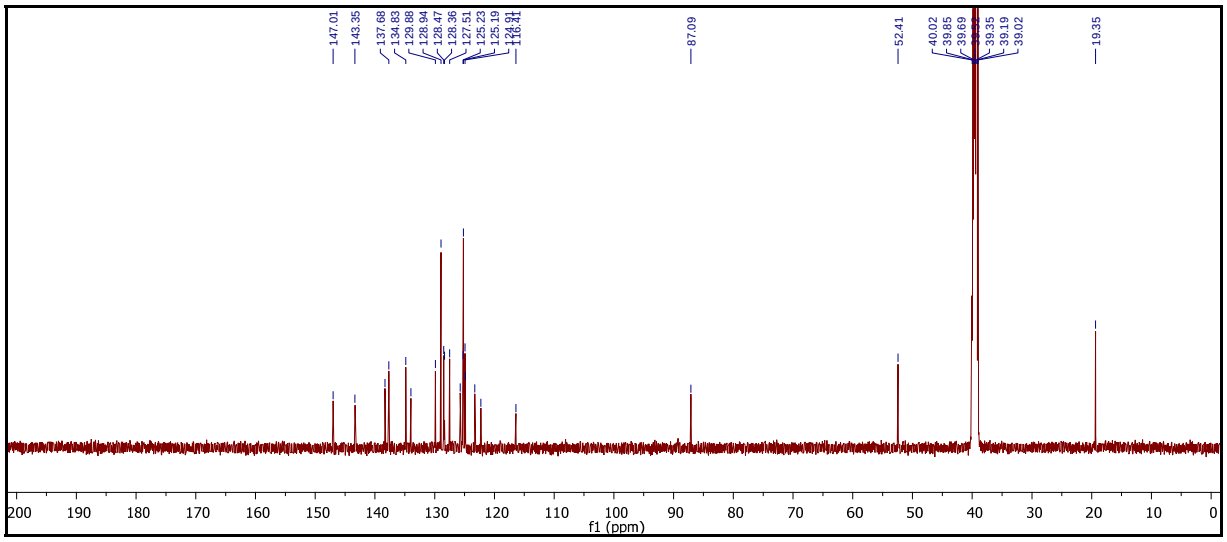
2.06
2.11
3.03
f1 (ppm)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52.41
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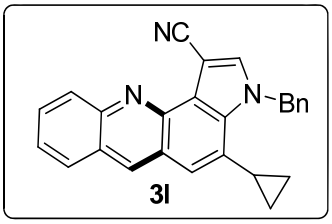
39.85
39.69
39.35
39.19
39.02
19.35
f1 (ppm)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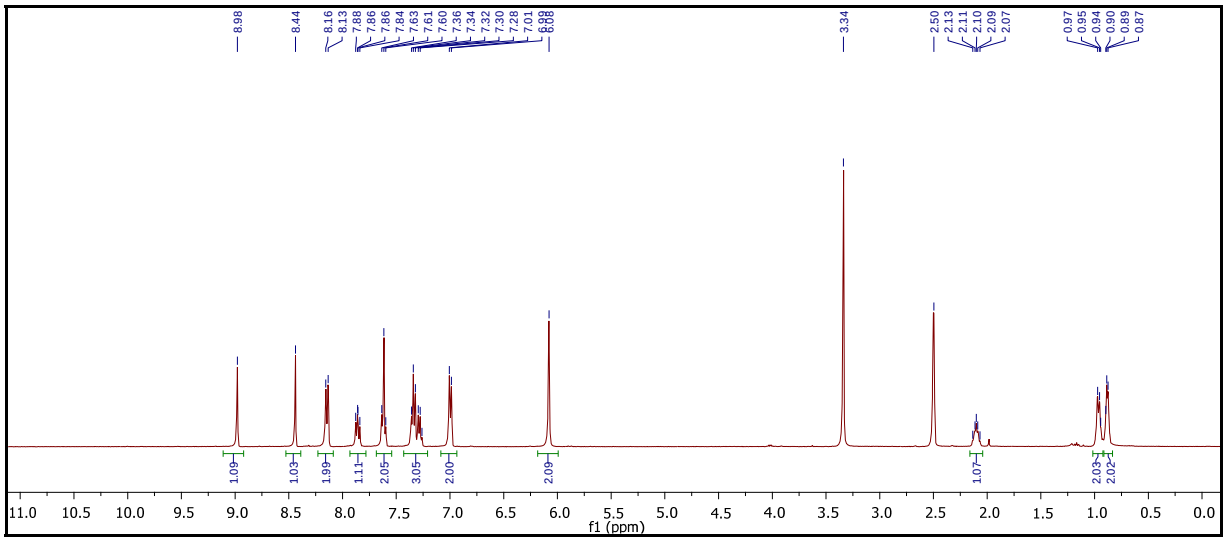
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6.98
3.34
2.50
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2.11
2.10
2.09
2.07
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0.94
0.90
0.89
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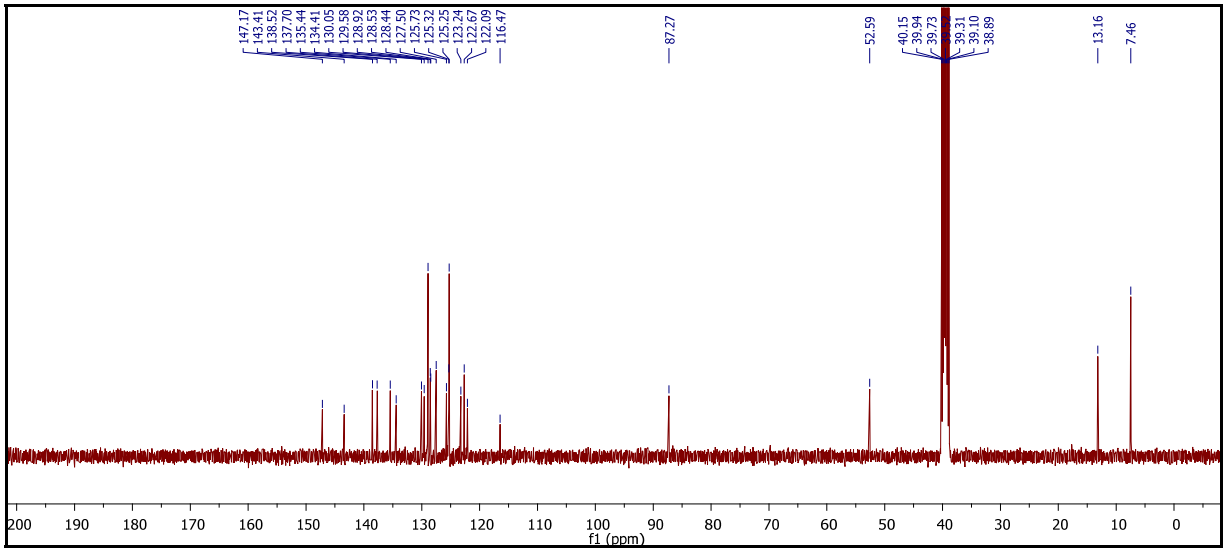
1.11
2.05
3.05
2.00
2.09
1.07
2.03
2.02
f1 (ppm)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87.27
52.59
40.15
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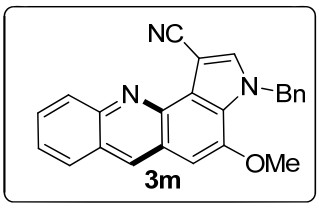
f1 (ppm)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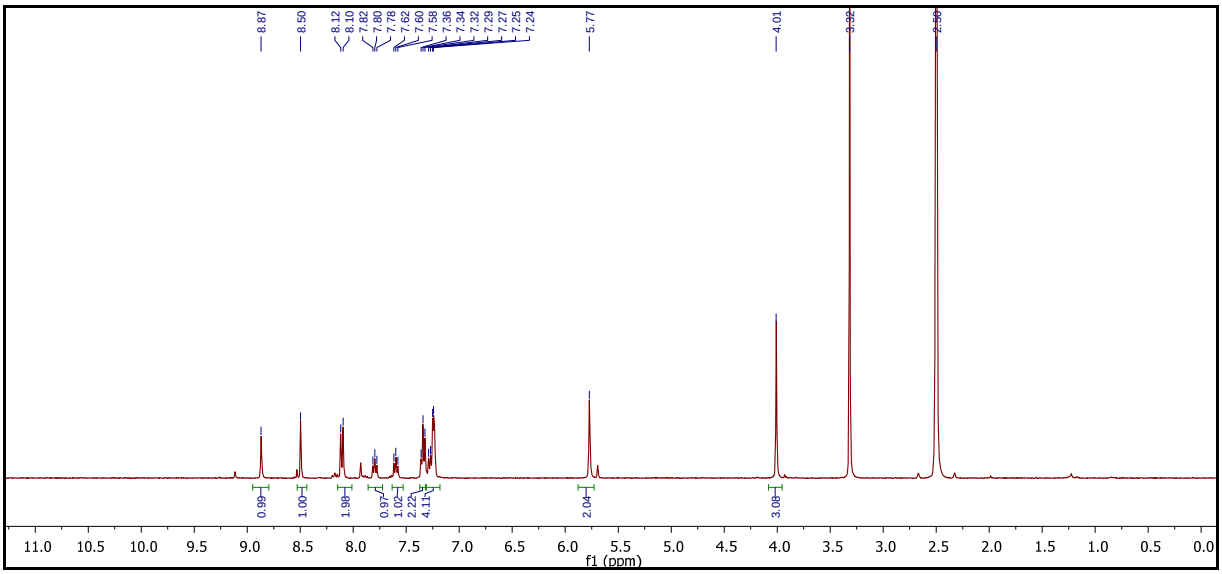
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7.27
7.25
7.24
5.77
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0.97
1.02
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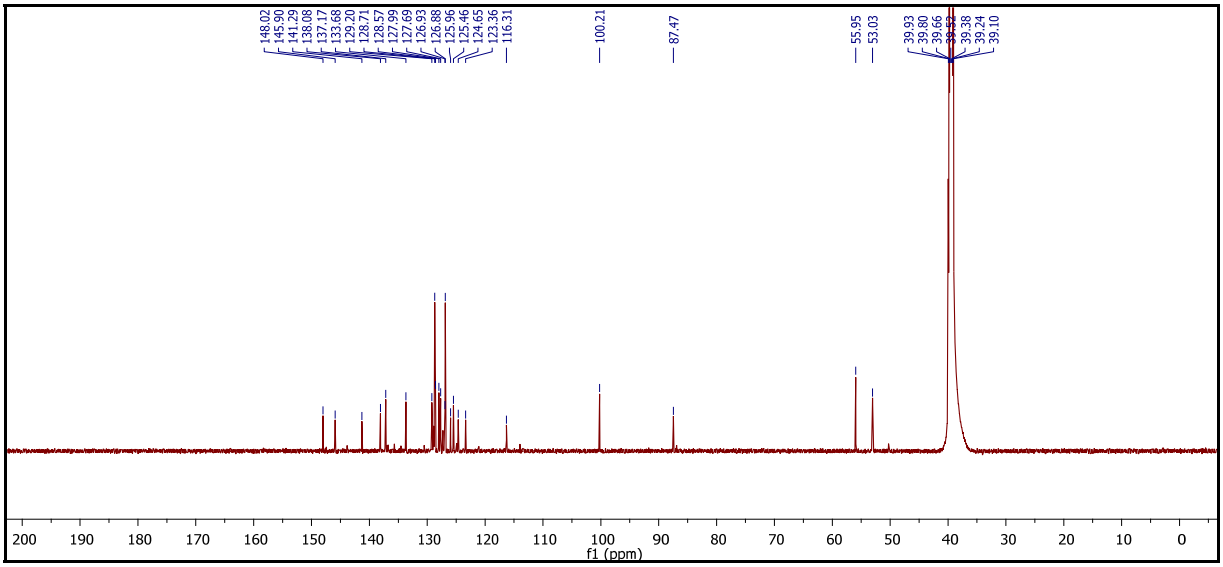
4.11
2.04
3.08
f1 (ppm)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124.65
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116.31
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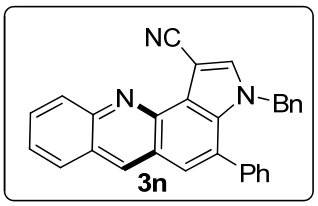
39.10
f1 (ppm)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Ph
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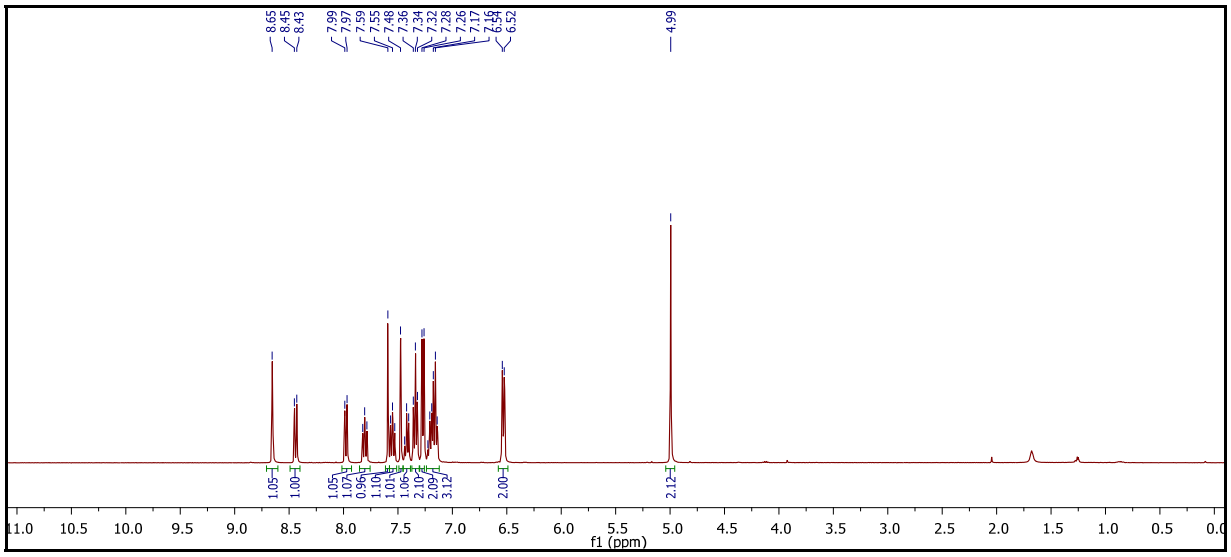
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7.16
6.54
6.52
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1.00
1.05
1.07
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1.10
1.01
1.06
2.10
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3.12
2.00
2.12
11.0
10.5
10.0
9.5
9.0
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6.5
6.0
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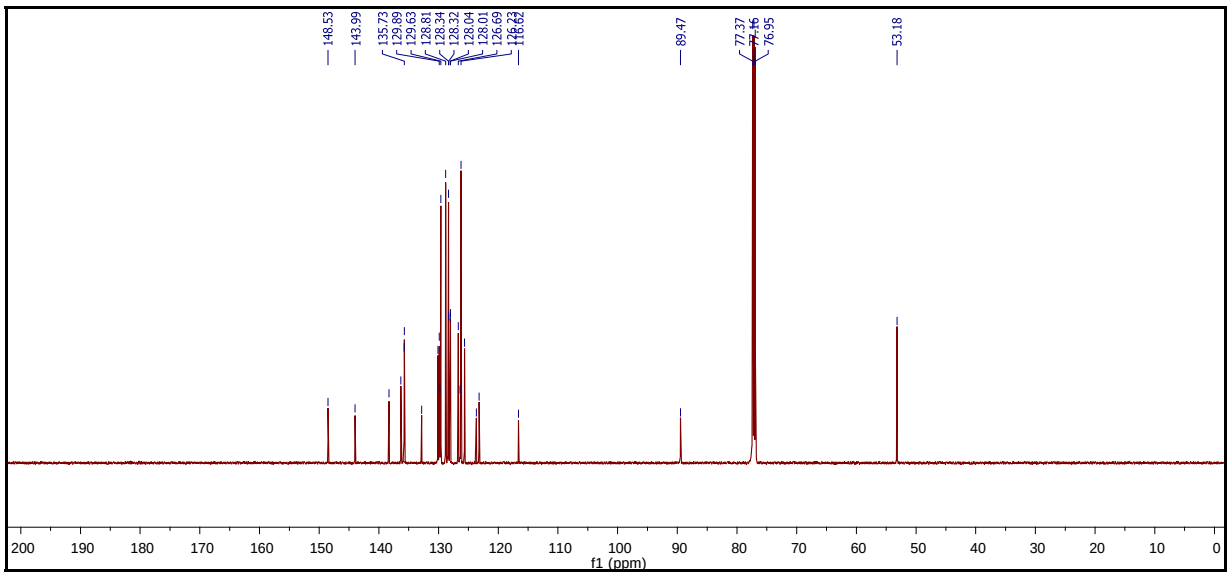
0.0
f1 (ppm)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77.37
77.16
76.95
53.18
200
190
180
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90
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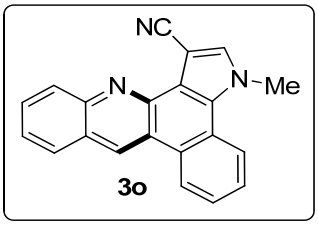
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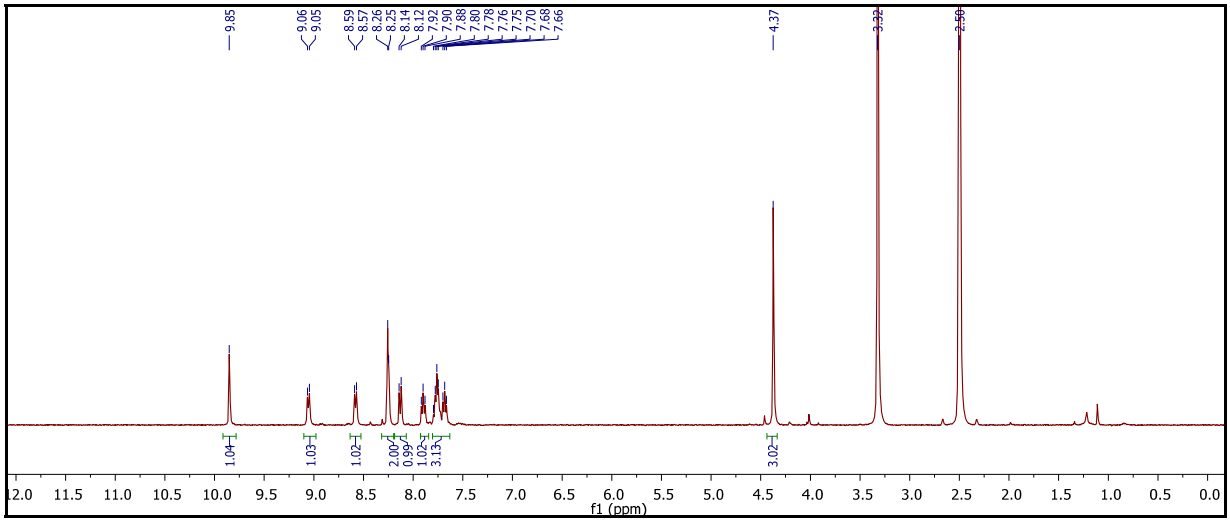
3o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8.25
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7.88
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7.78
7.76
7.75
7.70
7.68
7.66
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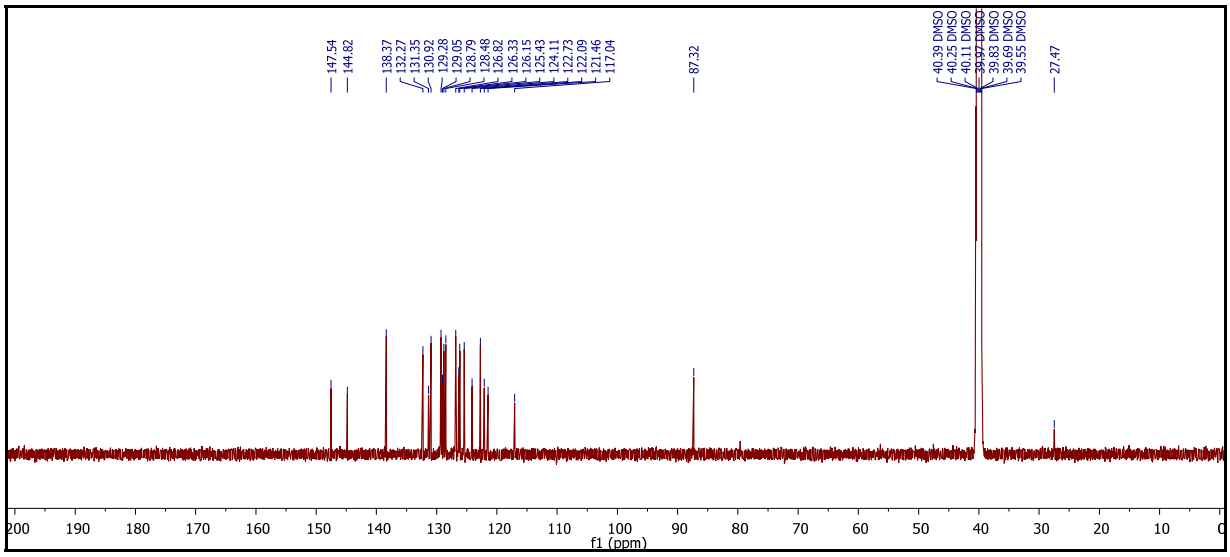
3.02
f1 (ppm)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130.92
129.28
129.05
128.79
128.48
126.82
126.33
126.15
125.43
124.11
122.73
122.09
121.46
117.04
87.32
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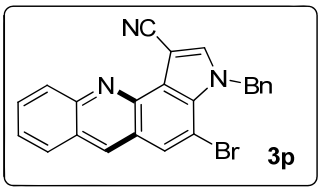
40.25 DMSO
40.11 DMSO
39.97 DMSO
39.83 DMSO
39.69 DMSO
39.55 DMSO
27.47
f1 (ppm)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Bn
Br
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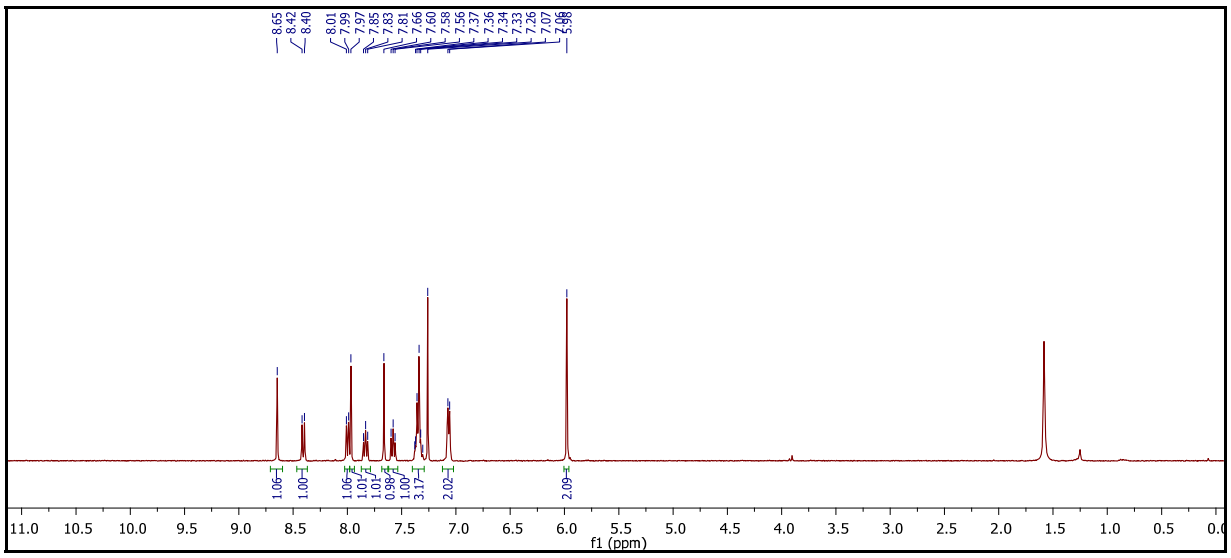
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7.83
7.81
7.66
7.60
7.58
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7.37
7.36
7.34
7.33
7.26
7.07
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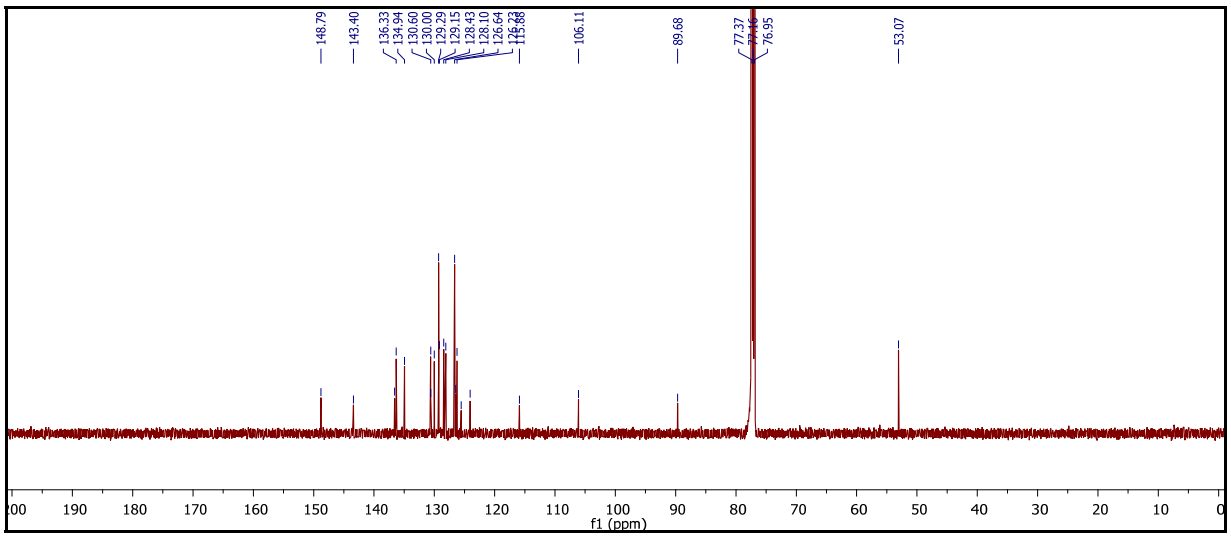
1.06
1.00
1.06
1.01
1.01
0.98
1.00
3.17
2.02
2.09
f1 (ppm)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130.00
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129.15
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128.10
126.64
106.11
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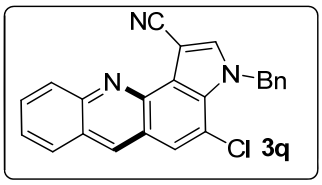
77.37
77.16
76.95
53.07
f1 (ppm)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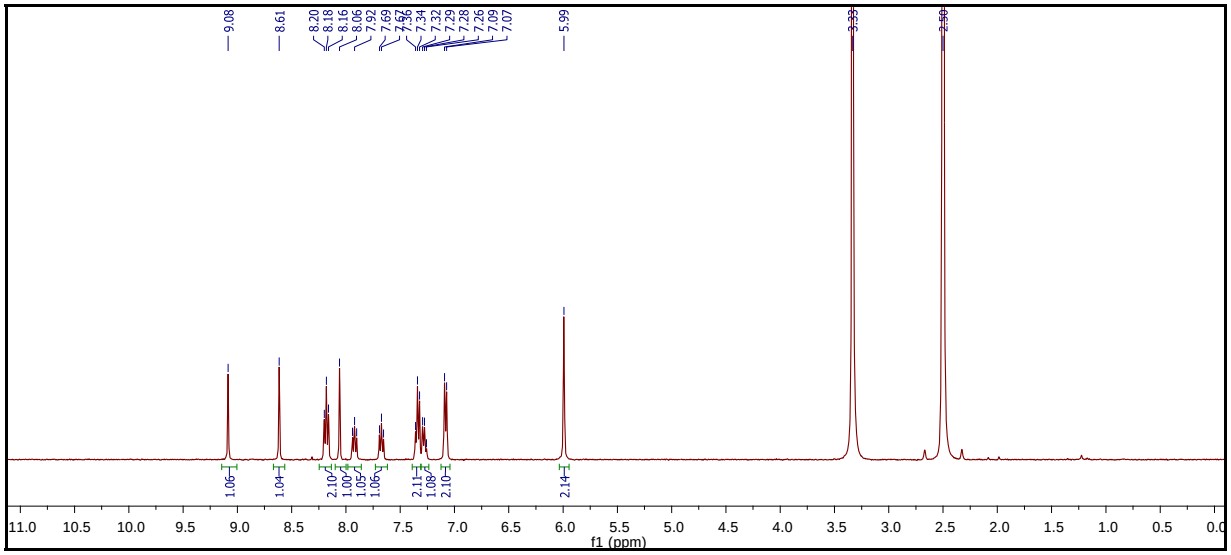
N–Bn
Cl
3q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7.92
7.69
7.67
7.36
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7.32
7.29
7.28
7.26
7.09
7.07
5.99
3.33
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1.06
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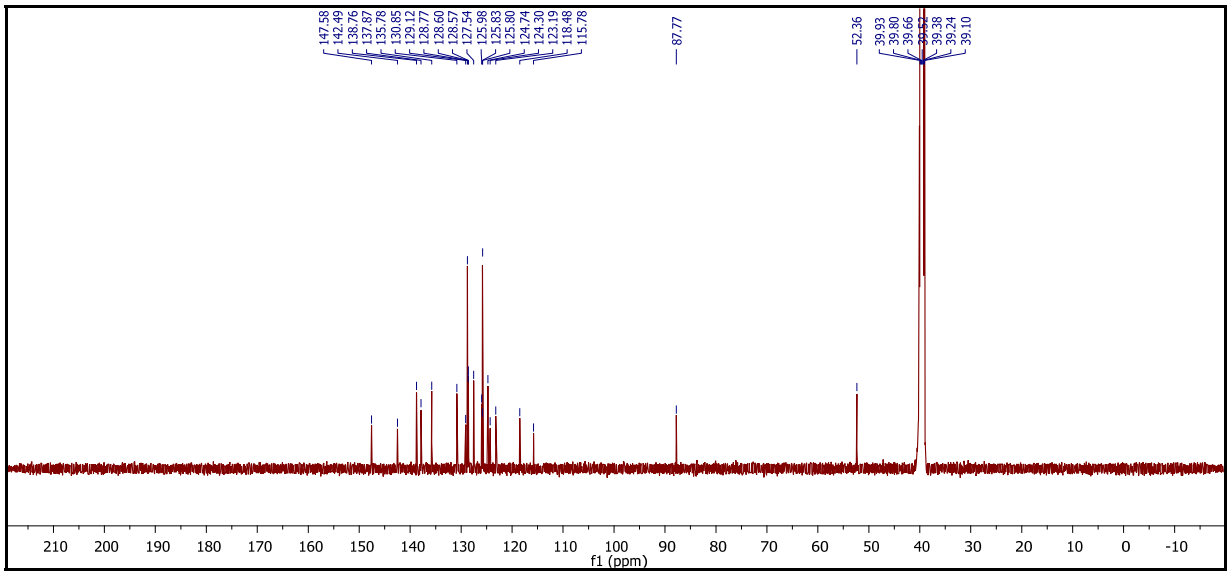
2.10
1.00
1.05
1.06
2.11
1.08
2.10
2.14
f1 (ppm)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125.80
124.74
124.30
123.19
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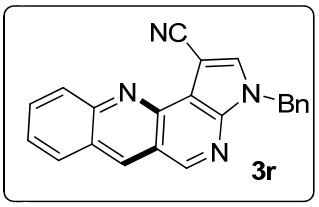
39.80
39.66
39.52
39.38
39.24
39.10
f1 (ppm)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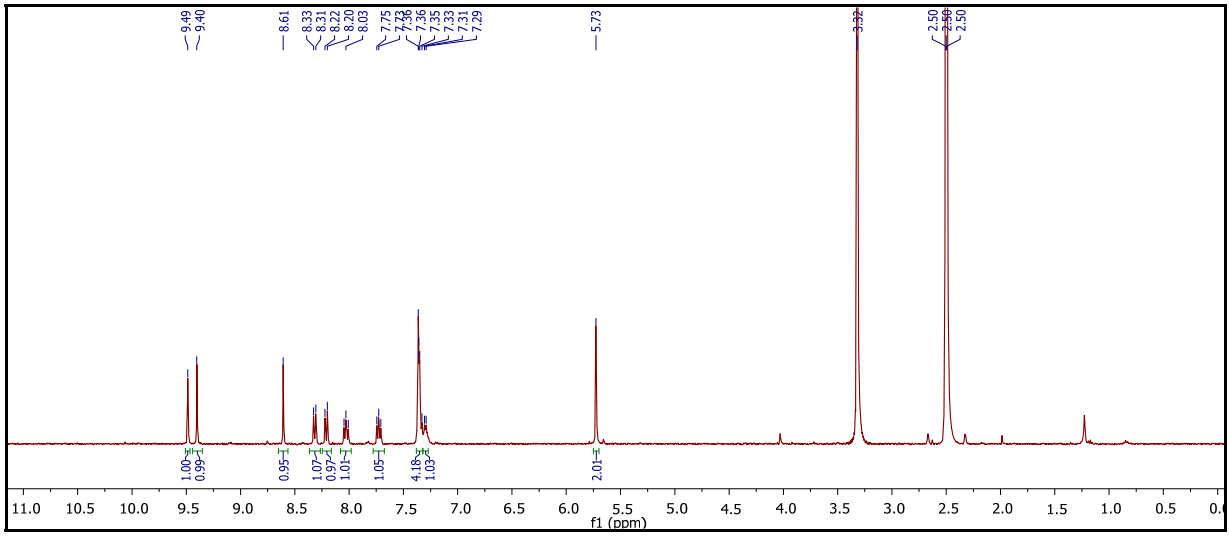
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8.03
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7.73
7.36
7.35
7.33
7.31
7.29
5.73
3.32
2.50
2.50
2.50
1.00
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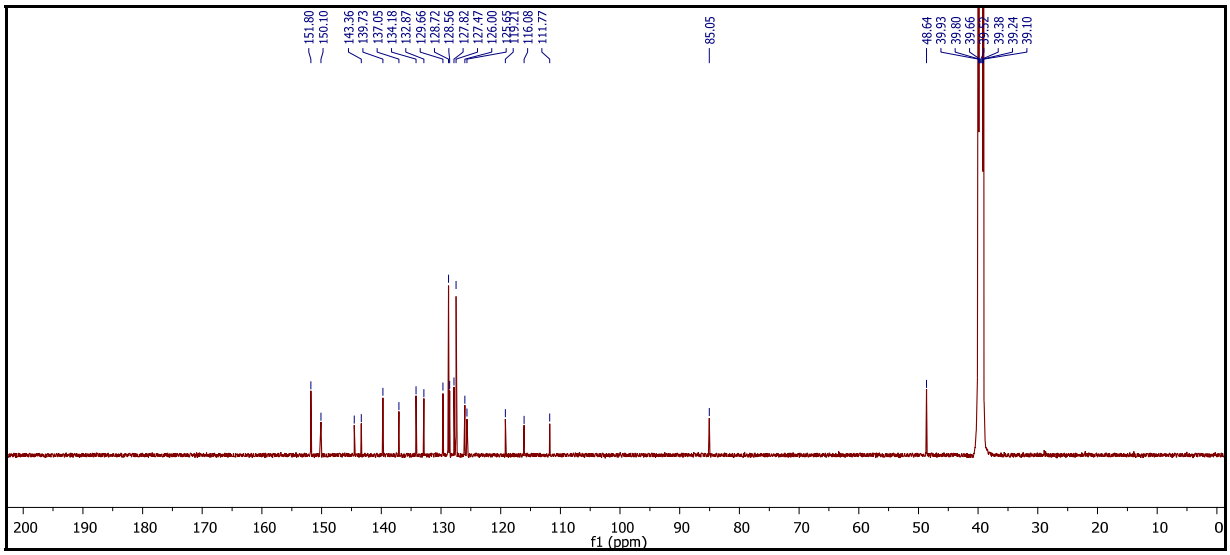
0.95
1.07
0.97
1.01
1.05
4.18
1.03
2.01
f1 (ppm)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126.00
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48.64
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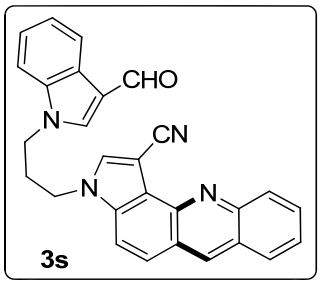
39.80
39.66
39.52
39.38
39.24
39.10
f1 (ppm)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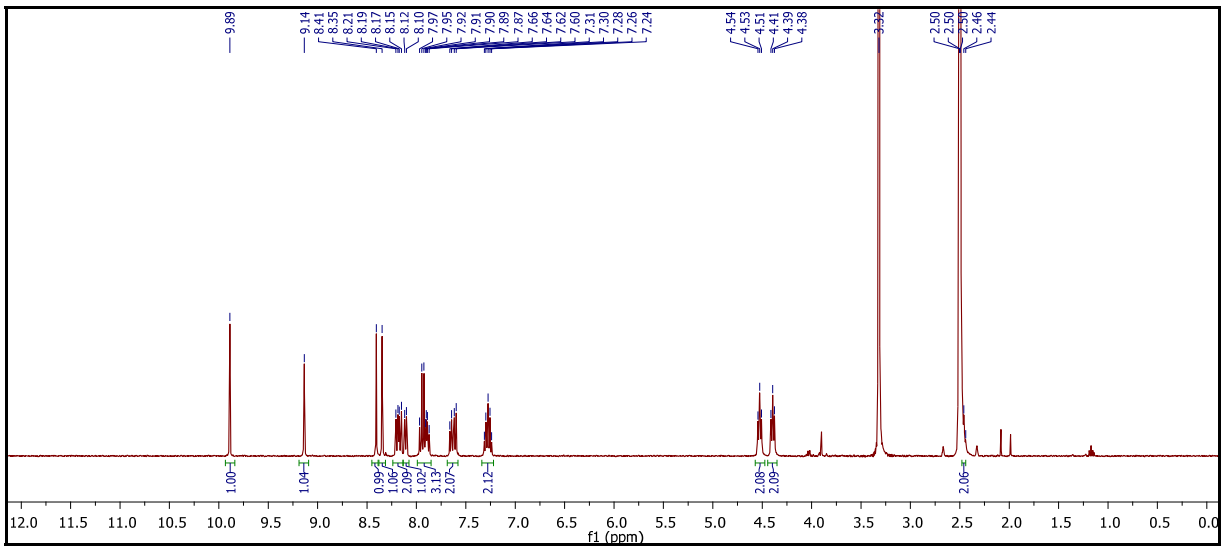
N
3s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8.10
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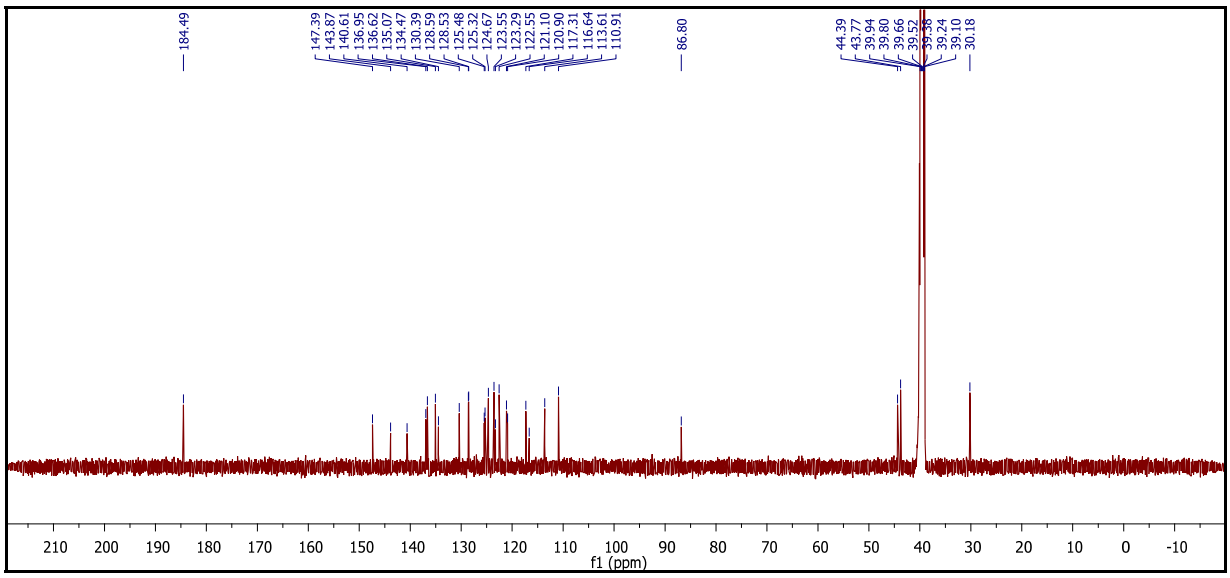
7.91
7.90
7.89
7.87
7.66
7.64
7.62
7.60
7.31
7.30
7.28
7.26
7.24
4.54
4.53
4.51
4.41
4.39
4.38
3.32
2.50
2.50
2.50
2.46
2.44
1.00
1.04
0.99
1.06
2.09
1.02
3.13
2.07
2.12
2.08
2.09
2.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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124.67
123.55
123.29
122.55
121.10
120.90
117.31
116.64
113.61
110.91
86.80
44.39
43.77
39.94
39.80
39.66
39.52
39.38
39.24
39.10
30.18
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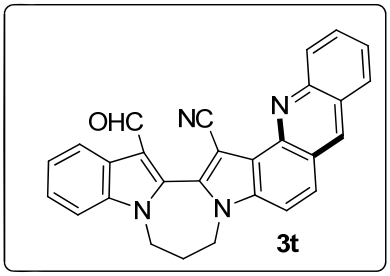
f1 (ppm)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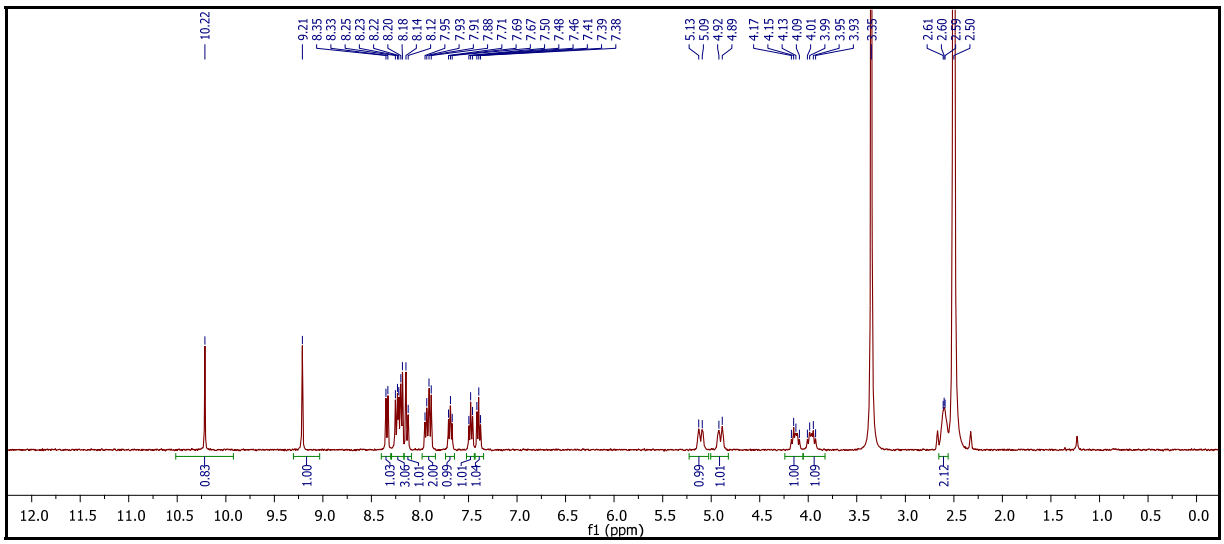
N
N

3t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7.93
7.91
7.88
7.71
7.69
7.67
7.50
7.48
7.46
7.41
7.39
7.38
5.13
5.09
4.92
4.89
4.17
4.15
4.13
4.09
4.01
3.99
3.95
3.93
3.35
2.61
2.60
2.59
2.50
0.83
1.00
1.03
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1.01
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0.99
1.01
1.04
0.99
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1.00
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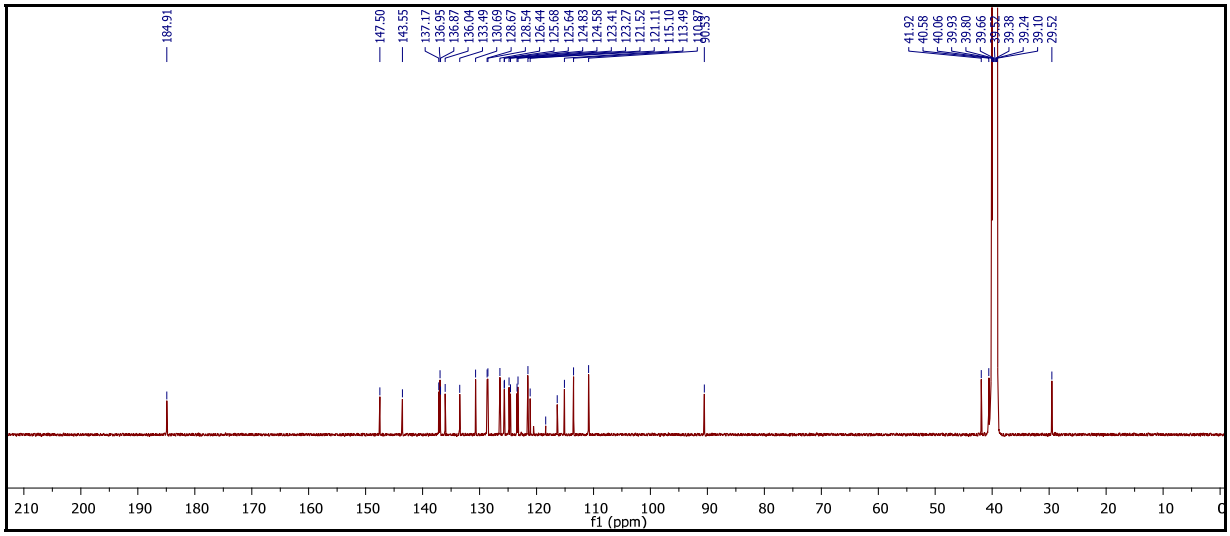
f1 (ppm)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39.52
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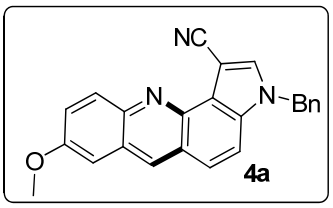
39.24
39.10
29.52
f1 (ppm)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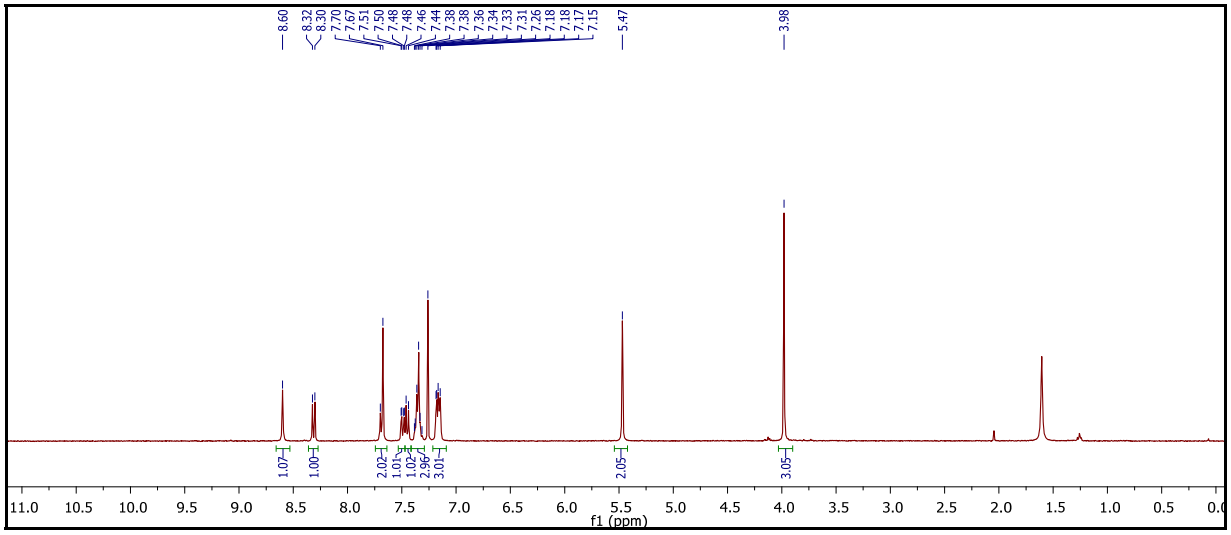
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7.44
7.38
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7.36
7.34
7.33
7.31
7.26
7.18
7.17
7.15
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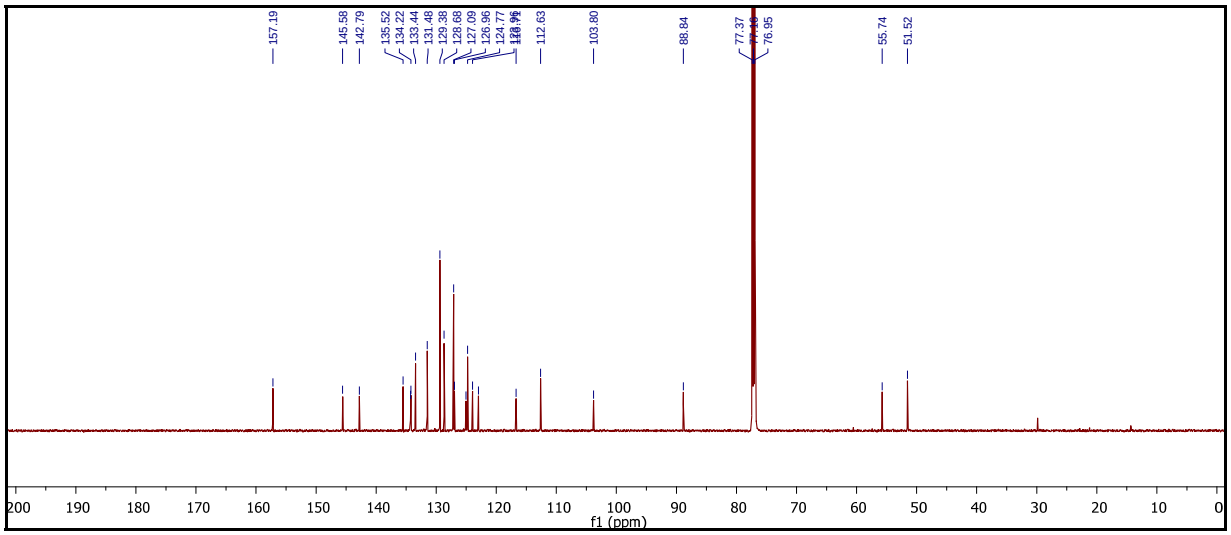
1.00
2.02
1.01
1.02
2.96
3.01
2.05
3.05
f1 (ppm)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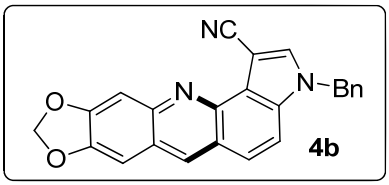
77.37
76.95
55.74
51.52
f1 (ppm)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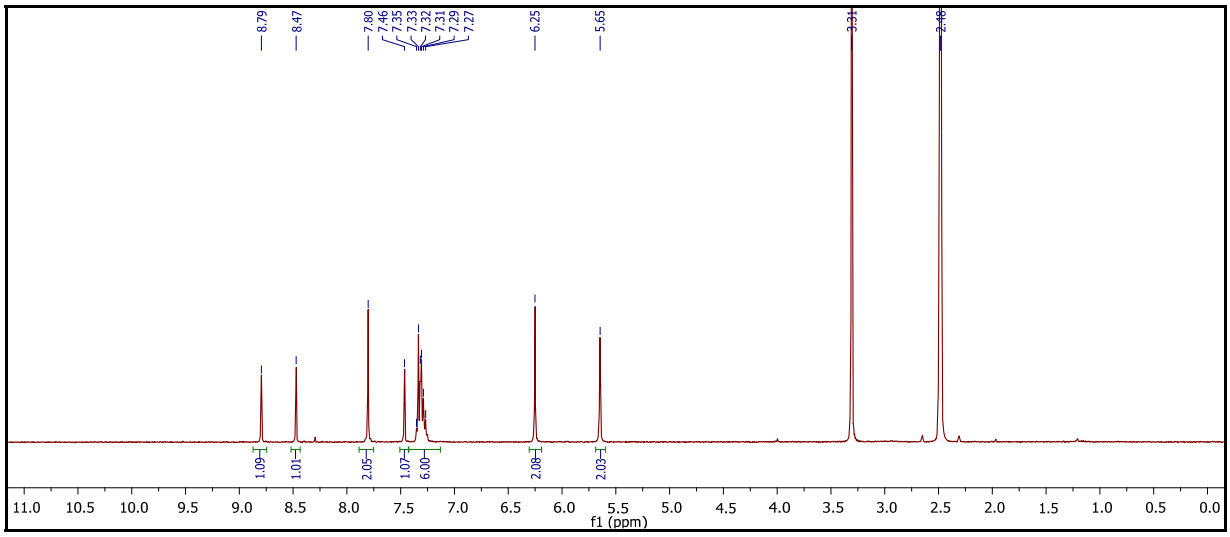
N–Bn
O
O
4b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7.27
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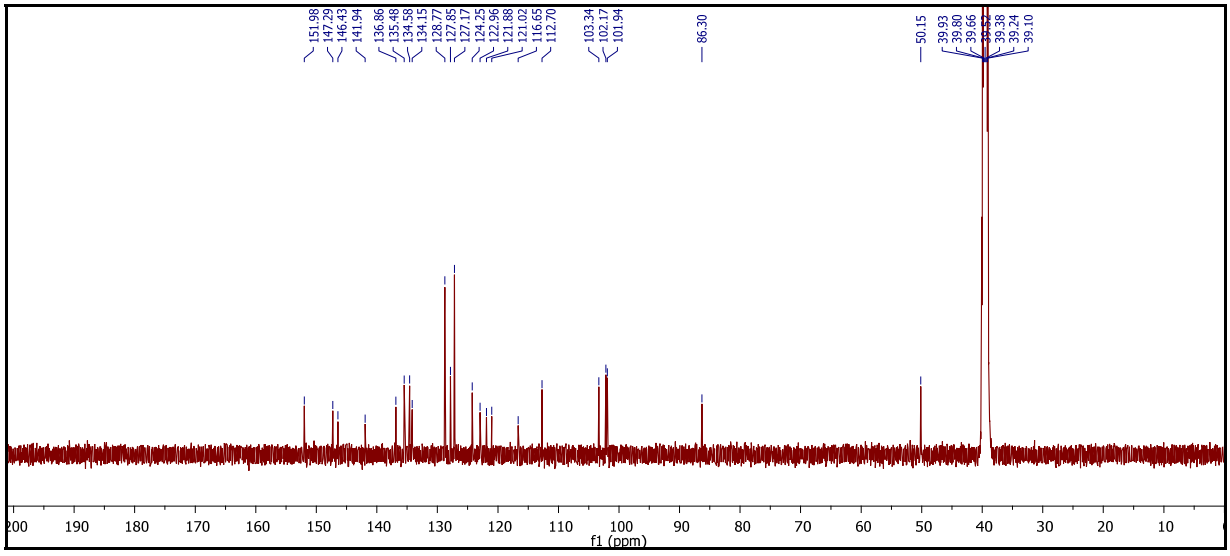
1.07
6.00
2.08
2.03
f1 (ppm)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122.96
121.88
121.02
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103.34
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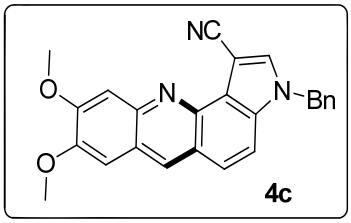
39.52
39.38
39.24
39.10
f1 (ppm)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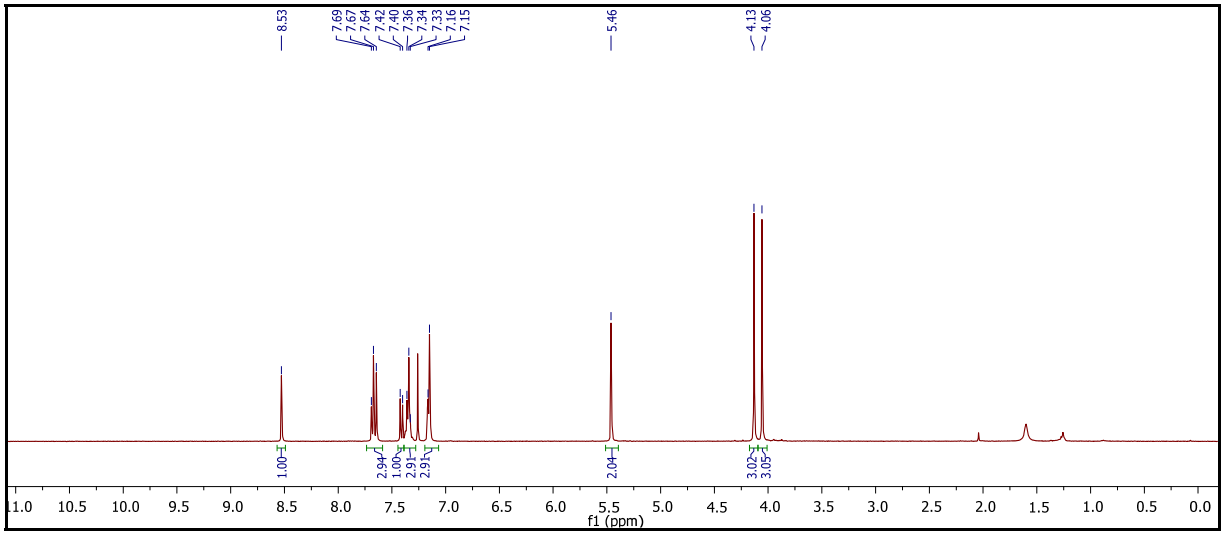
O
N
N
Bn
O
4c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2.04
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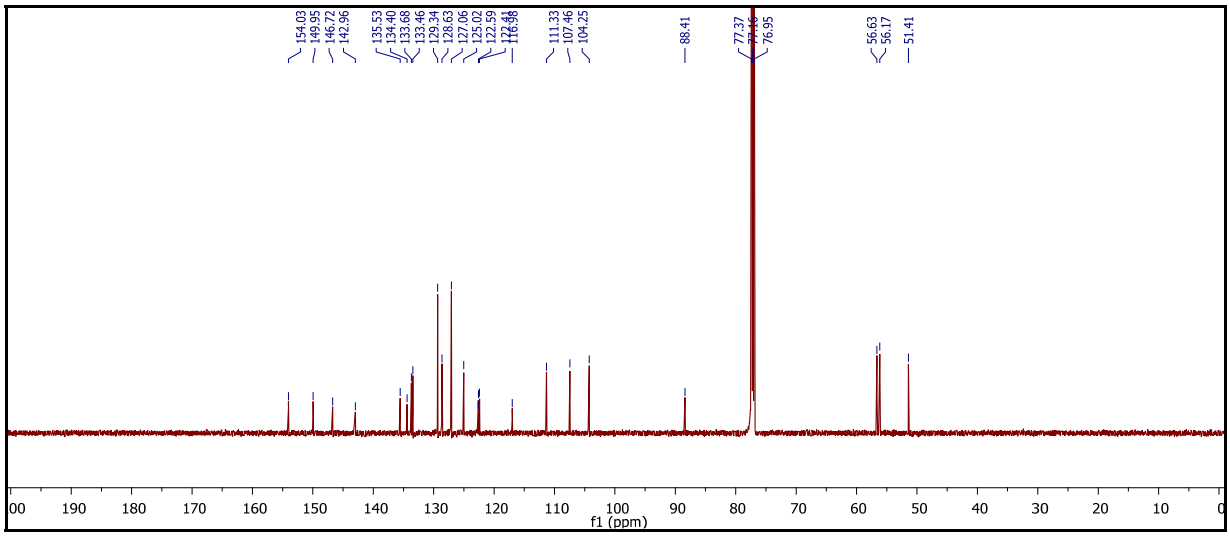
3.05
f1 (ppm)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132.46
129.34
128.63
127.06
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56.17
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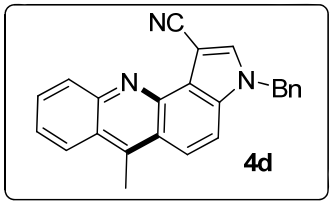
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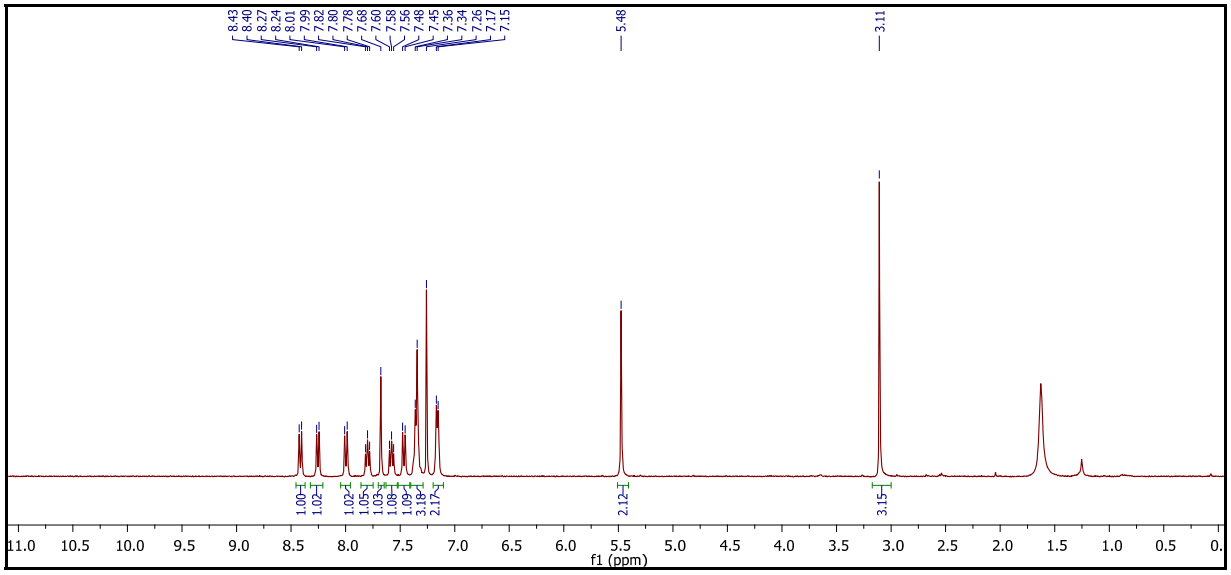
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7.34
7.26
7.17
7.15
5.48
3.11
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1.09
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2.17
2.12
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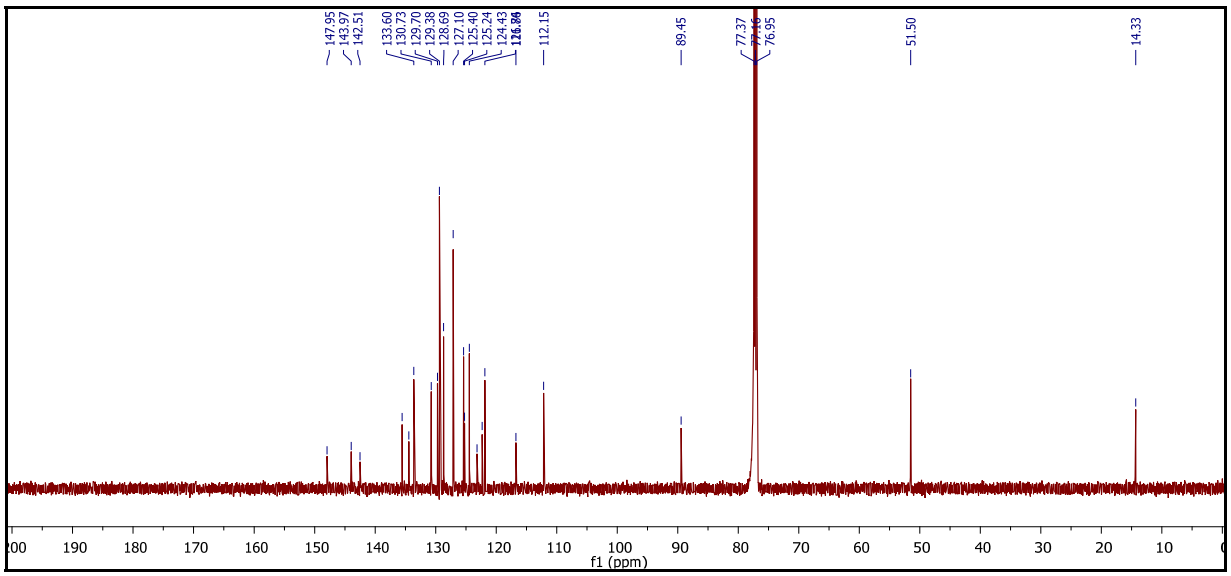
f1 (ppm)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125.24
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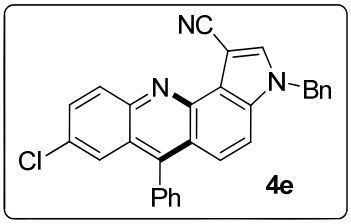
76.95
51.50
14.33
f1 (ppm)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Bn
Cl
Ph
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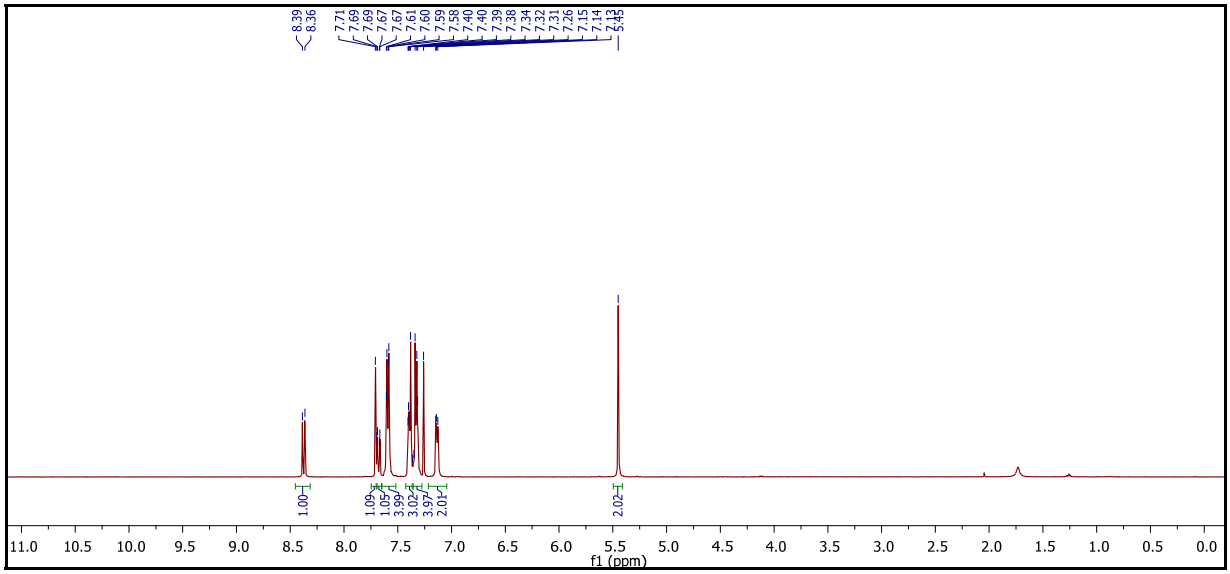
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7.38
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1.05
3.99
3.02
3.97
2.01
2.02
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9.0
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8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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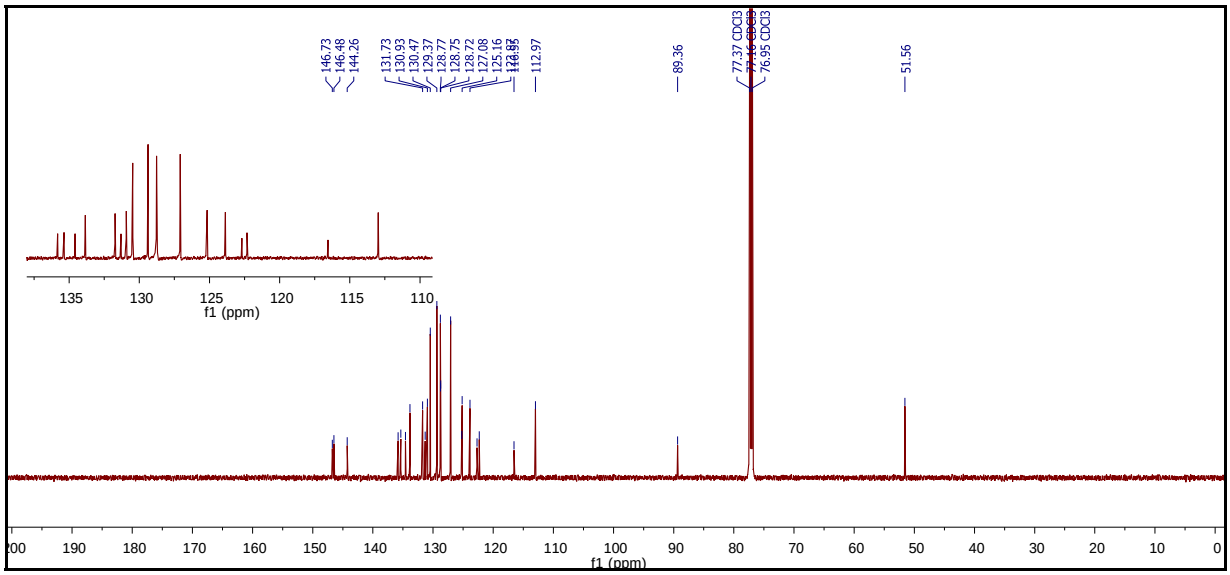
0.0
f1 (ppm)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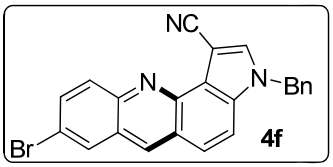
128.72
127.08
125.16
112.97
89.36
77.37 CDCl3
76.95 CDCl3
51.56
135
130
125
120
115
110
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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Br
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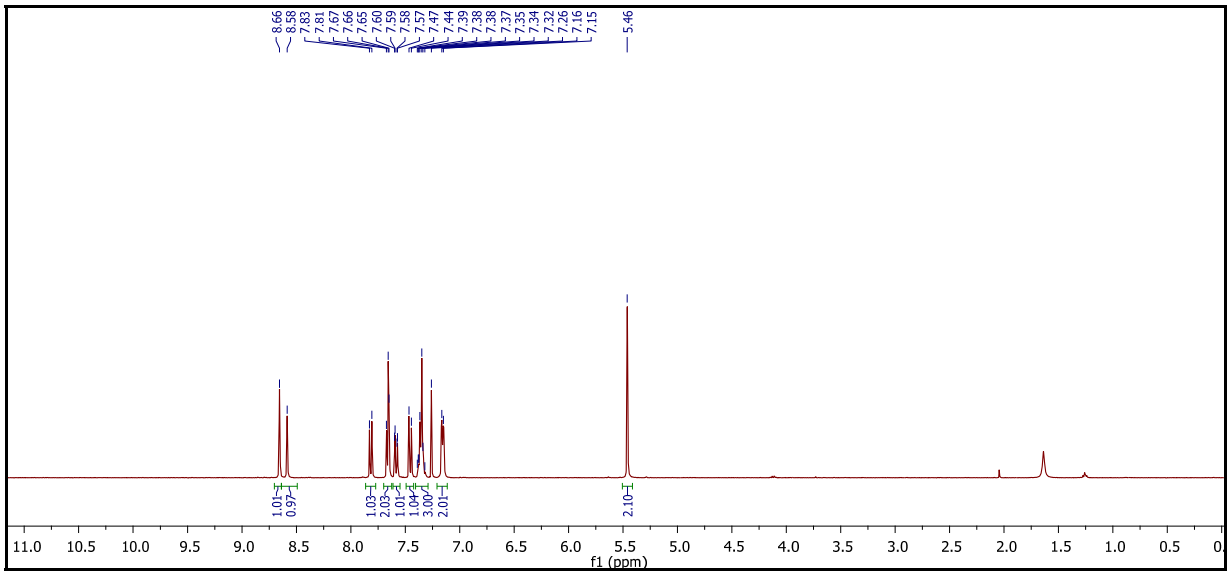
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7.44
7.39
7.38
7.37
7.35
7.34
7.32
7.26
7.16
7.15
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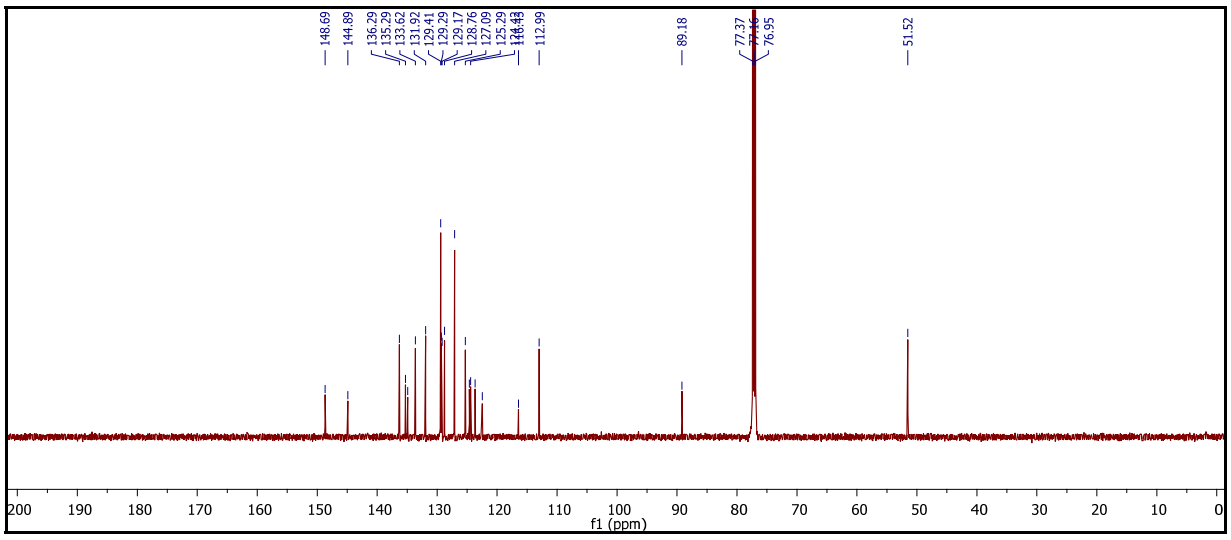
1.03
2.03
1.01
1.04
3.00
2.01
2.10
f1 (ppm)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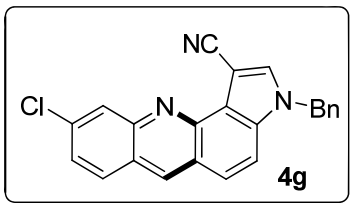
77.37
77.16
76.95
51.52
f1 (ppm)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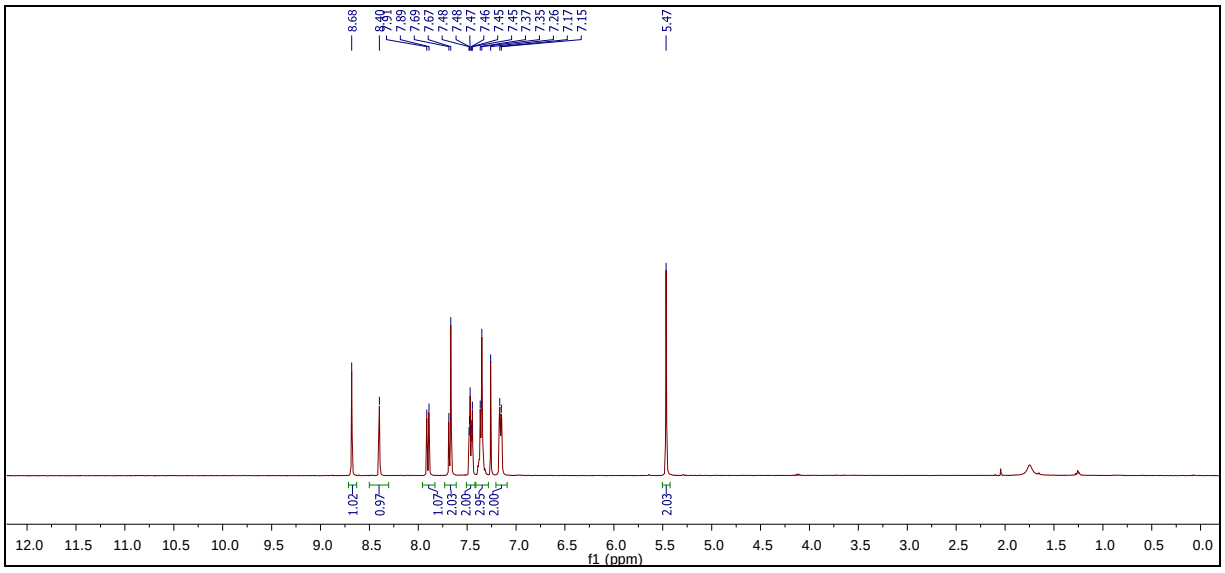
Cl
N
N
Bn
4g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7.46
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7.37
7.35
7.26
7.17
7.15
5.47
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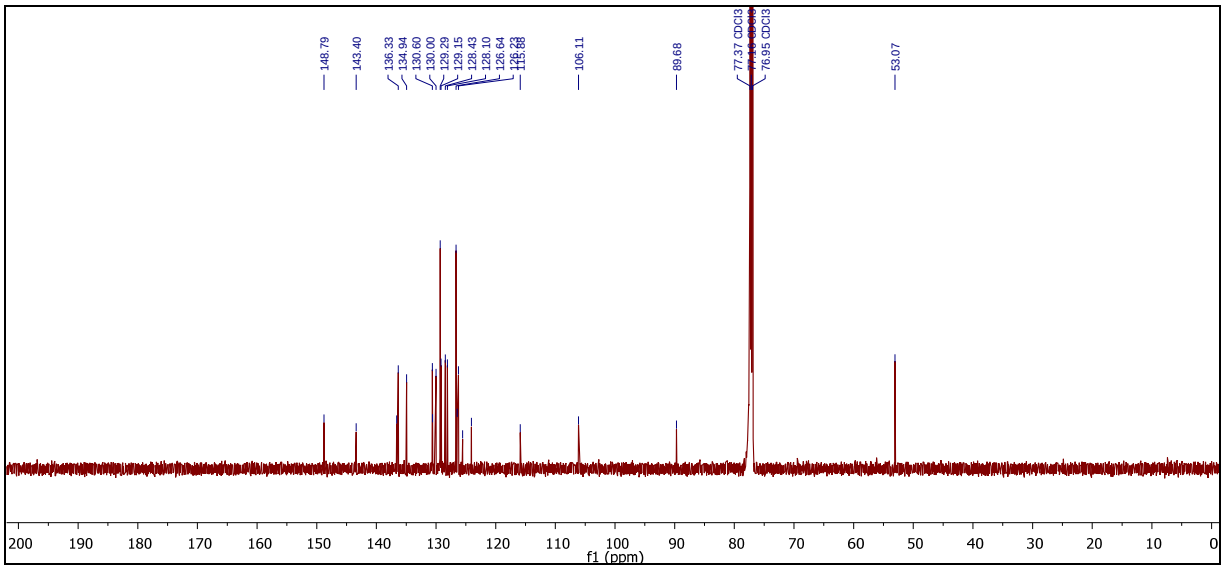
0.97
1.07
2.03
2.00
2.95
2.00
2.03
f1 (ppm)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128.10
126.64
106.11
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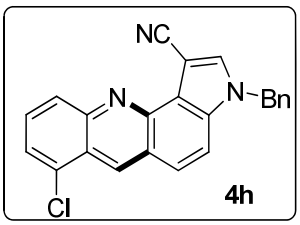
77.37 CDCl3
76.95 CDCl3
53.07
f1 (ppm)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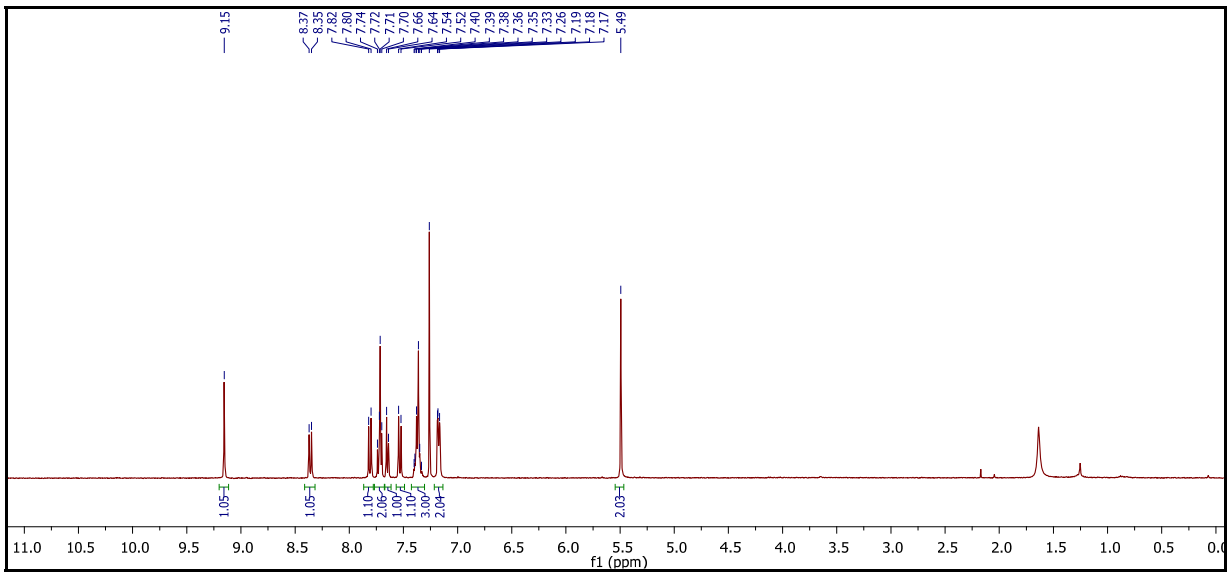
N-Bn
Cl
4h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7.52
7.40
7.39
7.38
7.36
7.35
7.33
7.26
7.19
7.18
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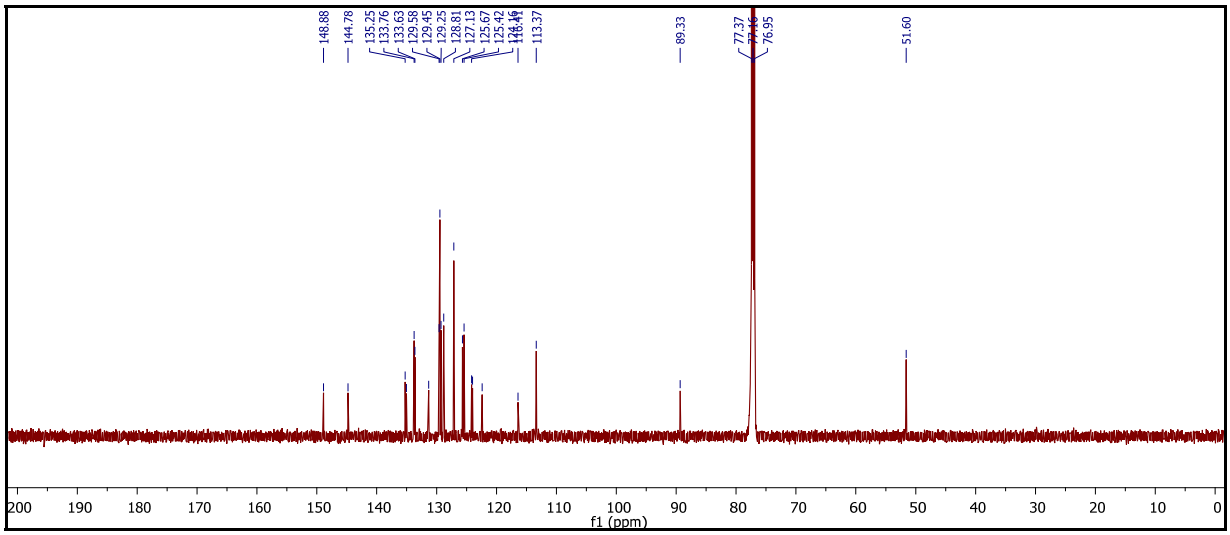
1.05
1.10
2.06
1.00
1.10
3.00
2.04
2.03
f1 (ppm)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125.42
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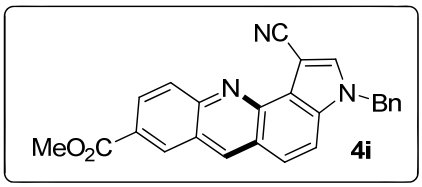
89.33
77.37
76.95
51.60
f1 (ppm)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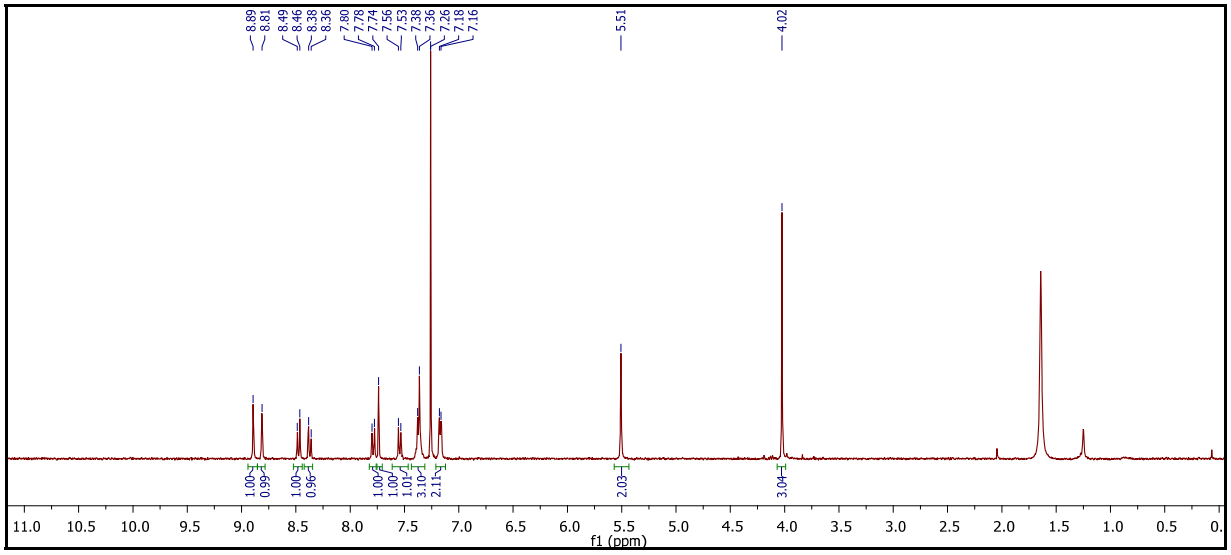
N
Bn
MeO2C
4i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7.74
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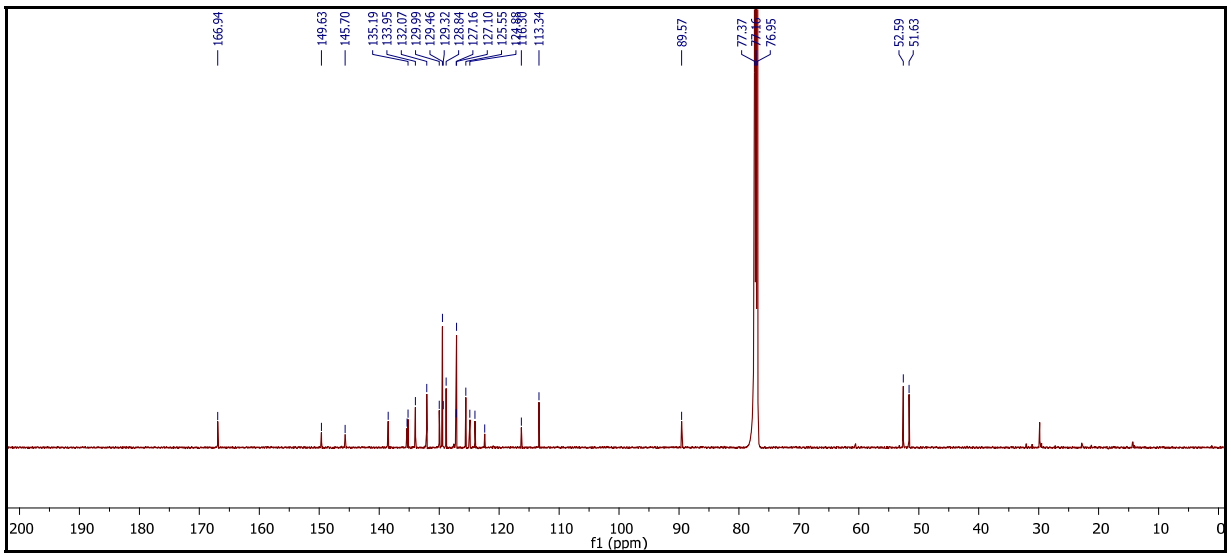
7.53
7.38
7.36
7.26
7.18
7.16
5.51
4.02
f1 (ppm)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129.46
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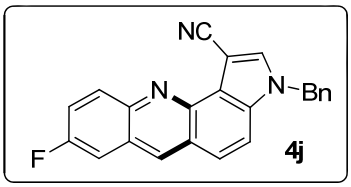
77.37
76.95
52.59
51.63
f1 (ppm)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Bn
F
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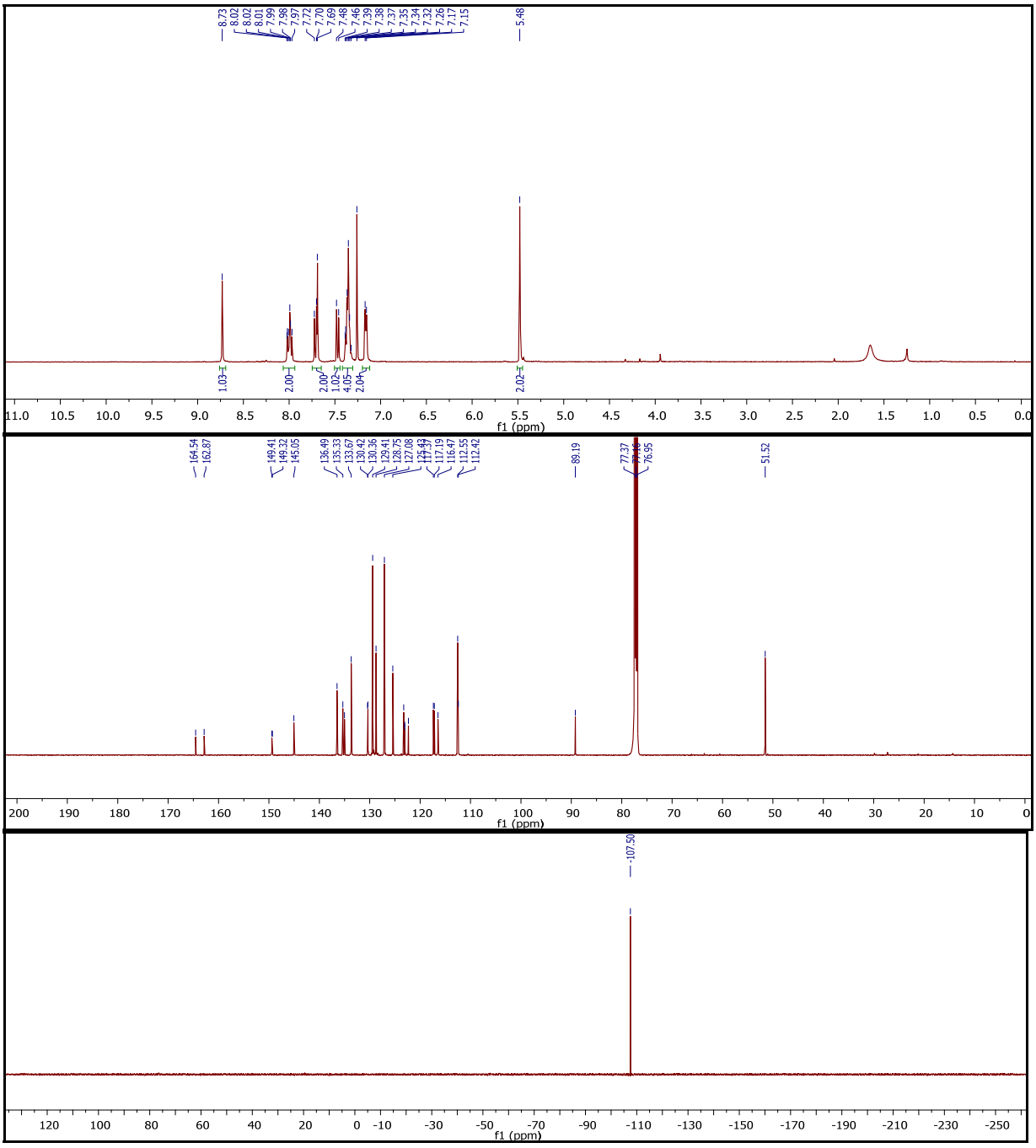
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7.46
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7.38
7.37
7.35
7.34
7.32
7.26
7.17
7.15
5.48
1.03
2.00
2.00
1.02
4.05
2.04
2.02
f1 (ppm)
164.54
162.87
149.41
149.32
145.05
136.49
135.33
133.67
130.42
130.36
129.41
128.75
127.08
125.43
117.37
117.19
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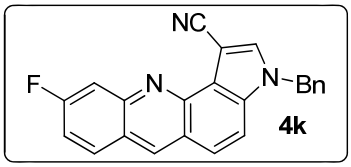
77.00
76.95
51.52
f1 (ppm)
-107.50
f1 (ppm)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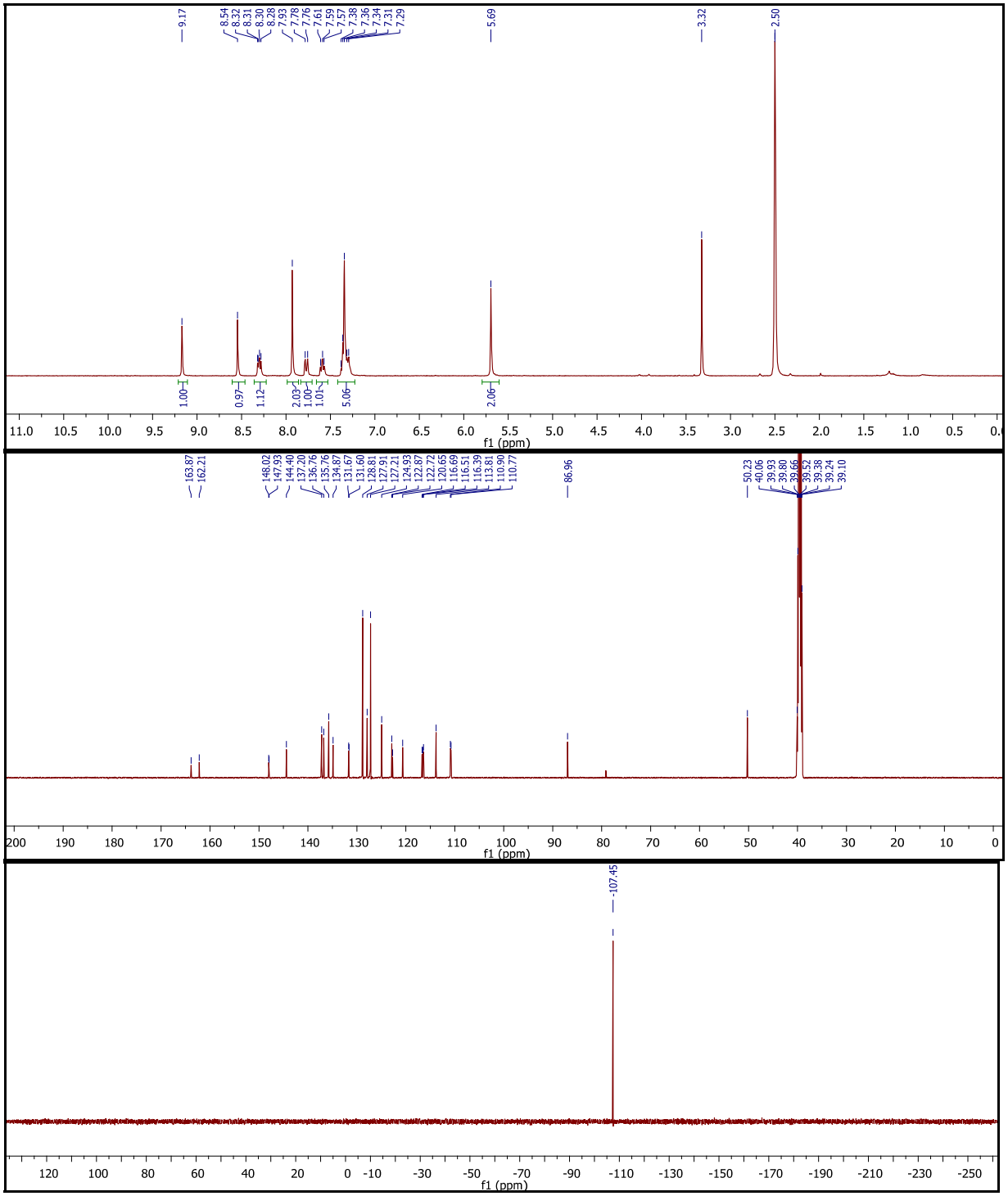
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7.38
7.36
7.34
7.31
7.29
5.69
3.32
2.50
1.00
0.97
1.12
2.03
1.00
1.01
5.06
2.06
f1 (ppm)
163.87
162.21
148.02
147.93
144.40
137.20
136.76
135.76
134.87
131.67
131.60
128.81
127.91
127.21
124.93
122.87
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120.65
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116.39
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50.23
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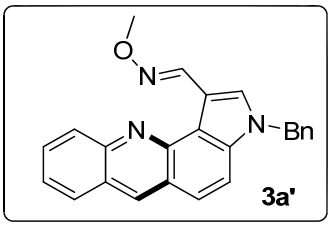
39.24
39.10
f1 (ppm)
-107.45
f1 (ppm)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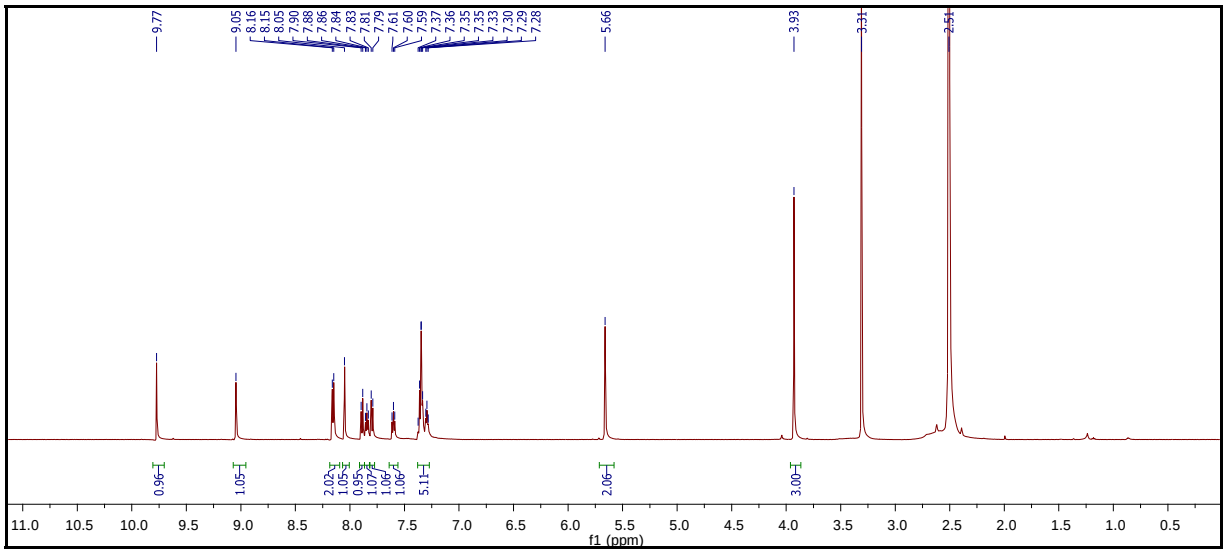
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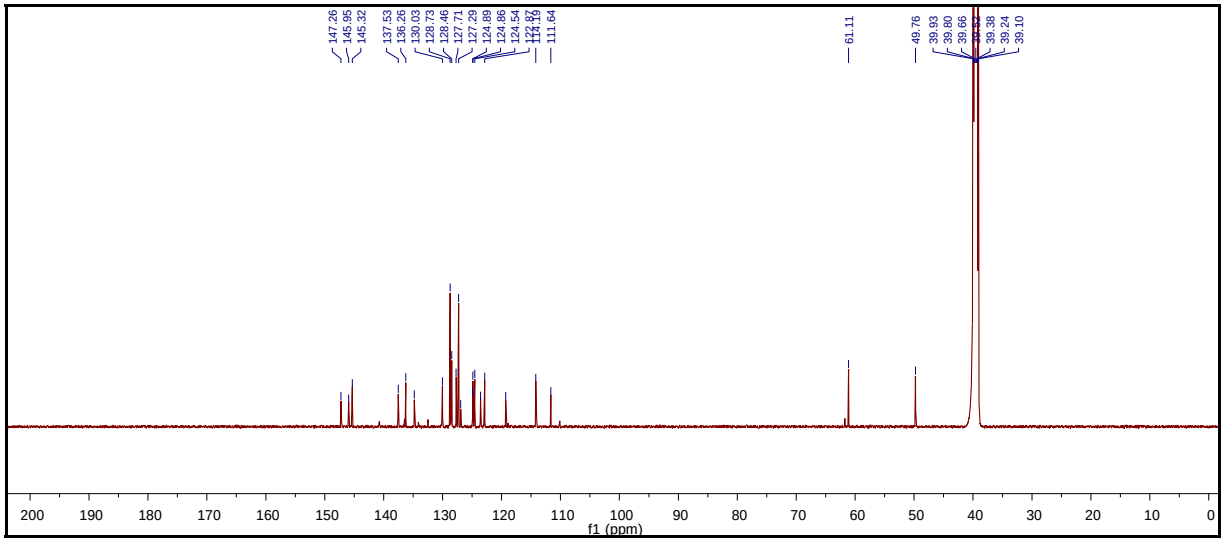
7.37
7.36
7.35
7.35
7.33
7.30
7.29
7.28
5.66
3.93
3.31
2.51
0.96
1.05
2.02
1.05
0.95
1.07
1.00
1.06
5.11
2.06
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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127.29
124.89
124.86
124.54
111.64
61.11
49.76
39.93
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39.52
39.38
39.24
39.10
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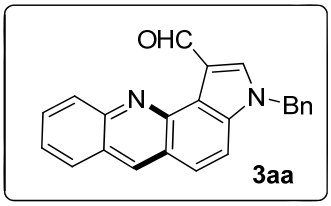
f1 (ppm)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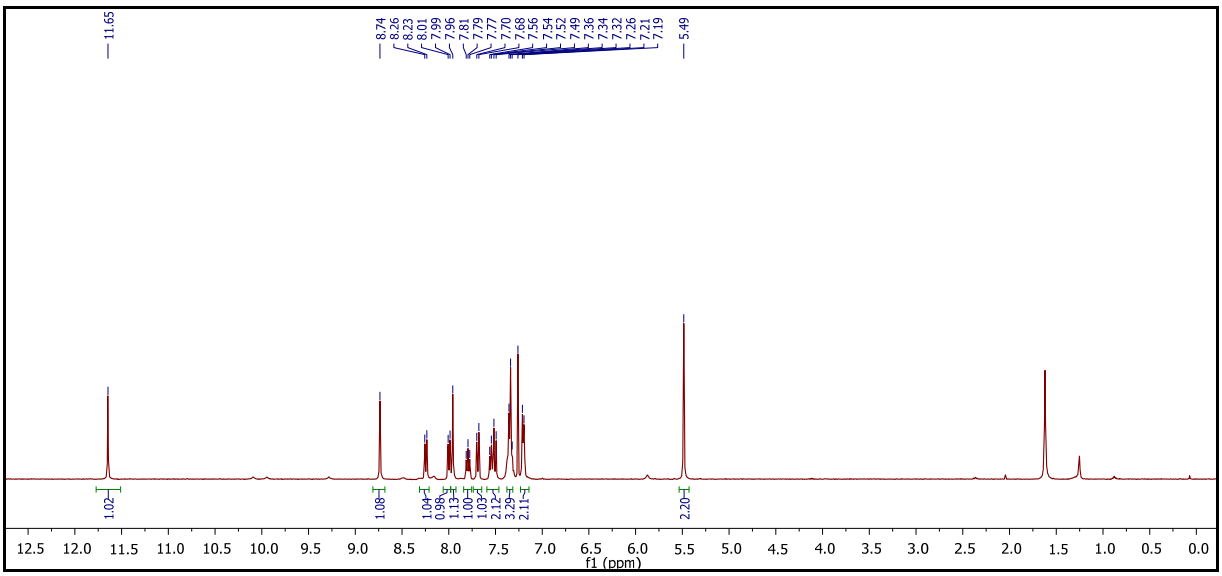
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7.52
7.49
7.36
7.34
7.32
7.26
7.21
7.19
5.49
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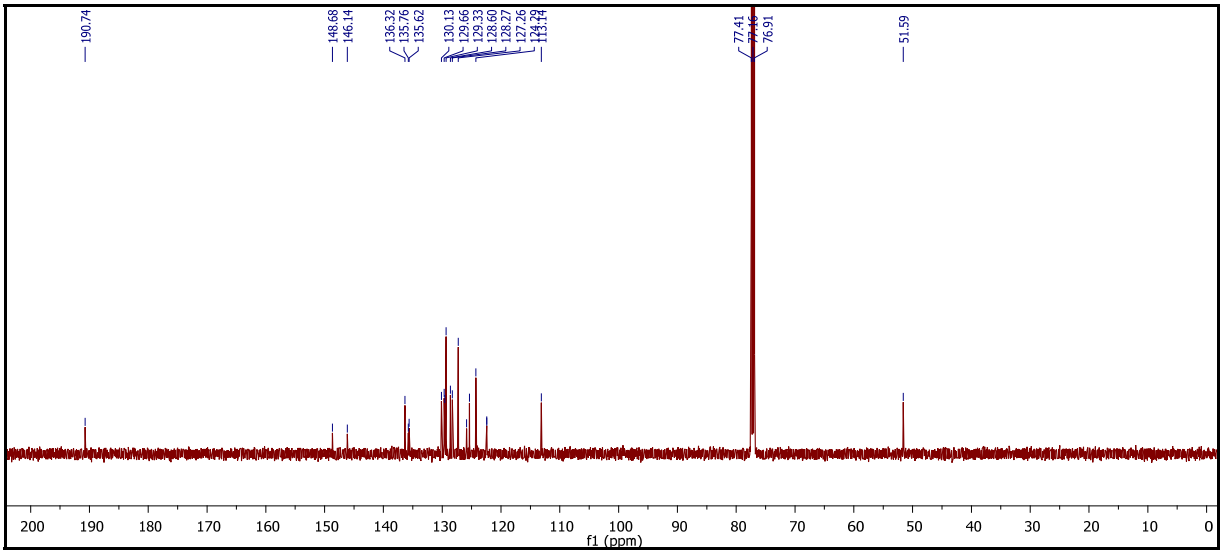
1.00
1.03
2.12
3.29
2.11
2.20
f1 (ppm)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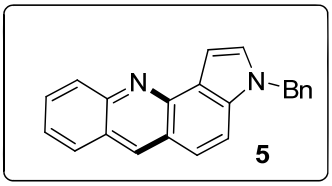
128.27
127.26
77.41
77.16
76.91
51.59
f1 (ppm)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Bn
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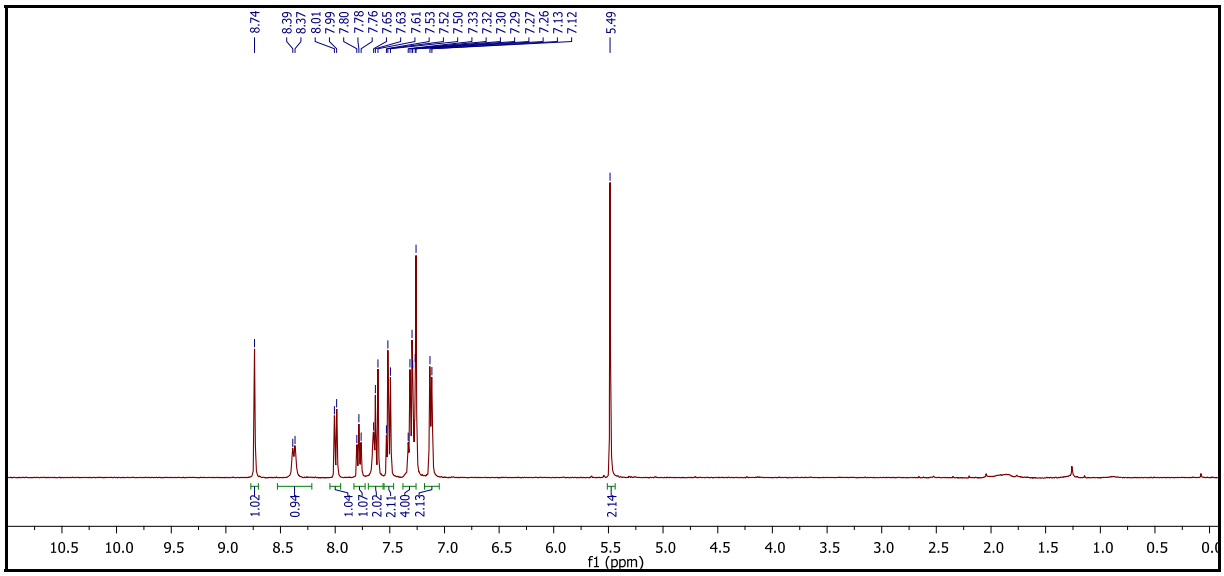
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7.52
7.50
7.33
7.32
7.30
7.29
7.27
7.26
7.13
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1.04
1.07
2.02
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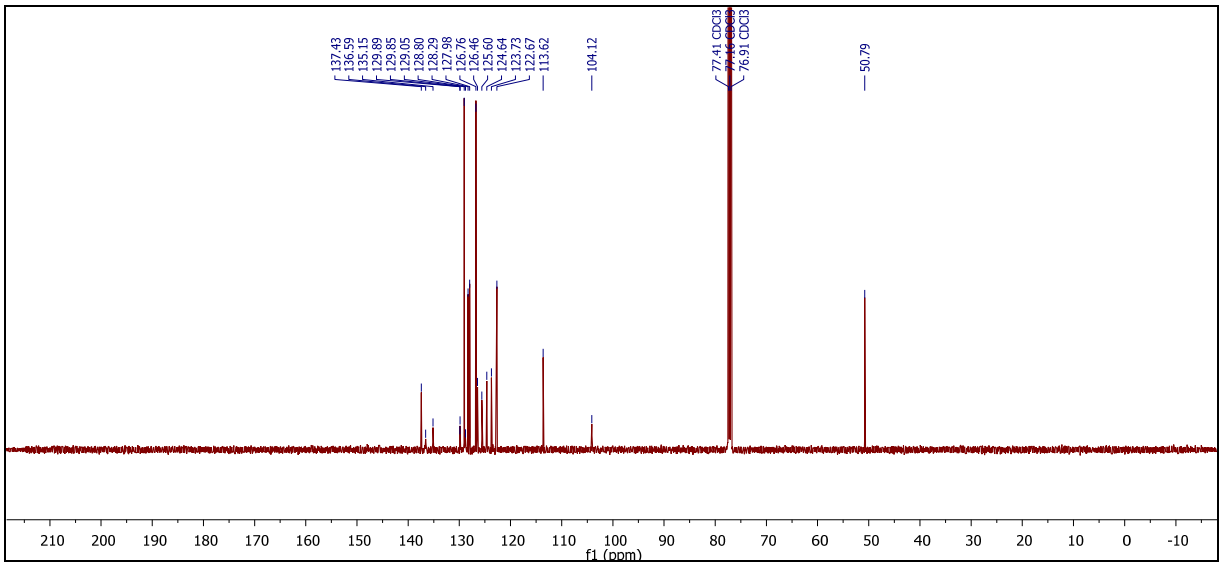
4.00
2.13
2.14
f1 (ppm)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126.76
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123.73
122.67
113.62
104.12
77.41 CDCl3
76.91 CDCl3
50.79
f1 (ppm)