Supplementary Information

Visible-light-driven metal-free iminyl radical cyanation for the synthesis of 3-cyanoindoles

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1. General Information

1.1 Reagent Information

Unless otherwise stated, all reactions were performed in oven-dried Schlenk tubes under air using screw-cap closures. All commercially available reagents and solvents were used as received without further purification (suppliers: Sigma-Aldrich, TCI, Alfa Aesar, BLD, Hyma, CDH). Crude products were purified by silica gel column chromatography (100–200 mesh). Organic solvents were removed under reduced pressure using an IKA rotary evaporator. Reaction progress was monitored by thin-layer chromatography (TLC) on silica gel F254 plates, visualized under UV light or iodine stain. Aldehyde formation was confirmed using the 2,4-dinitrophenylhydrazine (DNP) test.

1.2 Analytical Information

All isolated compounds were characterized by ^{1}H, $^{13}C\{^{1}H\}$, and high-resolution mass spectrometry (HRMS). NMR spectra were recorded on a JEOL ECZ 500R (500 MHz for ^{1}H; 126 MHz for ^{13}C). Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent peaks: $CDCl_3$ at 7.26 (^{1}H) and 77.16 ppm (^{13}C), DMSO-d_6 at 2.50 and 39.52 ppm, respectively. Multiplicities are indicated as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Coupling constants (J) are given in hertz (Hz).

HRMS (ESI-TOF) spectra were recorded in positive ion mode. Observed values are reported to four decimal places and compared to the most abundant isotope.

1.3 Computational details:

All calculations were performed using the Gaussian09 suite.[1] Geometry optimizations and frequency calculations were carried out using the wB97XD functional with the 6-311+G(d,p) basis set and ultrafine integration grids.[2,3] BSSE corrections (<0.04 eV) were applied. Transition states (TS) were confirmed by a single imaginary frequency along the reaction coordinate. All minima (reactants, intermediates, and products) were confirmed by the absence of imaginary frequencies. Gibbs free energies (ΔG, ΔG‡) were calculated as the difference between reactants and products or transition states, respectively.

1.4 Photochemical Reaction Setup

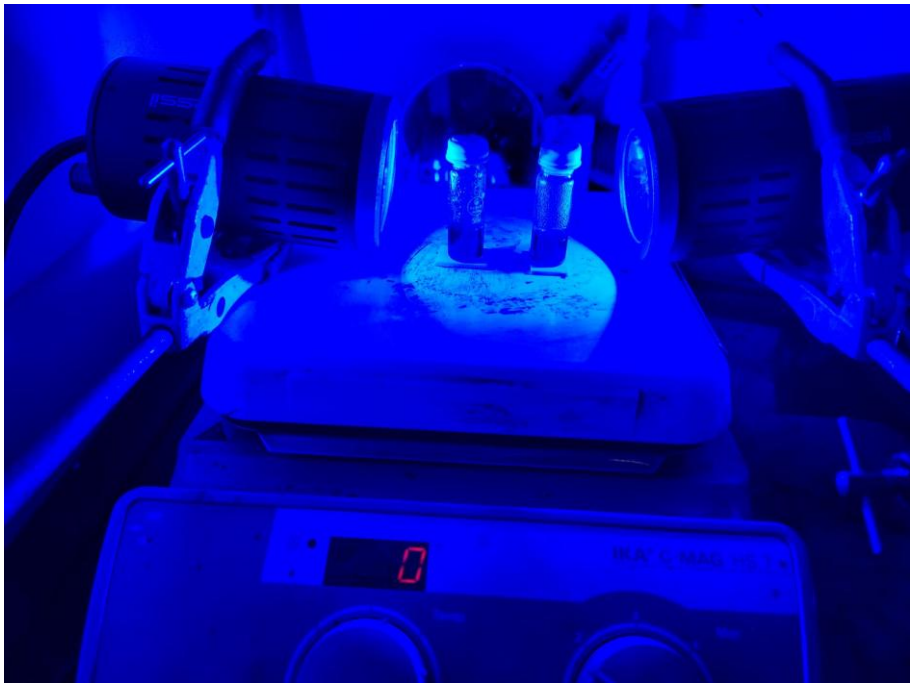
Reactions were irradiated using a 40 W Kessil Blue LED lamp (A160WE Tuna Blue) placed 1–2 cm from the reaction vessel to ensure efficient excitation. The compact design and high output of the light source made it ideal for photocatalytic conditions [Figure S1 (a)].

1.5 Light Source and Spectral Profile

The photocatalytic reactions were carried out using a Kessil A160WE Tuna Blue LED lamp (40 W) positioned approximately 1–2 cm from the reaction vessel to ensure optimal light penetration. This light source offers a broad emission spectrum in the blue region, tailored to excite photocatalysts such as 10-Ph-PTZ efficiently. The spectral intensity distribution of the lamp confirms peak emission in the 430–460 nm range [Figure S1 (b)], which overlaps with the absorption spectrum of the photocatalyst employed in this study.

The emission spectrum and additional specifications for the Kessil A160WE lamp are available from the manufacturer:
https://www.marine-aquatics.eu/en/kessil-a160we-tuna-blue-led-lighting-40w

(a)



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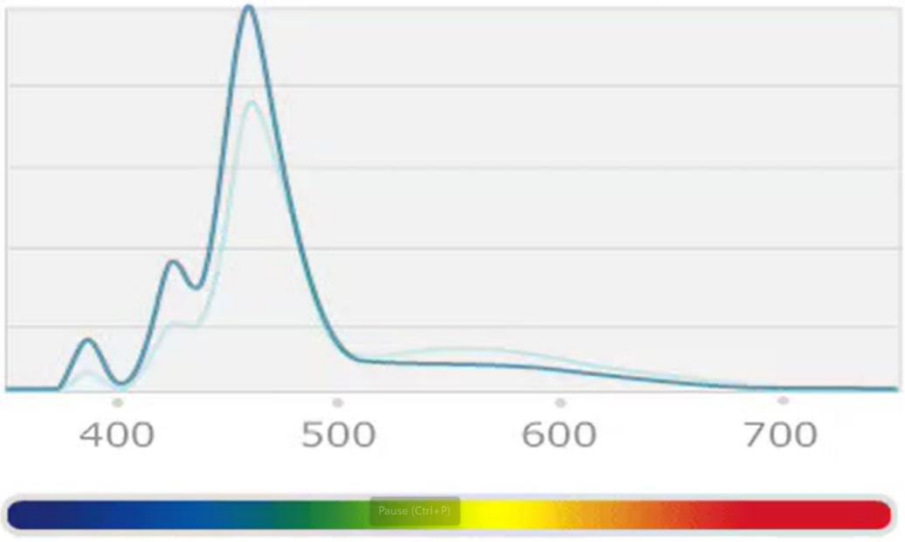
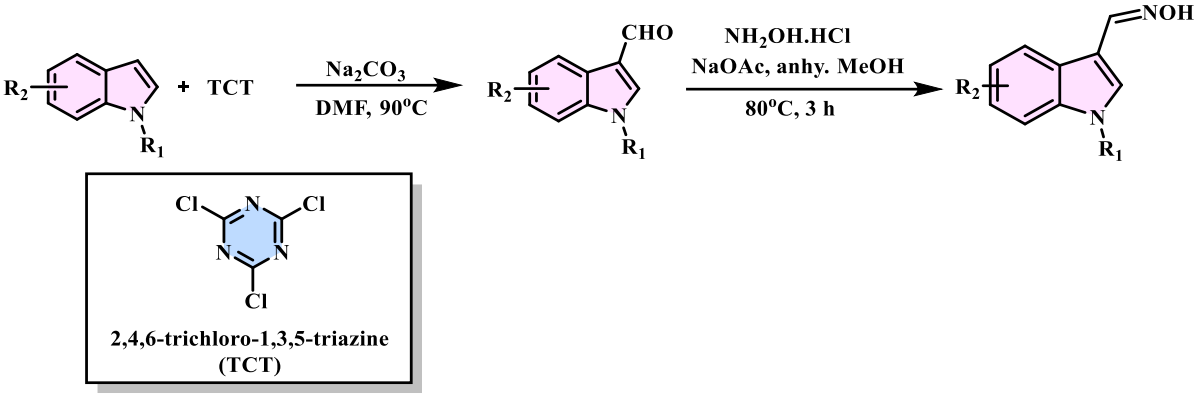


Figure S1: (a) Photochemical reaction setup & (b) Spectral Profile

2. General procedures

2.1 General procedure for the preparation of starting material



Scheme S1. Preparation of starting material

Step-1. Aldehyde formation[4]

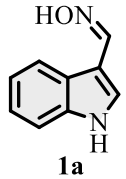
Into an RB, TCT (5.42 mmol, 1eq., 1 g) and DMF (2.6 mL) was added and permit is to stir for 1 h at room temperature. Then, the mixture was charged with either indole substrate (6.5mmol, 1.2 eq., 0.957g) and 3.5mL of DMF as solvent and stirred for 6 h at 90°C. When the reaction was completed (monitored by thin-layer chromatography), a saturated solution of Na_2CO_3 (25 mL) was add to the mixture in order to hydrolyse the iminium salt for the formation of formyl group. Then, EtOAc (25 mL) was added to the reaction mixture. After separation of ethyl acetate layer from H_2O, the aqueous phase was extracted with EtOAc (25 mL) again. The combined organic layers were then dried anhydrous Na_2SO_4, filtered, and concentrated in vacuum to yield the crude product. The crude product was purified by column chromatography (n-hexane/EtOAc) to obtain the desired purity.

Step-2. Oxime formation[5]

In a round-bottomed flask (50 mL) equipped with a football-shaped Teflon-coated magnetic stir bar is charged with aldehyde (0.2g, 1.1 mmol), hydroxylamine hydrochloride ($NH_2OH.HCl$) (0.11g, 1.7 mmol) and anhydrous sodium acetate (NaOAc) (0.21 g, 2.6 mmol) in anhydrous methanol (10 mL) were added by plastic syringe to the flask. The flask is fitted with a water-cooled condenser and the junction of the glassware is sealed with a teflon tape. The reaction vessel is placed in a pre-heated silicon oil bath (80°C, oil bath temperature). The mixture was stirred under reflux conditions for 3h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction vessel is removed from the oil bath and cooled to 24°C over 30 min. And then the reaction is quenched by H_2O (10 mL) and the reaction mixture was continued to stirring for 5 min. The product has been extracted with EtOAc (3x15 mL). The combined organic layers were dried over anhy. Na_2SO_4 and concentrated in vacuo to afford the pure carbaldehyde oxime products.

Substrates studied in this reaction protocol

Successful substrate



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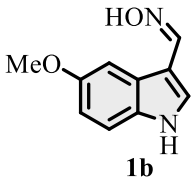

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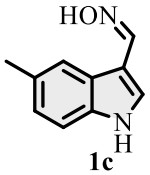

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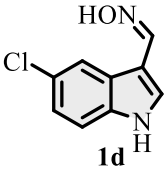

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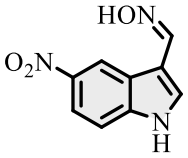

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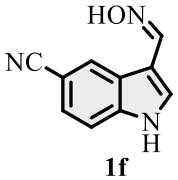

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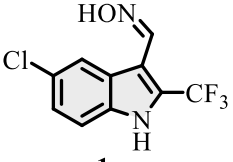

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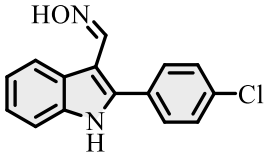

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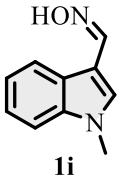

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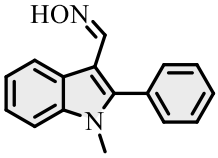

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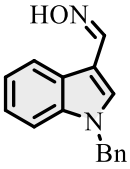

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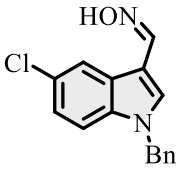

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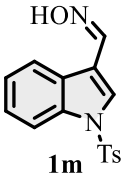

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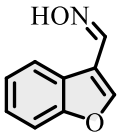

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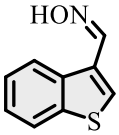

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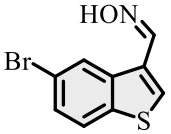

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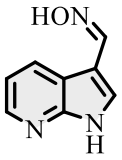

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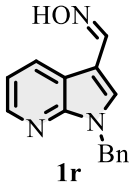
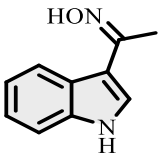


1r

Unsuccessful substrates



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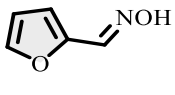

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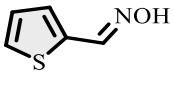

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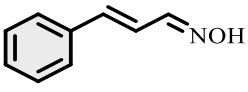

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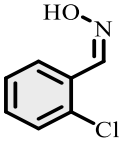

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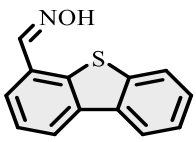

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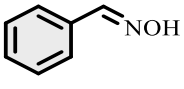
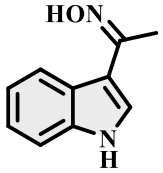
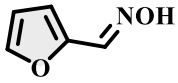
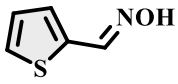
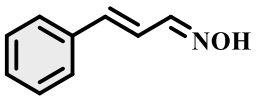
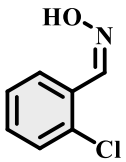
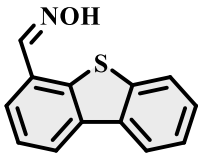
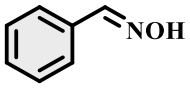


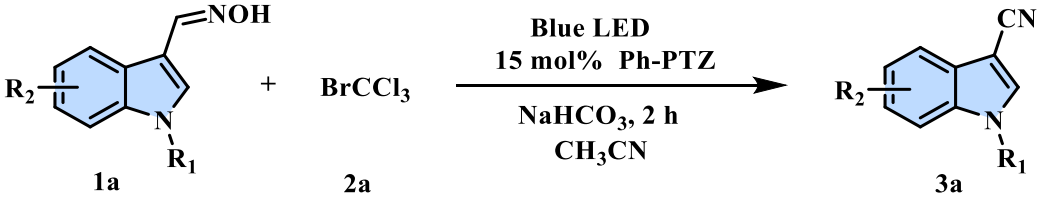
1z

Unsuccessful Oximes	Reason
(1t) 1-(1H-indol-3-yl)ethanone oxime  1t	The ketoxime structure is incompatible with the proposed mechanism because it lacks the necessary electronic and structural features required for key mechanistic steps. As in ketoxime there is methyl group in the place of H that's why ketoxime doesn't undergo HAT. As a result, ketoxime disfavored, preventing progression through the proposed reaction pathway.
(1u) furan-2-carbaldehyde oxime  1u	The furan ring is weakly aromatic and offers limited π-electron delocalization, resulting in poor stabilization of adjacent radical intermediates. In contrast, the benzene-fused indole framework in 1H-indole-3-carbaldehyde oxime enables efficient radical delocalization over an extended conjugated system, particularly at the C-3 position, providing significant stabilization. Consequently, the insufficient radical stabilization in the furan system makes it less compatible with the proposed radical pathway.
(1v) thiophene-2-carbaldehyde oxime  1v	Thiophene-2-carbaldehyde oxime provides much weaker heteroaromatic stabilization than 1H-indole-3-carbaldehyde oxime. The fused indole framework enables extensive π-delocalization and strong stabilization of radical intermediates, whereas the smaller thiophene ring offers limited conjugation with the oxime. As a result, radical delocalization and stabilization are insufficient in thiophene-2-carbaldehyde oxime, making the reaction pathway unfavorable.
(1w) cinnamaldehyde oxime  1w	Cinnamaldehyde oxime lacks a heteroaromatic framework and therefore cannot effectively stabilize radical intermediates through π-delocalization. In contrast, 1H-indole-3-carbaldehyde oxime benefits from extensive radical delocalization within the indole π system and a favorable HAT that promotes reaction progression. The absence of both features in cinnamaldehyde oxime renders the proposed mechanistic pathway unfavorable.
(1x) (Z)-2-chlorobenzaldehyde oxime  1x	(Z)-2-Chlorobenzaldehyde oxime lacks a heteroaromatic framework and therefore cannot provide effective π-conjugation or heteroatom-assisted radical delocalization. In contrast, 1H-indole-3-carbaldehyde oxime stabilizes radical intermediates through extensive delocalization within the indole π system and a favorable HAT. The absence of this hydrogen shift in the benzaldehyde oxime, together with the strong −I

	effect of the ortho-chloro substituent, further destabilizes reactive intermediates. As a result, (Z)-2-chlorobenzaldehyde oxime is incompatible with the proposed reaction mechanism.
(1y) dibenzo[b,d]thiophene-4-carbaldehyde oxime  1y	Although dibenzo[b,d]thiophene-4-carbaldehyde oxime contains a heteroaromatic framework, it is far less effective than 1H-indole-3-carbaldehyde oxime in stabilizing radical intermediates. In indole systems, the C-3 position allows efficient radical delocalization over the pyrrolic nitrogen and the fused benzene ring, and a favorable HAT further promotes rearomatization and stabilization. In contrast, dibenzo[b,d]thiophene lacks comparable heteroatom-assisted conjugation and an accessible C-3 hydrogen, leading to poor radical delocalization. Additionally, its rigid fused aromatic structure imposes steric hindrance around the oxime group. Together, these electronic and steric limitations make dibenzo[b,d]thiophene-4-carbaldehyde oxime incompatible with the proposed reaction mechanism.
(1z) benzaldehyde oxime  1z	Benzaldehyde oxime lacks a heteroaromatic framework and therefore cannot effectively delocalize or stabilize radical intermediates. In contrast, 1H-indole-3-carbaldehyde oxime enables efficient radical delocalization through its conjugated indole system and supports a favorable HAT. The absence of these stabilizing features in benzaldehyde oxime makes it incompatible with the proposed reaction mechanism.

Thus, the success of our protocol critically depends on **C3-activated heteroaryl aldehyde oximes** (like indole-3-carbaldehyde oxime) that can **stabilize radical intermediates**, allow **HAT**, and undergo smooth radical recombination under the photocatalytic cycle.

2.2 General Procedure for cyanation of indole

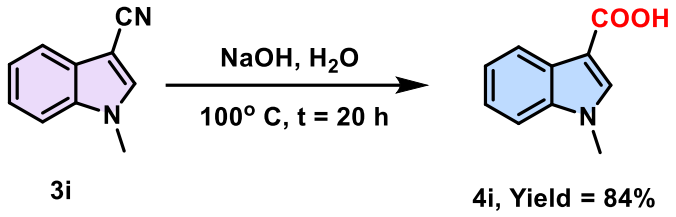


Scheme S2. Procedure for cyanation of indole

An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 1H-indole-3-carbaldehyde oxime (0.3 mmol, 1 equiv.), photocatalyst 10-Ph-PTZ (0.04 mmol, 15 mol%), $BrCCl_3$ (1.87 mmol, 6 equiv.), and $NaHCO_3$ (0.6 mmol, 2 equiv.). The tube was then sealed, and three argon backfilling cycles were performed. Dry CH_3CN (2 mL) was added under a flow of argon in the tightly sealed Schlenk tube. The reaction mixture was stirred at ambient temperature under irradiation with a 40 W Kessil Blue LED lamp (A160WE Tuna Blue) for 2 hours, as shown in Figure 1. After completion, the reaction was quenched with H_2O (1 mL) and extracted three times with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The

crude product was purified by column chromatography (hexanes/EtOAc 10:1, followed by 10:4) to afford the desired product.

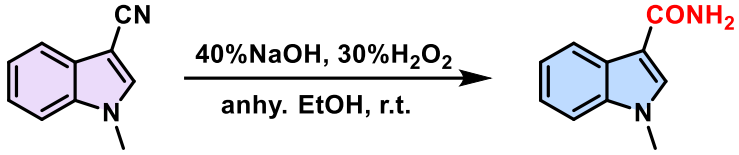
2.3 General Procedure for Carboxylation of 3-cyanoindole



3i **4i, Yield = 84%**

3i (50.71 mg, 0.2 mmol) was treated with NaOH (28.57mg, 0.4 mmol) in H_2O (0.71mL) at 100 °C for 20 h. Then the mixture was acidified with dilute HCl/H_2O to pH =5. The organic layer was washed with brine and dried by Na_2SO_4, and volatiles were evaporated to give 4i (490 mg, 84%) as a white solid.

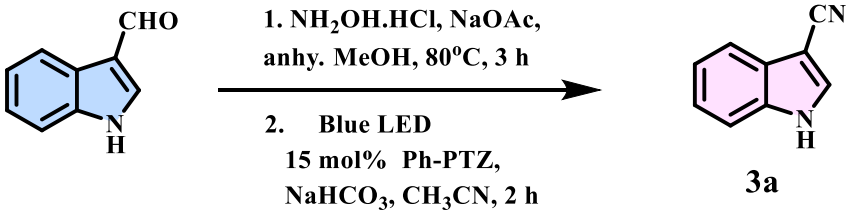
2.4 General Procedure for the Amidation of 3-cyanoindole



3i **5i, Yield = 71%**

Synthesis of indole-3-carboxamide derivative (5i). To a stirred solution of 3i (0.2 mmol) in anhydrous ethanol was added 40% NaOH (66 µL), then 41µL of 30% H2O2 (1.39 mmol) was slowly added to the mixture upon monitoring by TLC. The precipitated solid was filtered off, washed with water, recrystallized from anhydrous ethanol, and dried in vacuum to give the respective product 5i.

3. One pot reaction for cyanation of indoles from indole 3- carbaldehyde



3a

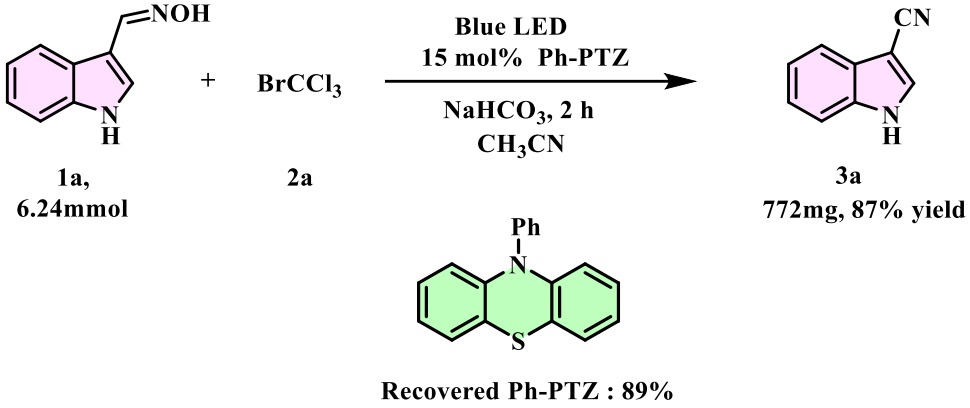
Scheme S3: Reaction in one pot

Procedure

In a one-pot procedure, a solution of 1H-indole-3-carbaldehyde (0.68 mmol), hydroxylamine $NH_2OH.HCl$ (1.03 mmol), and Sodium acetate NaOAc (1.58 mmol) in dry methanol (4 mL) was stirred at 80°C temperature for 3 h. After completion of the reaction (monitored by TLC), the dry methanol was evaporated under pressure in the rota vapour. An oven-dried round-bottom flask (RB) was equipped with a magnetic stir bar and charged with $BrCCl_3$ (3.74 mmol), 10-phenylphenothiazine (PC) (0.09 mmol), and sodium bicarbonate ($NaHCO_3$) (1.2 mmol). The flask was sealed and subjected to three cycles of evacuation and backfilling with argon to ensure an inert atmosphere. And then dry CH_3CN (3 mL) was added under a flow of argon in cork tight Schlenk tube. The mixture was then stirred at ambient temperature under the irradiation of 40W Kessil Blue LED (A 160WE Tuna Blue) for the stipulated time period (2 h) as shown in Figure 1. After 2 h of reaction, the reaction was quenched with H_2O (1 mL) and then extracted 3 times with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The products were purified by column chromatography (hexanes/EtOAc 10/1 followed by hexanes/EtOAc 10/4), and dried to afford the corresponding product in 82% yield.

***Note: $BrCCl_3$ was acquired commercially and stored in a refrigerator under below 10 ℃. Prior to the addition to the reaction mixture under inert condition in a well-ventilated fume hood, it has been broke down to room temperature.*

4. Gram-scale reaction procedure for the cyanation of indole

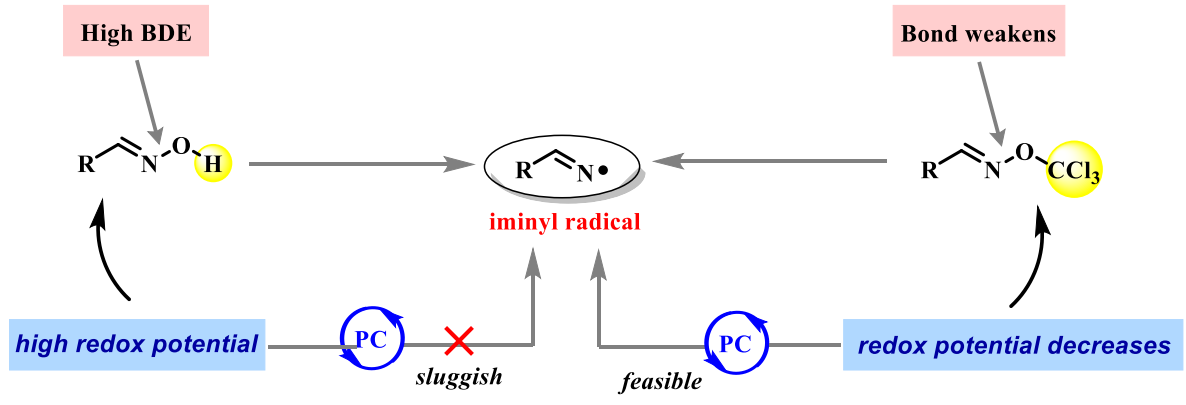


Scheme S4: Gram-scale reaction

An oven-dried 50 mL pear shaped round-bottom flask was charged with 1H-indole-3-carbaldehyde oxime (6.2 mmol, 1eq., 1 g), photocatalyst Ph-PTZ (0.93 mmol, 15mol%, 257.82 mg), $BrCCl_3$ (37.45 mmol, 6eq., 3.6ml), $NaHCO_3$(12.48 mmol, 2eq., 1.04g). The Schlenk tube was sealed and subjected to three cycles of evacuation and backfilling with argon to ensure an inert atmosphere. And then dry CH_3CN (30 mL) was added under a flow of argon in cork tight Schlenk tube. The mixture was then stirred at ambient temperature under the irradiation of 2×40W Kessil Blue LED (A 160WE Tuna Blue) for the stipulated time period (2 h) as shown in Figure 2. After 6 h of reaction, the reaction was quenched with H_2O (10 mL) and then extracted 3 times with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The products were purified by column chromatography (hexanes/EtOAc 10/1 followed by hexanes/EtOAc 10/4).

5. Mechanistic Investigation

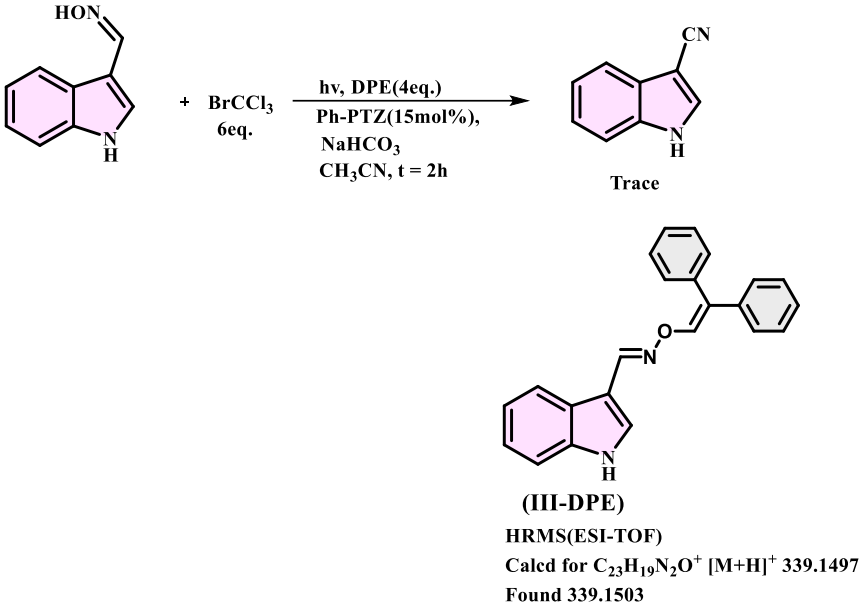
Although the formation of intermediate **IV** is **proposed based on the mechanistic sequence**, our experimental attempts to directly detect or isolate it were unsuccessful. TLC monitoring revealed a transient new spot during the reaction, which we attempted to isolate; however, it either decomposed rapidly or converted to downstream products before characterization was possible. Both the immediate precursor (**III**) and subsequent intermediate (**V**) were detected by high-resolution mass spectrometry (HRMS), which is consistent with the proposed placement of **IV** in the catalytic cycle, although its exact lifetime and point of formation remain uncertain. While intermediate **IV** shares some structural similarity with the starting material **I**, there is a significant difference in the strength of the N–O bond. In intermediate **IV**, the presence of the trichloromethyl group weakens the N–O bond, rendering it redox-active.[6,7]



In contrast, the starting material **I** possesses a stronger N–O bond, which makes it redox-inactive, as further evidenced by fluorescence quenching experiments. Nonetheless, these observations are consistent with the proposed mechanism.

5.1 Radical Trapping Experiment

5.1.1 Diphenylethylene(DPE) as a radical scavenger



Scheme S5. Radical III trapped by DPE.

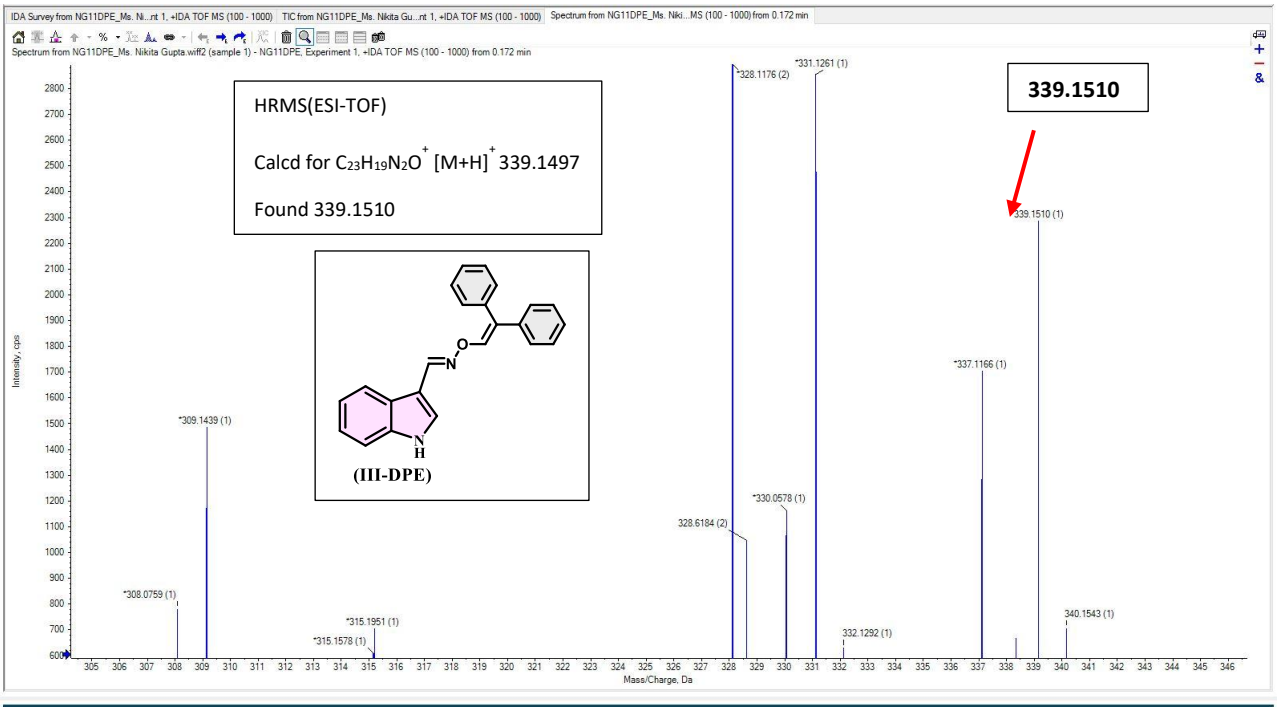


Figure S2. Radical III trapped by DPE.

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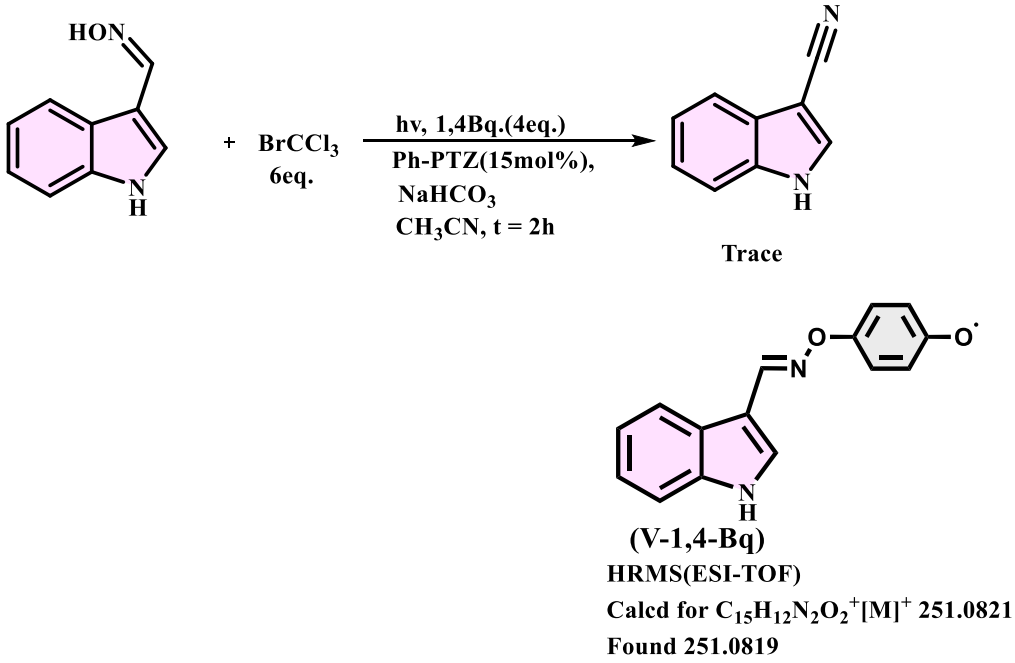
5.1.2 1,4-Benzoquinone(1,4-Bq) as a radical scavenger



Scheme S6. Radical V trapped by 1,4-Benzoquinone.

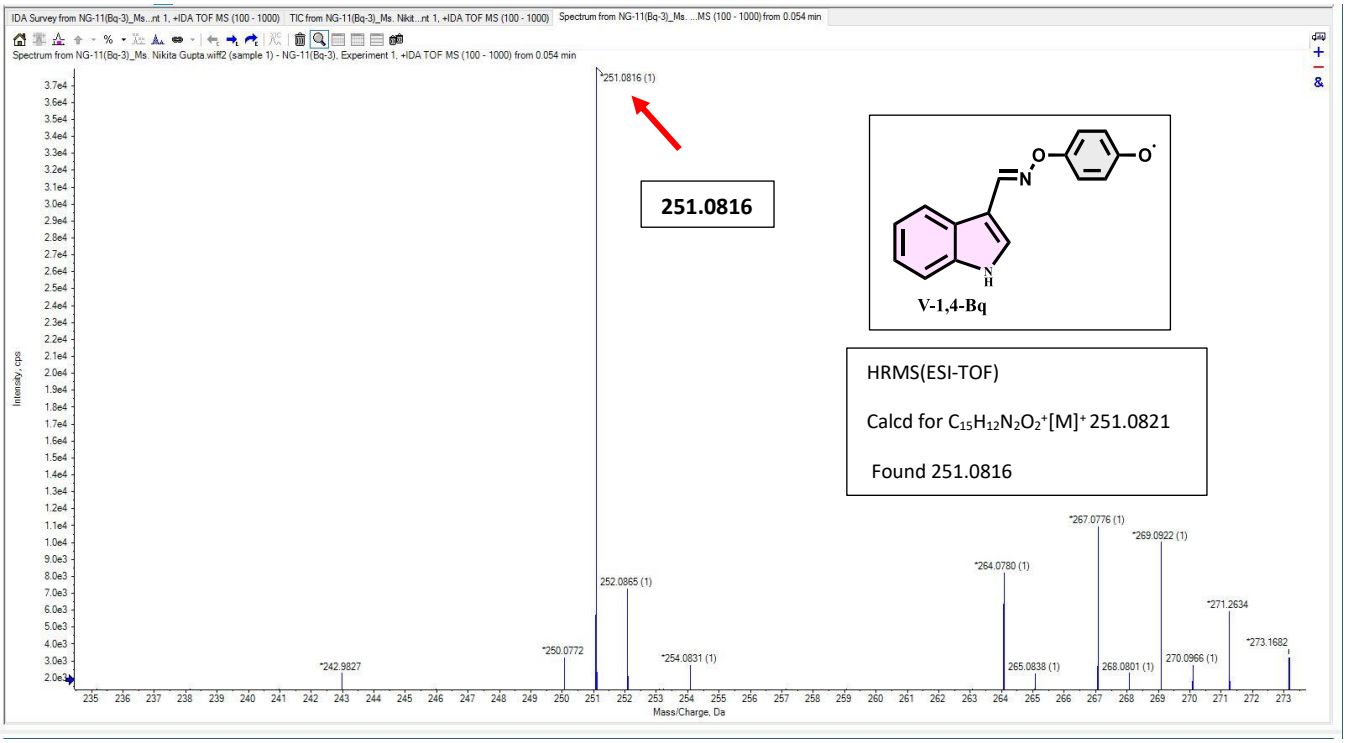


Figure S3. Radical V trapped by 1,4-Benzoquinone.

5.2 Luminescence Quenching Experiments

Fluorescence spectra were collected on JASCO Spectrofluorometer FP-8200 for all experiments. All Ph-PTZ solutions were excited at **320 nm** and the emission intensity was collected at **445 nm**. In each experiment, different samples were dissolved in CH_3CN and placed in **1.0 cm quartz cuvettes**.

Photocatalyst solution (10^{-3} M): To an oven dried 15 mL vial was added Ph-PTZ (2.7 mg) and acetonitrile (10 mL).

$BrCCl_3$ solution (10^{-3} M): To an oven dried 15 mL vial was added $BrCCl_3$ (9.8 mg) and acetonitrile (10 mL).

1H-indole-3-carbaldehyde oxime (10^{-3} M): To an oven dried 15 mL vial was added 1H-indole-3-carbaldehyde oxime (1.6 mg) and acetonitrile (10 mL).

Following preparation of these solutions, the solutions were allocated to the cuvettes and fluorescence quenching was determined with individual quenchers (**$BrCCl_3$, 1H-indole-3-carbaldehyde oxime**) with **Ph-PTZ**. And from the Figure S 5.3 it is clear that 1H-indole-3-carbaldehyde oxime does not act as a quencher and which give strength to our proposed mechanism. Fluorescence measurements were recorded at **445 nm**.

Table S1. Stern-Volmer quenching studies of oxidising agent $BrCCl_3$ (2a) with Ph-PTZ.

Quencher Concentration	I	I_o/I
0	1979.44	1
5	1731.67	1.14308
10	1463.47	1.35257
15	1239.17	1.59739
20	1096.78	1.80477
25	860.133	2.30132
30	817.233	2.42212
35	736.925	2.68608

Table S2. Stern-Volmer quenching studies of 1H-indole-3-carbaldehyde oxime (1a) with Ph-PTZ.

Quencher Concentration	I	I_o/I
0	1979.44	1
5	2185.47	0.90573
10	2173.36	0.91077
15	2166.02	0.91386
20	2166.02	0.91386
25	2149.25	0.92099
30	2131.89	0.92849

35	2128.7	0.92988

(a) Fluorescence Spectra for PC and 1H-indole-3-carbaldehyde oxime used as a quencher.

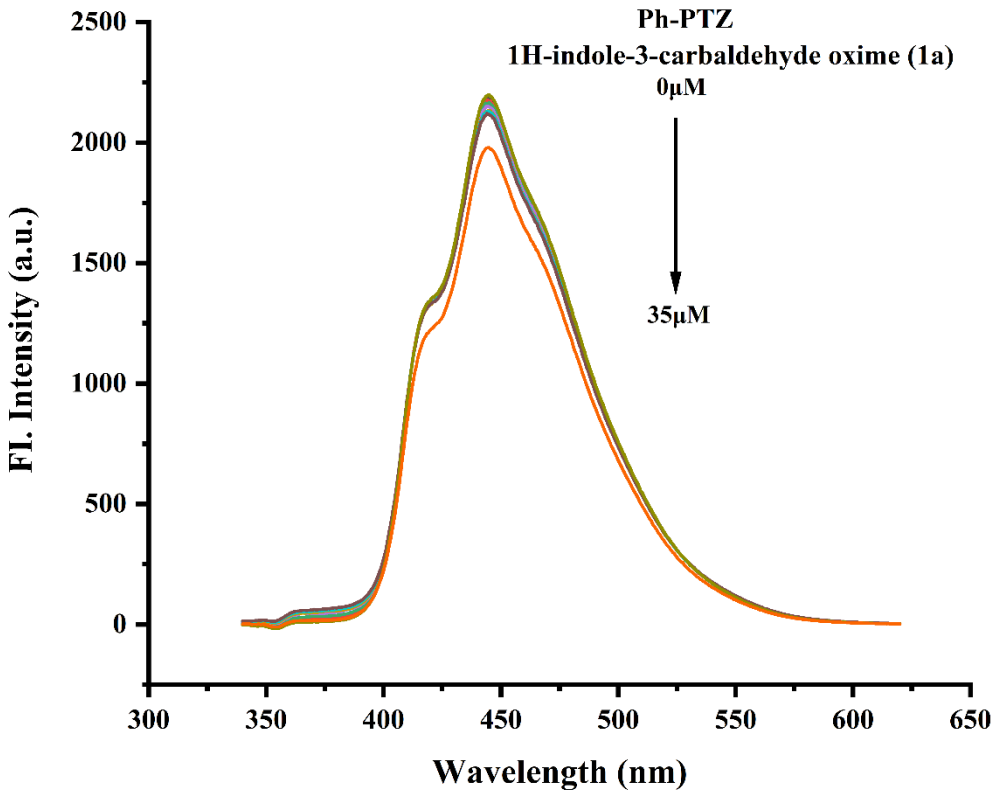


Figure S4. Fluorescence spectra of the photocatalyst (Ph-PTZ) in the presence of 1H-indole-3-carbaldehyde oxime.

(b) Fluorescence Spectra for PC and oxidising agent $BrCCl_3$ used as a quencher

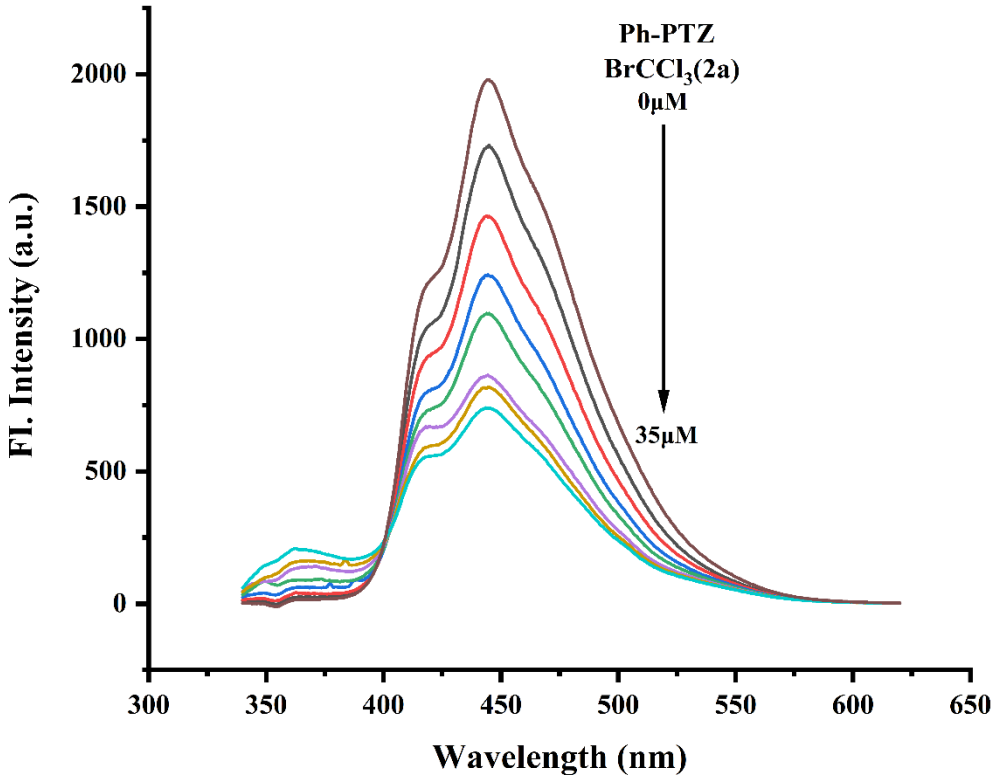


Figure S5. Fluorescence spectra of the photocatalyst (Ph-PTZ) in the presence of $BrCCl_3$ as a quencher.

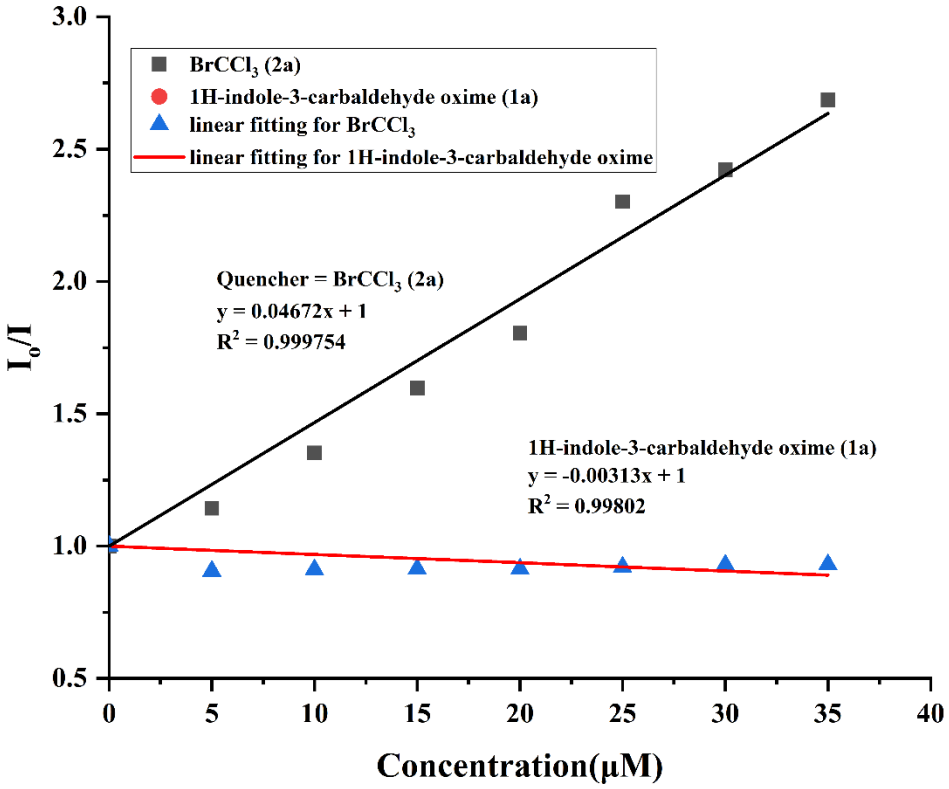


Figure S6. Stern−Volmer plot for the emission quenching of excited photocatalyst Ph-PTZ in CH_3CN by different quenchers.

Discussion of Stern- Volmer Data

The Stern-Volmer quenching experiments reveal a pronounced decrease in the photoluminescence intensity of Ph-PTZ upon incremental addition of bromotrichloromethane (**2a**), indicating efficient dynamic quenching and confirming a strong interaction between the photoexcited catalyst (Ph-PTZ*) and **2a**. In contrast, only a marginal decrease in luminescence intensity is observed upon addition of *1H*-indole-3-carbaldehyde oxime (**1a**), with the Stern-Volmer slope approaching zero (–0.007). This negligible quenching effect clearly establishes that **1a** does not engage in direct excited-state interactions with Ph-PTZ*, and therefore, does not function as an oxidative or reductive quencher in the catalytic cycle.

These results are fully consistent with our proposed redox-neutral radical cascade mechanism, in which $BrCCl_3$ serves as the primary electron acceptor from photoexcited Ph-PTZ*, thereby generating the trichloromethyl radical and oxidized photocatalyst species. The lack of quenching by **1a** supports its role as a ground-state reactant, entering the catalytic cycle only after radical initiation, rather than participating in the initial photoinduced electron-transfer event.

Conclusion of Stern- Volmer Data

From Stern-Volmer data we concluded that, $BrCCl_3$ (**2a**) acted as a quencher and *1H*-indole-3-carbaldehyde oxime (**1a**) didn't acts as a quencher.

6. Potential energy diagram of pathway 2

In pathway 2, the overall process is exergonic (ΔG = –233.14 kcal mol^{-1}), the large kinetic barrier and endergonic SET make this pathway thermally inaccessible under visible-light conditions.

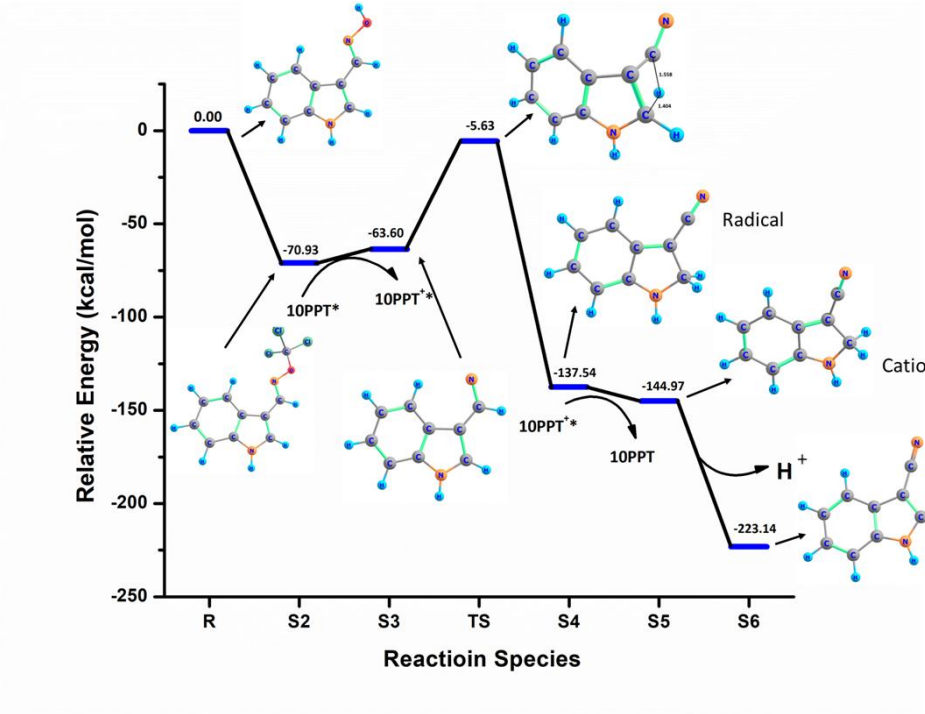


Figure S7. Potential energy diagram of pathway 2 calculated at wB97XD/6-311+G(d,p) level of theory.

Plausible Mechanisms for pathway 2

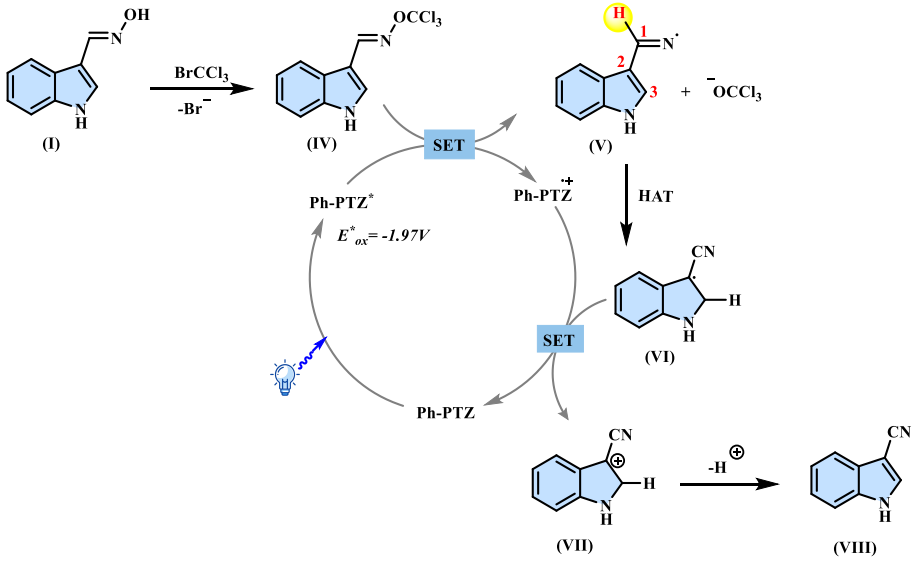


Figure S8. Plausible Mechanism of pathway 2.

7. Green Chemistry Metrics: Calculation of Eco-Scale

An important factor in green chemistry is the Eco Scale[8]. Eco Scale of the synthetic procedure to achieve the Cyano indole products have been calculated and based on this analysis, the environmental friendliness of the methodology has been determined. An Eco Scale of above 75 is considered an excellent green method, above 50 is acceptable, while scores below 50 indicate inadequate eco-friendliness. Eco Scale can be calculated as: Eco Scale = 100 - sum of the individual penalties

The individual penalties have been calculated as follows:

Table S3: Penalty points to calculate Eco Scale for product 3a

Sl No.	Parameters	Values	Penalty Points
1	Yield	(100-99)/2	0.5
2	Price of the substrate	< $10	0
3	Safety [a]	Not dangerous	0
4	Technical Setup	Kessil Blue LED	2
5	Temperature/Time	Room temperature, < 24 h	1
6	Workup add purification	Silica gel chromatography	10
		Total Penalty Points	13.5

[a] Based on the hazard warning symbols

Hence, Eco Scale = 100-13.5 = 88.5.

The calculated Eco Scale for the other synthesized cyano indoles are as follows:

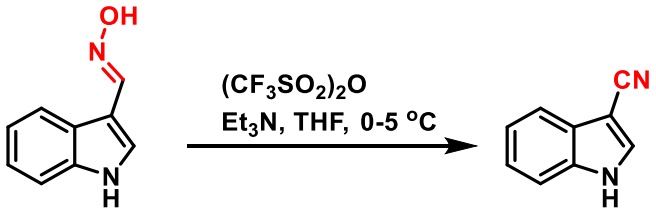
Compounds	Eco Scale	Compounds	Eco Scale
3b	**85**	**3k**	**73**
3c	**84**	**3l**	**72**
3d	**81**	**3m**	**67**
3e	**79.5**	**3n**	**66**
3f	**76**	**3o**	**85**
3g	**67.5**	**3p**	**82.5**
3h	**69**	**3q**	**80.5**
3i	**78.5**	**3r**	**81.5**
3j	**68**	**3s**	**70.5**

Excellent Green Method

Acceptable Method

Comparison of other's method

(A) Uludag's method

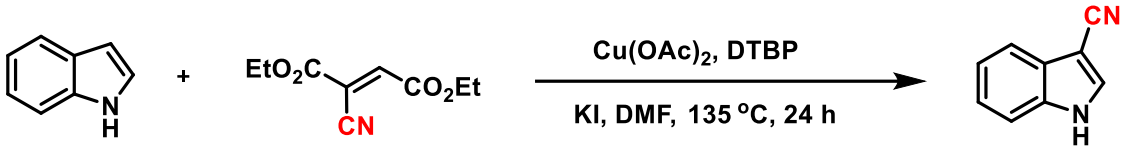


Sl No.	Parameters	Values	Penalty Points
1	Yield	(100-79)/2	10.5
2	Price of the substrate	< $10	0
3	Safety [a]	Not dangerous	0
4	Technical Setup	Simple stir	0
5	Temperature/Time	0 ℃	4
6	Workup add purification	Silica gel chromatography	10
		Total Penalty Points	24.5

[a] Based on the hazard warning symbols

Hence, Eco Scale = 100-24.5 = 75.5.

(B) Ze-lin Li and group's method



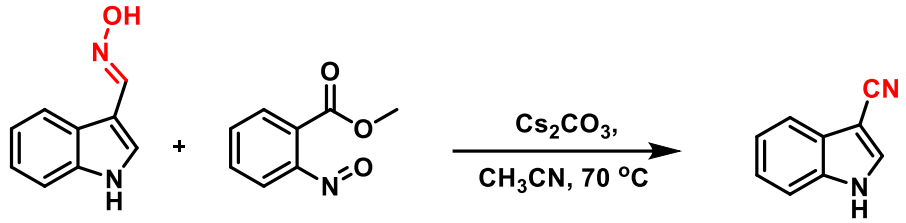
Sl No.	Parameters	Values	Penalty Points
1	Yield	(100-63)/2	18.5
2	Price of the substrate	< $10	0
3	Safety [a]	Not dangerous	0
4	Technical Setup	Simple stir	0
5	Temperature/Time	135 ℃/24 h	3
6	Workup add purification	Silica gel chromatography	10

		Total Penalty Points	31.5

[a] Based on the hazard warning symbols

Hence, Eco Scale = 100-31.5 = 68.5.

(C) Sanjeeva Thunga and group's method

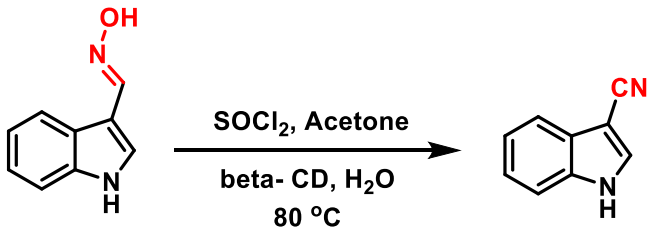


Sl No.	Parameters	Values	Penalty Points
1	Yield	(100-88)/2	6
2	Price of the substrate	< $10	0
3	Safety [a]	Not dangerous	0
4	Technical Setup	Simple stir	0
5	Temperature/Time	70℃ >1 h	3
6	Workup add purification	Silica gel chromatography	10
		Total Penalty Points	19

[a] Based on the hazard warning symbols

Hence, Eco Scale = 100-19 = 81.

(D) Dipak Patil and Dipak Dalal's method



Sl No.	Parameters	Values	Penalty Points
1	Yield	(100-94)/2	3
2	Price of the substrate	< $10	0

3	Safety [a]	Not dangerous	0
4	Technical Setup	Simple stir	0
5	Temperature/Time	80℃ < 1 h	2
6	Workup add purification	Silica gel chromatography	10
		Total Penalty Points	15

[a] Based on the hazard warning symbols

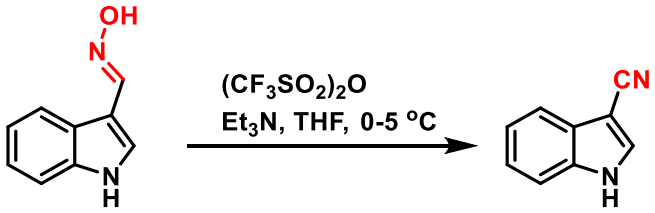
Hence, Eco Scale = 100-15 = 85.

Table S4: Eco scale comparison of our work with the previously reported ones

Prior report	Yield	Eco Scale
(a) N. Uludag[9]	79	75.5
(b) Ze-lin Li and group[10]	63	68.5
(c) Sanjeeva Thunga and group[11]	88	81
(d) Dipak Patil and Dipak Dalal[12]	94	85
(e) Our Work	**99**	**88.5**

8. Evaluation of Green metrics[13]

(A) Uludag's Method



Entry	Input		Output	
1	*1H*-indole-3-carbaldehyde oxime	240.27 mg	Indole-3-carbonitrile	168 mg
2	trifluoromethanesulfonic anhydride	846.42 mg		
3	Triethylamine	303.57 mg		
4	THF	10000 mg		
	Total mg	11390.26	Total	168 mg

$$\text{E-Factor} = \frac{Total\ input - Total\ output}{weight\ of\ product} = \frac{11390.26-168}{168} = 66.8$$

$$\text{Mass Intensity} = \frac{Total\ input}{weight\ of\ product} = \frac{11390.26}{168} = 67.8$$

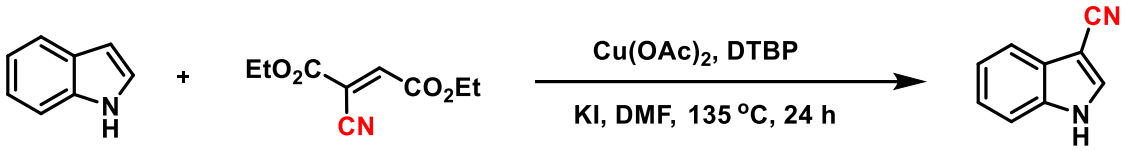
$$\text{Atom economy} = \frac{Molecular\ weight\ of\ Product}{Summation\ of\ Molecular\ weight\ of\ reagents\ used} \times 100$$

$$= \frac{142.16}{160.18+101.19+282.14} \times 100 = 26.15\ \%$$

Atom efficiency = Atom economy % × % Yield of the product

= 26.15 % × 79 % = 20.65 %

(B) Ze-lin Li and group's method



Entry	Input		Output	
1	*1H*-indole	58.57 mg	Indole-3-carbonitrile	44.7 mg
2	ethyl(ethoxymethylene)cyanoacetate	169.18 mg		
3	Cu(OAc)2	90.81 mg		
4	DTBP	255.9 mg		
5	KI	8.3 mg		
6	DMF	2000 mg		
	Total	2582.76 mg	Total	44.7 mg

$$\text{E-Factor} = \frac{Total\ input - Total\ output}{weight\ of\ product} = \frac{2582.76-44.7}{44.7} = 56.77$$

$$\text{Mass Intensity} = \frac{Total\ input}{weight\ of\ product} = \frac{2582.76}{44.7} = 57.77$$

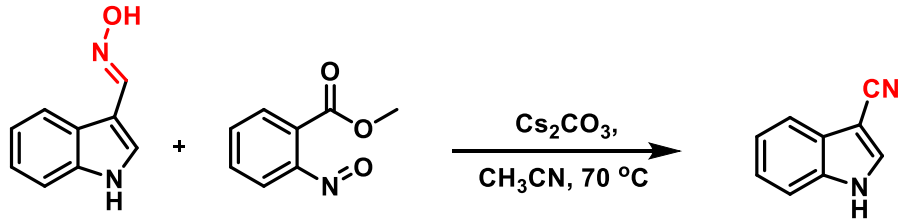
$$\text{Atom economy} = \frac{Molecular\ weight\ of\ Product}{Summation\ of\ Molecular\ weight\ of\ reagents\ used} \times 100$$

$$= \frac{142.16}{117.15+169.18+181.63+166+146.23} \times 100 = 18.22\ \%$$

Atom efficiency = Atom economy % × % Yield of the product

= 18.22 % × 63 % = 11.47 %

(C) Sanjeeva Thunga and group's method



Entry	Input		Output	
1	*1H*-indole-3-carbaldehyde oxime	160.18 mg	Indole-3-carbonitrile	125.1 mg
2	methyl 2-nitrosobenzoate	165.14 mg		
3	Cs2CO3	325.82 mg		
4	Dry CH3CN	2000 mg		
	Total	2651.14 mg	Total	125.1 mg

$$\text{E-Factor} = \frac{Total\ input - Total\ output}{weight\ of\ product} = \frac{2651.14 - 125.1}{125.1} = 20.19$$

$$\text{Mass Intensity} = \frac{Total\ input}{weight\ of\ product} = \frac{2651.14}{125.1} = 21.19$$

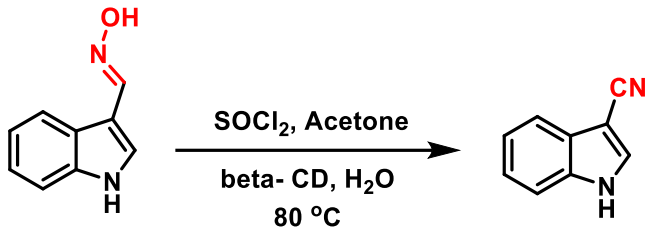
$$\text{Atom economy} = \frac{Molecular\ weight\ of\ Product}{Summation\ of\ Molecular\ weight\ of\ reagents\ used} \times 100$$

$$= \frac{142.16}{160.18+165.14+325.82} \times 100 = 21.83\ \%$$

Atom efficiency = Atom economy % × % Yield of the product

= 21.83 %× 88 % = 19.21 %

(D) Dipak Patil and Dipak Dalal's method



Entry	Input		Output	
1	*1H*-indole-3-carbaldehyde oxime	800.9 mg	Indole-3-carbonitrile	668.15 mg
2	SOCl2	713.82 mg		
3	beta-CD	567.5 mg		
4	H2O	10000 mg		
5	Acetone	2000 mg		
	Total mg	14082.22	Total mg	668.15

$$\text{E-Factor} = \frac{Total\ input - Total\ output}{weight\ of\ product} = \frac{14082.22 - 668.15}{668.15} = 20.07$$

$$\text{Mass Intensity} = \frac{Total\ input}{weight\ of\ product} = \frac{14082.22}{168} = 21.07$$

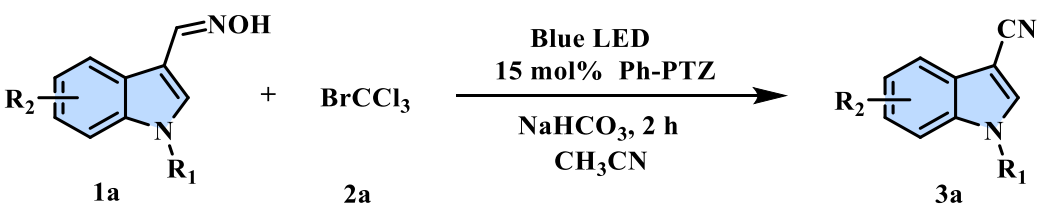
$$\text{Atom economy} = \frac{Molecular\ weight\ of\ Product}{Summation\ of\ Molecular\ weight\ of\ reagents\ used} \times 100$$

$$= \frac{142.16}{160.18+118.97+1135} \times 100 = 9.92\ \%$$

Atom efficiency = Atom economy % × % Yield of the product

= 9.92 % × 94 % = 9.32 %

(E) Our Method



Entry	Input		Output	
1	*1H*-indole-3-carbaldehyde oxime	50 mg	Indole-3-carbonitrile	42.22 mg
2	BrCCl3	370.76 mg	Ph-PTZ	10.05 mg
3	Ph-PTZ	12.39 mg	Dry CH3CN	2000 mg
4	NaHCO3	50.4mg		
5	Dry CH3CN	2000 mg		
	Total	2483 mg	Total mg	2052.27

$$\text{E-Factor} = \frac{Total\ input - Total\ output}{weight\ of\ product} = \frac{2483 - 2052.27}{42.22} = 10.2$$

$$\text{Mass Intensity} = \frac{Total\ input}{weight\ of\ product} = \frac{2483}{42.22} = 58.81$$

$$\text{Atom economy} = \frac{Molecular\ weight\ of\ Product}{Summation\ of\ Molecular\ weight\ of\ reagents\ used} \times 100$$

$$= \frac{142.16}{160.18+198.27+275.37+84} \times 100 = 19.8\ \%$$

Atom efficiency = Atom economy % × % Yield of the product

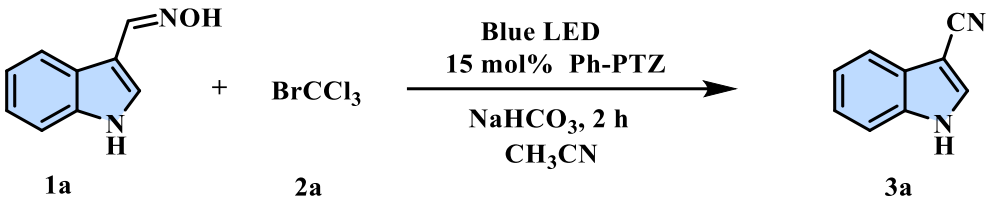
= 19.8 % × 99 % = 19.6 %

Table S5. A comparison of "green-ness" among the catalysts/reagents in the cyanation of indole oxime and indole

Prior Report/Catalyst/Reagent	**Eco-scale**	**E-factor[a]**	**MI[b]**	**AE[c] (%)**	**AEff[d] (%)**	**Time**	**Yield (%)**	**Key Features**
N. Uludag[9]: Oxime, trifluoromethanesulfonic anhydride, NEt_3, THF	75.5	66.8	67.8	26.15	20.65	3.5 h	79	Uses corrosive and hygroscopic $(CF_3SO_2)_2O$
Ze-lin Li and group[10]: Indole, ethyl(ethoxymethylene)cyanoacetate, $Cu(OAc)_2$, DTBP, KI, DMF	68.5	56.77	57.77	18.22	11.47	24 h	63	Uses activated cyanation reagent
Sanjeeva Thunga and group[11]: Oxime, methyl 2-nitrosobenzoate, Cs_2CO_3, dry CH_3CN	81	20.19	21.19	21.83	19.21	4 h	88	Thermal conditions
Dipak Patil and Dipak Dalal[12]: Oxime, $SOCl_2$, beta-CD, H_2O, Acetone	85	20.07	21.07	9.92	9.32	20 min	94	Requires heating
Our Work: Oxime, $BrCCl_3$, Ph-PTZ, $NaHCO_3$, dry CH_3CN	**88.5**	**10.2**	**58.81**	**19.8**	**19.6**	**2 h**	**99**	**Metal-free, visible light, no cyanide reagents, room temperature**

[a,b]: Mass intensity values were calculated including solvent mass, whereas E-factor values were determined excluding solvent contributions for consistency with literature reports. The mass intensity (58.81), which includes solvent contribution, reflects the total material input of the reaction system. [c]: AE-Atom Economy. [d]: AEff-Atom Efficiency.

9. Sensitivity test for the reaction[14]



Performed using general procedure 2.2. All experiments were performed on a 0.2 mmol scale (except scale-up).

Table S6: Sensitivity assessment for the formation of 3-cyanoindole.

Entry	*Modification*	*Deviation from standard Conditions*	*Yield*[a]	*Deviation from optimal yield*
1	High concentration	500 µL CH3CN	70%	-29%
2	Low concentration	4 mL CH3CN	83%	-16%
3	Low H_2O	Solvent: CH3CN (2mL) + 25% H_2O (0.5mL)	46%	-53%
4	Medium O_2	solvent sparged with air, reaction then carried out under argon atmosphere	73%	-26%
5	High O_2	reactions set up and carried out on air	63%	-36%
6	Low intensity	reaction carried out with minimum light intensity	70%	-29%
7	High intensity	reaction carried out with highest light intensity	99%	0
8	Scale up	6.2 mmol scale according to general procedure 4	87%	-12%

Based on the deviation yields from the **Table S8**, a radar diagram is plotted.

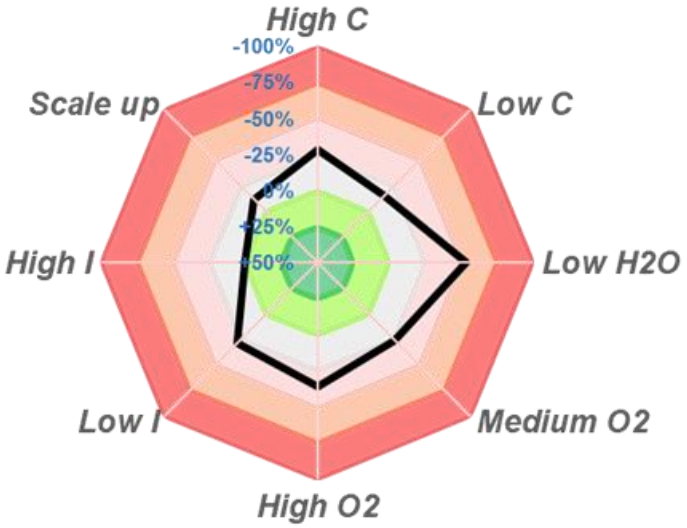
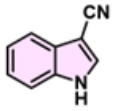


Figure S9: Sensitivity Screening.

10. Cyano-indoles accessible by prior methods and our method

Table S7. Table of comparison of cyano-indoles accessible by prior methods and our method

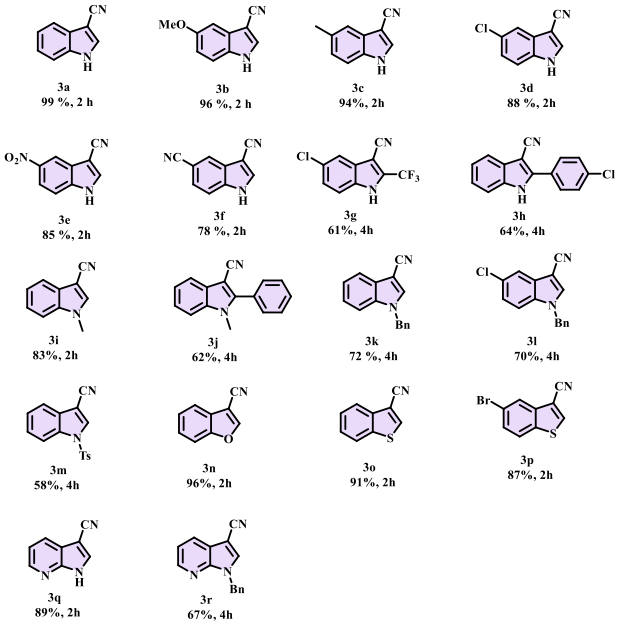
Cyano-indoles accessible by prior methods



Only one example

Yield	Time	Reference
72 %	2 h	*J. Org. Chem.* 2009, 74, 8, 3079–3084
79 %	3.5 h	*Russ. J. Org. Chem.* 2020, Vol. 56, No. 9, pp. 1640–1645.
95 %	6 h	*AsianJ.Org.Chem.*2024,13,e202400291(2of 4)
88 %	4 h	*ChemistrySelect* 2018,3,4425–4429
89 %	-	*Synthesis* 2007, No. 20, 3179–3184
87 %	-	*Synlett* 2004, No. 11, 2019–2021
94 %	20 min	*Synthetic Communications*, 1, 43: 118-128, 2013
99 %	**2 h**	**Our work**

Cyano-indoles accessible by our method



11. X-ray crystal structure of 3a

To a 10 mL tube containing 3a (20.0 mg) was added to chloroform (4 mL). A clear solution was obtained and was kept at room temperature and the crystals were obtained after the solvent evaporated, which were characterized by single crystal X-ray diffraction. X-ray diffraction experiment was carried out on a XtaLAB Synergy-i and the data obtained were deposited at the Cambridge Crystallographic Data Centre.[15]

Identification code	N-11-R-1_auto
Empirical formula	$C_9H_6N_2$
Formula weight	142.16
Temperature/K	293(2)

Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	13.9424(4)
b/Å	5.9908(2)
c/Å	8.9036(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	743.68(4)
Z	4
ρ_{calc}g/cm^3	1.270
μ/mm^{-1}	0.623
F (000)	296.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	12.698 to 136.054
Index ranges	-16 ≤ h ≤ 16, -7 ≤ k ≤ 7, -9 ≤ l ≤ 10
Reflections collected	7801
Independent reflections	1188 [R_{int} = 0.0428, R_{sigma} = 0.0225]
Data/restraints/parameters	1188/1/100
Goodness-of-fit on F^2	1.145
Final R indexes [I>=2σ (I)]	R_1 = 0.0385, wR_2 = 0.0949
Final R indexes [all data]	R_1 = 0.0426, wR_2 = 0.0978
Largest diff. peak/hole / e Å^{-3}	0.11/-0.15
Flack parameter	-0.1(4)

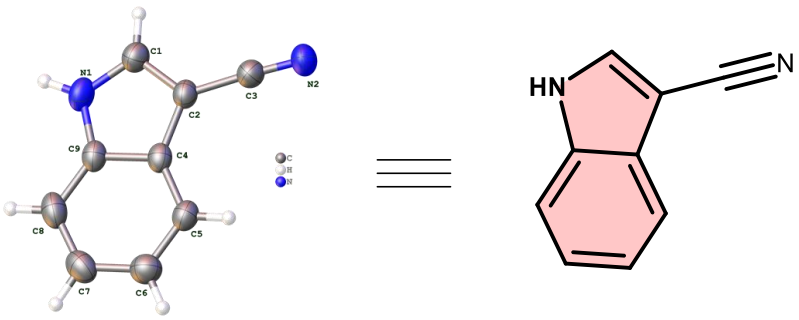


Figure S10. X-ray crystal structure of 1H-indole-3-carbonitrile (3a)

Table S8 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for N-11-R-1_auto. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
N1	3080.9(18)	4391(4)	4035(3)	74.0(7)
C2	2959(2)	7455(4)	5414(4)	57.3(7)
N2	2288(2)	10575(4)	7091(4)	81.1(9)

Table S8 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for N-11-R-1_auto. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C4	3875.0(18)	7503(4)	4684(3)	54.8(7)
C9	3925(2)	5542(4)	3821(4)	60.5(7)
C1	2503(2)	5527(4)	4977(4)	67.4(8)
C3	2568(2)	9155(4)	6346(4)	65.2(8)
C5	4643(2)	8990(4)	4658(3)	63.6(7)
C7	5455(2)	6557(6)	2922(4)	79.2(9)
C6	5420(2)	8498(5)	3780(4)	75.9(9)
C8	4714(2)	5041(5)	2930(4)	76.2(9)

Table S9 Anisotropic Displacement Parameters (Å^2×10^3) for N-11-R-1_auto. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	88.8(16)	55.6(11)	77.6(19)	-18.1(13)	-2.9(16)	-8.2(11)
C2	66.8(14)	49.4(12)	55.8(17)	-5.5(11)	0.9(14)	-0.1(11)
N2	86.2(18)	64.7(13)	92(2)	-20.6(14)	19.2(16)	-1.3(12)
C4	66.5(15)	46.9(12)	51.0(16)	-0.8(11)	-4.2(13)	5.8(10)
C9	72.3(15)	50.3(12)	58.8(18)	-5.6(14)	-4.5(13)	5.2(11)
C1	73.1(16)	59.7(13)	69(2)	-8.6(14)	0.8(16)	-7.6(14)
C3	67.2(15)	58.9(13)	70(2)	-4.3(16)	6.4(15)	-6.1(14)
C5	72.4(17)	52.6(13)	65.6(19)	-3.7(13)	-3.3(14)	-2.4(12)
C7	74.2(19)	85(2)	78(2)	1.4(19)	11.3(17)	18.6(17)
C6	68.7(17)	77.6(18)	81(2)	4(2)	4.4(17)	-2.6(14)
C8	95(2)	66.8(17)	67(2)	-10.5(16)	1.1(18)	20.2(17)

Table S10 Bond Lengths for N-11-R-1_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C9	1.377(4)	C4	C9	1.406(3)
N1	C1	1.348(4)	C4	C5	1.393(4)
C2	C4	1.433(4)	C9	C8	1.389(4)
C2	C1	1.375(3)	C5	C6	1.368(4)
C2	C3	1.422(4)	C7	C6	1.392(5)
N2	C3	1.148(4)	C7	C8	1.376(5)

Table S11. Bond Angles for N-11-R-1_auto.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	N1	C9	110.2(2)	N1	C9	C8	130.4(3)
C1	C2	C4	107.5(2)	C8	C9	C4	122.2(3)
C1	C2	C3	126.1(3)	N1	C1	C2	108.9(2)
C3	C2	C4	126.3(2)	N2	C3	C2	177.1(3)
C9	C4	C2	106.0(2)	C6	C5	C4	118.7(3)
C5	C4	C2	134.8(2)	C8	C7	C6	121.5(3)
C5	C4	C9	119.2(2)	C5	C6	C7	121.5(3)
N1	C9	C4	107.5(2)	C7	C8	C9	117.1(3)

Table S12. Torsion Angles for N-11-R-1_auto.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
N1	C9	C8	C7	178.7(3)	C1	N1	C9	C8	-178.6(3)
C2	C4	C9	N1	-0.2(3)	C1	C2	C4	C9	-0.1(3)
C2	C4	C9	C8	178.9(3)	C1	C2	C4	C5	179.1(3)

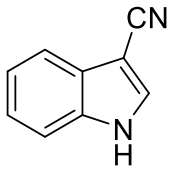
Table S12. Torsion Angles for N-11-R-1_auto.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	C4	C5	C6	-178.5(3)	C3	C2	C4	C9	-176.5(3)
C4	C2	C1	N1	0.3(3)	C3	C2	C4	C5	2.7(5)
C4	C9	C8	C7	-0.1(5)	C3	C2	C1	N1	176.7(3)
C4	C5	C6	C7	-0.1(5)	C5	C4	C9	N1	-179.5(3)
C9	N1	C1	C2	-0.4(4)	C5	C4	C9	C8	-0.5(4)
C9	C4	C5	C6	0.6(4)	C6	C7	C8	C9	0.6(5)
C1	N1	C9	C4	0.3(3)	C8	C7	C6	C5	-0.5(5)

Table S13. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for N-11-R-1_auto.

Atom	*x*	*y*	*z*	U(eq)
H1	2942.62	3130.71	3626.24	89
H1A	1894.31	5079.89	5282.06	81
H5	4628.38	10291.16	5227.58	76
H7	5991.85	6278.4	2330.94	95
H6	5935.31	9482.03	3754.36	91
H8	4740.01	3737.35	2364.08	91

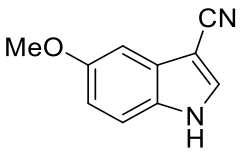
12. NMR Data of cyanide product
1H-indole-3-carbonitrile[16] (3a)



According to the general procedure for cyanation (2.2), compound 3a was prepared from the corresponding 1H-indole-3-carbaldehyde oxime as a white solid in 99% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ 12.14 (s, 1H), 8.20 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, DMSO-d6) δ 135.7, 134.9, 127.2, 123.8, 122.1, 118.9, 116.8, 113.4, 84.7.(see spectra)
HRMS(ESI-TOF) Calcd for $C_9H_7N_2$ $[M+H]^+$ 143.0604, Found $[M+H]^+$ 143.0575.

5-methoxy-1H-indole-3-carbonitrile[16] (3b)

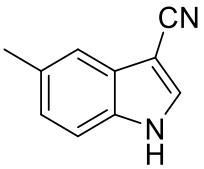


According to the general procedure for cyanation (2.2), compound 3b was prepared from the corresponding 5-methoxy-1H-indole-3-carbaldehyde oxime as an orange solid in 96% yield.

^{1}H NMR (500 MHz, DMSO-d6) δ 12.01 (s, 1H), 8.10 (d, *J* = 3.5 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.03 (s, 1H), 6.86 (dd, *J* = 9.3, 2.4 Hz, 1H), 3.76 (s, 3H). (see spectra)
^{13}C NMR (126 MHz, DMSO-d6) δ 155.8, 134.8, 130.5, 128.0, 117.1, 114.3, 100.3, 84.4, 55.9. (see spectra)

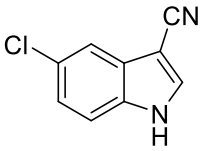
HRMS(ESI-TOF) Calcd for $C_{10}H_9N_2O[M+H]^+$ 173.0710, Found $[M+H]^+$ 173.0710

5-methyl-1H-indole-3-carbonitrile[16] (3c)



According to the general procedure for cyanation (2.2), compound 3c was prepared from the corresponding 5-methyl-1H-indole-3-carbaldehyde oxime as an off-white solid in 94% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.68 (d, *J* = 2.6 Hz, 1H), 7.54 (s, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 2.47 (s, 3H). (see spectra)
^{13}C NMR (126 MHz, $CDCl_3$) δ 133.3, 132.0, 127.3, 126.0, 119.2, 116.4, 111.9, 86.4, 21.5. (see spectra)
HRMS(ESI-TOF) Calcd for $C_{10}H_9N_2$ $[M+H]^+$ 157.0761, Found $[M+H]^+$ 157.0747

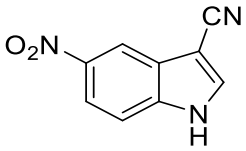
5-chloro-1H-indole-3-carbonitrile[16] (3d)



According to the general procedure for cyanation (2.2), compound 3d was prepared from the corresponding 5-chloro-1H-indole-3-carbaldehyde oxime as a white solid in 88% yield.
^{1}H NMR (500 MHz, DMSO-d6) δ 12.33 (s, 1H), 8.25 (d, *J* = 2.6 Hz, 1H), 7.60 (s, 1H), 7.53 (d, *J* = 9.1 Hz, 1H), 7.25 (d, *J* = 10.1 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, DMSO-d6) δ 136.5, 134.3, 128.3, 127.0, 124.1, 118.1, 116.1, 115.1, 84.6. (see spectra)

HRMS(ESI-TOF) Calcd for $C_9H_6N_2Cl[M+H]^+$ 177.0215, Found $[M+H]^+$ 177.0210.

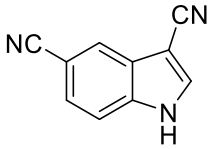
5-nitro-1H-indole-3-carbonitrile[16] (3e)



According to the general procedure for cyanation (2.2), compound 3e was prepared from the corresponding 5-nitro-1H-indole-3-carbaldehyde oxime as a yellow solid in 85% yield.
^{1}H NMR (500 MHz, DMSO-d6) δ 12.70 (s, 1H), 8.40 (d, *J* = 2.1 Hz, 1H), 8.36 (s, 1H), 8.02 (d, *J* = 9.8 Hz, 1H), 7.62 (d, *J* = 9.2 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, DMSO-d6) δ 143.0, 138.8 (d, *J* = 11.6 Hz), 126.4, 119.0, 115.4 (d, *J* = 17.0 Hz), 114.2, 87.3. (see spectra)

HRMS(ESI-TOF) Calcd for $C_9H_6N_3O_2[M+H]^+$ 188.0455, Found $[M+H]^+$ 188.0452.

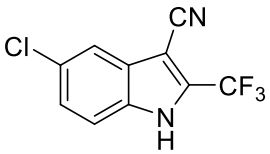
1H-indole-3,5-dicarbonitrile[16] (3f)



According to the general procedure for cyanation (2.2), compound 3f was prepared from the corresponding 3-((hydroxyimino)methyl)-1H-indole-5-carbonitrile as a yellow solid in 78% yield.

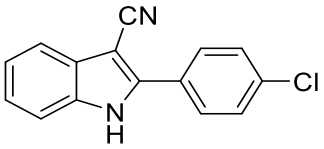
^{1}H NMR (500 MHz, DMSO-d6) δ 12.65 (s, 1H), 8.42 (s, 1H), 8.14 (s, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, DMSO-d6) δ 137.9, 137.7, 137.5, 126.8 (d, *J* = 12.2 Hz), 124.6 (dd, *J* = 22.5, 3.3 Hz), 120.1, 115.7, 114.8, 104.6, 85.9. (see spectra)
HRMS(ESI-TOF) Calcd for $C_{10}H_6N_3$ $[M+H]^+$ 168.0557, Found $[M+H]^+$ 168.0557.

5-chloro-2-(trifluoromethyl)-1H-indole-3-carbonitrile(3g)



According to the general procedure for cyanation (2.2), compound 3g was prepared from the corresponding 5-chloro-2-(trifluoromethyl)-1H-indole-3-carbaldehyde oxime as a white solid in 61% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.81 (s, 1H), 7.47 (d, *J* = 8.9 Hz, 1H), 7.42 (d, *J* = 9.7 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1, 132.7, 130.0, 127.7 (dd, *J* = 20.0, 7.5 Hz), 120.5, 120.1, 114.2, 113.5, 111.9, 29.7. (see spectra)
HRMS(ESI-TOF) Calcd for $C_{10}H_5ClF_3N_2$ $[M+H]^+$ 245.0088, Found $[M+H]^+$ 245.0091.

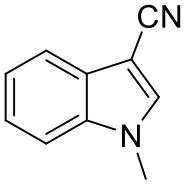
2-(4-chlorophenyl)-1H-indole-3-carbonitrile[17](3h)



According to the general procedure for cyanation (2.2), compound 3h was prepared from the corresponding 2-(4-chlorophenyl)-1H-indole-3-carbaldehyde oxime as a light-yellow solid in 64% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 6.9 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 135.4, 134.4, 133.1, 129.8, 129.6, 129.0 (d, *J* = 18.6 Hz), 128.7 (d, *J* = 7.8 Hz), 127.3, 123.8, 121.1, 119.6, 111.2, 90.6. (see spectra)

HRMS(ESI-TOF) Calcd for $C_{15}H_{10}N_2Cl$ $[M+Na]^+$ 275.0352 Found $[M+Na]^+$ 275.0356.

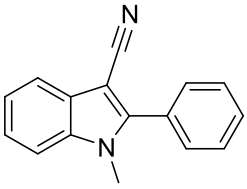
1-methyl-1H-indole-3-carbonitrile[16] (3i)



According to the general procedure for cyanation (2.2), compound 3i was prepared from the corresponding 1-methyl-1H-indole-3-carbaldehyde oxime as an off-white solid in 83% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.55 (s, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 3.85 (s, 3H). (see spectra)
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.1, 135.5, 127.9, 123.9, 122.2, 119.9, 115.9, 110.3, 85.7, 33.6. (see spectra)

HRMS(ESI-TOF) Calcd for $C_{10}H_9N_2$ $[M+H]^+$ 157.0761, Found $[M+H]^+$ 157.0744.

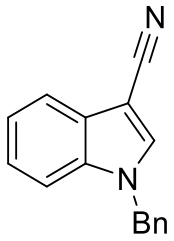
1-methyl-2-phenyl-1H-indole-3-carbonitrile[16] (3j)



According to the general cyanation procedure 2.2, compound 3j was prepared from the corresponding 1-methyl-2-phenyl-1H-indole-3-carbaldehyde oxime as a white solid in 62% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.54 (dd, *J* = 15.7, 6.6 Hz, 5H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 3.75 (s, 3H). (see spectra)
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 136.9, 129.9 (d, *J* = 6.0 Hz), 128.9 (d, *J* = 35.8 Hz), 127.6, 123.9 (dd, *J* = 17.8, 8.8 Hz), 122.9 – 122.0 (m), 119.6 (d, *J* = 8.5 Hz), 110.9 – 110.02 (m), 85.6, 31.8. (see spectra)

HRMS(ESI-TOF) Calcd for $C_{16}H_{13}N_2$ $[M+H]^+$ 233.1074, Found $[M+H]^+$ 233.1074.

1-benzyl-1H-indole-3-carbonitrile[18](3k)



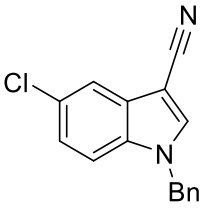
According to the general cyanation procedure 2.2, compound 3k was prepared from the corresponding 1-benzyl-1H-indole-3-carbaldehyde oxime as a yellow oil in 72% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.37 – 7.31 (m, 4H), 7.30(t, 2H), 7.14 (d, *J* = 6.5 Hz, 2H), 5.32 (s, 2H). (see spectra)

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 135.3, 135.1, 129.2, 128.5, 128.0, 127.2, 124.1, 122.4, 120.0, 115.9, 110.9, 86.3, 50.9. (see spectra)

HRMS(ESI-TOF) Calcd for $C_{16}H_{13}N_2$ $[M+H]^+$233.1074, Found $[M+H]^+$ 233.1059.

1-benzyl-5-chloro-1H-indole-3-carbonitrile[18] (3l)



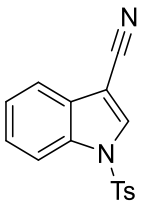
According to the general cyanation procedure 2.2, compound 3l was prepared from the corresponding 1-benzyl-5-chloro-1H-indole-3-carbaldehyde oxime as a brown solid in 70% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.59 (s, 1H), 7.34 (d, *J* = 7.1 Hz, 3H), 7.25 – 7.21 (m, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 5.31 (s, 2H). (see spectra)

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.0, 134.8, 134.0, 129.3, 129.0, 128.7, 128.5, 127.1, 124.6, 119.5, 115.1, 112.1, 86.0, 77.4, 77.1, 76.9, 51.2. (see spectra)

HRMS(ESI-TOF) Calcd for $C_{16}H_{12}N_2Cl$ $[M+H]^+$ 267.0684, Found $[M+H]^+$ 267.0686.

1-tosyl-1H-indole-3-carbonitrile[19](3m)



According to the general cyanation procedure 2.2, compound 3m was prepared from the corresponding 1-tosyl-1H-indole-3-carbaldehyde oxime as a white solid in 58% yield.

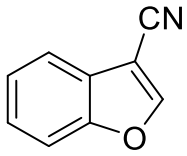
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 2.37 (s, 3H). (see spectra)

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 134.2, 133.7, 133.2, 130.4, 128.4, 127.3, 126.6, 124.8, 120.3, 113.8, 113.5, 93.7, 77.2 (d, *J* = 32.0 Hz), 21.7. (see spectra)

HRMS(ESI-TOF) Calcd for $C_{16}H_{12}N_2O_2SNa[M+Na]^+$ 319.0512

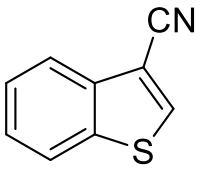
Found $[M+Na]^+$319.0522.

benzofuran-3-carbonitrile[20](3n)



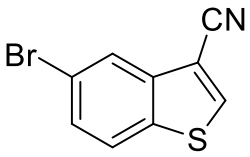
According to the general cyanation procedure 2.2, compound 3n was prepared from the corresponding benzofuran-3-carbaldehyde oxime as a white solid in 96% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 152.0, 126.7, 124.8 (d, *J* = 4.4 Hz), 120.3, 112.3 (d, *J* = 8.2 Hz), 95.0. (see spectra)
HRMS(ESI-TOF) Calcd for C_9H_6NO $[M+H]^+$144.0444, Found $[M+H]^+$144.0445.

benzo[b]thiophene-3-carbonitrile[21]**(3o)**



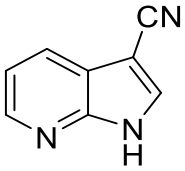
According to the general procedure for cyanation 2.2, compound 3o was prepared from the corresponding benzo[b]thiophene-3-carbaldehyde oxime as a brown solid in 91% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 1H), 7.73 (s, 1H), 7.72 (s, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.0, 136.2, 133.7, 126.6, 124.5, 124.0, 121.1, 113.2, 108.4. (see spectra)
HRMS(ESI-TOF) Calcd for C_9H_6NS $[M+H]^+$ 160.0216, Found $[M+H]^+$ 160.0209.

5-bromobenzo[b]thiophene-3-carbonitrile(3p)



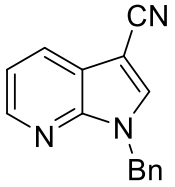
According to the general procedure for cyanation 2.2, compound 3p was prepared from the corresponding 5-bromobenzo[b]thiophene-3-carbaldehyde oxime as a brown solid in 87% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9 (d, *J* = 8.1 Hz), 137.1, 129.6, 125.4, 124.1, 120.5, 113.7, 106.6. (see spectra)
HRMS(ESI-TOF) Calcd for C_9H_5BrNS $[M+H]^+$160.0216, Found $[M+H]^+$160.0209.

1H-pyrrolo[2,3-b]pyridine-3-carbonitrile[22]**(3q)**



According to the general procedure for cyanation 2.2, compound 3q was prepared from the corresponding 1H-pyrrolo[2,3-b]pyridine-3-carbaldehyde oxime as a white solid in 89% yield.
^{1}H NMR (500 MHz, DMSO-d6) δ 12.77 (s, 1H), 8.37 (s, 1H), 8.34 (d, *J* = 4.3 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.21 (dd, *J* = 7.7, 4.8 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, DMSO-d6) δ 147.9, 145.5, 135.9, 127.7, 119.4, 118.3, 116.0, 83.8. (see spectra)
HRMS(ESI-TOF) Calcd for $C_8H_5N_3$ $[M+H]^+$ 144.0557, Found $[M+H]^+$ 144.0547.

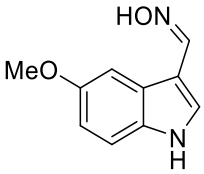
1-benzyl-1H-pyrrolo[2,3-b]pyridine-3-carbonitrile[22](3r)



According to the general procedure for cyanation 2.2, compound 3r was prepared from the corresponding 1-benzyl-1H-pyrrolo[2,3-b]pyridine-3-carbaldehyde oxime as a white solid in 67% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.7 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.67 (s, 1H), 7.36 – 7.30 (m, 3H), 7.26 (dt, *J* = 7.7, 3.8 Hz, 3H), 5.50 (s, 2H). (see spectra)
^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 145.5, 135.8, 134.9, 129.1, 128.4 (d, *J* = 16.2 Hz), 128.0, 120.0, 118.4, 115.0, 85.0, 48.7. (see spectra)
HRMS(ESI-TOF) Calcd for $C_{15}H_{11}N_3$ $[M+H]^+$ 234.1026, Found $[M+H]^+$ 234.1008.

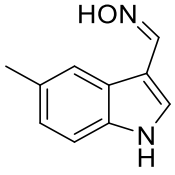
13. NMR Data of Successful Oximes

5-methoxy-1H-indole-3-carbaldehyde oxime(1b)



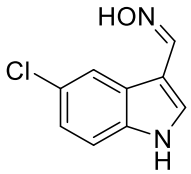
^{1}H NMR (500 MHz, DMSO) δ 11.22 (s, 1H), 10.46 (s, 1H), 8.22 (s, 1H), 7.53 (d, *J* = 2.3 Hz, 1H), 7.43 (d, *J* = 2.3 Hz, 1H), 7.28 (d, *J* = 9.1 Hz, 1H), 6.77 (d, *J* = 5.8 Hz, 1H), 3.71 (s, 3H). (see spectra)
^{13}C NMR (126 MHz, DMSO) δ 154.6, 145.4, 132.3, 129.4, 125.1, 113.0, 109.8, 103.6, 55.8. (see spectra)

5-methyl-1H-indole-3-carbaldehyde oxime(1c)



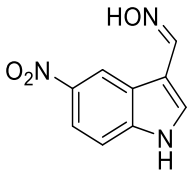
^{1}H NMR (500 MHz, DMSO) δ 11.41 (s, 1H), 11.10 (s, 1H), 8.15 (d, *J* = 2.3 Hz, 1H), 7.70 (s, 1H), 7.59 (s, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 2.37 (s, 3H). (see spectra)
^{13}C NMR (126 MHz, DMSO) δ 138.9, 133.8, 131.0, 129.1, 127.0, 123.9, 118.2, 111.9, 106.4, 21.8. (see spectra)

5-chloro-1H-indole-3-carbaldehyde oxime(1d)



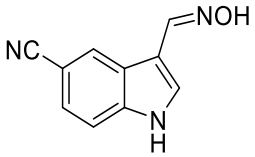
^{1}H NMR (500 MHz, DMSO) δ 11.67 (s, 1H), 11.19 (s, 1H), 8.22 (d, *J* = 2.4 Hz, 1H), 7.90 (s, 1H), 7.73 (s, 1H), 7.41 (d, *J* = 9.0 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, DMSO) δ 138.5, 133.9, 132.4, 127.8, 125.2, 122.3, 118.3, 113.8, 106.8. (see spectra)

5-nitro-1H-indole-3-carbaldehyde oxime(1e)



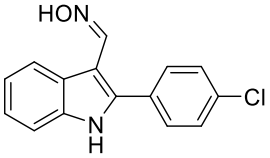
^{1}H NMR (500 MHz, DMSO) δ 12.02 (s, 1H), 10.88 (s, 1H), 8.92 (s, 2H), 8.29 (s, 1H), 8.03 (d, *J* = 9.1 Hz, 2H), 7.88 (d, *J* = 44.3 Hz, 2H), 7.60 – 7.55 (m, 2H). (see spectra)
^{13}C NMR (126 MHz, DMSO) δ 149.0, 146.7 (d, *J* = 8.4 Hz), 145.3, 143.4, 142.9, 139.1, 136.9, 130.7, 128.7, 123.7, 123.0, 122.5, 121.4, 117.6, 117.1, 114.0. (see spectra)

3-((hydroxyimino)methyl)-1H-indole-5-carbonitrile(1f)



^{1}H NMR (500 MHz, DMSO) δ 12.04 (s, 1H), 11.41 (s, 1H), 8.46 (s, 1H), 8.37 (s, 1H), 7.86 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 9.2 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, DMSO) δ 138.2, 137.2, 133.2, 126.5, 125.1, 124.9, 121.0, 113.6, 107.7, 102.6. (see spectra)

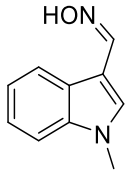
2-(4-chlorophenyl)-1H-indole-3-carbaldehyde oxime(1h)



^{1}H NMR (500 MHz, DMSO) δ 11.25 (s, 5H), 7.78 (d, *J* = 8.2 Hz, 4H), 7.64 (d, *J* = 8.0 Hz, 4H), 7.32 (d, *J* = 8.1 Hz, 7H), 7.11 (q, *J* = 8.6 Hz, 24H), 6.97 (t, *J* = 7.4 Hz, 6H), 6.90 (d, *J* = 8.1 Hz, 5H), 6.60 (t, *J* = 7.5 Hz, 5H). (see spectra)

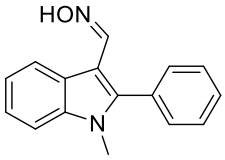
^{13}C NMR (126 MHz, DMSO) δ 147.9, 136.6, 134.2, 132.1 (d, *J* = 19.8 Hz), 130.0, 129.5, 129.1, 128.3, 124.4, 123.0, 121.6 (d, *J* = 9.7 Hz), 121.1, 119.2, 116.7, 112.6, 111.8. (see spectra)

1-methyl-1H-indole-3-carbaldehyde oxime(1i)



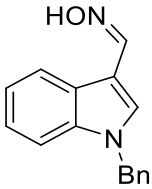
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.27 (s, 1H), 7.80 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.31 (t, 1H), 7.25 (t, 1H), 3.82 (s, 3H). (see spectra)
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.1, 135.5, 127.9, 123.9, 122.2, 119.9, 115.9, 110.3, 85.7, 33.6. (see spectra)

1-methyl-2-phenyl-1H-indole-3-carbaldehyde oxime(1j)



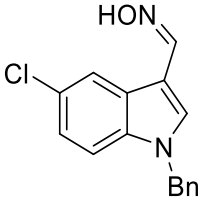
^{1}H NMR (500 MHz, DMSO) δ 10.65 (s, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.90 (s, 1H), 7.56 – 7.48 (m, 4H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 3.57 (s, 3H). (see spectra)
^{13}C NMR (126 MHz, DMSO) δ 144.8, 142.7, 137.8, 131.1, 130.1, 129.5, 129.1, 124.7, 123.3, 122.3, 121.3, 110.8, 107.4, 31.3. (see spectra)

1-benzyl-1H-indole-3-carbaldehyde oxime(1k)



^{1}H NMR (500 MHz, DMSO) δ 11.26 (s, 1H), 8.36 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.77 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.21 (d, *J* = 6.7 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.46 (s, 2H). (see spectra)
^{13}C NMR (126 MHz, DMSO) δ 138.5, 138.1, 135.3, 134.3, 129.1, 128.0, 127.6, 127.4, 122.6, 120.8, 119.0, 111.1, 106.4, 49.7. (see spectra)

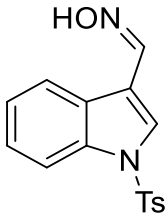
1-benzyl-5-chloro-1H-indole-3-carbaldehyde oxime(1l)



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 45.6 Hz, 1H), 7.74 (s, 1H), 7.29 (d, *J* = 7.4 Hz, 3H), 7.17 (s, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 5.28 (d, *J* = 31.5 Hz, 2H). (see spectra)
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 138.9, 136.1 (d, *J* = 9.6 Hz), 135.7, 133.9, 131.8, 129.07 (d, *J* = 2.3 Hz), 128.5 (d, *J* = 16.6 Hz), 128.2, 128.2 (d, *J* = 6.3 Hz), 127.8 (d, *J* = 20.1 Hz), 127.1 (d, *J* = 2.6

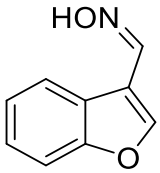
Hz), 126.8 (d, *J* = 13.1 Hz), 126.4, 123.6, 123.2, 121.8, 118.1, 111.5, 111.1, 109.1, 105.6, 50.9, 50.6. (see spectra)

1-tosyl-1Hindole-3-carbaldehyde oxime(1n)



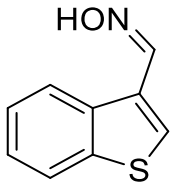
^{1}H NMR (500 MHz, DMSO) δ 11.21 (s, 2H), 8.29 (s, 2H), 8.10 (s, 2H), 8.01 (d, *J* = 7.9 Hz, 2H), 7.92 (t, *J* = 7.3 Hz, 4H), 7.86 (d, *J* = 15.0 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 5H), 7.36 (t, *J* = 7.4 Hz, 3H), 7.30 (d, *J* = 8.6 Hz, 7H), 7.27 (d, *J* = 7.7 Hz, 2H), 2.22 (s, 9H). (see spectra)
^{13}C NMR (126 MHz, DMSO) δ 146.5, 146.2, 143.6, 136.9, 135.2, 134.2, 133.4, 130.8 (d, *J* = 12.6 Hz), 130.0, 129.1, 128.9, 127.5, 127.3, 126.1, 125.9, 124.6, 124.3, 123.3, 120.3, 117.0, 113.6 (d, *J* = 15.7 Hz), 112.1, 21.5. (see spectra)

benzofuran-3-carbaldehyde oxime(1o)



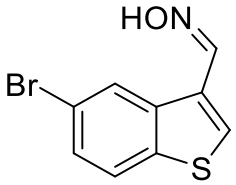
^{1}H NMR (500 MHz, DMSO) δ 12.44 (s, 1H), 11.65 (s, 1H), 9.14 (s, 1H), 8.71 (s, 1H), 8.64 (s, 1H), 8.39 (d, *J* = 7.7 Hz, 1H), 8.34 (d, *J* = 7.5 Hz, 1H), 8.26 (s, 1H), 8.02 – 7.96 (m, 2H), 7.75 (t, *J* = 7.7 Hz, 2H), 7.71 (dd, *J* = 8.3, 6.2 Hz, 2H). (see spectra)
^{13}C NMR (126 MHz, DMSO) δ 155.9, 154.3, 150.1, 148.0, 142.5, 136.9, 126.3, 126.0, 125.0, 124.5, 124.3, 123.5, 120.8, 116.6, 112.4 (d, *J* = 5.3 Hz), 112.1. (see spectra)

benzo[b]thiophene-3-carbaldehyde oxime(1p)



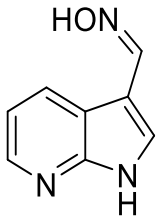
^{1}H NMR (500 MHz, DMSO) δ 12.10 (s, 2H), 11.51 (s, 4H), 8.41 (s, 4H), 7.95 – 7.92 (m, 5H), 7.89 – 7.85 (m, 7H), 7.80 – 7.77 (m, 4H), 7.74 (s, 3H), 7.57 (s, 4H), 7.39 – 7.36 (m, 5H), 7.34 – 7.31 (m, 8H). (see spectra)
^{13}C NMR (126 MHz, DMSO) δ 144.5, 142.1, 140.9, 139.6, 139.1, 137.9, 137.5, 131.8, 128.2, 126.7, 126.2, 125.2 (d, *J* = 15.1 Hz), 124.8, 124.5, 122.9, 122.8. (see spectra)

5-bromobenzo[b]thiophene-3-carbaldehyde oxime(1q)



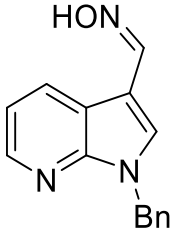
^{1}H NMR (500 MHz, DMSO) δ 11.33 (s, 1H), 8.68 (s, 1H), 8.39 (s, 1H), 8.07 (s, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 10.0 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, DMSO) δ 145.3, 139.5, 137.8, 133.1, 129.1, 128.2, 127.6, 125.4, 118.9. (see spectra)

1H-pyrrolo[2,3-b]pyridine-3-carbaldehyde oxime(1r)



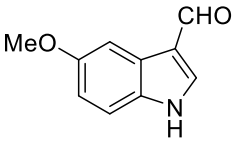
^{1}H NMR (600 MHz, DMSO) δ 12.14 (s, 1H), 11.96 (s, 1H), 11.39 (s, 1H), 10.72 (s, 1H), 8.36 (d, *J* = 7.9 Hz, 1H), 8.31 (d, *J* = 14.4 Hz, 5H), 7.81 (d, *J* = 14.7 Hz, 2H), 7.20 (dd, *J* = 12.2, 7.0 Hz, 2H). (see spectra)
^{13}C NMR (126 MHz, DMSO) δ 149.6, 148.0, 144.8, 144.2, 143.9, 138.5, 131.2, 130.0, 129.0, 127.8, 118.7, 117.0, 116.8, 109.0, 106.0. (see spectra)

1H-pyrrolo[2,3-b]pyridine-3-carbaldehyde oxime(1s)



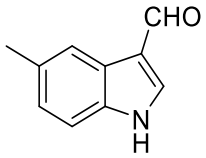
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 8.6, 4.5 Hz, 2H), 8.32 (d, *J* = 7.2 Hz, 2H), 8.25 (s, 1H), 8.10 (d, *J* = 7.2 Hz, 1H), 7.69 (s, 1H), 7.33 (s, 1H), 7.31 – 7.19 (m, 11H), 7.16 (dd, *J* = 7.8, 5.1 Hz, 1H), 5.51 (d, *J* = 25.8 Hz, 4H). (see spectra)
^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 148.3, 146.9, 145.3, 144.3, 144.0, 138.5, 136.9 (d, *J* = 4.5 Hz), 134.3, 130.7, 130.1, 128.9 (d, *J* = 4.0 Hz), 128.0 (d, *J* = 7.3 Hz), 127.7 (d, *J* = 11.7 Hz), 127.3, 119.4, 117.7, 117.3 (d, *J* = 19.9 Hz), 108.2, 104.7, 48.4, 48.1, 20.8. (see spectra)

13. NMR Data of Aldehyde
5-methoxy-1H-indole-3-carbaldehyde(1b')



^{1}H NMR (500 MHz, DMSO-d6) δ 11.98 (s, 1H), 9.86 (s, 1H), 8.17 (s, 1H), 7.55 (s, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H). (see spectra)
^{13}C NMR (126 MHz, DMSO-d6) δ 185.3, 156.1, 138.8, 132.3, 125.4, 118.5, 113.8, 103.0, 55.8. (see spectra)

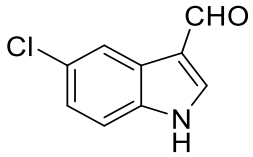
5-methyl-1H-indole-3-carbaldehyde(1c')



^{1}H NMR (500 MHz, $CDCl_3$+DMS0-d6) δ 11.45 (s, 1H), 9.85 (s, 1H), 7.93 (s, 1H), 7.74 (s, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 2.36 (s, 3H). (see spectra)

^{13}C NMR (126 MHz, $CDCl_3$+DMS0-d6) δ 185.0, 162.5, 137.1, 135.7, 131.9 (d, *J* = 10.9 Hz), 125.3, 124.8, 121.2, 118.5, 111.9, 21.5. (see spectra)

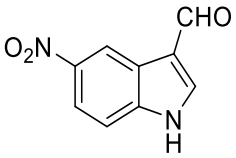
5-chloro-1H-indole-3-carbaldehyde(1d')



^{1}H NMR (500 MHz, $CDCl_3$) δ 12.26 (s, 1H), 9.88 (s, 1H), 8.30 (s, 1H), 8.03 (s, 1H), 7.49 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 1H). (see spectra)

^{13}C NMR (126 MHz, $CDCl_3$) δ 128.1, 124.8, 122.2, 120.4, 120.0(d, *J* = 16.8 Hz), 118.3, 111.6, 110.3. (see spectra)

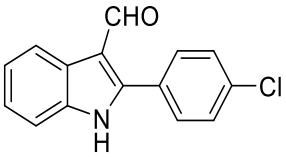
5-nitro-1H-indole-3-carbaldehyde(1e')



^{1}H NMR (500 MHz, DMSO-d6) δ 12.63 (s, 1H), 9.97 (s, 1H), 8.87 (d, *J* = 2.3 Hz, 1H), 8.50 (s, 1H), 8.09 (d, *J* = 9.5 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H). (see spectra)

^{13}C NMR (126 MHz, DMSO-d6) δ 186.0, 143.4, 141.8, 140.6, 124.0, 119.6, 119.3, 117.5, 113.7. (see spectra)

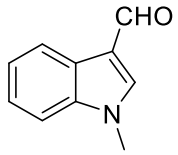
2-(4-chlorophenyl)-1H-indole-3-carbaldehyde(1h')



^{1}H NMR (500 MHz, DMSO-d6) δ 12.43 (s, 1H), 9.94 (s, 1H), 8.20 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H). (see spectra)

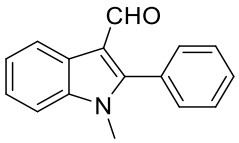
^{13}C NMR (126 MHz, DMSO-d6) δ 185.9, 147.9, 136.4, 135.3, 132.0, 129.5, 129.1, 126.3, 124.3, 123.0, 121.6, 114.2, 112.5. (see spectra)

1-methyl-1H-indole-3-carbaldehyde(1i')



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.83 (s, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.26 – 7.24 (m, 1H), 3.83 (s, 3H). (see spectra)

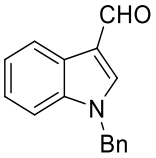
1-methyl-2-phenyl-1H-indole-3-carbaldehyde(1j')



^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.43 (d, *J* = 8.3 Hz, 1H), 7.57 – 7.53 (m, 3H), 7.48 (dd, *J* = 5.9, 2.8 Hz, 2H), 7.37 (tt, *J* = 6.7, 4.8 Hz, 3H), 3.66 (s, 3H). (see spectra)

^{13}C NMR (126 MHz, $CDCl_3$) δ 186.6, 151.4, 137.4, 130.9, 129.9, 128.8, 125.2, 124.1, 123.3, 122.3, 115.8, 109.8, 31.0. (see spectra)

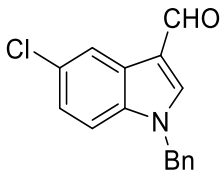
1-benzyl-1H-indole-3-carbaldehyde(1k')



^{1}H NMR (500 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.30 (s, 1H), 7.69 (s, 1H), 7.37 – 7.30 (m, 3H), 7.20 (s, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 5.31 (s, 2H). (see spectra)

^{13}C NMR (126 MHz, $CDCl_3$) δ 184.4, 139.3, 135.8, 134.9, 129.2 (d, *J* = 17.9 Hz), 128.5 (d, *J* = 19.9 Hz), 127.8 (d, *J* = 18.5 Hz), 127.2, 126.5, 124.6, 121.8, 117.9, 111.5, 51.2. (see spectra)

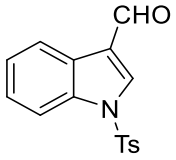
1-benzyl-5-chloro-1H-indole-3-carbaldehyde(1l')



^{1}H NMR (500 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.30 (s, 1H), 7.69 (s, 1H), 7.37 – 7.30 (m, 3H), 7.20 (s, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 5.31 (s, 2H). (see spectra)

^{13}C NMR (126 MHz, $CDCl_3$) δ 184.4, 139.4, 135.8, 134.9, 129.2 (d, *J* = 17.9 Hz), 128.5 (d, *J* = 19.9 Hz), 127.8 (d, *J* = 18.5 Hz), 127.2, 126.5, 124.6, 121.8, 117.9, 111.5, 51.2. (see spectra)

1-tosyl-1H-indole-3-carbaldehyde(1m')



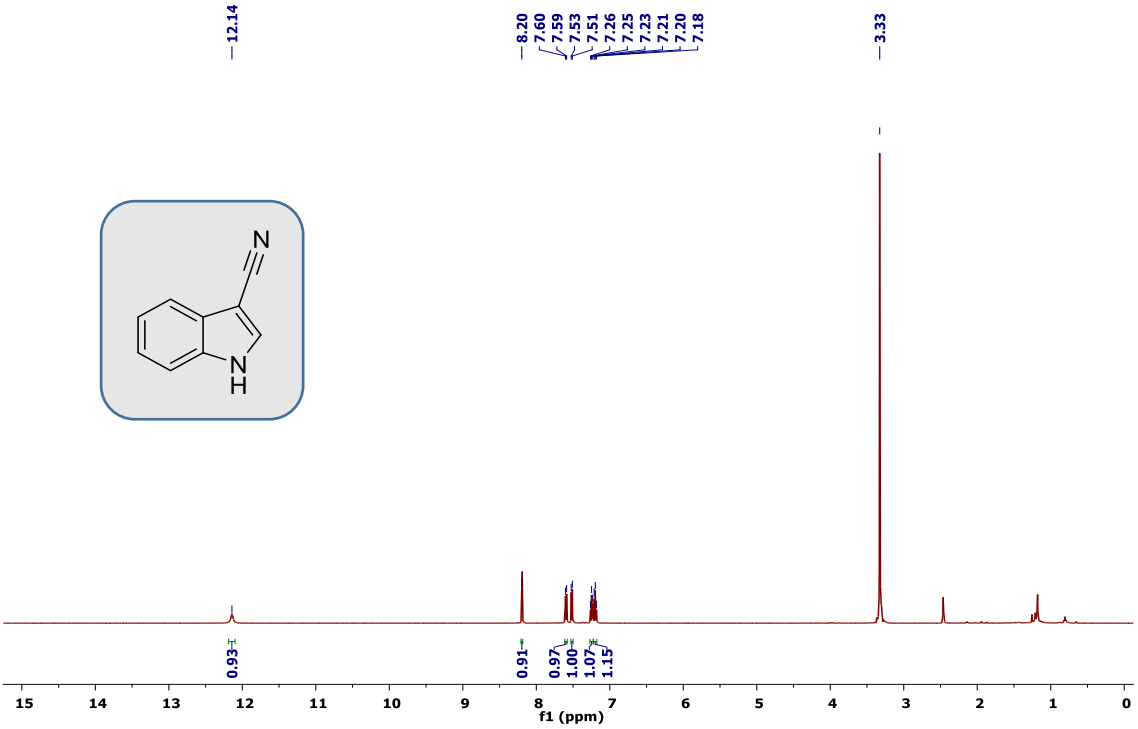
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.07 (s, 1H), 8.26 – 8.21 (m, 2H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.26 (s, 1H), 7.24 (s, 1H), 2.32 (s, 3H). (see spectra)

^{13}C NMR (126 MHz, $CDCl_3$) δ 185.5, 146.2, 136.4, 135.2, 134.3, 130.4, 127.3, 126.3, 125.1, 122.6, 122.4, 113.3, 21.7. (see spectra)

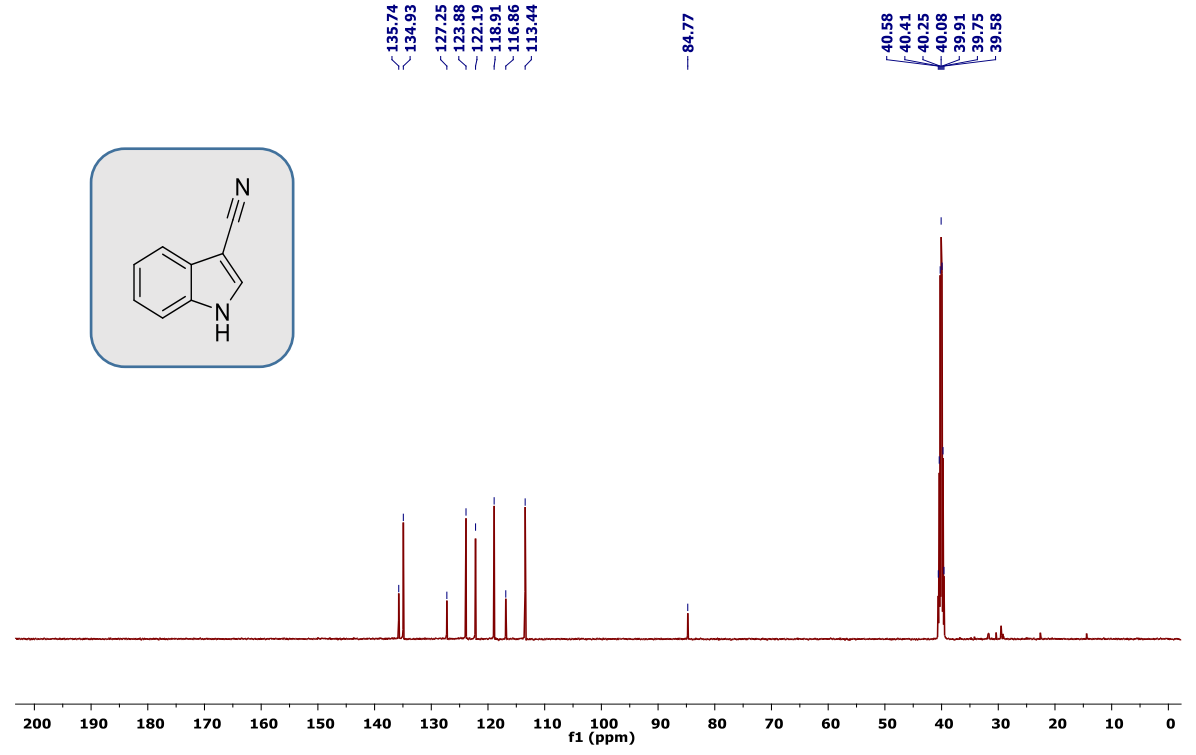
14. NMR and HRMS Spectra of cyanide products

1H-indole-3-carbonitrile(3a)

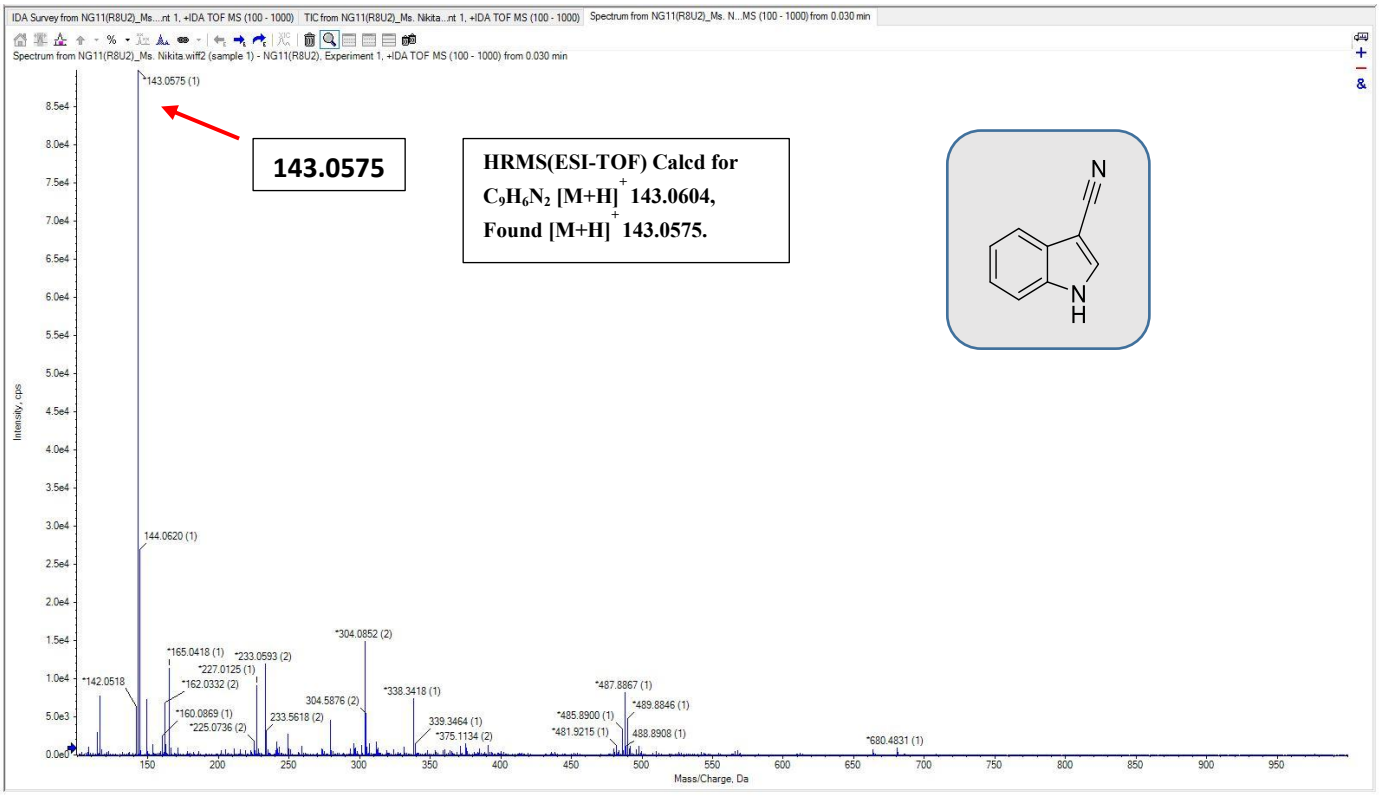
^{1}H NMR (500 MHz, DMSO-d6)



^{13}C NMR (126 MHz, DMSO-d6)

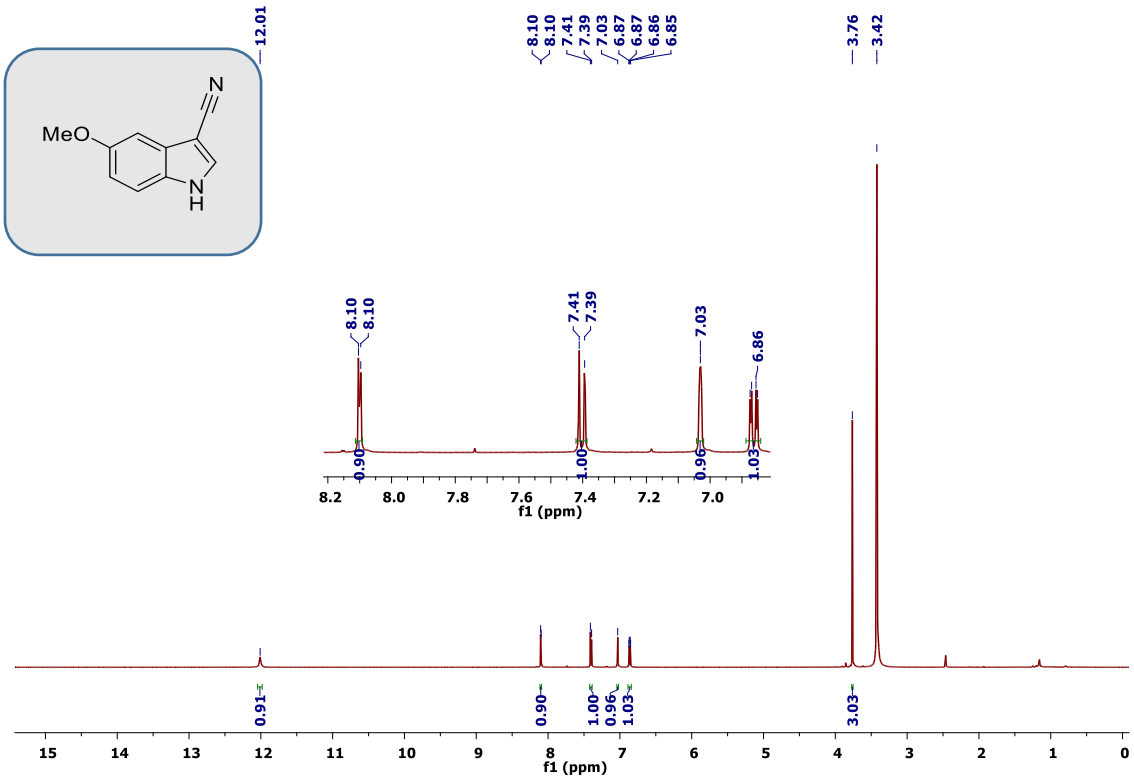


HRMS-Spectra

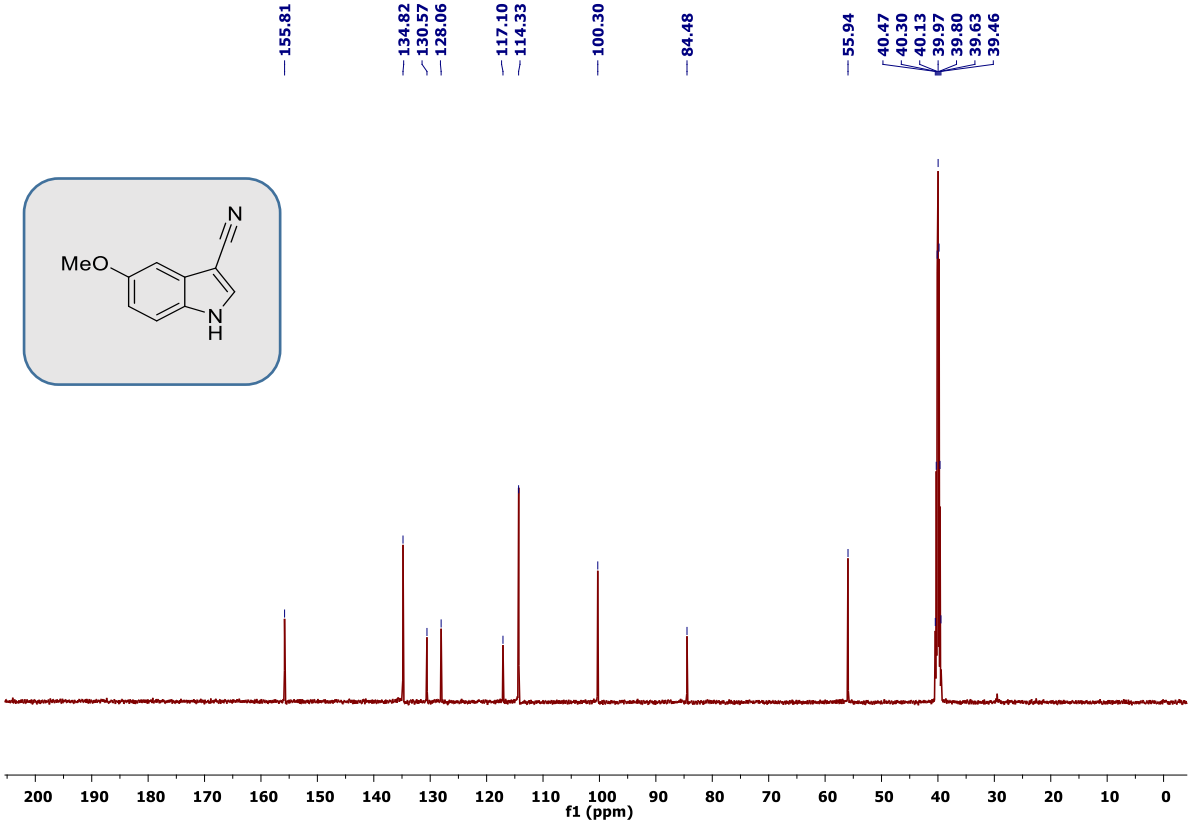


5-methoxy-1H-indole-3-carbonitrile(3b)

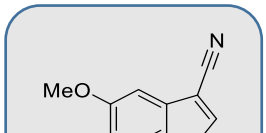
^{1}H NMR (500 MHz, DMSO-d6)



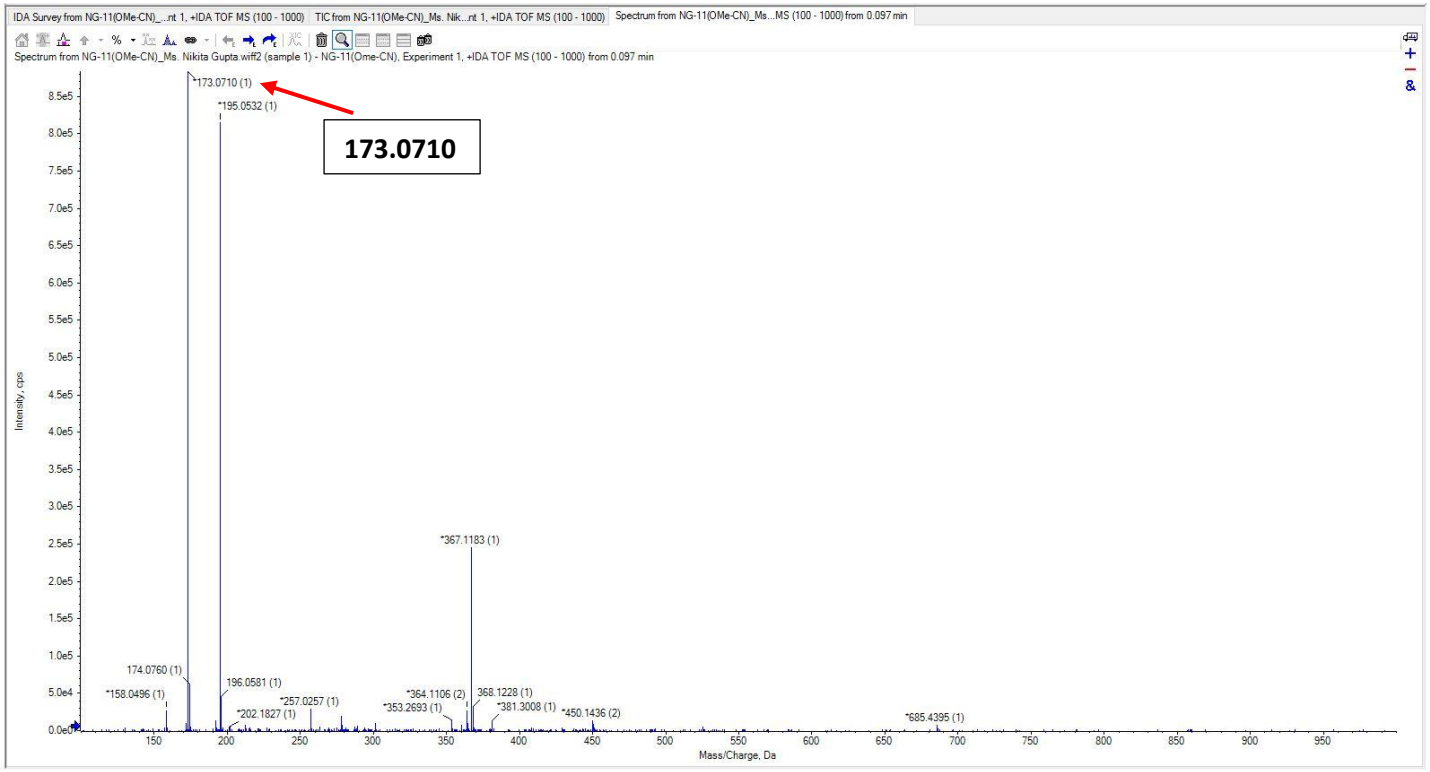
^{13}C NMR (126 MHz, DMSO-d6)



HRMS-Spectra

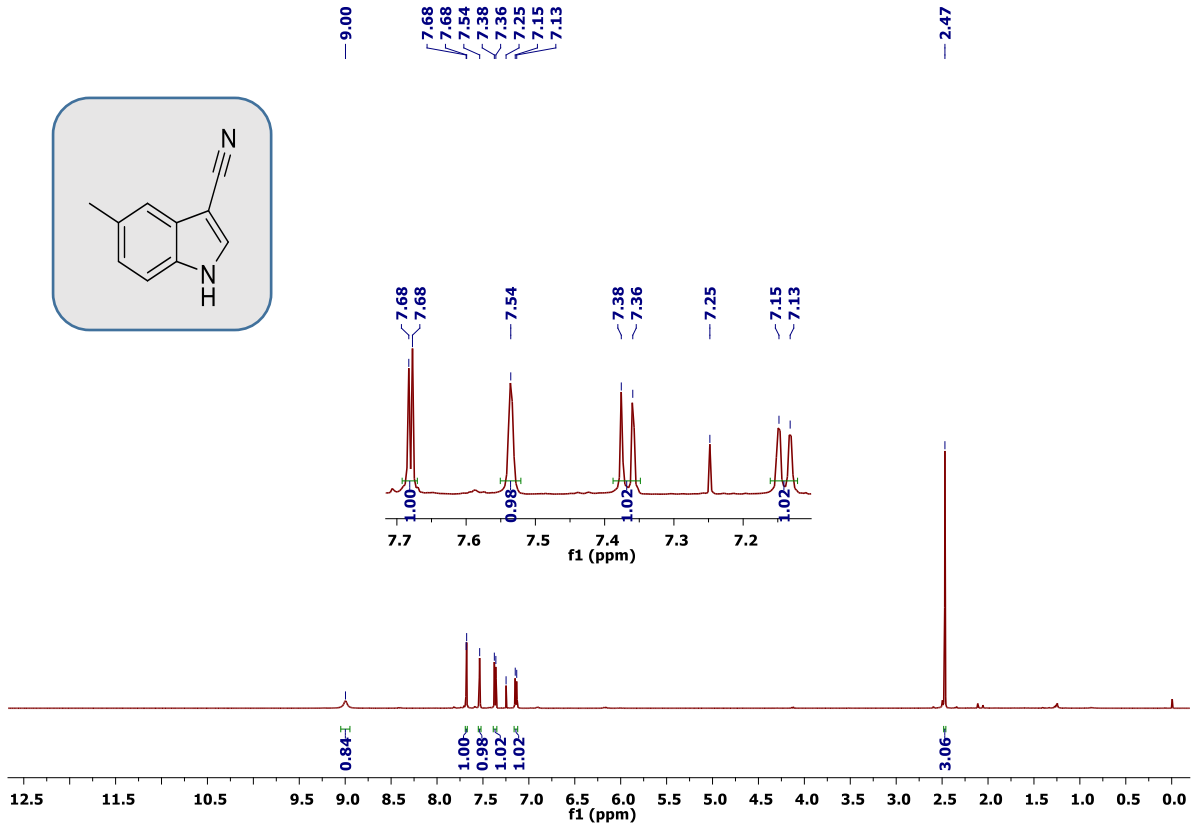


HRMS(ESI-TOF) Calcd for

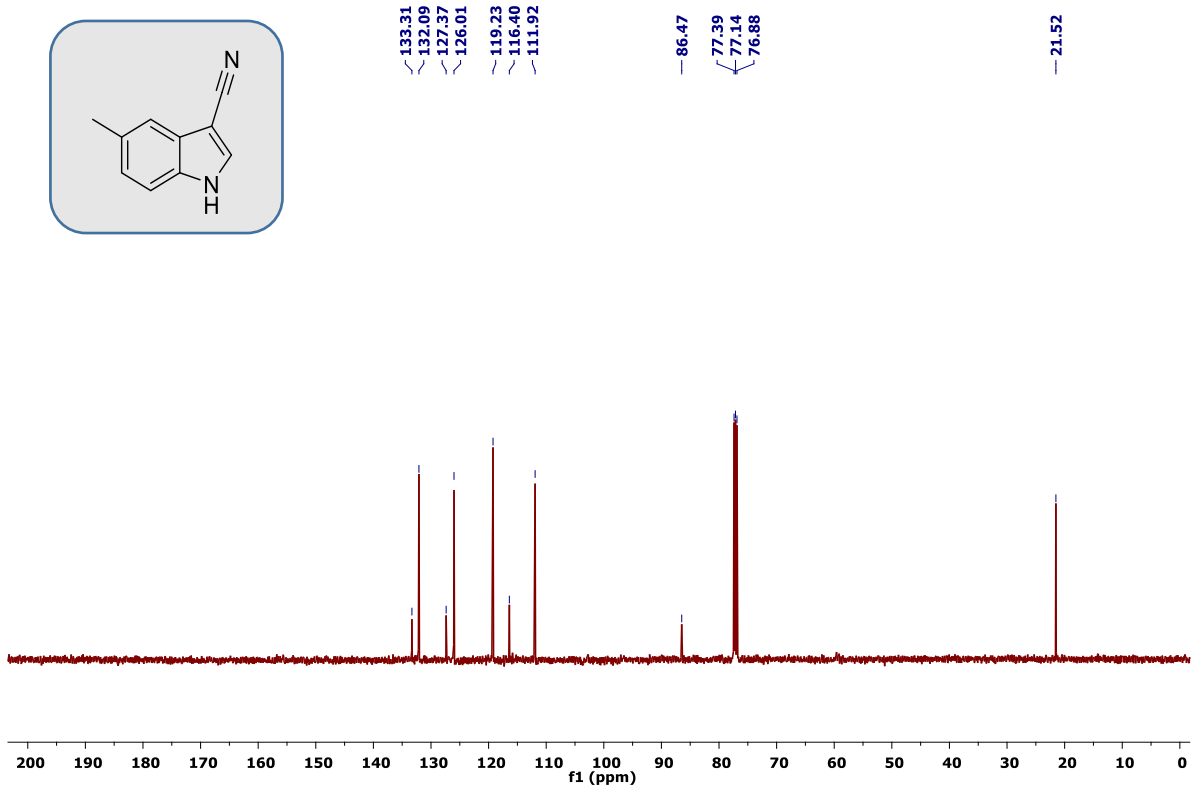


5-methyl-1H-indole-3-carbonitrile(3c)

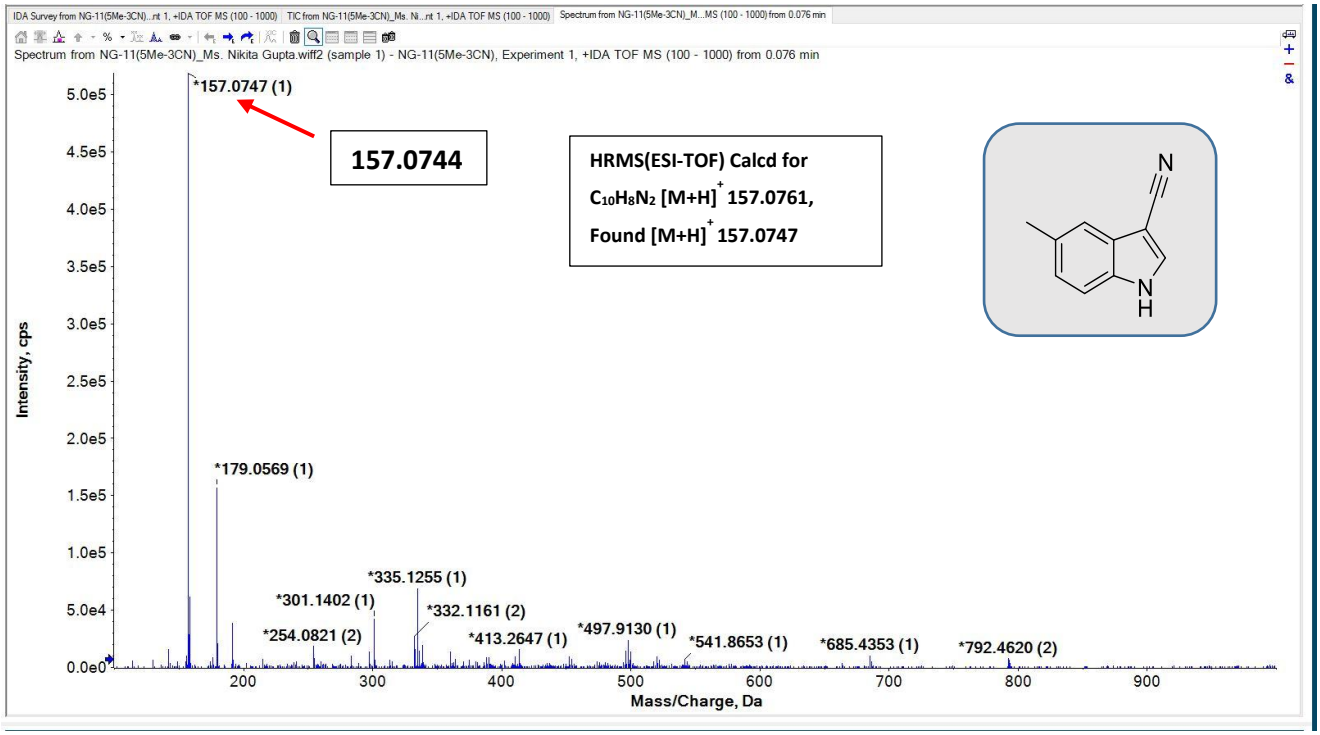
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

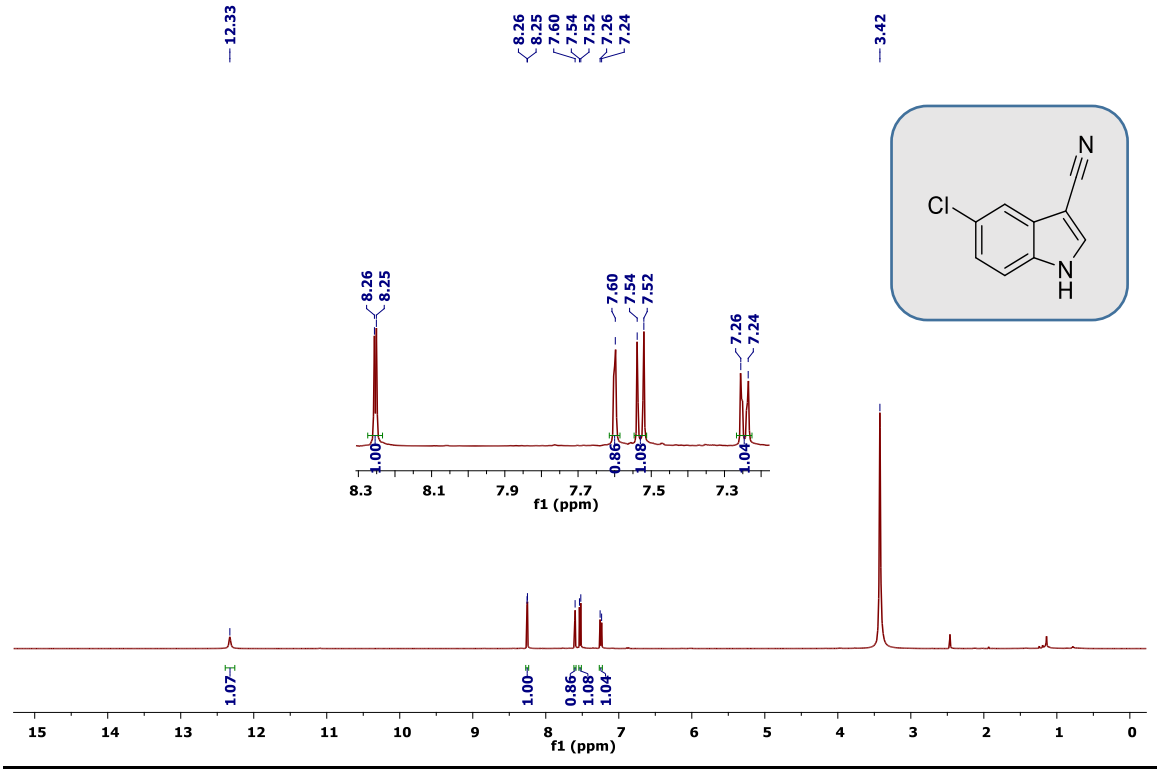


HRMS-Spectra

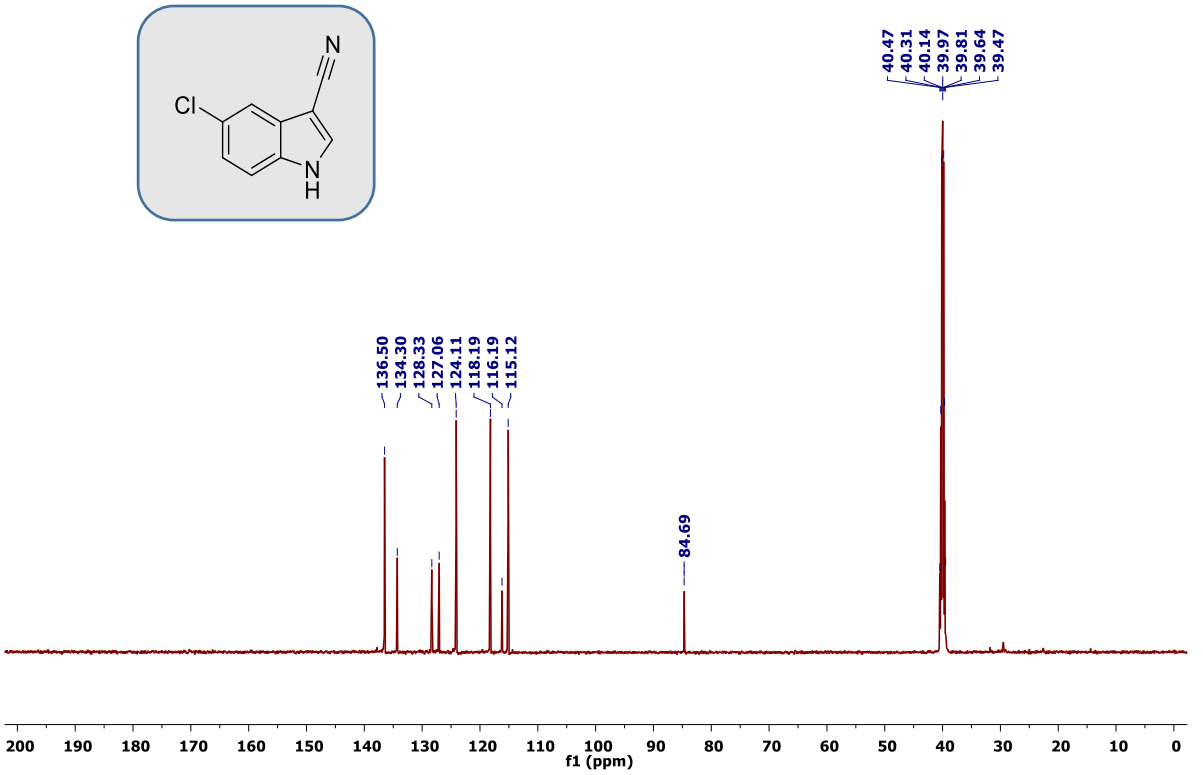


5-chloro-1H-indole-3-carbonitrile(3d)

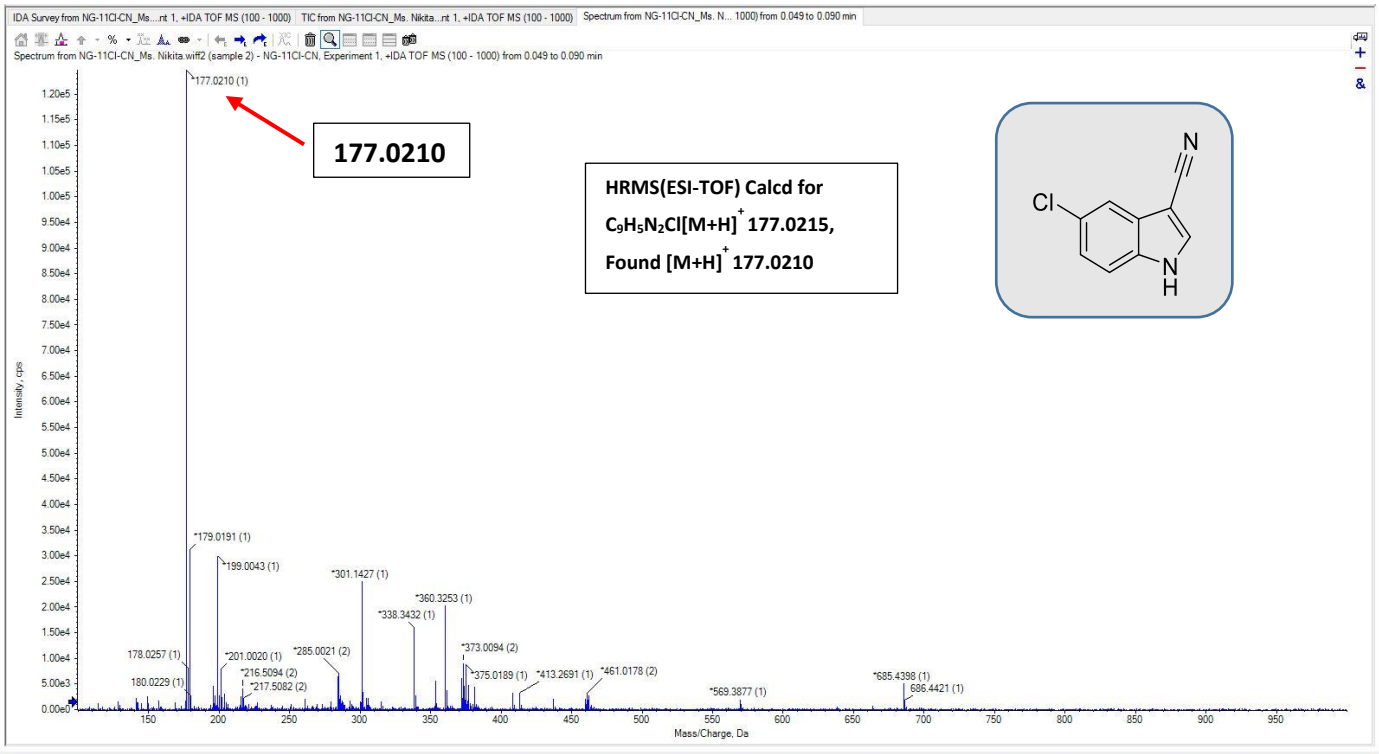
^{1}H NMR (500 MHz, DMSO-d6)



^{13}C NMR (126MHz, DMSO-d6)

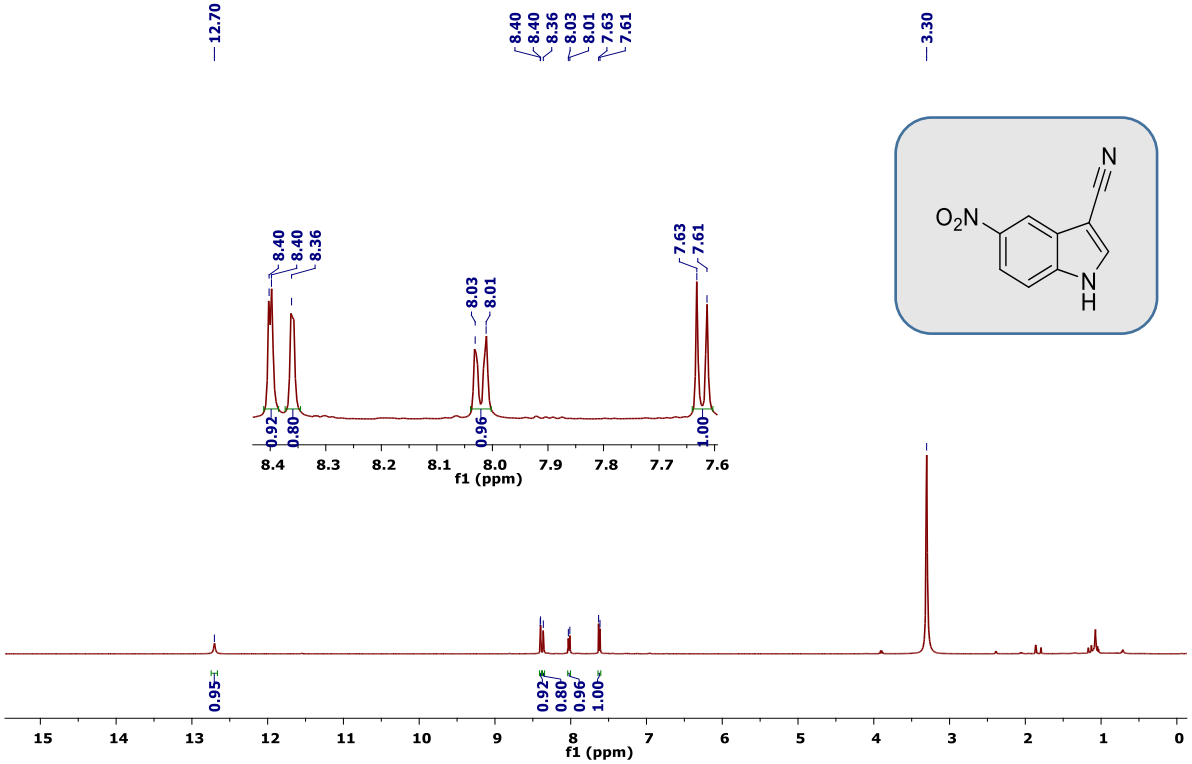


HRMS-Spectra

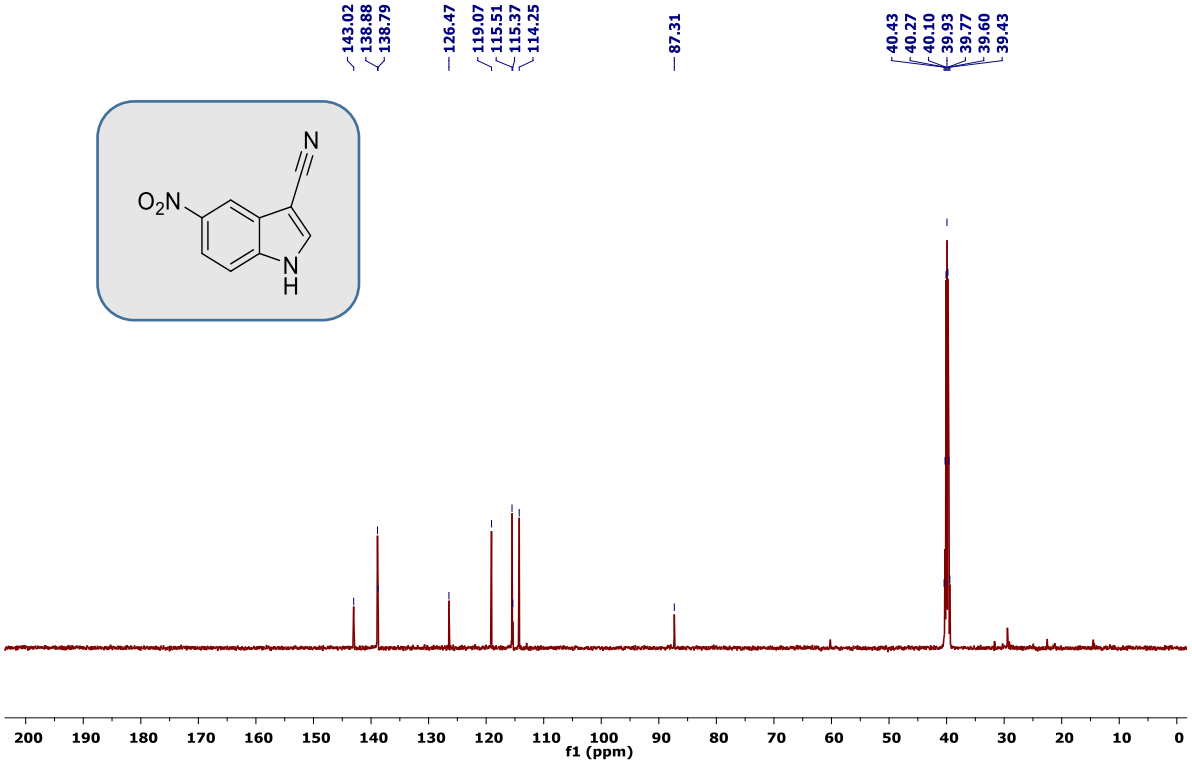


5-nitro-1H-indole-3-carbonitrile(3e)

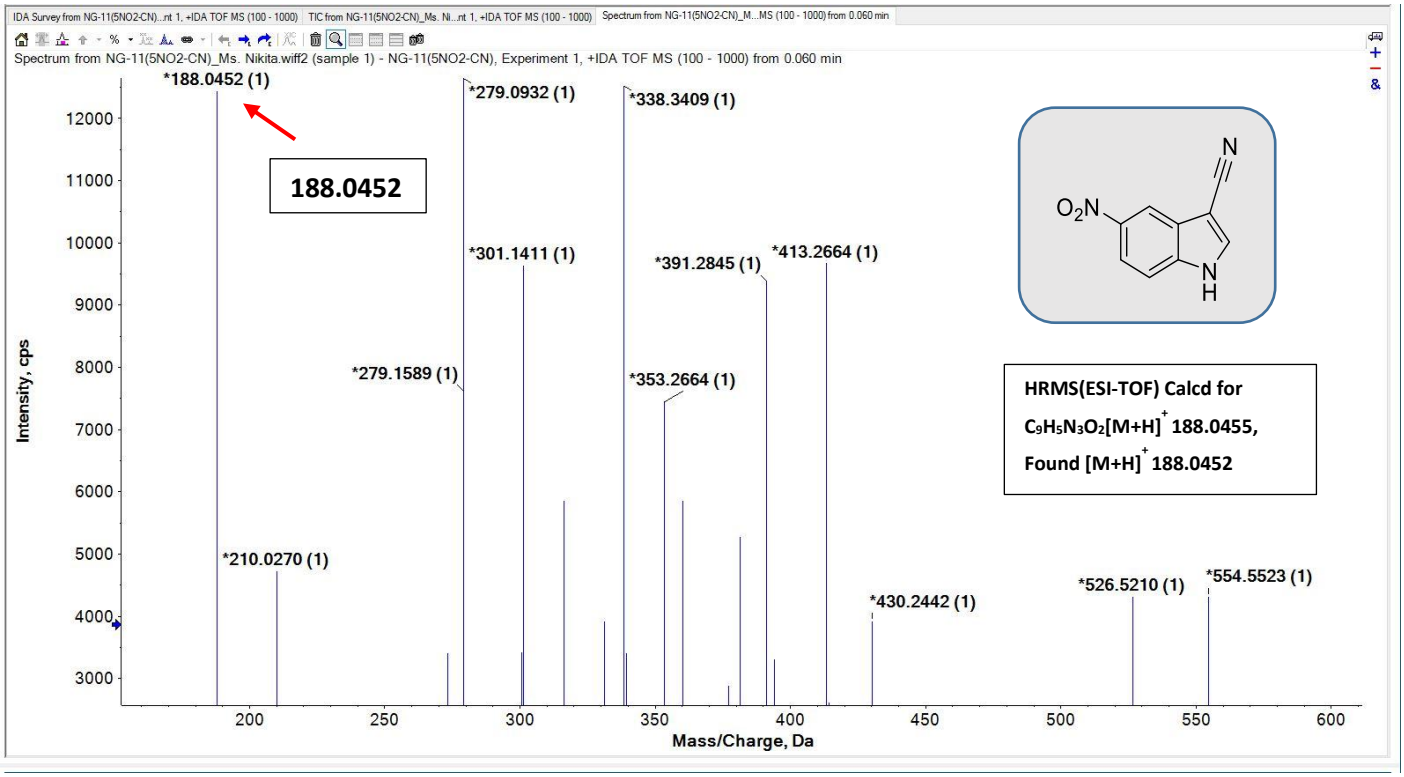
^{1}H NMR (500 MHz, DMSO-d6)



^{13}C NMR (126 MHz, DMSO-d6)

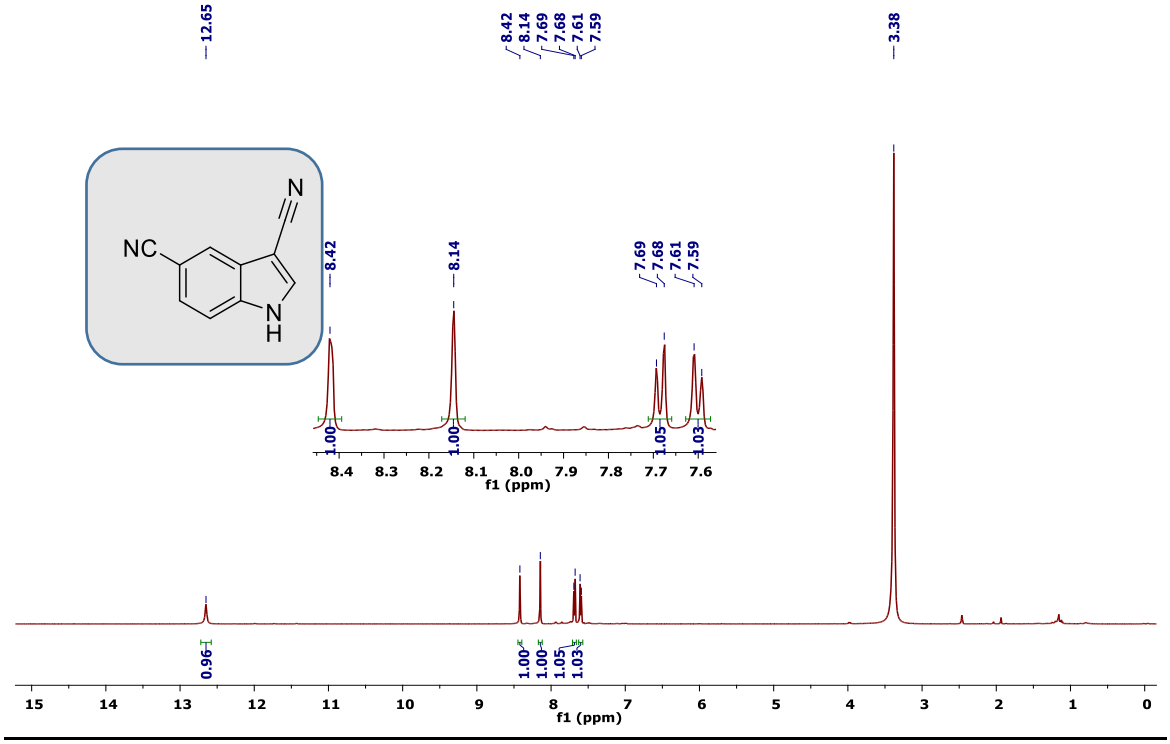


HRMS-Spectra

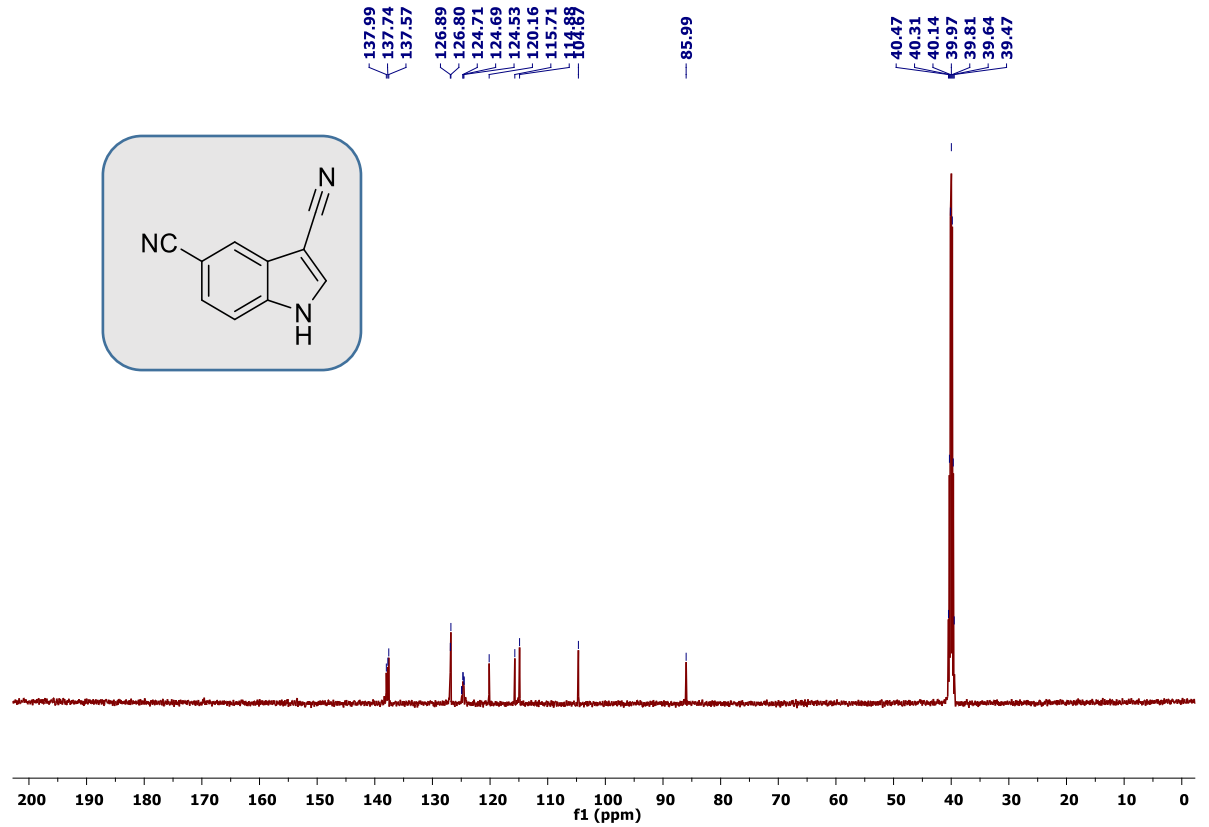


1H-indole-3,5-dicarbonitrile(3f)

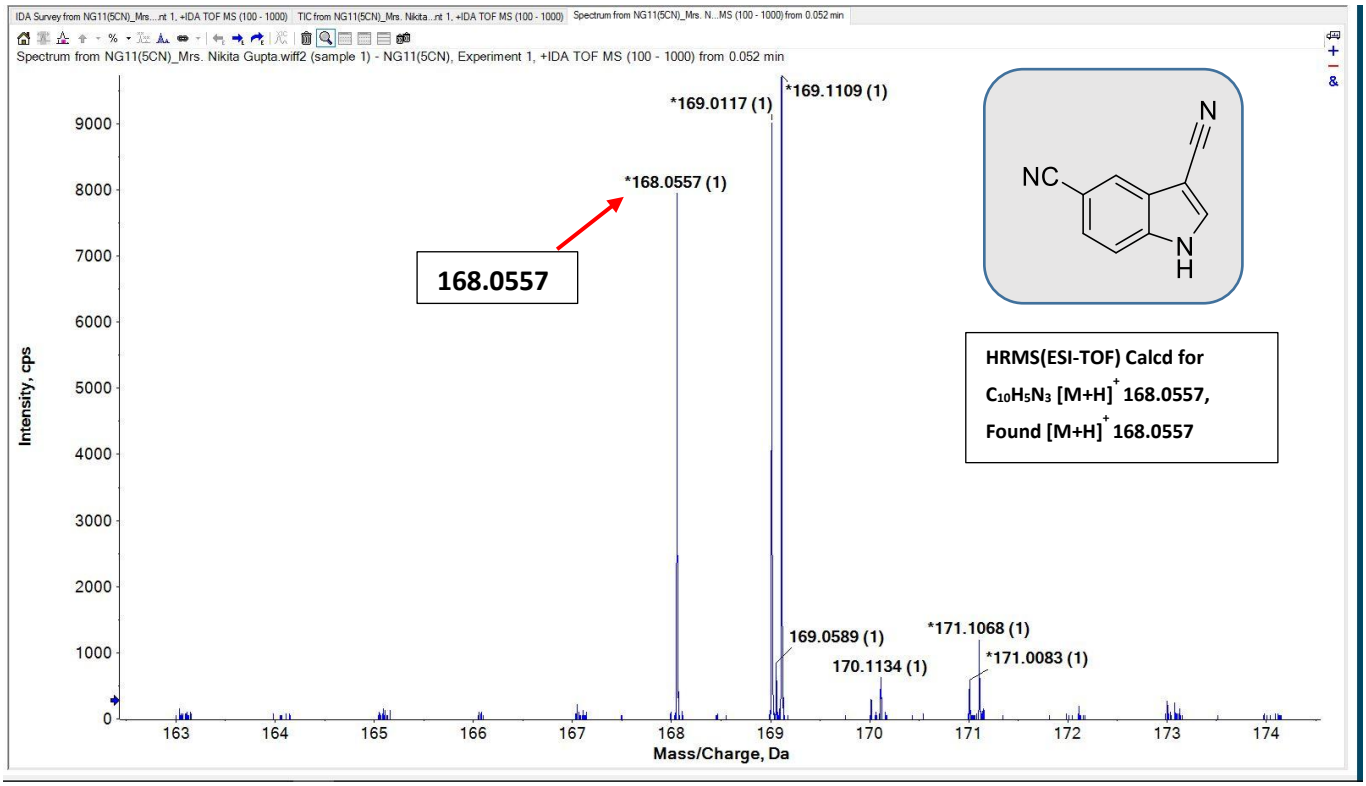
^{1}H NMR (500 MHz, DMSO-d6)



^{13}C NMR (126 MHz, DMSO-d6)

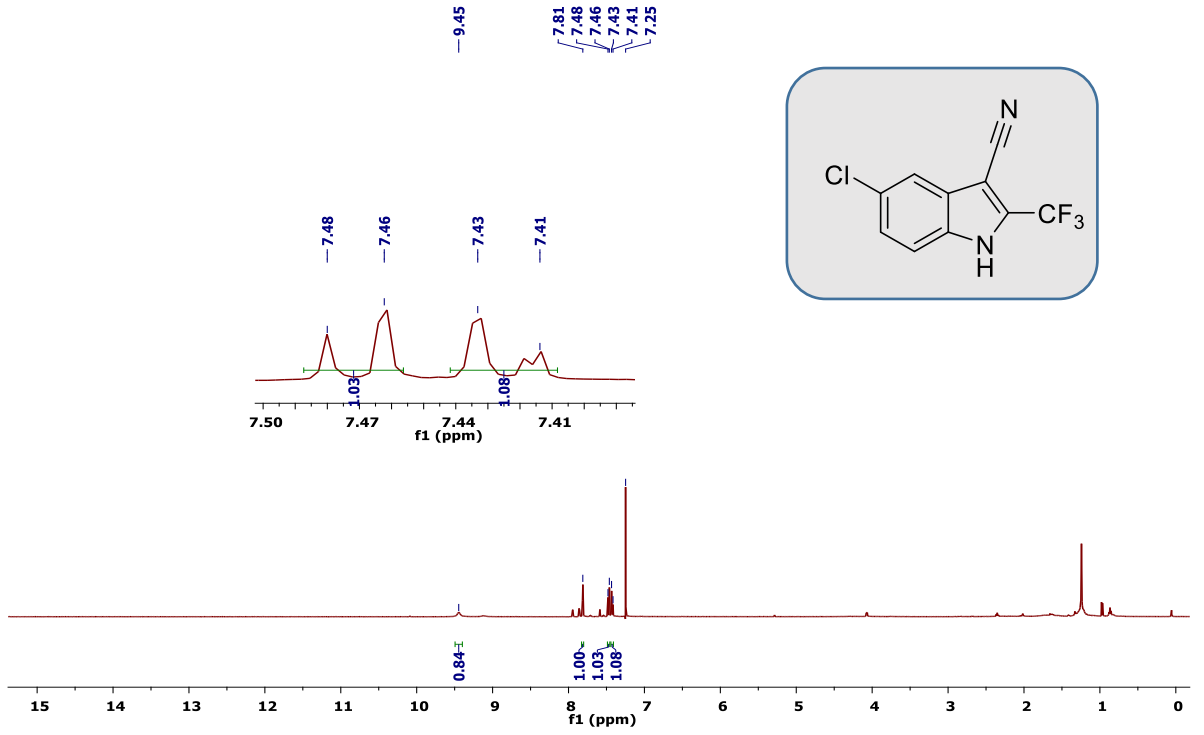


HRMS-Spectra

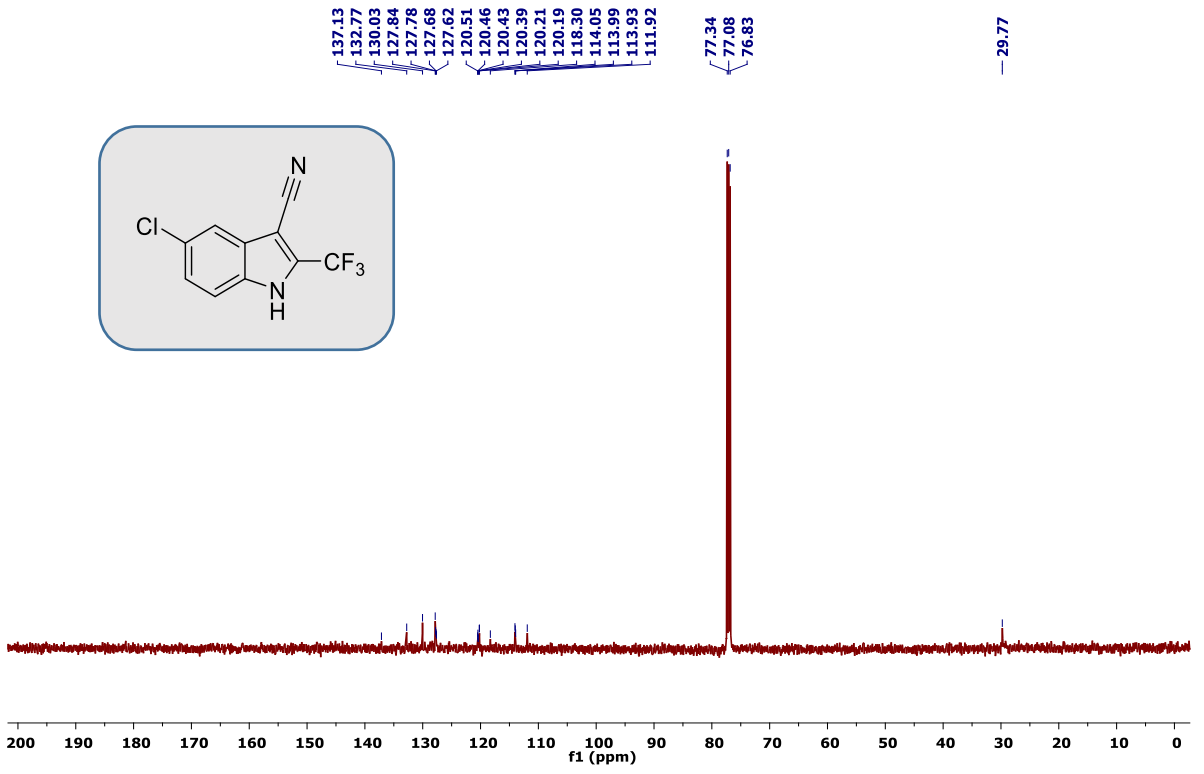


5-chloro-2-(trifluoromethyl)-1H-indole-3-carbonitrile(3g)

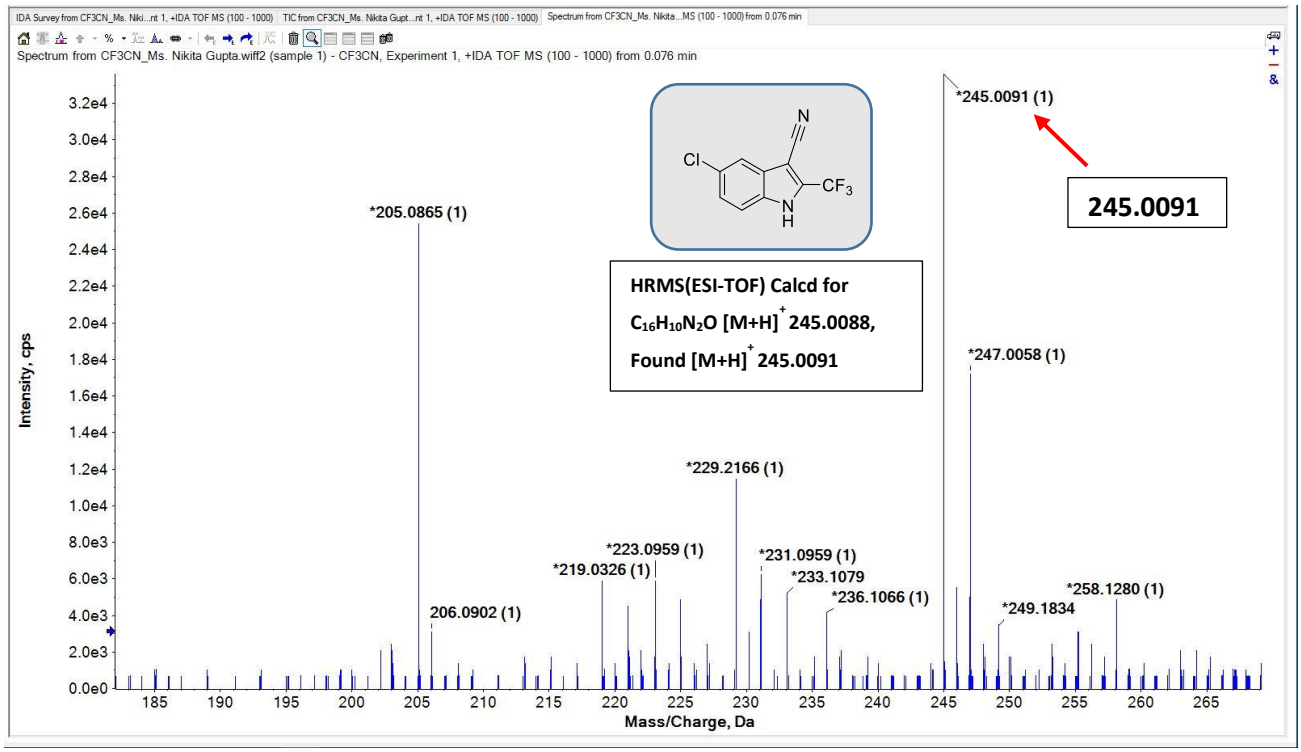
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



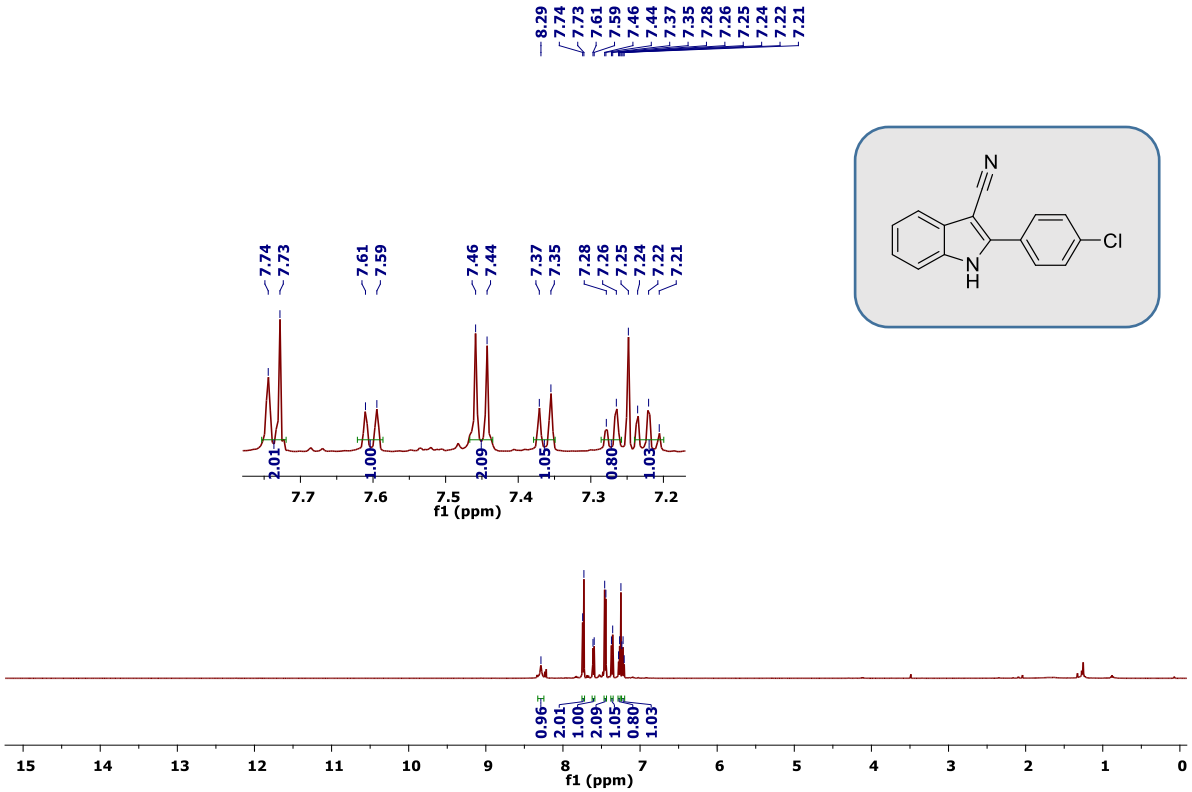
HRMS-Spectra



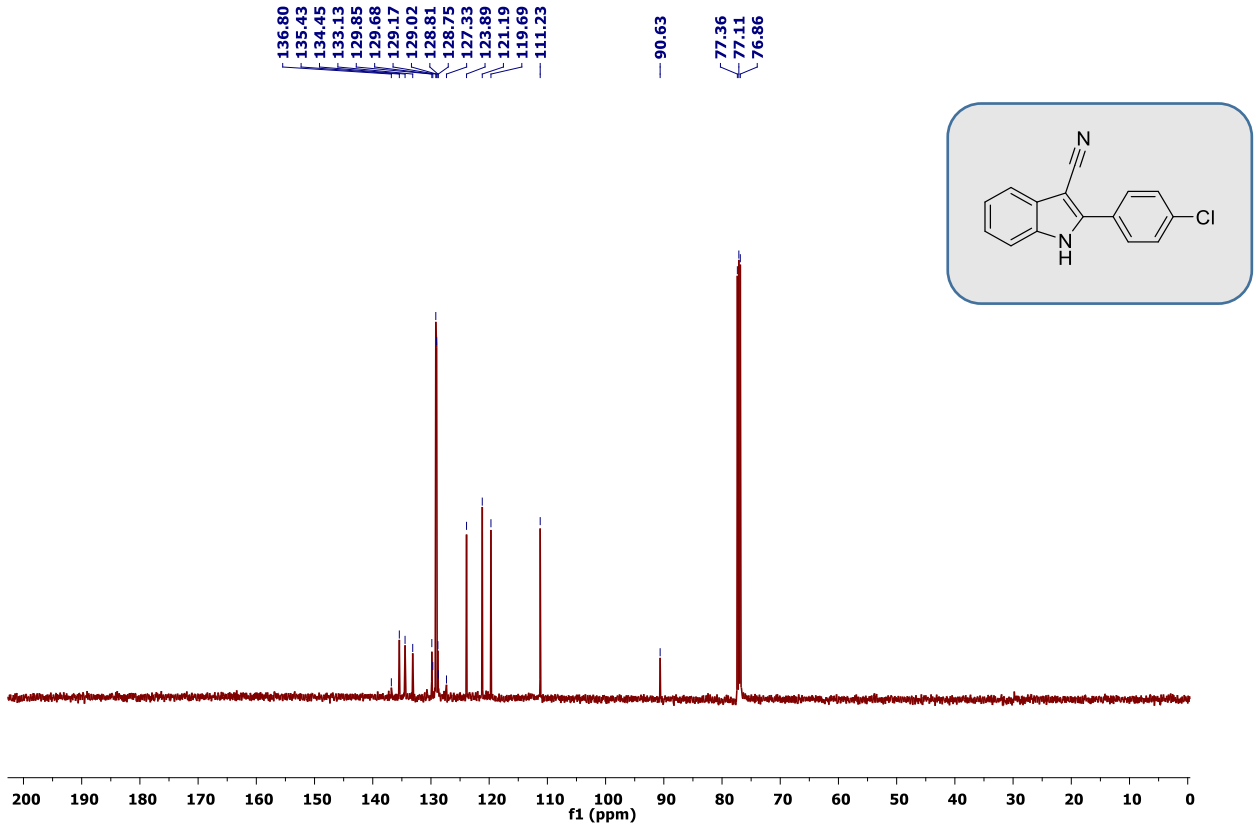
2-(4-

chlorophenyl)-1-methyl-1H-indole-3-carbonitrile(3h)

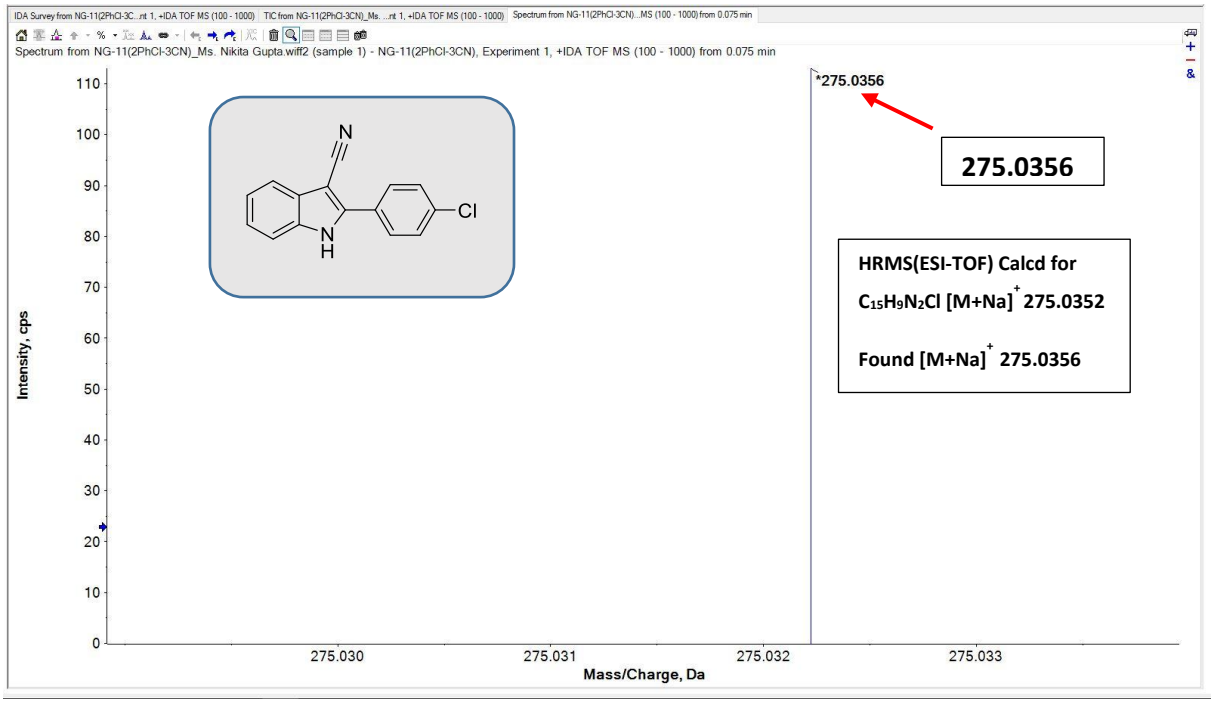
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

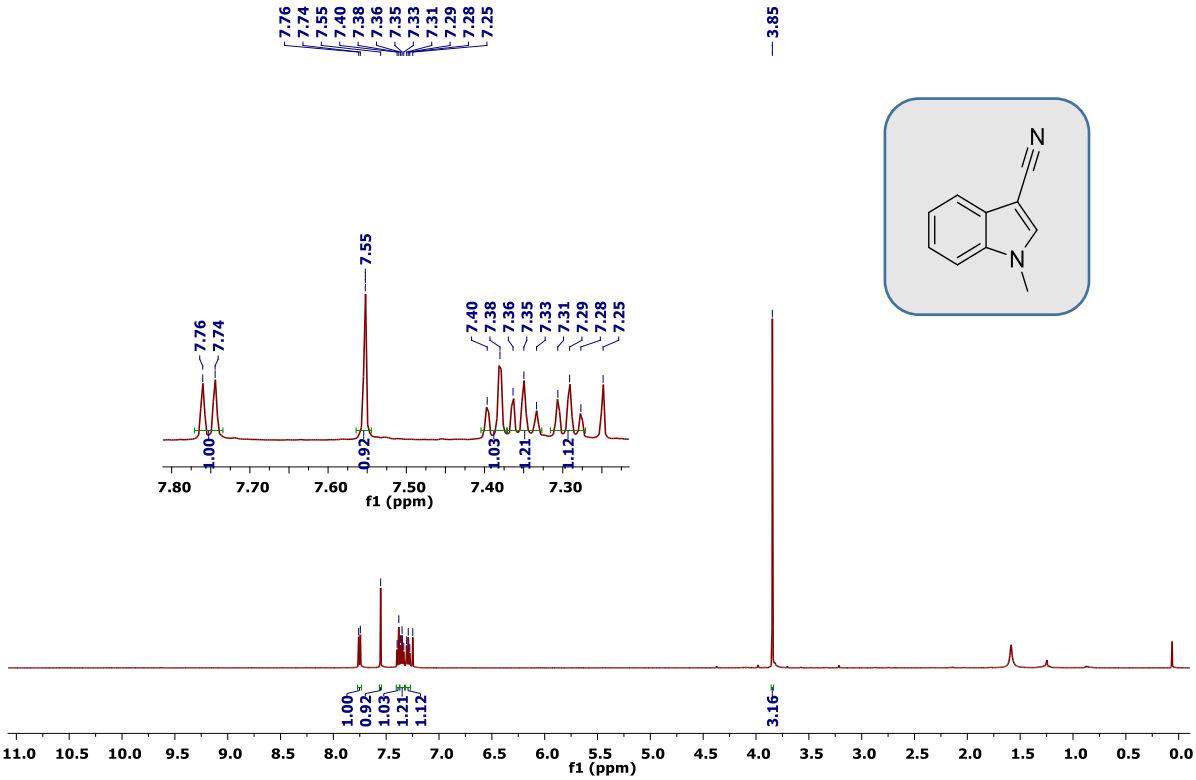


HRMS-Spectra

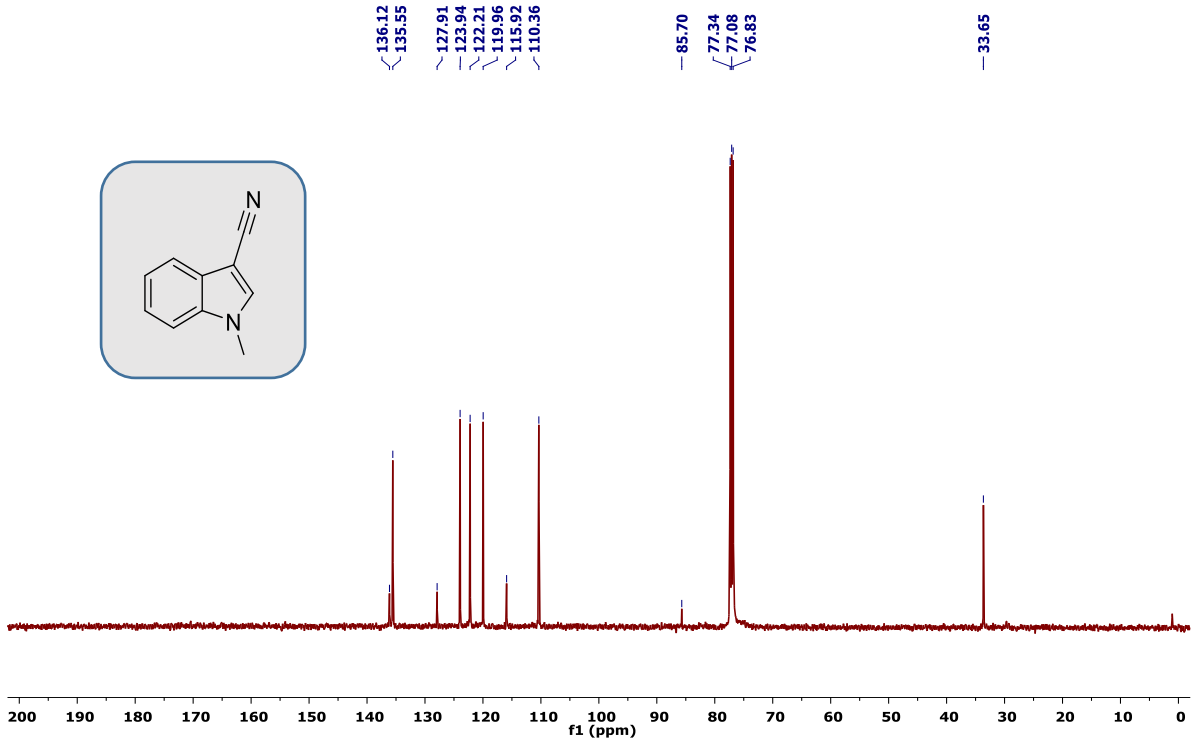


1-methyl-1H-indole-3-carbonitrile(3i)

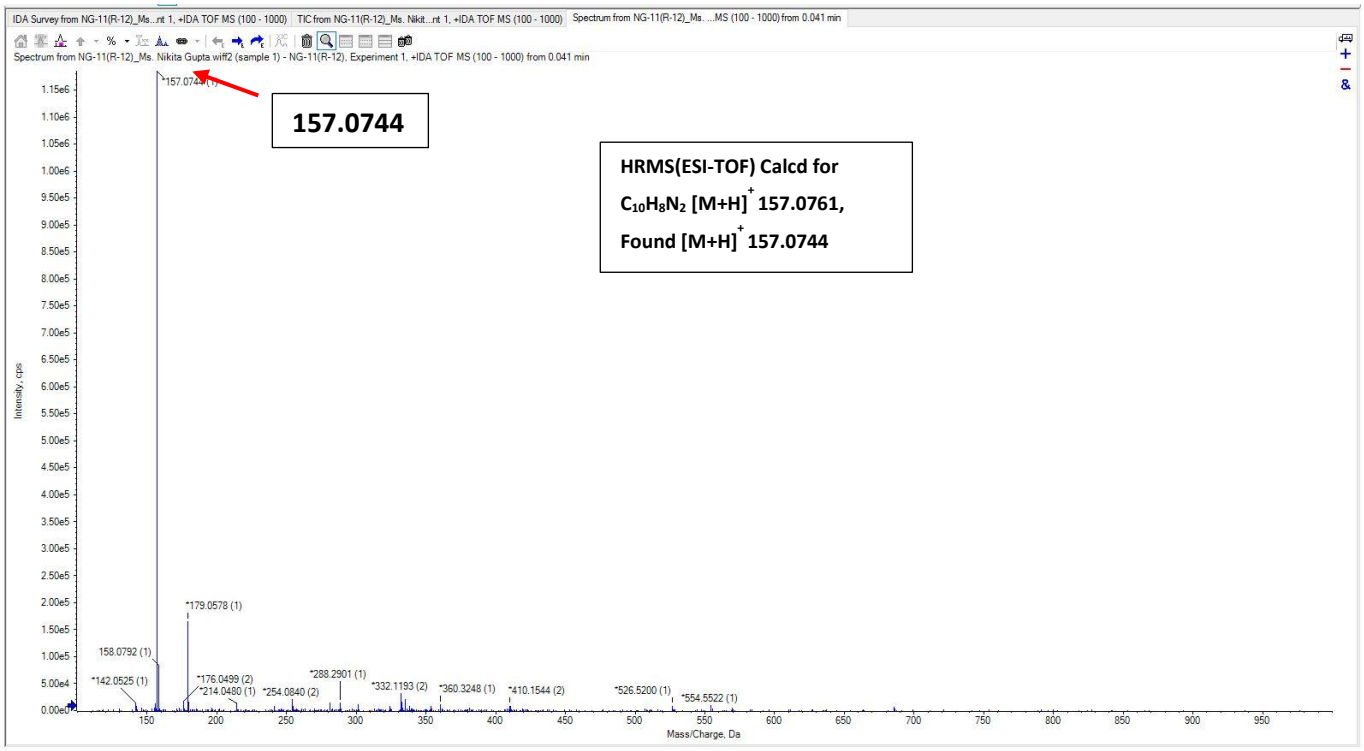
^{1}H NMR (500 MHz, $CDCl_3$)

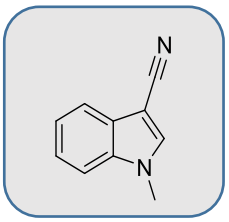


^{13}C NMR (126 MHz, $CDCl_3$)



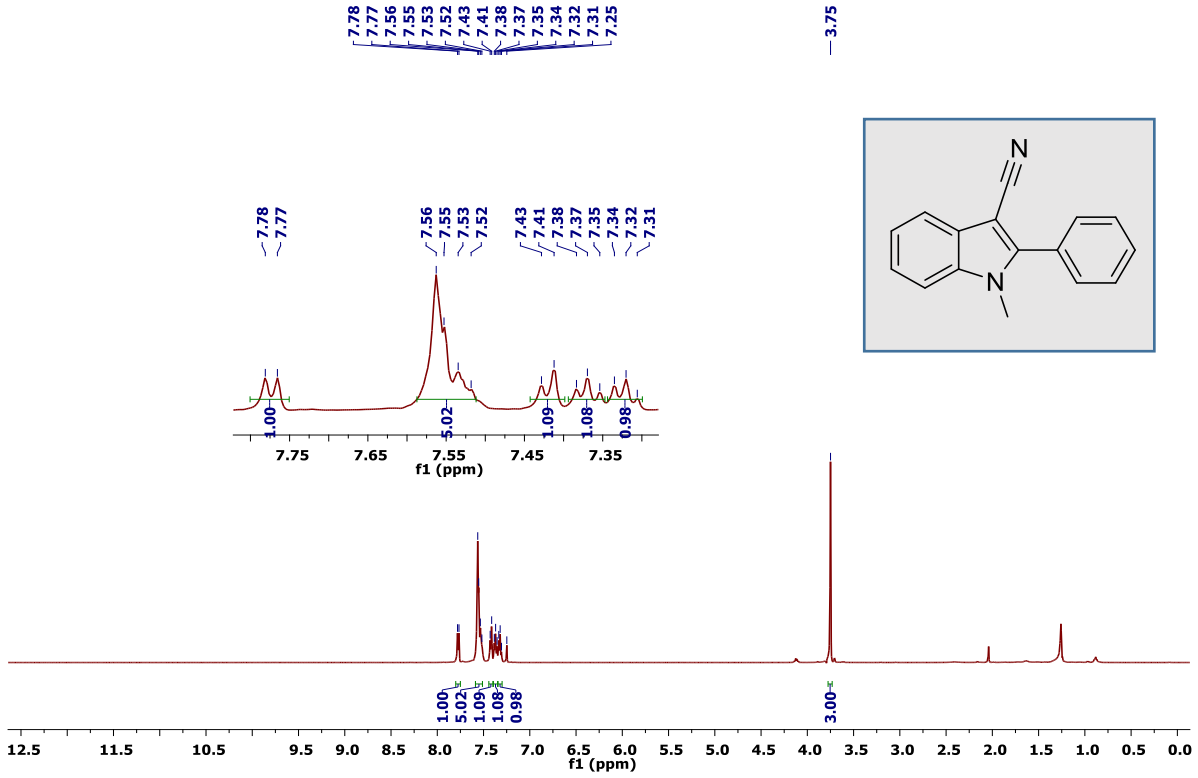
HRMS-Spectra



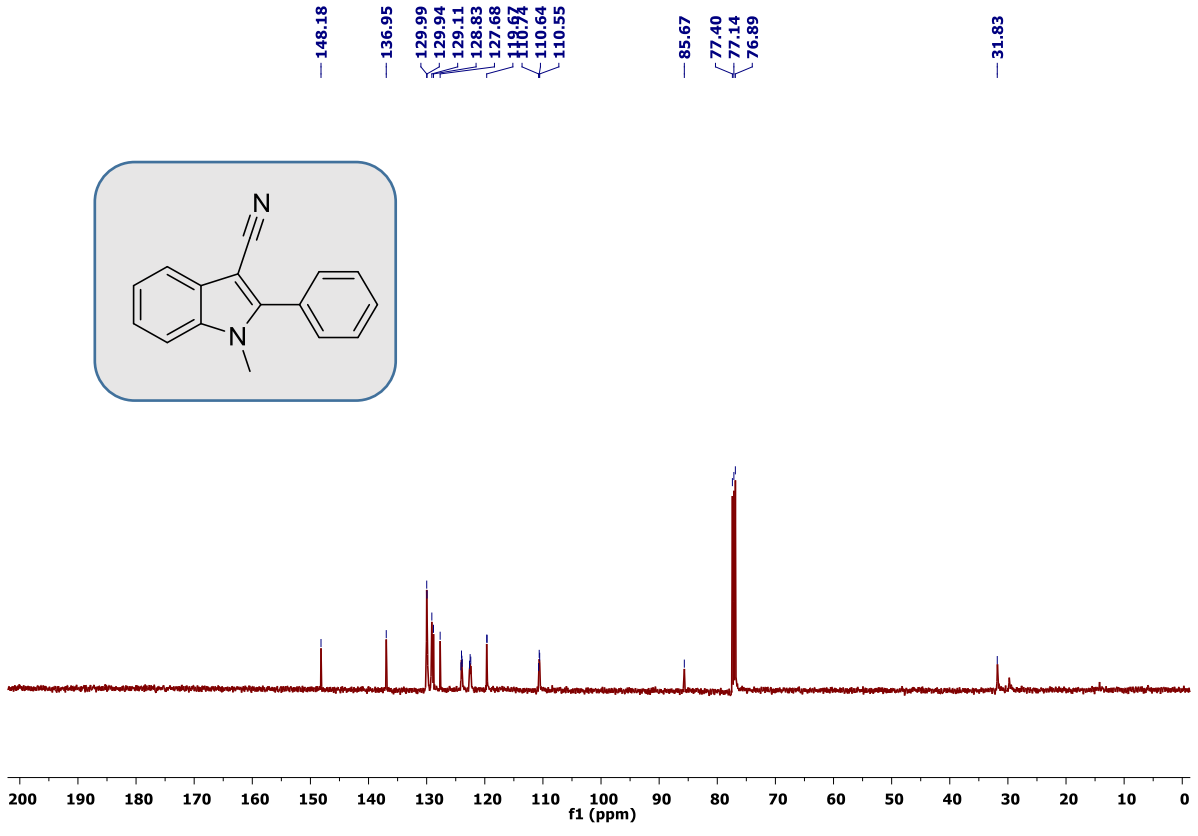


1-methyl-2-phenyl-1H-indole-3-carbonitrile(3j)

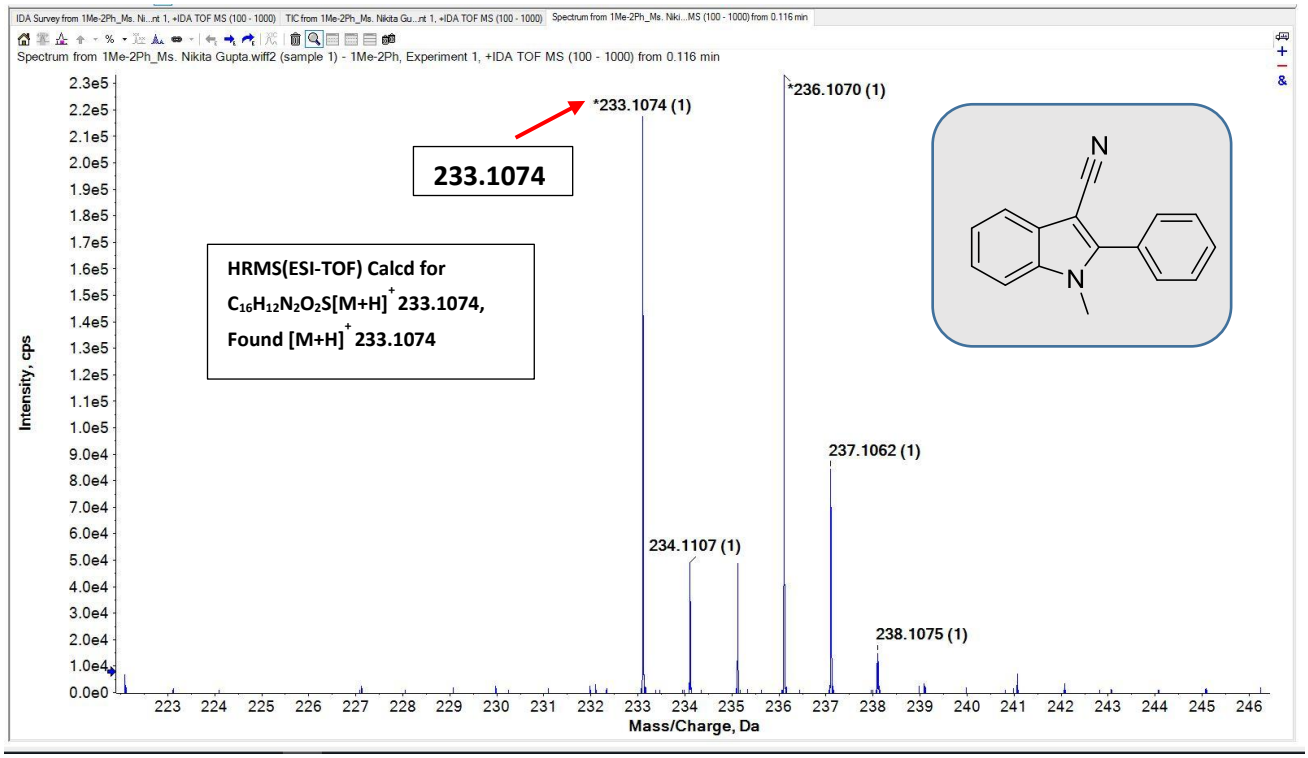
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

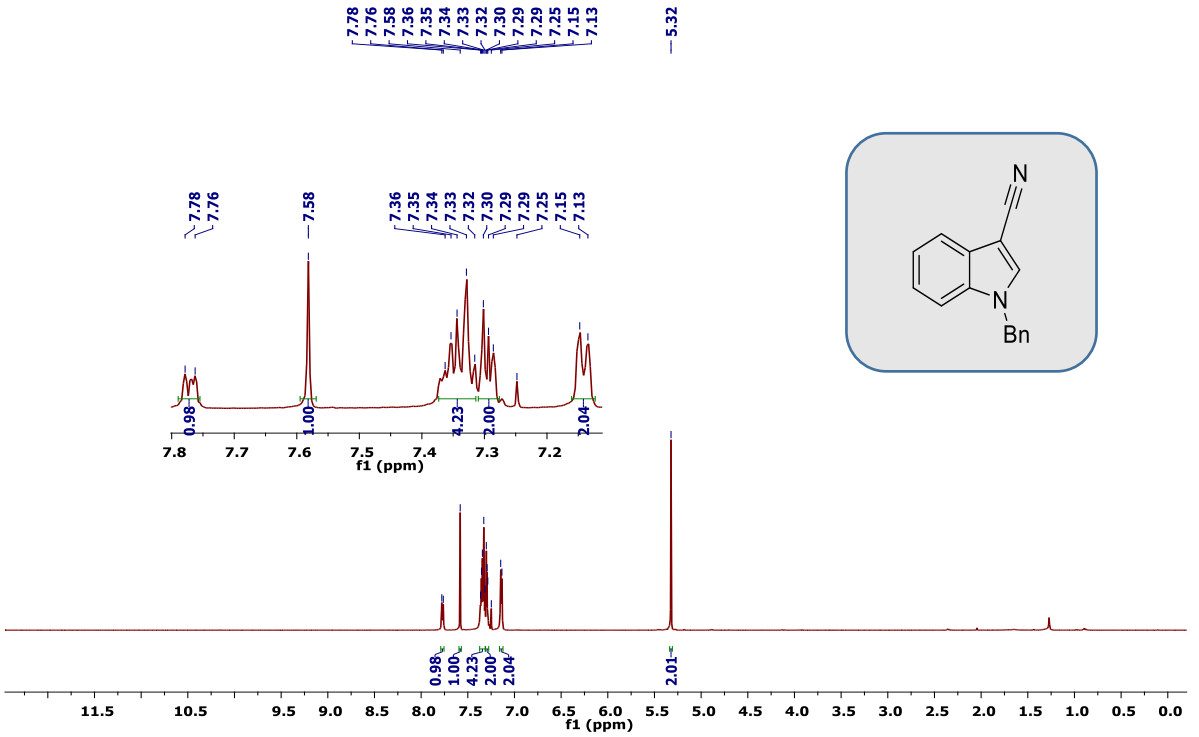


HRMS-Spectra

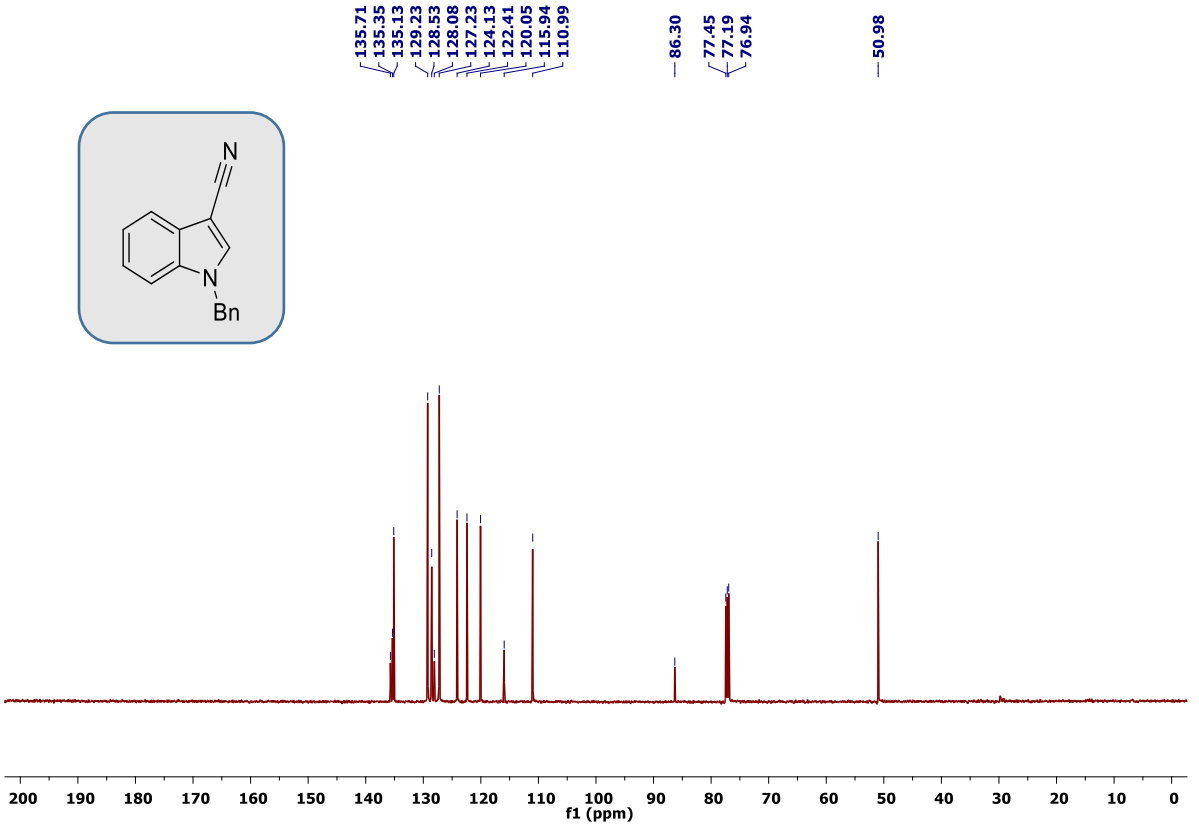


1-benzyl-1H-indole-3-carbonitrile(3k)

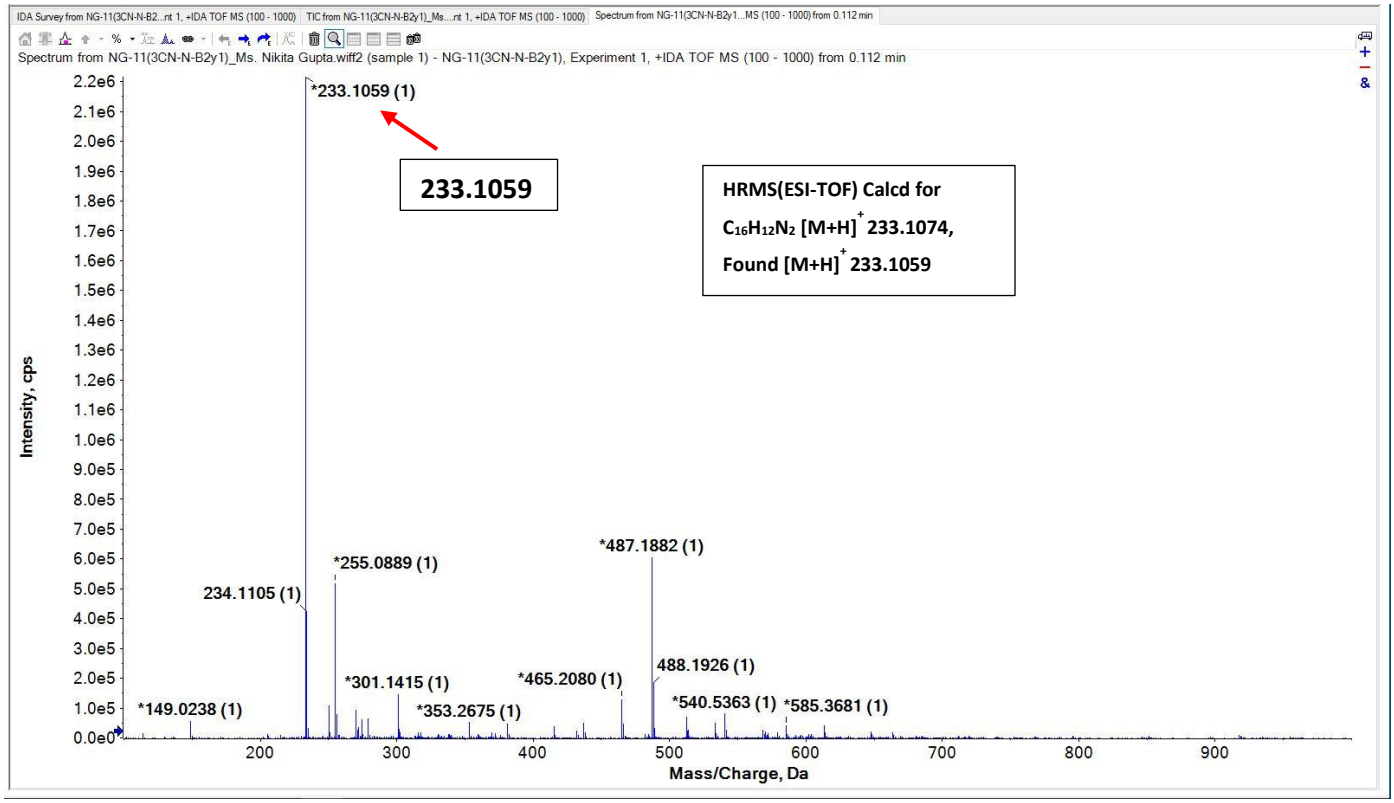
^{1}H NMR (500 MHz, $CDCl_3$)

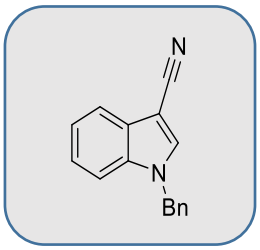


^{13}C NMR (126 MHz, $CDCl_3$)



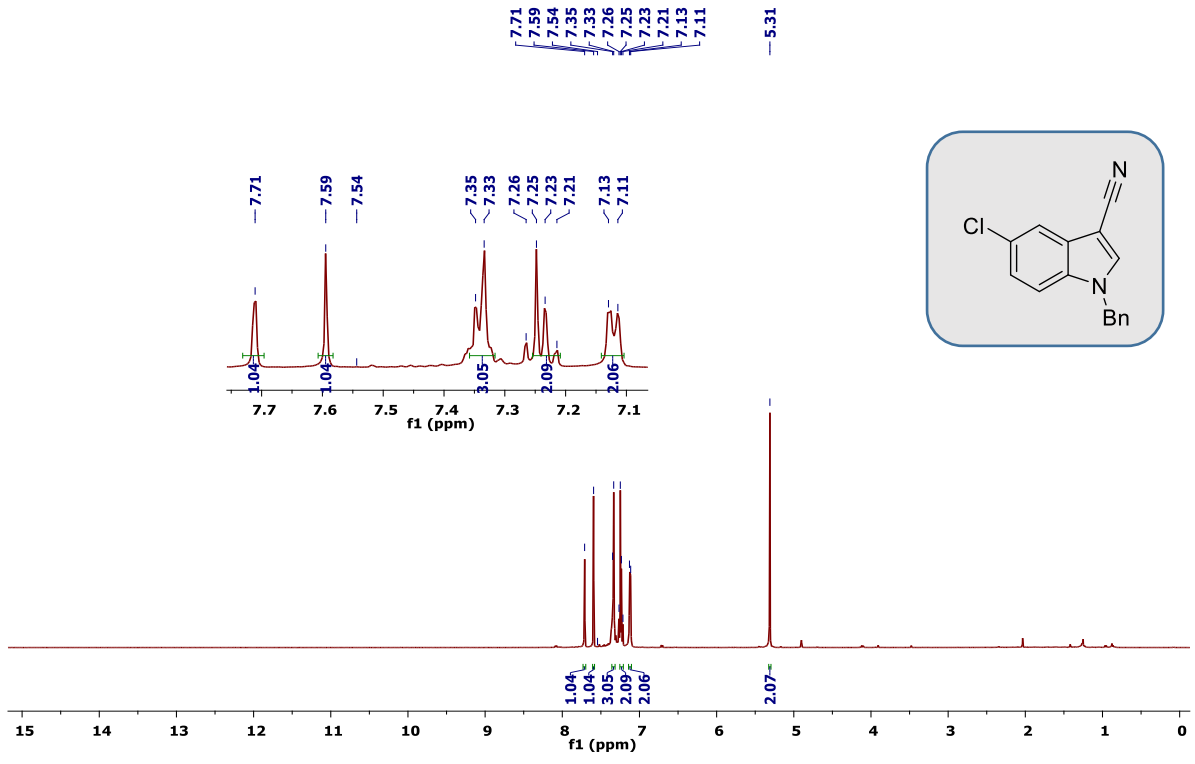
HRMS-Spectra



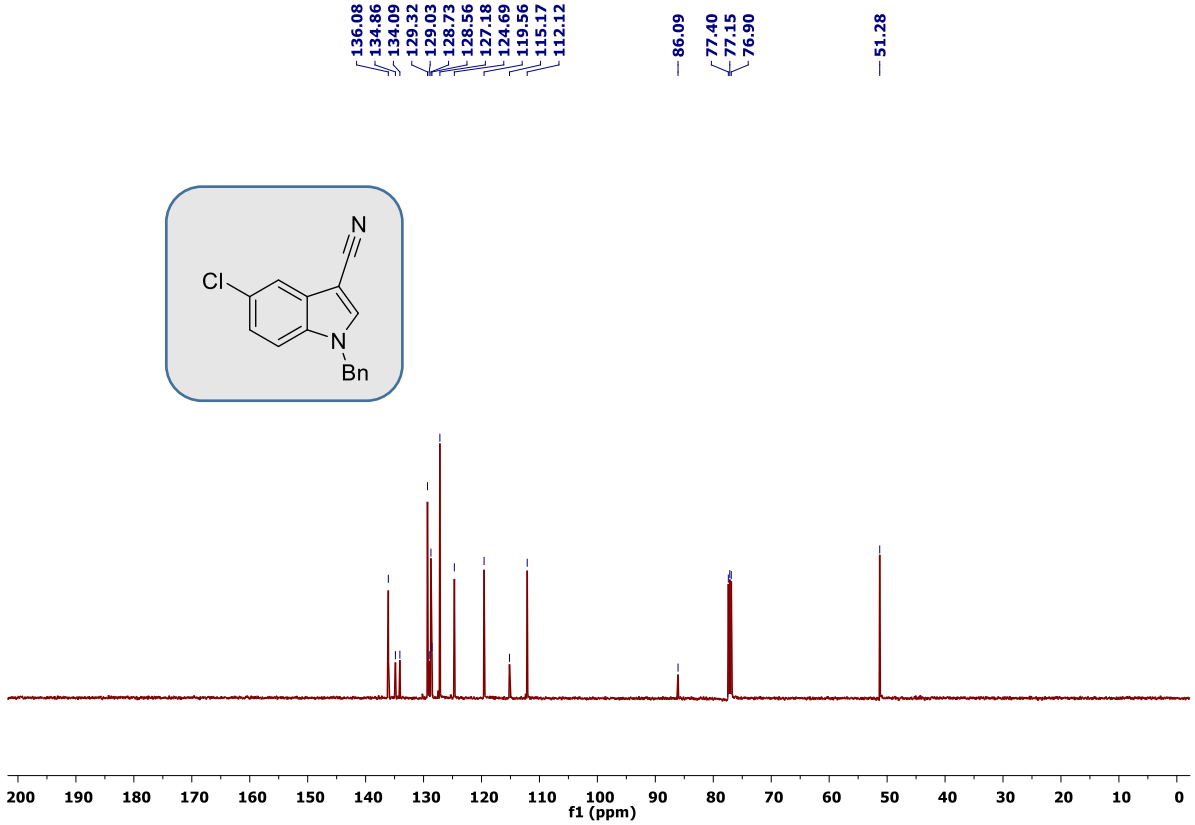


1-benzyl-5-chloro-1H-indole-3-carbonitrile(3l)

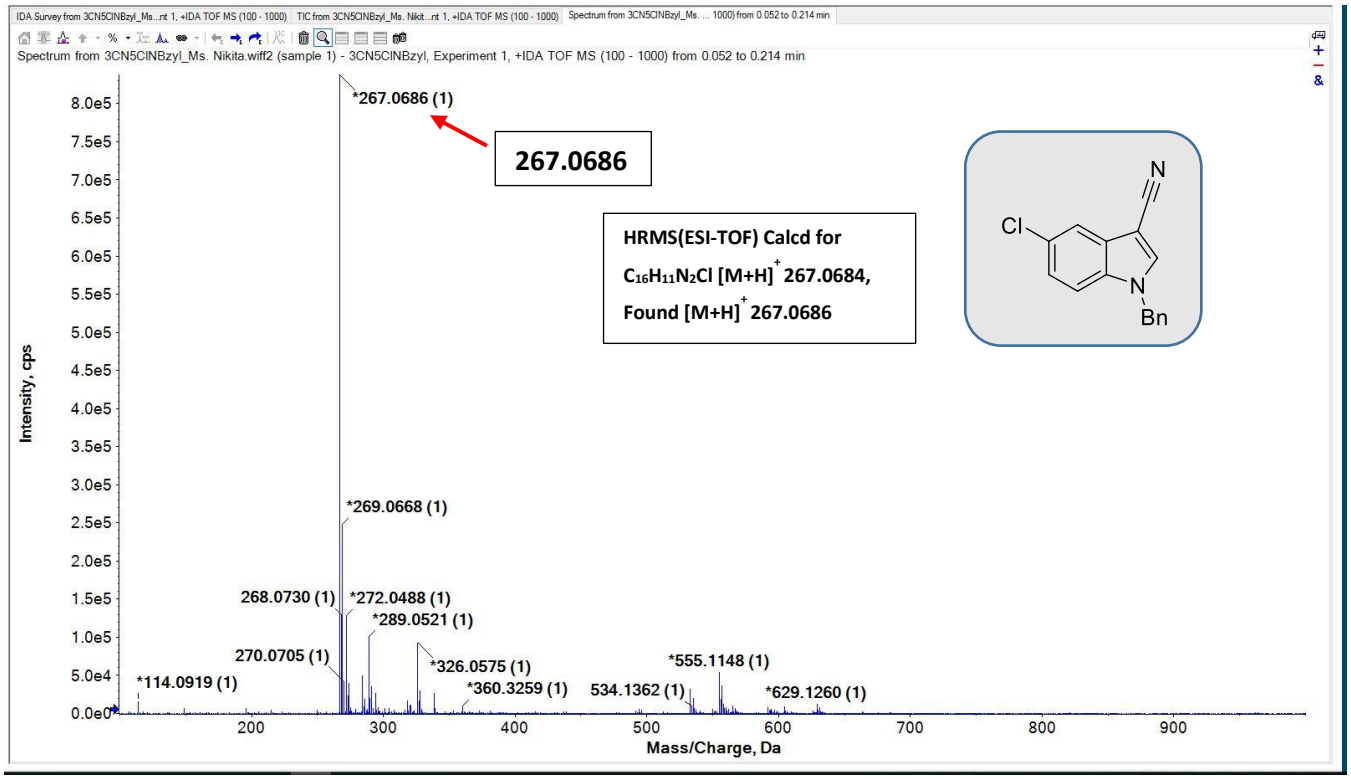
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



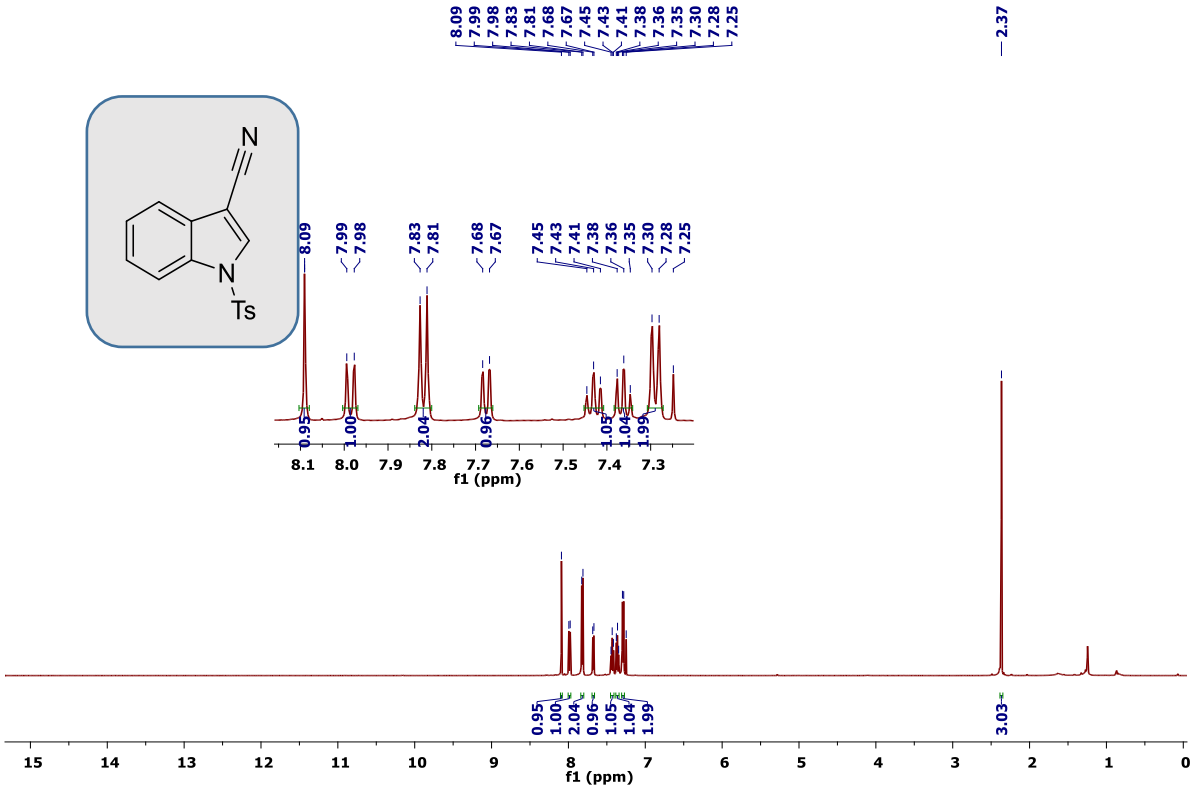
HRMS-Spectra



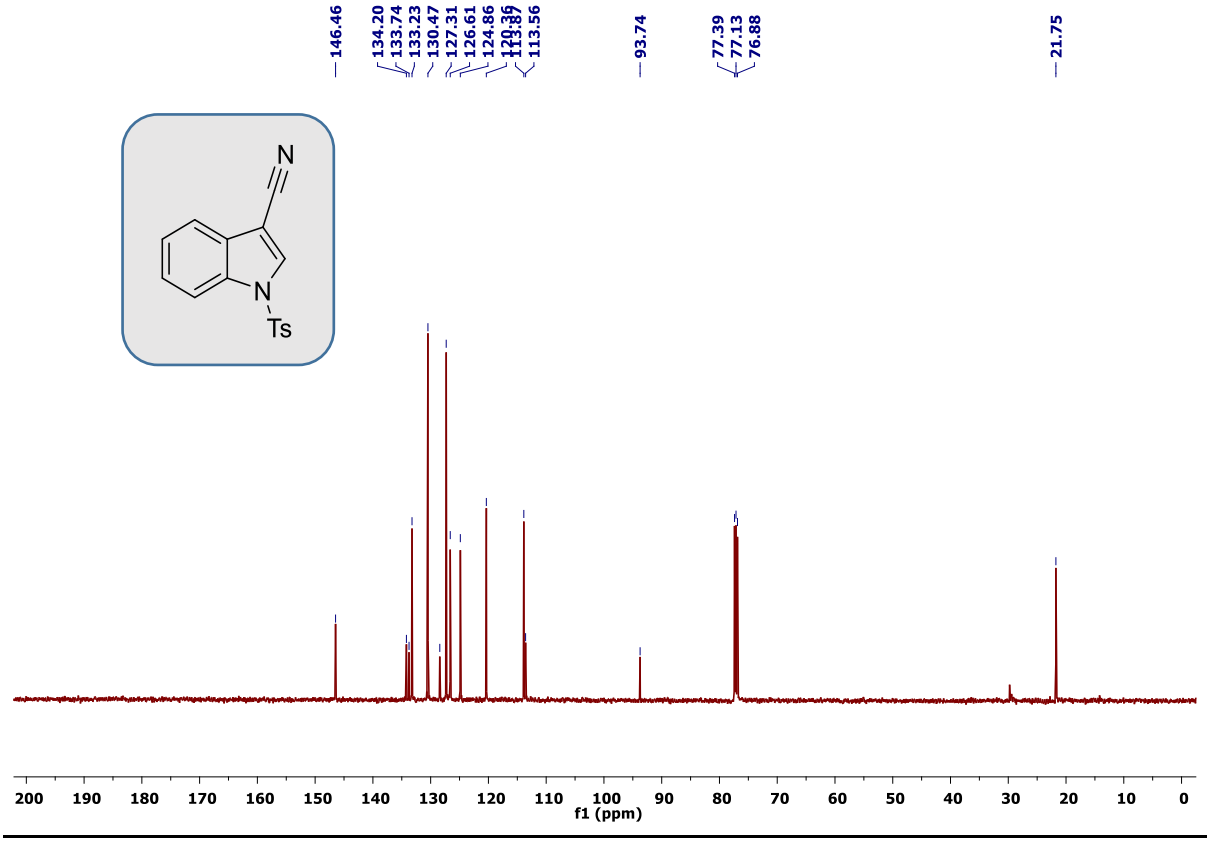
1-

tosyl-1H-indole-3-carbonitrile(3m)

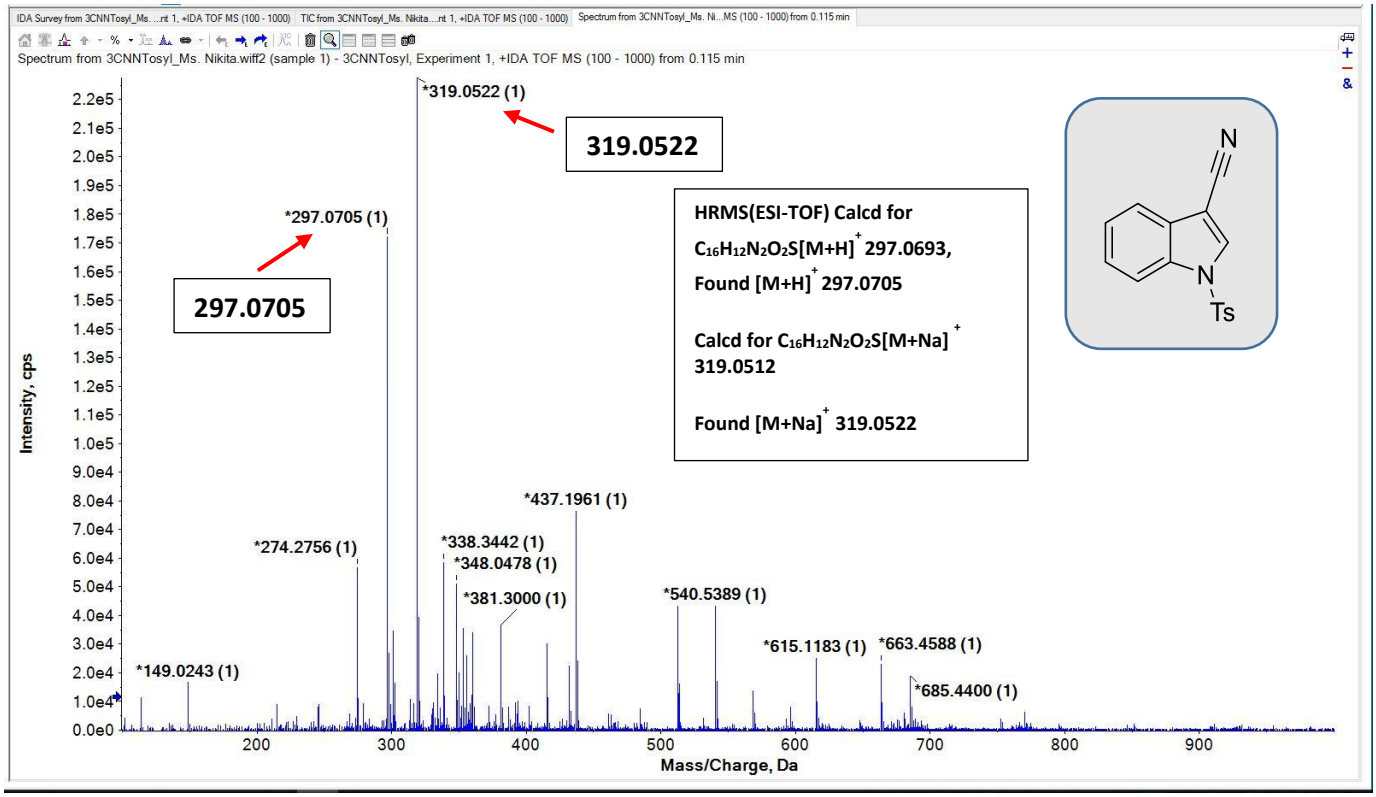
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126MHz, $CDCl_3$)

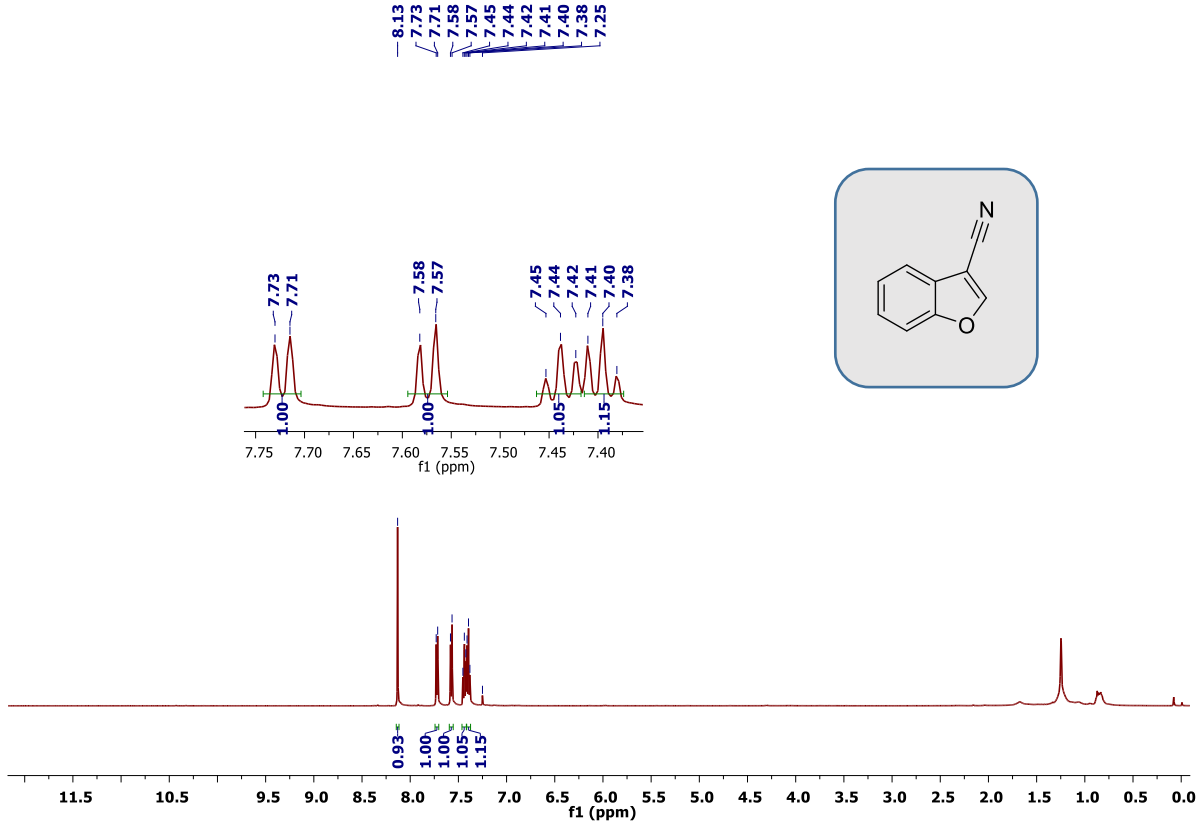


HRMS-Spectra

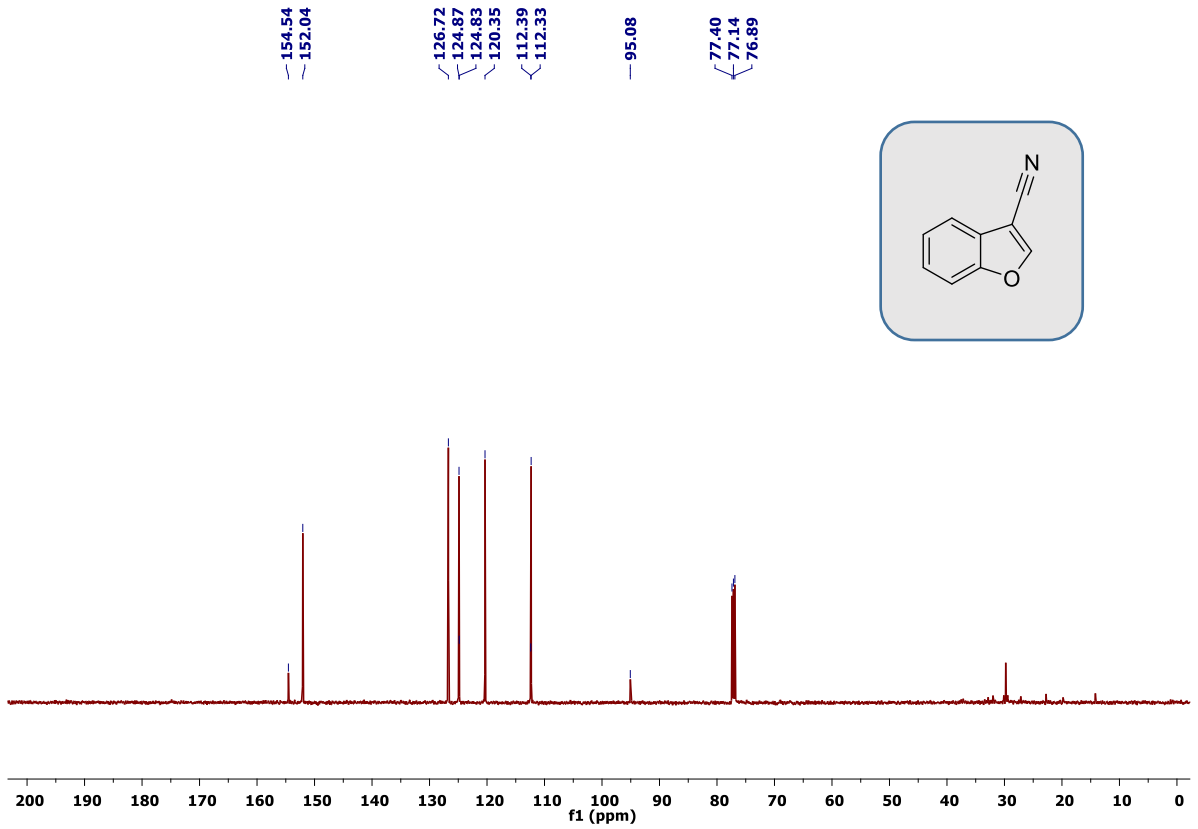


benzofuran-3-carbonitrile(3n)

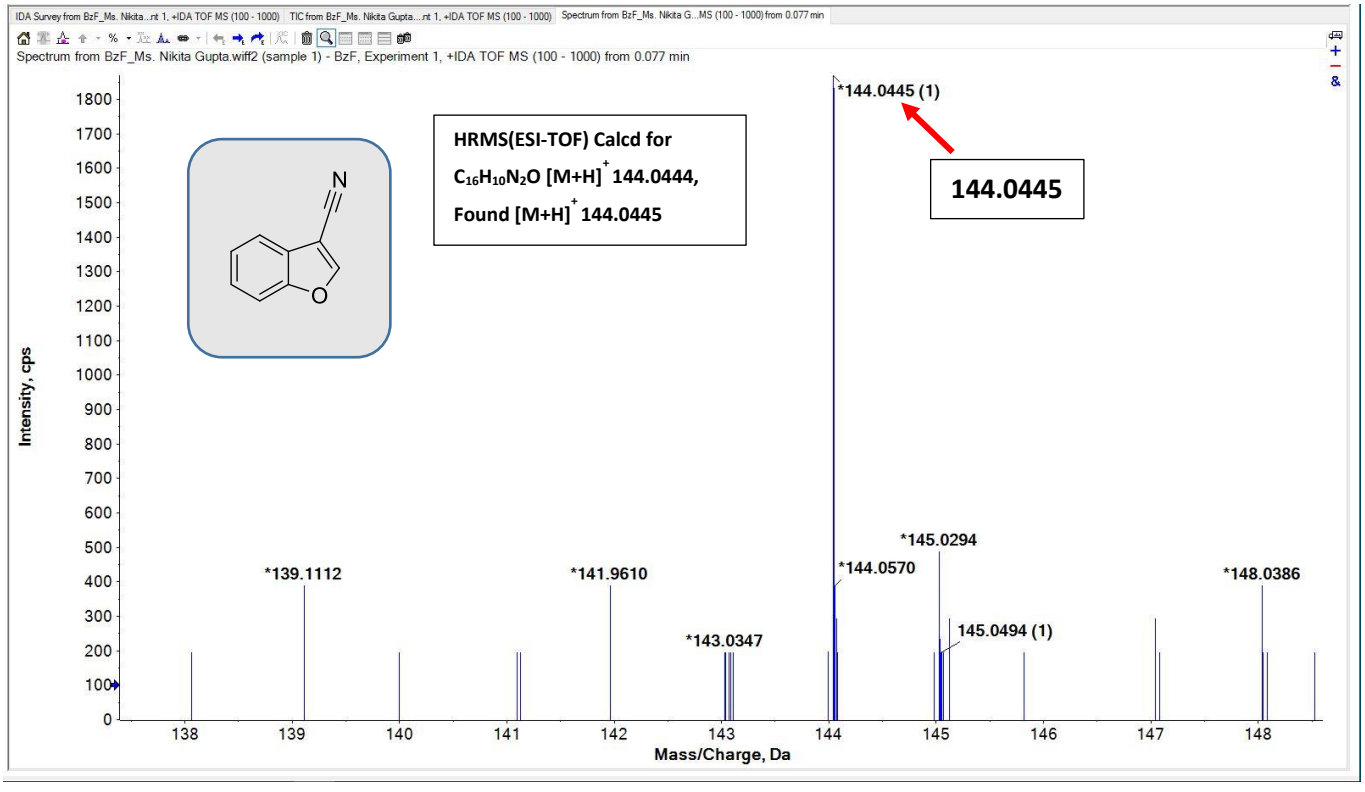
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

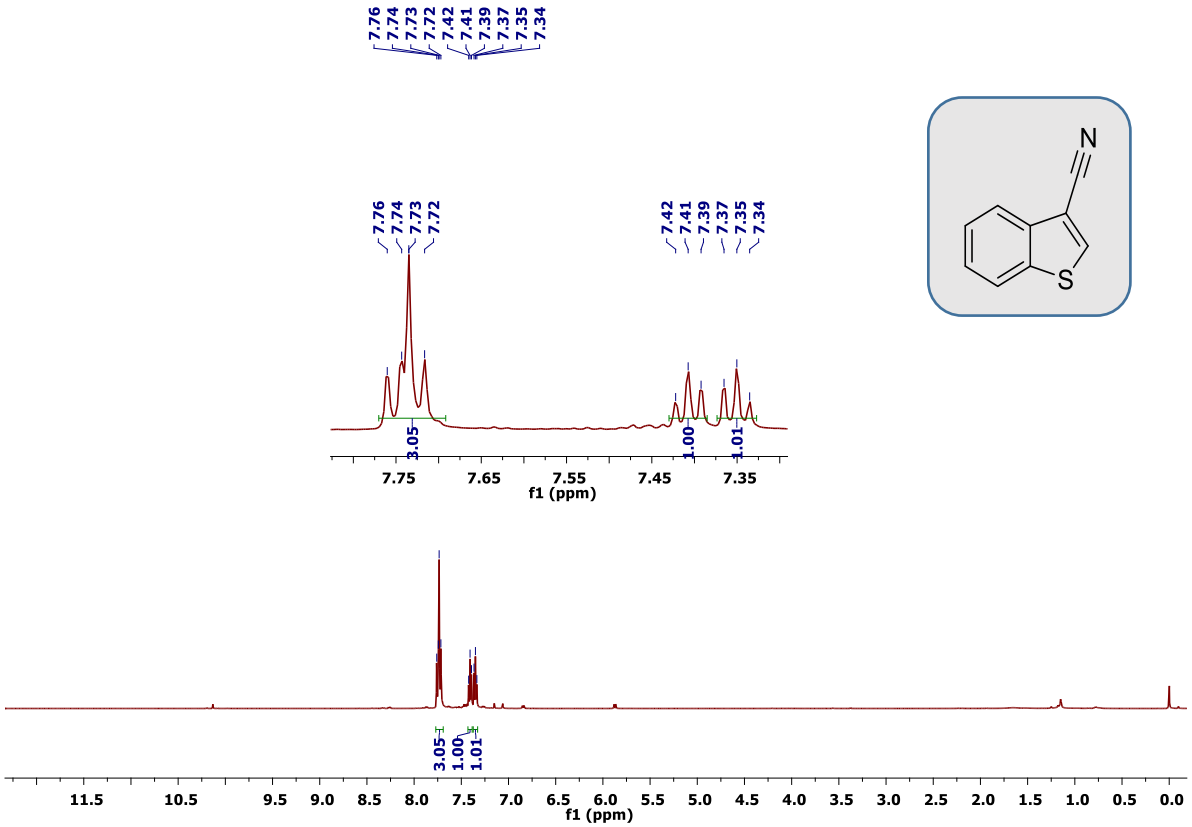


HRMS-Spectra

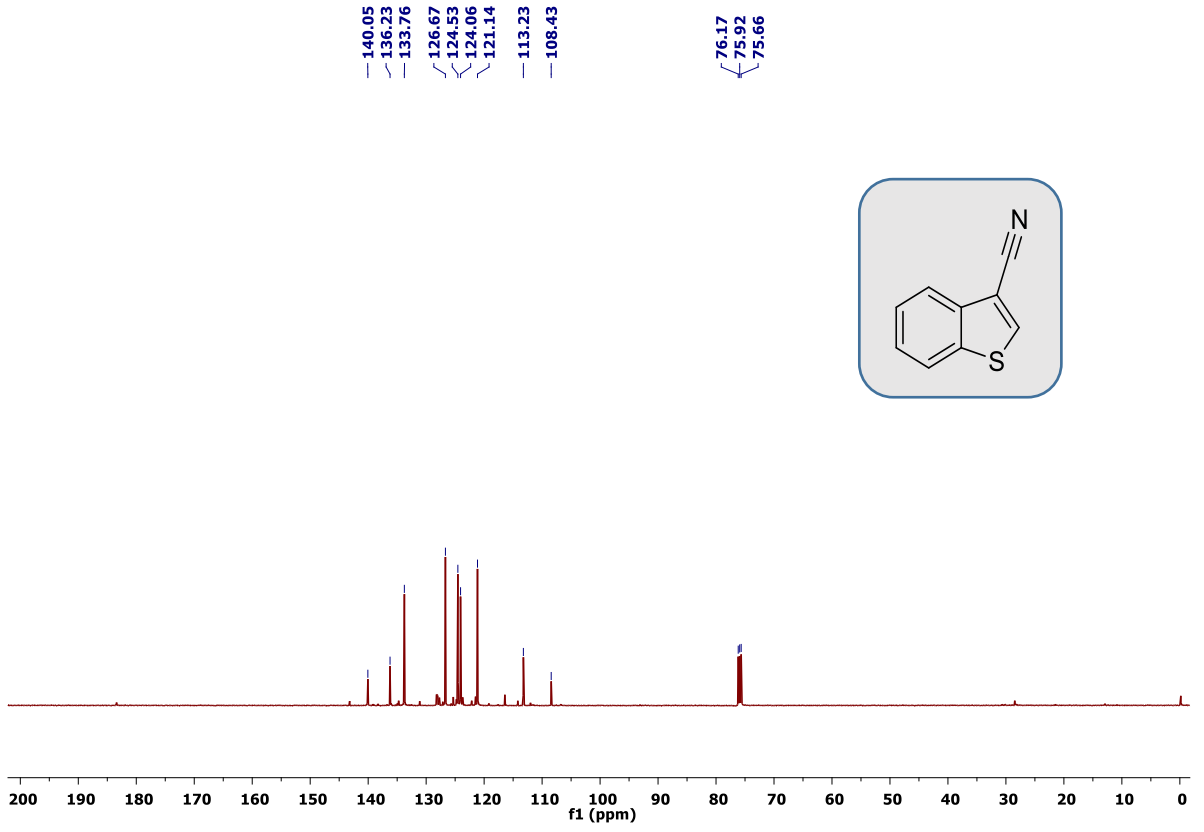


benzo[b]thiophene-3-carbonitrile(3o)

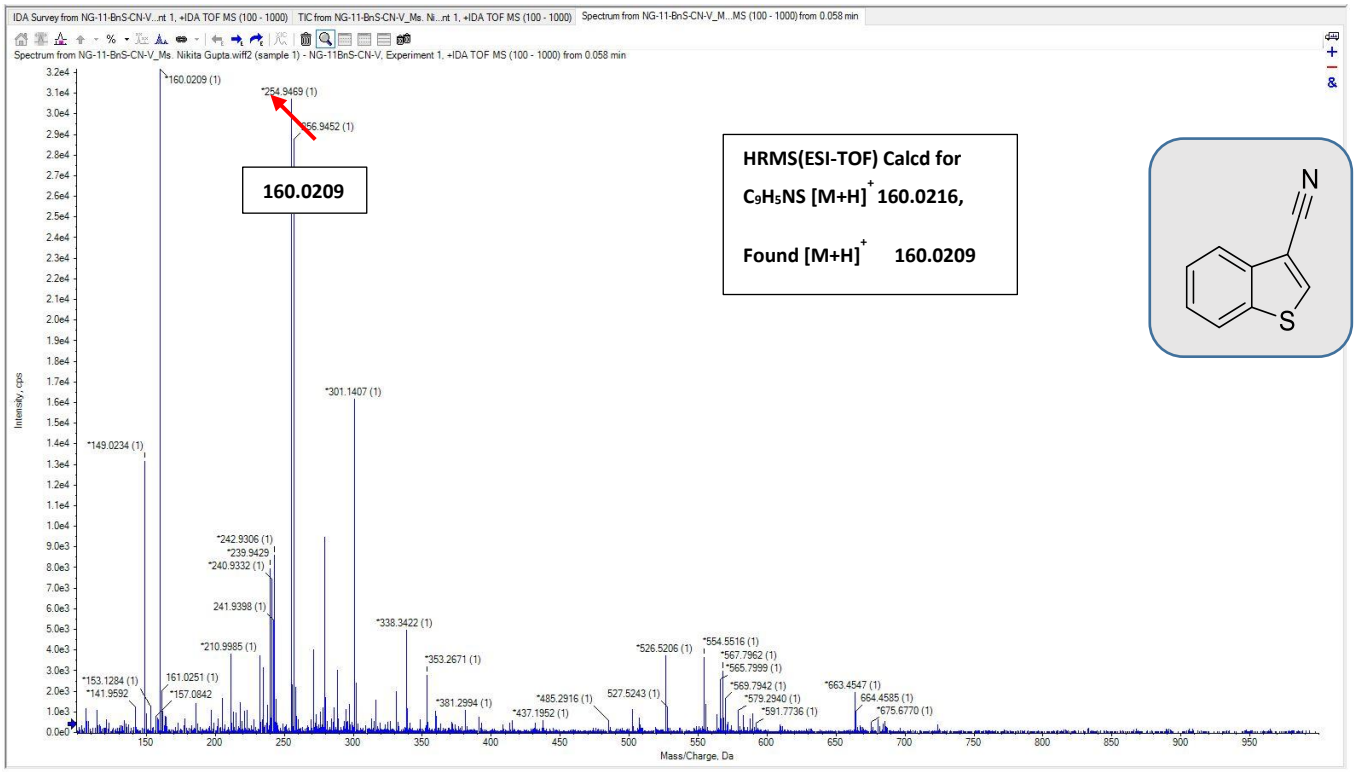
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}CNMR (126 MHz, $CDCl_3$)

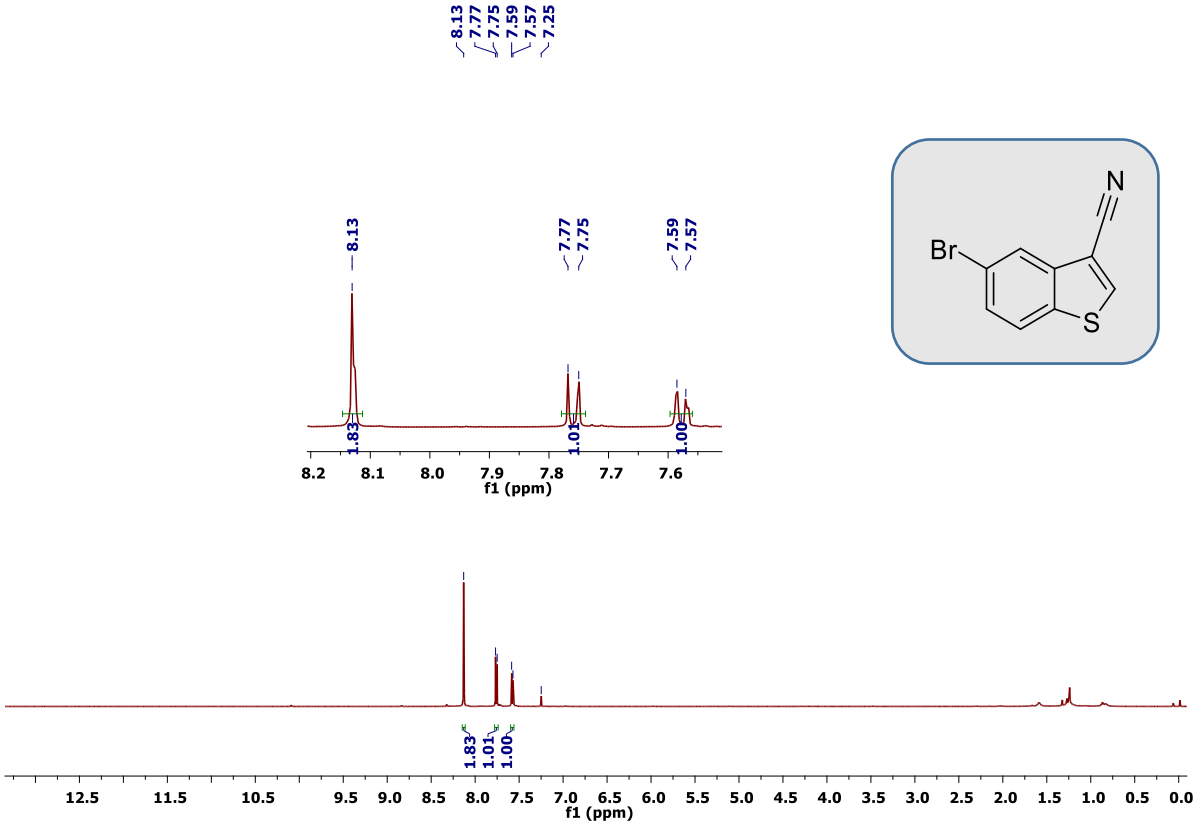


HRMS-Spectra

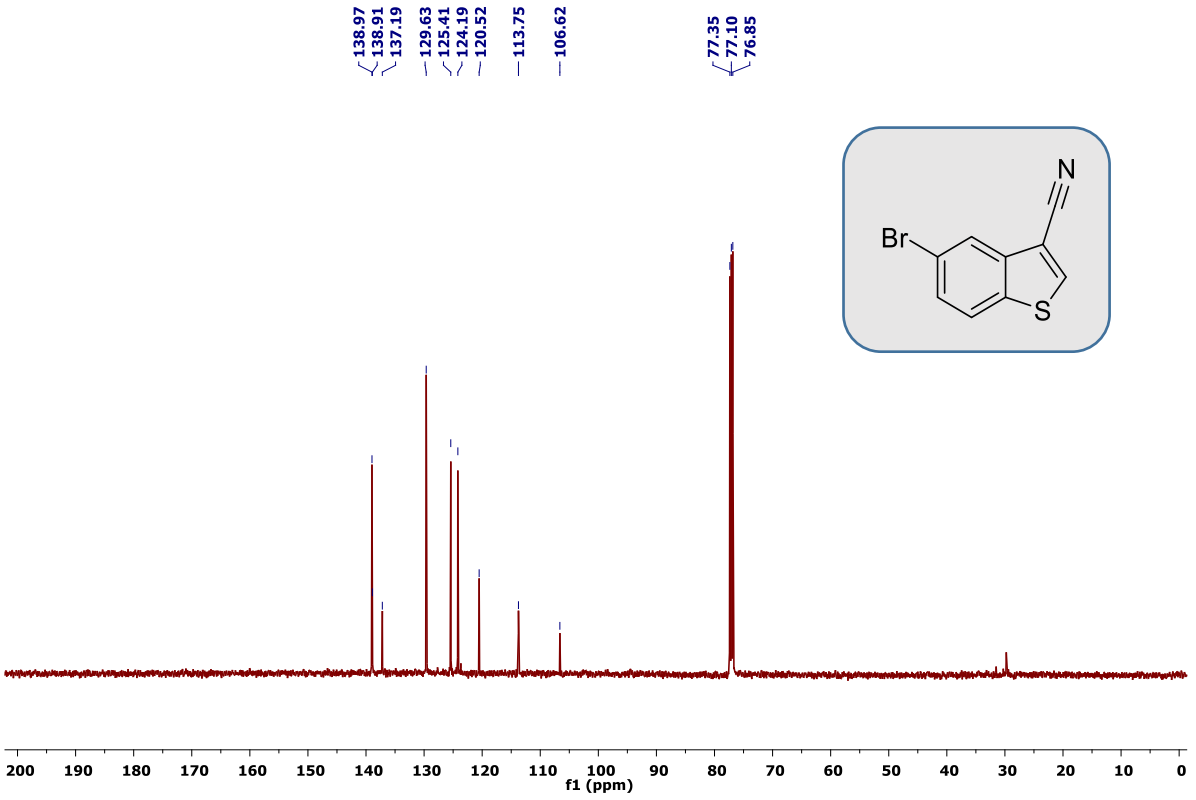


5-bromobenzo[b]thiophene-3-carbonitrile(3p)

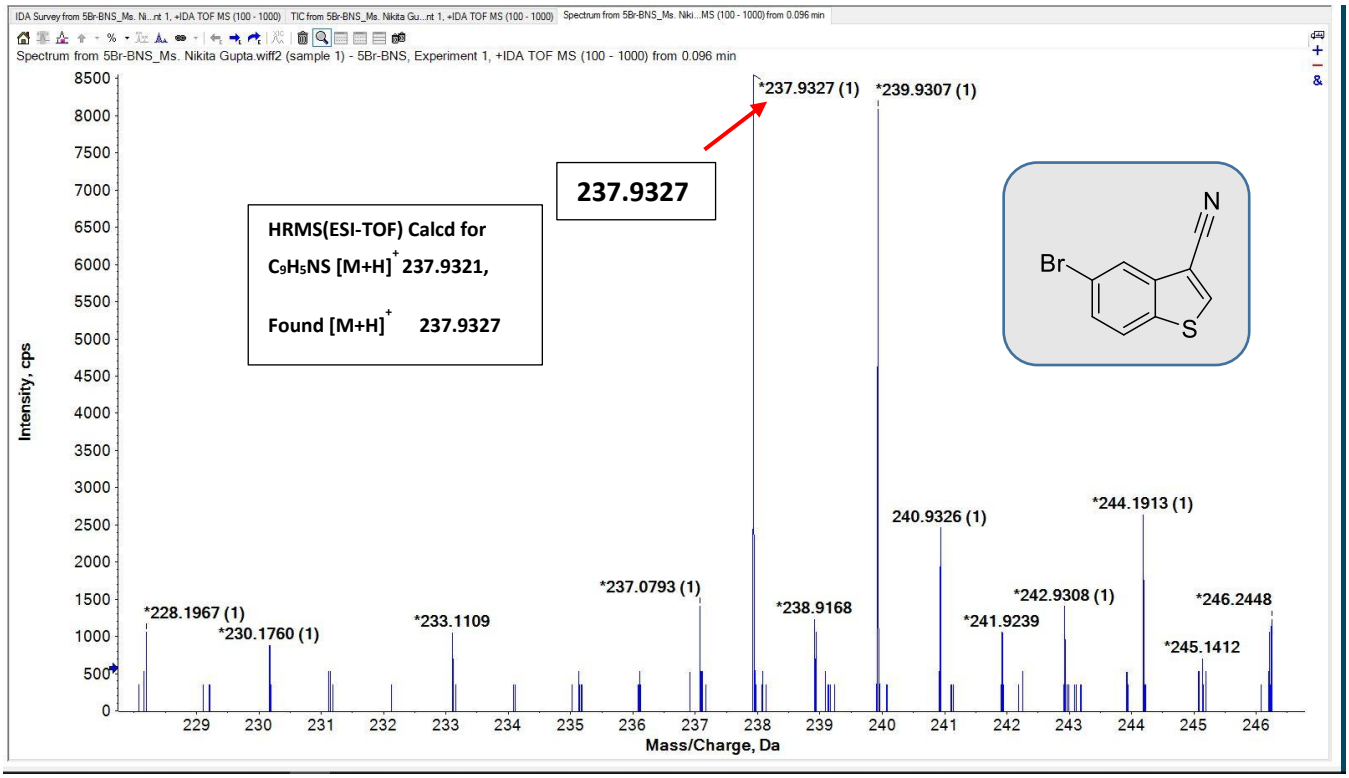
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

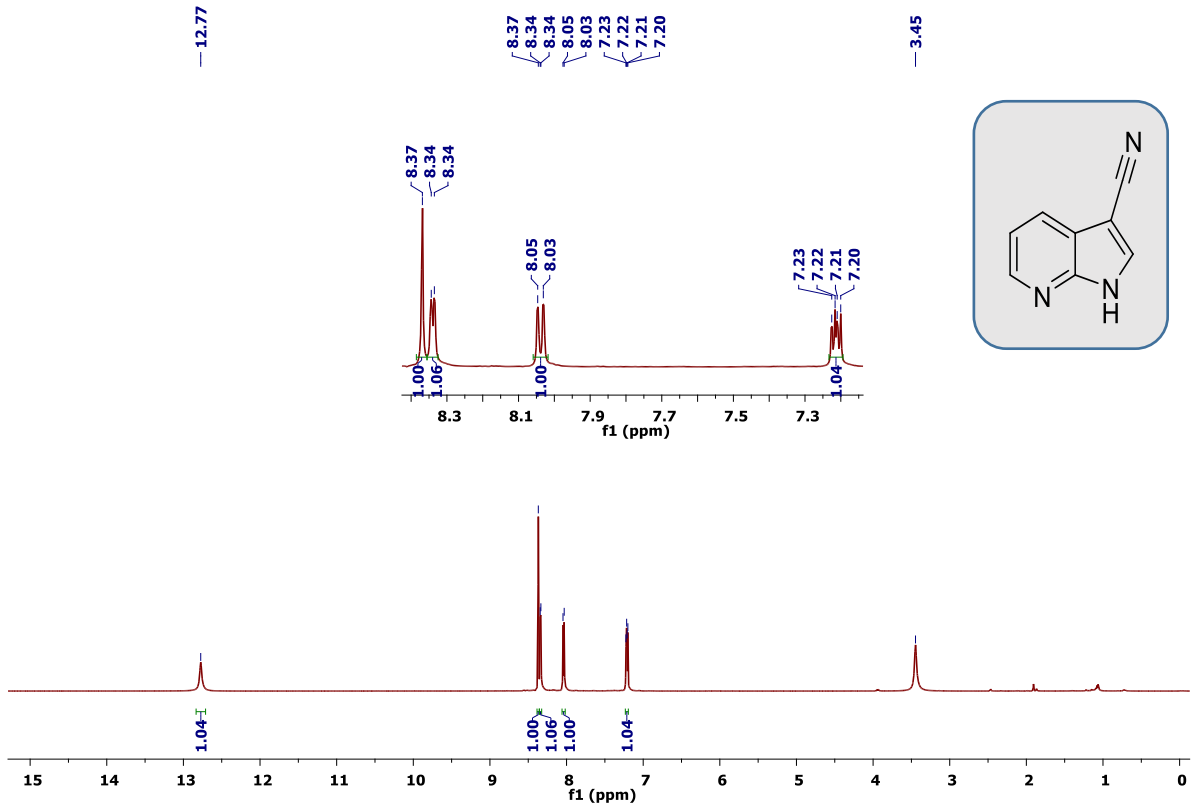


HRMS-Spectra

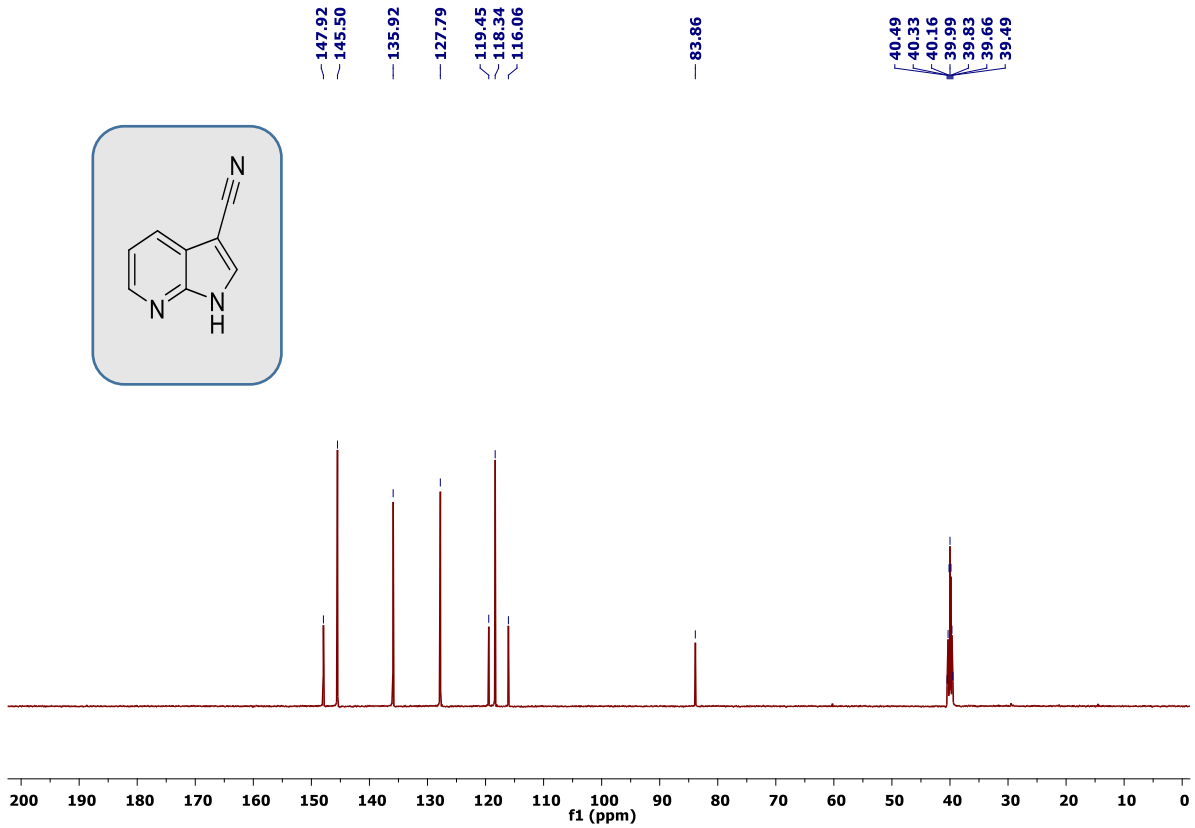


1H-pyrrolo[2,3-b]pyridine-3-carbonitrile(3q)

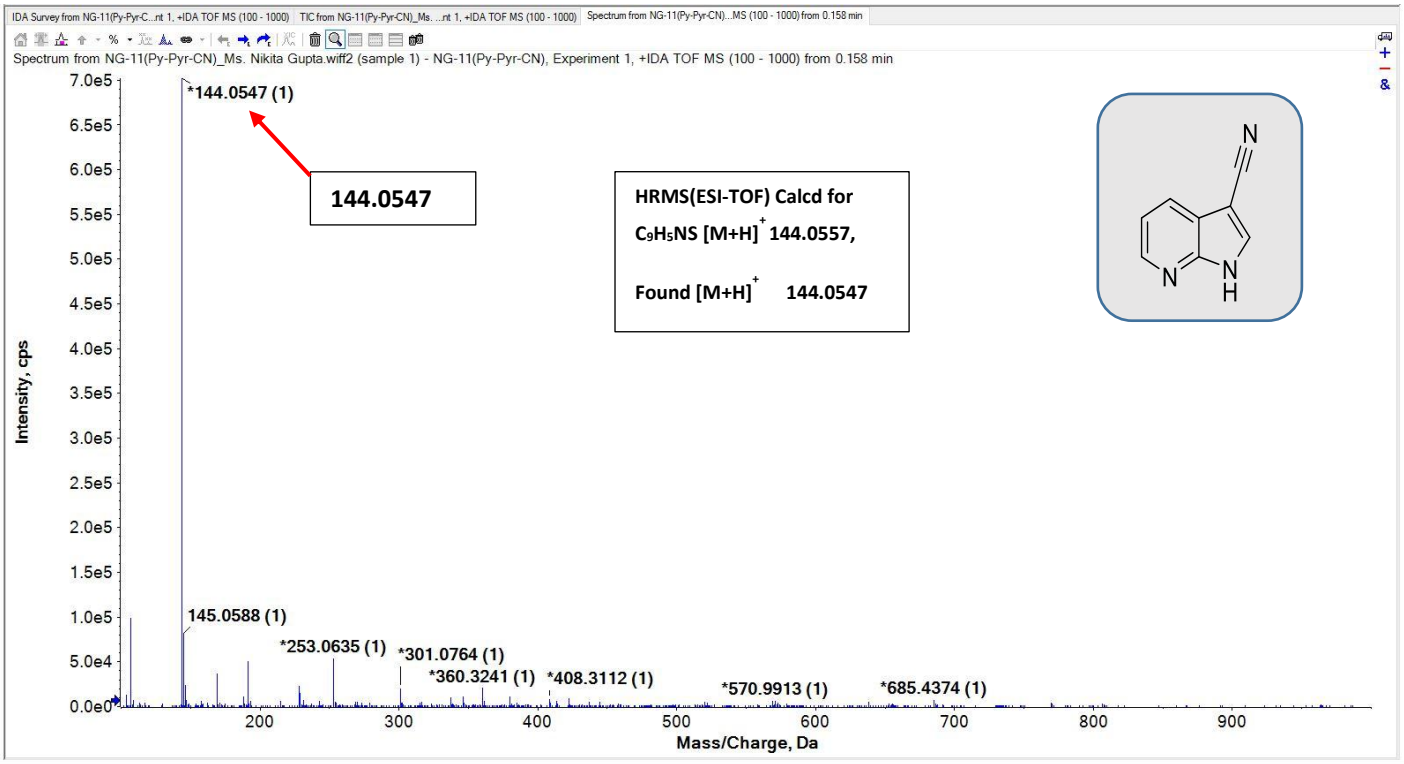
^{1}H NMR (500 MHz, DMSO-d6)



^{13}C NMR (126 MHz, DMSO-d6)

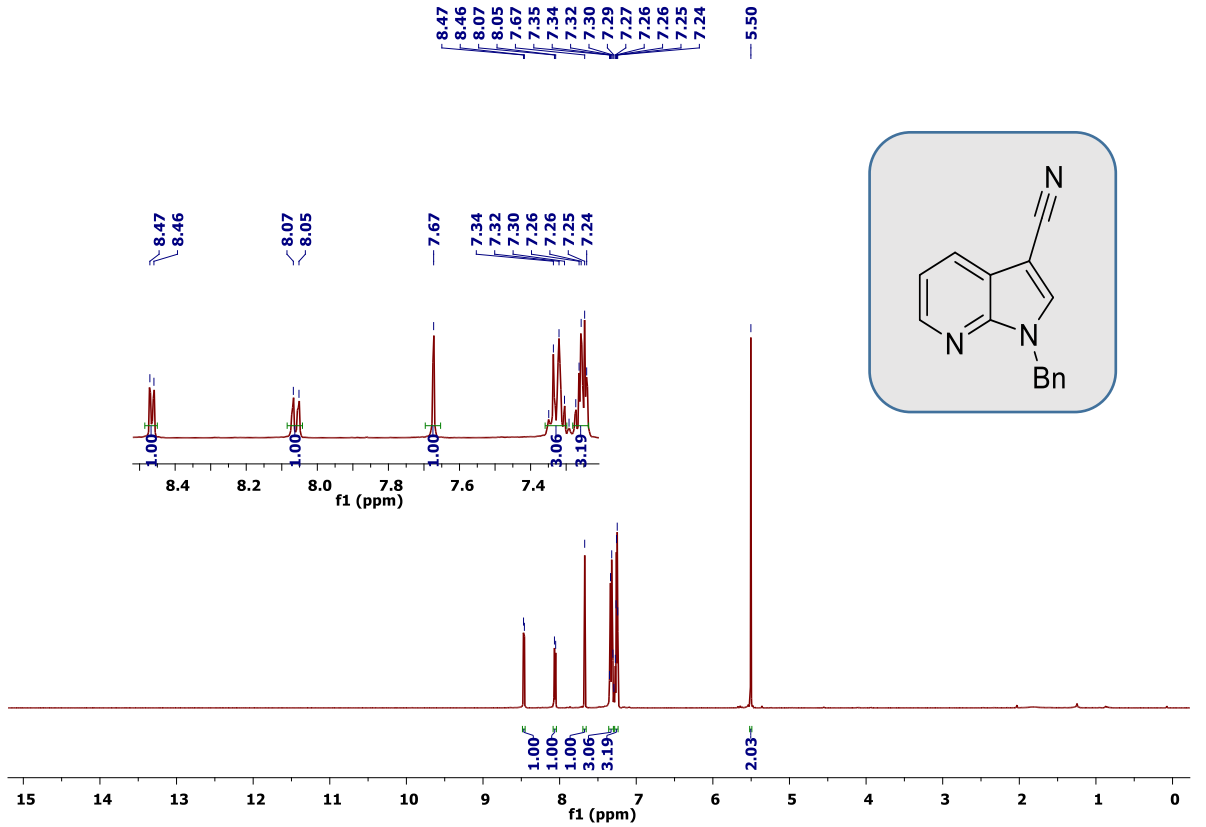


HRMS-Spectra

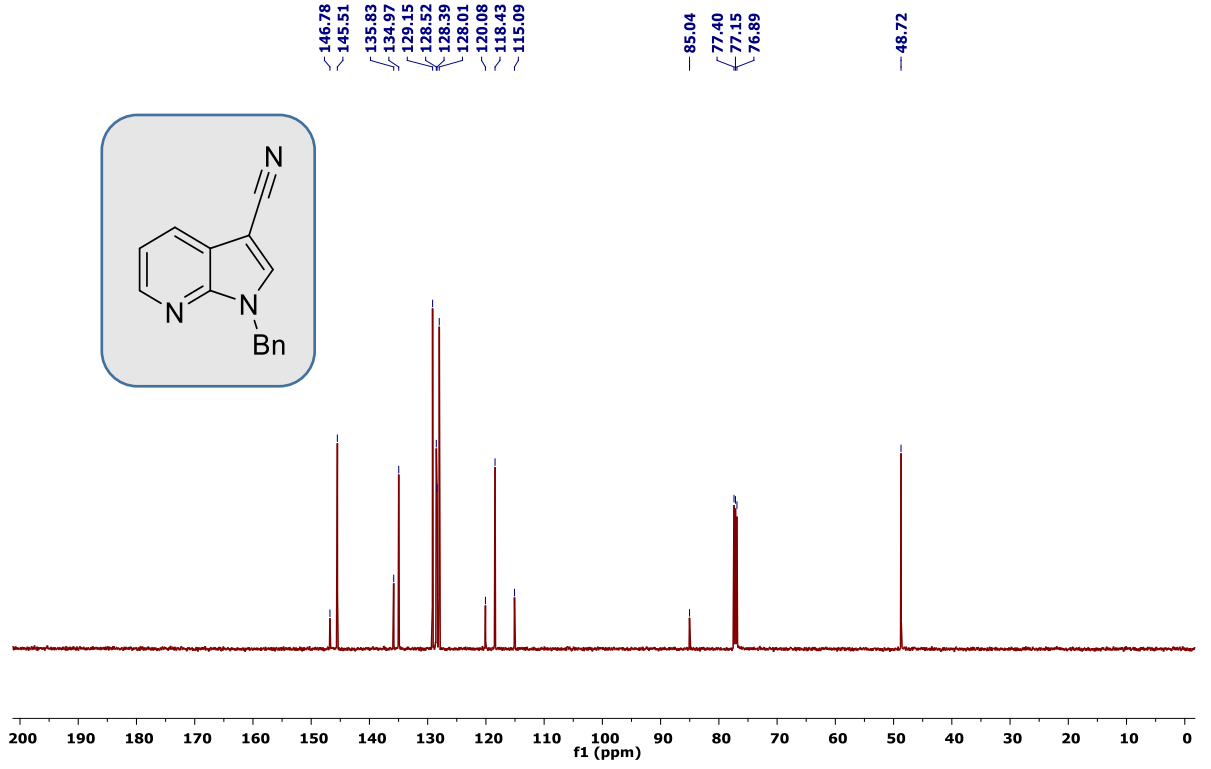


1-benzyl-1H-pyrrolo[2,3-b]pyridine-3-carbonitrile(3r)

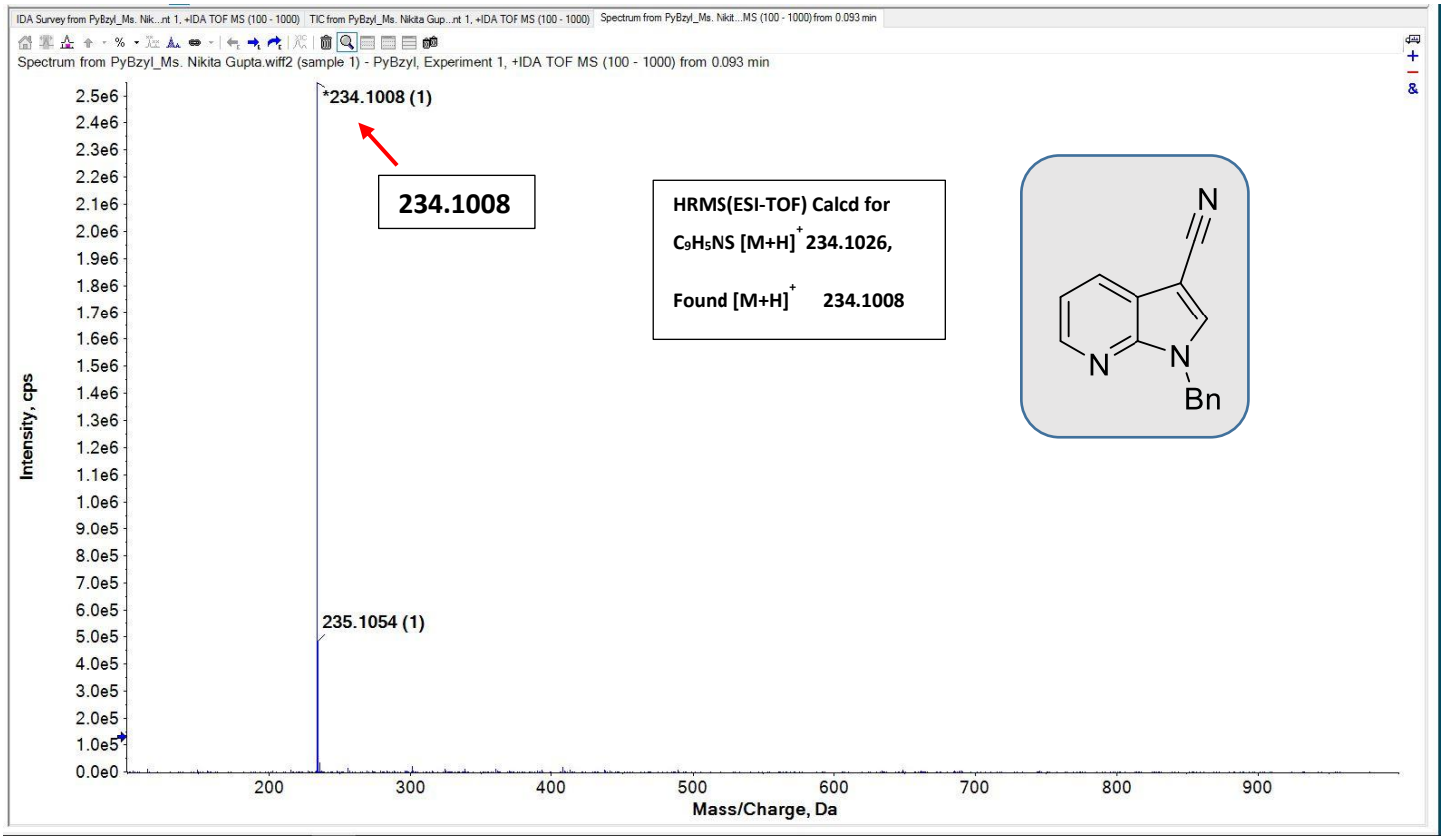
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



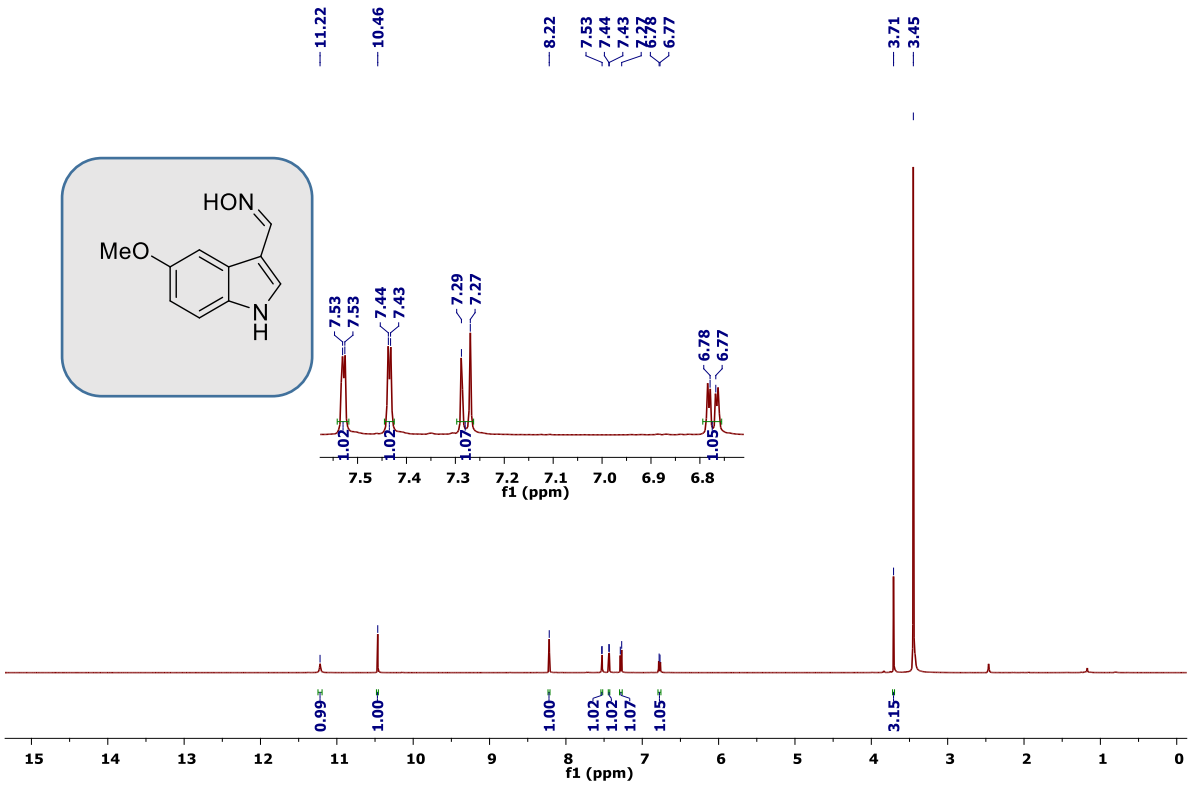
HRMS-Spectra



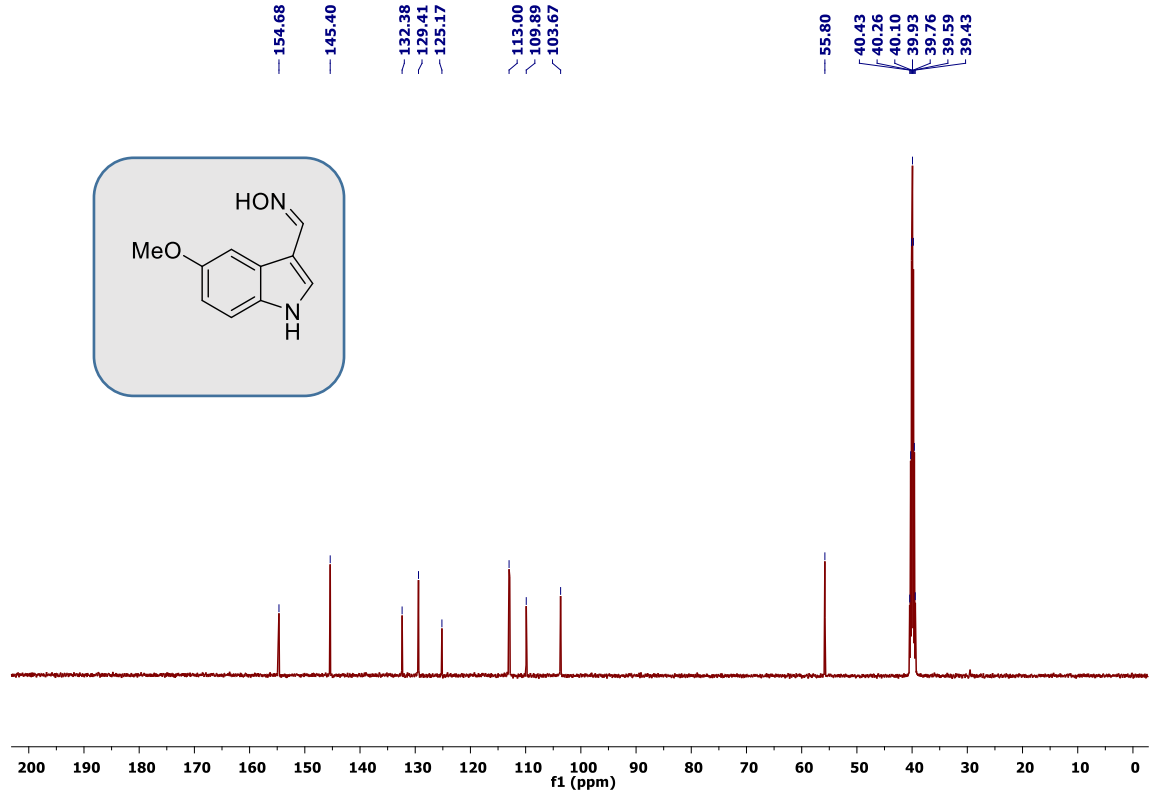
15. NMR Spectra of starting material Oxime

5-methoxy-1H-indole-3-carbaldehyde oxime(1b)

^{1}H NMR (500 MHz, DMSO-d6)

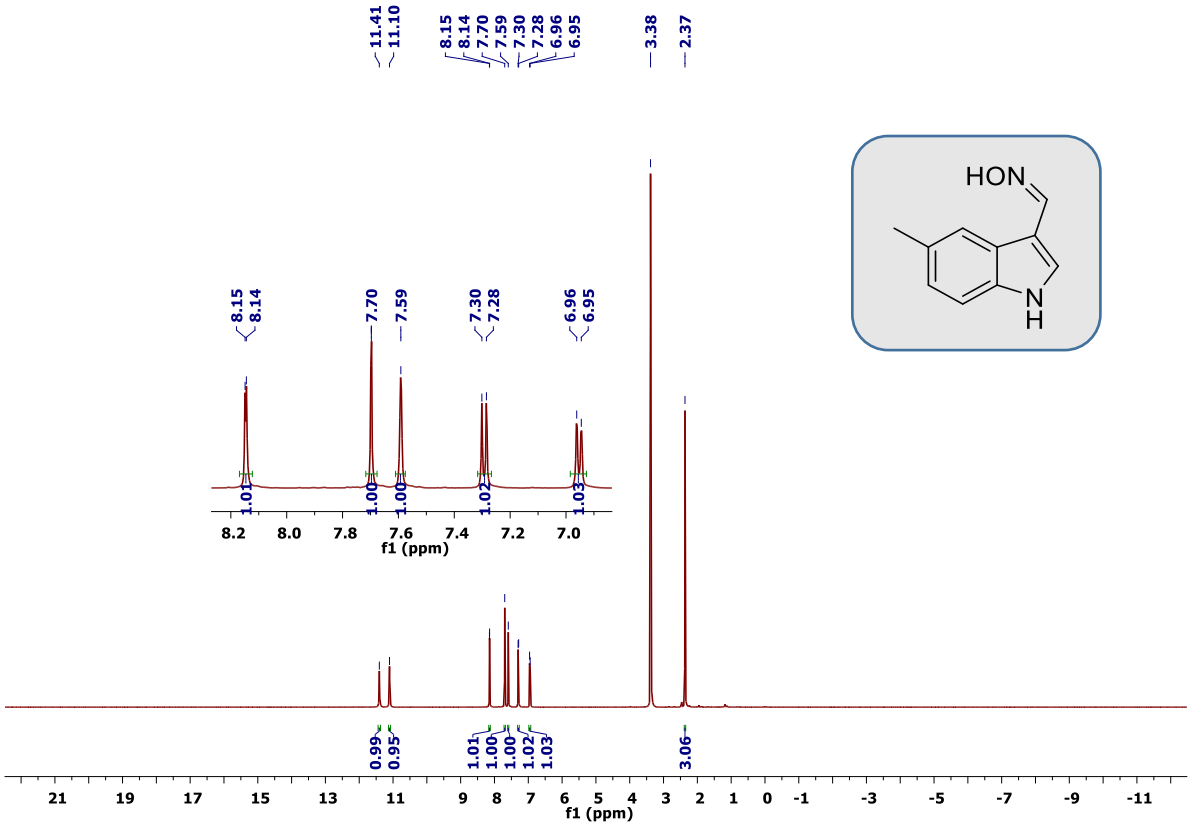


^{13}C NMR (126 MHz, DMSO-d6)

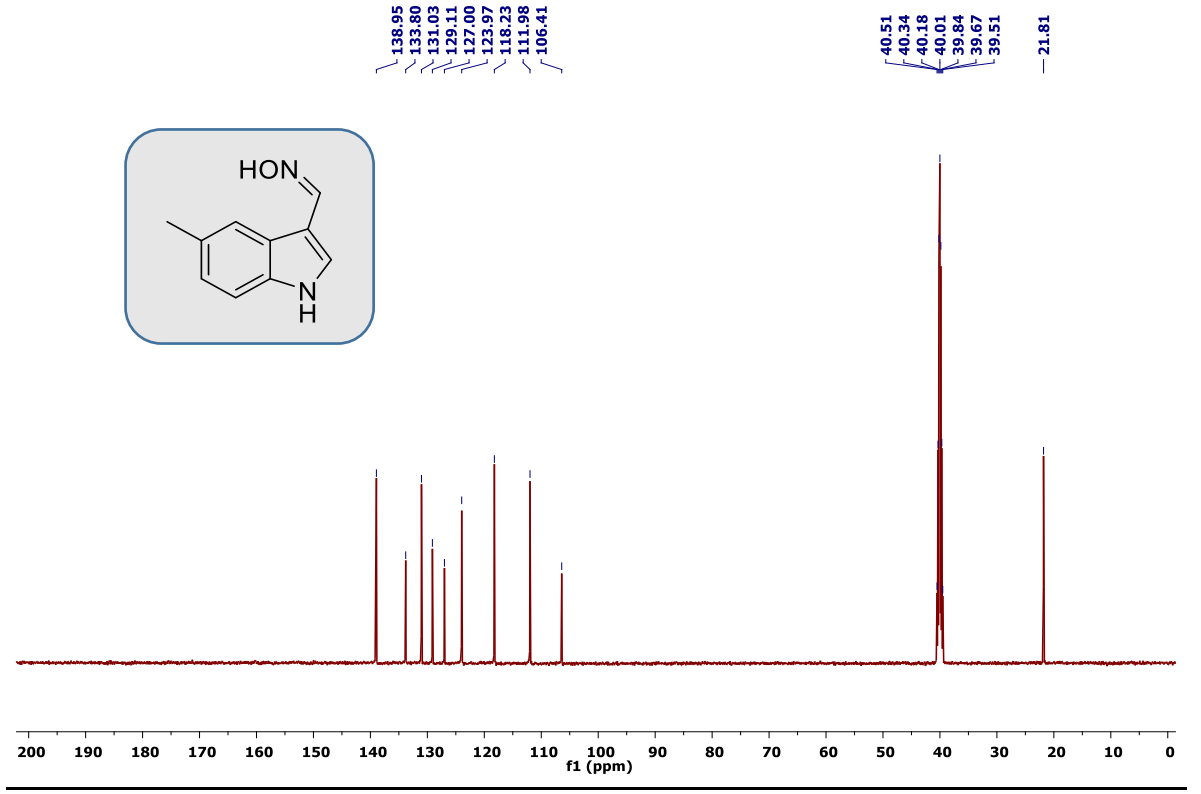


5-methyl-1H-indole-3-carbaldehyde oxime(1c)

^{1}H NMR (500 MHz, DMSO-d6)

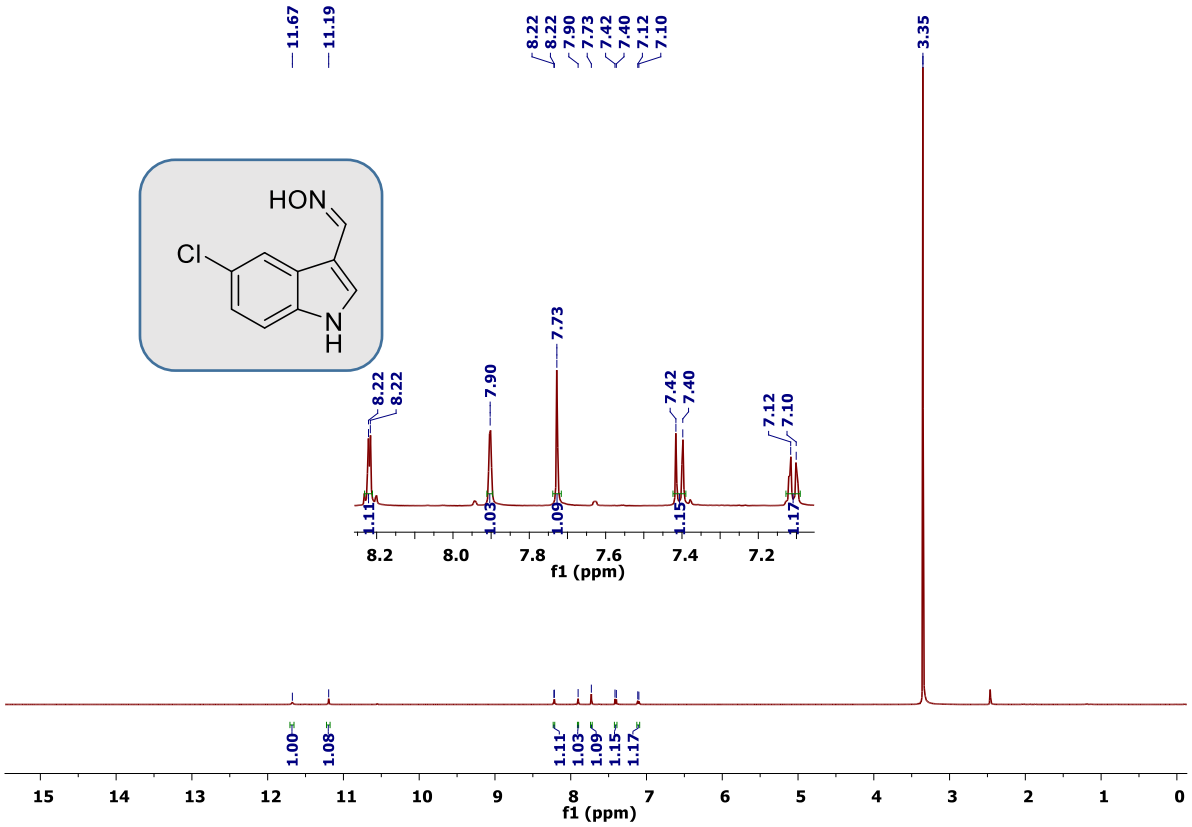


^{13}C NMR (126 MHz, DMSO-d6)

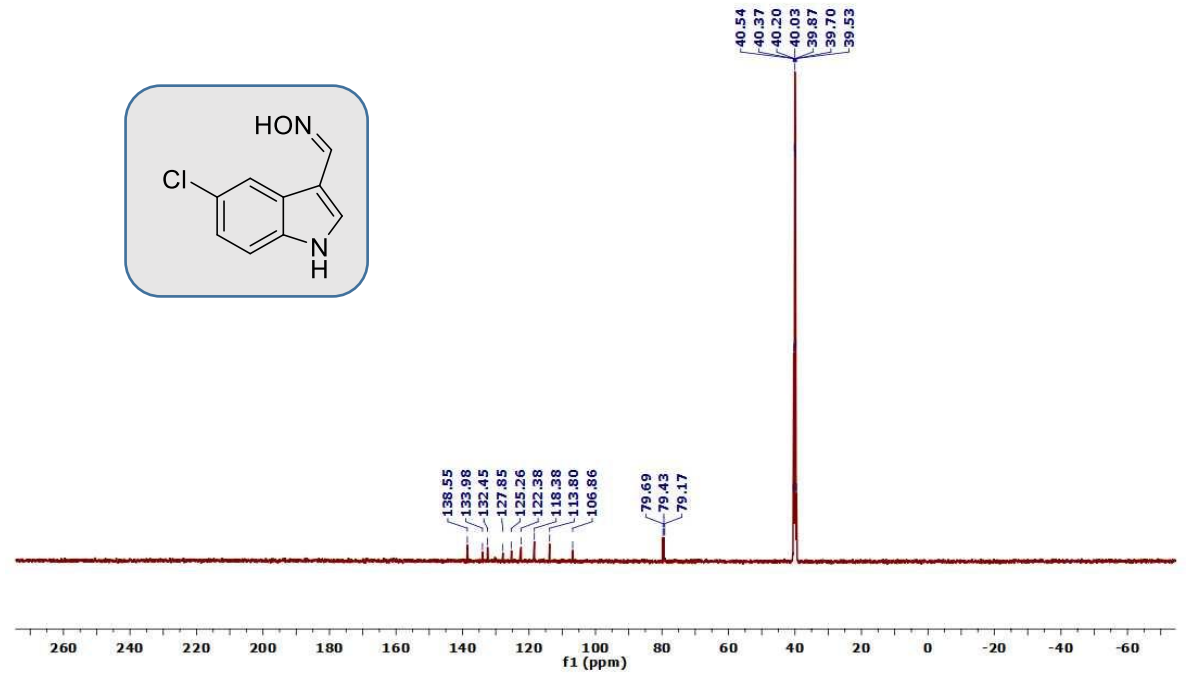


5-chloro-1H-indole-3-carbaldehyde oxime(1d)

^{1}H NMR (500 MHz, DMSO-d6)

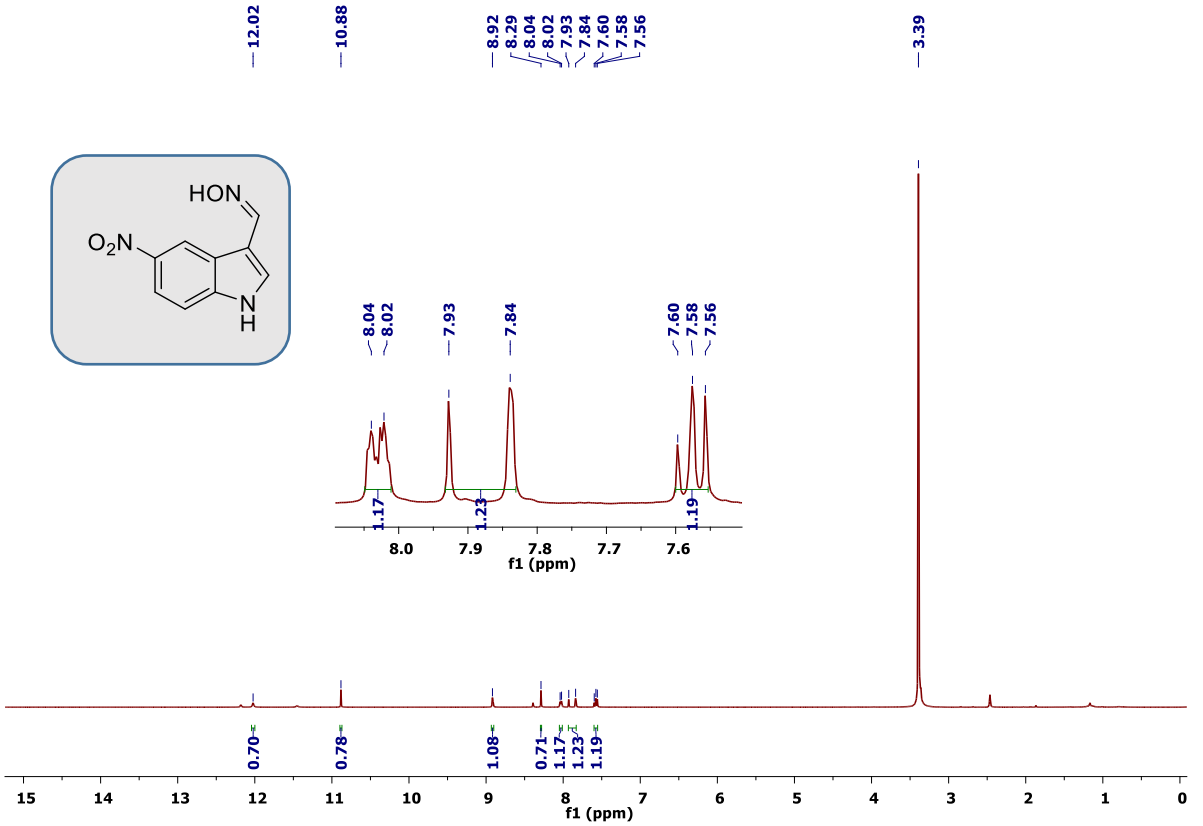


^{13}C NMR (126 MHz, DMSO-d6)

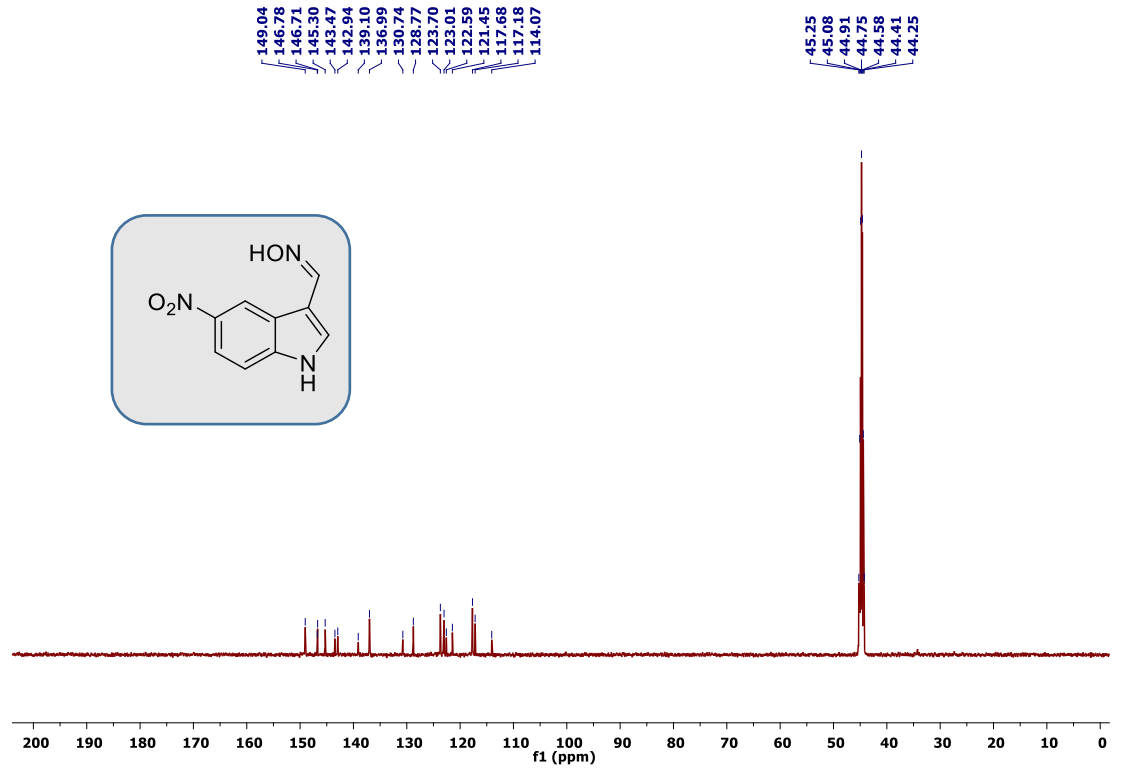


5-nitro-1H-indole-3-carbaldehyde oxime(1e)

^{1}H NMR (500 MHz, DMSO-d6)

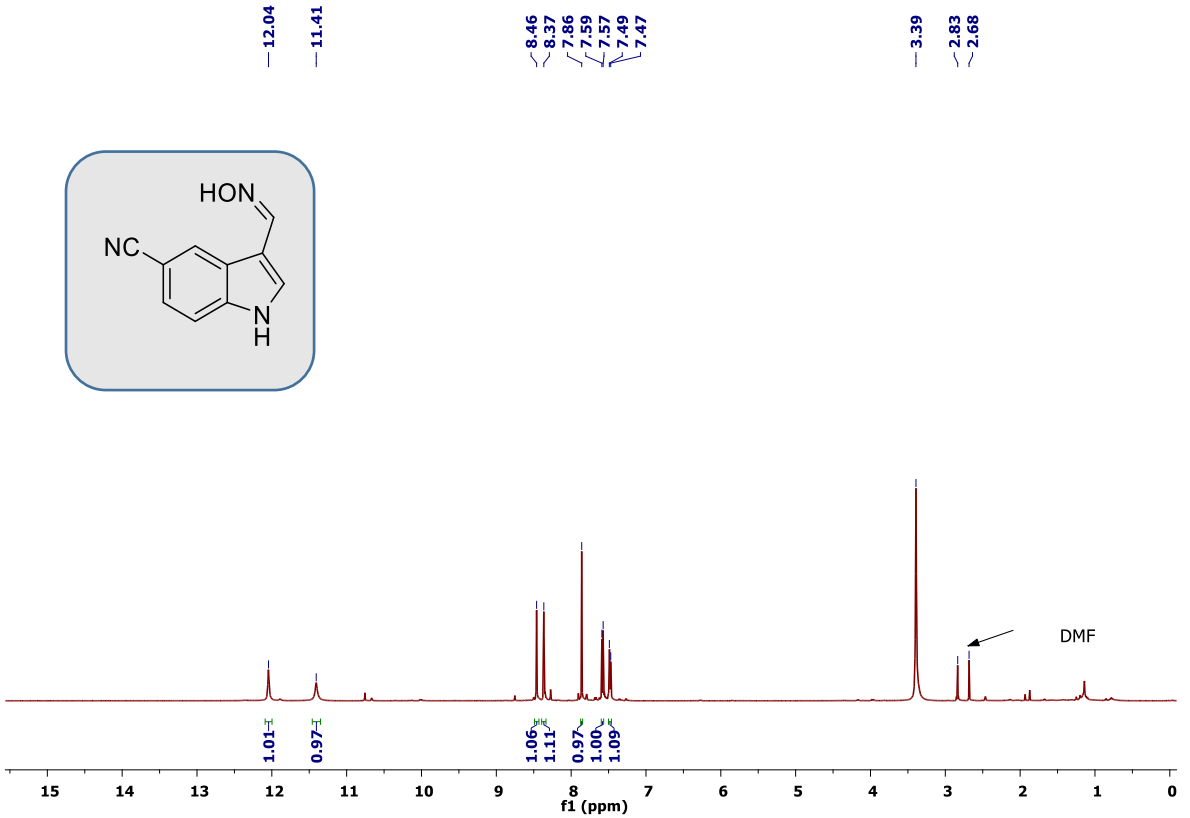


^{13}C NMR (126 MHz, DMSO-d6)

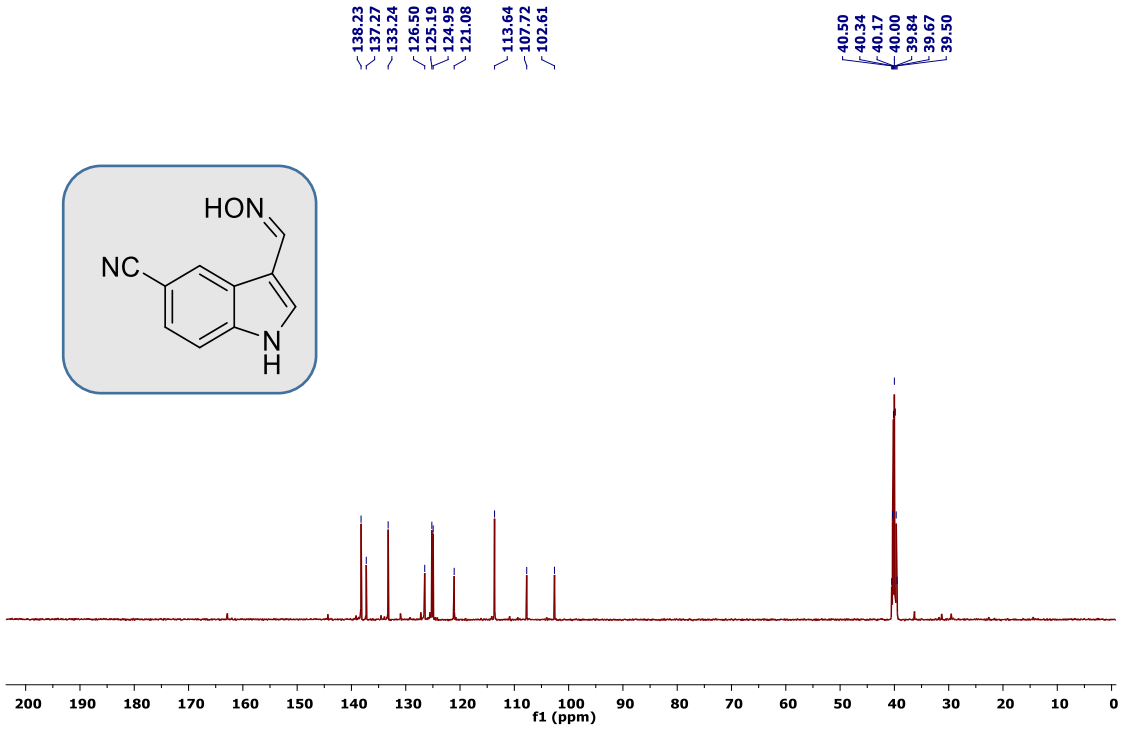


3-((hydroxyimino)methyl)-1H-indole-5-carbonitrile(1f)

^{1}H NMR (500 MHz, DMSO-d6)

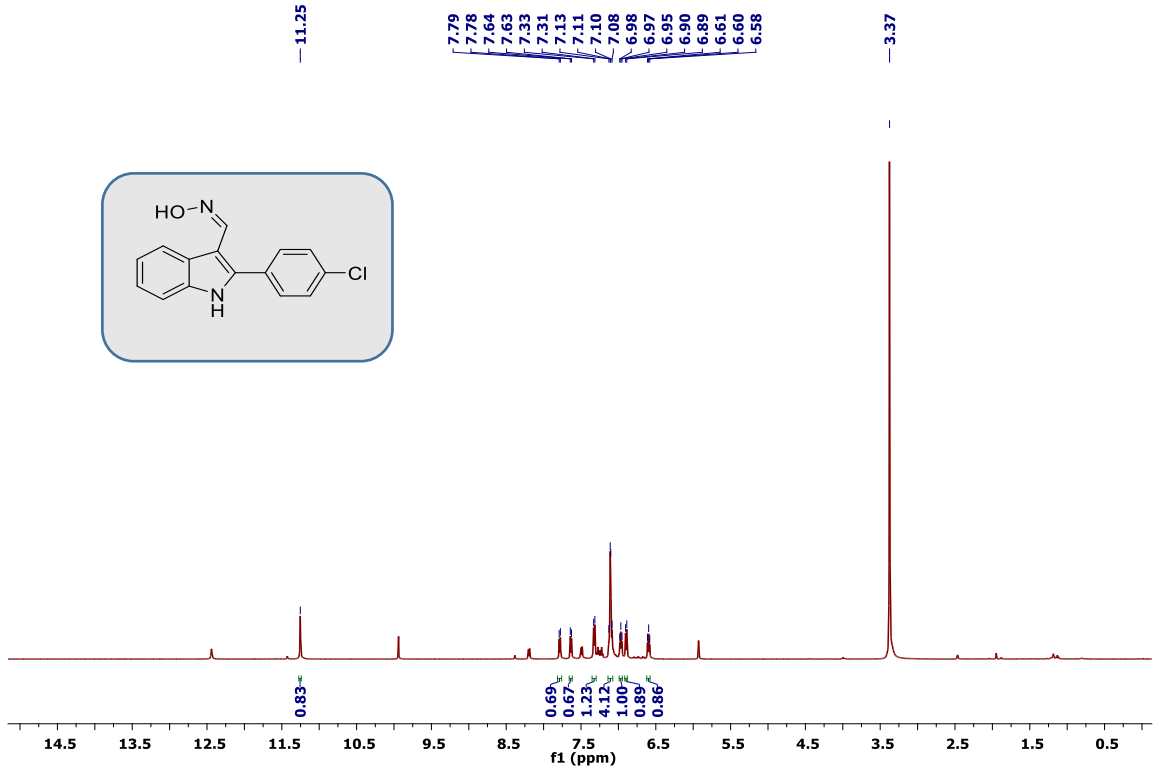


^{13}C NMR (126 MHz, DMSO-d6)

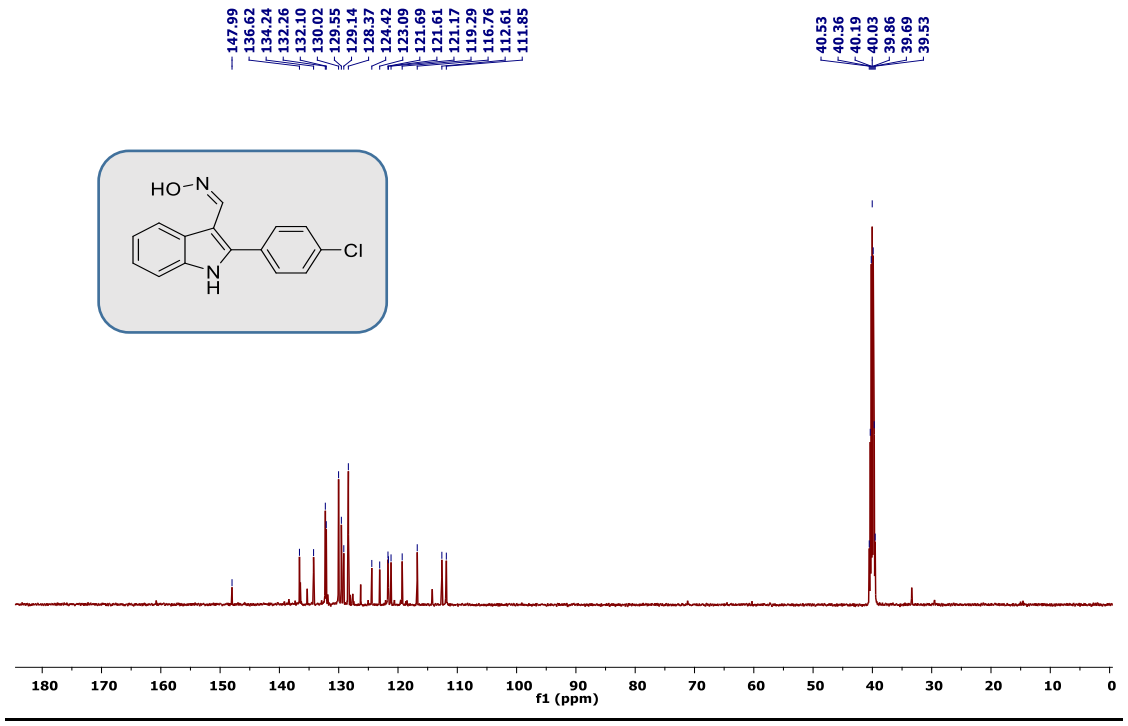


2-(4-chlorophenyl)-1H-indole-3-carbaldehyde oxime(1h)

^{1}H NMR (500 MHz, DMSO-d6)

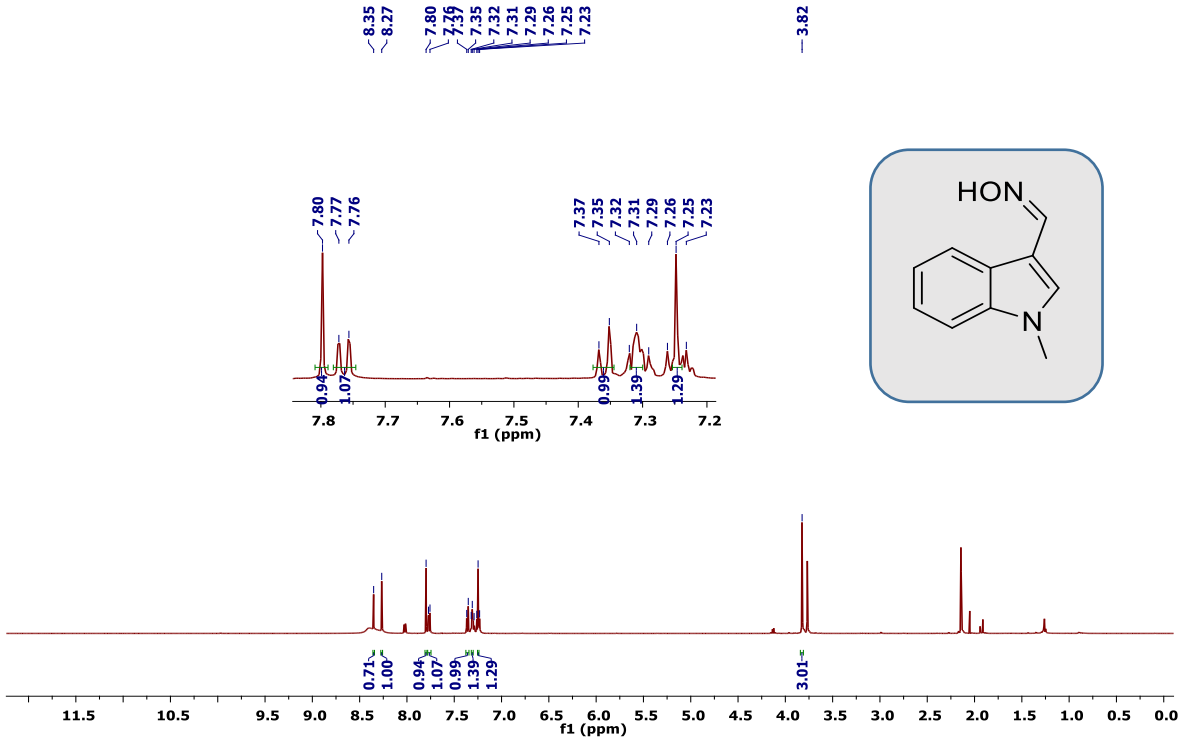


^{13}C NMR (126 MHz, DMSO-d6)

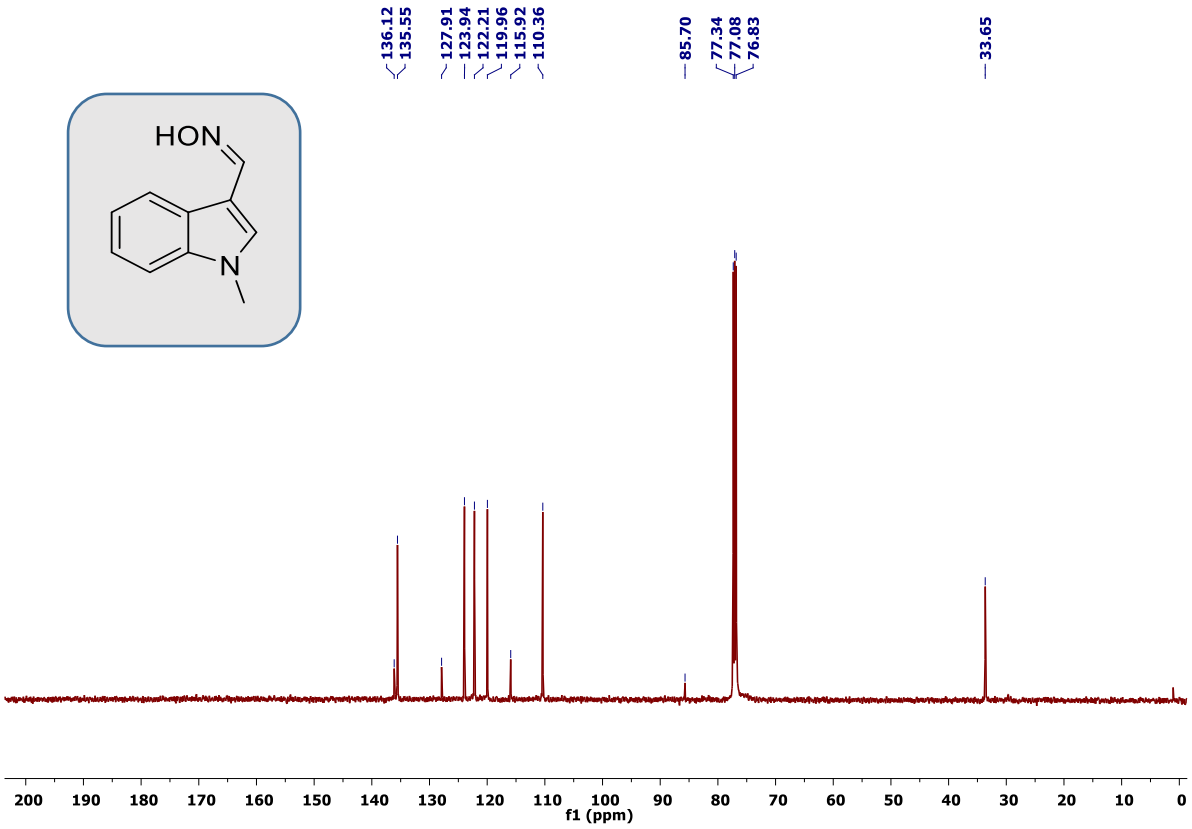


1-methyl-1H-indole-3-carbaldehyde oxime(1i)

^{1}H NMR (500 MHz, $CDCl_3$)

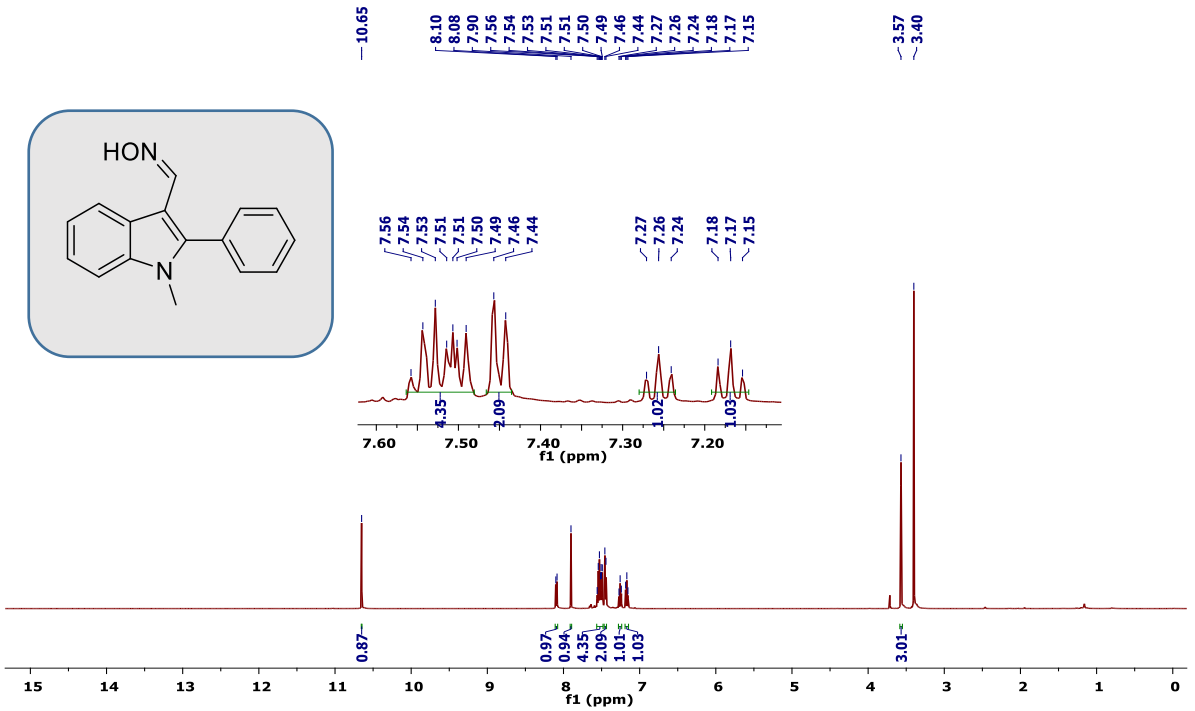


^{13}C NMR (126 MHz, $CDCl_3$)

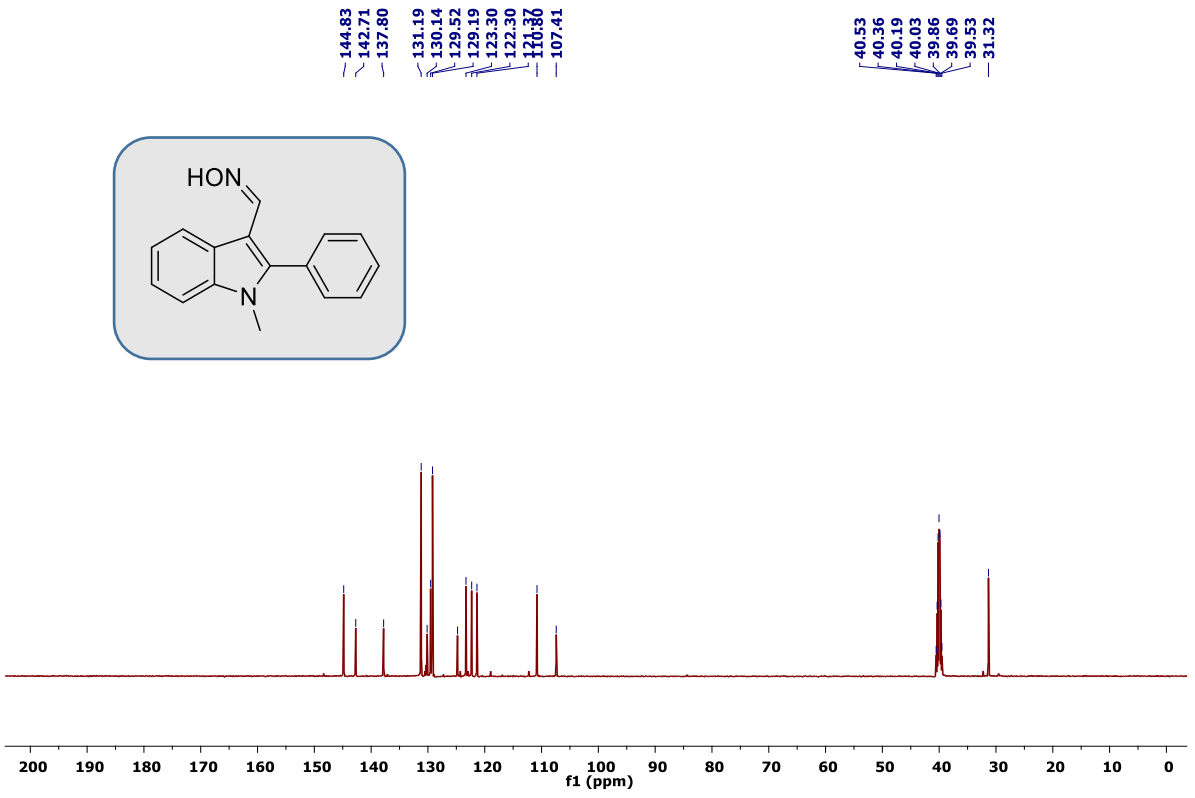


1-methyl-2-phenyl-1H-indole-3-carbaldehyde oxime(1j)

^{1}H NMR (500 MHz, DMSO-d6)

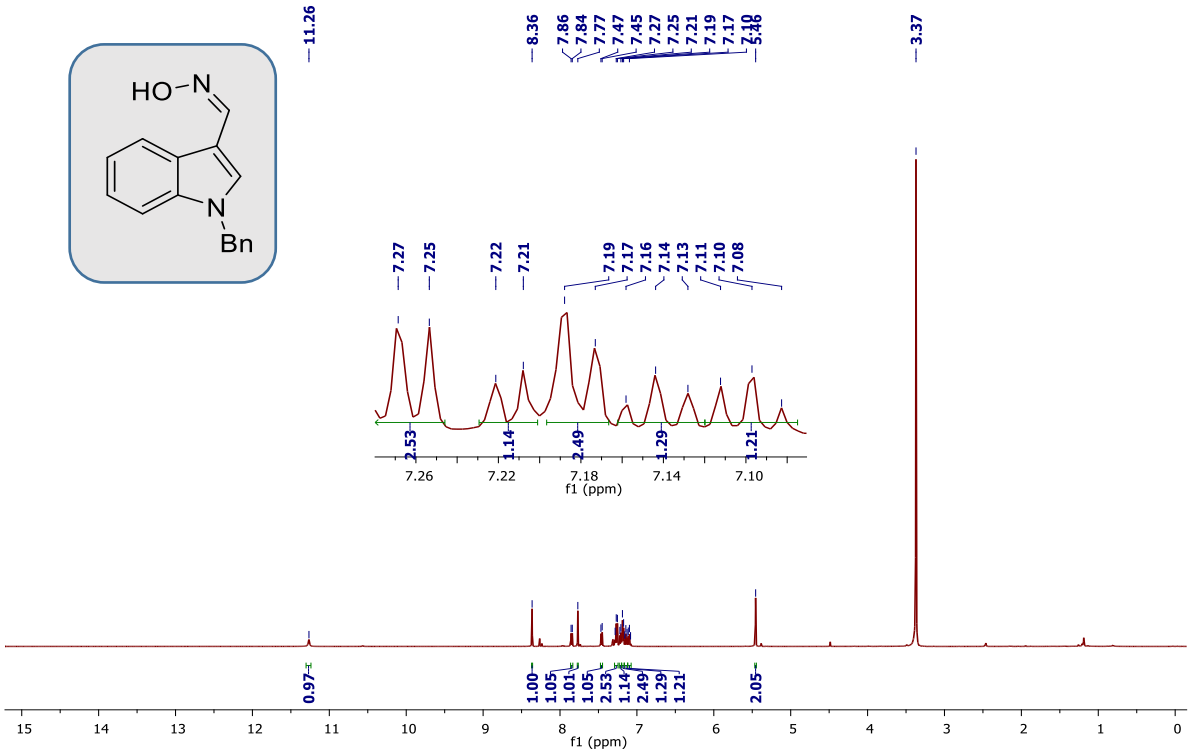


^{13}C NMR (126 MHz, DMSO-d6)

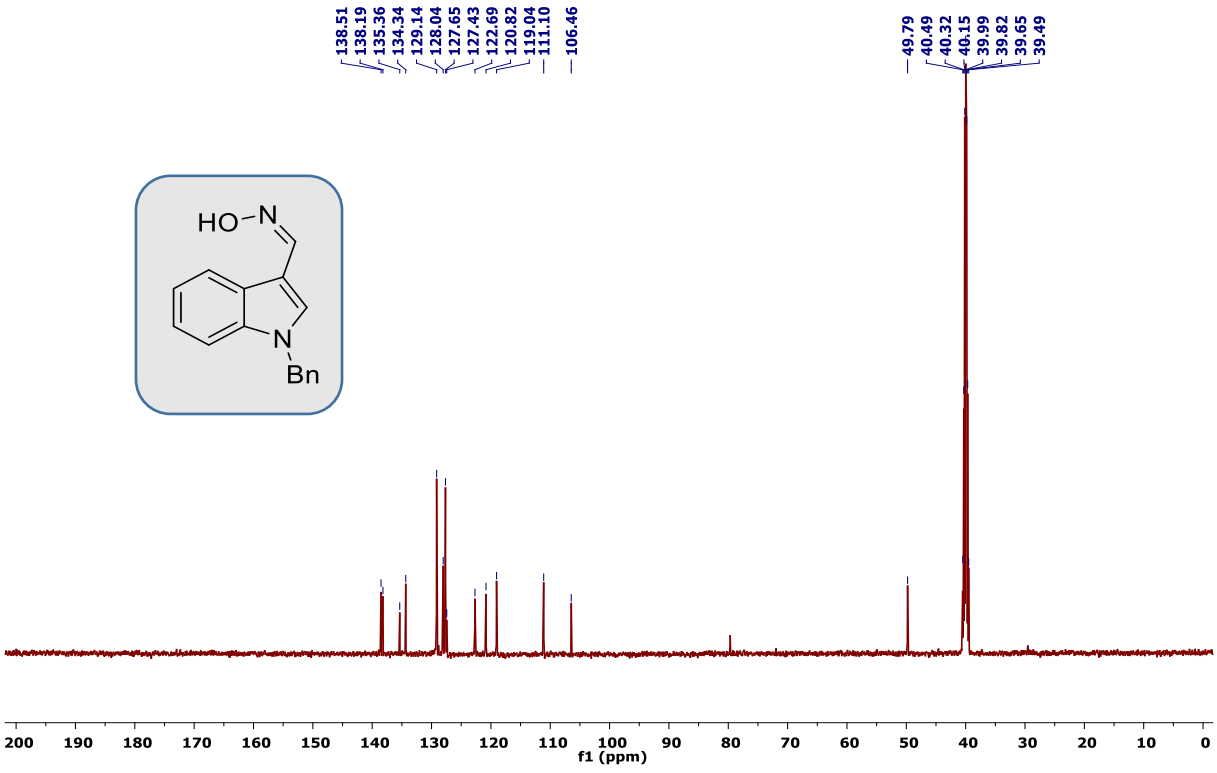


1-benzyl-1H-indole-3-carbaldehyde oxime(1k)

^{1}H NMR (500 MHz, DMSO-d6)

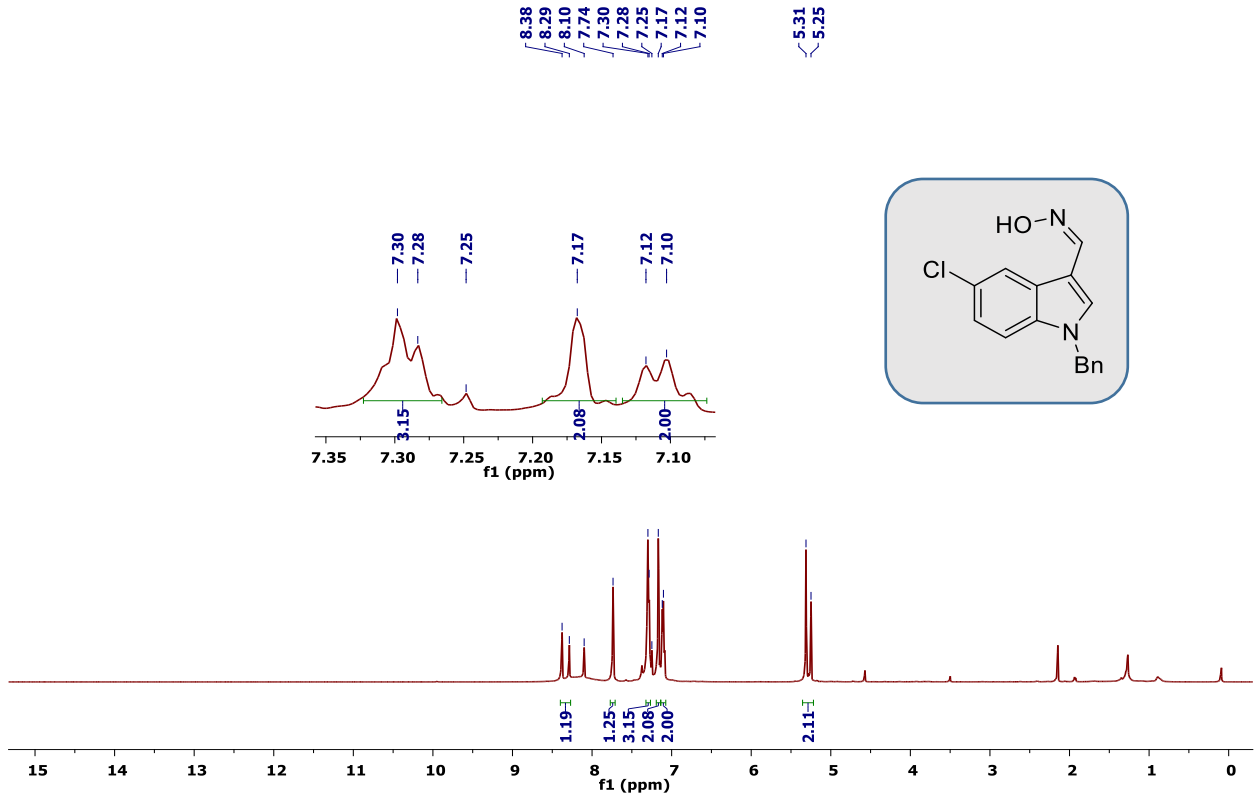


^{13}C NMR (126 MHz, DMSO-d6)

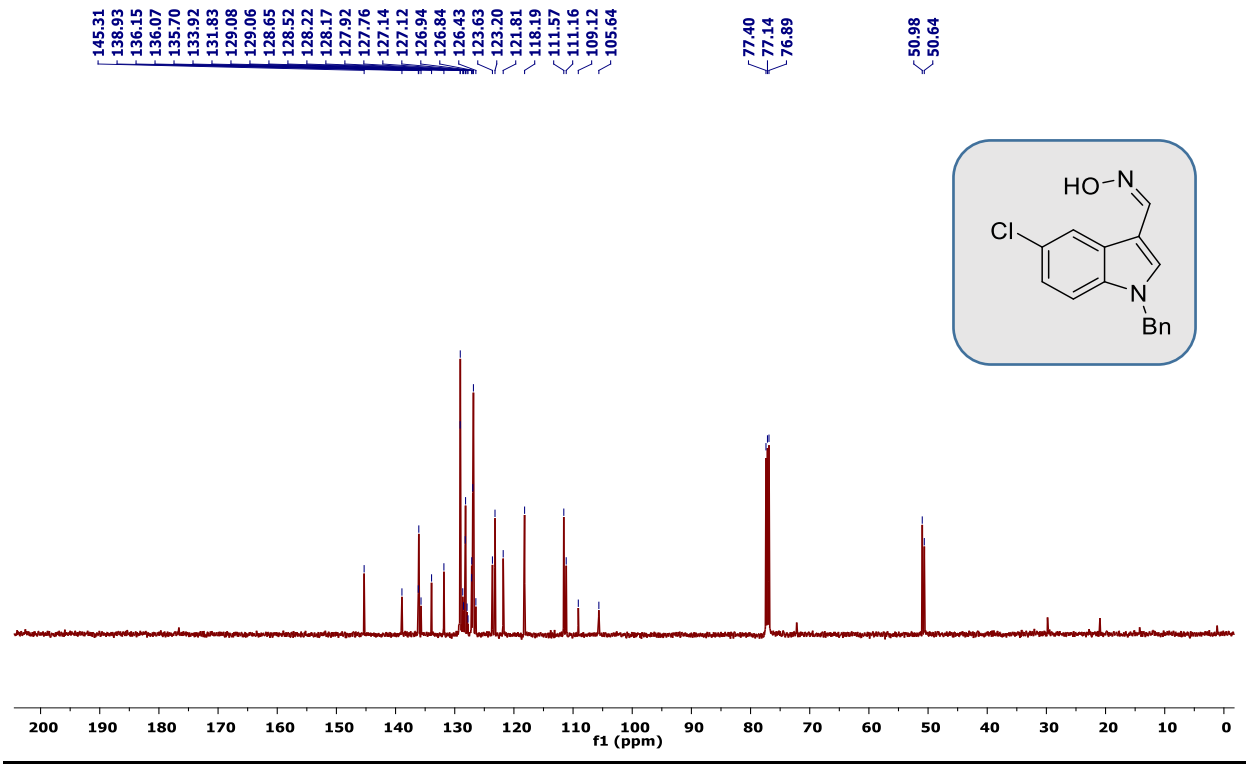


1-benzyl-5-chloro-1H-indole-3-carbaldehyde oxime(1l)

^{1}H NMR (500 MHz, $CDCl_3$)

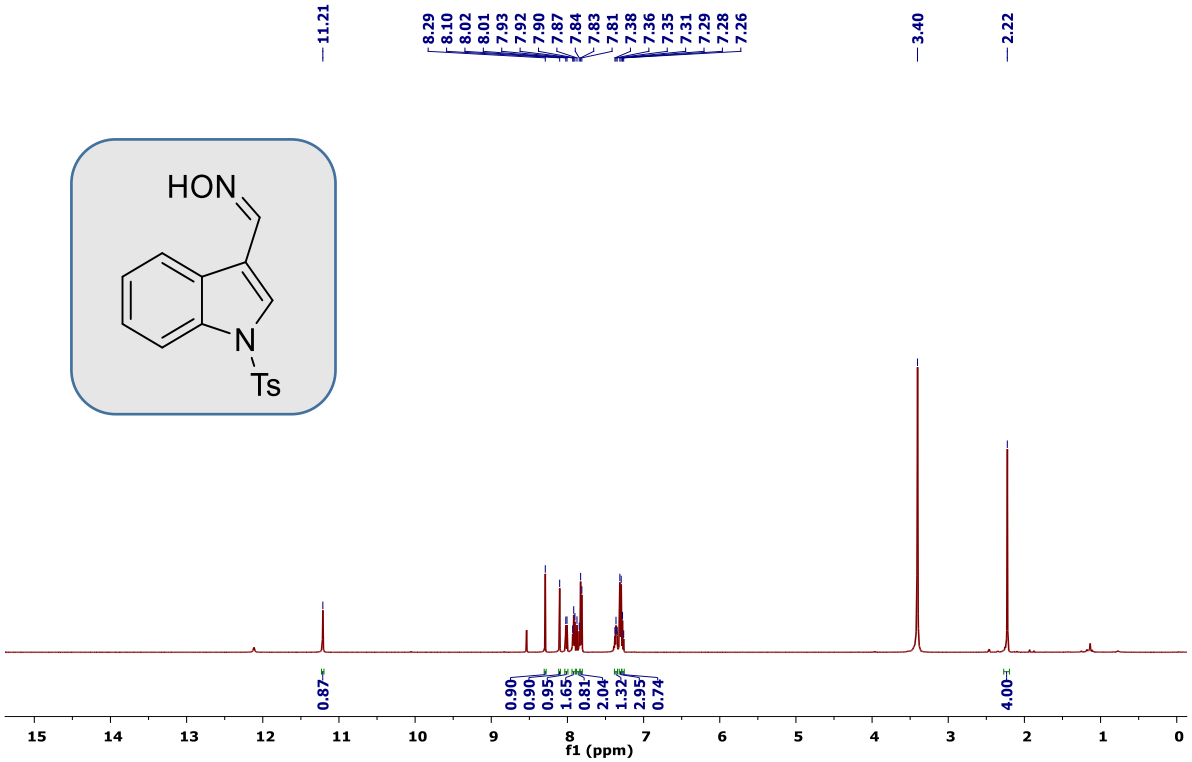


^{13}C NMR (126MHz, $CDCl_3$)

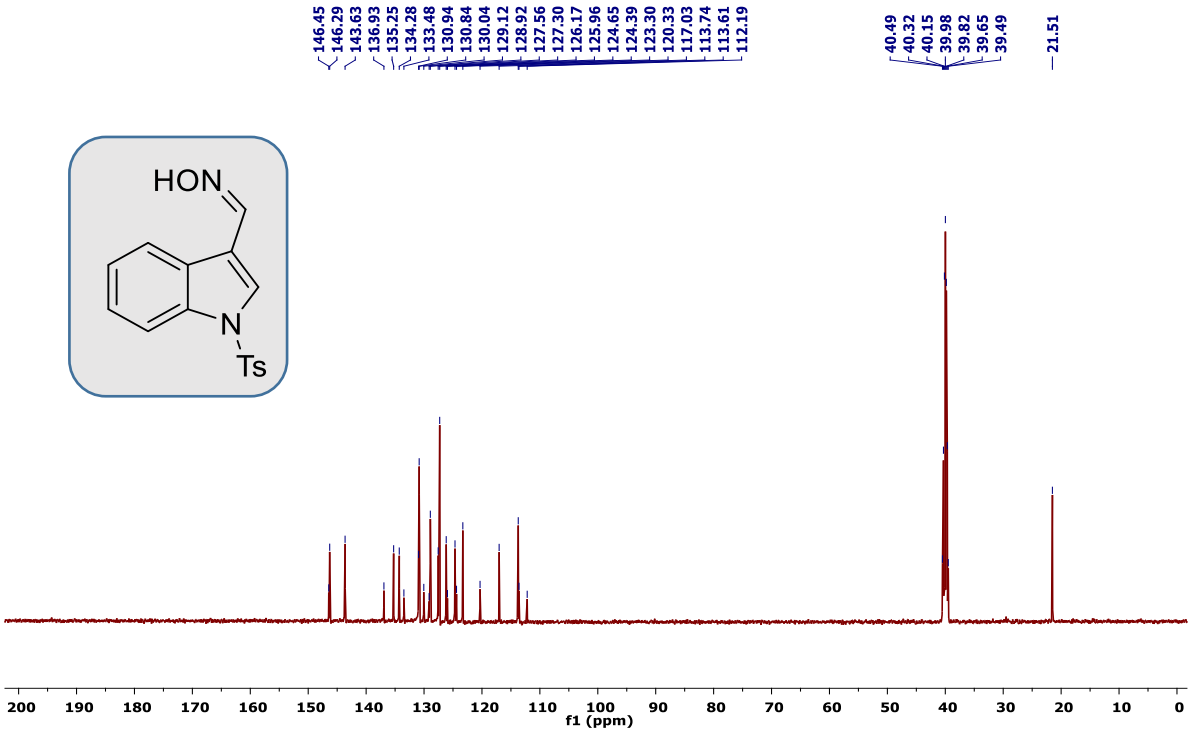


1-tosyl-1H-indole-3-carbaldehyde oxime(1n)

^{1}H NMR (500 MHz, DMSO-d6)

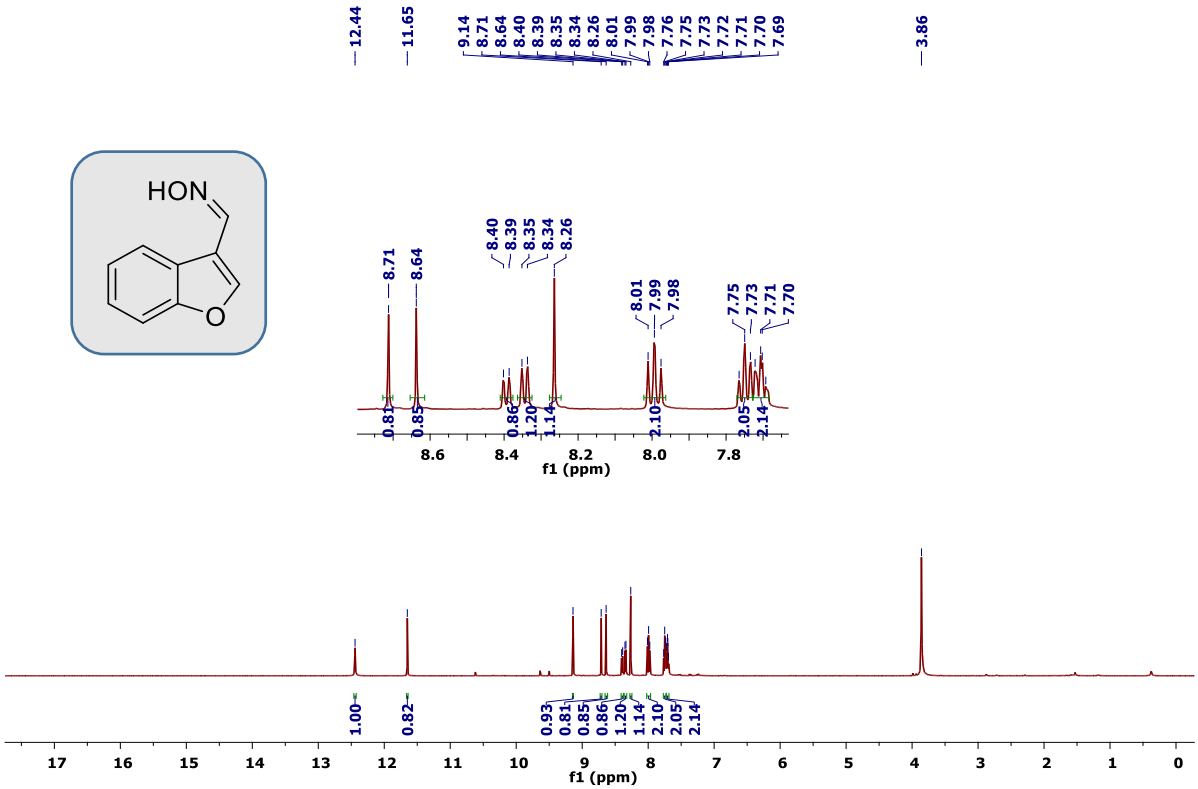


^{13}C NMR (126 MHz, DMSO-d6)

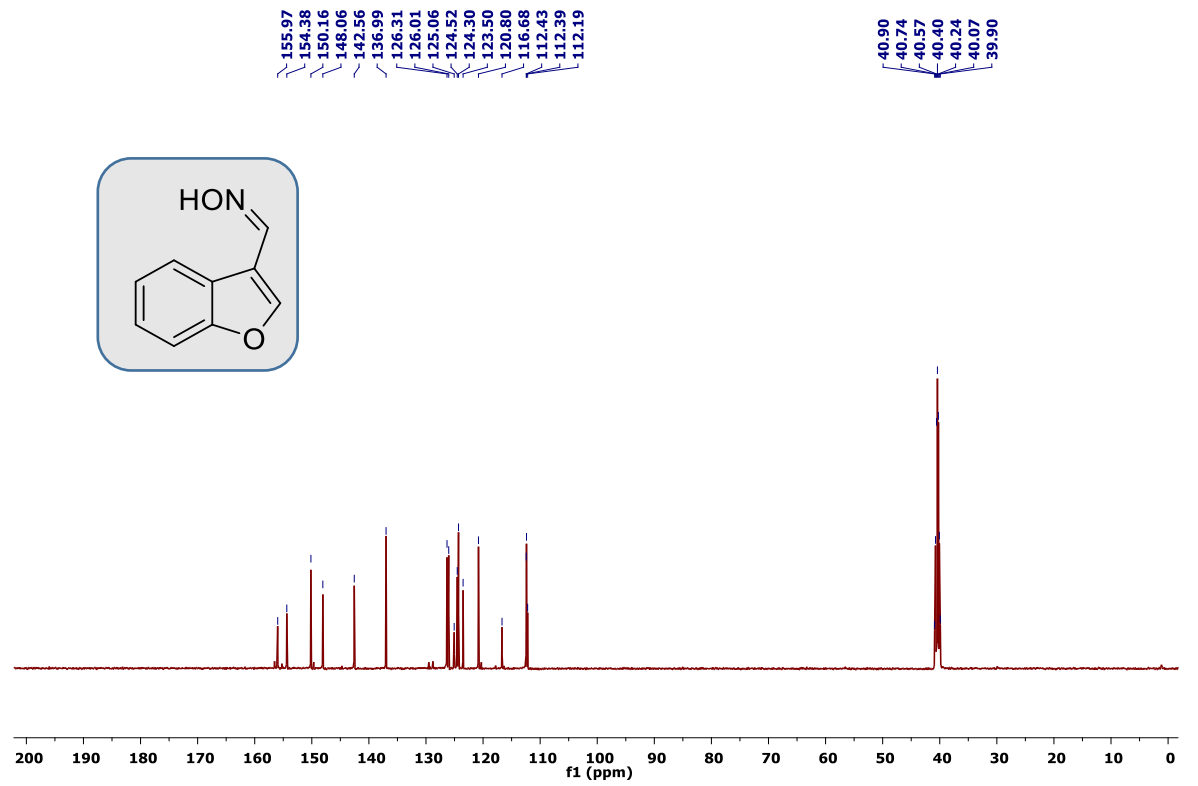


benzofuran-3-carbaldehyde oxime(1o)

^{1}H NMR (500 MHz, DMSO-d6)

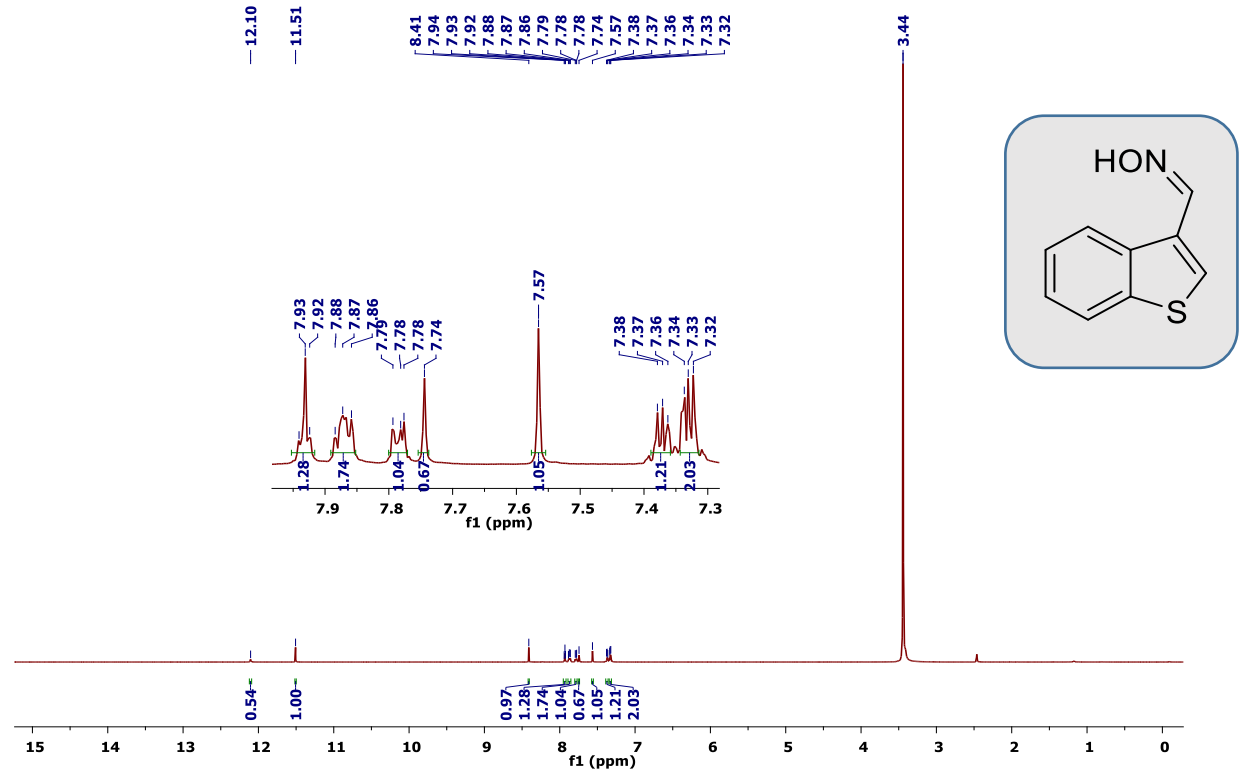


^{13}C NMR (126 MHz, DMSO-d6)

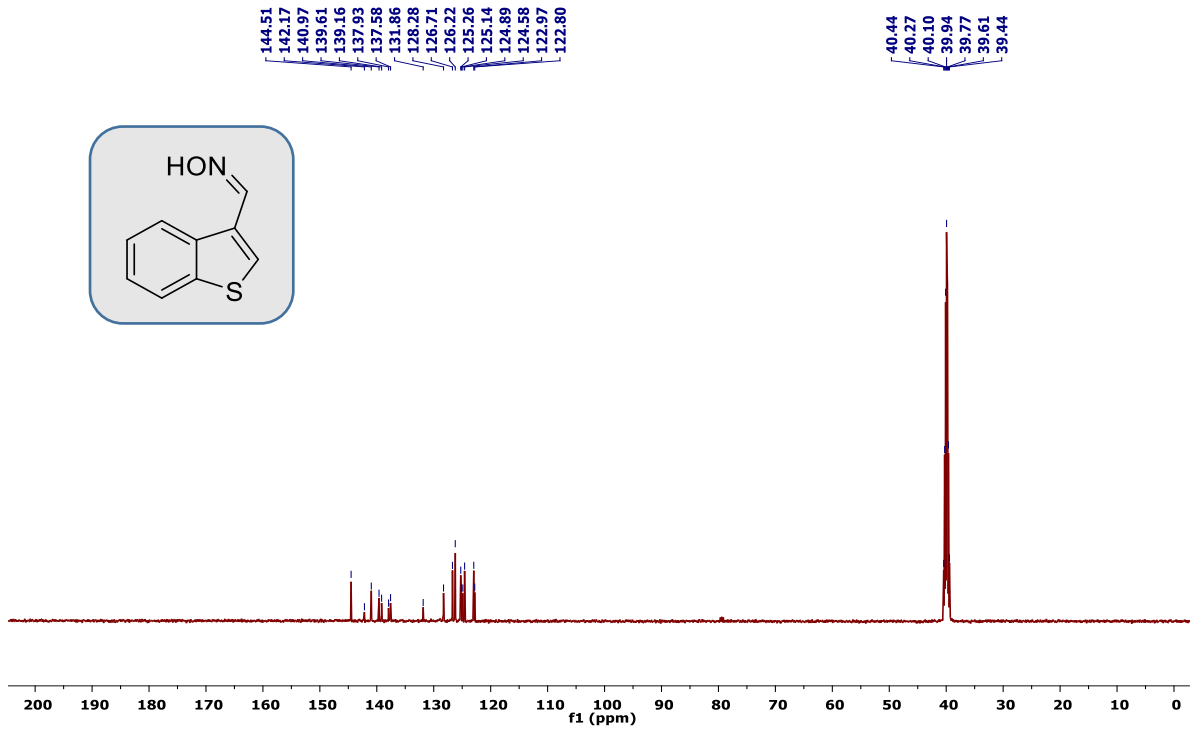


benzo[b]thiophene-3-carbaldehyde oxime(1p)

^{1}H NMR (500 MHz, DMSO-d6)

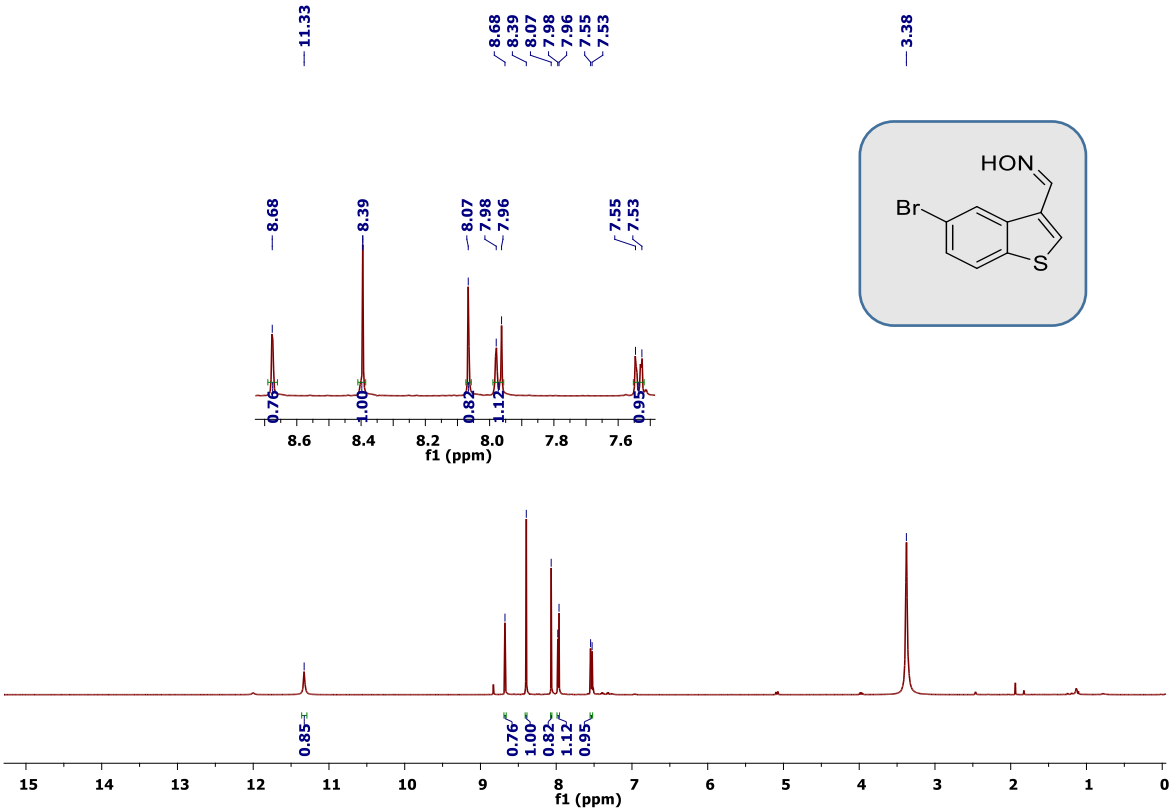


^{13}C NMR (126 MHz, DMSO-d6)

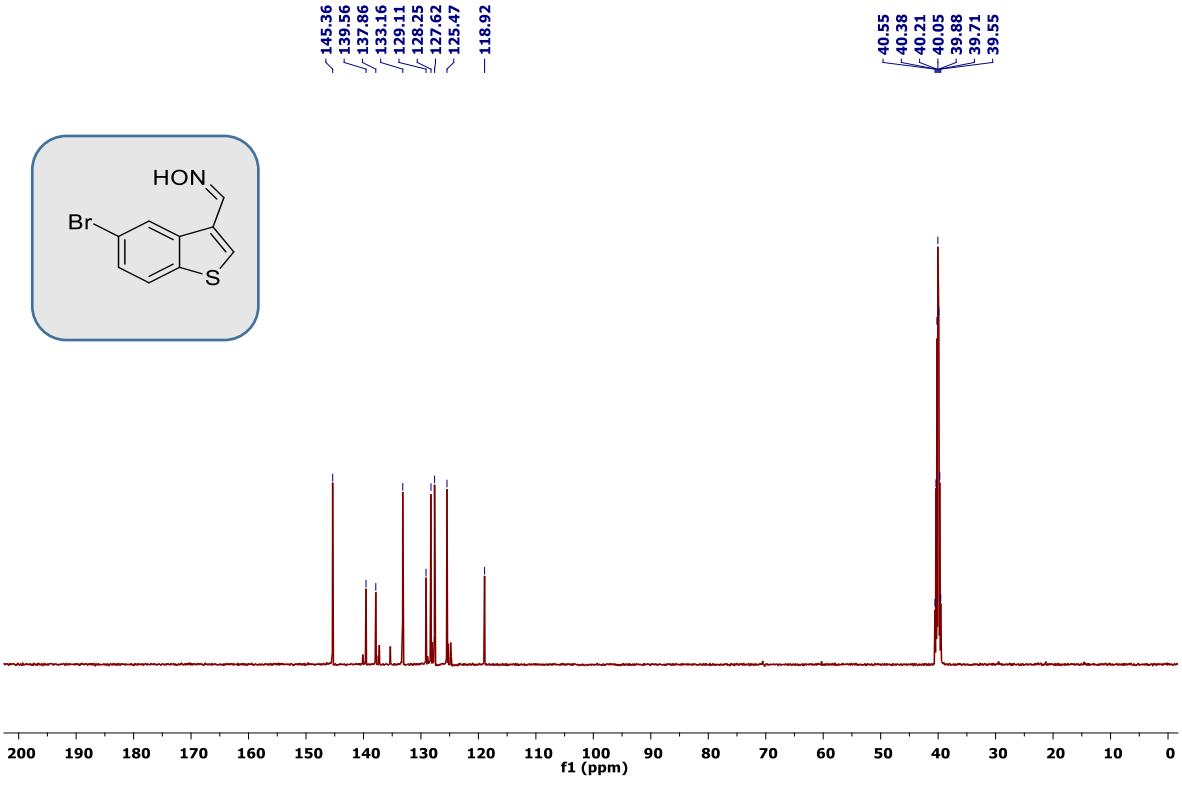


5-bromobenzo[b]thiophene-3-carbaldehyde oxime(1q)

^{1}H NMR (500 MHz, DMSO-d6)

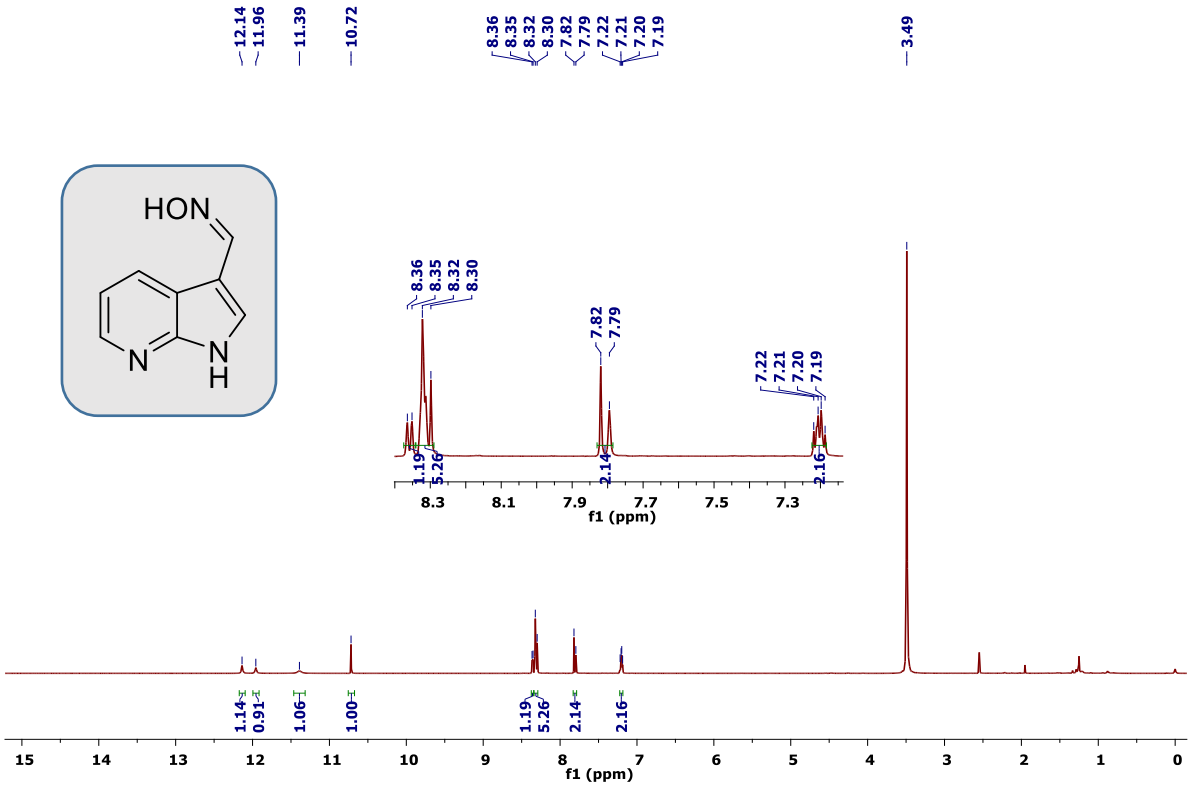


^{13}C NMR (500 MHz, DMSO-d6)

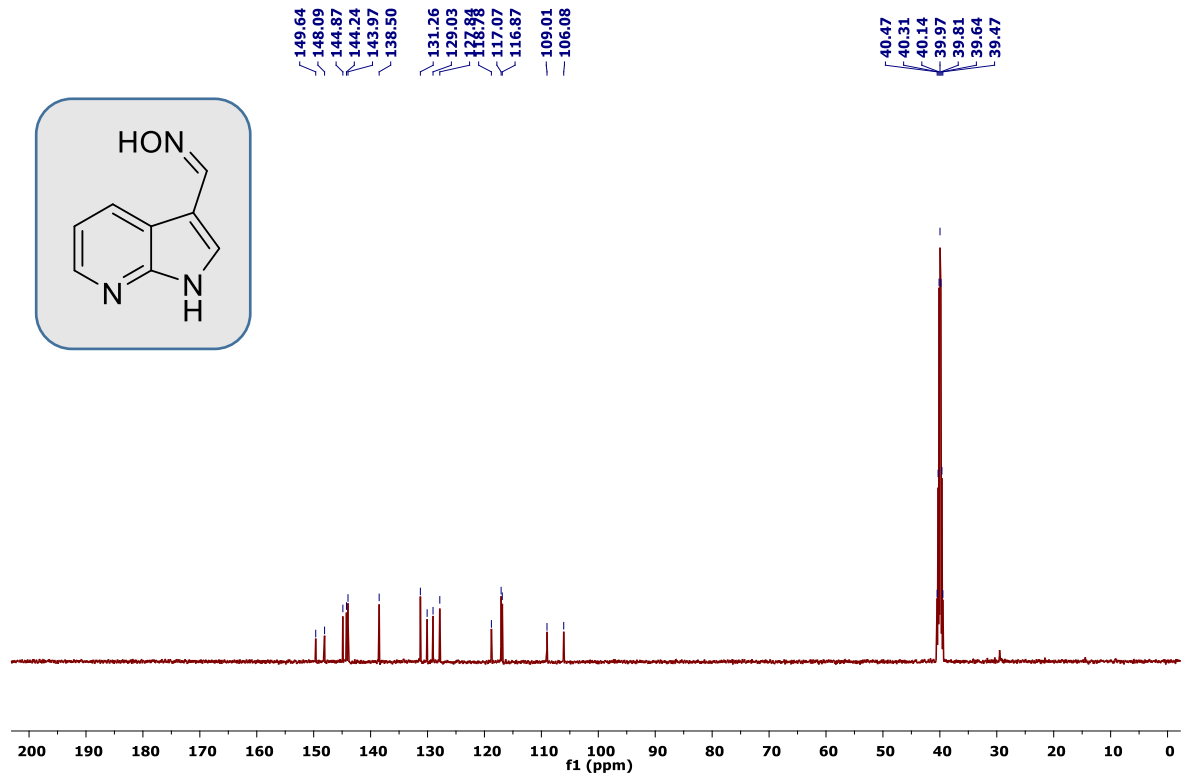


1H-pyrrolo[2,3-b]pyridine-3-carbaldehyde oxime(1r)

^{1}H NMR (500 MHz, DMSO-d6)

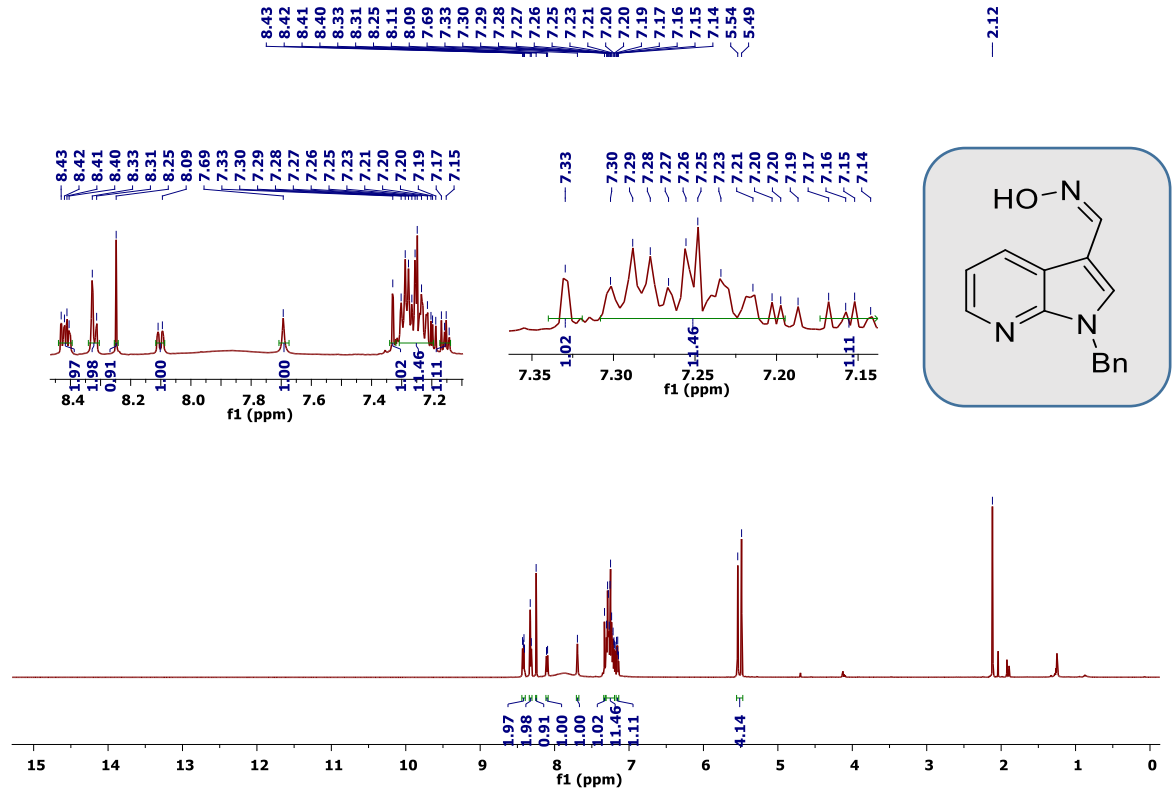


^{13}C NMR (126 MHz, DMSO-d6)

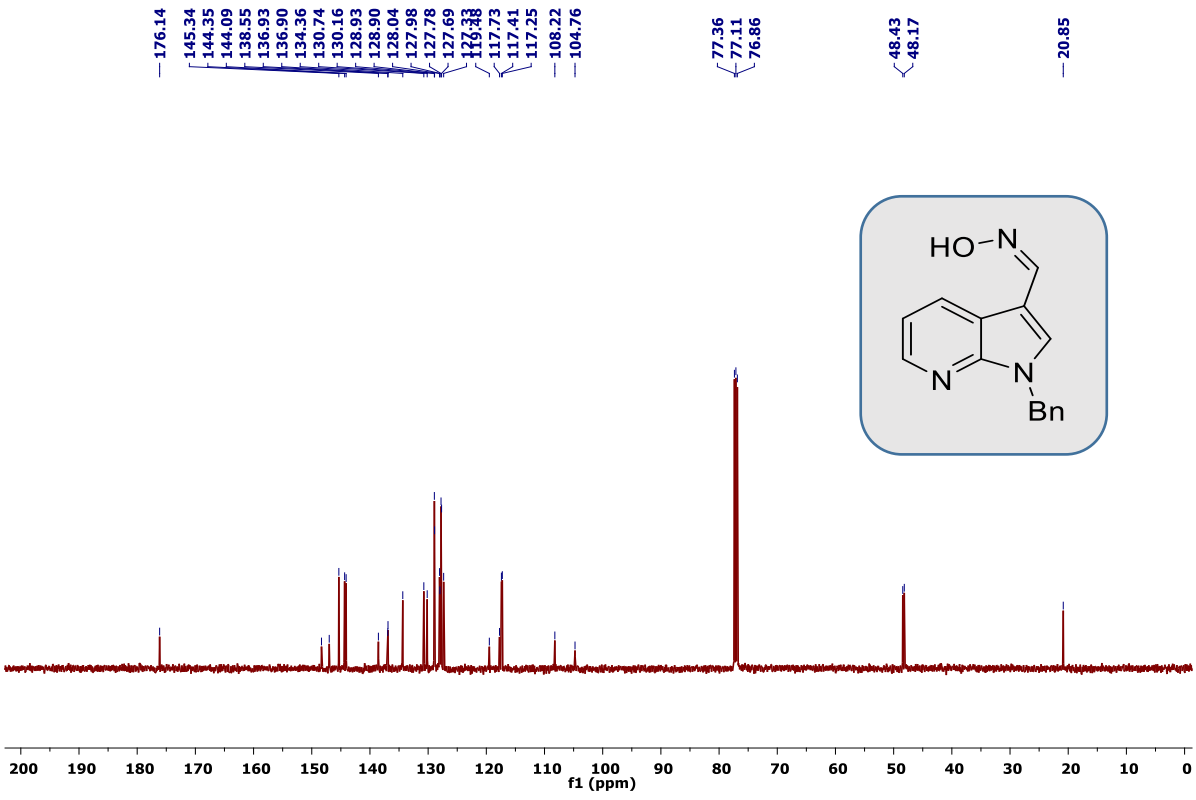


1-benzyl-1H-pyrrolo[2,3-b]pyridine-3-carbaldehyde oxime(1s)

^{1}H NMR (500 MHz, $CDCl_3$)

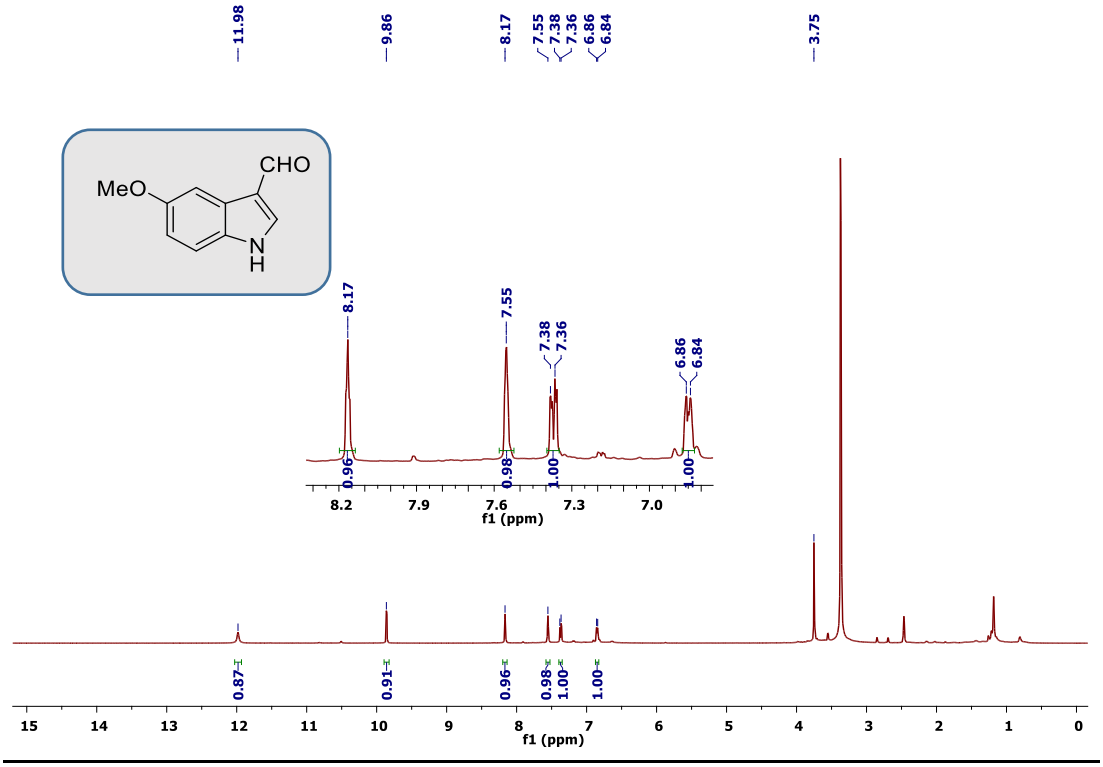


^{13}C NMR (126 MHz, $CDCl_3$)

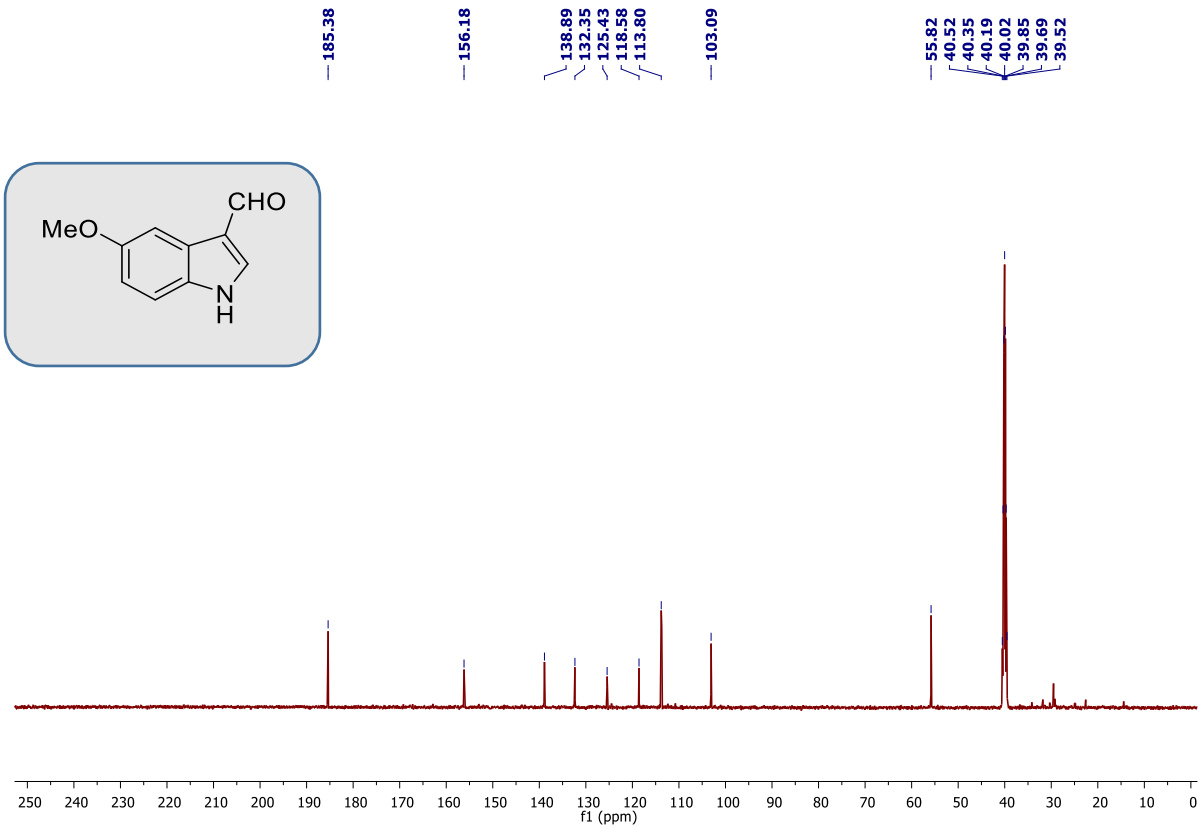


16. NMR Spectra of starting material: Aldehyde
5-methoxy-1H-indole-3-carbaldehyde(1b')

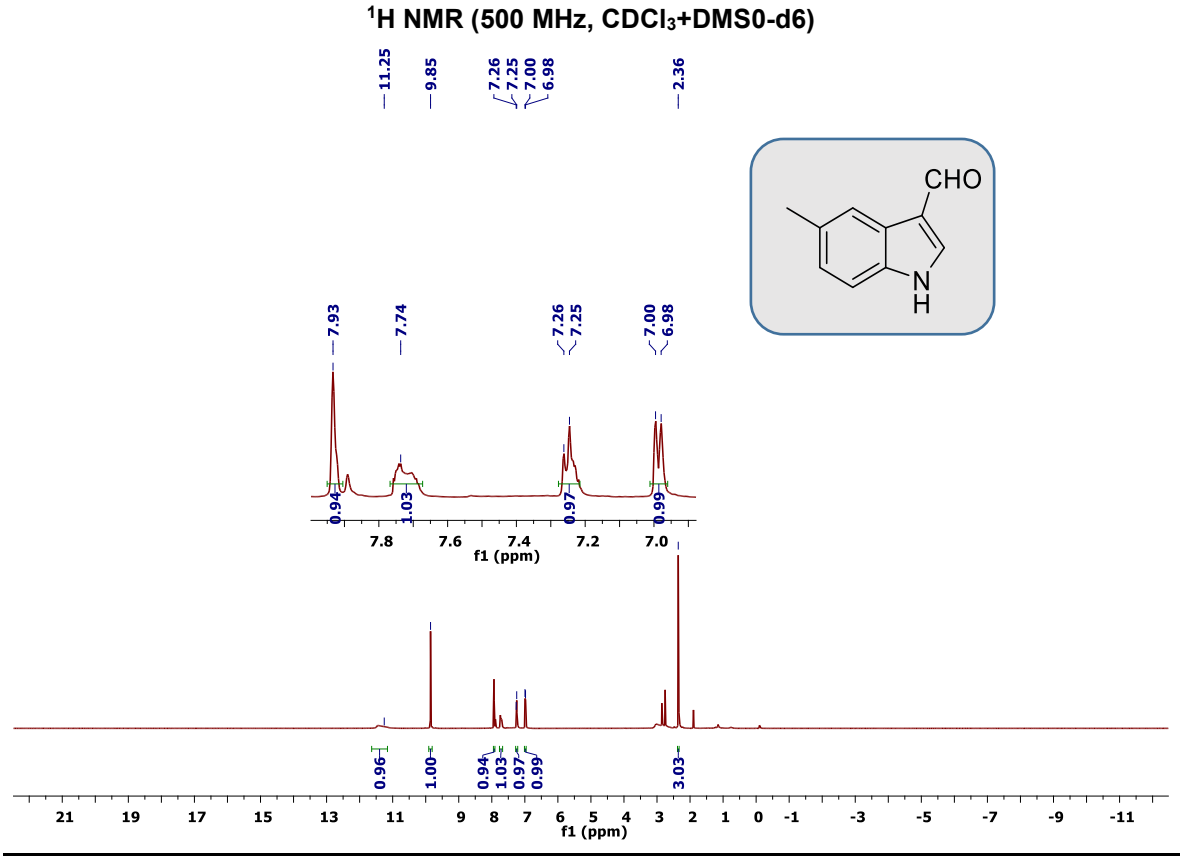
^{1}H NMR (500 MHz, DMSO-d6)



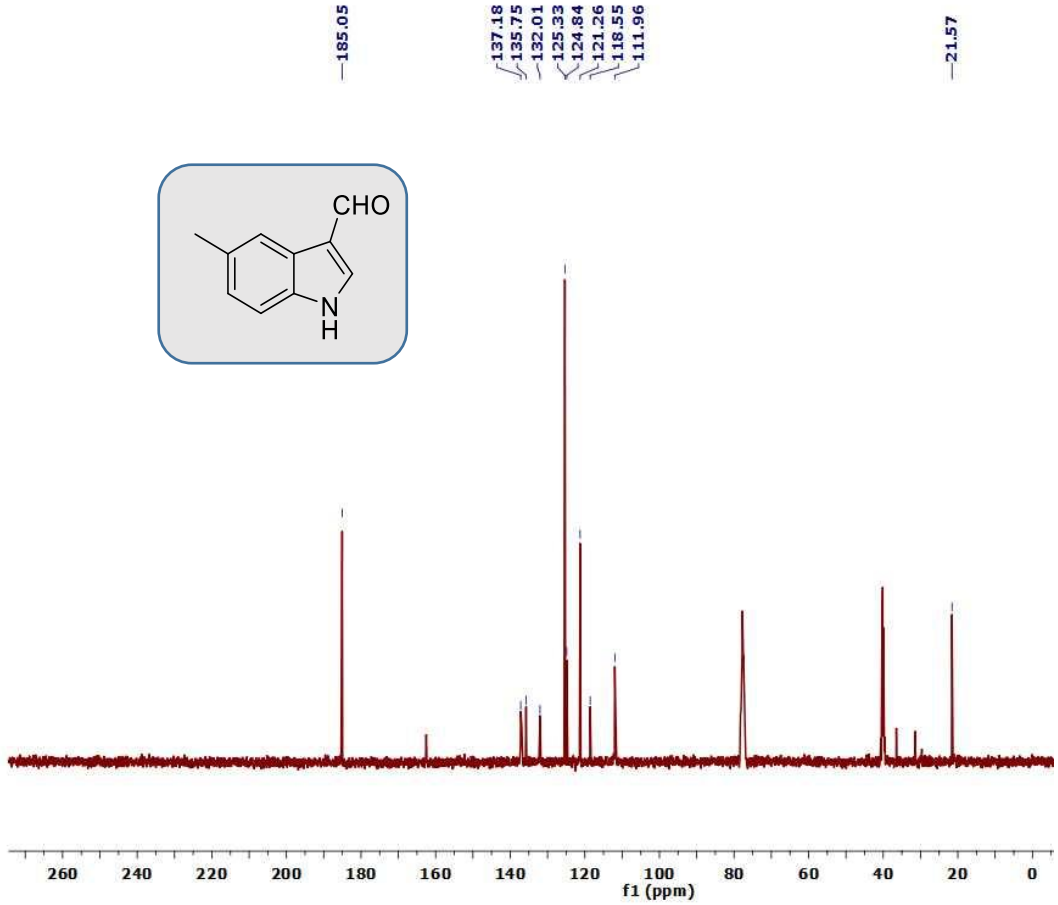
^{13}C NMR (126 MHz, DMSO-d6)



5-methyl-1H-indole-3-carbaldehyde(1c')

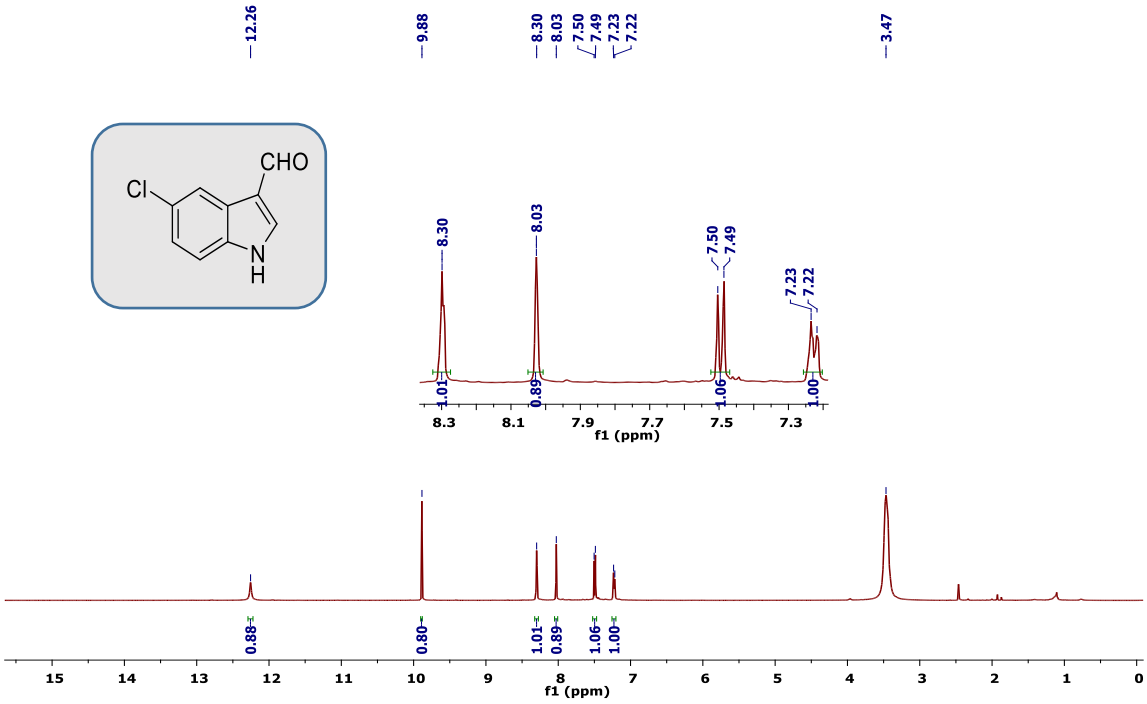


^{13}C NMR (126 MHz, $CDCl_3$+DMS0-d6)

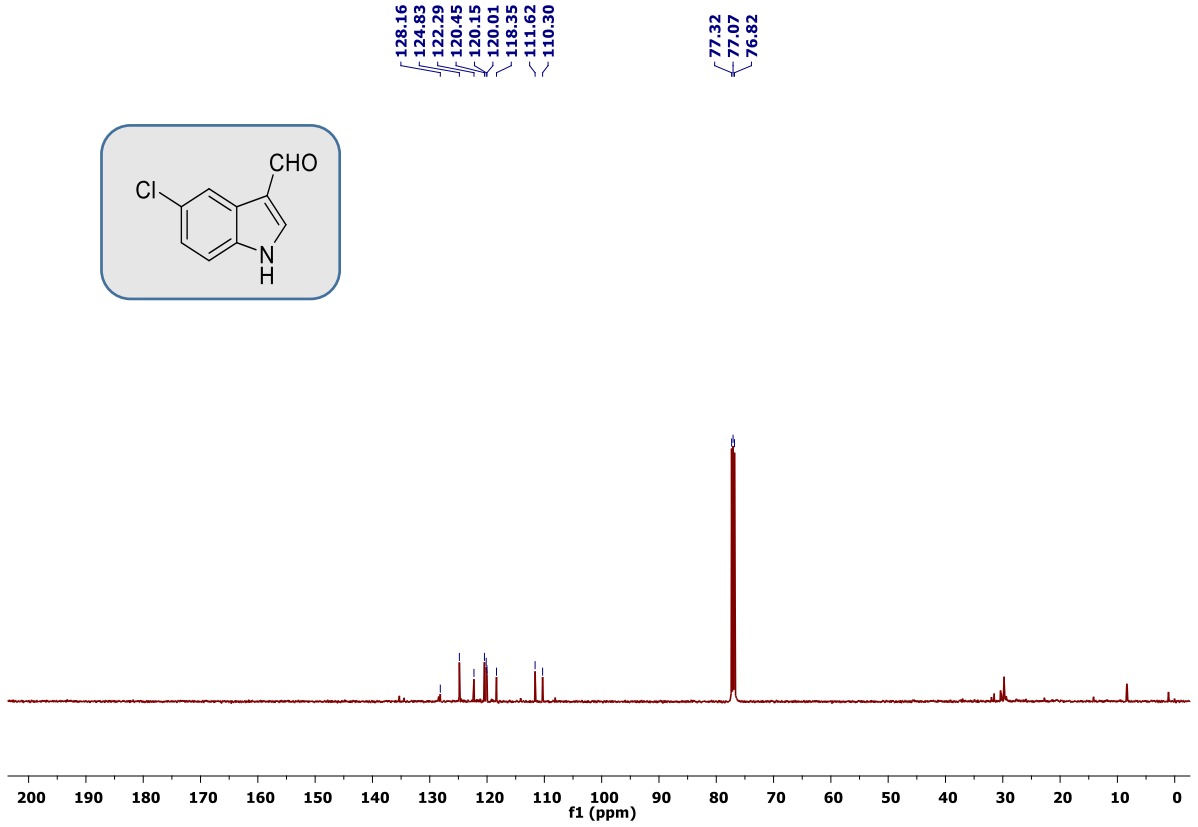


5-chloro-1H-indole-3-carbaldehyde(1d')

^{1}H NMR (500 MHz, $CDCl_3$)

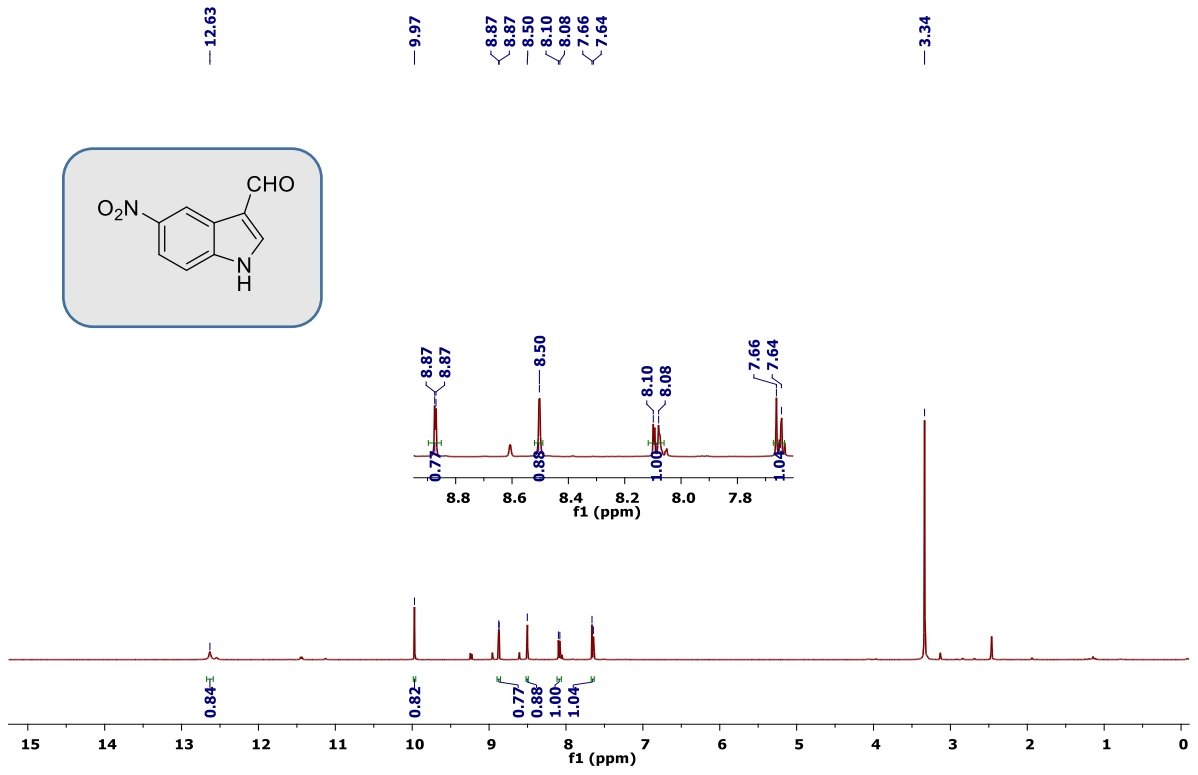


^{13}C NMR (126 MHz, $CDCl_3$)

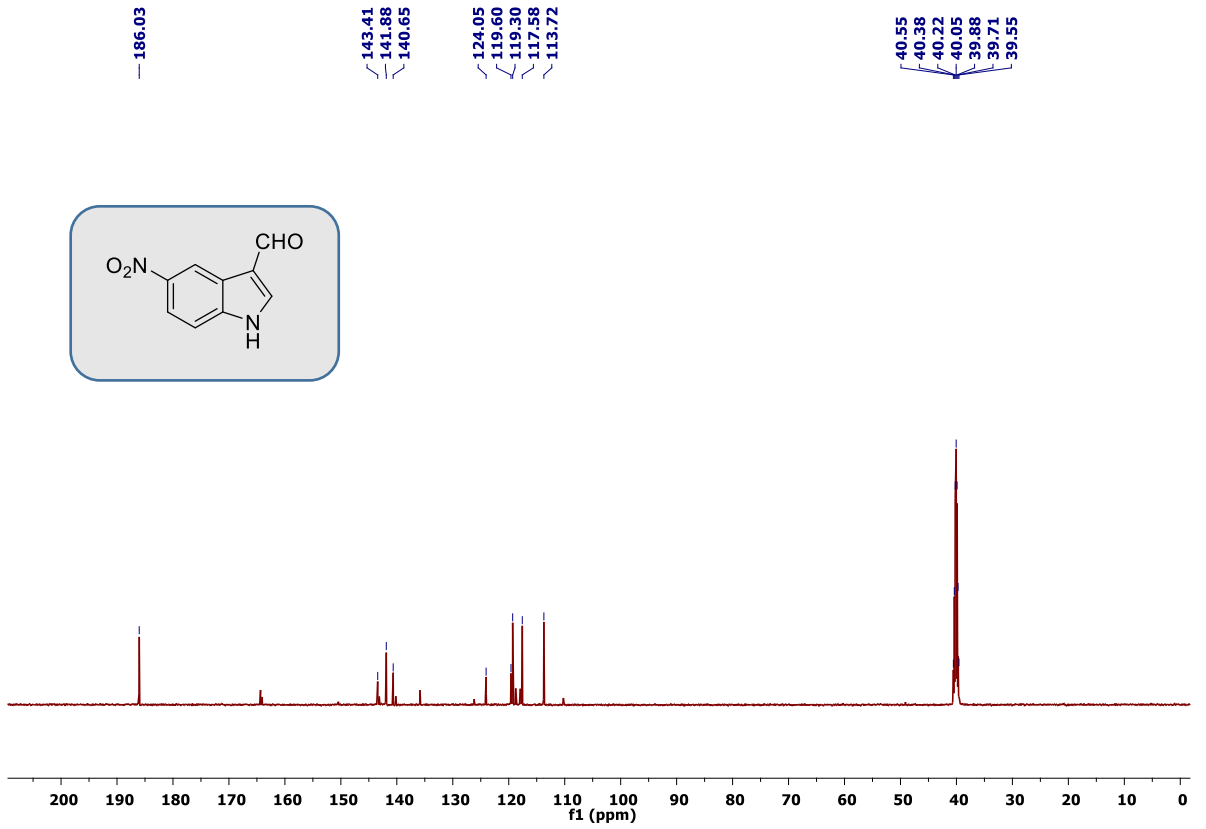


5-nitro-1H-indole-3-carbaldehyde(1e')

^{1}H NMR (500 MHz, DMSO-d6)

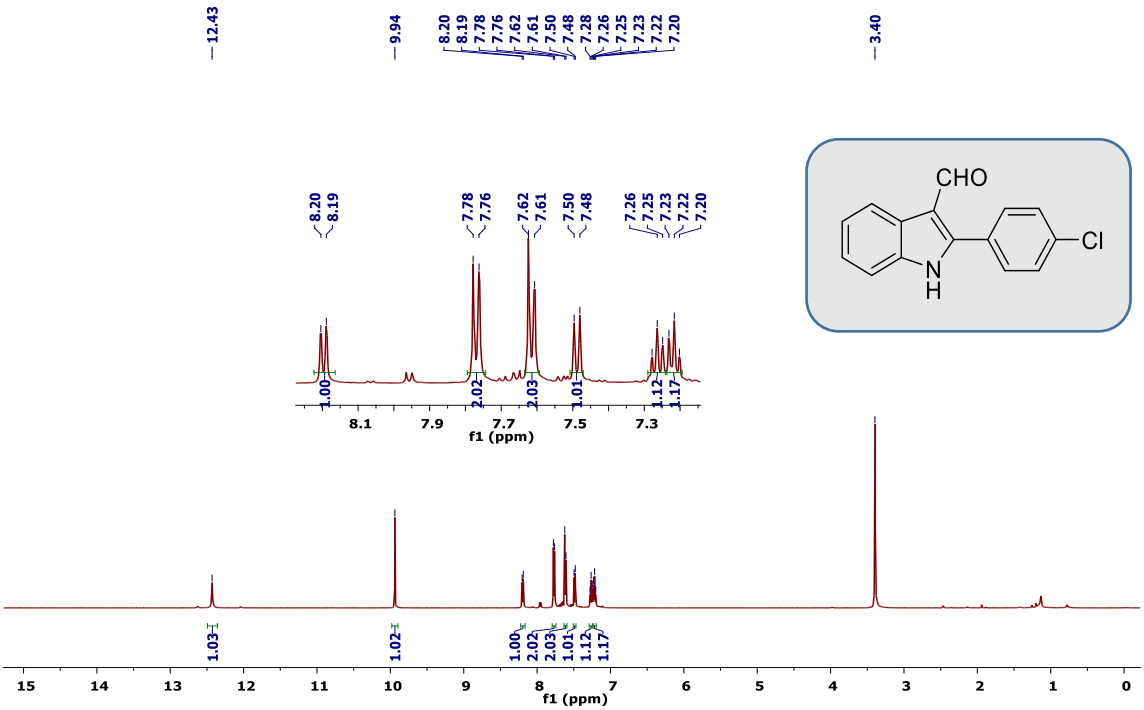


^{13}C NMR (126MHz, DMSO-d6)

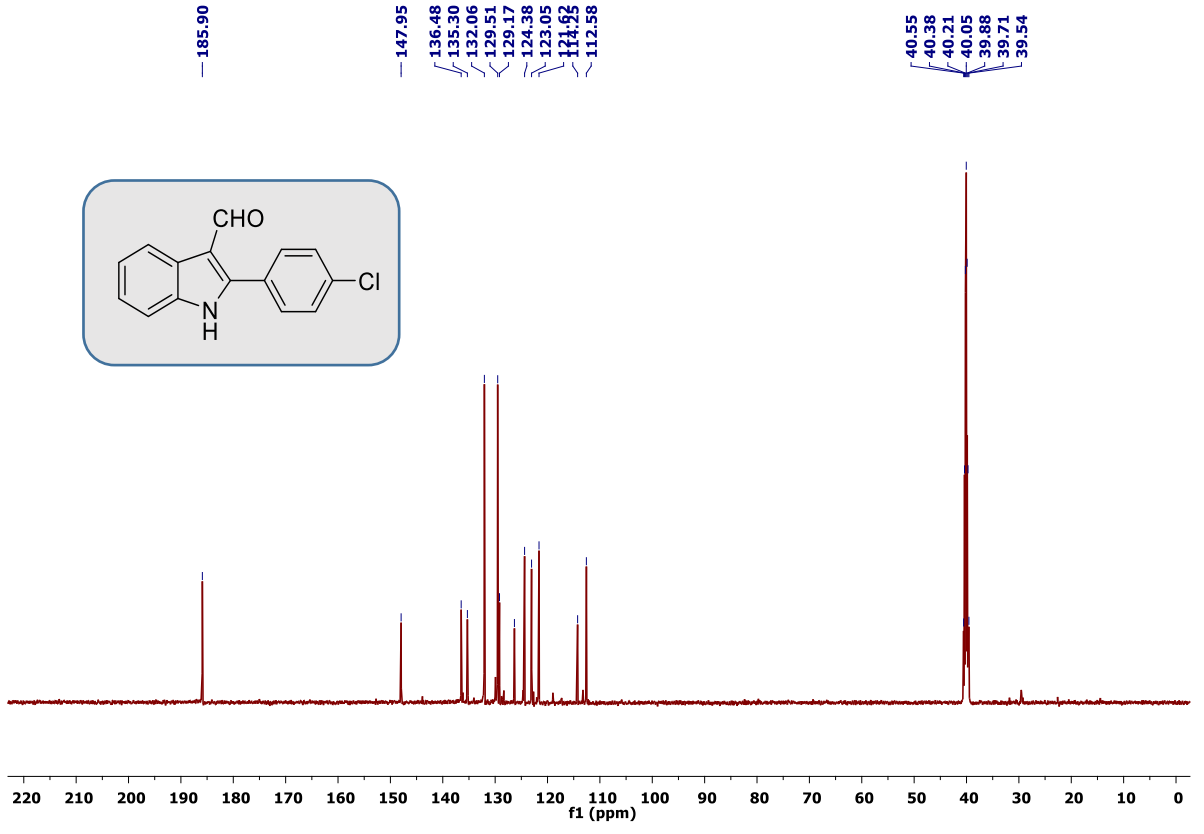


2-(4-chlorophenyl)-1H-indole-3-carbaldehyde(1h')

^{1}H NMR (500 MHz, DMSO-d6)

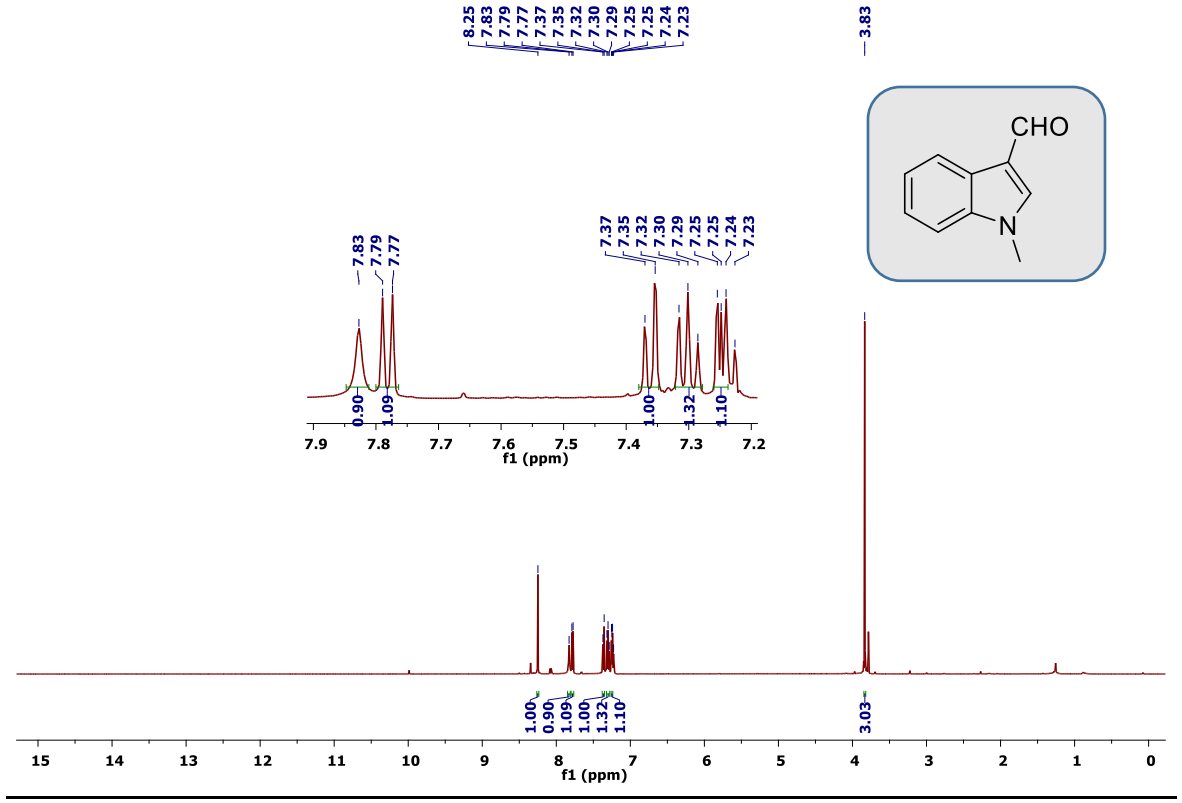


^{13}C NMR (126 MHz, DMSO-d6)



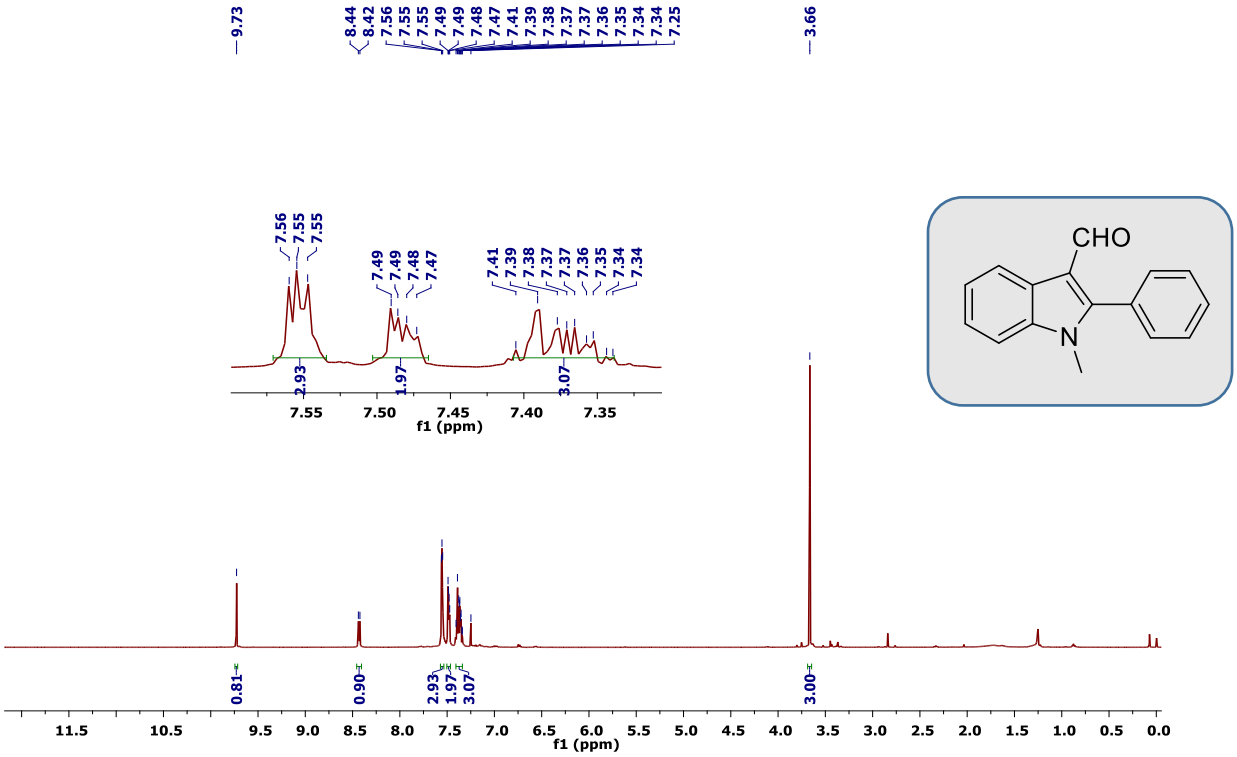
1-methyl-1H-indole-3-carbaldehyde(1i')

^{1}H NMR (500 MHz, $CDCl_3$)

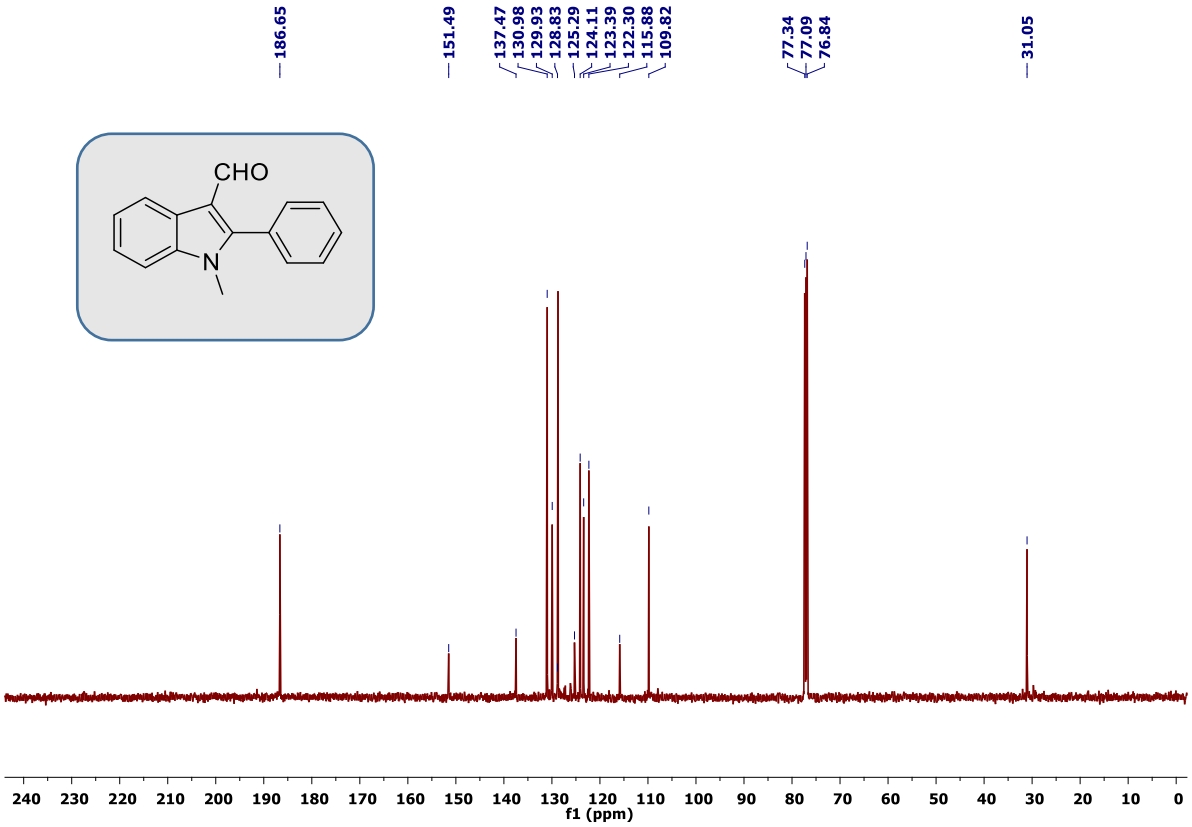


1-methyl-2-phenyl-1H-indole-3-carbaldehyde(1j')

^{1}H NMR (500 MHz, $CDCl_3$)

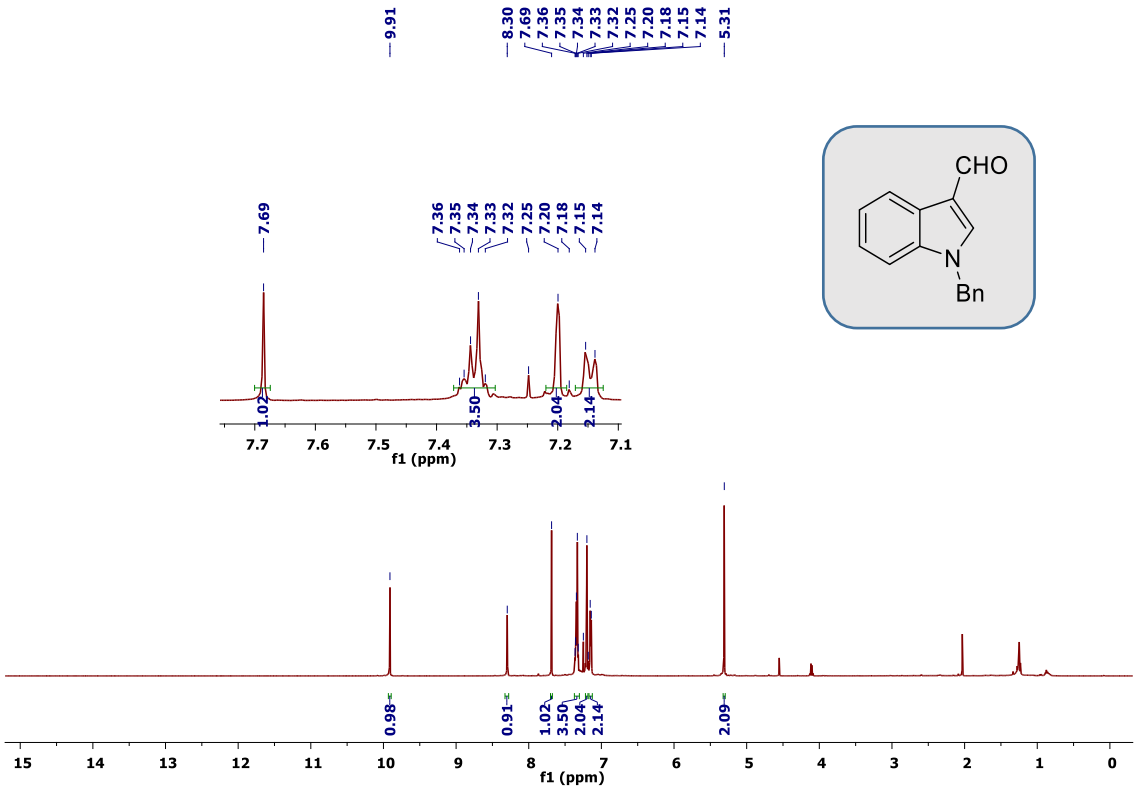


^{13}C NMR (126 MHz, $CDCl_3$)

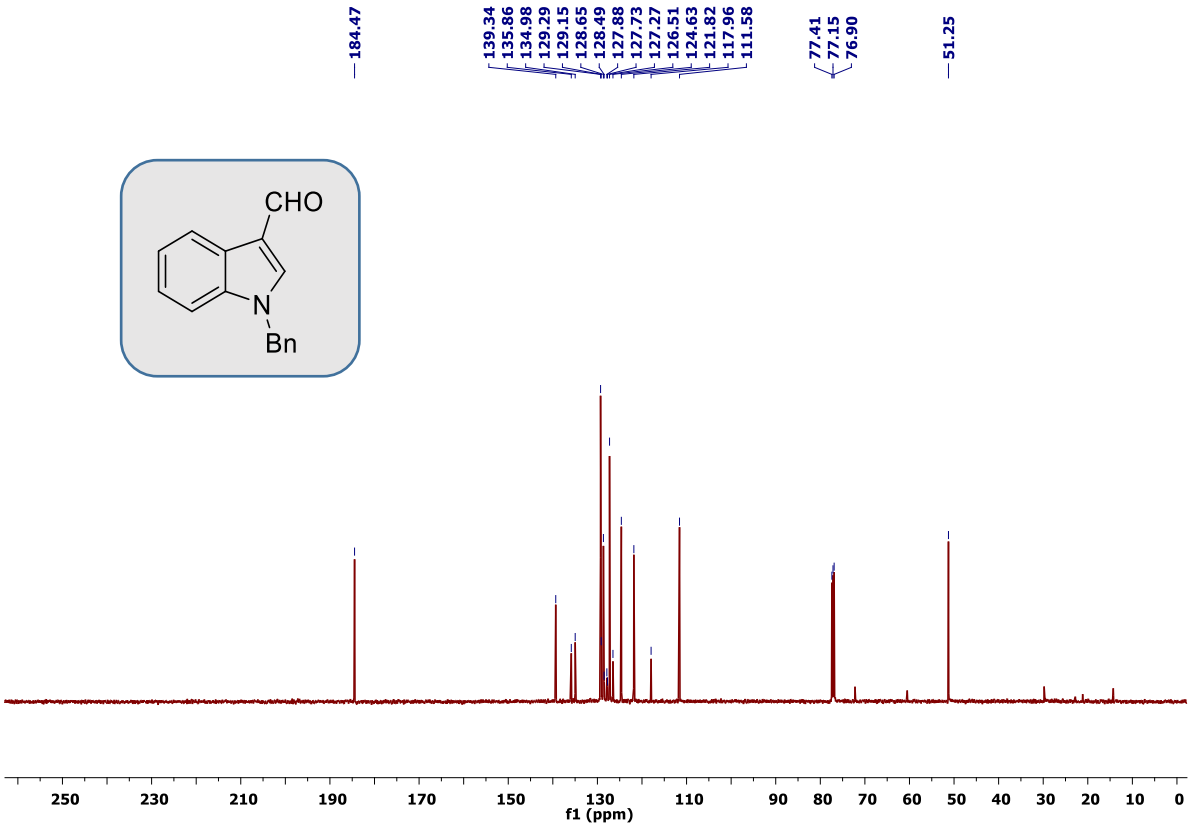


1-benzyl-1H-indole-3-carbaldehyde(1k')

^{1}H NMR (500 MHz, $CDCl_3$)

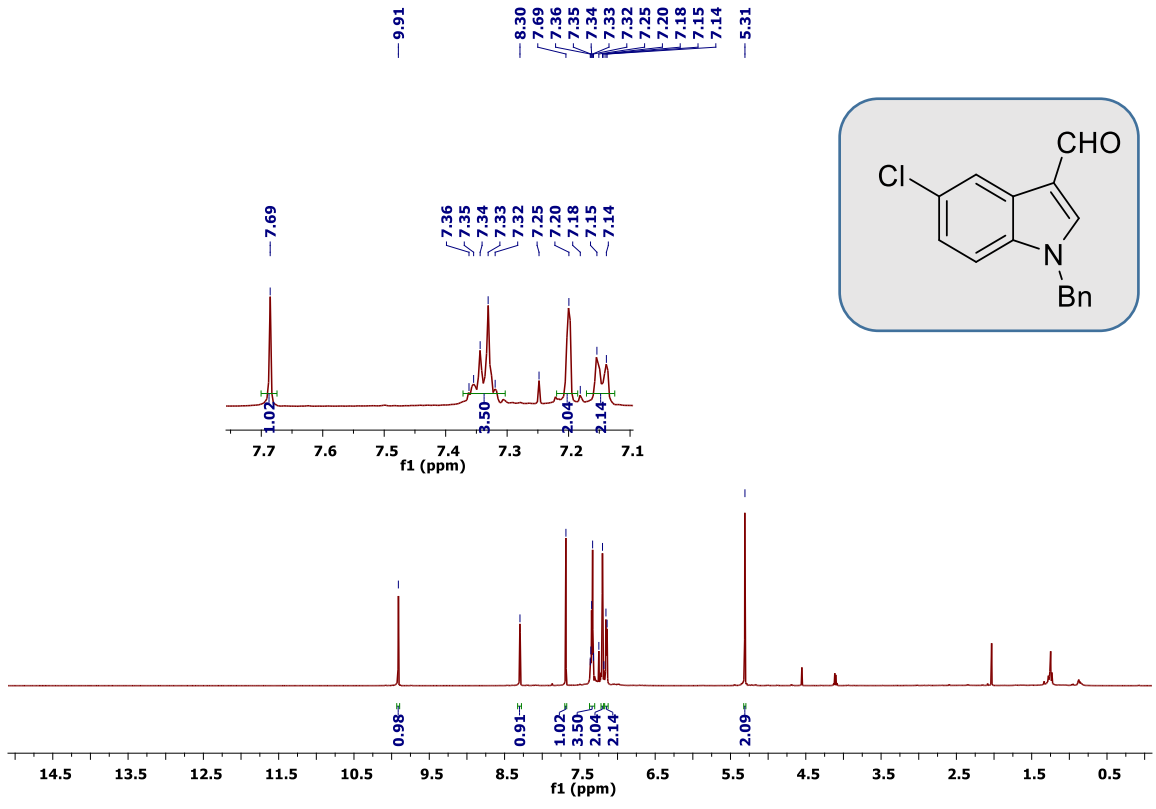


^{13}C NMR (126 MHz, $CDCl_3$)

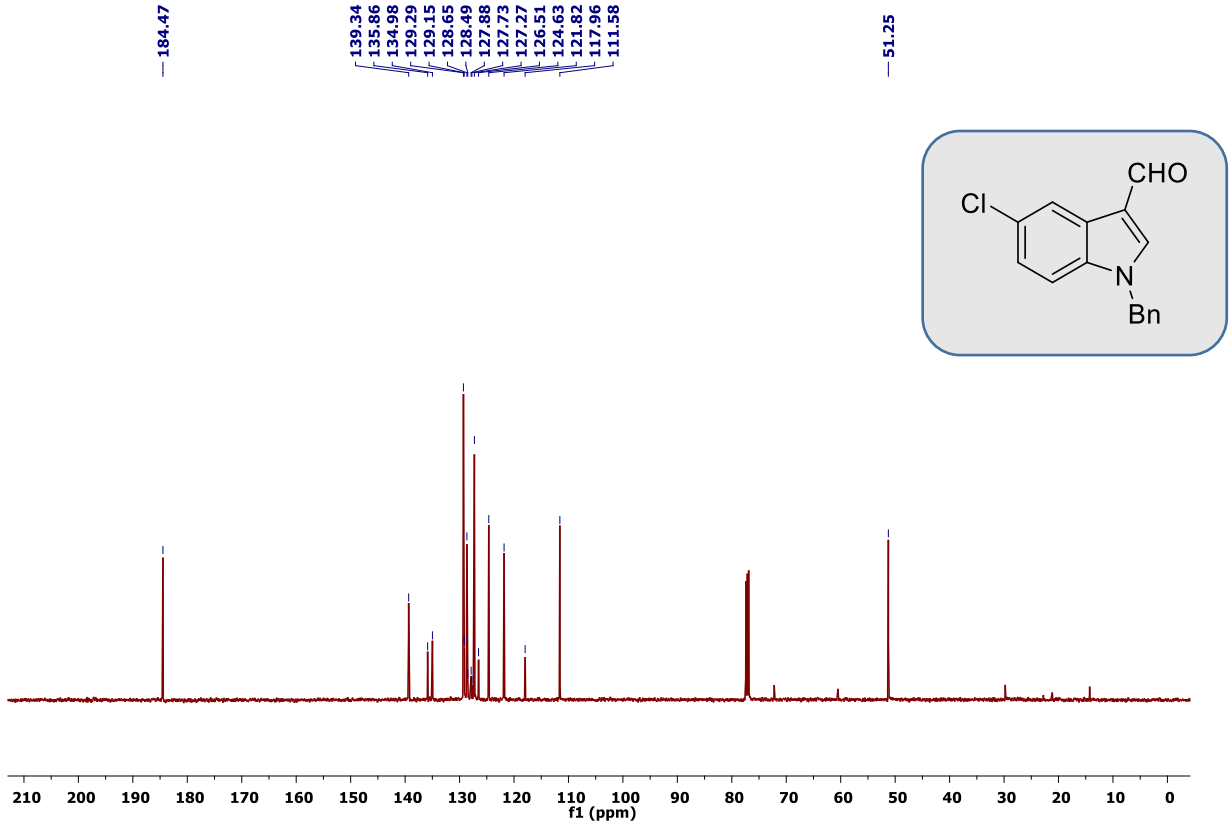


1-benzyl-5-chloro-1H-indole-3-carbaldehyde(1l')

^{1}H NMR (500 MHz, $CDCl_3$)

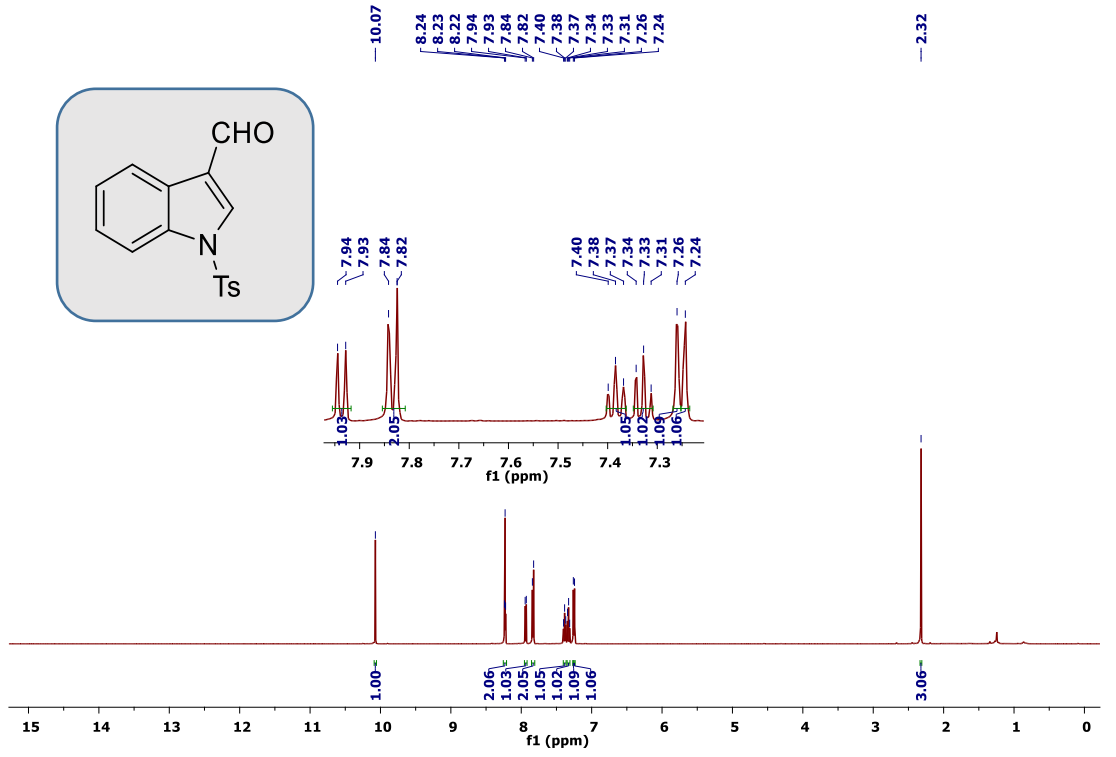


^{13}C NMR (126 MHz, $CDCl_3$)

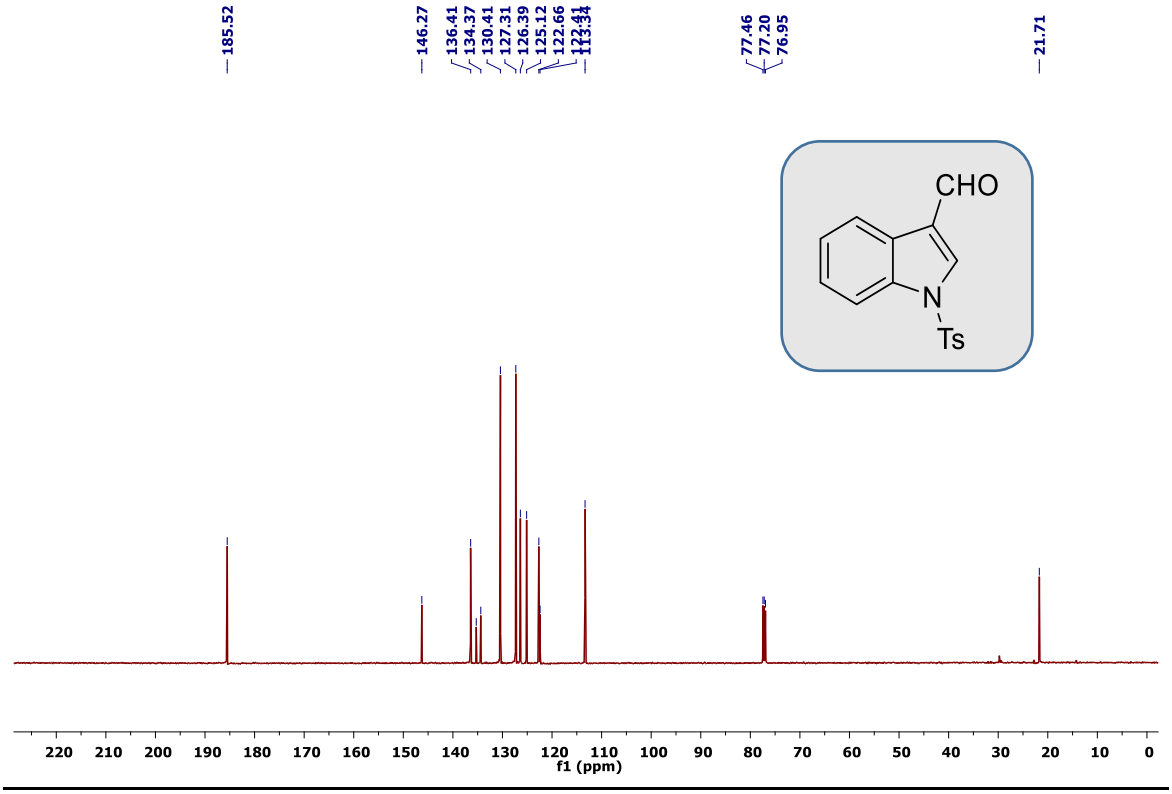


1-tosyl-1H-indole-3-carbaldehyde(1m')

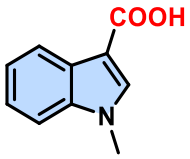
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



17. NMR Data and Spectra of 1-methyl-1H-indole-3-carboxylic acid (4i)

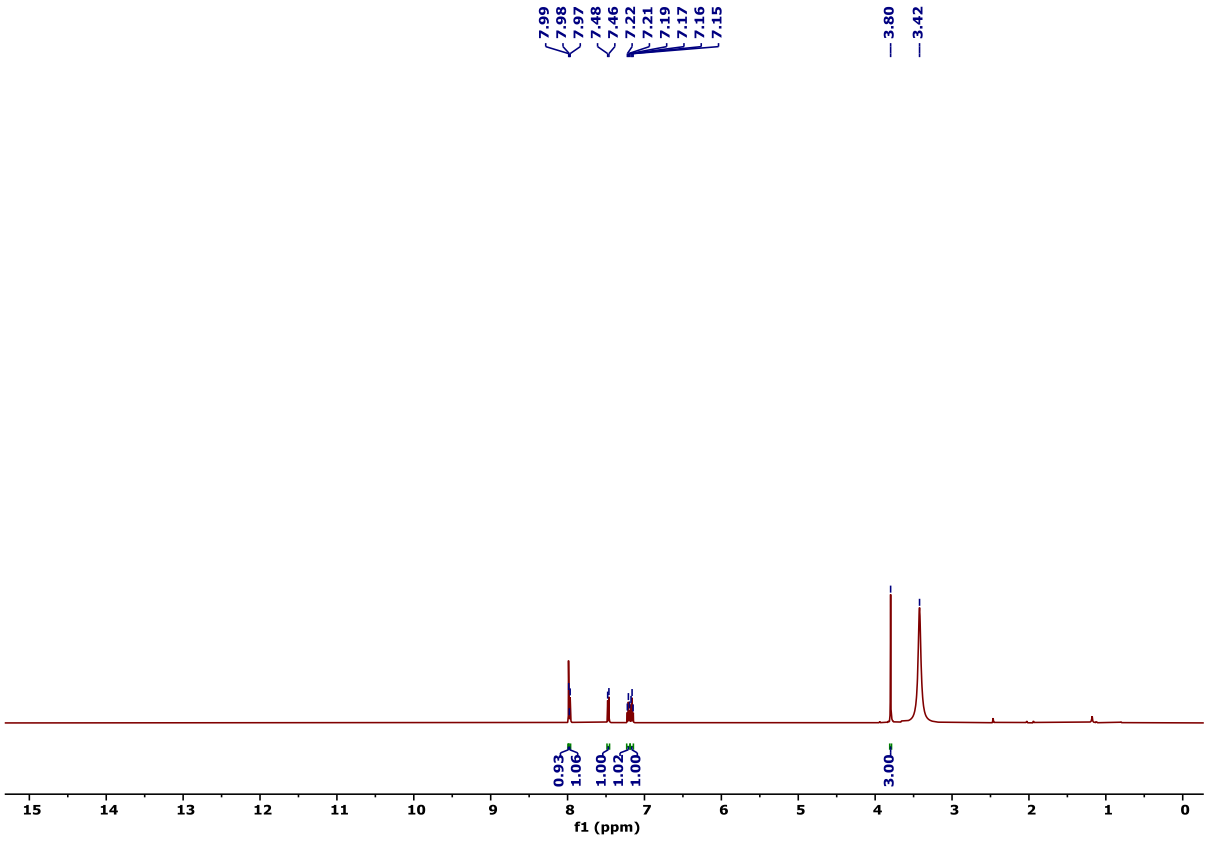


Known Compound. White solid; isolated yield 84%.

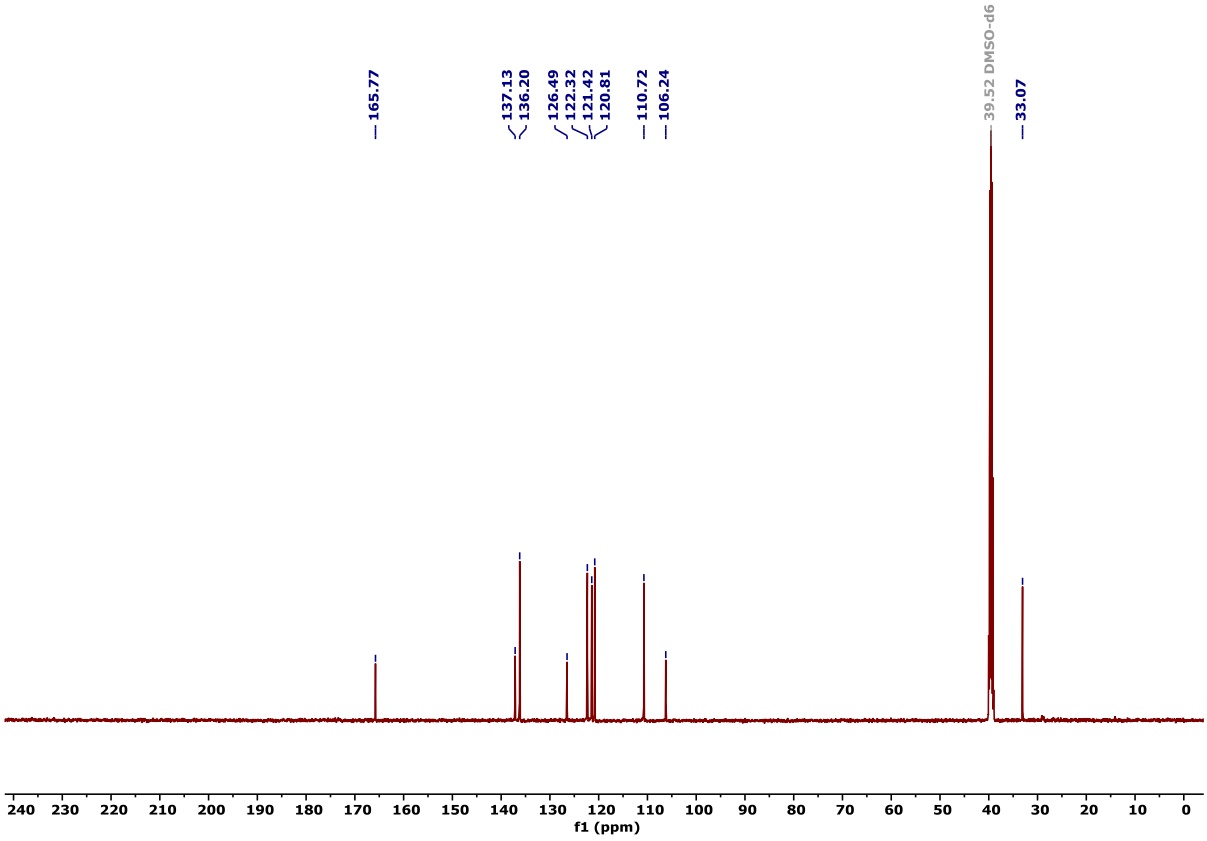
^{1}H NMR (500 MHz, DMSO-D_6) δ 7.99 (s, 1H), 7.97 (d, J = 5.3 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.3 Hz, 1H), 7.16 (t, J = 6.7 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (126 MHz, DMSO-D_6) δ 165.77, 137.13, 136.20, 126.49, 122.32, 121.42, 120.81, 110.72, 106.24, 33.07.

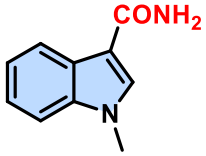
^{1}H NMR (500 MHz, DMSO-D_6)



^{13}C NMR (500 MHz, DMSO-D_6)



18. NMR Data and Spectra of 1-methyl-1H-indole-3-carboxamide (5i)

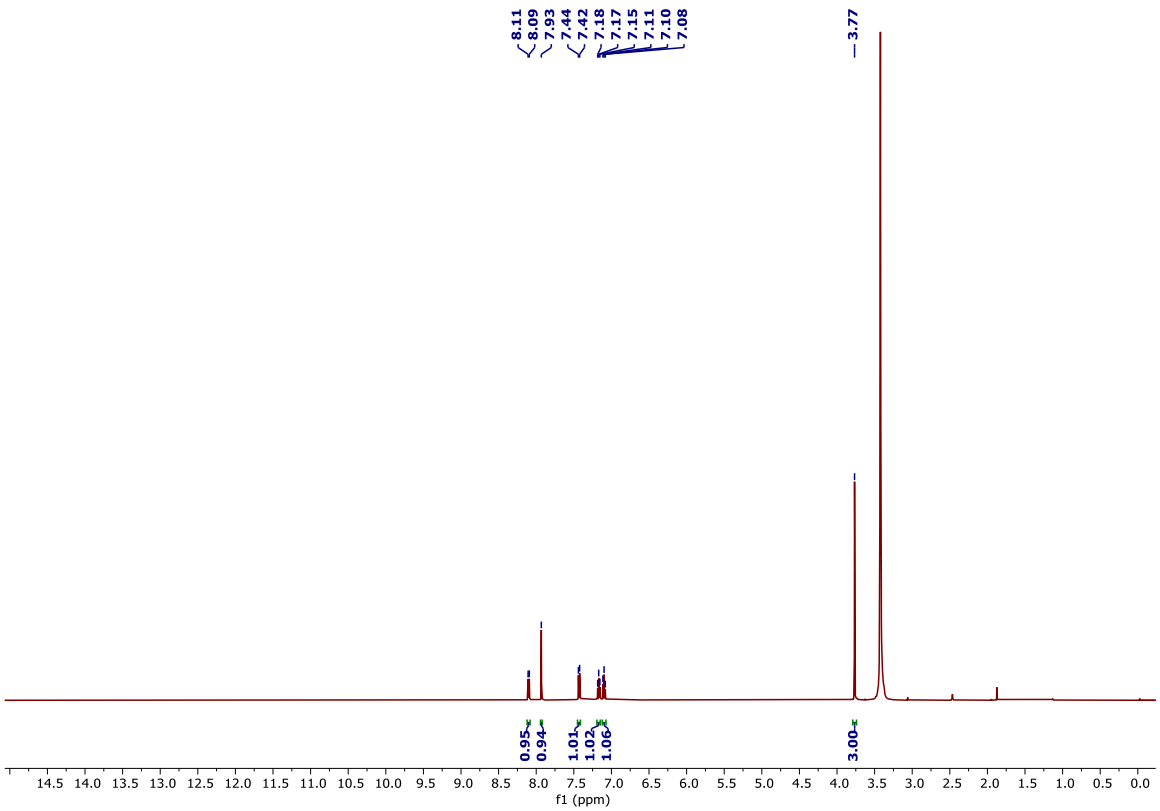


Known Compound. White solid, yield 71%.

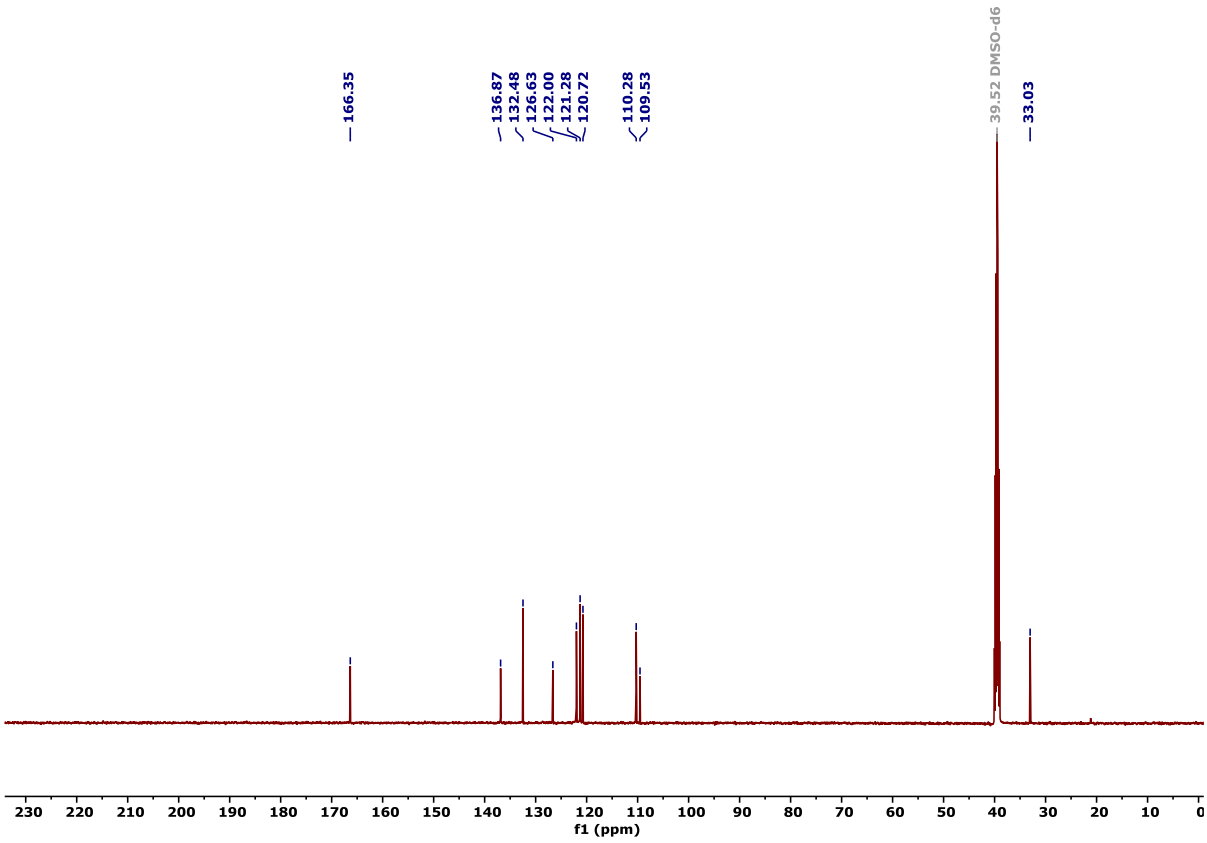
^{1}H NMR (500 MHz, DMSO-D_6) δ 8.10 (d, J = 8.0 Hz, 1H), 7.93 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.17 (t, J = 7.3 Hz, 1H), 7.10 (t, J = 8.0 Hz, 1H), 3.77 (s, 3H).

^{13}C NMR (126 MHz, DMSO-D_6) δ 166.35, 136.87, 132.48, 126.63, 122.00, 121.28, 120.72, 110.28, 109.53, 33.03.

^{1}H NMR (500 MHz, DMSO-D_6)



^{13}C NMR (500 MHz, DMSO-D_6)



19. DFT Calculation
Computational details:

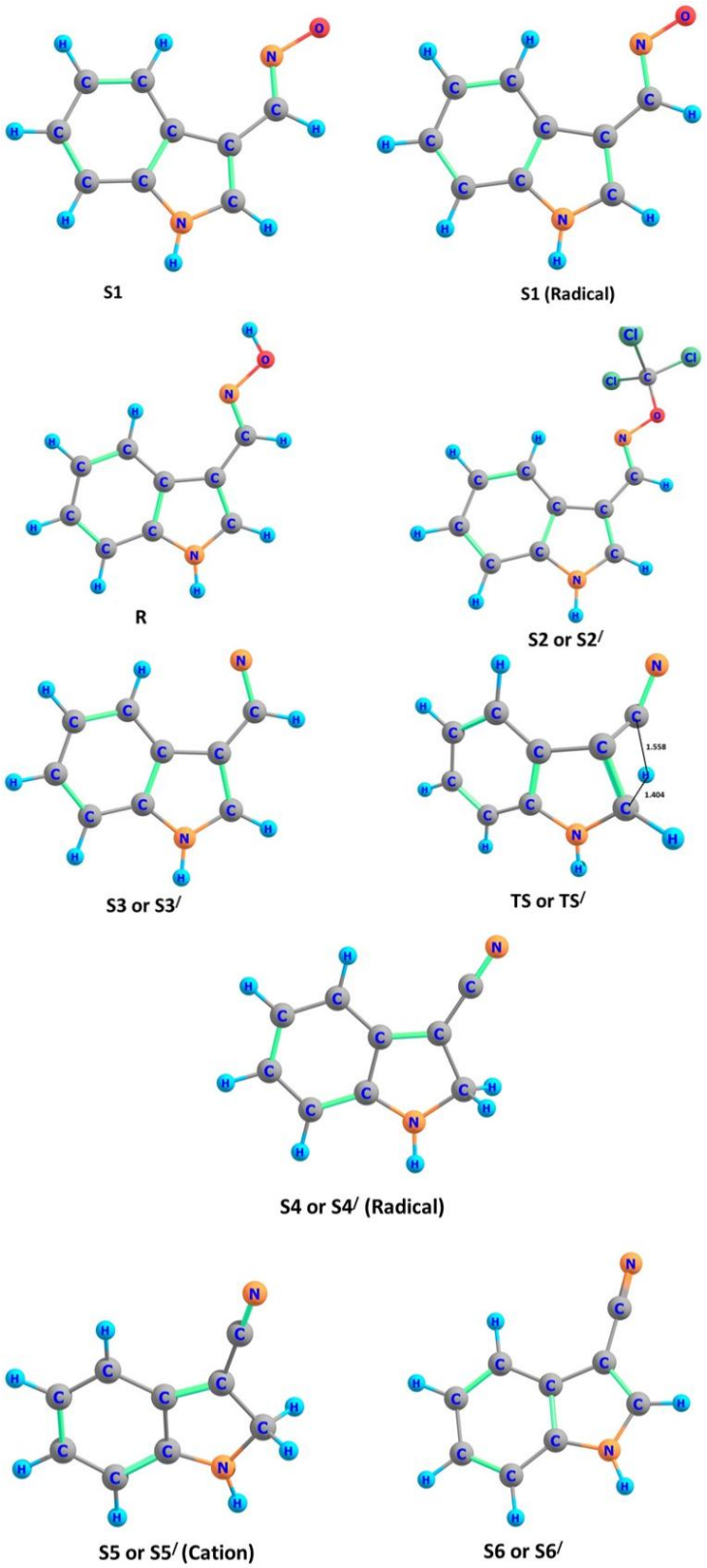
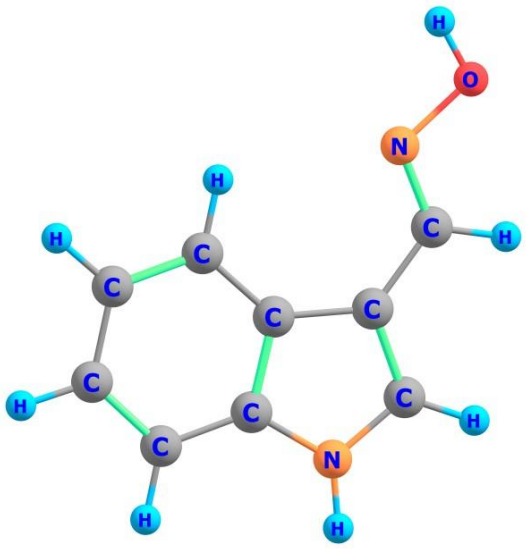


Figure 12: Structures of each and every species involved in both Pathway I and Pathway II calculated at wB97XD/6-311+G(d,p) level of theory.

Coordinates

R



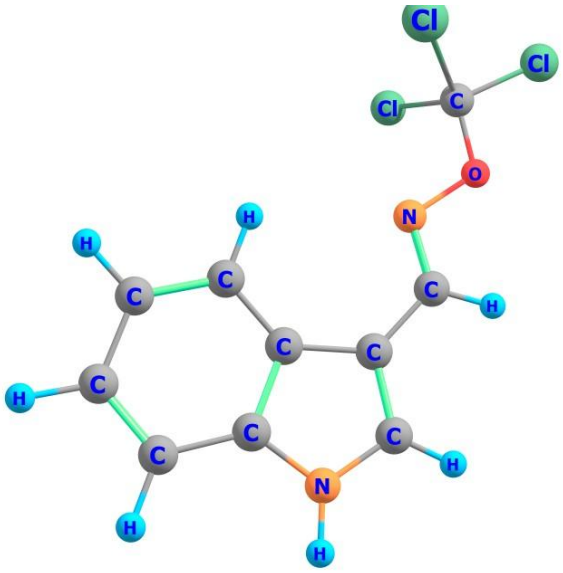
20

symmetry c1

C	0.360510000	-0.092507000	0.000002000
C	1.505156000	0.733610000	0.000075000
C	2.801230000	0.217658000	0.000063000
C	2.936414000	-1.159553000	-0.000024000
C	1.810213000	-2.002218000	-0.000096000
C	0.526457000	-1.484723000	-0.000085000
C	-0.783310000	0.789219000	0.000039000
C	-0.286741000	2.071597000	0.000132000
H	3.666150000	0.870747000	0.000118000
H	3.928492000	-1.596772000	-0.000035000
H	1.954148000	-3.076860000	-0.000163000
H	-0.338564000	-2.135986000	-0.000142000
H	-0.820107000	3.010295000	0.000185000
N	1.075000000	2.042941000	0.000154000
C	-2.194692000	0.476620000	-0.000008000

N	-2.621989000	-0.725869000	-0.000096000
O	-4.019144000	-0.757112000	-0.000126000
H	1.669634000	2.854830000	0.000220000
H	-4.225887000	-1.694704000	-0.000190000
H	-2.903205000	1.307628000	0.000033000

S-2 or S2$^{\prime}$



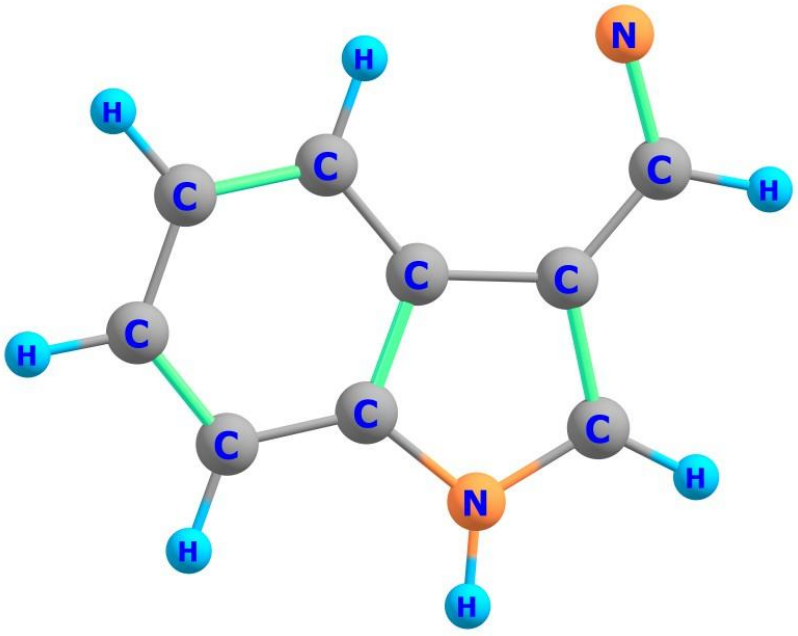
23

symmetry c1

C	-2.430624000	0.054961000	-0.000411000
C	-3.790902000	0.424447000	0.000158000
C	-4.821959000	-0.513805000	0.000637000
C	-4.461162000	-1.850149000	0.000515000
C	-3.110628000	-2.240960000	-0.000051000
C	-2.091258000	-1.304457000	-0.000508000
C	-1.674612000	1.285732000	-0.000833000
C	-2.593006000	2.313672000	-0.000506000
H	-5.861771000	-0.208238000	0.001075000
H	-5.234719000	-2.609568000	0.000862000

H	-2.866366000	-3.297188000	-0.000135000
H	-1.051903000	-1.608767000	-0.000930000
H	-2.424255000	3.379871000	-0.000657000
N	-3.849287000	1.805066000	0.000100000
C	-0.253179000	1.488180000	-0.001508000
N	0.550176000	0.492581000	-0.001448000
O	1.886828000	0.990356000	-0.002472000
H	-4.692829000	2.354734000	0.000445000
H	0.128527000	2.509174000	-0.002074000
C	2.793610000	-0.008699000	-0.000127000
Cl	2.653225000	-1.061912000	-1.456722000
Cl	2.653256000	-1.054821000	1.461572000
Cl	4.376154000	0.797914000	-0.002119000

S-3 or S3′



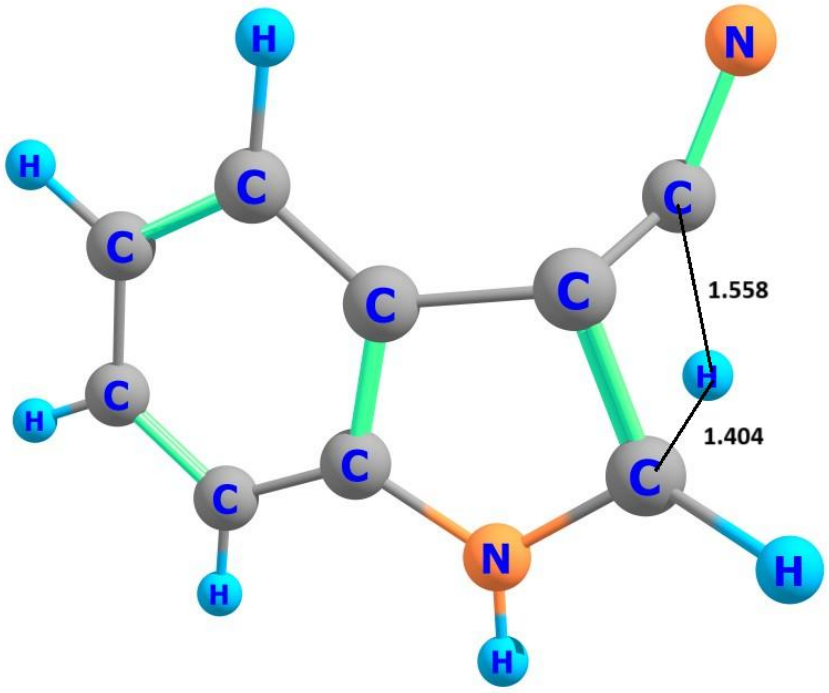
18

symmetry c1

C	0.068518000	-0.210207000	0.000039000

C	-0.787441000	0.910523000	-0.000021000
C	-2.164609000	0.776627000	-0.000049000
C	-2.684558000	-0.520881000	-0.000026000
C	-1.857398000	-1.640842000	0.000025000
C	-0.468857000	-1.490492000	0.000054000
C	1.445974000	0.281821000	0.000066000
C	1.320060000	1.756092000	0.000218000
H	-2.816587000	1.641506000	-0.000092000
H	-3.760688000	-0.653411000	-0.000048000
H	-2.292286000	-2.632763000	0.000041000
H	0.181654000	-2.357399000	0.000092000
H	2.090568000	2.507234000	-0.000512000
N	-0.015870000	2.064134000	-0.000045000
C	2.613008000	-0.444064000	-0.000027000
N	2.659445000	-1.792021000	-0.000101000
H	-0.387674000	2.999046000	-0.000108000
H	3.571807000	0.079538000	-0.000020000

TS or TS$^{/}$



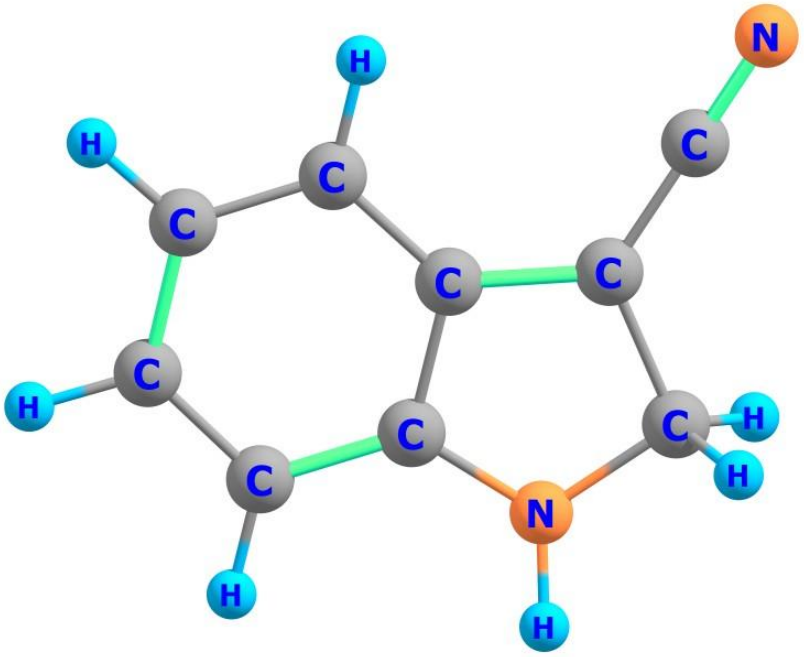
18

symmetry c1

C	0.043193000	-0.338462000	0.317923000
C	0.692431000	0.876390000	-0.007130000
C	2.045161000	0.934947000	-0.297791000
C	2.763496000	-0.259194000	-0.240804000
C	2.138244000	-1.467042000	0.070599000
C	0.770667000	-1.520242000	0.340368000
C	-1.367887000	-0.036732000	0.458802000
C	-1.511151000	1.443949000	0.299767000
H	2.524288000	1.868184000	-0.567509000
H	3.826042000	-0.247110000	-0.452590000
H	2.724197000	-2.377976000	0.099326000
H	0.285913000	-2.460742000	0.573393000
H	-2.143972000	2.070079000	0.926193000
N	-0.241544000	1.905622000	-0.004257000
C	-2.430382000	-0.520920000	-0.450894000

N	-3.146696000	-1.534567000	-0.362439000
H	-0.019801000	2.867715000	-0.212372000
H	-2.341620000	1.006288000	-0.744612000

S-4 or S4′ (Radical)



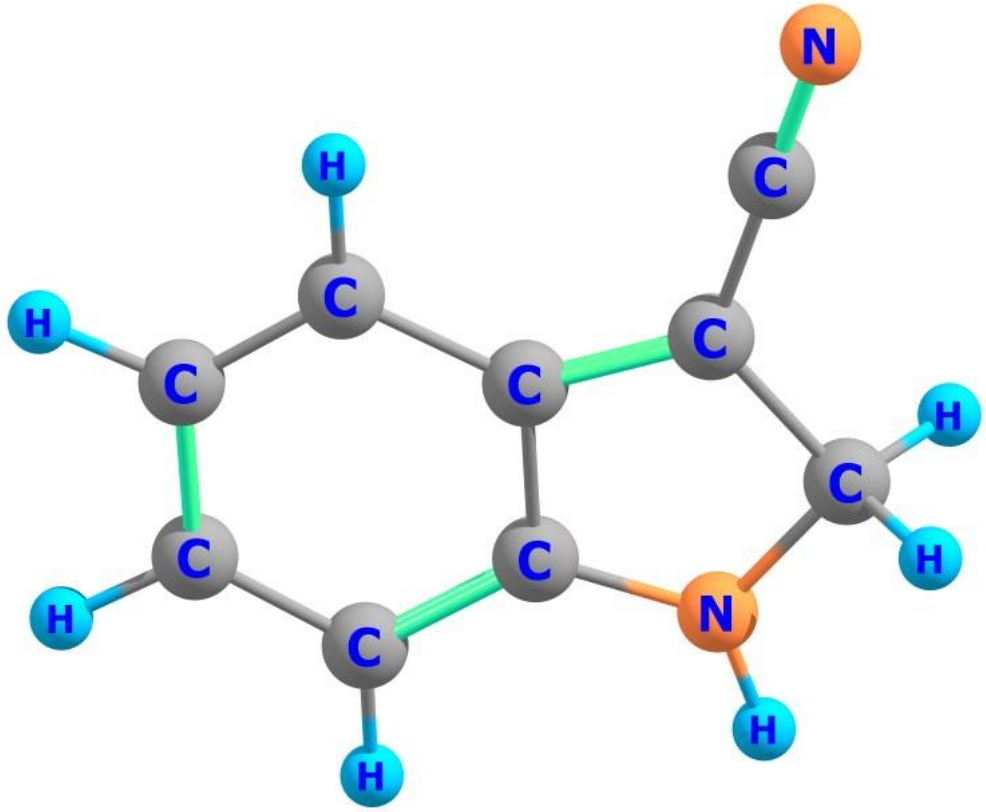
18

symmetry c1

C	-0.009926000	-0.289747000	-0.009569000
C	0.797395000	0.884814000	-0.018559000
C	2.189068000	0.795554000	0.001131000
C	2.758373000	-0.470295000	0.013983000
C	1.973051000	-1.637991000	0.006028000
C	0.594158000	-1.559324000	-0.005691000
C	-1.356972000	0.127977000	0.004884000
C	-1.405089000	1.632618000	0.031544000
H	2.804015000	1.687286000	0.002427000
H	3.838591000	-0.561318000	0.028515000

H	2.459179000	-2.606194000	0.013103000
H	-0.017887000	-2.454239000	-0.004744000
H	-1.984713000	2.046456000	-0.801648000
N	0.000672000	1.987849000	-0.068564000
C	-2.482581000	-0.695485000	0.000228000
N	-3.418487000	-1.382339000	-0.003642000
H	0.328525000	2.910882000	0.160987000
H	-1.847868000	2.009836000	0.962926000

S-5 or S5′ (Cation)



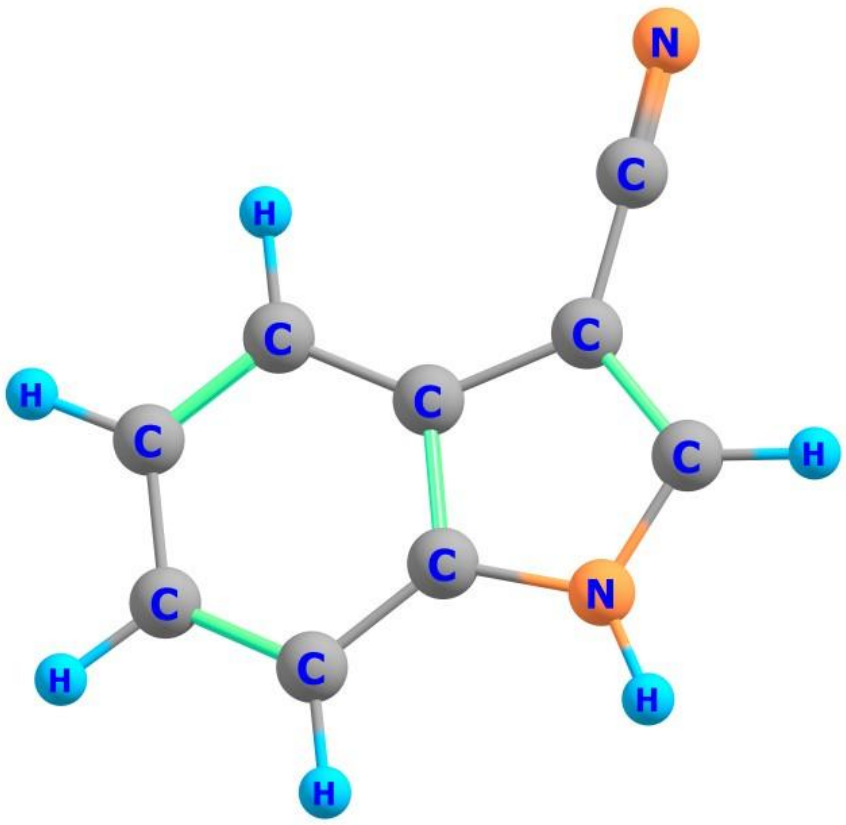
18

symmetry c1

C	-0.037911000	-0.291382000	-0.000048000
C	0.809460000	0.893165000	-0.000114000
C	2.221810000	0.776142000	-0.000179000

C	2.725449000	-0.486406000	-0.000149000
C	1.900918000	-1.673730000	-0.000064000
C	0.551868000	-1.597548000	-0.000021000
C	-1.325308000	0.148444000	0.000053000
C	-1.348469000	1.635477000	0.000017000
H	2.854696000	1.652474000	-0.000244000
H	3.800681000	-0.620393000	-0.000191000
H	2.393957000	-2.637126000	-0.000040000
H	-0.077245000	-2.478162000	0.000022000
H	-1.848751000	2.040776000	-0.886205000
N	0.053215000	1.969264000	-0.000046000
C	-2.492615000	-0.657157000	0.000222000
N	-3.438866000	-1.312380000	0.000369000
H	0.393740000	2.921365000	-0.000128000
H	-1.848727000	2.040855000	0.886213000

S-6 or or S6$^{\prime}$



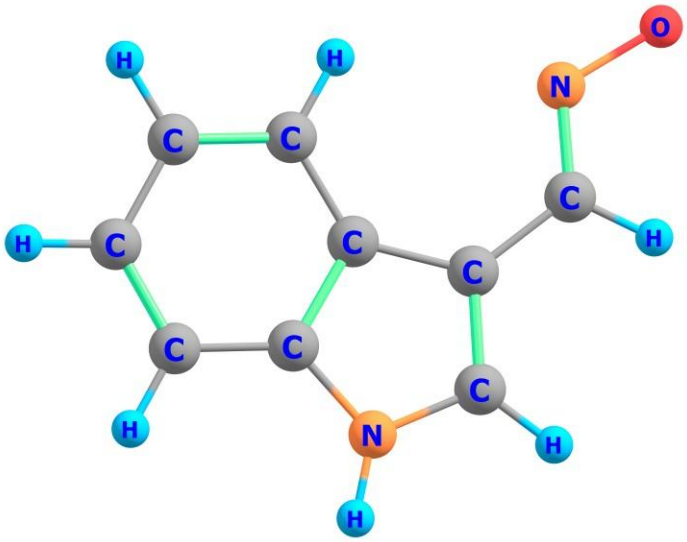
17

symmetry c1

C	0.022061000	-0.276022000	0.000009000
C	-0.790006000	0.874191000	-0.000020000
C	-2.183392000	0.799447000	-0.000009000
C	-2.748733000	-0.462561000	0.000032000
C	-1.951775000	-1.622588000	0.000062000
C	-0.571622000	-1.543702000	0.000050000
C	1.384788000	0.196993000	-0.000015000
C	1.337954000	1.573195000	-0.000056000
H	-2.795206000	1.693514000	-0.000032000
H	-3.828128000	-0.560651000	0.000042000
H	-2.432458000	-2.594041000	0.000094000
H	0.038107000	-2.440217000	0.000073000
N	0.044282000	1.974362000	-0.000059000

C	2.555137000	-0.592935000	0.000000000
N	3.498418000	-1.259761000	0.000013000
H	-0.254481000	2.936510000	-0.000088000
H	2.146795000	2.286562000	-0.000083000

S-1 (Anionic)



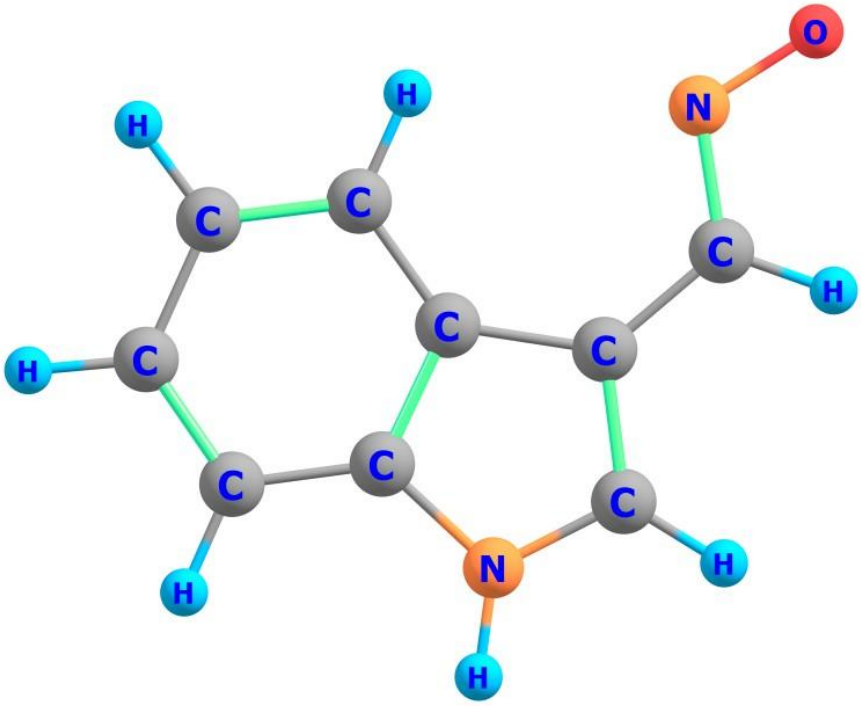
19

symmetry c1

C	0.313583000	-0.085997000	0.000260000
C	1.466005000	0.744404000	-0.000171000
C	2.763601000	0.222142000	-0.000228000
C	2.900323000	-1.159346000	0.000285000
C	1.769822000	-2.003801000	0.000843000
C	0.482939000	-1.480790000	0.000792000
C	-0.844725000	0.789362000	0.000204000
C	-0.352230000	2.076228000	-0.000153000
H	3.629251000	0.871505000	-0.000640000
H	3.890761000	-1.595995000	0.000279000
H	1.912103000	-3.076900000	0.001306000

H	-0.384689000	-2.124528000	0.001144000
H	-0.888395000	3.009981000	-0.000297000
N	1.032781000	2.056139000	-0.000417000
C	-2.259341000	0.449285000	0.000371000
N	-2.698651000	-0.772823000	-0.000928000
O	-4.072835000	-0.939741000	-0.000792000
H	1.621541000	2.867603000	-0.000809000
H	-2.976661000	1.274124000	0.001549000

S-1 (radical)



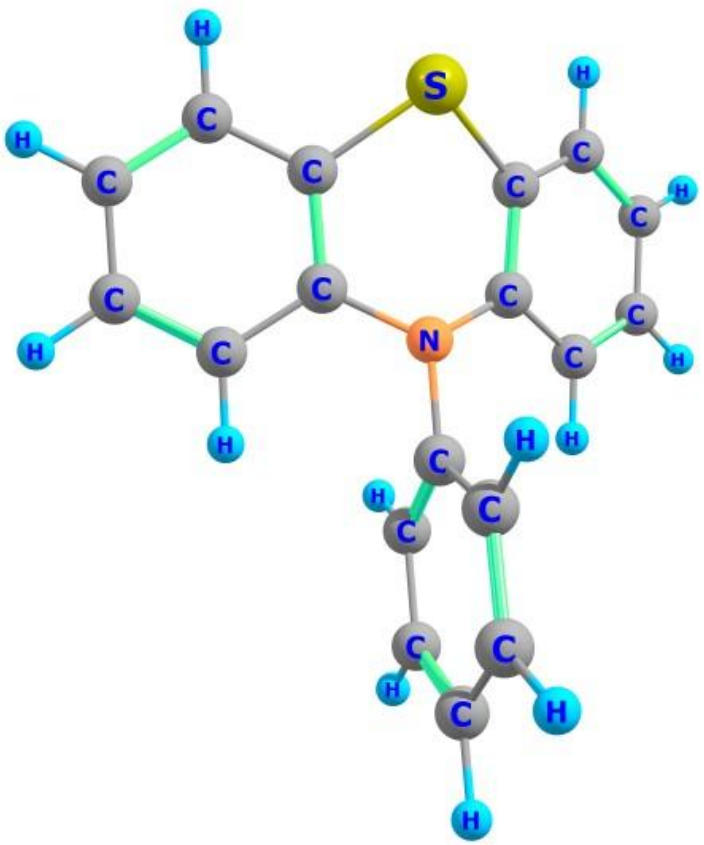
19

symmetry c1

C	0.313583000	-0.085997000	0.000260000
C	1.466005000	0.744404000	-0.000171000
C	2.763601000	0.222142000	-0.000228000
C	2.900323000	-1.159346000	0.000285000

C	1.769822000	-2.003801000	0.000843000
C	0.482939000	-1.480790000	0.000792000
C	-0.844725000	0.789362000	0.000204000
C	-0.352230000	2.076228000	-0.000153000
H	3.629251000	0.871505000	-0.000640000
H	3.890761000	-1.595995000	0.000279000
H	1.912103000	-3.076900000	0.001306000
H	-0.384689000	-2.124528000	0.001144000
H	-0.888395000	3.009981000	-0.000297000
N	1.032781000	2.056139000	-0.000417000
C	-2.259341000	0.449285000	0.000371000
N	-2.698651000	-0.772823000	-0.000928000
O	-4.072835000	-0.939741000	-0.000792000
H	1.621541000	2.867603000	-0.000809000
H	-2.976661000	1.274124000	0.001549000

10PPT



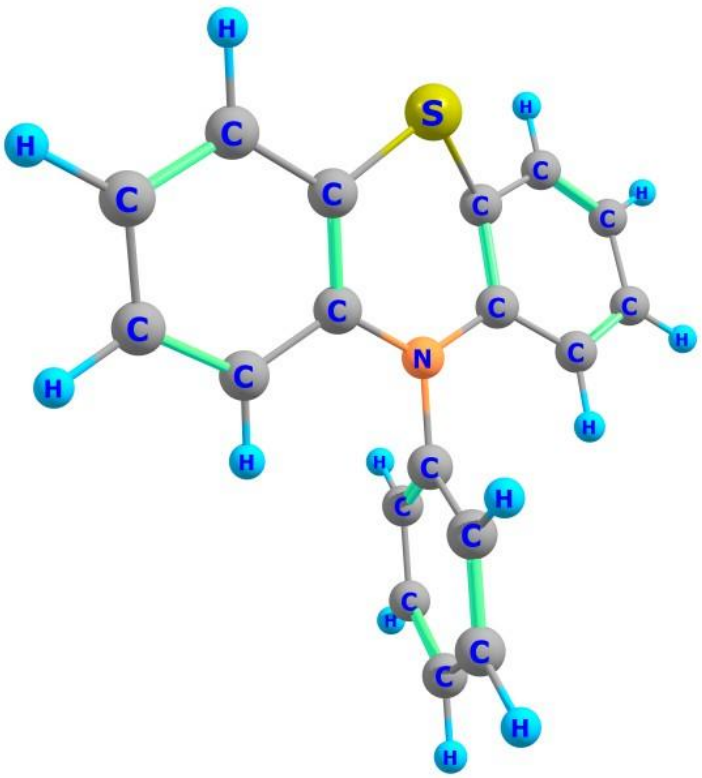
33

symmetry c1

C	-0.404678000	3.552957000	-0.744110000
C	0.267204000	2.355466000	-0.528002000
C	-0.414115000	1.226604000	-0.063129000
C	-1.788439000	1.344012000	0.188105000
C	-2.462539000	2.532077000	-0.068274000
C	-1.772678000	3.647510000	-0.527725000
C	-1.788445000	-1.344006000	0.188106000
C	-0.414120000	-1.226604000	-0.063129000
C	0.267194000	-2.355469000	-0.528001000
H	1.331487000	-2.306311000	-0.713194000
C	-0.404692000	-3.552957000	-0.744109000
C	-1.772692000	-3.647504000	-0.527724000

C	-2.462549000	-2.532068000	-0.068273000
H	0.153555000	4.413177000	-1.095205000
H	1.331496000	2.306304000	-0.713195000
H	-3.529496000	2.585923000	0.117651000
H	-2.299800000	4.576587000	-0.707778000
H	0.153537000	-4.413179000	-1.095204000
H	-2.299819000	-4.576579000	-0.707776000
H	-3.529506000	-2.585910000	0.117651000
C	3.800406000	-0.000007000	-0.960681000
C	4.460001000	-0.000006000	0.265405000
C	3.728760000	-0.000004000	1.447965000
C	2.337950000	-0.000003000	1.407365000
C	1.682144000	-0.000004000	0.182747000
C	2.412164000	-0.000006000	-1.003737000
H	4.367541000	-0.000008000	-1.884259000
H	5.543493000	-0.000007000	0.297511000
H	4.239080000	-0.000003000	2.404198000
H	1.752913000	-0.000001000	2.319898000
H	1.888787000	-0.000006000	-1.953531000
N	0.247159000	-0.000001000	0.172725000
S	-2.653664000	0.000005000	0.955460000

10PPT*



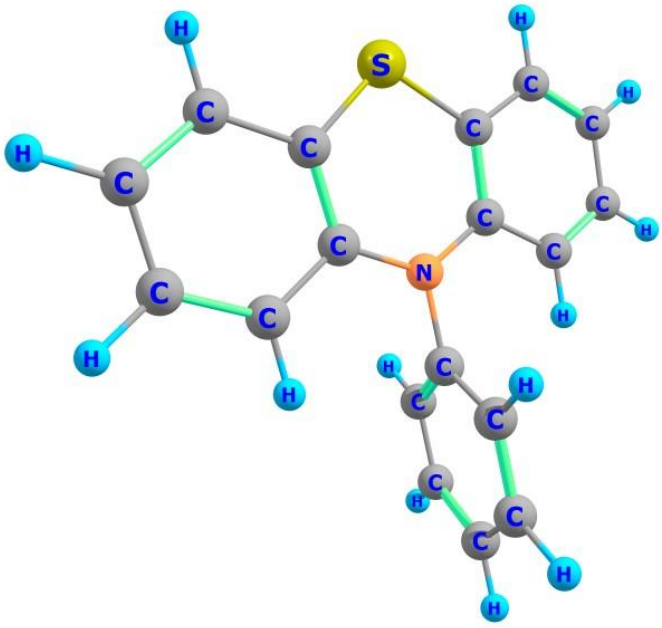
33

symmetry c1

C	0.462026000	-3.629557000	0.265564000
C	-0.211160000	-2.417151000	0.326710000
C	0.432926000	-1.220298000	0.019904000
C	1.877506000	-1.230389000	-0.302466000
C	2.520791000	-2.526036000	-0.440376000
C	1.843969000	-3.663949000	-0.169137000
C	1.755314000	1.410509000	0.111427000
C	0.376365000	1.235901000	-0.128958000
C	-0.397216000	2.390433000	-0.378440000
H	-1.452215000	2.286941000	-0.592625000
C	0.165674000	3.647056000	-0.345997000
C	1.526985000	3.812565000	-0.066204000
C	2.307512000	2.697576000	0.153305000

H	-0.052755000	-4.550592000	0.505787000
H	-1.266952000	-2.409574000	0.569561000
H	3.556983000	-2.558765000	-0.762682000
H	2.334244000	-4.623976000	-0.292896000
H	-0.458867000	4.510855000	-0.540997000
H	1.969324000	4.800725000	-0.039353000
H	3.369813000	2.803467000	0.345083000
C	-3.784073000	-0.437019000	-1.100277000
C	-4.441610000	-0.148142000	0.091750000
C	-3.712042000	0.187811000	1.227905000
C	-2.323941000	0.236406000	1.175351000
C	-1.678407000	-0.051817000	-0.020016000
C	-2.396370000	-0.390867000	-1.159204000
H	-4.351312000	-0.696903000	-1.986278000
H	-5.523956000	-0.184876000	0.135195000
H	-4.222729000	0.410253000	2.157434000
H	-1.739989000	0.496897000	2.050599000
H	-1.866845000	-0.614333000	-2.078097000
N	-0.241148000	-0.013223000	-0.078502000
S	2.840487000	0.062765000	0.344608000

10PPT*+



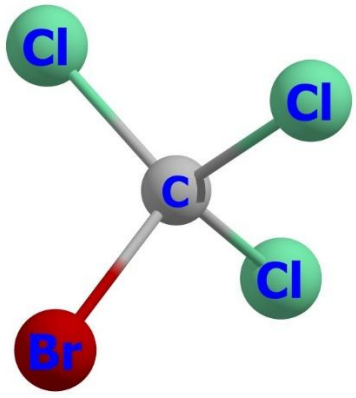
33

symmetry c1

C	0.259158000	3.647120000	-0.000190000
C	-0.352049000	2.417695000	-0.000077000
C	0.413616000	1.231562000	-0.000099000
C	1.820254000	1.352456000	-0.000226000
C	2.426364000	2.618439000	-0.000348000
C	1.657290000	3.756192000	-0.000332000
C	1.820299000	-1.352402000	-0.000059000
C	0.413659000	-1.231556000	0.000051000
C	-0.351962000	-2.417715000	0.000177000
H	-1.430194000	-2.359468000	0.000254000
C	0.259290000	-3.647119000	0.000201000
C	1.657426000	-3.756141000	0.000092000
C	2.426457000	-2.618359000	-0.000041000
H	-0.352828000	4.540281000	-0.000170000
H	-1.430279000	2.359409000	0.000031000
H	3.507872000	2.685123000	-0.000457000

H	2.130292000	4.729773000	-0.000427000
H	-0.352665000	-4.540301000	0.000301000
H	2.130463000	-4.729706000	0.000109000
H	3.507969000	-2.685001000	-0.000129000
C	-3.734128000	-0.000037000	1.206920000
C	-4.426425000	-0.000057000	0.000321000
C	-3.734301000	-0.000065000	-1.206377000
C	-2.344952000	-0.000054000	-1.212840000
C	-1.672175000	-0.000033000	0.000122000
C	-2.344778000	-0.000022000	1.213185000
H	-4.273883000	-0.000034000	2.146044000
H	-5.509962000	-0.000068000	0.000400000
H	-4.274191000	-0.000079000	-2.145423000
H	-1.787594000	-0.000059000	-2.142042000
H	-1.787288000	-0.000002000	2.142307000
N	-0.223409000	-0.000007000	0.000015000
S	2.895493000	0.000048000	-0.000236000

$BrCCl_3$



5

symmetry c1

C	-0.412239000	0.000076000	-0.000068000
Cl	-1.005911000	-0.233178000	1.659894000
Cl	-1.005288000	-1.321103000	-1.032070000
Cl	-1.005314000	1.554301000	-0.628206000
Br	1.535833000	-0.000023000	0.000197000

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