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Supporting Information

Cascade annulative-π-extension for the rapid construction of carbazole Based polyaromatic hydrocarbons

Samrat Kundu, Ankush Banerjee, Shyam Chand Pal, Meghna Ghosh, and Modhu Sudan Maji*

Department of Chemistry, Indian Institute of Technology Kharagpur

Kharagpur 721302, W.B., India.

E-mail: msm@chem.iitkgp.ac.in

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Experimental Sections

General Remarks: All reactions involving air or moisture-sensitive reagents were carried out in flame dried glassware under nitrogen/argon atmosphere. Ethyl-acetate was obtained from SRL India. All other solvents were acquired from Merck India and were dried according to the standard literature procedure. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F254 pre-coated plates (0.25 mm), and visualized under UV light or by dipping into $KMnO_4$ or DNP solution. Silica gel (particle size 100-200 mesh) was purchased from SRL India for performing column chromatography by using mixture of hexanes and ethyl-acetate eluent. The ^1H NMR spectroscopic data were recorded with a Bruker 400 or 500 or 600 MHz instruments. Proton decoupled ^{13}C NMR spectra ($^{13}C\{^1H\}$) were similarly recorded at 101 or 126 or 151 MHz NMR instruments by using a broadband decoupled mode. Proton and carbon NMR chemical shifts (δ) are reported in parts per million (ppm) relative to the residual proton or carbon signals in $CDCl_3$ (δ = 7.26, 77.16) or DMSO-d_6 (δ= 2.50, 39.52). Coupling constants (J) are reported in Hertz (Hz) and refer to apparent multiplicities. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, p: quintet, dd: doublet of doublets, dt: doublet of triplet, m: multiplet, br: broad. Infrared (IR) spectra were recorded by Perkin Elmer FTIR spectrometer, and reported in terms of wave number (cm^{-1}). High resolution mass spectra (HRMS) were recorded in ESI (+ Ve) method using a time-of-flight (TOF) mass analyzer.

Single Crystal X-ray Diffraction

The crystal and refinement data for **3v**, **6c**, **7c** and **7d** were collected and the results were summarized in Table S4. In those cases, a crystal of appropriate size was selected from the mother liquor and immersed in paratone oil, and then it was mounted on the tip of glass fibre and cemented using epoxy resin. Single crystal X-ray data were collected at 298 K on a Bruker SMART APEX II CCD diffractometer using graphite-monochromated Mo-K_α radiation (0.71073 Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were processed with SAINT[1a] software. Empirical absorption correction was applied to the collected reflections with SADABS using XPREP.[1b] The structures were solved by the direct method using SHELXTL[1c] and were refined on F^2 by a full-matrix least-squares technique using the SHELXL-2014[1d] program package. For all the cases, non-hydrogen atoms were refined anisotropically. All other hydrogen atoms are geometrically fixed using riding atom model. All other H atoms were placed in calculated positions using idealized geometries (riding model) and

assigned fixed isotropic displacement parameters. The solvent molecules present in the interspace of **3v** were highly disordered, no satisfactory disorder model could be achieved, and therefore PLATON/SQUEEZE routine was used to remove these electron densities.[1e]

Experimental section for photo-physical studies:

Steady state absorption and fluorescence measurements: All the steady state UV−Vis absorption spectra as well as emission spectra were recorded using the Shimadzu UV−Vis spectrophotometer (model UV 2450) and Shimadzu RF-6000 fluorimeter respectively. All samples were taken in micromolar concentrations using dichloromethane as solvent. Molar extinction coefficient (ε) for the highest absorption band was calculated by using Beer-Lambert's law (A= εcl) where path length (l) was kept as 1 cm and micro molar concentration (c) of the samples were maintained.

Determination of fluorescence Quantum yield (Φ): For calculating quantum yield, all the measurements were performed by maintaining the concentration of the samples and reference at a low value of 5μM to minimize error due or self-aggregation or self-quenching. The absorbance (A) values of all the solutions were kept below 0.1. Reference dye quinine sulphate (λ_{abs}= 350 nm) in 0.5 M H_2SO_4 (Φ_R = 0.546 at 298 K)[2] was used for measuring fluorescence quantum yields(Φ_s). The quantum yield was calculated by using the following equation:[3]

$$\frac{\phi_s}{\phi_R} = \frac{(Abs)_R}{(Abs)_s} \frac{A_s}{A_R} \frac{\eta_s^2}{\eta_R^2}$$

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

Result and Discussion:

Due to the wide range of substrate variety of the Brønsted acid-catalyzed annulation strategy, we were deeply concerned with the potential of the B[*a*]Cs and PAHs as optical materials. Therefore, we studied the photophysical properties of these moieties; the results are summarized in Table S2. The absorption spectra of the synthesized compounds were examined in dichloromethane solvent. All the samples were completely soluble in this solvent at the certain concentration range which has been shown in the Table S1. In dichloromethane, the compounds do not form hydrogen bond with the solvent, as a result the fine structure of the absorption band was observed. In Table S2, the values of λ (wavelengths corresponding to the various absorption bands), molar extinction coefficients, ε (at the λ_{max} of the band having highest absorbance), wavelength of emission maxima

(λ_{em}) and fluorescence quantum yield were summarized accordingly. It was seen that fluorescence excitation spectrum matched exactly with corresponding absorption spectrum confirming the purity of the compound.[3]

First, when we focused on assessing the effect of electron-donating aryl substituents on B[*a*]Cs (**3k**, **3l**, **3m**, **3n**), in the UV-vis spectrum the absorption bands ranging from 260 to 300 nm were attributed to the intense π-π* transitions whereas the weak *n*-π* transitions were detected in the range 345 to 380 nm (Figure S1).[4] Introduction of more electron donating group in C2 and C4 position of aryl moiety caused small red-shift of the λ_{em} along with reduction in ε (at the λ_{max} of band with highest absorption) (**3k** vs **3l**). Moreover, λ_{em} was found to be highly dependent on the methoxy group which resulted in red shift of the emission spectra (λ_{em} around 377-387 nm) leading to purple emission (**3k**, **3l** and **3m**).[4] Due to presence of extensive π-conjugation, **3n** exhibits higher fluorescence efficiency (Φ_F = 0.334 QS) along with highest molar extinction coefficient (ε= 6.99x10^4 M^{-1}cm^{-1}).

Next, we were concerned about evaluating structure-property correlations of HA[*a*]Cs (Figure S2). Introduction of pentacyclic core (**3p** vs **3q**) with extended conjugation triggered substantial red-shift in the absorption and emission band along with higher ε (at the λ_{max} of the band having highest absorbance). Benzofuro[*2,3-a*]carbazole **3o** having a furan ring was found to be the most emissive with higher fluorescence efficiency (Φ_F= 0.320). When studying the absorption and excitation spectra of compound **3r**, significant deviations were found. Hence, we deduced that the compound **3r** may have decomposed due to present of highly reactive free pyrrole moiety in dichloromethane solvent. Due to extensive π-delocalization, densely substituted *N*-methylated pyrrolo[2,3-*a*]carbazole **6e** displayed higher bathochromic effect in emission spectra with higher molar extinction coefficient (ε= 5.0299x10^4 M^{-1}cm^{-1}).

Furthermore, we were motivated to appraise the physical significance of similar or different aryl/alkyl substituted α-hydroxy aldehydes in B[*a*]Cs (Figure S3). Introduction of *N*-alkylated derivative along with methoxy substituted aryl moiety in aldehyde part may be wholly responsible for the bathochromic effect in emission spectra with highest fluorescence efficiency (Φ_F= 0.429) (**3n** vs **6f**). Negligible red shift was observed in absorption band when benzyl substituted α-hydroxy aldehydes were acquainted with B[*a*[Cs (**3t** vs **3k**). Incorporation of the alkyl moiety was always accompanied by a red-shift of the emission spectra regardless of the position of the alkyl group (**3w** vs **3n**).

Finally, we studied the photophysical properties of the more conjugated carbazole based PAHs (Figure S4). In contrast to the bathochromic effect in wavelength of fluorescence maxima,

introduction of furan moiety exhibited a hypsochromic effect along with sharp decrease in absorption band also (**7a** vs **7b**). **7d** was found to be most emissive in comparison with **7e**, in spite of being mostly annulated PAHs where, five, six and seven membered rings are connected simultaneously in contiguous fashion.

For further understanding about the photophysical properties of PAHs (**7d**, **7e**), we studied solvent dependence of the emission spectra by changing solvents from polar to nonpolar as well as protic to aprotic (Figure S5).[5]

Solubility of Synthesized PAH (7):

Solubility of all the polyaromatic hydrocarbons **7a-7e** have been checked thoroughly in dichloromethane solvent. Products **7a-7d** were completely soluble in dichloromethane for concentration of at least 5 x 10^{-3} M (approx. 2 mg/mL). The unique π-annulated moiety **7e** was least soluble in dichloromethane and was diluted 100 times to solubilize it completely (concentration around 5 x 10^{-5} M).

Table S1: Concentration of substituted benzo[*a*]carbazoles and carbazole based polyaromatic hydrocarbons used for photophysical studies.

Serial No	Substrate	Concentration used for absorption (μM)	Concentration (μM) used for Emission (excitation wavelength in nm)
1	**3k**	10	5 (330)
2	**3l**	10	5 (330)
3	**3m**	60	5 (330)
4	**3n**	10	5 (330)
5	**3o**	15	5 (330)
6	**3p**	10	5 (330)
7	**3q**	20	5 (330)
8	**6e**	20	5 (330)
9	**6f**	10	5 (350)
10	**3t**	20	5 (330)
11	**3u**	60	5 (350)
12	**3w**	10	5 (330)
13	**7a**	10	5 (330)
14	**7b**	10	5 (330)
15	**7c**	15	5 (350)
16	**7d**	40	5 (350)
17	**7e**	10	5 (350)

Table S2: Photophysical properties of substituted benzo[*a*]carbazoles and carbazole based polyaromatic hydrocarbons.

Sample	Absorption (nm)	Molar extinction coefficient ($10^4 M^{-1}cm^{-1}$) (at λ_{max} of the band of highest absorption)	Emission (nm)	Quantum yield[a] wrt quinine sulfate
3k	261, 286, 349, 366	6.11	377, 394	0.309
3l	283, 301, 349, 365	1.96	381, 397	0.371
3m	292	1.28	387, 373sh	0.074
3n	300, 361, 380	6.99	397, 412sh	0.334
3o	281, 318, 347	4.11	362, 376	0.321
3p	259, 297, 322, 344, 361	4.93	373, 385sh	0.049
3q	263, 314, 335, 350	4.16	364, 379	0.036
6e	296, 333	5.02	400	0.301
6f	265, 303, 371, 391	4.15	409, 426sh	0.429
3t	286, 350, 367	4.73	378, 395	0.195
3u	300, 362, 381	1.18	404, 418sh	0.380
3w	259, 300, 364, 383	4.99	409	0.364
7a	308,321,382,401	4.12	415, 430	0.039
7b	258, 320, 342, 379, 399	7.13	408, 429	0.195
7c	258, 302, 326, 375, 402, 425	6.13	439, 462sh	0.061
7d	303, 326, 340, 381, 402, 424, 450	1.16	458, 486, 518	0.374
7e	328, 343, 381, 402, 428, 454	6.36	469, 493sh	0.187

[a] Experimental error ±5%

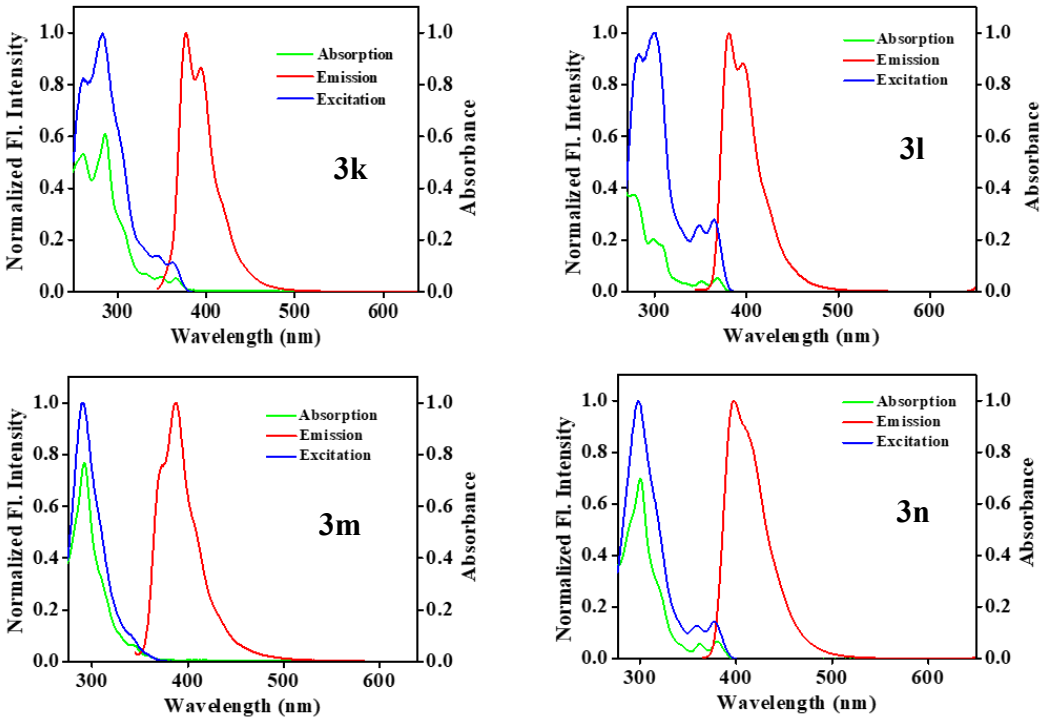


Figure S1: Absorption, excitation and emission spectra of densely substituted benzo[*a*]carbazoles **3k-3n**, synthesized from electron donating aromatic substitutions at C2 position of indole moiety.

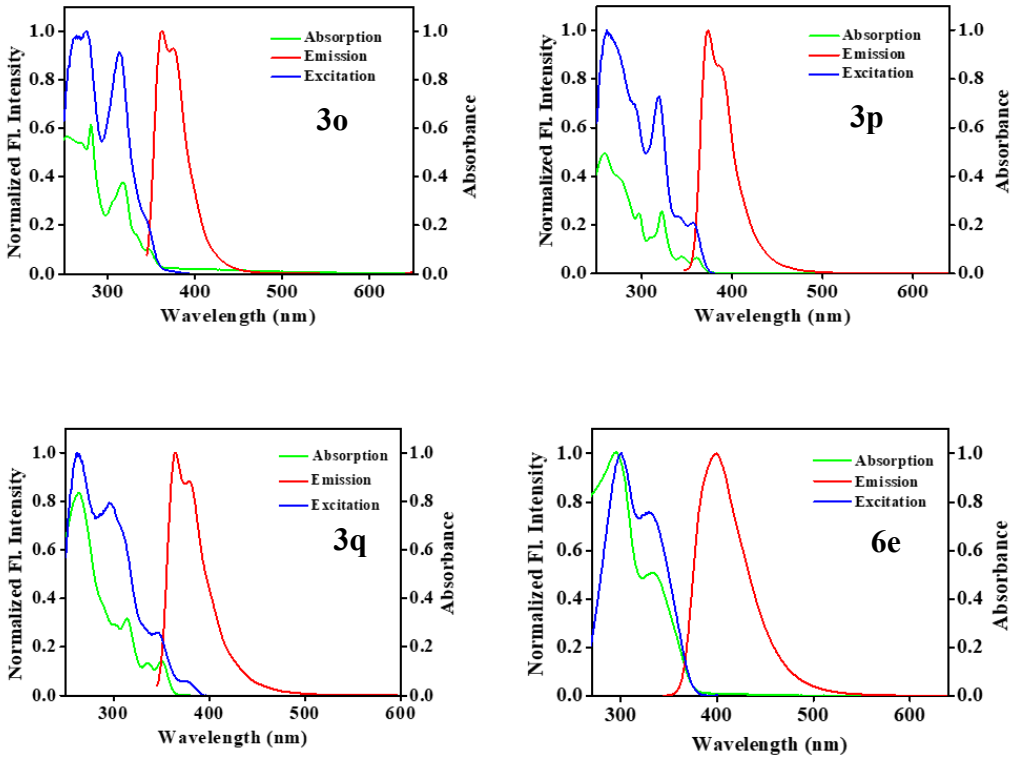


Figure S2: Absorption, excitation and emission spectra of heteroaryl-annulated densely substituted benzo[*a*]carbazoles **3o-3q** and **6e**.

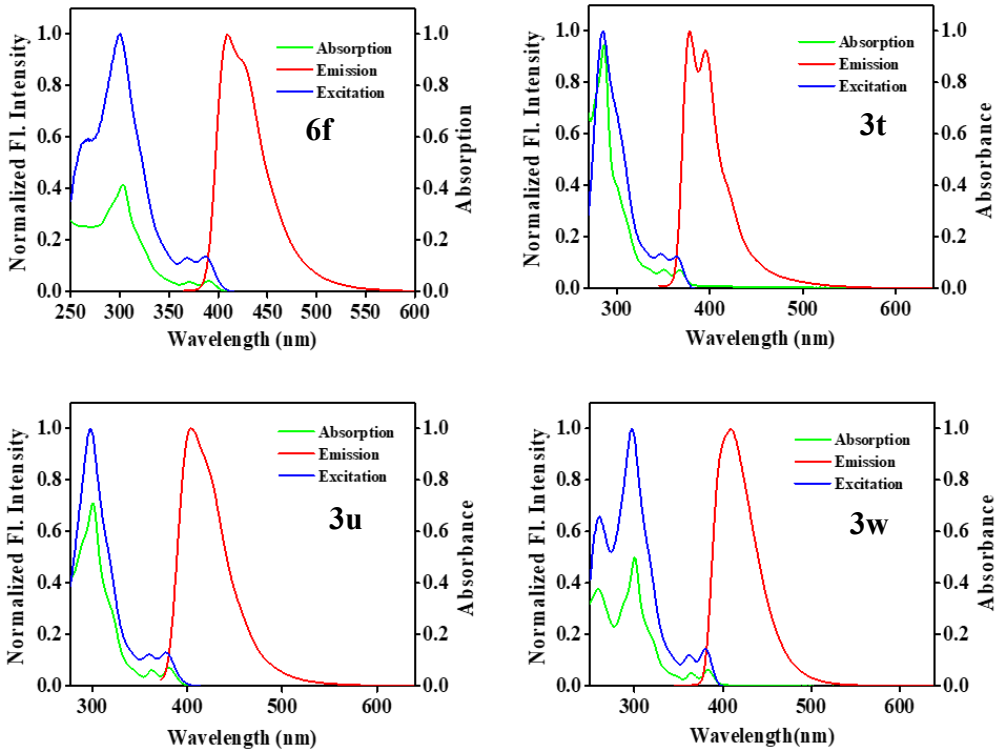


Figure S3: Absorption, excitation and emission spectra of densely functionalized benzo[*a*]carbazoles **3t-3u, 3w** and **6f**.

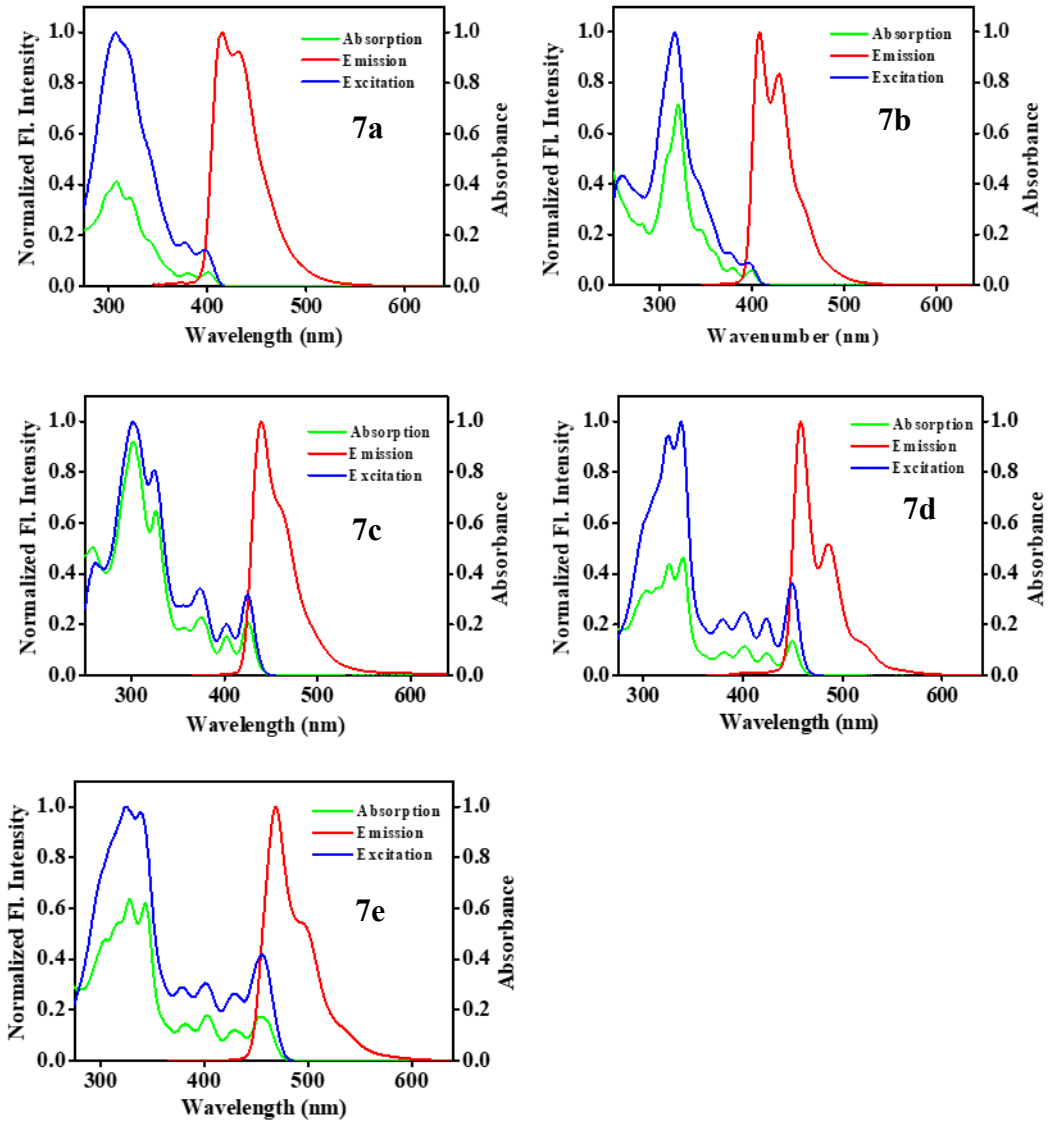


Figure S4: Absorption, excitation and emission spectra of densely functionalized carbazole based extensive π-annulated polyaromatic hydrocarbons **7a-7e**.

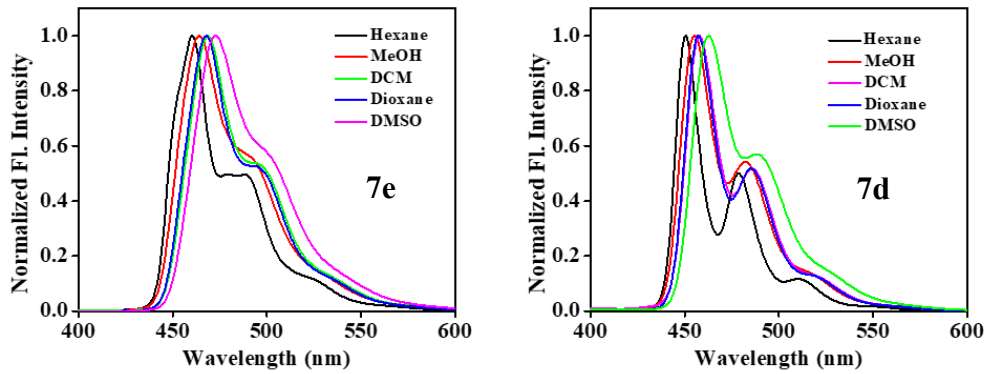
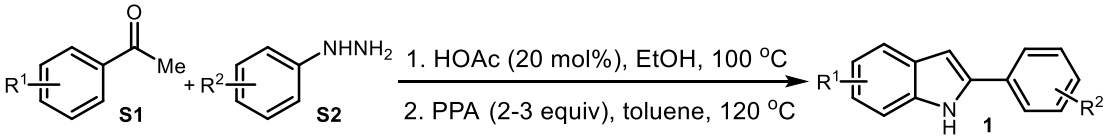


Figure S5: Solvent dependent emission spectra of compounds **7e** and **7d** by changing solvents from polar to nonpolar as well as protic to aprotic.

General procedure for the preparation of 2-arylindoles:

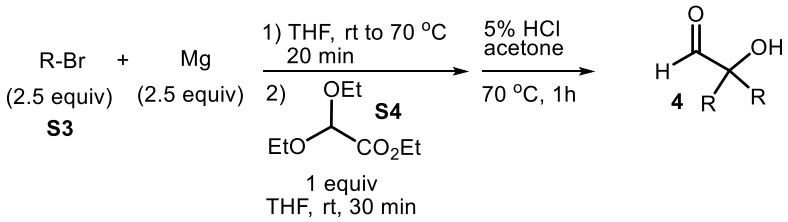
2-Aryl indoles **1a-1g** were synthesized according to the following reported method.[6a-6e]



Acetophenone **S1** (10 mmol), phenylhydrazine **S2** (1.2 equiv), HOAc (20 mol%) and EtOH (6 mL) were charged in a 25 mL round bottom flask. Then the reaction mixture was stirred at 100 °C. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature and ethanol was evaporated *under vacuo* to obtain crude phenylhydrazone. Next, crude phenylhydrazone was dissolved in toluene (6 mL), 2-3 equiv of polyphosphoric acid (PPA) was added and the resulting solution was refluxed at 120-140 °C. After completion of reaction, the reaction mixture was cooled down to room temperature, quenched with H_2O (10 mL) and extracted with EtOAc (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated under vacuo. The residue was purified by column chromatography on silica gel using ethyl acetate/hexane as the eluent to afford the corresponding 2-arylindoles **1a-1g** and **1i**.

Aryl indole **1h** was synthesized according to the reported procedure.[6f]

General procedure for the preparation of di-aryl or di-alkyl substituted *α*-hydroxyl aldehydes:[7a]

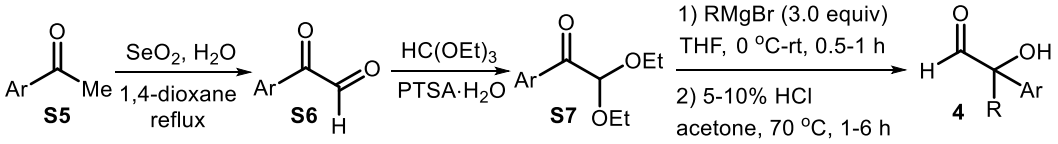


To a 25 mL two neck round bottom flask Mg-turnings (0.084 g, 3.5 mmol, 2.5 equiv) and a small crystal of I_2 were taken. After that, a condenser was fitted to the round bottom flask and the whole system was evacuated under vacuo and back-filled with nitrogen. This procedure was repeated twice. Then anhydrous THF (3.5 mL) and aryl or alkyl bromide **S3** (3.5 mmol, 2.5 equiv) were added slowly under constant stirring at 70°C (**Caution!!** Preparation of Grignard reagent is an exothermic reaction). The formation of the Grignard reagent started as soon as the colorless solution turned into grey. After complete dissolution of Mg-metal the reaction flask was cooled down to room temperature. Next, the flask was placed on a water bath and ethyl diethoxyacetate **S4** (0.25 mL in 2.0 mL THF, 1.4 mmol, 1.0 equiv.) was added dropwise via a syringe. The resulting mixture was stirred for another 30 min at room temperature and then quenched with 5 mL saturated

NH_4Cl solution. The two layers were separated and the aqueous layer was extracted with ether (3×5 mL). The combined organic layers were concentrated and the crude residue was subjected to hydrolysis without purification.

The crude acetal intermediate was transferred to a 20 mL round bottom flask, 0.5 mL of 5% HCl and acetone (~5 mL) were added to obtain a single layer homogenous solution. Thereafter, the flask was sealed and heated on an oil bath for 1 h at 70 °C. After cooling down to room temperature, the solution was diluted with 10 mL of CH_2Cl_2. The aqueous layer was separated and discarded; the organic layer was successively washed by $NaHCO_3$ solution and brine, dried over $MgSO_4$, and solvent was removed under reduced pressure. The crude residue containing **4** was purified by silica gel column chromatography using hexane and ethyl acetate as eluents.

General procedure for the preparation of different aryl or alkyl di-substituted *α*-hydroxyl: aldehydes:[7b, 7c]



To a 50 mL three-neck round bottom flask fitted with a condenser was added 1,4-dioxane, SeO_2 (25 mmol) and water (0.5 mL). The mixture was heated at 50-55 °C and stirred until the solid was dissolved. Then acetophenone **S5** (25 mmol) was added and the reaction mixture was refluxed for 6 h. The solid was removed by filtration and the filtrate was concentrated. The crude residue was purified by silica gel column chromatography to give arylglyoxal monohydrate **S6**.

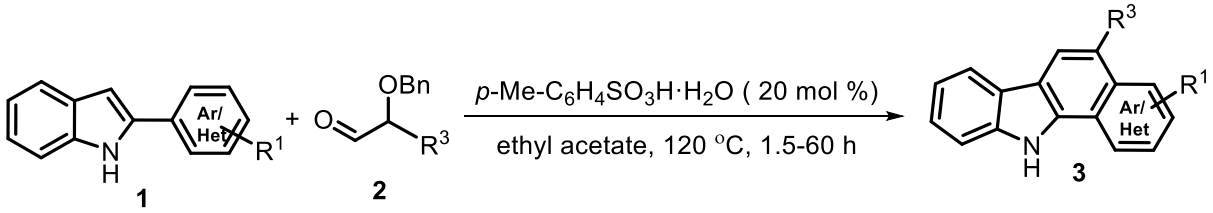
To a suspension of arylglyoxal monohydrate **S6** (10.0 mmol) and PTSA·H_2O (*p*-toluenesulfonic acid, 0.5 mmol) in CH_2Cl_2 (40 mL) at room temperature was added dropwise triethyl orthoformate ($HC(OEt)_3$, 10.0 mmol). The mixture was stirred for 30 min, triethylamine (0.20 mL) was added and the organic solvent was evaporated. The crude residue was purified by silica gel column chromatography to furnish *α,α*-diethoxymethyl aryl ketone **S7**.

The starting material **S7** was dissolved in anhydrous THF (1.0 M) and pre generated Grignard reagent was added dropwise to the solution. The reaction mixture was stirred at room temperature for 0.5 to 1.0 hours and quenched with saturated aqueous NH_4Cl-solution at 0 °C. The aqueous phase was separated and extracted twice with EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and the organic solvent was removed under reduced pressure. The crude product was treated with aqueous HCl-solution (5–10%) and acetone (~ 5 mL) to obtain a homogeneous solution. The resulting mixture was heated to 70 °C for 2 hours and then diluted

with CH_2Cl_2 and H_2O. The aqueous phase was extracted twice with CH_2Cl_2 and the combined organic layers were washed with saturated NaCl-solution, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude aldehyde **4** was purified by flash column chromatography using ethyl acetate/hexane eluent.

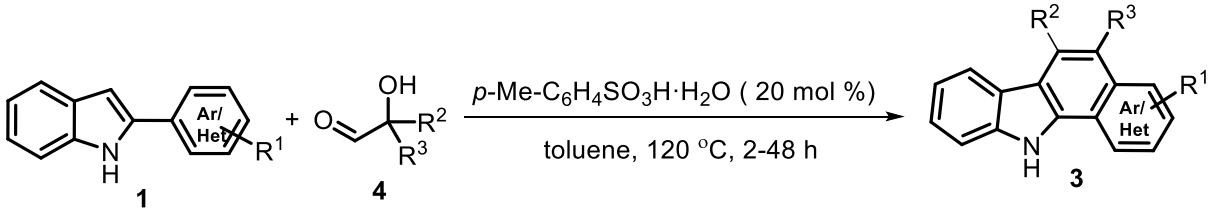
Aldehydes **2a** and **2b** were synthesized according to the reported procedures.[7d]

General Procedure IA (GP IA): Synthesis of benzo[*a*]carbazoles by cascade annulation protocol:



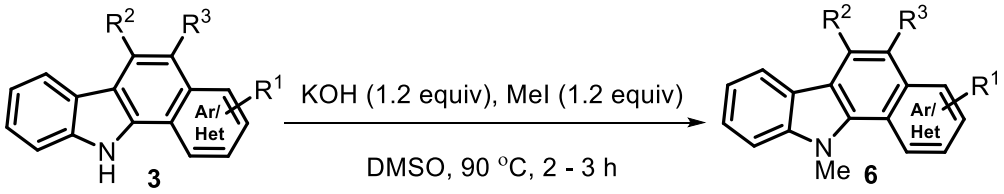
A 10 mL sealed pressure tube equipped with a magnetic stirring bar was charged with indole **1** (0.2 mmol, 1.0 equiv), *p*-toluenesulfonic acid monohydrate (PTSA·H_2O, 0.04 mmol, 20 mol %). To the mixture was added aldehyde **2** (0.4 mmol, 2 equiv) dissolved in ethyl acetate (3 mL) at room temperature. Finally, the resulting reaction mixture was heated to 120 °C under constant stirring. After complete consumption of starting material **1** (generally takes 1.5 to 60 h, check individual examples) as indicated by TLC (the products are $KMnO_4$ and DNP active), the crude reaction mixture was diluted with ethyl acetate, transferred to a round-bottomed flask, and the solvent was evaporated under vacuum. The crude residue was purified by silica gel column chromatography to obtain the pure desired products **3**.

General Procedure IB (GP IB): Synthesis of substituted benzo[*a*]carbazoles by cascade annulation through tandem pinacol-type rearrangement:



The indole **1** (0.2 mmol, 1.0 equiv) and *p*-toluenesulfonic acid monohydrate (PTSA·H_2O, 0.04 mmol, 20 mol %) were charged into an oven dried culture tube containing a stirring bar. To this stirring solution aldehyde **4** (0.22 mmol, 1.1 equiv, dissolved in 3 mL of toluene) was added drop-wise at the room temperature. The resulting mixture was then heated at 120 °C (on oil bath) for 2 to 48 h. Upon completion of the reaction (as monitored by TLC), the complete reaction mixture was transferred into a 25 mL round bottom flask by dissolving in ethyl acetate solvent and the organic layer was evaporated under vacuum. The crude residue was purified by silica gel column chromatography using ethyl acetate/hexane as an eluent to afford the desired products **3**.

General Procedure II (GP II): *N*-Methylation reaction:

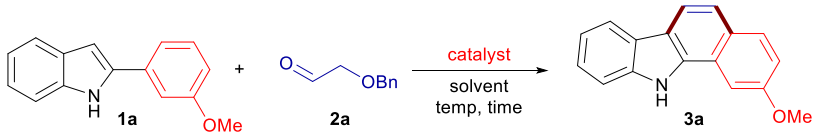


The benzocarbazole **3** (0.1 mmol, 1.0 equiv) was dissolved in 3 mL dimethyl sulfoxide, solid potassium hydroxide (0.12 mmol, 1.2 equiv) was added and the mixture was stirred for 30 min at room temperature. Then methyl iodide (0.15 mmol, 1.5 equiv) was added at room temperature and heated at 90 ^{o}C for 2 to 3 h. Upon completion of the reaction as indicated by TLC, water was added to the reaction mixture and extracted with ethyl acetate. The organic layers were dried over Na_2SO_4, evaporated under vacuum and purified by silica gel column chromatography using hexane as an eluent to afford the desired products **6**.

General Procedure III (GP III): Scholl reaction:

The *N*-methylated benzocarbazoles **6** (0.1 mmol, 1.0 equiv) was dissolved in dry dichloromethane (DCM) (9 mL) and cooled to 0 ^{o}C. To this solution, methanesulfonic acid (CH_3SO_3H) (1 mL) and solid 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.2 mmol, 2.0 equiv) were added, and the resulting highly colored mixture was stirred at room temperature. Upon completion of the reaction (as monitored by TLC), reaction mixture was quenched by pouring into saturated aqueous sodium bicarbonate (aq. $NaHCO_3$) solution. The organic layer was separated and the aqueous layer was extracted with DCM (3 x 10 mL). Combined organic layers were washed with water and brine, dried over anhydrous sodium sulfate (Na_2SO_4) and evaporated under vacuum. The crude residue was purified by silica gel column chromatography using ethyl acetate/hexane as an eluent to afford the desired products **7**.

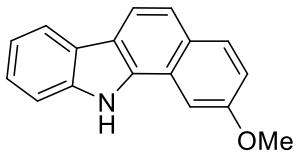
Table S3: Optimization of the benzannulation reaction



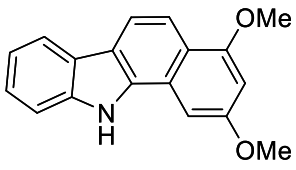
Entry	Solvent	Temperature [°C]	Time [h]	Catalyst (mol%)	Yield of [**3a**[b]]
1	EtOAc	rt	48	PTSA·H_2O (20)	NA
2	EtOAc	75	24	PTSA·H_2O (20)	59
3	EtOAc	100	14	PTSA·H_2O (20)	70
4	dioxane	100	14	PTSA·H_2O (20)	64
5	toluene	100	2	PTSA·H_2O (20)	32
6	1,2-DCE	100	2	PTSA·H_2O (20)	17
7	**EtOAc**	**120**	**12**	**PTSA·H_2O (20)**	**78**
8	EtOAc	120	24	$(PhO)_2P(O)OH$ (20)	56
9	EtOAc	120	24	TFA (20)	58

[a]Reactions were carried out in a sealed pressure tube using 0.2 mmol of **1a**, 0.4 mmol of **2a**; [b]Isolated yield.

*2-Methoxy-11H-benzo[a]carbazole (**3a**)*[8a]*:* The titled compound **3a** was synthesized according to the **GP IA** by using 2-(3-methoxyphenyl)-1*H*-indole **1a** (44.6 mg, 0.20 mmol, 1.0 equiv) and 2-(benzyloxy)acetaldehyde **2a** (60.0 mg, 0.40 mmol, 2.0 equiv). The reaction was continued for 12 h. The benzo[*a*]carbazole **3a** was isolated after column chromatography using 10% ethyl acetate/hexane as eluent (white solid, 38.6 mg, 78% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 8.70 (br s, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.20 (dd, *J* = 8.9, 2.3 Hz, 1H), 4.01 (s, 3H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ (ppm) 157.8, 138.7, 134.6, 130.8, 127.7, 125.0, 124.5, 122.0, 120.20, 120.16, 120.0, 119.1, 117.0, 111.2, 100.3, 55.6.

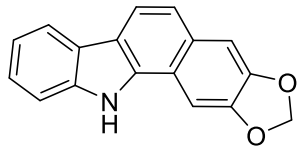


*2,4-dimethoxy-11H-benzo[a]carbazole (**3b**):* The titled compound **3b** was synthesized according to the **GP IA** by using 2-(3,5-dimethoxyphenyl)-1*H*-indole **1b** (50.7 mg, 0.20 mmol, 1.0 equiv) and 2-(benzyloxy)acetaldehyde **2a** (60.0 mg, 0.40 mmol, 2.0 equiv). The reaction was continued for 12 h. The benzo[*a*]carbazole **3b** was isolated after column chromatography using 12% ethyl acetate/hexane as eluent (white solid, 40 mg, 72% yield). **^{1}H NMR** (500 MHz, DMSO-d_6) δ(ppm) 11.98 (s, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 2.1 Hz, 1H), 3.99 (s, 3H), 3.97 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6) δ

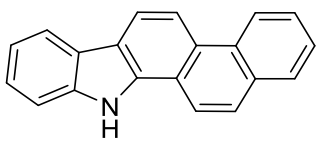


(ppm) 158.0, 156.8, 138.8, 134.9, 124.6, 123.1, 122.5, 119.8, 118.9, 118.6, 118.2, 115.9, 112.6, 111.2, 96.91, 93.8, 55.7, 55.4. **FTIR:** (neat)/ cm^{-1} = 3427, 3062, 2924, 2851, 1598, 1531, 1449, 1402, 1326, 1201, 1144, 1043, 929, 815. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{18}H_{16}NO_2$, 278.1176; found 278.1161.

*11H-[1,3]dioxolo[4',5':4,5]benzo[1,2-a]carbazole (**3c**):* The titled compound **3c** was synthesized according to the **GP IA** by using 2-(benzo[*d*][1,3]dioxol-5-yl)-1*H*-indole **1c** (47.5 mg, 0.20 mmol, 1.0 equiv) and 2-(benzyloxy)acetaldehyde **2a** (60.0 mg, 0.40 mmol, 2.0 equiv). The reaction was continued for 10 h. The benzo[*a*]carbazole **3c** was isolated after column chromatography using 10% ethyl acetate/hexane as eluent (white solid, 36.6 mg, 70% yield). **^{1}H NMR** (600 MHz, DMSO-d_6) δ (ppm) 11.85 (br s, 1H), 8.10 (d, *J* = 7.7 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.90 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.45 (s, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.16 (s, 2H). **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ (ppm) 146.8, 146.7, 138.6, 135.6, 128.6, 124.3, 123.3, 119.6, 118.9, 118.6, 117.5, 117.0, 116.7, 111.1, 105.2, 101.1, 98.8. **FTIR:** (neat)/ cm^{-1} = 3417, 3050, 2953, 2906, 2851, 1583, 1438, 1391, 1236, 1093, 1010, 936, 863. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{17}H_{12}NO_2$, 262.0863; found 262.0867.



*13H-Naphtho[2,1-a]carbazole **(3d)**:* The titled compound **3d** was synthesized according to the **GP IA** by using 2-(naphthalen-2-yl)-1*H*-indole **1d** (48.6 mg, 0.20 mmol, 1.0 equiv) and 2-(benzyloxy)acetaldehyde **2a** (60.0 mg, 0.40 mmol, 2.0 equiv). The reaction was continued for 1.5 h. The benzo[*a*]carbazole **3d** was isolated after column chromatography using 10% ethyl acetate/hexane as eluent (white solid, 38.4 mg, 72% yield). **^{1}H NMR** (600 MHz, DMSO-d6) δ (ppm) 12.20 (s, 1H), 8.91 (d, *J* = 8.4 Hz, 1H), 8.60 (d, *J* = 8.7 Hz, 1H), 8.51 (d, *J* = 8.8 Hz, 1H), 8.40 (d, *J* = 8.6 Hz, 1H), 8.24 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 8.9 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.67–7.63 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d6) δ (ppm) 139.4, 136.4, 131.3, 130.5, 128.8, 127.8, 127.0, 126.3, 126.2, 125.1, 123.4, 122.9, 120.9, 120.1, 119.7, 119.2, 119.0, 118.3, 114.0, 111.4. **FTIR:** (neat)/ cm^{-1} = 3401, 2920, 2853, 1608, 1456, 1309, 1250, 1177, 1124, 1071, 1014, 933, 871. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{20}H_{14}N$, 268.1121; found 268.1140.

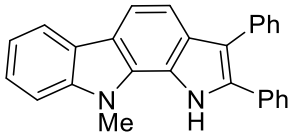


*12H-Benzofuro[2,3-a]carbazole (**3e**):* The titled compound **3e** was synthesized according to the **GP IA** by using 2-(benzofuran-2-yl)-1*H*-indole **1e** (46.6 mg, 0.20 mmol, 1.0 equiv) and 2-(benzyloxy)acetaldehyde **2a** (60 mg, 0.40 mmol, 2.0 equiv). The reaction was continued for 12 h. The benzo[*a*]carbazole **3e** was isolated after column chromatography using 10% ethyl acetate/hexane as eluent (white solid, 37.4 mg, 73% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 8.53 (br s, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 8.06 – 8.03 (m, 2H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ (ppm) 156.2, 141.9, 139.7, 126.4, 126.0, 125.6, 125.0, 124.2, 124.0, 123.1, 122.0, 120.6, 120.5, 120.3, 115.4, 112.0, 111.8, 111.3. **FTIR:** (neat)/ cm^{-1} = 3434, 2917, 2850, 1736, 1602, 1517, 1449, 1327, 1234, 1109, 1047923, 814. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{18}H_{12}NO$, 258.0913; found 258.0920.

*12H-Benzo[4,5]thieno[2,3-a]carbazole (**3f**)*[8b]*:* The titled compound **3f** was synthesized according to the **GP IA** by using 2-(benzo[*b*]thiophen-2-yl)-1*H*-indole **1f** (50.0 mg, 0.20 mmol, 1.0 equiv) and 2-(benzyloxy)acetaldehyde **2a** (60.0 mg, 0.40 mmol, 2.0 equiv). The reaction was continued for 12 h. The benzo[*a*]carbazole **3f** was isolated after column chromatography using 8% ethyl acetate/hexane as eluent (white solid, 49.5 mg, 91% yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 12.01 (br s, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 8.26 – 8.20 (m, 2H), 8.15 – 8.12 (m, 2H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6) δ (ppm) 139.7, 138.2, 136.3, 134.2, 133.4, 126.4, 125.6, 124.9, 123.4, 123.0, 122.0, 121.0, 120.7, 120.3, 119.3, 117.6, 113.0, 111.4.

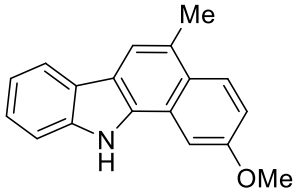
*10H-Thieno[2,3-a]carbazole (**3g**)*[8c]*:* The titled compound **3g** was synthesized according to the **GP IA** by using 2-(thiophen-2-yl)-1*H*-indole **1g** (40.0 mg, 0.20 mmol, 1.0 equiv) and 2-(benzyloxy)acetaldehyde **2a** (60 mg, 0.40 mmol. 2.0 equiv). The reaction was continued for 20 h. The benzo[*a*]carbazole **3g** was isolated after column chromatography using 8% ethyl acetate/hexane as eluent (pale yellow liquid, 30.4 mg, 63% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 8.30 (br s, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.45 – 7.41 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ (ppm) 139.3, 139.2, 134.3, 125.7, 125.4, 124.4, 124.0, 122.6, 120.31, 120.26, 119.5, 117.5, 116.0, 111.1.

*10-Methyl-2,3-diphenyl-1,10-dihydropyrrolo[2,3-a]carbazole (**3h**):* The titled compound **3h** was synthesized according to the **GP IA** by using 2-(4,5-diphenyl-1*H*-pyrrol-2-yl)-1-methyl-1*H*-indole

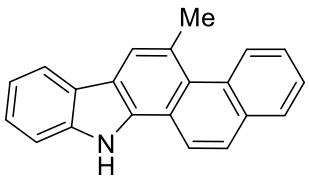


1h (69.7 mg, 0.20 mmol, 1.0 equiv) and 2-(benzyloxy)acetaldehyde **2a** (60.0 mg, 0.40 mmol, 2.0 equiv). The reaction was continued for 10 h. The benzo[*a*]carbazole **3h** was isolated after column chromatography using 12% ethyl acetate/hexane as eluent (yellow solid, 55.6 mg, 75% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 8.55 (s, 1H), 8.11 (d, *J* = 7.7 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.48 (m, 5H), 7.46 – 7.42 (m, 4H), 7.39 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H), 4.22 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ (ppm) 140.2, 135.3, 133.4, 133.1, 130.5, 128.9, 128.70, 128.67, 128.3, 127.9, 127.7, 126.6, 124.4, 124.2, 122.4, 119.8, 119.3, 118.5, 117.1, 113.9, 111.8, 108.4, 31.8. **FTIR:** (neat)/ cm^{-1} = 3466, 3243, 2918, 2853, 1730, 1608, 1487, 1419, 1373, 1265, 1184, 1117, 1016, 845. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{27}H_{21}N_2$, 373.1699; found 373.1758.

*2-Methoxy-5-methyl-11H-benzo[a]carbazole (**3i**):* The titled compound **3i** was synthesized according to the **GP IA** by using 2-(3-methoxyphenyl)-1*H*-indole **1a** (44.6 mg, 0.20 mmol, 1.0 equiv) and 2-(benzyloxy)propanal **2b** (65.7 mg, 0.40 mmol, 2.0 equiv). The reaction was continued for 60 h. The benzo[*a*]carbazole **3i** was isolated after column chromatography using 10% ethyl acetate/hexane as eluent (white solid, 44 mg, 84% yield). **^{1}H NMR** (600 MHz, DMSO-*d*$_6$) δ (ppm) 11.96 (br s, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 8.01 – 8.00 (m, 2H), 7.88 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.23 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 3.98 (s, 3H), 2.70 (s, 3H). **^{13}C{^{1}H} NMR** (151 MHz, DMSO-*d*$_6$) δ (ppm) 157.0, 138.7, 134.1, 126.7, 126.1, 124.5, 124.4, 123.2, 122.6, 119.7, 118.8, 117.2, 117.1, 116.4, 111.2, 102.2, 55.4, 19.5. **FTIR:** (neat)/ cm^{-1} = 3401, 2923, 2853, 1455, 1230, 1015, 737. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{18}H_{16}NO$, 262.1226; found 262.1231.

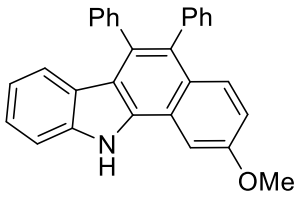


*7-Methyl-13H-naphtho[2,1-a]carbazole (**3j**):* The titled compound **3j** was synthesized according to the **GP IA** by using 2-(naphthalen-2-yl)-1*H*-indole **1d** (48.6 mg, 0.20 mmol, 1.0 equiv) and 2-(benzyloxy)acetaldehyde **2b** (65.7 mg, 0.40 mmol, 2.0 equiv). The reaction was continued for 24 h. The benzo[*a*]carbazole **3j** was isolated after column chromatography using 10% ethyl acetate/hexane as eluent (white solid, 23.4 mg, 42% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) 9.05 (d, *J* = 8.6 Hz, 1H), 8.68 (br s, 1H), 8.18 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.67 (t, *J* = 6.5 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 3.31 (s, 3H). **^{13}C{^{1}H} NMR** (151 MHz,



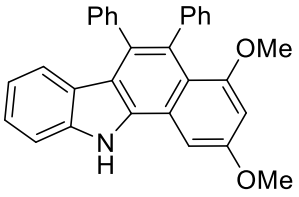
$CDCl_3$) δ (ppm) 139.6, 135.4, 133.2, 132.7, 129.1, 128.5, 127.7, 127.3, 127.2, 125.9, 125.59, 125.56, 123.8, 123.5, 120.4, 120.2, 120.0, 119.61, 119.55, 111.1, 28.1. **FTIR:** (neat)/ cm^{-1} = 3420, 3050, 2921, 2852, 1614, 1575, 1531, 1439, 1334, 1288, 1241, 1011, 928, 876. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{21}H_{16}N$, 282.1277; found 282.1259.

*2-Methoxy-5,6-diphenyl-11H-benzo[a]carbazole (**3k**):* The titled compound **3k** was synthesized



according to the **GP IB** by using 2-(3-methoxyphenyl)-1*H*-indole **1a** (44.6 mg, 0.20 mmol, 1.0 equiv) and 2-hydroxy-2,2-diphenylacetaldehyde **4a** (46.7 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 18 h. The substituted benzo[*a*]carbazole **3k** was isolated after column chromatography using 2% ethyl acetate/hexane as eluent (gray solid, 50 mg, 62% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 8.81 (br s, 1H), 7.58 – 7.54 (m, 2H), 7.48 (br s, 1H), 7.34 – 7.20 (m, 11H), 7.10 (d, *J* = 9.1 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 7.3 Hz, 1H), 4.03 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ (ppm) 157.6, 140.3, 139.6, 139.1, 134.0, 132.0, 130.6, 130.2, 128.32, 128.27, 128.0, 127.6, 126.8, 126.4, 124.8, 124.7, 122.3, 121.4, 119.8, 118.1, 117.0, 110.9, 100.3, 55.7. **FTIR:** (neat)/ cm^{-1} = 3375, 2924, 1623, 1501, 1438, 1366, 1216, 1101, 1025, 827, 751. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{29}H_{22}NO$, 400.1696; found 400.1693.

*2,4-Dimethoxy-5,6-diphenyl-11H-benzo[a]carbazole (**3l**):* The titled compound **3l** was synthesized



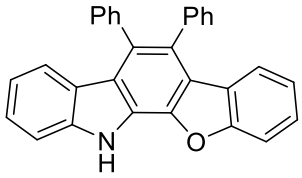
according to the **GP IB** by using 2-(3,5-dimethoxyphenyl)-1*H*-indole **1b** (50.7 mg, 0.20 mmol, 1.0 equiv) and 2-hydroxy-2,2-diphenylacetaldehyde **4a** (46.7 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 8 h. The substituted benzo[*a*]carbazole **3l** was isolated after column chromatography using 2% ethyl acetate/hexane as eluent (gray solid, 68 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.76 (br s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.30 – 7.19 (m, 5H), 7.12 – 7.04 (m, 6H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.54 (s, 1H), 4.04 (s, 3H), 3.39 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ (ppm) 159.6, 158.3, 143.5, 140.5, 139.2, 134.1, 133.4, 130.7, 130.6, 129.4, 127.8, 126.5, 126.1, 124.9, 124.8, 124.6, 122.6, 122.2, 119.7, 118.5, 118.4, 110.8, 99.1, 92.7, 55.7. **FTIR:** (neat)/ cm^{-1} = 3451, 3408, 3354, 3055, 2939, 2828, 1619, 1519, 1441, 1329, 1266, 1207, 1155, 1037, 911, 830. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{30}H_{24}NO_2$, 430.1802; found 430.1814.

*5,6-diphenyl-11H-[1,3]dioxolo[4',5':4,5]benzo[1,2-a]carbazole (**3m**):* The titled compound **3m** was synthesized according to the **GP IB** by using 2-(benzo[*d*][1,3]dioxol-5-yl)-1*H*-indole **1c** (47.5 mg, 0.20 mmol, 1.0 equiv) and 2-hydroxy-2,2-diphenylacetaldehyde **4a** (46.7 mg, 0.22 mmol. 1.10 equiv). The reaction was continued for 20 h. The substituted benzo[*a*]carbazole **3m** was isolated after column chromatography using 2% ethyl acetate/hexane as eluent (yellow solid, 60 mg, 72% yield). **^{1}H NMR** (500 MHz, DMSO-d_6) δ (ppm) 12.07 (br s, 1H), 8.04 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.18 (m, 8H), 7.15 (d, *J* = 7.2 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.68 (s, 1H), 6.48 (d, *J* = 7.9 Hz, 1H), 6.13 (s, 2H), 5.74 (s, 1H). **^{13}C{^{1}H NMR** (126 MHz, DMSO-d_6) δ (ppm) 146.9, 146.6, 140.0, 139.3, 139.0, 134.9, 132.6, 131.4, 129.9, 129.0, 127.8, 127.7, 127.5, 126.7, 126.3, 124.0, 123.3, 120.7, 118.5, 116.3, 115.5, 111.0, 103.7, 101.3, 98.9, 54.8. **FTIR:** (neat)/ cm^{-1} = 3443, 2915, 1605, 1464, 1355, 1249, 1180, 1038, 940, 862. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{29}H_{20}NO_2$, 414.1489; found 414.1502.

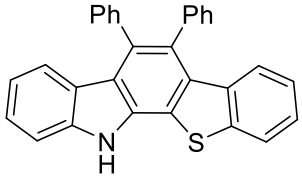
7,8-Diphenyl-13H-naphtho[2,1-a]carbazole (***3n**):* The titled compound **3n** was synthesized according to the **GP IB** by using 2-(naphthalen-2-yl)-1*H*-indole **1d** (48.7 mg, 0.20 mmol, 1.0 equiv) and 2-hydroxy-2,2-diphenylacetaldehyde **4a** (46.7 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 24 h. The substituted benzo[*a*]carbazole **3n** was isolated after column chromatography using 2% ethyl acetate/hexane as eluent (white solid, 68 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.81 (br s, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.91 – 7.88 (m, 2H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.25 – 7.16 (m, 7H), 7.08 (t, *J* = 8.5 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ (ppm) 143.2, 140.7, 139.7, 137.0, 135.5, 133.6, 131.9, 131.7, 131.2, 130.4, 128.9, 128.6, 128.3, 127.9, 127.7, 127.4, 126.7, 126.3, 125.6, 125.4, 125.3, 124.2, 122.3, 119.9, 119.5, 119.0, 118.7, 110.8. **FTIR:** (neat)/ cm^{-1} = 3426, 3053, 2920, 2850, 1601, 1442, 1331, 1255, 1183, 1072, 1026, 891. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{32}H_{22}N$, 420.1747; found 420.1747.

*5,6-Diphenyl-12H-benzofuro[2,3-a]carbazole (**3o**):* The titled compound **3o** was synthesized according to the **GP IB** by using 2-(benzofuran-2-yl)-1*H*-indole **1e** (46.7 mg, 0.20 mmol, 1.0 equiv) and 2-hydroxy-2,2-diphenylacetaldehyde **4a** (46.7 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 48 h. The substituted benzo[*a*]carbazole **3o** was isolated after column chromatography using 2% ethyl acetate/hexane as eluent (white solid, 60 mg, 73% yield). **^{1}H NMR**

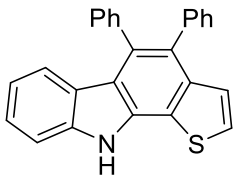
(400 MHz, $CDCl_3$) δ (ppm) 8.65 (br s, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.40 – 7.27 (m, 12H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.85 – 6.80 (m, 2H). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ (ppm) 156.6, 140.7, 140.1, 139.4, 138.9, 131.4, 131.0, 130.9, 128.2, 128.03, 127.98, 127.04, 126.95, 126.2, 125.7, 125.6, 124.3, 123.9, 122.8, 122.43, 122.38, 122.2, 120.7, 119.9, 111.5, 111.0. **FTIR:** (neat)/ cm^{-1} = 3420, 3056, 1657, 1603, 1434, 1311, 1166, 1095, 1013, 935, 885. **HRMS (ESI) *m*/*z*:** $[M + H]^+$ calcd for $C_{30}H_{20}NO$, 410.1539; found 410.1542.



*5,6-Diphenyl-12H-benzo[4,5]thieno[2,3-a]carbazole (***3p***):* The titled compound **3p** was synthesized according to the **GP IB** by using 2-(benzo[*b*]thiophen-2-yl)-1*H*-indole **1f** (50.0 mg, 0.20 mmol, 1.0 equiv) and 2-hydroxy-2,2-diphenylacetaldehyde **4a** (46.7 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 22 h. The substituted benzo[*a*]carbazole **3p** was isolated after column chromatography using 2% ethyl acetate/hexane as eluent (yellow solid, 64 mg, 76% yield). **^1H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.36 (br s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.25 (m, 12H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.74 – 6.68 (m, 2H). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ (ppm) 140.0, 139.7, 139.4, 139.0, 137.2, 133.9, 133.2, 132.1, 131.1, 130.4, 128.2, 127.9, 126.9, 126.8, 125.6, 125.0, 124.2, 124.1, 122.8, 122.3, 120.6, 119.9, 110.8. **FTIR:** (neat)/ cm^{-1} = 3409, 3054, 2922, 2852, 1602, 1420, 1323, 1172, 1024, 848. **HRMS (ESI) *m*/*z*:** $[M + H]^+$ calcd for $C_{30}H_{20}NS$, 426.1311; found 426.1312.



*4,5-Diphenyl-10H-thieno[2,3-a]carbazole (**3q**):* The titled compound **3q** was synthesized according to the **GP IB** by using 2-(thiophen-2-yl)-1*H*-indole **1g** (40.0 mg, 0.20 mmol, 1.0 equiv) and 2-hydroxy-2,2-diphenylacetaldehyde **4a** (46.7 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 18 h. The substituted benzo[*a*]carbazole **3q** was isolated after column chromatography using 2% ethyl acetate/hexane as eluent (yellow solid, 56 mg, 74% yield). **^1H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.42 (br s, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 5.3 Hz, 1H), 7.36 – 7.28 (m, 6H), 7.25 – 7.17 (m, 6H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$) δ (ppm) 139.9, 139.7, 139.5, 139.2, 133.3, 133.1, 131.4, 130.8, 129.4, 128.1, 127.6, 127.0, 126.4, 126.2, 125.1, 124.5, 123.9, 122.3, 121.5, 119.9, 118.4, 110.8. **FTIR:** (neat)/ cm^{-1} = 3432, 3055, 2909, 1601, 1548, 1429, 1329, 1239, 1159, 1018. **HRMS (ESI) *m*/*z*:** $[M + H]^+$ calcd for $C_{26}H_{18}NS$, 376.1154; found 376.1155.



*10-Methyl-2,3,4,5-tetraphenyl-1,10-dihydropyrrolo[2,3-a]carbazole (**3r**):* The titled compound **3r** was synthesized according to the **GP IB** by using 2-(4,5-diphenyl-1*H*-pyrrol-2-yl)-1-methyl-1*H*-indole **1h** (69.7 mg, 0.20 mmol, 1.0 equiv) and 2-hydroxy-2,2-diphenylacetaldehyde **4a** (46.7 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 2 h. The substituted benzo[*a*]carbazole **3r** was isolated after column chromatography using 2% ethyl acetate/hexane as eluent (yellow solid, 72 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 11.52 (br s, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.22 (m, 9H), 7.09 (d, *J* = 3.5 Hz, 2H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.79 – 6.75 (m, 3H), 6.70 – 6.67 (m, 5H), 6.59 (t, *J* = 7.2 Hz, 2H), 6.35 (d, *J* = 7.9 Hz, 1H), 4.41 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ (ppm) 140.6, 140.3, 138.2, 135.8, 135.7, 132.7, 131.3, 130.8, 130.7, 129.4, 128.9, 127.9, 127.7, 127.2, 127.0, 126.8, 126.3, 125.9, 125.7, 125.6, 124.80, 124.76, 123.53, 123.46, 121.3, 120.5, 118.3, 117.3, 115.6, 109.0, 31.9. **FTIR:** (neat)/ cm^{-1} = 3344, 3058, 2923, 1647, 1579, 1475, 1364, 1316, 1273, 1225, 1176, 1072, 1024, 864. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{39}H_{29}N_2$, 525.2325; found 525.2334.

*7,8-bis(3-Methoxyphenyl)-13H-naphtho[2,1-a]carbazole (**3s**):* The titled compound **3s** was synthesized according to the **GP IB** by using 2-(naphthalen-2-yl)-1*H*-indole **1d** (48.7 mg, 0.20 mmol, 1.0 equiv) and 2-hydroxy-2,2-bis(3-methoxyphenyl)acetaldehyde **4b** (60 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 48 h. The substituted benzo[*a*]carbazole **3s** was isolated in atropisomeric mixture due to presence of the methoxy group, which restricted the rotation of the molecule. The purification was performed by column chromatography using 2% ethyl acetate/hexane as eluent (white solid, 60 mg, 63% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 8.86 (s, 2H), 8.11 (d, *J* = 8.7 Hz, 2H), 7.88 (t, *J* = 9.0 Hz, 4H), 7.73 (d, *J* = 11.6 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.15 – 7.10 (m, 4H), 6.97 (q, *J* = 7.6 Hz, 3H), 6.85 (d, *J* = 8.3 Hz, 2H), 6.82 – 6.76 (m, 10H), 6.66 (s, 1H), 3.69 (s, 3H), 3.643 (s, 3H), 3.637 (s, 3H), 3.625 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ (ppm) 159.8, 159.7, 159.5, 159.3, 144.4, 142.00, 141.98, 139.8, 136.63, 136.61, 135.6, 133.5, 131.9, 130.91, 130.89, 129.4, 129.3, 129.1, 128.9, 128.8, 128.70, 128.65, 127.8, 127.33, 127.31, 125.7, 125.50, 125.45, 125.4, 124.52, 124.49, 124.2, 123.2, 123.1, 122.50, 122.48, 119.99, 119.98, 119.4, 118.84, 118.76, 116.9, 115.7, 115.5, 113.3, 113.1, 113.0, 112.9, 110.8, 55.43, 55.41, 55.39. **FTIR:** (neat)/ cm^{-1} = 3430, 2932, 2832, 1578, 1453, 1288, 1167, 1031, 870. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{34}H_{26}NO_2$, 480.1958; found 480.1964.

*5,6-Dibenzyl-2-methoxy-11H-benzo[a]carbazole (**3t**):* The titled compound **3t** was synthesized according to the **GP IB** by using 2-(3-methoxyphenyl)-1*H*-indole **1a** (44.7 mg, 0.20 mmol, 1.0 equiv) and 2-benzyl-2-hydroxy-3-phenylpropanal **4c** (53.0 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 7 h. The substituted benzo[*a*]carbazole **3t** was isolated after column chromatography using 2% ethyl acetate/hexane as eluent (greenish black solid, 52 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.87 (br s, 1H), 8.01 – 7.98 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.49 (s, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.20 (m, 6H), 7.19 – 7.13 (m, 4H), 7.10 (d, *J* = 7.1 Hz, 2H), 4.77 (s, 2H), 4.53 (s, 2H), 4.01 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ (ppm) 157.2, 141.2, 139.8, 139.0, 134.3, 130.0, 128.7, 128.5, 128.4, 128.2, 127.9, 127.1, 127.0, 126.1, 125.9, 124.6, 124.3, 122.5, 121.7, 120.2, 119.0, 117.2, 111.1, 100.8, 55.7, 36.3, 34.0. **FTIR:** (neat)/ cm^{-1} = 3398, 3021, 2923, 1629, 1492, 1448, 1371, 1324, 1222, 1169, 1031, 934, 844. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{31}H_{26}NO$, 428.2009; found 428.2009.

*8-(4-Methoxyphenyl)-7-phenyl-13H-naphtho[2,1-a]carbazole (**3u**)*: The titled compound **3u** was synthesized according to the **GP IB** by using 2-(naphthalen-2-yl)-1*H*-indole **1d** (48.7 mg, 0.20 mmol, 1.0 equiv) and 2-hydroxy-2-(4-methoxyphenyl)-2-phenylacetaldehyde **4d** (53.3 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 24 h. The substituted benzo[*a*]carbazole **3u** was isolated as mixture of two isomers. The purification was performed by column chromatography using 2% ethyl acetate/hexane as eluent (white solid, 68 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 12.34 (br s, 2H), 8.62 (dd, *J* = 8.9, 1.8 Hz, 2H), 8.05 (d, *J* = 8.9 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.65 (dd, *J* = 8.1, 2.2 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.36 – 7.31 (m, 5H), 7.26 – 7.23 (m, 3H), 7.17 – 7.15 (m, 2H), 7.13 – 7.10 (m, 2H), 7.07 – 6.96 (m, 6H), 6.91 – 6.82 (m, 4H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.51 (d, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 8.0 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ (ppm) 157.7, 157.5, 143.0, 140.7, 140.0, 136.8, 136.2, 135.8, 135.7, 134.9, 133.2, 132.5, 132.2, 131.3, 131.2, 131.03, 131.0, 130.0, 129.9, 129.2, 128.8, 128.2, 127.9, 127.5, 127.4, 127.1, 126.6, 126.3, 125.3, 125.0, 124.9, 123.0, 122.9, 121.2, 121.1, 121.0, 118.9, 118.8, 118.7, 118.3, 117.9, 113.7, 113.2, 111.2, 54.9. **FTIR:** (neat)/ cm^{-1} = 3370, 3044, 2920, 1609, 1512, 144, 1330, 1241, 1178, 1024, 819. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{33}H_{24}NO$, 450.1852; found 450.1852.

*7-(4-Chlorophenyl)-8-(4-methoxyphenyl)-13H-naphtho[2,1-a]carbazole (**3v**):* The titled compound **3v** was synthesized according to the **GP IB** by using 2-(naphthalen-2-yl)-1*H*-indole **1d** (48.7 mg, 0.20 mmol, 1.0 equiv) and 2-(4-chlorophenyl)-2-hydroxy-2-(4-methoxyphenyl)acetaldehyde **4g** (61.0 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 26 h. The substituted benzo[*a*]carbazole **3v** was isolated after column chromatography using 10% ethyl acetate/hexane as eluent (white solid, 78 mg, 81% yield). **^{1}H NMR** (500 MHz, DMSO-d_6) δ(ppm) 12.36 (s, 1H), 12.35 (s, 1H), 8.62 (d, *J* = 8.9 Hz, 2H), 8.06 (d, *J* = 8.9 Hz, 2H), 7.99 (t, *J* = 6.7 Hz, 2H), 7.67 – 7.64 (m, 2H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.46 – 7.42 (m, 3H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.09 – 7.03 (m, 6H), 6.92 – 6.90 (m, 4H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.49 (dd, *J* = 15.5, 8.0 Hz, 2H), 3.79 (s, 3H), 3.75 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6) δ 157.8, 157.7, 142.0, 140.01, 139.95, 139.9, 139.6, 136.23, 136.22, 135.9, 135.8, 135.3, 134.6, 133.2, 133.14, 133.05, 132.2, 132.1, 131.8, 131.2, 131.1, 130.9, 130.8, 130.7, 129.3, 128.9, 128.8, 128.5, 128.2, 127.9, 127.3, 127.2, 127.1, 126.5, 126.1, 125.40, 125.36, 125.0, 124.9, 122.9, 122.7, 122.6, 121.1, 120.89, 120.85, 120.8, 119.0, 118.9, 118.84, 118.80, 118.3, 117.5, 113.8, 113.3, 111.3, 111.2, 55.0. **FTIR:** (neat)/ cm^{-1} = 3382, 2923, 2853, 1609, 1512, 1456, 1394, 1331, 1178, 1090, 1014, 819. **HRMS (ESI) *m/z*:** [M + H]$^+$ calcd for $C_{33}H_{23}ClNO$, 484.1463; found 484.1477.

*7-Ethyl-8-phenyl-13H-naphtho[2,1-a]carbazole (**3w**):* The titled compound **3w** was synthesized according to the **GP IB** by using 2-(naphthalen-2-yl)-1*H*-indole **1d** (48.7 mg, 0.20 mmol, 1.0 equiv) and 2-hydroxy-2-phenylbutanal **4e** (36.0 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 18 h. The substituted benzo[*a*]carbazole **3w** was isolated after column chromatography using 2% ethyl acetate/hexane as eluent (pale yellow solid, 62 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 8.98 (d, *J* = 8.5 Hz, 1H), 8.73 (br s, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 8.9 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.68 – 7.56 (m, 5H), 7.53 – 7.48 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 3.43 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.3 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ (ppm) 141.6, 139.7, 137.6, 134.6, 133.5, 132.1, 130.9, 130.0, 129.3, 128.9, 128.3, 127.7, 127.5, 127.2, 126.0, 125.7, 125.2, 124.2, 122.2, 120.1, 119.8, 119.6, 119.2, 110.7, 26.2, 16.0. **FTIR:** (neat)/ cm^{-1} = 3425, 2971, 2910 1425, 1332 1253, 1101, 1019, 961,745. **HRMS (ESI) *m/z*:** [M + H]$^+$ calcd for $C_{28}H_{22}N$, 372.1747; found 372.1751.

*2-(4-Methoxyphenyl)-2-(2-(naphthalen-2-yl)-1H-indol-3-yl)-1 phenylethan-1-one (**5a**):* The titled compound **5a** was synthesized according to the **GP IB** by using 2-(naphthalen-2-yl)-1*H*-indole **1d** (48.7 mg, 0.20 mmol, 1.0 equiv) and 2-hydroxy-2-(4-methoxyphenyl)-2-phenylacetaldehyde **4d** (53.3 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 0.5 h. The *α*-(3-indolyl) ketone **5a** was isolated after column chromatography using 2% ethyl acetate/hexane as eluent (white solid, 65 mg, 69% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 8.36 (s, 1H), 7.95 – 7.90 (m, 3H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.53 (m, 3H), 7.40 – 7.28 (m, 4H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.28 (s, 1H), 3.81 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ (ppm) 198.7, 158.6, 137.0, 136.5, 133.6, 133.1, 132.6, 132.2, 130.5, 129.9, 129.0, 128.7, 128.4, 128.3, 128.0, 127.9, 126.94, 126.85, 126.0, 122.7, 121.5, 120.6, 114.1, 111.0, 110.4, 55.4, 50.8. **FTIR:** (neat)/ cm^{-1} = 3353, 3062, 2951, 1672, 1595, 1511, 1449, 1246, 1178, 1038, 996, 899. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{33}H_{26}NO_2$, 468.1958; found 468.1970. This compound was further treated under the standard reaction conditions and the desired product **3u** was isolated in 79% yield.

*3-(2-(Naphthalen-2-yl)-1H-indol-3-yl)-1,4-diphenylbutan-2-one (**5b**):* The titled compound **5b** was synthesized according to the **GP IB** by using 2-(naphthalen-2-yl)-1*H*-indole **1d** (48.7 mg, 0.20 mmol, 1.0 equiv) and 2-benzyl-2-hydroxy-3-phenylpropanal **4c** (53.0 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 36 h. The *α*-(3-indolyl) ketone **5b** was isolated after column chromatography using 2% ethyl acetate/hexane as eluent (white solid, 50 mg, 56% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.26 (s, 1H), 7.88 – 7.85 (m, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.64 (m, 1H), 7.56 – 7.50 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.18 – 7.14 (m, 5H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 2H), 6.90 – 6.88 (m, 2H), 6.64 (d, *J* = 7.2 Hz, 2H), 4.28 (dd, *J* = 9.6, 4.9 Hz, 1H), 3.55 – 3.48 (m, 1H), 3.43 (d, *J* = 6.3 Hz, 2H), 3.39 – 3.33 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ (ppm) 207.4, 140.7, 137.5, 136.4, 134.3, 133.4, 133.0, 129.6, 129.5, 129.4, 128.6, 128.34, 128.33, 127.9, 127.8, 127.4, 126.8, 126.7, 126.6, 126.2, 126.17, 122.8, 120.6, 111.2, 109.2, 51.4, 48.1, 36.1. **FTIR:** (neat)/ cm^{-1} = 3398, 2917, 1705, 1601, 1425, 1334, 1243, 1101, 959, 821. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{34}H_{28}NO$, 466.2165; found 466.2193.

*8-(2-(Naphthalen-2-yl)-1H-indol-3-yl)tetradecan-7-one (**5c**):* The titled compound **5c** was synthesized according to the **GP IB** by using 2-(naphthalen-2-yl)-1*H*-indole **1d** (48.7 mg, 0.20 mmol, 1.0 equiv) and 2-hexyl-2-hydroxyoctanal **4f** (50.2 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 36 h. The *α*-(3-indolyl) ketone **5c** was isolated after column chromatography using 1% ethyl acetate/hexane as eluent (white solid, 52 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.27 (s, 1H), 8.02 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.92 (dd, *J* = 9.4, 5.4 Hz, 2H), 7.68 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 4.05 (t, *J* = 7.3 Hz, 1H), 2.35 – 2.20 (m, 3H), 1.98 – 1.89 (m, 1H), 1.43 – 1.33 (m, 3H), 1.30 – 1.16 (m, 9H), 1.13 – 1.02 (m, 6H), 0.79 (t, *J* = 6.7 Hz, 3H), 0.74 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ (ppm) 211.2, 136.38, 136.36, 133.6, 133.1, 130.5, 128.9, 128.2, 128.02, 127.98, 127.6, 127.0, 126.8, 126.5, 122.7, 120.9, 120.3, 111.4, 111.0, 50.0, 41.5, 31.9, 31.6, 30.2, 29.5, 28.9, 28.1, 24.1, 22.7, 22.5, 14.2, 14.1. **FTIR:** (neat)/ cm^{-1} = 3354, 3057, 2929, 2855, 1699, 1603, 1455, 1340, 1240, 1132, 1014, 952, 819. **HRMS (ESI) *m*/*z*:** $[M + H]^+$ calcd for $C_{32}H_{40}NO$, 454.3104; found 454.3128.

*1-(4-Chlorophenyl)-2-(4-methoxyphenyl)-2-(2-(naphthalen-2-yl)-1H-indol-3-yl)ethan-1-one (**5d**):* The titled compound **5d** was synthesized according to the **GP IB** by using 2-(naphthalen-2-yl)-1*H*-indole **1d** (48.7 mg, 0.20 mmol, 1.0 equiv) and 2-(4-chlorophenyl)-2-hydroxy-2-(4-methoxyphenyl)acetaldehyde **4g** (61.0 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 2 h. The *α*-(3-indolyl) ketone **5d** was isolated after column chromatography using 5% ethyl acetate/hexane as eluent (white solid, 88.6 mg, 89% yield). **^{1}H NMR** (500 MHz, DMSO-d_6) δ (ppm) 11.69 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 8.00 – 7.97 (m, 2H), 7.87 – 7.85 (m, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.59 – 7.57 (m, 4H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 7.1 Hz, 4H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.97 – 6.92 (m, 3H), 6.31 (s, 1H), 3.76 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6) δ (ppm) 197.3, 158.0, 137.4, 136.4, 136.2, 135.3, 132.8, 132.4, 131.8, 130.3, 129.7, 129.5, 128.4, 128.3, 128.0, 127.7, 127.4, 127.2, 126.8, 126.6, 125.9, 121.6, 119.5, 113.6, 111.6, 108.4, 55.0, 50.4. **FTIR:** (neat)/ cm^{-1} = 3331, 2927, 1670, 1586, 1510, 1454, 1245, 1175, 1092, 1034, 821. **HRMS (ESI) *m*/*z*:** $[M + H]^+$ calcd for $C_{33}H_{25}NO_2Cl$, 502.1568; found 502.1593.

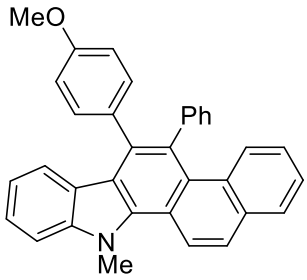
*4-(3-(2-Oxo-1-phenylbutyl)-1H-indol-2-yl)benzonitrile (**5e**):* The titled compound **5e** was synthesized according to the **GP IB** by using 4-(1*H*-indol-2-yl)benzonitrile **1i** (43.6 mg, 0.20 mmol, 1.0 equiv) and 2-hydroxy-2-phenylbutanal **4e** (36.0 mg, 0.22 mmol, 1.10 equiv). The reaction was continued for 48 h. The *α*-(3-indolyl) ketone **5e** was isolated after column chromatography using 10% ethyl acetate/hexane as eluent (white solid, 39.6 mg, 55% yield). **^{1}H NMR** (500 MHz, DMSO-d_6) δ (ppm) 11.78 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.25 (m, 3H), 7.23 – 7.15 (m, 4H), 7.01 (t, *J* = 7.5 Hz, 1H), 5.50 (s, 1H), 2.43 – 2.36 (m, 1H), 2.30 – 2.22 (m, 1H), 0.77 (t, *J* = 7.3 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6) δ (ppm) 208.8, 139.3, 136.63, 136.57, 134.9, 132.7, 128.83, 128.81, 128.0, 127.3, 126.4, 122.5, 119.9, 119.8, 118.6, 111.9, 110.2, 109.3, 54.7, 34.2, 7.9. **FTIR:** (neat)/ cm^{-1} = 3370, 2923, 2219, 1708, 1604, 1494, 1452, 1343, 1245, 1165, 1109, 843. **HRMS (ESI) *m/z*:** [M + H]$^{+}$ calcd for $C_{25}H_{21}N_2O$, 365.1654; found 365.1661.

*10-Methyl-4,5-diphenyl-10H-thieno[2,3-a]carbazole (**6a**):* The titled compound **6a** was synthesized according to the **GP II** by using 4,5-diphenyl-10*H*-thieno[2,3-*a*]carbazole **3q** (37.5 mg, 0.10 mmol, 1.0 equiv) and methyl iodide (10 μL, 0.15 mmol, 1.5 equiv). The reaction was continued for 2 h. The methylated product **6a** was isolated after column chromatography using hexane as eluent (yellow solid, 36 mg, yield 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 7.47 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.34 – 7.28 (m, 5H), 7.25 – 7.17 (m, 6H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.32 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ (ppm) 141.0, 140.0, 139.8, 139.6, 135.4, 133.3, 131.4, 130.7, 128.8, 128.2, 127.6, 127.0, 126.4, 125.8, 124.8, 124.0, 123.7, 122.3, 121.2, 119.3, 117.6, 108.6, 31.4. **FTIR:** (neat)/ cm^{-1} = 3052, 1575 1436 1386, 1327, 1283, 1311, 1026, 911, 843. **HRMS (ESI) *m/z*:** [M + H]$^{+}$ calcd for $C_{27}H_{20}NS$, 390.1311; found 390.1318.

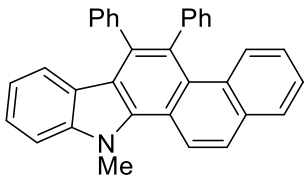
*12-Methyl-5,6-diphenyl-12H-benzofuro[2,3-a]carbazole (**6b**):* The titled compound **6b** was synthesized according to the **GP II** by using 5,6-diphenyl-12*H*-benzofuro[2,3-*a*]carbazole **3o** (41.0 mg, 0.10 mmol, 1.0 equiv) and methyl iodide (10 μL, 0.15 mmol, 1.5 equiv). The reaction was continued for 2 h. The methylated product **6b** was isolated after column chromatography using hexane as eluent (white solid, 38 mg, yield 90%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 7.67 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.34 – 7.31 (m, 10H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.84 – 6.80 (m, 2H), 4.42 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ (ppm) 156.5, 141.7, 141.1, 139.5, 139.1,

131.5, 131.0, 130.8, 128.2, 128.0, 127.3, 127.0, 126.9, 126.11, 126.06, 125.4, 125.3, 124.0, 122.7, 122.4, 122.2, 121.5, 121.0, 119.3, 111.5, 108.6, 31.9. **FTIR:** (neat)/ cm^{-1} = 3055, 1648, 1601, 1439, 1312, 1199, 1149, 1089, 1024, 961, 907, 851. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{31}H_{22}NO$, 424.1696; found 424.1701.

*8-(4-Methoxyphenyl)-13-methyl-7-phenyl-13H-naphtho[2,1-a]carbazole (**6c**):* The titled compound **6c** was synthesized according to the **GP II** by using 8-(4-methoxyphenyl)-7-phenyl-13*H*-naphtho[2,1-*a*]carbazole **3u** (45.0 mg, 0.10 mmol, 1.0 equiv) and methyl iodide (10 μL, 0.15 mmol, 1.5 equiv). The reaction was continued for 3 h. The methylated product **6c** was isolated as a mixture of isomers. The purification was performed by column chromatography using hexane as eluent (white solid, 43 mg, yield 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.72 (dd, *J* = 9.1, 1.2 Hz, 2H), 7.87 (t, *J* = 3.9 Hz, 3H), 7.85 (s, 3H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.53 (dd, *J* = 8.2, 2.0 Hz, 2H), 7.50 – 7.38 (m, 4H), 7.36 – 7.31 (m, 3H), 7.23 – 7.18 (m, 5H), 7.14 – 7.08 (m, 5H), 7.06 – 7.00 (m, 3H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 4.44 (s, 6H), 3.85 (s, 3H), 3.79 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ (ppm) 158.3, 158.0, 143.5, 142.8, 141.0, 137.2, 136.8, 136.6, 135.7, 133.2, 132.9, 132.8, 131.93, 131.88, 131.80, 131.77, 131.5, 130.9, 130.5, 129.2, 129.09, 129.05, 128.8, 128.3, 128.1, 126.7, 126.2, 126.1, 125.5, 125.3, 124.7, 124.6, 123.3, 123.2, 122.5, 122.3, 121.3, 120.23, 120.21, 120.16, 119.8, 119.60, 119.56, 113.7, 113.5, 109.1, 55.32, 55.28, 35.4. **FTIR:** (neat)/ cm^{-1} = 3045, 2918, 1607, 1512 1465, 1384, 1324, 1249, 1176, 1105, 1028, 901. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{34}H_{26}NO$,, 464.2009; found 464.2025.



*13-Methyl-7,8-diphenyl-13H-naphtho[2,1-a]carbazole (**6d**):* The titled compound **6d** was synthesized according to the **GP II** by using 7,8-diphenyl-13*H*-naphtho[2,1-*a*]carbazole **3n** (42 mg, 0.10 mmol, 1.0 equiv) and methyl iodide (10 μL, 0.15 mmol, 1.5 equiv). The reaction was continued for 3 h. The methylated product **6d** was isolated after column chromatography using hexane as eluent (yellow solid, 40 mg, yield 91%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.72 (d, *J* = 9.1 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.35 – 7.32 (m, 3H), 7.23 – 7.15 (m, 7H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 1H), 4.43 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ (ppm) 143.4, 142.8, 140.9, 136.9, 136.8, 132.9, 131.9, 131.8, 131.3, 130.5, 129.2, 128.7, 128.2, 128.1, 128.0, 126.7, 126.2, 126.1, 125.6, 125.3, 124.7, 123.2, 122.3, 121.3, 120.2, 119.8, 119.6, 109.1,



35.3. **FTIR:** (neat)/ cm^{-1} = 3046, 1521, 1443, 1381, 1324, 1206, 1123, 1071, 1023, 917, 796. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{33}H_{24}N$, 434.1903; found 434.1928.

*1,10-Dimethyl-2,3,4,5-tetraphenyl-1,10-dihydropyrrolo[2,3-a]carbazole (**6e**):* The titled compound **6e** was synthesized according to the **GP II** by using 10-methyl-2,3,4,5-tetraphenyl-1,10-dihydropyrrolo[2,3-*a*]carbazole **3r** (52.4 mg, 0.10 mmol, 1.0 equiv) and methyl iodide (10 μL, 0.15 mmol, 1.5 equiv). The reaction was continued for 3 h. The methylated product **6e** was isolated after column chromatography using hexane as eluent (yellow solid, 50 mg, yield 93%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 7.61 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.25 (m, 9H), 7.09 (d, *J* = 3.8 Hz, 2H), 6.83 – 6.79 (m, 2H), 6.73 – 6.67 (m, *J* = 20.7 Hz, 5H), 6.63 – 6.56 (m, 4H), 6.32 (d, *J* = 7.9 Hz, 1H), 4.25 (s, 3H), 3.92 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6) δ (ppm) 143.3, 141.7, 140.3, 137.9, 135.5, 131.6, 131.1, 130.9, 130.60, 130.55, 129.4, 129.1, 128.0, 127.7, 127.5, 126.5, 126.4, 126.3, 125.9, 125.8, 125.7, 124.8, 124.6, 124.5, 124.0, 120.5, 119.0, 118.9, 117.9, 110.3, 38.3, 36.5. **FTIR:** (neat)/ cm^{-1} = 3046, 2920, 1599, 1440, 1324, 1247, 1157, 1071, 1021, 955. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{40}H_{31}N_2$, 539.2482; found 539.2494.

*7,8-bis(3-Methoxyphenyl)-13-methyl-13H-naphtho[2,1-a]carbazole (**6f**):* The titled compound **6f** was synthesized according to the **GP II** by using 7,8-bis(3-methoxyphenyl)-13*H*-naphtho[2,1-*a*]carbazole **3s** (48 mg, 0.10 mmol, 1.0 equiv) and methyl iodide (10 μL, 0.15 mmol, 1.5 equiv). The reaction was continued for 3 h. The methylated product **6f** was isolated in atropisomeric mixture due to presence of the methoxy group, which restricted the rotation of the molecule. The purification was performed by column chromatography using 10% ethyl acetate/hexane as eluent (white solid, 47 mg, yield 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ(ppm) 8.72 (d, *J* = 9.2 Hz, 2H), 7.90 – 7.84 (m, 7H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.46 (dd, *J* = 14.9, 7.4 Hz, 4H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.18 – 7.11 (m, 4H), 7.03 (t, *J* = 7.1 Hz, 3H), 6.93 – 6.89 (m, 3H), 6.85 – 6.78 (m, 10H), 6.69 (dd, *J* = 2.1, 1.5 Hz, 1H), 4.42 (s, 6H), 3.74 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 3.66 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ(ppm) 159.6, 159.52, 159.45, 159.3, 144.5, 142.8, 142.08, 142.06, 136.8, 136.5, 136.4, 132.8, 131.7, 130.93, 130.90, 129.20, 129.15, 129.12, 129.10, 128.9, 128.59, 128.57, 128.0, 126.3, 125.6, 125.3, 124.79, 124.76, 124.6, 124.5, 123.3, 123.1, 123.0, 122.49, 122.46, 121.2, 120.2, 119.67, 119.65, 119.5, 116.97, 116.94, 115.8, 115.4, 113.2, 113.0, 112.71, 112.65, 109.1, 55.4, 55.3, 35.3. **FTIR:** (neat)/ cm^{-1} = 2925, 2852, 1577, 1465, 1324, 1244, 1168, 1039, 922. **HRMS (ESI) *m/z*:** $[M + H]^+$ calcd for $C_{35}H_{28}NO_2$, 494.2115; found 494.2131.

*8-Methyl-8H-phenanthro[9,10-c]thieno[2,3-a]carbazole (**7a**):* The titled compound **7a** was synthesized according to the **GP III** by using 10-methyl-4,5-diphenyl-10*H*-thieno[2,3-*a*]carbazole **6a** (39 mg, 0.10 mmol, 1.0 equiv) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (45.4 mg, 0.20 mmol, 2.0 equiv). The reaction was continued for 15 min. The PAH **7a** was isolated after column chromatography using hexane as eluent (yellow solid, 14 mg, yield 43%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 9.10 (d, *J* = 8.1 Hz, 1H), 8.76 – 8.72 (m, 2H), 8.68 (d, *J* = 8.1 Hz, 1H), 8.52 (d, *J* = 8.1 Hz, 1H), 8.45 (d, *J* = 5.5 Hz, 1H), 7.71 – 7.62 (m, 4H), 7.61 – 7.56 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 4.38 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ (ppm) 140.7 (C), 136.2 (C), 136.0 (C), 131.0 (C), 129.8 (C), 129.7 (C), 129.5 (C), 128.7 (CH), 127.3 (CH), 127.1 (CH), 127.0 (2 CH), 126.8 (C), 125.9 (CH), 125.7 (CH), 124.8 (CH), 124.6 (CH), 124.22 (C), 124.19 (C), 123.6 (CH), 123.5 (CH), 123.2 (CH), 122.3 (C), 119.2 (CH), 114.1 (C), 109.3 (CH), 31.6 (CH_3). **FTIR:** (neat)/ cm^{-1} = 3054, 2922, 2851, 1577, 1431,1326, 1240, 1150, 1067, 907, 851. **HRMS (ESI) *m*/*z*:** $[M + H]^+$ calcd for $C_{27}H_{18}NS$, 388.1154; found 388.1158.

*10-Methyl-10H-benzofuro[2,3-a]phenanthro[9,10-c]carbazole (**7b**):* The titled compound **7b** was synthesized according to the **GP III** by using 12-methyl-5,6-diphenyl-12*H*-benzofuro[2,3-*a*]carbazole **6b** (42.3 mg, 0.10 mmol, 1.0 equiv) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (45.4 mg, 0.20 mmol, 2.0 equiv). The reaction was continued for 10 min. The PAH **7b** was isolated after column chromatography using hexane as eluent (white solid, 19 mg, yield 46%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) 9.10 (d, *J* = 8.0 Hz, 1H), 8.94 (d, *J* = 7.7 Hz, 1H), 8.70 (d, *J* = 7.3 Hz, 2H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.49 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.64 – 7.59 (m, 2H), 7.56 – 7.49 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.3 Hz, 1H), 4.52 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ (ppm) 156.5 (C), 143.6 (C), 141.4 (C), 130.2 (C), 130.0 (C), 129.6 (C), 129.1 (C), 128.3 (CH), 127.7 (C), 127.4 (CH), 126.8 (CH), 126.4 (CH), 126.3 (CH), 126.1 (CH), 126.0 (CH), 125.8 (C), 125.53 (C), 125.51 (CH), 124.3 (C), 123.6 (CH), 123.54 (CH), 123.47 (CH), 123.3 (CH), 122.6 (CH), 122.1 (C), 119.2 (CH), 117.90 (C), 117.89 (C), 112.0 (CH), 109.4 (CH), 32.1 (CH_3). **FTIR:** (neat)/ cm^{-1} = 2919, 1850 1736 1633, 1542, 1432, 1326, 1213, 1156, 1023, 958, 852. **HRMS (ESI) *m*/*z*:** $[M + H]^+$ calcd for $C_{31}H_{20}NO$, 422.1539; found 422.1551.

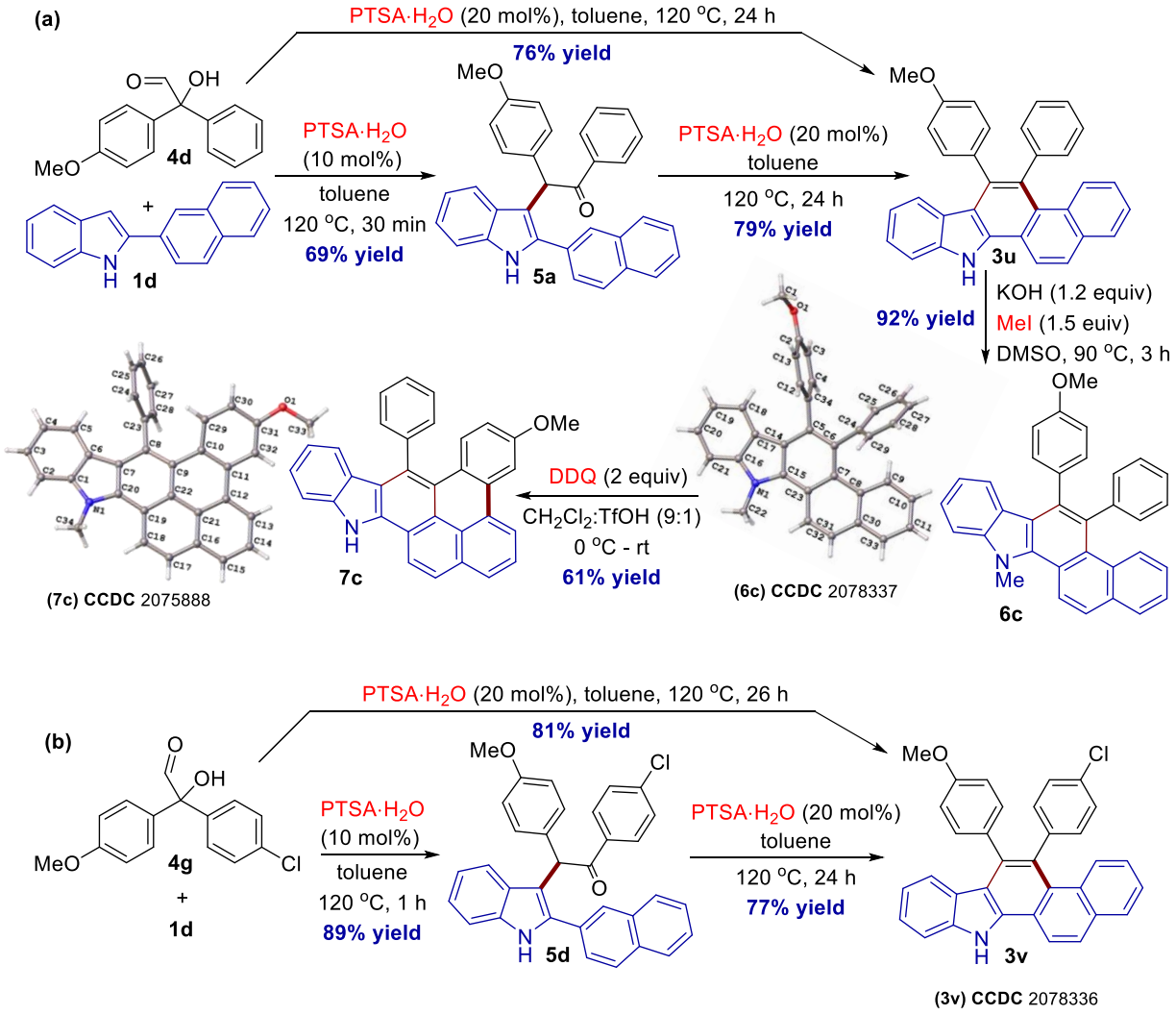
*18-Methoxy-11-methyl-11H-naphtho[2,1-a]phenanthro[9,10-c]carbazole (**7c**):* The titled compound **7c** was synthesized according to the **GP III** by using 8-(4-methoxyphenyl)-13-methyl-7-phenyl-13*H*-naphtho[2,1-*a*]carbazole **6c** (46.3 mg, 0.10 mmol, 1.0 equiv) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (45.4 mg, 0.20 mmol, 2.0 equiv). The reaction was continued for 10 min. The PAH **7c** was isolated after column chromatography using hexane as eluent (yellow solid, 28 mg, yield 61%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) 8.96 (d, *J* = 9.2 Hz, 1H), 8.76 (d, *J* = 7.7 Hz, 1H), 8.18 – 8.15 (m, 2H), 8.12 (d, *J* = 9.2 Hz, 1H), 7.98 (t, *J* = 7.7 Hz, 1H), 7.92 (d, *J* = 9.4 Hz, 1H), 7.70 – 7.66 (m, 3H), 7.63 – 7.60 (m, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.73 (dd, *J* = 9.4, 2.8 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 4.53 (s, 3H), 3.97 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ (ppm) 157.6, 144.0, 143.1, 135.8, 133.4, 132.5, 131.5, 131.1, 130.6, 130.1, 128.0, 126.3, 126.2, 126.1, 125.92, 125.85, 125.7, 125.0, 123.5, 123.3, 121.8, 121.6, 120.9, 119.9, 119.3, 117.3, 113.7, 108.9, 106.7, 55.5, 35.3. **FTIR:** (neat)/ cm^{-1} = 3051, 2928, 1849, 1612, 1553, 1485, 1400, 1328, 1237, 1173, 1110, 1039, 945, 833. **HRMS (ESI) *m*/*z*:** $[M + H]^+$ calcd for $C_{34}H_{24}NO$, 462.1852; found 462.1855.

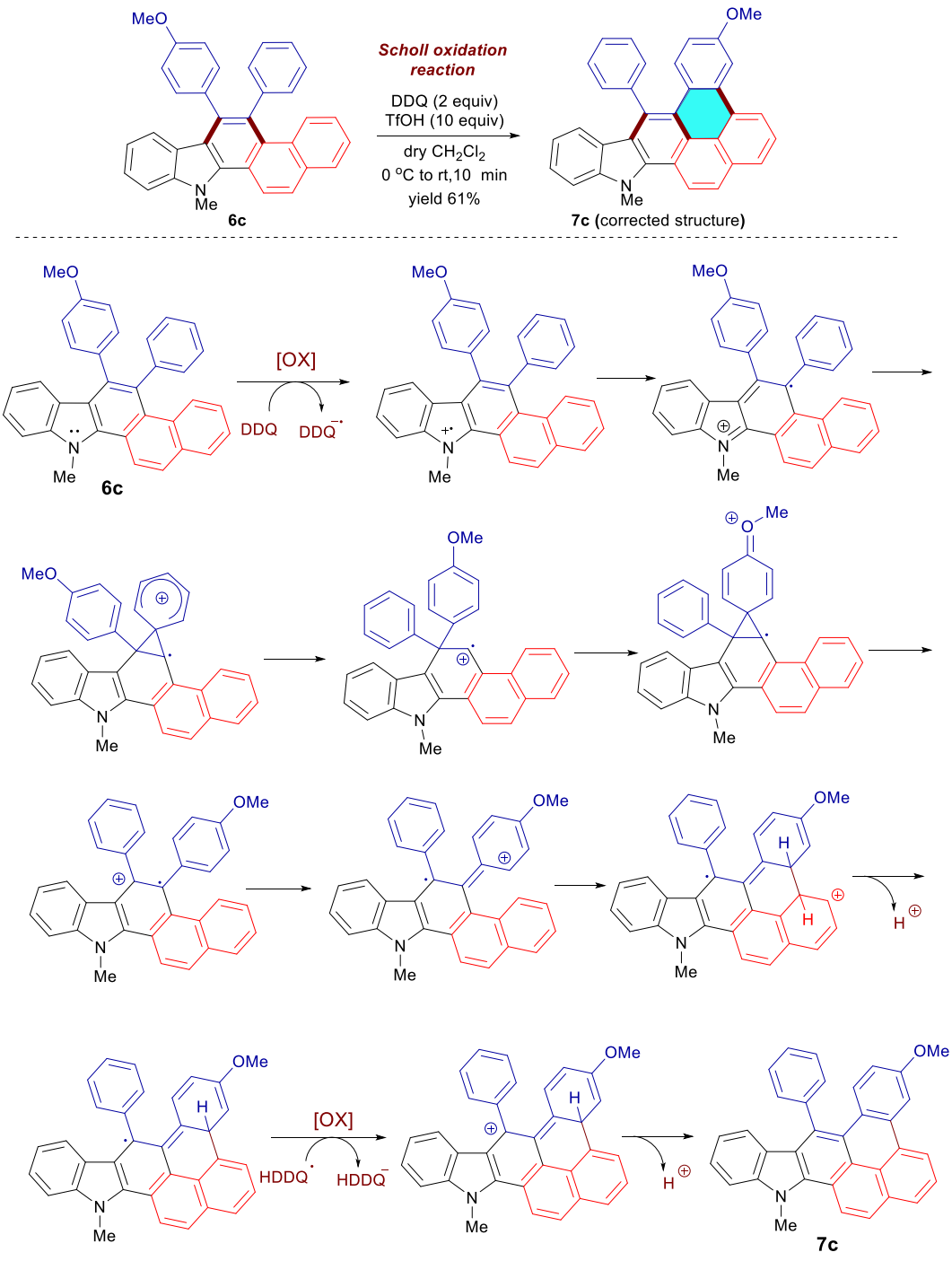
*17-Methyl-17H-benzo[10,11]peryleno[1,12-abc]carbazole **(7d)**:* The titled compound **7d** was synthesized according to the **GP III** by using 13-methyl-7,8-diphenyl-13*H*-naphtho[2,1-*a*]carbazole **6d** (43.3 mg, 0.10 mmol, 1.0 equiv) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (90.8 mg, 0.40 mmol, 4.0 equiv). The reaction was continued for 10 min. The PAH **7d** was isolated after column chromatography using hexane as eluent (yellow solid, 29 mg, yield 68%). **^{1}H NMR** (600 MHz, DMSO-d_6) δ (ppm) 9.21 (d, *J* = 9.1 Hz, 1H), 9.16 (dd, *J* = 7.7, 3.6 Hz, 2H), 9.12 (t, *J* = 7.2 Hz, 2H), 8.99 (d, *J* = 8.1 Hz, 1H), 8.63 (d, *J* = 8.1 Hz, 1H), 8.35 – 8.33 (m, 2H), 8.11 – 8.08 (m, 2H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.86 (t, *J* = 7.3 Hz, 1H), 7.76 (t, *J* = 7.3 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 4.65 (s, 3H). **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ (ppm) 141.7, 136.8, 131.4, 130.3, 129.6, 129.0, 128.8, 128.7, 128.5, 128.2, 126.8, 126.7, 126.33, 126.28, 125.9, 125.8, 125.2, 124.9, 124.3, 123.3, 122.71, 122.66, 122.5, 122.4, 122.3, 122.2, 121.2, 118.9, 118.4, 117.4, 115.4, 110.5, 35.0. **FTIR:** (neat)/ cm^{-1} = 3424, 3045, 2925, 2852, 1735, 1579, 1471, 1391, 1332, 1262, 1218, 1122, 1031, 939, 899. **HRMS (ESI) *m*/*z*:** $[M + H]^+$ calcd for $C_{33}H_{20}N$, 430.1590; found 430.1583.

*19,20-Dimethyl-19,20-dihydro-19,20-diazatribenzo[b,ij,l]benzo[6,7]-as-indaceno[2,3,4,5-nopq]pleiadene (**7e**):* The titled compound **7e** was synthesized according to the **GP III** by using 1,10-dimethyl-2,3,4,5-tetraphenyl-1,10-dihydropyrrolo[2,3-*a*]carbazole **6e** (53.8 mg, 0.10 mmol, 1.0 equiv) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (136.2 mg, 0.60 mmol, 6.0 equiv). The reaction was continued for 30 min. The PAH **7e** was isolated after column chromatography using 2% ethylacetate/hexane as eluent (yellow solid, 41 mg, yield 78%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ (ppm) 8.93 (d, *J* = 8.2 Hz, 1H), 8.79 (d, *J* = 8.3 Hz, 1H), 8.72 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 7.7 Hz, 1H), 8.56 – 8.52 (m, 2H), 8.28 (d, *J* = 8.2 Hz, 1H), 7.84 (t, *J* = 7.5 Hz, 1H), 7.80 – 7.72 (m, 3H), 7.70 – 7.64 (m, 4H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 4.46 (s, 3H), 4.32 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6) δ (ppm) 143.3 (C), 138.7 (C), 137.8 (C), 137.1 (C), 133.3 (C), 132.7 (CH), 132.6 (CH), 130.9 (C), 130.8 (C), 129.8 (C), 129.7 (C), 129.5 (C), 129.3 (C), 128.5 (CH), 127.8 (CH), 127.7 (C), 127.4 (C), 127.0 (CH), 126.8 (CH), 126.39 (CH), 126.36 (CH), 125.0 (CH), 124.9 (CH), 124.6 (CH), 124.5 (C), 124.3 (CH), 123.9 (CH), 123.52 (CH), 123.50 (CH), 122.5 (C), 122.2 (C), 122.1 (C), 121.3 (CH), 120.9 (C), 119.4 (CH), 118.8 (C), 116.6 (C), 111.1 (CH), 42.0 (CH_3), 35.3 (CH_3). **FTIR:** (neat)/ cm^{-1} = 3401, 2925, 2853, 2257, 2130, 1657, 1463, 1391, 1331, 1234, 1153, 1049, 1032, 998, 825. **HRMS (ESI) *m*/*z*:** [M + Na]$^{+}$ calcd for $C_{40}H_{24}N_2Na$, 555.1832; found 555.1814.

Isolation of the Intermediate Ketones and Successive Cyclization Reactions:

We first started the benzannulation reaction between indole derivative **1d** and aldehyde **4d** in presence of 20 mol% of catalyst PTSA·H_2O and the desired benzo[*a*]carbazole **3u** was isolated as mixture of two isomers. To establish our hypothesis, we performed the same reaction in presence of 10 mol% of catalyst and α-(3-indolyl) ketone **5a** was isolated as sole product, which converted to the benzo[*a*]carbazole derivative **3u** in presence of 20 mol% of the catalyst under optimized reaction conditions. It confirmed that, *para*-methoxyphenyl group was migrated selectively over phenyl group due to greater migratory amplitude. After converting ketone **5a** to the benzo[*a*]carbazole scaffold **3u**, two isomers were isolated as a mixture as observed by NMR spectra analysis. These experiments were also repeated with ketone **4g** and same observations were noted for **3v**. After *N*-methylation of **3u** and followed by Scholl reaction of **6c** using 2 equiv of DDQ resulted in a single product **7c** in 61% yield.


(a)
PTSA·H2O (20 mol%), toluene, 120 °C, 24 h
76% yield
4d
1d
PTSA·H2O
(10 mol%)
toluene
120 °C, 30 min
69% yield
5a
PTSA·H2O (20 mol%)
toluene
120 °C, 24 h
79% yield
3u
92% yield
KOH (1.2 equiv)
MeI (1.5 euiv)
DMSO, 90 °C, 3 h
6c
(6c) CCDC 2078337
DDQ (2 equiv)
CH2Cl2:TfOH (9:1)
0 °C - rt
61% yield
7c
(7c) CCDC 2075888
(b)
PTSA·H2O (20 mol%), toluene, 120 °C, 26 h
81% yield
4g
1d
PTSA·H2O
(10 mol%)
toluene
120 °C, 1 h
89% yield
5d
PTSA·H2O (20 mol%)
toluene
120 °C, 24 h
77% yield
3v
(3v) CCDC 2078336



Scheme S1. The plausible reaction mechanism for 1,2-aryl exchange under Scholl reaction conditions

Table S4: Crystal data and structure refinements for the molecules **7d, 7c, 3v, and 6c**.

Entry	**7d**	**7c**	**3v**	**6c**
CCDC	**2074598**	**2075888**	**2078336**	**2078337**
Empirical formula	C_{33} H_{19} N	C_{34} H_{23} N O	C_{33} H_{22} Cl N O	C_{34} H_{25} N O
Formula weight	429.49	461.53	483.96	463.55
Temperature (K)	298(2)	298(2)	298(2)	298(2)
Radiation	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
Wavelength(λ)	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$F\,d\,d\,2$
a[Å]	16.09(3)	10.249(4)	9.5167(14)	29.4033(13)
b[Å]	5.262(13)	10.824(6)	11.0235(17)	34.6034(15)
c[Å]	23.54(5)	11.279(4)	13.535(2)	9.5921(5)
α[°]	90	80.260(13)	94.069(11)	90
β[°]	96.07(2)	67.268(13)	97.179(10)	90
γ[°]	90	85.10(2)	99.905(11)	90
Volume[Å^3]	1982(7)	1137.1(9)	1381.6(4)	9759.5(8)
Z	4	2	2	16
Density (calculated) [Mg/m^3]	1.439	1.348	1.163	1.262
Absorption coefficient [mm^{-1}]	0.083	0.080	0.163	0.075
F(000)	896	484	504	3904
Refl. used [$I > 2\sigma(I)$]	2028	2403	1325	2408
Independent reflections	4124	4773	6112	5196
R_{int}	0.0946	0.0571	0.1039	0.1659
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
GOF	1.029	1.054	0.741	0.972
Final R indices	R_1= 0.0624; wR_2= 0.1510	R_1= 0.0613; wR_2= 0.1497	R_1= 0.0845; wR_2= 0.1889	R_1= 0.0686; wR_2= 0.1718
R indices (all data)	R_1= 0.1462; wR_2= 0.1961	R_1= 0.1253; wR_2= 0.2084	R_1= 0.2816; wR_2= 0.2585	R_1= 0.1599; wR_2= 0.2219

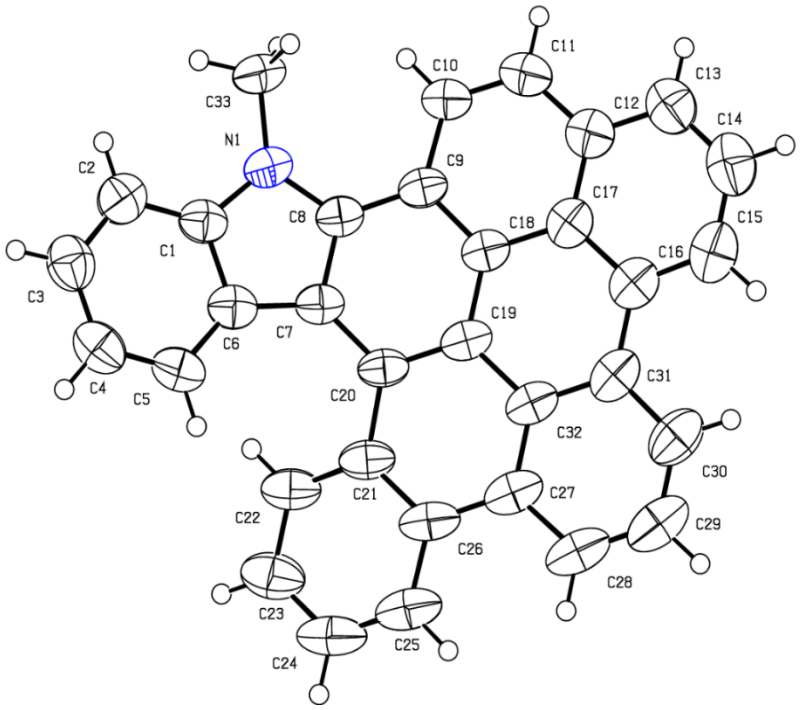


Figure S6: ORTEP view of the molecular structure of **7d** with thermal ellipsoids drawn at the 50% probability level.

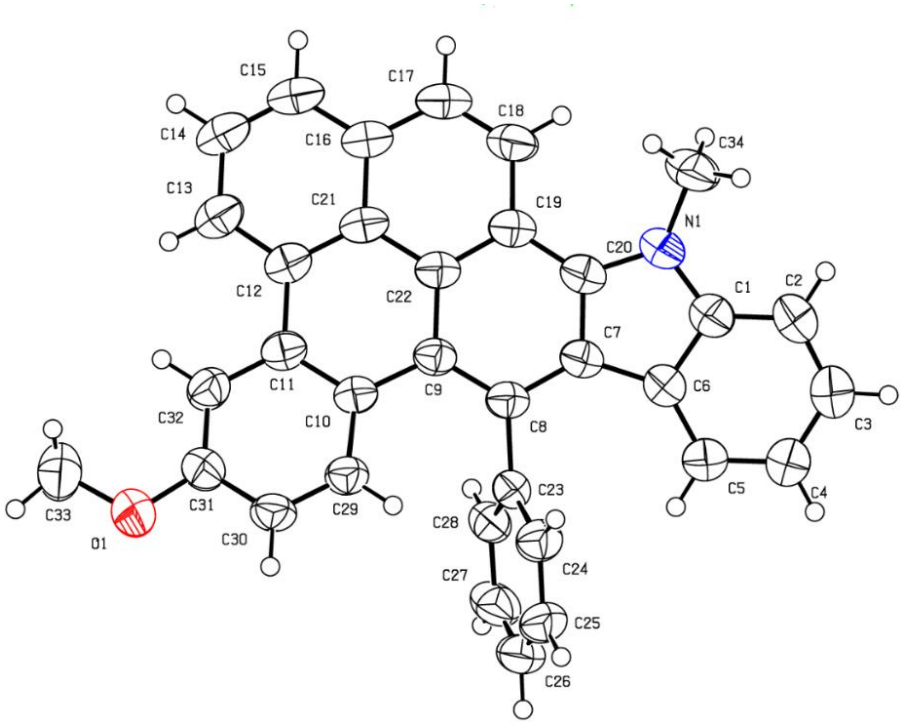


Figure S7: ORTEP view of the molecular structure of **7c** with thermal ellipsoids drawn at the 50% probability level.

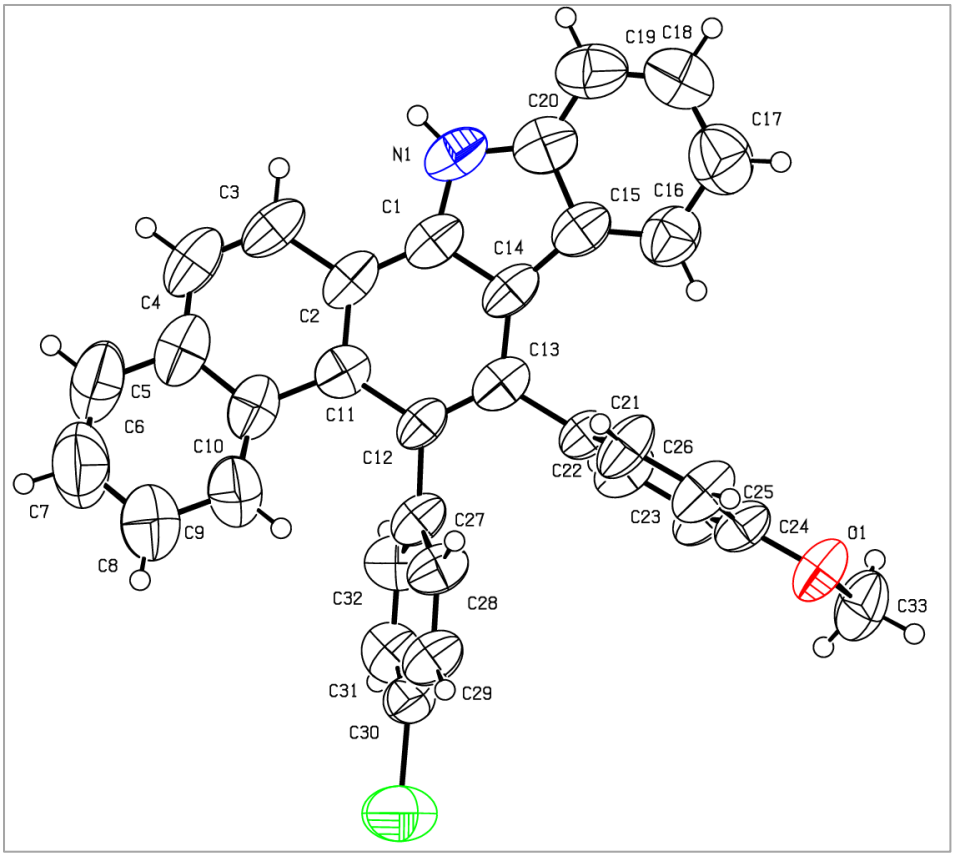


Figure S8: ORTEP view of the molecular structure of **3v** with thermal ellipsoids drawn at the 50% probability level.

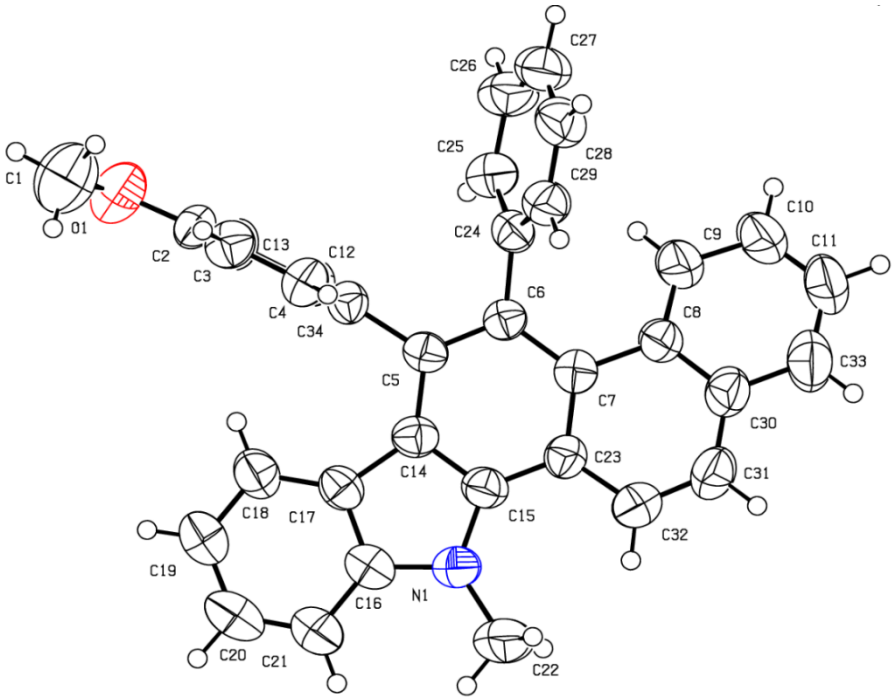


Figure S9: ORTEP view of the molecular structure of **6c** with thermal ellipsoids drawn at the 50% probability level.

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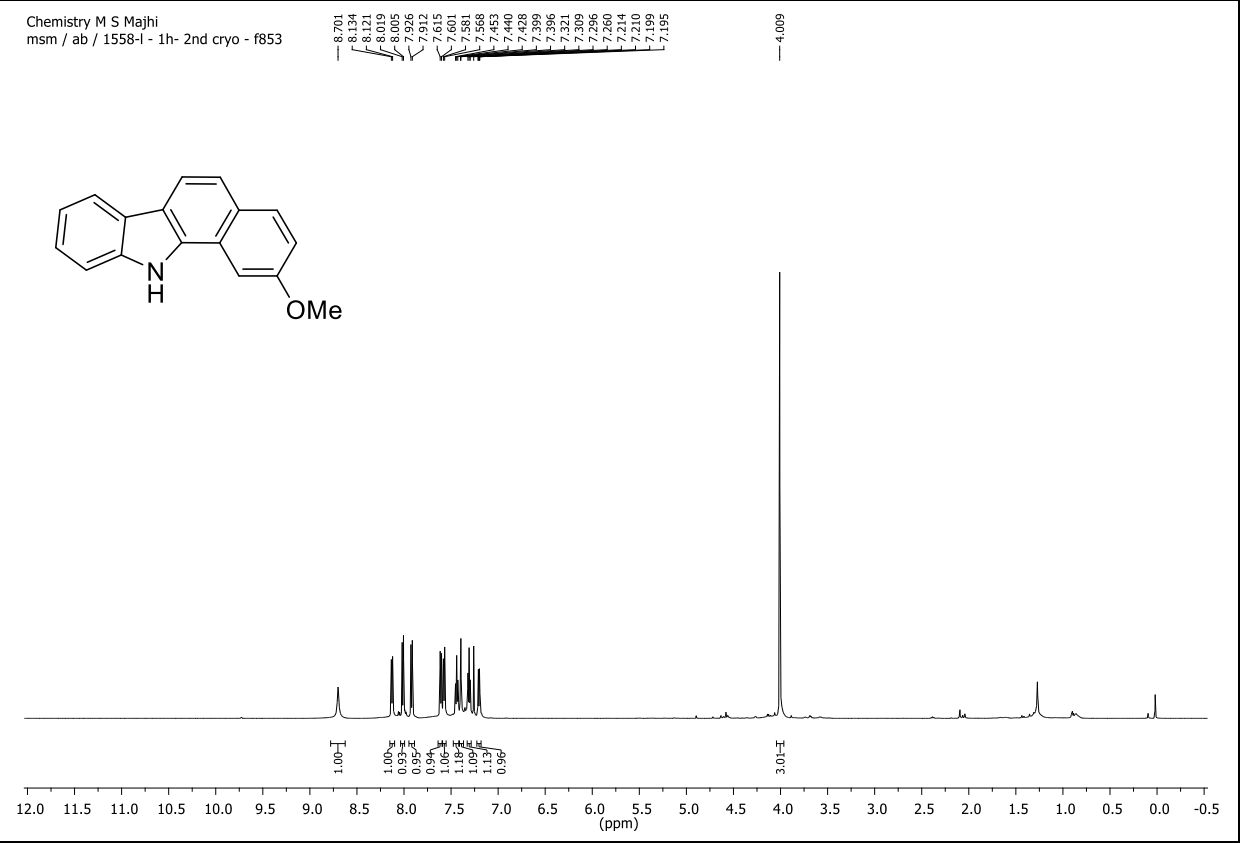
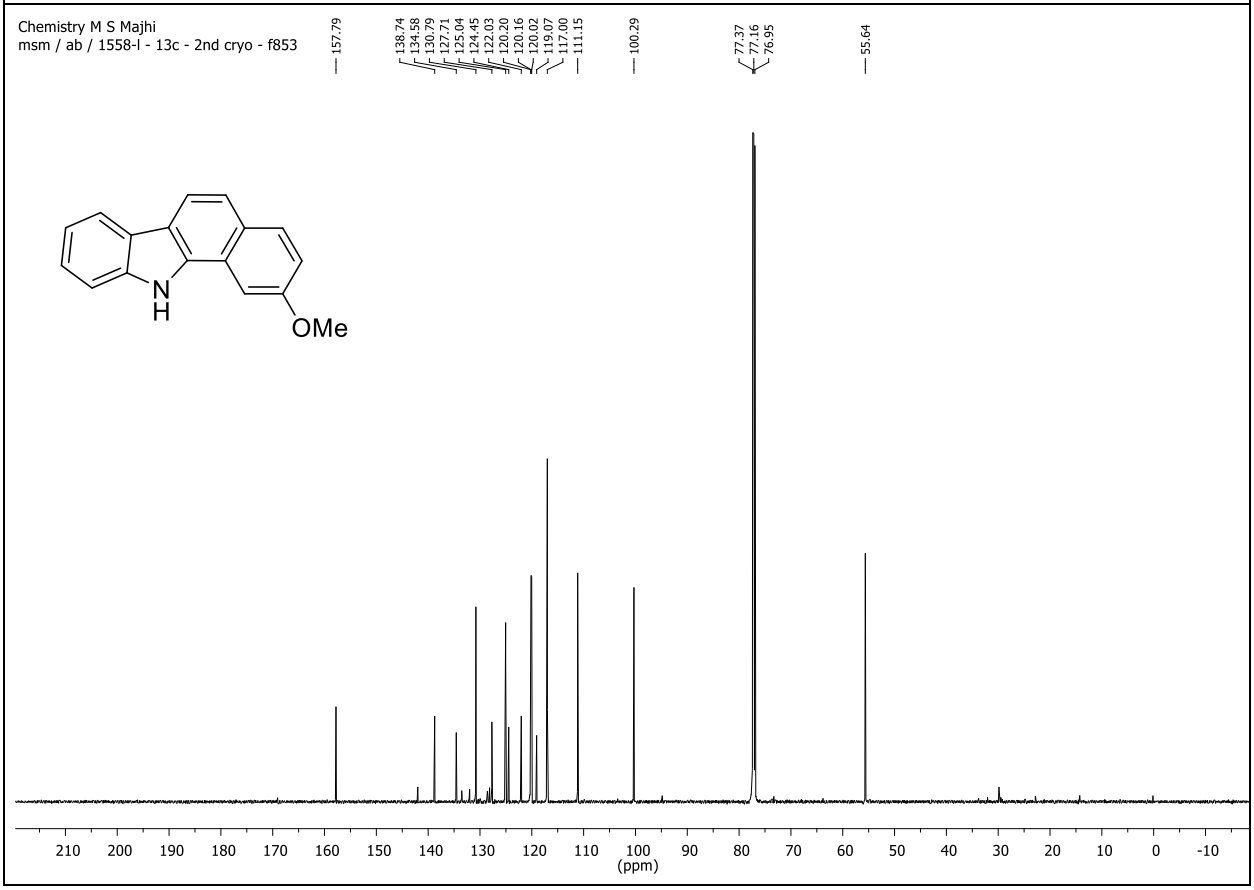
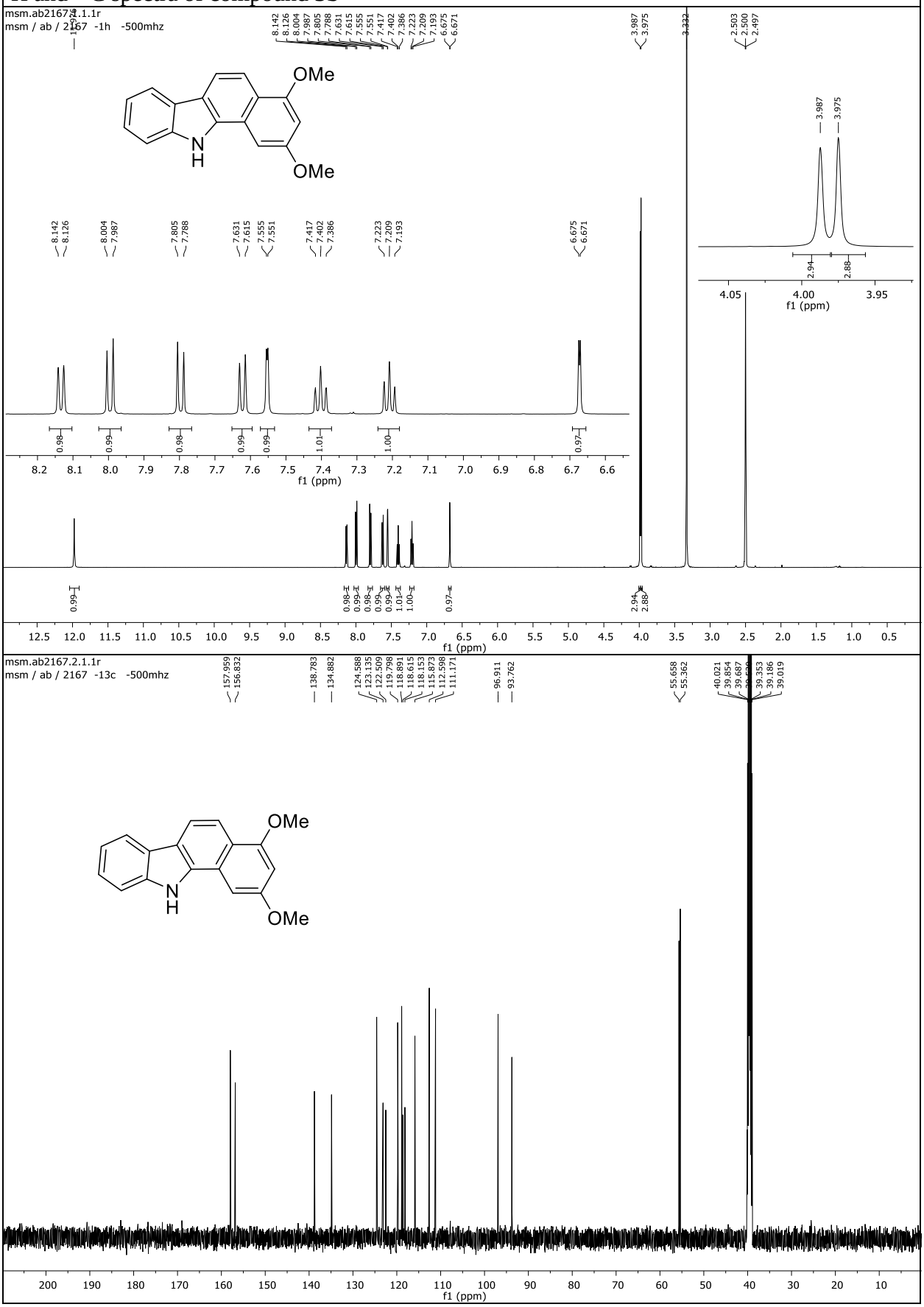
^{1}H and ^{13}C spectra of compound **3a**





^{1}H and ^{13}C spectra of compound **3b**



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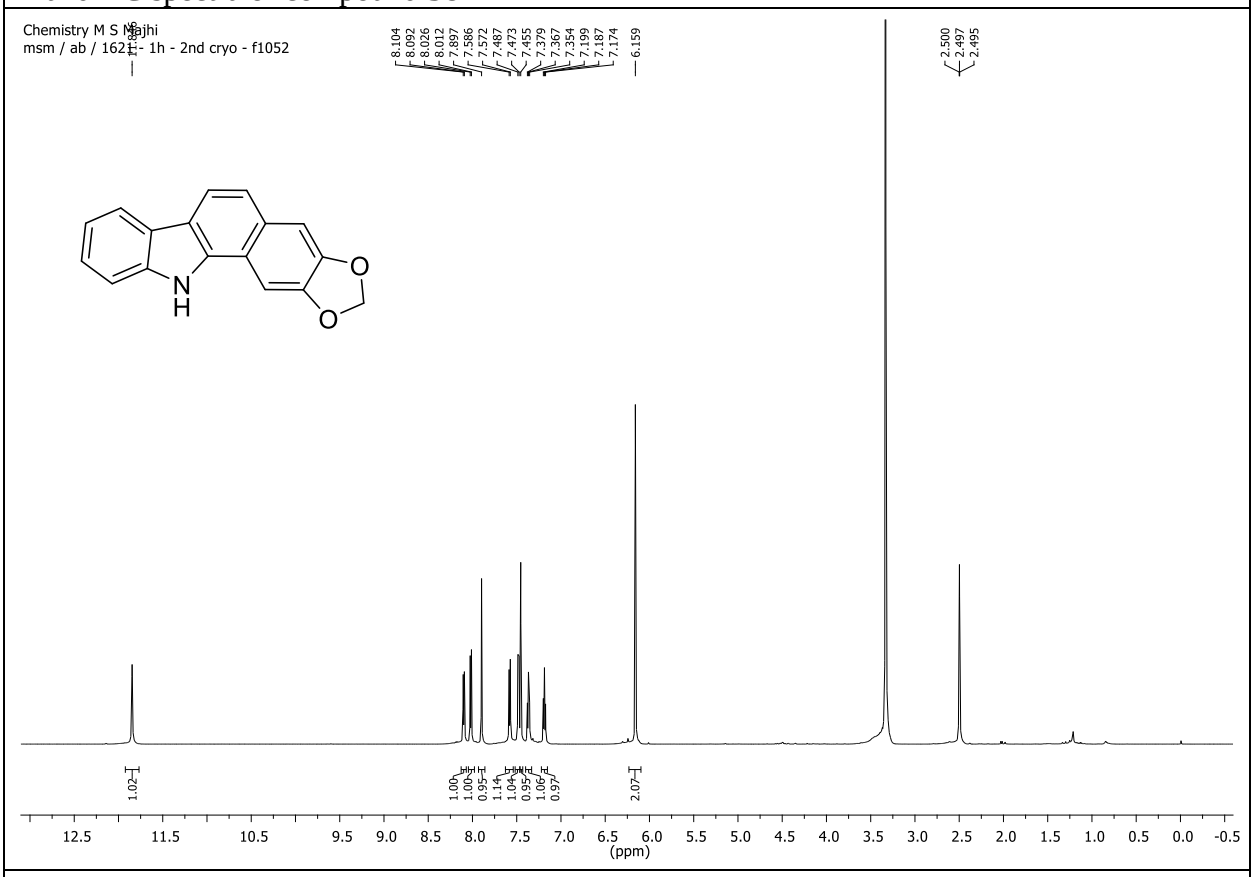

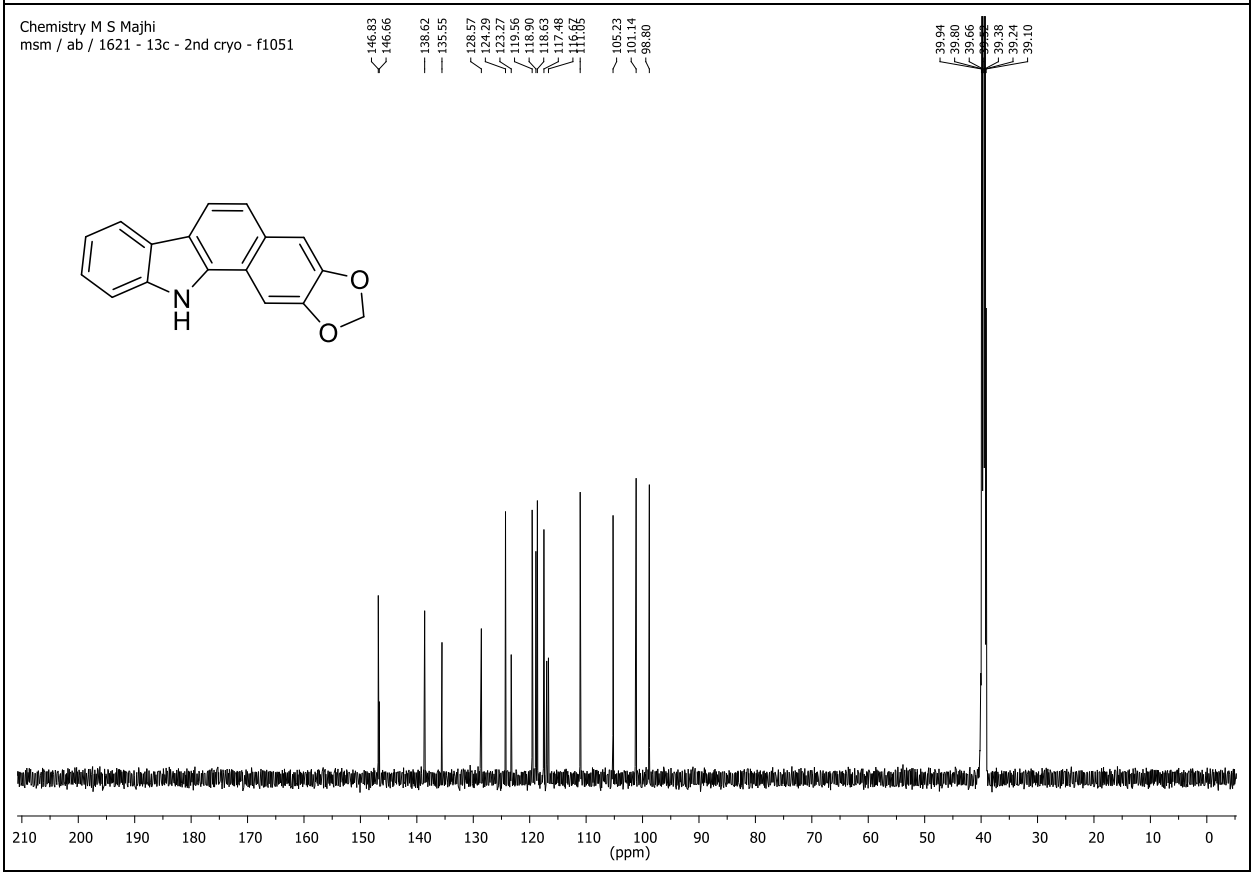

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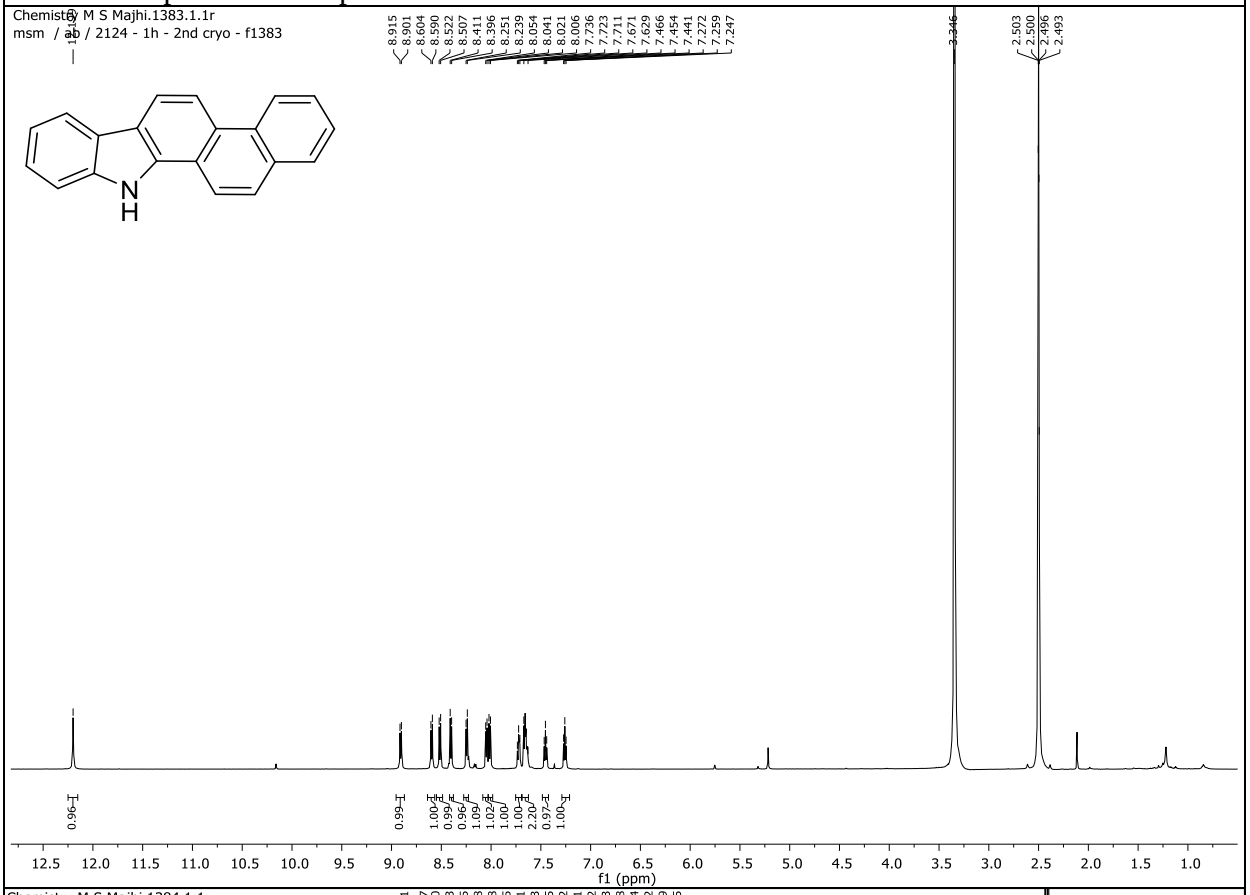

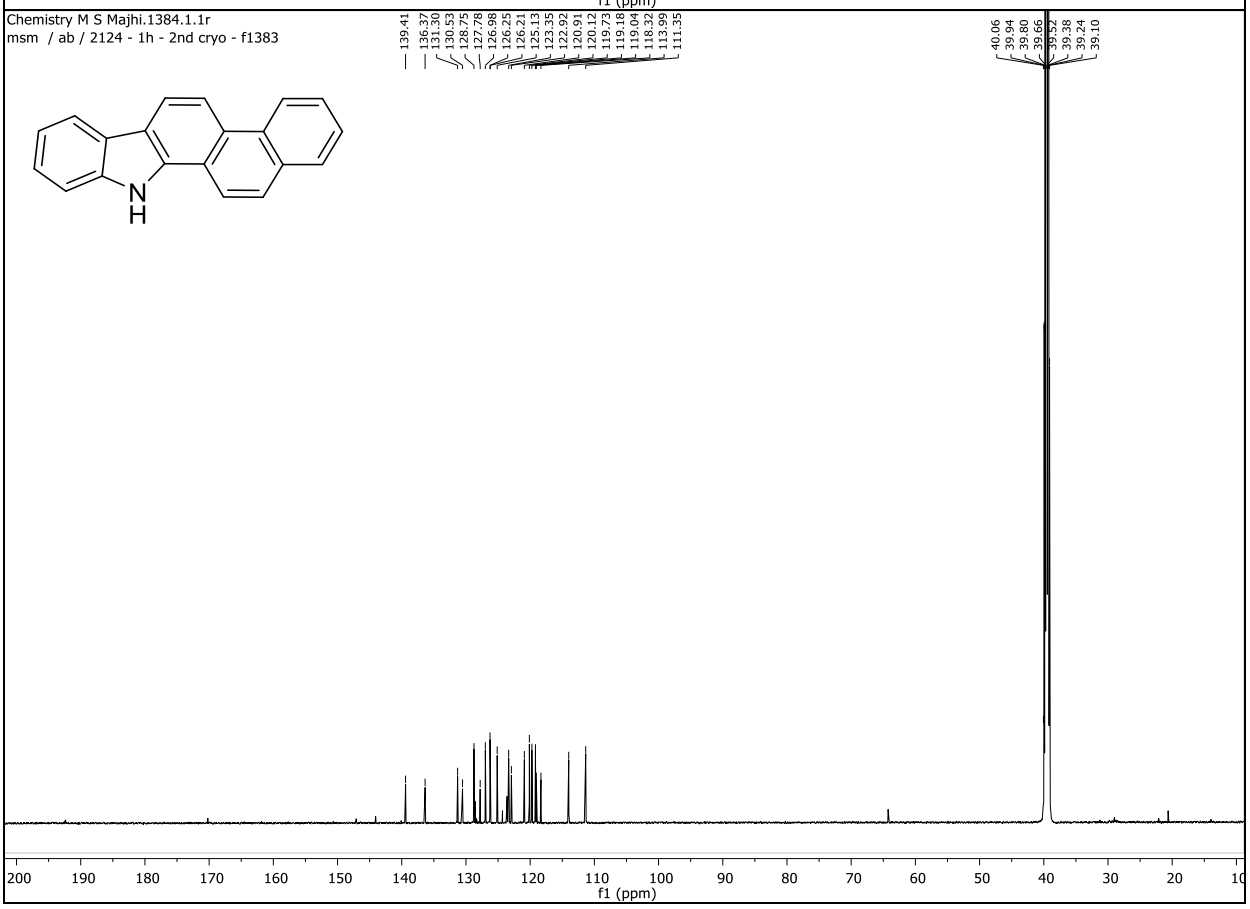

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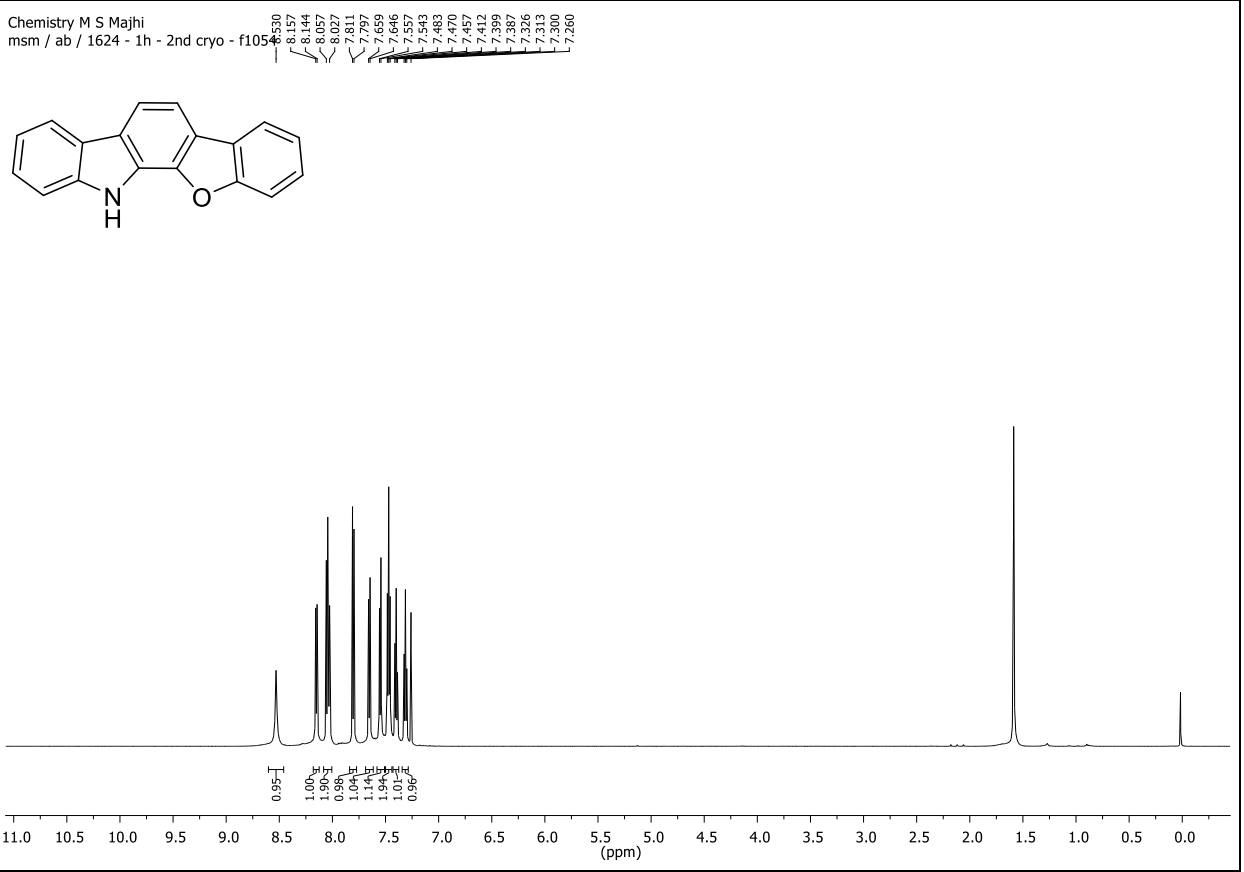

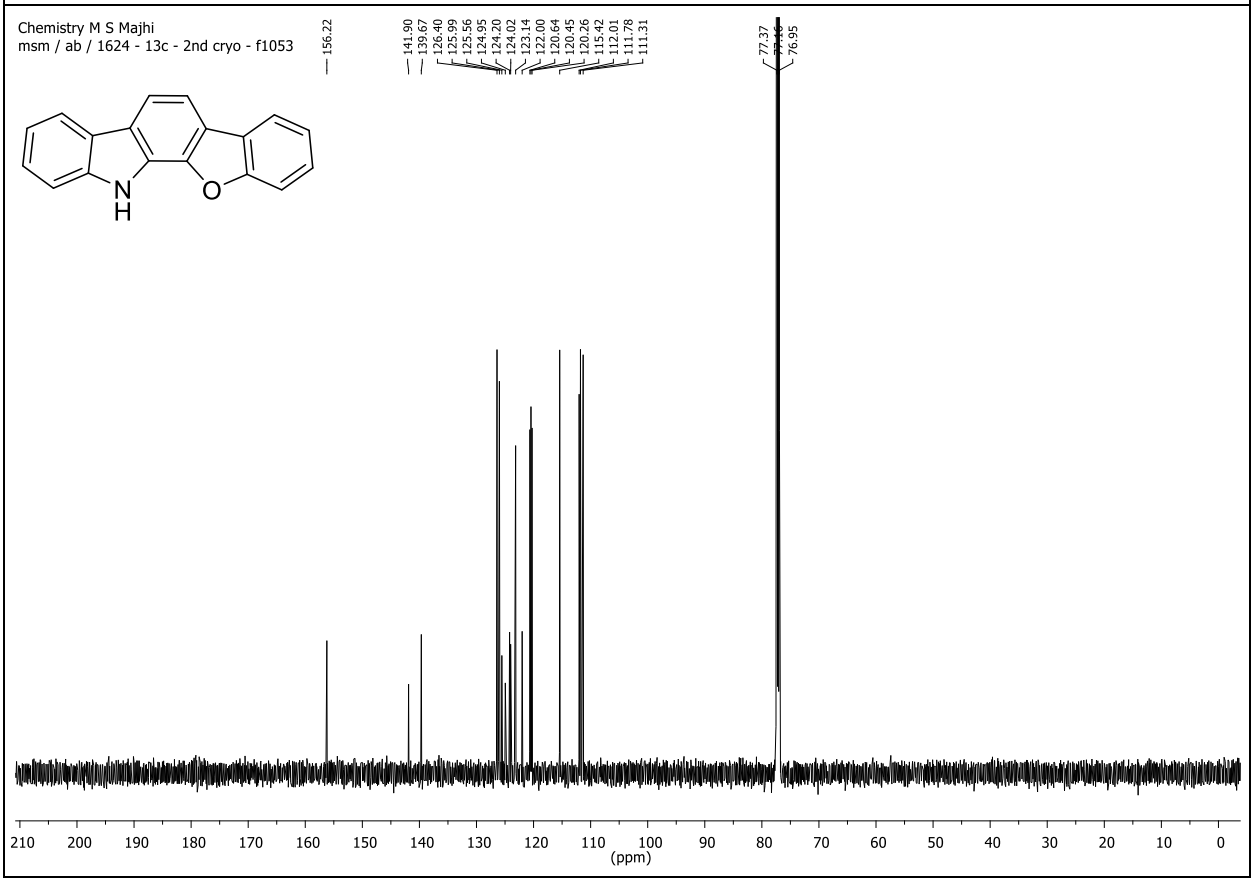

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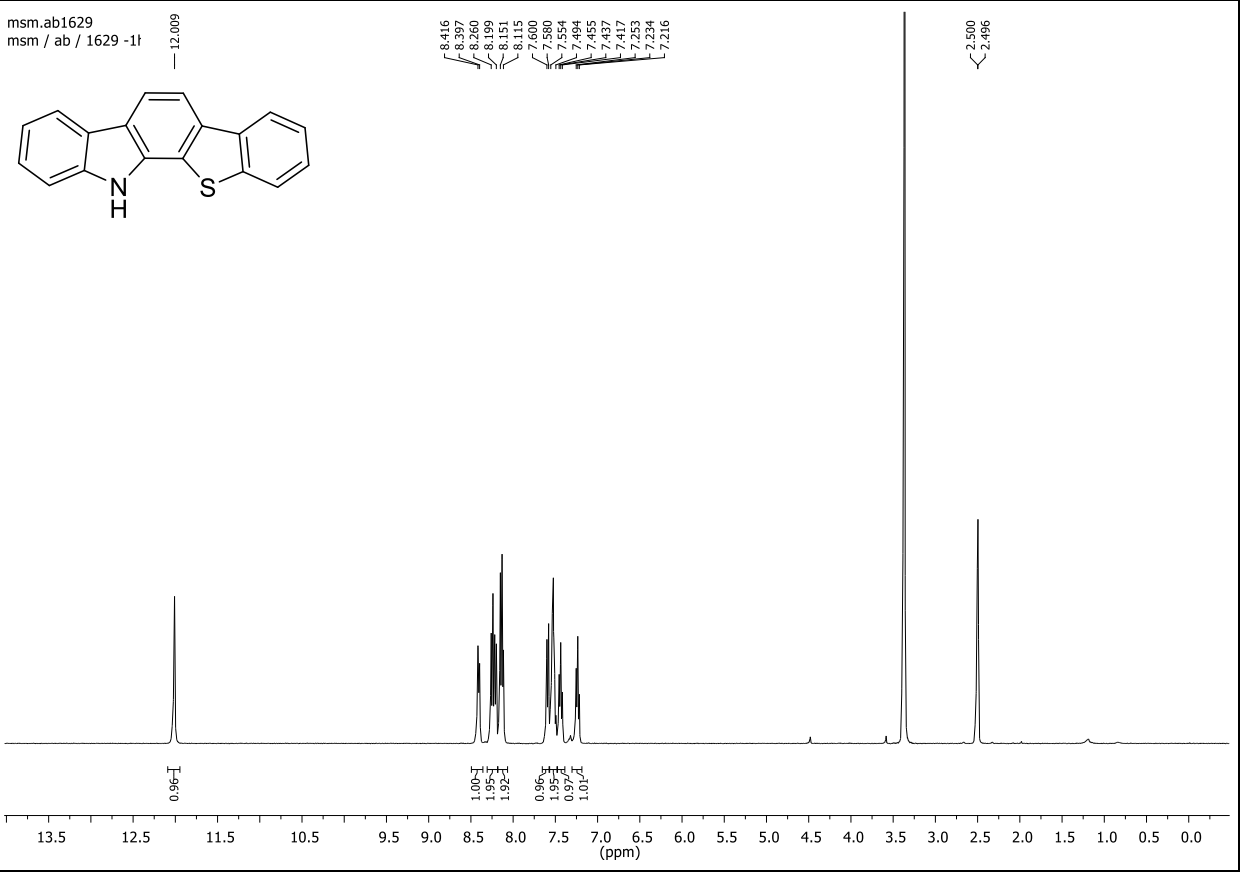

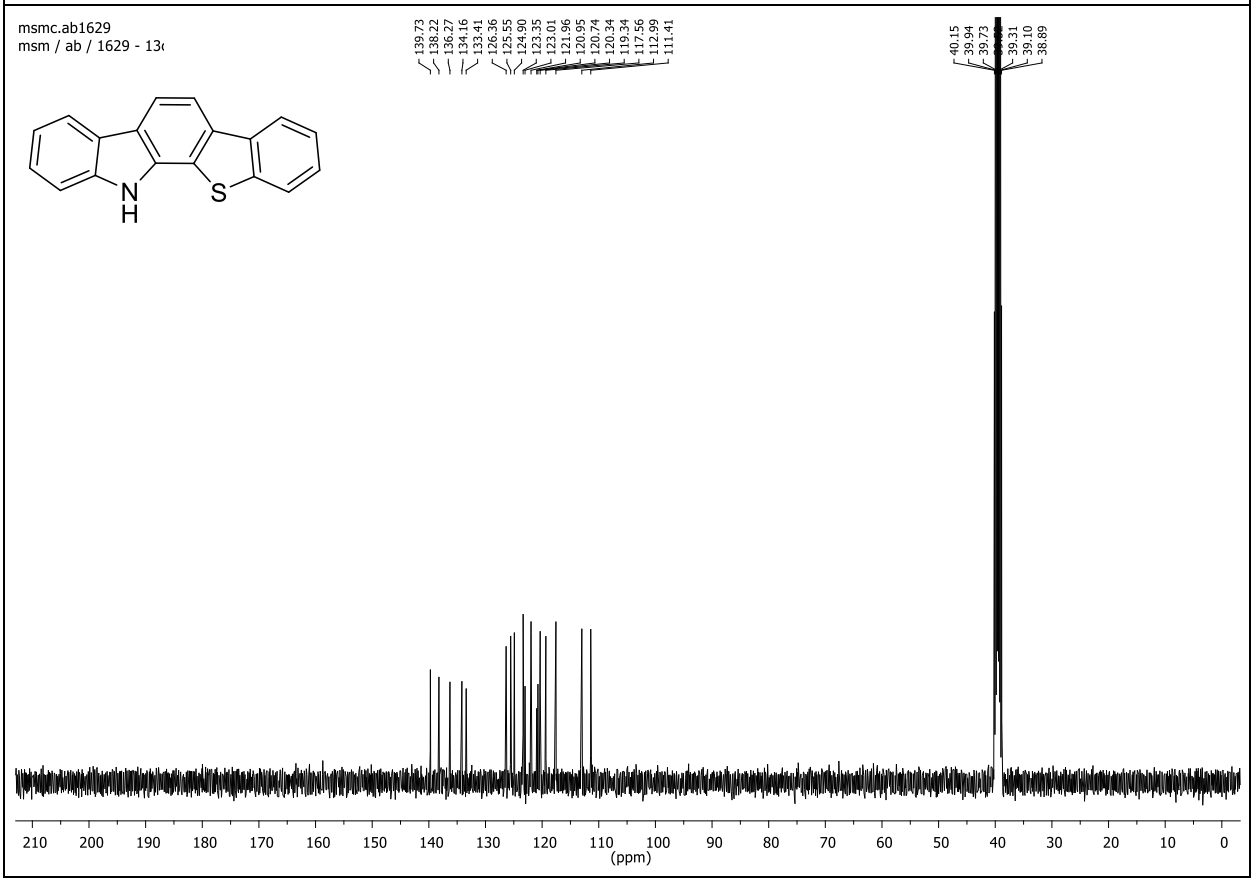

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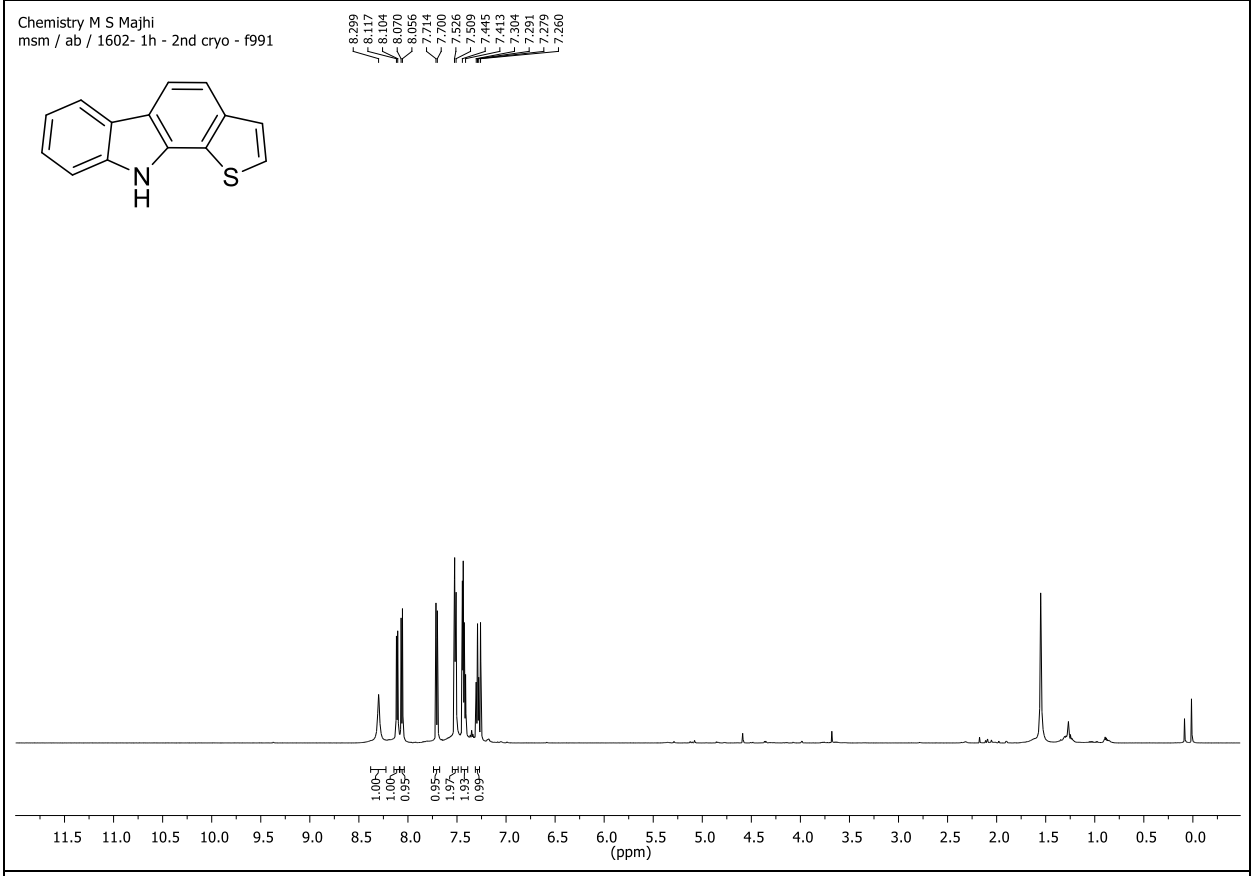

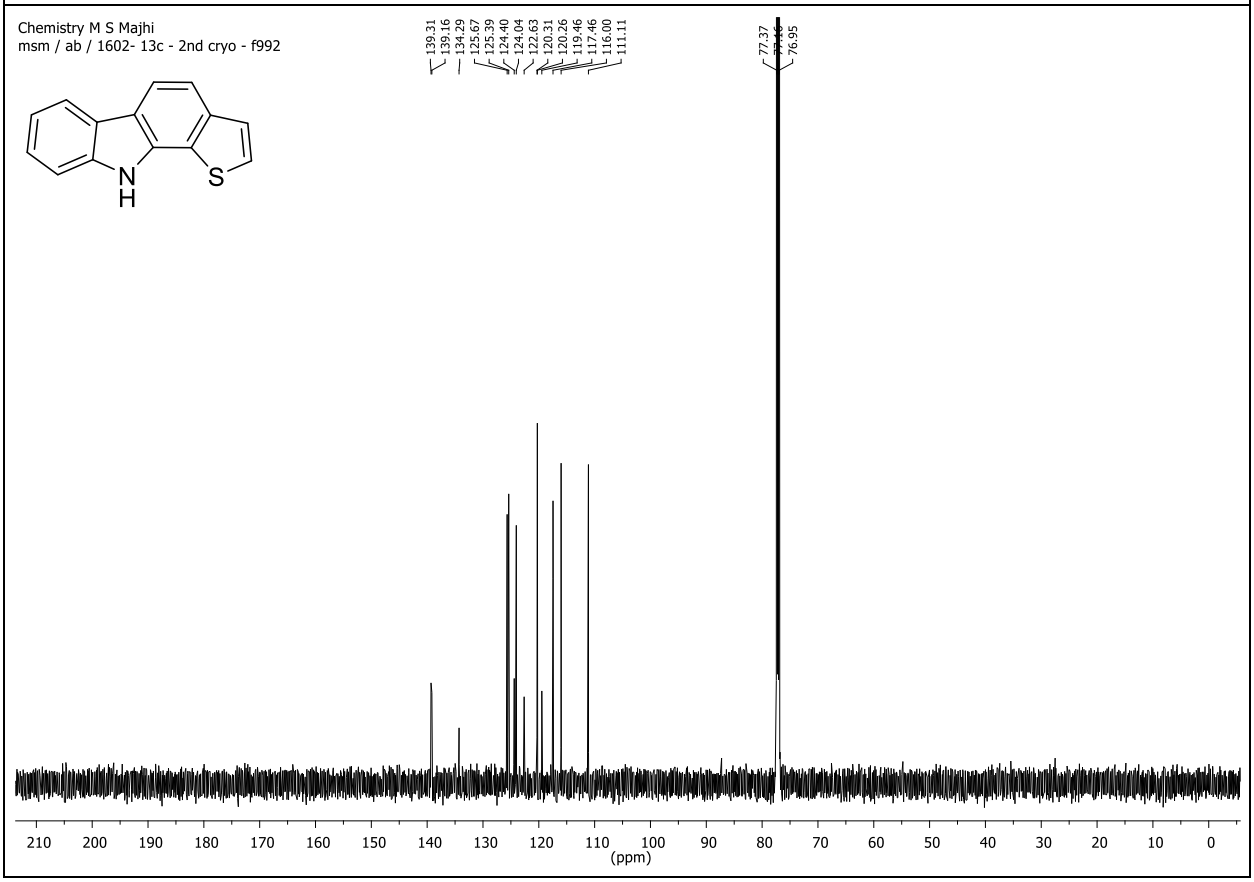

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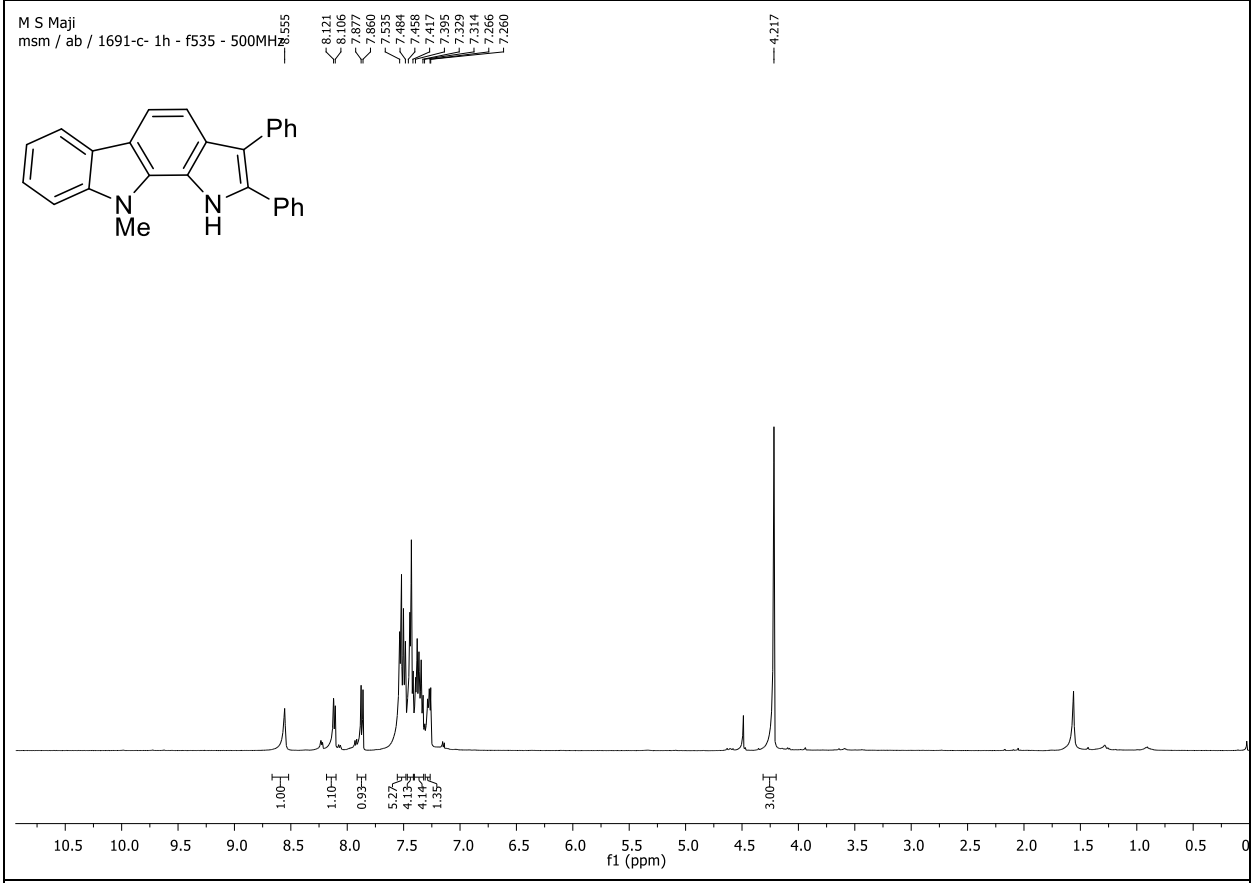

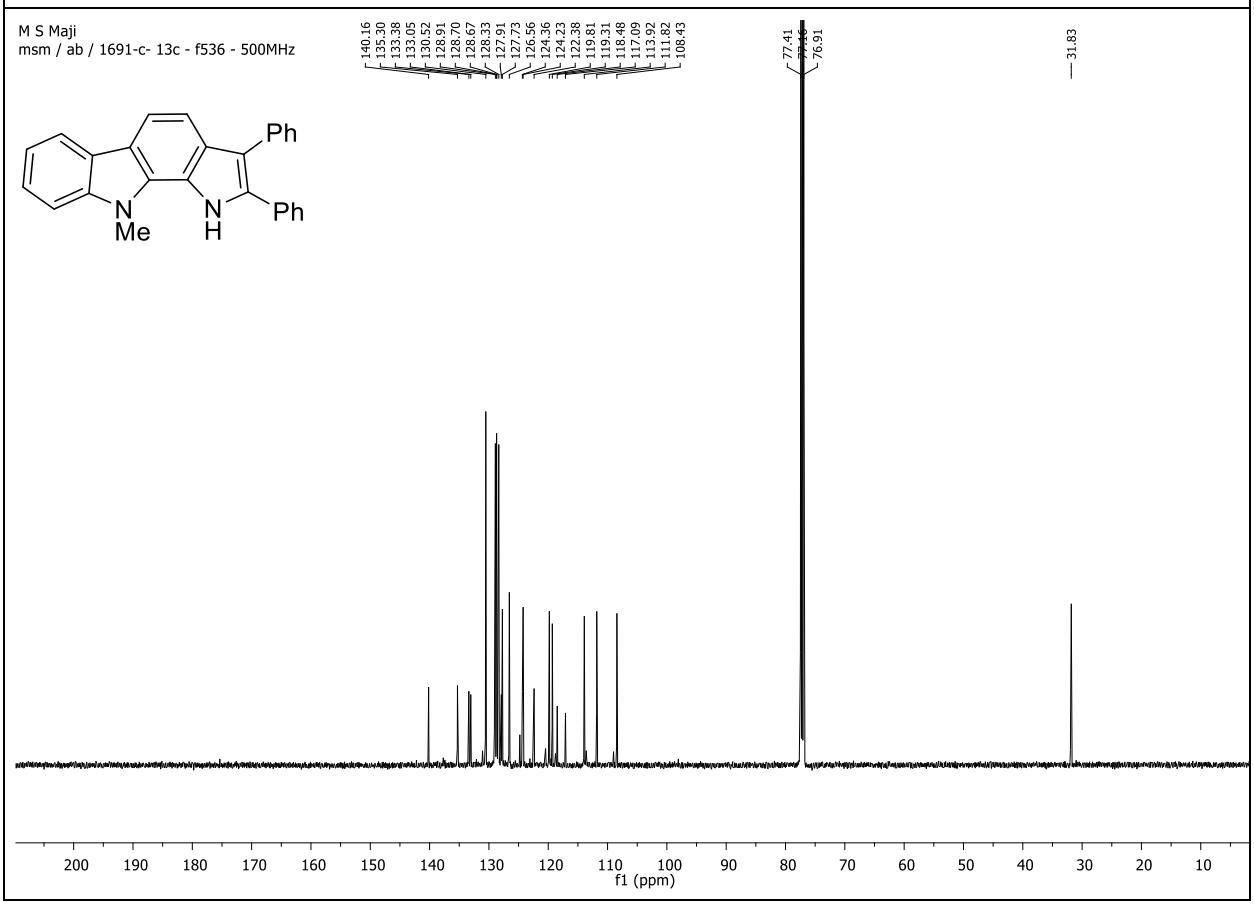

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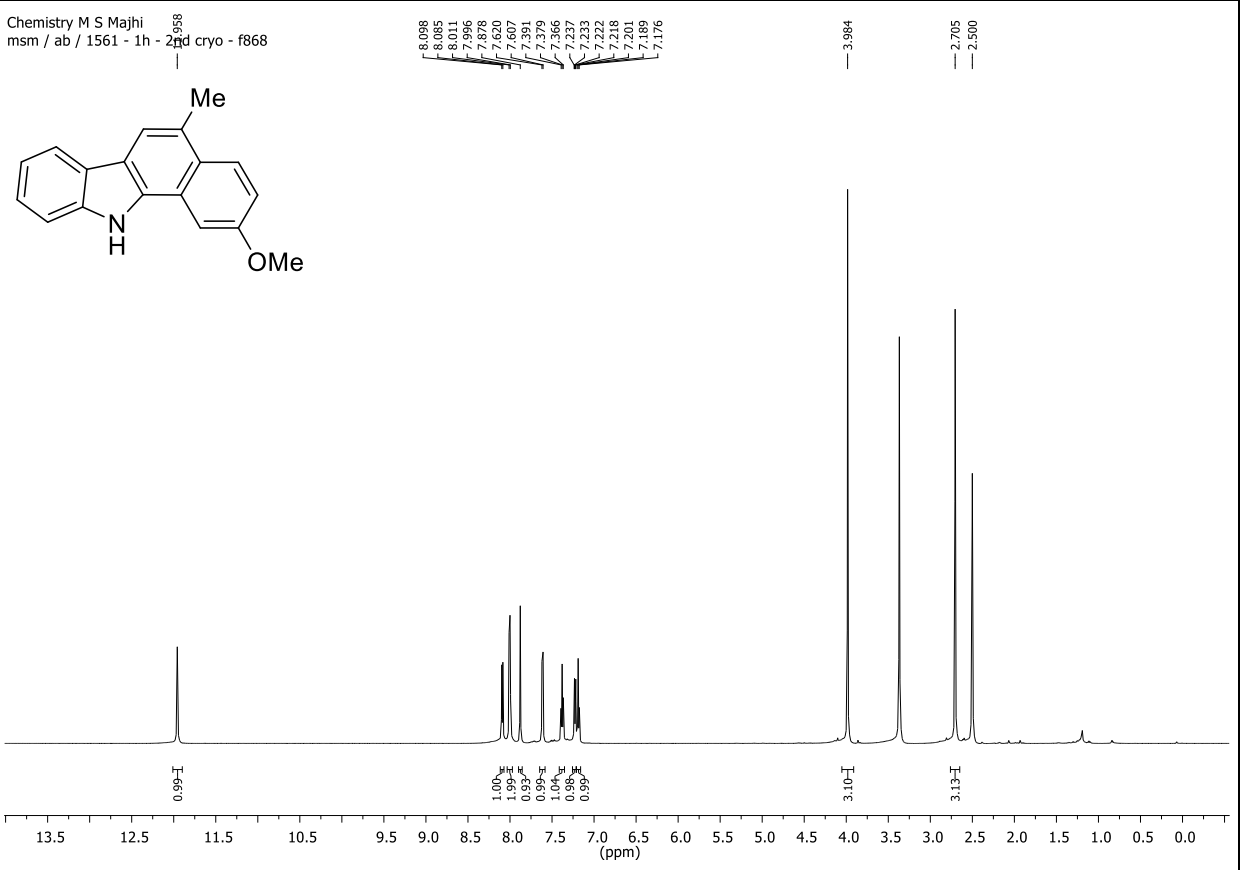

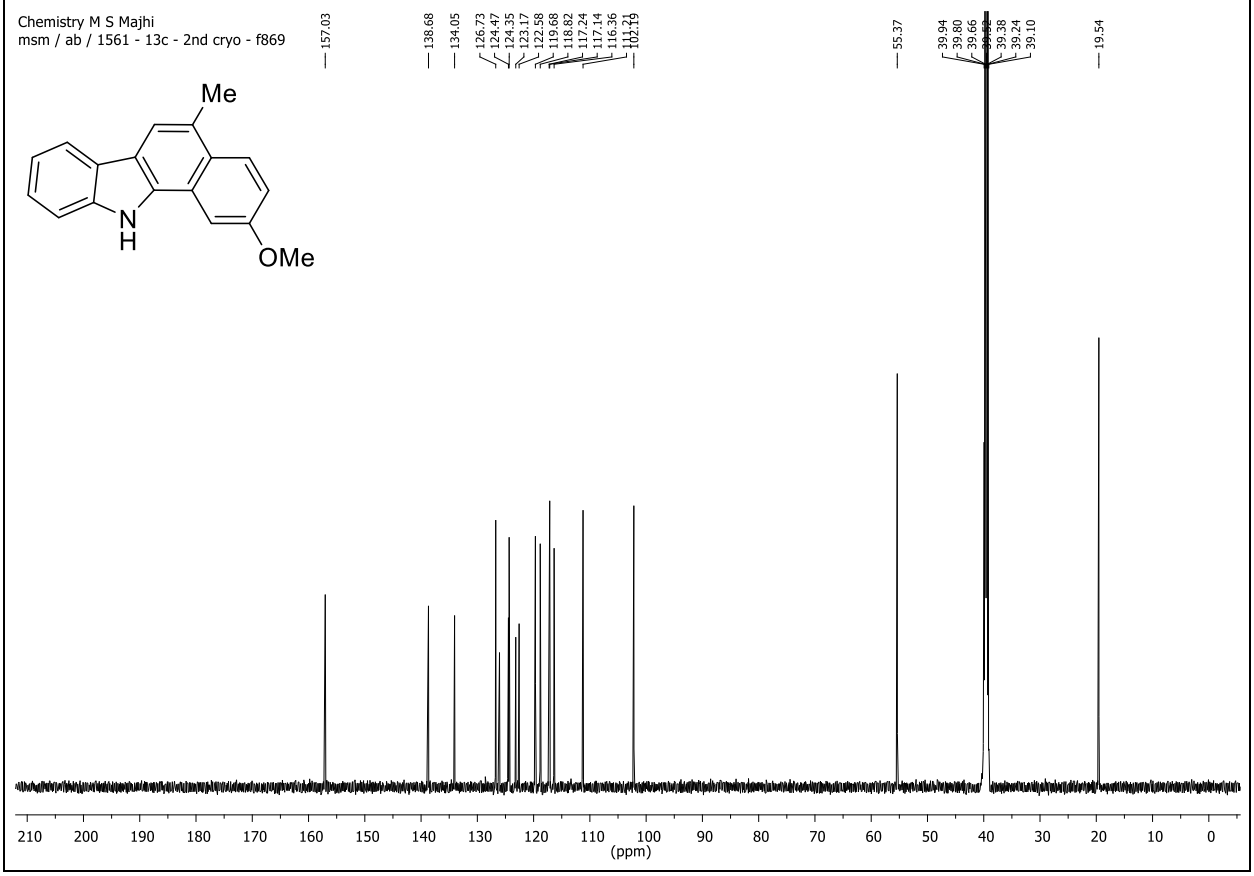

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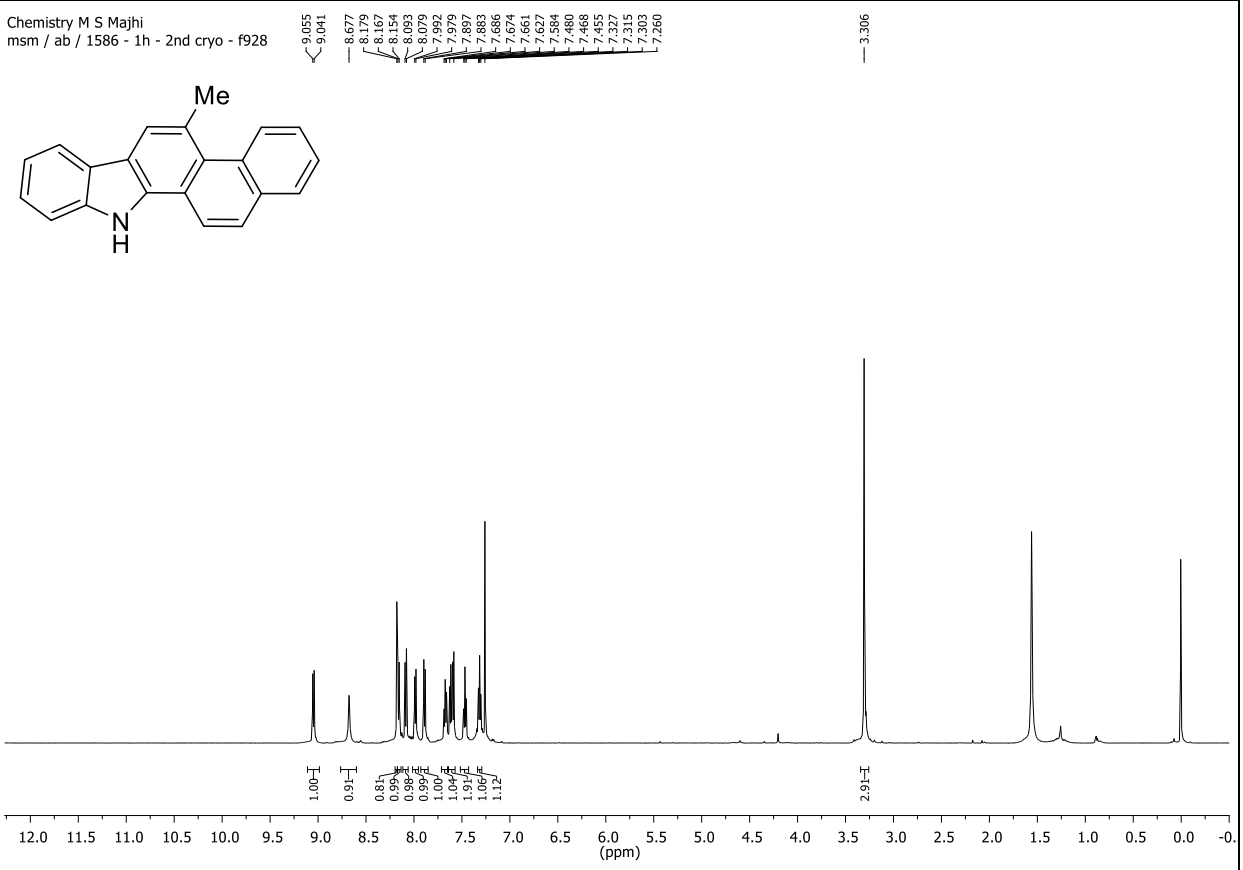

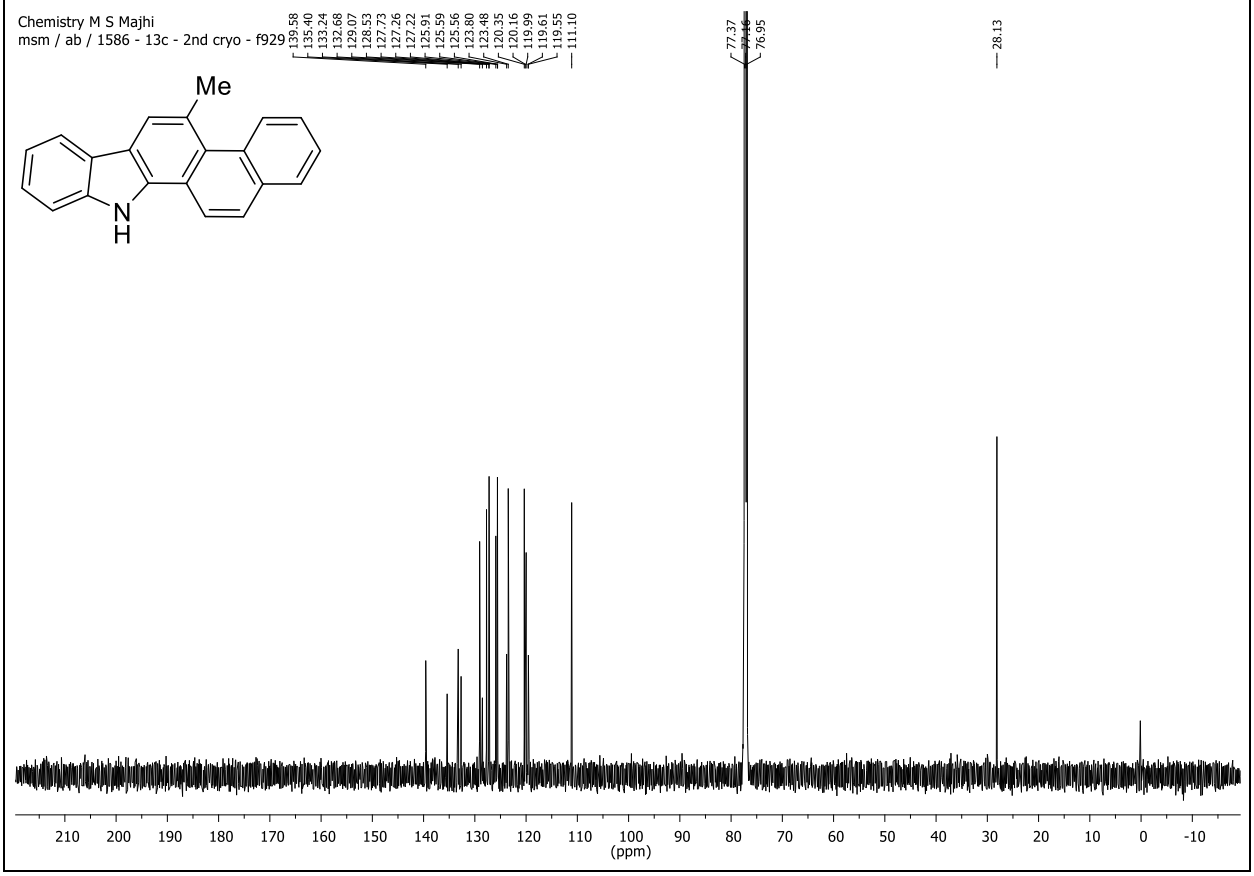

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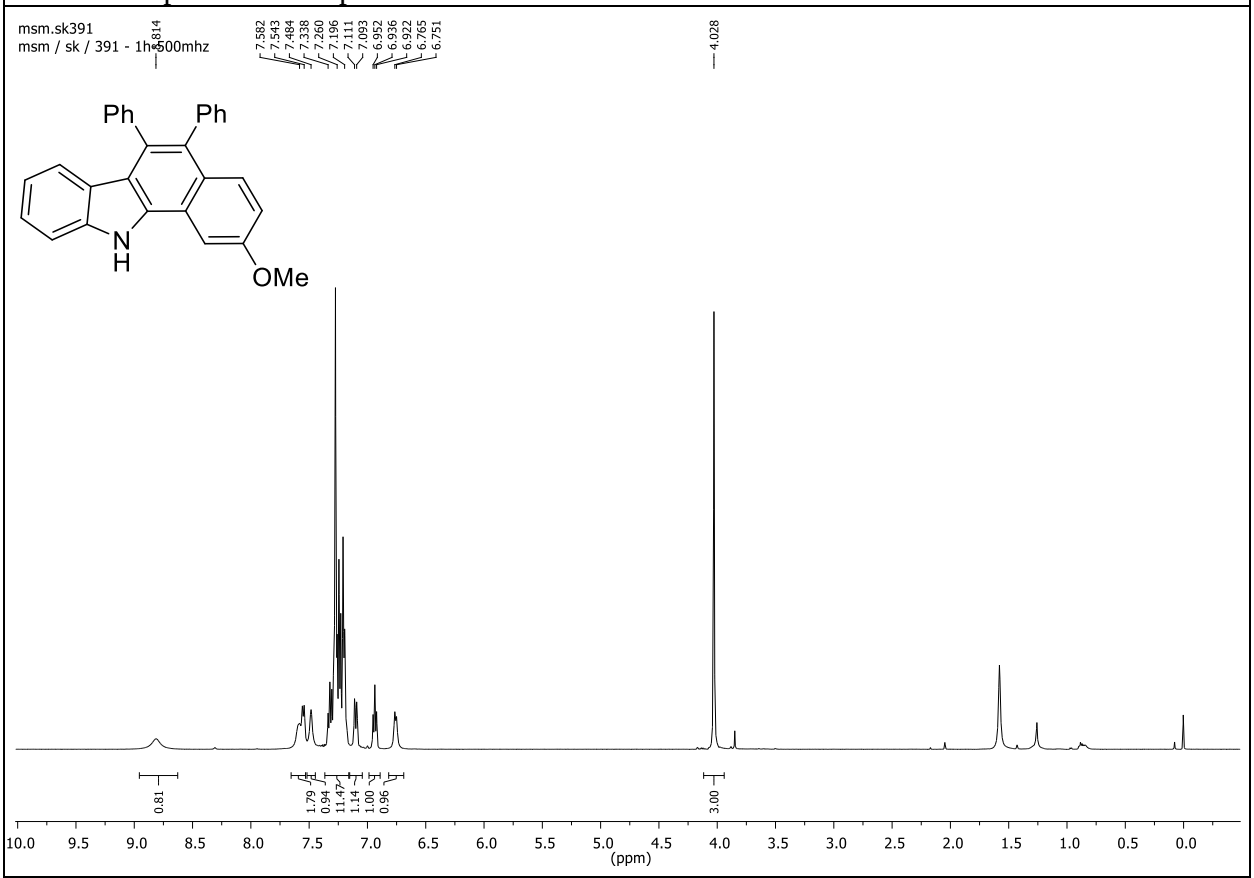

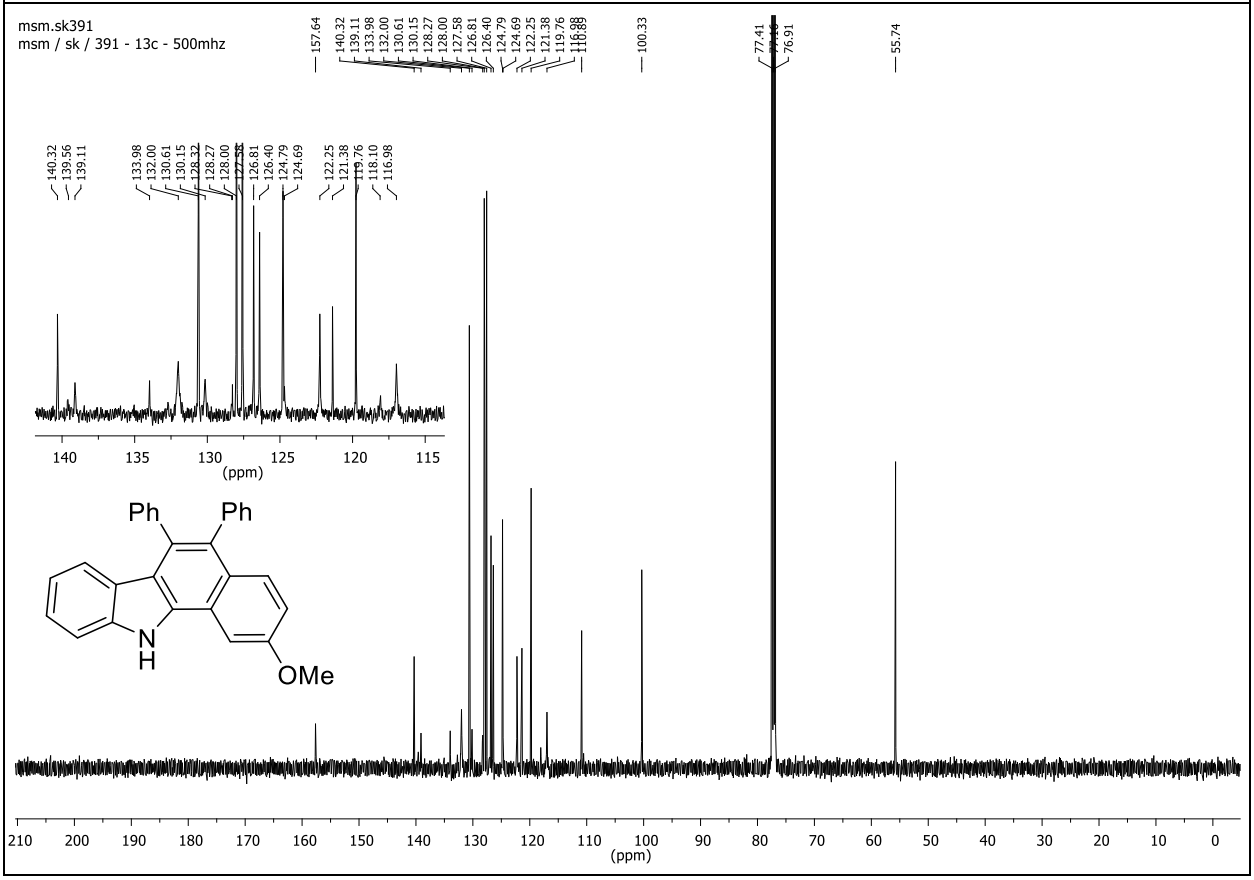

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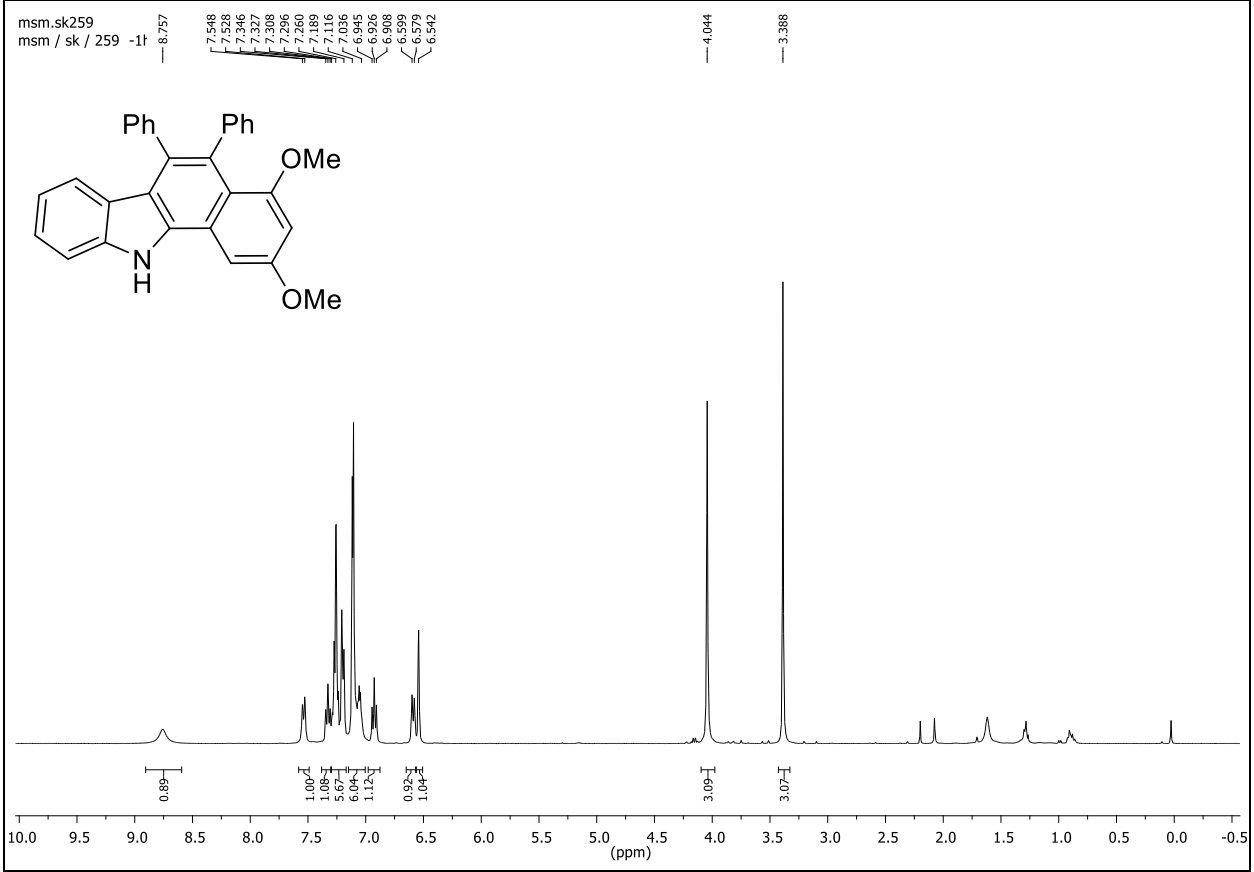

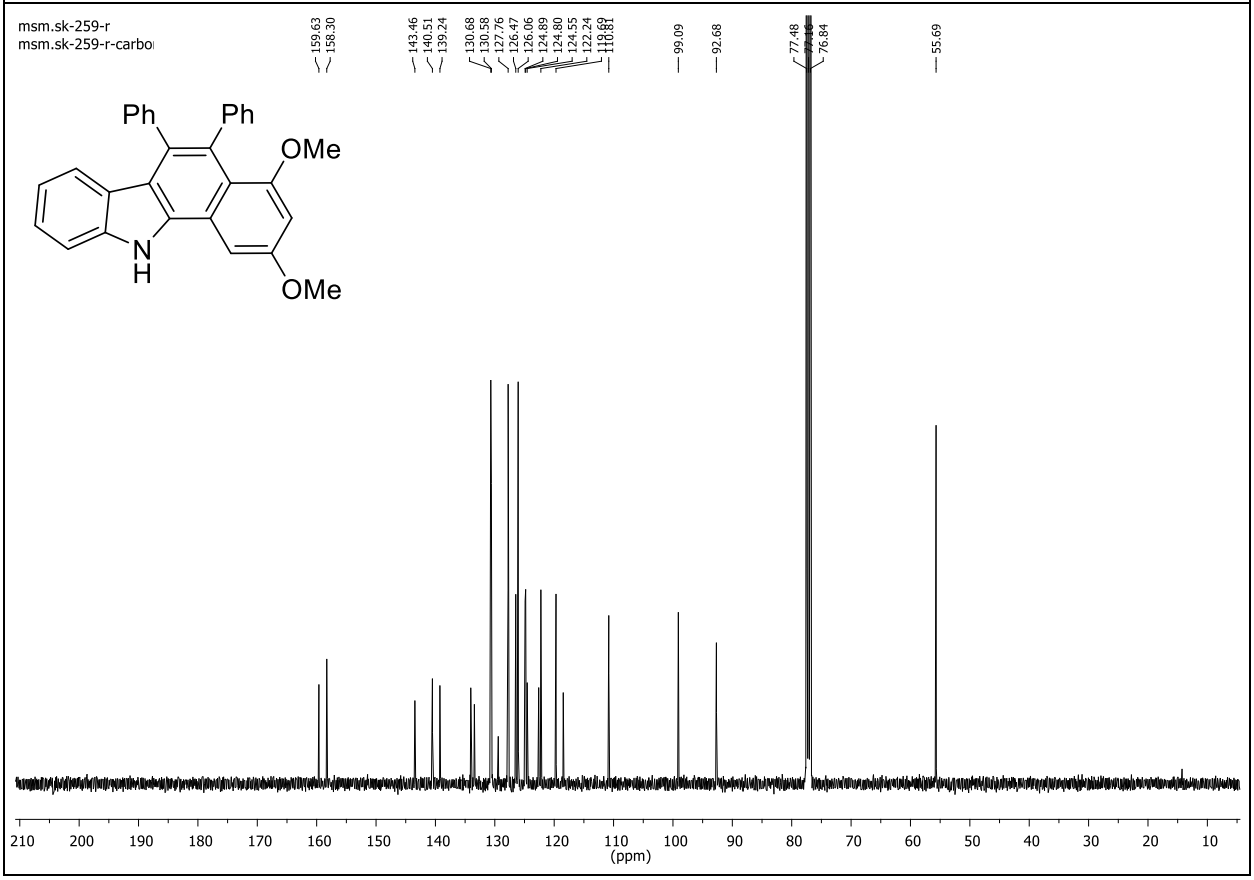

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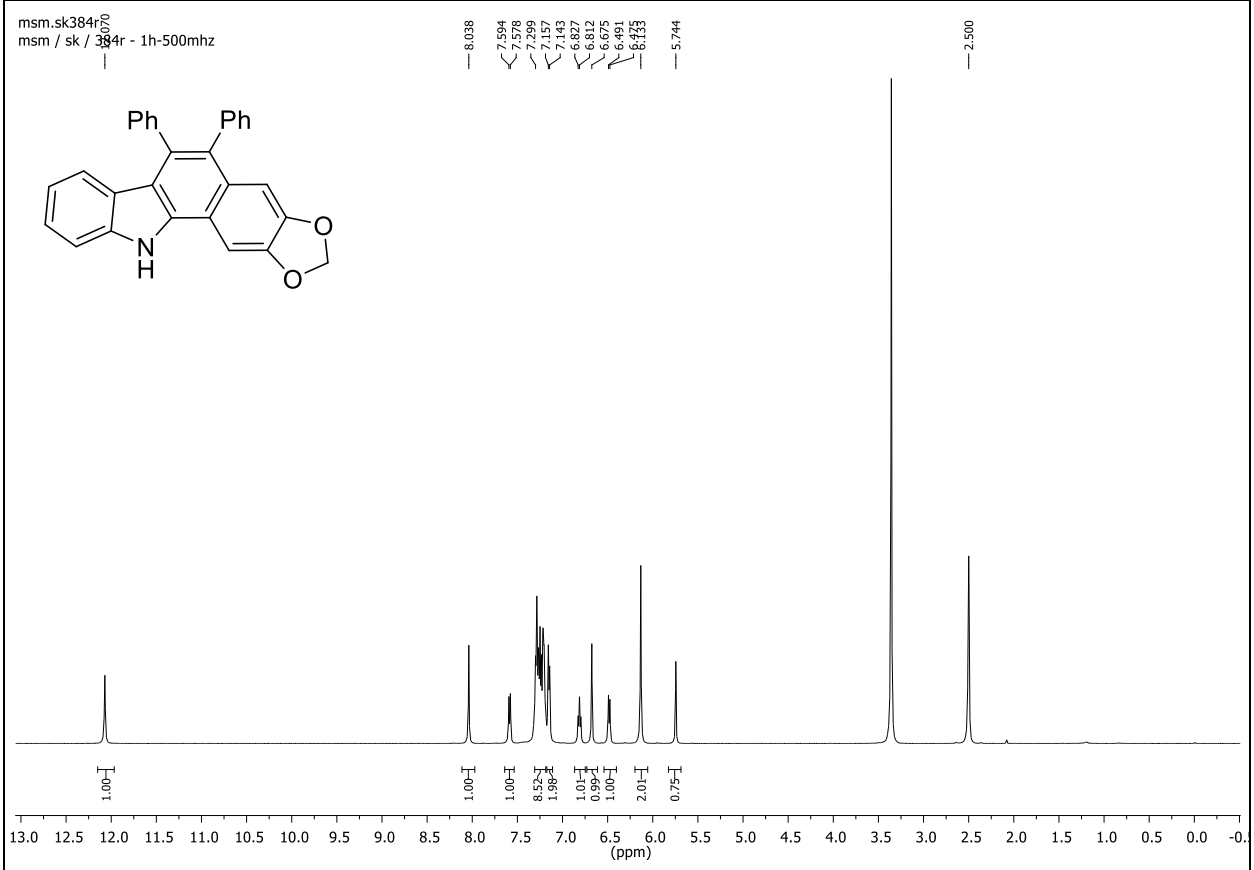

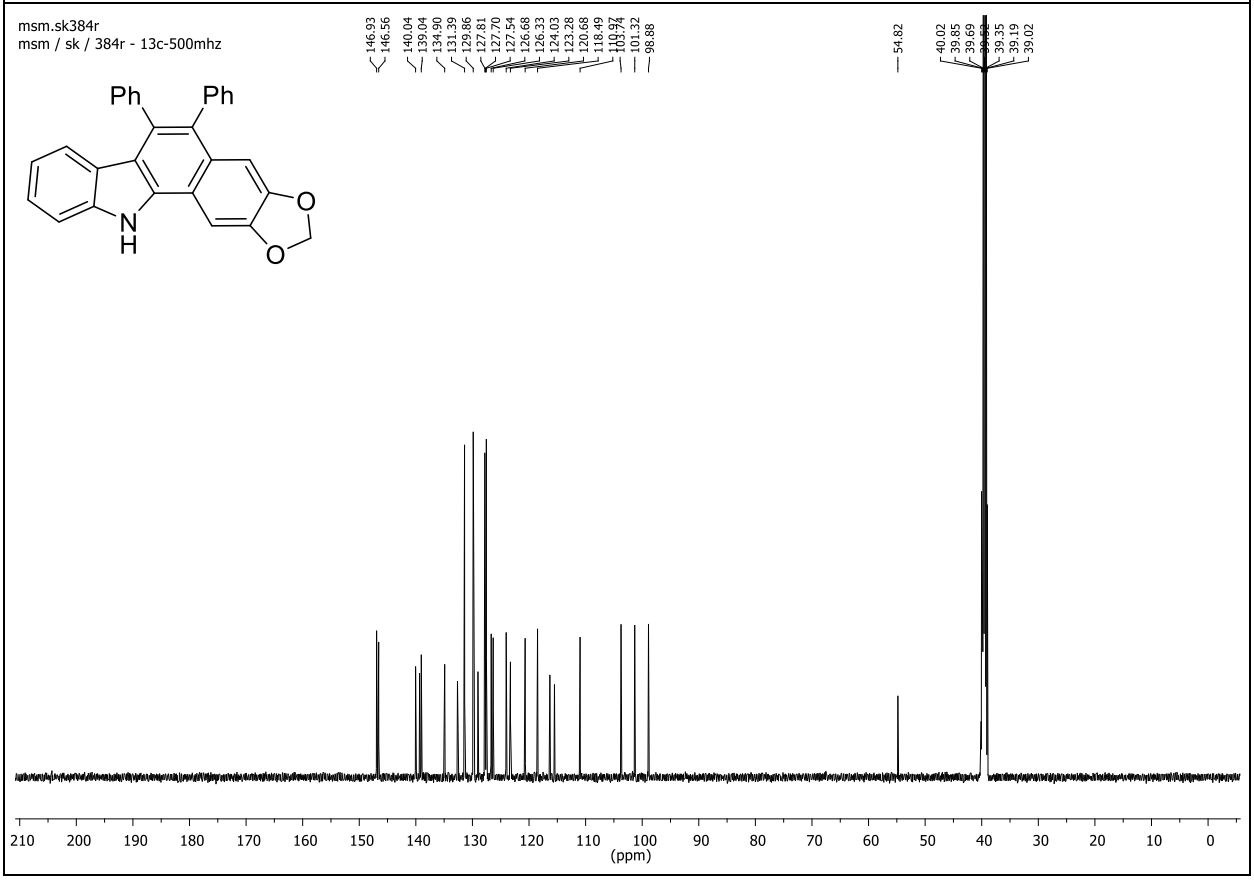

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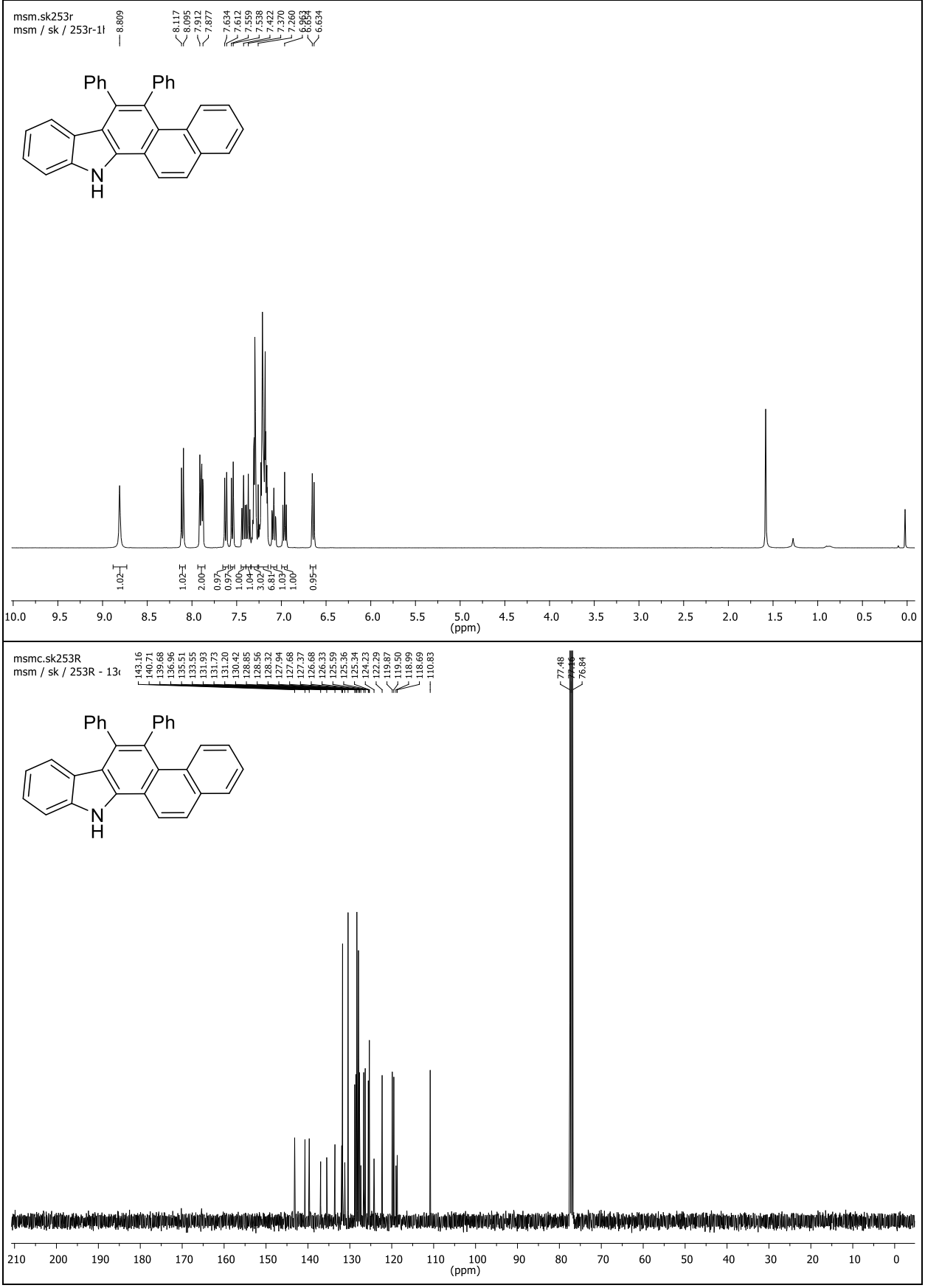

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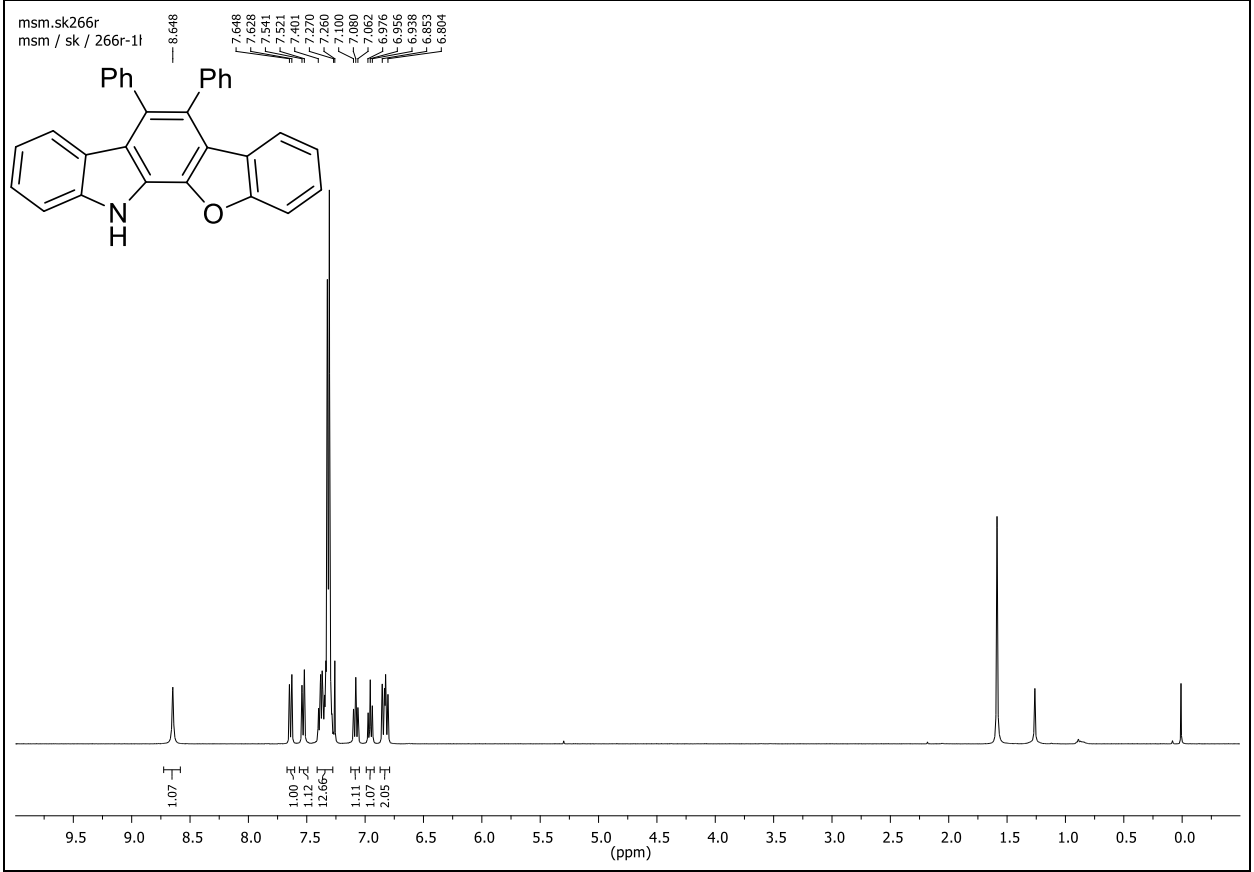

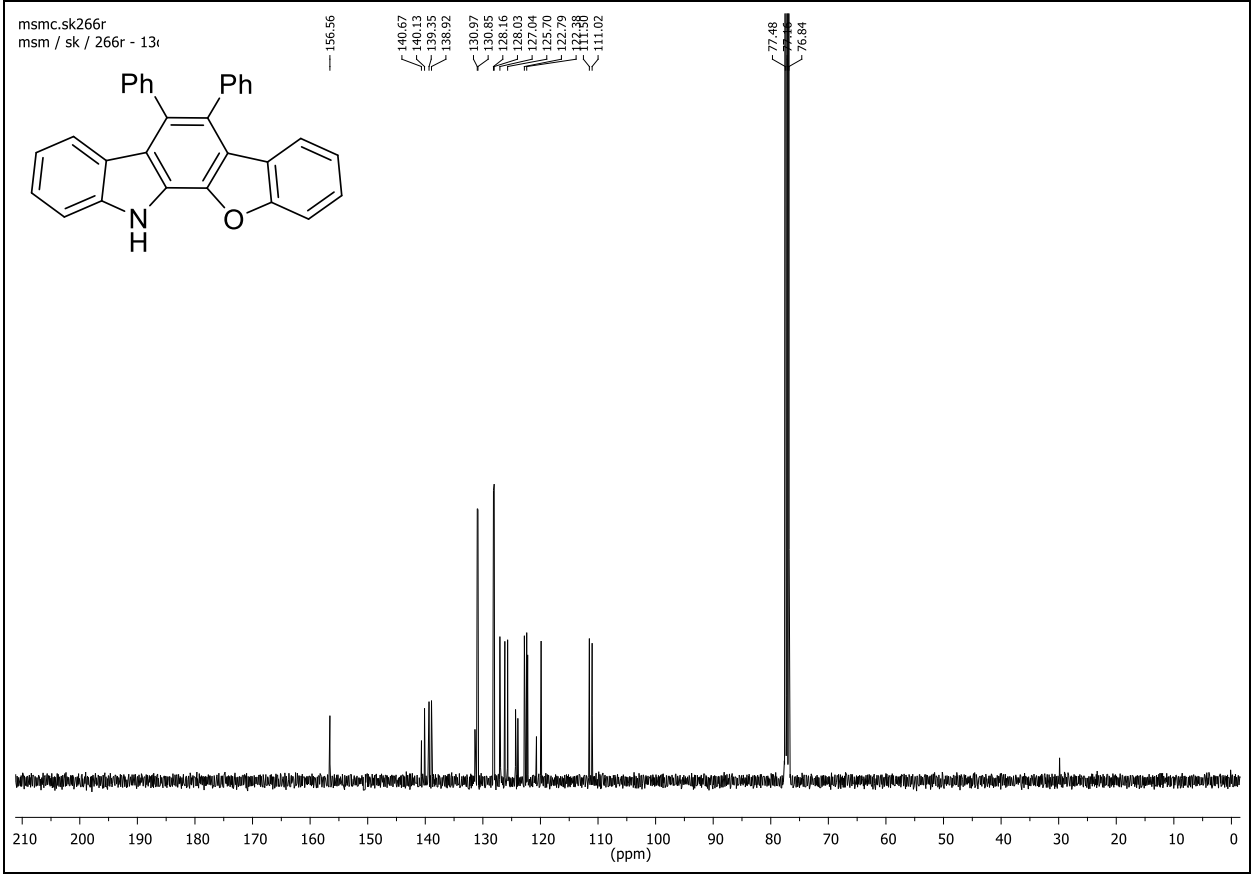

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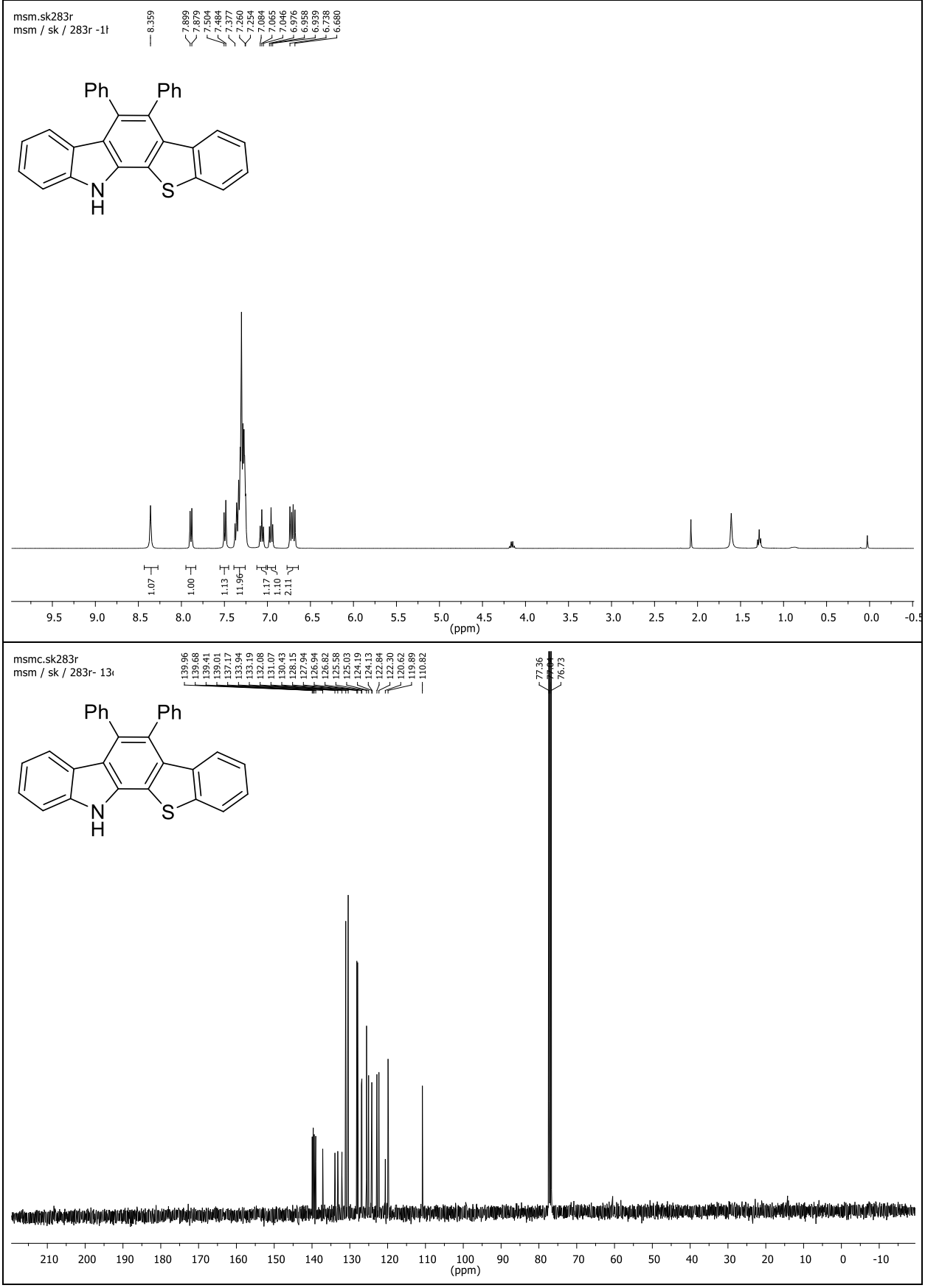

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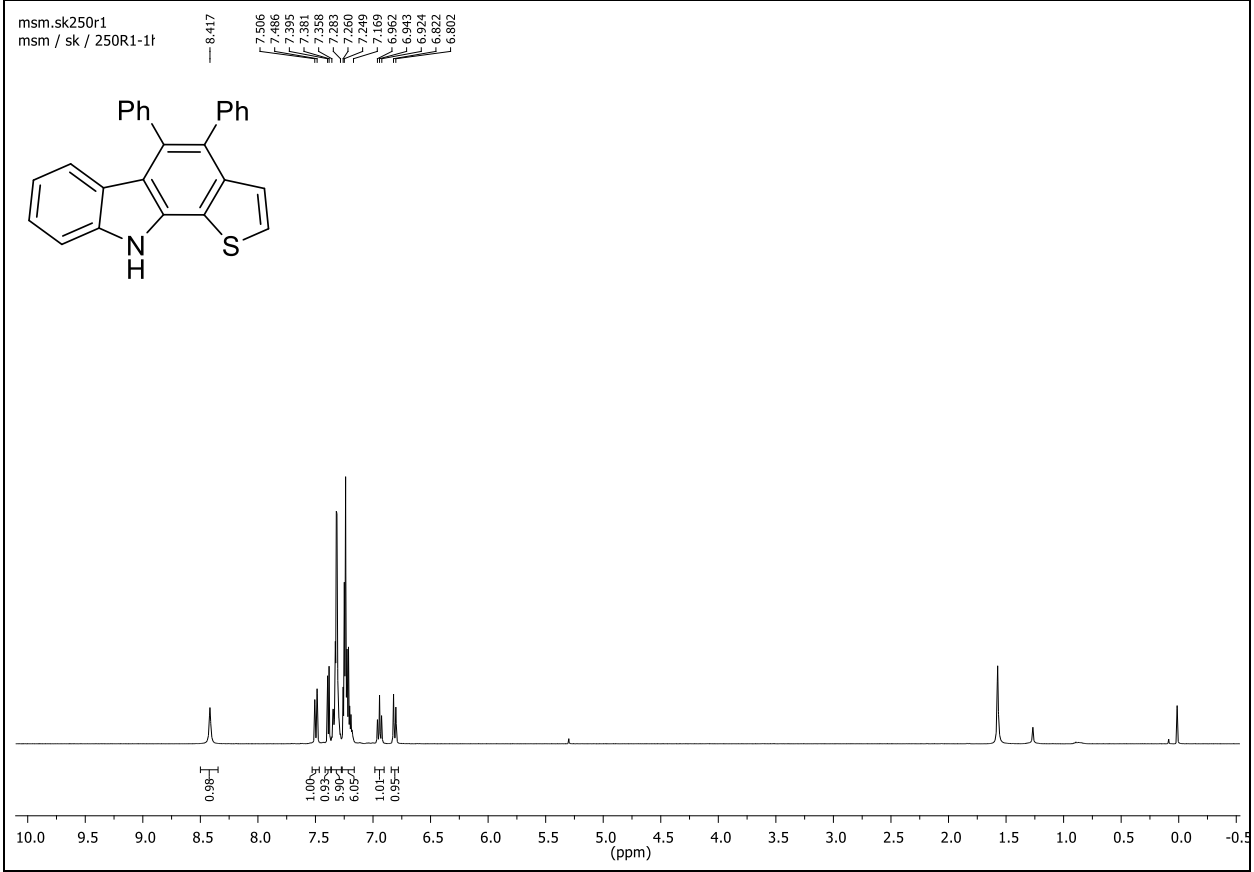

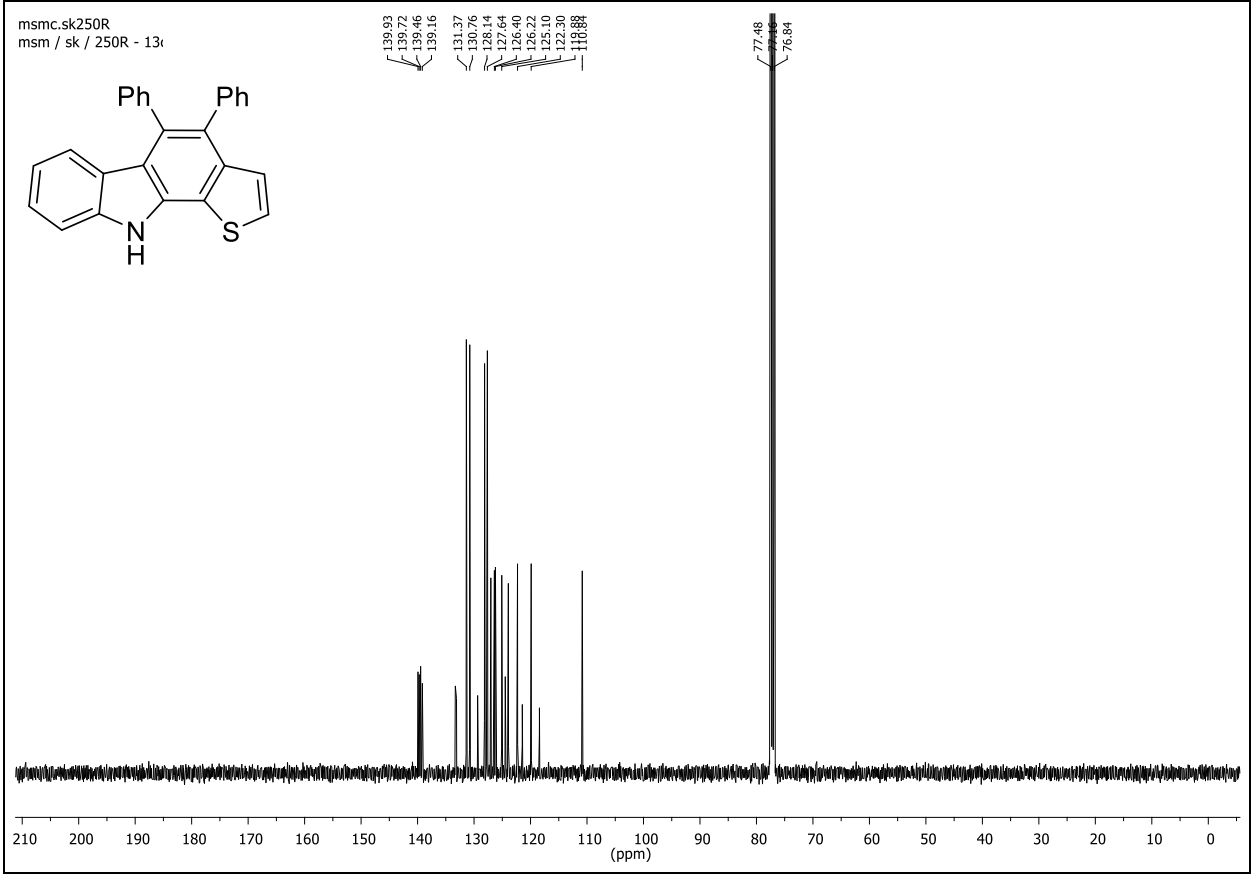

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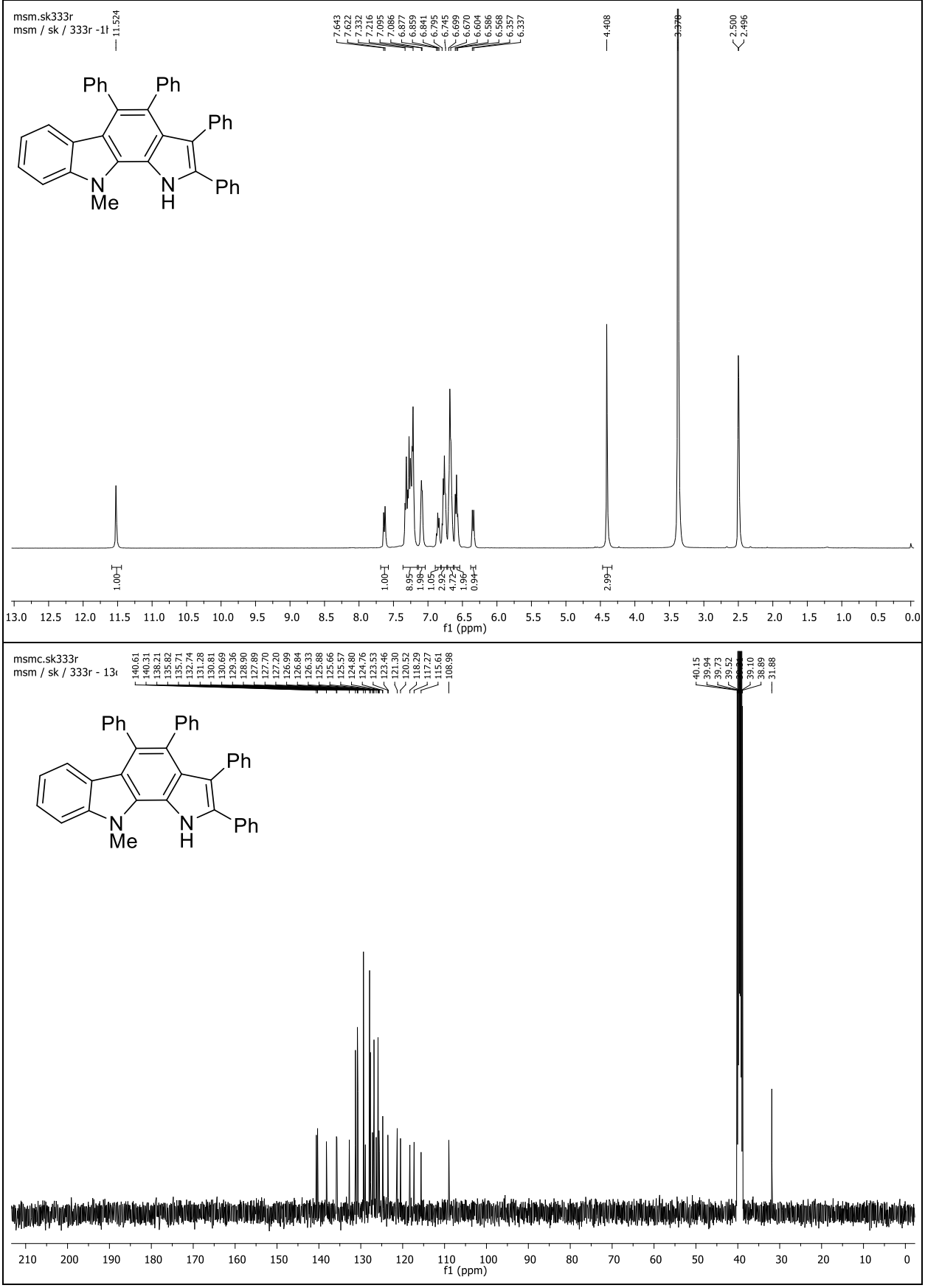

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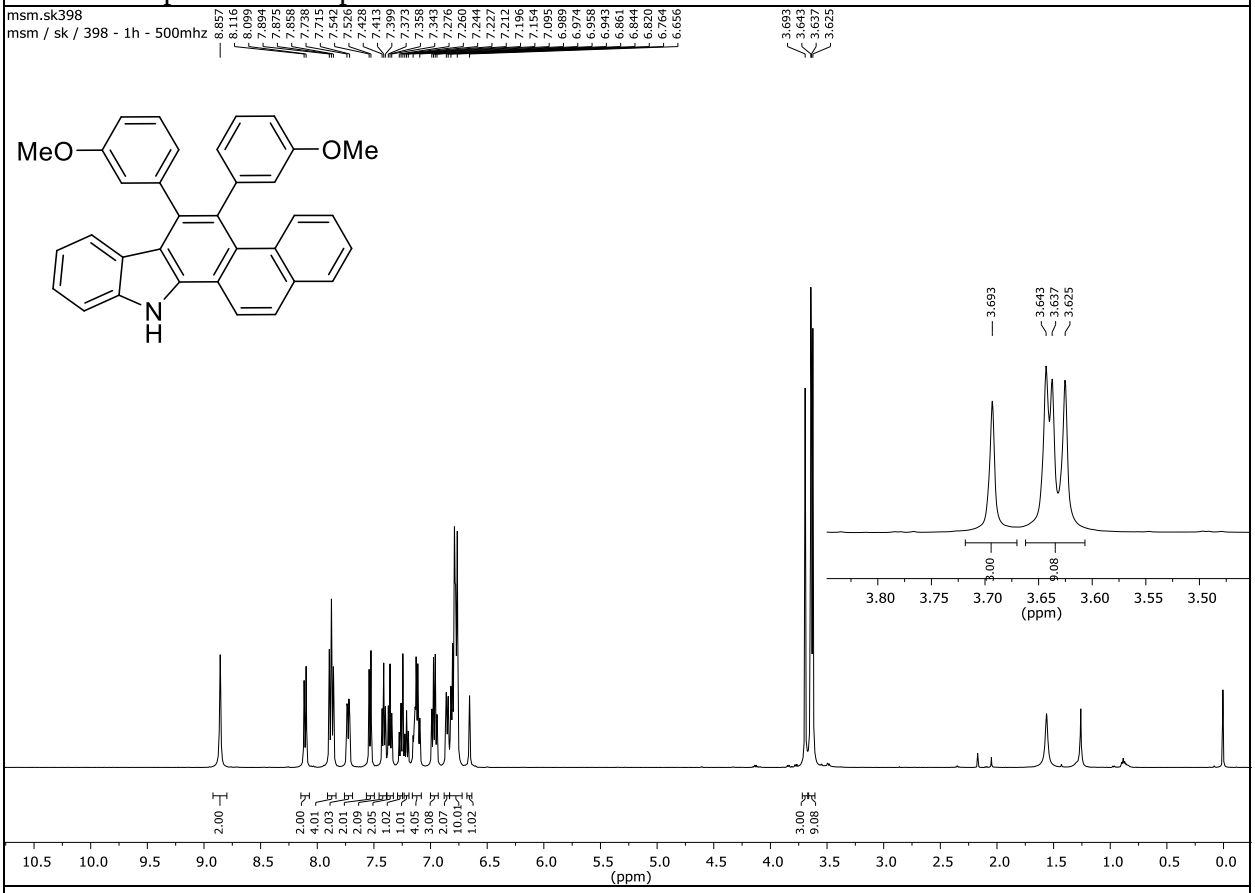

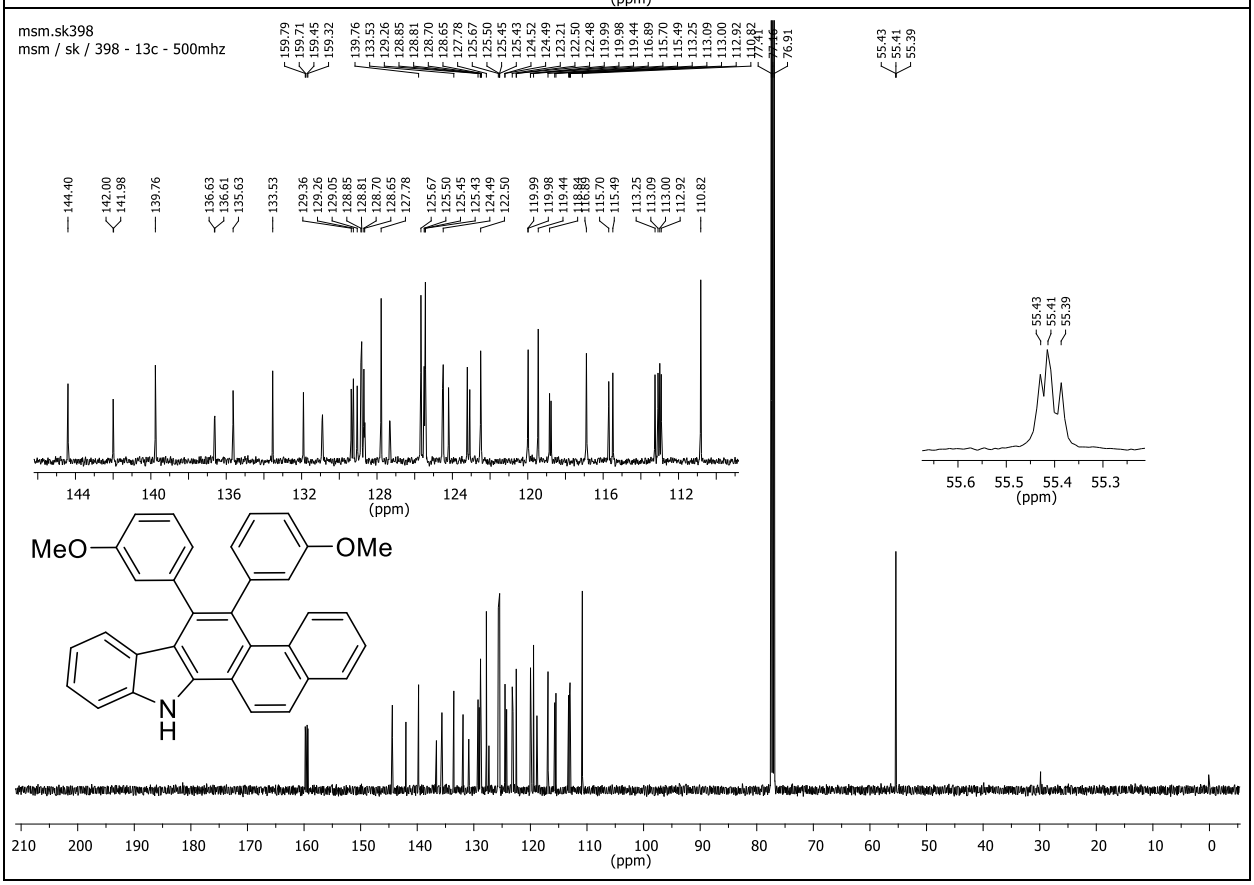

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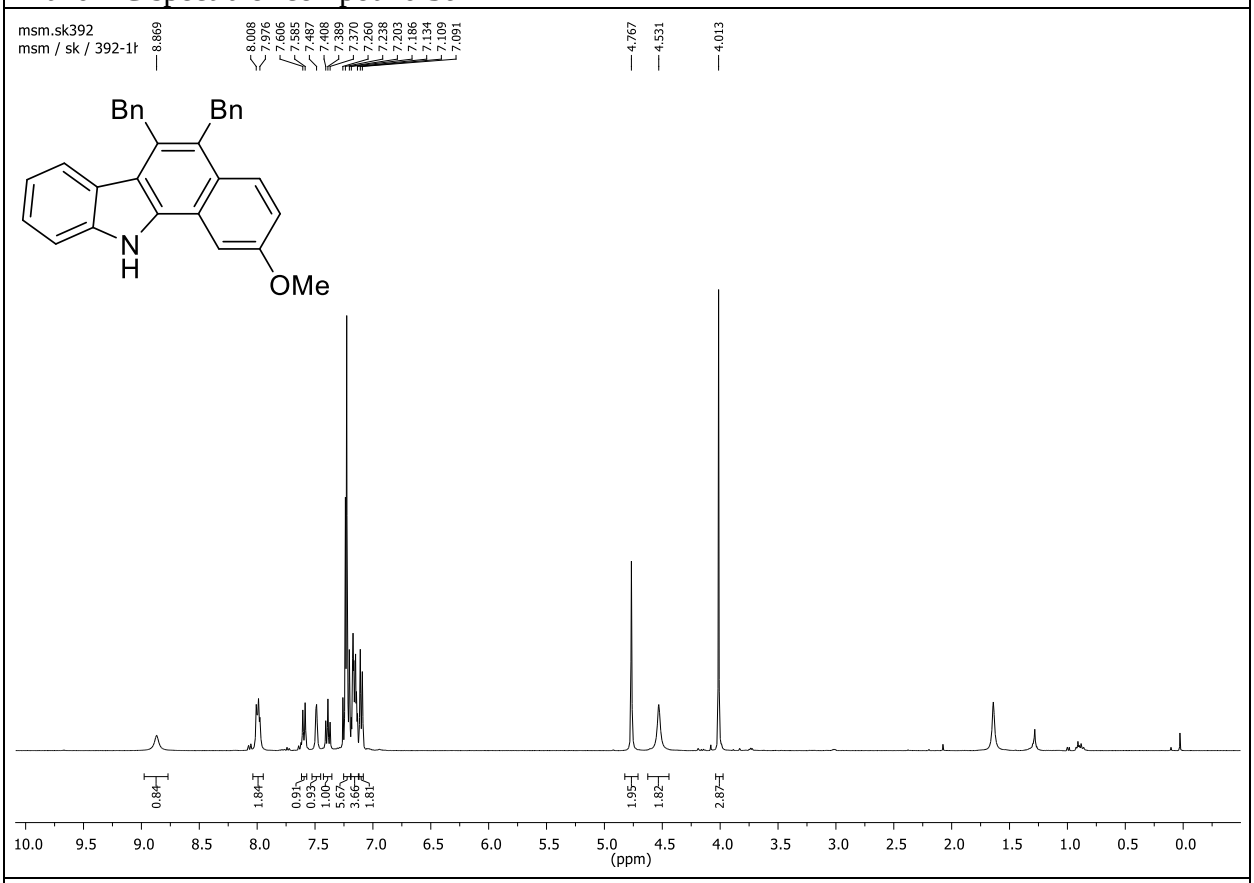

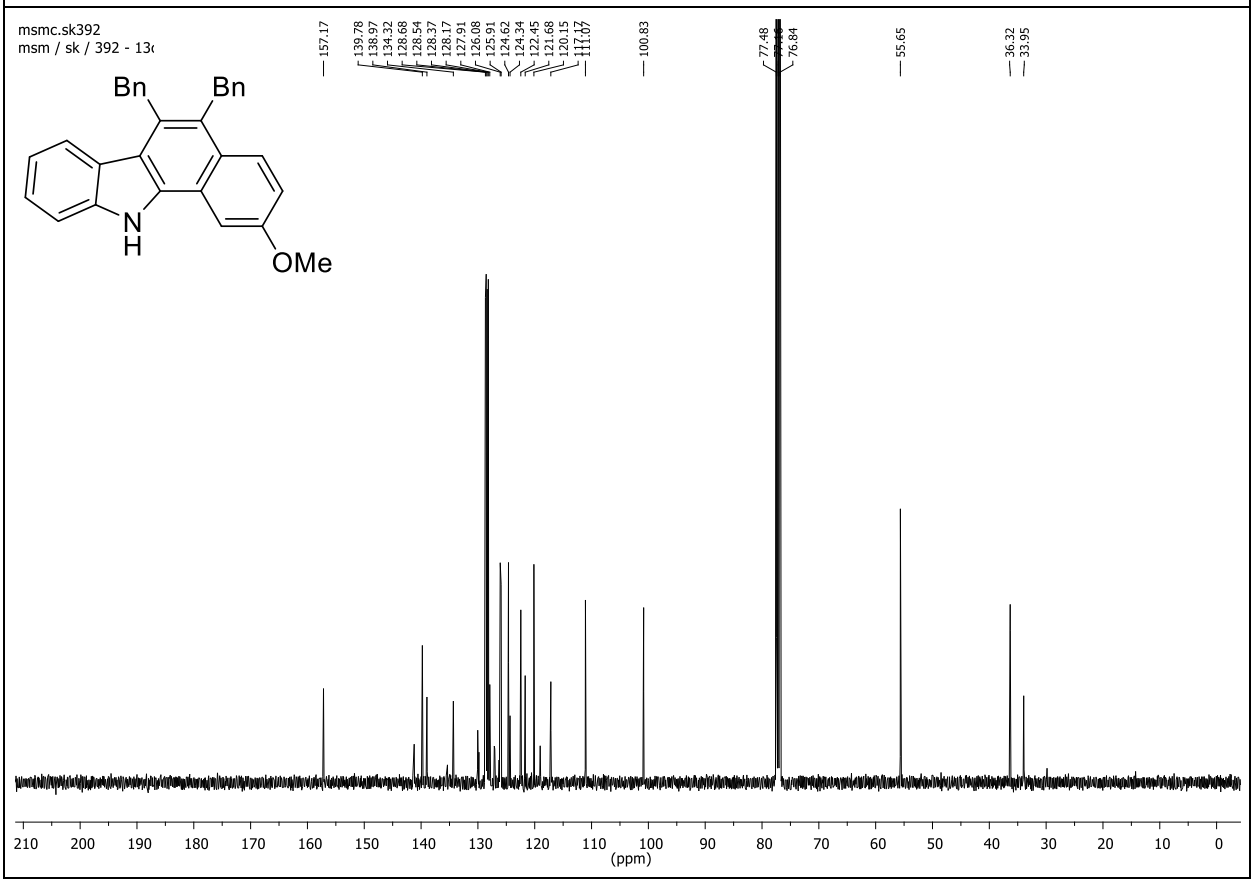

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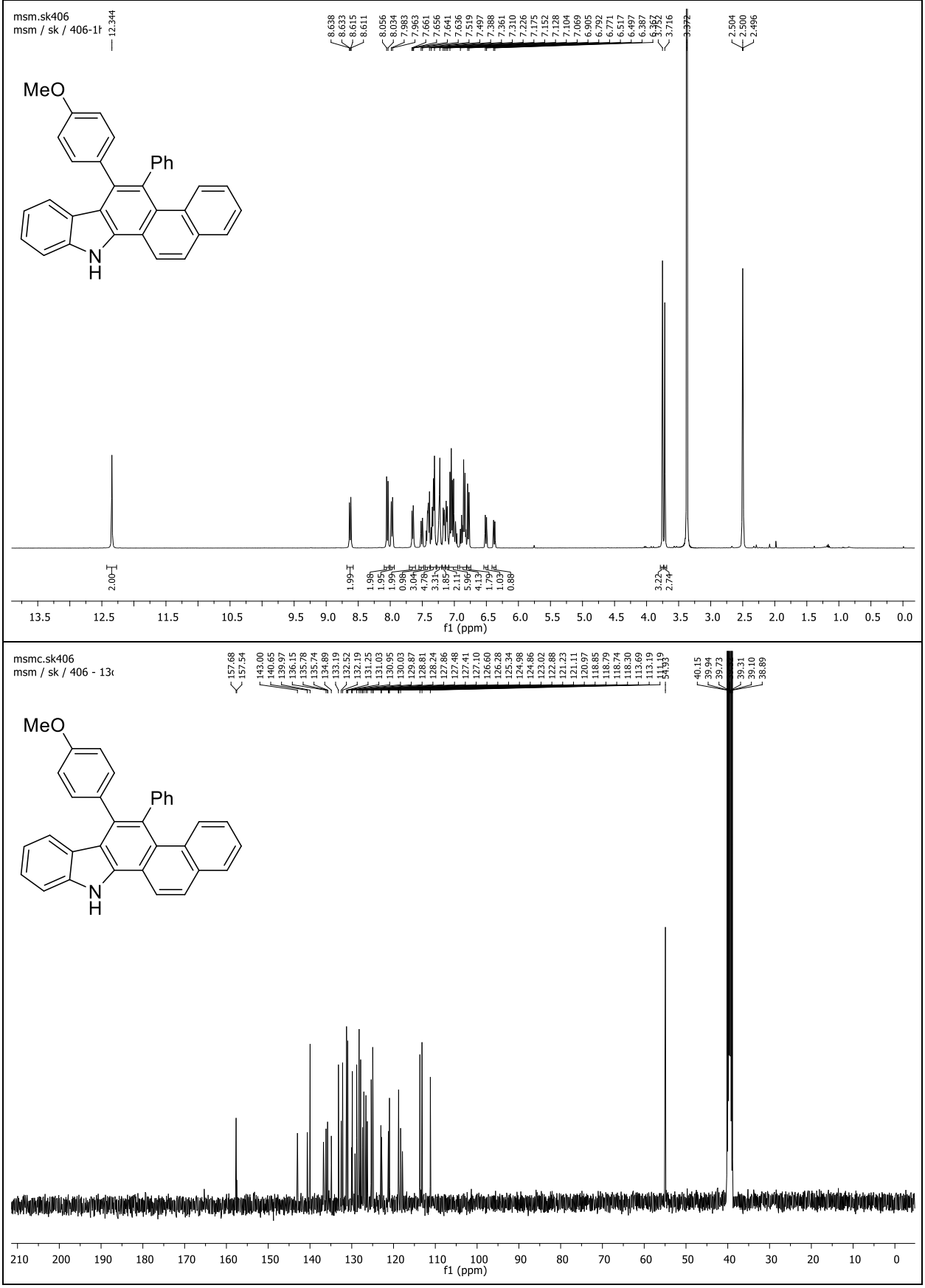

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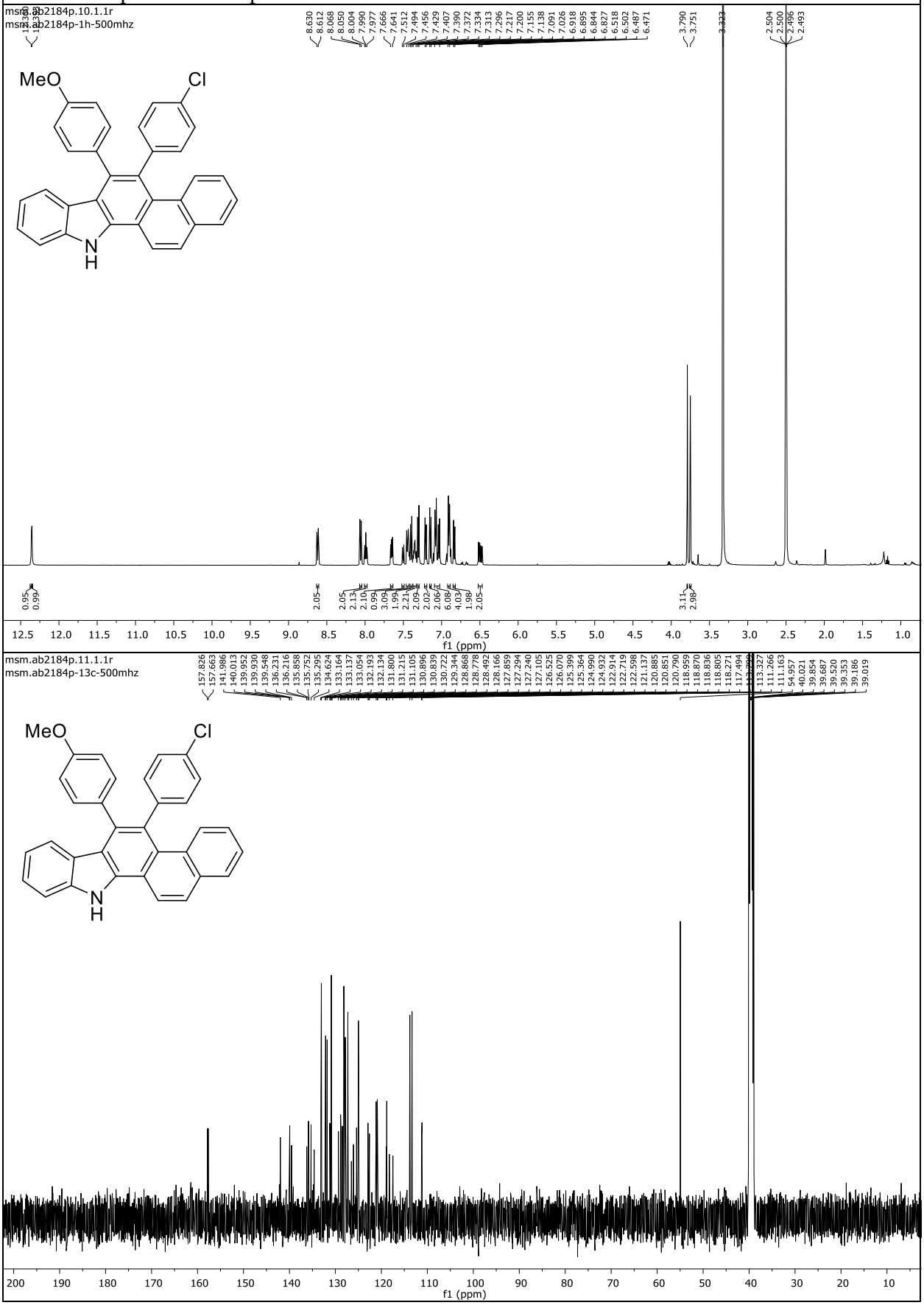

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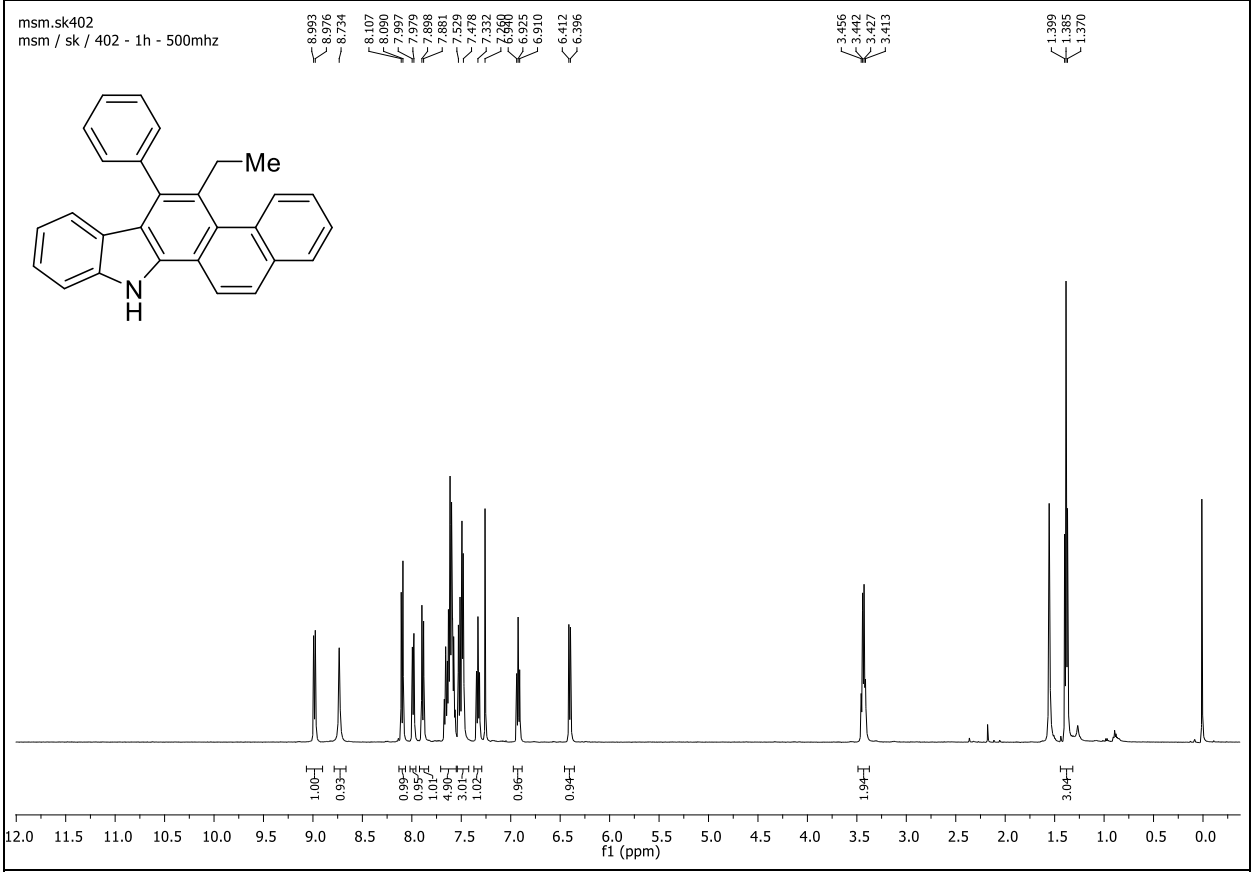

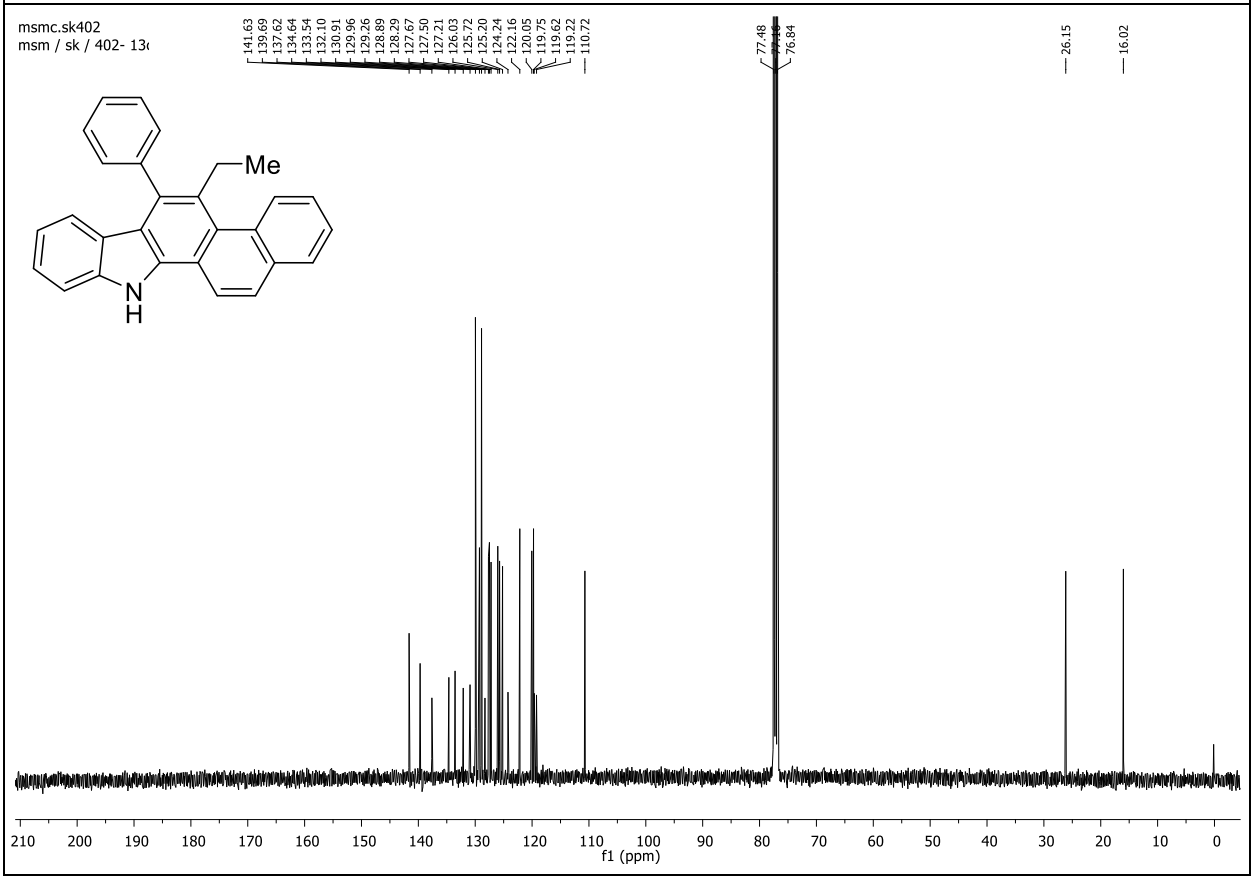

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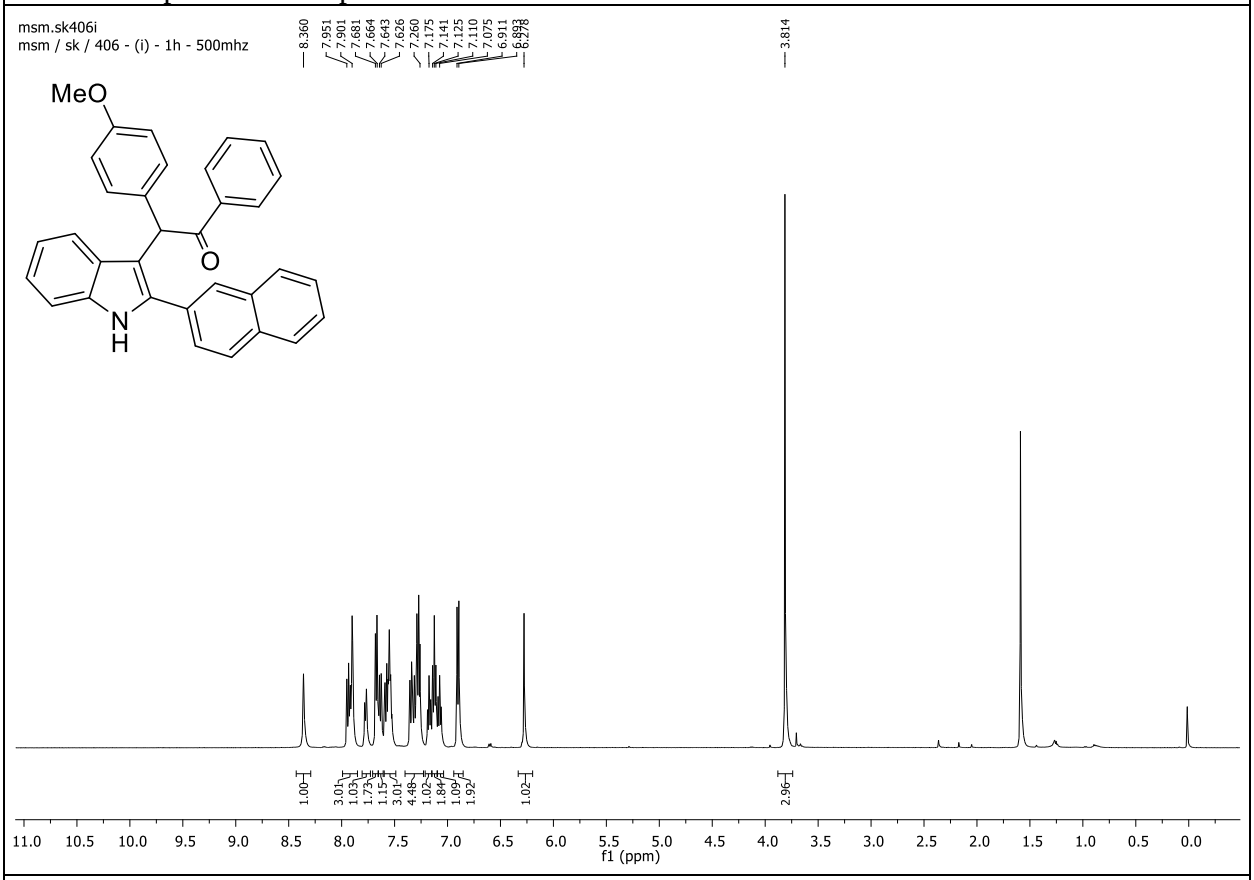

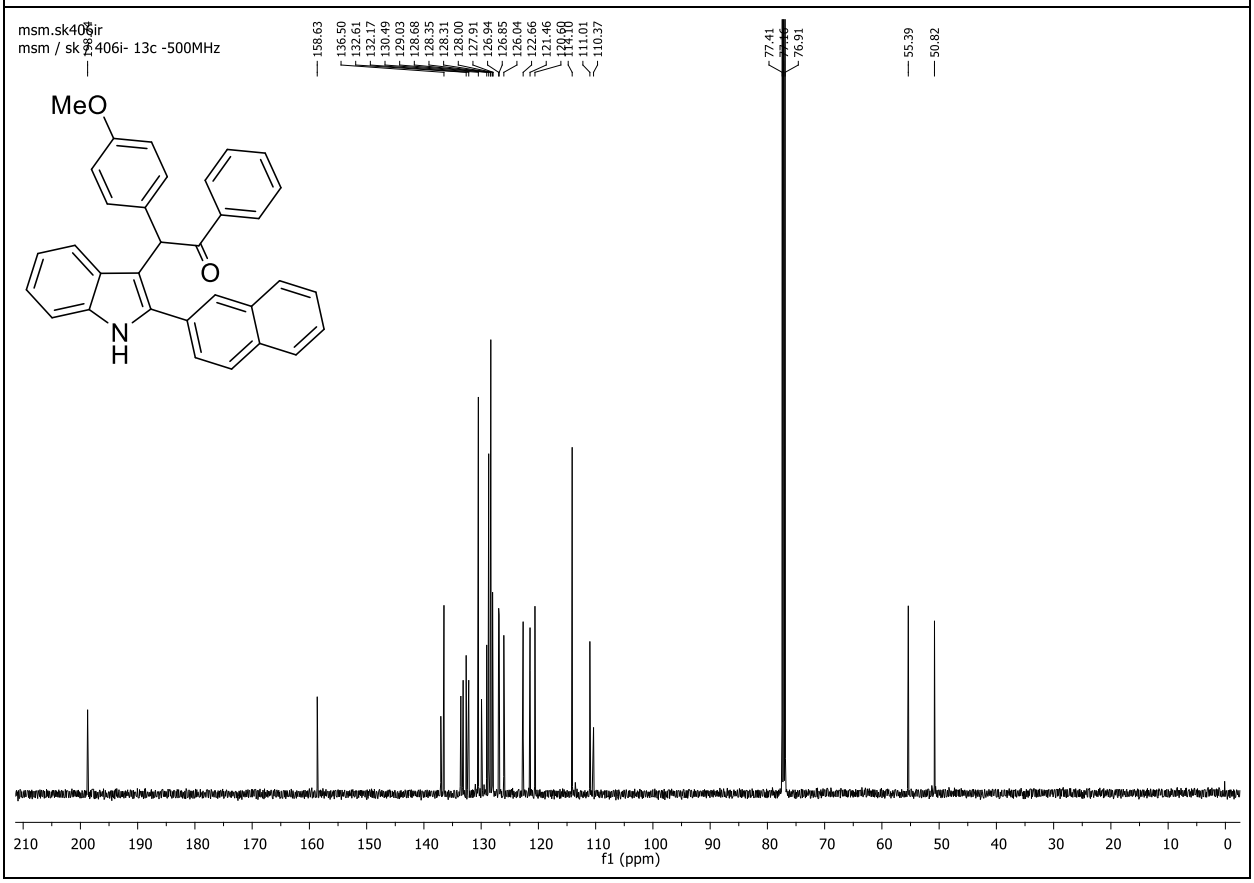

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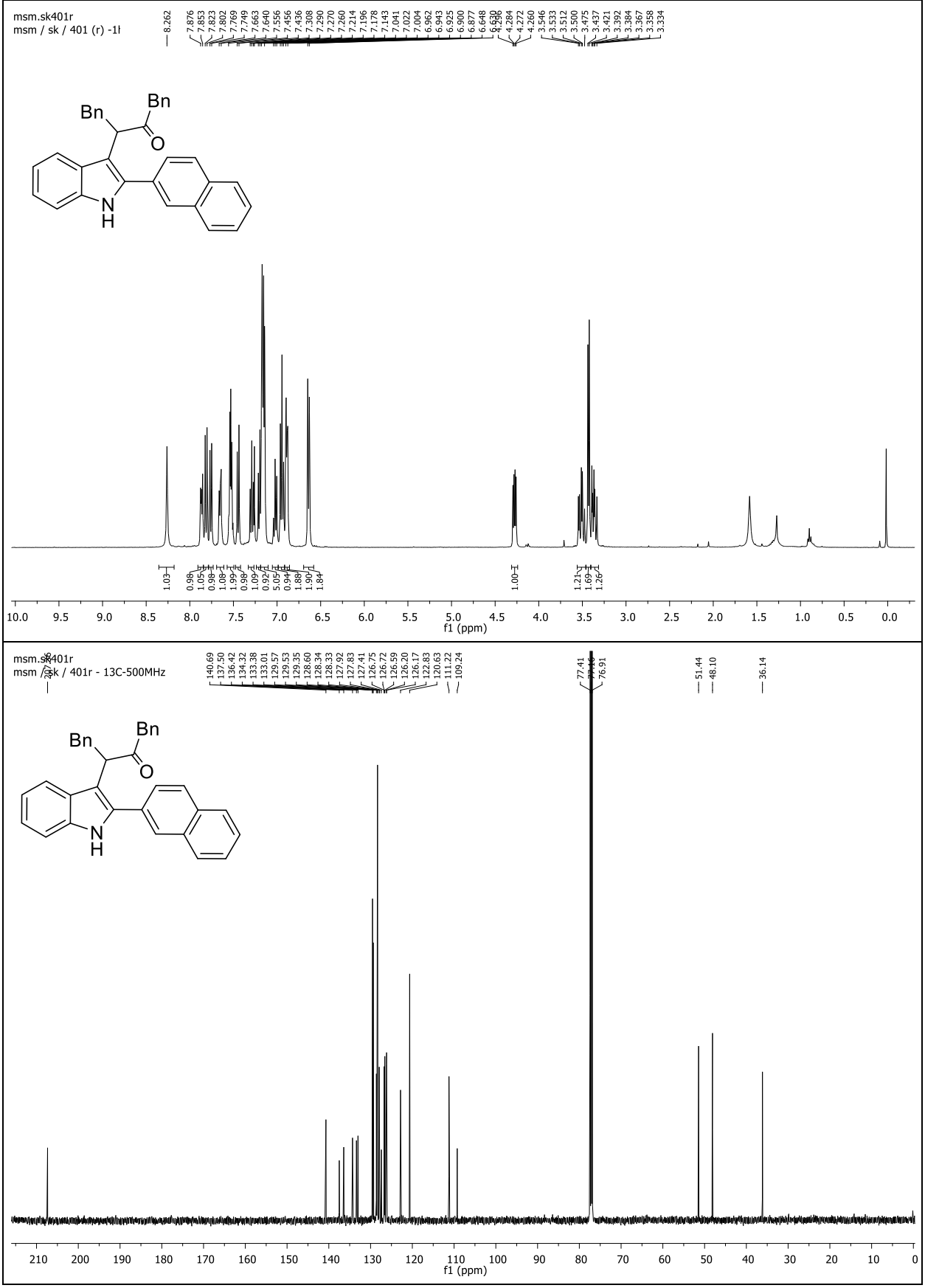

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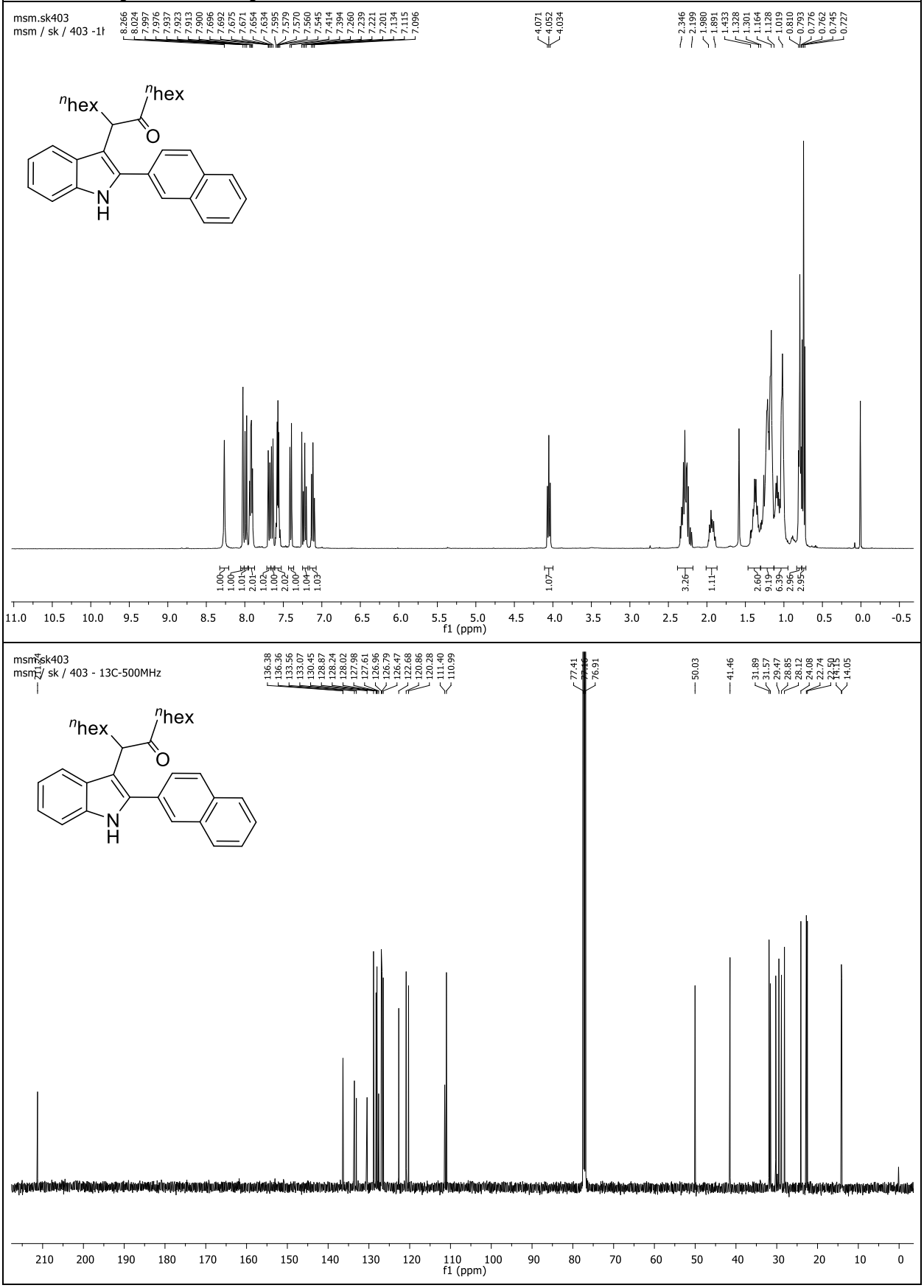

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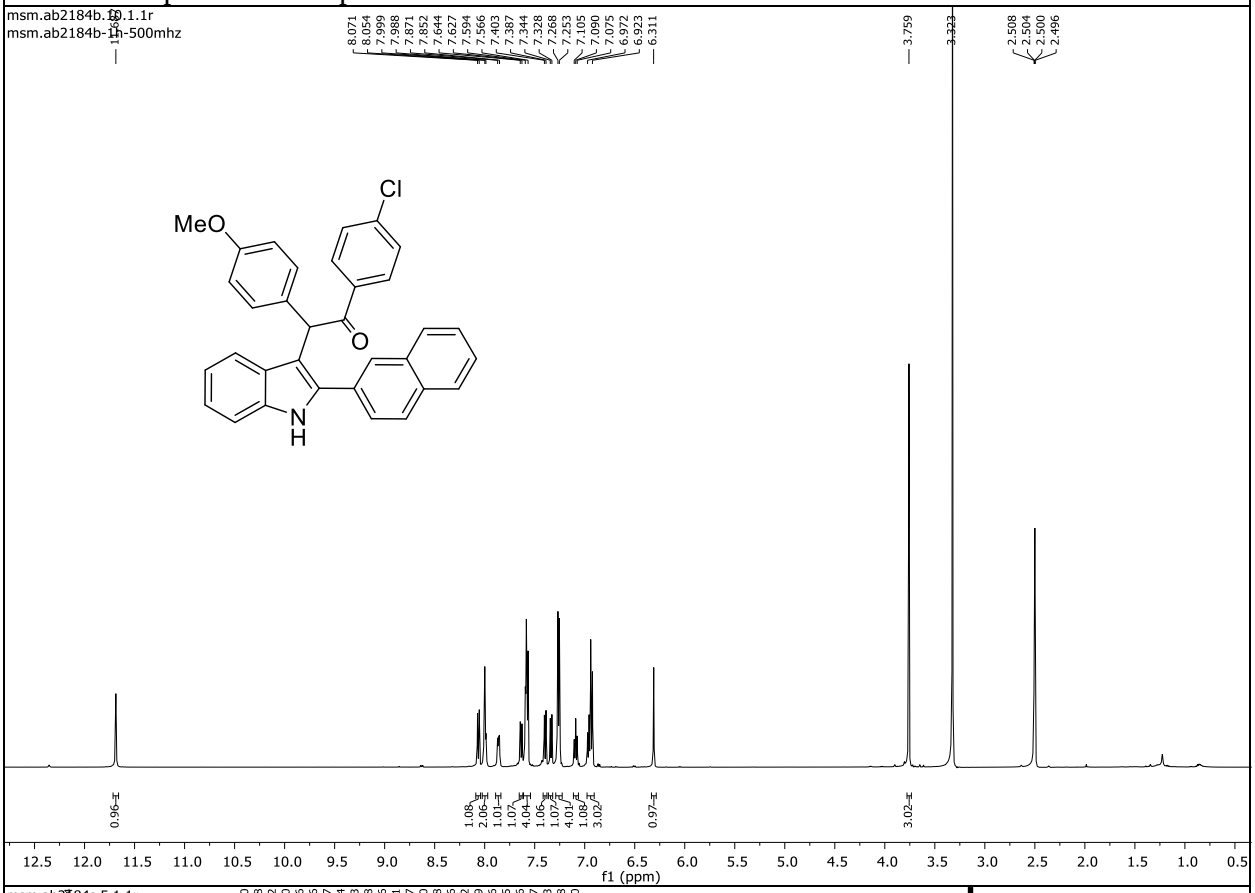

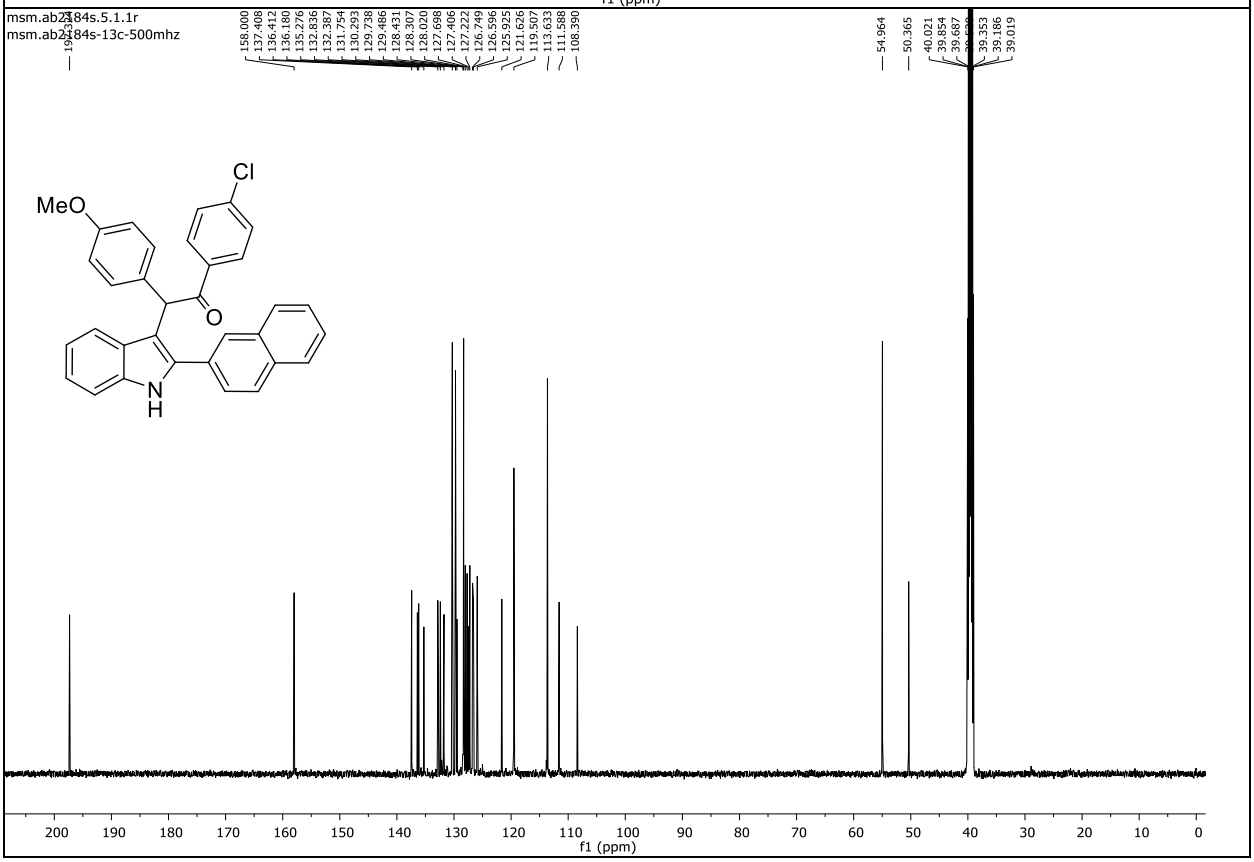

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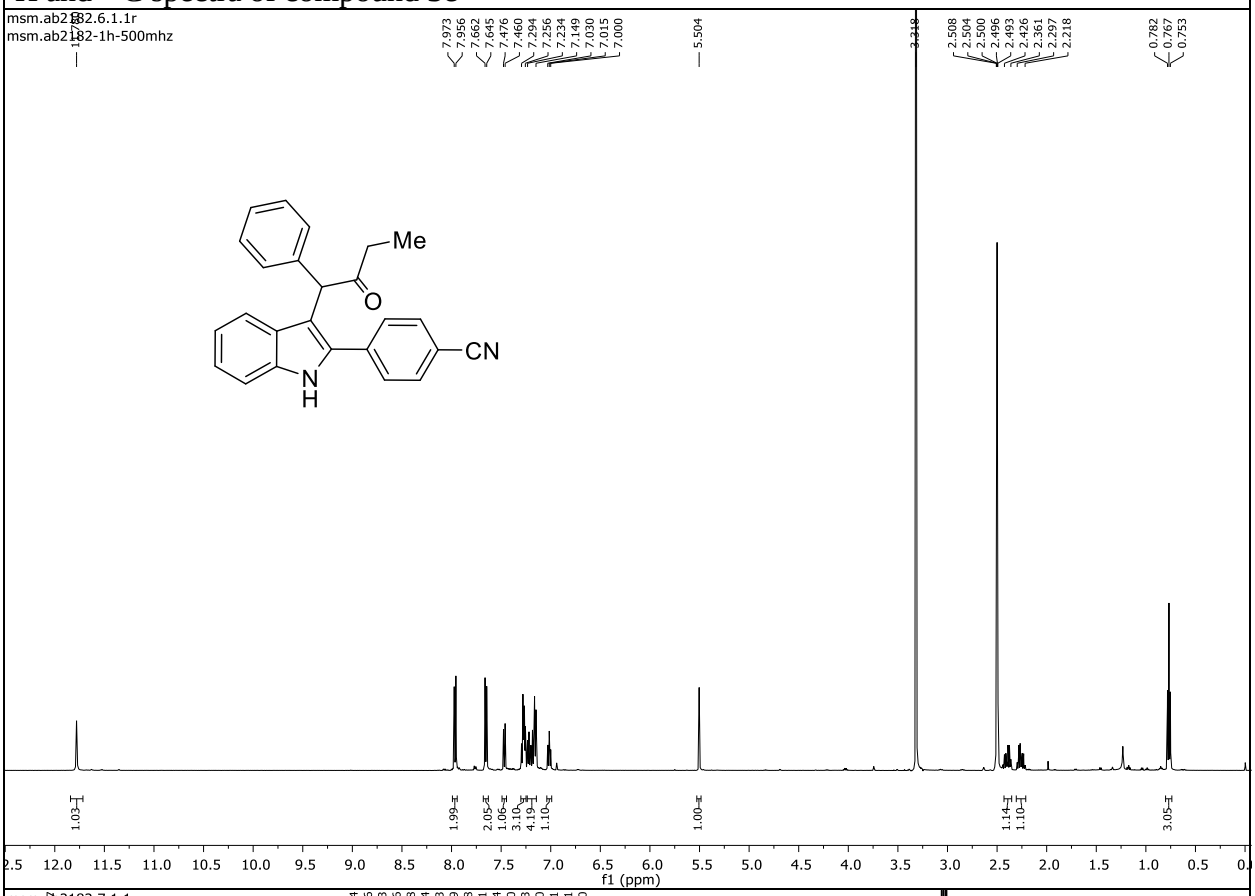

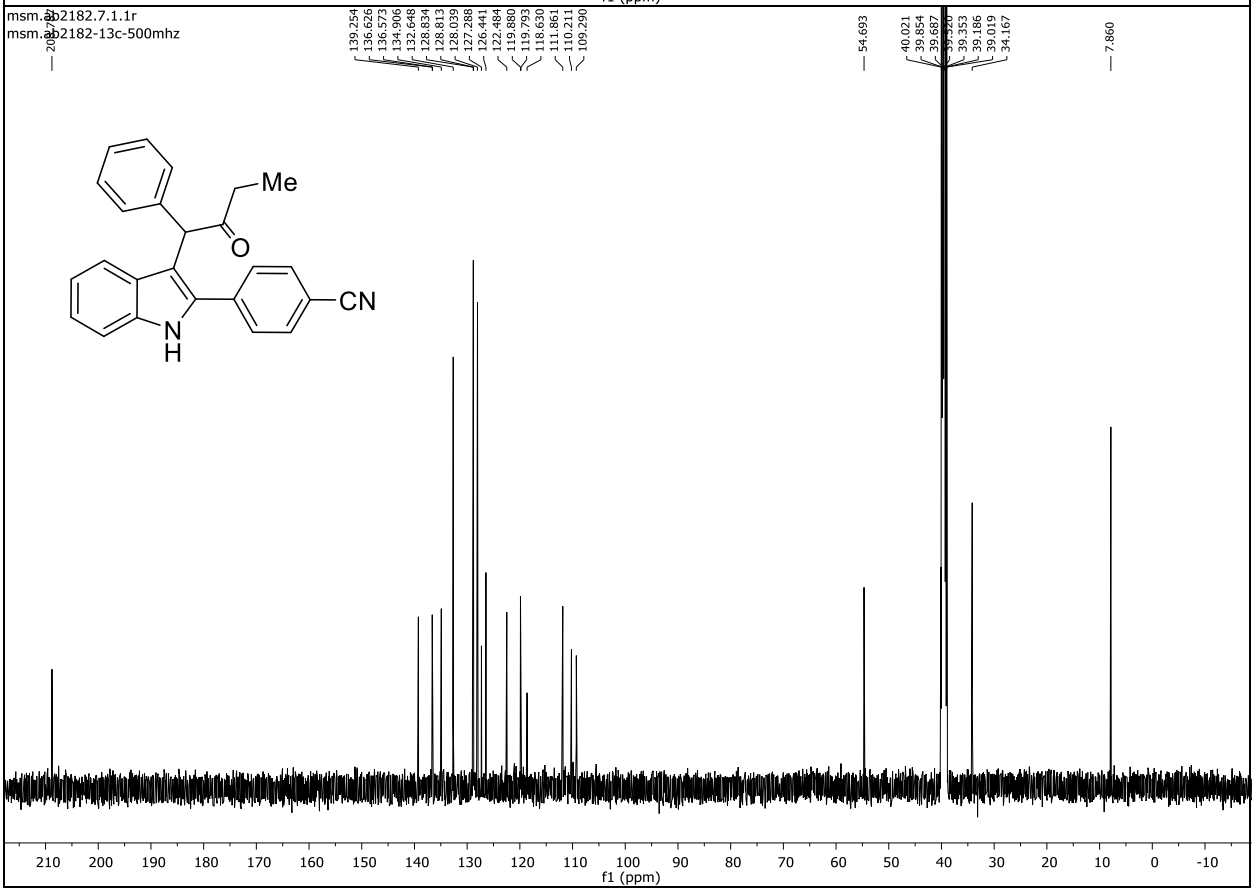

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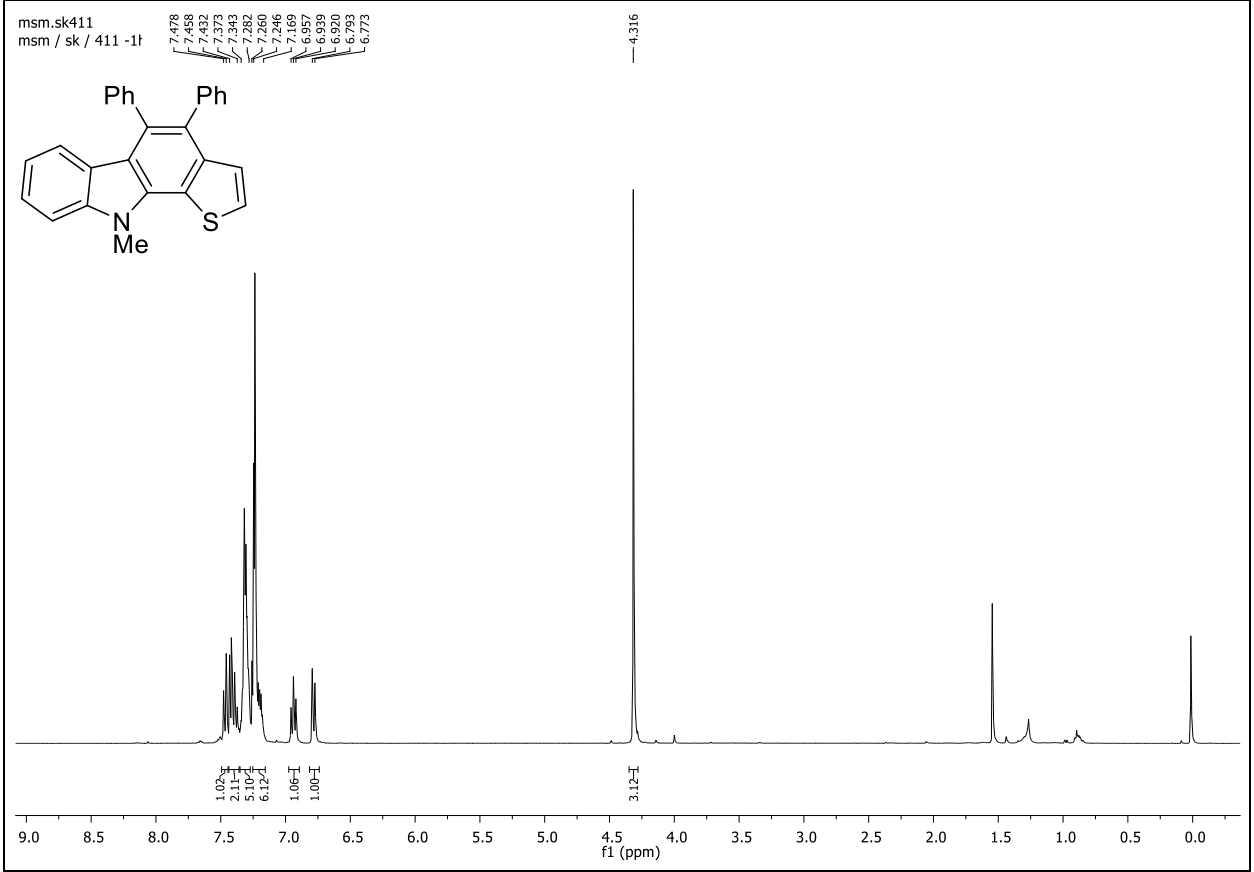
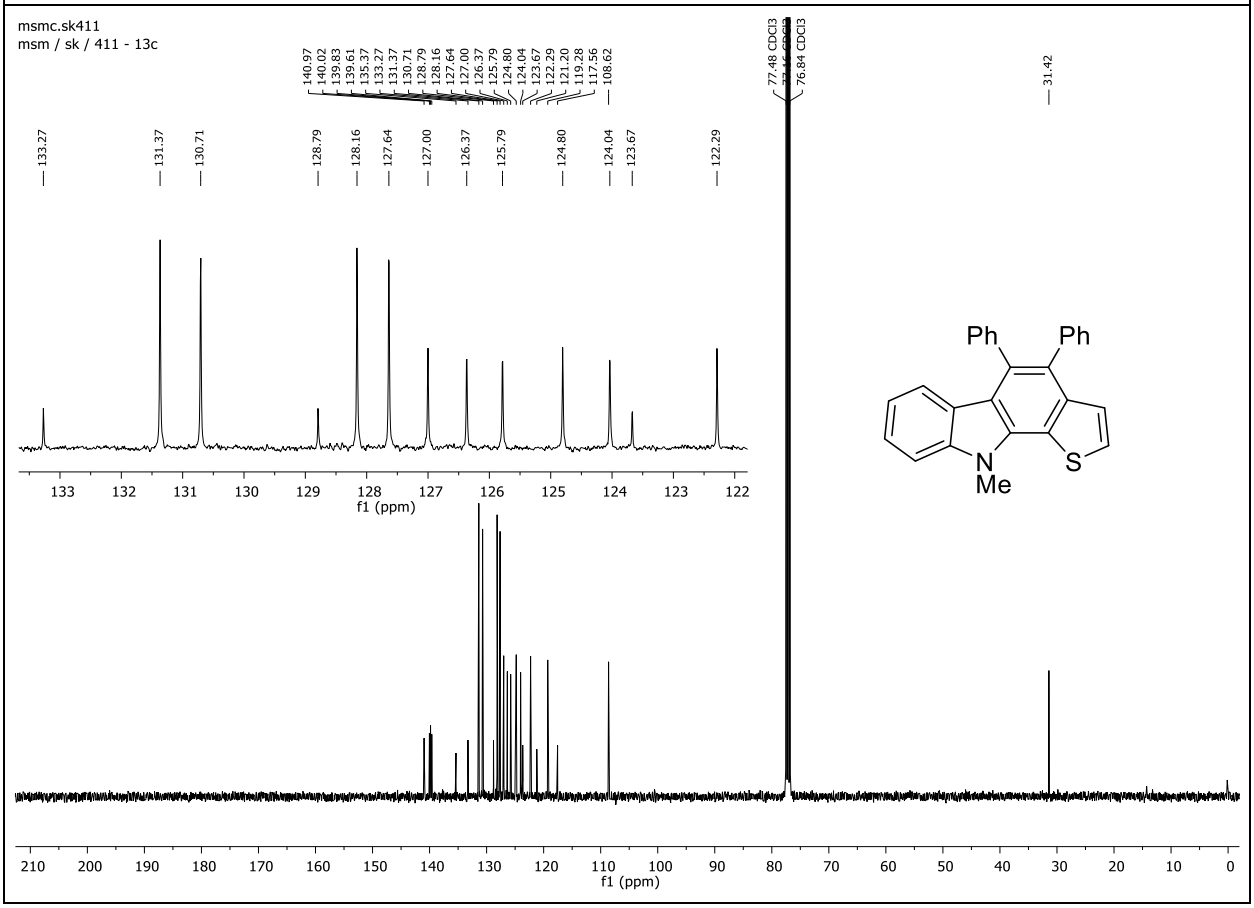
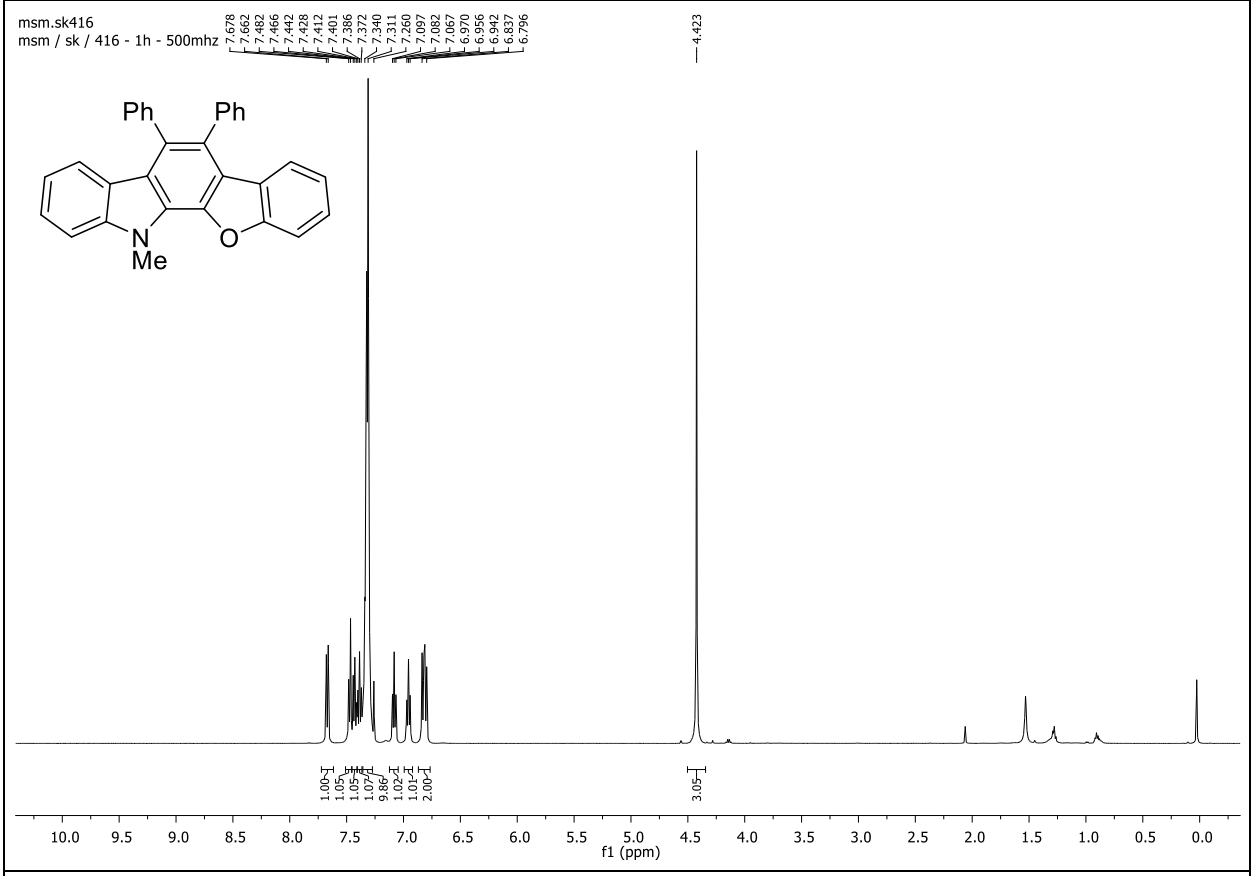
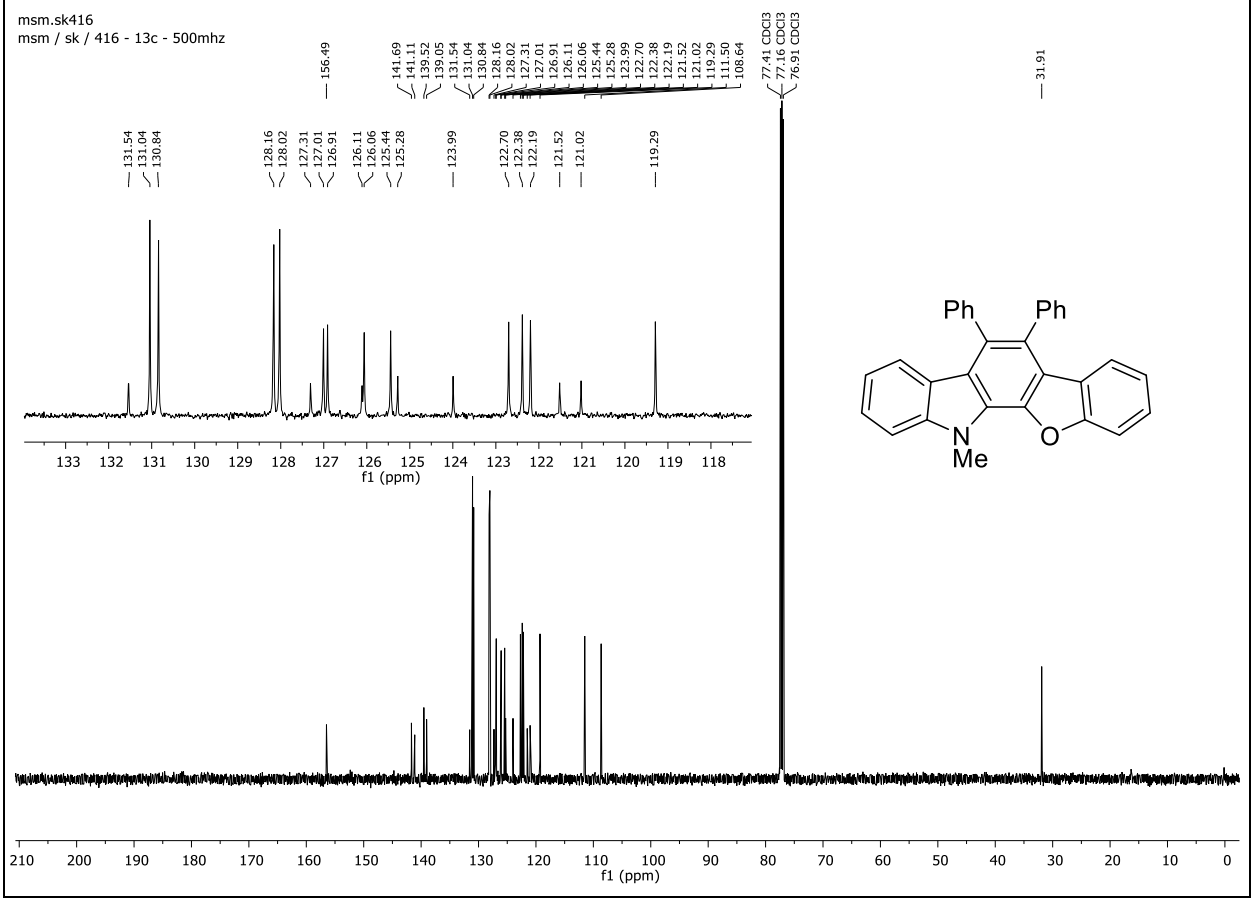


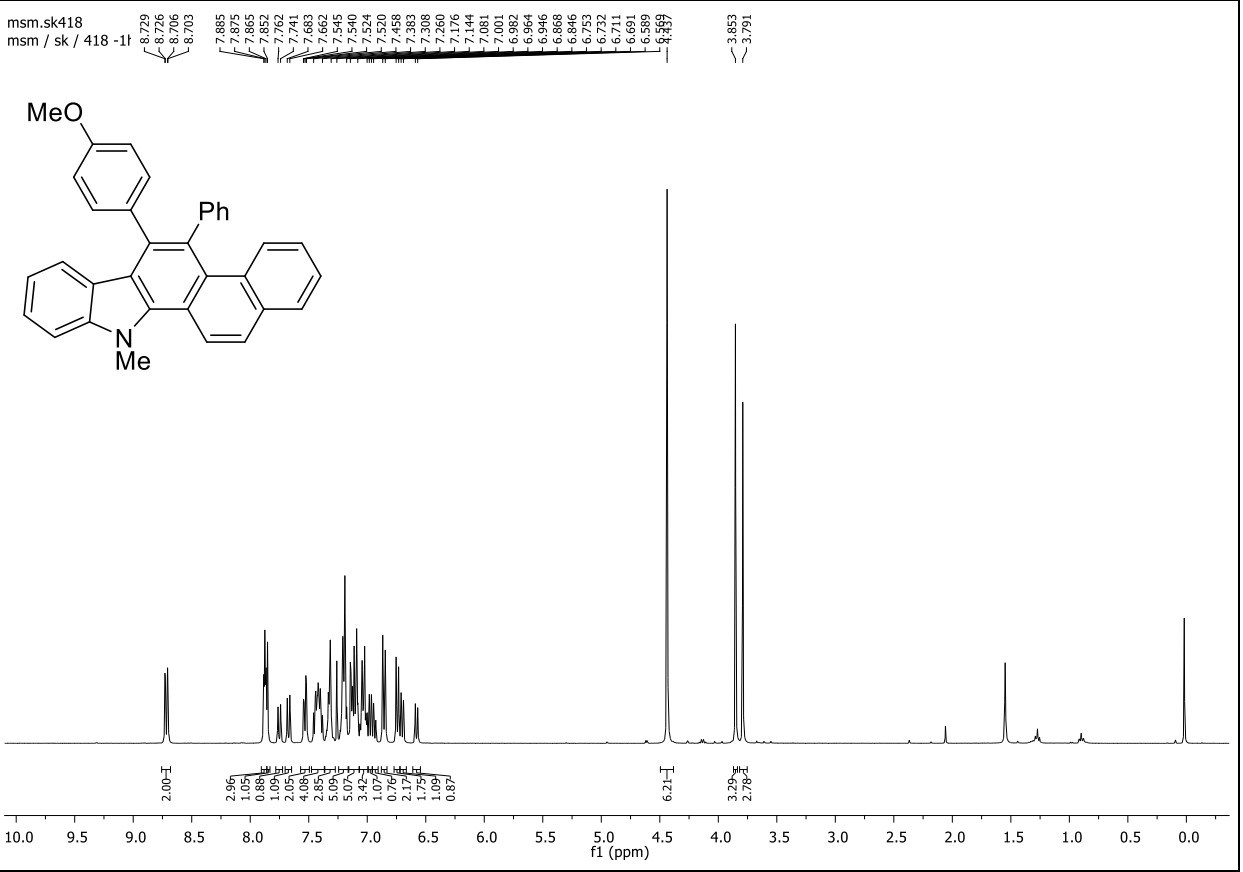


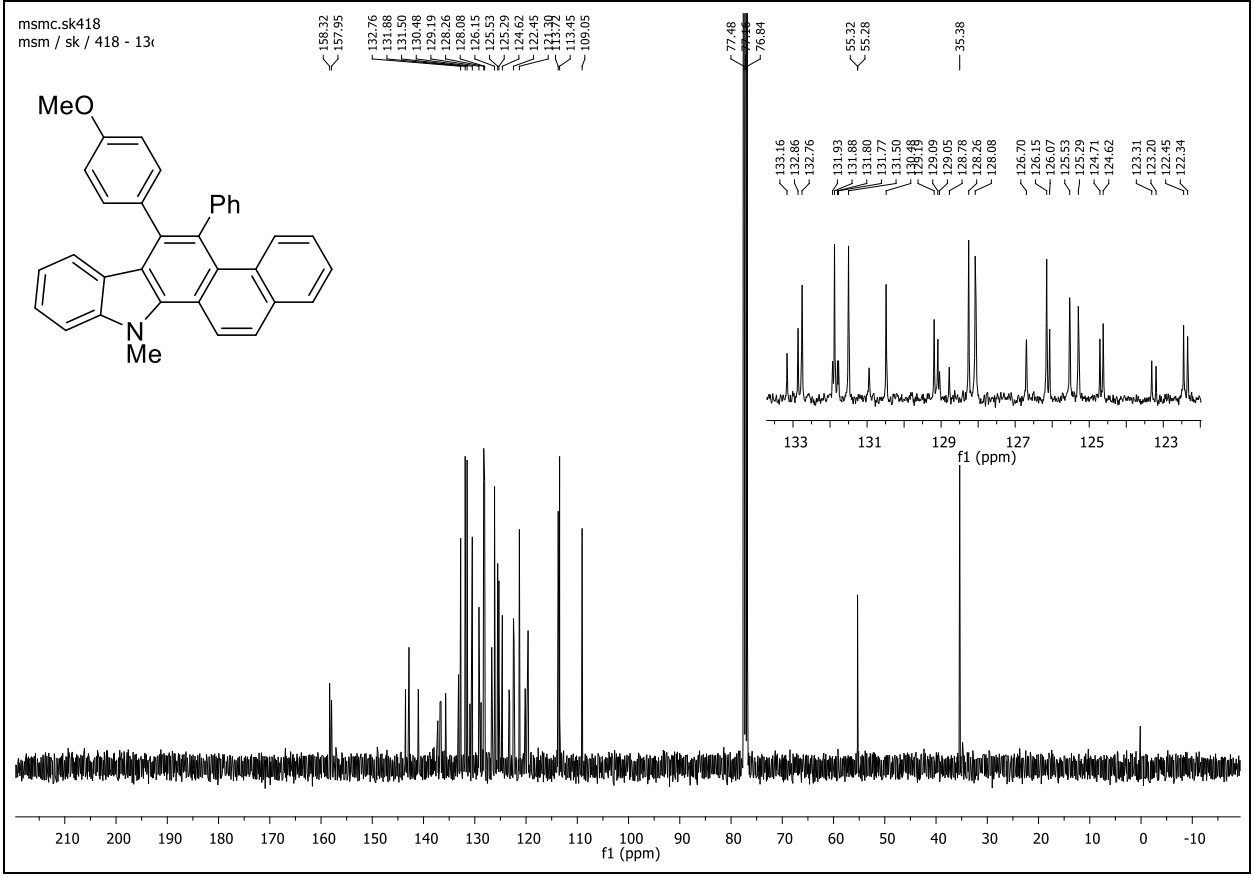
^{1}H and ^{13}C spectra of compound **6b**



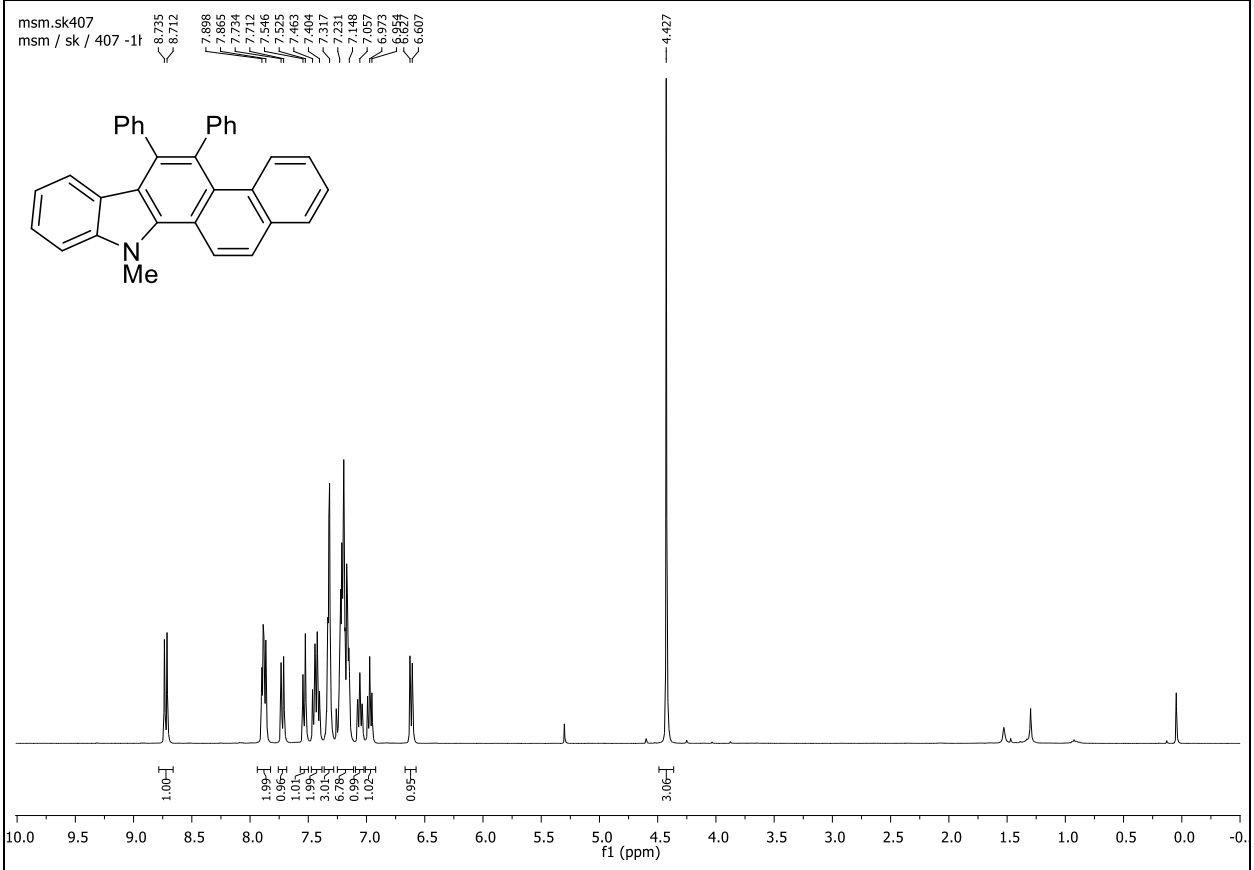


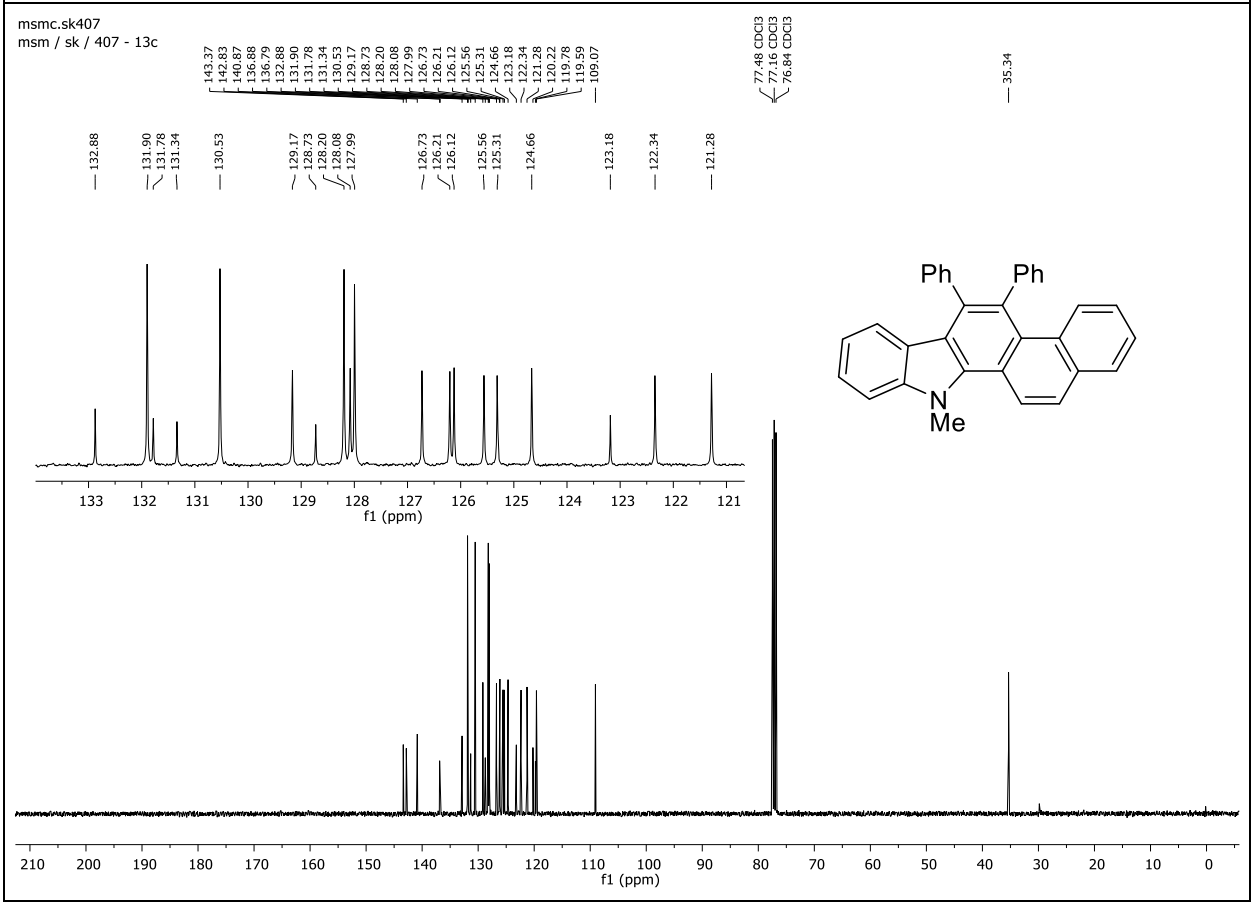
^{1}H and ^{13}C spectra of compound **6c**



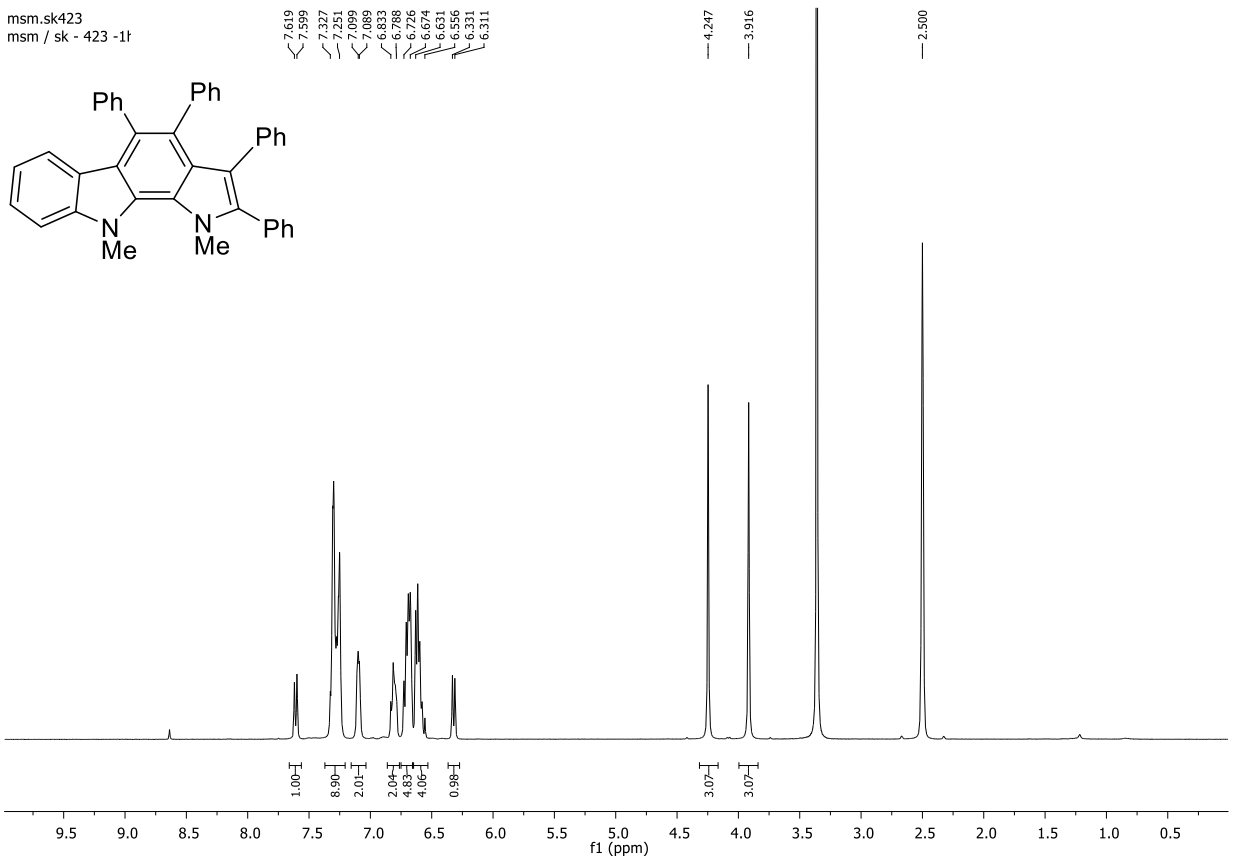


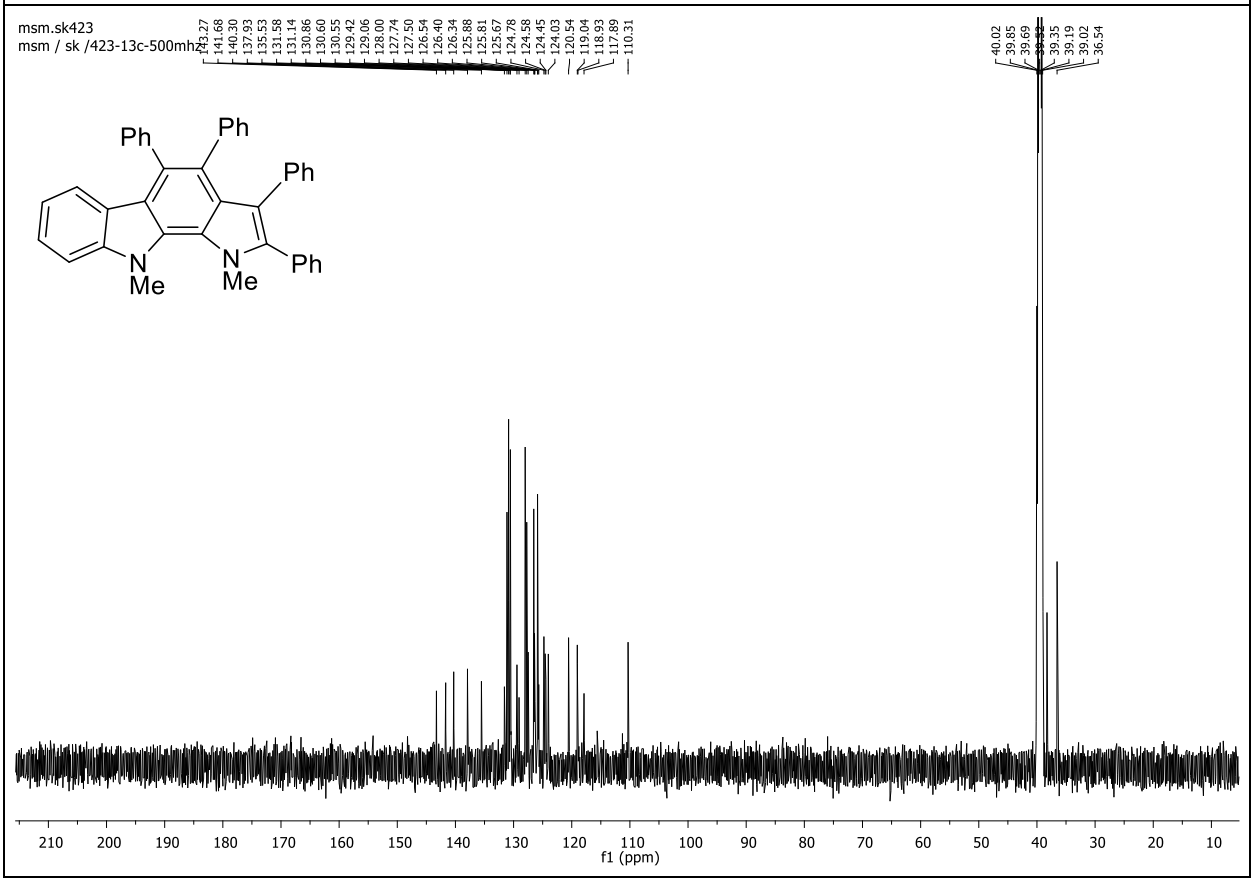
^{1}H and ^{13}C spectra of compound **6d**



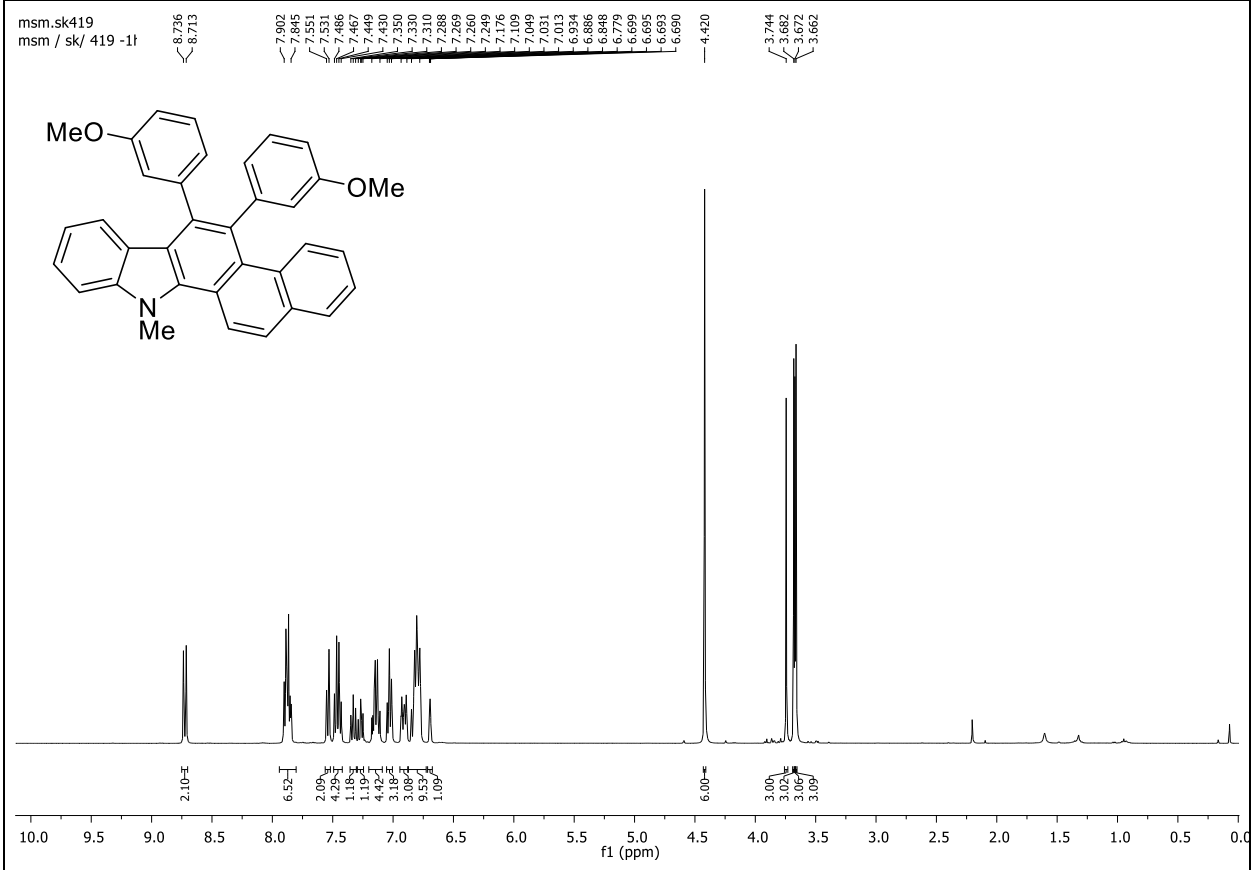


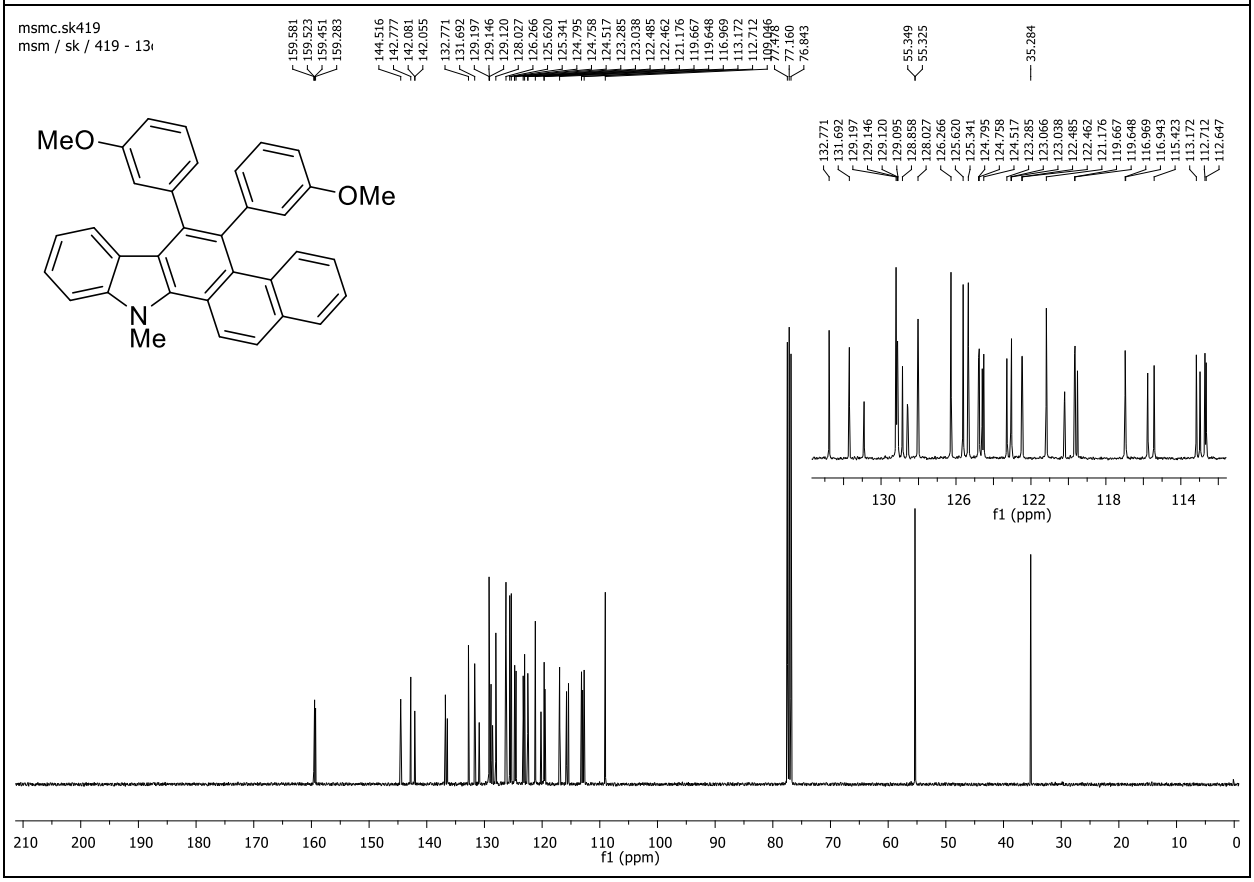
^{1}H and ^{13}C spectra of compound **6e**



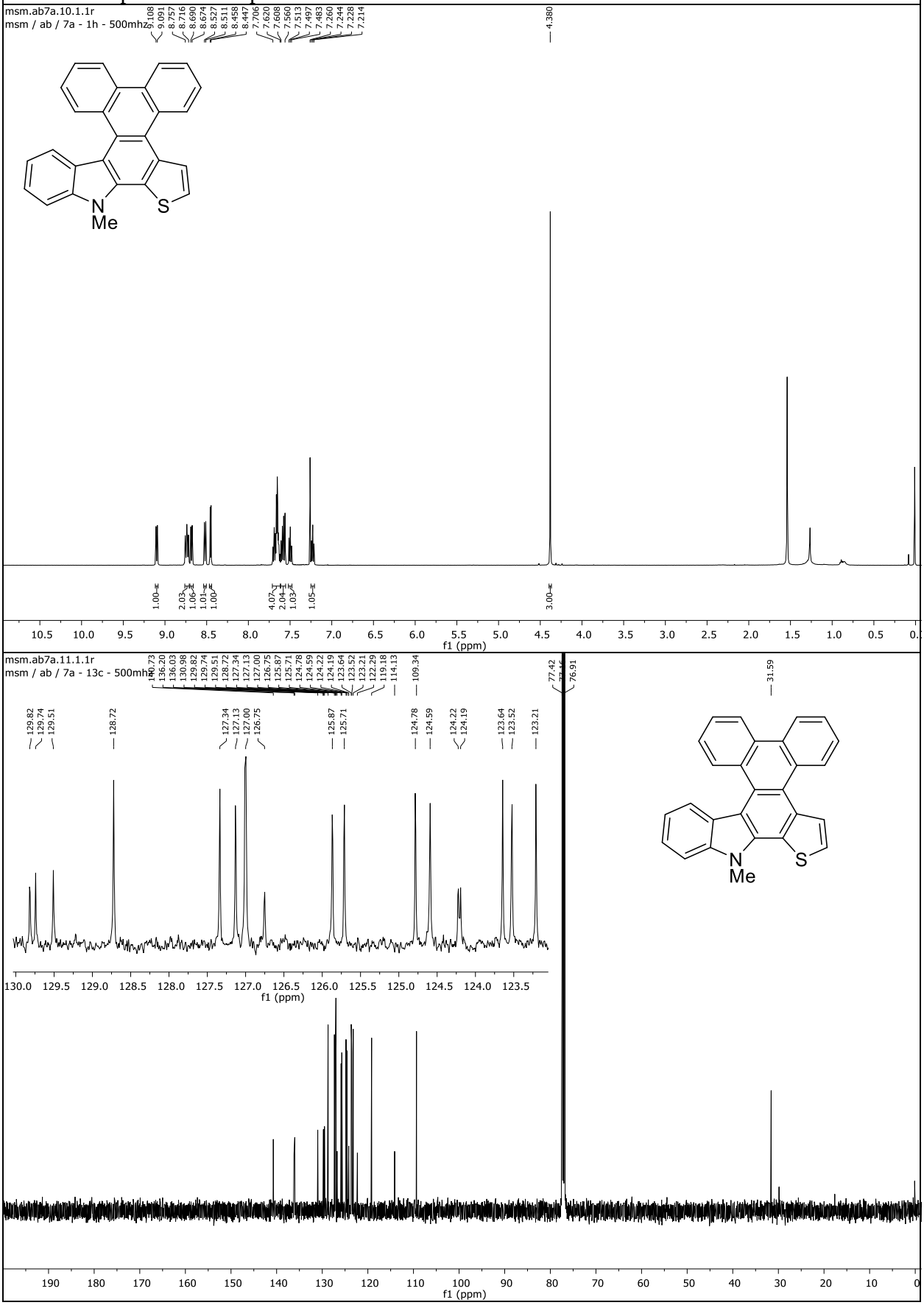


^{1}H and ^{13}C spectra of compound **6f**

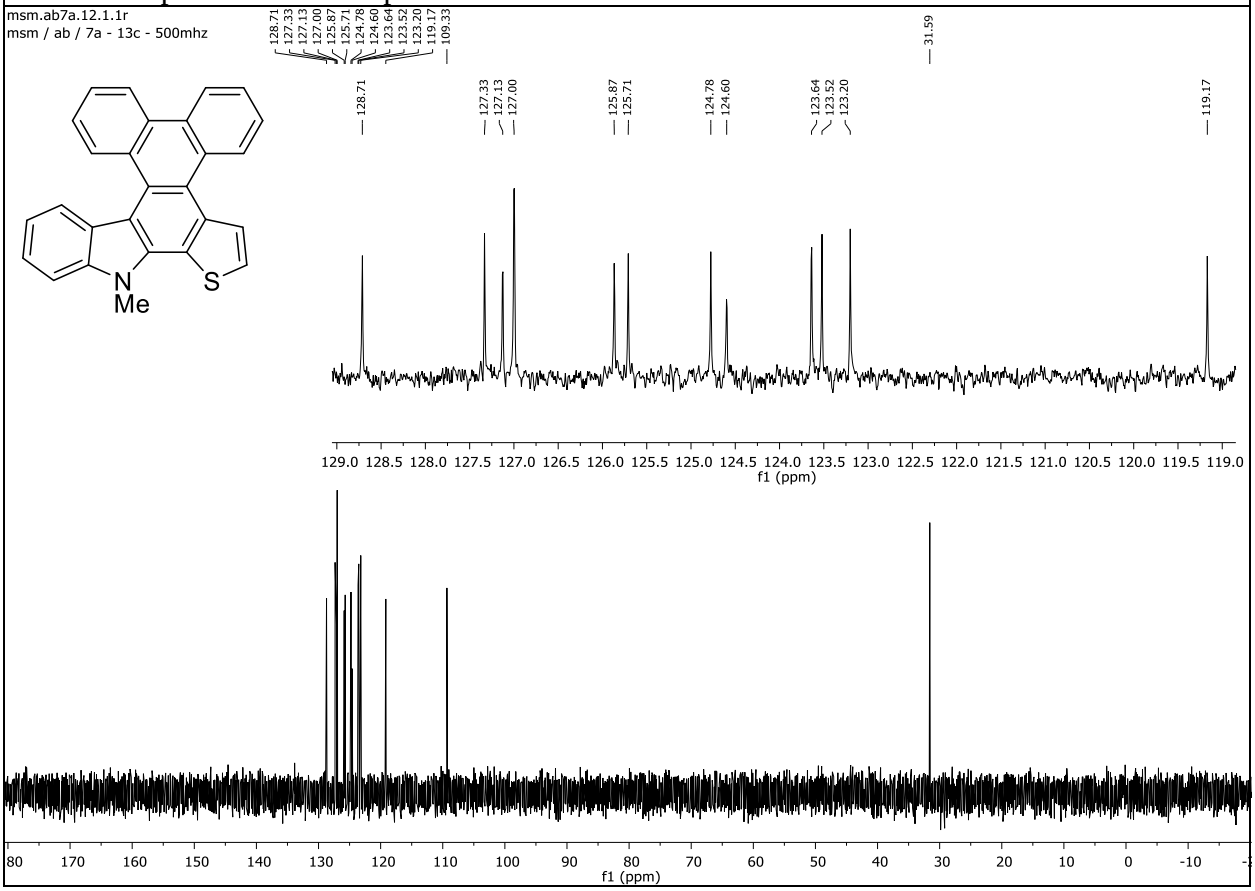




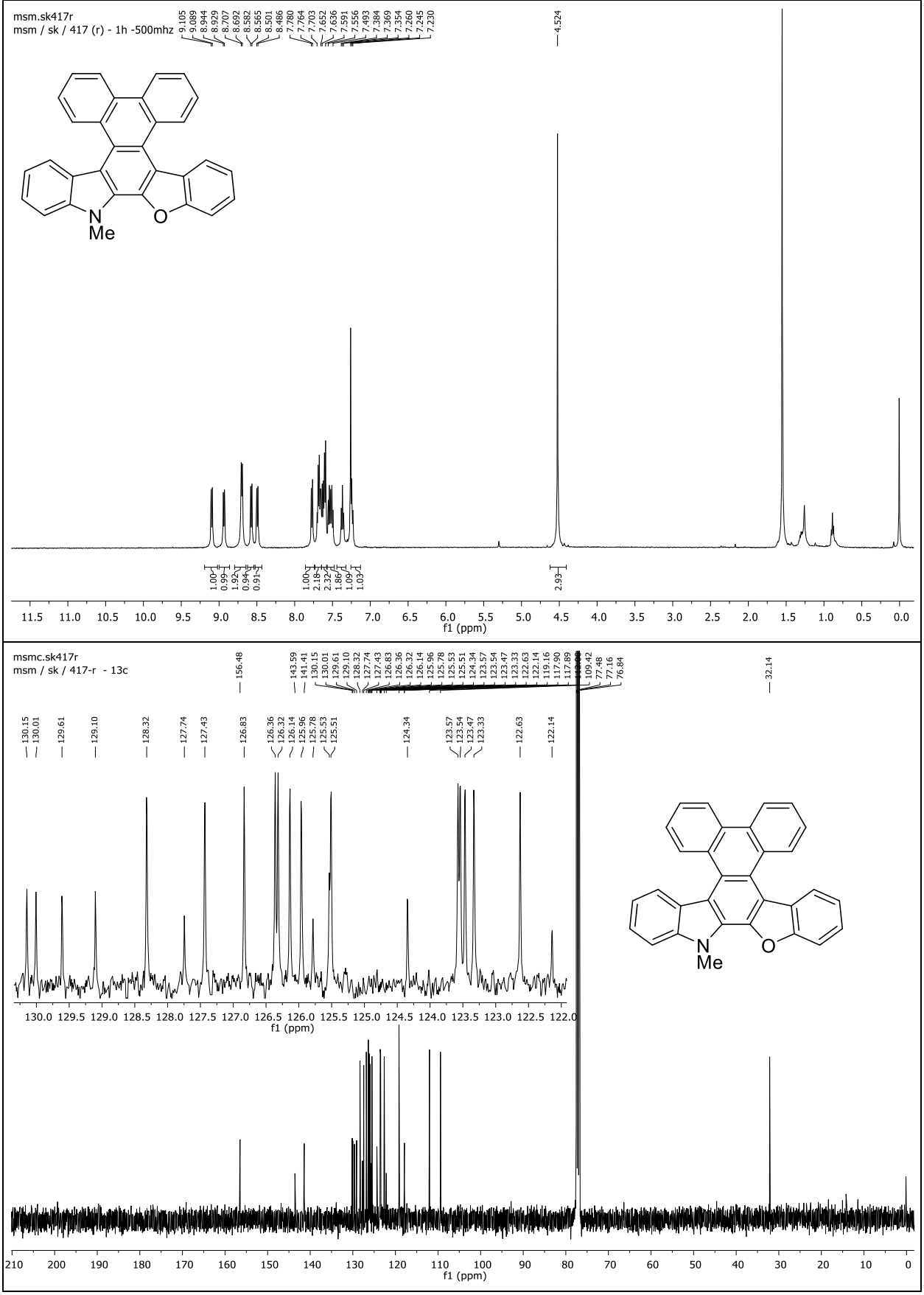
^{1}H and ^{13}C spectra of compound **7a**



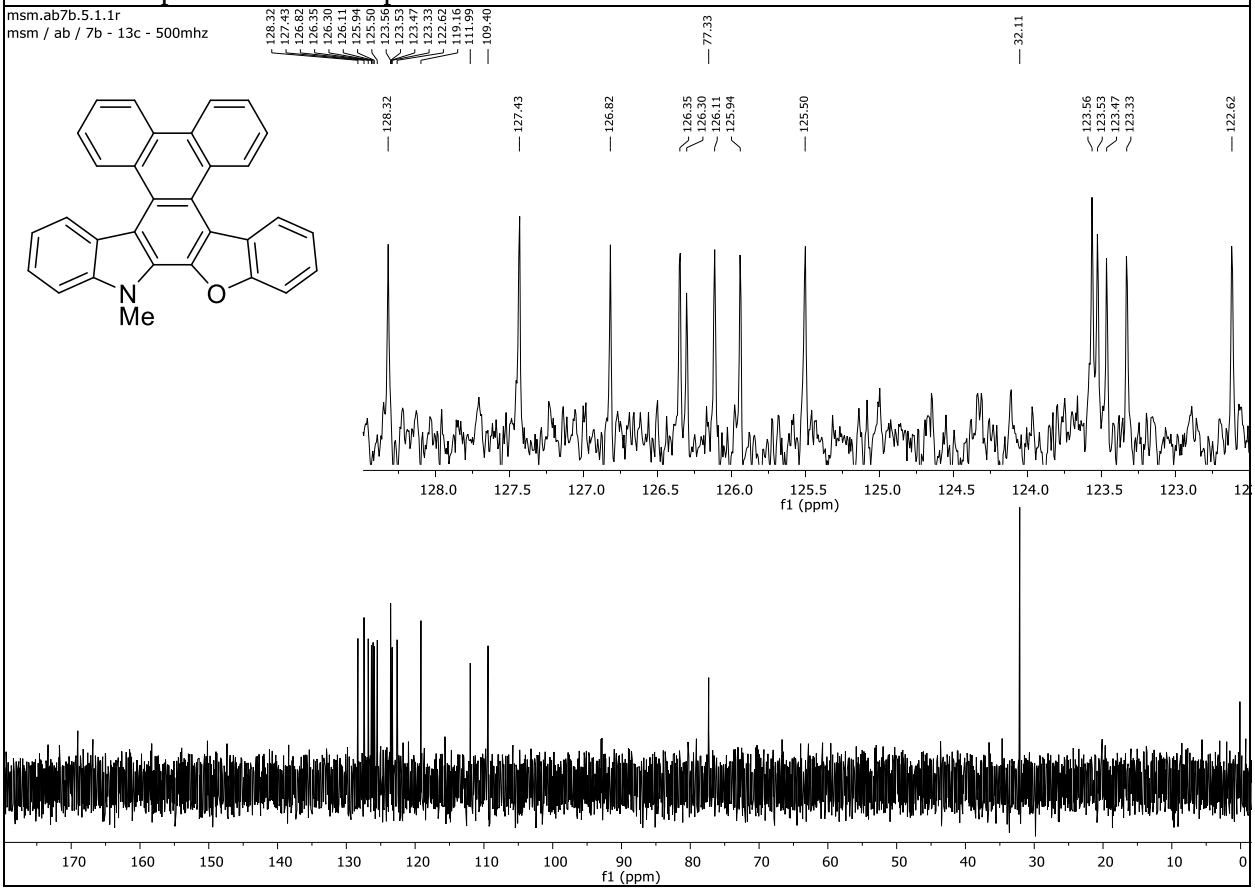
DEPT 135 spectra of the compound **7a**



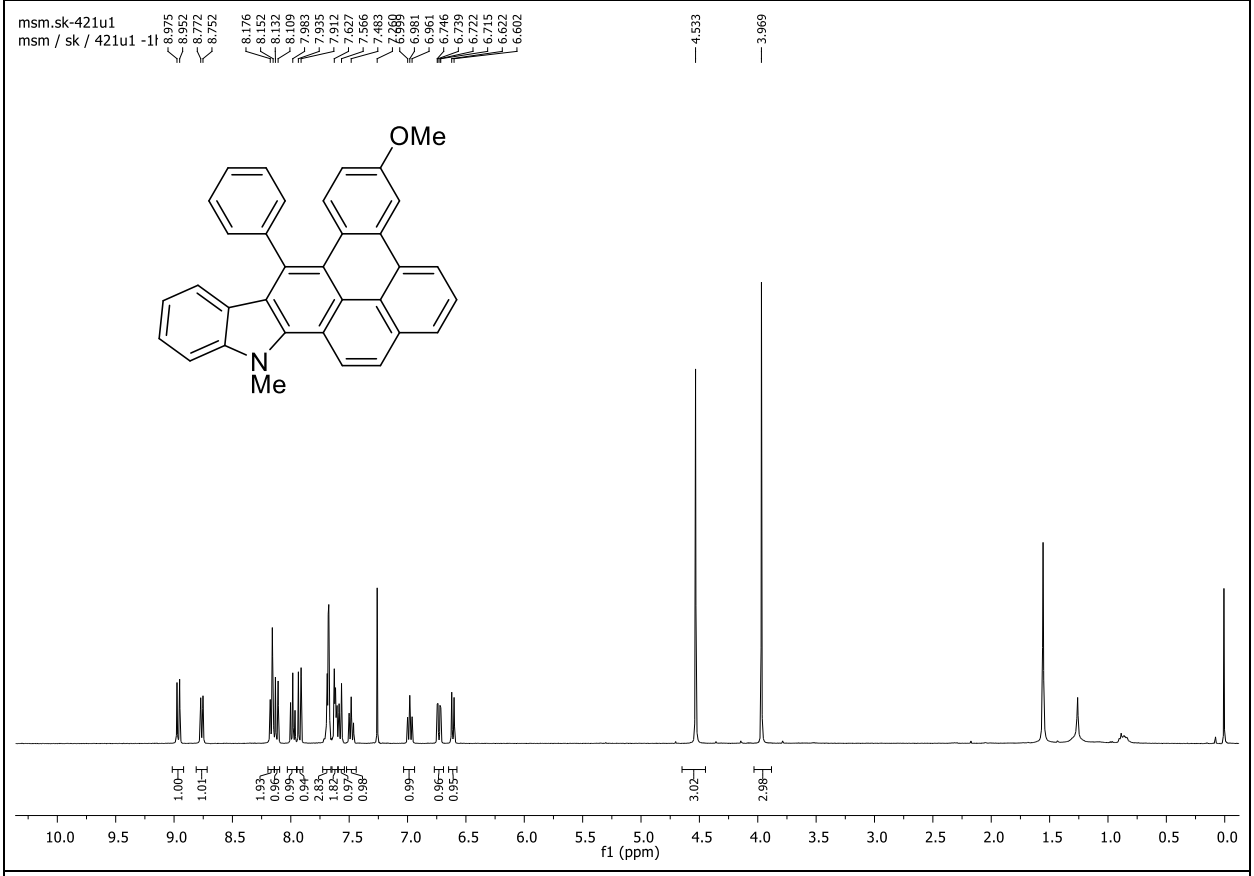
^{1}H and ^{13}C spectra of compound **7b**

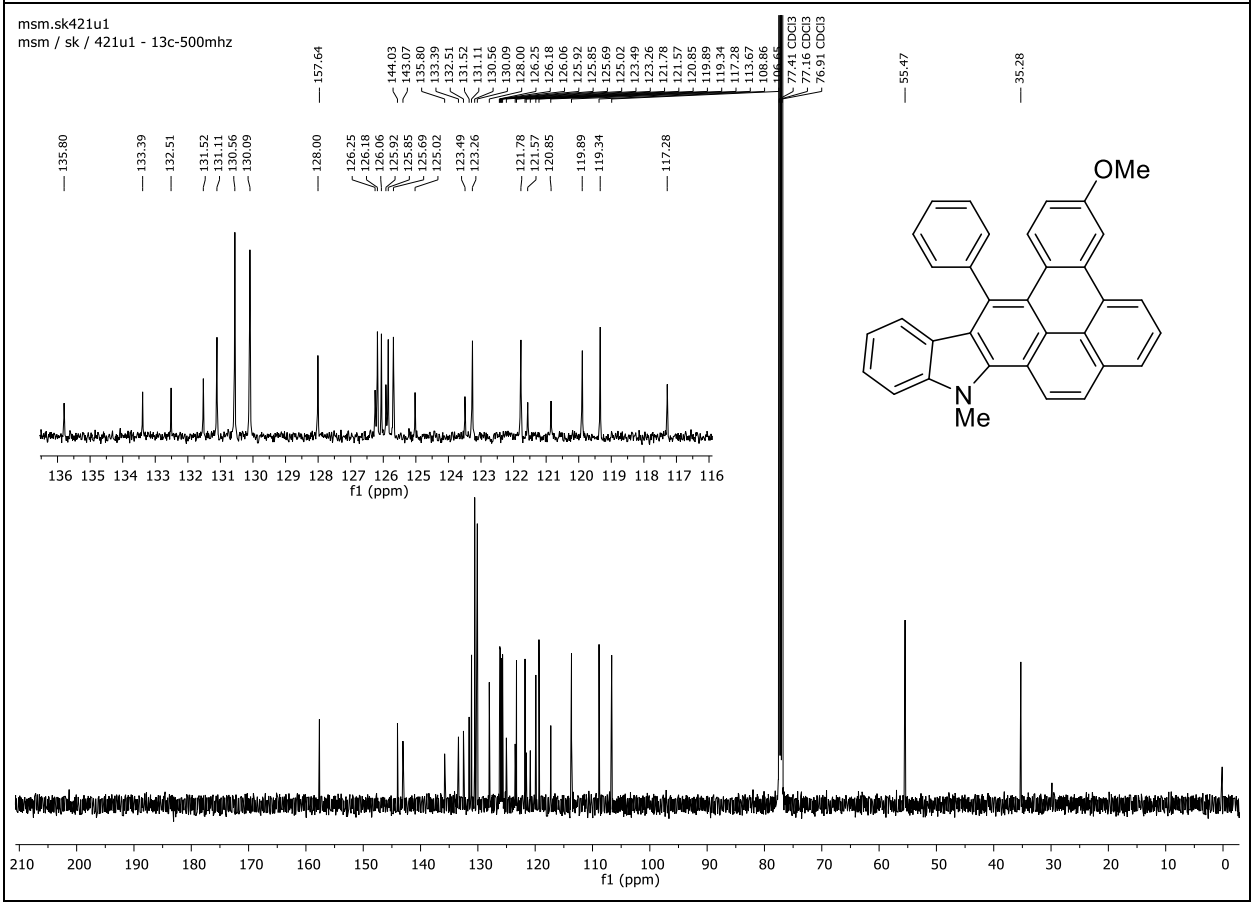


DEPT 135 spectra of the compound **7b**

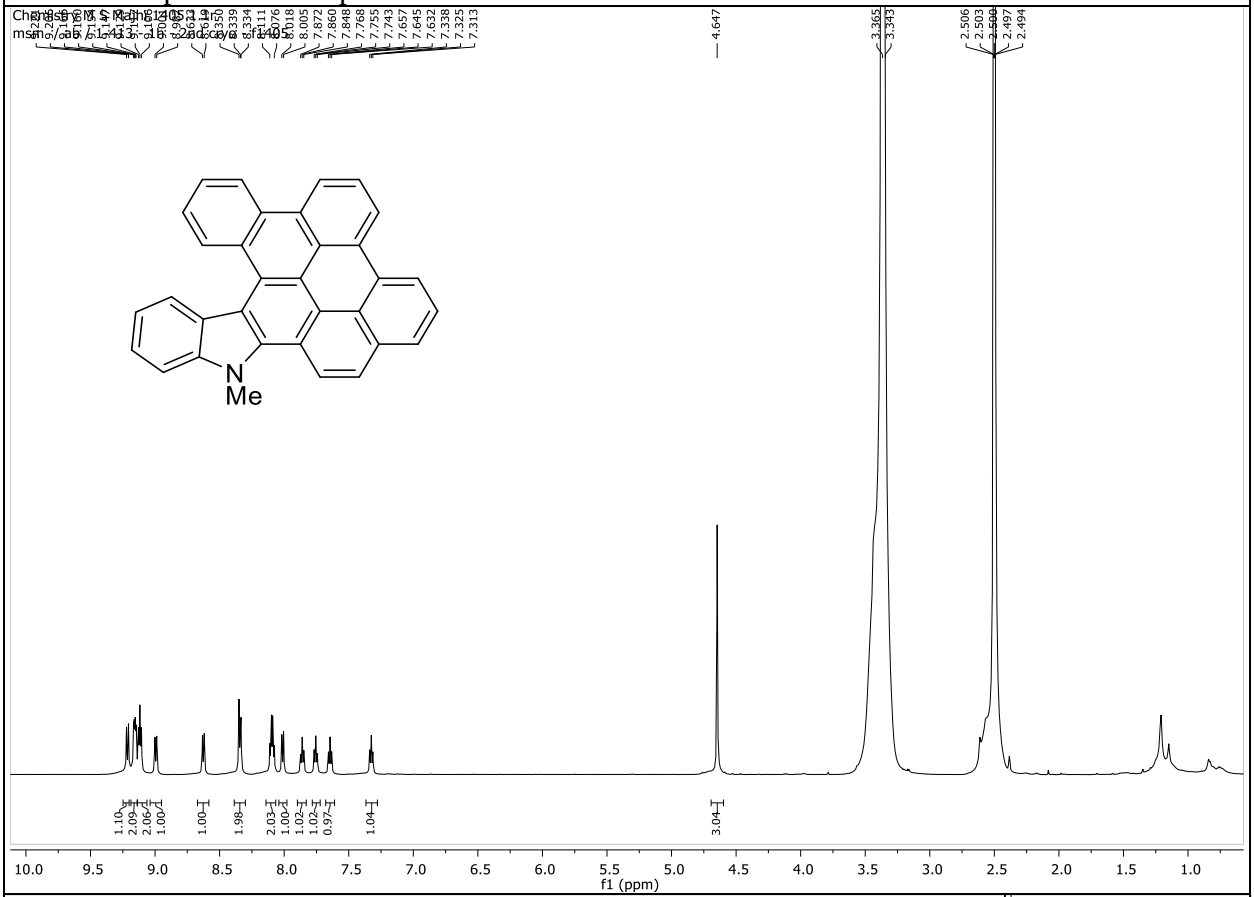


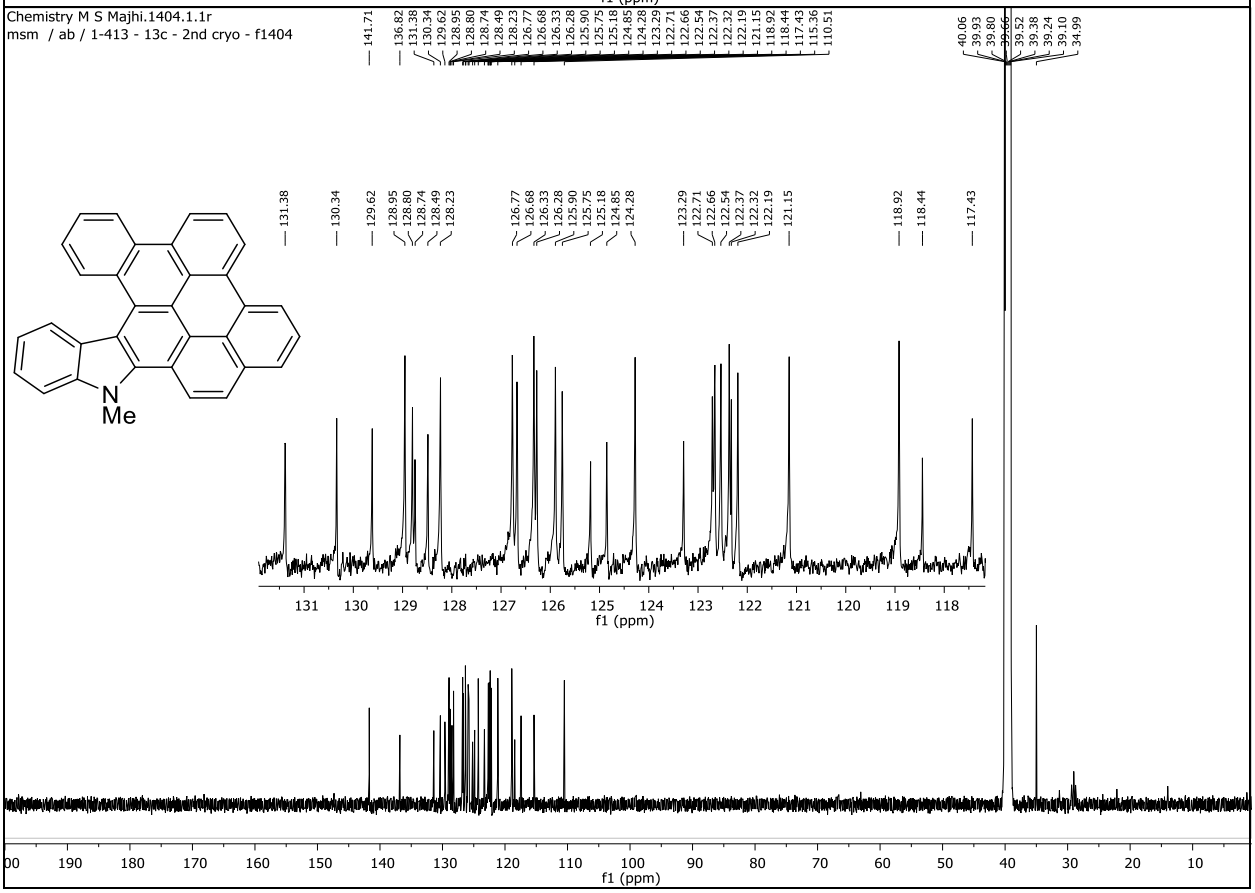
^{1}H and ^{13}C spectra of compound **7c**



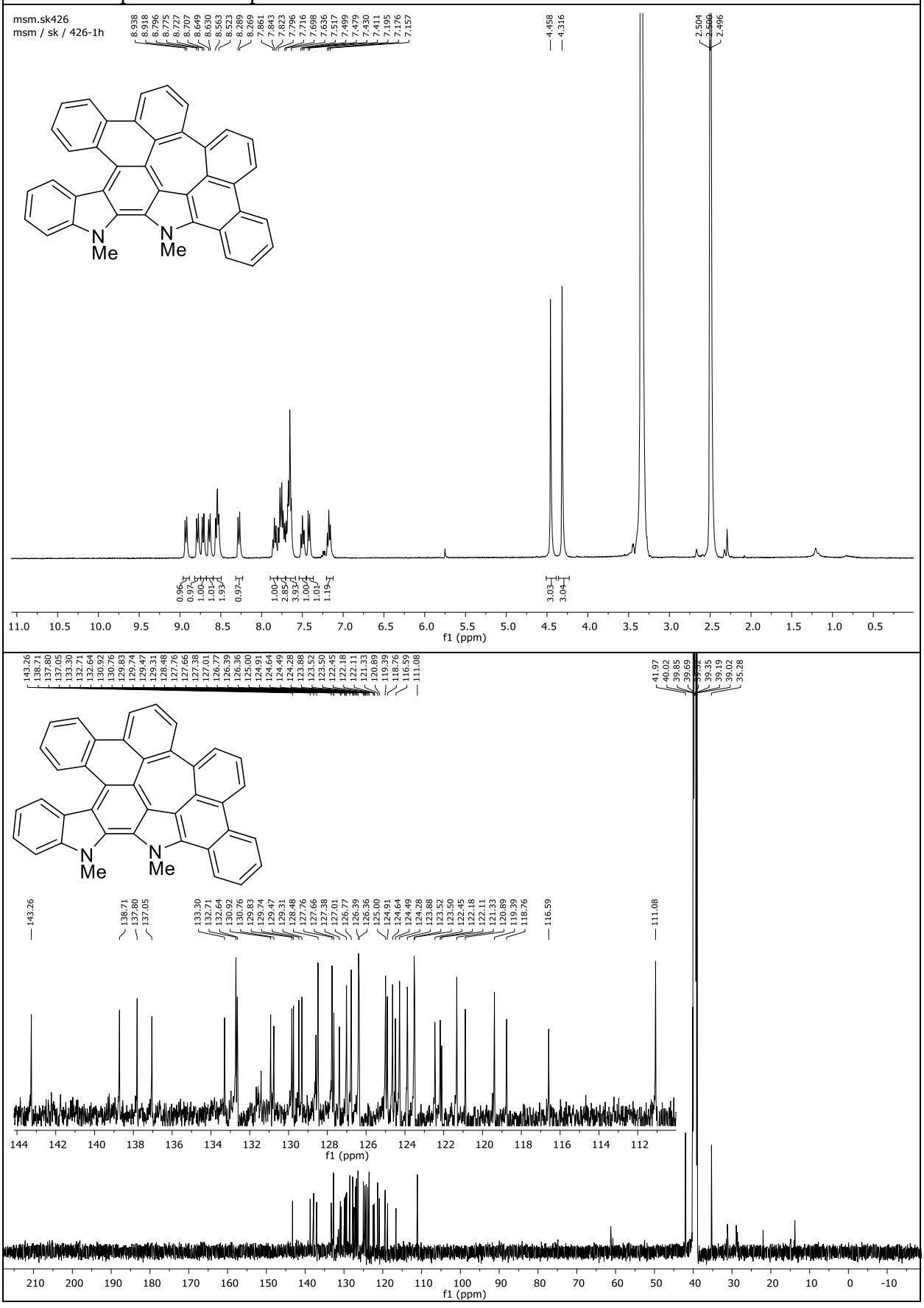


^{1}H and ^{13}C spectra of compound **7d**





^{1}H and ^{13}C spectra of compound **7e**



DEPT 135 spectra of the compound **7e**