Electronic Supplementary Material (ESI) for New Journal of Chemistry.

A Facile Access to 1, 2-Disubstituted Benzimidazoles and 2, 3-Dihydro-1H-Perimidines Using Biogenically Synthesized Single Phase δ-MnO_2 NPs Catalyst and its Dye Removal Study

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1. General Considerations

Unless otherwise specified, the presence of various phytochemicals in *Pongamia pinnata* (*P. pinnata)* leaves extract was analyzed *via* GC-MS technology using SHIMADZU GC-MS QP 2010SE system. UV-Visible analysis was carried out with the help of a PerkinElmer Lambda 360 UV-Visible spectrophotometer. The presence of different functional groups in *P. pinnata* leaves extract and δ-MnO_2 NPs was done by Fourier Transform Infrared Spectroscopy (FT-IR) in a Perkin Elmer FT-IR instrument by KBr pellets method in the range of 4000 to 500 cm^{-1}. The crystallographic nature and the phase of the δ-MnO_2 NPs were as examined and confirmed using powder X-ray diffraction spectroscopy (XRD) noted on a Rigaku X-Ray Diffraction Ultima IV (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 1.5406 Å) with a scan rate of 2^o min^{-1} and theta value range of 10-80° at 30 kV voltage and 15 mA current. The surface area analysis of δ-MnO_2 NPs microspheres was performed using Brunauer Emmet and Teller (BET) method on Belsorp-Max (M/s. Microtrac BEL, Japan) under an N_2 atmosphere at a temperature of -196 ºC. The corresponding pore size distribution of the catalyst was analyzed using Barrett Joyner Halenda's (BJH) method. The catalysts were degassed at 120 ºC for 4 h under vacuum before analysis to push out absorbed moisture. The thermal degradation of δ-MnO_2 NPs was determined by a thermal analyzer within the temperature window of 27 ºC to 900 ºC under continuous N_2 flow with a heating rate of 10 ºC min^{-1}. The morphology and structural identity of δ-MnO_2 NPs microspheres was investigated using Field Emission Scanning Electron Microscope (JEOL JSM-7100F, Singapore) coupled with energy dispersive X-Ray spectroscopy (EDX). The carbon tape on the aluminium metal stub was adequately covered with the powdered sample and subjected to sputtering using gold nanoparticles. All reactions were performed in completely dried glass wares if otherwise specified. All reagents were directly used as purchased without further purification unless otherwise specified. Column chromatography was performed using silica gel (60-120 mesh) and a proper eluent. Chemical shifts were expressed in parts per million (ppm) concerning the solvent peak ($CHCl_3$ in $CDCl_3$: 7.26 ppm). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Broadband proton decoupling was used to fully decouple ^{13}C {^1H} NMR and recorded on an Agilent Technologies DD2 (100 MHz). Chemical changes were measured in parts per million (ppm) and compared to the center of a triplet at 77.0 parts per million (ppm) of $CDCl_3$.

2. Experimental Section

2.1 Synthesis of Manganese Nanoparticles (δ-MnO_2 NPs) using *Pongamia pinnata* leaves extract

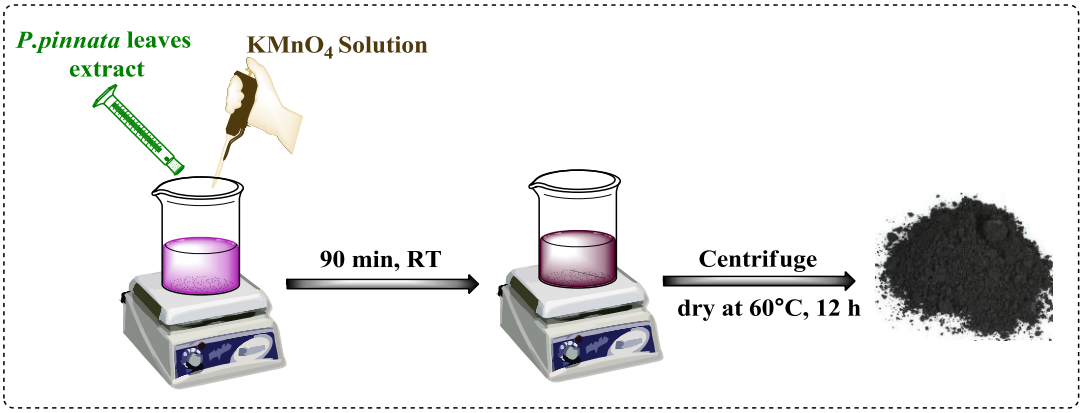
2.1.1. Preparation of *Pongamia pinnata* (*P. pinnata*) leaves extract

Scheme 1. Preparation of *Pongamia pinnata* (*P. pinnata*) leaves extract

P. pinnata is commonly known as Indian beech. Leaves of *P. pinnata* leaves were collected from the campus of Jain University, Ramanagara, India and dried under the sunlight for 3 days. It was then cut into small pieces and ground into a fine powder with the help of mortar and a piston. Later 10g of the leaves powder was taken in a 250ml Erlenmeyer flask containing 150 mL solvent (EtOH:H_2O, 1:1) and stirred at 80 ^oC for 90 minutes. After completion, the mixture was filtered using whatman filter paper and the obtained plant extract was stored in the refrigerator at 4 ^oC for further use.

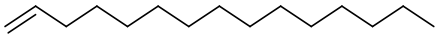
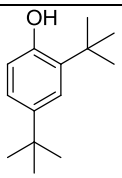
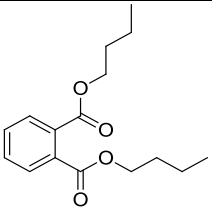
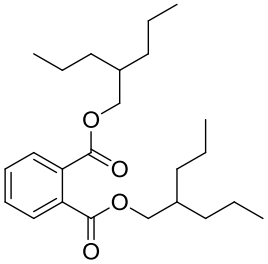
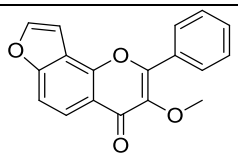
2.1.2. Preparation of δ-manganese oxide nanoparticles (δ-MnO_2 NPs) using *P. pinnata* leaves extract

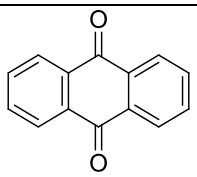
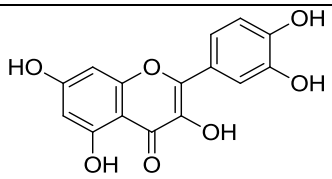
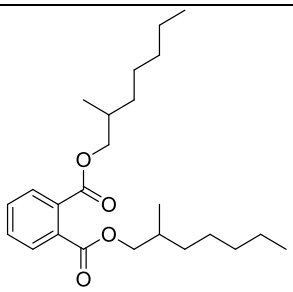
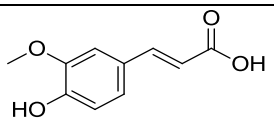
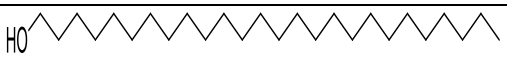
About 0.2 M $KMnO_4$ (948 mg) was weighed and dissolved in 30 ml of deionized water. To the same solution, 20 ml of plant extract was added slowly under continuous stirring at room temperature. During the addition of plant extract, a gradual color change from pink to dark brown was observed over a period. This was monitored and confirmed by the UV- Visible spectral analysis. The phytochemicals present in the plant extract (confirmed through GCMS) were responsible for the reduction indicating the reduction of Mn(VII) to Mn(IV).[79] After completion, the solution was collected and centrifuged at 3500 rpm for 10 minutes with water and acetone (1 x 3). The obtained wet solid δ-MnO_2 NPs were dried at 80 ^oC overnight. Further, the obtained δ-MnO_2 NPs were analyzed and characterized by various analytical techniques.



Scheme 2. Preparation of δ-MnO_2 NPs using Pongamia pinnata (P. pinnata) leaves Extract

2.2. GC-MS data of *P. pinnata* leaves extract:

RT	Area (%)	m/z	Compound Name	Structure
6.825	6.29	210.39	1-Pentadecene	
7.36	11.40	206.36	2,4-Di-tert-butyl-phenol	
8.91	7.35	278.34	Dibutyl phthalate	
8.91	3.27	390.27	Phthalic acid, di(2-propylpentyl) ester	
9.15	12.50	292.07	Karanjin (flavonoid)	

10.38	5.11	208.05	Anthraquinone	
10.38	5.11	302	Quercetin (polyphenol)	
10.86	17.90	390.27	Bis(2-ethylhexyl) phthalate	
11.04	3.08	194	Ferulic acid (phenolic)	
11.85	5.06	382.41	1-Hexacosanol	

2.3 The long term stability test for δ-MnO_2 NPs

The *P*-XRD of δ-MnO_2 NPs after 3 months of preparation shows the long term stability of the catalyst (Figure 1). The powdered sample δ-MnO_2 contains relatively smaller crystallite size organized in completely random orientation owing to the broader diffraction patterns with significant width and overlapping. That may lead to the occurrence of numerous lines in the (002) and (-111) planes, causing the broadening and intensification of 26.93° and 37.26° diffraction patterns.

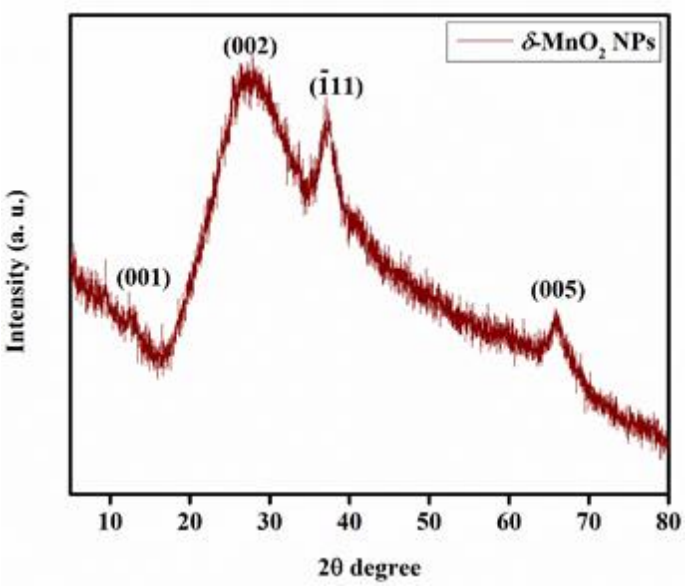
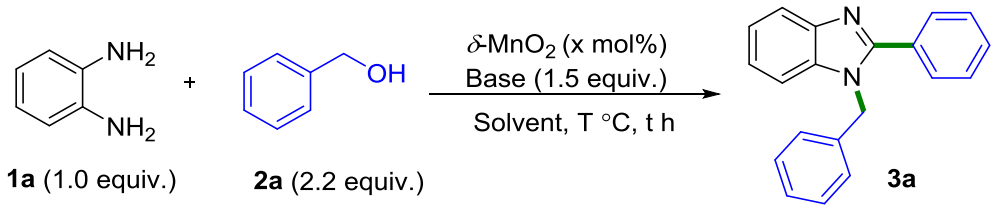


Figure 1. *P*-XRD of δ-MnO_2 NPs after 3 months: long term stability

3. General experimental procedure for synthesis of 1-benzyl-2-aryl-1H-benzo[d]imidazole derivatives and 2, 3-Dihydro-1H-Perimidine Derivatives:

The δ-MnO_2 NPs (0-20 mol%, Mn content: 59%w/w) were added in a 15 ml oven-dried sealed tube containing compound **1** (0.5 mmol, 1 equiv.). To the same reaction mixture, base (0-0.75 mmol, 0-1.5 equiv.) and benzyl alcohol **2** (1.2 mmol, 2.2 equiv.) were added along with the solvent (3 ml). The mixture was heated to 100-140 ^{o}C for 18-36 h. After complete conversion of starting material (monitored by TLC), the reaction mixture was filtered using whatman filter paper to remove the catalyst. Further, the extraction of the synthesized compound was carried out using ethyl acetate (EtOAc) and brine solution (10x3). Then the organic layer was dried over anhydrous Na_2SO_4 and evaporated using a rotary evaporator. The crude compound was purified by column chromatography (eluent: 10-12 % EA/Hexane) to get compound **3.** The reaction was repeated twice and product was isolated to determine the yield (by average of two run). Similar procedure was followed to synthesize 2, 3-Dihydro-1H-Perimidines by changing the base to get the compound **5**. The reaction was repeated twice and product was isolated to determine the yield (by average of two run).

Table 1. Optimization of reaction condition[a]



1a (1.0 equiv.) **2a** (2.2 equiv.) **3a**

Entry	Base	Solvent	T (°C) /t (h)	Yield 3a (%)[f]
1	*t*-BuOK	Toluene	100/36	(trace)
2	*t*-BuOK	Toluene	120/36	(50)
3	*t*-BuOK	**Toluene**	**140/36**	**(75)**
4	*t*-BuOK	Toluene	140/18	(trace)
5	*t*-BuOK	Toluene	140/24	(25)
6	NaOAc	Toluene	140/36	(65)
7	KOH	Toluene	140/36	(30)
8	K_2CO_3	Toluene	140/36	(32)
9	Cs_2CO_3	Toluene	140/36	(51)
10[b]	*t*-BuOK	Toluene	140/36	(53)
11[c]	-	Toluene	140/36	(trace)
12[d]	*t*-BuOK	Toluene	140/36	(40)
13	*t*-BuOK	Toluene	140/36	(trace)
14	*t*-BuOK	1,4-Dioxane	140/36	(67)
15	*t*-BuOK	THF	140/36	(45)
16	*t*-BuOK	MeCN	140/36	(trace)
17	*t*-BuOK	DMF	140/36	(trace)

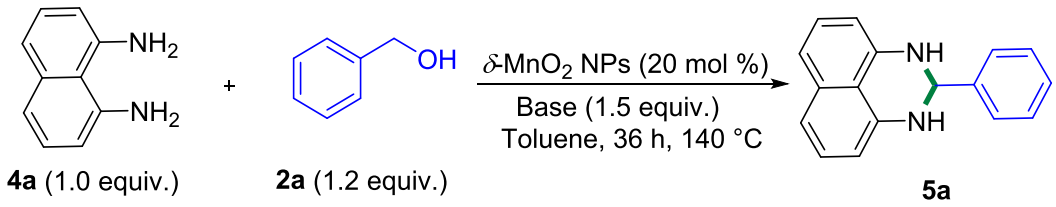
a) reaction condition: **1** (0.5 mmol), **2** (1.2 mmol), δ-MnO_2 NPs (0-20 mol%, 59% w/w), base (0-0.75 mmol, 1.5 equiv.), solvent (3 mL), at 100-140 °C in 20-36 h, b) 1.0 equiv. base, c) no base, d) δ-MnO_2 (10 mol%), e) no catalyst, f)Yields are reported after purification from the silica column (average of two runs).

4. Experimental Procedure for the synthesis of 1-benzyl-2-aryl-1H-benzo[d]imidazole and 2, 3-Dihydro-1H-Perimidine derivatives (5):

To the solution of Benzyl alcohol **2a** (1.2 mmol, 2.2 equiv.) in toluene solvent was added o-phenylenediamine **1a** (0.5 mmol, 1 equiv.) which is taken in oven-dried 15 ml sealed tube. To the same mixture, δ-MnO_2 NPs (20 mol%, 59 w/w) and *t*-BuOK (0.75mmol, 1.5 equiv.) were added

and the resulting reaction mixture was stirred at 140 °C for 36 h. After complete conversion of starting material (monitored by TLC) the reaction mixture was cooled to room temperature and was filtered using whatman filter paper to remove the catalyst followed by the extraction process using EtOAc and brine solution (10x3). Then the organic layer was dried over anhydrous Na_2SO_4, then the solvent was evaporated using a rotary evaporator. The crude compound obtained was purified by performing column chromatography (eluent: 18-25% EA/Hexane) to get compound **3a** as a white solid. Similar procedure was followed to synthesize 2, 3-Dihydro-1H-Perimidines by changing the base from *t*-BuOK to Cs_2CO_3. The crude compound was purified by column chromatography (eluent: 2-4% EA/Hexane) to get the compound **5a**. The reaction was repeated twice and product was isolated to determine the yield (by average of two run).

Table 2. Optimization of reaction condition[a]



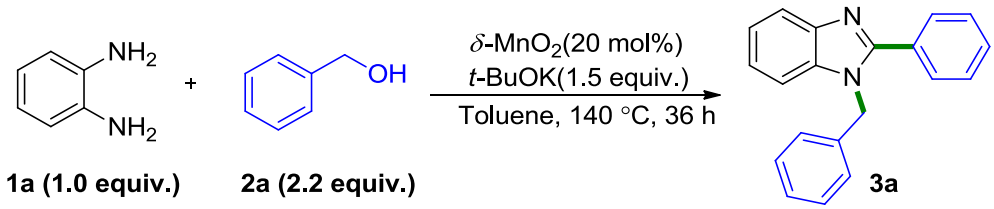
4a (1.0 equiv.) **2a** (1.2 equiv.) **5a**

Entry	Catalyst (mol %)	Solvent	Base	T(°C) /t (h)	Yield 5a (%)[b]
01	20	Toluene	*t*-BuOK	140/36	70
02	**20**	**Toluene**	**Cs_2CO_3**	**140/36**	**95**
03	20	Toluene	KOH	140/36	60
04	20	Toluene	NaOAc	140/36	65

a) Reaction condition: **4a** (0.5 mmol), **2a** (0.6 mmol), *δ*-MnO_2 NPs (20 mol%, Mn content: 59% w/w), base (0,75 mmol, 1.5 equiv.), solvent (2 mL), at 140 °C in oil bath for 36 h. b)Yields are reported after purification from the silica column (average of two runs).

Further, to improve the yield of **5a**, base screening was performed where in increase in the yield from 75 % to 95 % isolated yield was observed with respect to Cs_2CO_3.

5. Representative procedure for gram scale synthesis of disubstituted benzimidazole:



The δ-MnO_2 NPs (150 mg, 20 mol%, 59 w/w) was taken in oven dried 60 mL sealed tube containing *t*-BuOK (1.55g, 0.75mmol, 1.5 equiv.), compound **1a** (1g, 0.5 mmol, 1 equiv.) and Benzyl alcohol **2a** (2.19 g, 1.2mmol, 2.2 equiv.) followed by addition of 10 mL toluene. Then the reaction mixture was stirred at 140 °C for 36 h. The completion of the reaction was monitored by TLC, the reaction was quenched with water and the organic layer was extracted with EtOAc (30x3). The collected organic layer was dried over Na_2SO_4 and the solvent was evaporated using rotary evaporator. The obtained crude product was purified by column chromatography (eluent-25% EA/Hexane) to get the pure product **3a** (1.88 g, 72%).

6. Control Experiment:

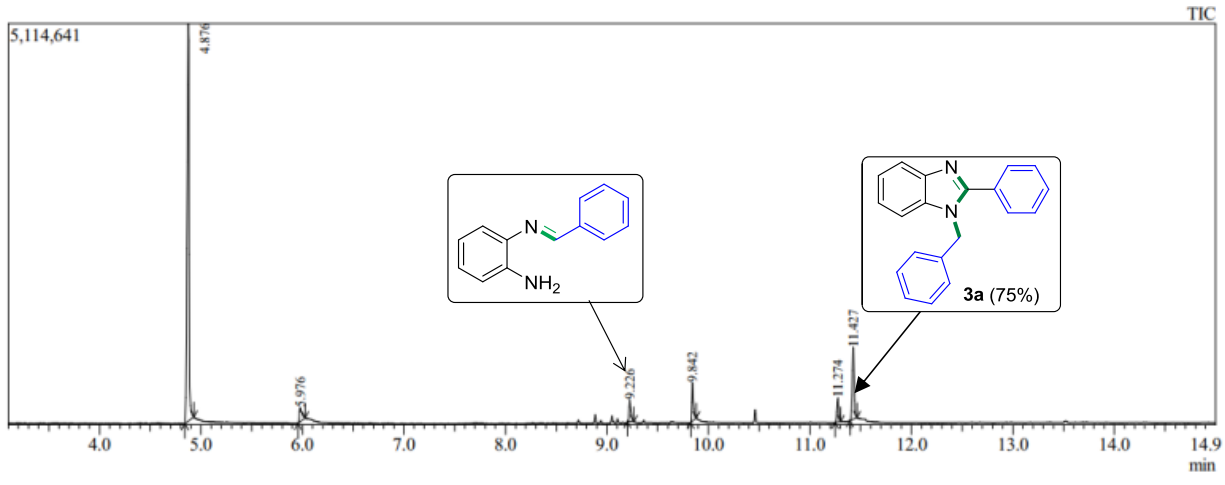


Figure 2. GCMS data for monoamine formation

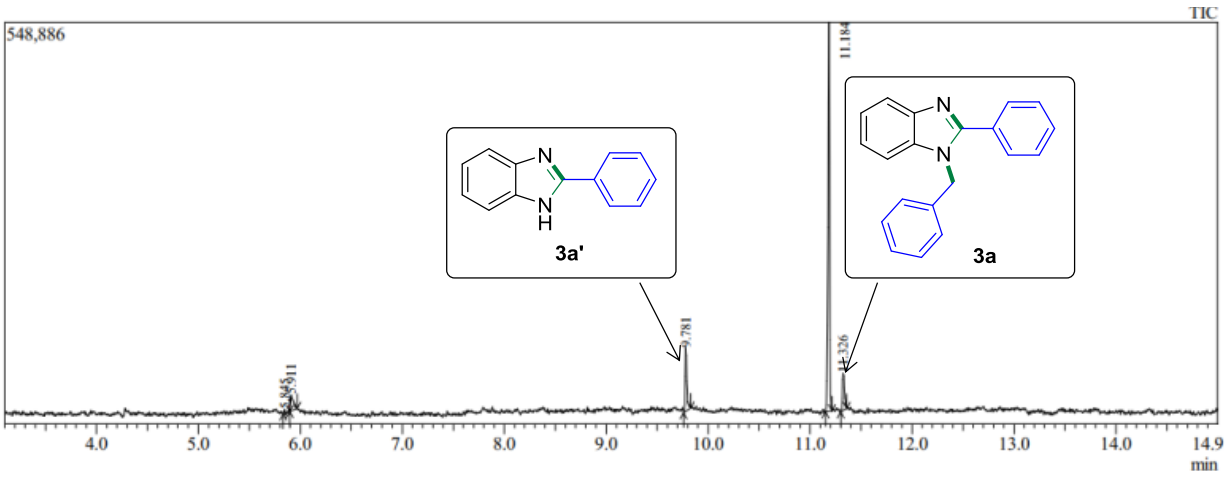


Figure 3. GCMS data for scheme 2b right

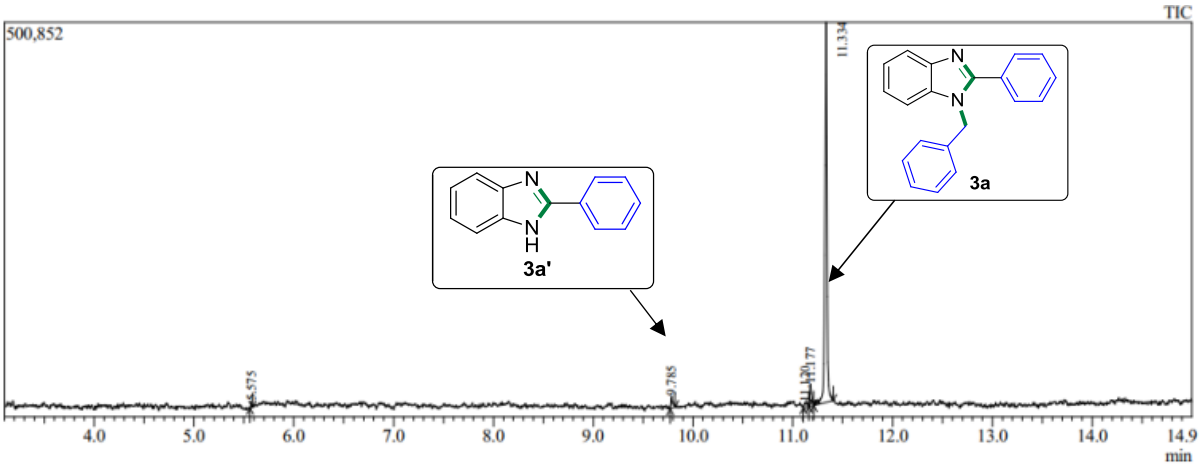


Figure 4. GCMS data for scheme 2b left

7. Catalyst recyclability study:

Recyclability of the catalyst was examined up to 3 cycles (Fig. S4) especially in the case of 1-benzyl-2-aryl-1H-benzo[d]imidazole synthesis under optimized conditions. Once the reaction is completed (indicated by TLC), the catalyst was separated from the reaction mixture by centrifugation. Then the catalyst was washed with water(3 x 10 mL) followed by ethanol (3 x 10 mL) and dried at 60 °C for 12 hours which is used for the next cycle. The desired product (**3a**) was isolated in every cycle where the drop in yield was observed. (75% in 1st cycle, 56% in 2nd cycle and 38 % in 3rd cycle). About 40 mg weight loss was observed in 1st cycle, while 50 mg and 55 mg weight loss was observed in consecutive 2nd and 3rd cycles. Further, the recycled catalyst was

subjected to different spectroscopic analyses in which the XRD of the recycled catalyst reflects the change in the crystalline phase which may be due to the change in the oxidation state of the metal under the standard reaction conditions (Figure 4a-4c). FESEM images of the recycled catalyst showed disrupted spherical morphology of δ-MnO_2 NPs which is due to the detachment of phytochemicals adhered to the metal center. (Figure 4d-4f).

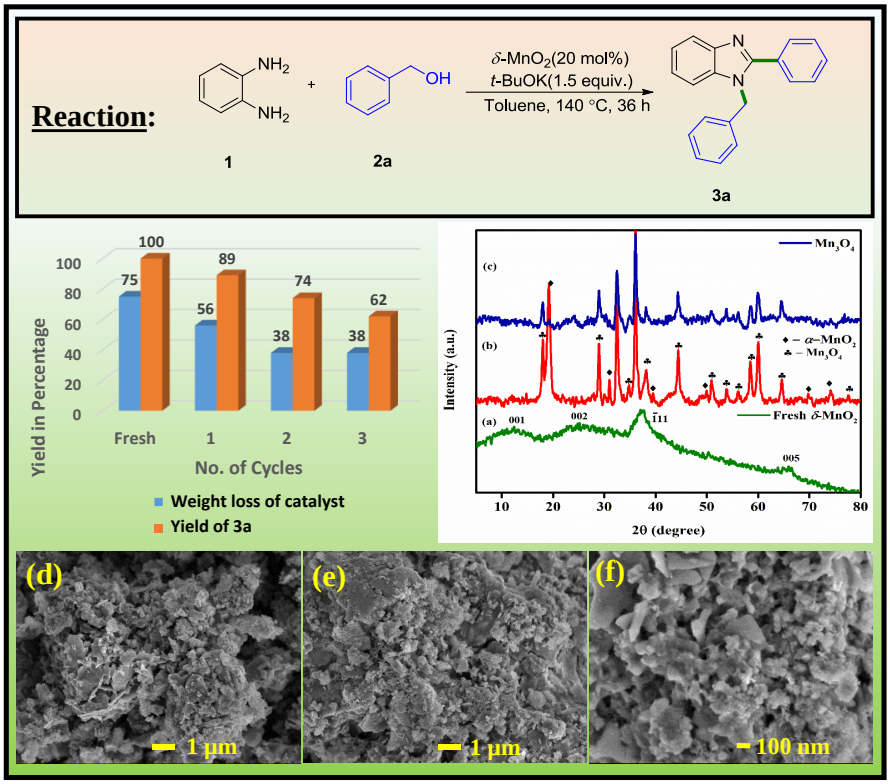


Figure. 5 Catalyst recyclability study

8. Hot filtration test

A hot filtration test was performed during the disubstituted benzimidazole synthesis process under typical reaction conditions for 12 hours, at the conclusion of which the reaction mixture was filtered to remove the catalyst in order to determine the leaching of the δ-MnO_2 NPs catalyst. The filtrate was additionally agitated for up to 36 hours, during which the presence of oxidized aldehyde caused a little rise in the yield of the desired product. The catalyst's heterogeneous nature during the benzimidazole synthesis was confirmed by this hot filtration test

9. Dye removal study:

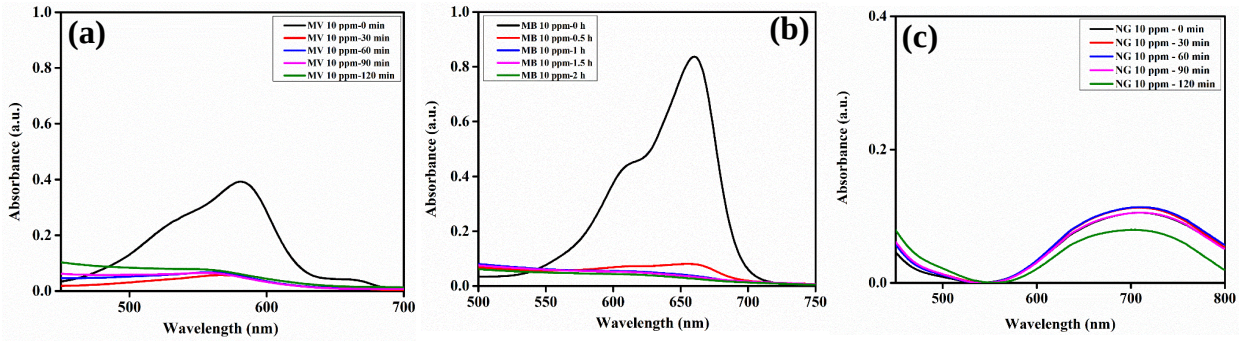


Figure 6: UV-Visible spectrum for 10 ppm concentration of (a) Methyl violet, (b) Methylene blue and (c) Naphthalene green removal study

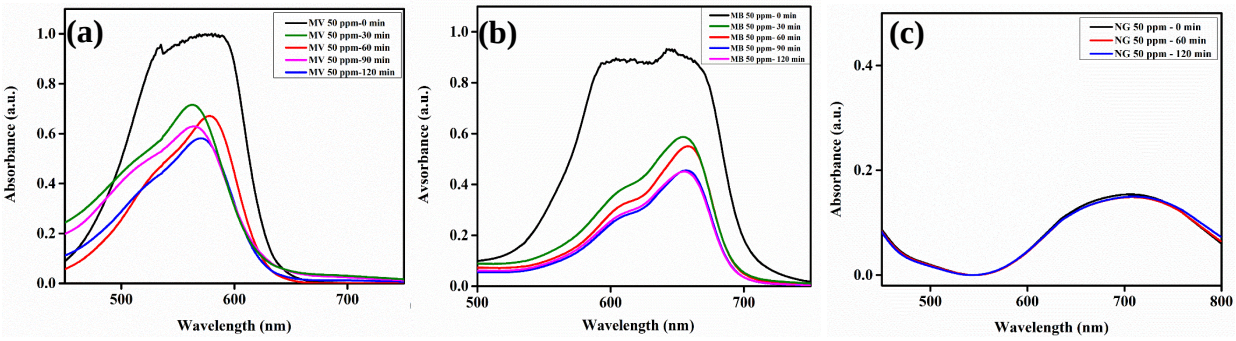
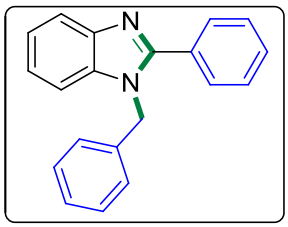


Figure 7: UV-Visible spectrum for 50 ppm concentration of (a) Methyl violet, (b) Methylene blue and (c) Naphthalene green removal study

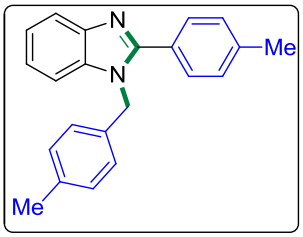
10. Spectroscopic data of 1-benzyl-2-aryl-1H-benzo[d]imidazole and 2, 3-Dihydro-1H-Perimidine derivatives

1-benzyl-2-phenyl-1H-benzo[d]imidazole (3a)



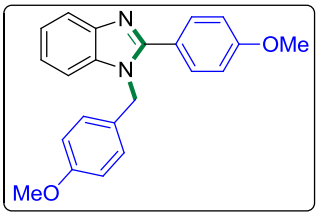
Purified by column chromatography, White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 (d, J = 6.4 Hz, 1H), 7.66 (d, J = 5.2 Hz, 2H), 7.42 – 7.38 (m, 3H), 7.26 (q, J = 12.8 Hz, 6.8 Hz, 4H), 7.20 – 7.14, m, 2H), 7.05 (d, J = 6.0 Hz, 2H), 5.39 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 154.2, 143.2, 136.4, 136.1, 129.9, 129.3, 129.1, 128.8, 127.8, 126.0, 123.0, 122.7, 120.0, 110.6, 48.1. MS m/z Calculated for $C_{20}H_{16}N_2$ $(M + H)^+$, 285.4, found: 285.1.[S1]

1-(4-methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole (3b)



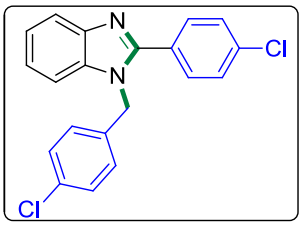
Purified by column chromatography, White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.26 – 7.23 (m, 2H), 7.21 – 7.17 (m, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 7.6 Hz, 2H), 5.39 (s, 2H), 2.39 (s, 2H);); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 154.2, 142.9, 140.1, 137.4, 136.0, 133.3, 129.9, 129.7, 129.4, 129.1, 128.8, 126.9, 125.8, 122.9, 122.6, 119.7, 110.5,48.1, 21.4, 21.1; HRMS for $C_{22}H_{21}N_2$ $(M+H)^+$, 313.1660 found, 313.1700. [S1]

1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (3c)



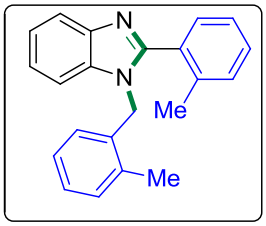
Purified by column chromatography, White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, J = 6.4 Hz, 1H), 7.63 (d, J = 7.2 Hz, 2H), 7.31 – 7.21 (m, 3H), 7.03 (d, J = 7.2 Hz, 2H), 6.95 (d, 6.8 Hz, 2H), 6.85 (d, J = 6.8 Hz, 2H), 5.38 (s, 2H), 3.83 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 161.0, 159.2, 154.2, 143.2, 136.2, 130.8, 128.6, 127.3, 122.9, 122.7, 122.5, 119.8, 114.5, 114.3, 110.6, 55.5, 55.4, 48.0; HRMS m/z calculated for $C_{22}H_{20}N_2O_2$ $(M+H)^+$, 345.1558 found: 345.1576. [S1]

1-(4-Chlorobenzyl)-2-(4-chlorobenzyl)-1H-benzo[d]imidazole (3d)



Purified by column chromatography, White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.21 – 7.17 (m, 4H), 7.09 (d, J = 6.91 (d, J = 8.4 Hz, 2H), 5.24 (s, 2H); 2H), 6.85 (d, J = 6.8 Hz, 2H), 5.38 (s, 2H), 3.83 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 153.0, 143.0, 139.7, 136.5, 135.9, 134.7, 134.0, 133.2, 130.5, 129.5, 129.3, 128.7, 128.3, 127.4, 123.6, 123.2, 120.2, 110.5, 64.4, 47.9; MS (APCI) m/z calculated for $C_{20}H_{14}Cl_2N_2$ $(M + H)^+$, 354.05, found: 354.2. [S1]

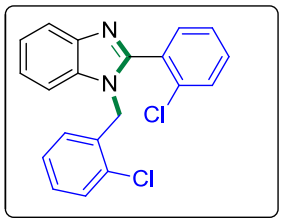
1-(2-methylbenzyl)-2-(o-tolyl)-1H-benzo[d]imidazole (3e)



Purified by column chromatography, White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79 (d, J = 8.0 Hz, 1H), 7.29 – 7.27 (m, 4H), 7.15 – 7.03 (m, 5H), 6.96 – 6.92 (m, 1H), 6.55 (d, J = 7.6 Hz, 1H), 5.09 (s, 2H), 2.15 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 153.9, 143.1, 138.4, 135.0, 134.8, 134.0, 130.6, 130.4, 129.9, 129.9, 129.8, 127.6, 126.4, 126.0,

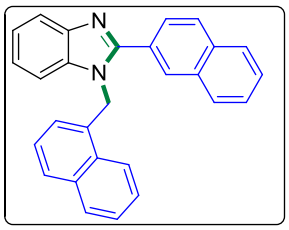
125.7, 122.9, 122.4, 120.0, 110.6, 45.8, 19.8, 19.1; HRMS: Calculated for $C_{22}H_{20}N_2$ $(M+H)^+$ 313.1660, found 313.1706. [S2]

1-(2-Chlorobenzyl)-2-(2-chlorobenzyl)-1H-benzo[d]imidazole (3f)



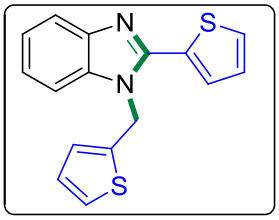
Purified by column chromatography, Brown solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79 (d, J = 8.0 Hz, 1H), 7.56 (dd, J = 7.6 Hz, 1.6 Hz, 2H), 7.38 – 7.34 (m, 3H), 7.24 – 7.15 (m, 3H), 7.06 (t, J = 7.0 Hz, 2H), 6.67 (d, J = 7.6 Hz, 1H), 5.41 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 154.2, 143.1, 135.9, 133.8, 132.3, 132.1, 130.9, 130.7, 130.1, 129.8, 129.0, 128.9, 127.5, 127.0, 123.3, 122.9, 120.1, 110.3, 46.4. MS (APCI) m/z calculated for $C_{20}H_{14}Cl_2N_2$ $(M + H)^+$, 354.05, found: 354.2. [S1]

1-(naphthalen-1-ylmethyl)-2-(naphthalen-2-yl)-1H-benzo[d]imidazole (3g)



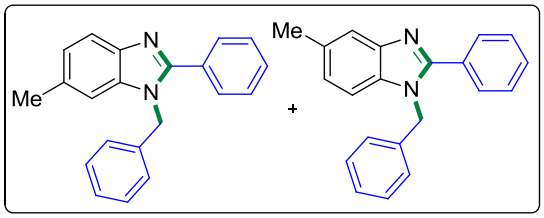
Purified by column chromatography, White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (d, J = 8.0 Hz, 2H), 7.93 – 7.85 (m, 3H), 7.74 (d, J = 8.0 Hz, 2H), 7.57 – 7.43 (m, 5H), 7.39 – 7.35 (m, 2H), 7.30 – 7.21 (m, 3H), 6.83 (d, J = 7.2 Hz, 1H), 5.72 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 153.2, 143.3, 135.4, 133.7, 133.6, 132.3, 131.2, 130.4, 130.2, 129.0, 128.4, 128.3, 128.2, 127.4, 127.3, 126.5, 126.4, 126.0, 125.6, 125.5, 124.9, 123.6, 123.2, 122.7, 122.1, 120.3, 110.8, 46.2; MS (APCI) m/z calculated for $C_{28}H_{20}N_2$ $(M + H)^+$ 385.1, found: 385.3. [S1]

2-(Thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1H-benzo[d]imidazole (3h)



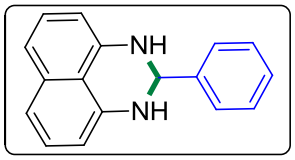
Purified by column chromatography, Brown solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (d, J = 6.8 Hz, 1H), 7.47 (d, J = 5.2 Hz, 1H), 7.43 (d, J = 3.6 Hz, 1H), 7.34 – 7.32 (m, 1H), 7.29 – 7.22 (m, 2H), 7.20 (d, J = 5.2 Hz, 1H), 7.14 – 7.09 (m, 1H), 6.92 – 6.90 (m, 1H), 6.83 – 6.82 (m, 1H), 5.65 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 147.6, 143.0, 138.8, 135.9, 131.9, 129.0, 128.1, 128.0, 127.3, 125.5, 125.5, 123.4, 123.1, 119.9, 110.0, 44; HRMS : m/z calculated for $C_{16}H_{12}N_2S_2$ HRMS m/z $(M + H)^+$ 297.0515, found: 297.0527. [S1]

1-benzyl-6-methyl-2-phenyl-1H-benzo[d]imidazole and 1-benzyl-5-methyl-2-phenyl-1H-benzo[d]imidazole (3i)



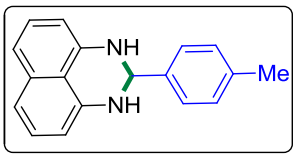
Purified by column chromatography, Brown solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, J = 8.0 Hz, 1H), 7.69 – 7.66 (m, 5H), 7.47 – 7.43 (m, 6H), 7.37 – 7.29 (m, 6H), 7.15 – 7.07 (m, 7H), 7.00 (s, 1H), 5.43 (s, 4H), 2.50 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 154.2, 153.8, 143.6, 141.4, 130.3, 129.9, 129.9, 129.3, 129.3, 129.2, 129.1, 128.8, 128.8, 127.8, 127.8, 126.1, 126.0, 124.4, 119.6, 110.4, 48.5, 48.3, 22.0, 21.7. MS: m/z calculated for $C_{42}H_{36}N_4$ $(M + H)^+$ 597.29.

2-phenyl-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3-dihydroperimidine (5a)



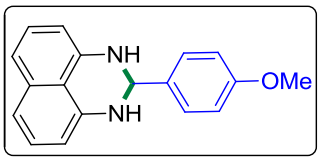
Purified by column chromatography, White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 – 7.61 (m, 2H), 7.43 – 7.41 (m, 3H), 7.23 – 7.21 (m, 4H), 6.50 (dd, J = 6.8 Hz, 1.2 Hz, 2H), 5.47 (s, 1H), 4.52 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 142.1, 140.1,134.9, 129.6, 128.9, 127.9, 126.9, 117.9, 113.5, 105.9, 68.4; HRMS: m/z calculated for $C_{17}H_{15}N_2$ $(M + H)^+$ 247.1191, found: 247.1236. [S3]

2-(p-tolyl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine (5b)



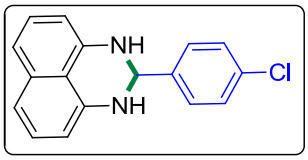
Purified by column chromatography, White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (d, J = 8.0 Hz, 2H), 7.24 – 7.19 (m, 6H), 6.50 (d, J = 7.2 Hz, 2H), 5.42 (s, 1H), 4.49 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 142.4, 139.7, 137.3, 135.0, 129.6, 127.9, 127.0, 118.0, 113.6, 105.9, 68.3, 21.4; HRMS : m/z calculated for $C_{18}H_{17}N_2$ $(M + H)^+$ 261.1347, found: 261.1397. [S3]

2-(4-methoxyphenyl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine (5c)



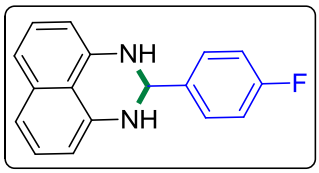
Purified by column chromatography, White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 – 7.55 (m, 2H), 7.26 – 7.20 (m, 4H), 6.97 – 6.95 (m, 2H), 6.51, (d, J = 6.8 Hz, 2H), 5.42, (s, 1H), 4.50 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 160.7142.4, 135.1, 132.4, 129.3, 127.0, 117.9, 114.2, 113.6, 105.9, 68.1, 55.5 HRMS : m/z calculated for $C_{18}H_{17}N_2O$ $(M + H)^+$ 277.1296, found: 277.1338. [S3]

2-(4-chlorophenyl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine (5d)



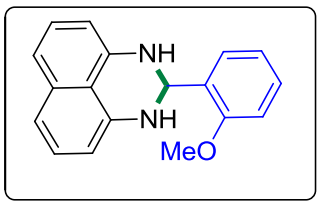
Purified by column chromatography, White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 – 7.56 (m, 2H), 7.44 – 7.40 (m, 2H), 7.28 – 7.22 (m, 4H), 6.53 (d, J = 6.4 Hz, 2H), 5.45 (s, 1H), 4.48 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 142.1, 141.8, 138.6, 135.4, 134.9, 129.6, 129.3, 129.1, 128.9, 127.9, 126.9, 118.1, 117.9, 113.4, 106.0, 105.8, 67.7; HRMS: m/z calculated for $C_{17}H_{14}ClN_2$ $(M + H)^+$ 282.0738, found 282.0780. [S3]

2-(4-fluorophenyl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine (5e)



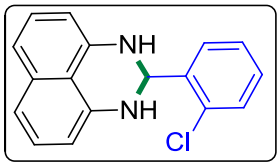
Purified by column chromatography, light brown solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 – 7.55 (m, 2H), 7.24 – 7.19 (m, 4H), 7.12 – 7.07 (m, 2H), 6.49 (dd, J = 6.6 Hz, 1.4 Hz, 2H), 5.40 (s, 1H), 4.45 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 164.7, 162.2, 142.0, 136.0, 136.0, 134.9, 129.9, 129.8, 126.9, 118.1, 115.9, 115.7, 113.4, 105.9, 67.7; calculated for C_{17} $H_{13}N_2F$: C, 77.24; H, 4.97; N, 10.60%. found: C, 77.41; H, 4.67; N, 10.86%. [S3]

2-(2-methoxyphenyl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine (5f)



Purified by column chromatography, Light pink solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (dd, J = 7.6, 1.4 Hz, 2H), 7.26 (td, J = 8.3 Hz, 1.6 Hz, 2H), 7.18 (t, J = 7.7 Hz, 5H), 7.19 – 7.11 (m, 4H), 6.93 (t, J = 7.5 Hz, 2H), 6.87 (d, J = 8.3 Hz, 2H), 6.48 (d, J = 7.2 Hz, 4H), 5.85 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 157.0, 142.1, 134.9, 129.8, 128.6, 127.4, 126.9, 121.1, 117.6, 113.5, 110.6, 106.0, 61.4, 55.5; MS-MS (ESI): m/z calculated for $C_{18}H_{17}N_2O$ $(M + H)^+$ 277, found: 277. [S3]

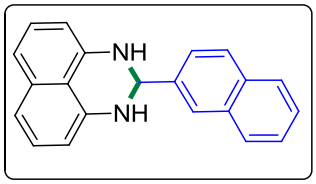
2-(2-chlorophenyl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3-dihydroperimidine (5g)



Purified by column chromatography, Light pink solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 – 7.72 (m, 1H), 7.35 – 7.32 (m, 1H), 7.24 – 7.22 (m, 2H), 7.20 – 7.13 (m, 4H), 6.47 (d, J = 6.9 Hz, 2H), 5.88 (s, 1H), 4.51 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 141.7, 137.7, 134.9, 133.3, 130.3, 129.8, 129.1, 127.7,

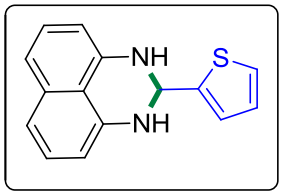
127.0, 118.1, 113.3, 106.2, 63.9; HRMS : m/z calculated for $C_{17}H_{14}ClN_2$ $(M + H)^+$ 282.0738, found: 282.0774.[S3]

2-(naphthalen-2-yl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine (5h)



Purified by column chromatography, White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.63 (s, 1H), 7.94 – 7.85 (m, 3H), 7.55 – 7.51 (m, 3H), 7.30 – 7.26 (m, 4H), 6.55 (dd, *J* = 6.6 Hz, 1.4 Hz, 2H), 6.16 (s, 1H), 4.70 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 142.4, 135.0, 134.8, 134.2, 131.2, 130.1, 128.9, 126.9, 126.5, 126.1, 125.4, 117.9, 113.6, 113.6, 106.0, 67.0; HRMS : m/z calculated for $C_{21}H_{17}N_2(M + H)^+$ 297.1347, found: 297.1392. [S3]

2-(thiophen-2-yl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine(5i)



Purified by column chromatography, White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (d, *J* = 5.2 Hz, 1H), 7.30 – 7.24 (m, 5H), 7.06 - 7.04 (m, 1H), 6.56 (dd, *J* = 6.7 Hz, 1.3 Hz, 2H), 5.83 (s, 1H), 4.68 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ = 144.0, 141.4, 134.8, 126.9, 126.5, 126.4, 118.2, 113.7, 106.2, 63.8; HRMS : m/z calculated for $C_{15}H_{13}N_2S$ $(M + H)^+$ 253.0755, found 253.0797.[S3]

11. References:

S1 R. Chebolu, D. N. Kommi, D. Kumar, N. Bollineni, and A. K. Chakraborti, *J. Org. Chem.*, 2012, **77**, 10158-10167.

S2. Z. Xu, D. S. Wang, X. Yu, Y. Yang, and D. Wang, *Adv. Syn. Catal.*, 2017, **359**, 3332-3340.

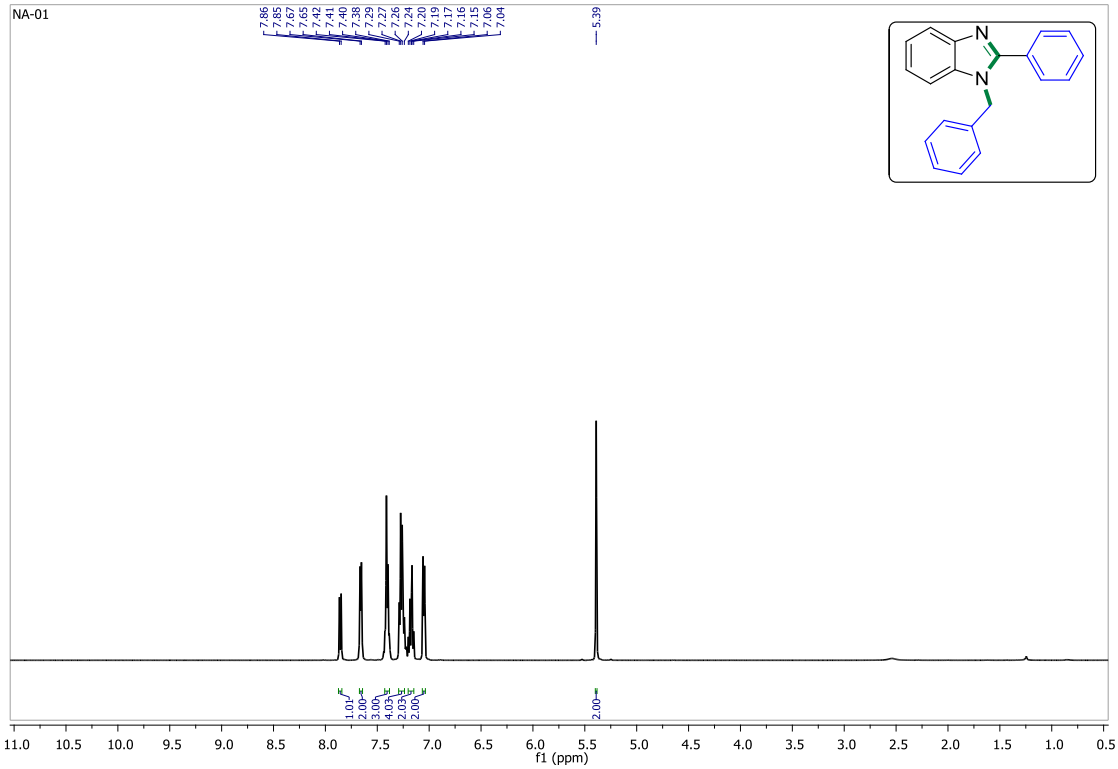
S3. N. A. Harry, S. Radhika, M. Neetha, and G. Anilkumar, *J. Heterocyl. Chem.*, 2020, **57**, 2037-2043

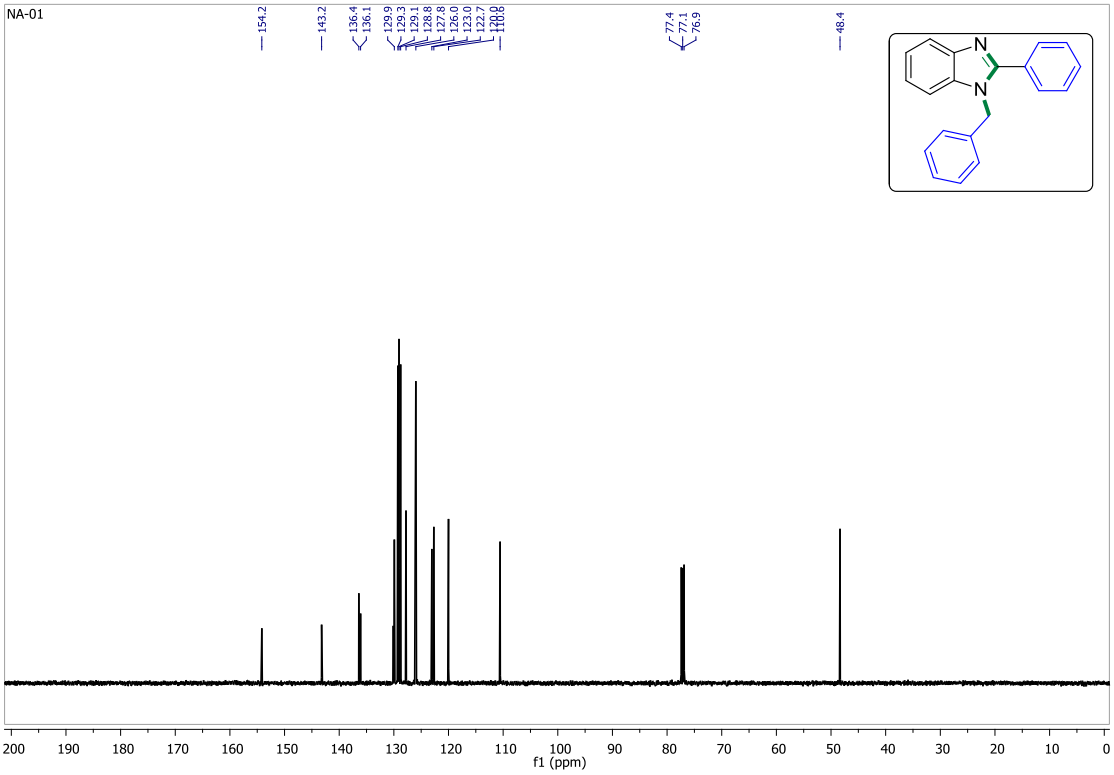
S4. A. Ghosh, R. V. Hegde, A. S. Limaye, R. Thrilokraj, S. A. Patil, R. B. Dateer, *Appl. Organomet. Chem.*, 2023, **37**, 7119.

Appendix-I

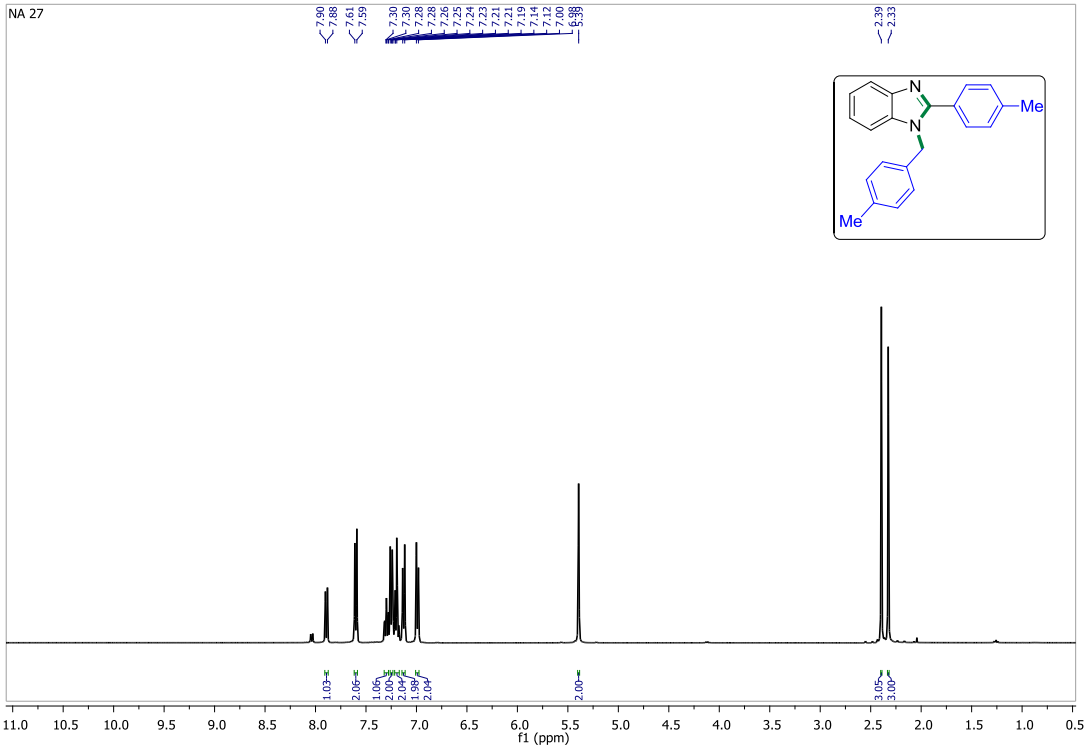
Spectral copies of ^{1}H and ^{13}C NMR of compounds

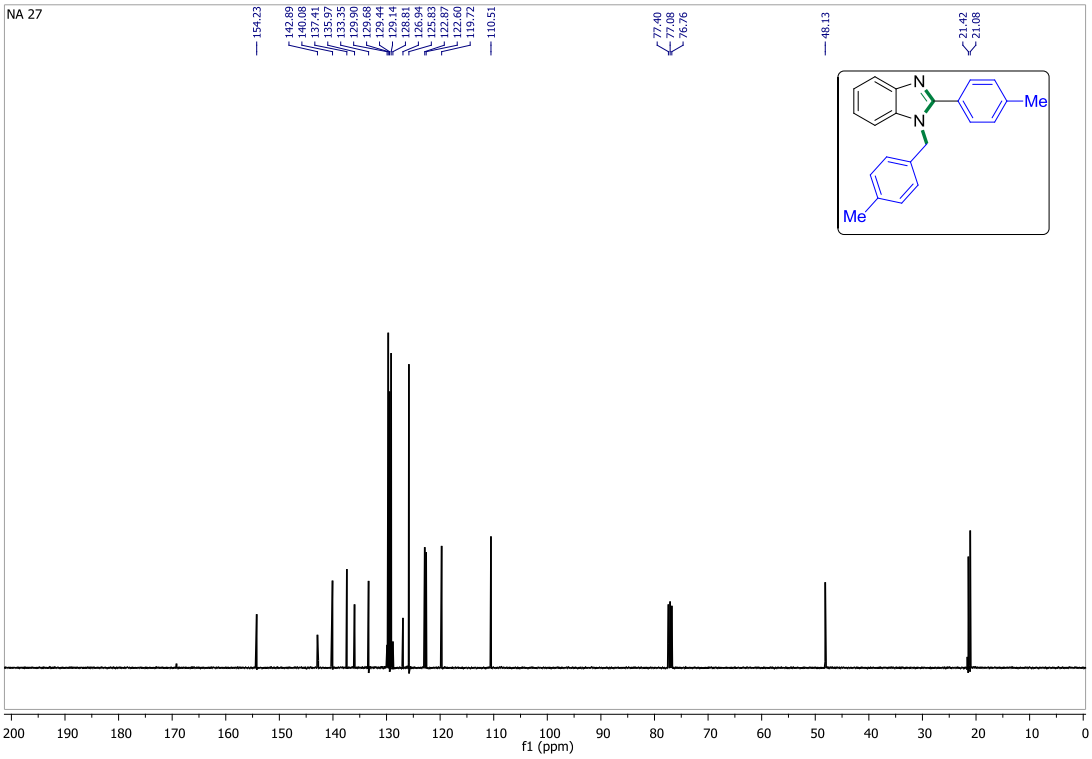
1-benzyl-2-phenyl-1H-benzo[d]imidazole (3a)



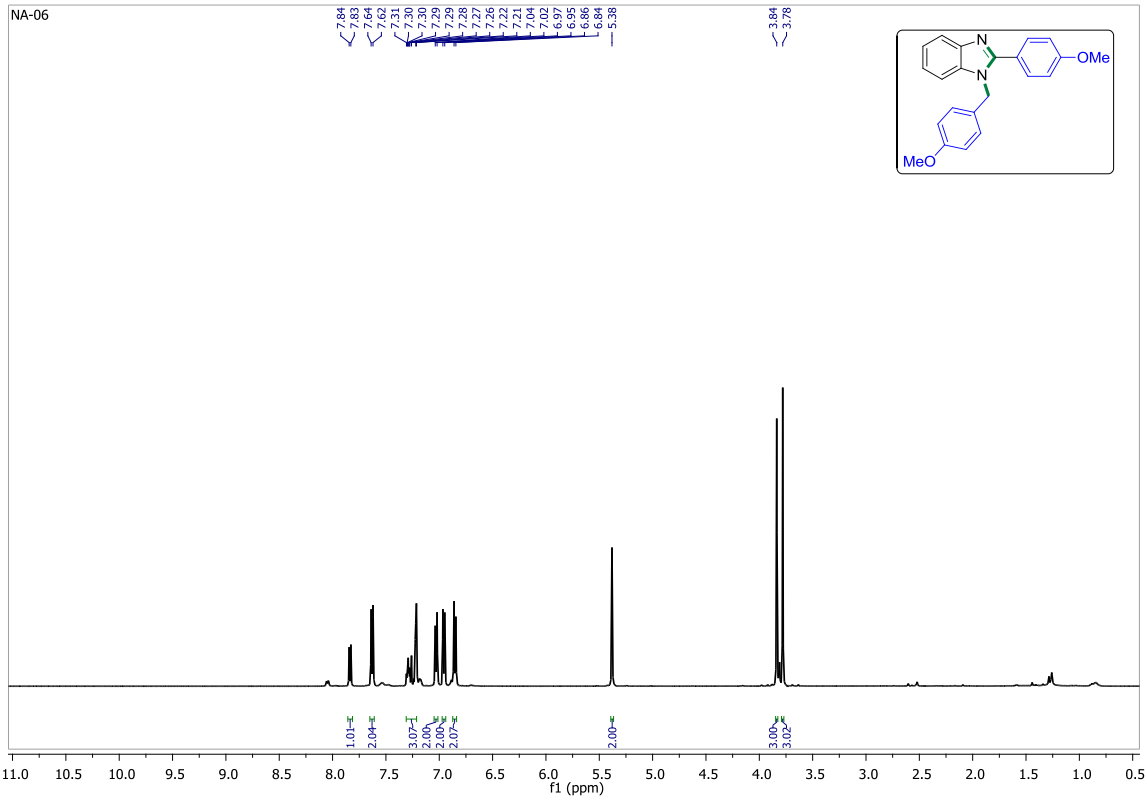


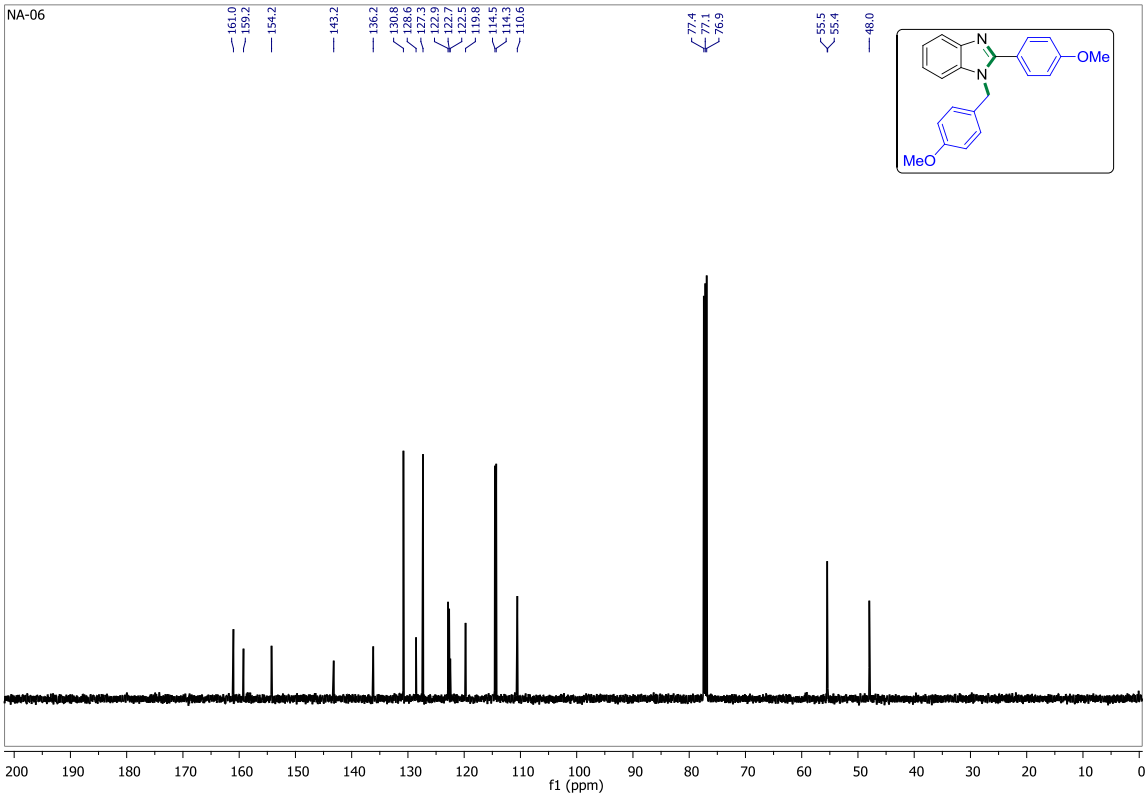
1-(4-methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole (3b)



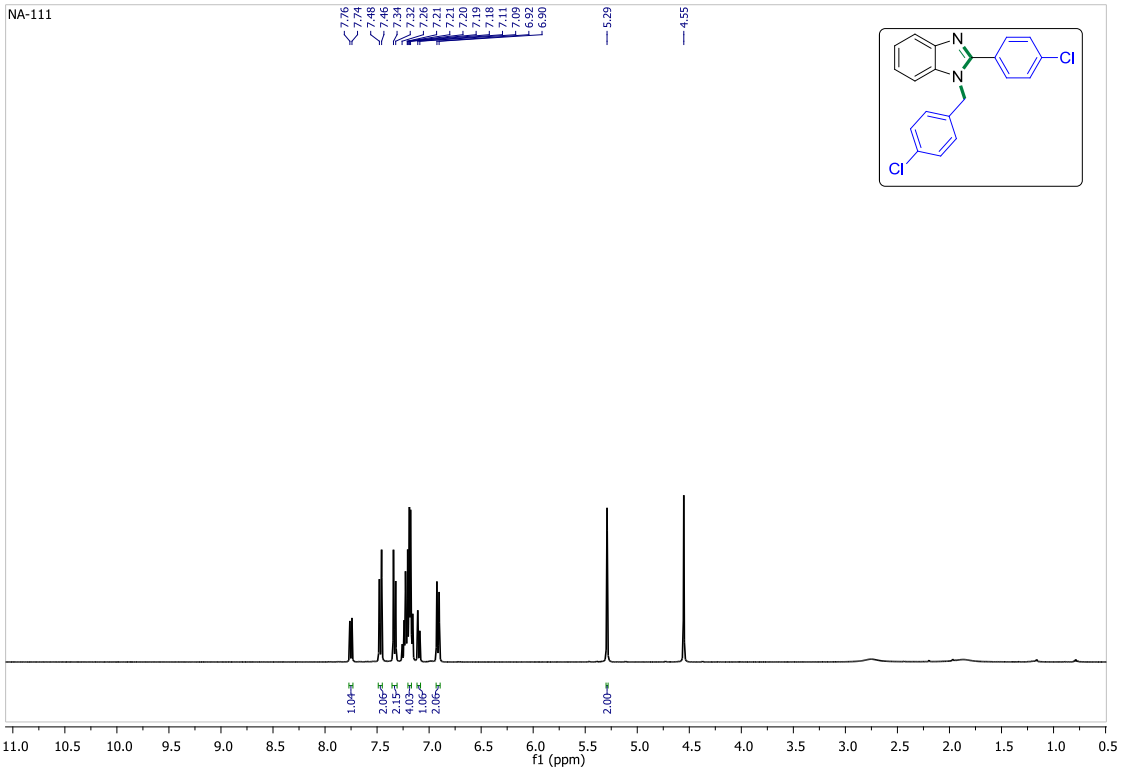


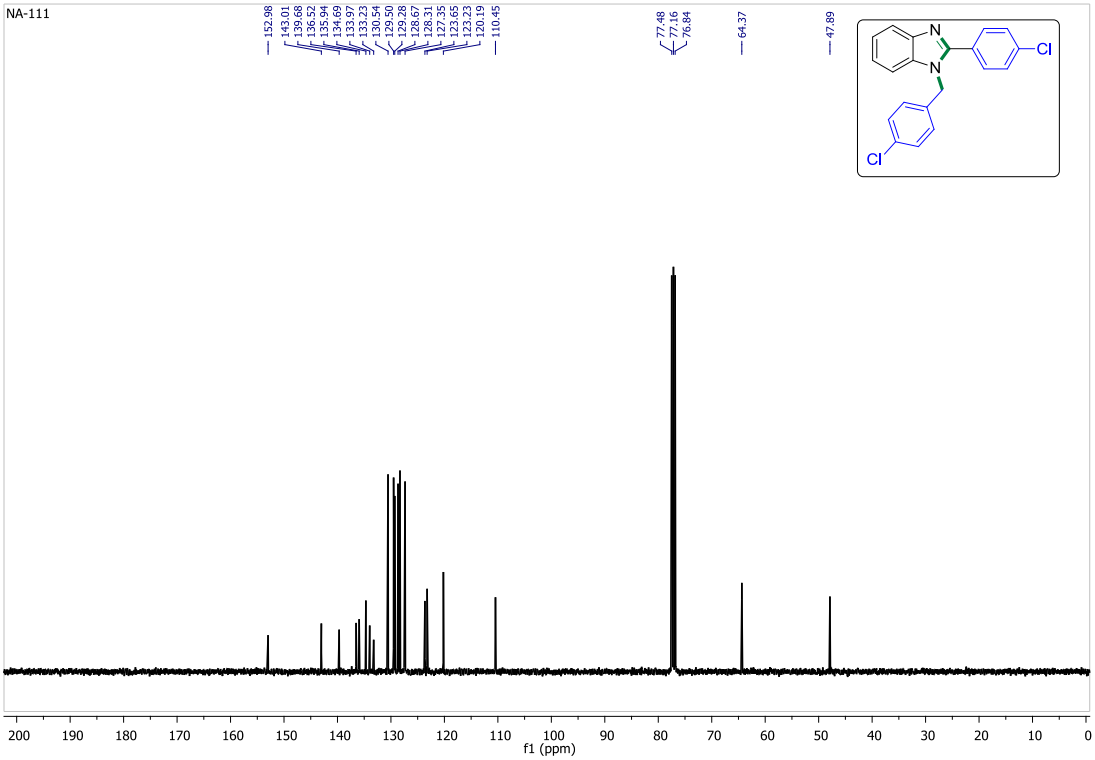
1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (3c)



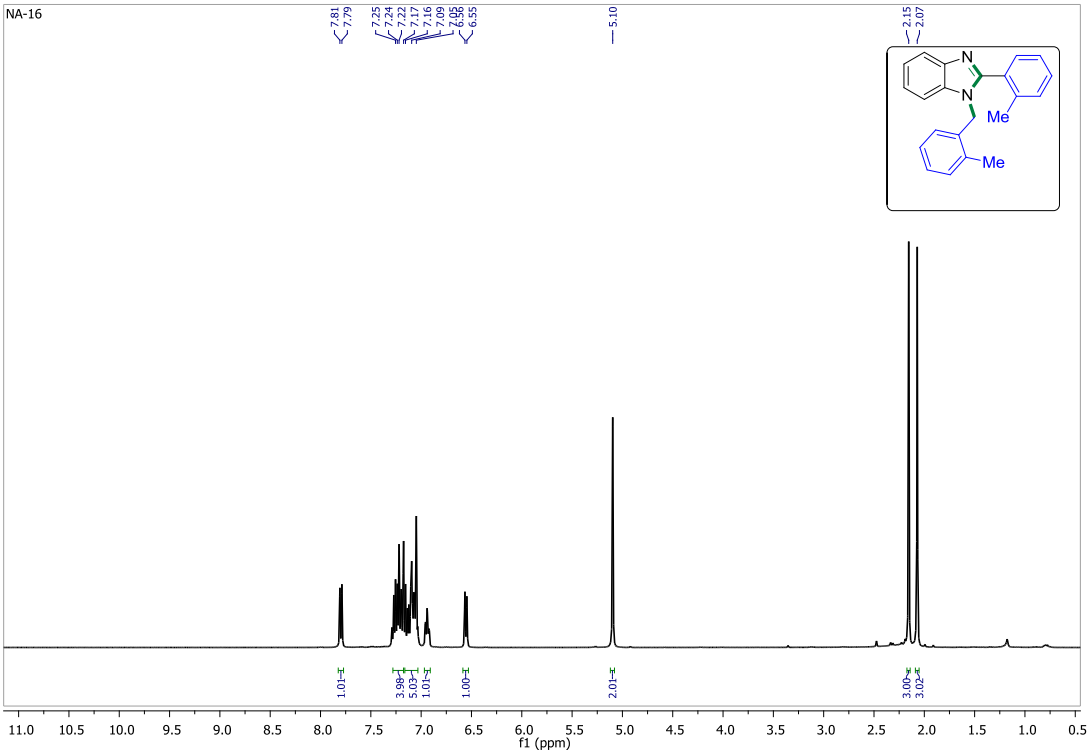


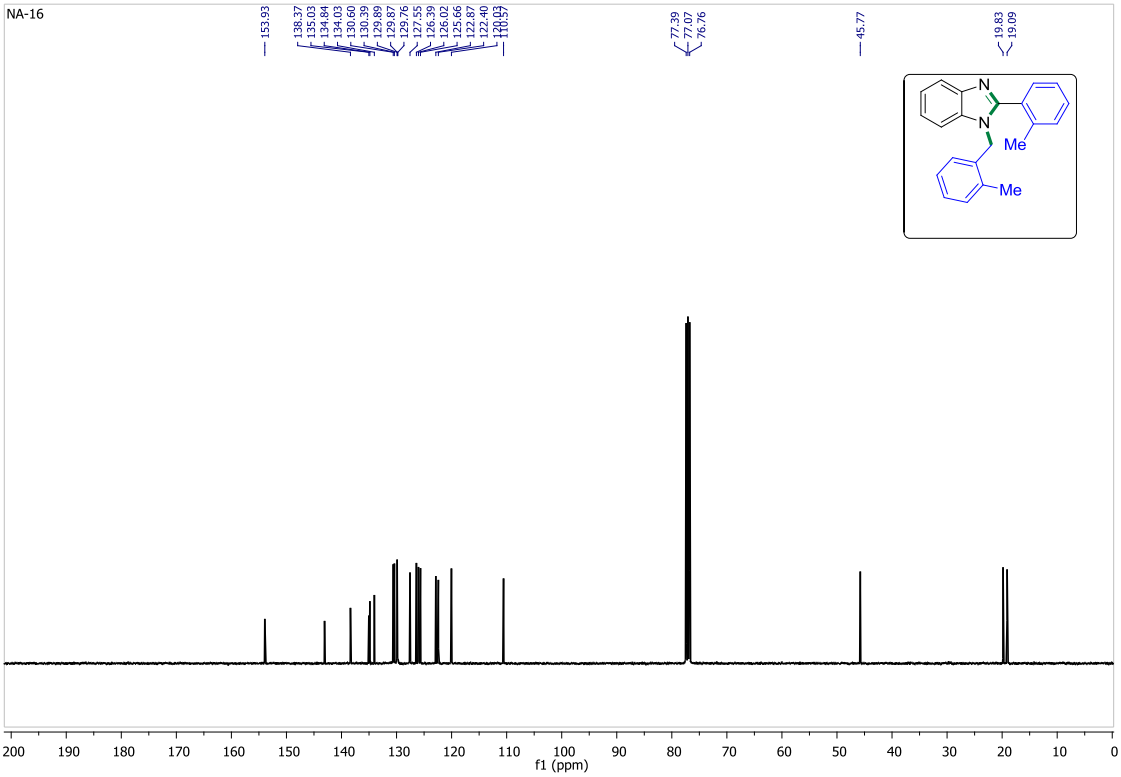
1-(4-Chlorobenzyl)-2-(4-chlorobenzyl)-1H-benzo[d]imidazole (3d)



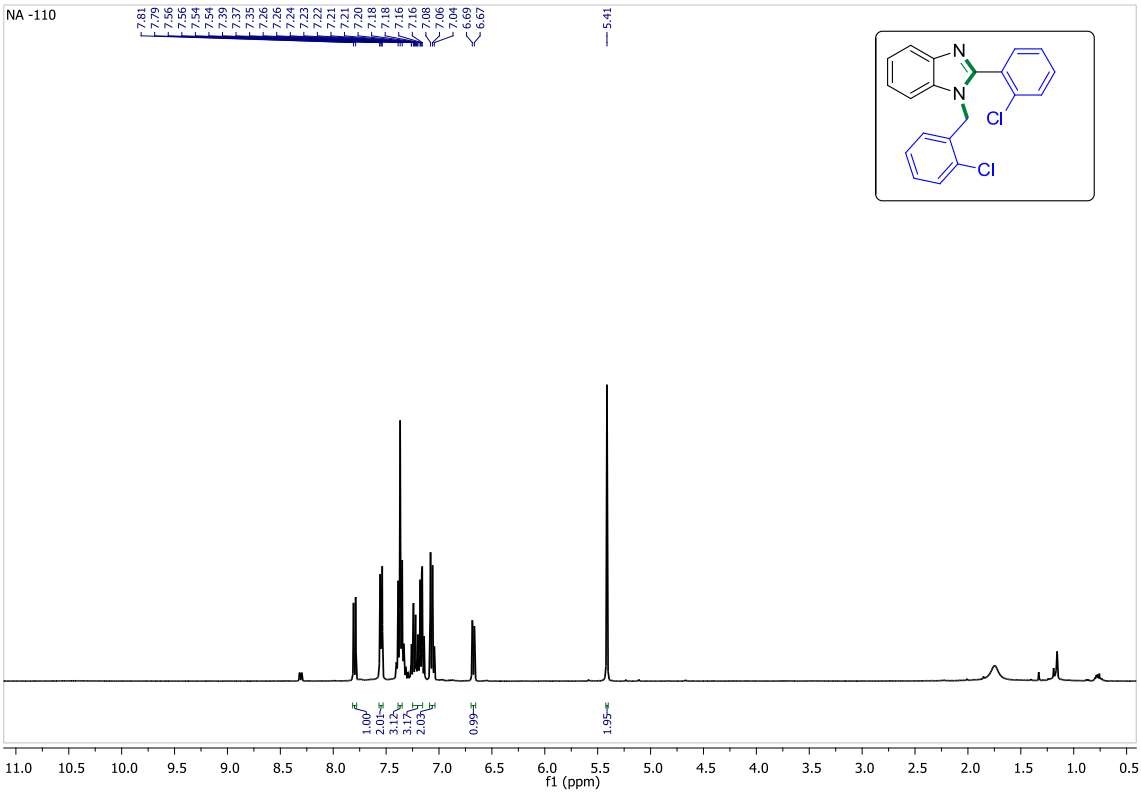


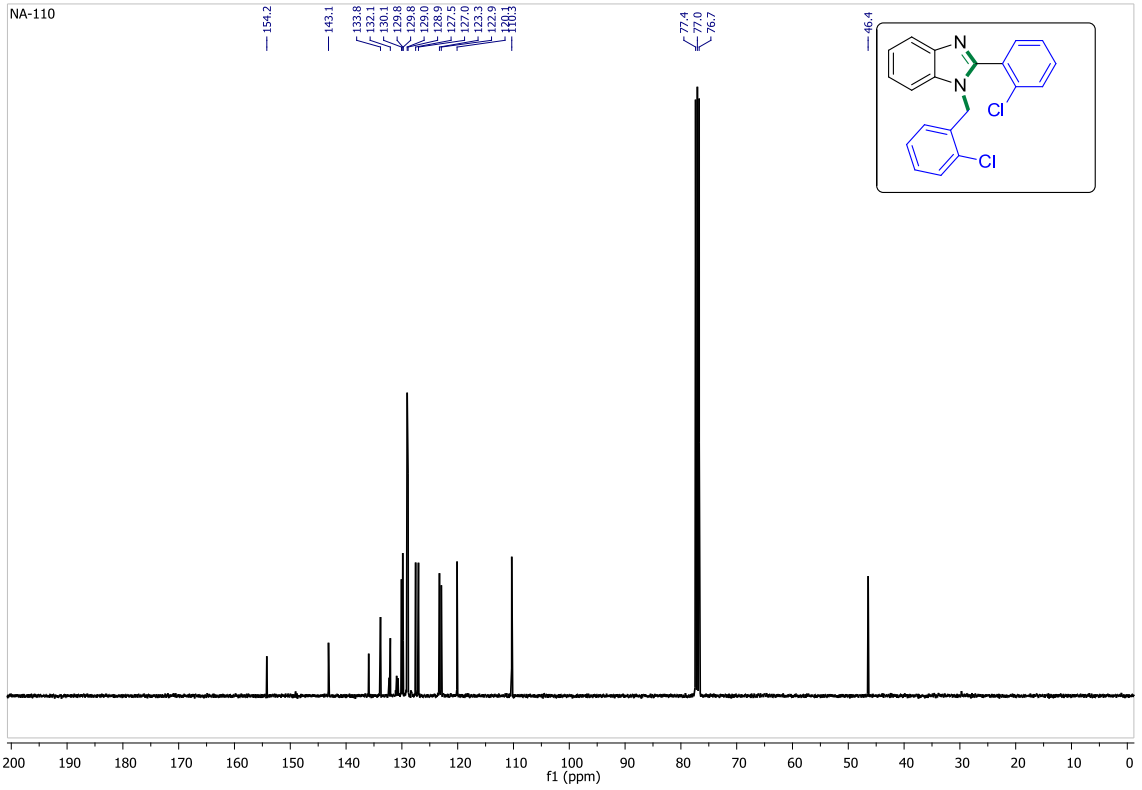
1-(2-methylbenzyl)-2-(o-tolyl)-1H-benzo[d]imidazole (3e)



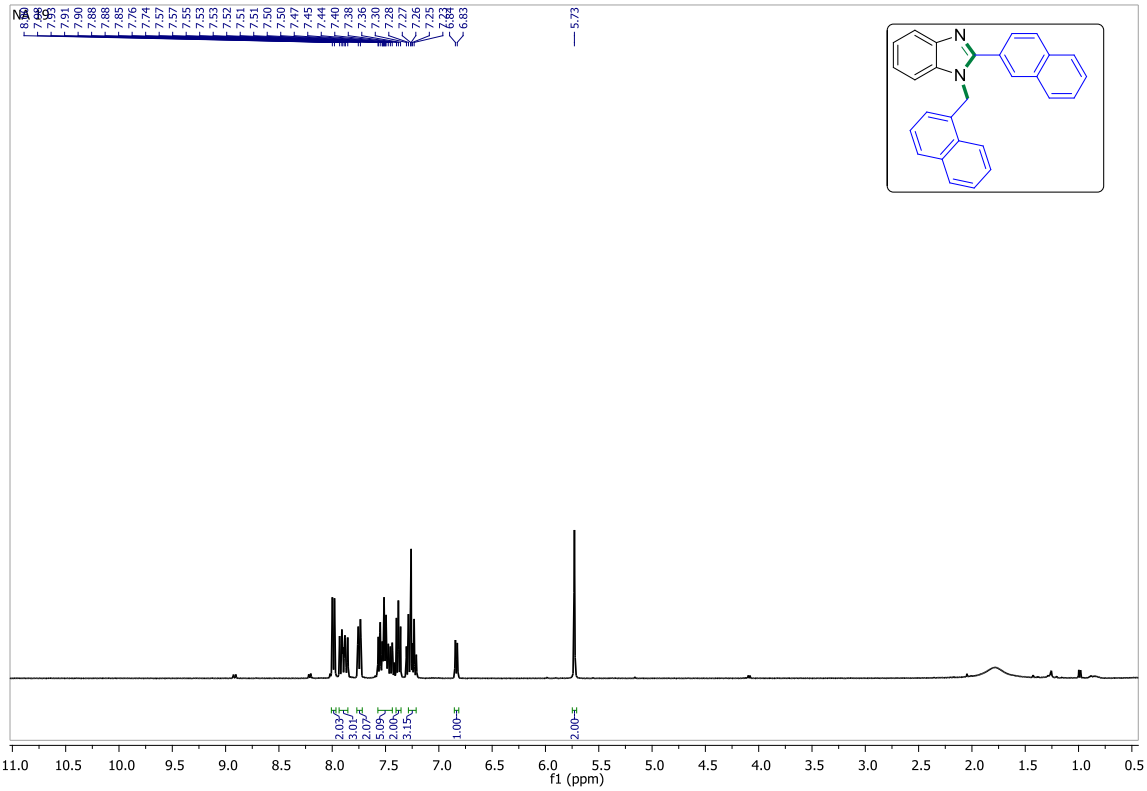


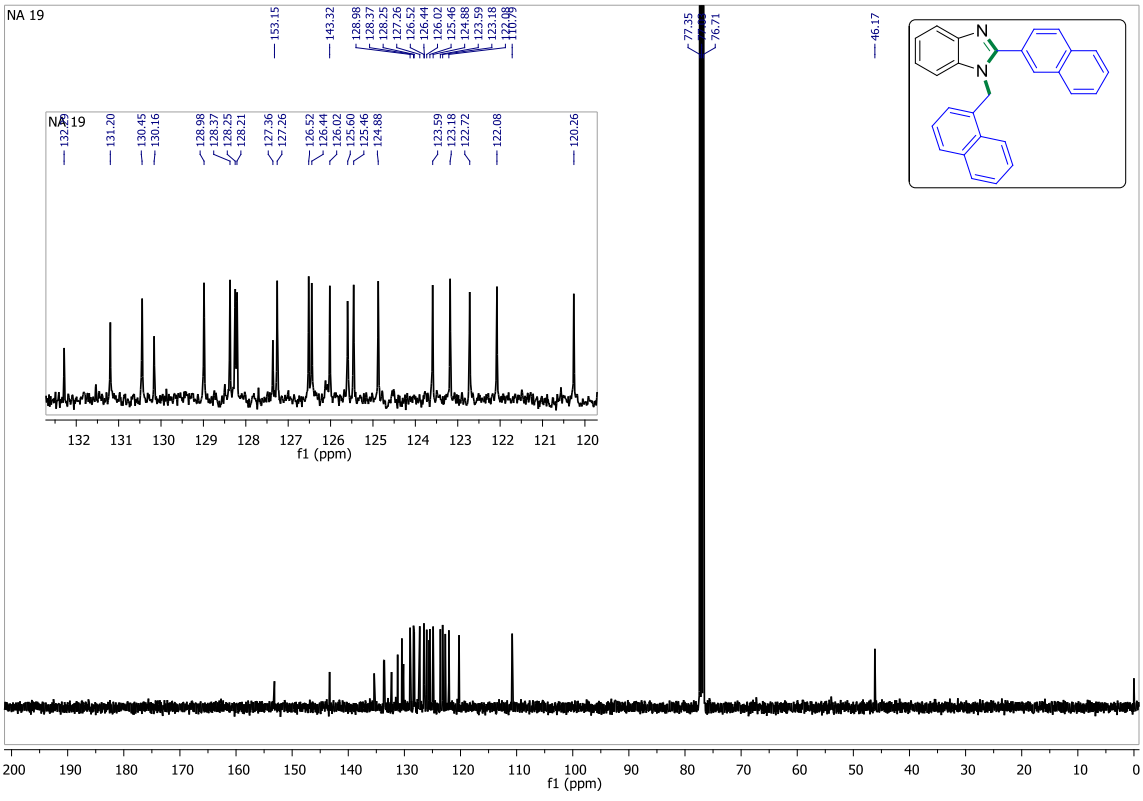
1-(2-Chlorobenzyl)-2-(2-chlorobenzyl)-1H-benzo[d]imidazole (3f)



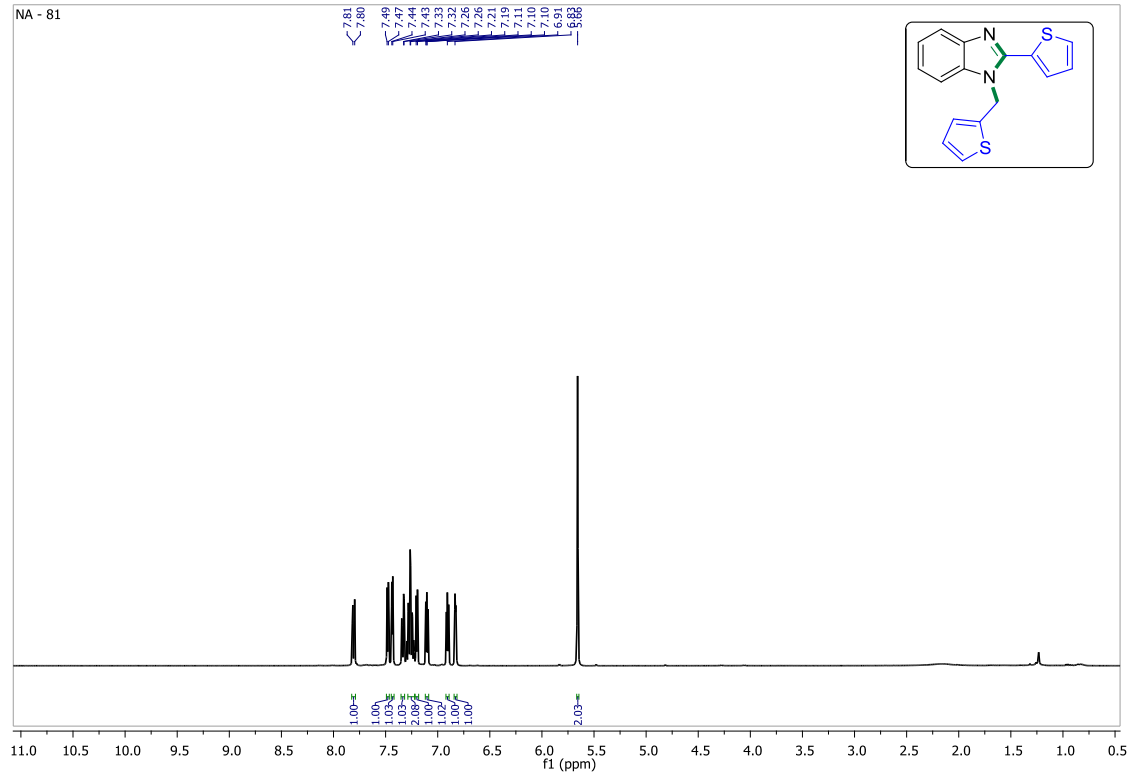


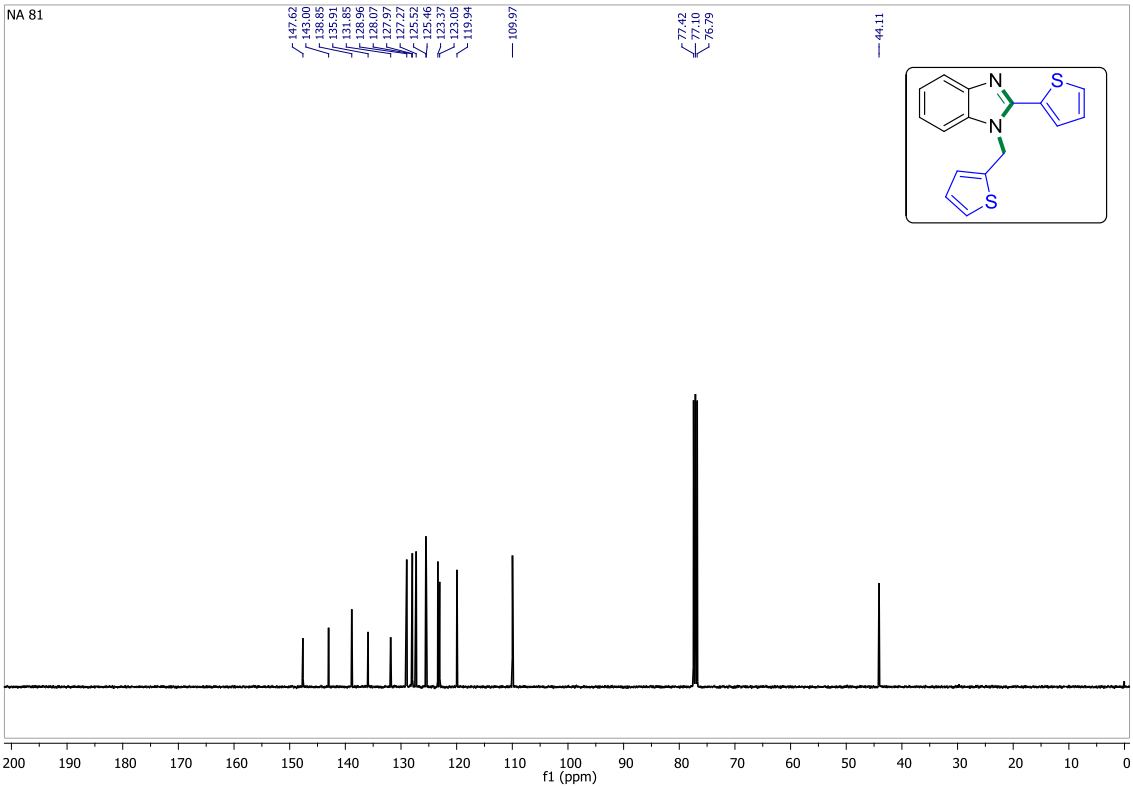
1-(naphthalen-1-ylmethyl)-2-(naphthalen-2-yl)-1H-benzo[d]imidazole (3g)



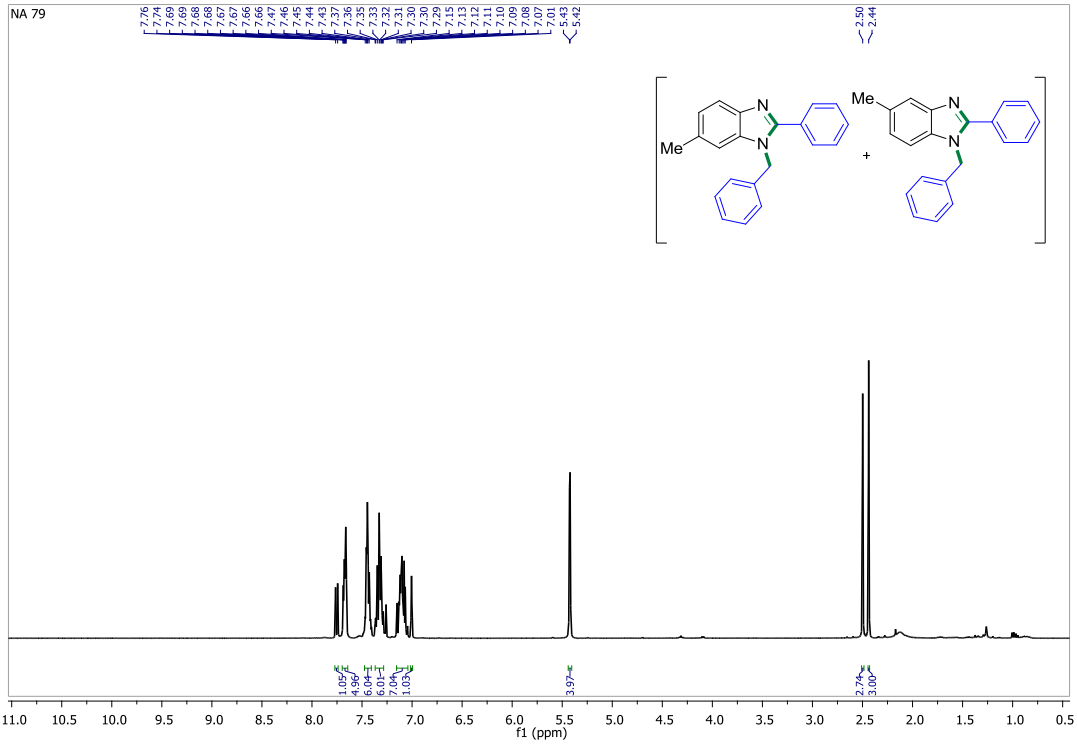


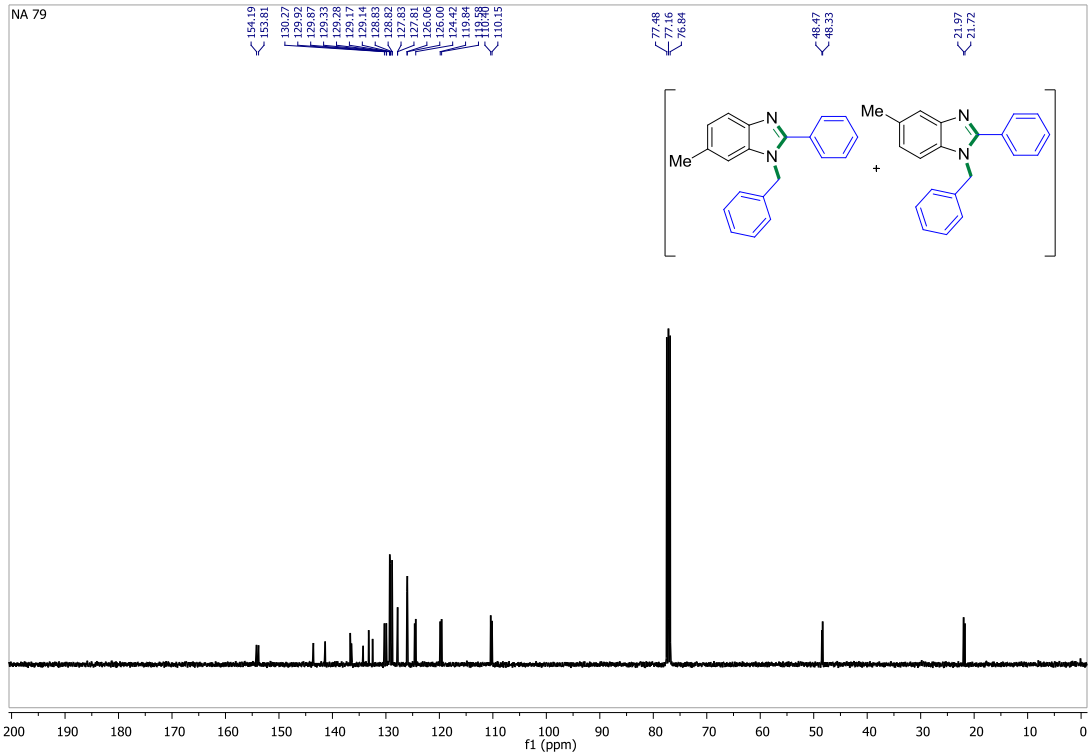
2-(Thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1H-benzo[d]- imidazole (3h)



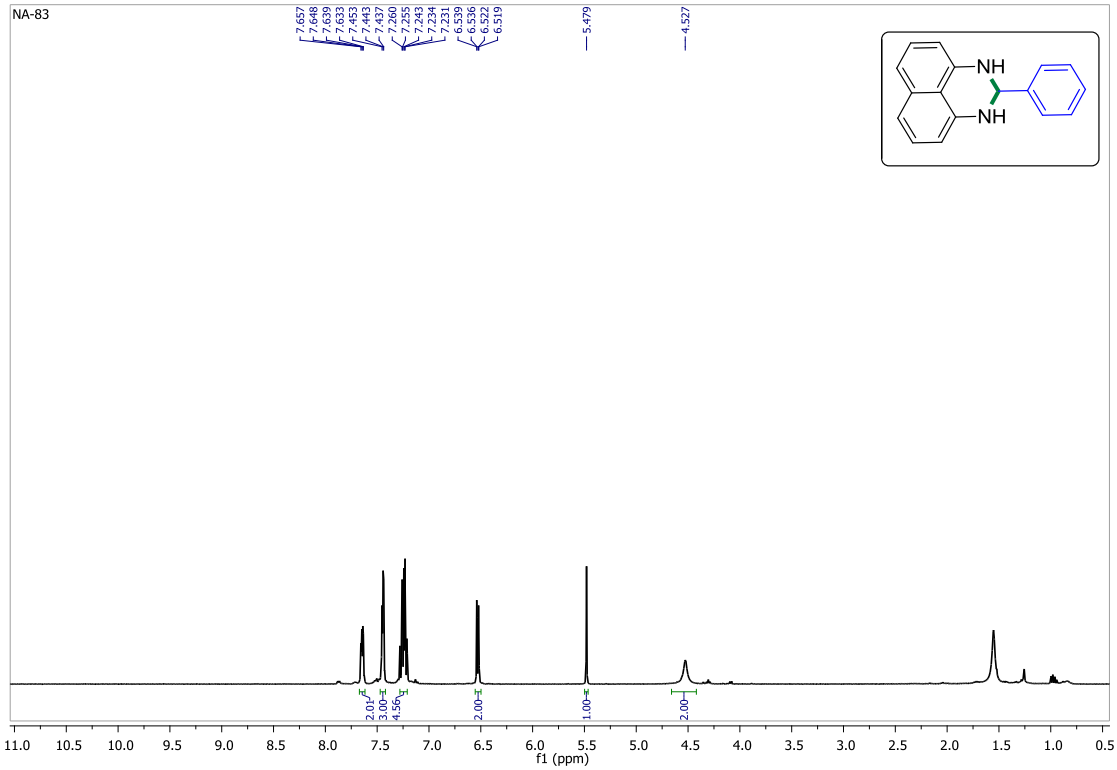


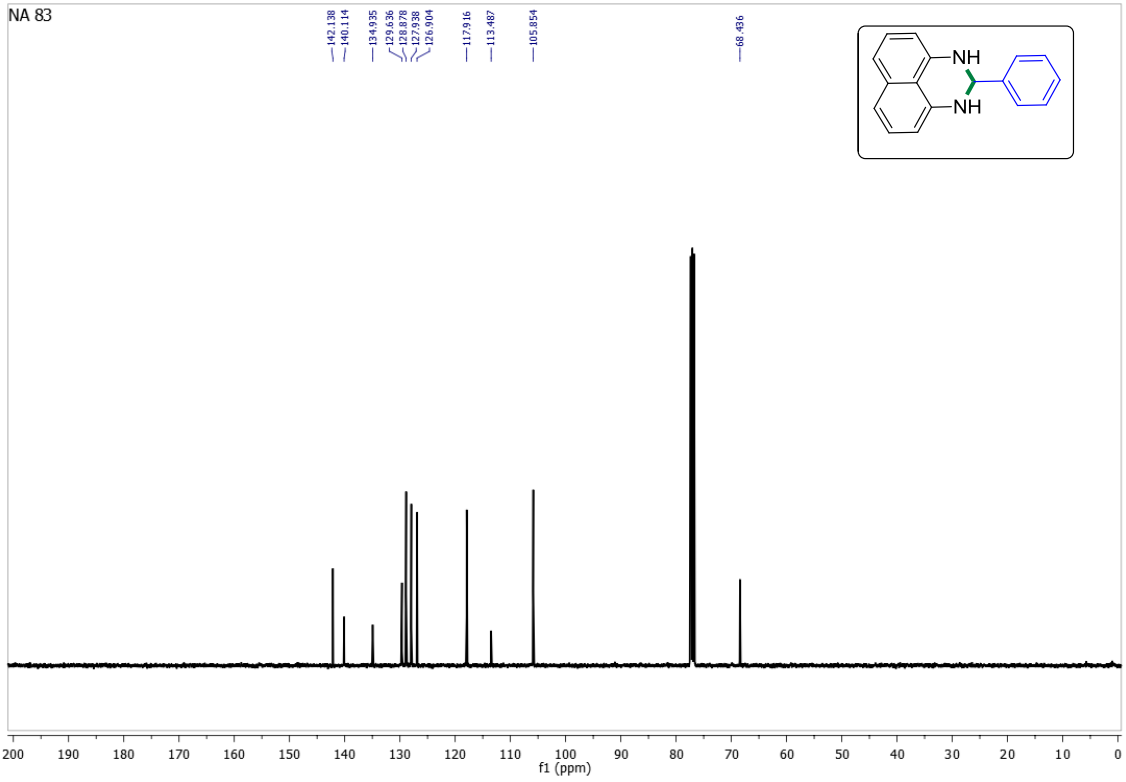
1-benzyl-6-methyl-2-phenyl-1H-benzo[d]imidazole and 1-benzyl-5-methyl-2-phenyl-1H-benzo[d]imidazole (3i)



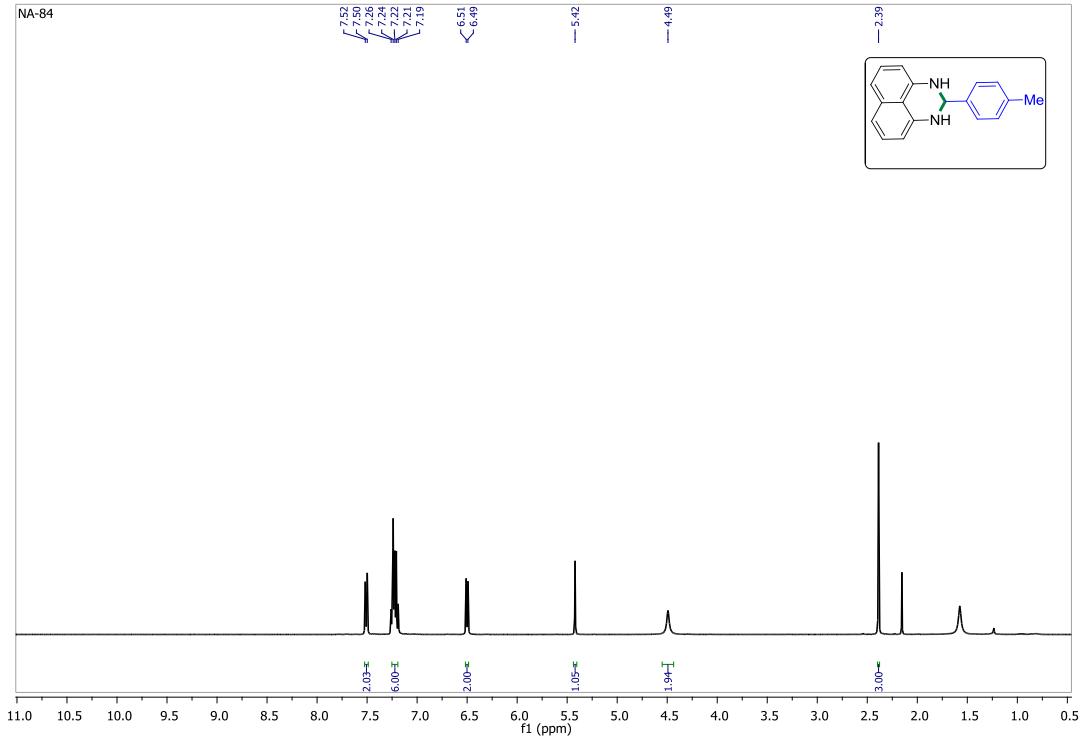


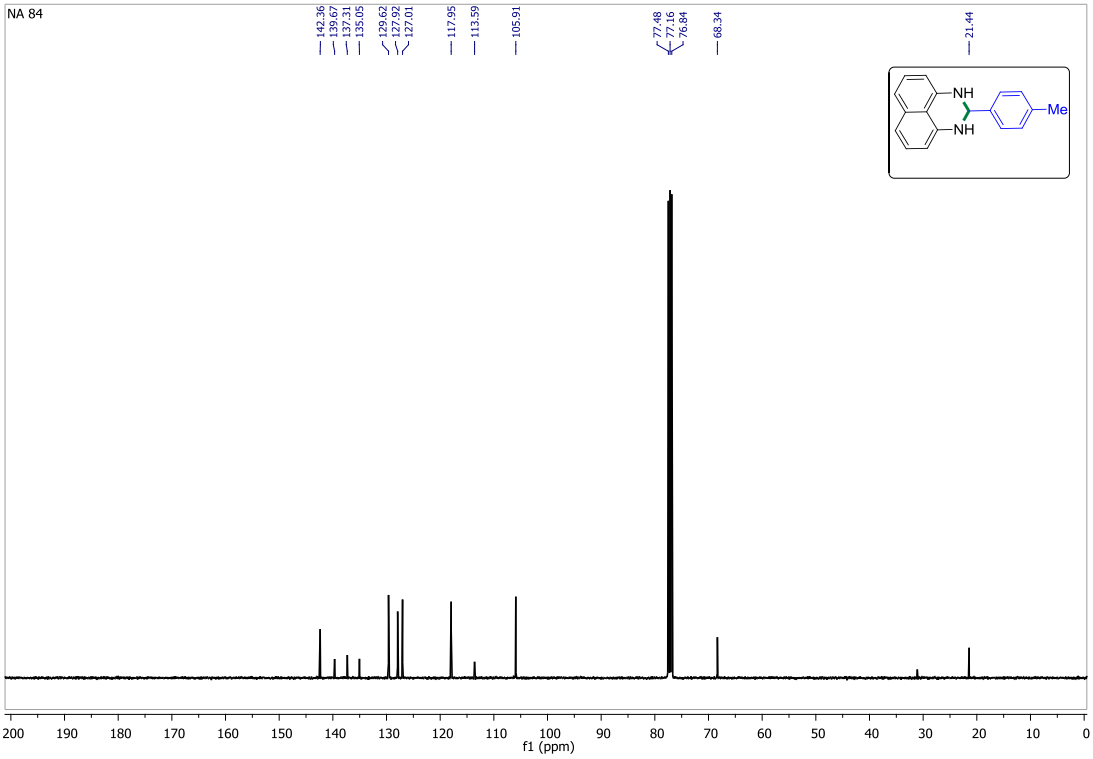
2-phenyl-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3-dihydroperimidine (5a)



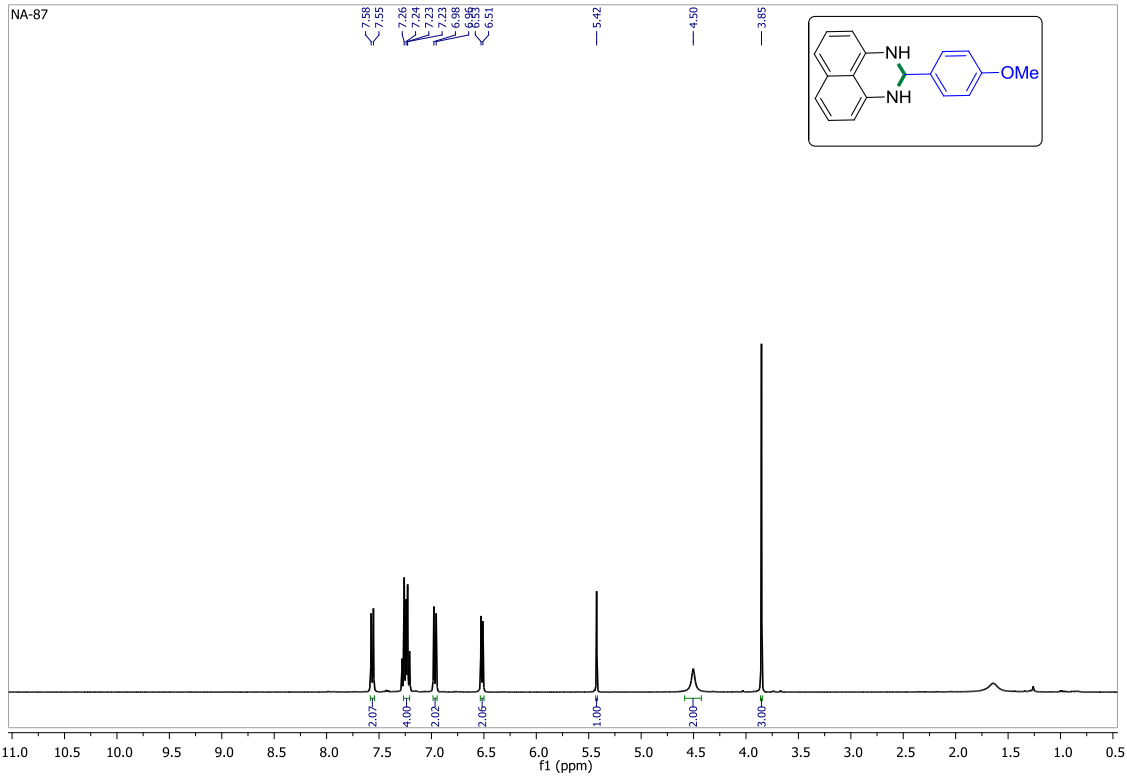


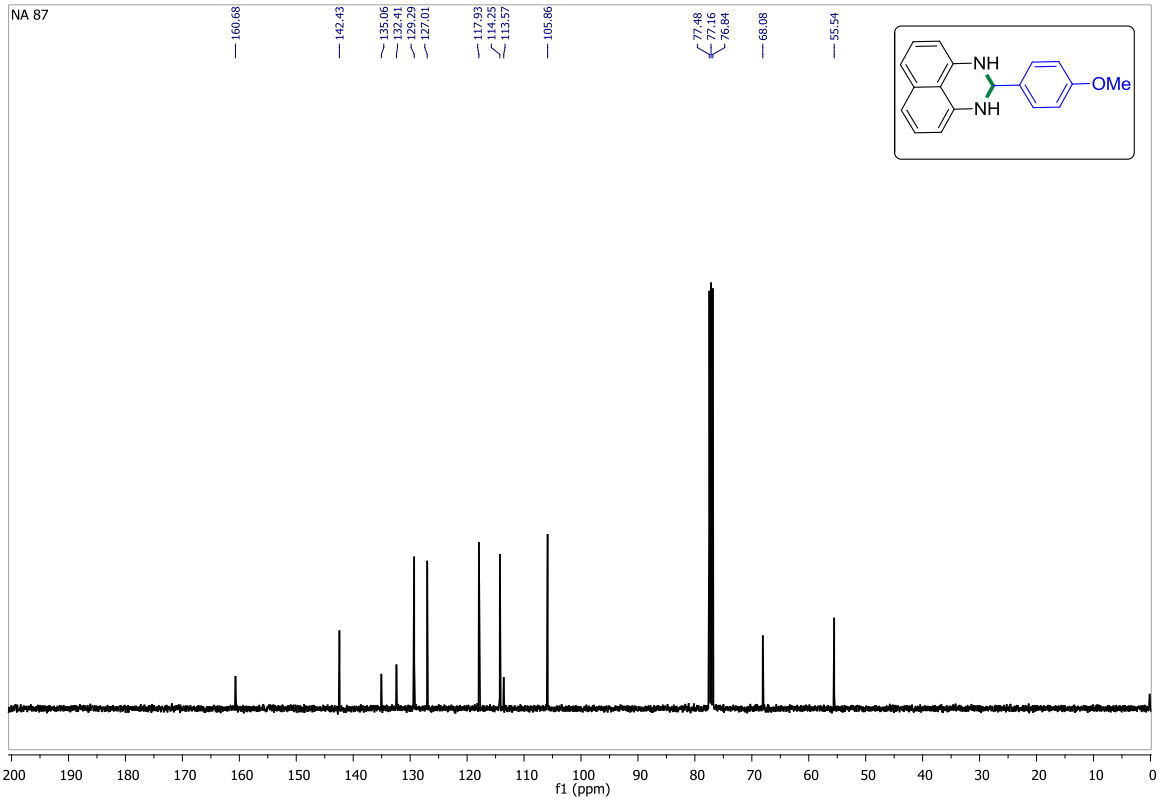
2-(p-tolyl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine (5b)



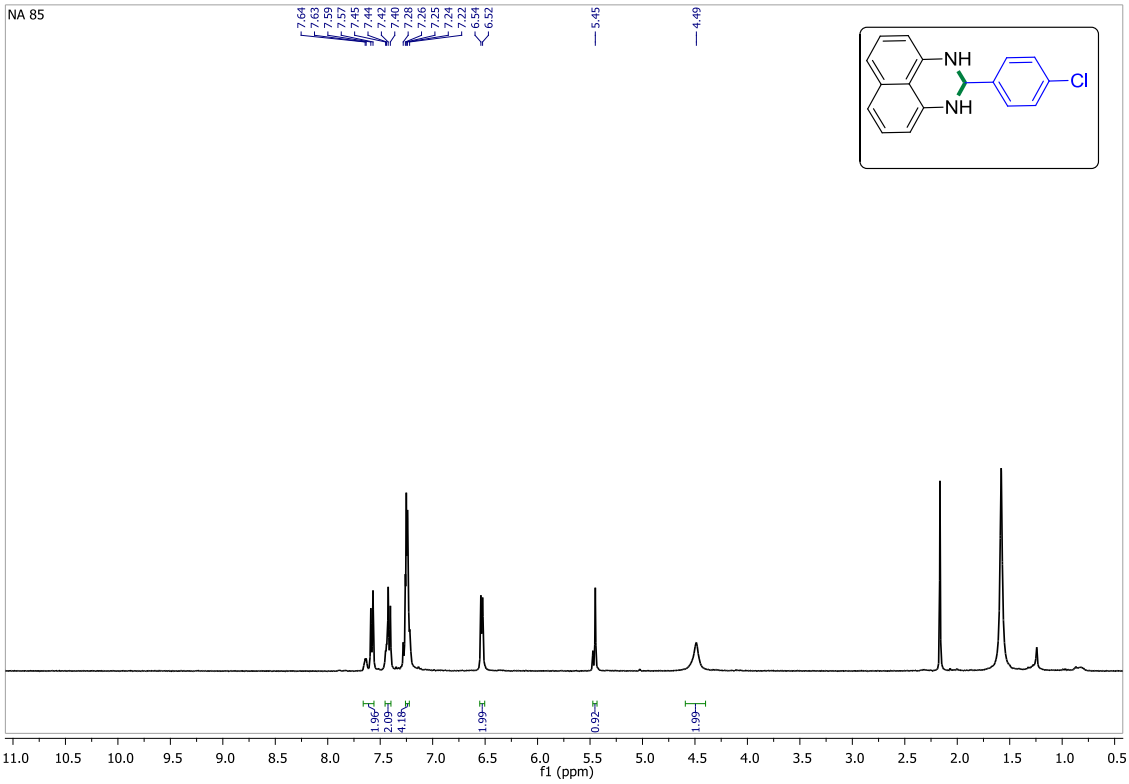


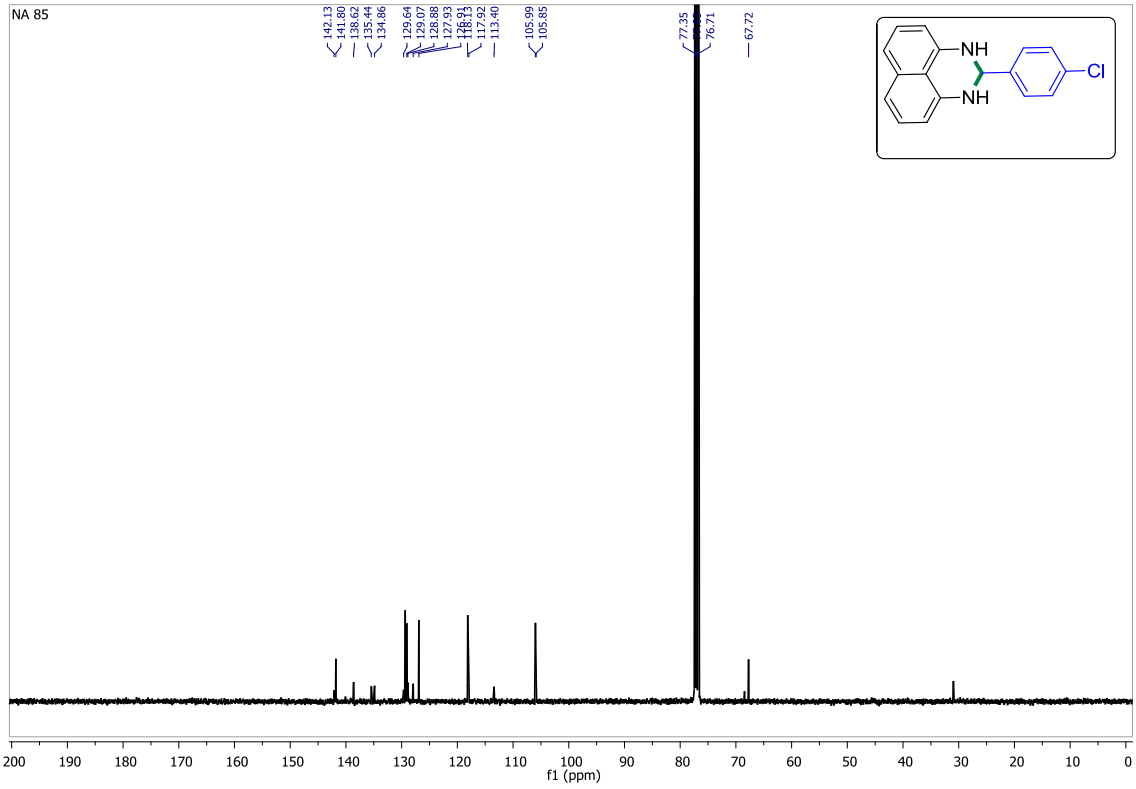
2-(4-methoxyphenyl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine (5c)



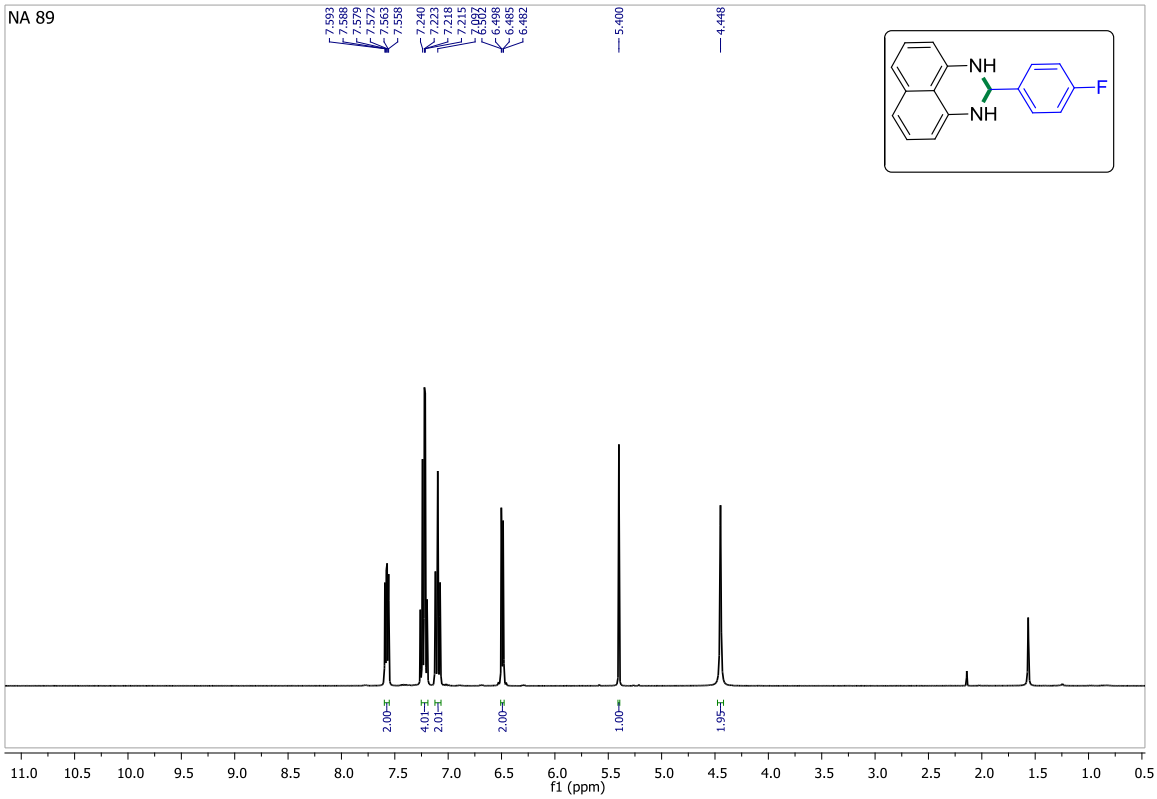


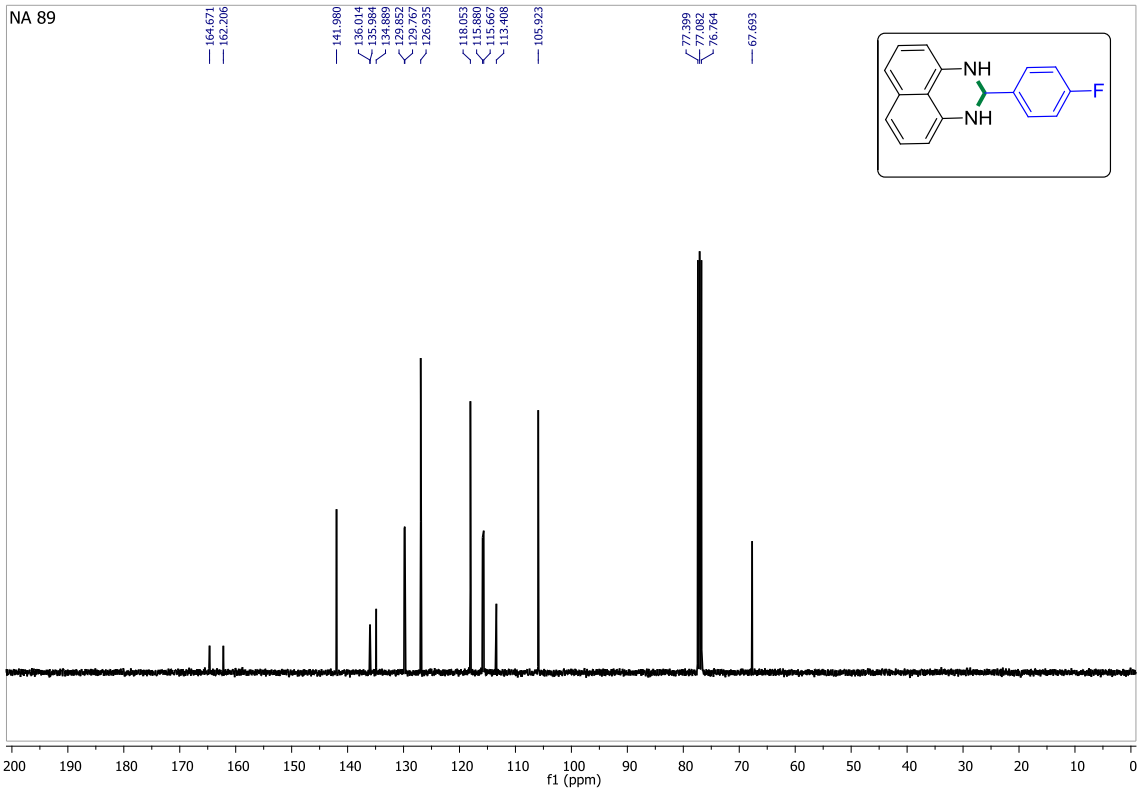
2-(4-chlorophenyl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine (5d)



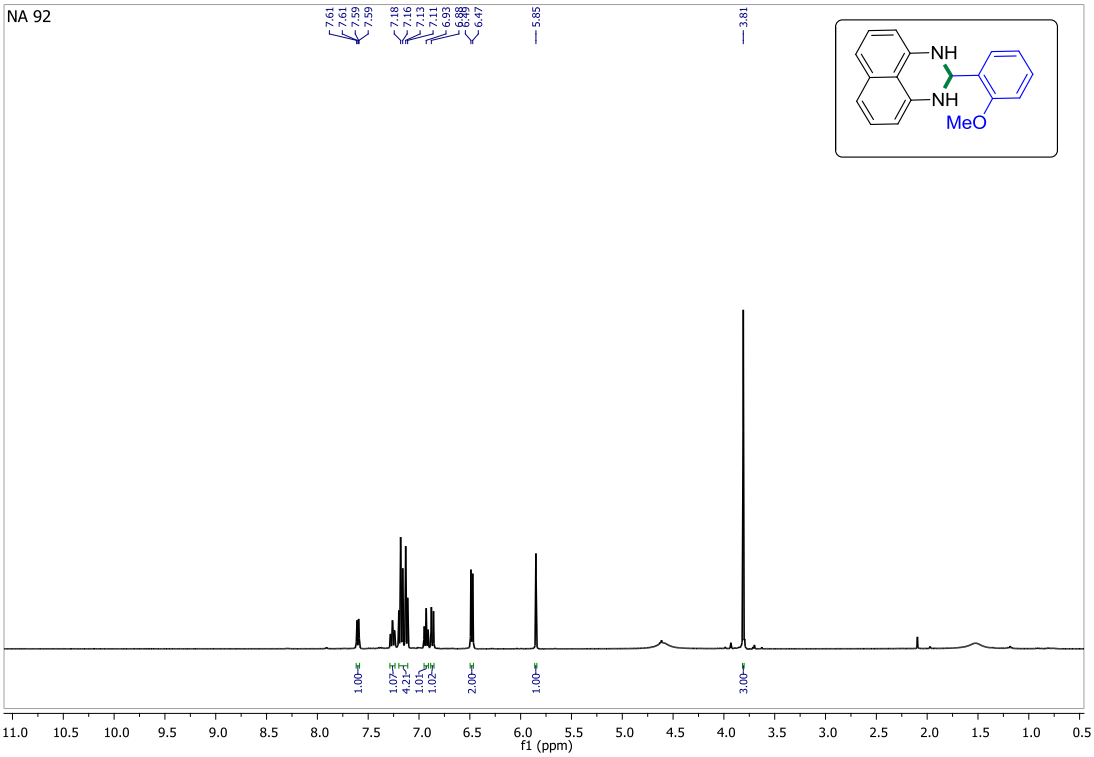


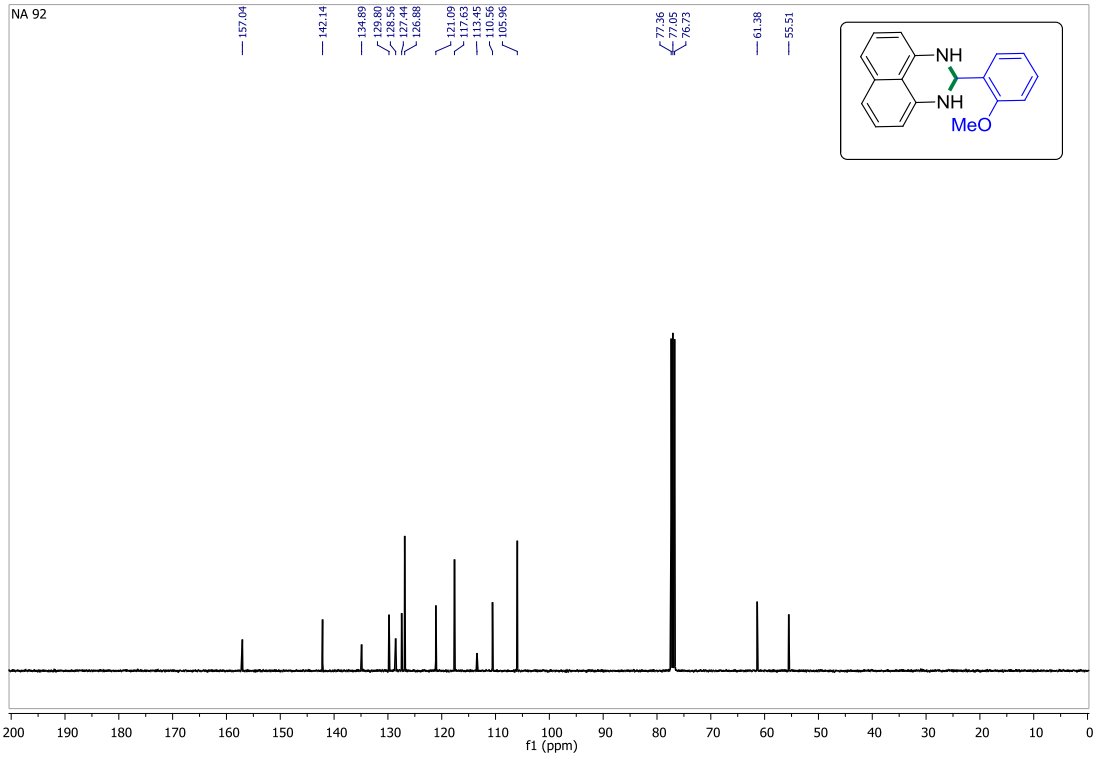
2-(4-fluorophenyl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine (5e)



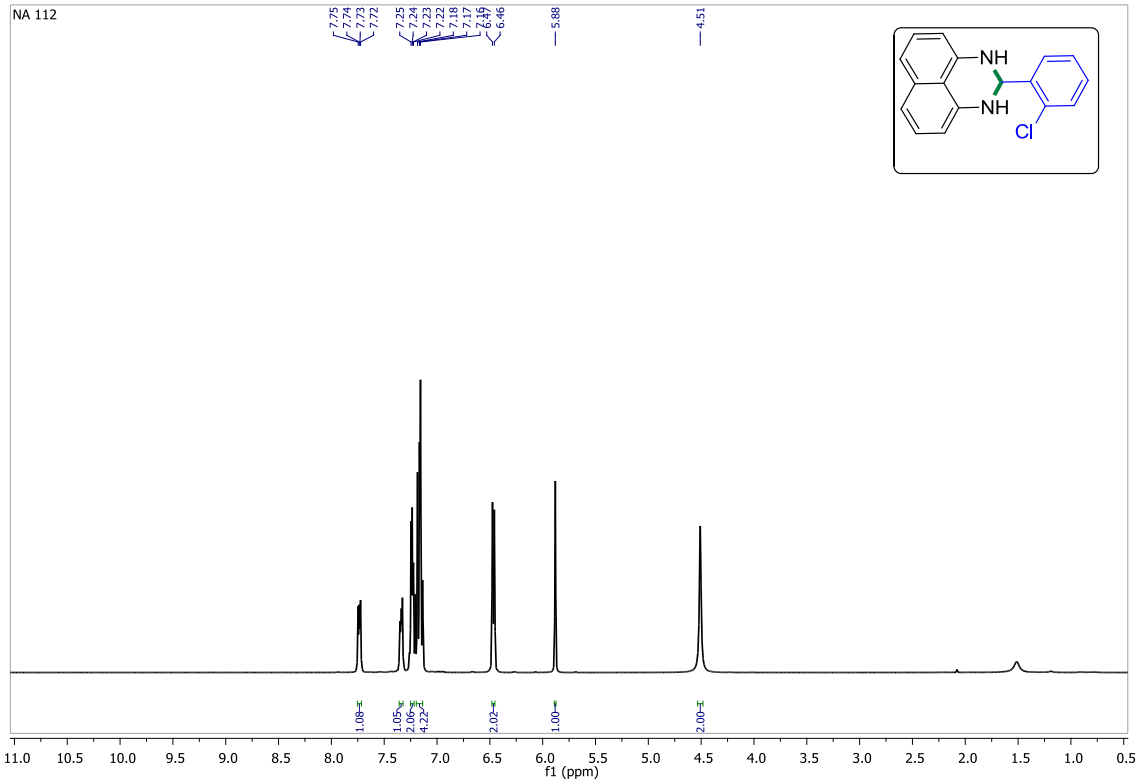


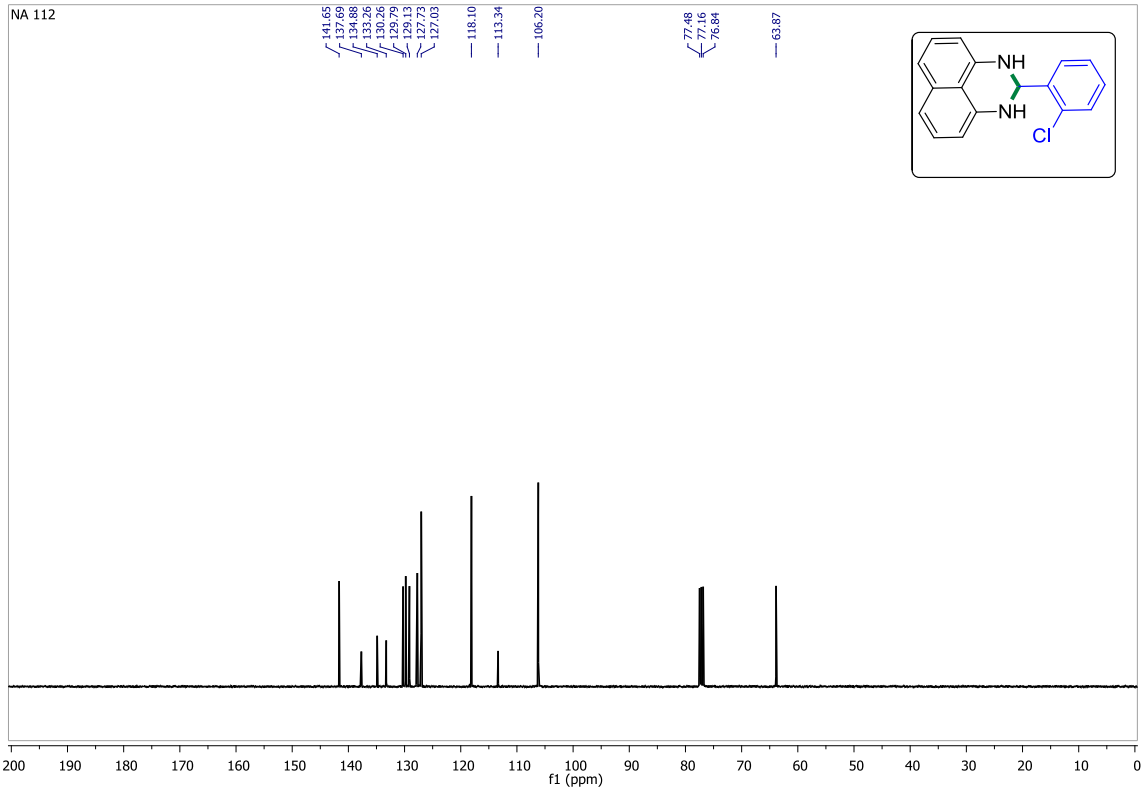
2-(2-methoxyphenyl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine (5f)



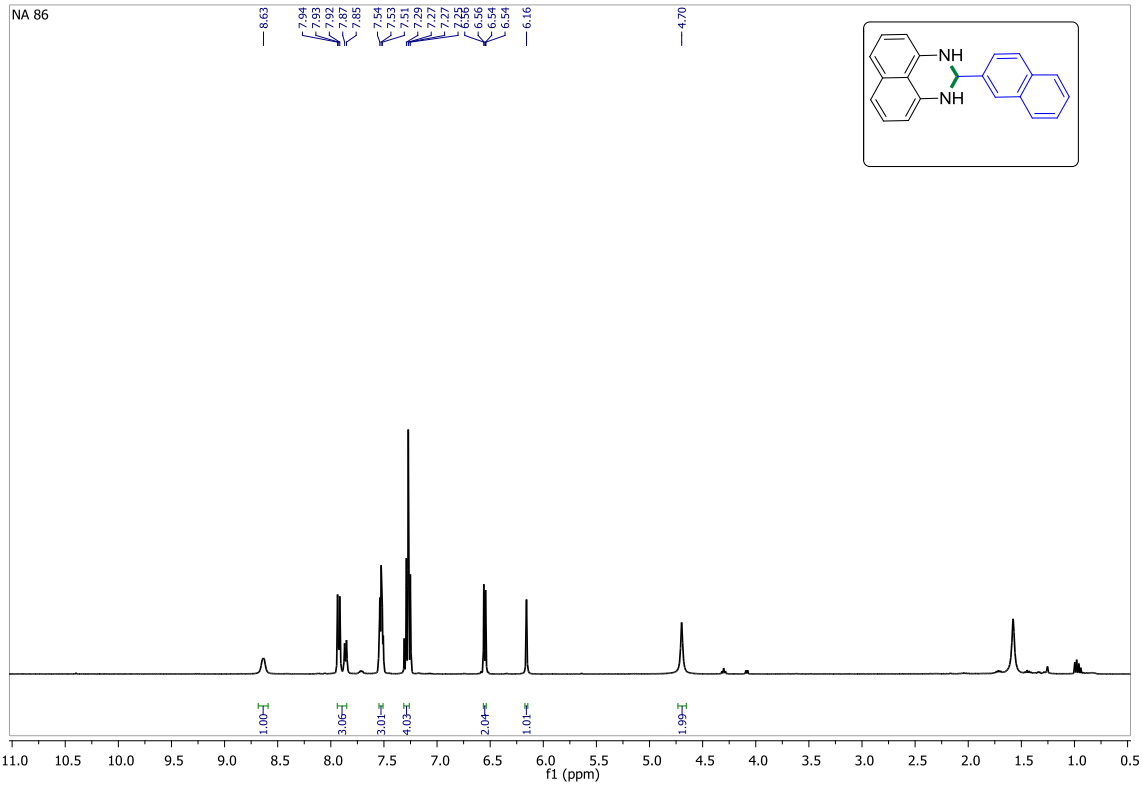


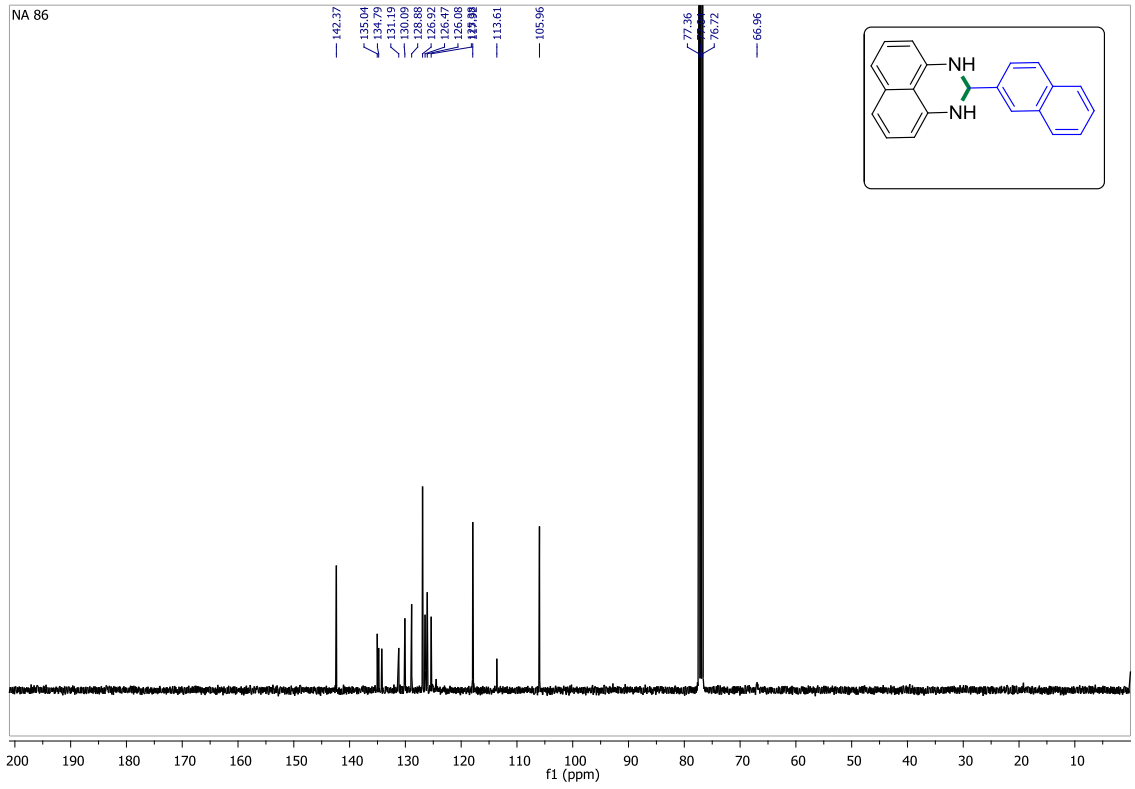
2-(2-chlorophenyl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3-dihydroperimidine (5g)



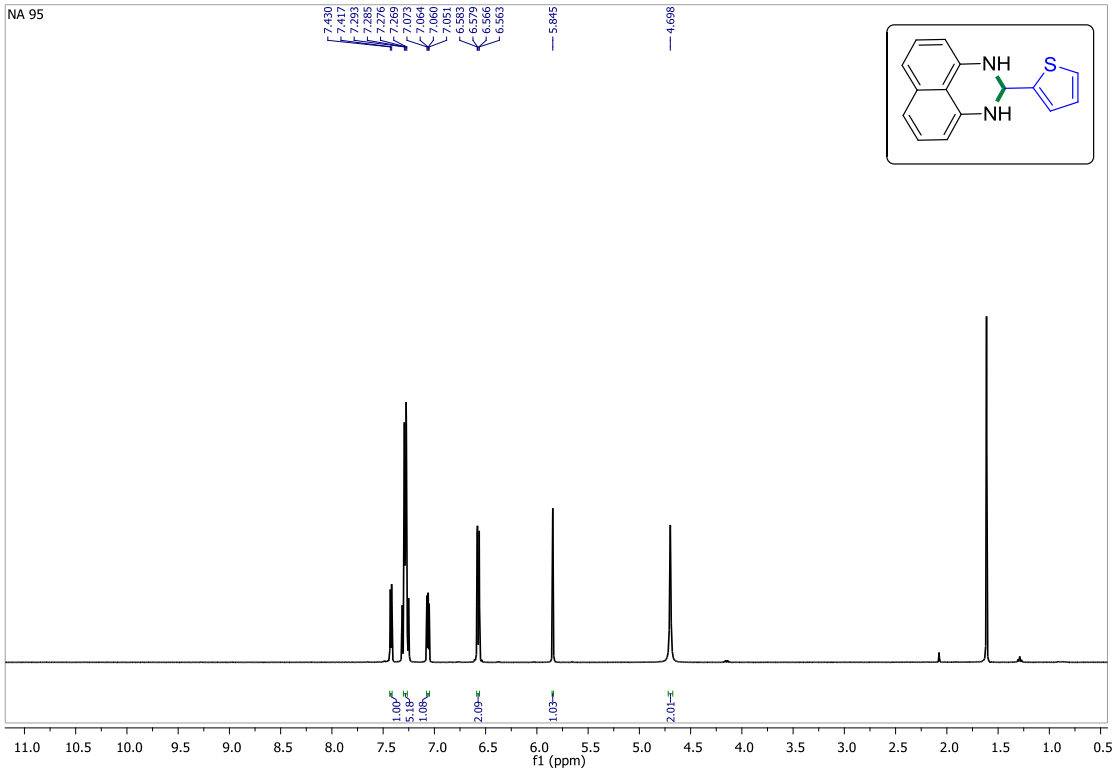


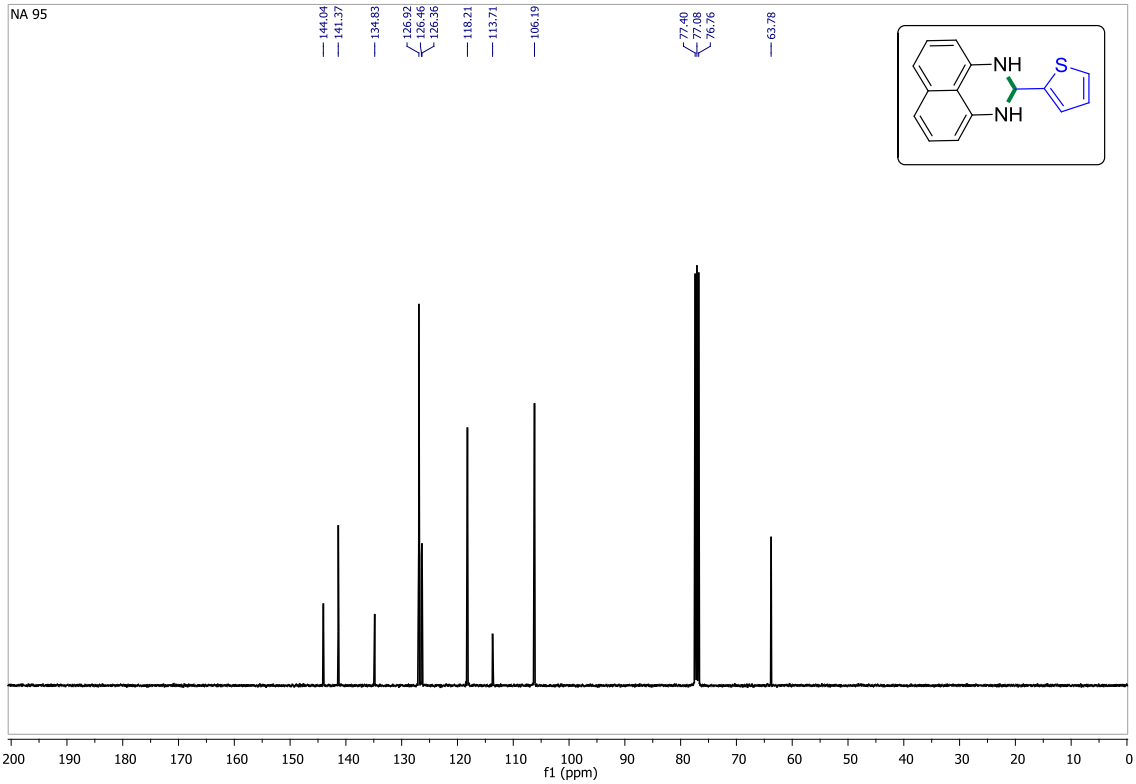
2-(naphthalen-2-yl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine (5h)





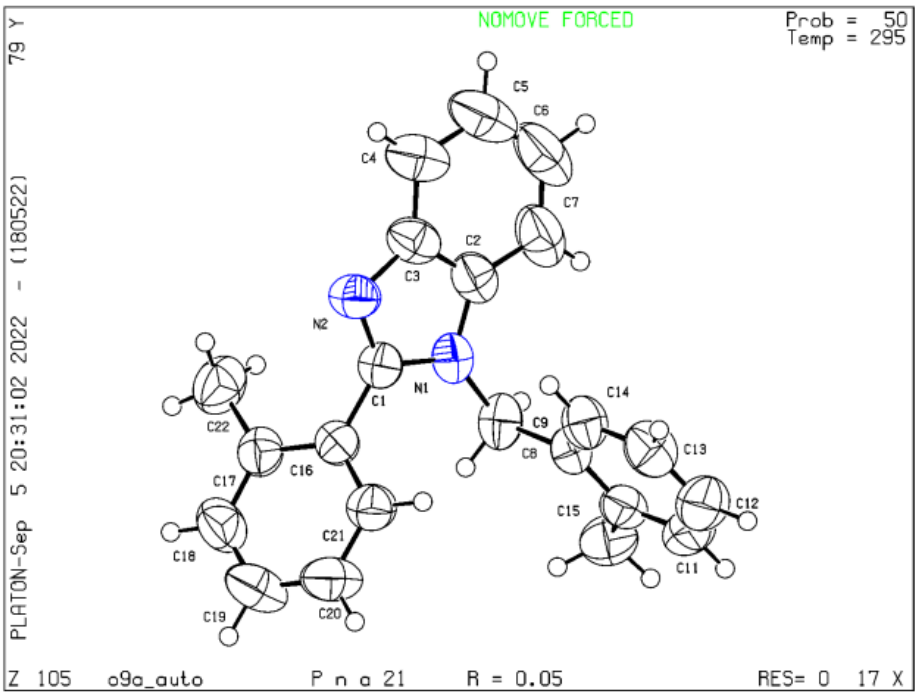
2-(thiophen-2-yl)-2,3-dihydro-1H-1H-2,3-dihydro1H-2,3- dihydroperimidine(5i)





Appendix-II

Crystallographic data of compound 3e



Single Crystal X-ray Crystallography

The crystals were mounted in turn, on a Gemini A Ultra Oxford Diffraction automatic diffractometer equipped with a CCD detector, and used for data collection. X–ray intensity data were collected with graphite monochromated MoKα radiation (λ=0.71073 Å) at a temperature of 295(2) K, with ω scan mode. Lorentz, polarization and empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm (CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.37.46) were applied. All the non–hydrogen atoms were refined anisotropically using full–matrix, least–squares technique. All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement and refined as "riding" on the adjacent carbon atom with individual isotropic temperature factor equal 1.2 times the value of equivalent temperature factor of the parent atom. The Olex2[3] and SHELXS, SHELXL[4] programs were used for all the calculations. Four fluorine atoms of the hexafluorophosphate anion were disordered over two sets. The geometrical calculations were carried out using the PLATON program. The graphics for molecular structures, pi-pi stacking and packing images for publication were obtained using Olex2 and MERCURY software packages.

Crystal sample preparation of 3e

Crystal of **3e** was prepared by using dichloromethane and pentane as solvent, the solution of which was kept at room temperature for a period of 4 days to get the single crystal.

Characterization

2.1 Table S1. Crystallographic data and the structure refinement detail for 1-(2-methylbenzyl)-2-(o-tolyl)-1H-benzo[d]imidazole

	1-(2-methylbenzyl)-2-(o-tolyl)-1H-benzo[d]imidazole
Formula	$C_{22}H_{20}N_2$
Formula weight	312.40
Crystal system	orthorhombic
Space group	Pna21
Unit cell dimensions	
a (Å)	9.9094
b (Å)	11.0437
c (Å)	15.9662
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	90
Z	1747.30(18)
Density(calcd) (g/cm^3)	1.188
Abs. coeff. (mm^{-1})	10.070
F(000)	664.0
Crystal size (mm)	0.28 x 0.13 x 0.06
Temperature (K)	295 (2)
Radiation (Å)	0.71073
θ Min, Max (°)	7.38, 58.54
Data set	13:-9, 10:-15, 20:-21
R (int)	0.0374
N_{ref}, N_{par}	4045, 219

R, wR_2, S	0.0882, 0.1030,

Important bond distances of 1-(2-methylbenzyl)-2-(o-tolyl)-1H-benzo[d]imidazole

Bond distances	
Module	Bond distance (Å)
N1-C1	1.370 (3)
N1-C2	1.386 (4)
N1-C8	1.456 (3)
N2-C1	1.318 (4)
C1-C16	1.474 (4)
C2-C3	1.390 (4)
C2-C7	1.385 (4)
C3-C4	1.391 (4)
C4-C5	1.371 (5)
C5-C6	1.390(6)
C6-C7	1.378 (5)
C8-C9	1.517 (4)
C9-C10	1.396 (4)
C9-C14	1.381(4)
C10-C11	1.379(4)
C10-C15	1.503(4)
C11-C12	1.377(5)
C12-C13	1.365(5)
C13-C14	1.383(4)
C16-C17	1.395(4)
C16-C21	1.392(4)
C17-C18	1.383(4)
C17-C21	1.507(4)
C18-C19	1.368(5)

C19-C20	1.365(5)
C20-C21	1.371(4)

Important bond angles of 1-(2-methylbenzyl)-2-(o-tolyl)-1H-benzo[d]imidazole

Module	Bond angle (^{o})
C1-N1-C2	106.2(2)
C1-N1-C8	128.2(2)
C2-N1-C8	125.5(2)
C1-N2-C3	105.1(2)
N1-C1-C16	122.3(2)
N2-C1-N1	112.9(2)
N2-C1-C16	124.8(2)
N1-C2-C3	105.8(2)
C7-C2-N1	131.4(3)
C7-C2-C3	122.8(3)
N2-C3-C2	110.0(2)
N2-C3-C4	130.1(3)
C2-C3-C4	119.9(3)
C5-C4-C3	117.7(4)
C4-C5-C6	121.5(4)
C7-C6-C5	121.8(4)
C6-C7-C2	116.1(4)
N1-C8-C9	114.2(2)
C10-C9-C8	118.0(2)
C14-C9-C8	122.3(3)
C14-C9-C10	119.7(3)
C9-C10-C15	120.9(3)
C11-C10-C9	118.3(3)
C11-C10-C15	120.9(3)

C12-C11-C10	121.8(3)
C13-C12-C11	119.7(3)
C12-C13-C14	119.7(3)
C9-C14-C13	120.9(3)
C17-C16-C1	120.6(2)
C21-C16-C1	120.0(2)
C21-C16-C17	119.5(3)
C16-C17-C22	122.5(3)
C18-C17-C16	118.0(3)
C18-C17-C22	119.5(3)
C19-C18-C17	121.8(3)
C20-C19-C18	120.3(3)
C19-C20-C21	119.4(3)
C20-C21-C16	121.1(3)