Unveiling a carbazole-based photocatalyst for visible-light-driven synthesis of indolyl diarylmethanes and 2-benzimidazoles

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1. General information

The analytical grade solvents and commercially available reagents were purchased from SDFCL, AVARICE, Fisher Scientific, MERCK, THOMAS BAKER, Spectrochem, AVRA, and LOBA Chemie., TCI chemicals. Progress of the reactions was measured by thin-layer chromatography (TLC) on pre-coated aluminium backed plates. Purification of the derivatives was done by column chromatography on Silica gel (100-200 mess sizes well as 200-400 mess size). NMR spectra were acquired on a BRUKER 500 MHZ spectrometer and JEOL 500 MHZ spectrometer for ^{1}H and 125 MHZ for ^{13}C. Chemical shifts (δ) are reported in ppm relative to residual solvent signals $CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.10 ppm for ^{13}C NMR, DMSO-D_6: 2.50 ppm for ^{1}H NMR and 39.50 ppm for ^{13}C NMR, Optical measurements, such as absorption and emission, have been conducted at room temperature on a UV−Vis spectrophotometer (Cary 300 UV-Vis spectrophotometer) and spectrofluorometer (Horiba Scientific Fluoromax4C spectrophotometer). HRMS spectra were acquired on Agilent Mass Hunter Qualitative Analysis 10 Software.

2. Experimental section

2.1. Photophysical and electrochemical analysis for E^*_{ox} and photoinduced electron transfer

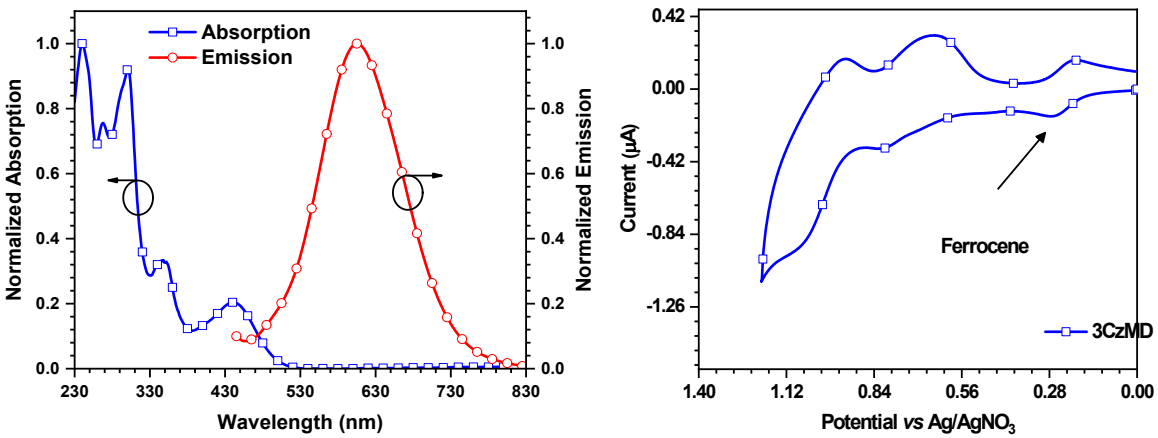


Fig. 1 a) Absorption (2 × 10^{-5}M) and emission (2 × 10^{-6}M) spectra b) Cyclic voltammograms of **MD** recorded in dichloromethane (0.1 mM).

The excited-state oxidation potential (E^*_{ox}) is a key parameter in photocatalysis and photochemistry, calculated using photophysical and electrochemical data. It provides insight into the oxidative power of a molecule in its excited state.[1]

$$E^*_{ox} = E_{ox} - E_{0\text{-}0} \quad \text{..... (i)}$$

E_{ox} : Ground-state oxidation potential

$E_{0\text{-}0}$: Singlet or triplet excitation energy, obtained from the intersection of absorption and emission spectra.

$$E^*_{ox} = -1.87 \text{ V} \quad \text{..... (ii)}$$

Photoinduced electron transfer in MD–*p*-QMs / O_2 *via* Rehm-Weller equation[2]

Rehm-Weller equation was used to compute ΔG_{S1}, the associated free energy change (ΔG), in order to examine the photoinduced electron transfer that occurred between the acceptor (*p*-QMs / O_2) and the donor (**MD**).

Rehm-Weller equation:

$\Delta G_{et} = E_{ox} - E_{red} - E_{exc} + C$……..(iii)

E_{ox} is the oxidation potential of the donor

E_{red} is the reduction potential of the acceptor

E_{exc} is the energy of the first excited state

C is the Coulomb term of the initially formed ion pair, respectively. C is negligible in polar solvents

Δ*G* for photoinduced electron transfer in MD–*p*-QMs

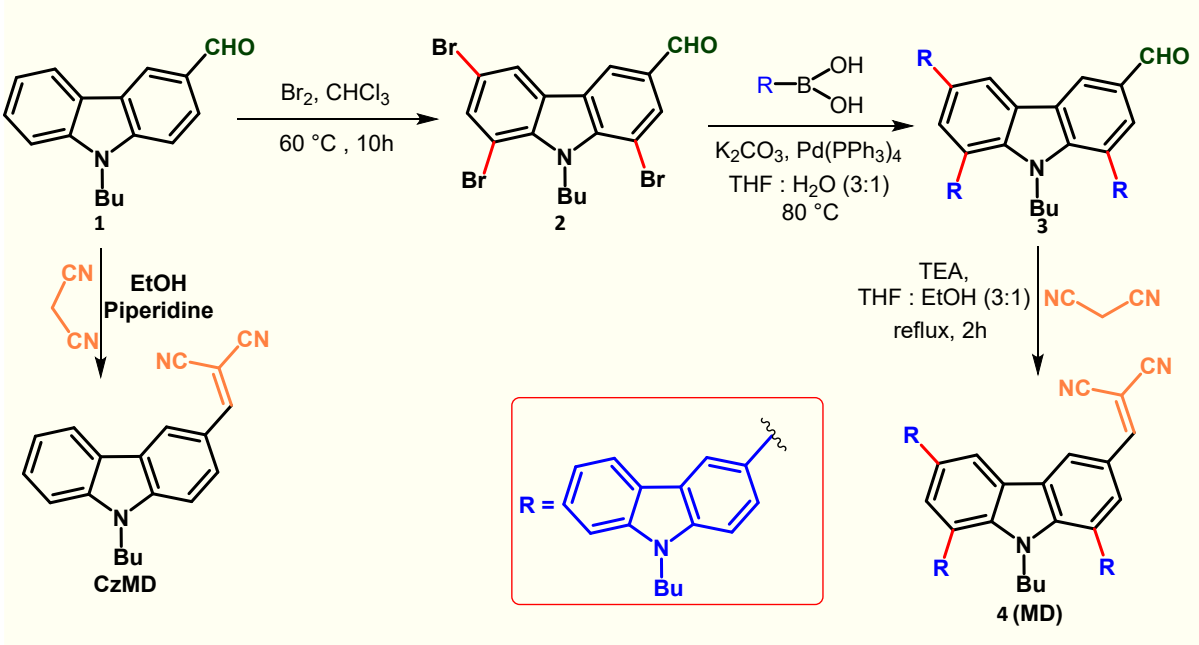
$\Delta G_{et} = E_{ox} - E_{red} - E_{exc} + C$

ΔG_{et} = -1.67 kcal/mol……..(iv)

Δ*G* for photoinduced electron transfer in MD–O_2

ΔG_{et} = -1.09 kcal/mol……..(v)

2.2. Synthesis procedure for MD



1, 6, 8-Tribromo-9-butyl-9*H*-carbazole-3-carbaldehyde (2)

9-Butyl-9*H*-carbazole-3-carbaldehyde (1.98 mmol) was dissolved in 5 mL of chloroform and stirred at room temperature. A bromine solution (9.75 mmol) diluted in 5 mL of chloroform was added dropwise to the reaction mixture. The solution was then stirred and heated to 60 °C for 10 hours, with the reaction progress monitored via TLC. Upon completion, excess bromine was quenched by adding a sodium hydrogen sulfite solution. The organic phase was extracted using chloroform, dried over sodium sulfate, and concentrated under reduced pressure. It was further purified by silica gel column chromatography, employing a 1:1 mixture of hexanes and dichloromethane as the eluent, yielding a white solid product (78%). The spectroscopic data for this compound were identical to those reported in the literature.[3] ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 10.02 (s, 1H), 8.45 (d, *J* = 1.6 Hz, 1H), 8.20 (d, *J* = 1.5 Hz, 1H), 8.18 (d, *J* = 1.9 Hz, 1H), 7.84 (d, *J* = 1.8 Hz, 1H), 5.33 – 5.11 (m, 2H), 1.94 – 1.75 (m, 1H), 1.47 – 1.38 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

9-Butyl-1, 6, 8-tris (9-butyl-9*H*-carbazole-3-yl)-9*H*-carbazole-3-carbaldehyde (3)

A reaction mixture containing 1, 6, 8-tribromo-9-butyl-9*H*-carbazole-3-carbaldehyde (0.6 mmol), 9-butyl-9*H*-carbazole-3-boronic acid (5 equivalents), $Pd(PPh_3)_4$ (4 mol%), and potassium carbonate (5 mmol) in a 3:1 mixture of THF and water was refluxed at

80 °C for 8 hours under a nitrogen atmosphere. The reaction progress was monitored using TLC. After completion, the mixture was cooled to room temperature, washed with water, and extracted with chloroform. The organic phase was thoroughly washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. The crude product was purified via silica column chromatography using a 1:2 mixture of hexanes and dichloromethane as the eluent, yielding a light yellow solid (80%). The spectroscopic data for this compound were identical to those reported in the literature.[3] ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 10.19 (s, 1H), 8.80 (s, 1H), 8.58 (s, 1H), 8.51 (s, 1H), 8.30 (s, 1H), 8.25 (s, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 8.11 (s, 2H), 7.94 (d, *J* = 1.8 Hz, 1H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.49 – 7.42 (m, 11H), 4.37 – 4.32 (m, 6H), 3.49 (m, 2H), 1.88 (m, 8H), 1.45 (m, 4H), 1.38 (t, *J* = 7.6 Hz, 4H), 0.97 – 0.92 (m, 12H).

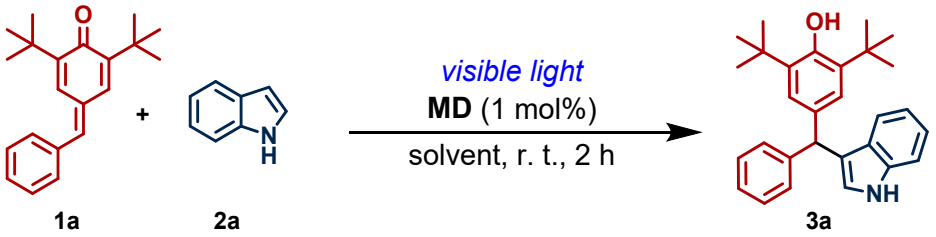
3-Dicyanovinyl-9-butyl-1, 6, 8-tris (9-butyl-9*H*-carbazole-3-yl)-9*H*-carbazole (MD)

9-Butyl-1, 6, 8-tris (9-butyl-9*H*-carbazole-3-yl)-9*H*-carbazole-3-carbaldehyde (0.4 mmol) and malononitrile (1.5 equivalents) were dissolved in a 3:1 mixture of THF and ethanol. The solution was stirred at 65 °C for 10 minutes, followed by the addition of 2–3 drops of triethylamine (TEA). The reaction was then heated at 65 °C for an additional 2 hours. The progress of the reaction was monitored using TLC. After confirming completion, the reaction mixture was poured into 50 mL of methanol, and the resulting solid was filtered and dried to yield an orange solid (90%). The spectroscopic data for this compound were identical to those reported in the literature.[3] ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 8.91 (s, 1H), 8.52 (s, 1H), 8.48 (s, 1H), 8.28 (s, 1H), 8.21 – 8.18 (m, 2H), 8.10 (s, 1H), 7.93 – 7.90 (m, 2H), 7.89 (s, 1H), 7.87 (s, 1H), 7.66 (d, *J* = 10.1 Hz, 1H), 7.58 (s, 1H), 7.52 – 7.43 (m, 13H), 4.37 – 4.34 (m, 6H), 3.48 (m, 2H), 1.96 – 1.85 (m, 8H), 1.47 – 1.36 (m, 8H), 1.01 – 0.90 (m, 12H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 160.13, 140.94, 140.05, 135.59, 132.61, 131.99, 130.97, 128.87, 126.02, 125.82, 125.50, 123.51, 123.04, 122.64, 121.01, 120.64, 120.48, 119.09, 118.92, 117.55, 115.37, 114.32, 109.15, 108.90, 108.39, 77.36, 76.85, 45.73, 43.00, 31.54, 31.14, 20.59, 19.06, 13.92, 13.13, 1.10.

HRMS (ESI) calcd for $C_{65}H_{62}N_6^+$ $(M+H)^+$ 963.5116, found 963.5159.

2.3. Reaction optimization

Table 1 Optimization of reaction conditions for indolyldiarylmethane synthesis[a]



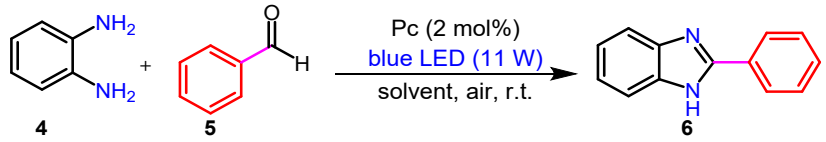
1a 2a 3a

Entry	Solvent	Light Source	Yield [%][g]
1	CH_3CN	Blue LED (427 nm)	26
2	DMSO	Blue LED (427 nm)	trace
3	DMF	Blue LED (427 nm)	15
4	MeOH	Blue LED (427 nm)	N. D.
5	EtOH	Blue LED (427 nm)	N. D.
6	CH_2Cl_2	Blue LED (427 nm)	32
7	$CHCl_3$	Blue LED (427 nm)	38
8	CCl_4	Blue LED (427 nm)	25
9[b]	$CHCl_3/CH_3CN$	Blue LED (427 nm)	73
10[c]	$CHCl_3/CH_3CN$	Blue LED (427 nm)	88
11[c]	$CHCl_3/CH_3CN$	Blue LED (440 nm)	47
12[c]	$CHCl_3/CH_3CN$	Green LED (530 nm)	N. D.
13[c]	$CHCl_3/CH_3CN$	White CFL	N. D.
14[d,c]	$CHCl_3/CH_3CN$	-	N. D.
15[e,c]	$CHCl_3/CH_3CN$	Blue LED (427 nm)	N. D.
16[f,c]	$CHCl_3/CH_3CN$	-	N. D.
17[h,c]	$CHCl_3/CH_3CN$	Blue LED (427 nm)	35
18[i,c]	$CHCl_3/CH_3CN$	Blue LED (427 nm)	76

[a]Reaction conditions: **1a** (0.15 mmol), **2a** (0.15 mmol), solvent (2 mL). Reaction time: 2 hours. [b]$CHCl_3/CH_3CN$ (3:2). [c]$CHCl_3/CH_3CN$ (3:1). [d]Reaction in dark. [e]Reaction

without catalyst. [f]Reaction without catalyst and light. [g]Isolated yields. [h]CzMD instead of 3CzMD. [i]2CzMD instead of MD.

Table 2 Optimizations for MD catalysed benzimidazole synthesis[a]

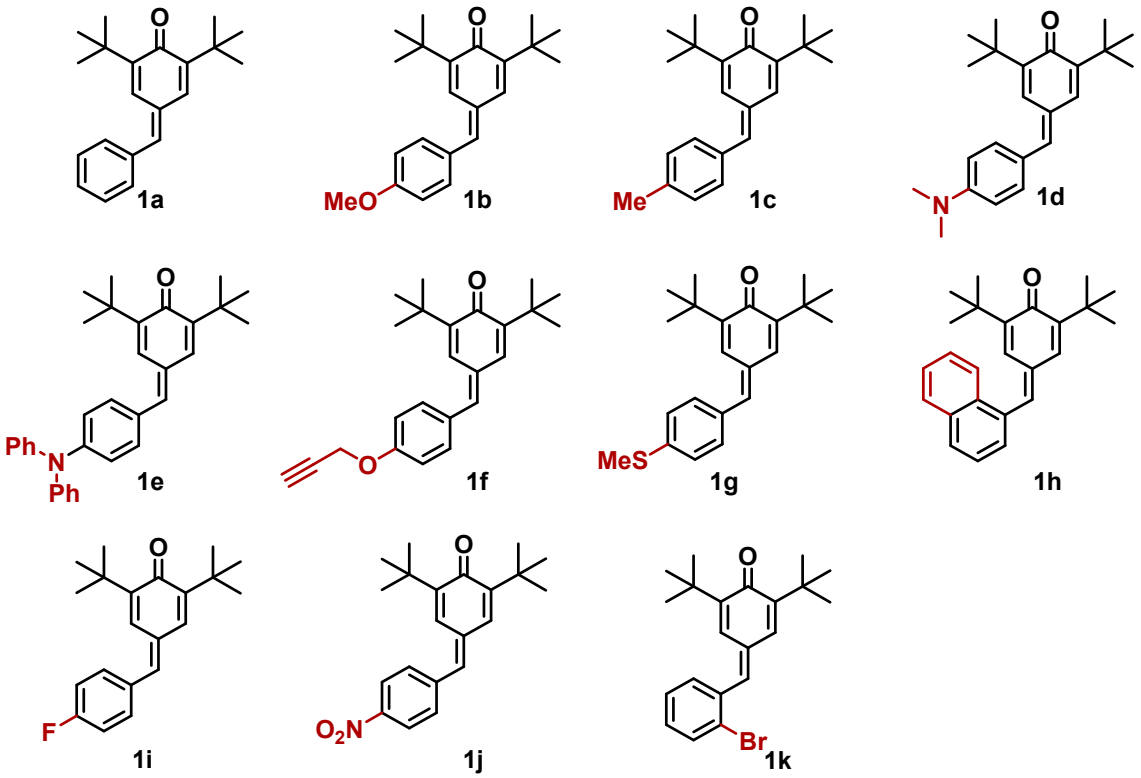


4 5 6

Entry	PC	Time (h)	solvent	Yield[%][b]
1	MD	1.5	CH_3CN	92
2	MD	1.5	MeOH	62
3	MD	1.5	DMF	10
4	MD	1.5	1,4-dioxane	48
5	MD	1	CH_3CN	67
6[c]	-	1.5	CH_3CN	18
7[d]	-	1.5	CH_3CN	8
8[e]	MD	1.5	CH_3CN	17
9[f]	MD	1.5	CH_3CN	12
10[g]	MD	1	CH_3CN	86

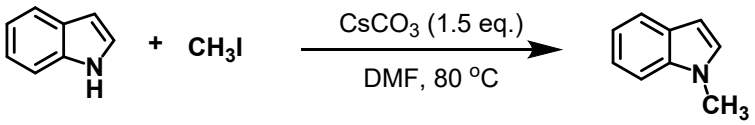
Reaction Conditions: [a]*o*-phenylenediamine (0.25 mmol), benzaldehyde (0.25 mmol). [b]isolated yield. [c]Without catalyst under blue light irradiation. [d]Without catalyst and light. [e]Reaction carried out in absence of visible-light (dark). [f] Inert atmosphere (three times freeze pump thaw). [g]The reaction was carried out in the presence of O_2.

2.4. Synthesis of *para*-quinone methides



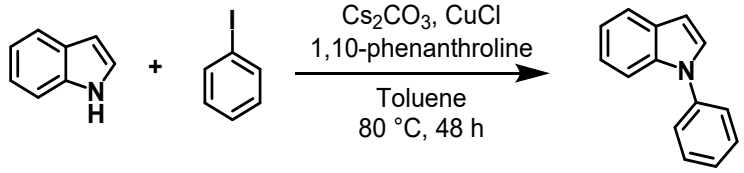
p-Quinone methides were prepared according to established protocols. Using a Dean-Stark apparatus, a mixture of aldehyde (1 eq.) and 2,6-di-*tert*-butylphenol (1 eq.) in toluene (0.25 M) was refluxed. Piperidine (2 eq.) was added dropwise over one hour, and the reaction mixture was stirred at reflux for 12 hours. After cooling the reaction to 100 °C, acetic anhydride (2 eq.) was introduced, and stirring continued for an additional 30 minutes at the same temperature. The mixture was then cooled to room temperature, poured into 100–200 mL of ice-cold water, and extracted with dichloromethane (2 × 50 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to yield a yellow residue. Purification by column chromatography using hexane and ethyl acetate as the eluent produced the final product. The spectroscopic data for these compounds were identical to those reported in the literature.[4]

2.5. Synthesis of *N*-methyl indole



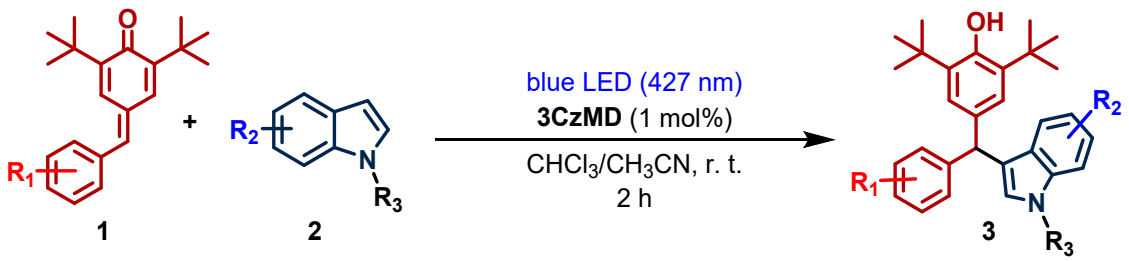
Indole (5 mmol), methyl iodide (7.5 mmol), and cesium carbonate (1.5 eq.) were mixed with DMF (10 mL) in 100 mL RB. The mixture was stirred at 80 °C for 8 hours. Upon completion, the reaction was quenched by adding ice-cold water, and the organic components were extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to yield a colorless residue. The crude product was purified via column chromatography using hexane as the eluent, affording the desired product as a colorless liquid in 78% yield. The spectroscopic data matched previously reported literature values.[5]

2.6. Synthesis of *N*-phenyl indole



The desired product was synthesized following a literature procedure.[6] Indole (1 g, 8.59 mmol), cesium carbonate (12.84 mmol), copper chloride (0.85 mmol), and 1,10-phenanthroline (1.28 mmol) were dissolved in 25 mL of anhydrous toluene in a 50 mL round-bottom flask under a nitrogen atmosphere. Iodobenzene (10.25 mmol) was added to the reaction mixture, which was then refluxed for 48 hours. After cooling to room temperature, the mixture was diluted with 40 mL of diethyl ether and filtered through a Celite pad. The filtrate was concentrated under vacuum and distilled at reduced pressure to obtain the crude product as a yellow oil. The product was purified by column chromatography using hexane as the eluent, yielding the desired compound in 95% yield as a colorless liquid. The spectroscopic data matched those reported in the literature.[6]

2.7. General procedure for the synthesis of indolyldiarylmethanes



To an oven dried 30 mL vial, *para*-quinone methide, **1a** (0.15 mmol) was dissolved in solvent (2 mL) and to this solution **MD** (1 mol%) was added followed by addition of indole, **2a** (0.15 mmol). The reaction vial was then irradiated under Kessil blue LED light (427 nm) irradiation at a distance of 4-6 Cm. The progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was removed through rota evaporator and reddish yellow residue was obtained. It was purified by column chromatography using hexane / ethyl acetate as eluent. The spectroscopic data for these compounds were identical to those reported in the literature.[7]

2.8. Light on/off study of MD-catalyzed indolyldiarylmethanes

In a 30 mL vial, 2,6-di-*tert*-butyl-4-(naphthalen-1-ylmethylene)cyclohexa-2,5-dien-1-one (0.25 mmol) was dissolved in $CDCl_3/CH_3CN$ (3 mL) and to this solution **MD** (1 mol%) was added followed by addition of indole, **2a** (0.25 mmol). After 10 minutes of stirring in the dark, (0.1 mL) of the solution was taken from the reaction vial, 0.4 mL of $CDCl_3$ was added, and NMR was recorded. The reaction vial was then exposed to 10 minutes of Kessil blue LED light (427 nm) irradiation at a distance of 4-6 cm, and NMR data was obtained. A % conversion vs. time graph was then plotted after this cycle was repeated for 120 minutes.

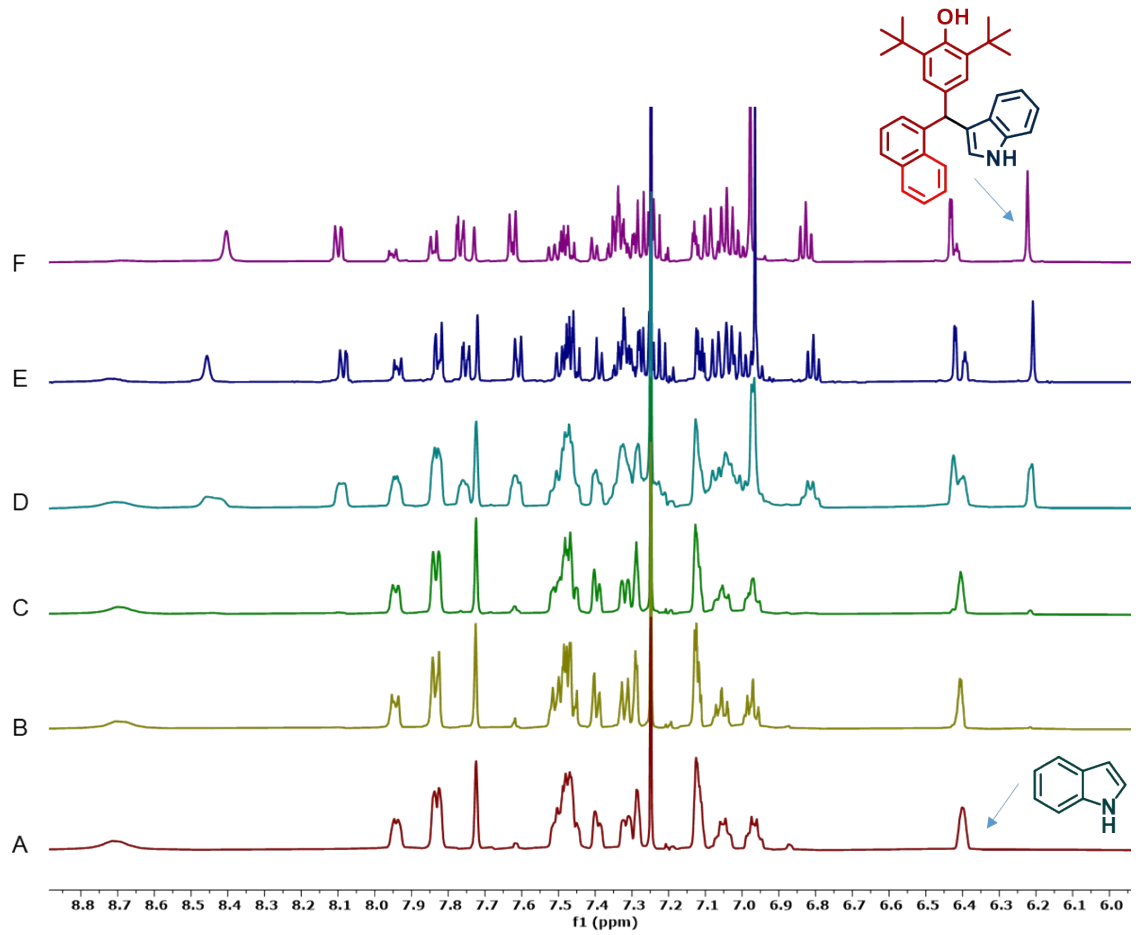


Fig. 2 Light On/Off Experiment. A: Dark, 10 minutes; B: Light 20 minutes; C: Dark, 30 minutes; D: Light, 60 minutes; E: Dark, 90 minutes; F: Light, 120 minutes.

2.9. Radical trapping in MD-catalyzed indolyldiarylmethane synthesis

To an oven dried 30 mL vial, *para*-quinone methide, **1a** (0.15 mmol) was dissolved in solvent (2 mL) and to this solution **MD** (1 mol%) was added followed by addition of indole, **2a** (0.15 mmol) and TEMPO (2 eq.). The reaction vial was then irradiated under Kessil blue LED light (427 nm) irradiation at a distance of 4-6 Cm. The progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was removed through rota evaporator and reddish yellow residue was obtained. It was purified by column chromatography using hexane / ethyl acetate as eluent.

2.10. Fluorescence quenching studies

The fluorescence emission intensities were measured using a Horiba Scientific Fluoromax4C spectrophotometer. **MD** was excited at a wavelength of 400 nm, with the emission recorded at 415 nm. In a standard experiment, the emission spectrum of

a 2×10^{-5} M solution of **MD** was obtained in a $CHCl_3/CH_3CN$ mixture, while varying the concentration of **1a** and **2a**.

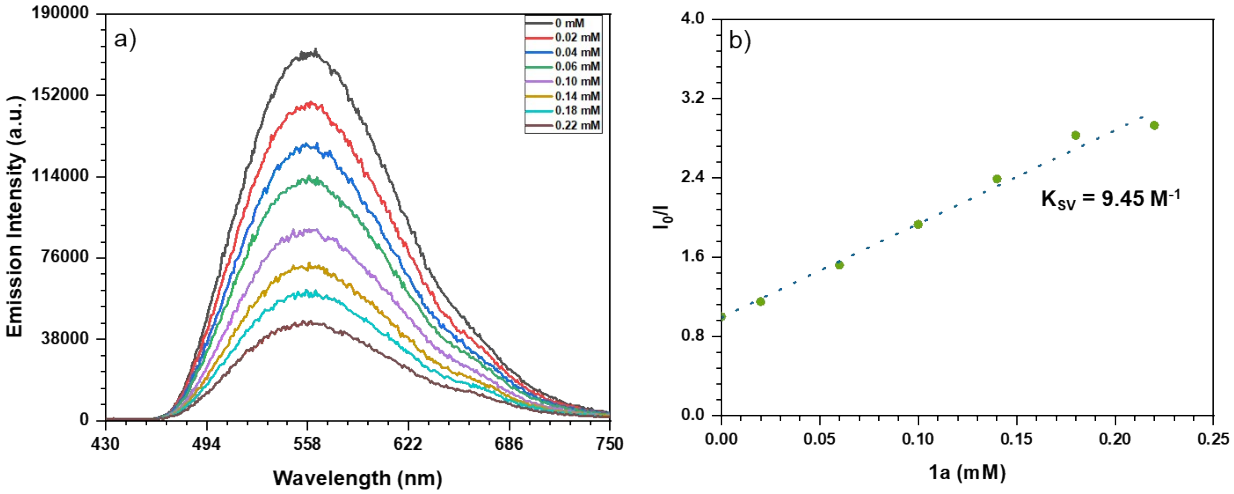


Fig. 3 (a) Fluorescence Quenching of **MD** upon Addition of *p*-QMs (**1a**); (b) stern-volmer quenching plot for **MD** in the presence of ***p*-QM (1a).**

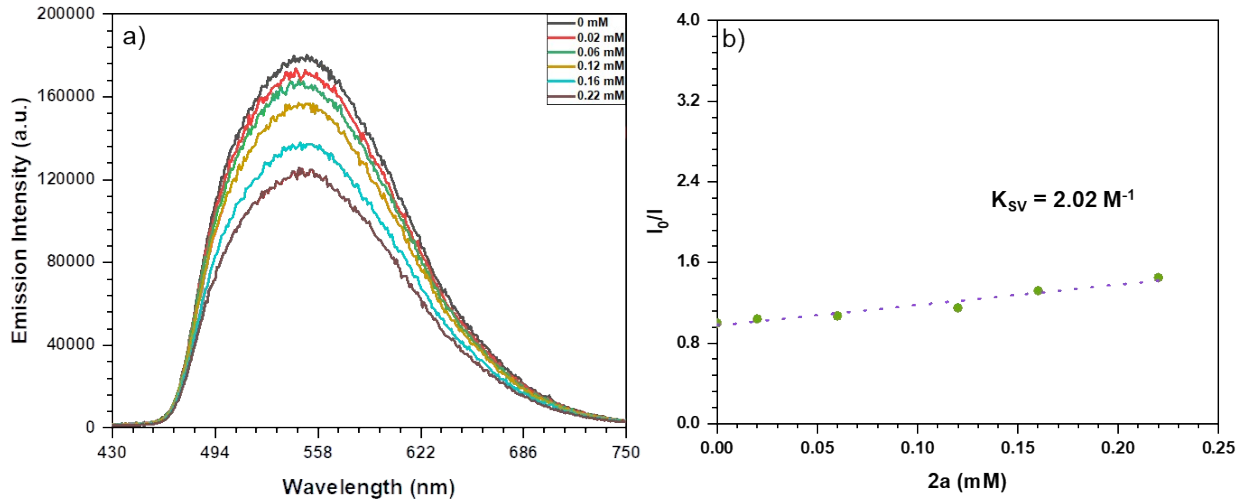
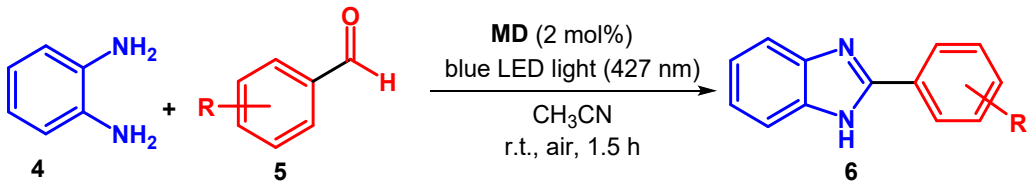


Fig. 4 (a) Fluorescence Quenching of **MD** upon addition of indole (**2a**); (b) stern-volmer quenching plot for **MD** in the presence of indole (**2a).**

2.11. Procedure for the synthesis of 2-benzimidazoles



In an oven-dried 30 mL glass vial charged with magnetic bead, aromatic aldehyde (0.25 mmol), o-phenylenediamine (0.25 mmol), acetonitrile (1.5 mL), 2 mol% of **MD** (PC) were taken. The reaction mixture was irradiated under blue LED light irradiation (427 nm) for 1.5 h in an open air at room temperature. After the completion of the reaction, solvent was evaporated under vacuum and the residue was purified by the column chromatography by using hexane/ethyl acetate as eluent to afford the final product. The spectroscopic data for these compounds were identical to those reported in the literature.[8]

2.12. Singlet oxygen detection *via* DABCO

In an oven-dried 30 mL glass vial charged with magnetic bead, aromatic aldehyde (0.25 mmol), o-phenylenediamine (0.25 mmol), acetonitrile (1.5 mL), 2 mol% of **MD** (PC) were taken. To this solution DABCO (1 eq.) was added. The reaction mixture was then irradiated under blue LED light irradiation (427 nm) for 1.5 h in an open air at room temperature. After the completion of the reaction, solvent was evaporated under vacuum and the residue was purified by the column chromatography by using hexane/ethyl acetate as eluent to afford the final product.

2.13. Reaction with 1,4-benzoquinone to detect superoxide radical anion

In an oven-dried 30 mL glass vial charged with magnetic bead, aromatic aldehyde (0.25 mmol), o-phenylenediamine (0.25 mmol), acetonitrile (1.5 mL), 2 mol% of **MD** (PC) were taken. To this solution 1,4-benzoquinone (1 eq.) was added. The reaction mixture was then irradiated under blue LED light irradiation (427 nm) for 1.5 h in an open air at room temperature. After the completion of the reaction, solvent was evaporated under vacuum and the reddish-brown residue was purified by the column chromatography by using hexane/ethyl acetate as eluent to afford the final product.

2.14. Test for the detection of H_2O_2

In an oven-dried 30 mL glass vial charged with magnetic bead, aromatic aldehyde (0.5 mmol), *o*-phenylenediamine (0.5 mmol), acetonitrile (1.5 mL), 2 mol% of **MD** (PC) were taken. The reaction mixture was irradiated under 427 blue LED light irradiation for 1.5 h in an open air at room temperature. After the completion of the reaction, chloroform (70 mL) was added to the reaction mixture and was four times extracted with water (4 × 25 mL). The aqueous layer was collected in a 250 mL conical flask. To this aqueous

layer, 1N H_2SO_4 (6 mL) was added. 3 mL (3wt.%) starch solution and 1 mmol KI were added in 20 mL water in another conical flask. The contents of the two flasks were mixed and stirred well. Within 20 seconds, the pale blue colour started appearing which became dark in the next 3-5 min (Figure 5).

Fig. 5 Conformation of H_2O_2.

2.15. Crude NMR spectra for intermediate detection

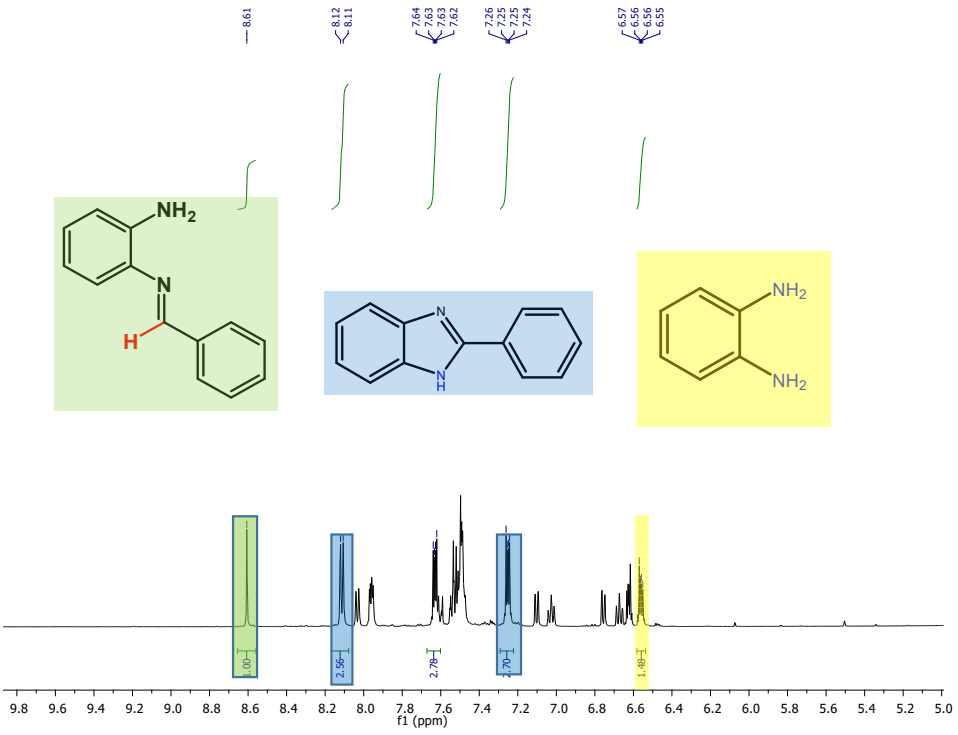


Fig. 6 ^1H NMR spectrum in CD_3CN of the reaction mixture after 30 min. of irradiation.

2.16. Experimental setup

25 Watt Kessil PR160L blue LED with a wavelength of 427 nm was used for the experiments. The reaction was carried out in a 30 mL borosilicate glass vial and a magnetic bar. During the reaction, the distance of light from the borosilicate glass vials was kept at 4-6 cm and the room temperature was 20-25 ^{0}C for all the reactions.

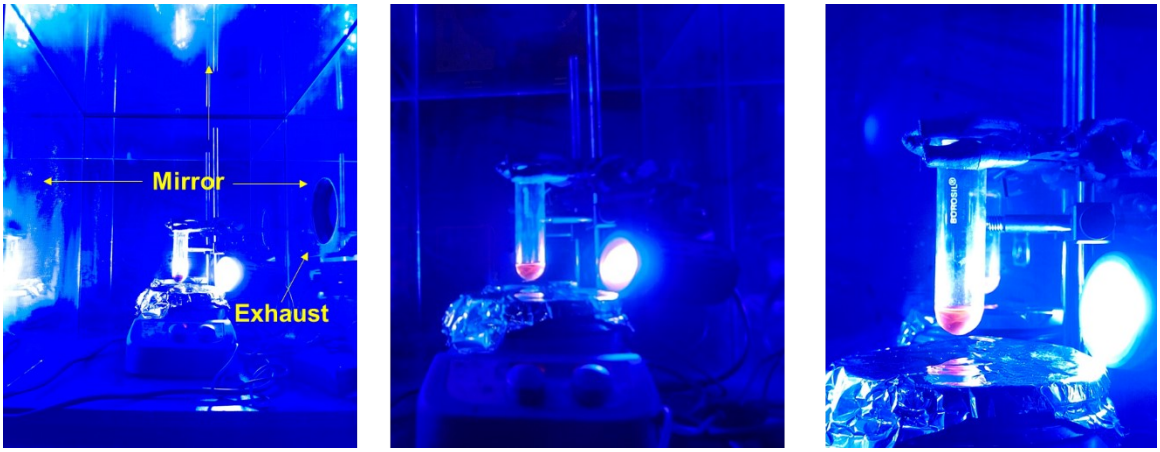


Fig. 7 Reaction setup for **MD** catalyzed synthesis of indolyldiarylmethanes and 2-benzimidazoles.

3. Spectroscopic characterizations

4-((1*H*-indol-3-yl)(phenyl)methyl)-2,6-di-*tert*-butylphenol (3aa)

The reaction was carried out according to general method **2.7.** The title compound **3aa** was obtained in **88%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.95 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 16.7 Hz, 2H), 7.25 – 7.21 (m, 5H), 7.19 – 7.13 (m, 2H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.60 (s, 1H), 5.56 (s, 1H), 5.05 (s, 1H), 1.35 (s, 18H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 157.81, 152.02, 136.94, 136.78, 135.39, 134.83, 129.90, 127.19, 125.51, 123.81, 121.95, 121.28, 120.21, 119.25, 113.53, 110.98, 55.27, 48.01, 34.40, 30.45.

2,6-di-*tert*-butyl-4-((4-fluorophenyl)(1*H*-indol-3-yl)methyl)phenol (3ba)

The reaction was carried out according to general method **2.7.** The title compound **3ba** was obtained in **91%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.93 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.16 (m, 4H), 7.03 (s, 2H), 7.03 – 6.95 (m, 3H), 6.59 (s, 1H), 5.57 (s, 1H), 5.10 (s, 1H), 1.39 (s, 18H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 162.35, 160.41, 152.16, 140.37, 136.80, 135.56, 134.37, 130.38 (d, *J* = 7.8 Hz), 127.03, 125.50, 123.91, 122.10, 120.77, 120.04, 119.37, 115.00, 114.91 (d, *J* = 21.1 Hz), 111.08, 48.05, 34.42, 30.43. ^{19}F NMR (471 MHz, CHLOROFORM-*D*) δ -117.56 – -117.60 (m).

4-((1*H*-indol-3-yl)(4-nitrophenyl)methyl)-2,6-di-*tert*-butylphenol (3ca)

The reaction was carried out according to general method **2.7.** The title compound **3ca** was obtained in **85%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 8.13 (d, *J* = 8.8 Hz, 1H), 8.03 (s, 1H), 7.39 – 7.37 (m, 3H), 7.20 – 7.15 (m, 2H), 7.02 – 6.99 (m, 3H), 6.62 (s, 1H), 5.65 (s, 1H), 5.13 (s, 1H), 1.36 (s, 18H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 152.62, 146.46, 136.82, 135.94, 132.95, 129.81, 126.71, 125.50, 124.13, 123.60, 122.44, 119.69, 119.33, 111.29, 48.77, 34.45, 30.38.

4-((2-Bromophenyl)(1*H*-indol-3-yl)methyl)-2,6-di-*tert*-butylphenol (3da)

The reaction was carried out according to general method **2.7.** The title compound **3da** was obtained in **72%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.93 (s, 1H), 7.58 (d, *J* = 9.5 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.16 (m, 4H), 7.07 (s, 2H), 7.06 – 7.03 (m, 1H), 7.00 – 6.98 (m, 1H), 6.60 (s, 1H), 5.98 (s, 1H), 5.07 (s, 1H), 1.38 (s, 18H).

4-((1*H*-indol-3-yl)(4-methoxyphenyl)methyl)-2,6-di-*tert*-butylphenol (3ea)

The reaction was carried out according to general method **2.7.** The title compound **3ea** was obtained in **78%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.91 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.17 – 7.15 (m, 3H), 7.05 (s, 2H), 7.00 – 6.97 (m, 1H), 6.81 (d, *J* = 6.6 Hz, 2H), 6.59 (s, 1H), 5.52 (s, 1H), 5.06 (s, 1H), 3.79 (s, 3H), 1.37 (s, 18H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 157.81, 152.02, 136.94, 136.78, 135.39, 134.83, 129.90, 127.19, 125.51, 123.81, 121.95, 121.28, 120.21, 119.25, 113.53, 110.98, 55.27, 48.01, 34.40, 30.45.

4-((1*H*-indol-3-yl)(*p*-tolyl)methyl)-2,6-di-*tert*-butylphenol (3fa)

The reaction was carried out according to general method **2.7.** The title compound **3fa** was obtained in **85%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.91 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.16 – 7.12 (m, 3H), 7.07 – 7.05 (m, 4H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.60 (s, 1H), 5.52 (s, 1H), 5.04 (s, 1H), 2.31 (s, 3H), 1.36 (s, 18H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 152.03, 141.72, 136.78, 135.39, 134.71, 128.88, 128.83, 127.25, 125.56, 123.80, 121.94, 121.16, 120.21, 119.24, 110.95, 48.52, 34.41, 30.45, 21.14.

2,6-di-*tert*-butyl-4-((4-(dimethylamino)phenyl)(1*H*-indol-3-yl)methyl)phenol (3ga)

The reaction was carried out according to general method **2.7.** The title compound **3ga** was obtained in **64%** yield as a red solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.89 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.15 – 7.10 (m, 3H), 7.06 (s, 2H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.1 Hz, 2H), 6.61 (s, 1H), 5.47 (s, 1H), 5.02 (s, 1H), 2.90 (s, 6H), 1.36 (s, 18H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 151.91, 149.01, 136.77, 135.27,

135.18, 133.21, 129.50, 127.33, 125.52, 123.71, 121.82, 121.66, 120.35, 119.15, 112.78, 110.89, 47.96, 40.96, 34.39, 30.47.

2,6-di-*tert*-butyl-4-((4-(diphenylamino)phenyl)(1*H*-indol-3-yl)methyl)phenol (3ha)

The reaction was carried out according to general method **2.7.** The title compound **3ha** was obtained in **71%** yield as a red solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.95 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.22 – 7.19 (m, 5H), 7.18 – 7.15 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 7.5 Hz, 2H), 7.04 (s, 2H), 7.03 – 6.99 (m, 3H), 6.96 (t, *J* = 7.3 Hz, 2H), 6.64 (s, 1H), 5.54 (s, 1H), 5.06 (s, 1H), 1.38 (s, 18H).

4-((1*H*-indol-3-yl)(4-(prop-2-yn-1-yloxy)phenyl)methyl)-2,6-di-*tert*-butylphenol (3ia)

The reaction was carried out according to general method **2.7.** The title compound **3ia** was obtained in **75%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.92 (s, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.15 – 7.13 (m, 3H), 7.02 (s, 2H), 7.00 – 6.96 (m, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.59 (s, 1H), 5.52 (s, 1H), 5.05 (s, 1H), 4.66 (d, *J* = 2.4 Hz, 2H), 2.49 (t, *J* = 2.4 Hz, 1H), 1.36 (s, 18H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 135.44, 134.72, 129.95, 125.53, 123.84, 122.00, 121.14, 120.20, 119.28, 114.59, 111.00, 76.85, 75.35, 55.99, 48.03, 34.42, 30.45.

4-((1*H*-indol-3-yl)(4-(methylthio)phenyl)methyl)-2,6-di-*tert*-butylphenol (3ja)

The reaction was carried out according to general method **2.7.** The title compound **3ja** was obtained in **80%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.94 (s, 1H), 7.34 (d, *J* = 9.2 Hz, 1H), 7.23 – 7.21 (m, 1H), 7.17 (s, 4H), 7.15 – 7.13 (m, 1H), 7.04 (s, 2H), 7.00 – 6.97 (m, 1H), 6.60 (s, 1H), 5.52 (s, 1H), 5.06 (s, 1H), 2.46 (s, 3H), 1.37 (s, 18H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 152.13, 141.95, 136.79, 135.51, 135.35, 134.33, 129.51, 127.11, 126.76, 125.52, 123.89, 122.04, 120.74, 120.14, 119.32, 111.02, 48.37, 34.41, 30.44, 16.19.

4-((1*H*-indol-3-yl)(naphthalen-1-yl)methyl)-2,6-di-*tert*-butylphenol (3ka)

The reaction was carried out according to general method **2.7.** The title compound **3ka** was obtained in **77%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 8.18 (d, *J* = 9.6 Hz, 1H), 7.90 (s, 1H), 7.86 (d, *J* = 9.6 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.36 – 7.32 (m, 2H), 7.15 (dd, *J* = 10.7, 7.0 Hz, 1H), 7.17 – 7.14 (m, 2), 7.06 (s, 2H),6.98 – 6.95 (m, 1H), 6.50 (s, 1H), 6.33 (s, 1H), 5.04 (s, 1H), 1.33 (s, 18H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 152.12, 140.55, 136.79, 135.45, 134.01, 133.77, 132.09, 128.68, 127.19, 126.87, 126.64, 125.82, 125.49, 125.42, 125.24, 124.54, 124.49, 122.01, 120.92, 120.04, 119.29, 111.00, 44.58, 34.39, 30.46.

4-((5-Bromo-1*H*-indol-3-yl)(phenyl)methyl)-2,6-di-*tert*-butylphenol (3ab)

The reaction was carried out according to general method **2.7.** The title compound **3ab** was obtained in **84%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.97 (s, 1H), 7.33 (s, 1H), 7.29 – 7.26 (m, 2H), 7.25 – 7.15 (m, 5H), 7.00 (s, 2H), 6.64 (s, 1H), 5.50 (s, 1H), 5.07 (s, 1H), 1.36 (s, 18H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 152.21, 144.28, 135.56, 135.37, 134.08, 128.92, 128.30, 126.21, 125.56, 125.08, 124.89, 122.71, 120.63, 112.62, 112.48, 48.62, 34.42, 30.42.

2,6-di-*tert*-butyl-4-((1-methyl-1H-indol-3-yl)(phenyl)methyl)phenol (3cb)

The reaction was carried out according to general method **2.7.** The title compound **3cb** was obtained in **88%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.28 – 7.25 (m, 5H), 7.22 – 7.16 (m, 3H), 7.05 (s, 2H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.45 (s, 1H), 5.55 (s, 1H), 5.05 (s, 1H), 3.71 (s, 3H), 1.37 (s, 18H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 152.05, 144.93, 137.51, 135.40, 134.67, 129.01, 128.55, 128.16, 127.58, 125.94, 125.63, 121.49, 120.25, 119.23, 118.69, 109.06, 48.88, 34.42, 32.77, 30.46.

2,6-di-*tert*-butyl-4-(phenyl(1-phenyl-1H-indol-3-yl)methyl)phenol (3cc)

The reaction was carried out according to general method **2.7.** The title compound **3cc** was obtained in **81%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.57 (d, *J* = 8.4 Hz, 1H), 7.51 – 7.45 (m, 5H), 7.32 – 7.30 (m, 5H), 7.23 – 7.18 (m, 2H), 7.11 (s, 2H), 7.06 – 7.03 (m, 1H), 6.80 (s, 1H), 5.64 (s, 1H), 5.09 (s, 1H), 1.39 (s, 18H). ^{13}C NMR

(126 MHz, CHLOROFORM-*D*) δ 152.17, 144.45, 140.02, 136.55, 135.50, 134.23, 129.61, 129.56, 129.04, 128.69, 128.27, 127.54, 126.11, 125.64, 124.26, 124.20, 122.43, 121.93, 120.51, 119.92, 110.45, 48.83, 34.44, 30.46.

2-Phenyl-1*H*-benzo[*d*]imidazole (6a)

The reaction was carried out according to general method **2.11.** The title compound **6a** was obtained in **92%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.90 (s, 1H), 8.18 (d, *J* = 7.0 Hz, 2H) 7.69 – 7.60 (m, 1H), 7.55 (m, 2H), 7.53 – 7.47 (m, 2H), 7.20 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 151.22, 143.80, 130.16, 129.87, 128.98, 126.43, 122.56, 121.69, 118.89, 111.34.

2-(4-Fluorophenyl)-1*H*-benzo[*d*]imidazole (6b)

The reaction was carried out according to general method **2.11.** The title compound **6b** was obtained in **89%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.93 (s, 1H), 8.26 – 8.18 (m, 2H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 8.9 Hz, 2H), 7.20 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 149.44, 147.78, 133.11, 131.38 (d, *J* = 5.4 Hz), 124.74 (d, *J* = 5.4 Hz), 123.53, 122.38, 119.72, 115.00, 112.14. ^{19}F NMR (471 MHz, DMSO) δ -110.90 – -111.12 (m).

2-(4-Chlorophenyl)-1*H*-benzo[*d*]imidazole (6c)

The reaction was carried out according to general method **2.11.** The title compound **6c** was obtained in **94%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.98 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.27 – 7.16 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 150.11, 143.71, 134.98, 134.45, 129.05, 129.03, 128.10, 122.75, 121.81, 118.93, 111.38.

2-(4-Bromophenyl)-1*H*-benzo[*d*]imidazole (6d)

The reaction was carried out according to general method **2.11.** The title compound **6d** was obtained in **84%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.99 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 61.8 Hz, 2H), 7.22 (s, 2H).

2-(4-Nitrophenyl)-1*H*-benzo[*d*]imidazole (6e)

The reaction was carried out according to general method **2.11.** The title compound **6e** was obtained in **67%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 13.30 (s, 1H), 8.44 – 8.40 (m, 4H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.27 (dd, *J* = 16.5, 7.9 Hz, 2H).

2-(Pyridin-4-yl)-1*H*-benzo[*d*]imidazole (6f)

The reaction was carried out according to general method **2.11.** The title compound **6f** was obtained in **89%** yield as a reddish-brown solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 13.28 (s, 1H), 8.76 (d, *J* = 6.0 Hz, 2H), 8.10 (d, *J* = 6.1 Hz, 2H), 7.67 (d, *J* = 63.2 Hz, 2H), 7.27 (s, 2H).

2-(*p*-Tolyl)-1*H*-benzo[*d*]imidazole (6g)

The reaction was carried out according to general method **2.11.** The title compound **6g** was obtained in **88%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.82 (s, 1H), 8.06 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 6.9 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.23 – 7.14 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 150.94, 143.39, 139.13, 134.52, 129.09, 127.03, 125.96, 121.90, 121.13, 118.28, 110.76, 20.55.

2-(4-Isopropylphenyl)-1*H*-benzo[*d*]imidazole (6h)

The reaction was carried out according to general method **2.11.** The title compound **6h** was obtained in **92%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.82 (s, 1H), 8.11 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.222 – 7.16 (m, 2H), 3.02 – 2.91 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 6H).

2-(4-Methoxyphenyl)-1*H*-benzo[*d*]imidazole (6i)

The reaction was carried out according to general method **2.11.** The title compound **6i** was obtained in **85%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.73 (s, 1H), 8.11 (d, *J* = 8.8

Hz, 2H), 7.55 (dd, *J* = 62.8, 7.4 Hz, 2H), 7.19 – 7.14 (m, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H).

4-(1*H*-benzo[*d*]imidazol-2-yl)-*N,N*-dimethylaniline (6j)

The reaction was carried out according to general method **2.11.** The title compound **6a** was obtained in **82%** yield as a reddish-brown solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.54 (s, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 42.1 Hz, 2H), 7.12 (dd, *J* = 5.9, 2.9 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 2.99 (s, 6H).

4-(1*H*-benzo[*d*]imidazol-2-yl)phenol (6k)

The reaction was carried out according to general method **2.11.** The title compound **6k** was obtained in **75%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.61 (s, 1H), 9.96 (s, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.53 (s, 2H), 7.15 (dd, *J* = 5.8, 3.1 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H).

2-(2-Bromophenyl)-1*H*-benzo[*d*]imidazole (6l)

The reaction was carried out according to general method **2.11.** The title compound **6l** was obtained in **87%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.73 (s, 1H), 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.76 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.67 – 7.52 (m, 2H), 7.47 (td, *J* = 7.8, 1.8 Hz, 1H), 7.25 – 7.23 (m, 2H).

2-(2-Nitrophenyl)-1*H*-benzo[*d*]imidazole (6m)

The reaction was carried out according to general method **2.11.** The title compound **6m** was obtained in **55%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.92 (s, 1H), 8.22 (ddd, *J* = 8.4, 5.3, 2.5 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.45 – 7.36 (m, 2H), 7.23 – 7.17 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 164.52, 162.56, 150.86, 144.21, 135.48, 129.23, 129.16, 127.28, 127.25, 123.04, 122.20, 119.30, 116.57, 116.39, 111.79.

2-(Pyridin-2-yl)-1*H*-benzo[*d*]imidazole (6n)

The reaction was carried out according to general method **2.11.** The title compound **6n** was obtained in **86%** yield as a brown solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 13.09 (s, 1H), 8.73 (d, *J* = 4.6 Hz, 1H), 8.33 (d, *J* = 7.9 Hz, 1H), 8.00 (td, *J* = 7.7, 1.8 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.23 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 151.19, 149.84, 149.00, 144.33, 138.01, 135.39, 125.18, 123.58, 122.34, 121.87, 119.75, 112.53.

2-(1*H*-benzo[*d*]imidazol-2-yl)quinolone (6o)

The reaction was carried out according to general method **2.11.** The title compound **6o** was obtained in **91%** yield as a brown solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 13.18 (s, 1H), 8.55 (d, *J* = 8.6 Hz, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.10 – 8.05 (m, 1H), 7.87 (t, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 151.18, 149.21, 147.68, 144.42, 137.87, 135.67, 130.92, 129.22, 128.71, 128.56, 127.76, 124.04, 122.51, 120.02, 119.68, 112.74.

2-(naphthalen-1-yl)-1*H*-benzo[*d*]imidazole (6p)

The reaction was carried out according to general method **2.11.** The title compound **6p** was obtained in **86%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.92 (s, 1H), 9.11 (d, *J* = 7.2 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 8.07 – 7.97 (m, 2H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.72 – 7.56 (m, 4H), 7.31 – 7.21 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 151.82, 144.38, 134.92, 134.10, 130.99, 130.61, 128.85, 128.32, 128.02, 127.52, 126.82, 126.80, 125.74, 123.10, 122.06, 119.55, 111.82.

1,4-bis(1*H*-benzo[*d*]imidazol-2-yl)benzene (6q)

The reaction was carried out according to general method **2.11.** The title compound **6q** was obtained in **81%** yield as a off-white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 13.05 (s, 1H), 8.35 (s, 4H), 7.63 (s, 4H), 7.24 (dd, *J* = 5.8, 3.0 Hz, 4H).

2-(anthracen-9-yl)-1*H*-benzo[*d*]imidazole (6r)

The reaction was carried out according to general method **2.11.** The title compound **6r** was obtained in **82%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 13.01 (s, 1H), 8.85 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.64 – 7.57 (m, 3H), 7.55 – 7.48 (m, 2H), 7.33 (m, 2H).

2-ethyl-1*H*-benzo[*d*]imidazole (6s)

The reaction was carried out according to general method **2.11.** The title compound **6s** was obtained in **88%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.18 (s, 1H), 7.46 (dd, *J* = 5.9, 3.2 Hz, 2H), 7.11 – 7.08 (m, 2H), 2.82 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-D_6) δ 156.17, 121.06, 115.16, 21.98, 12.25. ^{13}C NMR (126 MHz, DMSO) δ 155.16, 121.01, 110.80 30.90, 28.50, 27.30, 21.87, 13.88.

2-pentyl-1*H*-benzo[*d*]imidazole (6t)

The reaction was carried out according to general method **2.11.** The title compound **6t** was obtained in **93%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, DMSO) δ 12.17 (s, 1H), 7.45 (s, 2H), 7.11 – 7.08 (m, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 1.76 (p, *J* = 7.4 Hz, 2H), 1.34 – 1.31 (m, 3H), 0.98 – 0.85 (m, 3H). ^{13}C NMR (126 MHz, DMSO) δ 155.16, 121.01, 110.80 30.90, 28.50, 27.30, 21.87, 13.88.

5-methyl-2-phenyl-1*H*-benzo[*d*]imidazole (6u)

The reaction was carried out according to general method **2.11.** The title compound **6u** was obtained in **87%** yield as a white solid after passing through a short silica gel column chromatography. ^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 8.05 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.51 – 7.39 (m, 5H), 7.09 (d, *J* = 9.8 Hz, 1H), 2.47 (s, 3H).

4. Computational analysis

The ground state (S_0) geometries optimizations of all compounds were performed by DFT using B3LYP functional with the def2-SVP basis set and D3BJ (dispersion interaction) in ORCA 5.0.3 software. All the optimized structures were characterized by frequency analysis, and all the frequencies were positive. The Time dependent method was utilized for TD-DFT calculations in gaseous state at optimized S_0 geometry. Natural transition orbitals (NTO) were obtained using wavefunction analyser program (Multiwfn)[9] and plotted in GaussView software.

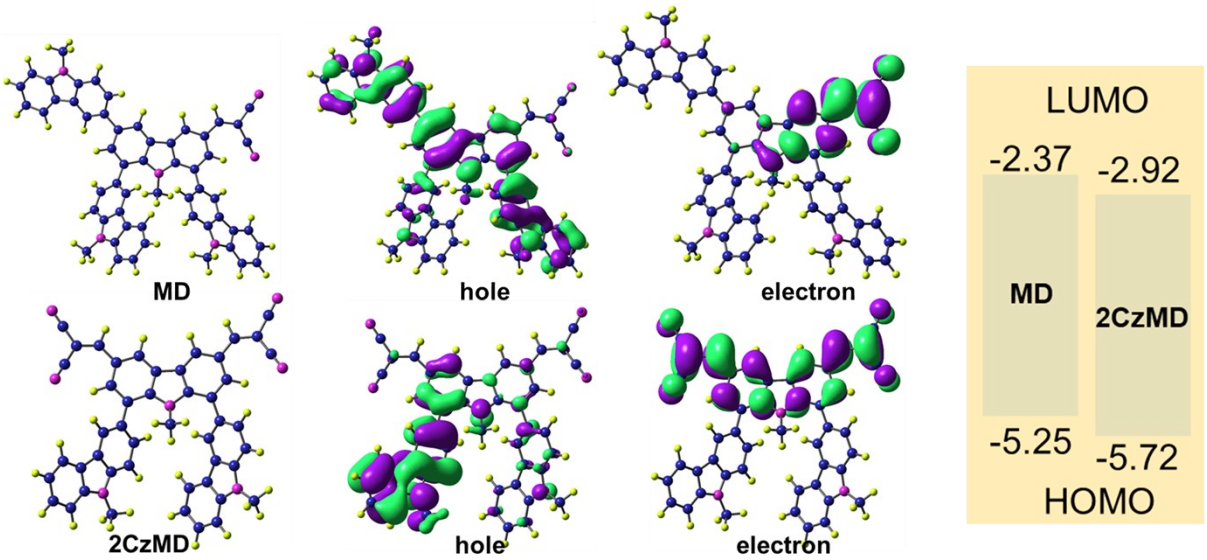


Fig. 8 HOMO-LUMO distribution in **MD** and **2CzMD.**

Table 3 Electronic Properties of Photocatalysts: HOMO-LUMO Levels, Energy Gaps (S1 and T1), and ΔE_{ST}

MD	HOMO (eV)	LUMO (eV)	EGap (eV)	S1 (eV)	T1 (eV)	ΔE_{ST} (eV)
	-5.2540	-2.3739	2.8801	2.576	2.141	0.435
2CzMD	HOMO (eV)	LUMO (eV)	EGap (eV)	S1 (eV)	T1 (eV)	ΔE_{ST} (eV)

-5.7286	-2.9214	2.8072	2.477	2.149	0.328

5. References

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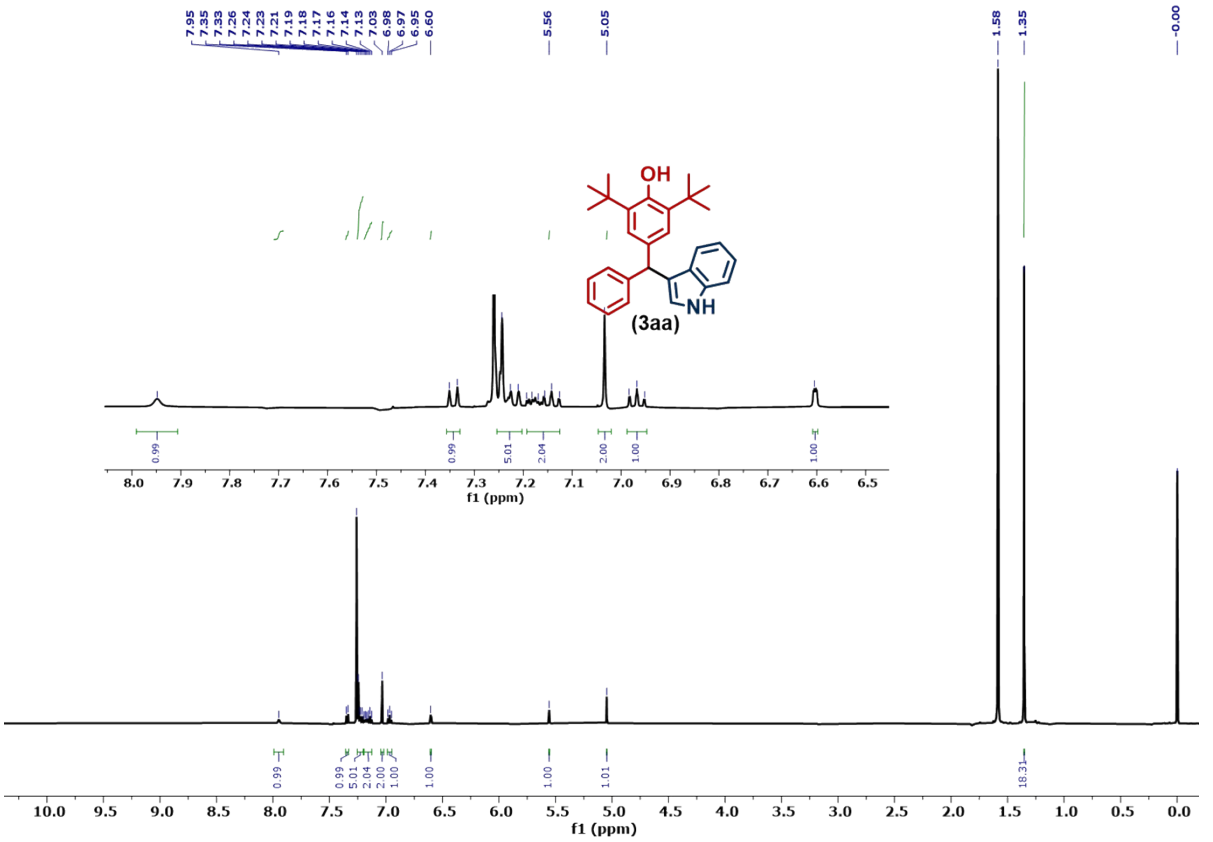
6. NMR data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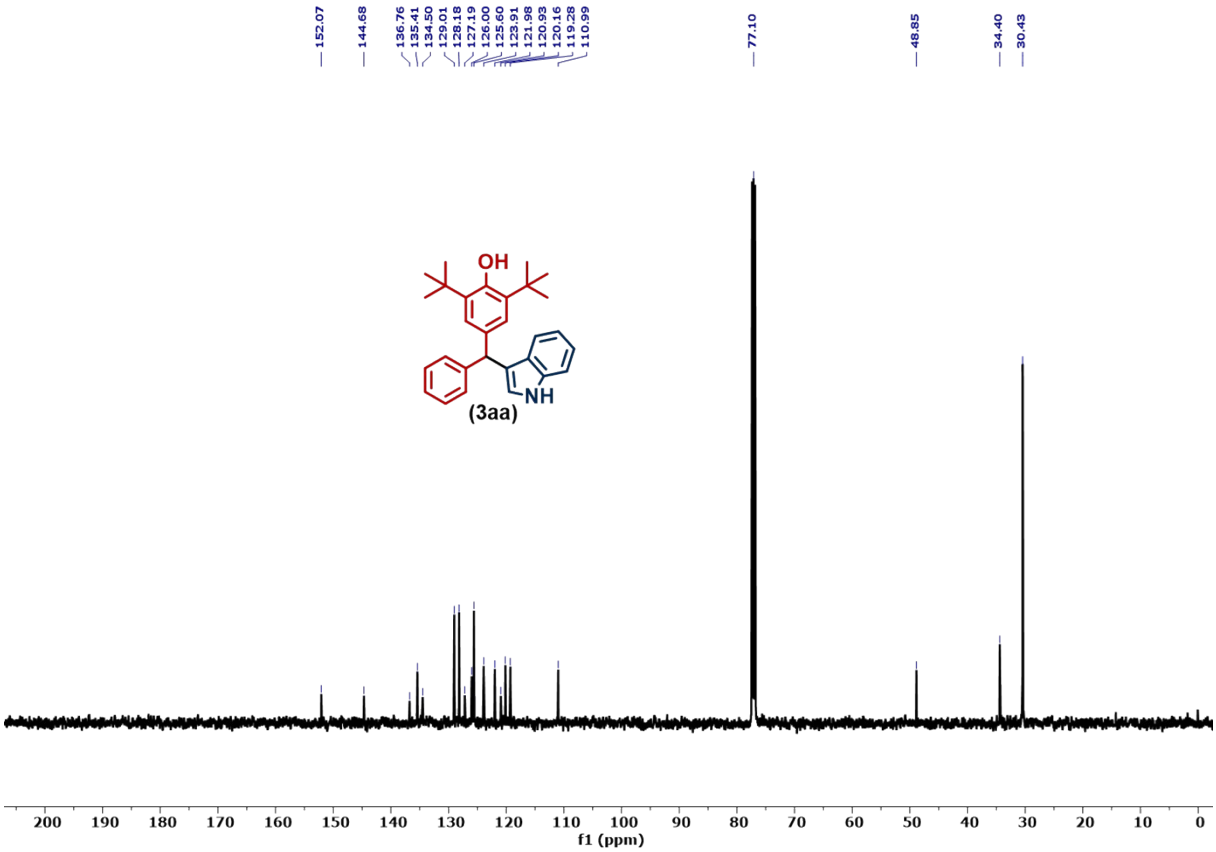
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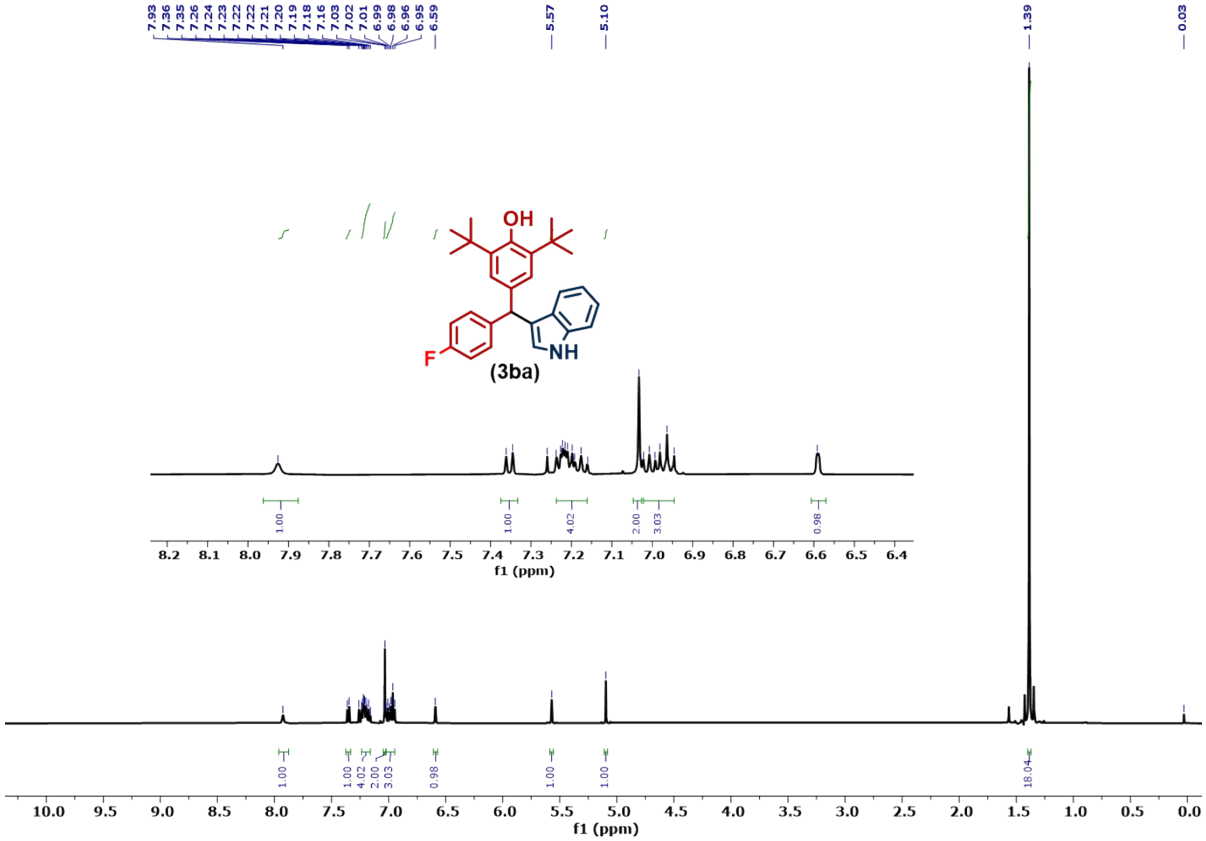
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7.01
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6.95
6.59
5.57
5.10
1.39
0.03
OH
F
NH
(3ba)
1.00
1.00
4.02
2.00
3.03
0.98
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4
f1 (ppm)
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2.00
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1.00
1.00
18.04
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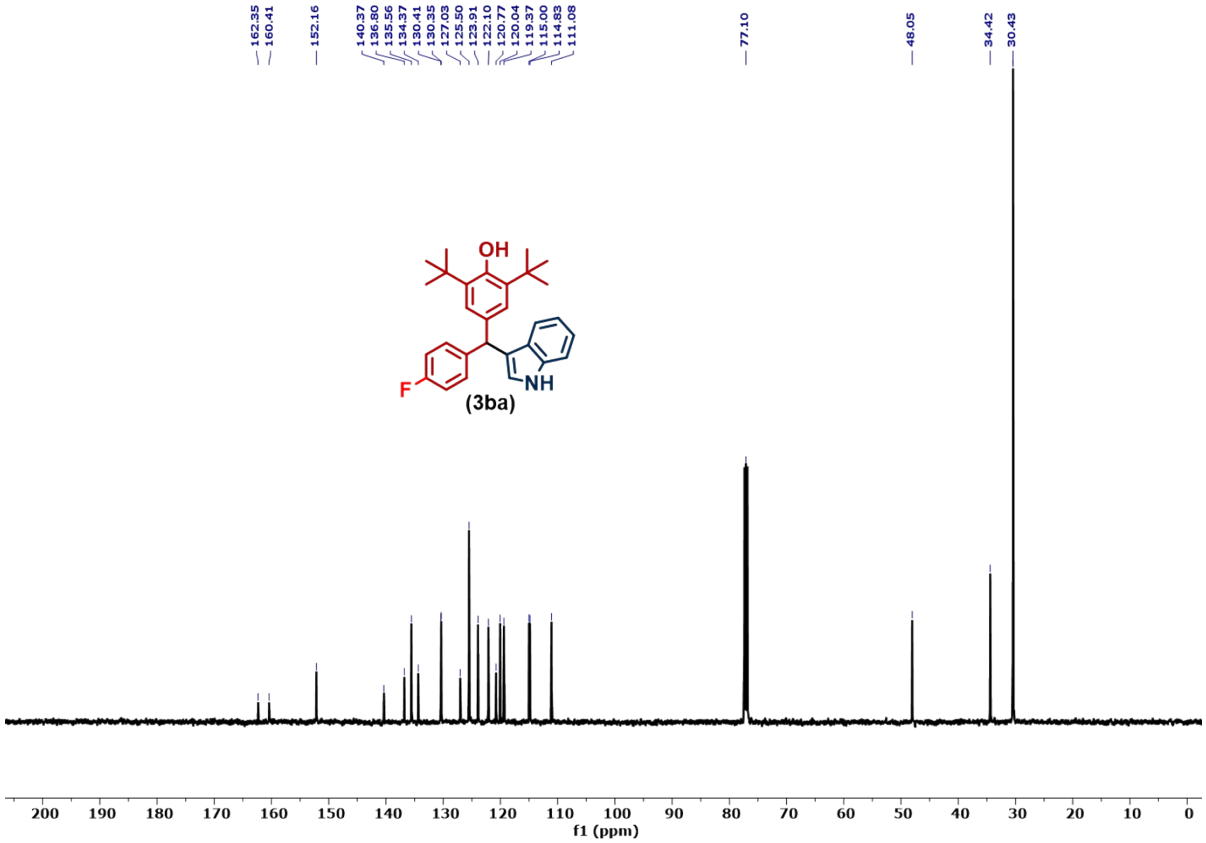
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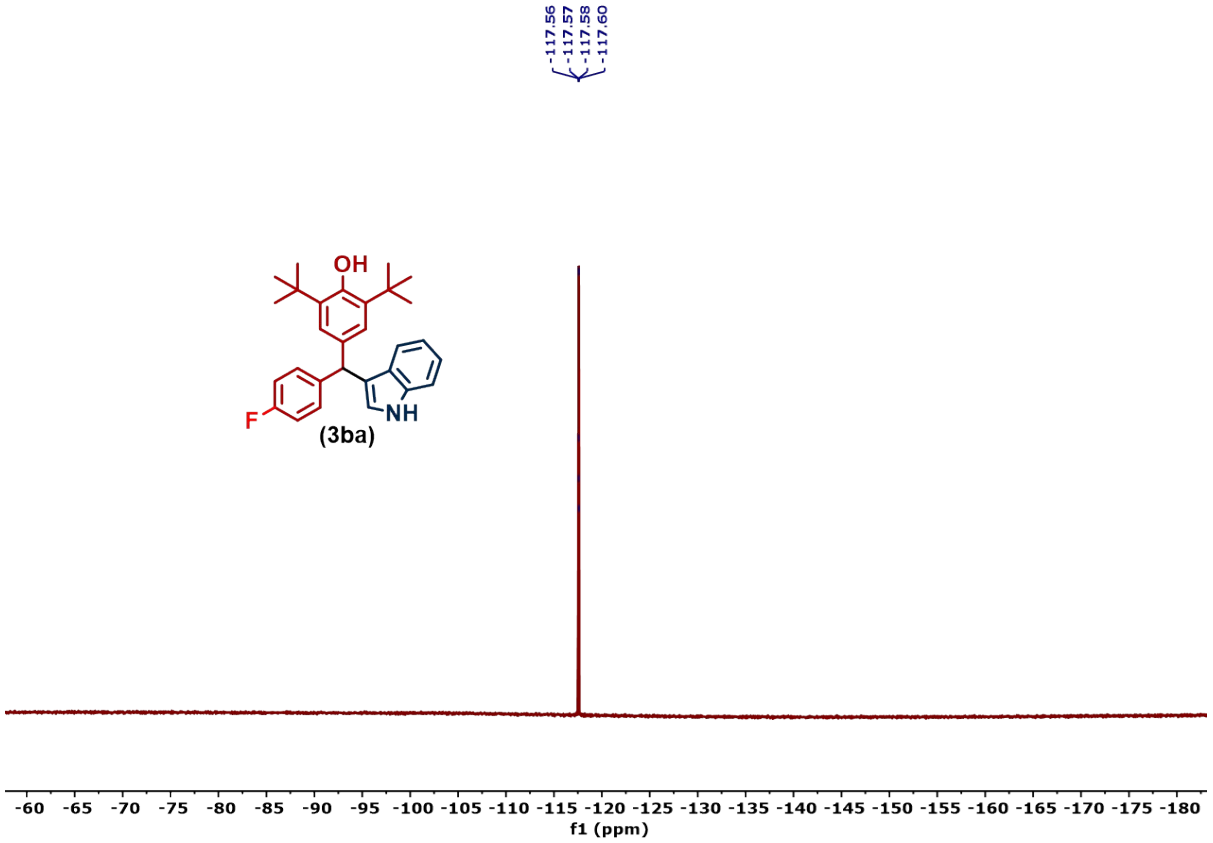
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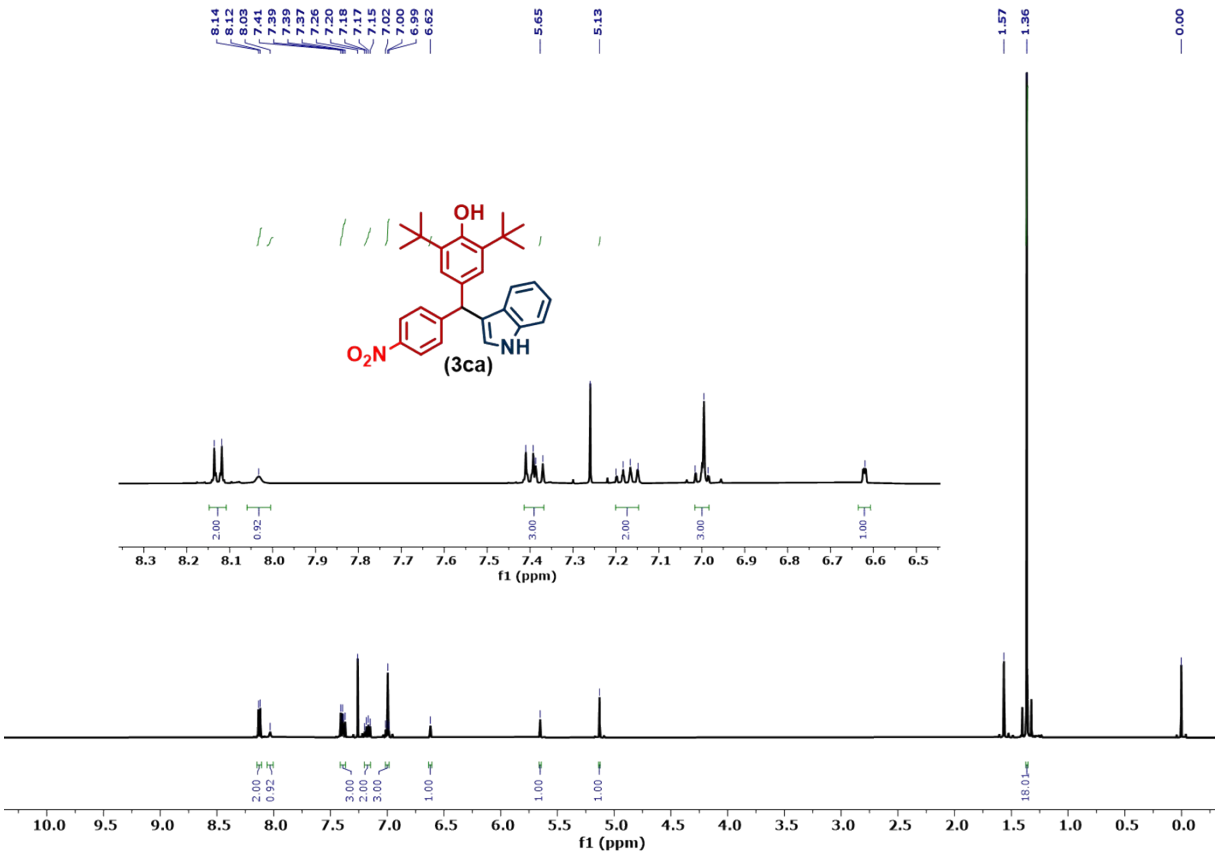
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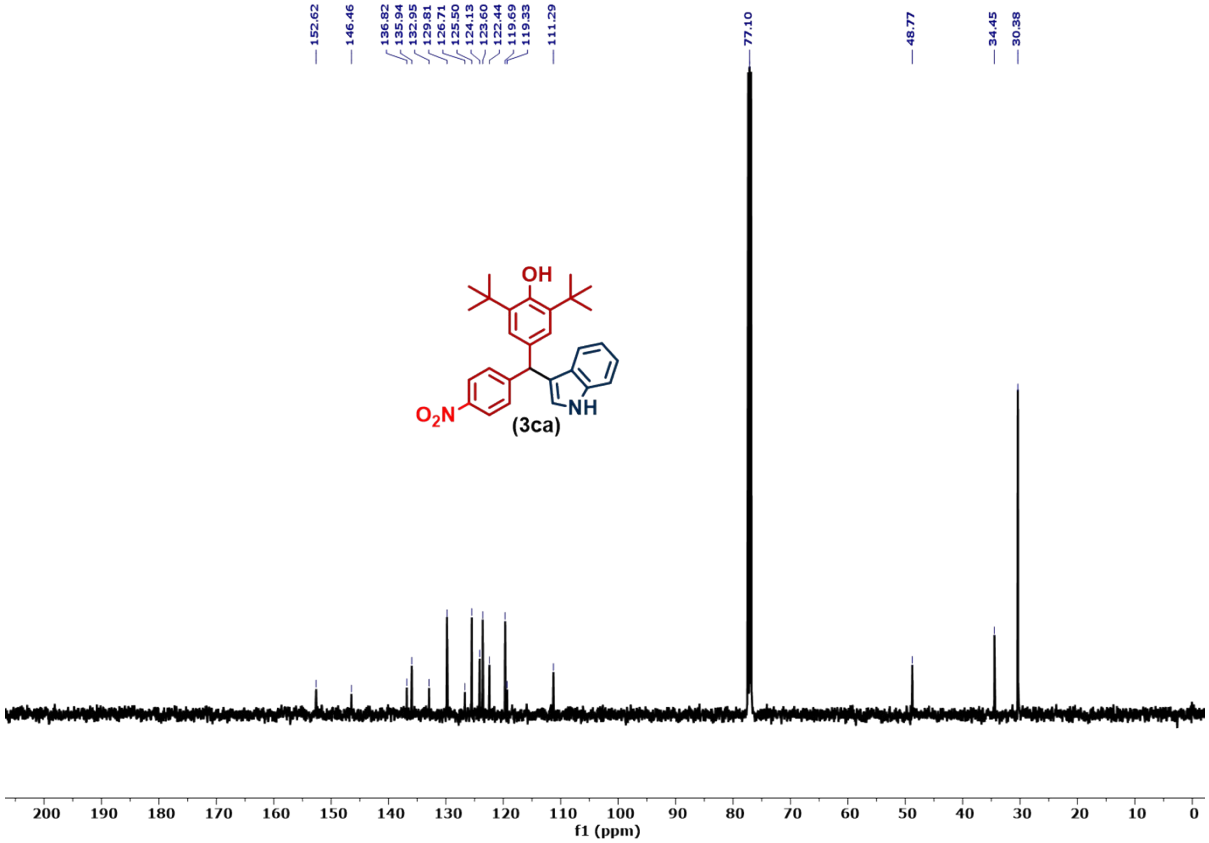
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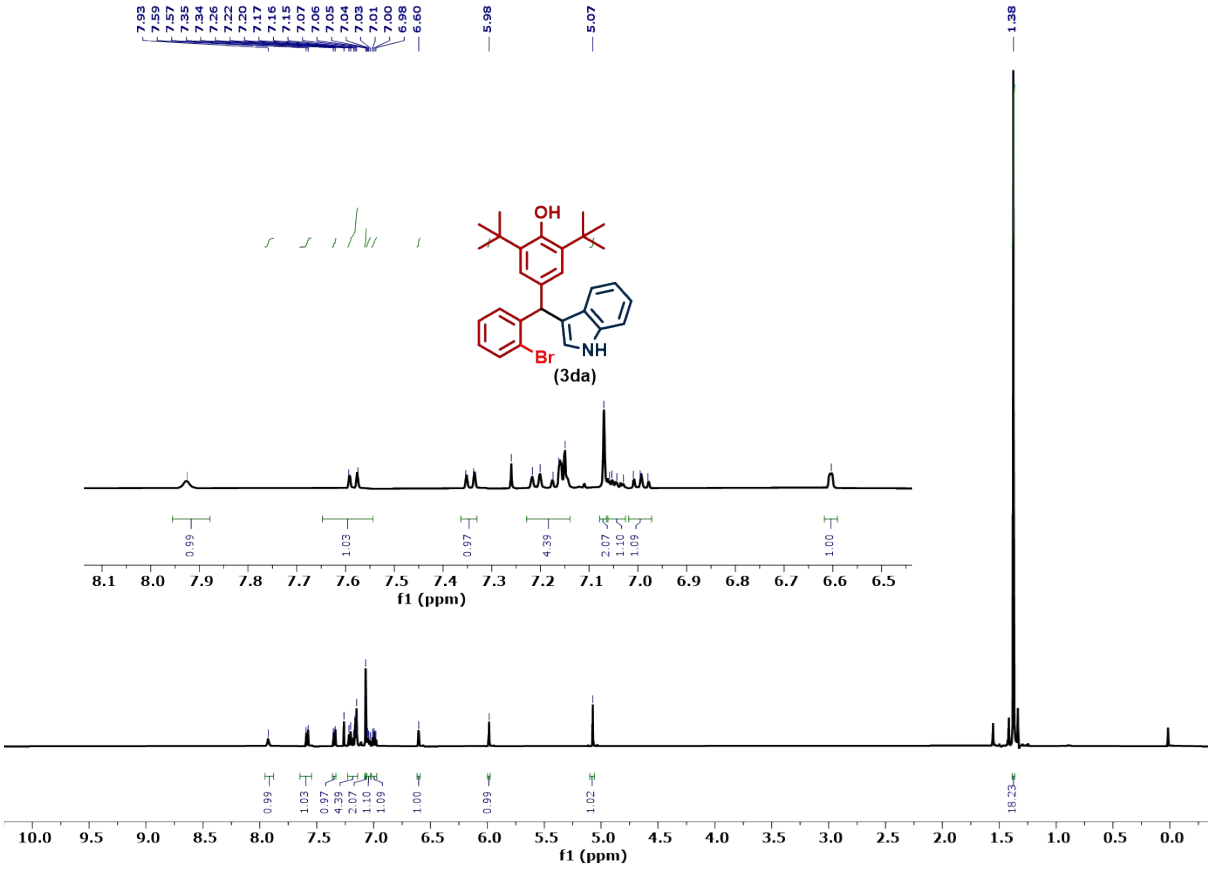
f1 (ppm)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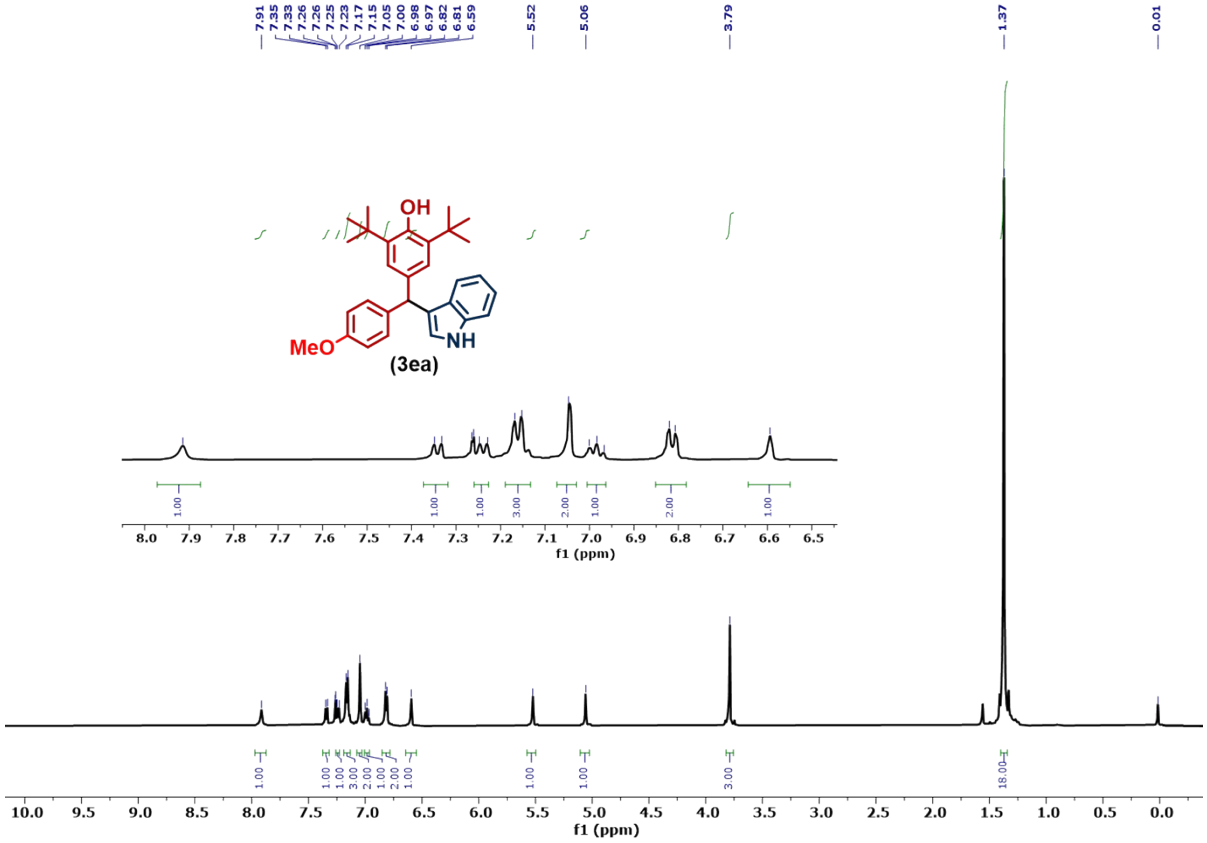
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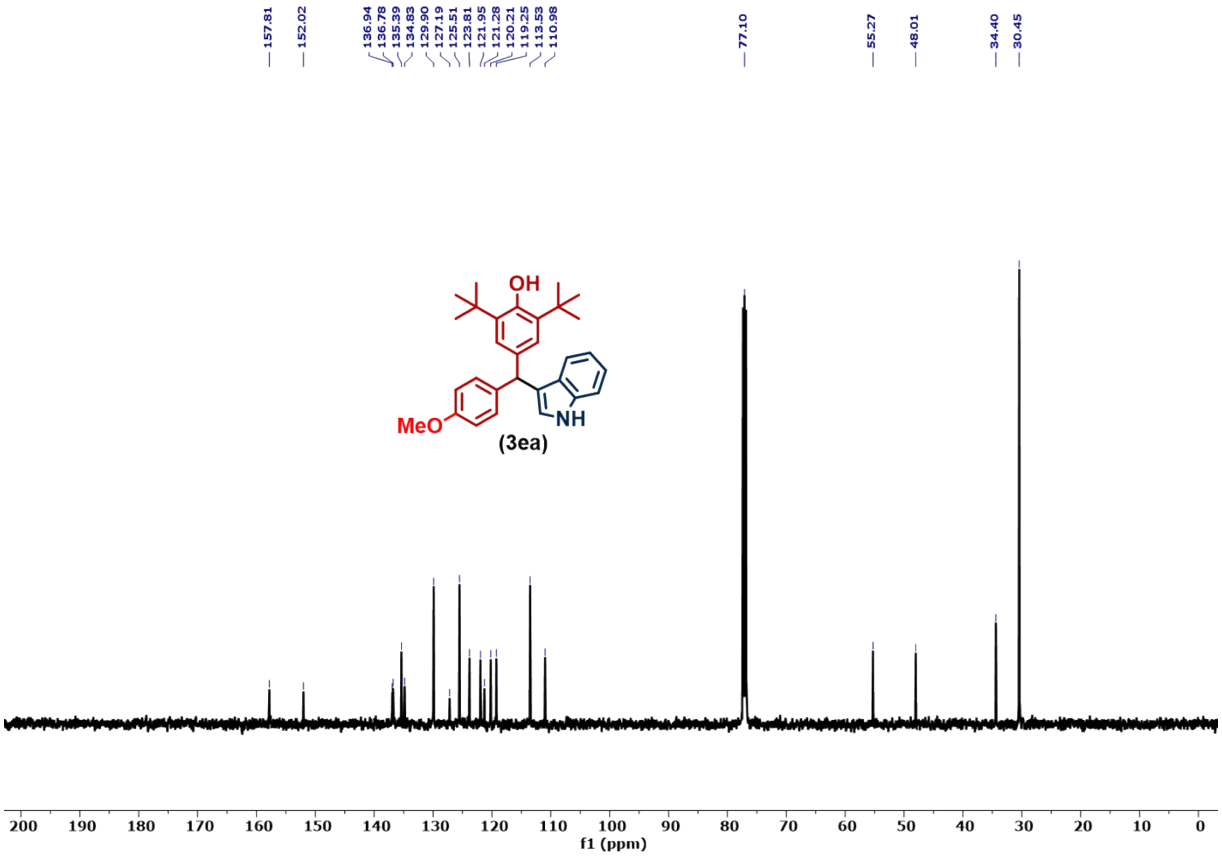
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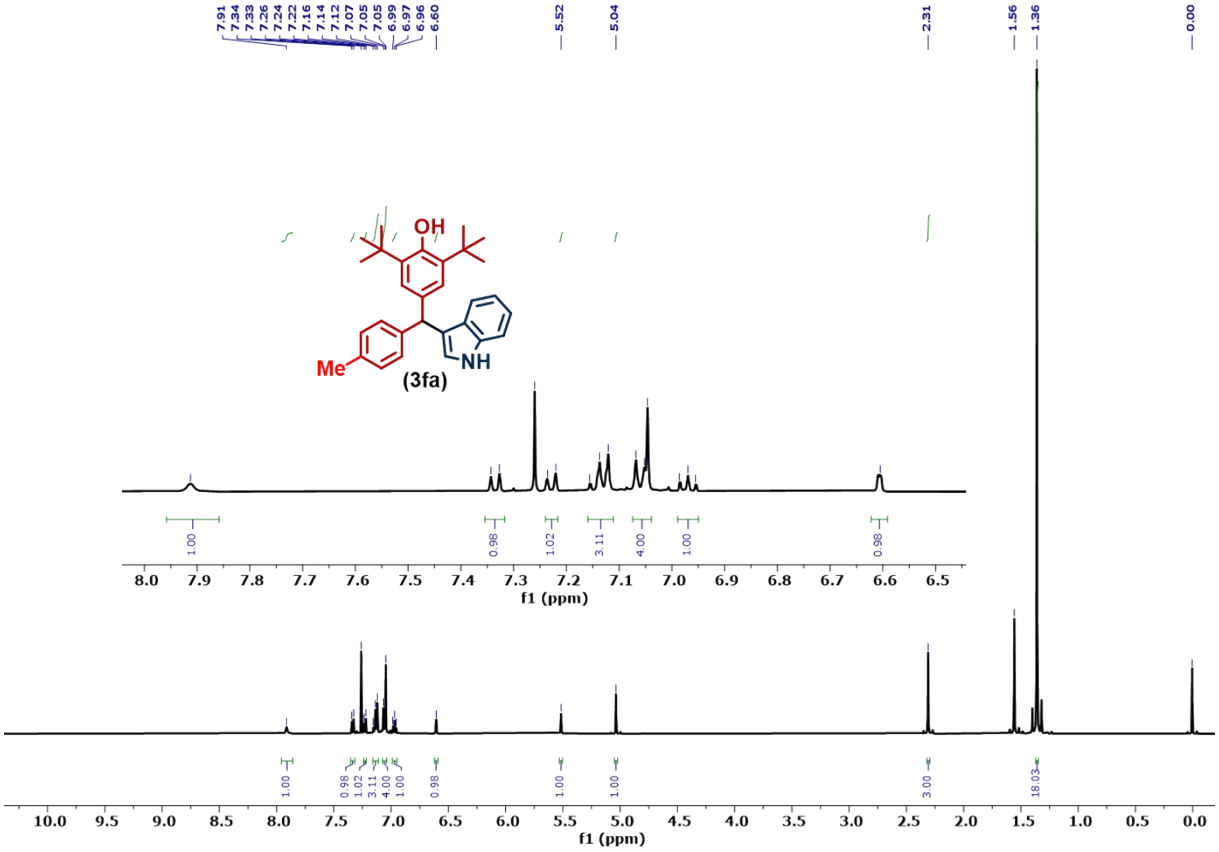
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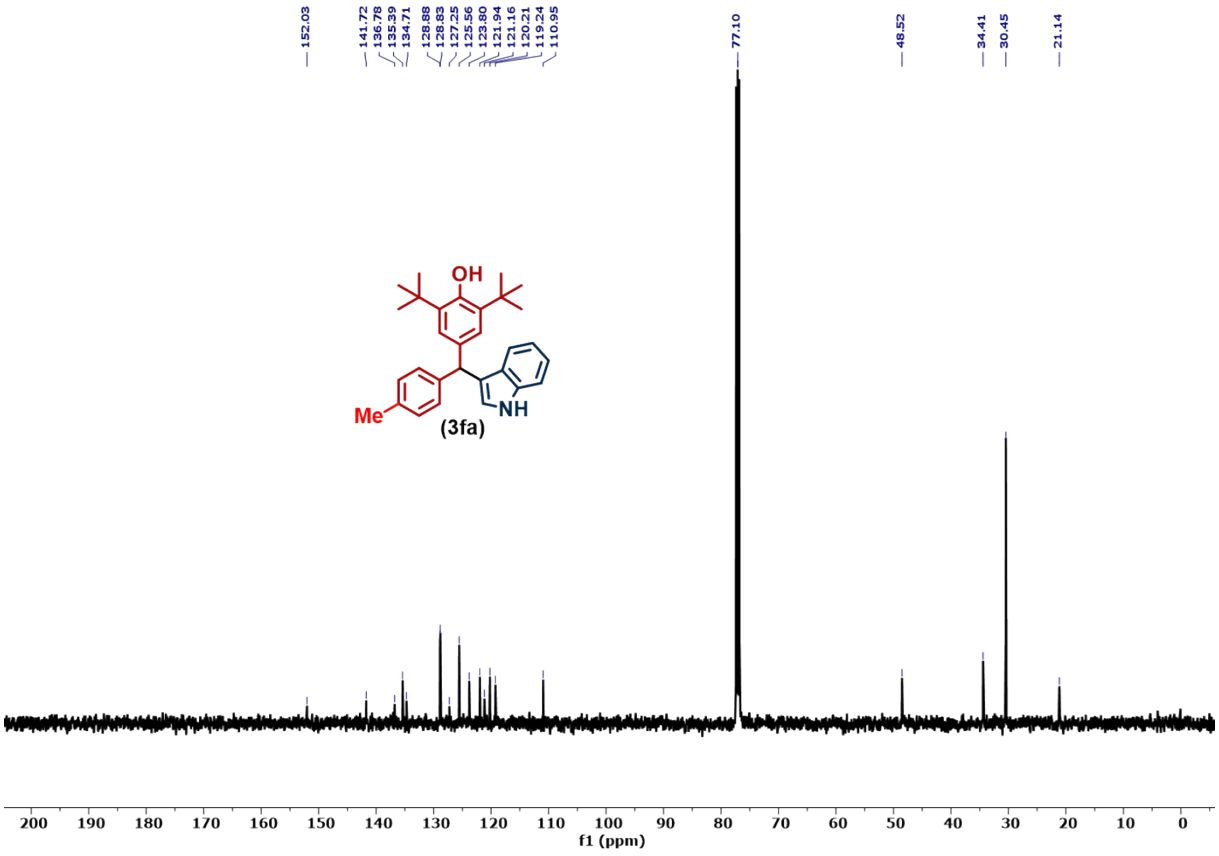
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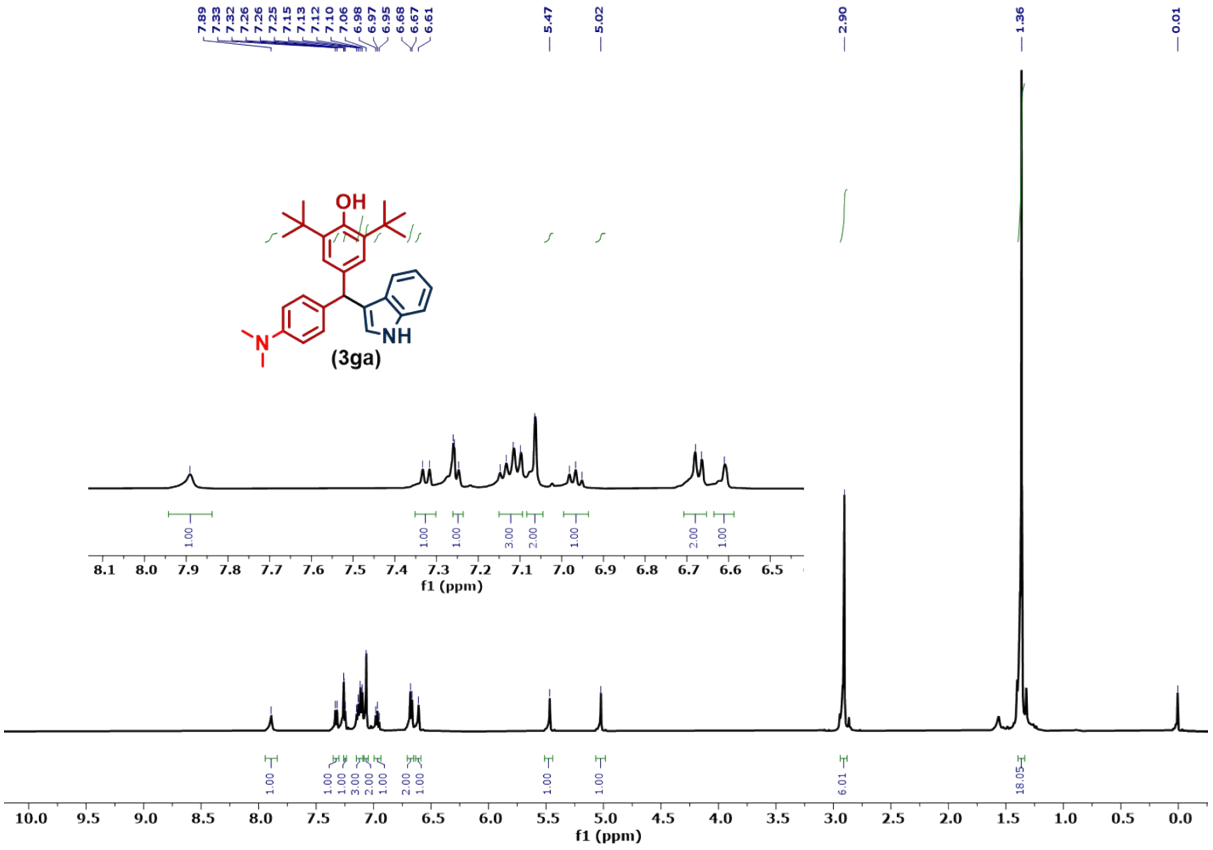
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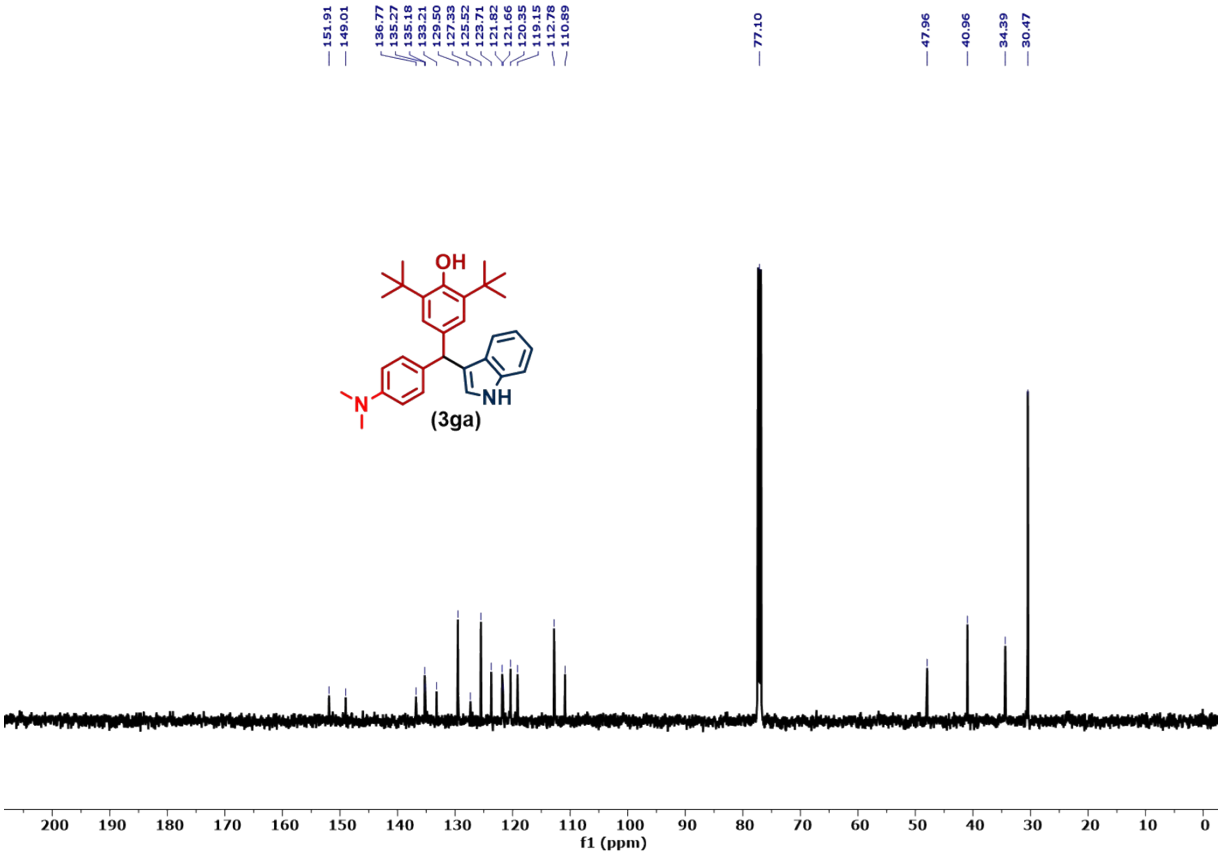
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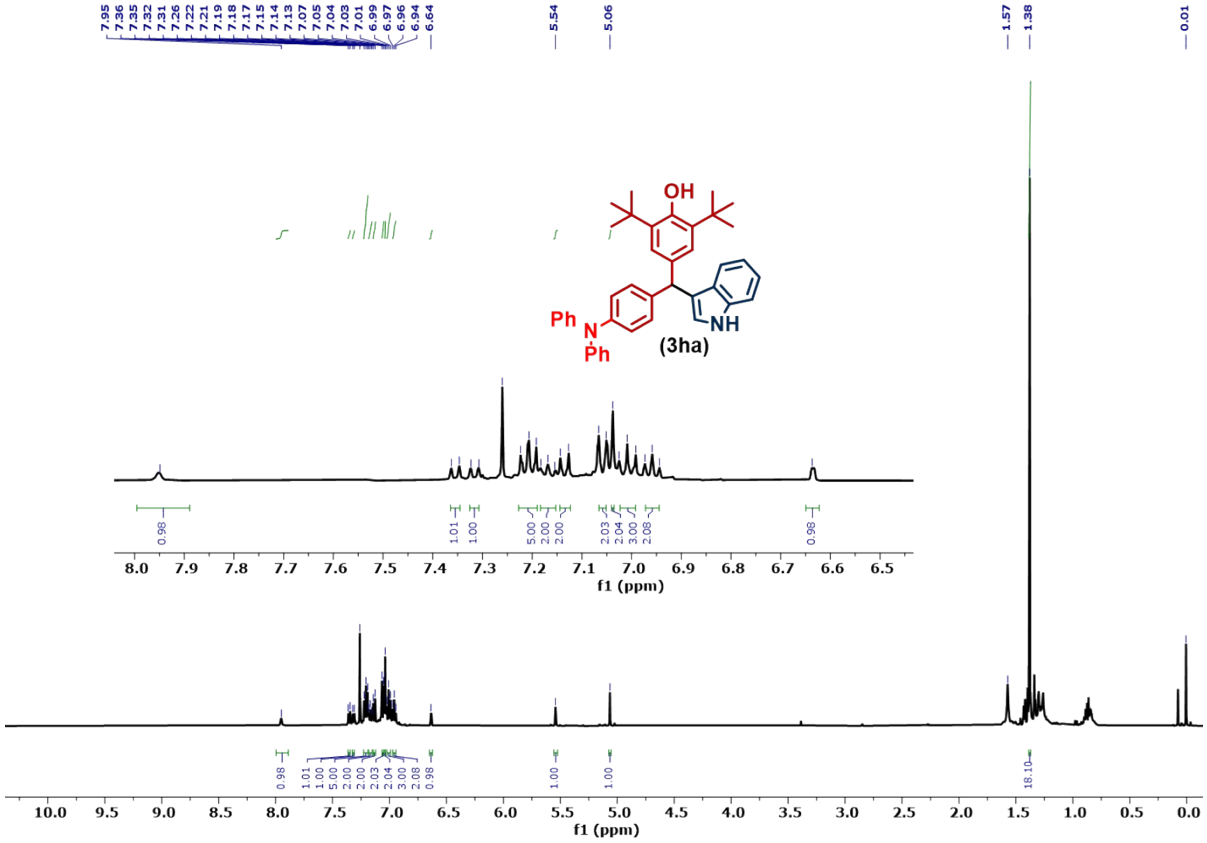
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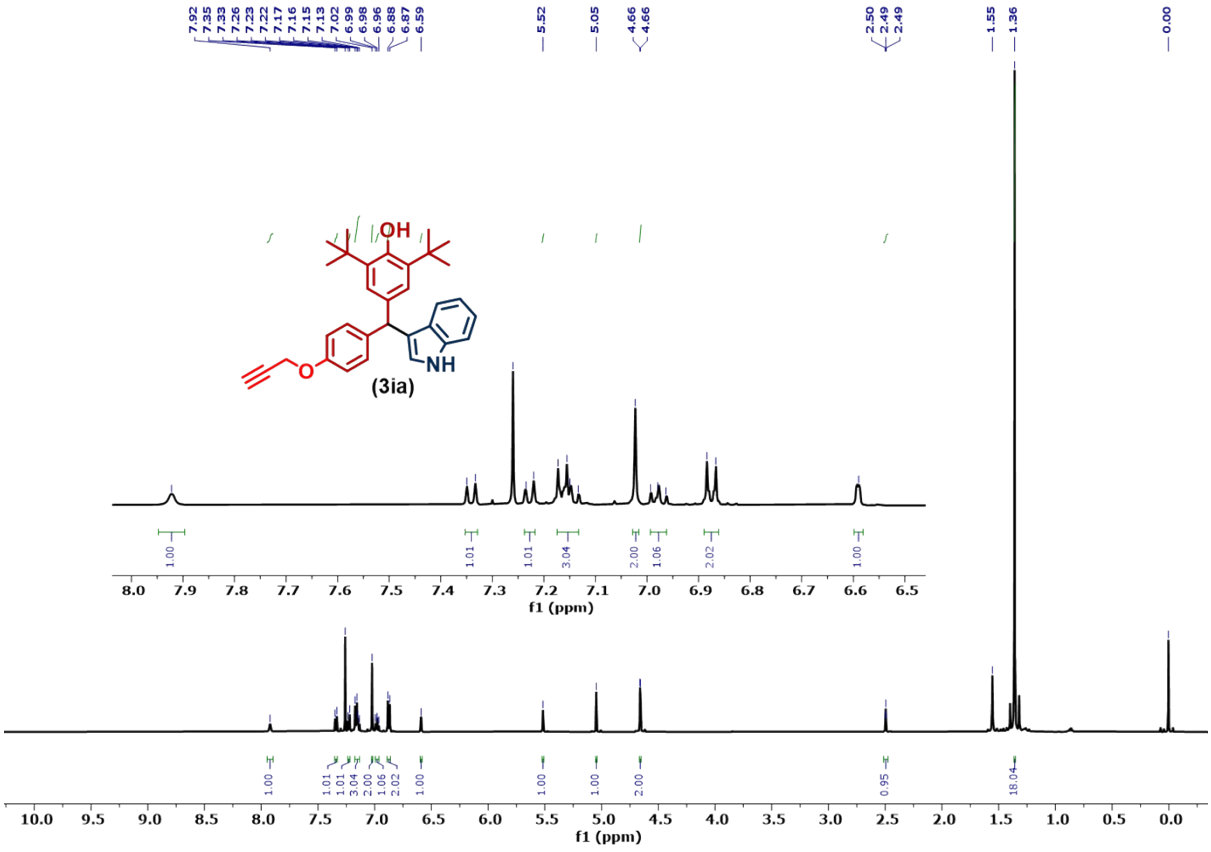
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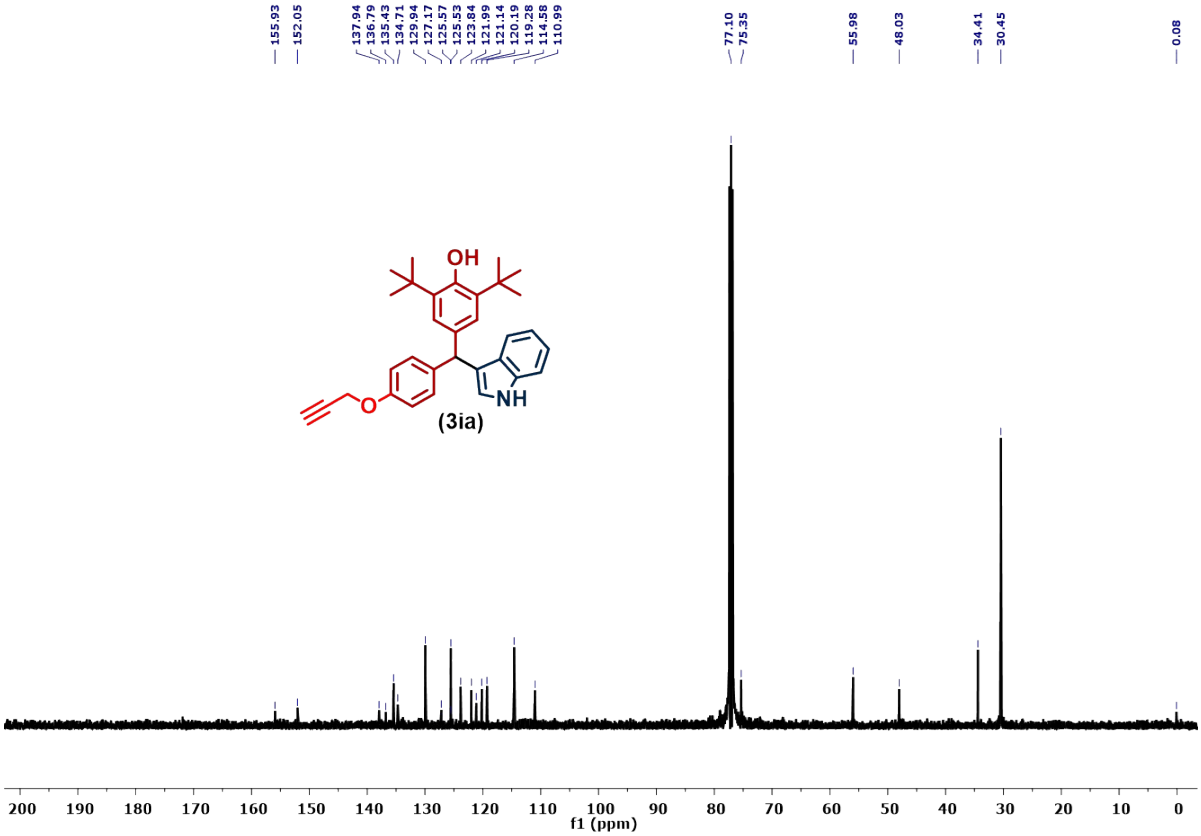
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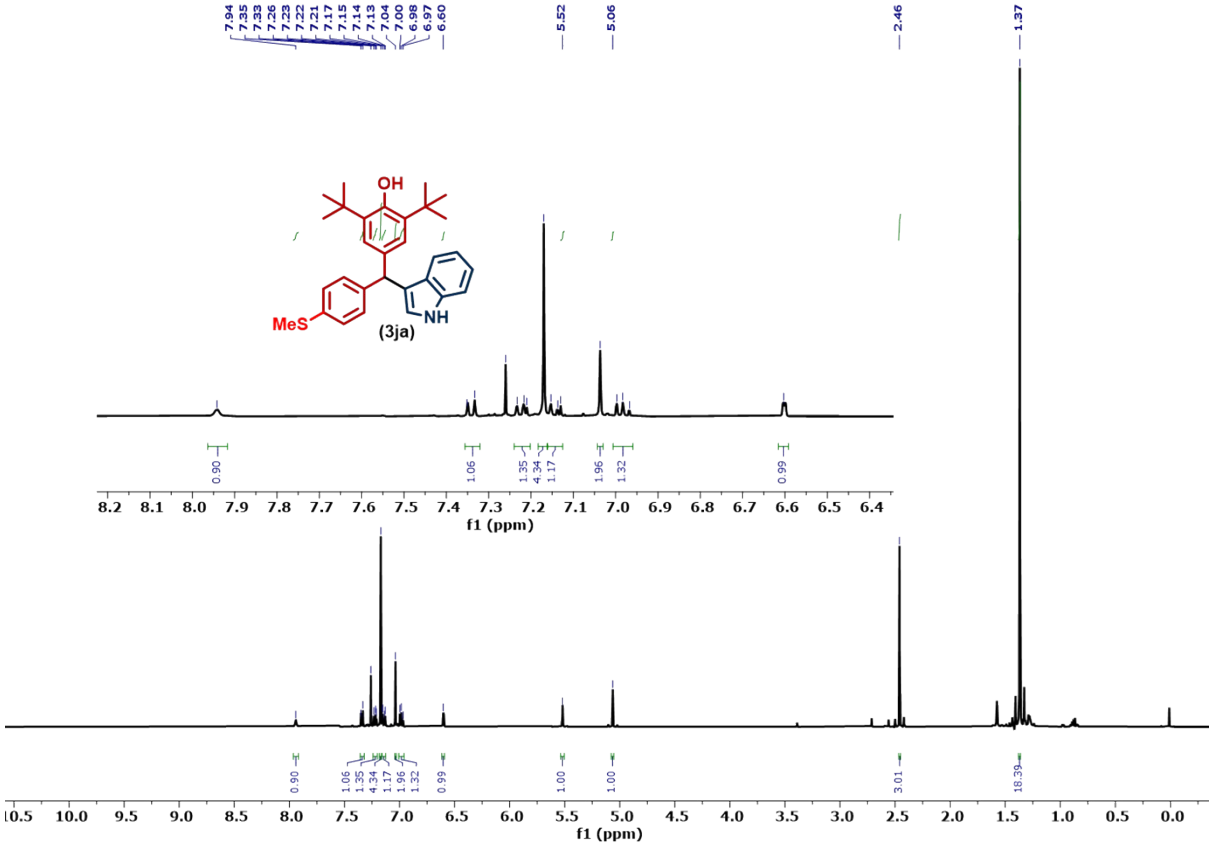
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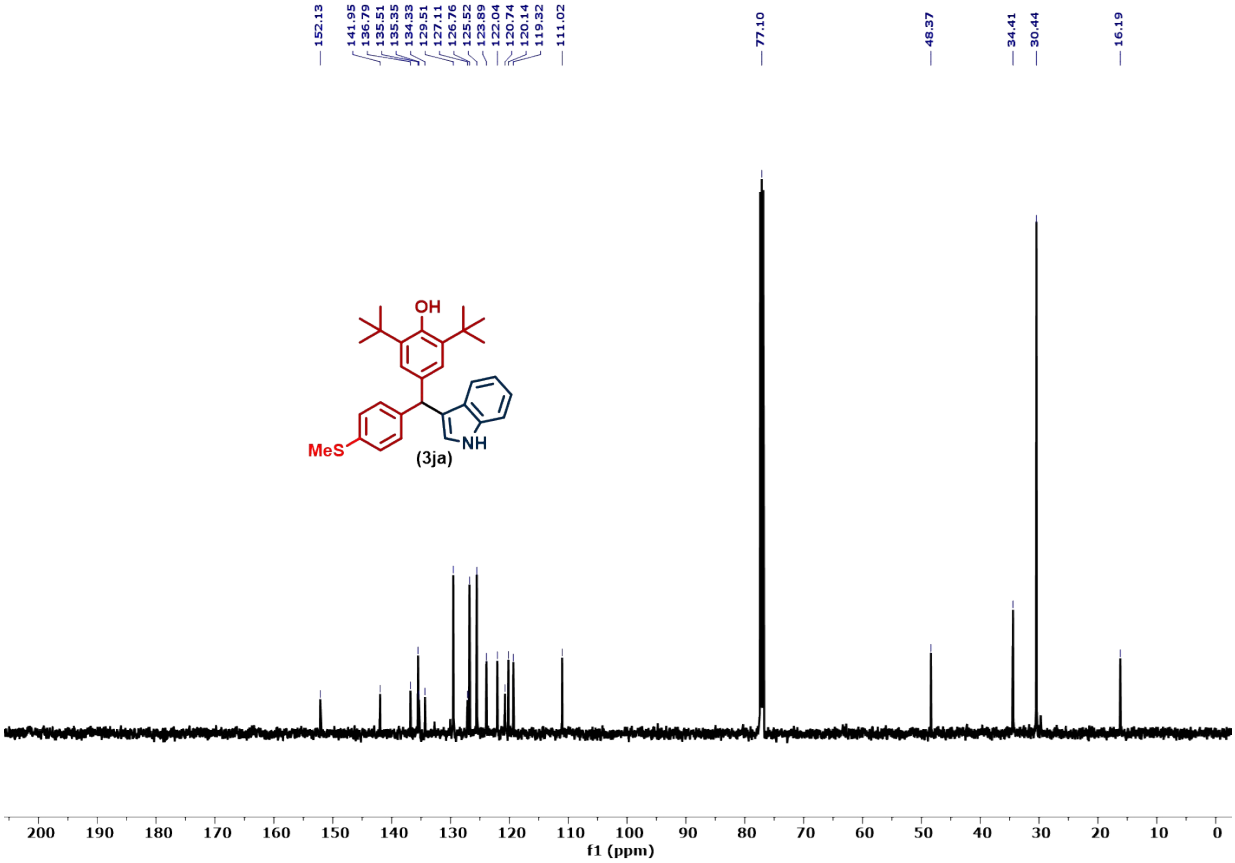
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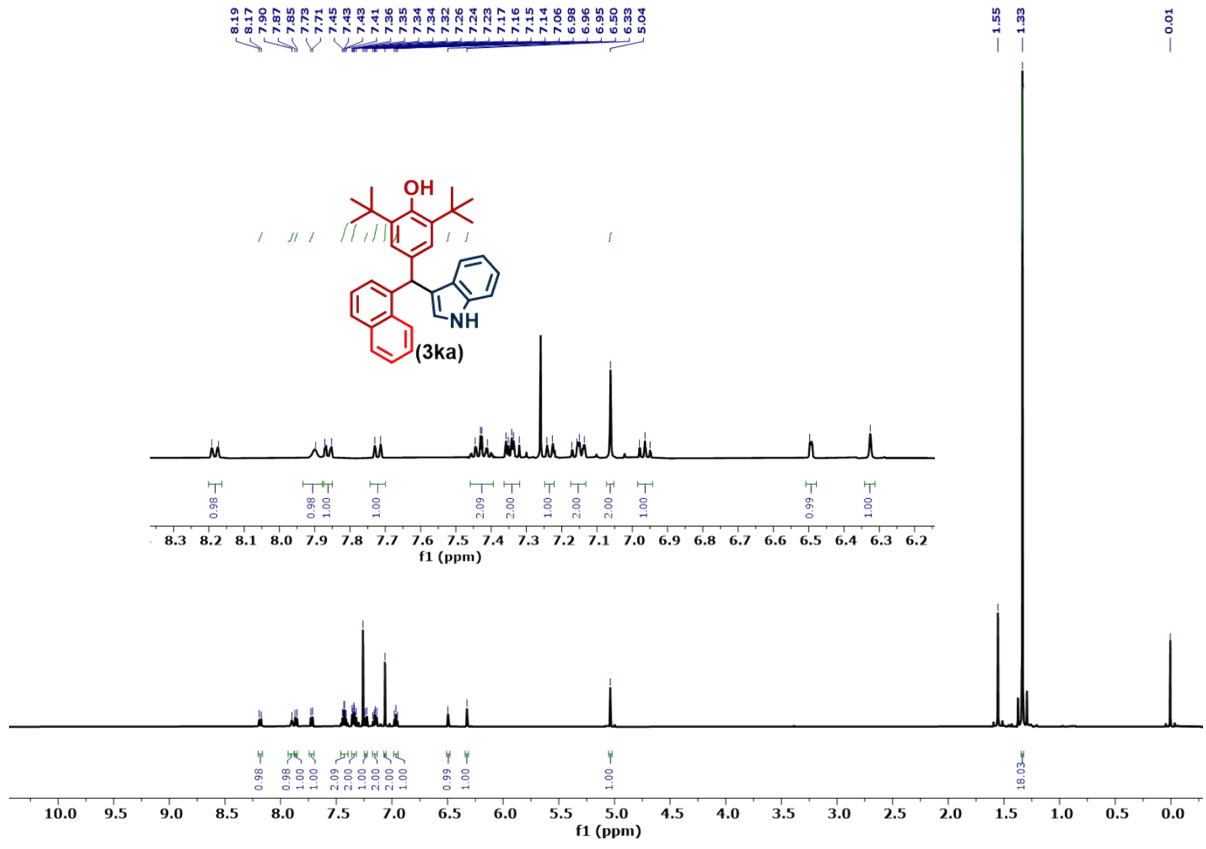
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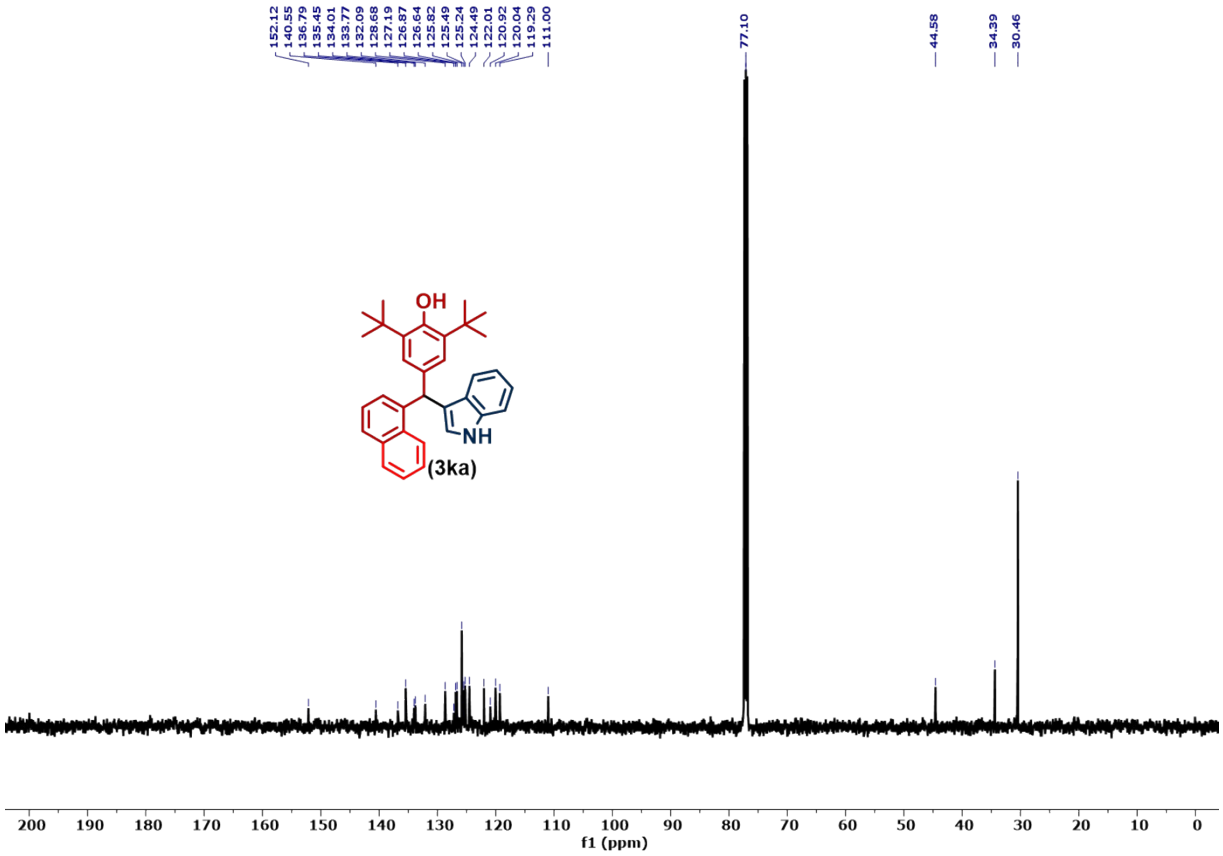
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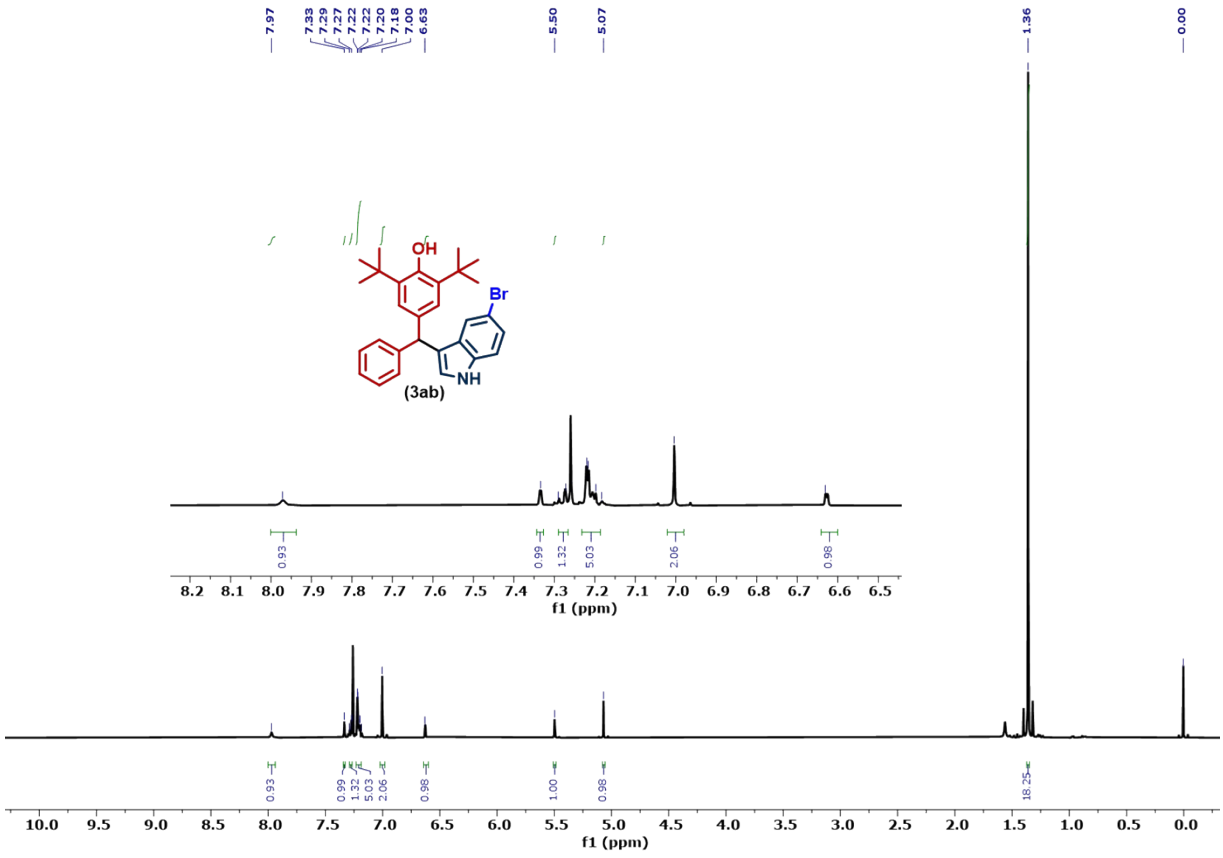
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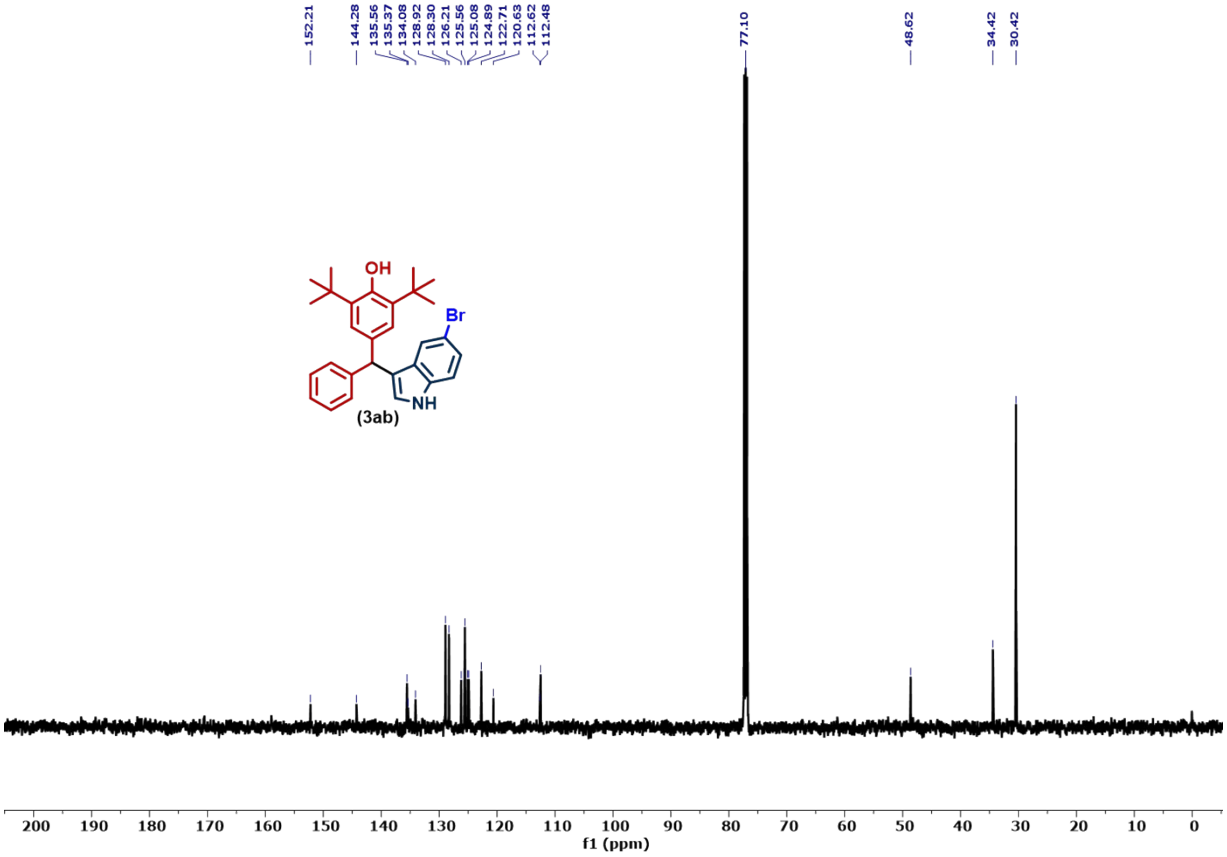
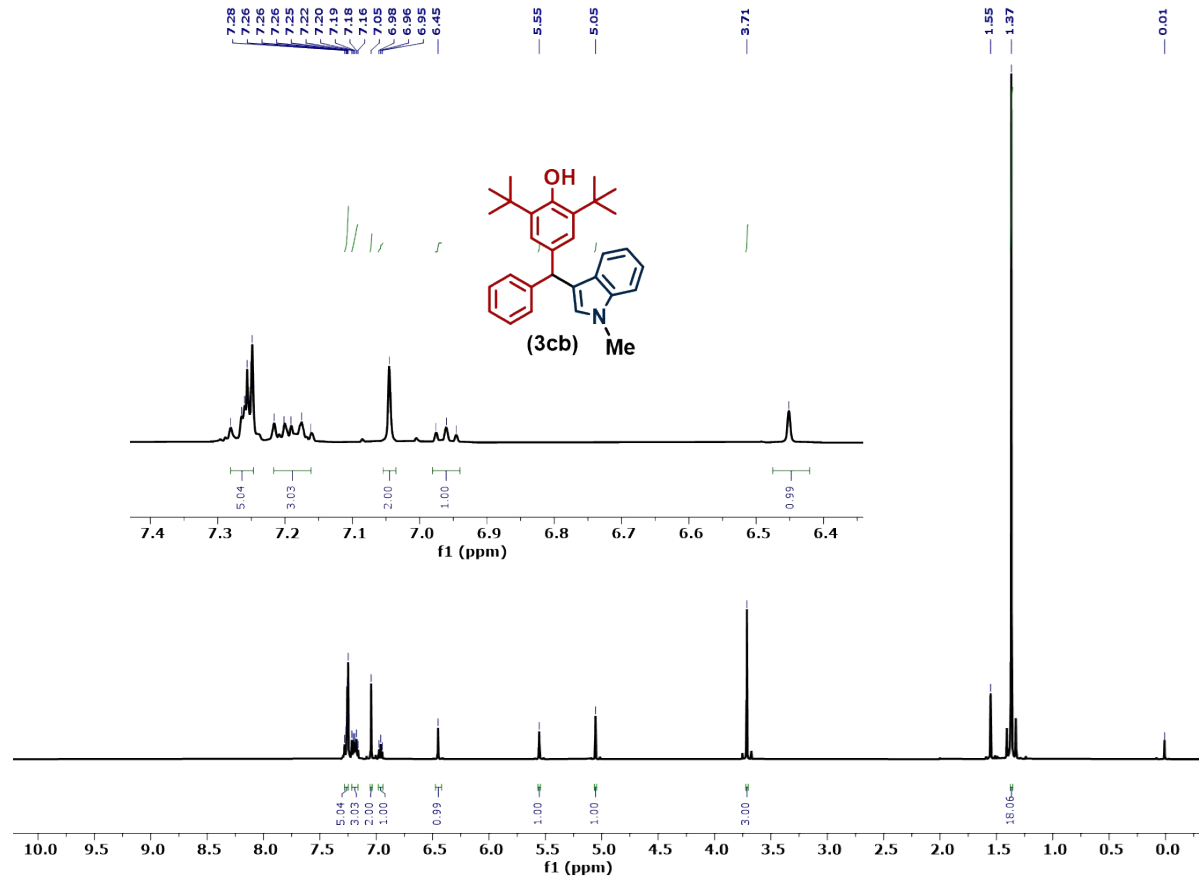
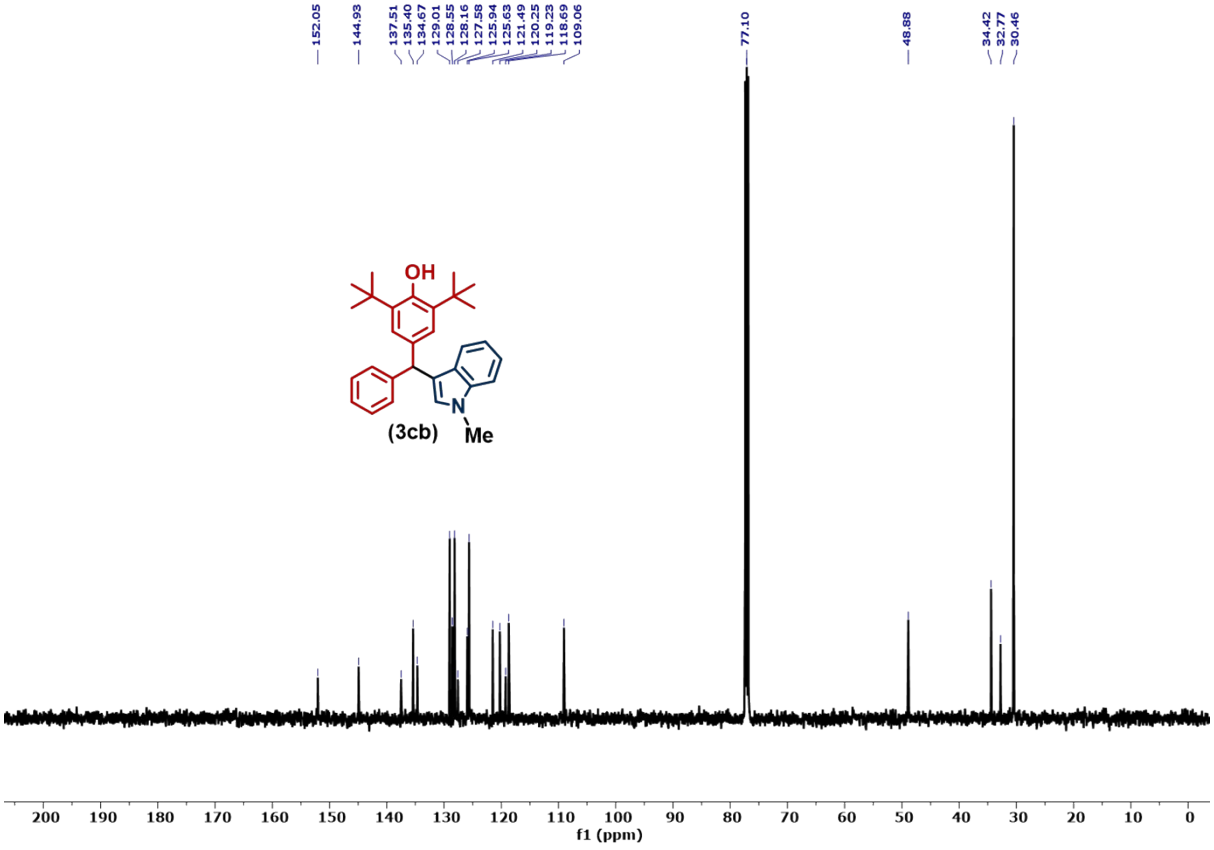
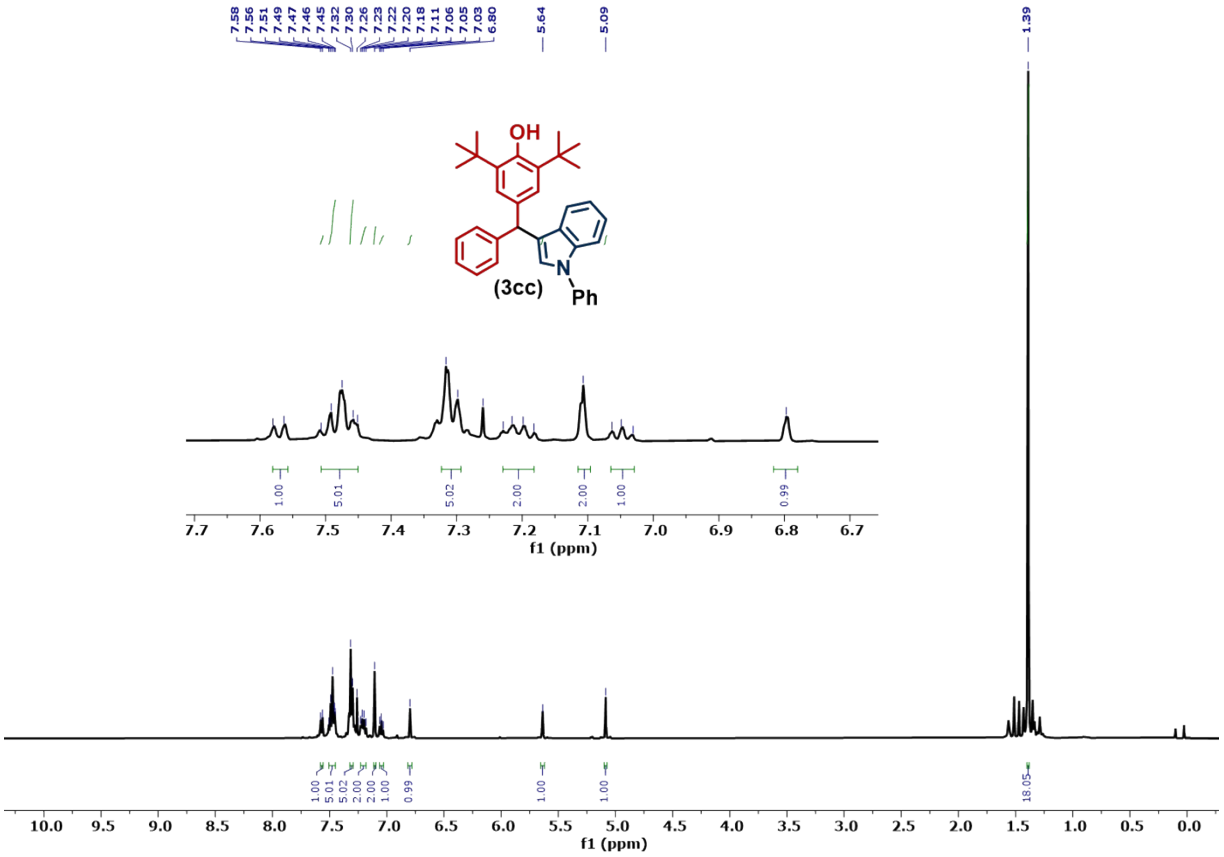
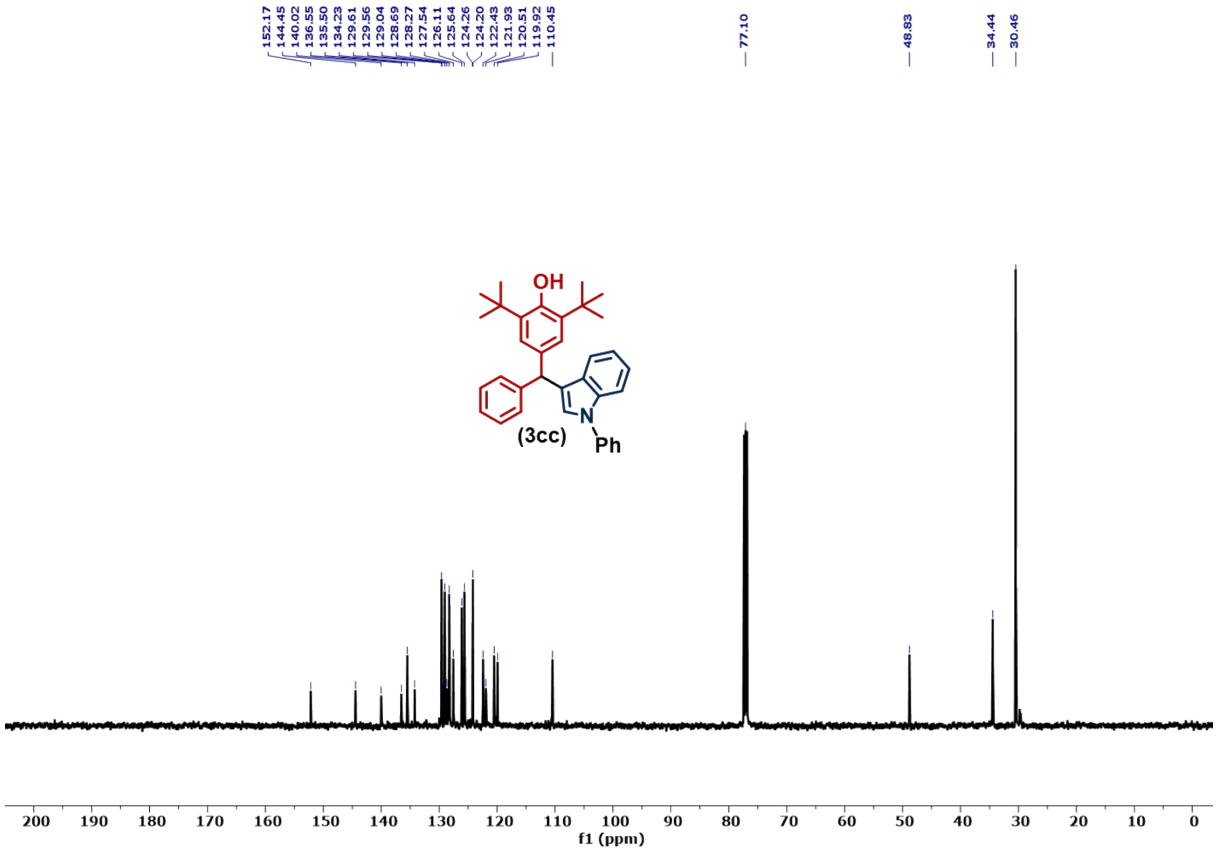
18.25
f1 (ppm)

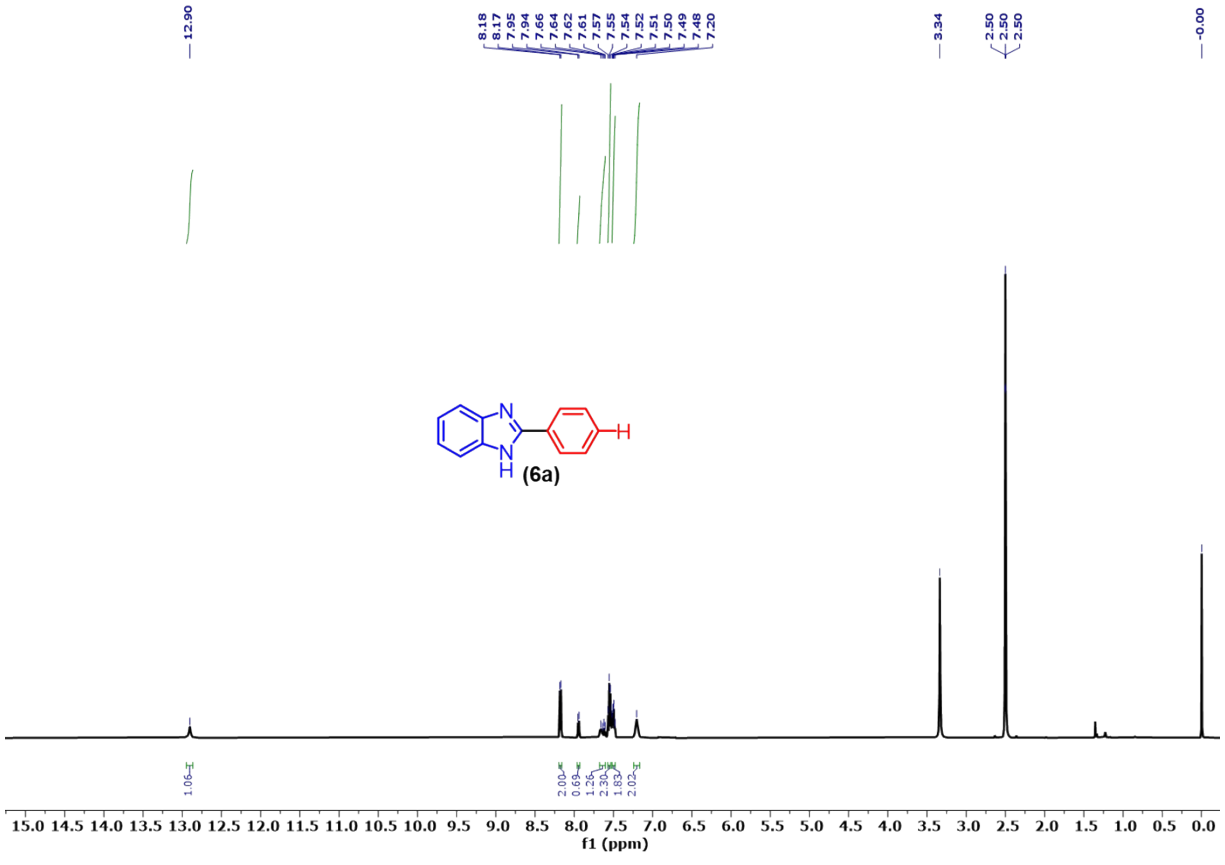

152.21
144.28
135.56
135.37
134.08
128.92
128.30
126.21
125.56
125.08
124.89
122.71
120.63
112.62
112.48
77.10
48.62
34.42
30.42
OH
Br
NH
(3ab)
f1 (ppm)

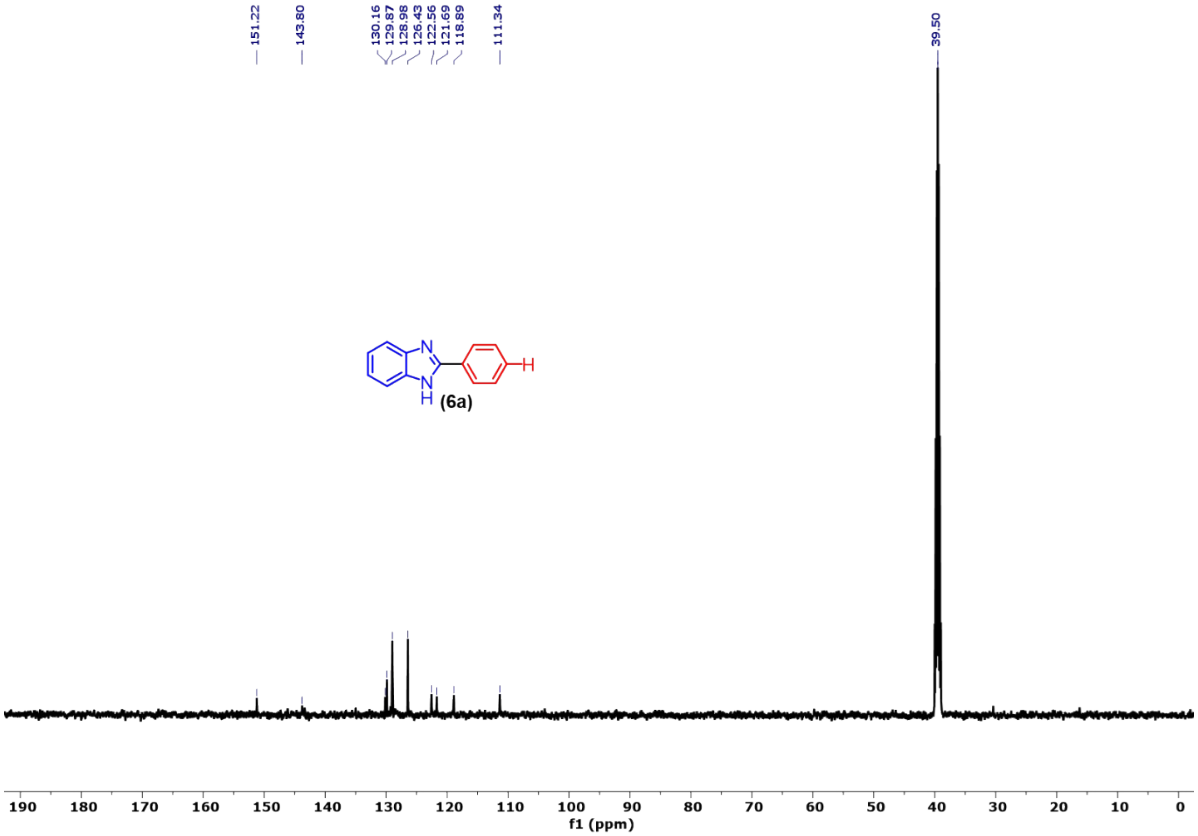

7.28
7.26
7.26
7.26
7.25
7.22
7.20
7.19
7.18
7.16
7.05
6.98
6.96
6.95
6.45
5.55
5.05
3.71
1.55
1.37
0.01
OH
N
Me
(3cb)
5.04
3.03
2.00
1.00
0.99
f1 (ppm)

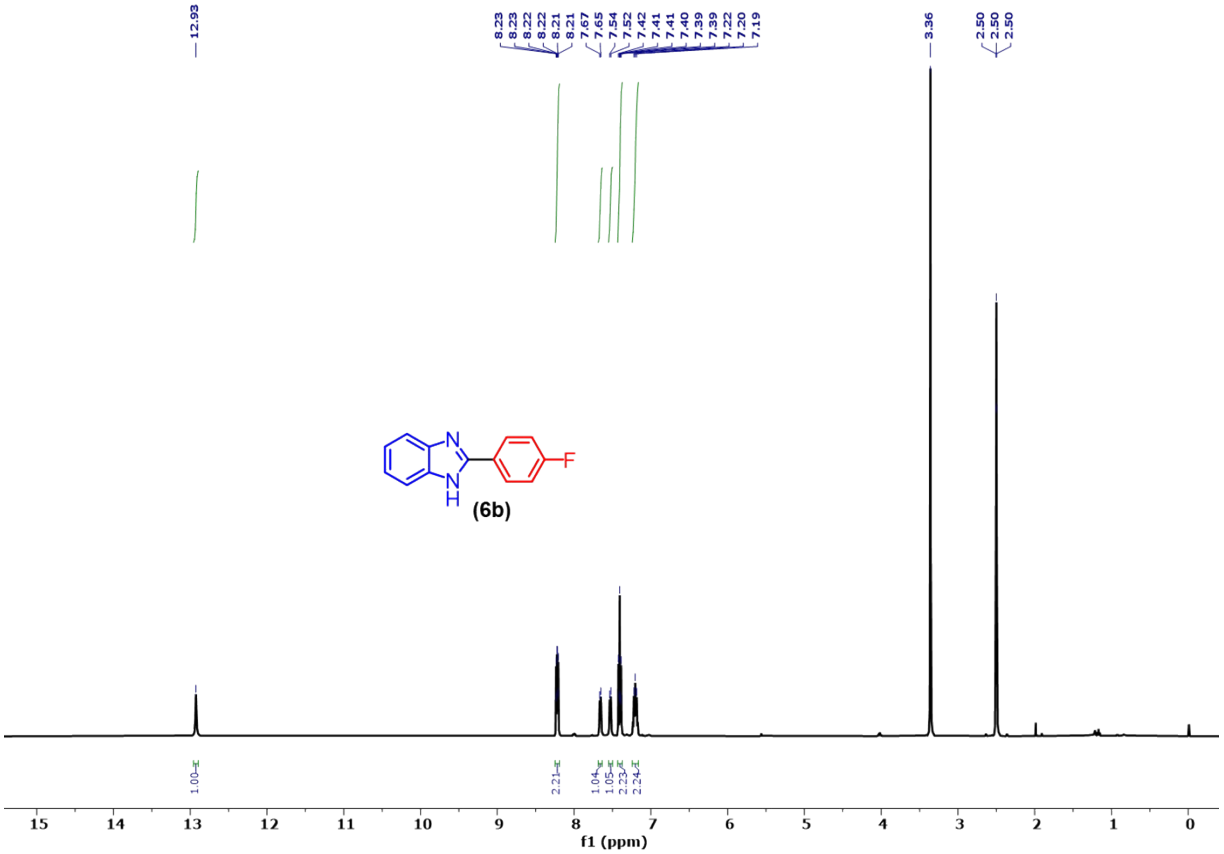

152.05
144.93
137.51
135.40
134.67
129.01
128.55
128.16
127.58
125.94
125.63
121.49
120.25
119.23
118.69
109.06
77.10
48.88
34.42
32.77
30.46
OH
N
Me
(3cb)
f1 (ppm)

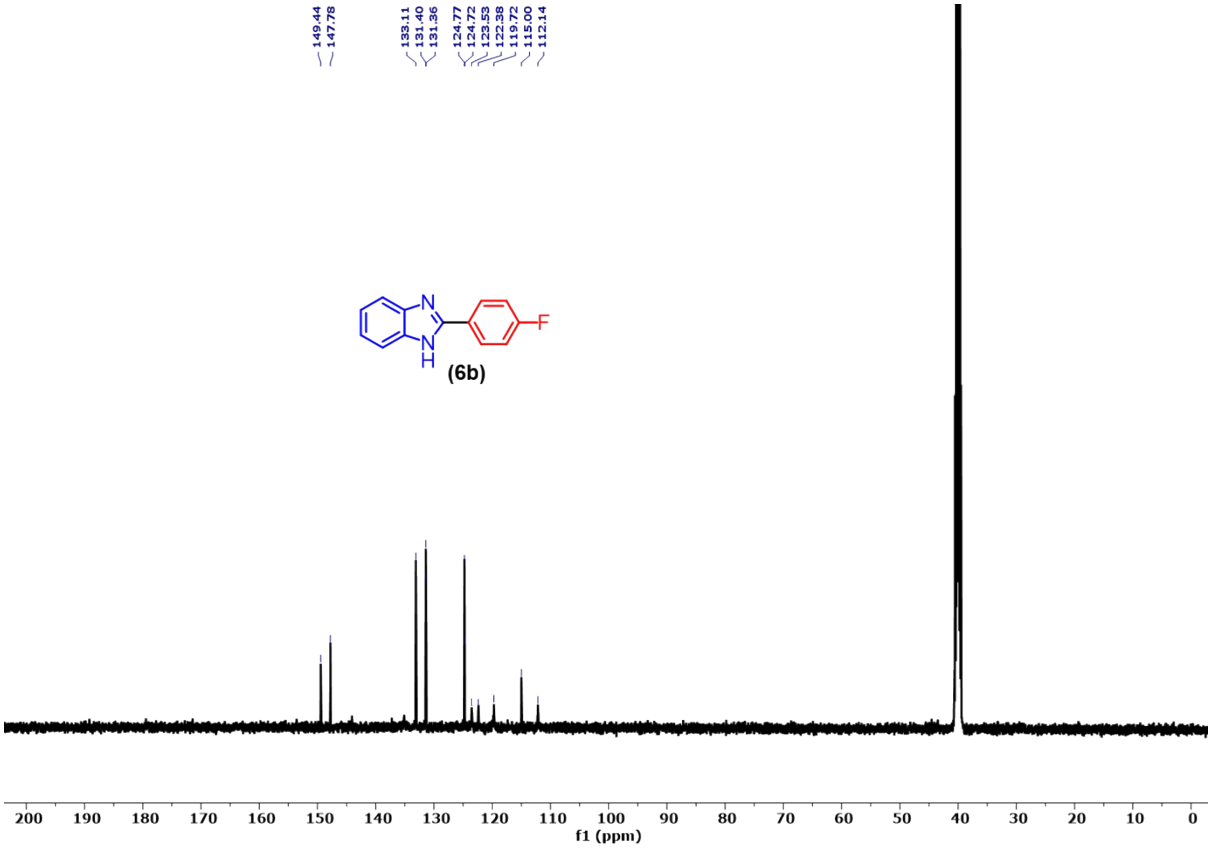

7.58
7.56
7.51
7.49
7.47
7.46
7.45
7.32
7.30
7.26
7.23
7.22
7.20
7.18
7.11
7.06
7.05
7.03
6.80
5.64
5.09
1.39
OH
N
Ph
(3cc)
1.00
5.01
5.02
2.00
2.00
1.00
0.99
1.00
1.00
18.05
f1 (ppm)

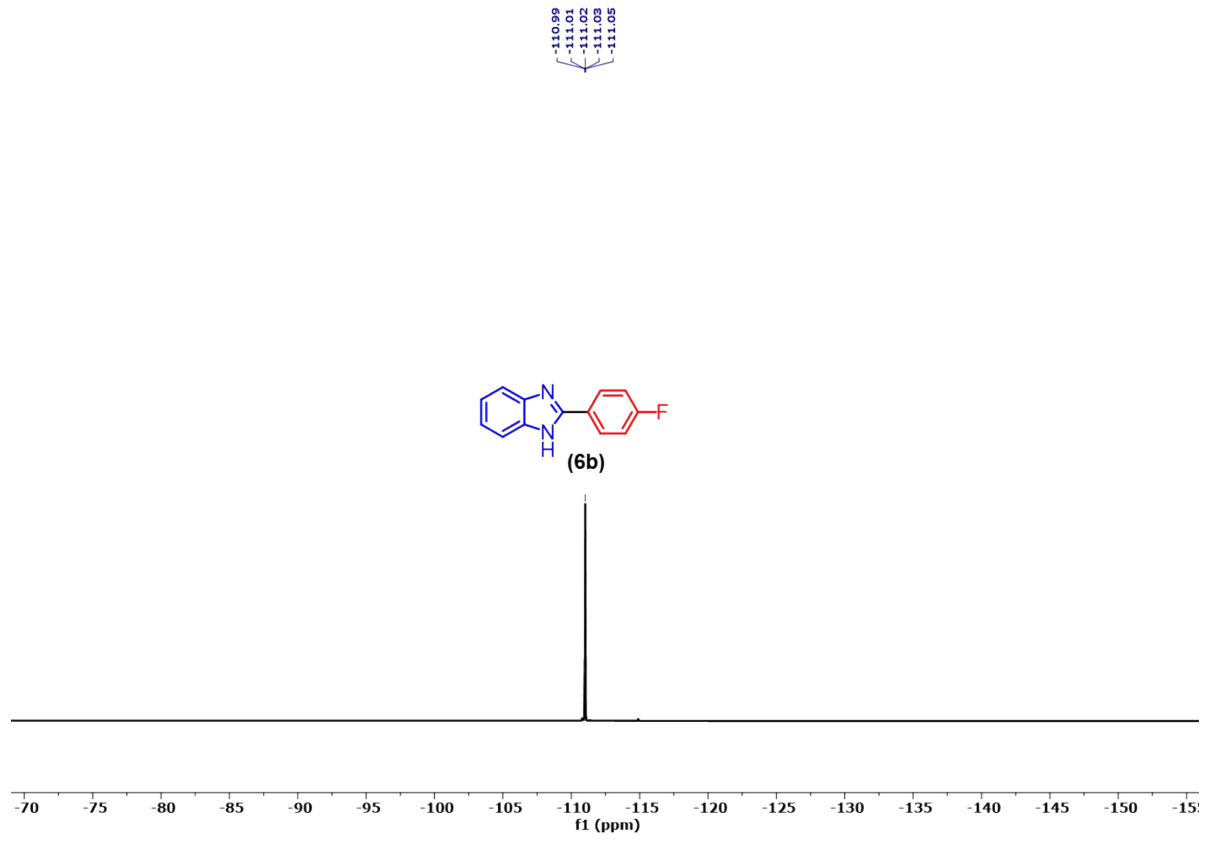

152.17
144.45
140.02
136.55
135.50
134.23
129.61
129.56
129.04
128.69
128.27
127.54
126.11
125.64
124.26
124.20
122.43
121.93
120.51
119.92
110.45
77.10
48.83
34.44
30.46
OH
N
Ph
(3cc)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

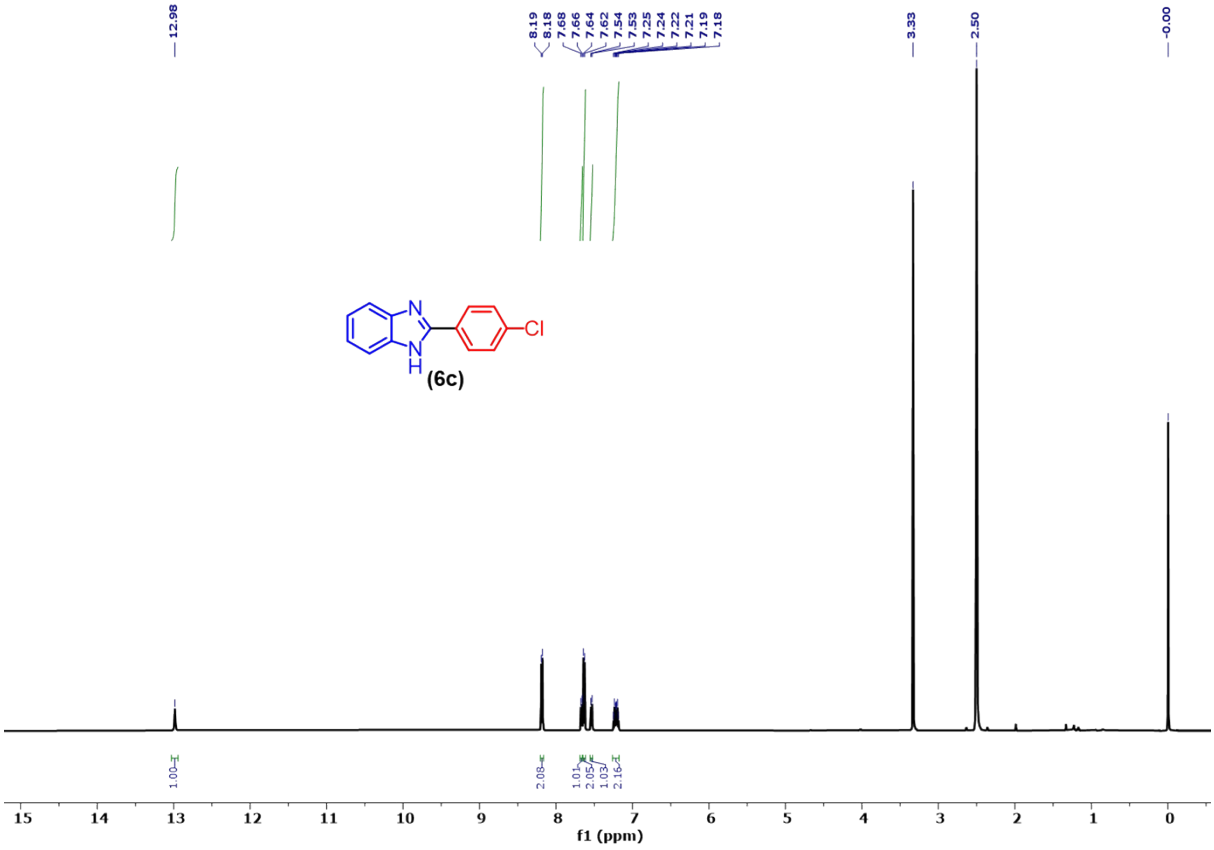

12.90
8.18
8.17
7.95
7.94
7.66
7.64
7.62
7.61
7.57
7.55
7.54
7.52
7.51
7.50
7.49
7.48
7.20
3.34
2.50
2.50
2.50
-0.00
N
N
H
H
(6a)
1.06
2.00
0.69
1.26
2.30
1.83
2.02
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

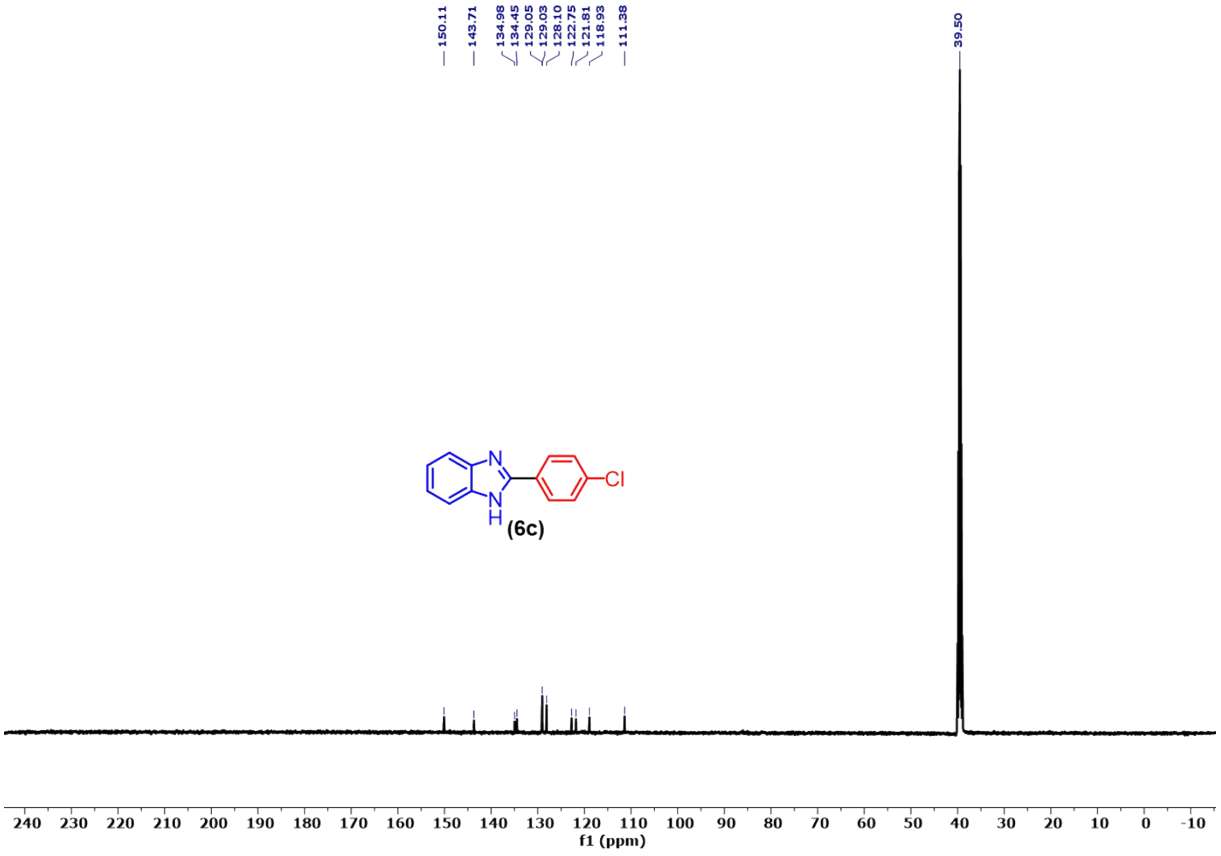

151.22
143.80
130.16
129.87
128.98
126.43
122.56
121.69
118.89
111.34
39.50
(6a)
f1 (ppm)

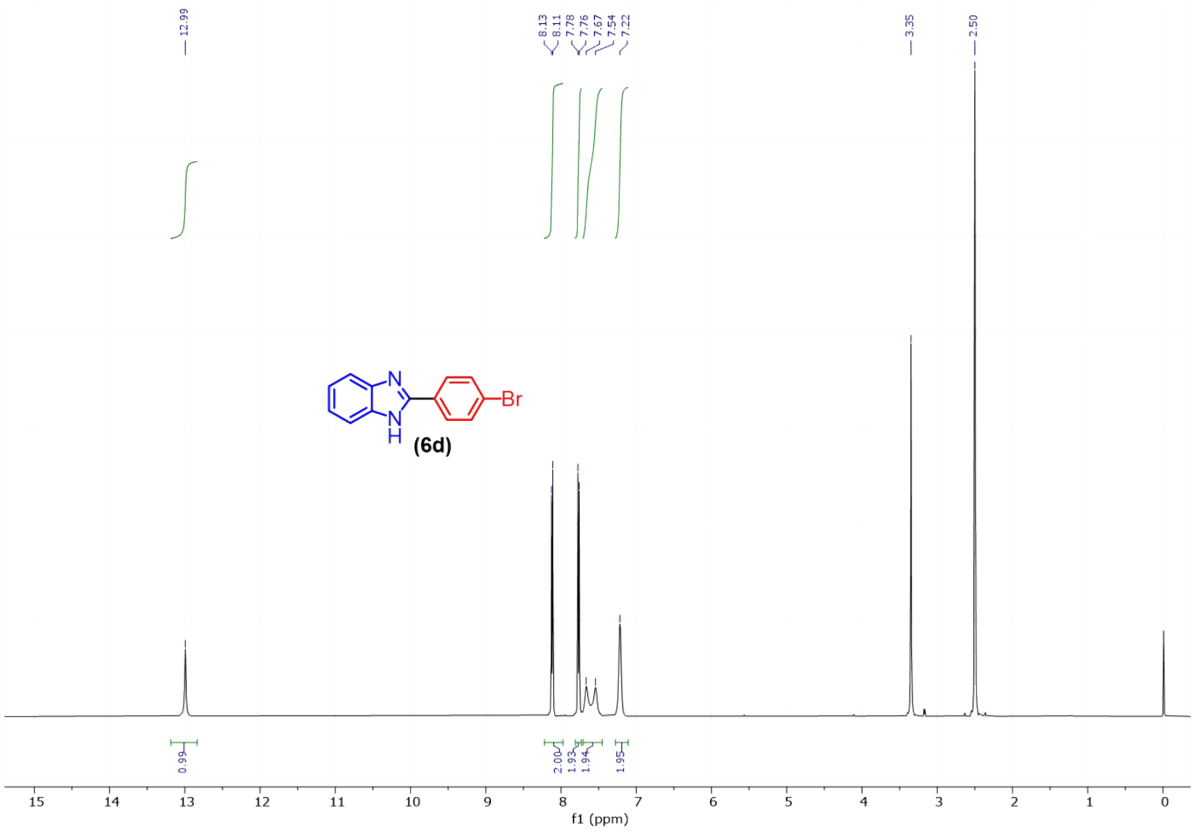

12.93
8.23
8.23
8.22
8.22
8.21
8.21
7.67
7.65
7.54
7.52
7.42
7.41
7.41
7.40
7.39
7.39
7.22
7.20
7.19
3.36
2.50
2.50
2.50
(6b)
1.00
2.21
1.04
1.05
2.23
2.24
f1 (ppm)

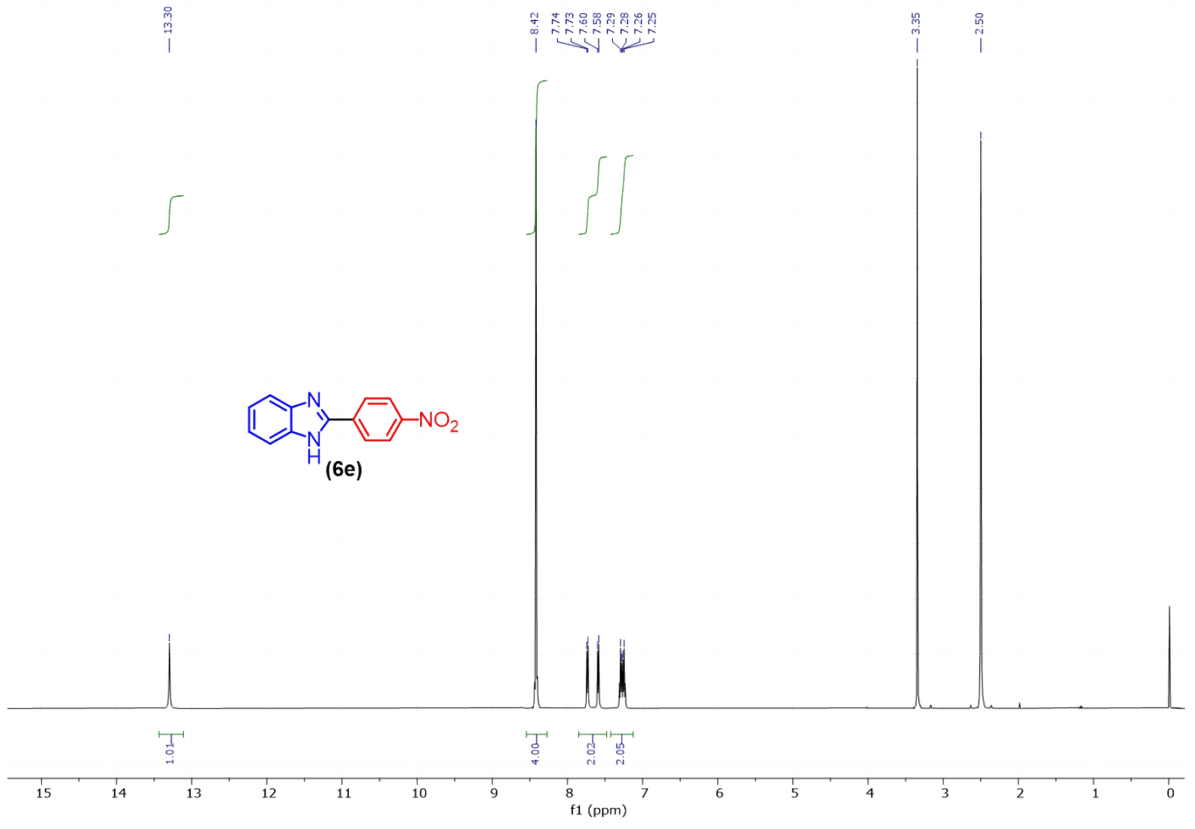

149.44
147.78
133.11
131.40
131.36
124.77
124.72
123.53
122.38
119.72
115.00
112.14
N
H
F
(6b)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

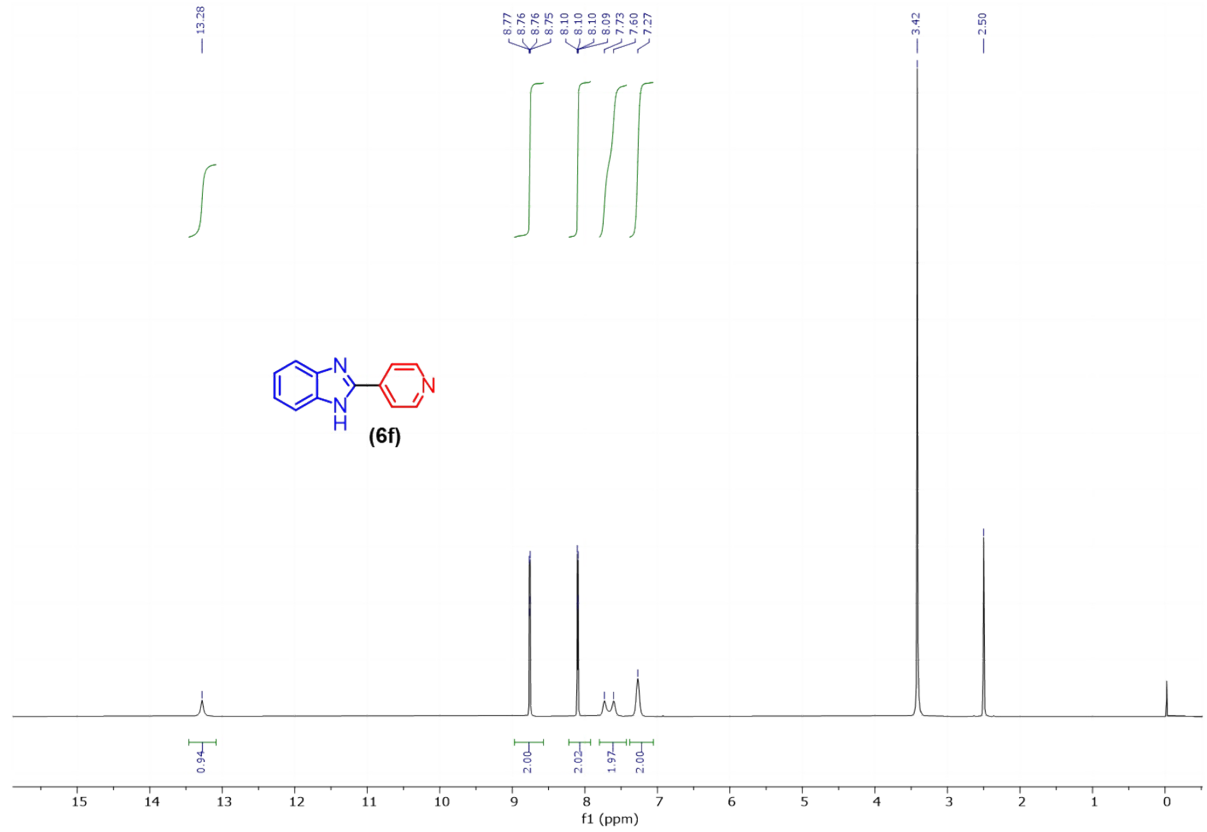

-110.99
-111.01
-111.02
-111.03
-111.05
N
H
F
(6b)
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)

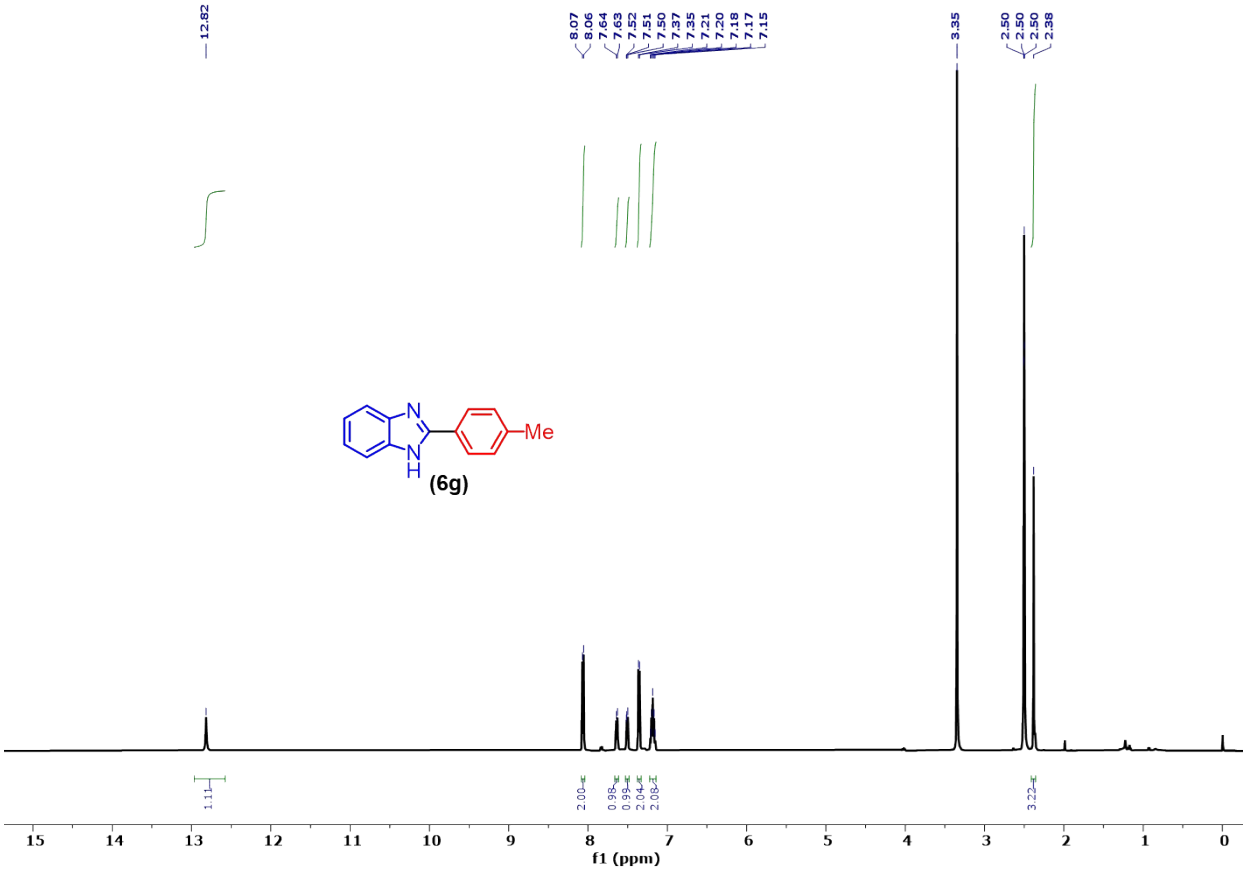

12.98
8.19
8.18
7.68
7.66
7.64
7.62
7.54
7.53
7.25
7.24
7.22
7.21
7.19
7.18
3.33
2.50
-0.00
Cl
(6c)
1.00
2.08
1.01
2.05
1.03
2.16
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

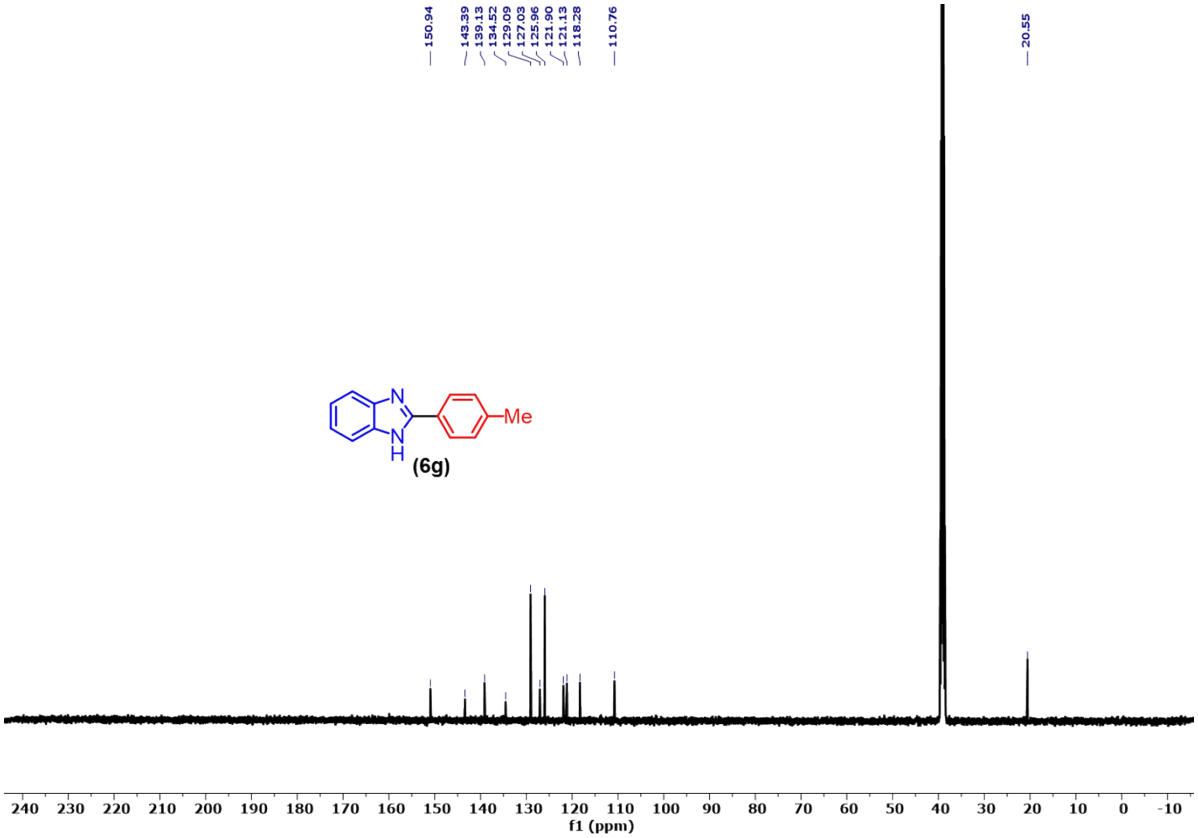

150.11
143.71
134.98
134.45
129.05
129.03
128.10
122.75
121.81
118.93
111.38
39.50
Cl
(6c)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

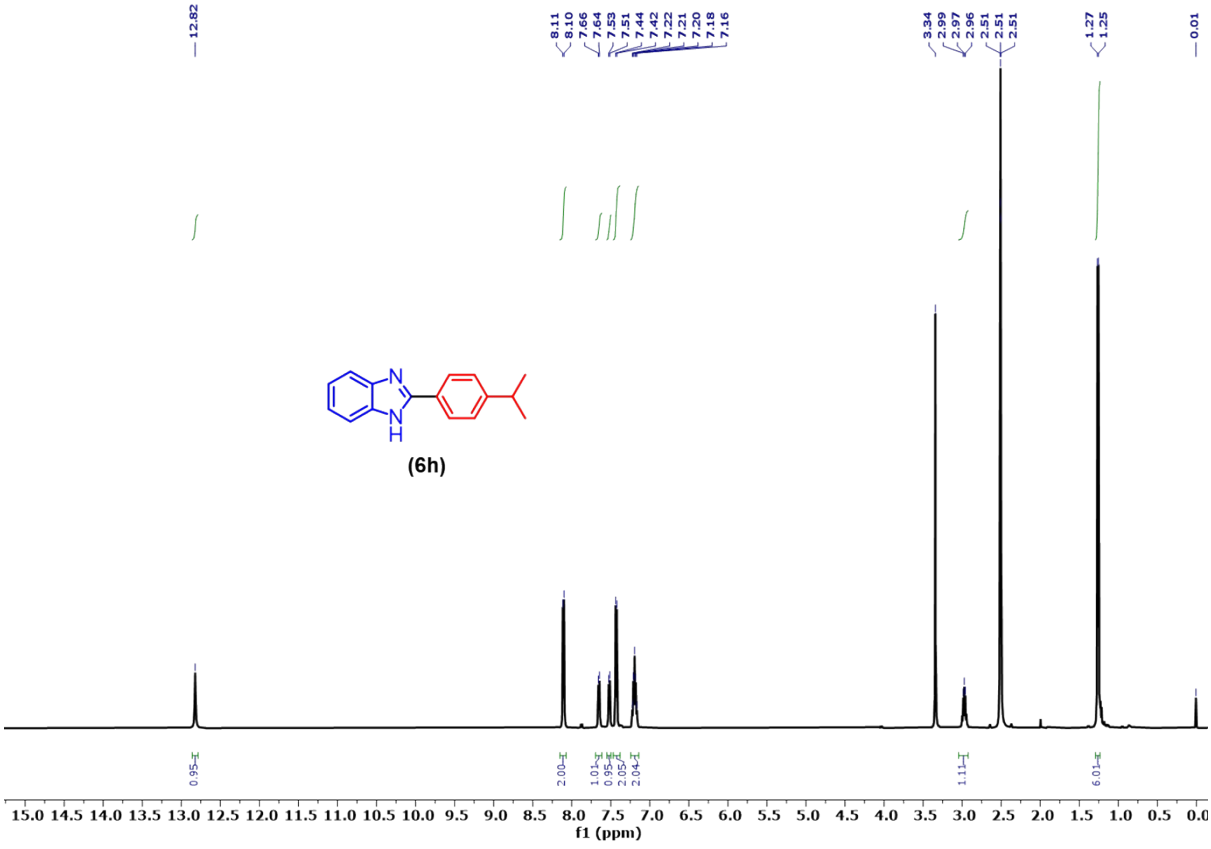

12.99
8.13
8.11
7.78
7.76
7.67
7.54
7.22
3.35
2.50
Br
(6d)
0.99
2.00
1.93
1.94
1.95
f1 (ppm)

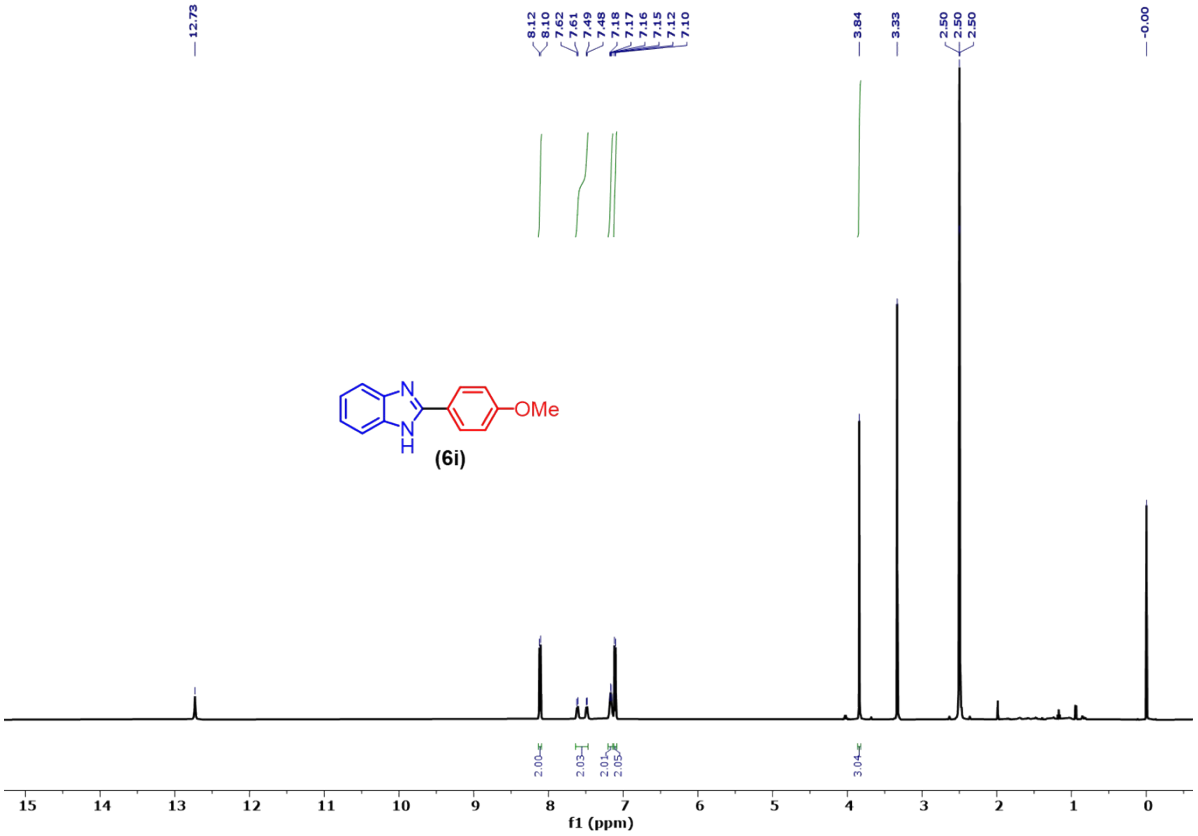

13.30
8.42
7.74
7.73
7.60
7.58
7.29
7.28
7.26
7.25
3.35
2.50
NO2
(6e)
1.01
4.00
2.02
2.05
f1 (ppm)

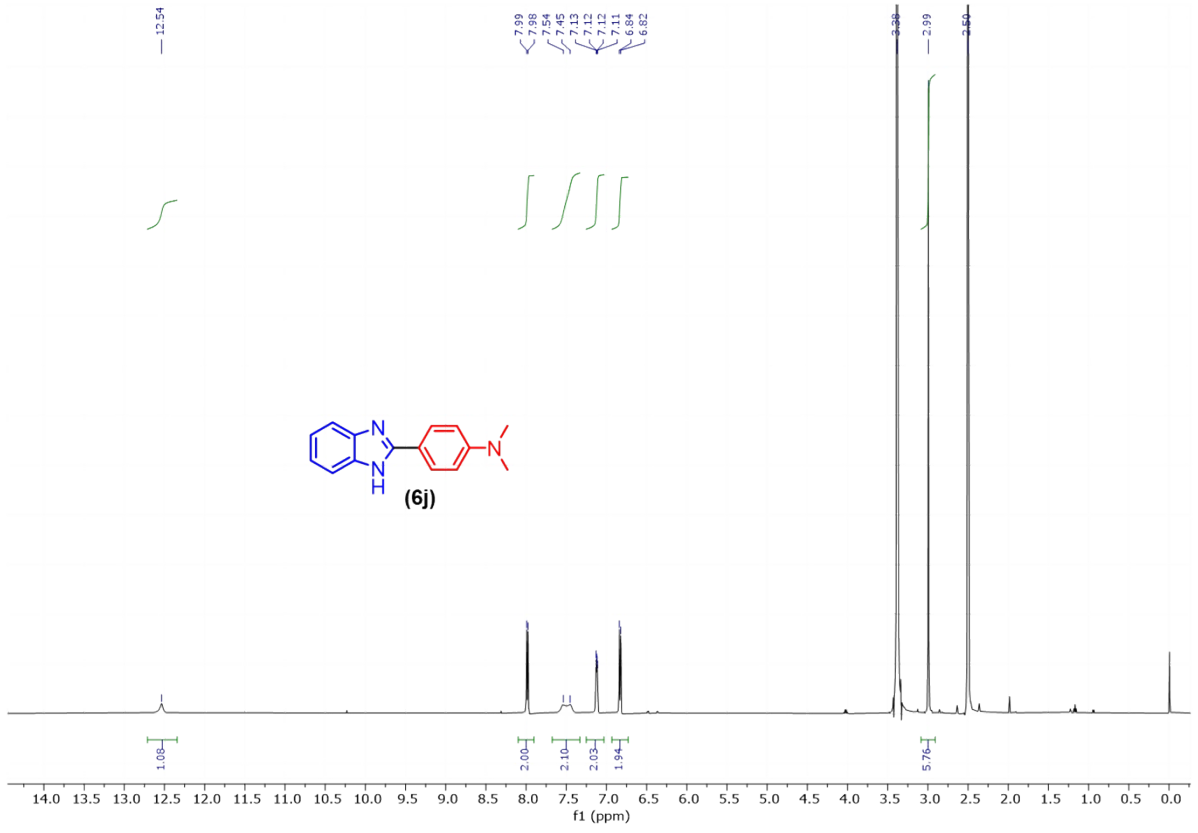

13.28
8.77
8.76
8.76
8.75
8.10
8.10
8.10
8.09
7.73
7.60
7.27
3.42
2.50
(6f)
0.94
2.00
2.02
1.97
2.00
f1 (ppm)

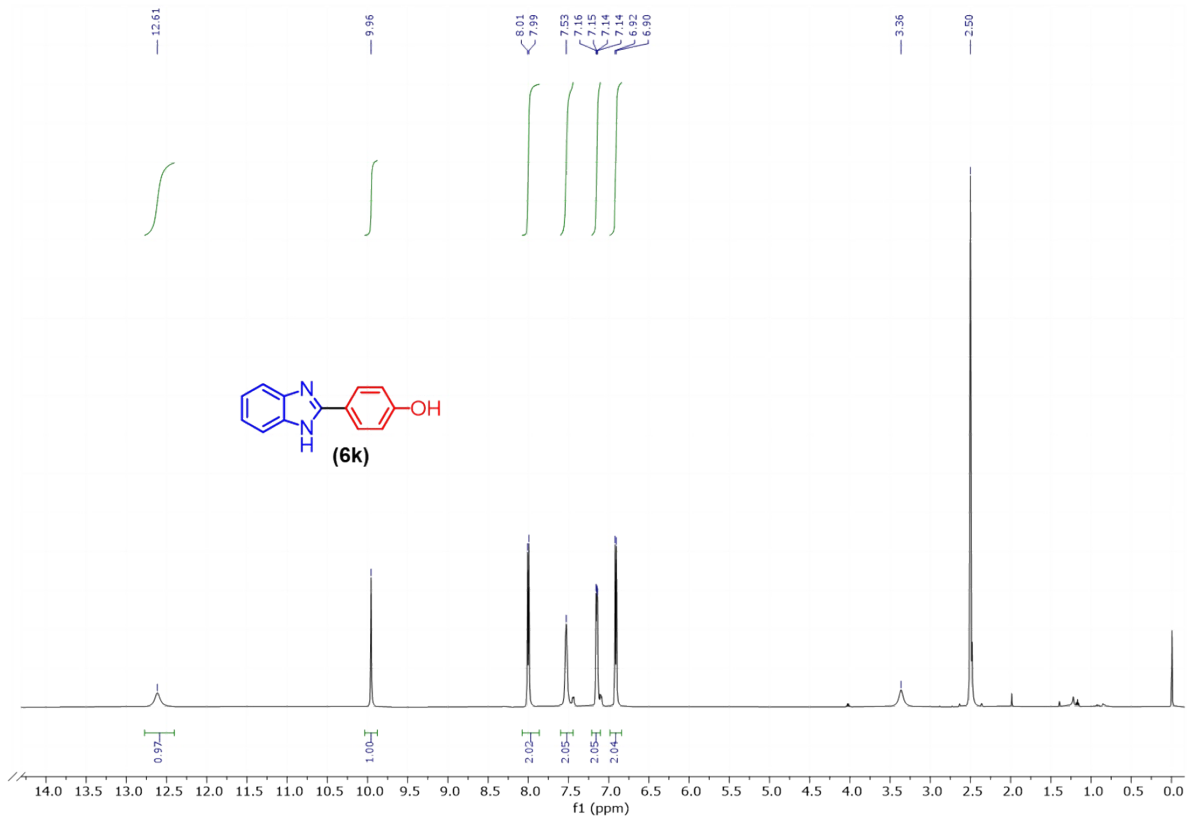

12.82
8.07
8.06
7.64
7.63
7.52
7.51
7.50
7.37
7.35
7.21
7.20
7.18
7.17
7.15
3.35
2.50
2.50
2.50
2.38
Me
(6g)
1.11
2.00
0.98
0.99
2.04
2.08
3.22
f1 (ppm)

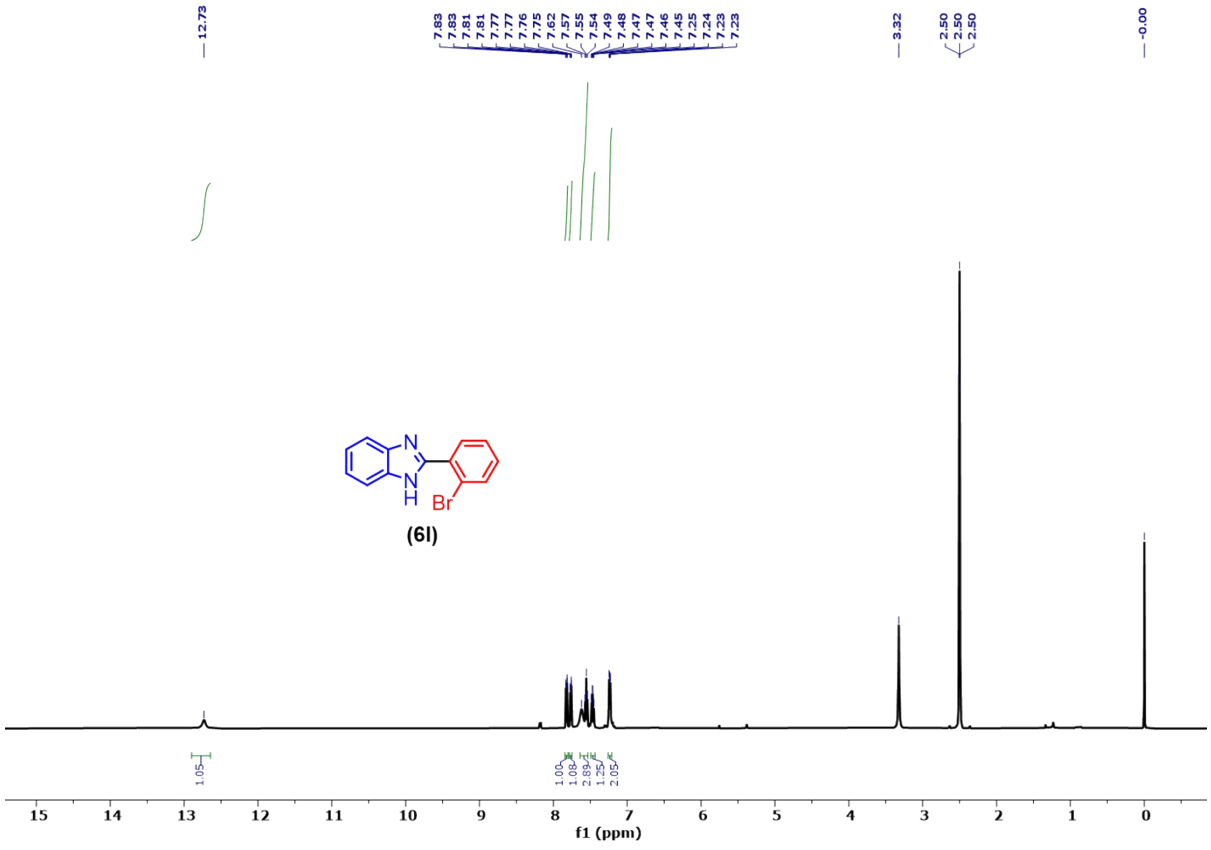

150.94
143.39
139.13
134.52
129.09
127.03
125.96
121.90
121.13
118.28
110.76
20.55
Me
(6g)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

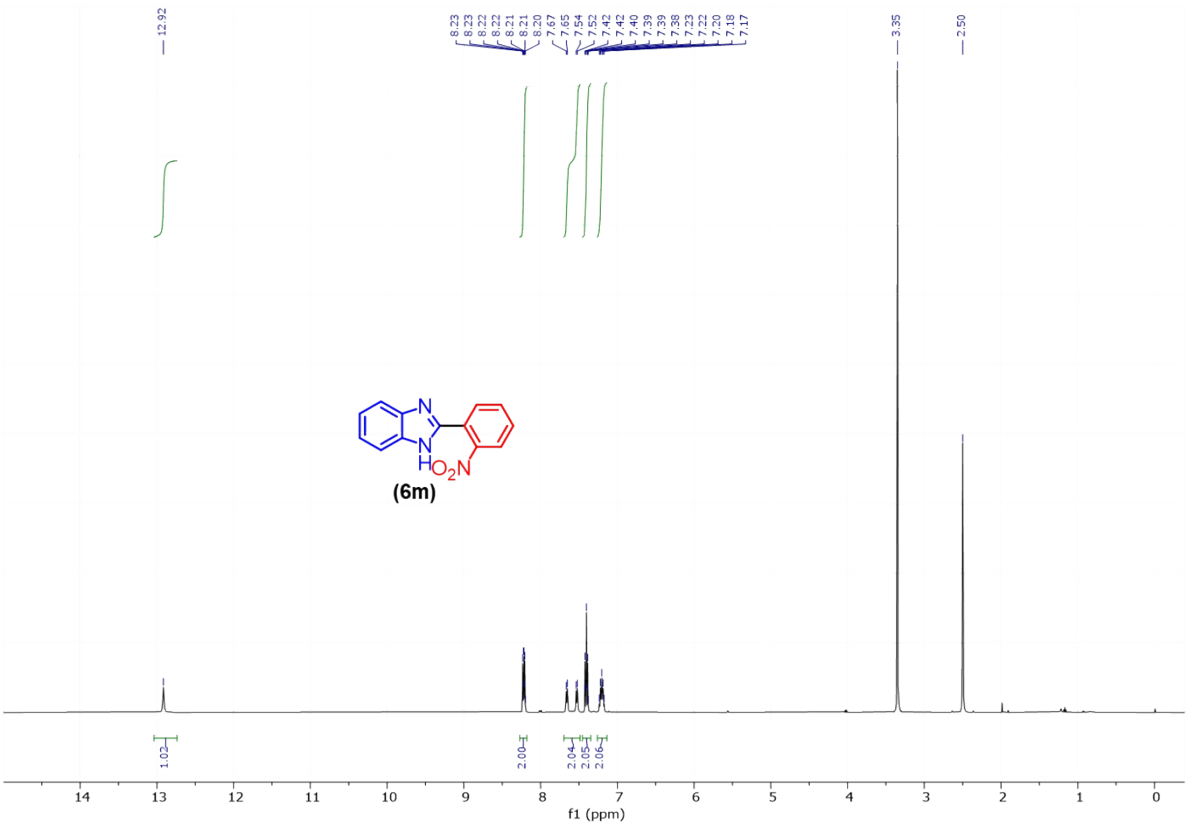

12.82
8.11
8.10
7.66
7.64
7.53
7.51
7.44
7.42
7.22
7.21
7.20
7.18
7.16
3.34
2.99
2.97
2.96
2.51
2.51
2.51
1.27
1.25
0.01
(6h)
0.95
2.00
1.01
0.95
2.05
2.04
1.11
6.01
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


12.73
8.12
8.10
7.62
7.61
7.49
7.48
7.18
7.17
7.16
7.15
7.12
7.10
3.84
3.33
2.50
2.50
2.50
-0.00
OMe
(6i)
2.00
2.03
2.01
2.05
3.04
f1 (ppm)

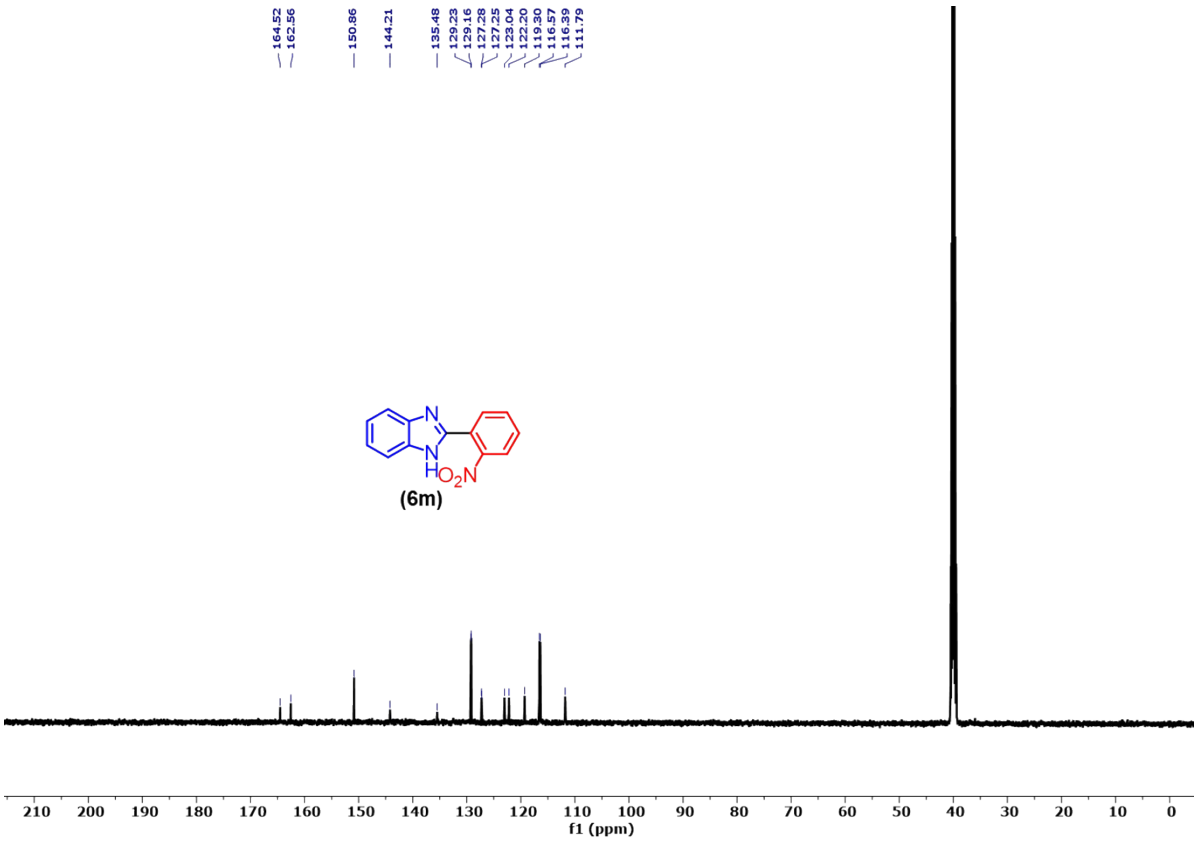

12.54
7.99
7.98
7.54
7.45
7.13
7.12
7.12
7.11
6.84
6.82
3.38
2.99
2.50
(6j)
1.08
2.00
2.10
2.03
1.94
5.76
f1 (ppm)


12.61
9.96
8.01
7.99
7.53
7.16
7.15
7.14
7.14
6.92
6.90
3.36
2.50
OH
(6k)
0.97
1.00
2.02
2.05
2.05
2.04
f1 (ppm)

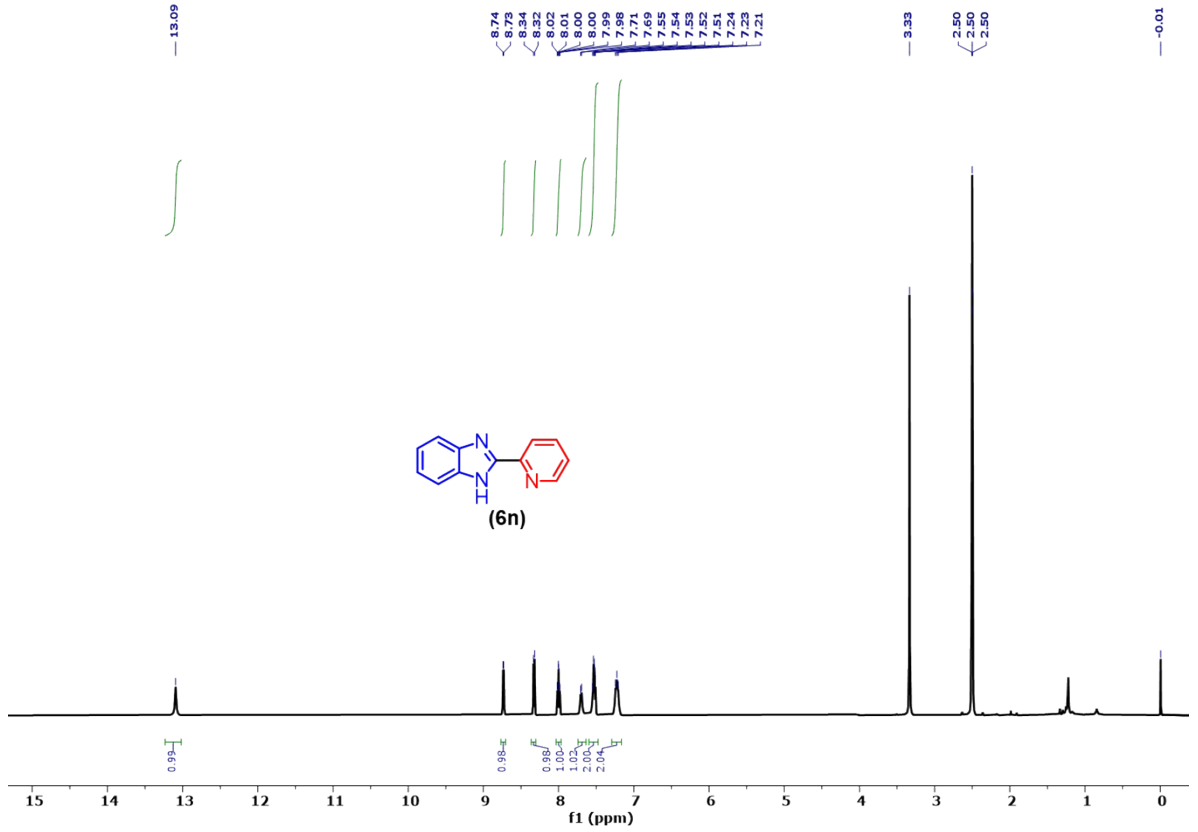

12.73
7.83
7.83
7.81
7.81
7.77
7.77
7.76
7.75
7.62
7.57
7.55
7.54
7.49
7.48
7.47
7.47
7.46
7.45
7.25
7.24
7.23
7.23
3.32
2.50
2.50
2.50
-0.00
Br
(6l)
1.05
1.00
1.08
2.89
1.25
2.05
f1 (ppm)

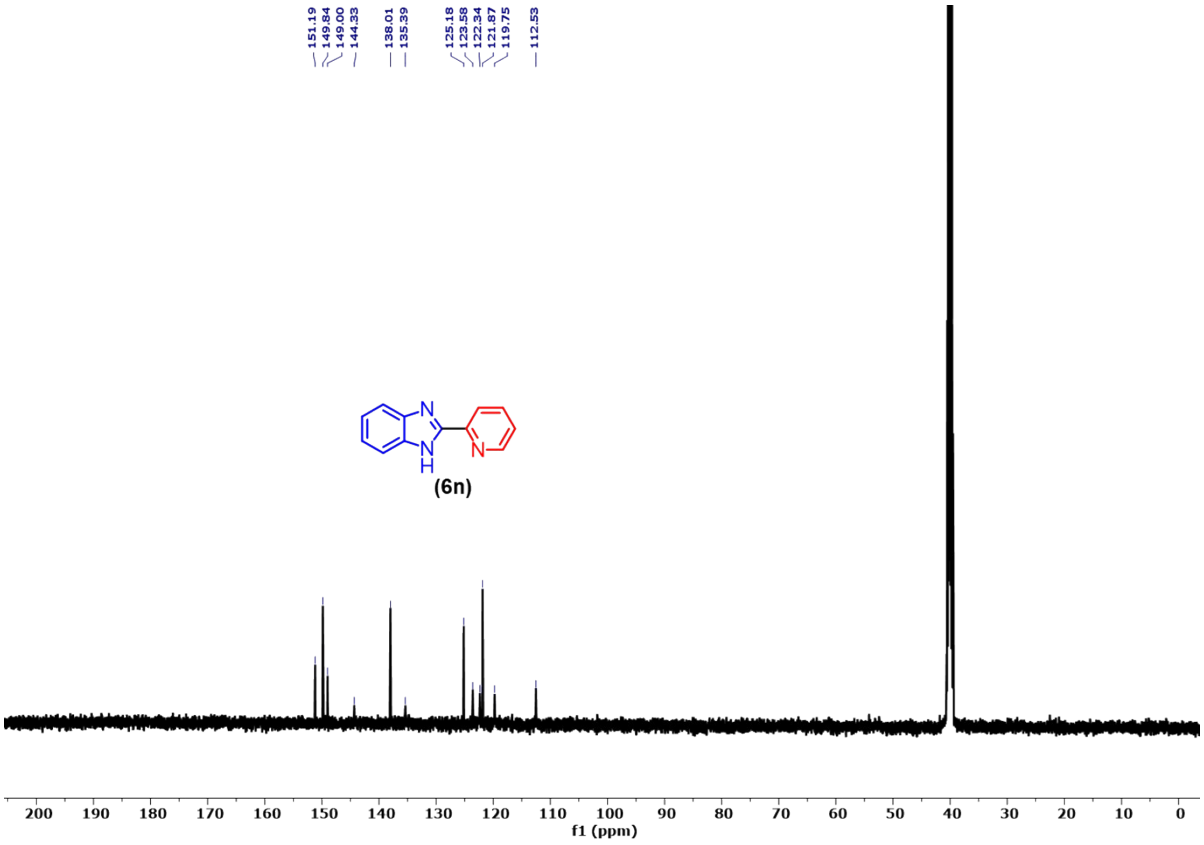

12.92
8.23
8.23
8.22
8.22
8.21
8.21
8.20
7.67
7.65
7.54
7.52
7.42
7.42
7.40
7.39
7.39
7.38
7.23
7.22
7.20
7.18
7.17
3.35
2.50
1.02
2.00
2.04
2.05
2.06
f1 (ppm)

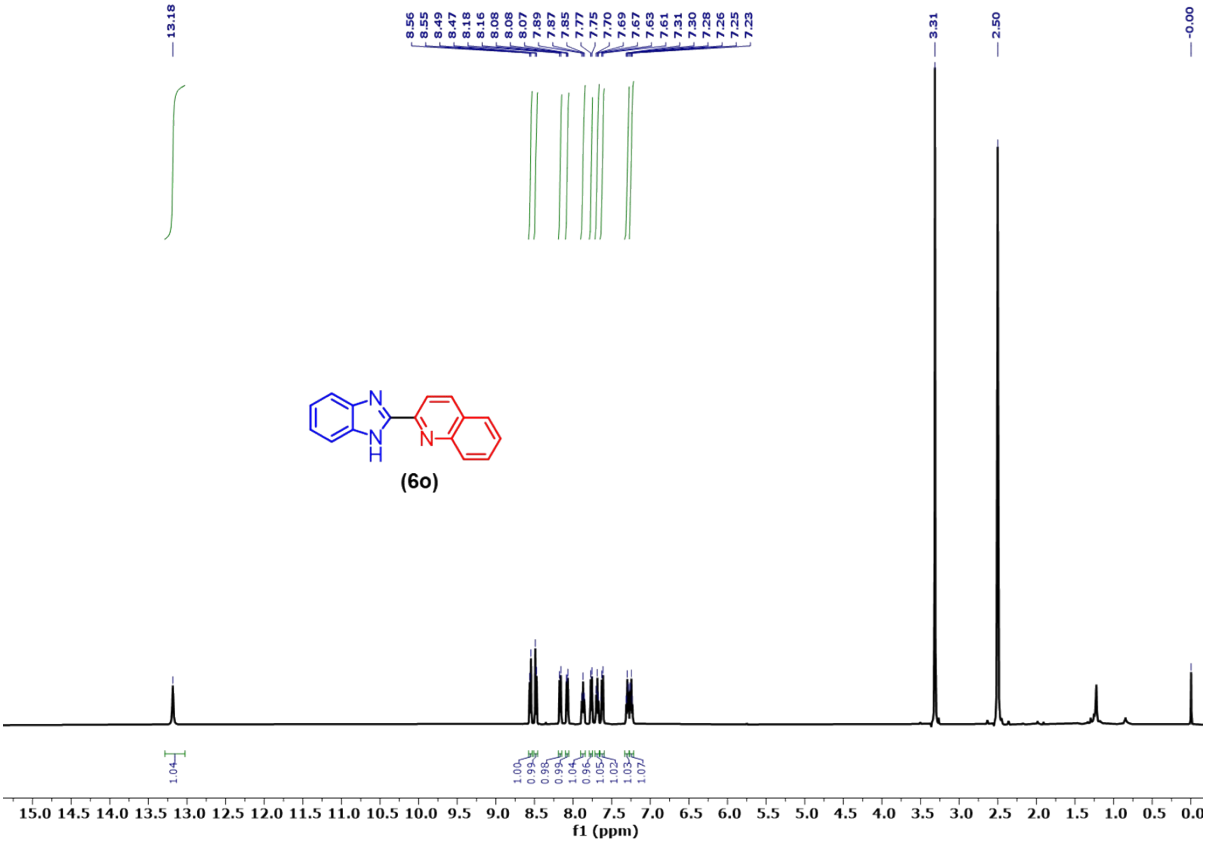
(6m)


164.52
162.56
150.86
144.21
135.48
129.23
129.16
127.28
127.25
123.04
122.20
119.30
116.57
116.39
111.79
f1 (ppm)

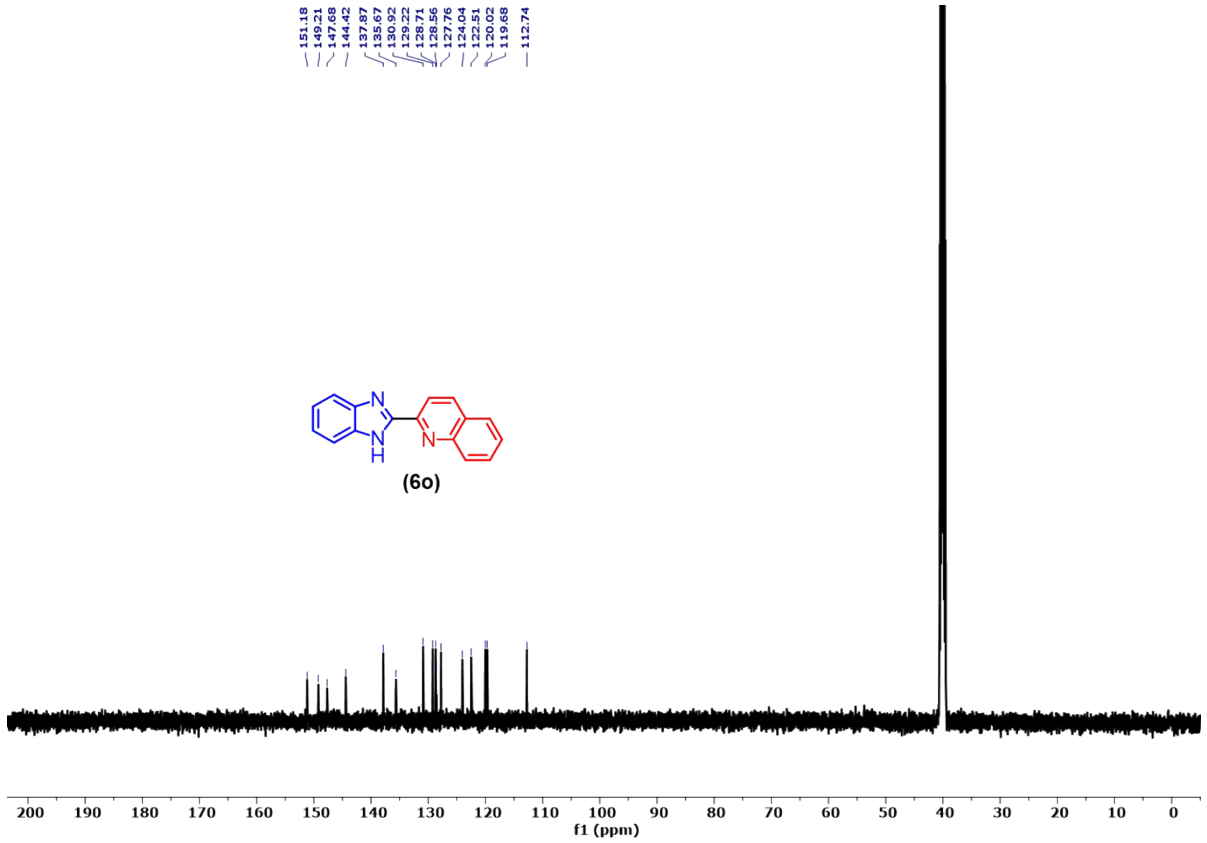
(6m)


13.09
8.74
8.73
8.34
8.32
8.02
8.01
8.00
8.00
7.99
7.98
7.71
7.69
7.55
7.54
7.53
7.52
7.51
7.24
7.23
7.21
3.33
2.50
2.50
2.50
-0.01
(6n)
f1 (ppm)

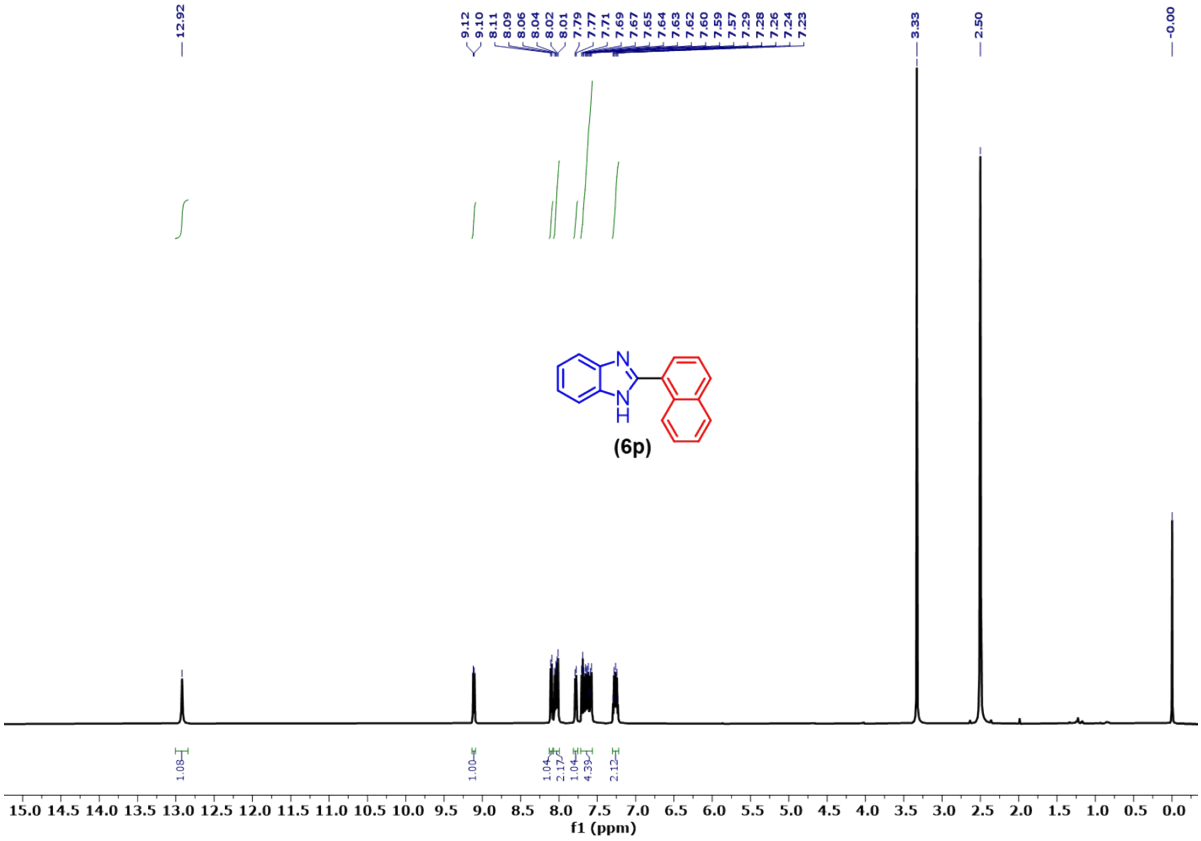

151.19
149.84
149.00
144.33
138.01
135.39
125.18
123.58
122.34
121.87
119.75
112.53
(6n)
f1 (ppm)

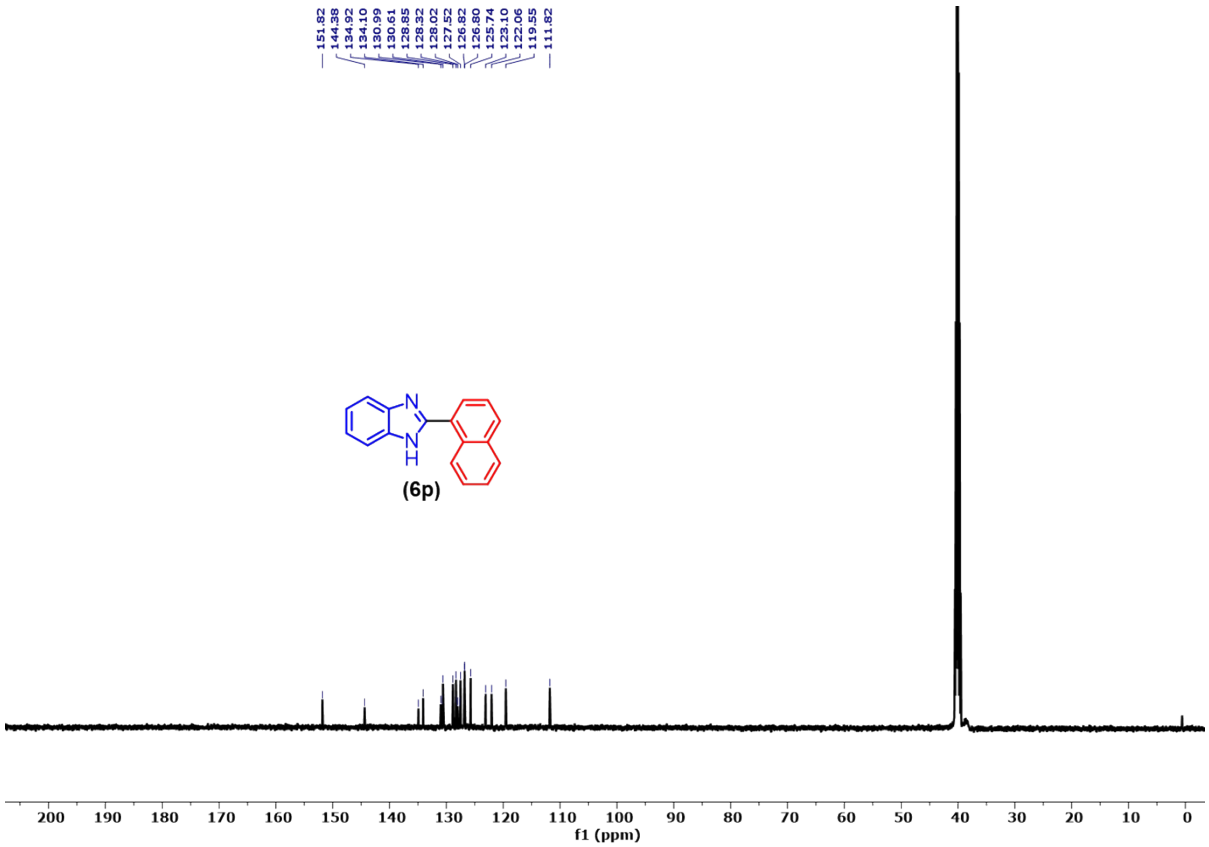

13.18
8.56
8.55
8.49
8.47
8.18
8.16
8.08
8.08
8.07
7.89
7.87
7.85
7.77
7.75
7.70
7.69
7.67
7.63
7.61
7.31
7.30
7.28
7.26
7.25
7.23
3.31
2.50
-0.00
1.04
1.00
0.99
0.98
0.99
1.04
0.96
1.05
1.02
1.03
1.07
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

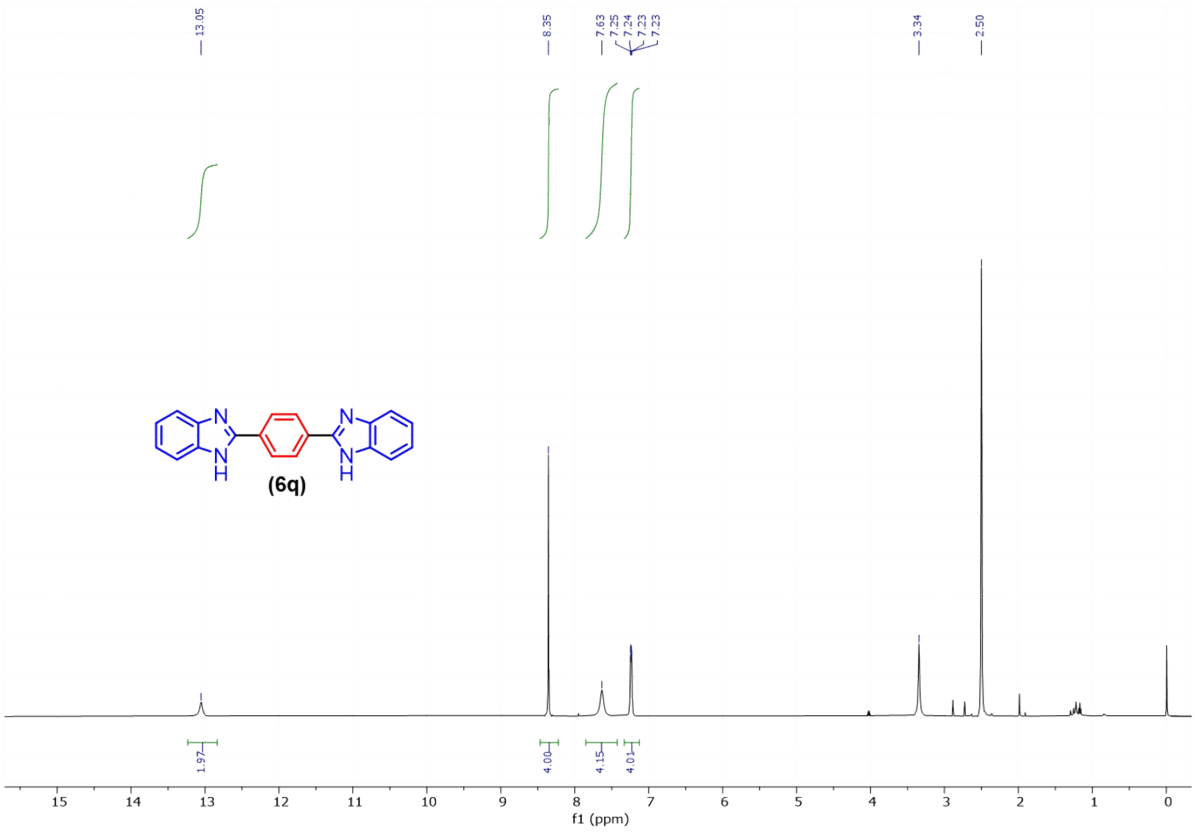
(6o)

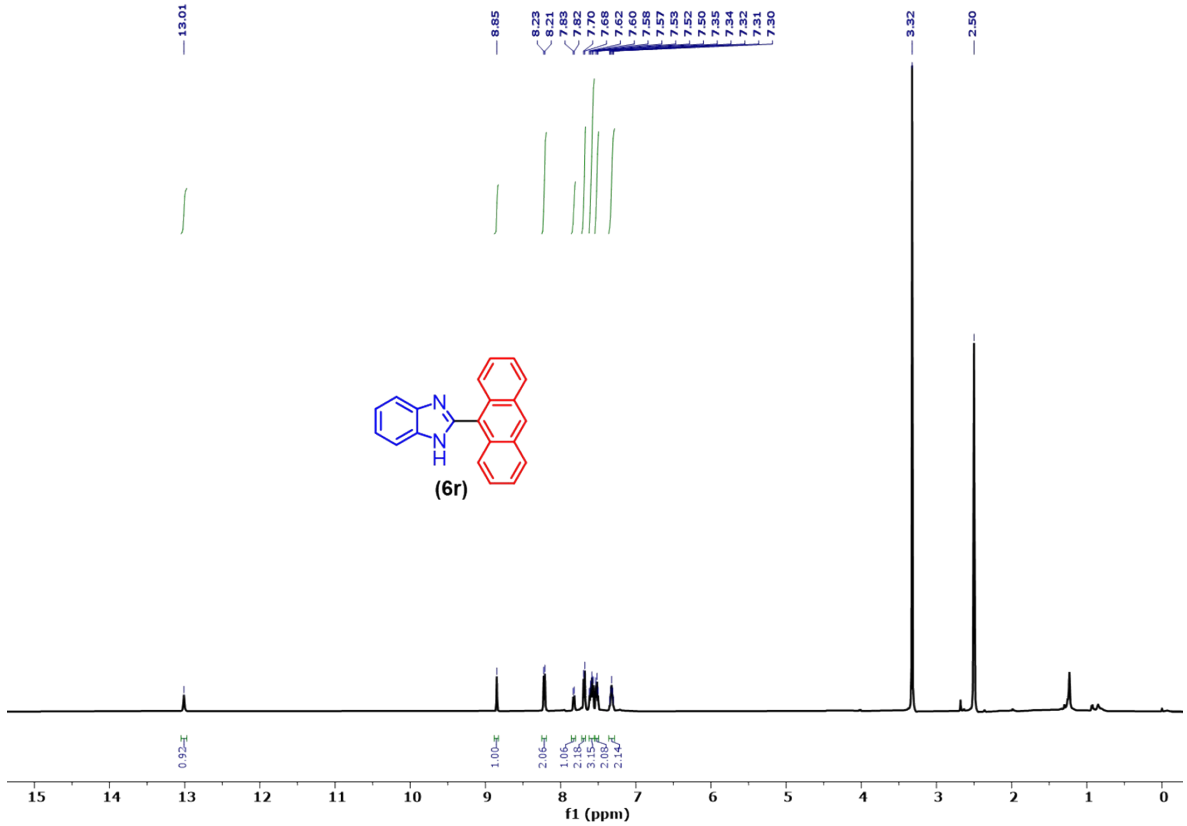

151.18
149.21
147.68
144.42
137.87
135.67
130.92
129.22
128.71
128.56
127.76
124.04
122.51
120.02
119.68
112.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

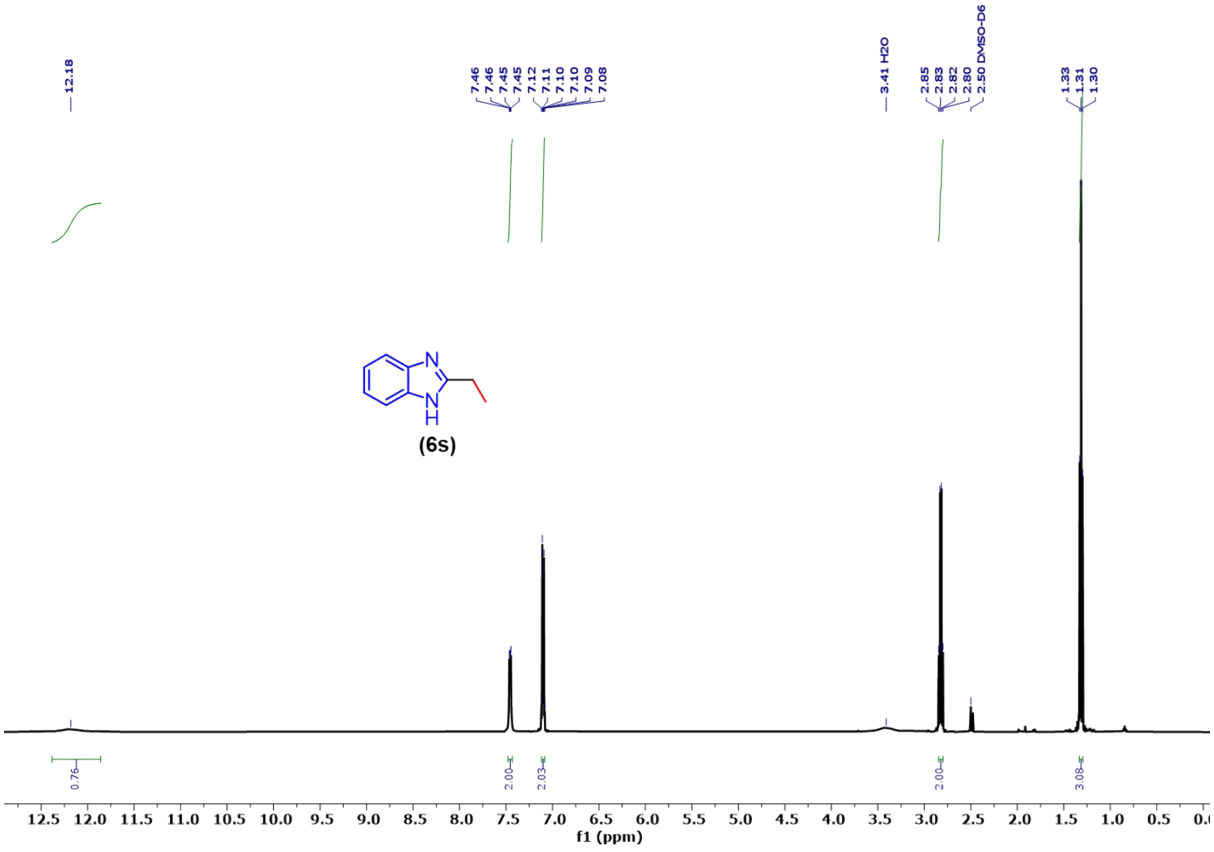
(6o)

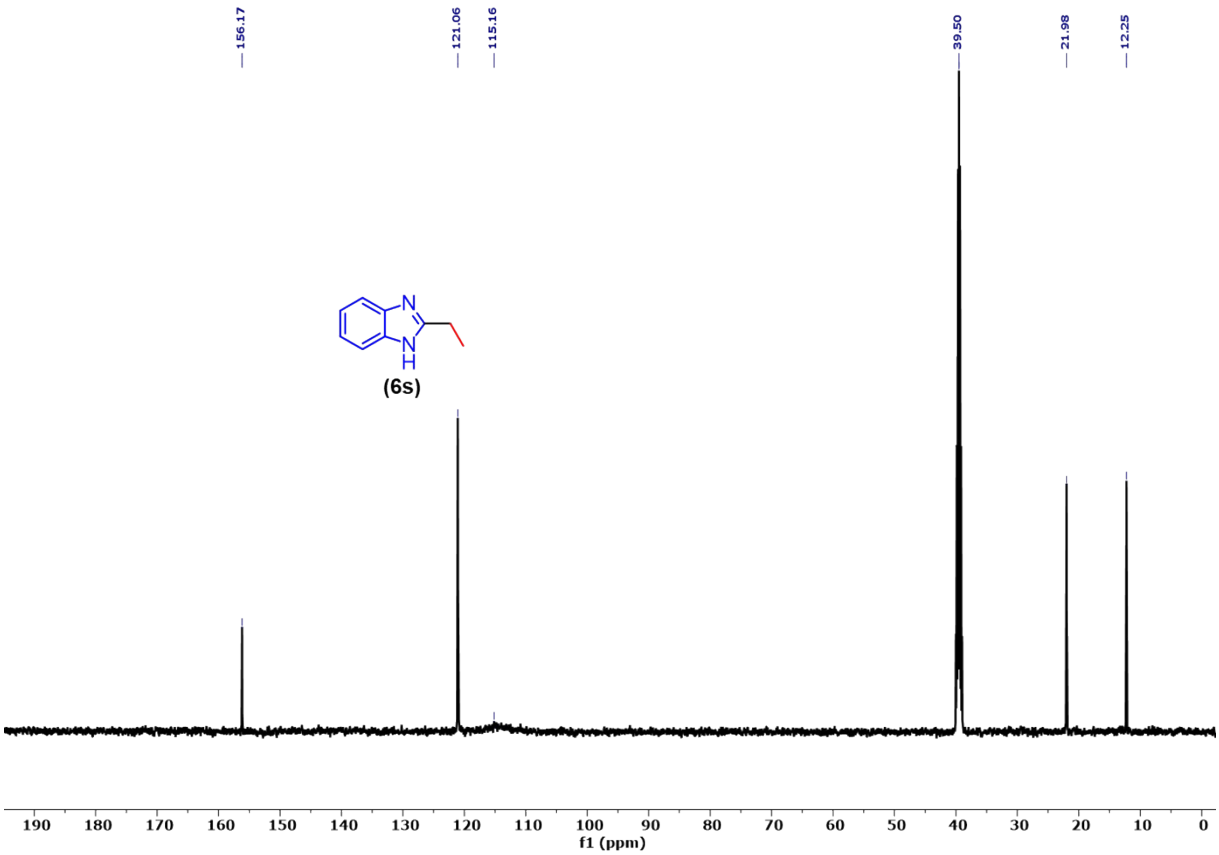

12.92
9.12
9.10
8.11
8.09
8.06
8.04
8.02
8.01
7.79
7.77
7.71
7.69
7.67
7.65
7.64
7.63
7.62
7.60
7.59
7.57
7.29
7.28
7.26
7.24
7.23
3.33
2.50
-0.00
(6p)
1.08
1.00
1.04
2.12
1.04
4.39
2.13
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

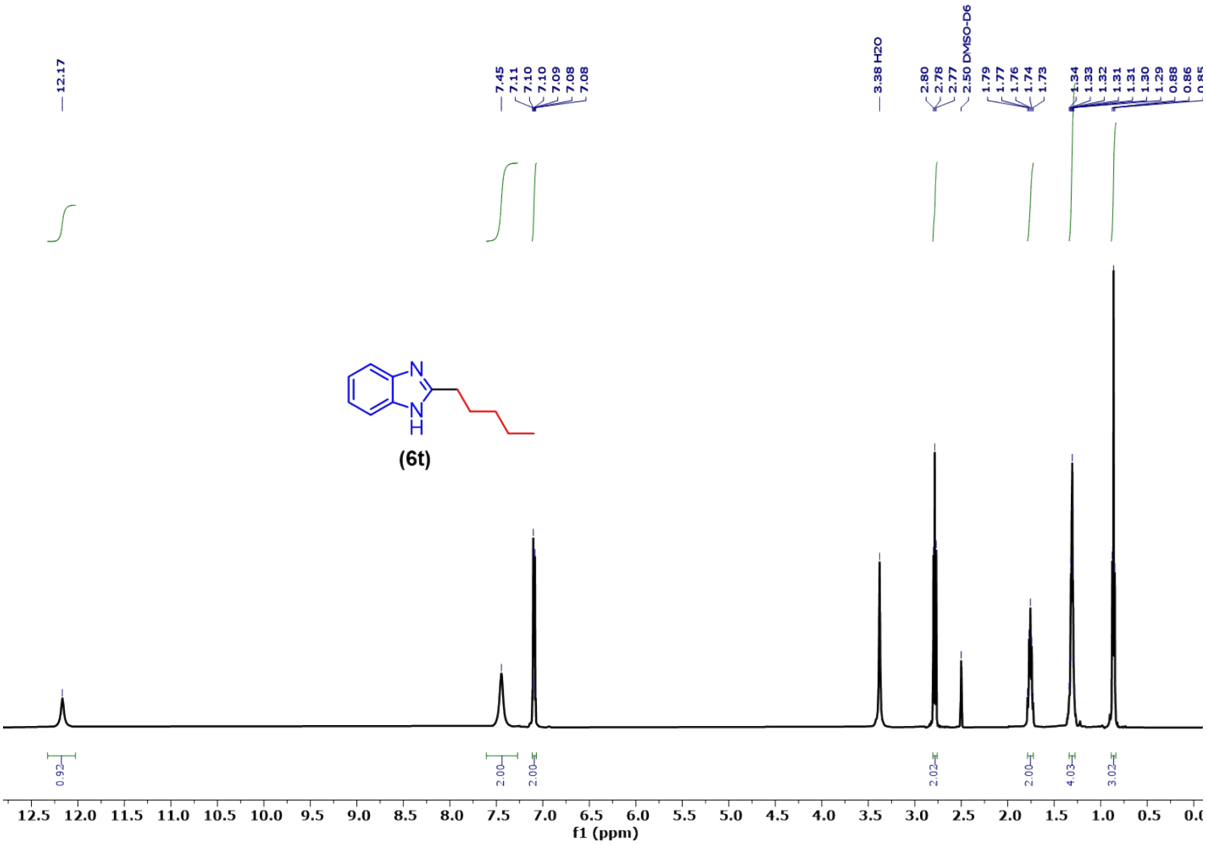

151.82
144.38
134.92
134.10
130.99
130.61
128.85
128.32
128.02
127.52
126.82
126.80
125.74
123.10
122.06
119.55
111.82
(6p)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


13.05
8.35
7.63
7.25
7.24
7.23
7.23
3.34
2.50
(6q)
1.97
4.00
4.15
4.01
f1 (ppm)

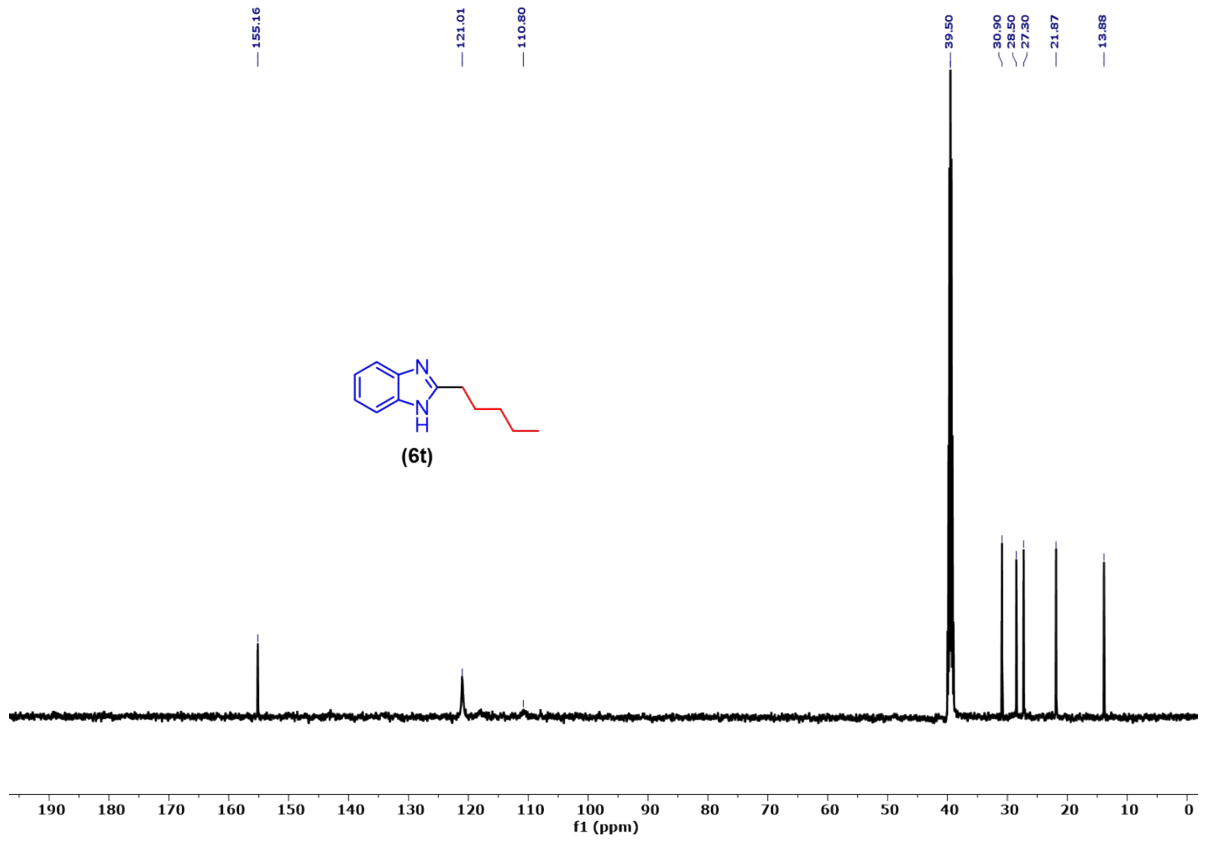

13.01
8.85
8.23
8.21
7.83
7.82
7.70
7.68
7.62
7.60
7.58
7.57
7.53
7.52
7.50
7.35
7.34
7.32
7.31
7.30
3.32
2.50
(6r)
f1 (ppm)


12.18
7.46
7.46
7.45
7.45
7.12
7.11
7.10
7.10
7.09
7.08
3.41 H2O
2.85
2.83
2.82
2.80
2.50 DMSO-D6
1.33
1.31
1.30
(6s)
0.76
2.00
2.03
2.00
3.08
f1 (ppm)

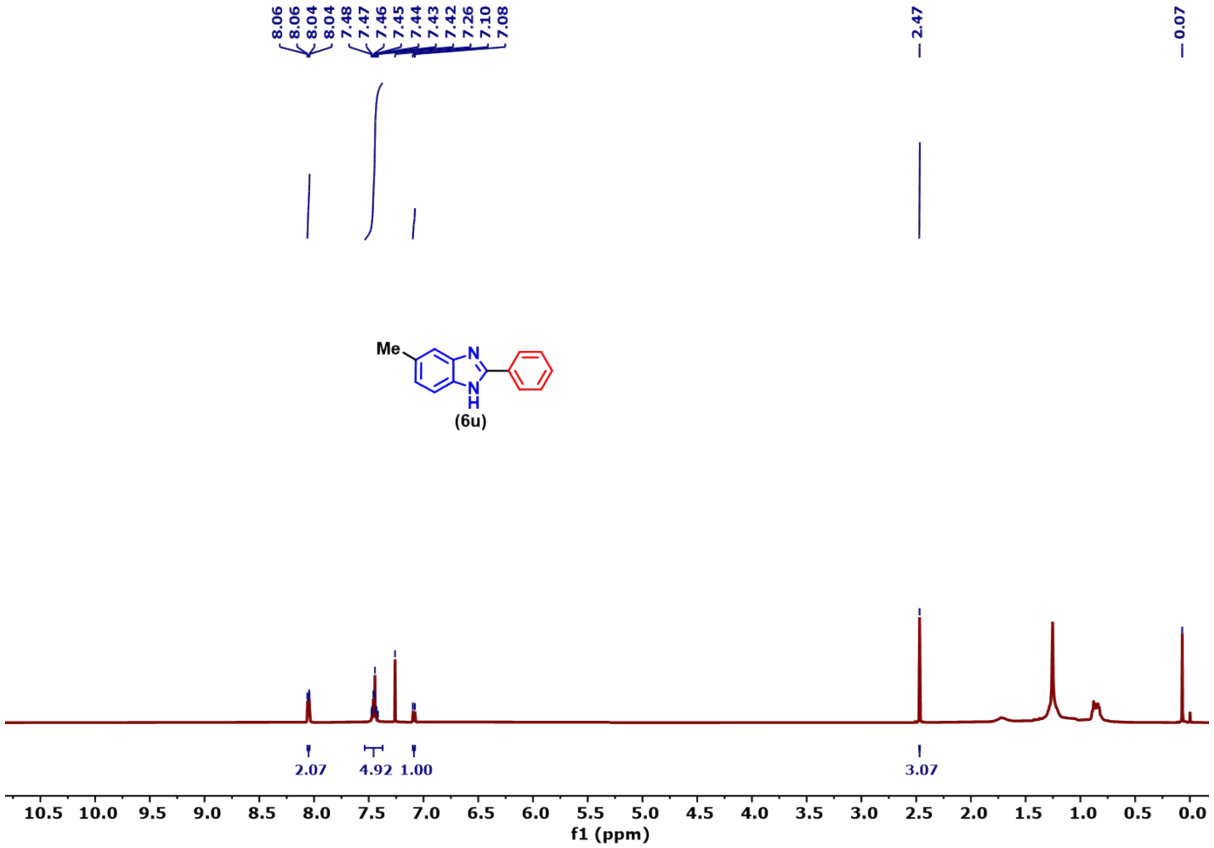

156.17
121.06
115.16
39.50
21.98
12.25
(6s)
f1 (ppm)

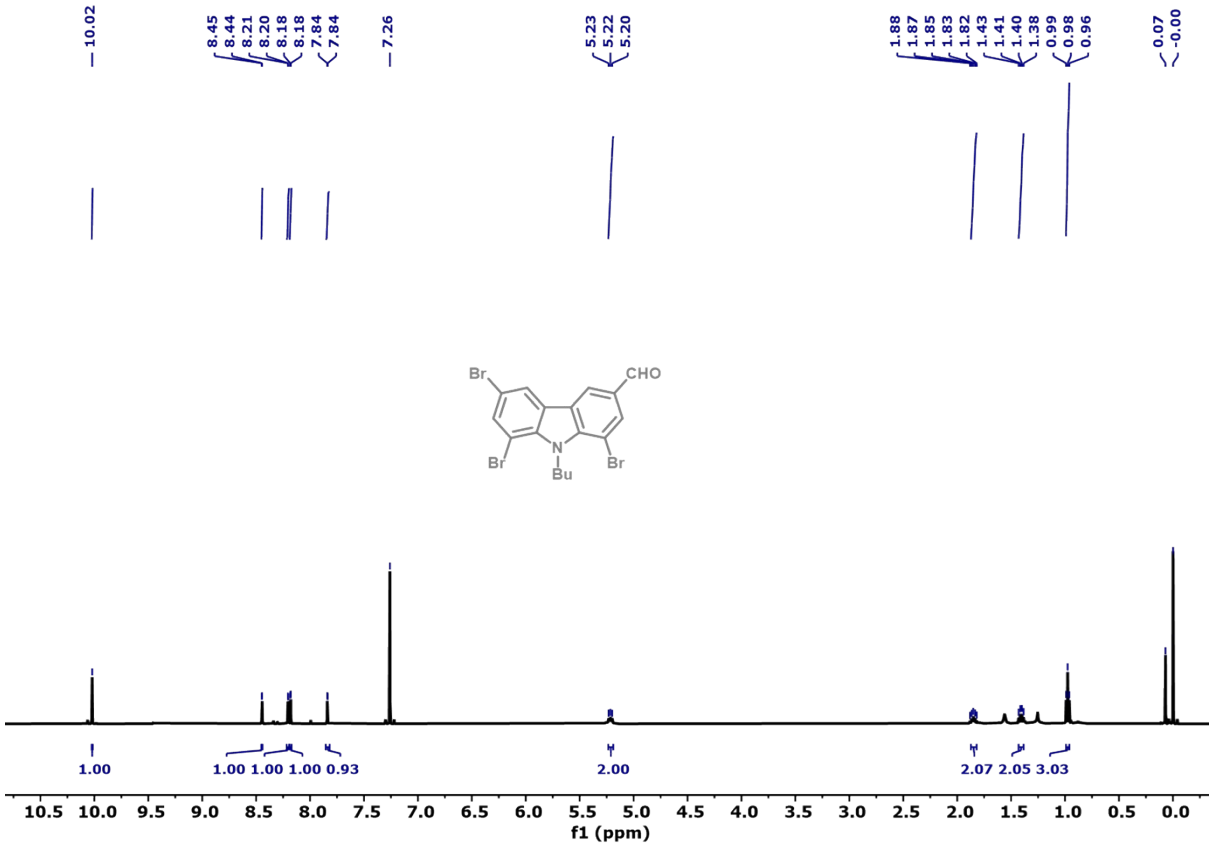

12.17
7.45
7.11
7.10
7.10
7.09
7.08
7.08
3.38 H2O
2.80
2.78
2.77
2.50 DMSO-D6
1.79
1.77
1.76
1.74
1.73
1.34
1.33
1.32
1.31
1.31
1.30
1.29
0.88
0.86
0.92
2.00
2.00
2.02
2.00
4.03
3.02
f1 (ppm)

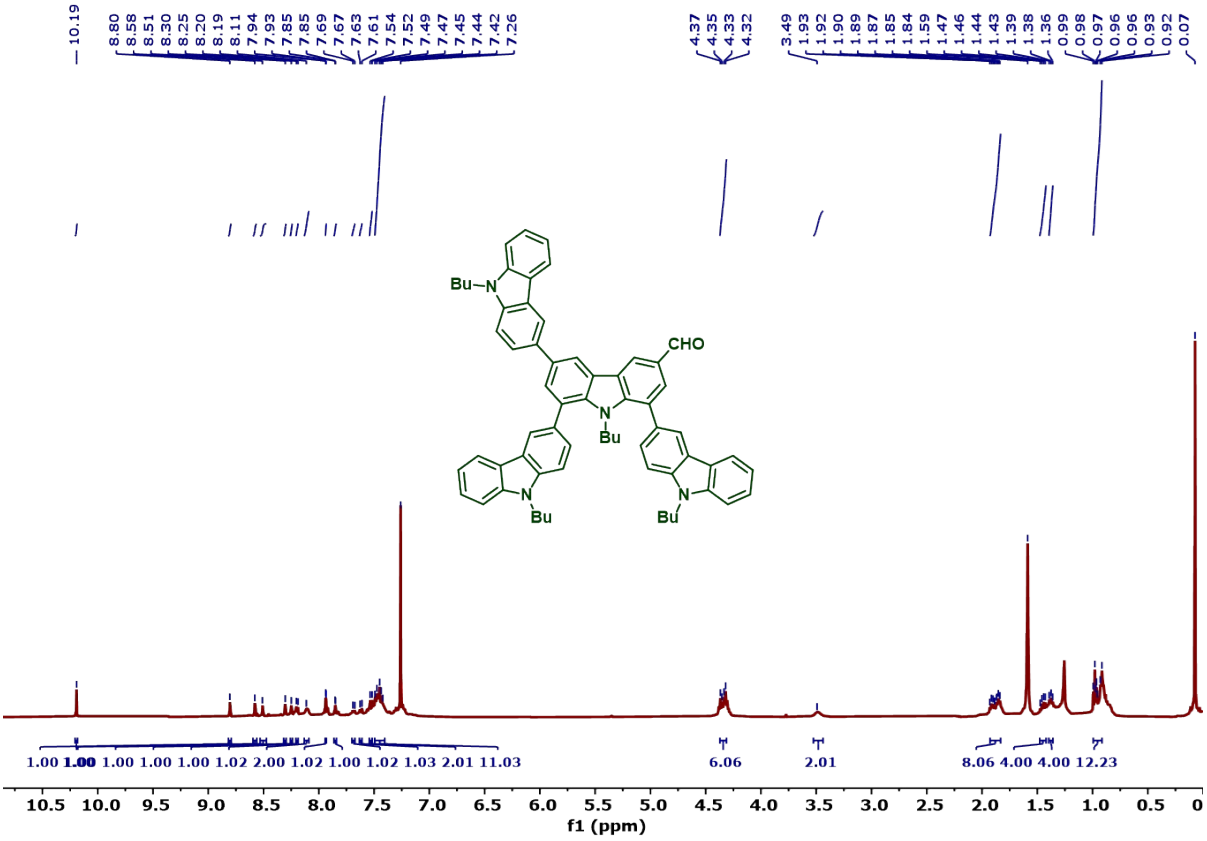
(6t)

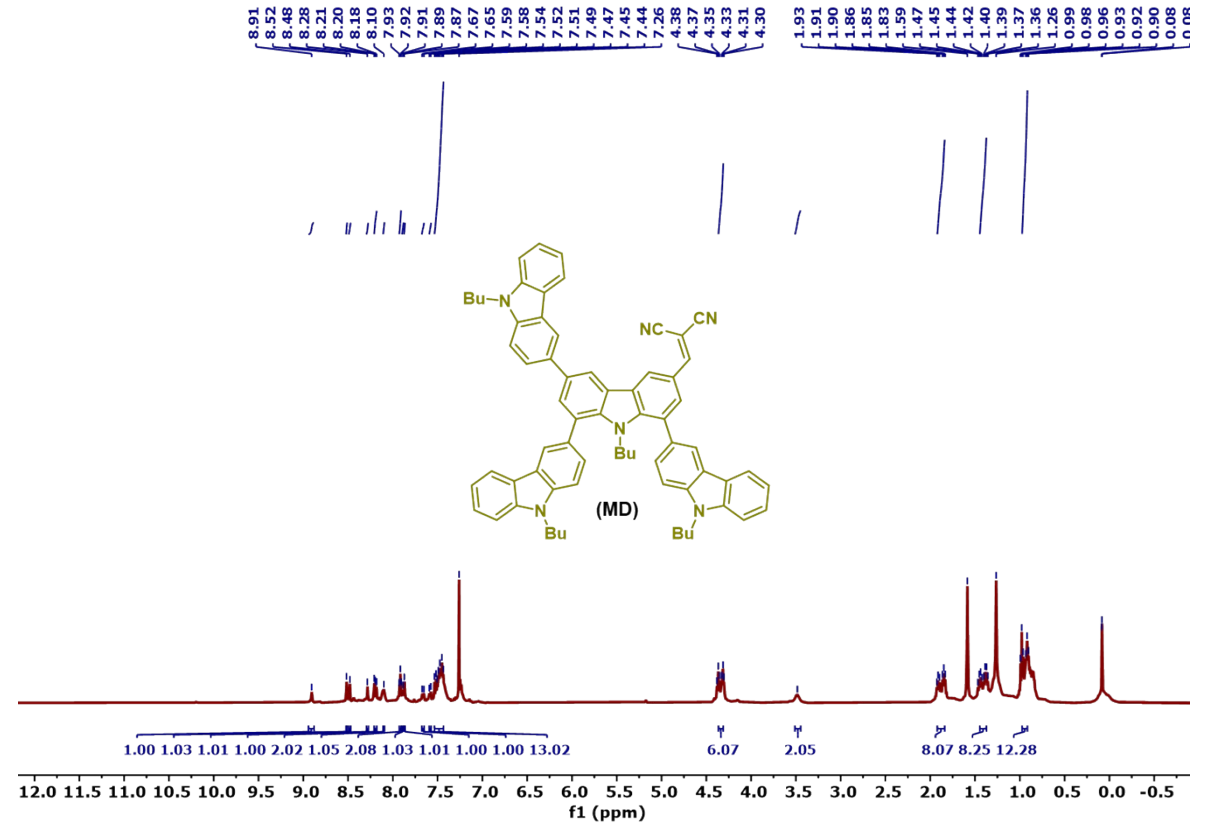

155.16
121.01
110.80
39.50
30.90
28.50
27.30
21.87
13.88
f1 (ppm)

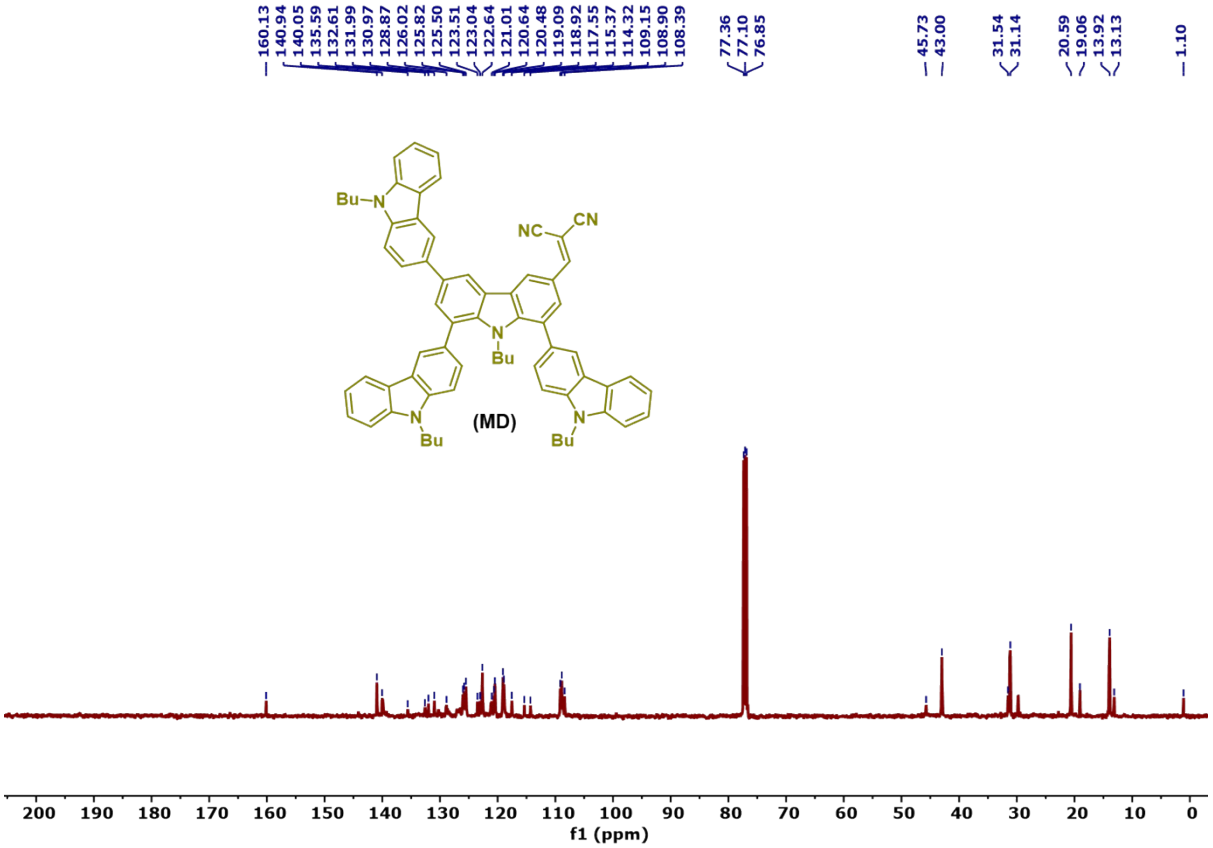
(6t)


8.06
8.06
8.04
8.04
7.48
7.47
7.46
7.45
7.44
7.43
7.42
7.26
7.10
7.08
2.47
0.07
Me
N
N
H
(6u)
2.07
4.92
1.00
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


10.02
8.45
8.44
8.21
8.20
8.18
8.18
7.84
7.84
7.26
5.23
5.22
5.20
1.88
1.87
1.85
1.83
1.82
1.43
1.41
1.40
1.38
0.99
0.98
0.96
0.07
-0.00
Br
CHO
Br
N
Br
Bu
1.00
1.00 1.00 1.00 0.93
2.00
2.07 2.05 3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


10.19
8.80
8.58
8.51
8.30
8.25
8.20
8.19
8.11
7.94
7.93
7.85
7.85
7.69
7.67
7.63
7.61
7.54
7.52
7.49
7.47
7.45
7.44
7.42
7.26
4.37
4.35
4.33
4.32
3.49
1.93
1.92
1.90
1.89
1.87
1.85
1.84
1.59
1.47
1.46
1.44
1.43
1.39
1.38
1.36
0.99
0.98
0.97
0.96
0.96
0.93
0.92
0.07
Bu–N
CHO
N
Bu
N
Bu
N
Bu
1.00 1.00 1.00 1.00 1.00 1.02 2.00 1.02 1.00 1.02 1.03 2.01 11.03
6.06
2.01
8.06 4.00 4.00 12.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


8.91
8.52
8.48
8.28
8.21
8.20
8.18
8.10
7.93
7.92
7.91
7.89
7.87
7.67
7.65
7.59
7.58
7.54
7.52
7.51
7.49
7.47
7.45
7.44
7.26
4.38
4.37
4.35
4.33
4.31
4.30
1.93
1.91
1.90
1.86
1.85
1.83
1.59
1.47
1.45
1.44
1.42
1.40
1.39
1.37
1.36
1.26
0.99
0.98
0.96
0.93
0.92
0.90
0.08
Bu–N
NC
CN
N
Bu
N
Bu
N
Bu
(MD)
1.00 1.03 1.01 1.00 2.02 1.05 2.08 1.03 1.01 1.00 1.00 13.02
6.07
2.05
8.07 8.25 12.28
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



7. HRMS of TEMPO adduct