Electronic Supplementary Material (ESI) for Chemical Communications.

Nickel-Catalysed Dehydrogenative Coupling of Aromatic Diamines with Alcohols: Selective Synthesis of Substituted Benzimidazoles and Quinoxalines

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[1.1] General Experimental Details:

All solvents and reagents were used, as received from the suppliers. TLC was performed on Merck Kiesel gel 60, GF_{254} plates with the layer thickness of 0.25 mm. Column chromatography was performed on silica gel (100-200 mesh) using a gradient of ethyl acetate and hexane as mobile phase. ^{1}H NMR spectral data were collected at, 400 MHz (JEOL), 500 MHz (Bruker) and ^{13}C NMR were recorded at 100 MHz. ^{1}H NMR spectral data are given as chemical shifts in ppm followed by multiplicity (s- singlet; d- doublet; t- triplet; q- quartet; m- multiplet), number of protons and coupling constants. ^{13}C NMR chemical shifts are expressed in ppm. Elemental analysis data were recorded in Vario Micro Cube. GC-MS were recorded using Agilent GC Mass Spectrometer. All the reactions were performed in a closed system using Schlenk tube. All nickel salts were purchased from Sigma Aldrich. Nickel(II) chloride (Assay- 98%; CAS Number 13462-88-9; EC Number 236-665-0; Pack Size- No 217891-10G). Potassium *tert*-butoxide was purchased from Avra Synthesis Pvt. Ltd., India. (Purity-98%, CAS No: 865-47-4, Catalog No- ASP2012).

[1.2] General Procedure for Nickel-Catalysed Synthesis of substituted Benzimidazoles and Quinoxaline *via* Dehydrogenative Coupling of Aromatic diamines and Alcohols:

<u>Procedure A:</u>

In a 15 mL oven dried Schlenk tube, *o*-phenylenediamine (0.5 mmol), *t*-BuOK (0.5 mmol), $NiCl_2$ (2.5 mol%), Phen (3.0 mol%), and alcohols (1.0 mmol) were added followed by toluene 2.0 mL under an atmosphere of N_2 and the reaction mixture was heated at 140 ^{o}C for 24 h in a closed system. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated *in vacuo*. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

<u>Procedure B:</u>

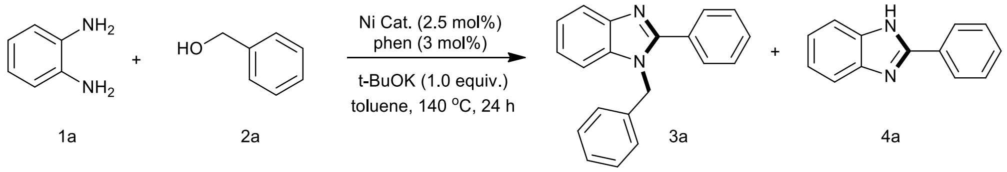
In a 15 mL oven dried Schlenk tube, *o*-phenylenediamine (0.5 mmol), *t*-BuOK (0.5 mmol), $NiCl_2$ (2.5 mol%), Phen (3.0 mol%) and alcohols (0.5 mmol) were added followed by toluene 2.0 mL under an atmosphere of N_2 and the reaction mixture was heated at 140 ^{o}C for 24 h in a closed system. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated *in vacuo*. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

Procedure C:

In a 15 mL oven dried Schlenk tube, *o*-phenylenediamine (0.5 mmol), *t*-BuOK (1.0 mmol), $NiCl_2$ (6.0 mol%), Phen (12.0 mol%) and alcohols (2.5 mmol) were added followed by toluene 2.0 mL under an atmosphere of N_2 and the reaction mixture was heated at 140 °C for 36 h in a closed system. The reaction mixture was cooled to room temperature and 3.0 mL of ethyl acetate was added and concentrated *in vacuo*. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

[1.3] Optimisation studies for the synthesis of Benzimidazole from diamine and benzyl alcohol:

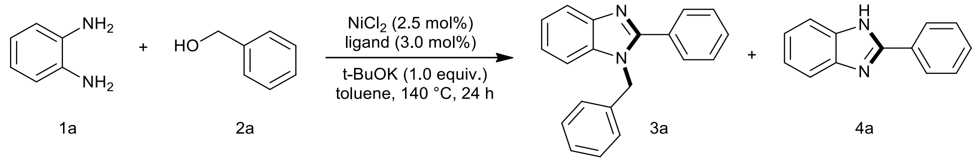
Table S1: Screening of catalyst [a]

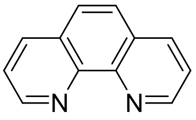
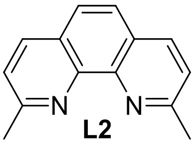
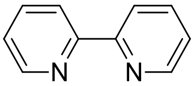
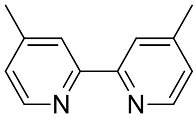
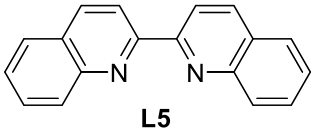


Entry	**Ni-Catalyst**	GC-MS Conversion **3a** (%)	GC-MS Conversion **4a** (%)
1	$NiBr_2$	65	5
2	**$NiCl_2$**	**98 (91%)**[b]	**2**
2	$Ni(acac)_2$	56	11
3	$NiCl_2(DME)$	54	6
5	No Catalyst	21	0

Reaction condition: [a] *o*-phenylenediamine **1a** (0.5 mmol), benzyl alcohol **2a** (1.0 mmol), **Ni Cat. (2.5 mol%)**, phen (3.0 mol%), *t*-BuOK (0.5 mmol), toluene (2.0 mL), Schlenk tube under N_2 atmosphere, 140 °C oil bath, 24 h reaction time. [b] Isolated yield.

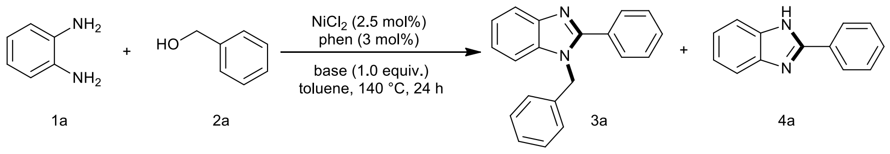
Table S2: Screening of ligands[a]



Entry	**Ligand**	GC-MS Conversion **3a** (%)	GC-MS Conversion **4a** (%)
1	 **L1**	**98 (91%)**[b]	2
2	 **L2**	57	20
3	 **L3**	76	12
4	 **L4**	55	6
5	 **L5**	33	5
6	No Ligand	35	4

Reaction condition: [a] *o*-phenylenediamine **1a** (0.5 mmol), benzyl alcohol **2a** (1.0 mmol), NiCl$_2$ (2.5 mol%), **ligand (3.0 mol%),** *t*-BuOK (0.5 mmol), toluene (2.0 mL), Schlenk tube under N$_2$ atmosphere, 140 ^{o}C oil bath, 24 h reaction time. [b] Isolated yield.

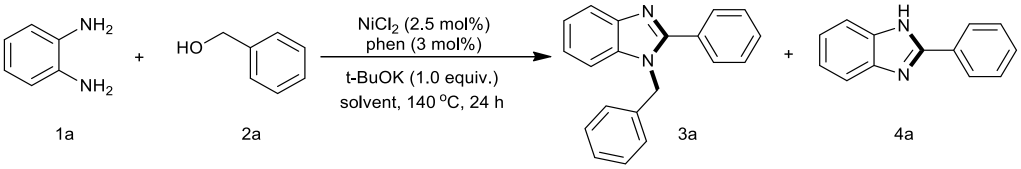
Table S3: Screening of base[a]



Entry	**Base**	GC-MS Conversion **3a** (%)	GC-MS Conversion **4a** (%)
1	***t*-BuOK**	**98(91%)** [b]	**2**
2	*t*-BuONa	75	9
3	K$_3$PO$_4$	0	2
4	K$_2$CO$_3$	0	3
5	Cs$_2$CO$_3$	0	43

Reaction condition: [a] *o*-phenylenediamine **1a** (0.5 mmol), benzyl alcohol **2a** (1.0 mmol), $NiCl_2$ (2.5 mol%), phen (3.0 mol%), **base (0.5 mmol),** toluene (2.0 mL), Schlenk tube under N_2 atmosphere, 140 ^oC oil bath, 24 h reaction time. [b] Isolated yield.

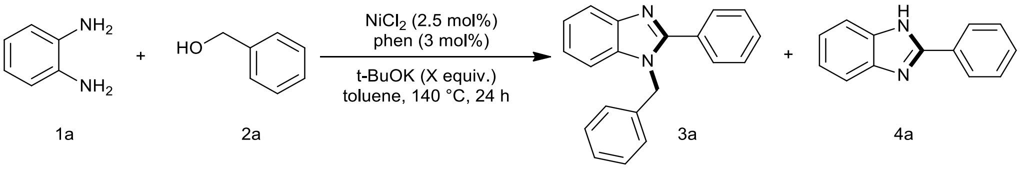
Table S4: Screening of solvents[a]



Entry	**Solvent**	GC-MS Conversion **3a** (%)	GC-MS Conversion **4a** (%)
1	**Toluene**	**98 (91%)** [b]	**2**
2	P-Xylene	30	2
3	1,4-Dioxane	75	10
4	DMA	0	0
5	*n*-BuOH	2	0
6	DMF	4	2

Reaction condition: [a] *o*-phenylenediamine **1a** (0.5 mmol), benzyl alcohol **2a** (1.0 mmol), $NiCl_2$ (2.5 mol%), phen (3.0 mol%), *t*-BuOK (0.5 mmol), **solvent (2.0 mL),** Schlenk tube under N_2 atmosphere, 140 ^oC oil bath, 24 h reaction time. [b] Isolated yield.

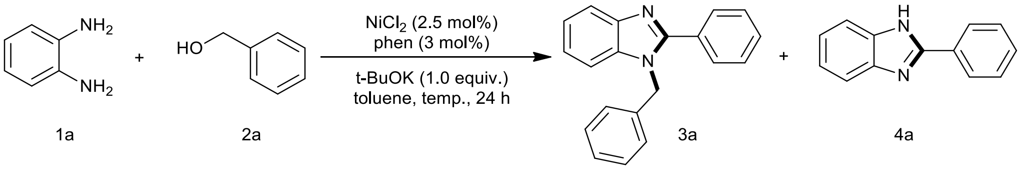
Table S5: Screening of base equivalents [a]



Entry	**Base Equivalent**	GC-MS Conversion **3a** (%)	GC-MS Conversion **4a** (%)
1	***t*-BuOK (1.0 equiv.)**	**98 (91%)** [b]	**2**
2	*t*-BuOK (0.75 equiv.)	75	15
3	*t*-BuOK (0.50 equiv.)	50	9
4	*t*-BuOK (0.25 equiv.)	40	2
5	No base	0	0

Reaction condition: [a] *o*-phenylenediamine **1a** (0.5 mmol), Benzyl alcohol **2a** (1.0 mmol), $NiCl_2$ (2.5 mol%), phen (3.0 mol%), *t*-BuOK (X equiv.), Toluene (2.0 mL), Schlenk tube under N_2 atmosphere, 140 ^oC oil bath, 24 h reaction time. [b] Isolated yield.

Table S6: Screening of temperature[a]

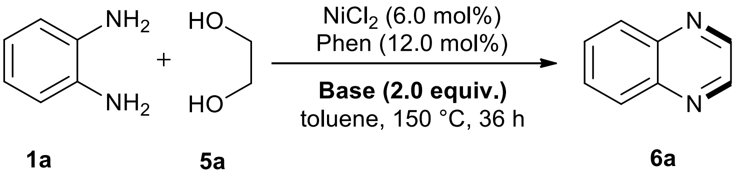


Entry	**Temp.**	GC-MS Conversion **3a** (%)	GC-MS Conversion **4a** (%)
1	**140°C**	**98 (91%)**[b]	**2**
2	130°C	85	5
3	120°C	30	4

Reaction condition: [a] *o*-phenylenediamine **1a** (0.5 mmol), benzyl alcohol **2a** (1.0 mmol), $NiCl_2$ (2.5 mol%), phen (3.0 mol%), *t*-BuOK (1.0 equiv.), toluene (2.0 mL), Schlenk tube under N_2 atmosphere, temp. (X ^{0}C) oil bath, 24 h reaction time. [b] Isolated yield.

[1.4] Synthesis of Quinoxaline from Diamine with ethylene glycol:

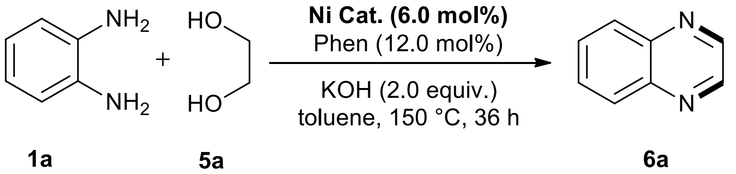
Table S7: Screening of Bases[a]



S. No	Base	GC-MS Conversion (%)
1	*t*-BuONa	22
2	*t*-BuOK	17%
3	**KOH**	**23%**

Reaction Conditions: [a] *o*-phenylenediamine **1a** (0.25 mmol), ethylene glycol **5a** (1.25 mmol), $NiCl_2$ (6.0 mol %), Phen (12 mol %), **Base (0.50 mmol)**, toluene (2.0 mL), Pressure tube under N_2 atmosphere, 150 ^{0}C oil bath, 36 h reaction time.

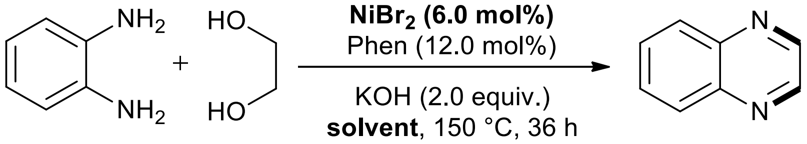
Table S8: Screening of Catalysts[a]



S. No	Base	GC-MS Conversion (%)
1	$NiCl_2$	20%
2	**$NiBr_2$**	**26%**
3	$NiCl_2$.DME	11%
4	Ni(acac)$_2$	21%

Reaction Conditions: [a] *o*-phenylenediamine **1a** (0.25 mmol), ethylene glycol **5a** (1.25 mmol), **Ni-Catalyst (6.0 mol %),** Phen (12 mol %), KOH (0.50 mmol), toluene (2.0 mL), Pressure tube under N_2 atmosphere, 150 ^{0}C oil bath, 36 h reaction time.

Table S9: Screening of Solvents[a]

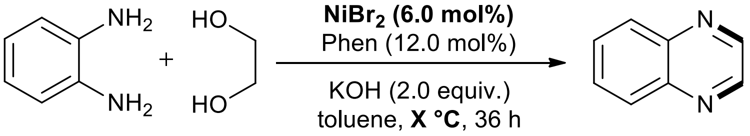


1a **5a** **6a**

S. No	Solvents	GC-MS Conversion (%)
1	**Toluene**	**26%**
2	p-Xylene	12%
3	1,4-Dioxane	8%

Reaction Conditions: [a] *o*-phenylenediamine **1a** (0.25 mmol), ethylene glycol **5a** (1.25 mmol), $NiBr_2$ (6.0 mol %), Phen (12 mol %), KOH (0.50 mmol), **solvent (2.0 mL)**, Pressure tube under N_2 atmosphere, 150 ^{0}C oil bath, 36 h reaction time.

Table S10: Screening of Reaction temperature[a]

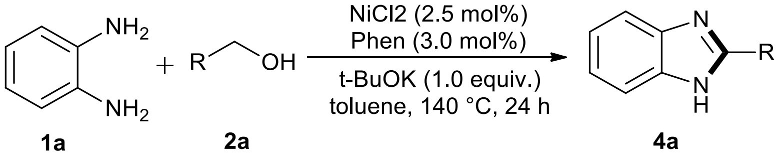


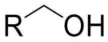
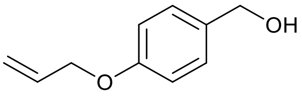
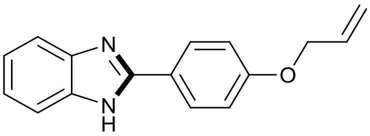
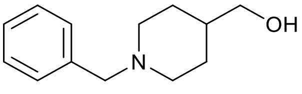
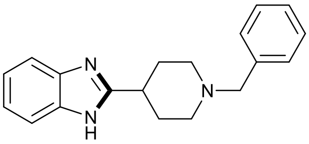
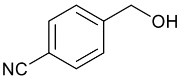
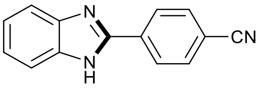
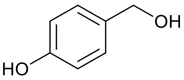
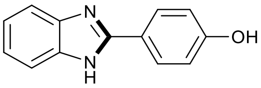
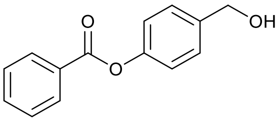
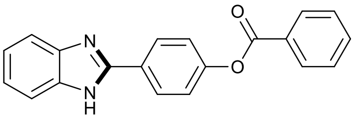
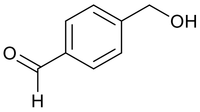
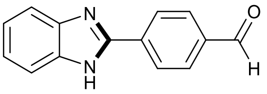
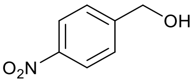
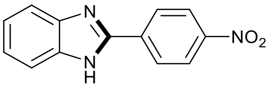
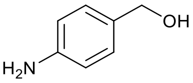
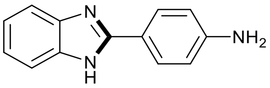
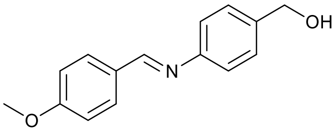
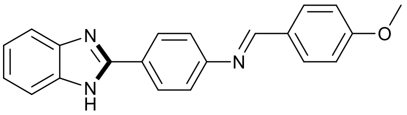
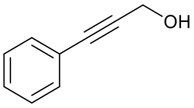
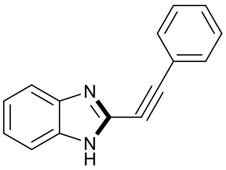
1a **5a** **6a**

S. No	Temperature	GC-MS Conversion (%)
1	130 ^{o}C	3%
2	140 ^{o}C	12%
3	**150 ^{o}C**	**26%**

Reaction Conditions: [a] *o*-phenylenediamine **1a** (0.25 mmol), ethylene glycol **5a** (1.25 mmol), $NiBr_2$ (6.0 mol %), Phen (12 mol %), KOH (0.50 mmol), toluene (2.0 mL), Pressure tube under N_2 atmosphere, **X ^{o}C** oil bath, 36 h reaction time.

[1.5] Table S11: Substrates with poor reactivity for 2-substituted benzimidazole reaction:

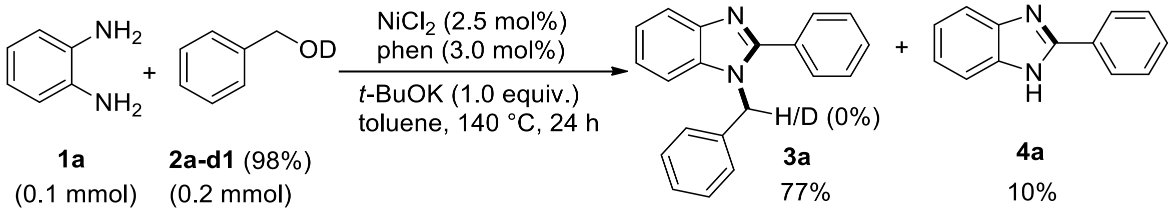


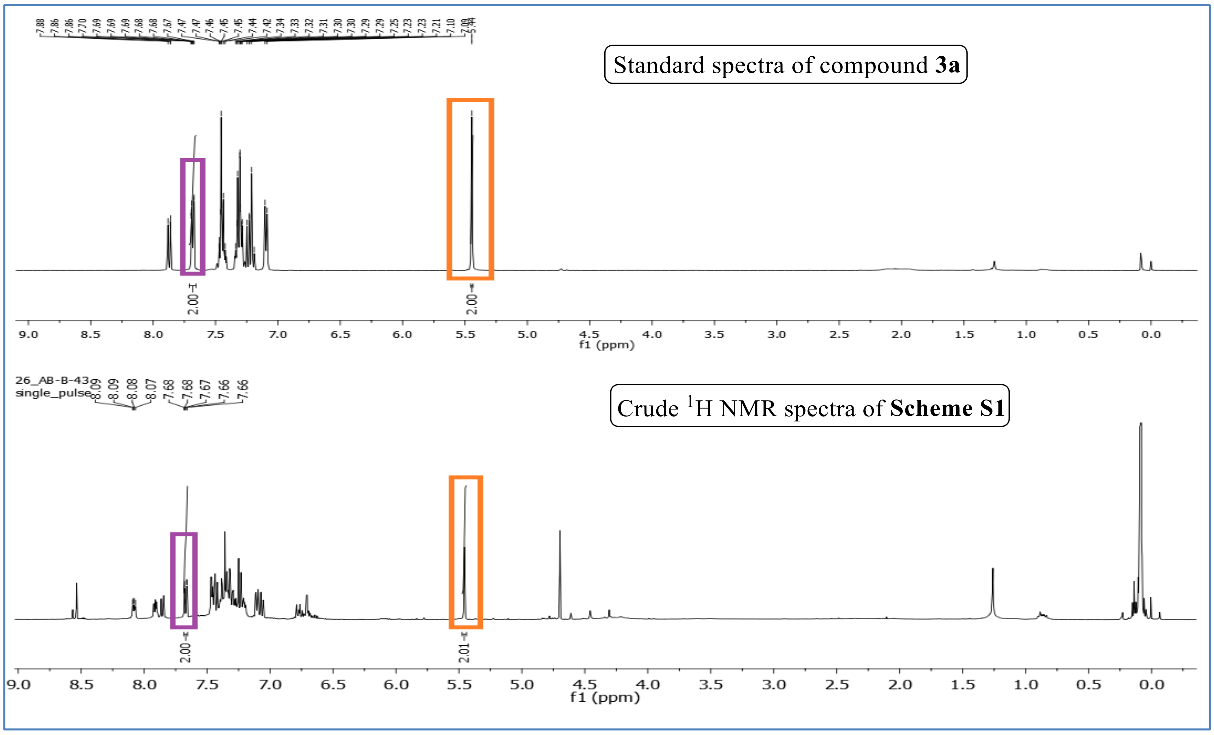
S. No		Product	GC-MS Conversion (%)
1			15
2			0
3			5
4			10
5			20
6			0
7			0
8			trace
9			0
10			15

Reaction condition: [a] o-phenylenediamine **1a** (0.5 mmol), benzyl alcohol **2a** (0.5 mmol), $NiCl_2$ (2.5 mol %), phen (3.0 mol %), t-BuOK (1.0 equiv.), toluene (2.0 mL), Schlenk tube under N_2 atmosphere, 140 ° C in oil bath, 24 h reaction time. [b] Isolated yield.

[1.6] Deuterium Incorporation Experiments:

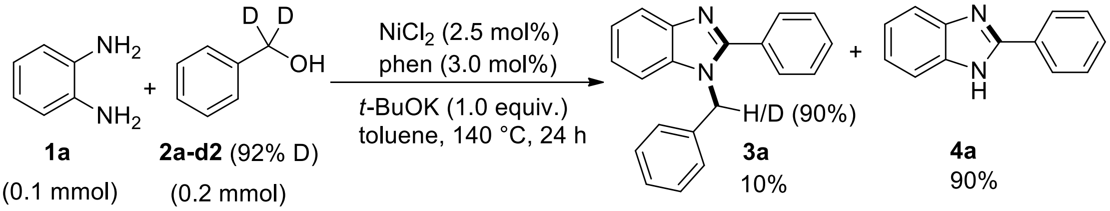
Scheme S1:

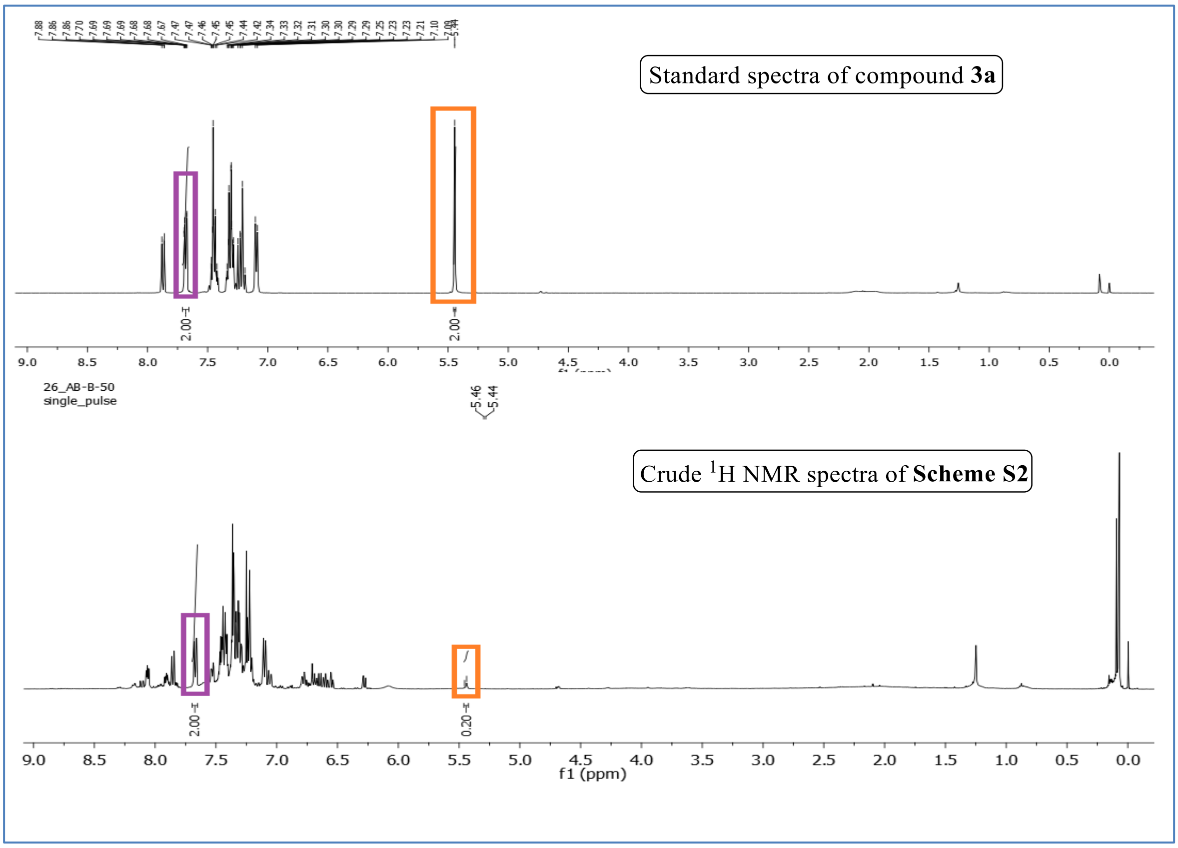




Reaction Conditions: **1a** (0.10 mmol), **2a-d1** (0.20 mmol), $NiCl_2$ (0.0025 mmol), Phen (0.0030 mmol), *t*-BuOK (0.10 mmol), toluene (1.0 mL) in a pressure tube under N_2 atmosphere at 140 ^{0}C in an oil bath for 24 h reaction time.

Scheme S2:



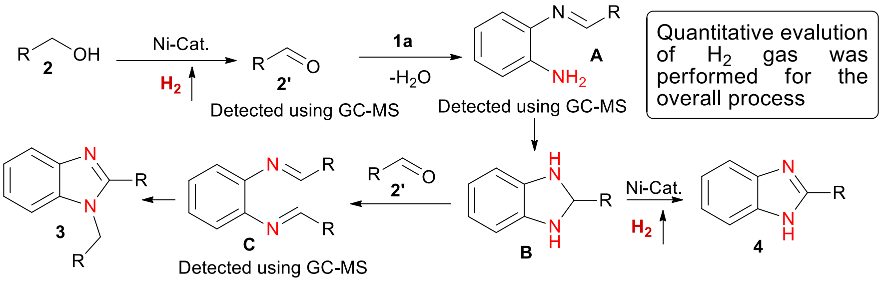


Conversion was calculated by ^{1}H NMR integration value:

		Deuterium incorporation in **H** position
Signal δ ppm	5.44 [s, -CH$_2$, (2H)]	5.45(2H)
Integral value	2.0	0.20
Calculated ratio		**(2-0.20)×100 = 180** **Deuterium incorporation in per H** = **180/2 = 90%**

Reaction Conditions: 1a (0.10 mmol), **2a-d2** (0.20 mmol), NiCl$_2$ (0.0025 mmol), Phen (0.0030 mmol), *t*-BuOK (0.10 mmol), toluene (1.0 mL) in a pressure tube under N$_2$ atmosphere at 140 ^{0}C in an oil bath for 24 h reaction time.

[1.7] Scheme S3: Plausible Mechanism



Initially, Ni-catalysed dehydrogenation of primary alcohol gave aldehyde **2’** followed by condensation with **1a** to imine intermediate **A**, which subsequently undergoes cyclisation and dehydrogenation to product **4** *via* intermediate **B**. It is noteworthy to mention that, in the GC-MS analysis of the crude reaction mixture we detected intermediate **2’** as well as intermediate **A.** Another possibility is that, intermediate **B** could couple with **2’** to intermediate **C**, which subsequently undergoes intra-molecular cyclisation and rearrange to 1,2-disubstituted imidazoles **3**.

[1.8] Quantitative determination of hydrogen gas produced in the reaction of 3a.

In a 10 mL oven dried Schlenk tube, o-Phenylenediamine (0.5 mmol), $NiCl_2$ (2.5 mol%), Phen (3.0 mol%), benzyl alcohol (1.0 mmol) and *t*-BuOK (0.5 mmol), were added followed by toluene 2.0 mL and connected to the gas burette as shown in **Fig. 1**. Then the reaction mixture was heated at 140 °C until the production of hydrogen gas ceased. The procedure was repeated three times to get concordant reading.

Fig. 1

Total volume of water displaced, V = 0.0155 L

Vapor pressure of water at 298K, P_{H2O} = 23.7695 Torr

Atmospheric pressure at 298K, P_{atm} = 758.3124 Torr

Pressure of H_2 gas, $P_{H2} = P_{atm} - P_{H2O}$ = (758.3124 - 23.7695) Torr = 734.5429 Torr

P_{H2} * V = nH_2*R*T

$nH_2 = P_{H2}$ * V / R*T

= 734.5429 Torr * 0.0155 L / 62.3635 L Torr K^{-1} mol^{-1} * 298K

= 0.000612 mol

≈ 0.61 mmol

Quantitative determination of hydrogen gas produced in the reaction of 4a.

In a 10 mL oven dried Schlenk tube, o-Phenylenediamine (0.5 mmol), $NiCl_2$ (2.5 mol%), Phen (3.0 mol%), benzyl alcohol (0.5 mmol) and *t*-BuOK (0.5 mmol), were added followed by toluene 2.0 mL and connected to the gas burette as shown in **Fig. 1**. Then the reaction mixture was heated at 140 °C until the production of hydrogen gas ceased. The procedure was repeated three times to get concordant reading.

Total volume of water displaced, V = 0.0160 L

Vapour pressure of water at 298K, P_{H2O} = 23.7695 Torr

Atmospheric pressure at 298K, P_{atm} = 758.3124 Torr

Pressure of H_2 gas, $P_{H2} = P_{atm} - P_{H2O}$ = (758.3124 - 23.7695) Torr = 734.5429 Torr

P_{H2} * V = nH_2*R*T

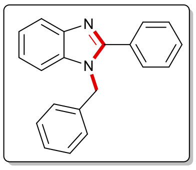
$nH_2 = P_{H2}$ * V / R*T

= 734.5429 Torr * 0.0160 L / 62.3635 L Torr K^{-1} mol^{-1} * 298K

= 0.000632 mol

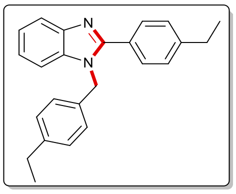
≈ 0.63 mmol

[1.9] Spectroscopic and analytical data:

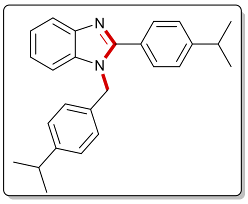


1-benzyl-2-phenyl-1*H*-benzo[*d*]imidazole (3a)[1]: Following the general procedure A, the title compound was isolated as a white solid using silica-gel column chromatography eluting with 15% ethyl acetate in hexane. (Yield: 91%, 129 mg); mp 132-133 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.86 (m, 1H), 7.70 – 7.67 (m, 2H), 7.47 – 7.42 (m, 3H), 7.34 – 7.25 (m, 4H), 7.23 – 7.19 (m, 2H), 7.09 (d, *J* = 6.7 Hz, 2H), 5.44 (s, 2H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ 154.1, 143.1, 136.3, 136.0, 129.9, 129.2, 129.0, 128.7, 127.7, 125.9, 123.0, 122.6, 119.9, 110.5, 48.3.

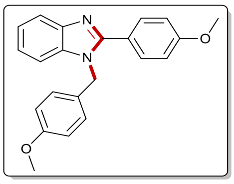
1-(4-ethylbenzyl)-2-(4-ethylphenyl)-1*H*-benzo[*d*]imidazole (3b)[2]: Following the general procedure A, the title compound was isolated as a white solid using silica-gel column chromatography eluting with 15% ethyl acetate in hexane. (Yield: 72%, 122 mg); mp 148-149 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.21 – 7.18 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 5.42 (s, 2H), 2.72 – 2.60 (m, 4H), 1.27 – 1.20 (m, 6H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 154.3, 146.2, 143.7, 143.0, 136.0, 133.6, 129.2, 128.5, 128.2, 127.2, 125.9, 122.8, 122.5, 119.7, 110.5, 48.1, 28.7, 28.4, 15.4, 15.3.



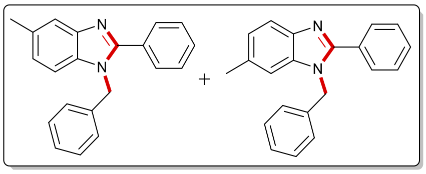
1-(4-isopropylbenzyl)-2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole (3c)[3]: Following the general procedure A, the title compound was isolated as a white solid using silica-gel column chromatography eluting with 15% ethyl acetate in hexane. (Yield: 70%, 128 mg); mp 170-172 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.62 (m, 2H), 7.31 – 7.25 (m, 3H), 7.21 – 7.16 (m, 4H), 7.03 (d, *J* = 8.3 Hz, 2H), 5.43 (s, 2H), 2.98 – 2.85 (m, 2H), 1.24 (dd, *J* = 13.9, 6.9 Hz, 12H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 154.4, 151.0, 148.5, 143.3, 136.2, 133.9, 129.4, 127.1, 126.9, 126.0, 122.9, 122.6, 119.9, 110.7, 48.3, 34.1, 33.8, 24.0, 23.9.



1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole (3d)[1]: Following the general procedure A, the title compound was isolated as a brownish solid using silica-gel column chromatography eluting with 20% ethyl acetate in hexane. (Yield: 64%, 110 mg); mp 131-132 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.28 – 7.25 (m, 1H), 7.21 – 7.19 (m, 2H), 7.03 – 7.01 (m, 2H), 6.97 – 6.95 (m, 2H), 6.85 – 6.83 (m, 2H), 5.37 (s, 2H), 3.83 (s, 3H), 3.77 (s, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 161.0, 159.2, 154.2, 143.3, 136.2, 130.8, 128.6, 127.3, 122.8, 122.6, 122.5, 119.8, 114.5, 114.3, 110.5, 55.5, 55.4, 48.0.

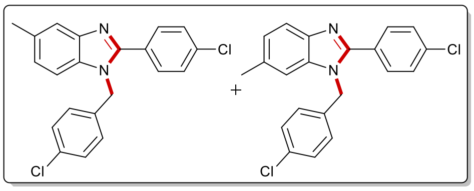


1-benzyl-5-methyl-2-phenyl-1*H*-benzo[*d*]imidazole (3e)+(3e')[4]**:** Following the general procedure A, the title compound was isolated as a mixture of two isomers of ratio 3:1 and appears as white solid using silica-gel column chromatography eluting with 15% ethyl acetate in hexane. (Yield: 69%, 102 mg); mp 189-190 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.66 (m, 3H), 7.45 – 7.43 (m,



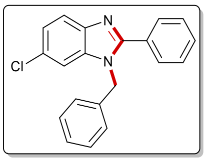
4H), 7.35 – 7.31 (m, 4H), 7.15 – 7.08 (m, 4H), 7.01 (d, J = 0.6 Hz, 1H), 5.43 (s, 1H), 5.42 (s, 2H), 2.50 (s, 1H), 2.44 (s, 3H). ^{13}C{1H} NMR (100 MHz, CDCl$_3$) δ 153.9, 141.4, 136.8, 136.5, 133.3, 130.0, 129.4, 129.3, 128.9, 127.9, 126.1, 124.5, 119.7, 110.5, 48.4, 22.1.

1-(4-chlorobenzyl)-2-(4-chlorophenyl)-5-methyl-1*H*-benzo[*d*]imidazole (3f)+(3f')[2]**:**

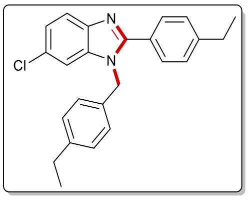


Following the general procedure A, the title compound was isolated as a mixture of two isomers of ratio 3:1 and appears as a white solid using silica-gel column chromatography eluting with 15-18% ethyl acetate in hexane. (Yield: 56%, 102 mg); mp 131-133 ^{0}C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74 (d, J = 8.2 Hz, 1H), 7.60 – 7.54 (m, 3H), 7.45 – 7.40 (m, 3H), 7.34 – 7.28 (m, 3H), 7.16 (dd, J = 8.3, 1.1 Hz, 1H), 7.10 – 7.06 (m, 1H), 7.04 – 6.97 (m, 4H), 5.37 (s, 2H), 5.36 (s, 2H), 2.50 (s, 3H), 2.45 (s, 3H).^{13}C{1H} NMR (100 MHz, CDCl$_3$) δ 152.5, 141.2, 136.3, 134.9, 133.7, 130.4, 130.3, 129.7, 128.6, 128.5, 128.0, 127.3, 124.8, 119.8, 110.1, 48.0, 22.1.

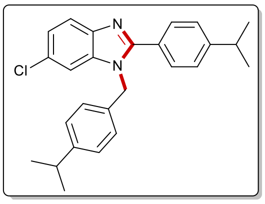
1-benzyl-6-chloro-2-phenyl-1*H*-benzo[*d*]imidazole (3g)[4]: Following the general procedure A, the title compound was isolated as a white solid using silica-gel column chromatography eluting with 15-18% ethyl acetate in hexane. (Yield: 59%, 94 mg); mp 168-170 ^{0}C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 – 7.85 (m, 1H), 7.69 – 7.67 (m, 2H), 7.46 – 7.44 (m, 2H), 7.35 – 7.29 (m, 4H), 7.25 – 7.21 (m, 2H), 7.11 – 7.09 (m, 2H), 5.45 (s, 2H). ^{13}C{1H} NMR (100 MHz, CDCl$_3$) δ 154.1, 143.1, 136.4, 136.0, 130.0, 129.9, 129.2, 129.0, 128.7, 127.7, 125.9, 123.0, 122.6, 120.0, 110.5, 48.4.



6-chloro-1-(4-ethylbenzyl)-2-(4-ethylphenyl)-1*H*-benzo[*d*]imidazole (3h): Following the general procedure A, the title compound was isolated as a brownish solid using silica-gel column chromatography eluting with 15-18% ethyl acetate in hexane. (Yield: 67%, 125 mg), mp 100-102 ^{0}C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87-7.85 (d, J = 8.0 Hz, 1H), 7.63-7.61 (d, J = 8.1 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.22 – 7.20 (m, 1H), 7.17-7.15 (d, J = 8.0 Hz, 2H), 7.04-7.02 (d, J = 7.9 Hz, 2H), 5.43 (s, 2H), 2.71 – 2.63 (m, 4H), 1.28 – 1.22 (m, 6H). ^{13}C{1H} NMR (100 MHz, CDCl$_3$) δ 154.3, 146.3, 143.7, 143.2, 136.1, 133.7, 129.2, 128.5, 128.2, 127.3, 125.9, 122.8, 122.5, 119.8, 110.5, 48.2, 28.7, 28.4, 15.4, 15.3. Elemental Analysis: $C_{24}H_{23}ClN_2$: Calculated C, 76.89; H, 6.18; N, 7.47; Found C, 85.44; H, 7.10; N, 8.30. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{24}H_{23}ClN_2$ 375.1623; Found 375.1616.

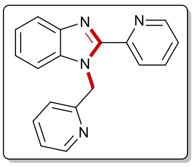


6-chloro-1-(4-isopropylbenzyl)-2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole (3i):

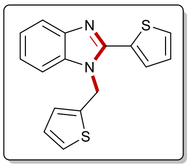


Following the general procedure A, the title compound was isolated as a brownish solid using silica-gel column chromatography eluting with 15-18% ethyl acetate in hexane. (Yield: 71%, 143 mg); mp 165-166 ⁰C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.84 (m, 1H), 7.65 – 7.63 (m, 2H), 7.32 – 7.26 (m, 3H), 7.22 – 7.17 (m, 3H), 7.03 (d, J = 8.2 Hz, 2H), 5.43 (s, 2H), 2.95 – 2.89 (m, 2H), 1.28 – 1.23 (m, 12H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 154.3, 150.8, 148.4, 143.2, 136.1, 133.8, 129.2, 127.5, 127.0, 126.8, 125.9, 122.8, 122.5, 119.8, 110.6, 48.2, 34.0, 33.7, 23.9, 23.8. Elemental Analysis: $C_{26}H_{27}ClN_2$: Calculated C, 77.50; H, 6.75; N, 6.95; Found C, 83.39; H, 7.55; N, 7.81. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calculated for $C_{24}H_{27}ClN_2$ 425.1755; Found 425.1762.

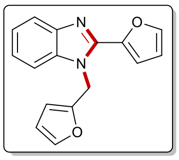
2-(pyridine-2-yl)-1-(pyridine-2-ylmethyl)-1*H*-benzo[*d*]imidazole (3j)[1]: Following the general procedure A, the title compound was isolated as a brownish solid using silica-gel column chromatography eluting with 20-25% ethyl acetate in hexane. (Yield: 78%, 112 mg); mp 102-103 ⁰C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.47 (m, 2H), 8.40 – 8.38 (m, 1H), 7.82 – 7.71 (m, 2H), 7.41-7.37 (m, 1H), 7.31 – 7.14 (m, 4H), 7.08 – 7.02 (m, 1H), 6.81 (d, J = 7.9 Hz, 1H), 6.21 (s, 2H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 157.3, 150.2, 149.8, 149.1, 148.6, 142.6, 137.2, 136.6, 124.5, 123.9, 123.6, 122.9, 120.9, 120.0, 110.7, 51.0.



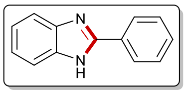
2-(thiophen-2-yl)-1-(thiophen-2-ylmethyl)-1*H*-benzo[*d*]imidazole (3k)[1]: Following the general procedure A, the title compound was isolated as a pale yellow solid using silica-gel column chromatography eluting with 10-12% ethyl acetate in hexane. (Yield: 32%, 47 mg); mp 149-150 ⁰C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 1H), 7.53-7.51 (m, 1H), 7.47 – 7.46 (m, 1H), 7.38-7.36 (m, 1H), 7.31-7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 7.16-7.12 (m, 1H), 6.97-6.93 (m, 1H), 6.95 – 6.86 (m, 1H), 5.71 (s, 2H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 143.1, 138.9, 136.0, 132.1, 129.0, 128.1, 128.0, 127.3, 125.6, 125.5, 123.4, 123.4, 123.1, 120.0, 110.0, 44.2.



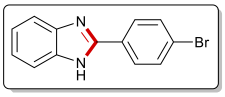
2-(furan-2-yl)-1-(furan-2-ylmethyl)-1*H*-benzo[*d*]imidazole (3l)[1]: Following the general procedure A, the title compound was isolated as a white solid using silica-gel column chromatography eluting with 10-12% ethyl acetate in hexane. (Yield: 34%, 44 mg), mp 74-76 ⁰C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 1H), 7.66 – 7.65 (m, 1H), 7.52 – 7.50 (m, 1H), 7.33 – 7.26 (m, 3H), 7.26 – 7.22 (m, 1H), 6.63 – 6.61 (m, 1H), 6.29 – 6.27 (m, 2H), 5.66 (s, 2H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 149.7,



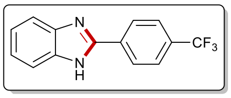
145.5, 144.1, 143.1, 142.8, 135.6, 123.3, 123.0, 119.9, 113.0, 112.2, 110.6, 110.6, 110.1, 108.4, 41.8.



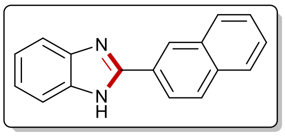
2-phenyl-1*H*-benzo[*d*]imidazole (4a)[5]: Following the general procedure B, the title compound was isolated as a reddish solid using silica-gel column chromatography eluting with 15-20% ethyl acetate in hexane. (Yield: 52%, 50 mg); mp 289-290 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.08 (m, 2H), 7.68 – 7.67 (m, 2H), 7.52 – 7.50 (m, 3H), 7.32 – 7.29 (m, 2H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$ + DMSO d_6) δ 152.1, 130.4, 129.8, 128.8, 126.9, 122.4.



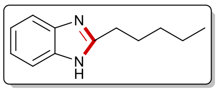
2-(4-bromophenyl)-1*H*-benzo[*d*]imidazole (4b)[1]: Following the general procedure B, the title compound was isolated as a white solid using silica-gel column chromatography eluting with 15-20% ethyl acetate in hexane. (Yield: 35%, 47 mg); 290-291 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO d_6) δ 7.95 – 7.93 (m, 2H), 7.47 – 7.45 (m, 4H), 7.09 – 7.07 (m, 2H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$ + DMSO d_6) δ 151.0, 132.0, 129.5, 128.4, 124.0, 122.6.



2-[4-(trifluromethyl)phenyl)-1*H*-benzo[*d*]imidazole (4c)[5]: Following the general procedure B, the title compound was isolated as a white solid using silica-gel column chromatography eluting with 15-20% ethyl acetate in hexane. (Yield: 38%, 50 mg); mp 263-265 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.17 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.2 Hz, 3H), 7.34 – 7.31 (m, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$ + DMSO d_6) δ 145.6, 127.2, 125.8, 124.2, 123.3, 119.6, 39.5.

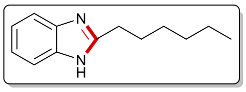


2-(naphthalene-2-yl)-1*H*-benzo[*d*]imidazole (4d)[1]: Following the general procedure B, the title compound was isolated as a white solid using silica-gel column chromatography eluting with 15-20% ethyl acetate in hexane. (Yield: 56%, 68 mg); mp 269-271 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$ +DMSO d_6) δ 12.38 (s, 1H), 8.86 – 8.82 (m, 1H), 7.99 – 7.93 (m, 4H), 7.61-7.55 (m, 4H), 7.29 – 7.26 (m, 2H).

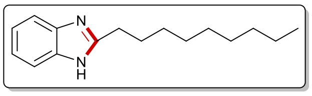


2-pentyl-1*H*-benzo[*d*]imidazole (4e)[8]: Following the general procedure B, the title compound was isolated as a white solid using silica-gel column chromatography eluting with 15-20% ethyl acetate in hexane. (Yield: 56%, 53 mg); mp 157-158 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 2H), 7.25-7.20 (m, 2H), 2.92 – 2.88 (m, 2H), 1.87 – 1.81 (m, 2H), 1.38 – 1.36 (m, 4H), 0.88 (t, J = 7.1 Hz, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 154.9, 122.3, 31.6, 29.4, 27.9, 22.4, 14.0.

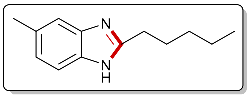
2-hexyl-1H-benzo[d]imidazole (4f)[5]: Following the general procedure B, the title compound was isolated as a white solid using silica-gel column chromatography eluting with 15-20% ethyl acetate in hexane. (Yield: 30%, 30 mg); mp 136-137 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.53 (m, 2H), 7.26 – 7.19 (m, 2H), 2.95 – 2.91 (m, 2H), 1.89 – 1.81 (m, 2H), 1.42 – 1.25 (m, 6H), 0.86 – 0.82 (m, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 155.4, 122.2, 31.6, 29.5, 29.1, 28.4, 22.6, 14.1.



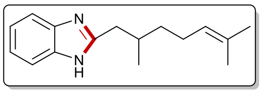
2-nonyl-1*H*-benzo[*d*]imidazole (4g)[6]: Following the general procedure B, the title compound was isolated as a white solid using silica-gel column chromatography eluting with 15-20% ethyl acetate in hexane. (Yield: 41%, 50 mg); mp 116-117 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 2H), 7.26 – 7.20 (m, 2H), 2.93 – 2.89 (m, 2H), 1.89 – 1.81 (m, 2H), 1.44 – 1.24 (m, 12H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 155.0, 122.3, 31.9, 29.8, 29.5, 29.5, 29.4, 29.4, 29.4, 29.2, 28.3, 22.8, 14.2.



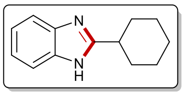
5-methyl-2-pentyl-1*H*-benzo[*d*]imidazole (4h)[5]: Following the general procedure B, the title compound was isolated as white solid using silica-gel column chromatography eluting with 15-20% ethyl acetate in hexane. (Yield: 45%, 45 mg); mp 165-166^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 1H), 7.32 (s, 1H), 7.05-7.03 (m, 1H), 2.90 – 2.86 (m, 2H), 2.45 (s, 3H), 1.86 – 1.80 (m, 2H), 1.35 – 1.34 (m, 4H), 0.89 – 0.86 (m, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 154.8, 132.1, 123.7, 31.6, 29.4, 28.0, 22.4, 21.7, 14.0.



2-(2,6-dimethylhept-5-en-1-yl)-1*H*-benzo[*d*]imidazole (4i)[7]: Following the general procedure B, the title compound was isolated as a white solid using silica-gel column chromatography eluting with 15-20% ethyl acetate in hexane. (Yield: 37%, 45 mg); mp 94-95^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.58 (s, 2H), 7.26 – 7.20 (m, 2H), 5.08 – 5.05 (m, 1H), 2.96 – 2.90 (m, 1H), 2.73 – 2.68 (m, 1H), 2.09 – 2.06 (m, 3H), 2.05 – 1.98 (m, 3H), 1.66 – 1.53 (m, 3H), 1.44 – 1.30 (m, 1H), 1.29 – 1.27 (m, 1H), 0.97 (t, J = 5.8 Hz, 3H). ^{13}C NMR{1H} (100 MHz, $CDCl_3$) δ 154.2, 131.8, 124.3, 122.3, 37.1, 37.0, 32.9, 25.8, 25.6, 19.7, 17.7.

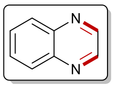


2-cyclohexyl-1*H*-benzo[*d*]imidazole (4j)[9]: Following the general procedure B, the title compound was isolated as a white solid using silica-gel column chromatography eluting with 15-20% ethyl acetate in hexane. (Yield: 39%, 59 mg); mp >280 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO d_6) δ 7.46 (s, 2H), 7.09 – 7.07 (m, 2H), 2.86 – 2.80 (m, 1H), 2.07 – 2.04 (m, 2H), 1.81 – 1.77 (m, 2H), 1.66 – 1.60 (m, 3H), 1.35

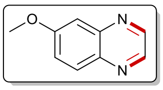


– 1.23 (m, 3H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$ + DMSO d_6) δ 159.5, 121.6, 40.5, 40.3, 40.1, 39.9, 39.7, 38.6, 31.8, 26.1, 25.9.

Quinoxaline (5a)[11]: Following the general procedure C, the title compound was isolated as a white semi solid using silica-gel column chromatography eluting with 10% ethyl acetate in hexane. (Yield: 25%, 16 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.87 – 8.86 (m, 1H), 8.15 – 8.11 (m, 1H), 7.81 – 7.78 (m, 1H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.1, 143.1, 130.2, 129.6.



6-methoxyquinoxaline (6b)[10]: Following the general procedure C, the title compound was isolated as a pale yellow solid using silica-gel column chromatography eluting with 10% ethyl acetate in hexane. (Yield: 40%, 32 mg); mp 59-60 ^{0}C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.76 – 8.70 (m, 2H), 7.99 – 7.98 (m, 1H), 7.44 – 7.42 (m, 1H), 7.38 (d, 1H), 3.98 (s, 3H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 160.8, 144.9, 144.7, 142.4, 139.3, 130.4, 123.5, 106.7, 55.8.



[2.0] References:

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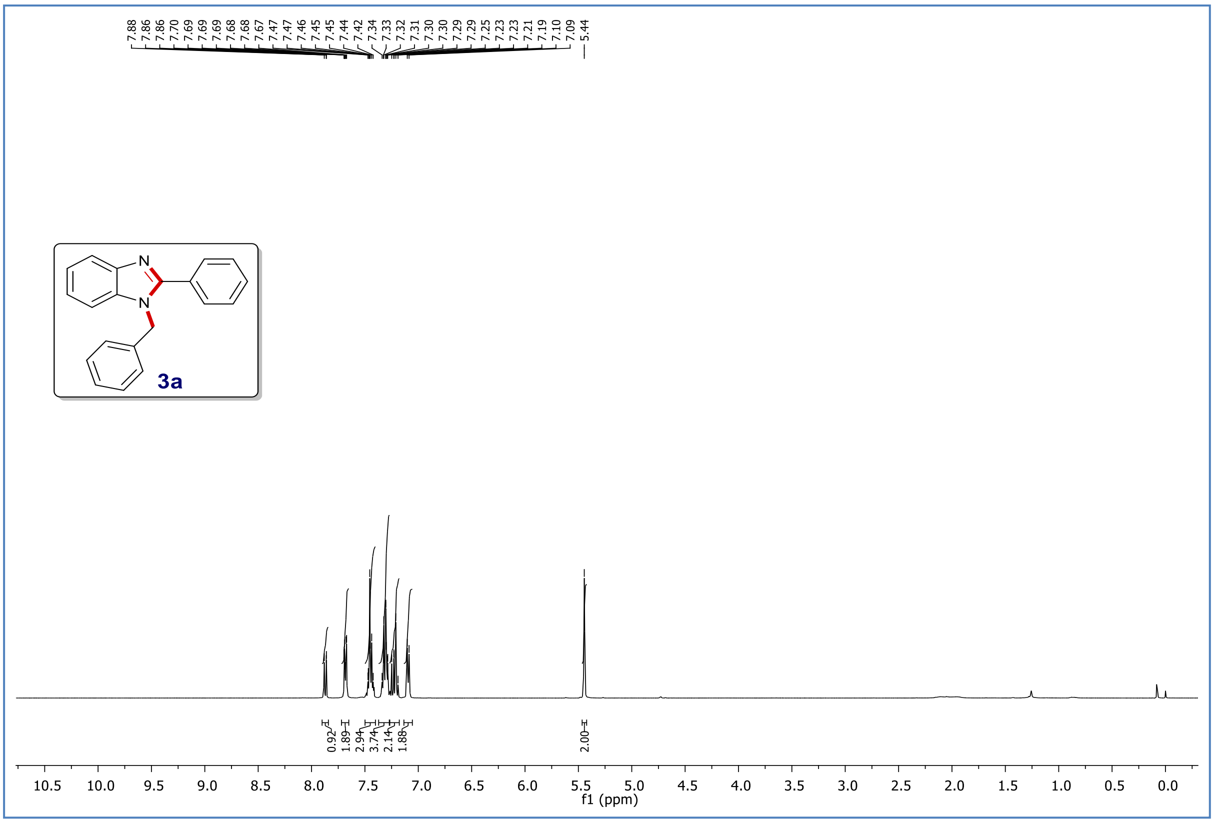
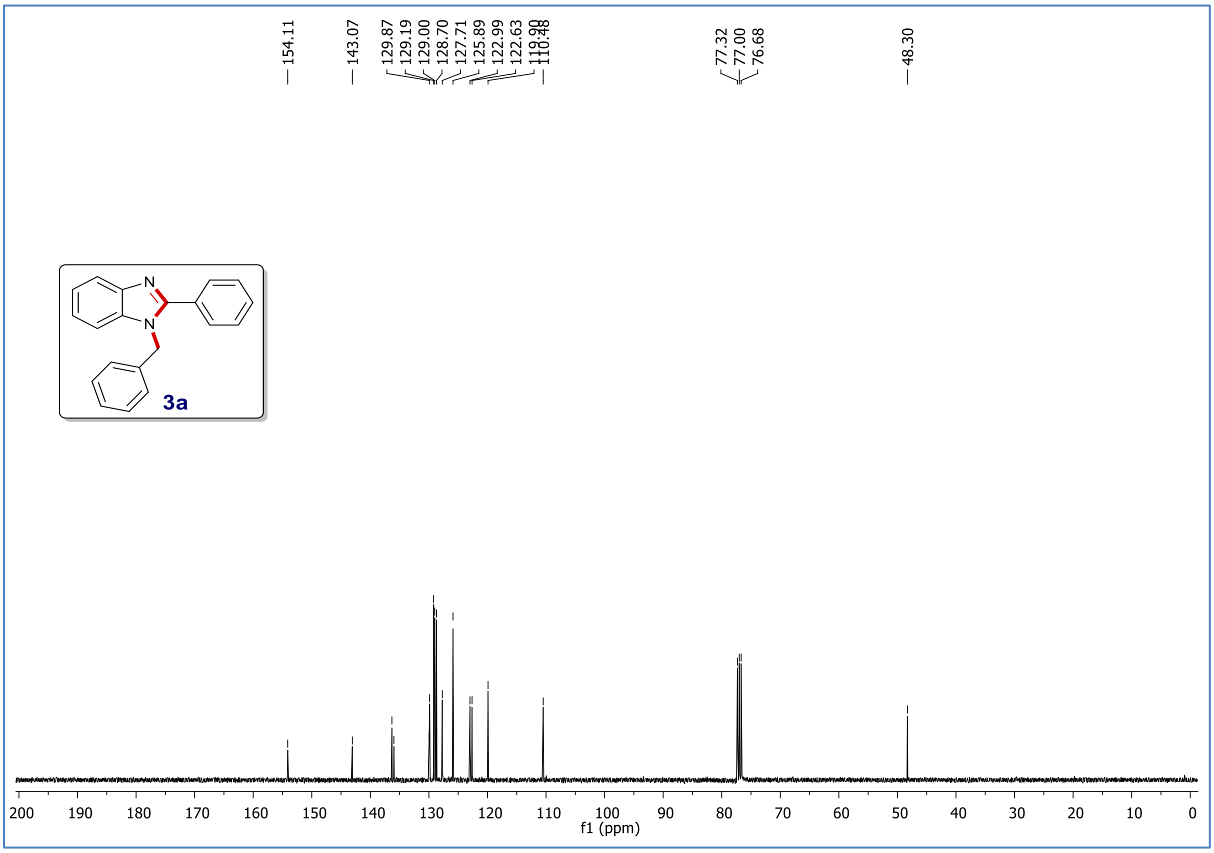
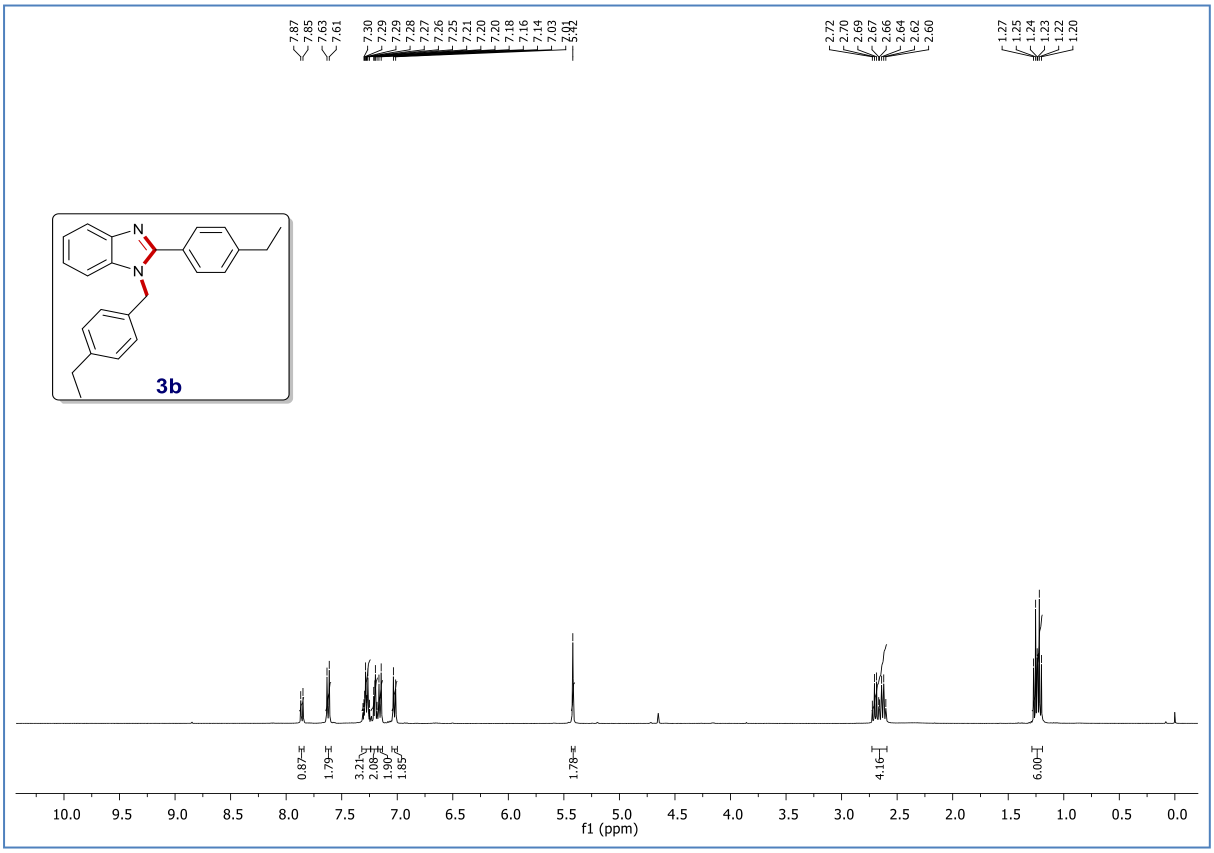
[2.1] Copies of ^{1}H NMR & ^{13}C NMR for selected compounds:



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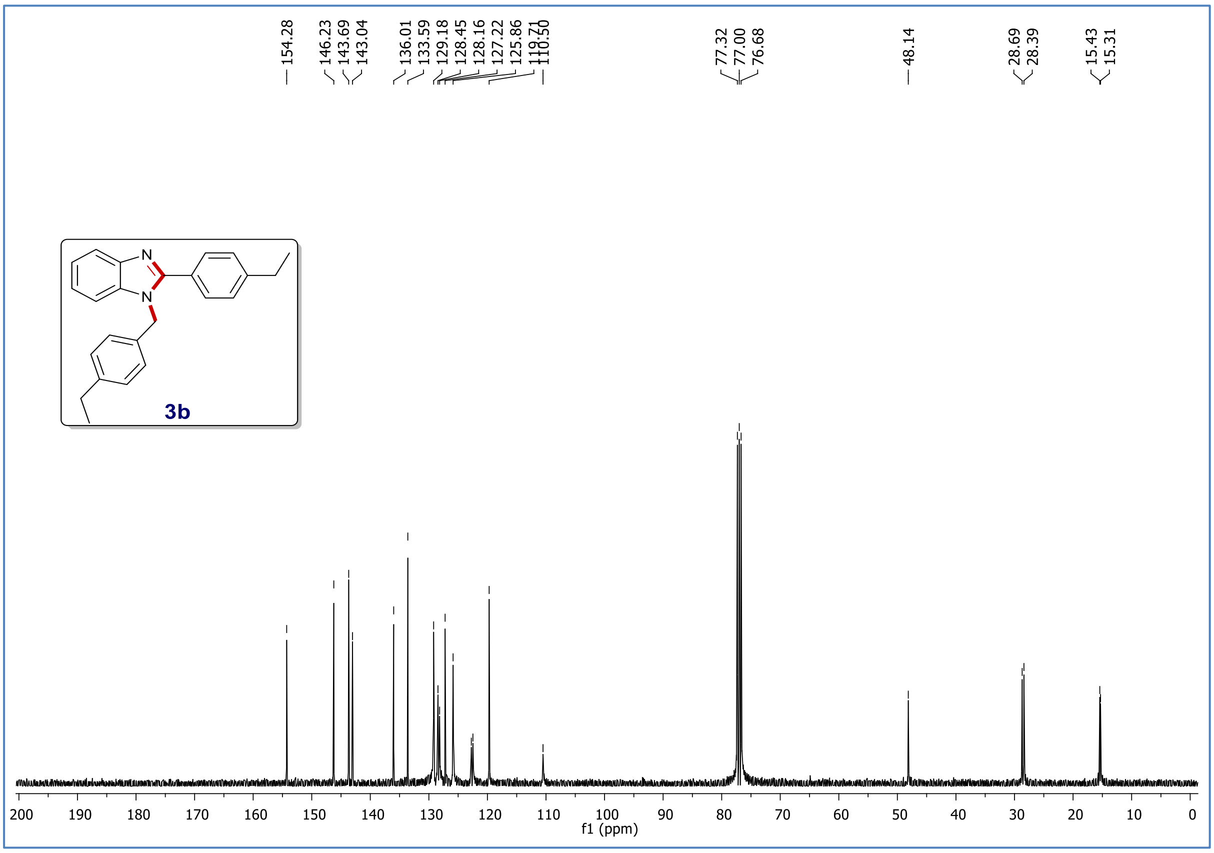
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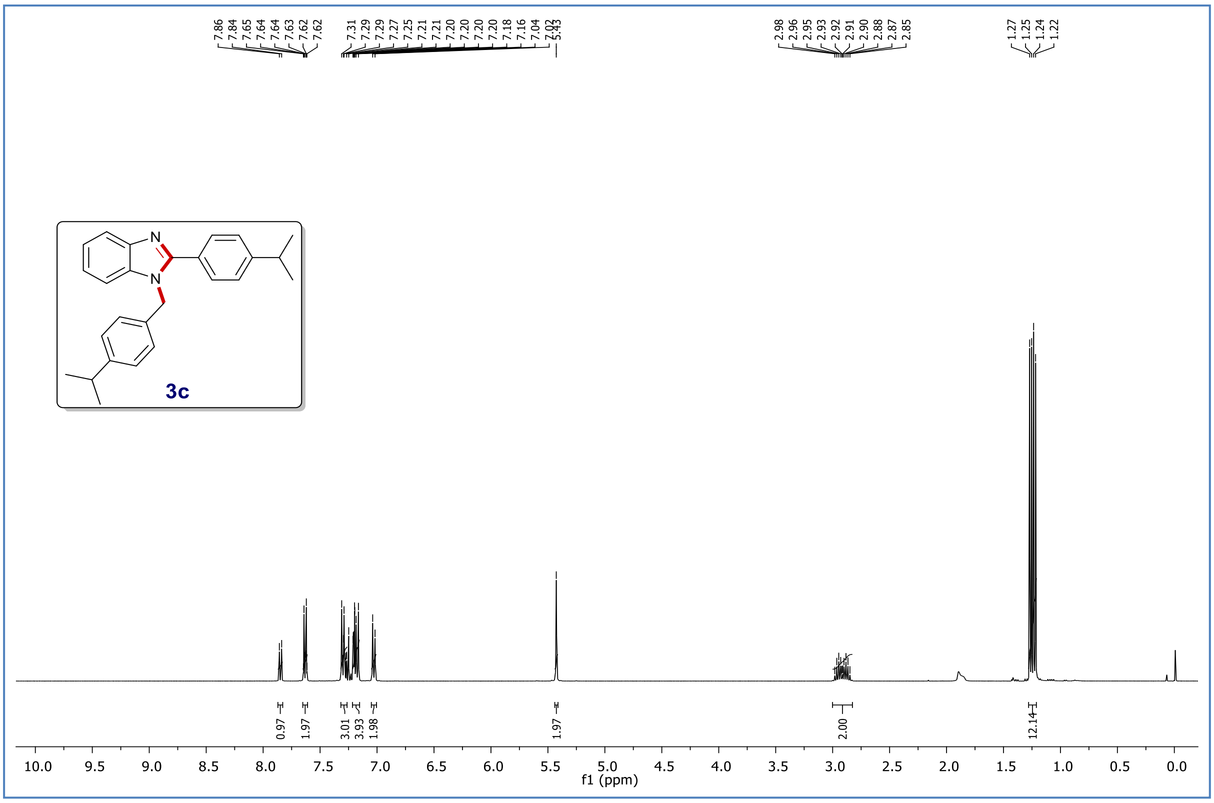
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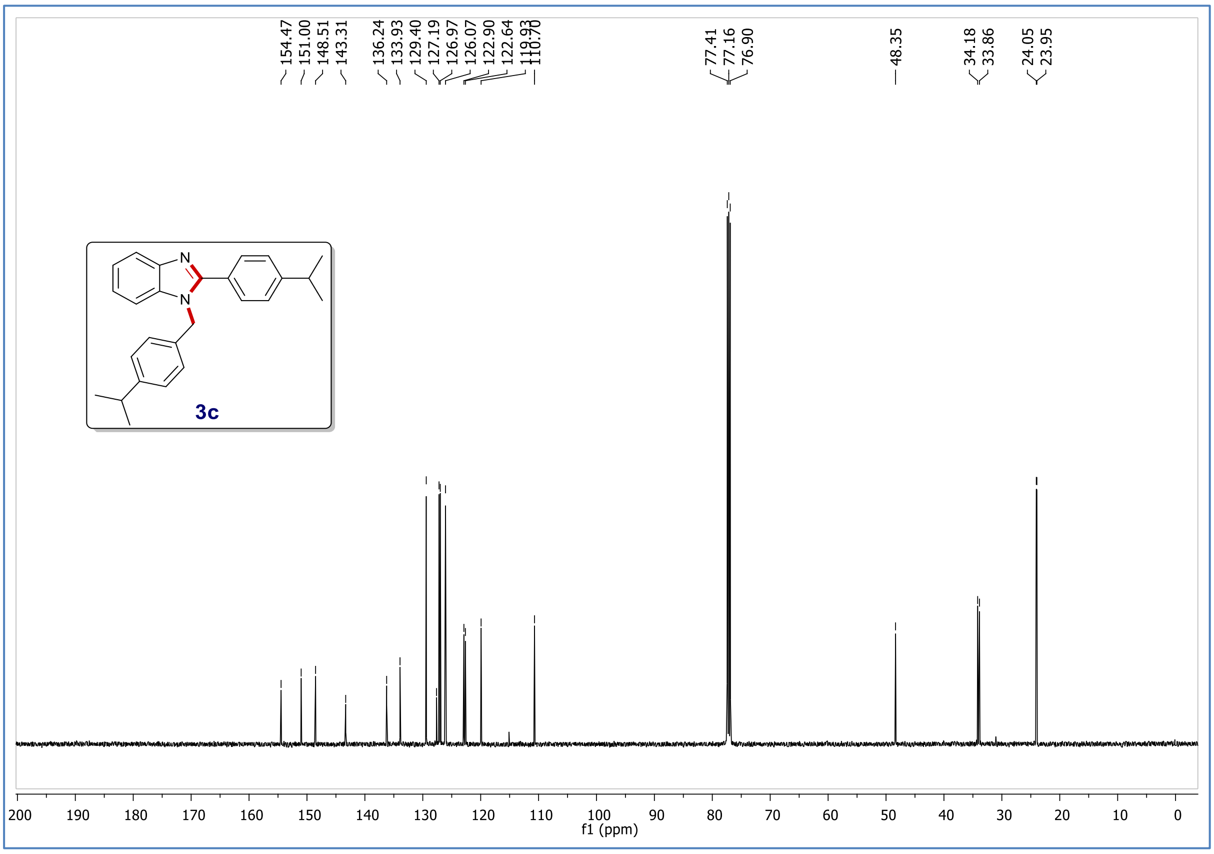
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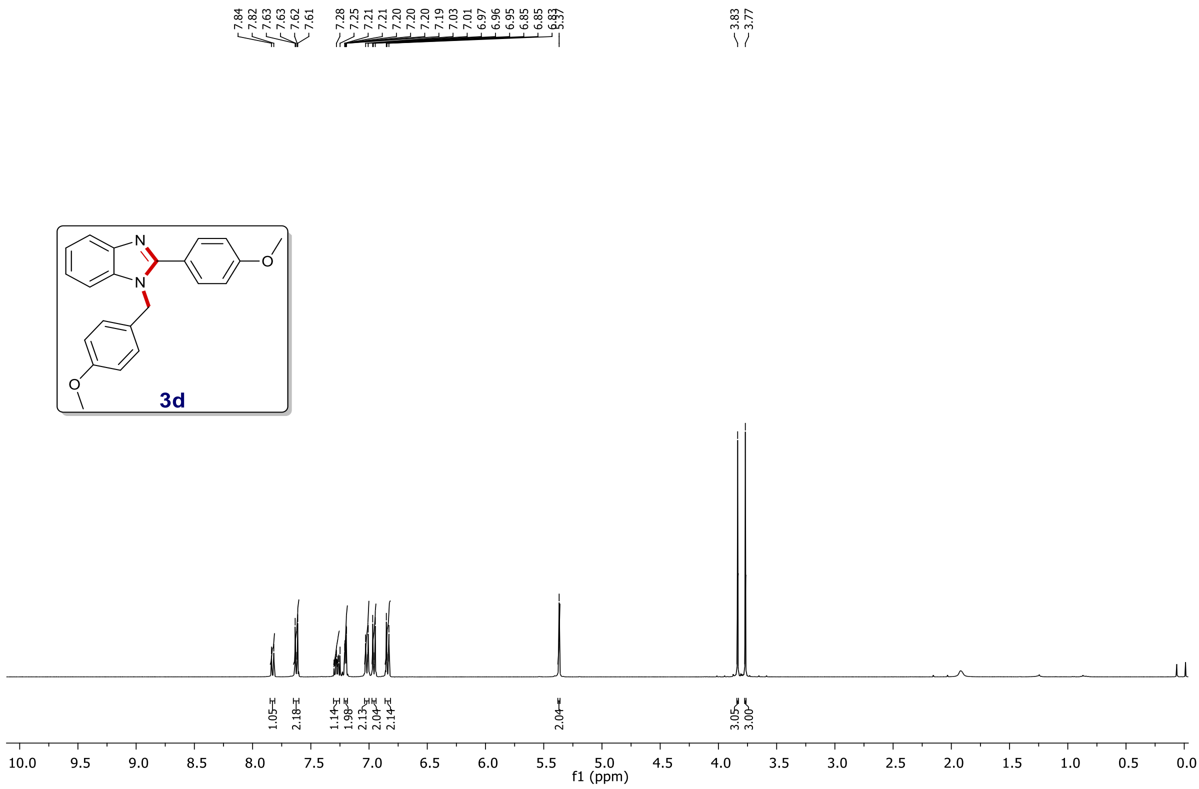
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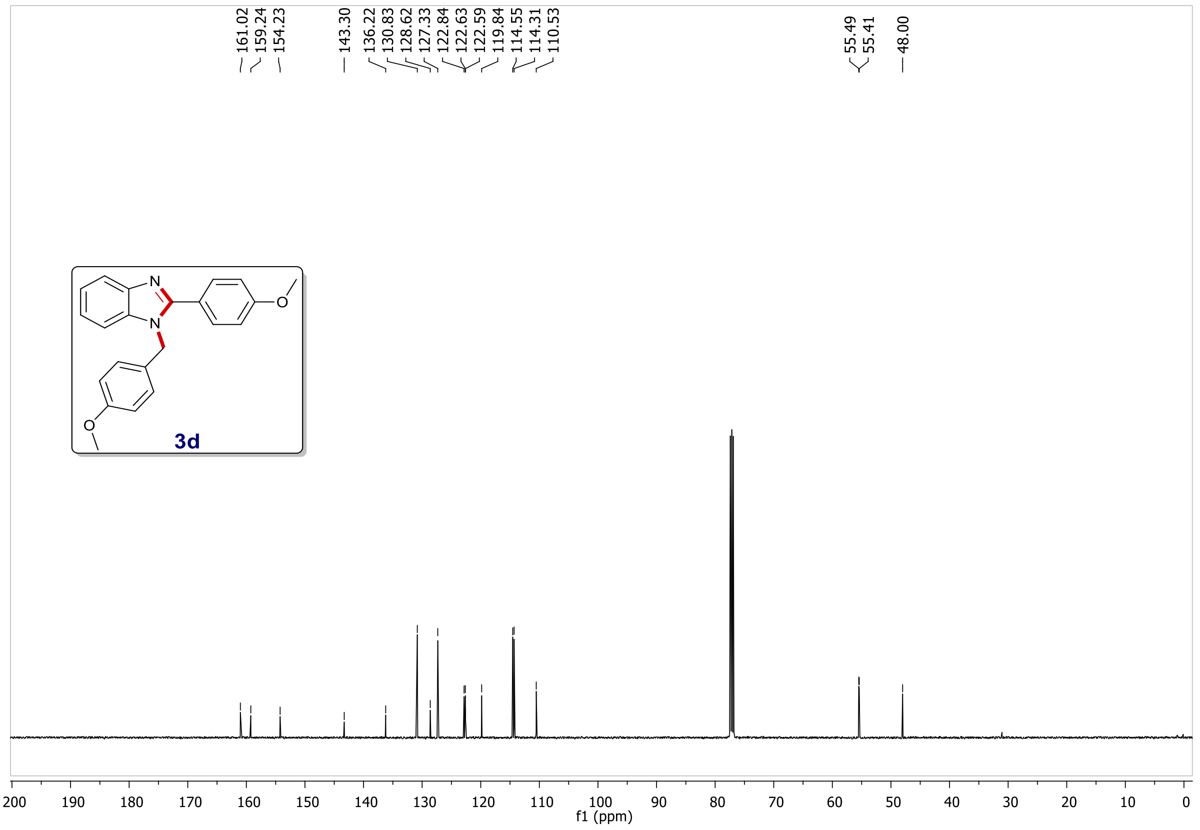
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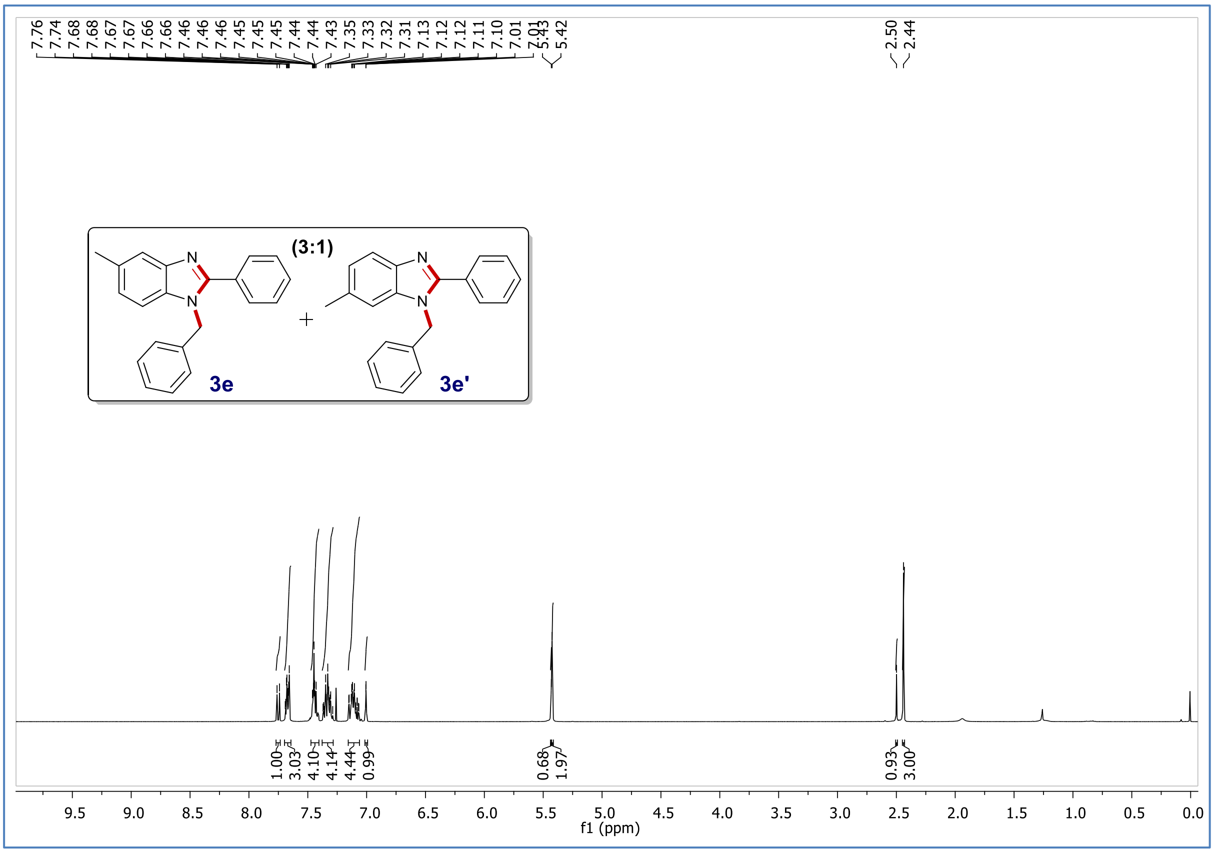
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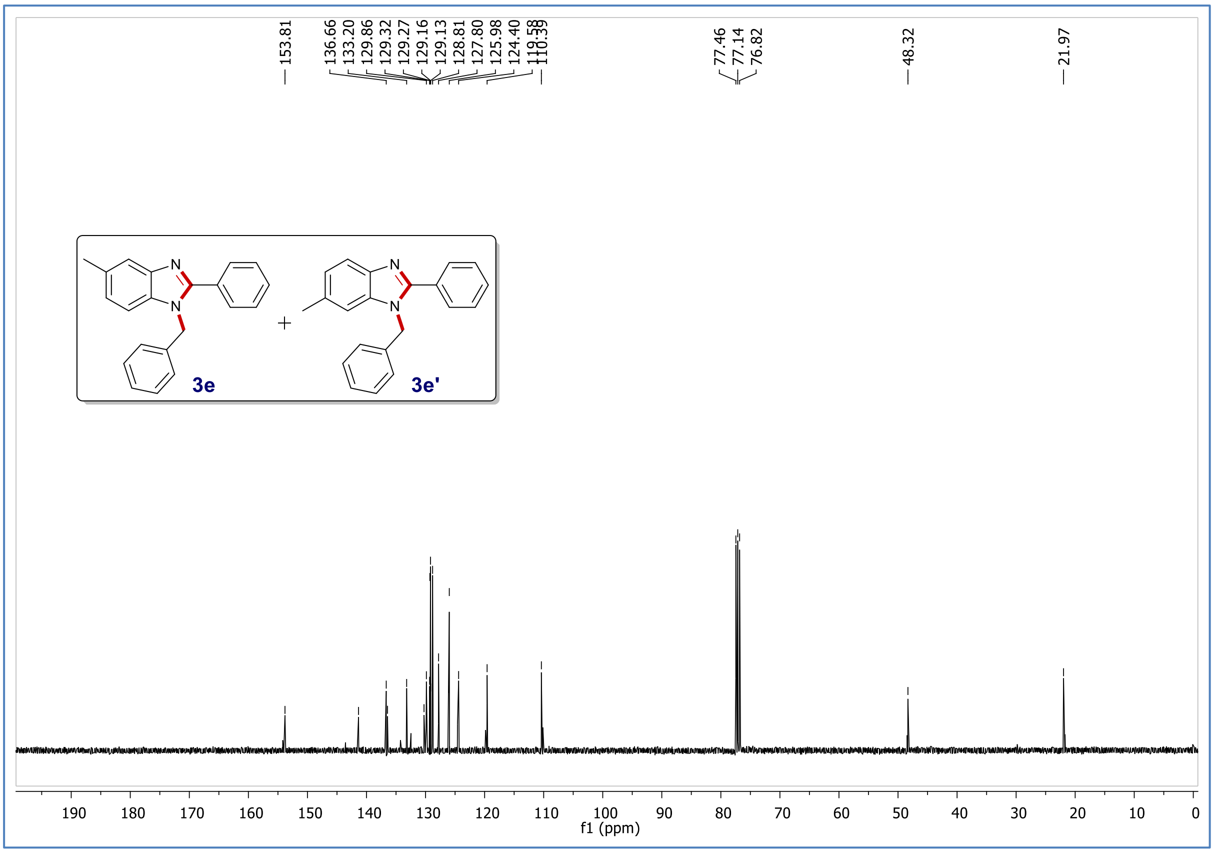
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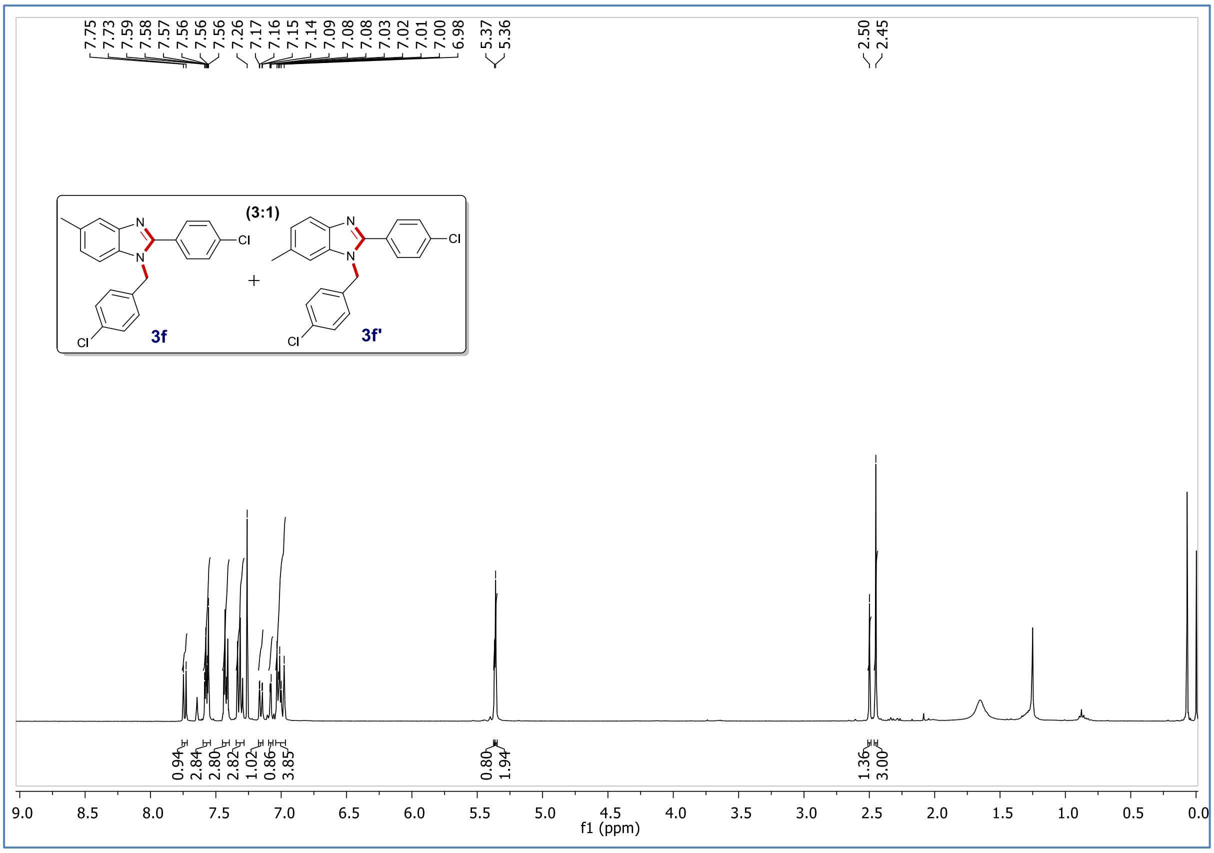
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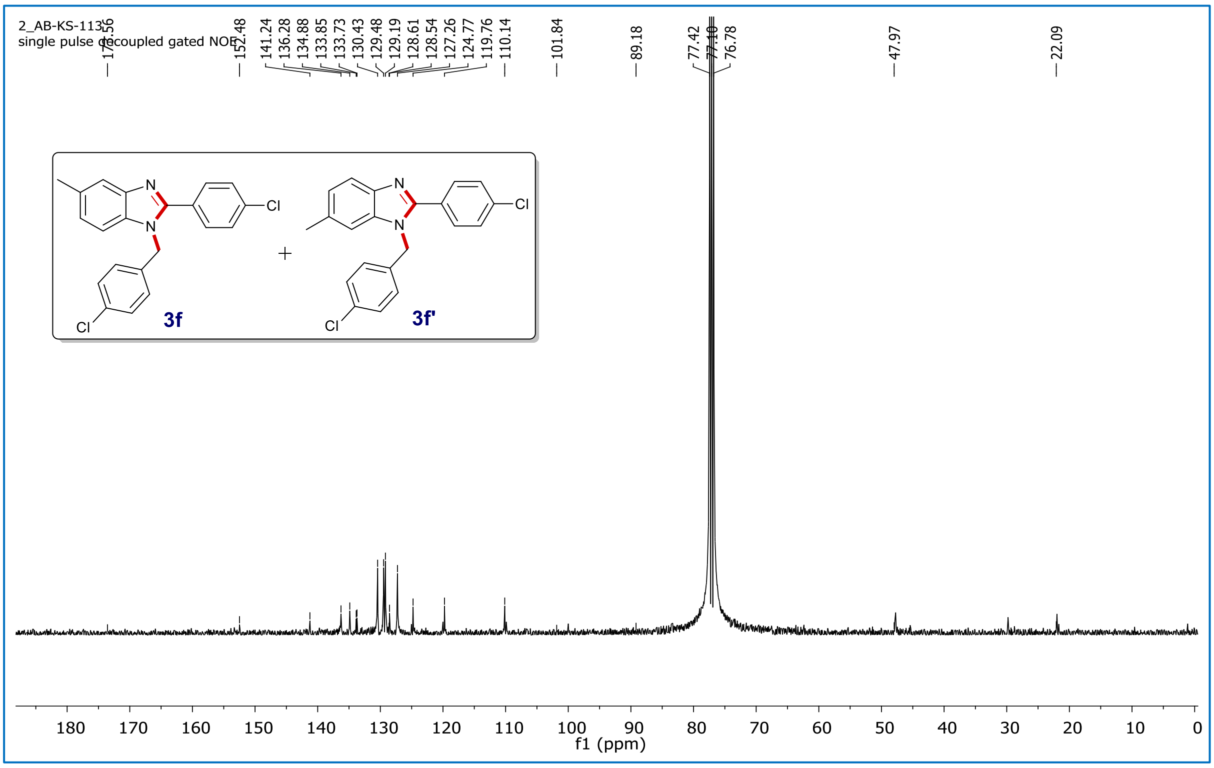
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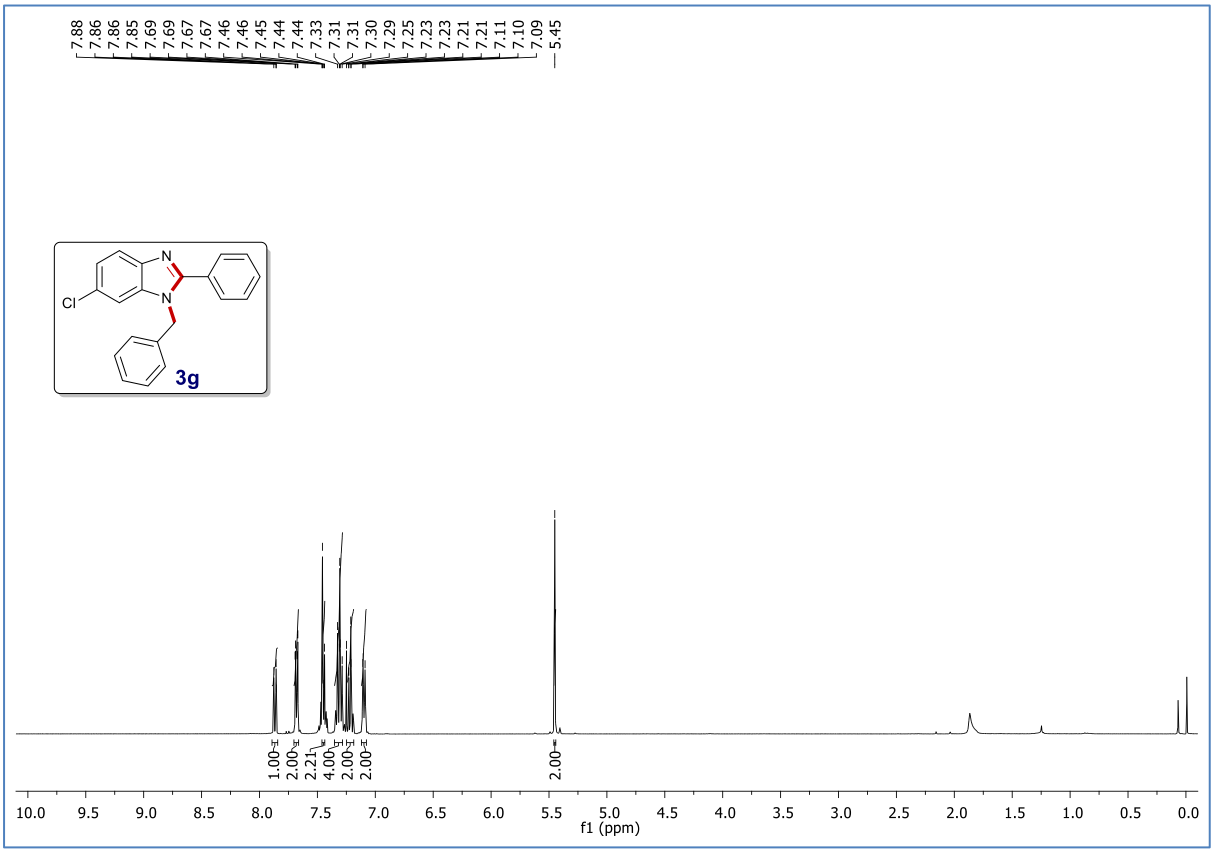
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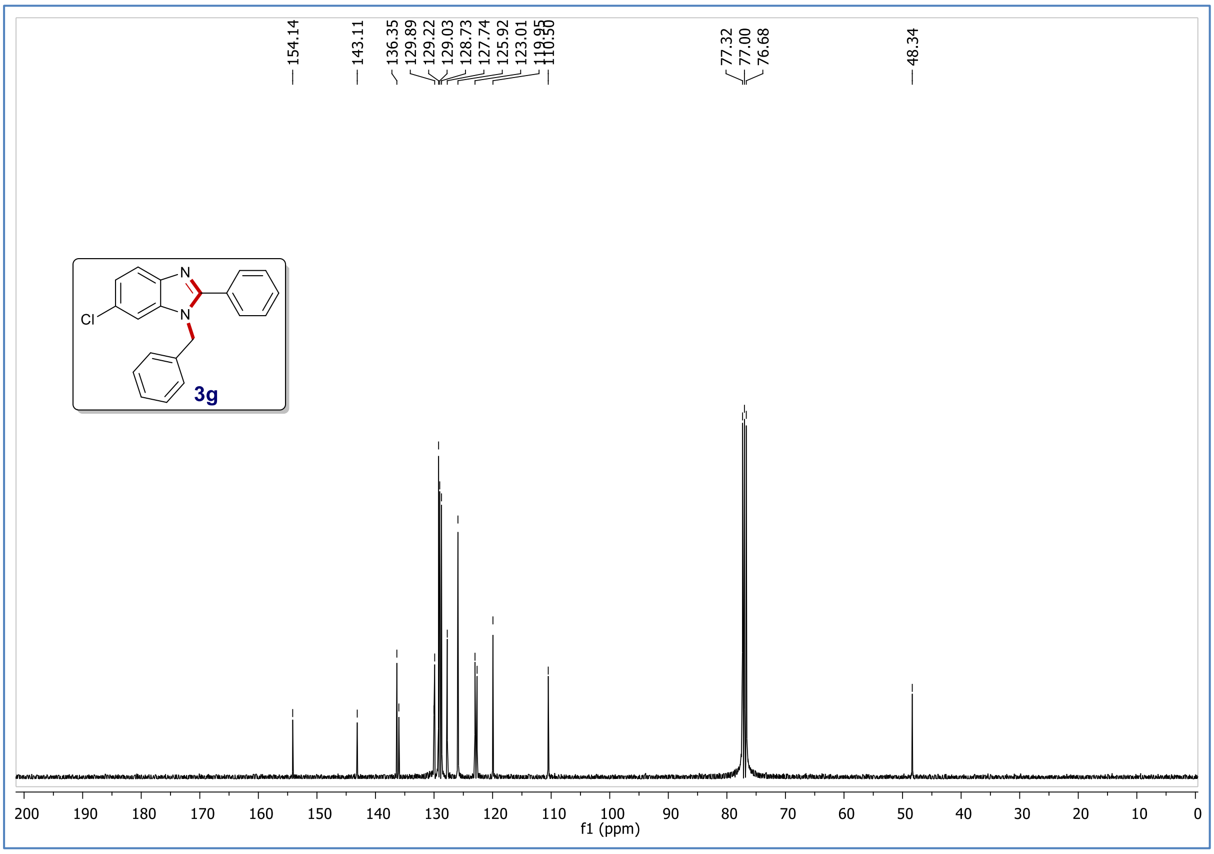
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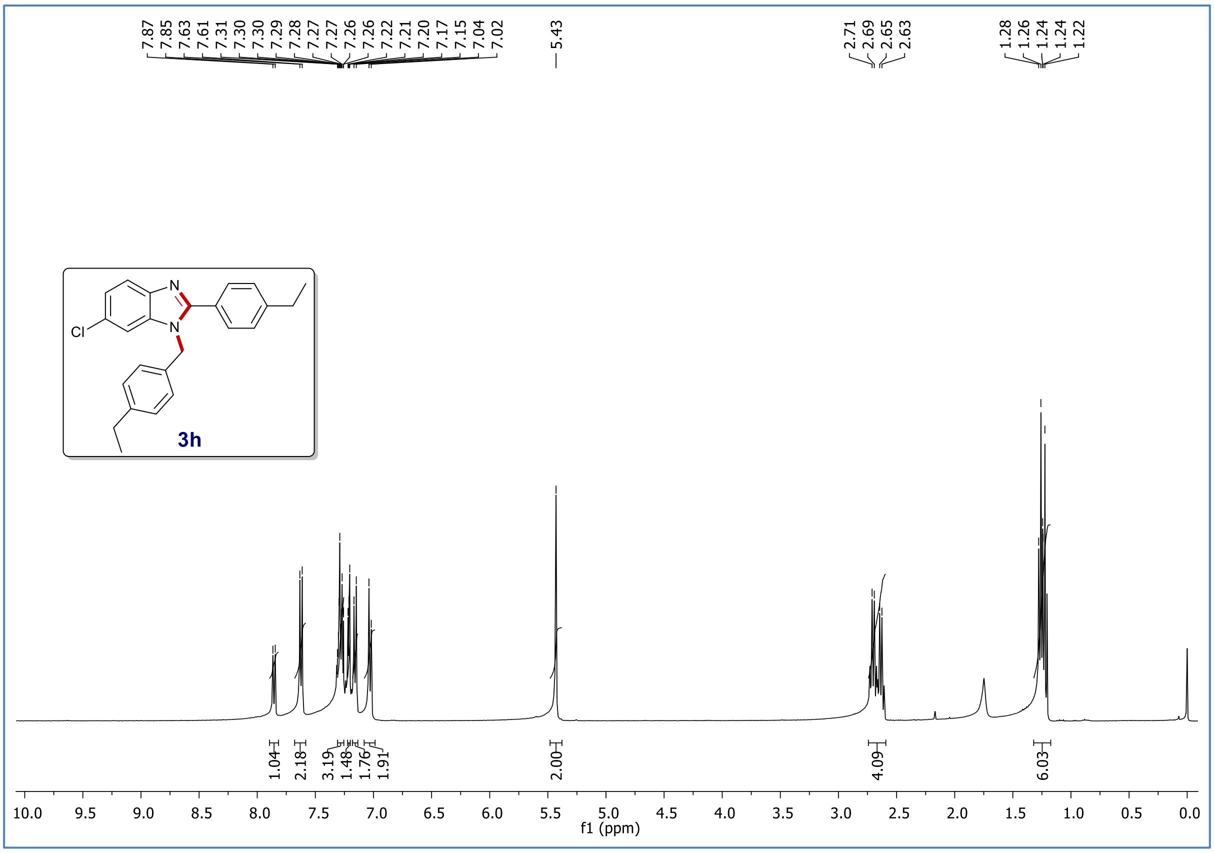
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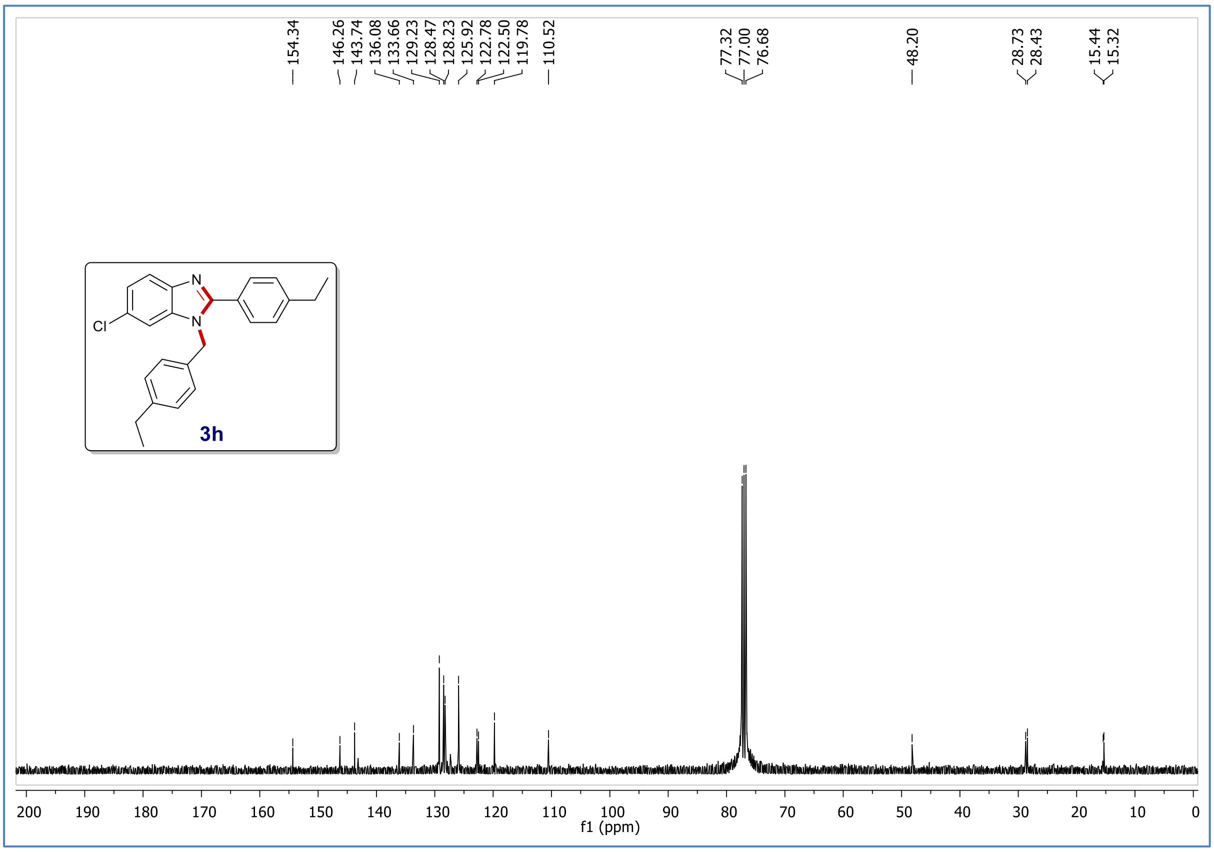
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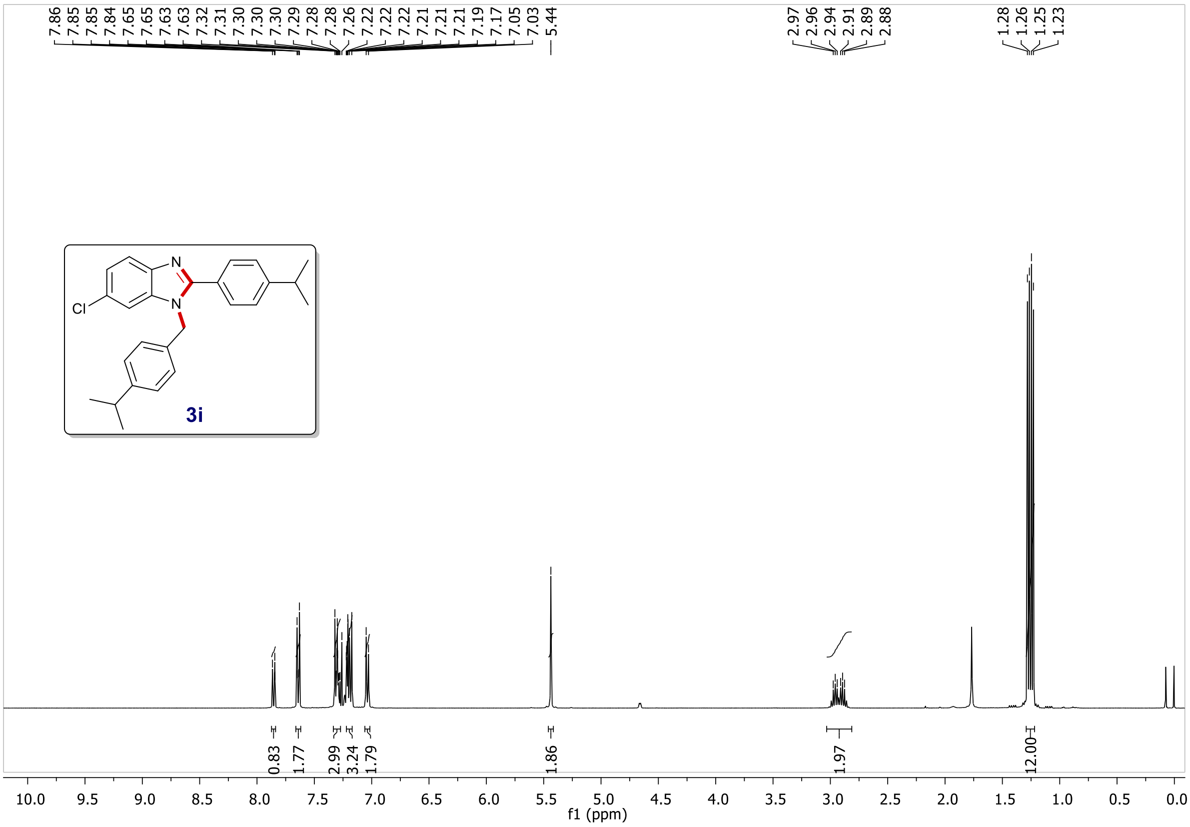
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1.25
1.23
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1.97
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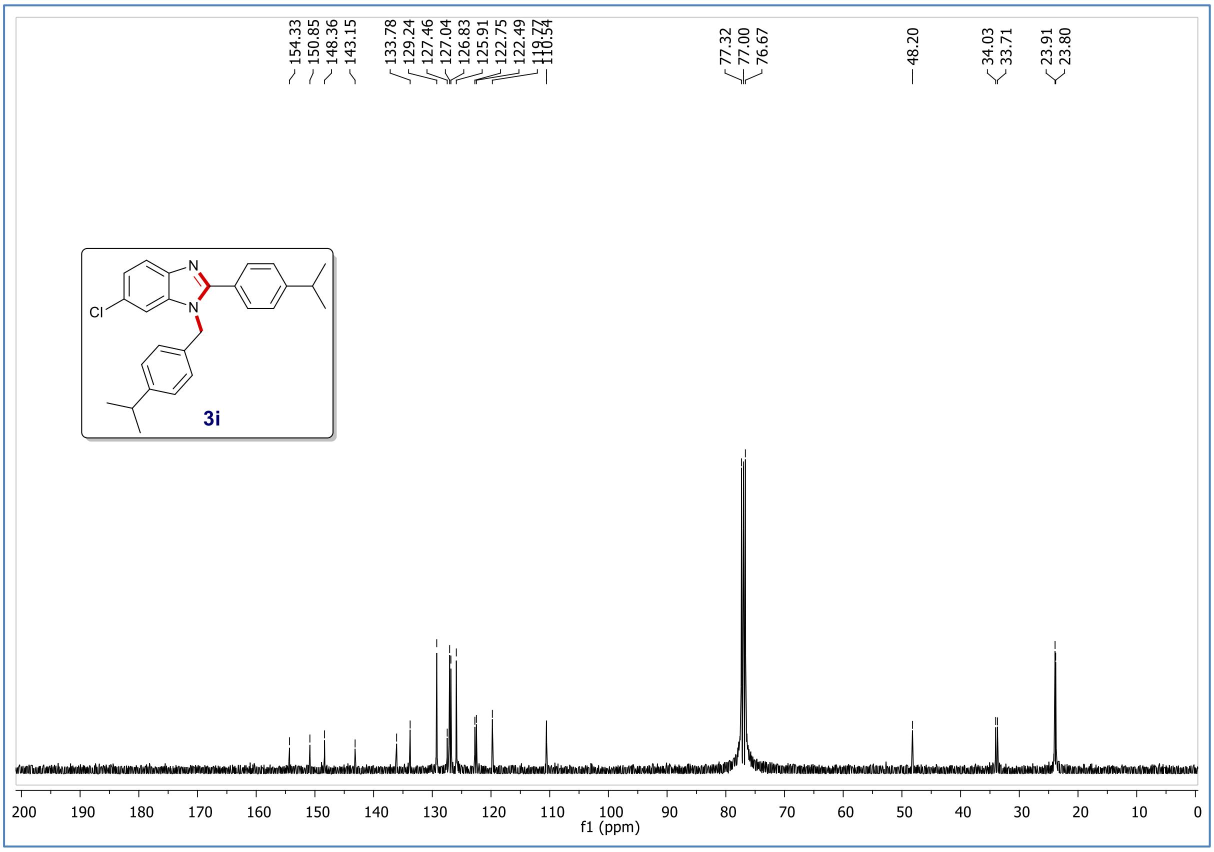
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23.80
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N
Cl
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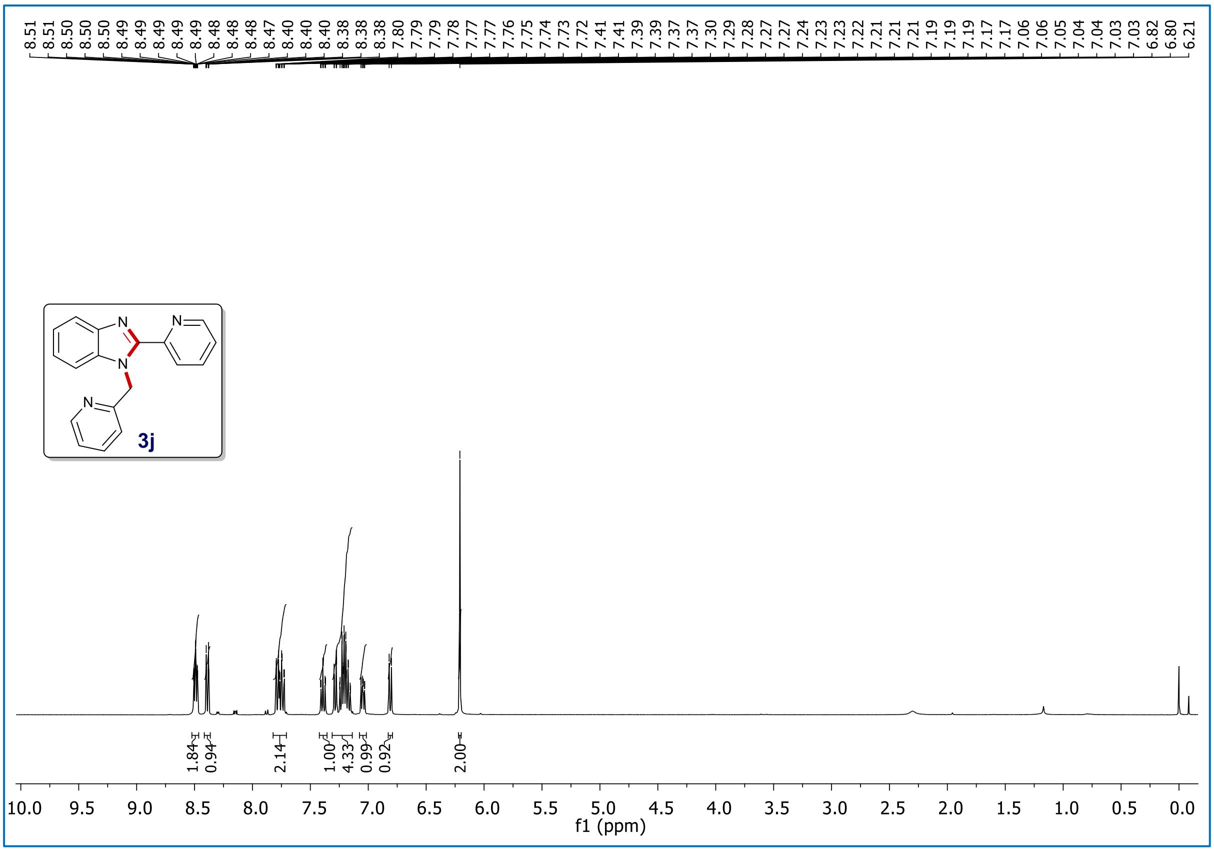
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7.05
7.04
7.04
7.03
7.03
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6.80
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N
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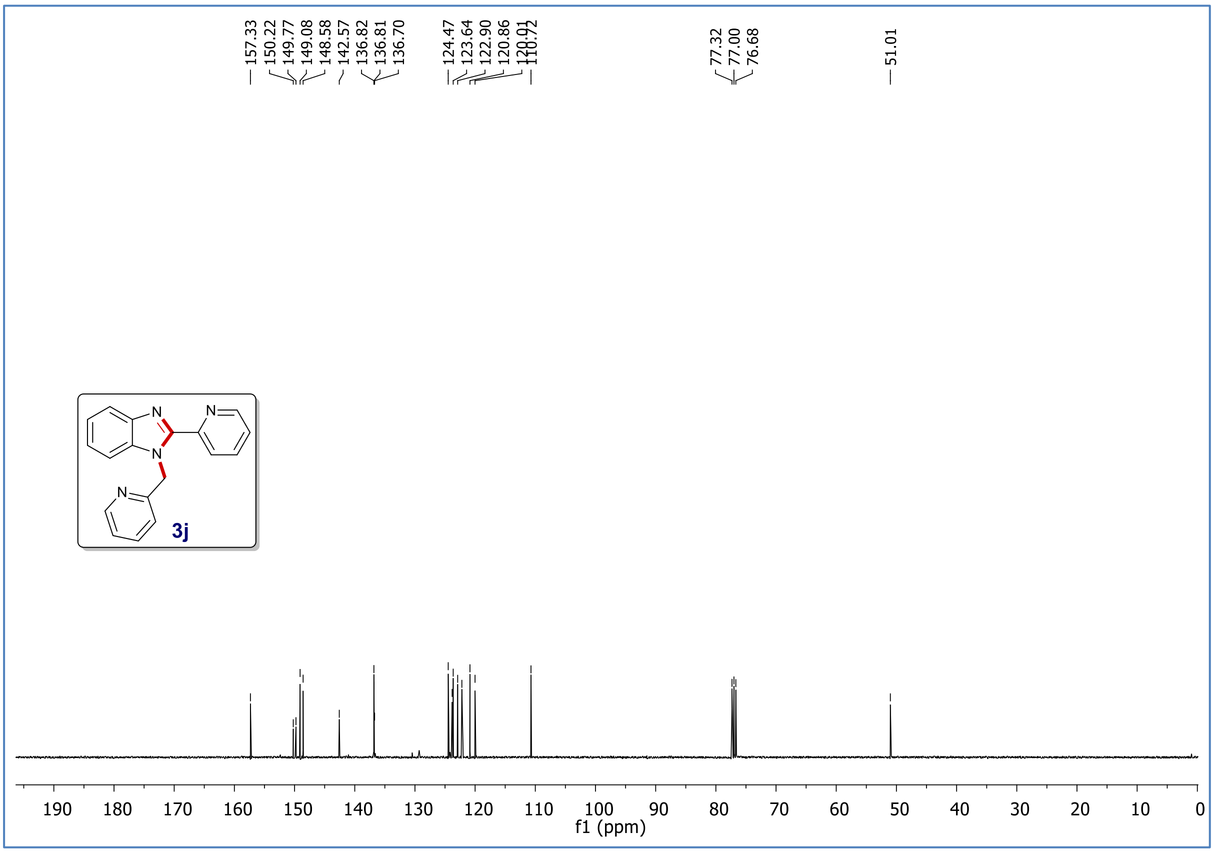
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77.32
77.00
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N
N
3j
190
180
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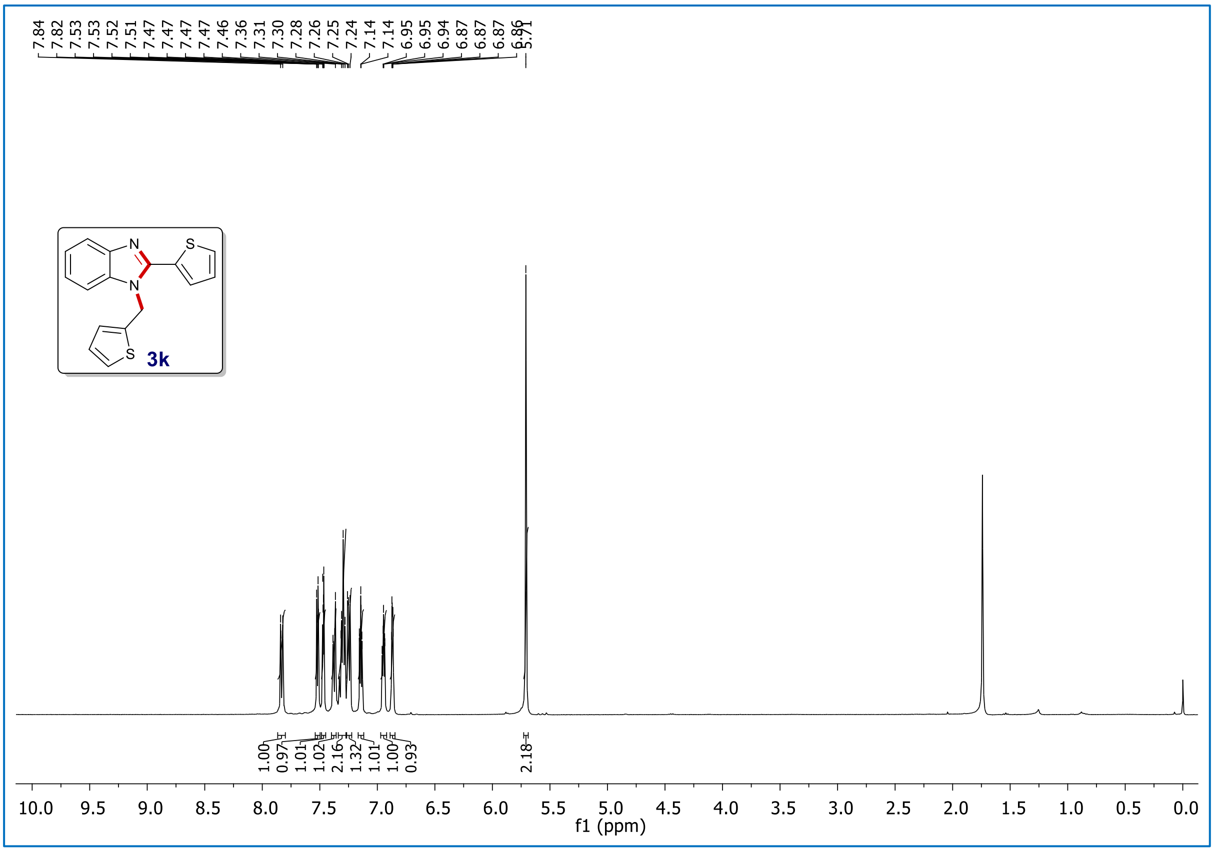
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7.28
7.26
7.25
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7.14
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6.87
6.87
6.86
5.71
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N
S
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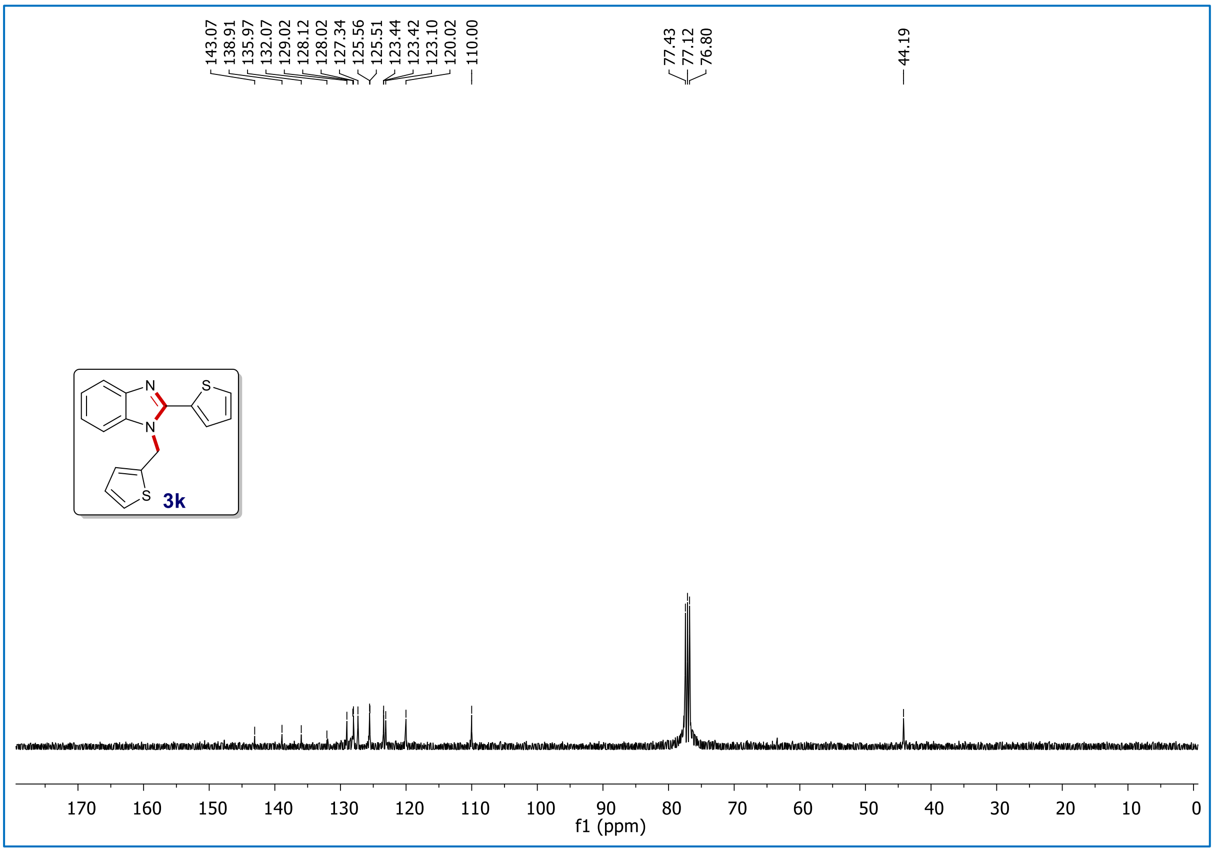
f1 (ppm)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123.10
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77.43
77.12
76.80
44.19
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S
N
S
3k
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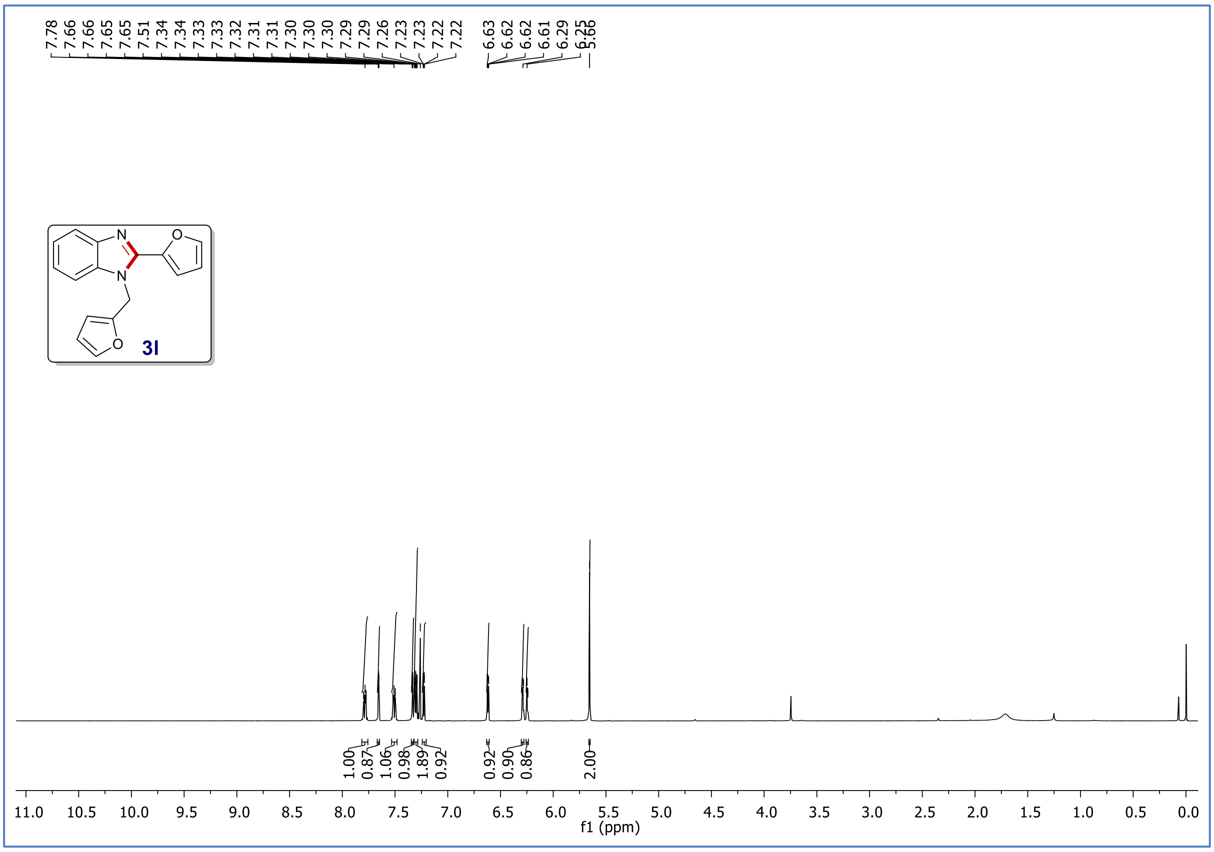
f1 (ppm)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7.29
7.26
7.23
7.23
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7.22
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6.62
6.62
6.61
6.29
6.25
5.66
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O
N
O
3l
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1.06
0.98
1.89
0.92
0.92
0.90
0.86
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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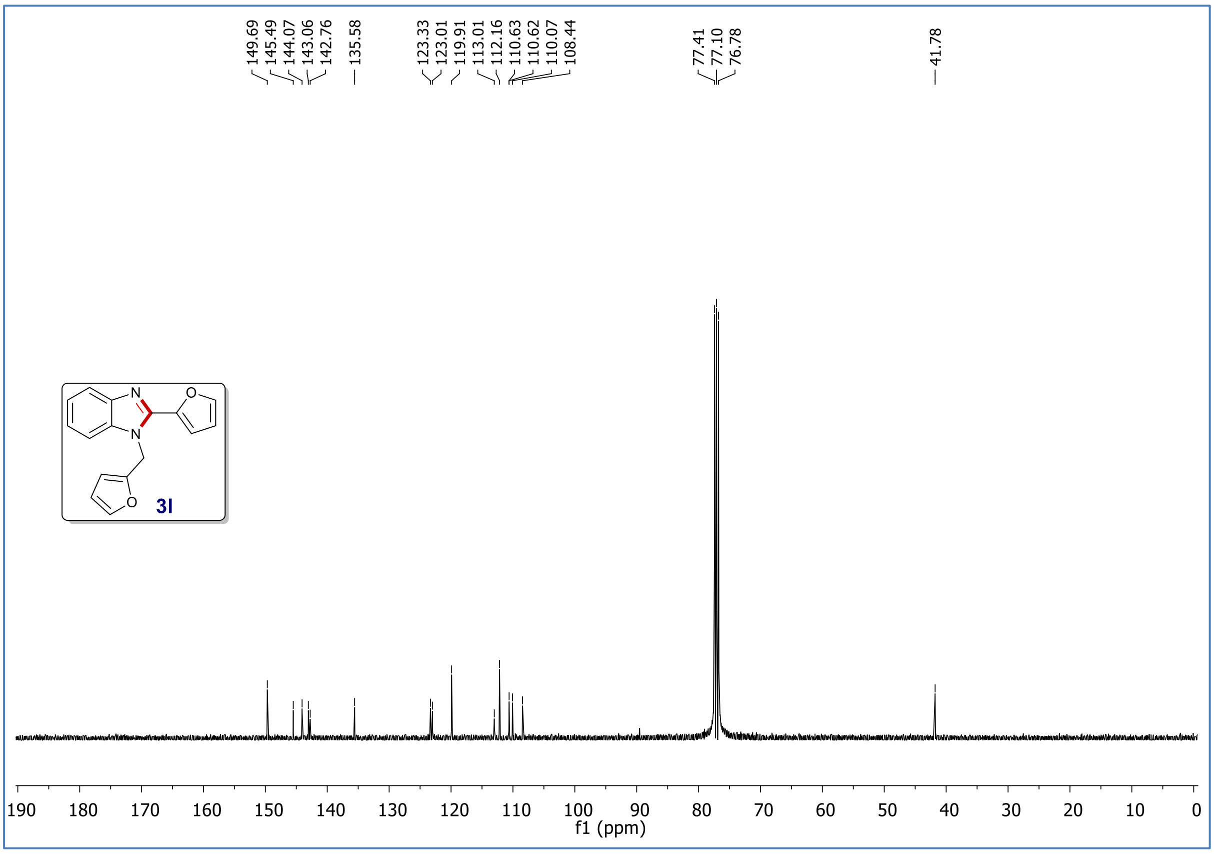
f1 (ppm)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113.01
112.16
110.63
110.62
110.07
108.44
77.41
77.10
76.78
41.78
N
O
N
O
3l
190
180
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150
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130
120
110
100
90
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70
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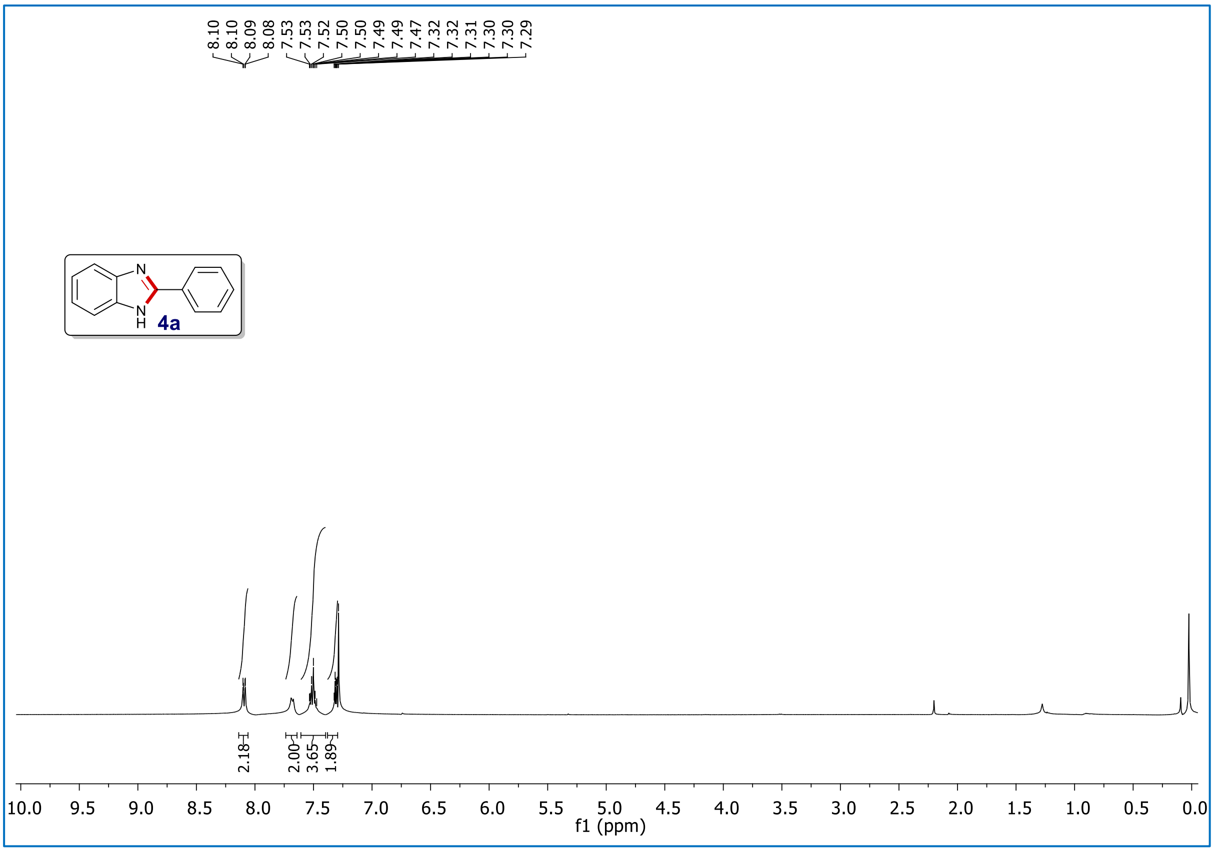
10
0
f1 (ppm)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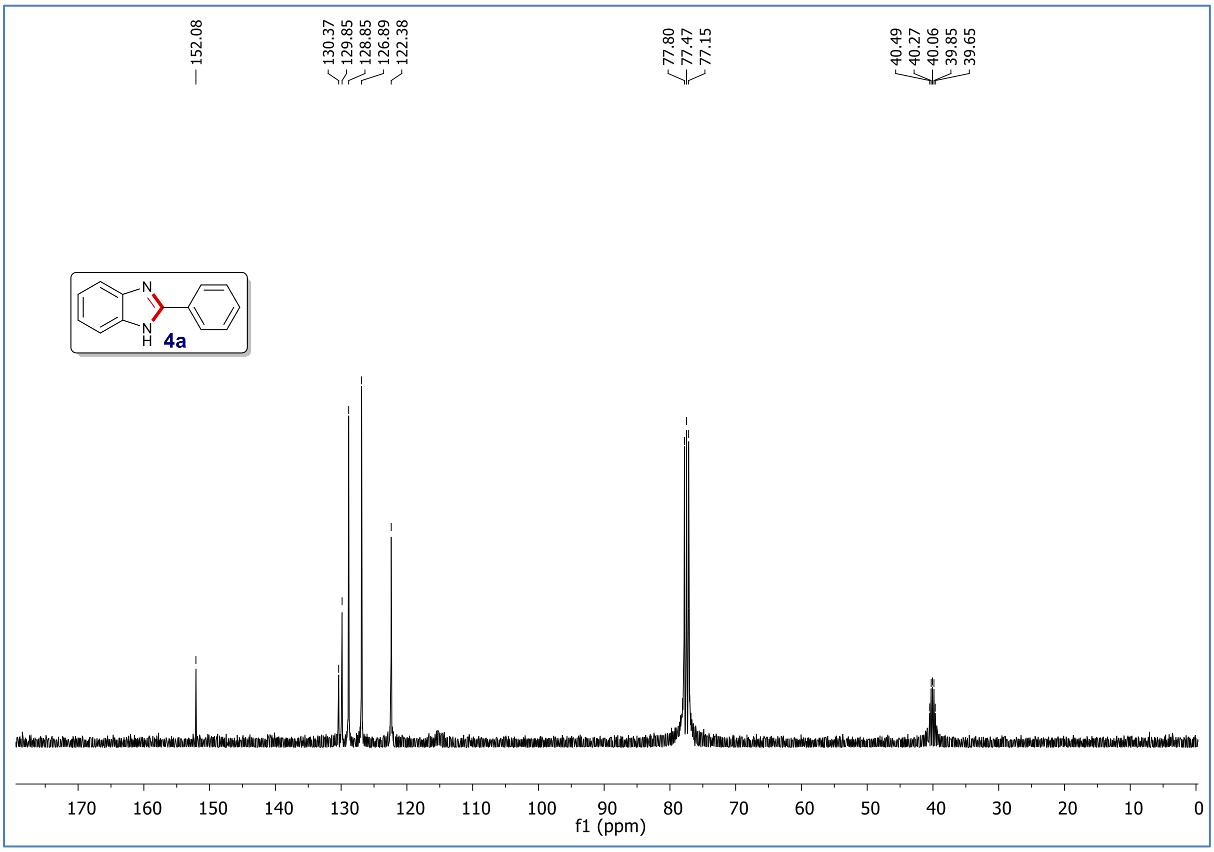
7.49
7.47
7.32
7.32
7.31
7.30
7.30
7.29
N
N
H
4a
2.18
2.00
3.65
1.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.85
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40.49
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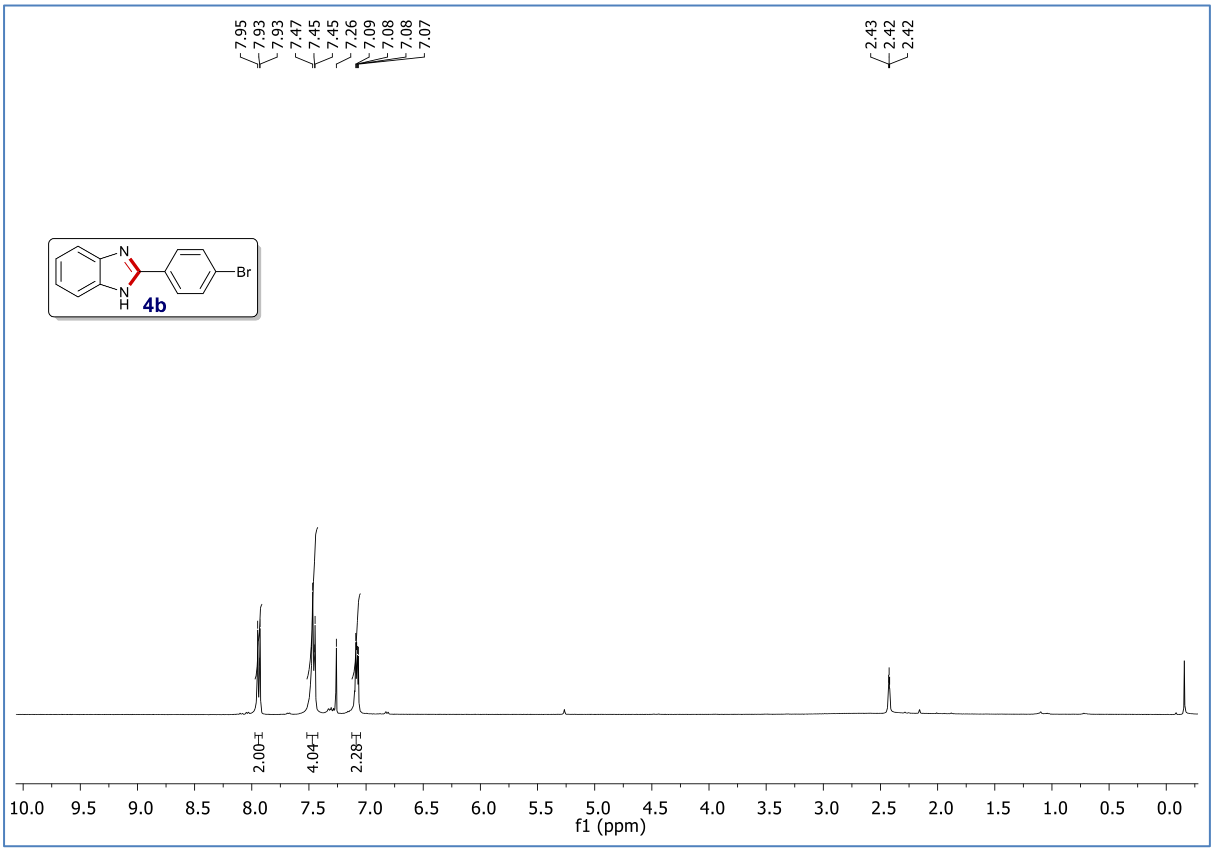
40.06
39.85
39.65
N
N
H
4a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.93
7.93
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7.45
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7.08
7.08
7.07
2.43
2.42
2.42
N
N
H
Br
4b
2.00
4.04
2.28
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
1.5
1.0
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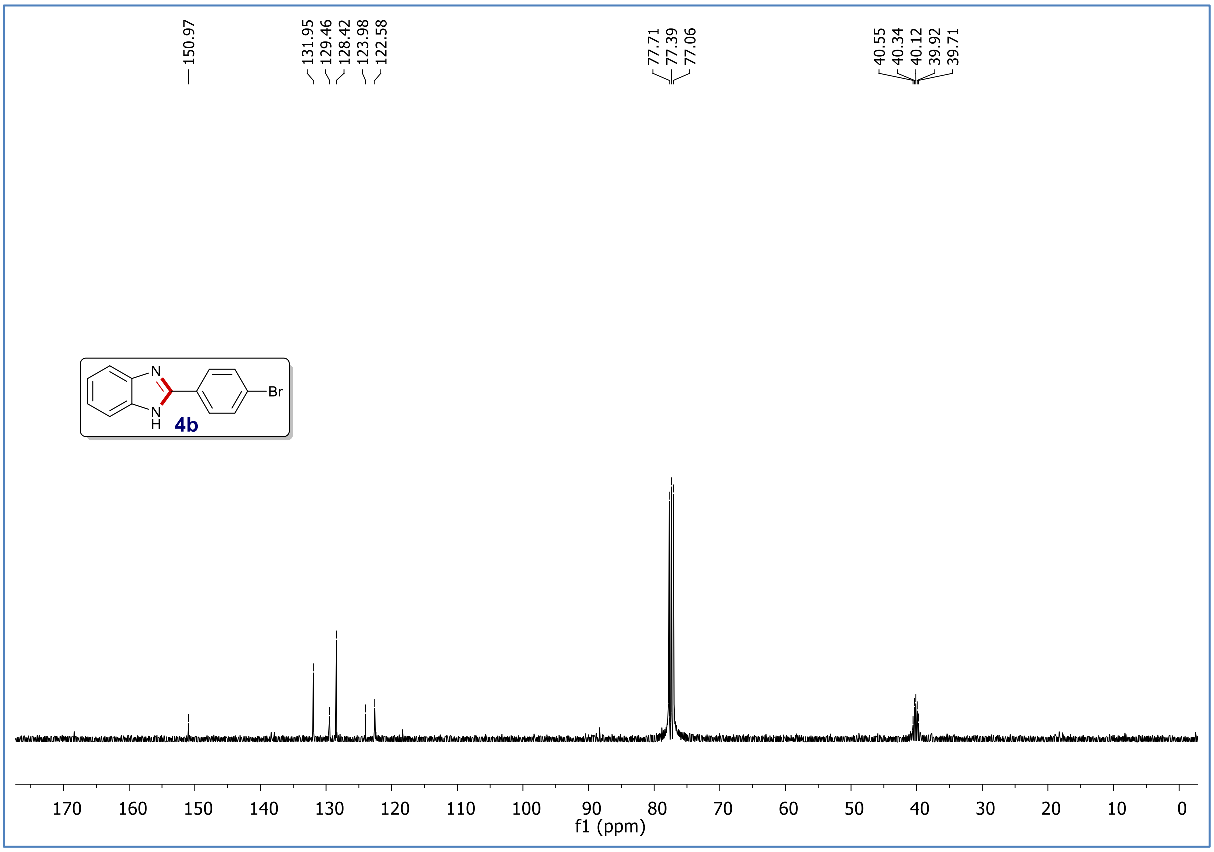
0.0
f1 (ppm)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H
Br
4b
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130
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110
100
90
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50
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10
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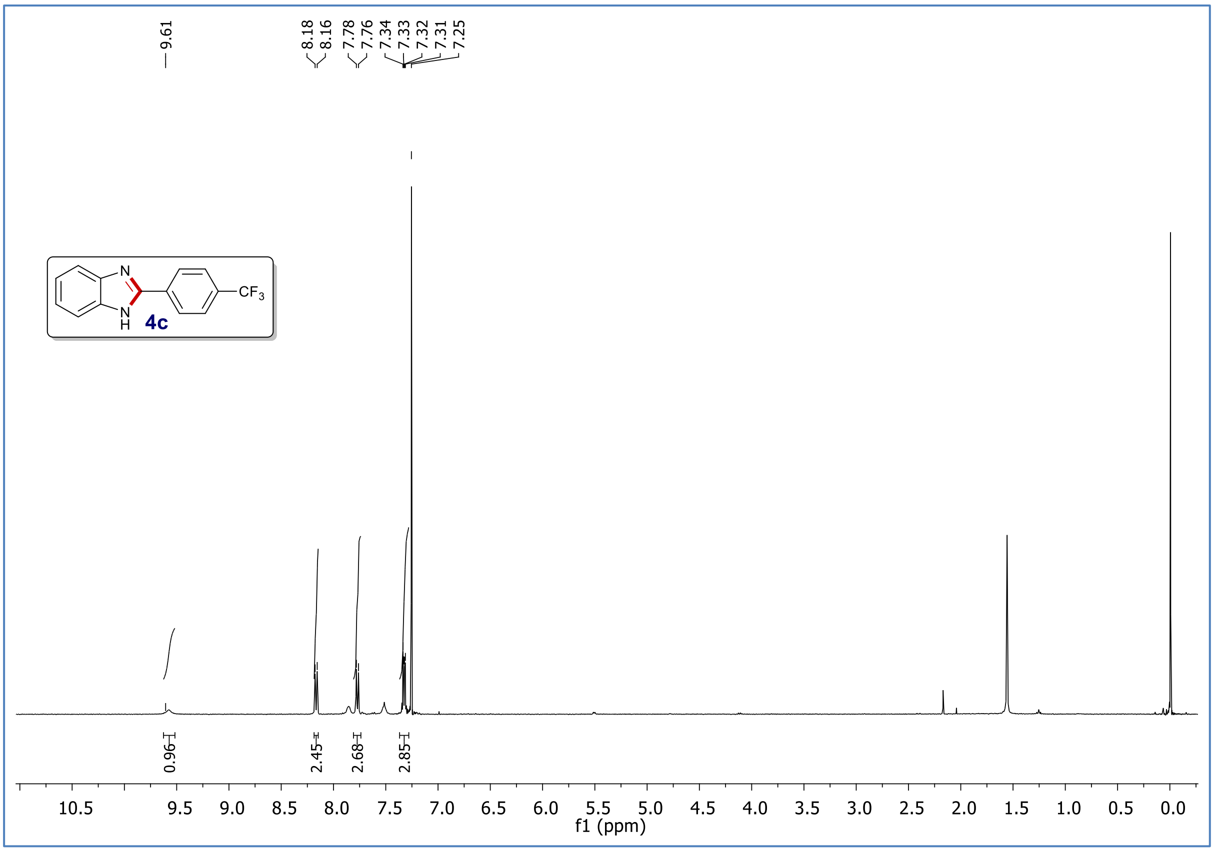
f1 (ppm)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4c
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2.68
2.85
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.0
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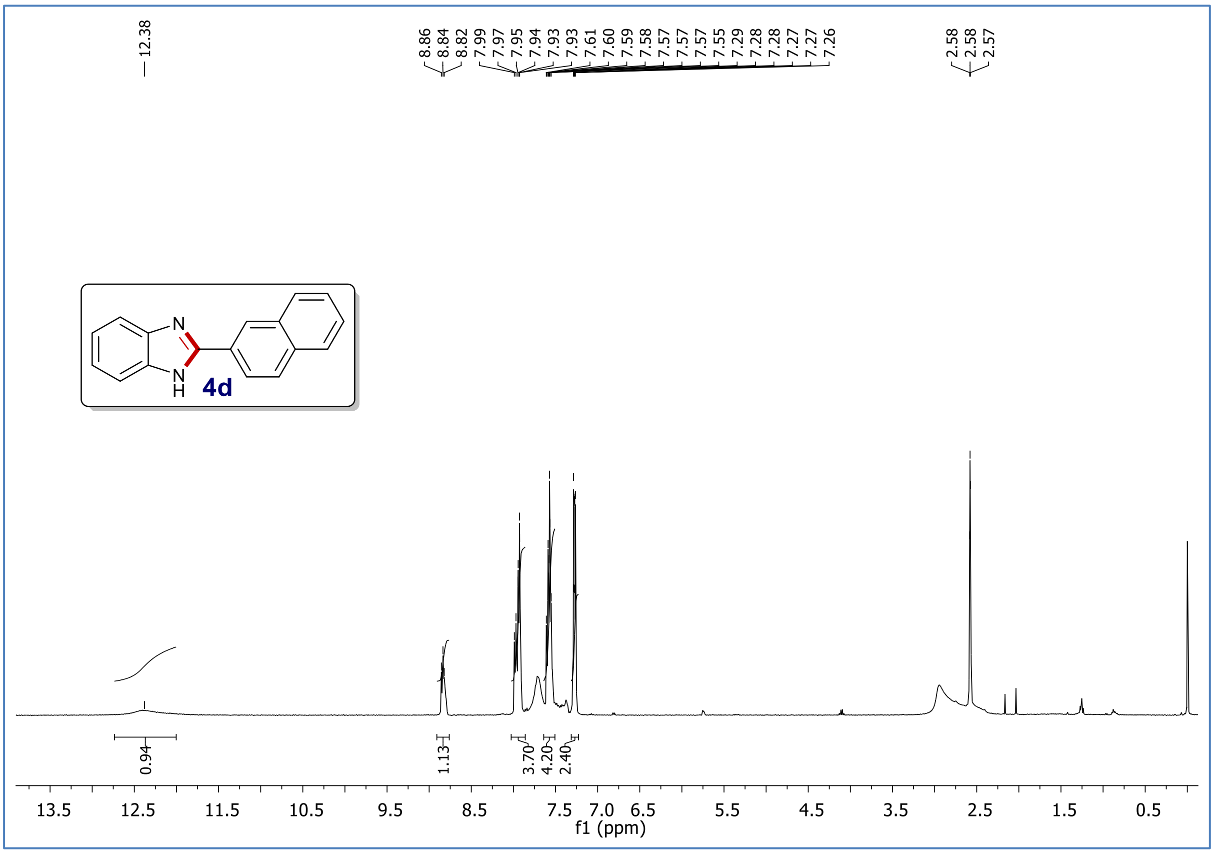
f1 (ppm)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7.57
7.57
7.55
7.29
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7.27
7.27
7.26
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2.58
2.57
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H
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3.70
4.20
2.40
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11.5
10.5
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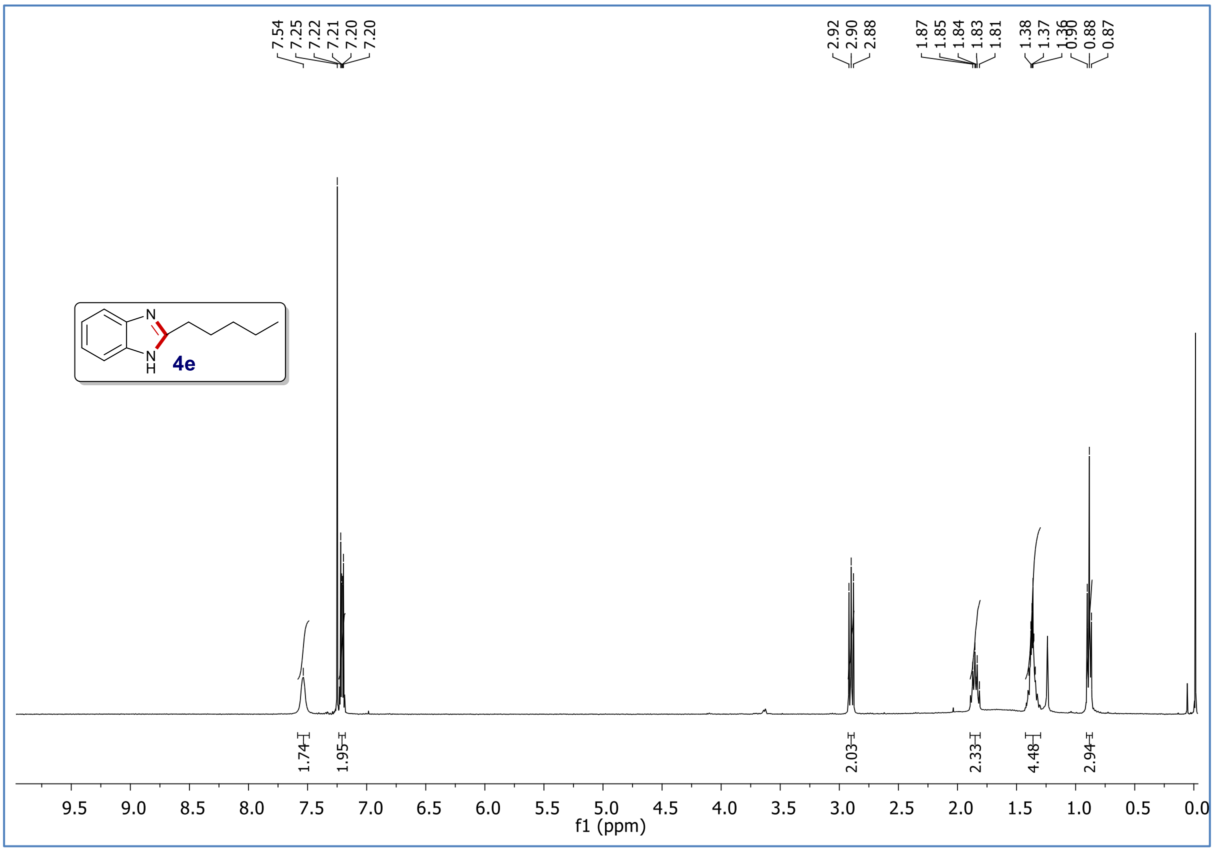
f1 (ppm)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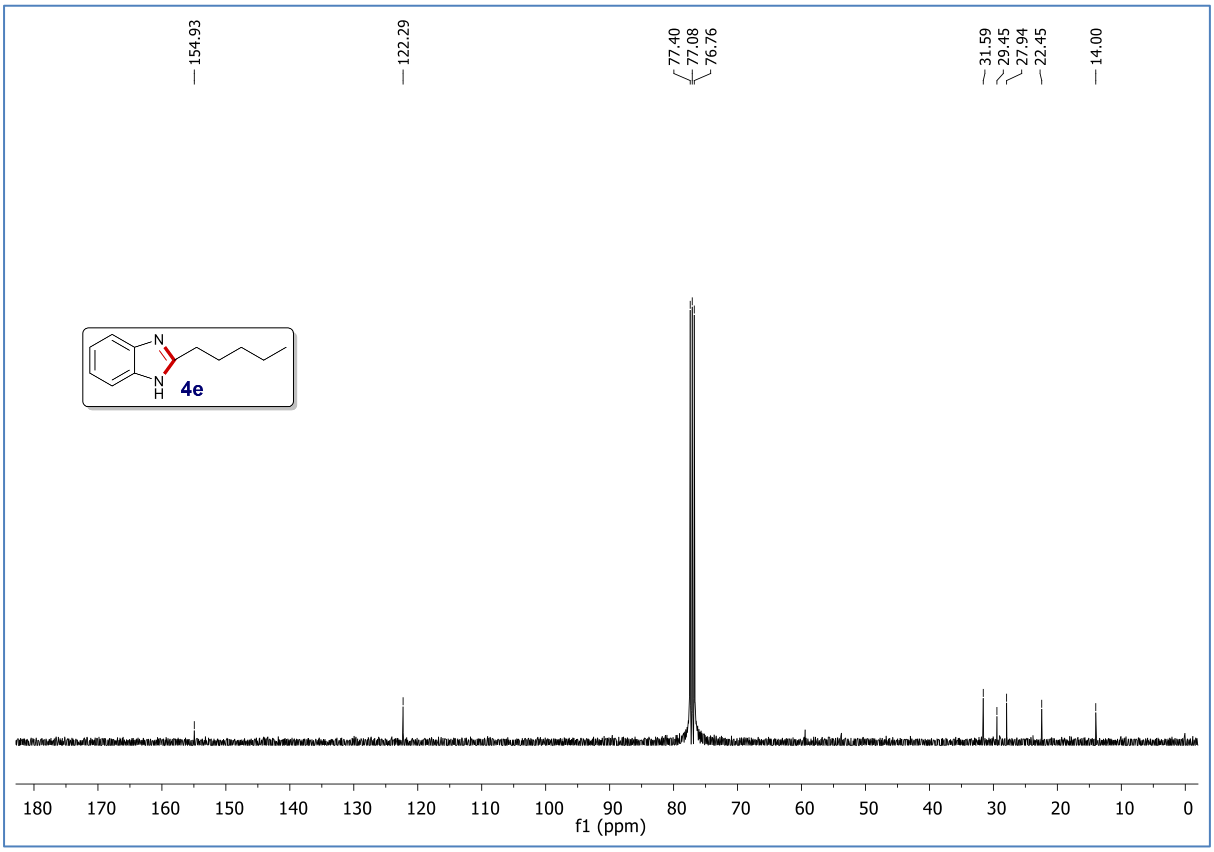
1.85
1.84
1.83
1.81
1.38
1.37
1.36
0.90
0.88
0.87
N
N
H
4e
1.74
1.95
2.03
2.33
4.48
2.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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H
4e
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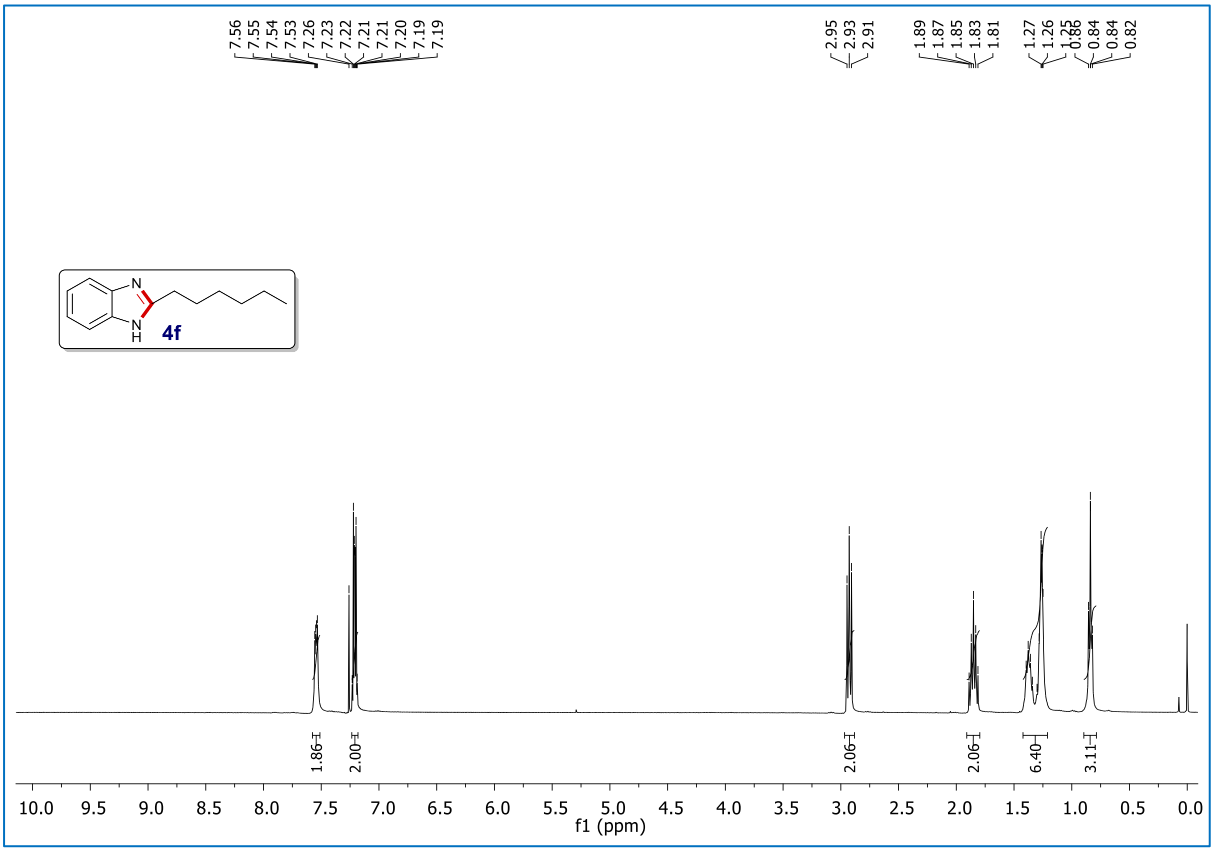
f1 (ppm)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2.91
1.89
1.87
1.85
1.83
1.81
1.27
1.26
1.25
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0.84
0.84
0.82
N
N
H
4f
1.86
2.00
2.06
2.06
6.40
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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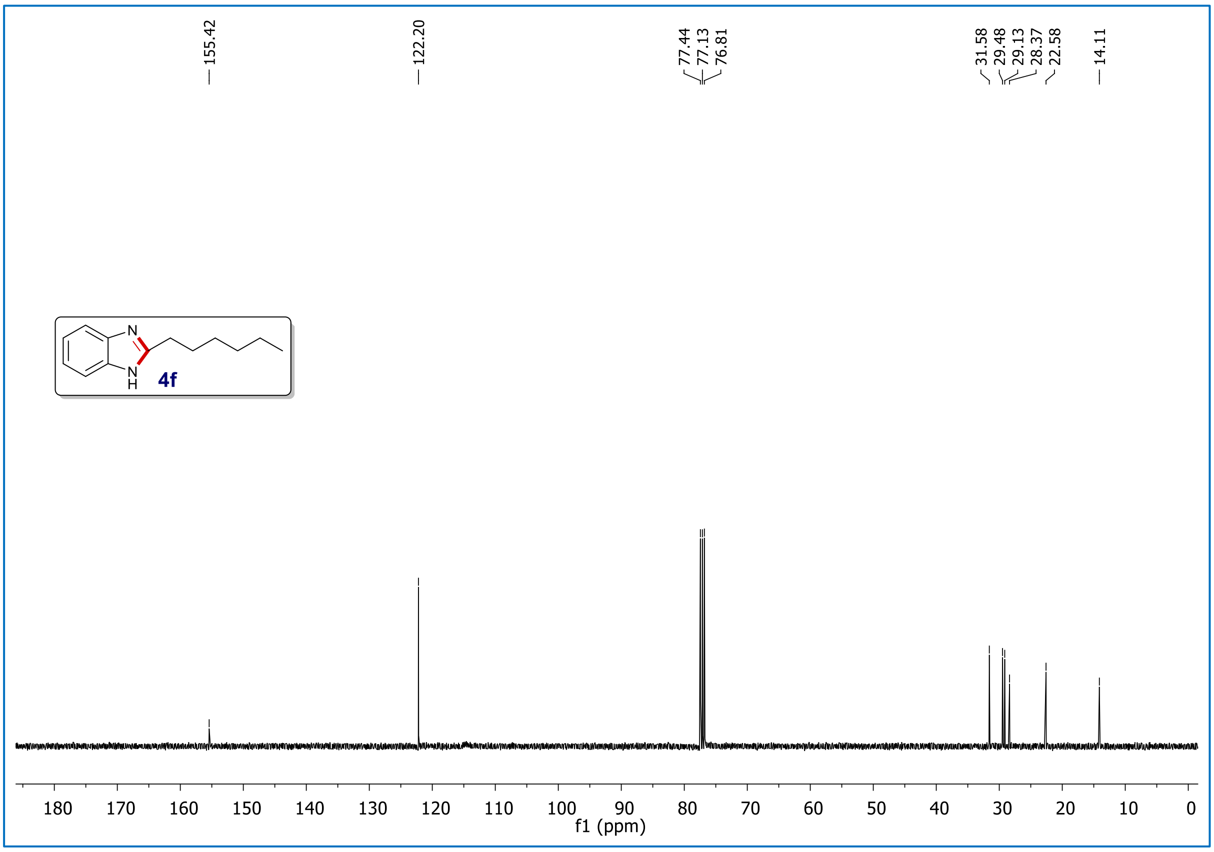
f1 (ppm)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22.58
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N
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H
4f
180
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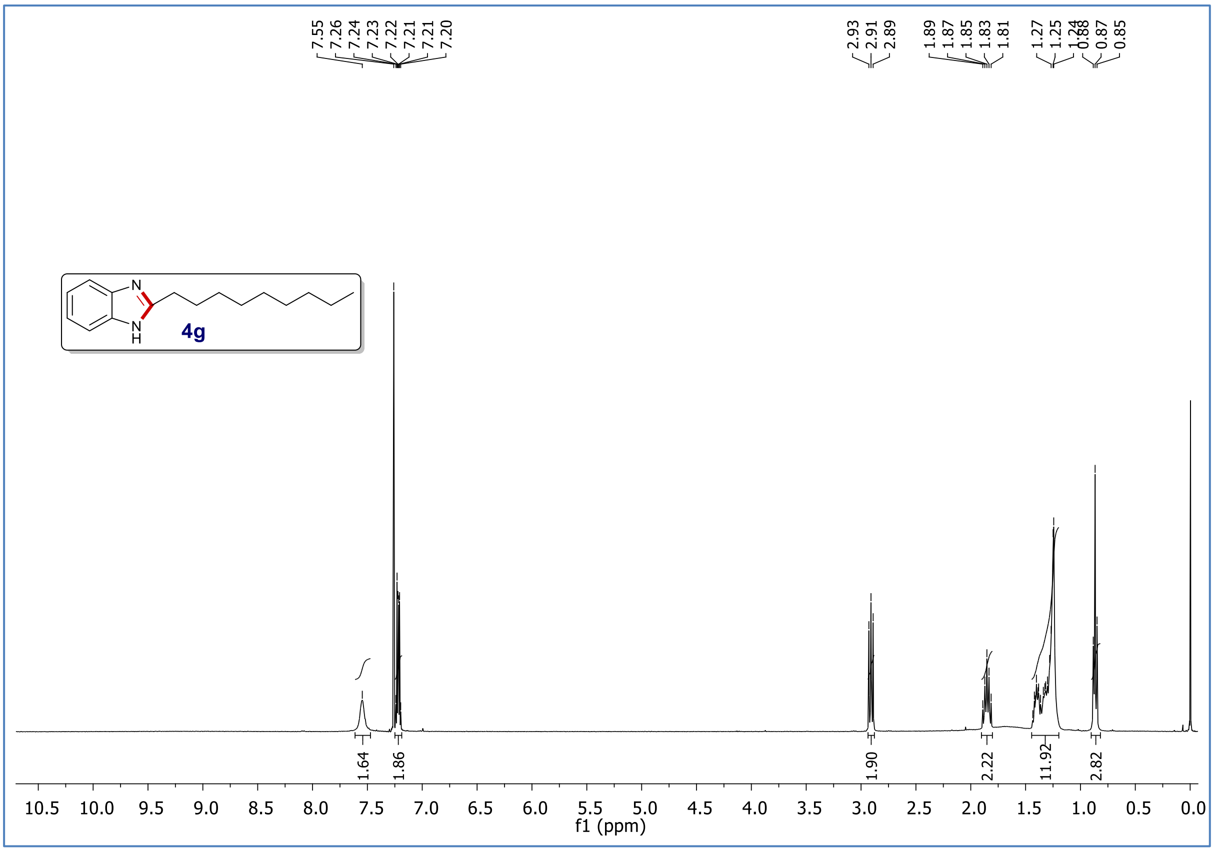
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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2.91
2.89
1.89
1.87
1.85
1.83
1.81
1.27
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1.24
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0.87
0.85
N
N
H
4g
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2.82
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9.5
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7.5
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6.0
5.5
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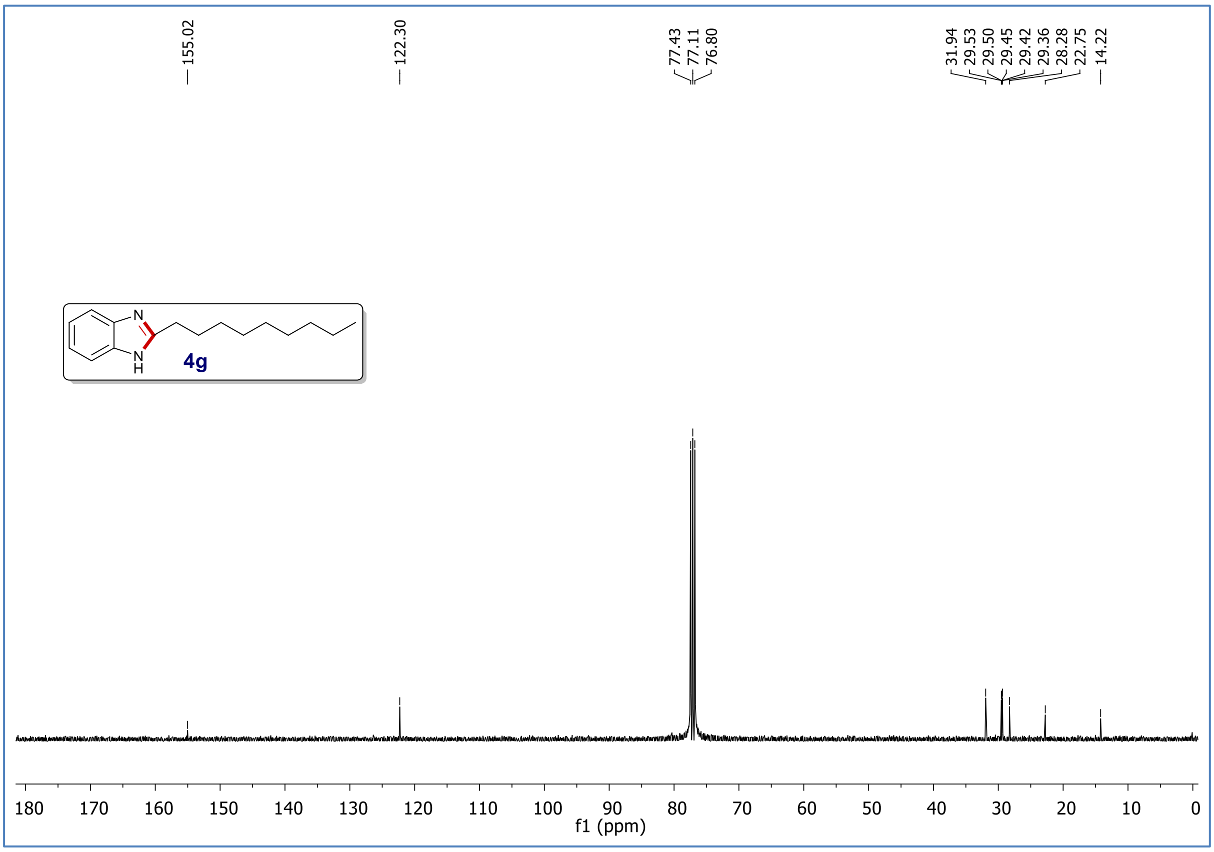
f1 (ppm)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29.42
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28.28
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N
N
H
4g
180
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110
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90
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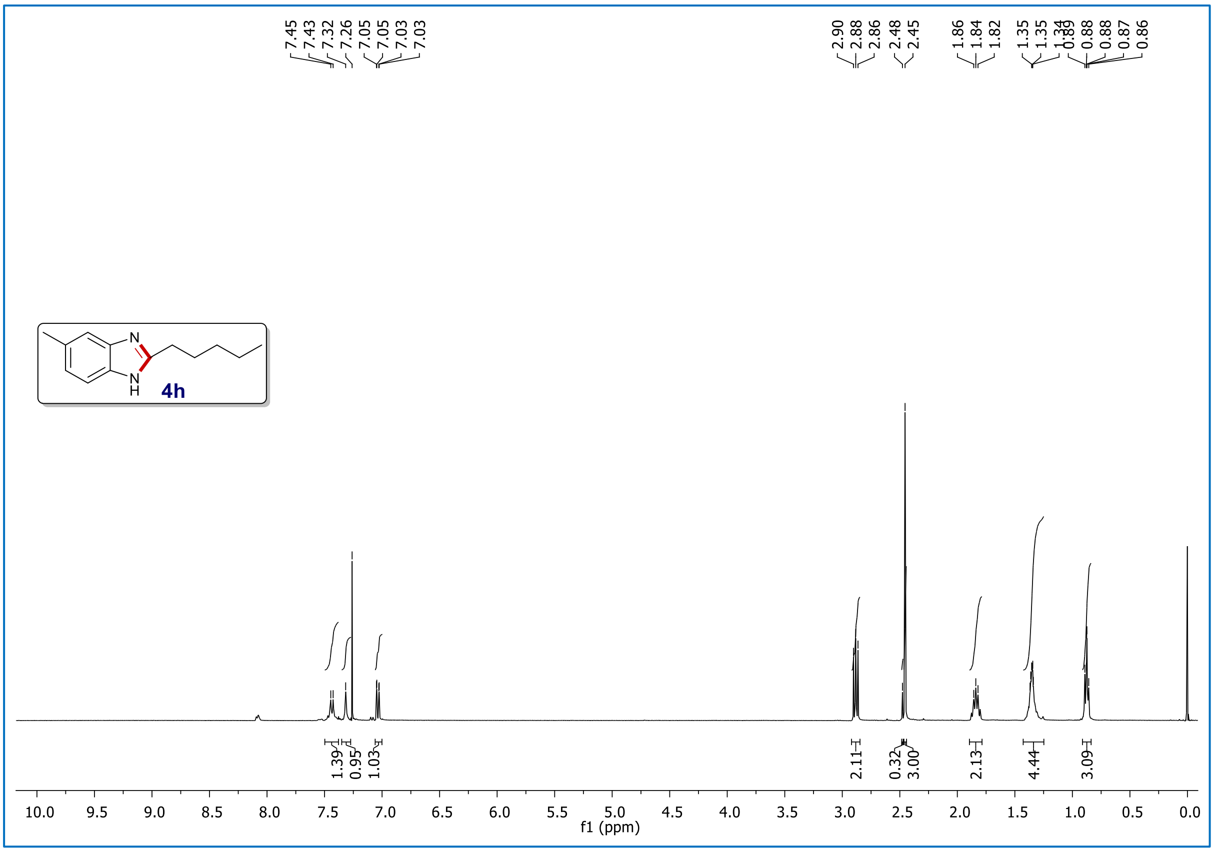
f1 (ppm)



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7.05
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7.03
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2.45
1.86
1.84
1.82
1.35
1.35
1.34
0.89
0.88
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0.87
0.86
N
H
4h
1.39
0.95
1.03
2.11
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3.00
2.13
4.44
3.09
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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2.0
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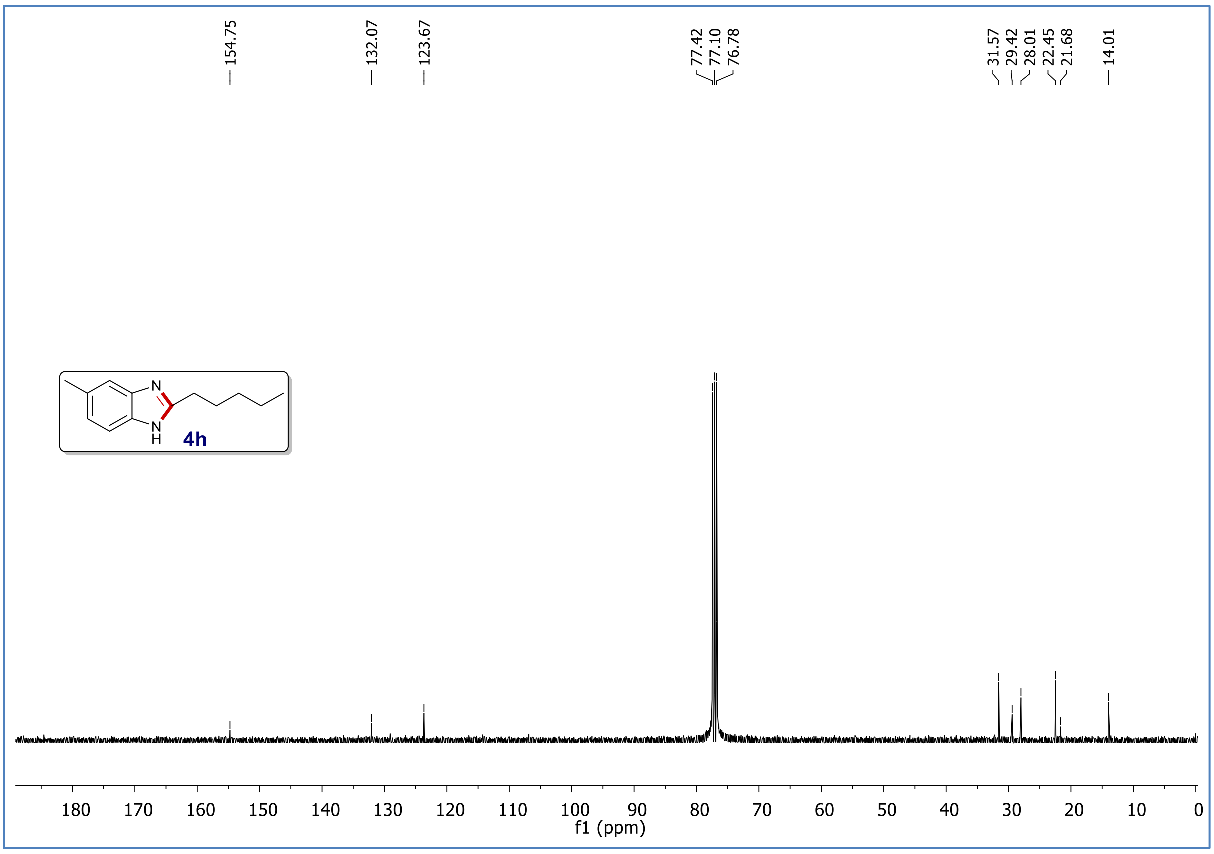
f1 (ppm)



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H
4h
180
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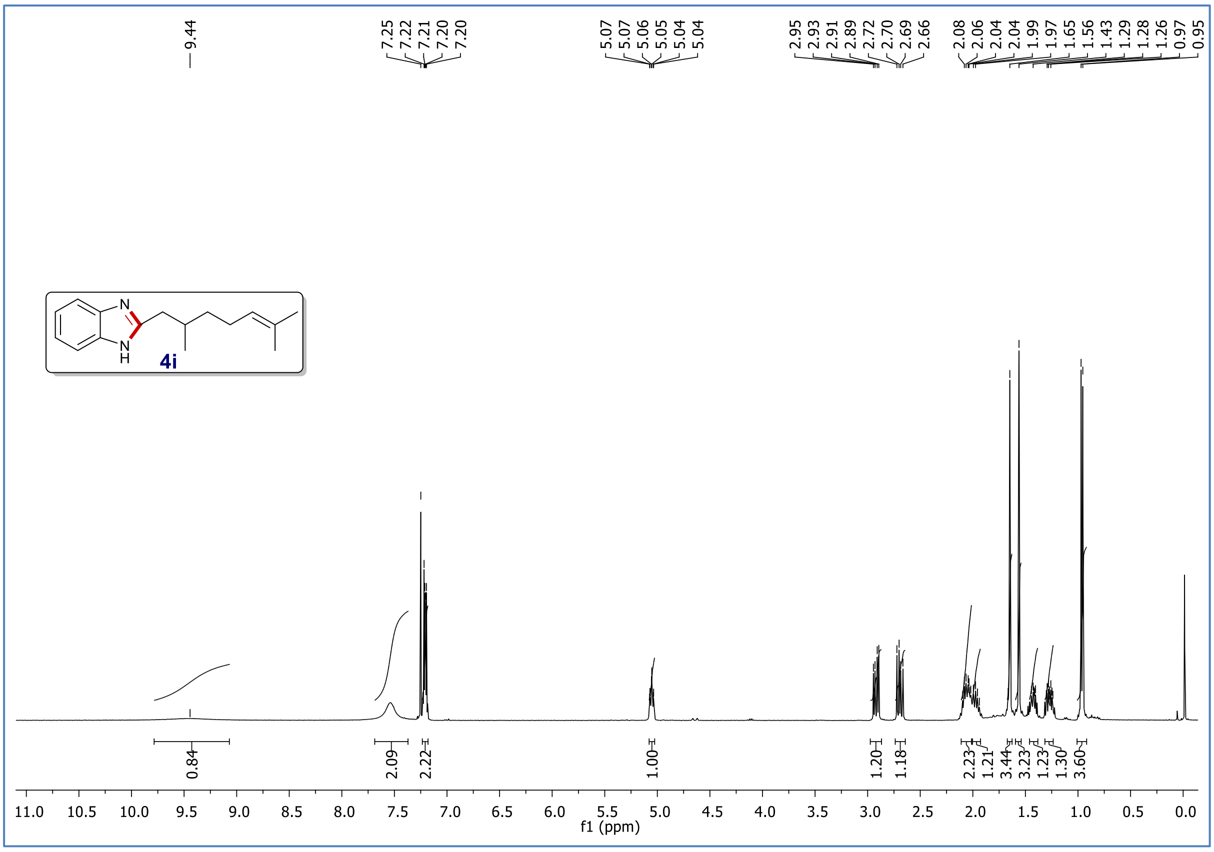
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2.91
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2.72
2.70
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2.06
2.04
2.04
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1.65
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1.29
1.28
1.26
0.97
0.95
N
N
H
4i
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2.09
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1.00
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2.23
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1.30
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7.5
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6.5
6.0
5.5
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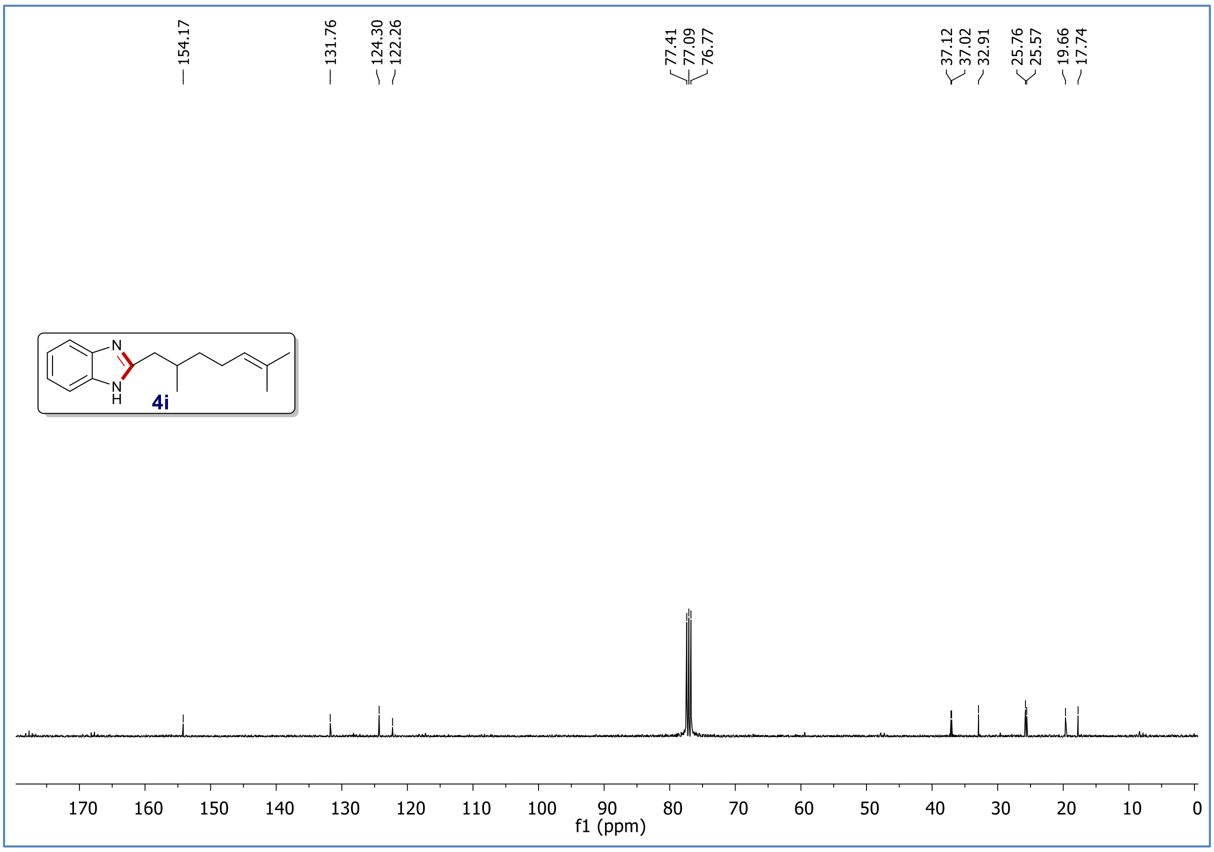
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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37.02
32.91
25.76
25.57
19.66
17.74
N
N
H
4i
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80
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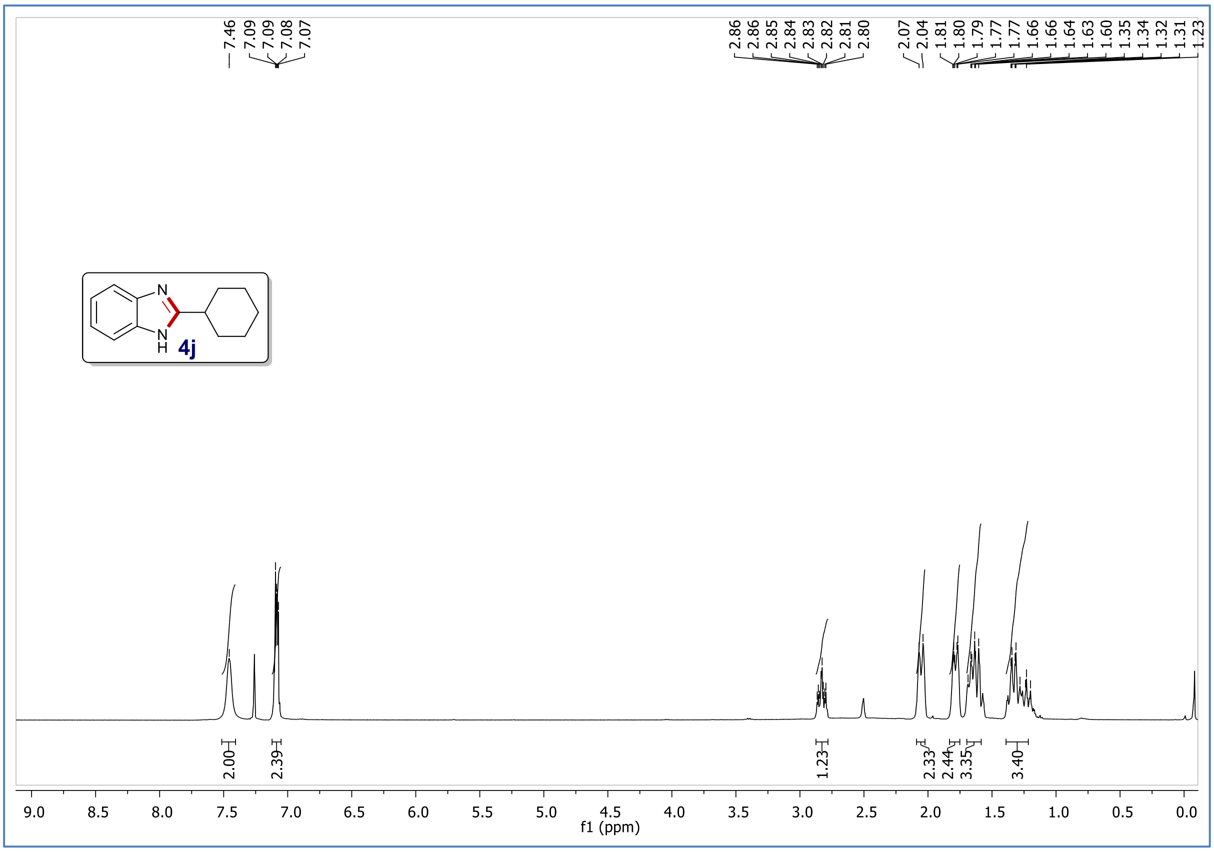
0
f1 (ppm)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1.79
1.77
1.77
1.66
1.66
1.64
1.63
1.60
1.35
1.34
1.32
1.31
1.23
N
N
H
4j
2.00
2.39
1.23
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2.44
3.35
3.40
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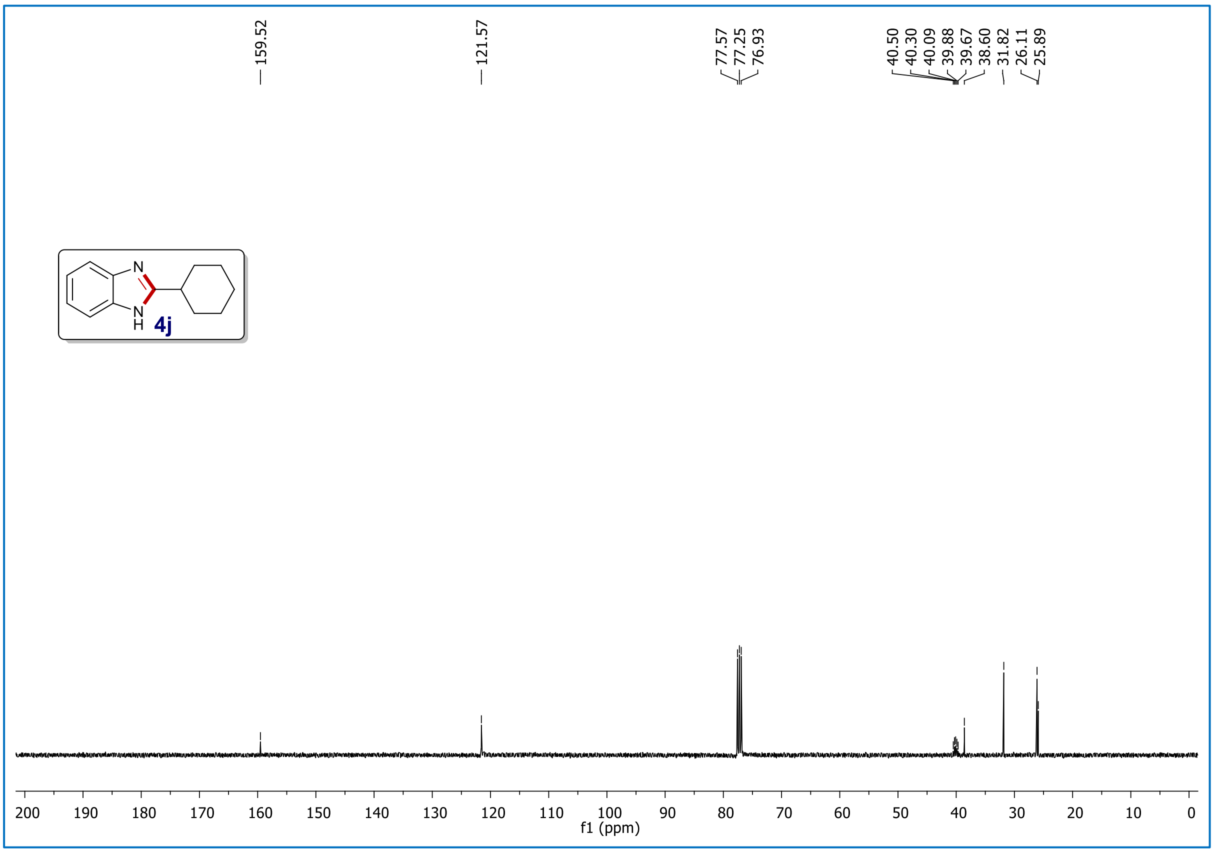
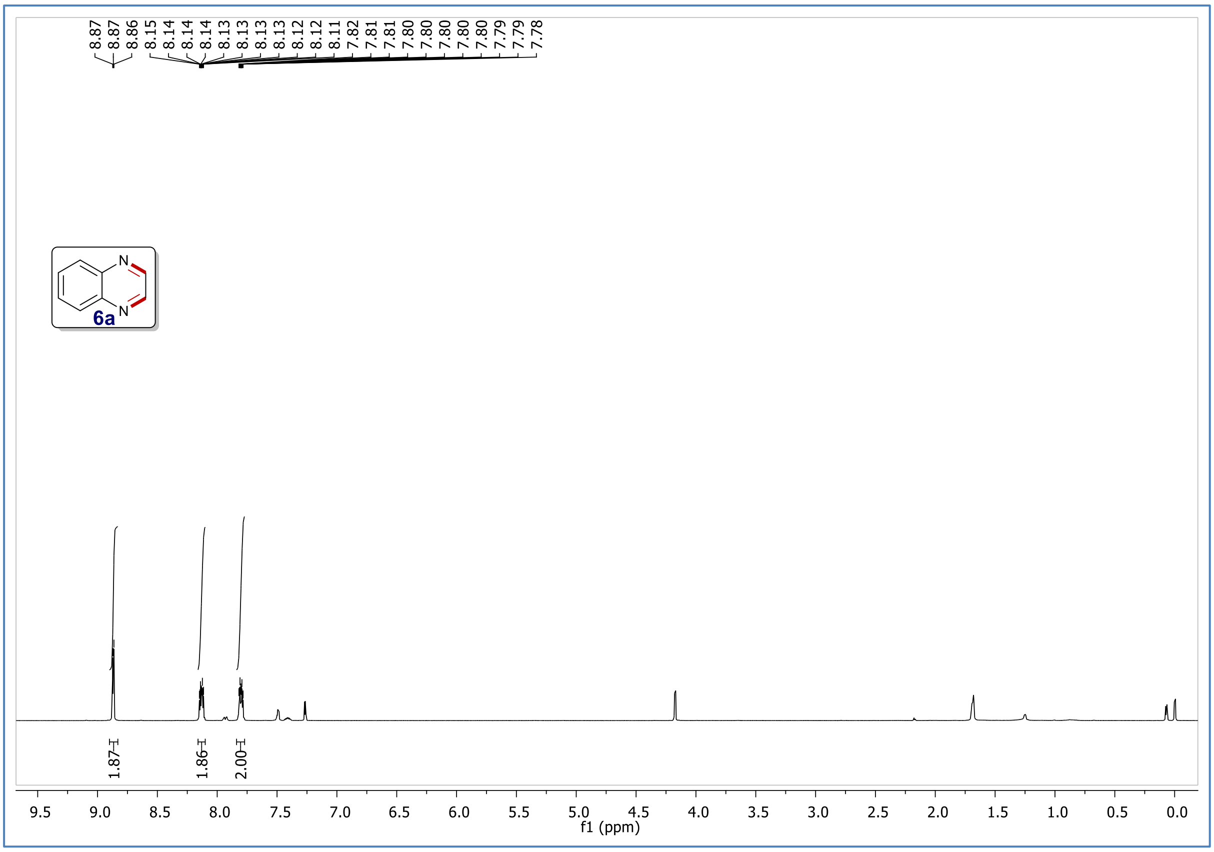
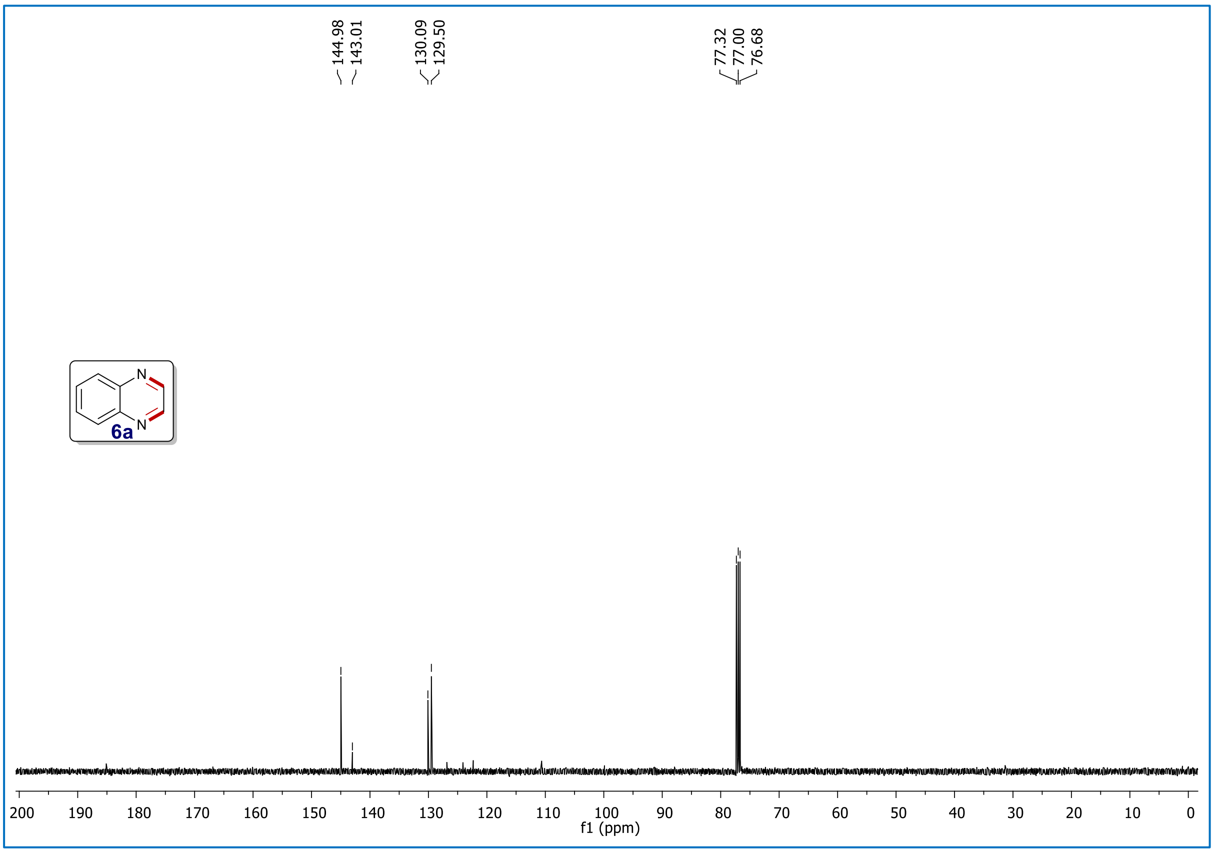
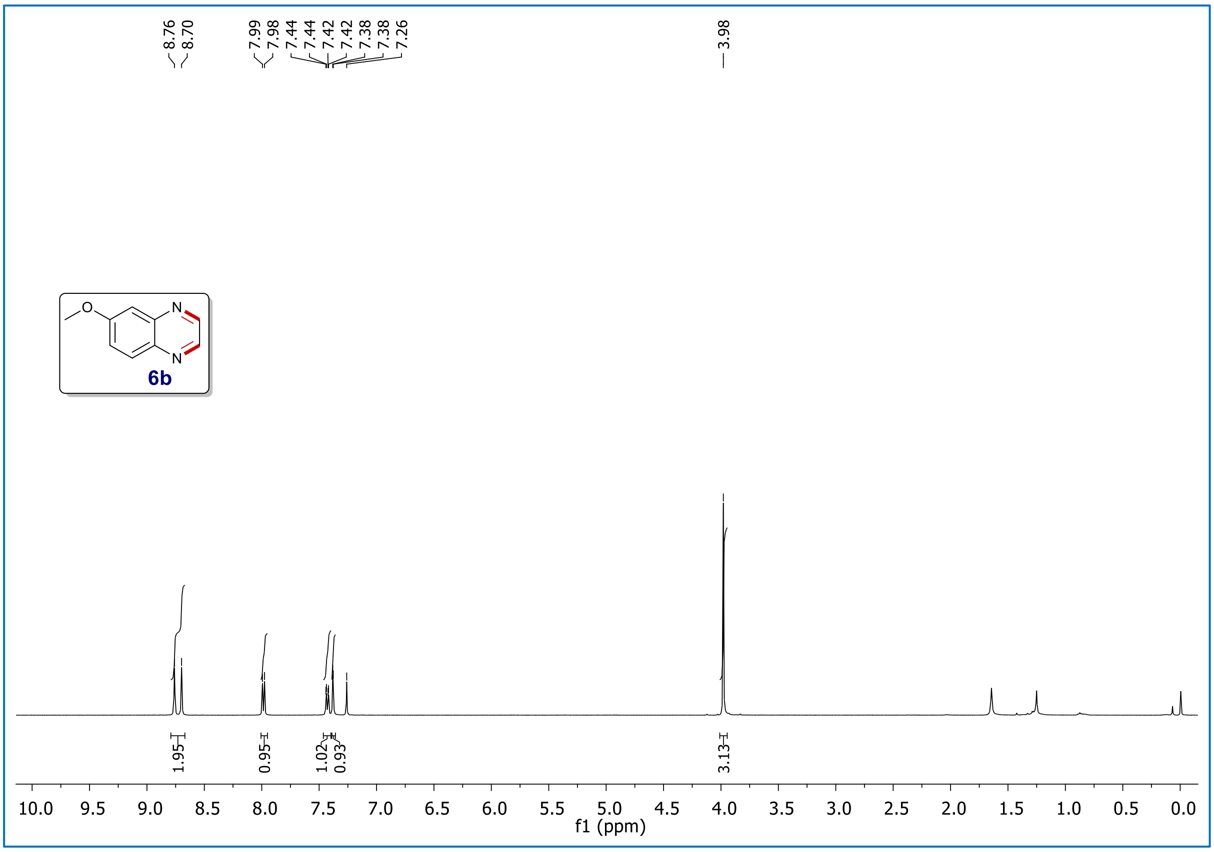
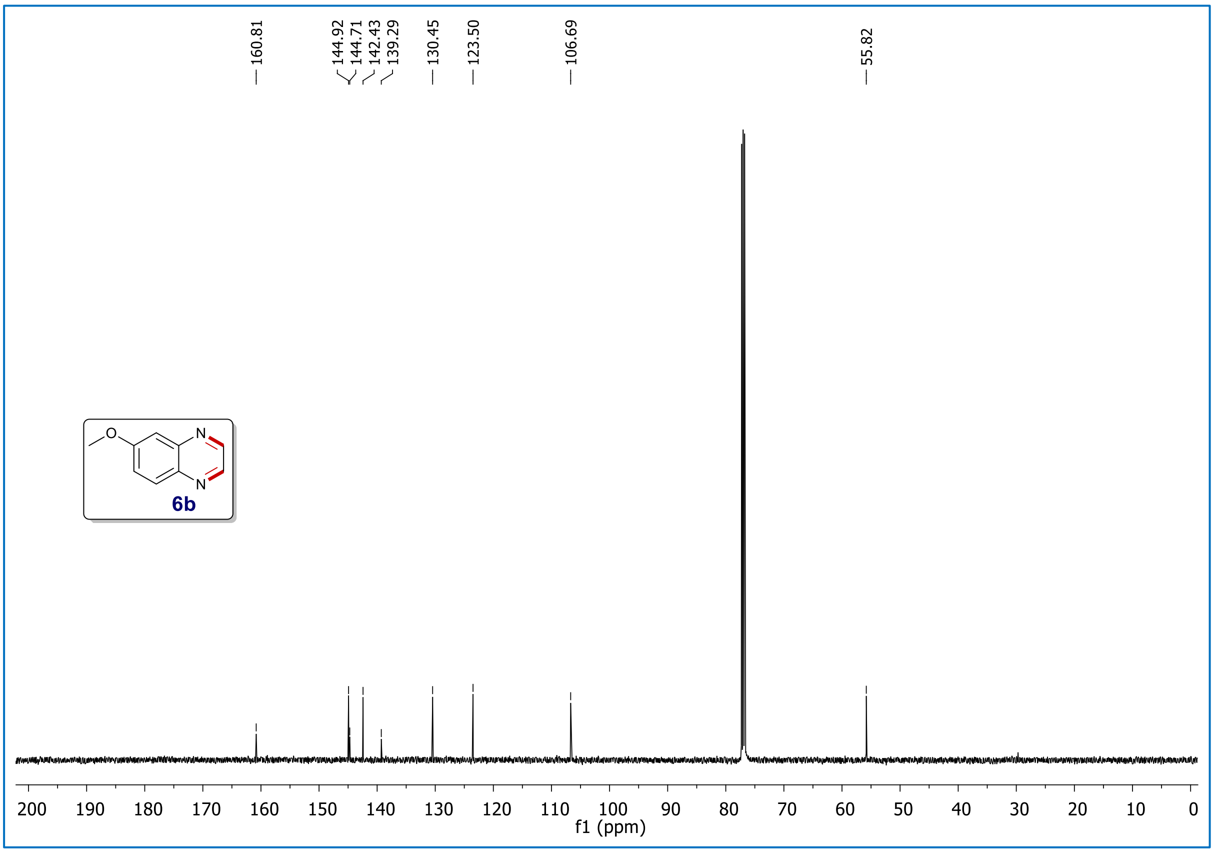
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.52
121.57
77.57
77.25
76.93
40.50
40.30
40.09
39.88
39.67
38.60
31.82
26.11
25.89
N
N
H
4j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.87
8.87
8.86
8.15
8.14
8.14
8.14
8.13
8.13
8.13
8.13
8.12
8.12
8.11
7.82
7.81
7.81
7.80
7.80
7.80
7.80
7.80
7.79
7.79
7.78
N
N
6a
1.87
1.86
2.00
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)


144.98
143.01
130.09
129.50
77.32
77.00
76.68
N
N
6a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.76
8.70
7.99
7.98
7.44
7.44
7.42
7.42
7.38
7.38
7.26
3.98
O
N
N
6b
1.95
0.95
1.02
0.93
3.13
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)


160.81
144.92
144.71
142.43
139.29
130.45
123.50
106.69
55.82
O
N
N
6b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)