Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Polynapthoquinone Mediated Metal-Free Direct N-Alkylation of (Hetero)Aryl Amines Using Alcohols

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1. General Consideration

All chemicals were purchased from commercial sources (Sigma-Aldrich, TCI, Avra Synthesis Pvt. Ltd., SRL Pvt. Ltd.) and used as received unless otherwise mentioned. Liquid anilines were distilled under vacuum before using in catalytic reactions. Potassium tert-butoxide was purchased from Sigma Aldrich. All the catalytic reactions were carried out under inert conditions in a 15 ml pressure reaction tube. Reactions were monitored using thin layer chromatography (TLC) and gas chromatography. Column chromatography and thin layer chromatography (TLC) were performed on silica gel (Merck silica gel 100–200 mesh). The 1H and 13CNMR spectra were recorded on 400 and 500 MHz spectrometers in $CDCl_3$ with residual undeuterated solvent ($CDCl_3$, 7.26/77.0) as an internal standard using tetramethylsilane ($\delta = 0.00$) as a reference. Chemical shifts (δ) are given in ppm, and J values are given in Hz. Chemical shifts (δ) downfield from the reference standard were assigned positive values. All catalytic reactions were carried out with 15 ml pressure reaction tube and the temperature corresponds to oil bath temperature.

2. Preparation of polynapthoquinone:

The synthesis protocol used for the synthesis of polynapthoquinone (PNQ) was identical as reported literature[1-7]. In a typical procedure 200 ml of 25% nitric acid was aged with 500 mg of sodium nitrite ($NaNO_2$) placed in an ice bath at 10˚-20˚C with. 1,7-Naphthalenediol (1.0 g) was dissolved in 50 ml absolute ethanol and was added to the acid solution drop wise by using dropping funnel for 15 minutes. The reaction mixture turns dark and stirring was continued for an additional 15 min. Before filtration, the reaction mixture was diluted to 600 ml with distilled water and filtered through a buchner funnel. The dark brown precipitate was washed several times with distilled water until the filtrate becomes netural. Finally, product (0.7g) was dried in air at 100˚C for 16 hr. Thus, obtained brown powder was washed with distilled water and divided into 2 parts and heated with temperature 300˚C for 3 hr in air for further thermal polymerization resulting a black powder. The obtained sample (PNQ) were utilised as a catalyst for synthesis of N-alkylated amines via hydrogen auto-transfer process.

3. Characterization of catalyst polynapthoquinone

3.1 Fourier transform infrared (FTIR) spectroscopy:

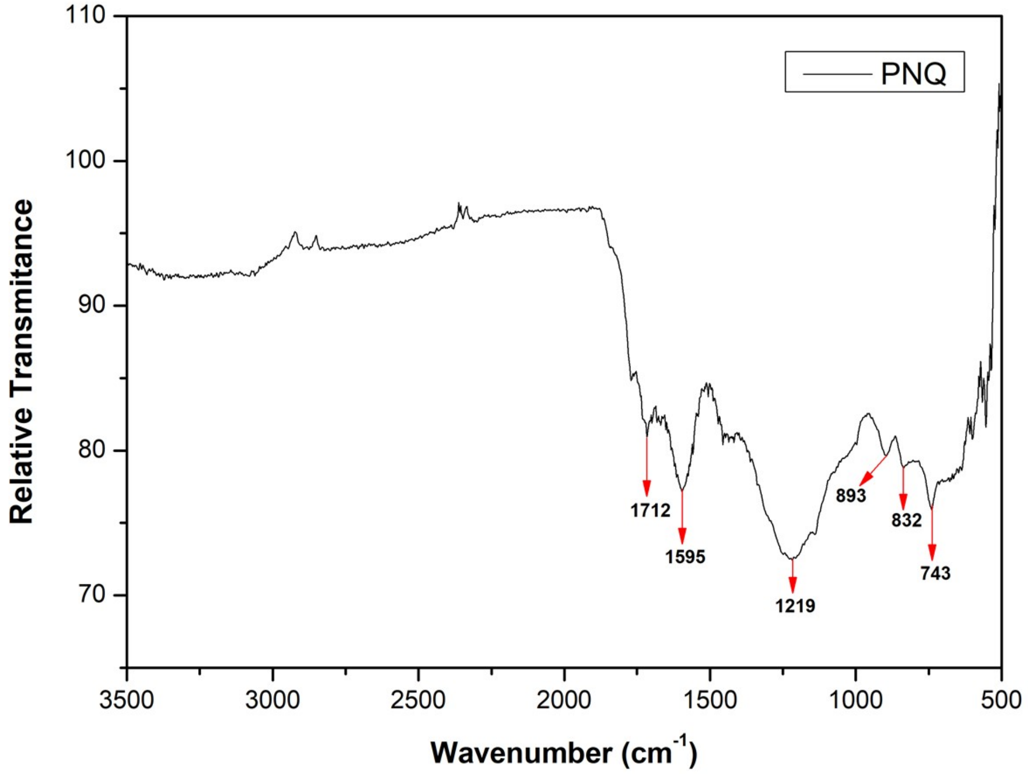


Figure 4. FT-IR Spectrum of Polynapthoquinone catalyst

3.2 X-ray photoelectron spectroscopy (XPS):

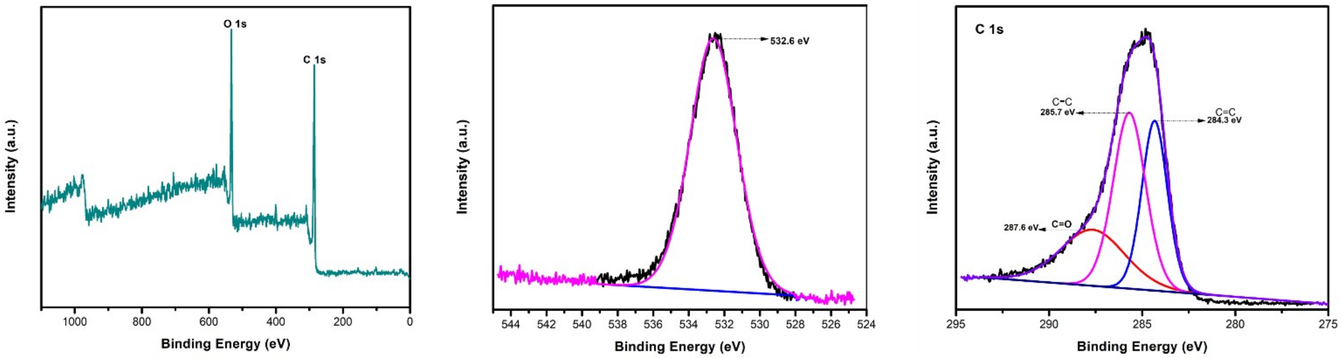


Figure 5. XPS Spectra of Polynapthoquinone catalyst

3.3 Thermogravimetric analysis (TGA)

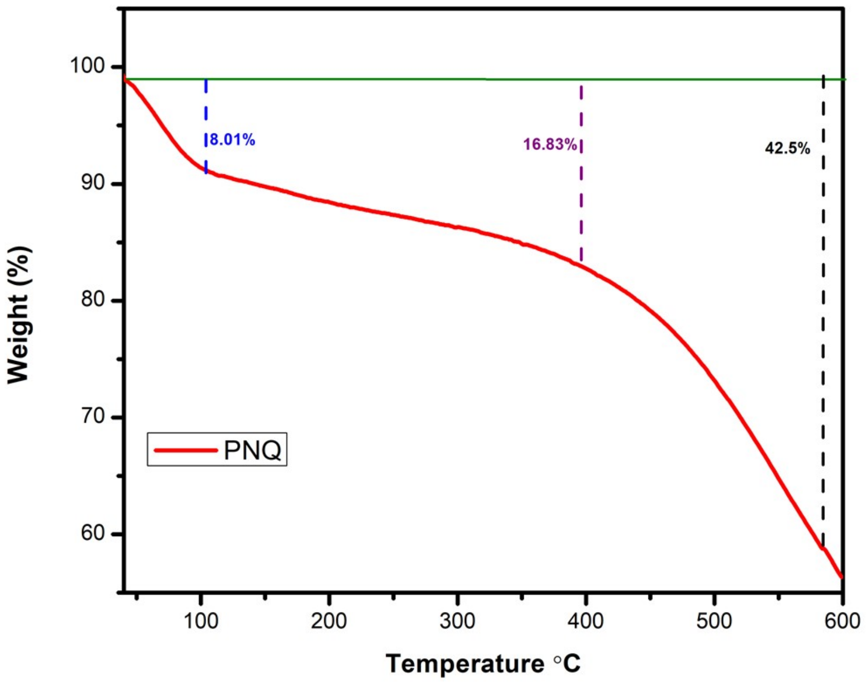


Figure 6. TGA Curve of Polynapthoquinone catalyst

3.4 ^{13}C NMR of Oolynapthoquinone Catalyst

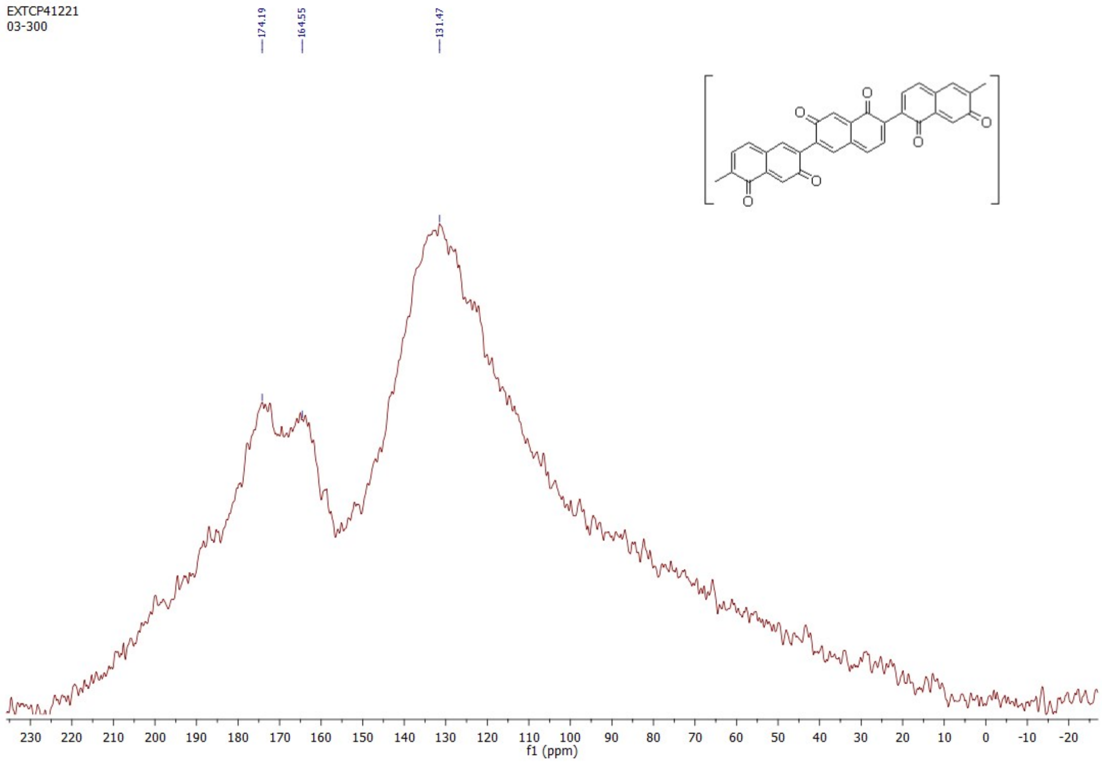


Figure 7. Carbon NMR of Polynapthoquinone catalyst

3.5 Scanning electron microscope (SEM) studies:

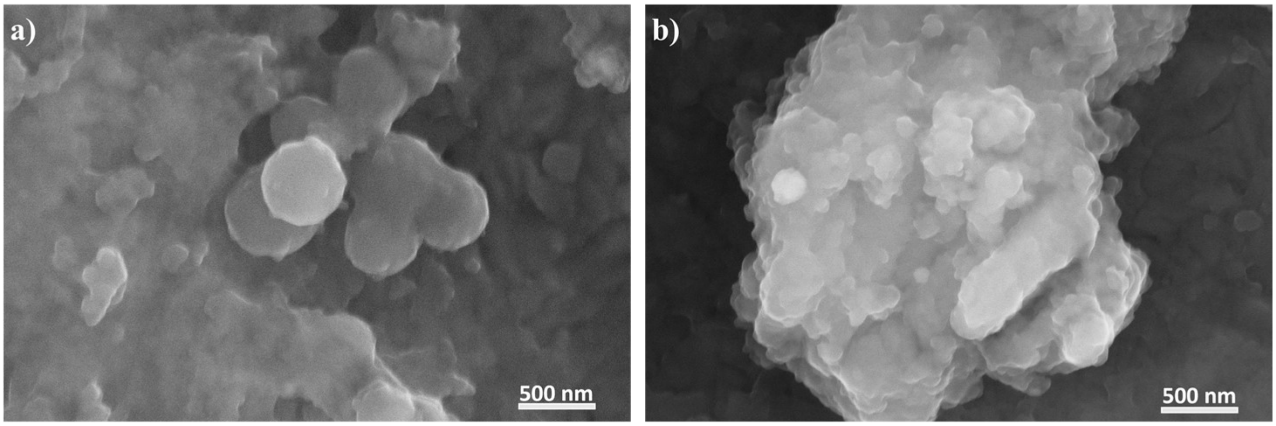


Figure 8. Scanning electron microscope images of Polynapthoquinone nanocatalyst, a) as synthesized b) after catalytic reaction

3.5 EDAX studies:

Element	Wt%
C	51.93
O	8.97
Al	39.10
Total:	100.00

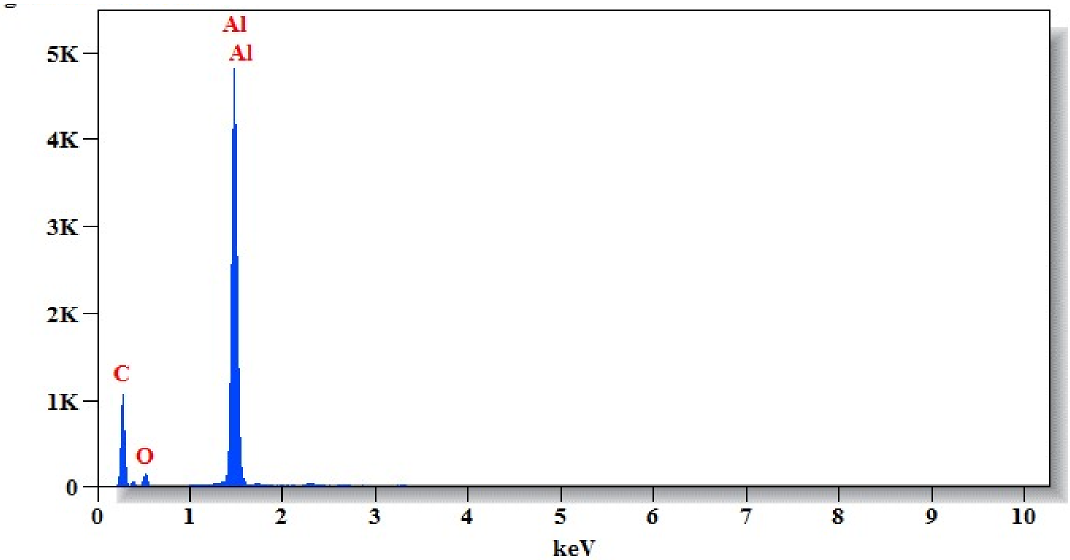


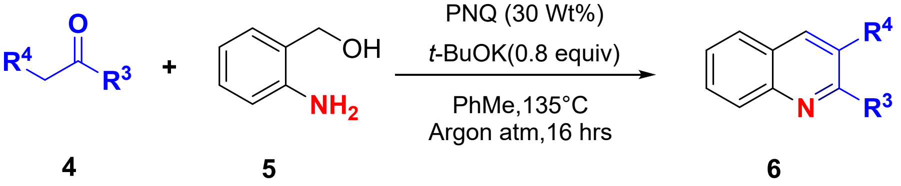
Figure 9. EDAX Polynapthoquinone catalyst

4. Experimental methods for polynapthoquinone (PNQ) catalysed reactions:

Proceure A: N alkylation of anilines with alcohols

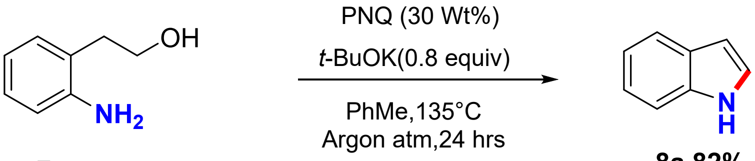
In a typical reaction 32 mg (30 wt%) catalyst, *t*-BuOK (90 mg, 0.8 mmol), benzyl alcohol (104 μL, 1.0 mmol), aniline (137 μL, 1.5 mmol) was loaded in an oven dried 15 ml PTFE pressure reaction tube followed by 1 ml of toluene as a solvent respectively at room temperature under argon atmosphere. The pressure reaction tube was kept in a pre-heated oil bath at 135 °C with constant stirring for 24 hrs. The reaction mixture was analysed by gas chromatography to obtain the conversion and selectivity. The residual part was purified using column chromatography through a mixture of hexane/ethyl acetate as mobile phase and characterisied by ^{1}H and ^{13}C NMR spectroscopies.

Procedure B: Dehydrogenative quinoline synthesis



A 15 ml pressure reaction tube, previously oven-dried, was equipped with a magnetic stirring bar and loaded with 41 mg (30 wt%) of PNQ catalyst, potassium tert-butoxide (0.8 mmol), 120 mg (1 mmol) of acetophenone, and 148 mg (1.2 mmol) of 2-aminobenzyl alcohol. Toluene (1 ml) was added as the solvent. The tube was purged with argon, sealed with a PTFE cap, and heated in a pre-heated oil bath at 130 °C with stirring for 16hrs. Upon completion, the reaction mixture was allowed to cool to room temperature. The catalyst was separated by filtration washed with ethyl acetate followed by water. The final product was isolated by column chromatography on silica gel (100-200 mesh) using a hexane/ethyl acetate (98:3) mixture

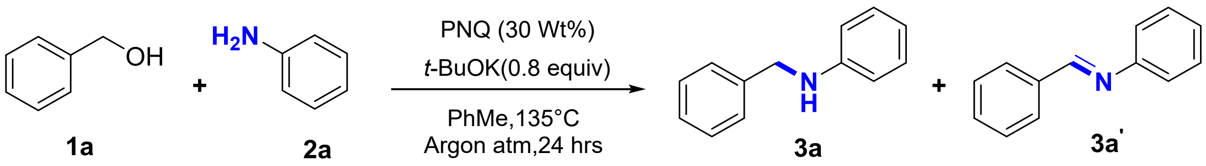
Proceure C: Synthesis of Indole



7a **8a,82%**

A 15 ml pressure reaction tube, previously oven-dried, was equipped with a magnetic stirring bar and charged with 41 mg (30 wt%) of PNQ catalyst, potassium tert-butoxide (0.8 mmol), and 2-aminophenethyl alcohol (1.0 mmol). Toluene (1 ml) was added as the solvent at room temperature. The tube was purged with argon, sealed with a PTFE cap, and heated in a pre-heated oil bath at 130 °C with stirring for 24 hours. Upon completion, the reaction mixture was allowed to cool to room temperature. The catalyst was then separated using an external magnet and washed with ethyl acetate followed by water. The final product was purified by column chromatography on silica gel (100-200 mesh) using a hexane/ethyl acetate (98:3) mixture.

4. Optimization data for the N-alkylation of aniline with alcohol:



Crude 1H NMR spectra of reaction mixture:

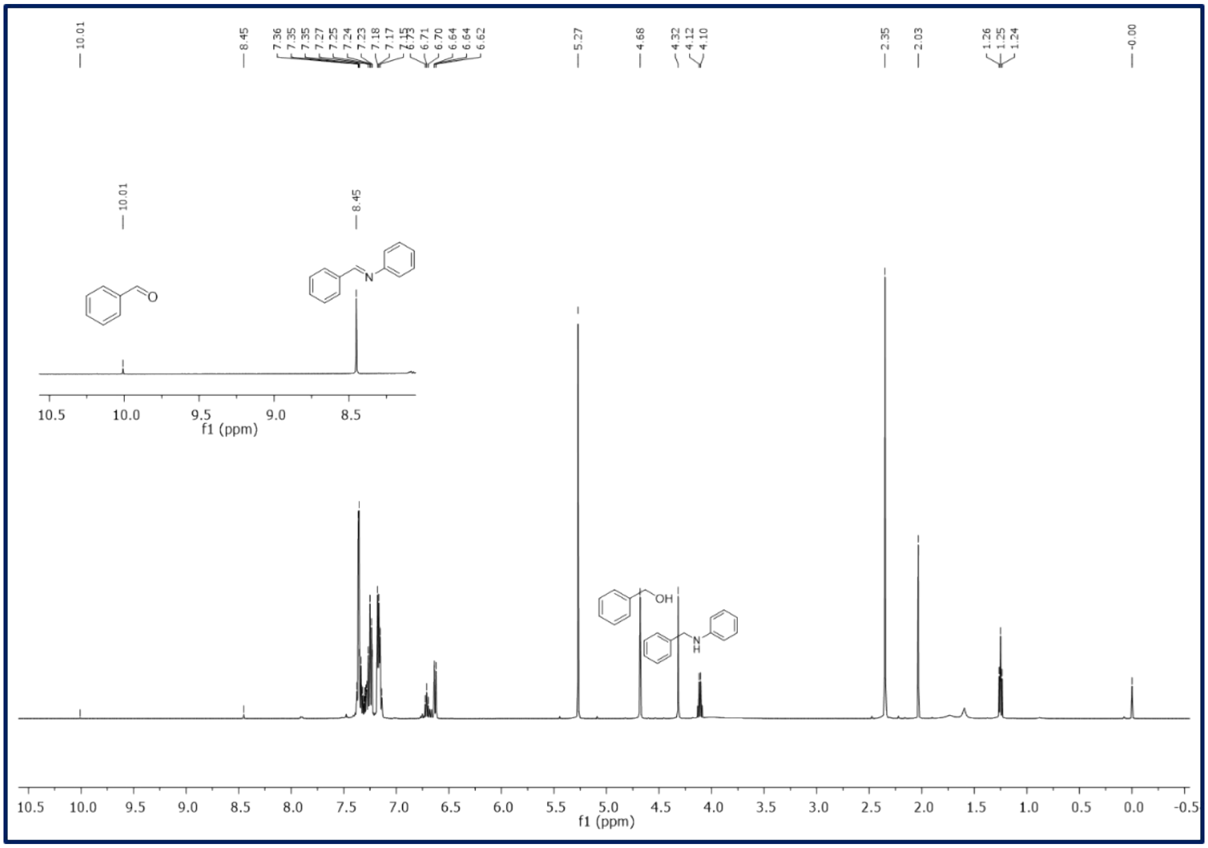


Figure 10. *Crude reaction mixture* ^{1}H *NMR*

Table S1: Screening of catalyst loading

Entry	Catalyst	Catalyst loading (wt%)	Amine **3a**(%)	Imine **3a'** (%) [c]
1	PNQ-100	50	34	10
2	PNQ-200	50	55	1
3	PNQ	50	97	3
4	PNQ	40	98	2
5	PNQ	30	97 (94)[d]	3
6	PNQ	20	71	2
7	PNQ	10	58	4
8	No catalyst	-	0	0

Reaction Conditions: [a] Benzyl alcohol (1.0 mmol), Aniline (1.5 mmol), **PNQ (X wt%)**, *t*-BuOK (1 mmol), Toluene (1 ml), 135˚C, Pressure reaction tube under argon atmosphere, 24 hrs.

Table S2: Screening of base[a]

Entry	Base	Amine **3a** (%) [c]	Imine **3a′** (%) [c]
1	t-BuOK	97	3
2	K_2CO_3	1	1
3	Na_2CO_3	2	1
4	KOH	28	11
5	NaOH	15	7
6	TEA	0	0
7	$NaHCO_3$	0	0
8	Cs_2CO_3	0	0
9	No Base	0	0

Reaction Conditions: [a] Benzyl alcohol (1.0 mmol), Aniline (1.5 mmol), PNQ (30 wt%), **base (1.0 mmol),** Toluene (1.0 ml), 135˚C, Pressure reaction tube under argon atmosphere, 24 hours.

Table S3: Screening of time [a]

Entry	Time (Hrs)	Amine **3a** (%) c]	Imine **3a′** (%) [c]
1	12	33	8
2	18	73	9
3	24	99	1

Reaction Conditions: [a] Benzyl alcohol (1.0 mmol), Aniline (1.5 mmol), PNQ (30 wt%), t-BuOK (0.8 mmol), Toluene (1 ml), 135˚C, Pressure reaction tube under argon atmosphere. [c] Determined via GC.

Table S4: Screening of *t*-BuOK Loading[a]

Entry	t-BuOK Loading (equiv.)	Amine **3a**(%) [c]	Imine **3a′**(%)
1	1.2	87	0.6
2	1.0	99	1
3	0.8	97	3
4	0.6	73	trace
5	0.5	65	2

Reaction Conditions: [a] Benzyl alcohol (1.0 mmol), Aniline (1.5 mmol), PNQ (30 wt%), t-BuOK (**X equiv.**), Toluene (1 ml), 135 ˚C, Pressure reaction tube under argon atmosphere, 24 hours. [c] Determined via GC.

Table S5: Screening of solvent[a]

Entry	Solvents	Amine **3a**(%) [c]	Imine **3a′**(%)[c]
	No Solvent	0	0
1	DMF	0	0
2	1,4-Dioxane	21	28
3	Toluene	99	1
4	Chloroform	0	0
5	m-xylene	63	4
6	THF	0	0
7	DMSO	0	0
8	*i*-PrOH	0	0

Reaction Conditions: [a] Benzyl alcohol (1.0 mmol), Aniline (1.5 mmol), PNQ (30 wt%), *t*-BuOK (0.8 mmol), **Solvent (1 ml)**, 135˚C, Pressure reaction tube under argon atmosphere, 24 hours.

Table S6: Screening of temperature [a]

Entry	Temperature (°C)	Amine **3a**(%)[c][%]
1	100	8
2	115	19
3	125	37
4	135	99

Reaction Conditions: [a] Benzyl alcohol (1.0 mmol), Aniline (1.5mmol), PNQ (30 wt%), t-BuOK (0.8 mmol), Toluene (1.0 ml),135 ˚C, Pressure reaction tube under argon atmosphere, 24 hours. [c] Determined via GC

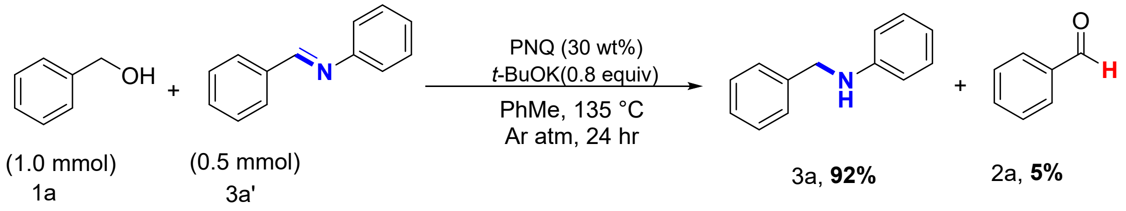
Table S7: Optimization of Substrate ratio [a]

Entry	Benzyl alcohol [mmol]	Aniline [mmol]	Amine **3a**(%)[c] [%]
1	1.0	1.5	97
2	1.0	1.2	93
3	1.0	1.0	78
4	1.2	1.0	63

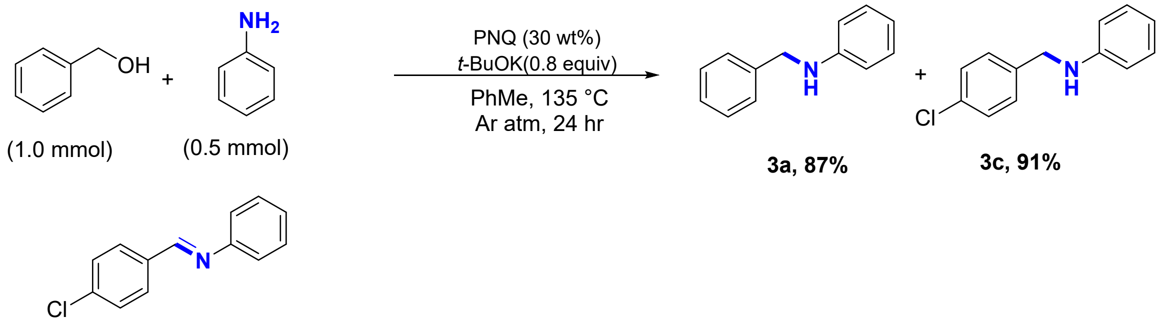
Reaction Conditions: [a] Benzyl alcohol (1.0 mmol), Aniline (X), PNQ (30 wt%), t-BuOK (0.8 mmol), Toluene (1.0 ml),135 ˚C, Pressure reaction tube under argon atmosphere, 24 hours. [c] Determined via GC

5. Controlled Reaction

Procedure: Benzyl alcohol (1.0mmol), imine (0.5 mmol), PNQ catalyst (30 wt%) with respect to benzyl alcohol, t-BuOK (0.8 mmol) and toluene (1ml) were added to a pressure reaction tube and was placed in a pre-heated oil bath at 135 °C with stirring for 24 hr.



Procedure: A controlled N-alkylation reaction was set up (following general procedure A) with benzyl alcohol (1.0 mmol), 1-(4-chlorophenyl)-N-phenylmethanimine (0.5 mmol),aniline (1.5 mmol), PNQ catalyst (30 wt%), t-BuOK (0.8 mmol) and toluene (1ml) in a pressure reaction tube purged with argon gas and kept at 135˚C in a preheated oil bath for 24 hours.



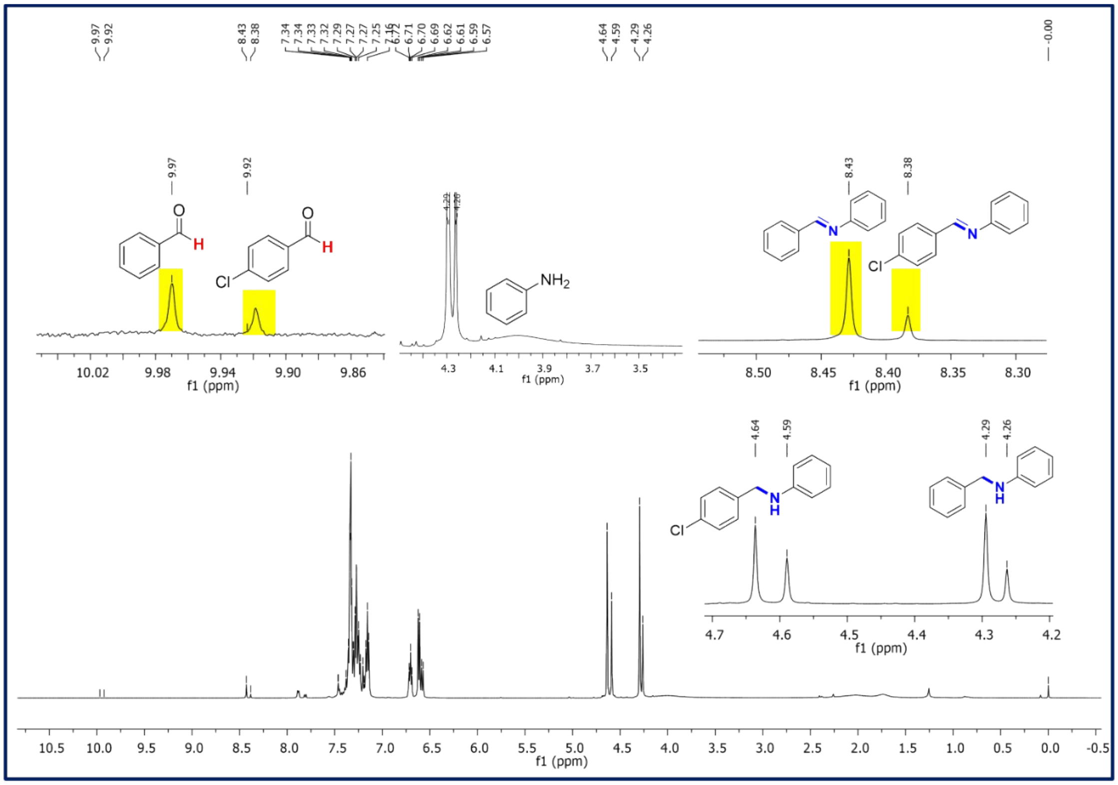


Figure 11. *Crude reaction mixture ^1H NMR*

6. Recyclability test of Polynapthoquinone catalyst

The catalyst was filtered and washed several times with ethyl acetate and dried at 100˚C in oven. The above model reaction was chosen to investigate the recyclability of polynapthoquinone (PNQ) catalyst. A oven dried 15 ml pressure tube reaction was loaded with magnetic stirring bar, polynapthoquinone catalyst, *t*-BuOK (90 mg, 0.8 mmol), benzyl alcohol (104 μL, 1.0 mmol), aniline (137 μL, 1.5 mmol) was loaded in an oven dried 15ml PTFE pressure reaction tube followed by 1 ml of toluene as a solvent respectively at room temperature under inert atmosphere. The sealed tube was kept in a pre-heated oil bath at 135 °C with constant stirring for 24 hours and then cooled down to room temperature. The reaction mixture was analysed by gas chromatography**.**

Table S8: Recyclability Test [a]

Entry	Catalytic cycle	Yield [c] [%]
1	1	99
2	2	97
3	3	97
4	4	96
5	5	91

6	6	87
7	7	58

Reaction Conditions: [a] Benzyl alcohol (1.0 mmol), Aniline (1.5 mmol), PNQ (30 wt%), t-BuOK (0.8 mmol), Toluene (1.0 ml), 135 ˚C, Pressure reaction tube under argon atmosphere, 24 hours. [c] Determined via GC

6. Hot filtration test

A standard N-alkylation reaction between anilines and benzyl alcohol was carried out at 135 °C for 10 hr. The catalyst was separated from the hot reaction mixture by using filtration method and the reaction was continued for additional 14 hr. No increase in yield was observed.

Table S9:

Catalyst	Time (Hr)	GC Yield [%]
Polynapthoquinone(PNQ)	12	40
-	12+12	42

7.0 Course of reaction

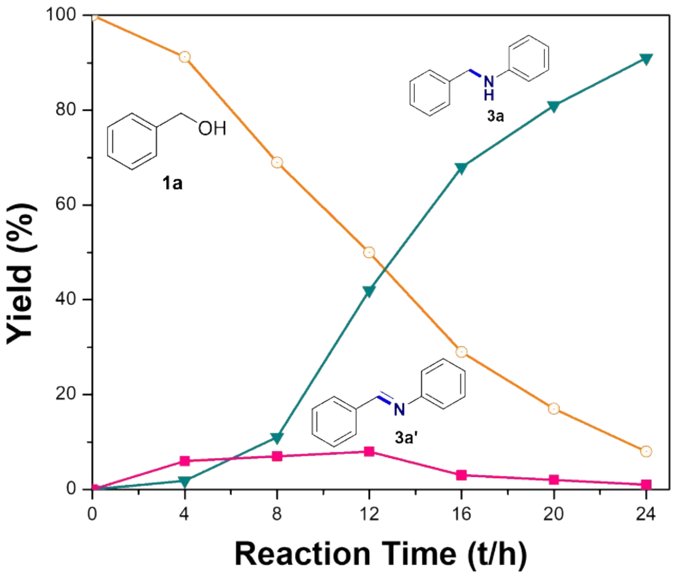
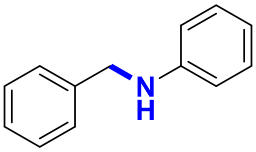
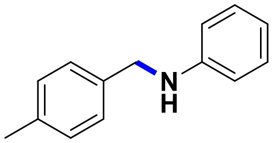
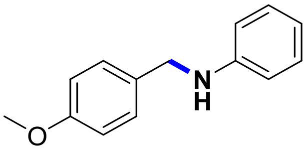
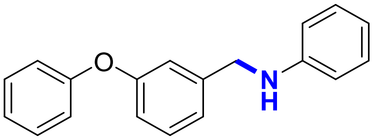
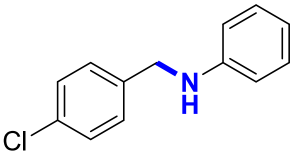
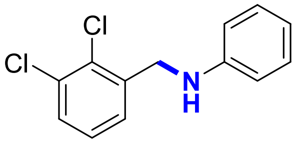
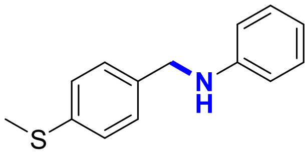
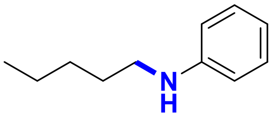
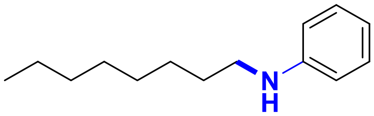
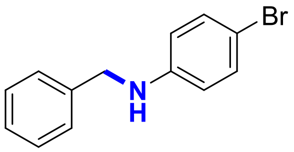
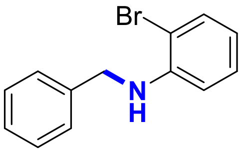
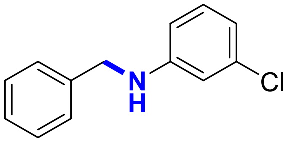
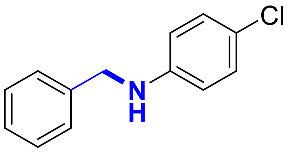
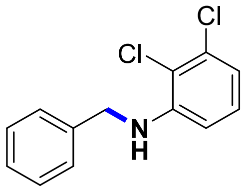
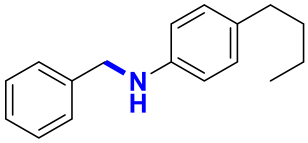
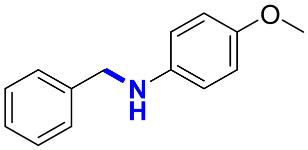
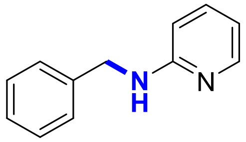
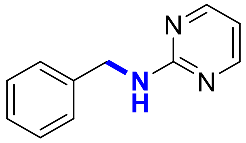
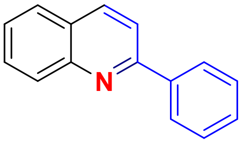


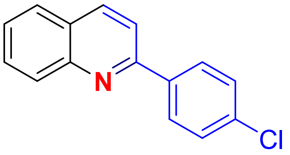
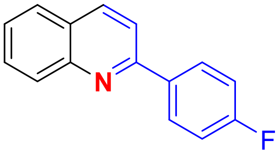
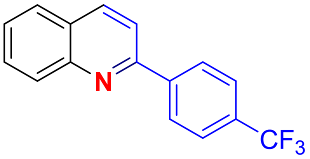
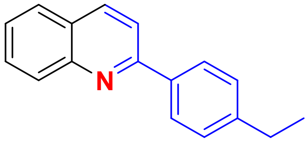
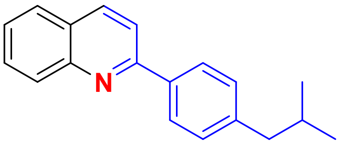
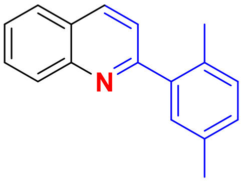
Figure 12. Yields of unreacted benzyl alcohol (1a), amine (3a), imine(3a') for N-alkylation by polynapthoquinone at 135 ˚C

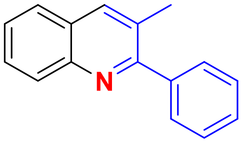
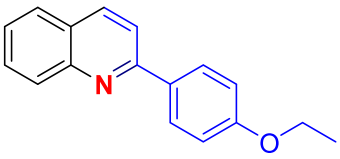
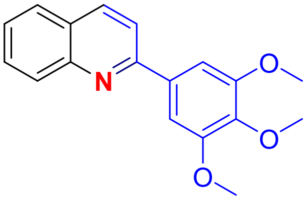
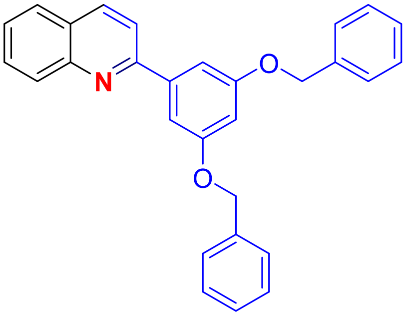
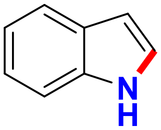
7.0 Characterization data:

	The product **N-Benzylaniline**[8] **(3a)** was obtained as a yellow liquid according to general procedure (95% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, J = 19.8, 7.2 Hz, 4H), 7.27 (d, J = 6.7 Hz, 1H), 7.17 (t, J = 7.5 Hz, 2H), 6.71 (t, J = 7.2 Hz, 1H), 6.63 (d, J = 7.7 Hz, 2H), 4.32 (s, 2H), 3.24 (s, 1H).; ^{13}C NMR (126 MHz, CDCl3) δ 148.34, 139.64, 129.55, 128.91, 127.81, 127.52, 117.90, 113.18, 48.62.
	The product **N-(4-methylbenzyl)aniline**[9] **(3b)** was obtained as a yellow liquid according to general procedure (91% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.26 (t,J = 7.1 Hz, 2H), 7.20 – 7.15 (m, 4H), 6.74 – 6.72 (m, 1H), 6.71–6.63 (m, 2H), 4.292 (s, 2H), 4.00 (s, 1H), 2.36 (s, 3H).; 13C NMR (126 MHz, CDCl3) δ 148.31, 136.99, 136.46, 129.42, 129.37, 127.65, 117.62, 112.96, 48.2, 21.2
	The product **N-(4-methoxybenzyl)aniline**[10] **(3c)** was obtained as a yellow liquid according to general procedure (167 mg, 98% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, J = 8.7 Hz, 2H), 7.22 (dd,J=8.5, 7.4 Hz 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.67 – 6.60 (m, 2H), 4.24 (s, 2H), 3.79 (s, 3H), 3.03 (s, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.89, 148.19, 131.40, 129.28, 128.86, 117.58, 114.05, 112.91, 55.35, 47.86.
	The product **N-(3-phenoxybenzyl)aniline**[11] **(3d)** was obtained as a yellow liquid according to general procedure (87% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 3H), 7.19 – 7.12 (m, 2H), 7.12 – 7.05 (m, 2H), 7.06 – 6.93 (m, 3H), 6.89 (dd, J = 8.1, 2.0 Hz, 1H), 6.71 (dd, J = 10.6, 4.1 Hz, 1H), 6.60 (dd, J = 8.5, 0.9 Hz, 2H), 4.29 (s, 2H), 4.04 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.56 , 157.01, 147.91 , 141.63, 129.9, 129.75, 129.25, 123.30, 122.14, 118.93, 117.70, 117.65, 117.47 , 112.89, 48.02.
	The product **N-(4-chlorobenzyl)aniline**[10] **(3e)** was obtained as a yellow liquid according to the general procedure (84% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.4 – 7.35 (m, 1H), 7.32-7.3 (s, 3H), 7.22 – 7.18 (m, 2H), 6.77 – 6.73 (m, 1H), 6.64 – 6.61(m, 2H), 4.32 (s, 2H), 4.06 (br, 1H); 13C NMR (126 MHz, $CDCl_3$) δ 147.9, 138.1, 132.9, 129.4, 128.82, 127.6, 117.9, 113.0, 47.7.
	The product **N-(2,3-dichlorobenzyl)aniline (3f)** was obtained as a yellow liquid according to the general procedure (81% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, J = 8.6 Hz, 1H), 7.22 – 7.15 (m, 2H), 6.90 – 6.84(m, 2H), 6.72 (dd, J = 10.6, 4.1 Hz, 1H), 6.63 (dd, J = 8.5, 0.9 Hz, 2H), 4.24 (s, 1H), 3.79 (s, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 158.90, 148.24, 131.44, 129.29, 128.86, 117.55, 114.06, 112.87, 29.75.

	The product **N-(4-(methylthio)benzyl)aniline[10] (3g)** was obtained as a yellow liquid according to the general procedure (87% yield); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.25-7.22 (dd, J = 27.9, 8.3 Hz, 4H), 7.17 (dd, J = 8.3, 7.5 Hz, 2H), 6.70-6.73 (t, J = 7.3 Hz,1H), 6.61-6.63 (d, J = 7.7 Hz, 2H), 4.28 (s, 1H), 4.01 (s, 1H), 2.47 (s, 3H).;13C NMR (126 MHz, CDCl$_3$) δ 148.03, 137.14, 136.38, 129.27, 128.02, 126.95, 117.61, 112.85, 47.87,16.04.
	The product **N-pentylaniline[12] (3h)** was obtained as a yellow liquid according to the general procedure (167 mg, 73% yield); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.17-7.14 (dd, J = 8.5, 7.4 Hz, 2H), 6.67 (s, 1H), 6.60-6.58 (dd, J = 8.6, 1.0 Hz, 2H), 3.51 (s,1H), 3.08 (t, J = 7.2 Hz, 2H), 1.62 (dt, J = 11.8, 7.4 Hz, 2H), 1.24 (s, 4H), 0.93 – 0.87 (m,3H).;^{13}C NMR (126 MHz, CDCl3) δ 129.27, 117.18, 112.78, 44.06, 29.75, 29.39, 29.29, 22.56, 14.09.
	The product **N-octylaniline[13] (3i)** was obtained as a yellow liquid according to the general procedure (79% yield); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.17-7.14 (t, J = 7.6 Hz, 2H), 6.68-6.65 (t, J = 7.3 Hz, 1H), 6.59 (d, J = 8.1 Hz, 2H), 3.52-3.49 (t,J = 6.6 Hz, 1H), 3.09-3.06 (t, J = 7.1 Hz, 2H), 1.61 (m, 2H), 1.30 – 1.26 (m, 10H), 0.87 (t,J = 5.7 Hz, 3H).^{13}C NMR (126 MHz, CDCl$_3$) δ 148.58, 129.26, 117.11, 112.72, 44.04, 31.88, 29.75, 29.62, 29.47, 29.32, 27.23, 22.71, 14.16.
	The product **N-benzyl-4-bromoaniline[14] (3j)** was obtained as a yellow liquid according to the general procedure (65% yield); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39- 7.33 (m, 5H), 7.28 (d, J = 6.2 Hz, 2H), 6.54 (d, J = 8.0 Hz, 2H), 4.34 (s, 2H), 3.65 (s,br, 1H).; 13C NMR (126 MHz, CDCl$_3$) δ 147.03, 138.85, 131.95, 128.72, 127.42, 114.46, 109.15, 48.24.
	The product **N-benzyl-2-bromoaniline[15] (3k)** was obtained as a yellow liquid according to the general procedure (64% yield); The desired product was obtained as a yellow liquid (219 mg, 84% yield); 1 HNMR (500 MHz, CDCl$_3$) δ 7.43 (dd, J = 7.9, 1.5 Hz, 1H), 7.38 – 7.32 (m, 4H), 7.31 – 7.26 (m, 1H), 7.15 –7.10 (m, 1H), 6.63 – 6.53 (m, 2H), 4.76 (s, 1H), 4.40 (s, 2H).; 13CNMR (126 MHz, CDCl$_3$) δ 144.80, 138.70, 132.40, 128.75, 128.51, 127.37, 127.25, 117.98, 111.63, 109.68, 48.01.
	The product **N-benzyl-3-chloroaniline [11](3l)** was obtained as a yellow liquid according to general procedure (87% yield); 1H NMR (500 MHz, CDCl$_3$) δ 7.33 (s, 4H), 7.28 (s, 1H), 7.05 (t, J = 7.7 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H), 6.60 (s, 1H), 6.47 (d, J = 8.0 Hz, 1H), 4.29 (s, 2H), 2.71 (s, 1H).; 13C NMR (126 MHz, CDCl$_3$) δ 146.64, 138.95, 129.11, 128.75, 127.47, 127.42, 122.16, 114.00, 48.38.
	The product **N-benzyl-4-chloroaniline[16] (3m)** was obtained as a yellow liquid according to general procedure (93% yield); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.38 – 7.28 (m, 5H), 7.15 (d, J = 8.1 Hz, 2H), 6.59 (d, J = 8.1 Hz, 2H), 4.34 (s, 2H), 3.64 (s, 1H).; ^{13}C NMR (126 MHz, CDCl$_3$) δ 146.63, 138.94, 129.12, 128.76, 127.5, 127.4, 122.2, 114.01, 48.40.

	The product **N-benzyl-2, 3-dichloroaniline[17] (3n)** was obtained as a yellow liquid according to general procedure (84% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H), 6.99 (t, J = 8.1 Hz, 1H), 6.79 (dd, J = 8.0, 1.3 Hz, 1H), 6.51 (dd, J = 8.3, 1.3 Hz, 1H), 4.90 (s, 1H), 4.40 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.32, 138.27, 132.89, 128.83 (s), 127.76, 127.53, 127.23, 118.16, 117.17, 109.40, 47.99.
	The product **N-benzyl-4-butylaniline[16] (3o)** was obtained as a yellow liquid according to general procedure (89% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 5H), 6.98 (d, J = 8.5 Hz, 2H), 6.61 – 6.55 (m, 2H), 4.30 (s, 2H), 3.97 (s, 1H), 2.53 – 2.46 (m, 2H), 1.56 – 1.51 (m, 2H), 1.36 – 1.31 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.06, 139.63, 132.13, 129.15, 128.62, 127.59, 127.20, 112.94 , 48.71, 34.74, 34.03, 22.36, 14.02.
	The product **N-benzyl-4-methoxyaniline[18] (3p)** was obtained as a brown solid according to general procedure (83% yield, m.p. 48-50 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.30(m, 4H), 7.29 – 7.20 (m, 1H), 6.84-6.72 (d,2H), 6.64 – 6.55 (d,2H), 4.27(s, 2H), 3.92 (br, 1H),3.73(s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.20, 142.47, 139.70, 128.64, 127.59, 127.22, 114.92, 114.15, 55.83,49.27.
	The product **N-benzylpyridin-2-amine[19] (3q)** was obtained as a colourless crystalline solid according to general procedure (145 mg, 79% yield, m.p. 94-95 ºC);^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.41 – 7.32 (m, 6H), 6.59 (ddd, *J* = 7.1, 5.0, 0.9 Hz, 1H), 6.37 (d, *J* = 8.4 Hz, 1H), 4.90 (s, 1H), 4.50 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.56, 148.06, 139.11, 137.59, 128.67, 127.41, 127.28, 113.19, 106.88, 46.35.
	The product **N-benzylpyrimidin-2-amine[20] (3r)** was obtained as a colourless liquid according to general procedure (118 mg, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 2.3 Hz, 2H), 7.25 (m, 5H), 6.45 (t, *J* = 4.8 Hz, 1H), 5.77 (s, 1H), 4.56 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.29, 158.07, 139.08, 128.62, 127.55, 127.26, 126.99, 110.75, 45.46.
	The product **2-phenylquinoline[21] (6a)** was obtained as colourless solid according to general procedure (186 mg, 91% yield, m.p. 84-85 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 – 8.19 (m, 4H), 7.89 (d, J = 8.6 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 8.4, 6.9, 1.4 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.48 (dd, J = 4.8, 3.7 Hz, 1H).;^{13}C NMR (126 MHz, $CDCl_3$) δ 157.41, 148.31, 139.72, 136.80, 129.76, 129.68, 129.33, 128.86, 127.60, 127.47, 127.21, 126.30, 119.05.

	The product **2-(4-chlorophenyl)quinoline[21] (6b)** was obtained as a colourless solid according to general procedure (186 mg, 78% yield, m.p. 111-112 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.24 (d, J = 8.6 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 8.14 – 8.11 (m, 2H), 7.84 (dd, J = 10.2, 4.8 Hz, 2H), 7.74 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.54 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 7.52 – 7.48 (m, 2H).^{13}C NMR (126 MHz, CDCl$_3$) δ 156.06, 148.24, 138.07, 137.01, 135.56, 129.88, 129.70, 129.05, 128.84, 127.51, 127.24, 126.53, 118.62.
	The product **2-(4-fluorophenyl)quinoline[22] (6c)** was obtained as a colourless solid according to general procedure (166 mg, 75% yield, m.p. 95-96 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.23 (d, J = 8.6 Hz, 1H), 8.16 (ddd, J = 8.8, 4.5, 2.5 Hz, 3H), 7.84 (d, J = 8.6 Hz, 2H), 7.74 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.24 – 7.18 (m, 2H).^{13}C NMR (126 MHz, CDCl$_3$) δ 163.75 (d, J$_{C-F}$ = 249.0 Hz) 155.26, 147.14, 135.95,134.76 (d, J$_{C-F}$ = 2.5 Hz) 128.80, 128.53, 128.43 (t, J$_{C-F}$ = 8.8 Hz), 126.46, 126.04, 125.34, 117.67, 114.84 (d, J$_{C-F}$ = 21.4 Hz).
	The product **2-(4-(trifluoromethyl)phenyl)quinoline[23] (6d)** was obtained as a yellow liquid according to general procedure (199 mg, 73% yield, m.p. 124-126 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.46 (s, 1H), 8.36 (d, J = 7.7 Hz, 1H), 8.28 (d, J = 8.5 Hz, 1H), 8.19 (d, J = 8.5 Hz, 1H), 7.88 (dd, J = 21.6, 8.3 Hz, 2H), 7.77 (t, J = 7.7 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H).^{13}C NMR (126 MHz, CDCl$_3$) δ 155.63, 148.26, 140.38, 137.22, 130.02 (q, J$_{C-F}$ = 25.4 Hz), 129.82, 129.34, 127.54, 127.40, 126.81, 125.93, 124.43 (q, J$_{C-F}$ = 188.7 Hz), 118.64.
	The product **2-(4-ethylphenyl)[24](6e)** was obtained as a colourless solid according to general procedure (197 mg, 84% yield, m.p. 47-49 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.21 (d, J = 8.6 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 8.11 – 8.06 (m, 2H), 7.87 (d, J = 8.6 Hz, 1H), 7.82 (dd, J = 8.1, 1.1 Hz, 1H), 7.72 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.52 (td, J = 6.9, 3.4 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H), 2.74 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H).^{13}C NMR (126 MHz, CDCl$_3$) δ 157.45, 148.31, 145.78, 137.17, 136.70, 129.67, 129.60, 128.43, 127.57, 127.46, 127.11, 126.11, 118.97, 28.75, 15.61.
	The product **2-(4-isobutylphenyl)quinoline[25] (6f)** was obtained as a colourless solid according to general procedure (238 mg, 81% yield, m.p. 55-57 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.20 (d, J = 8.6 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 8.10 – 8.05 (m, 2H), 7.87 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.72 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.51 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 7.31 (d, J = 8.2 Hz, 2H), 2.56 (d, J = 7.2 Hz, 2H), 1.99 – 1.88 (m, 1H), 0.94 (d, J = 6.6 Hz, 6H).^{13}C NMR (126 MHz, CDCl$_3$) δ 157.52, 148.32, 143.24, 137.21, 136.69, 129.69, 129.60, 127.47, 127.35, 127.11, 126.11, 119.00, 45.26, 30.30, 22.40.
	The product **2,5-dimethylphenyl)quinoline[17] (6g)** was obtained as a yellow liquid according to general procedure (218 mg, 79% yield): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.17 (d, J = 8.4 Hz, 2H), 7.83 (dd, J = 8.1, 0.9 Hz, 1H), 7.72 (ddd, J = 8.4, 7.0, 1.4 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.33 (s, 1H), 7.24 – 7.17 (m, 1H), 7.15 (dd, J = 7.8, 1.4 Hz, 1H), 2.37 (s, 3H), 2.35 (s, 3H).^{13}C NMR (126 MHz, CDCl$_3$) δ 160.48, 147.97, 140.59, 135.98, 135.51, 132.76, 130.83, 130.35, 129.63, 129.30, 127.55, 126.76,

	126.39, 122.49, 21.03, 19.91.
	The product **3-methyl-2-phenylquinoline[21] (6h)** was obtained as a Colourless solid according to general procedure (193 mg, 83% yield, m.p. 92-93 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 8.02 (s, 1H), 7.78 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.66 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.55 – 7.47 (m, 3H), 7.46 – 7.41 (m, 1H), 2.46 (d, *J* = 0.8 Hz, 3H);^{13}C NMR (126 MHz, CDCl$_3$) δ 160.57, 146.63, 140.88, 136.77, 129.30, 129.25, 128.87, 128.78, 128.34, 128.22, 127.62, 126.74, 126.44, 20.65 .
	The product **2-(4-ethoxyphenyl)quinoline[26] (6i)** was obtained as a colourless solid according to general procedure (211 mg, 85% yield, m.p. 129-131 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.14 – 7.99 (m, J = 15.6, 8.1 Hz, 4H), 7.77 – 7.67 (m, J = 13.8, 8.4 Hz, 2H), 7.61 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 6.94 (d, J = 8.1 Hz, 2H), 4.01 (q, J = 6.9 Hz, 2H), 1.36 (t, J = 6.9 Hz, 3H).^{13}C NMR (126 MHz, CDCl$_3$) δ 160.21, 156.99, 148.30, 136.65, 132.08, 129.59, 129.52, 128.90, 127.47, 126.91, 125.91, 118.59, 114.77, 63.58, 14.86.
	The product **2-(3,4,5-trimethoxyphenyl)quinoline[22] (6j)** was obtained as a colourless solid according to general procedure (381 mg, 86% yield, m.p. 84-86 °C); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.20 (dd, *J* = 23.7, 8.5 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.40 (s, 2H), 4.01 (s, 6H), 3.93 (s, 3H).^{13}C NMR (126 MHz, CDCl$_3$) δ 157.01, 153.59, 148.11, 139.43, 136.88, 135.29, 129.81, 129.58, 127.49, 127.14, 126.34, 118.93, 104.84, 60.98, 50.29.
	The product **2-(3,5-bis(benzyloxy)phenyl)quinoline[17] (6k)** was obtained as colourless solid according to general procedure (370 mg, 89% yield, m.p. 105-107 °C); 1H NMR (500 MHz, CDCl$_3$) δ 8.18 (s, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.72 (t, J = 7.7 Hz, 1H), 7.57 – 7.43 (m, 7H), 7.39 (d, J = 7.4 Hz, 4H), 7.34 (d, J = 7.4 Hz, 2H), 6.73 (s, 1H), 5.15 (s, 4H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 160.39, 156.98, 148.15, 141.86, 136.86, 129.78, 129.74, 128.67, 128.11, 127.75, 127.66, 127.51, 127.39, 126.45 , 119.15, 106.88 , 103.16 , 70.30.
	The product **1H-indole[16] (8a)** was obtained as colourless solid crystal (103 mg, 88% yield, m.p. 52- 54 °C); 1H NMR (500 MHz, CDCl3) δ 8.04 (s,br, 1H), 7.65 (d, J = 7.9, 0.8 Hz, 1H), 7.36 (dd, J = 8.1, 0.8 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.17 – 7.15 (m, 1H), 7.13 – 7.10 (m, 1H), 6.55 (ddd, J = 3.1, 2.0, 0.9 Hz, 1H).;13C NMR (126 MHz, CDCl3) δ 135.80, 127.88, 124.18,122.02, 120.78, 119.86, 111.07 , 102.64 .

8.0 References

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2. Y. Iwasawa, H. Nobe and S. Ogasawara, *J. Catal.*, 1973, **31**, 444-449.
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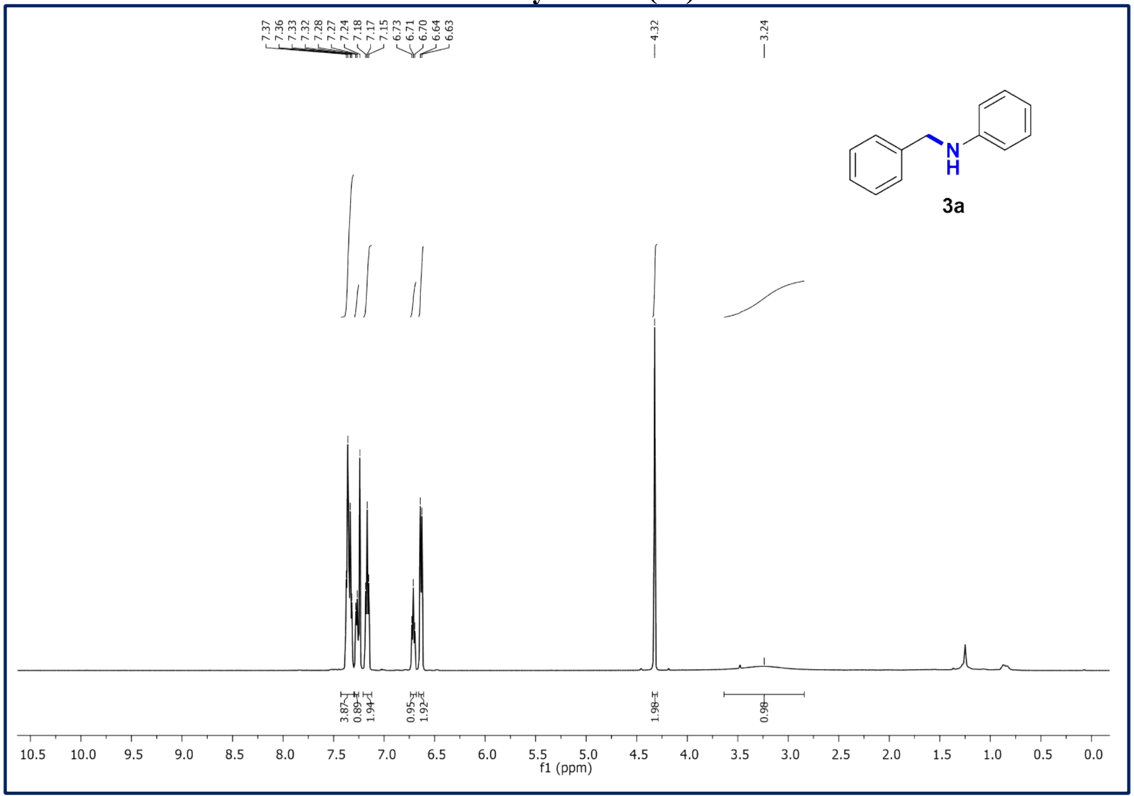
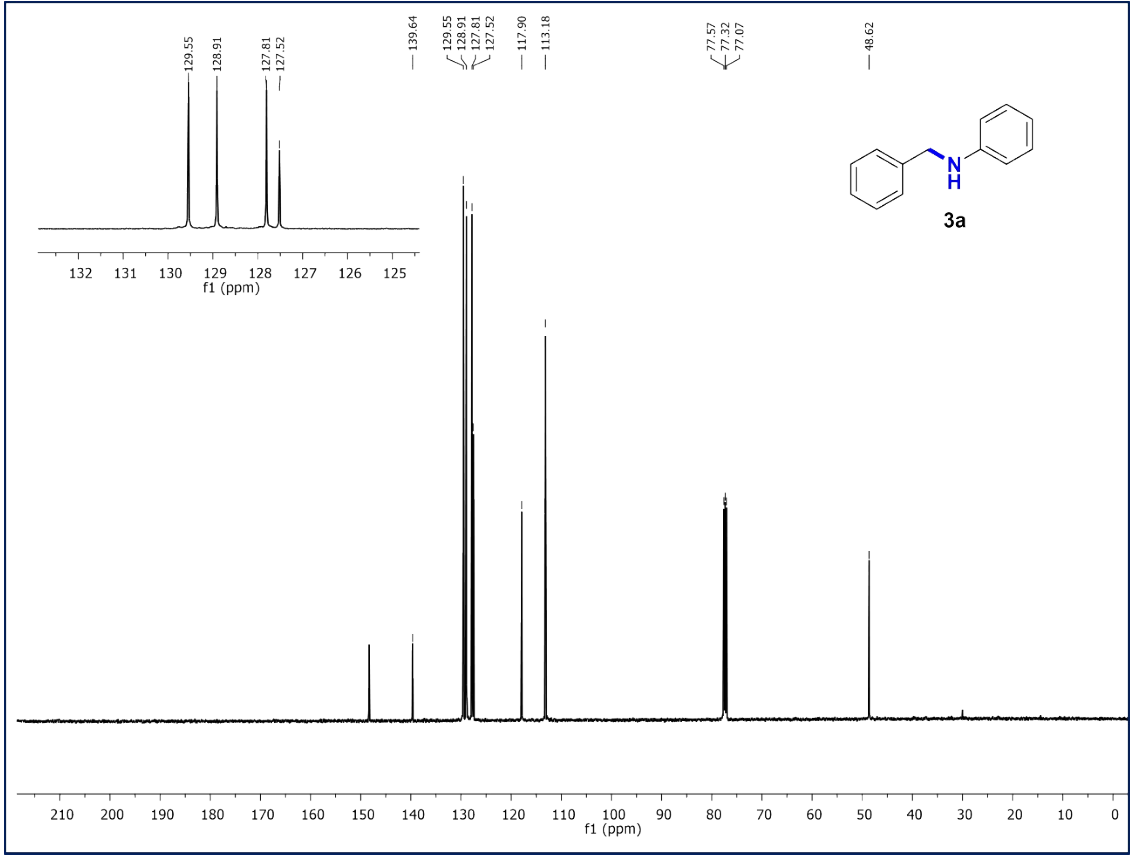
^{1}H and ^{13}C NMR Spectra of Compounds

N-Benzylaniline (3a)





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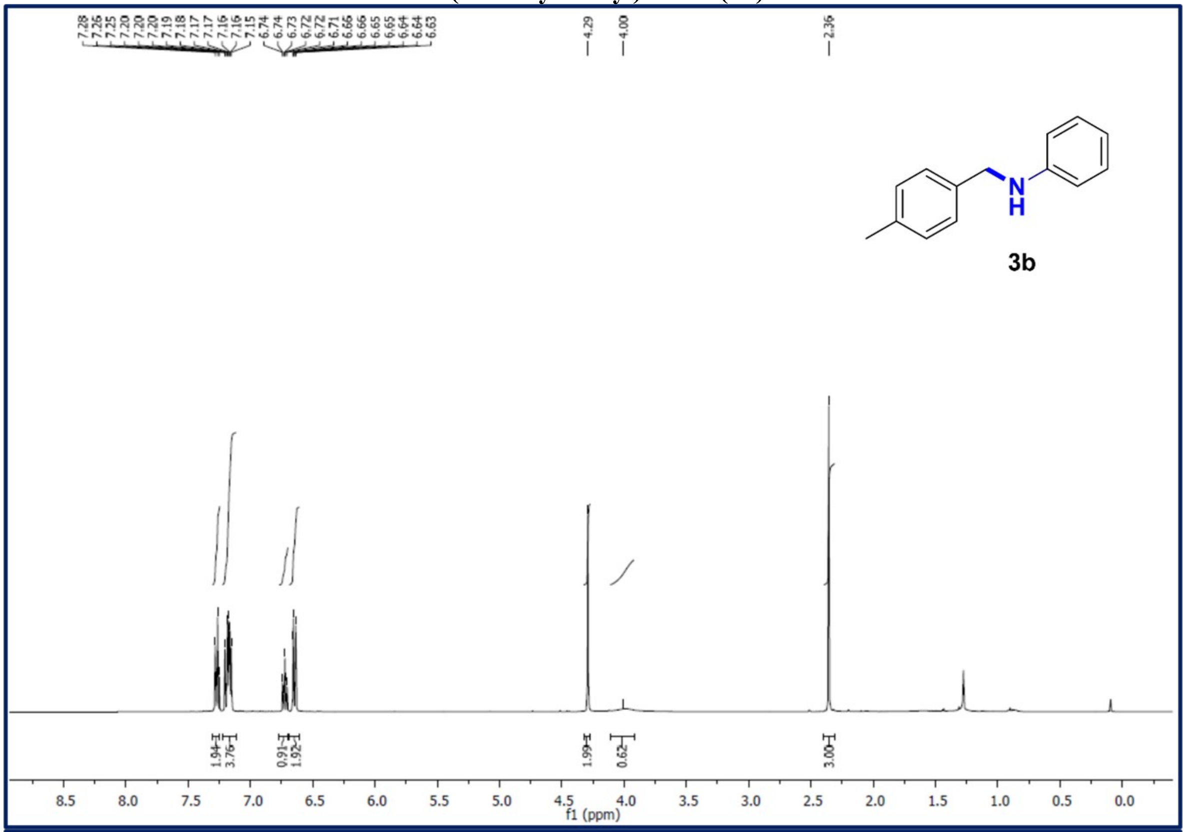

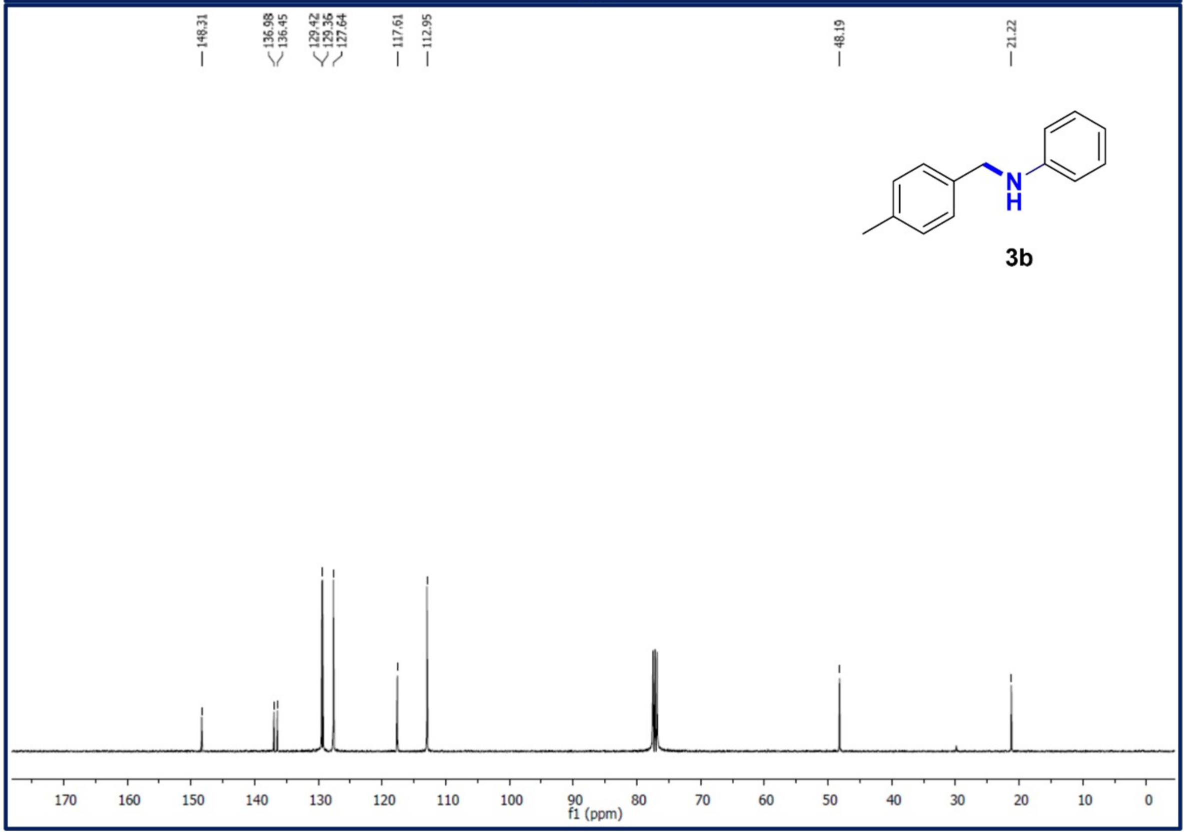

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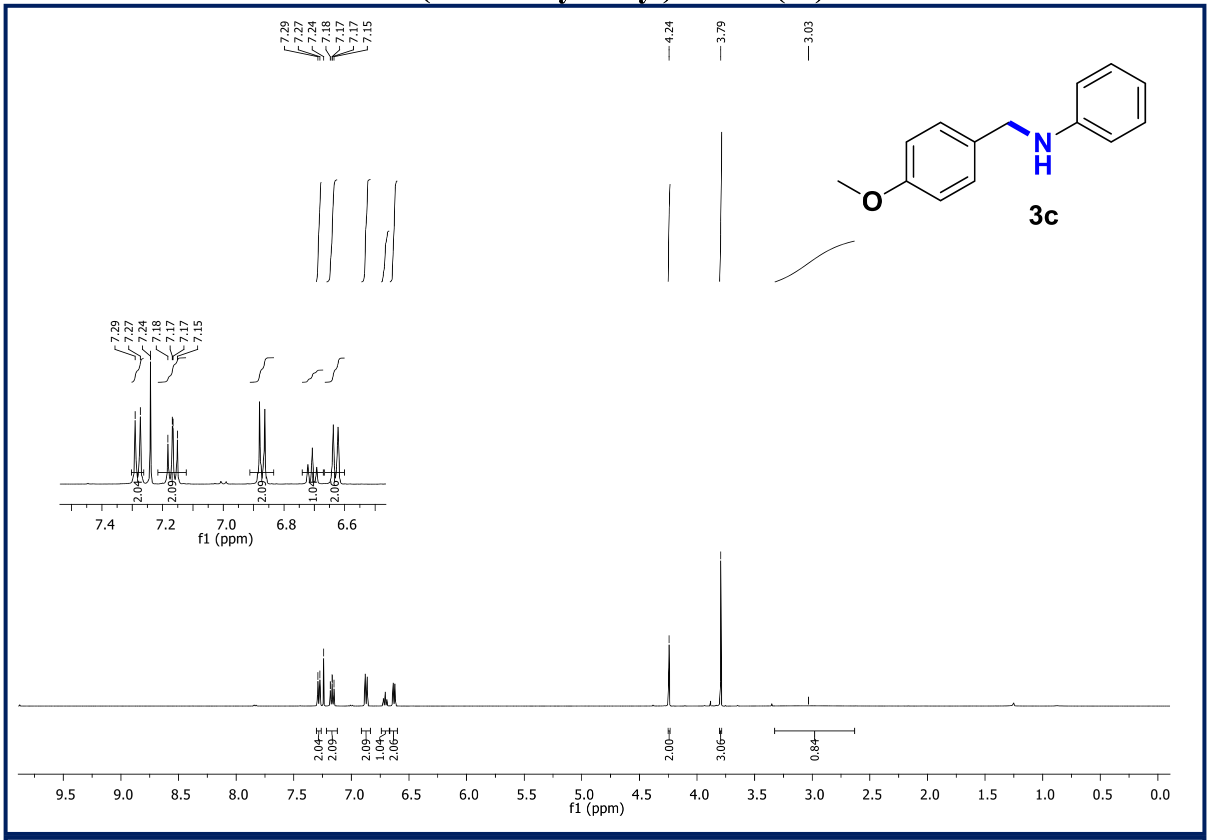

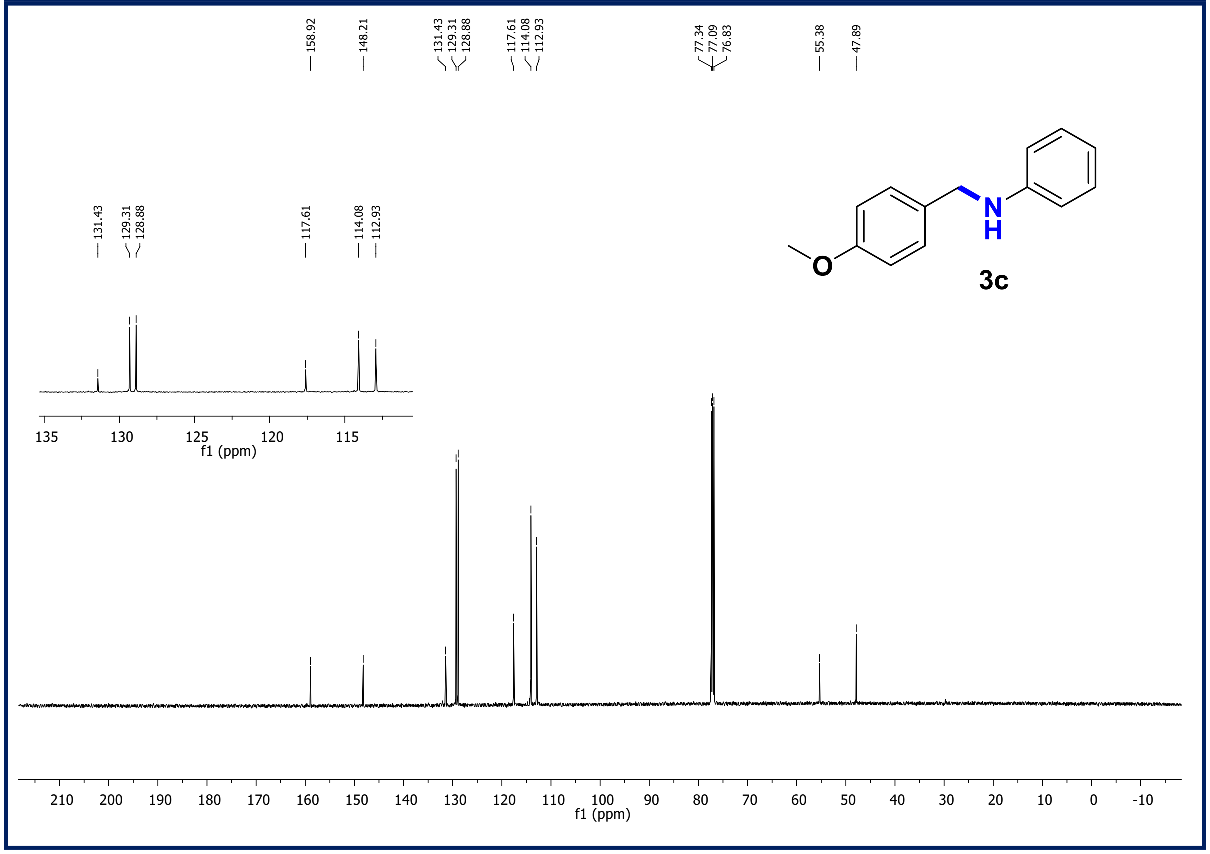

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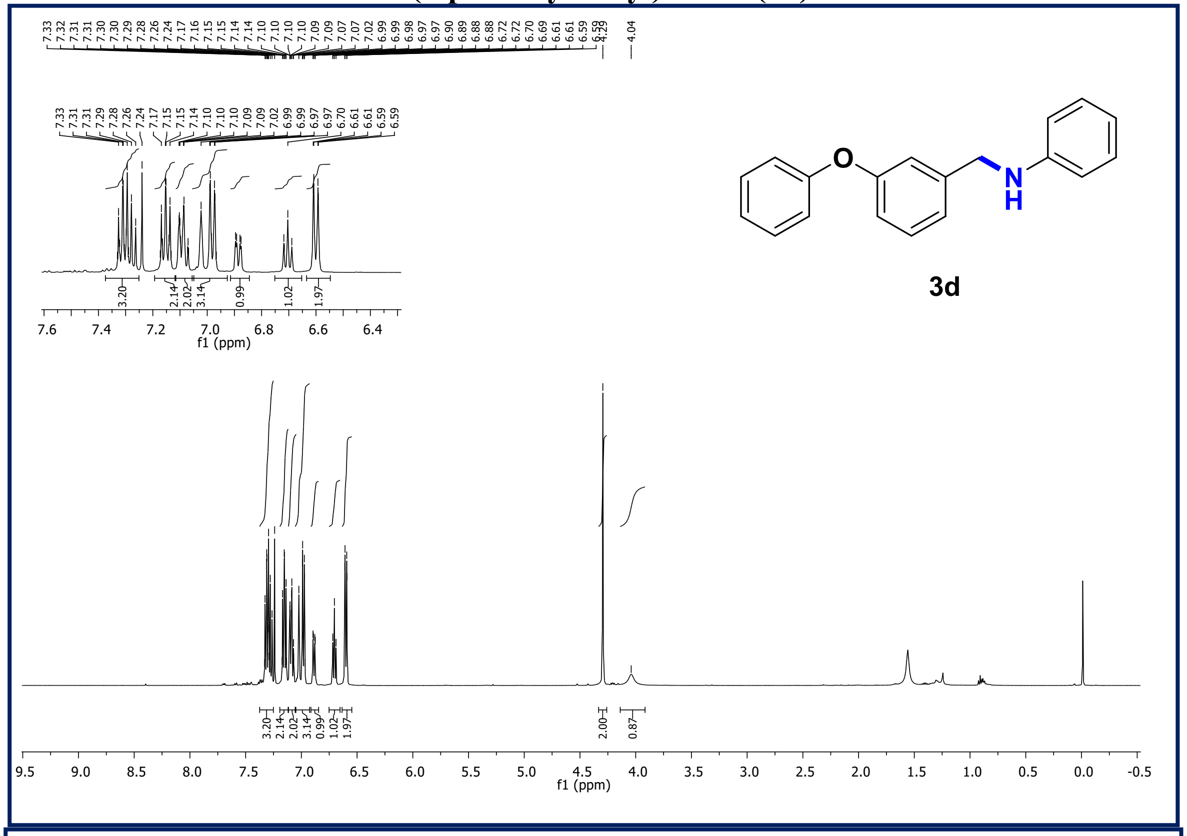

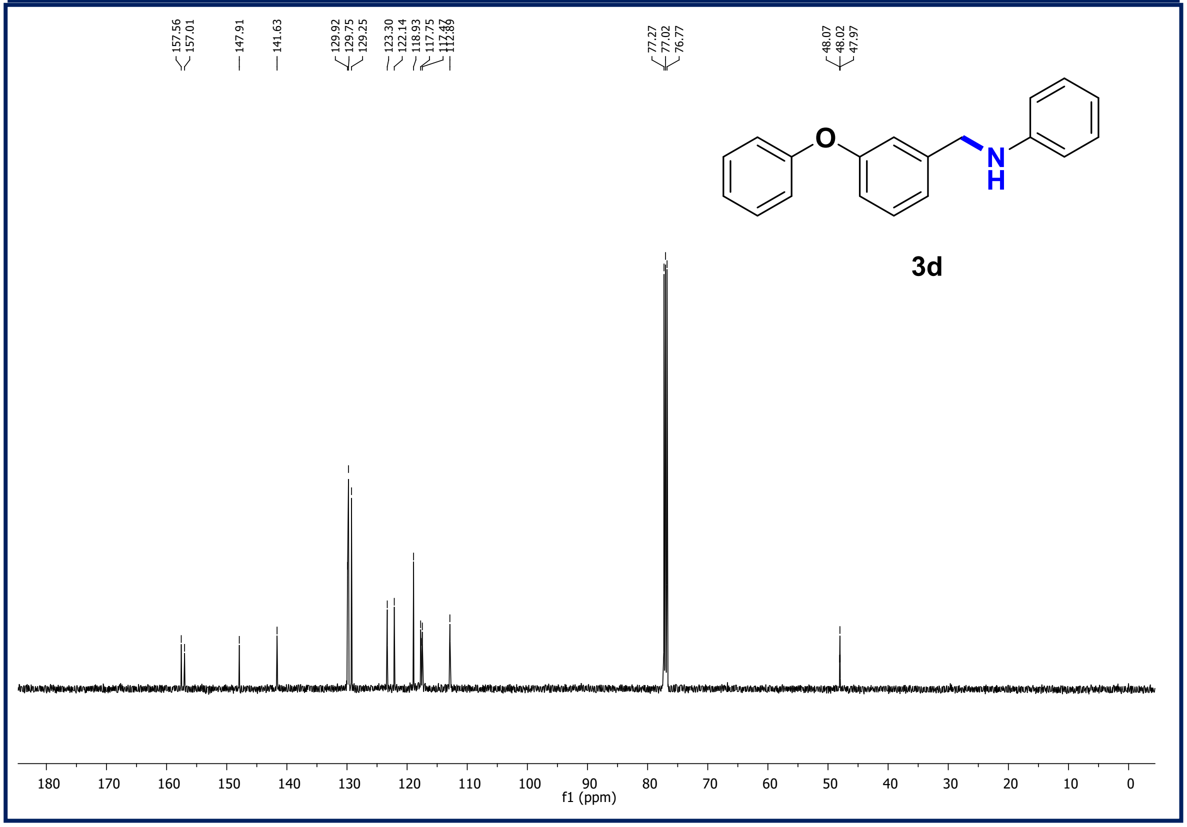

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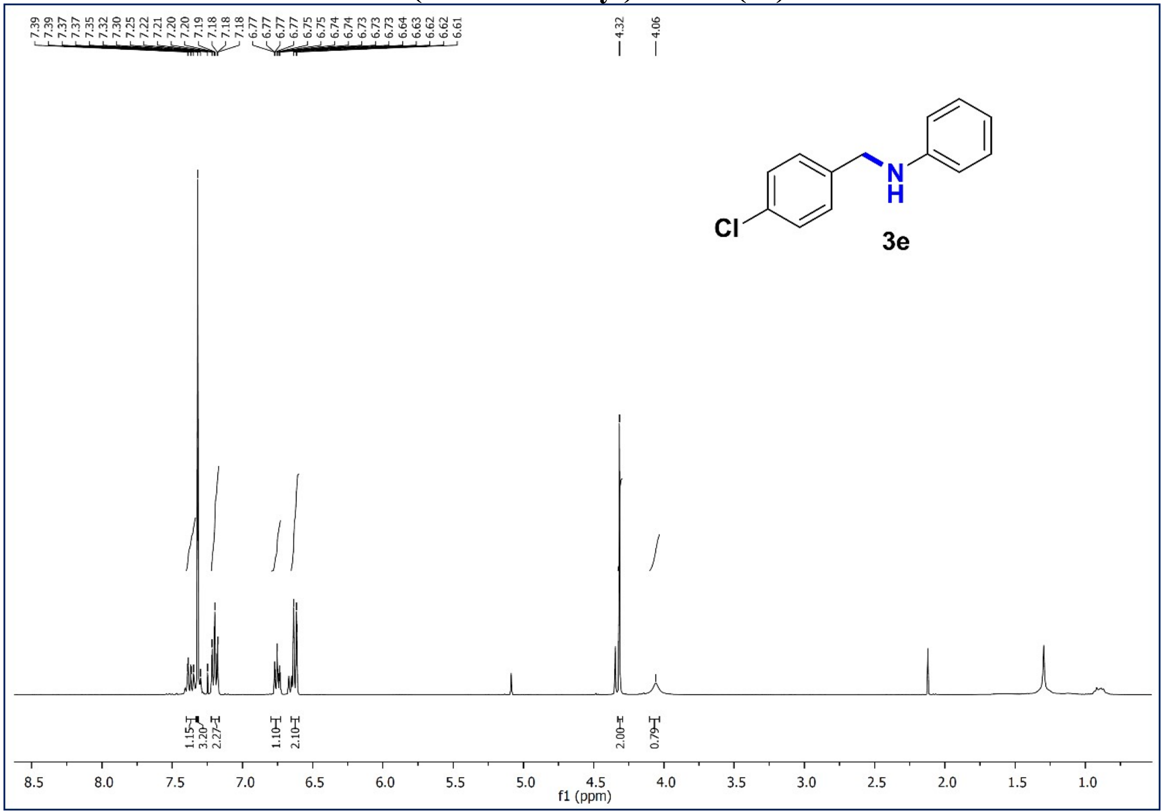

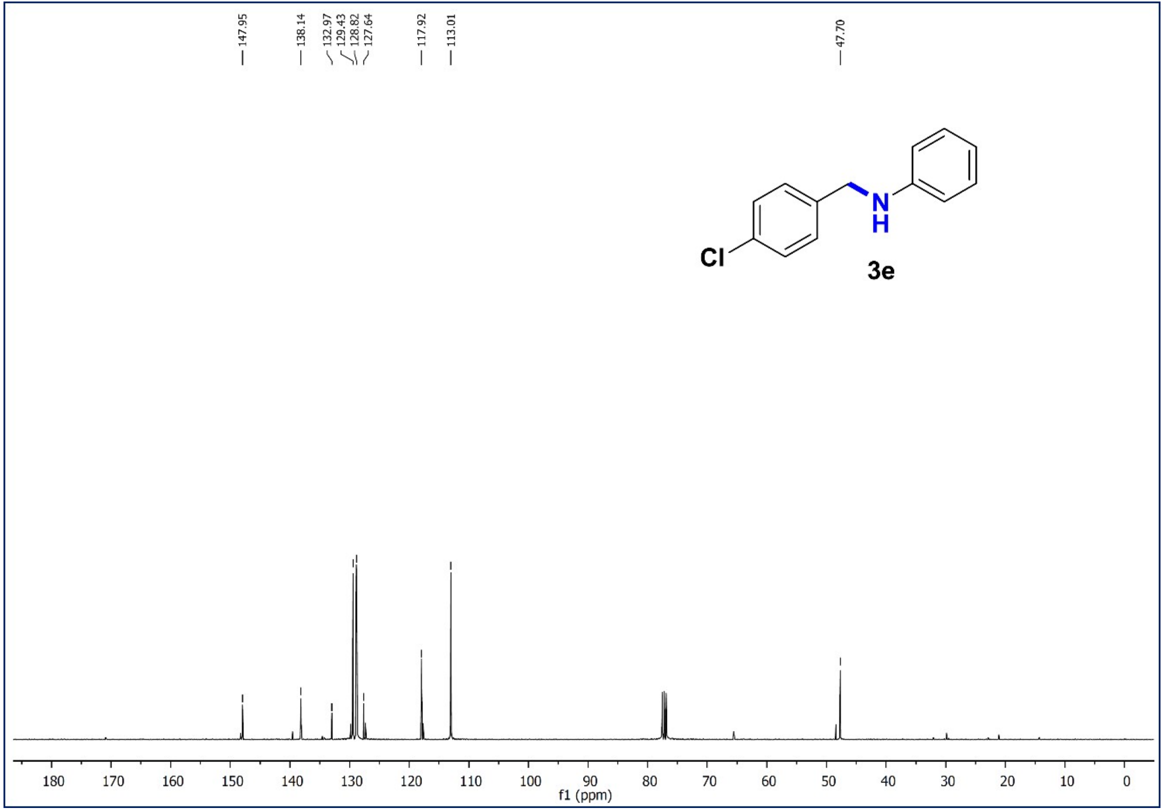

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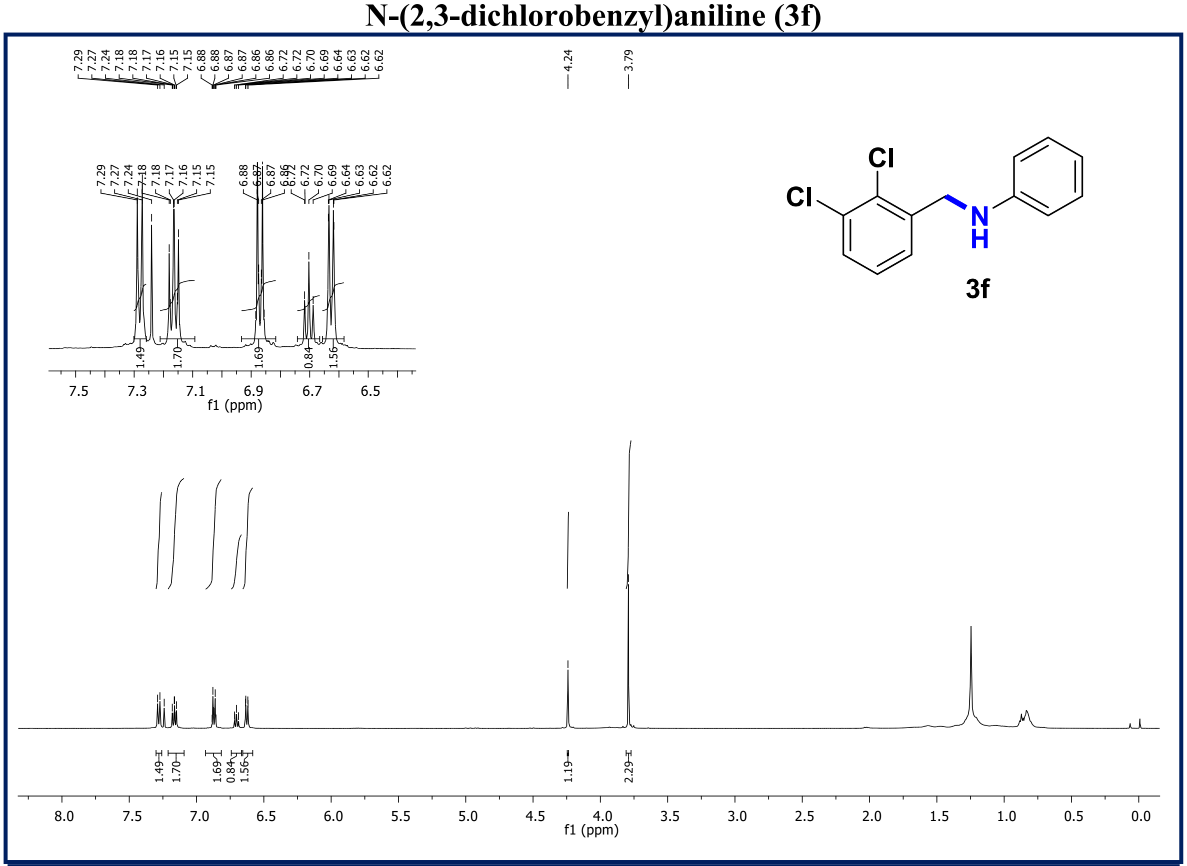

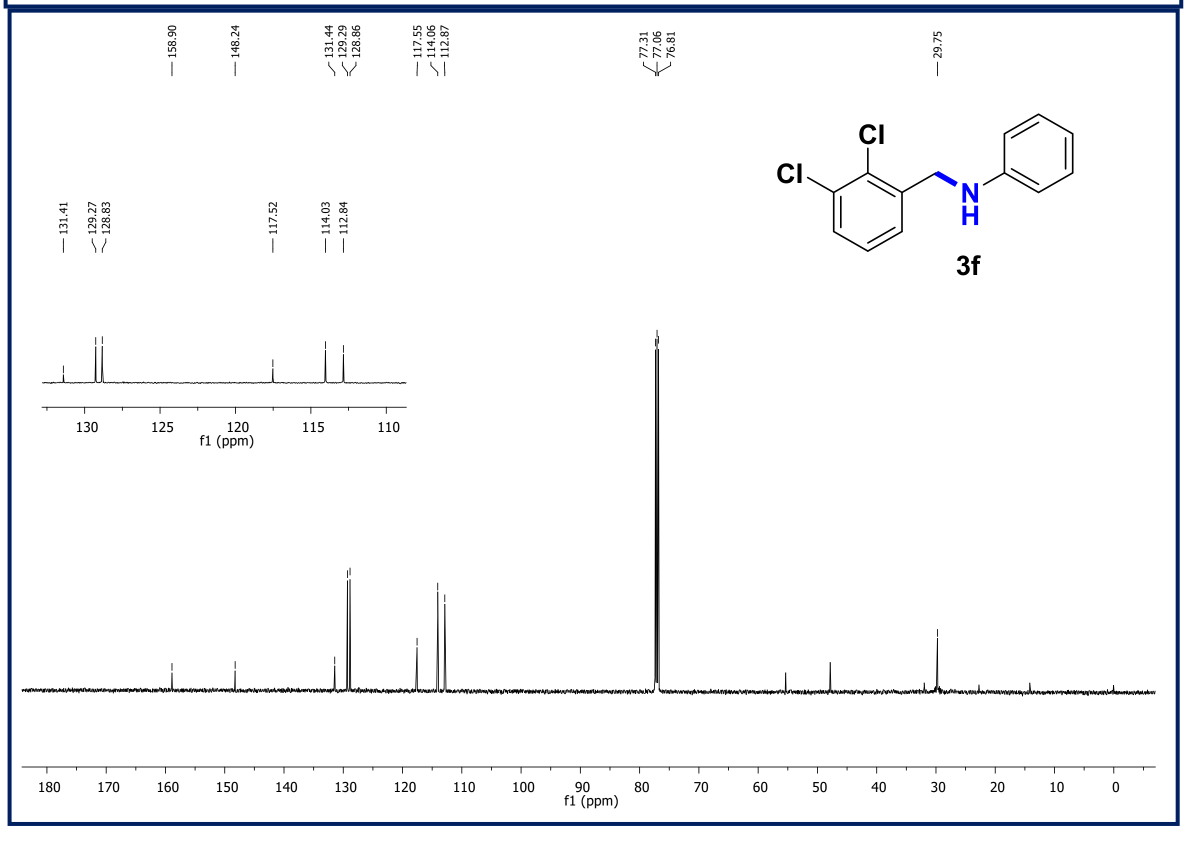

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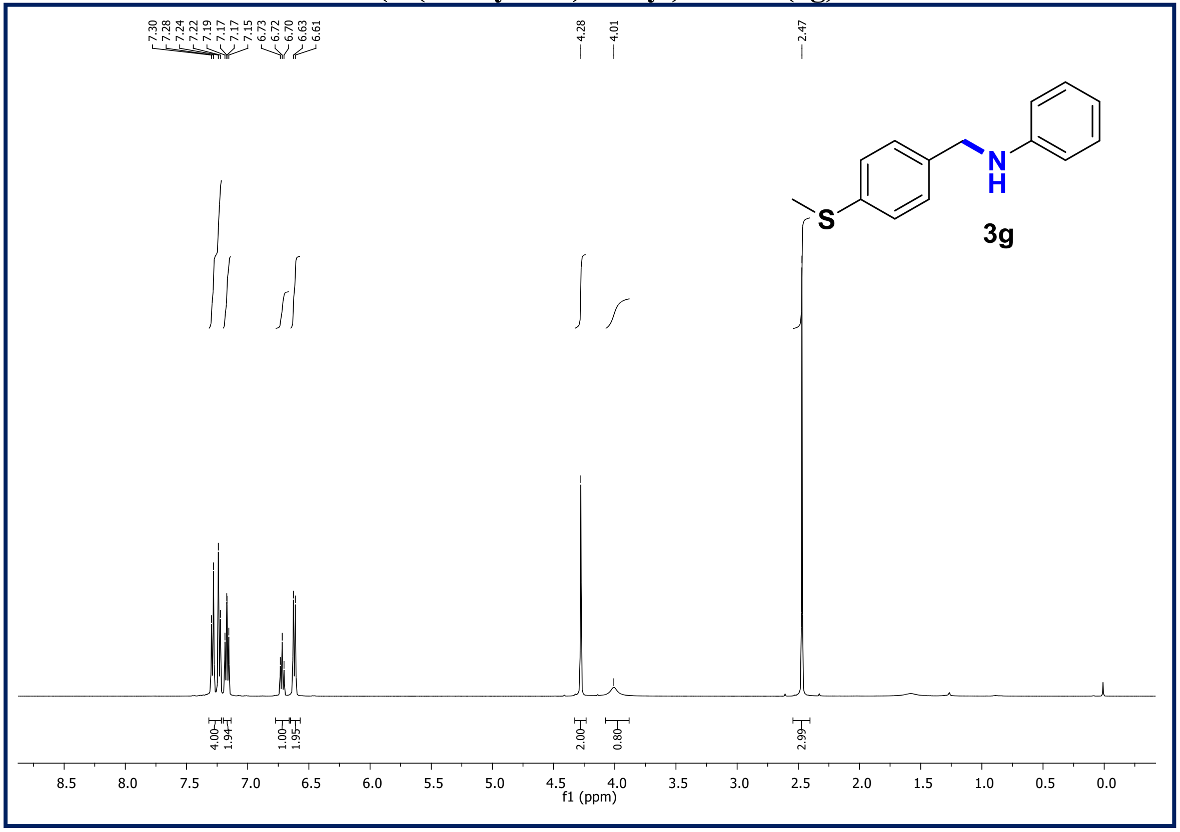

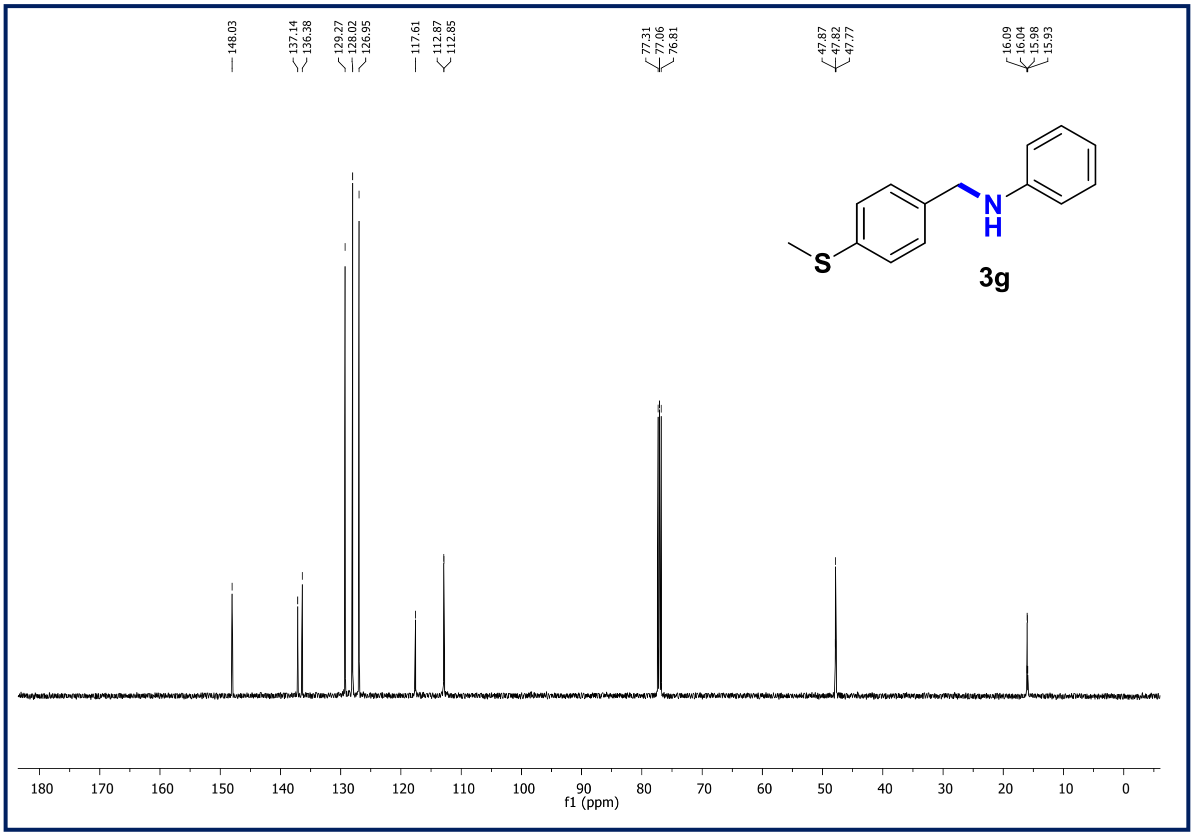

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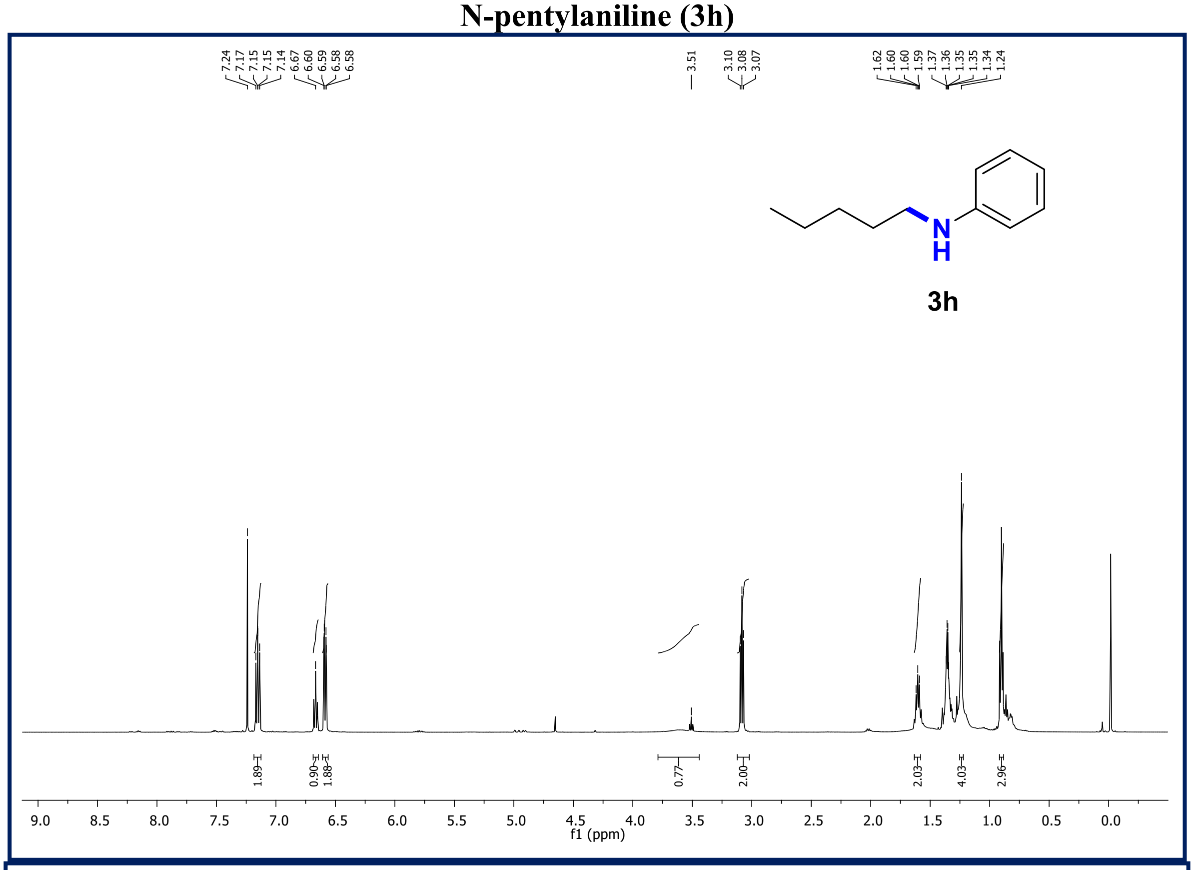

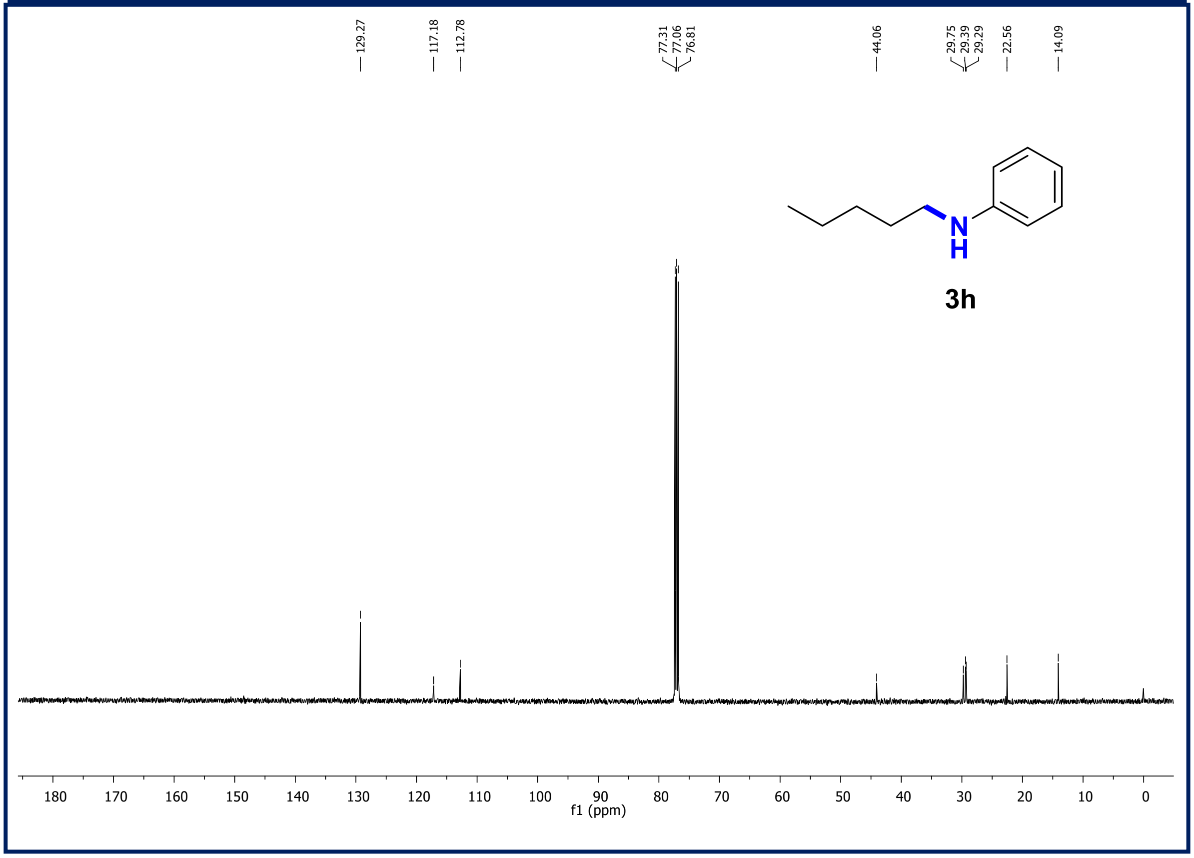

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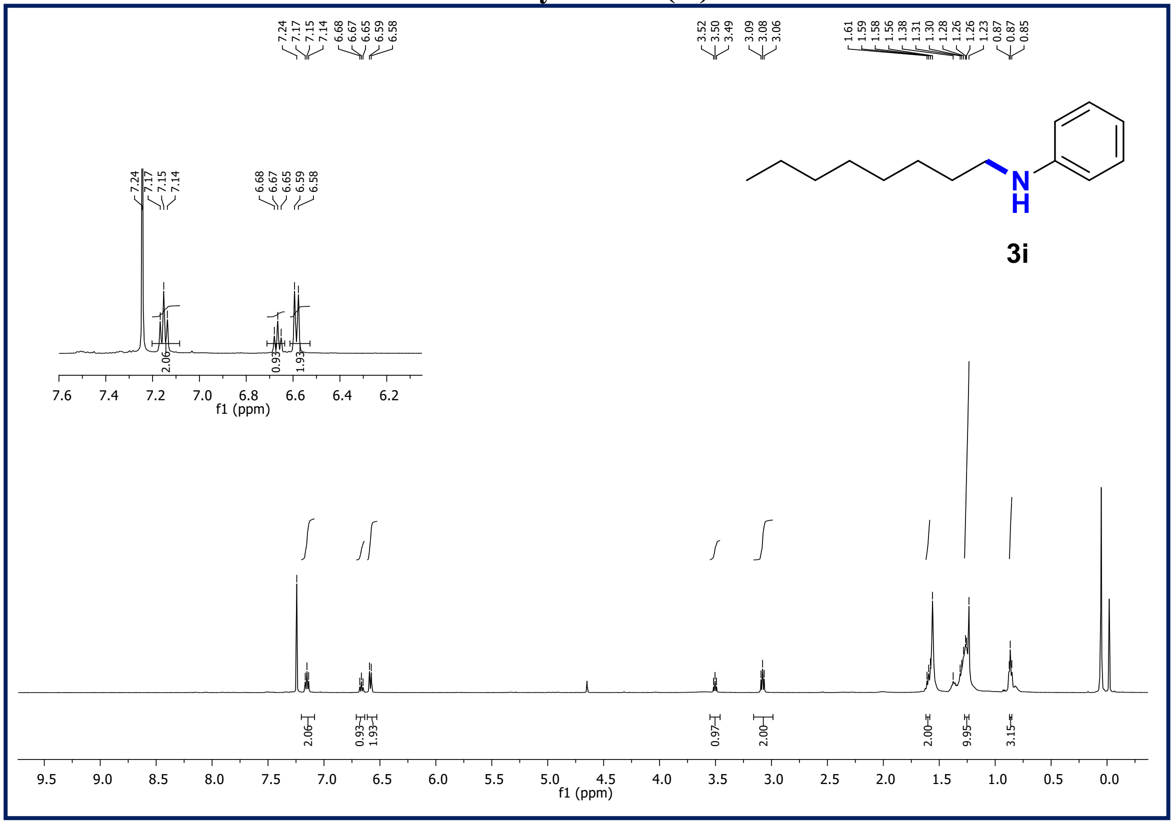

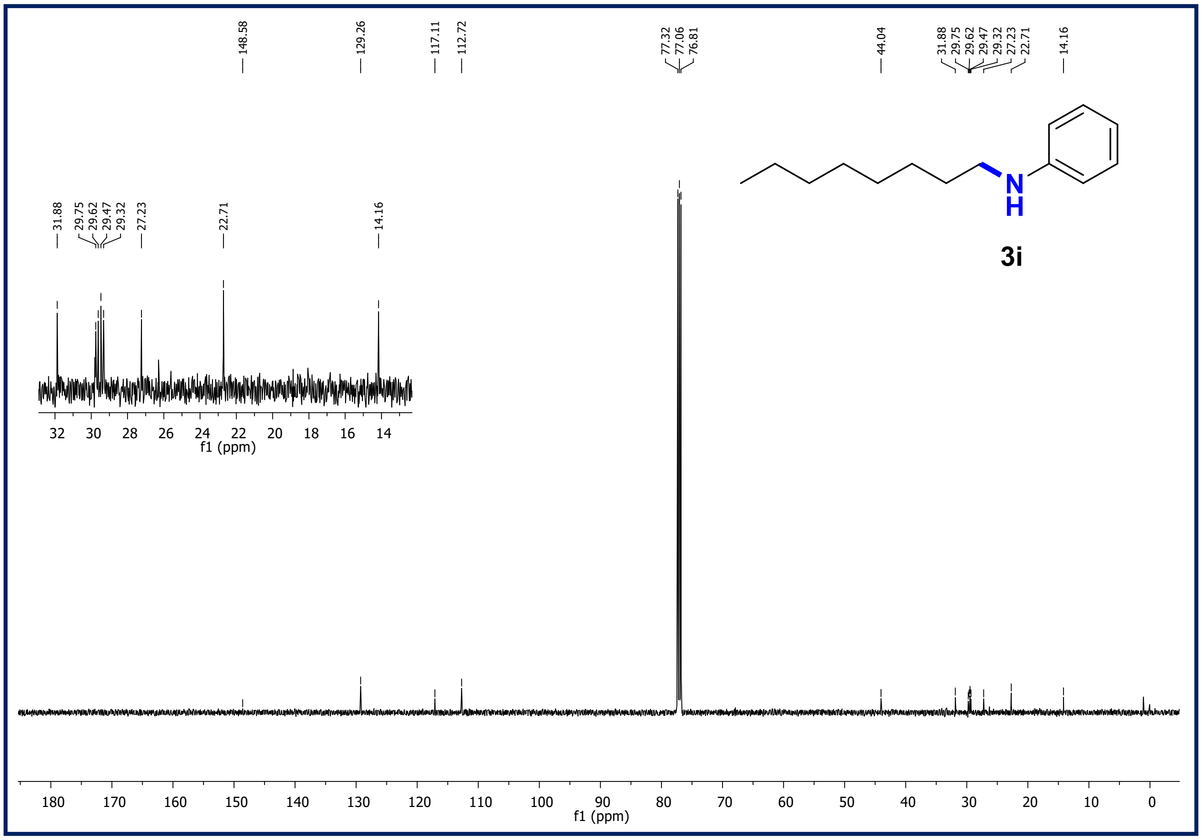

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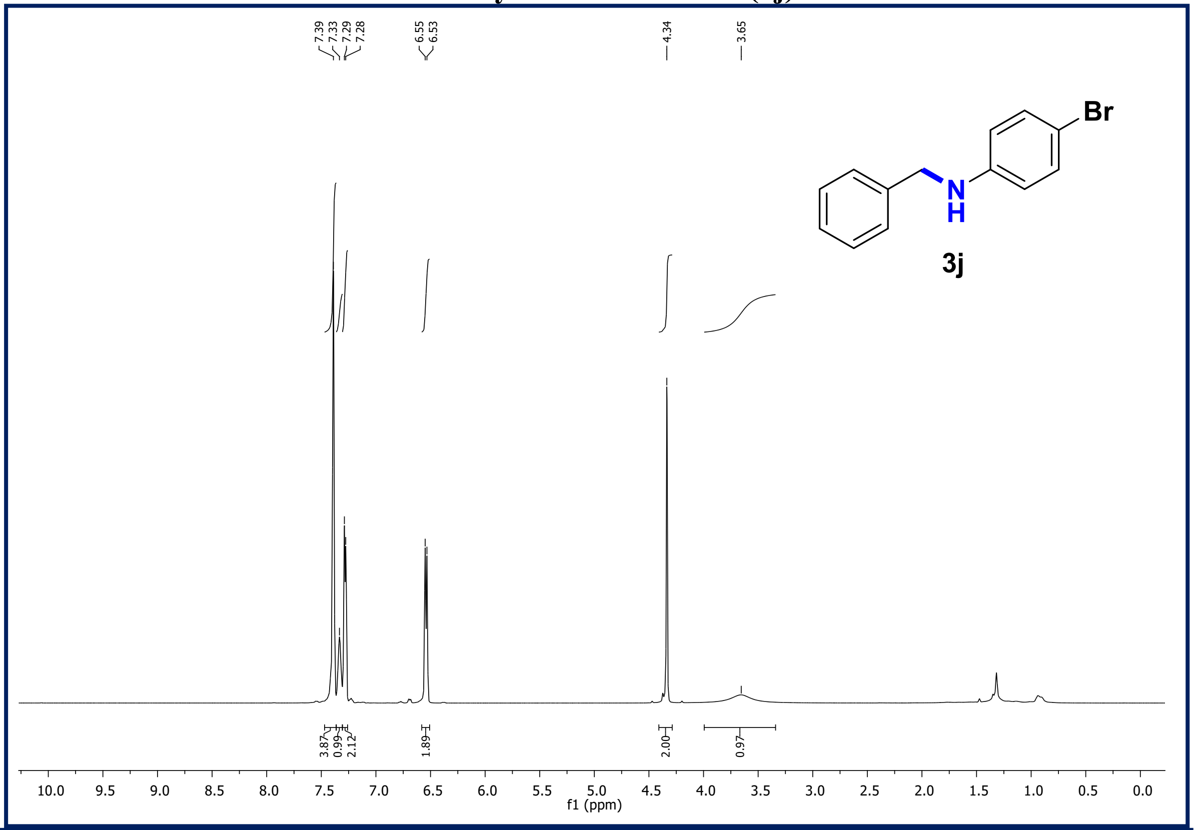

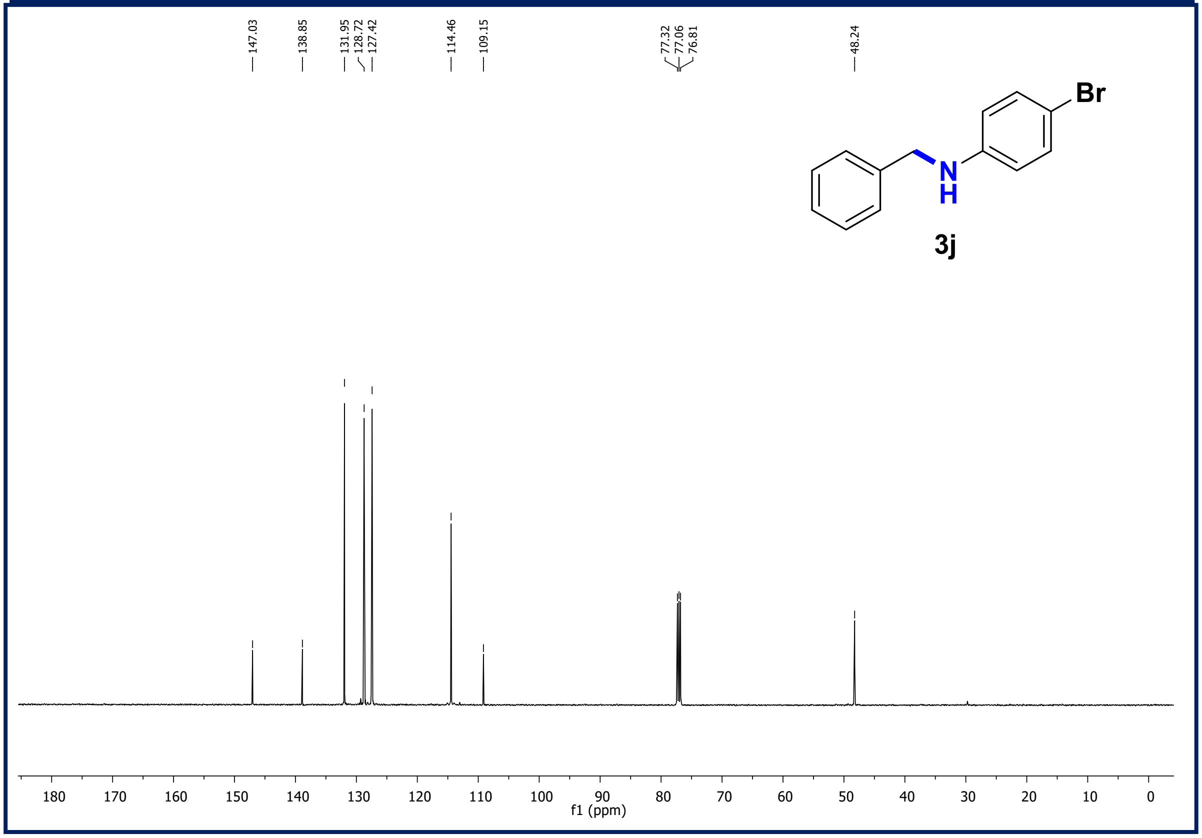

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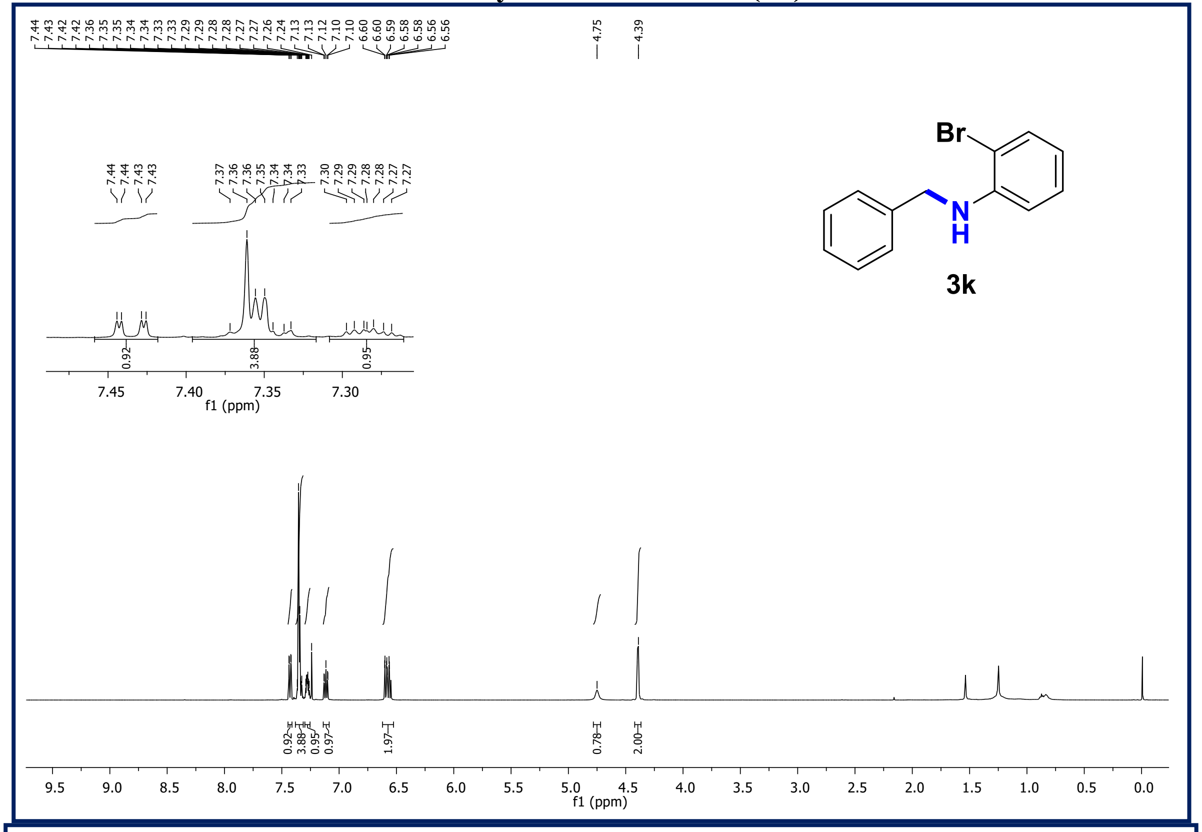

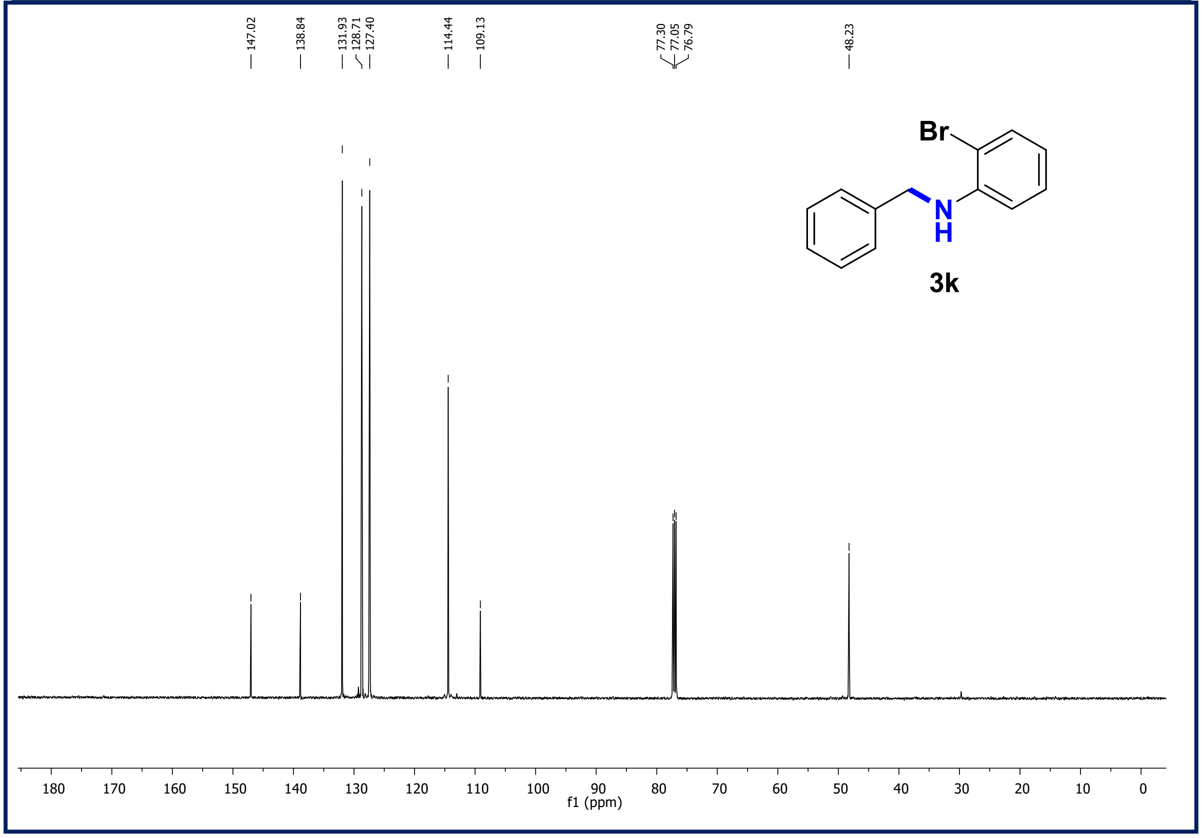

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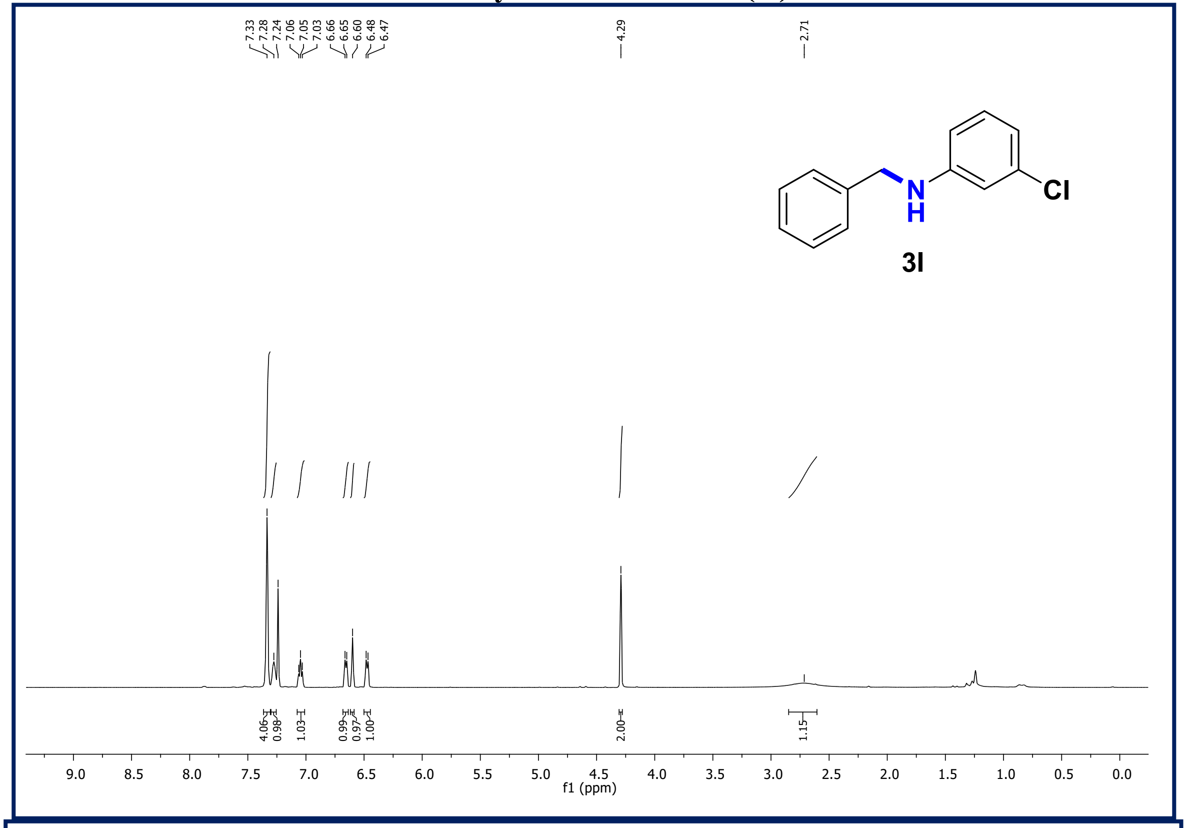

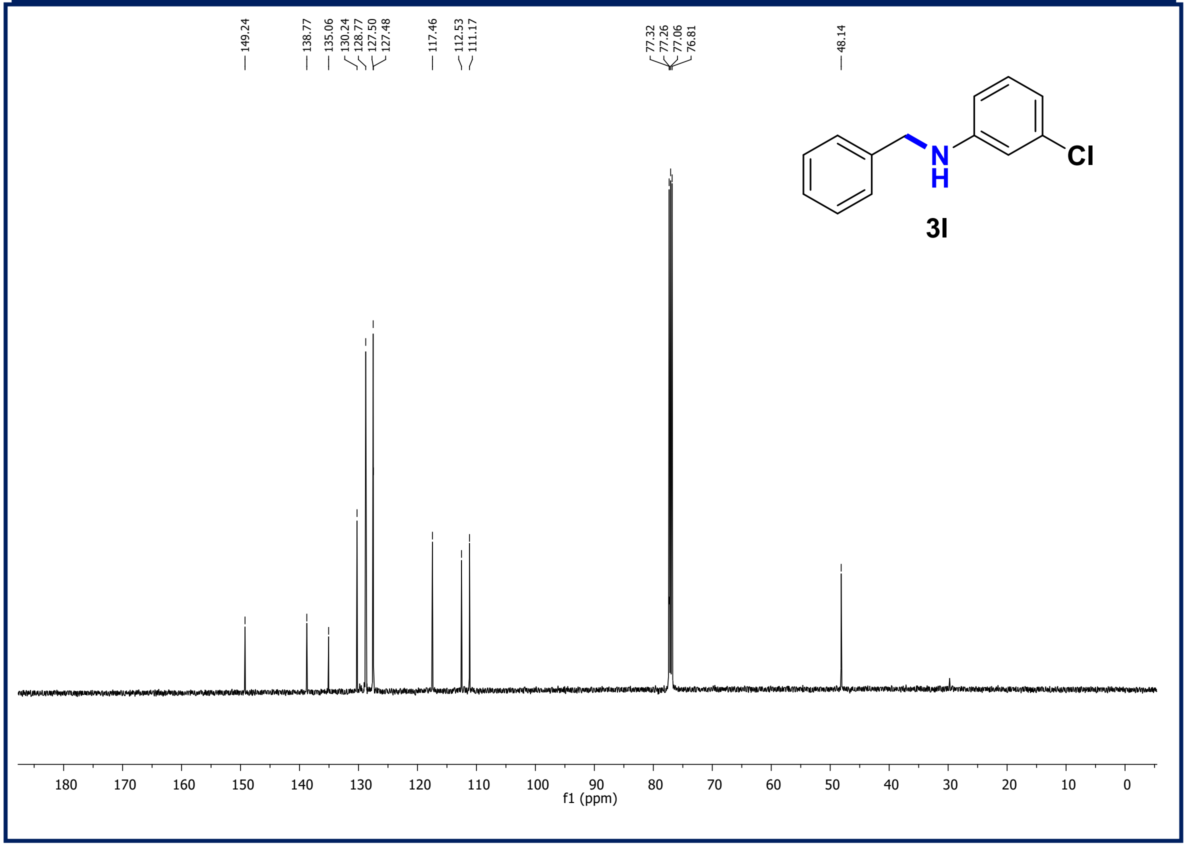

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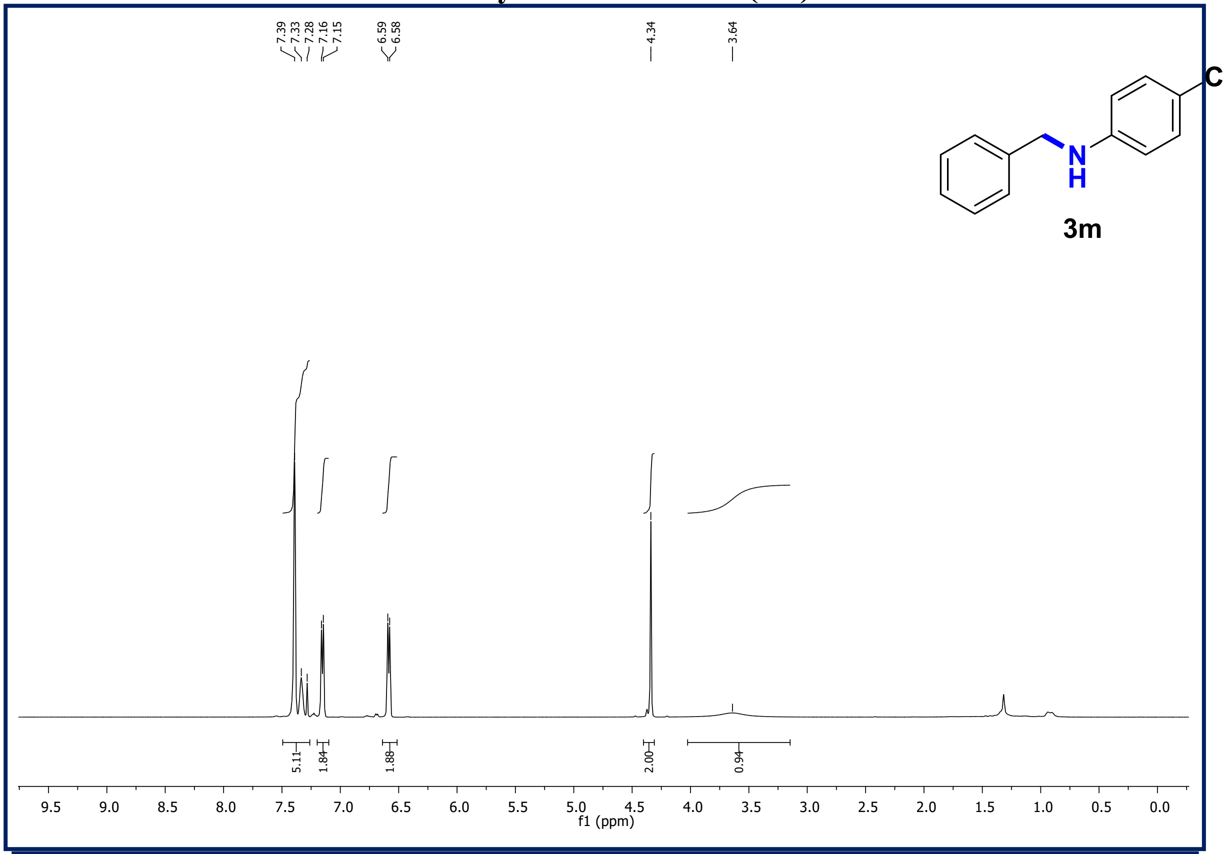

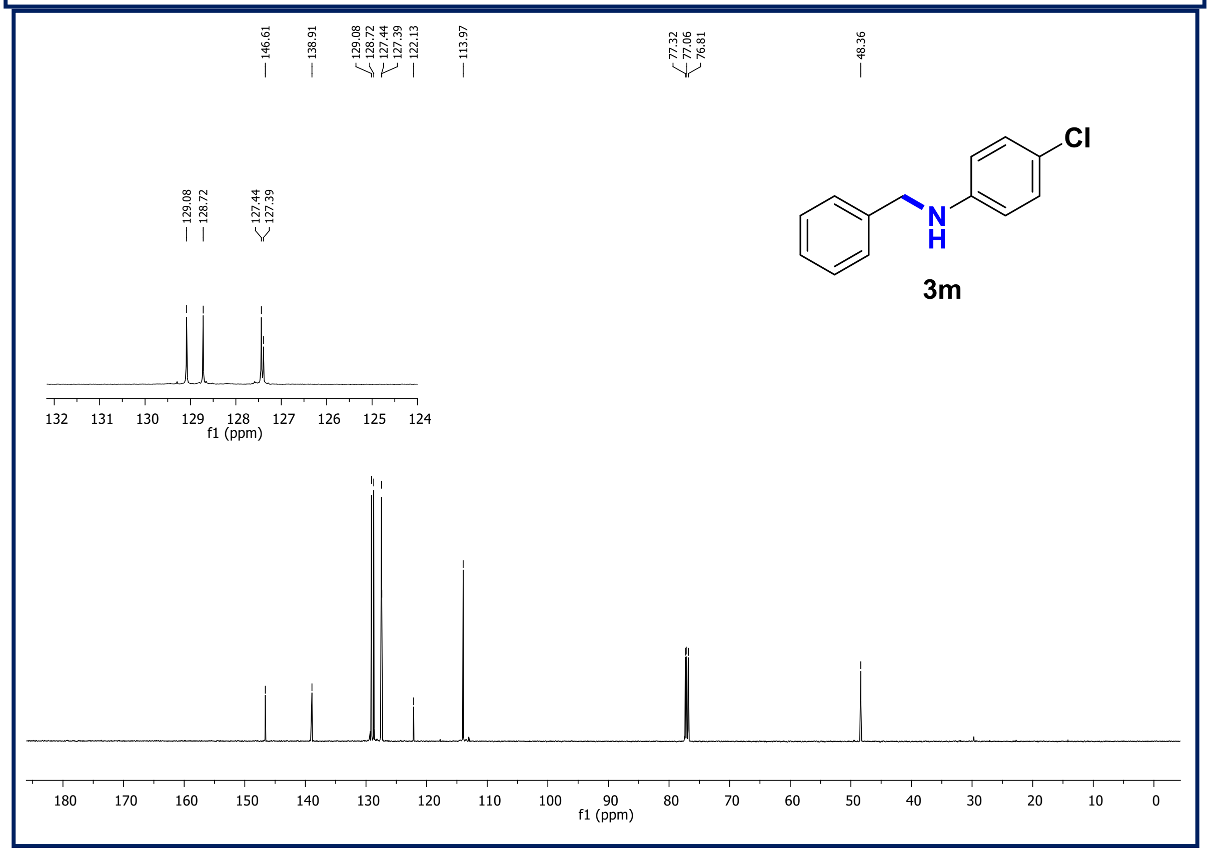

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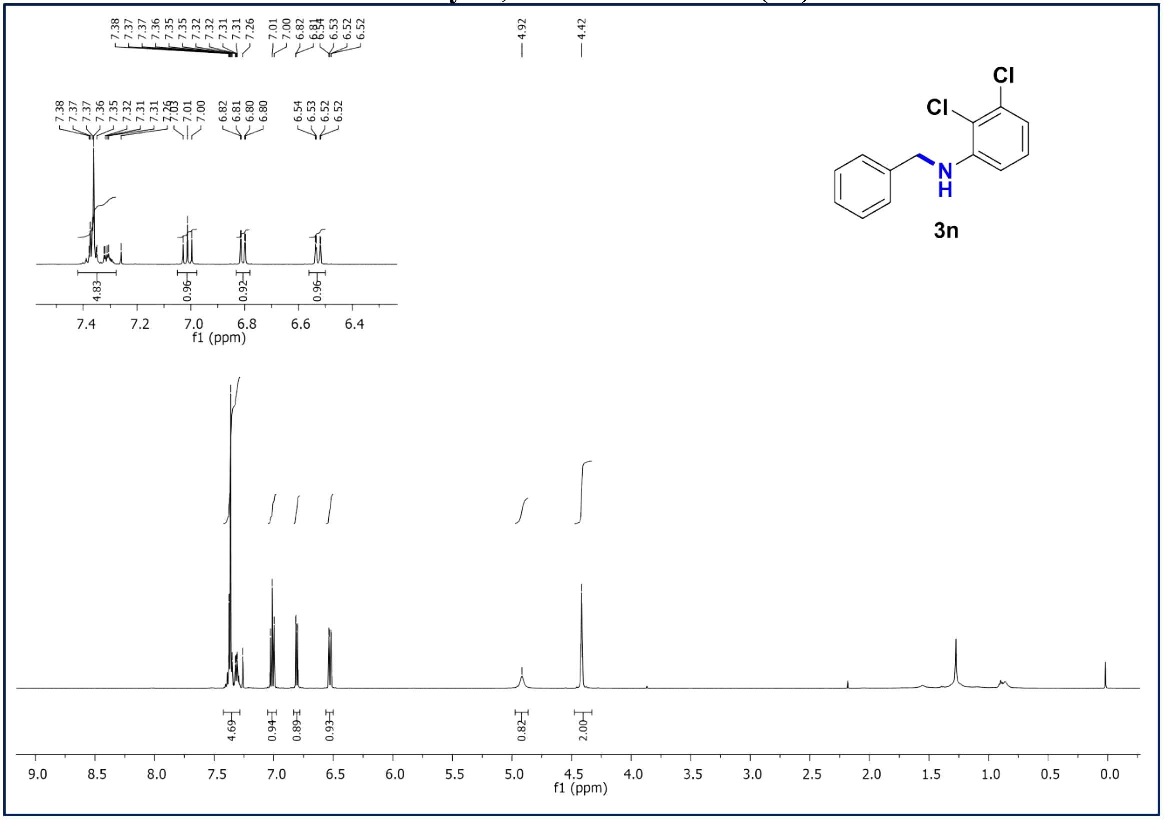

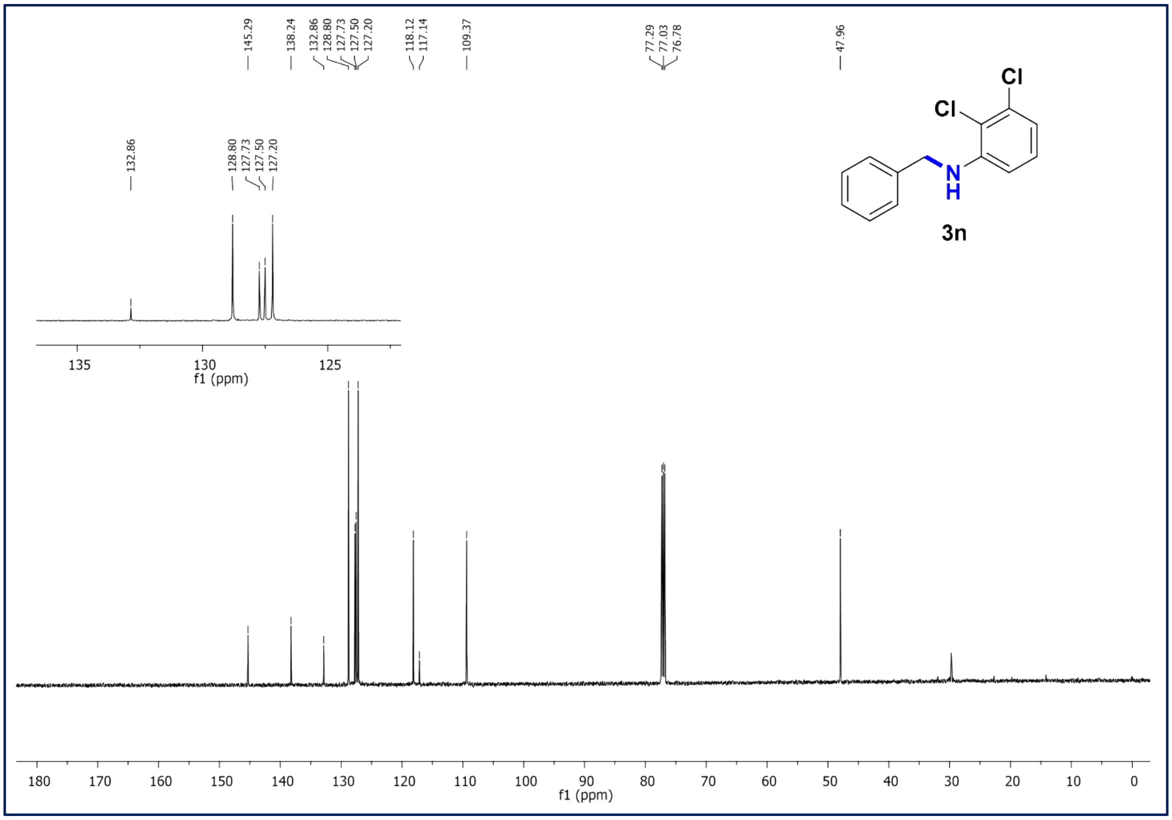

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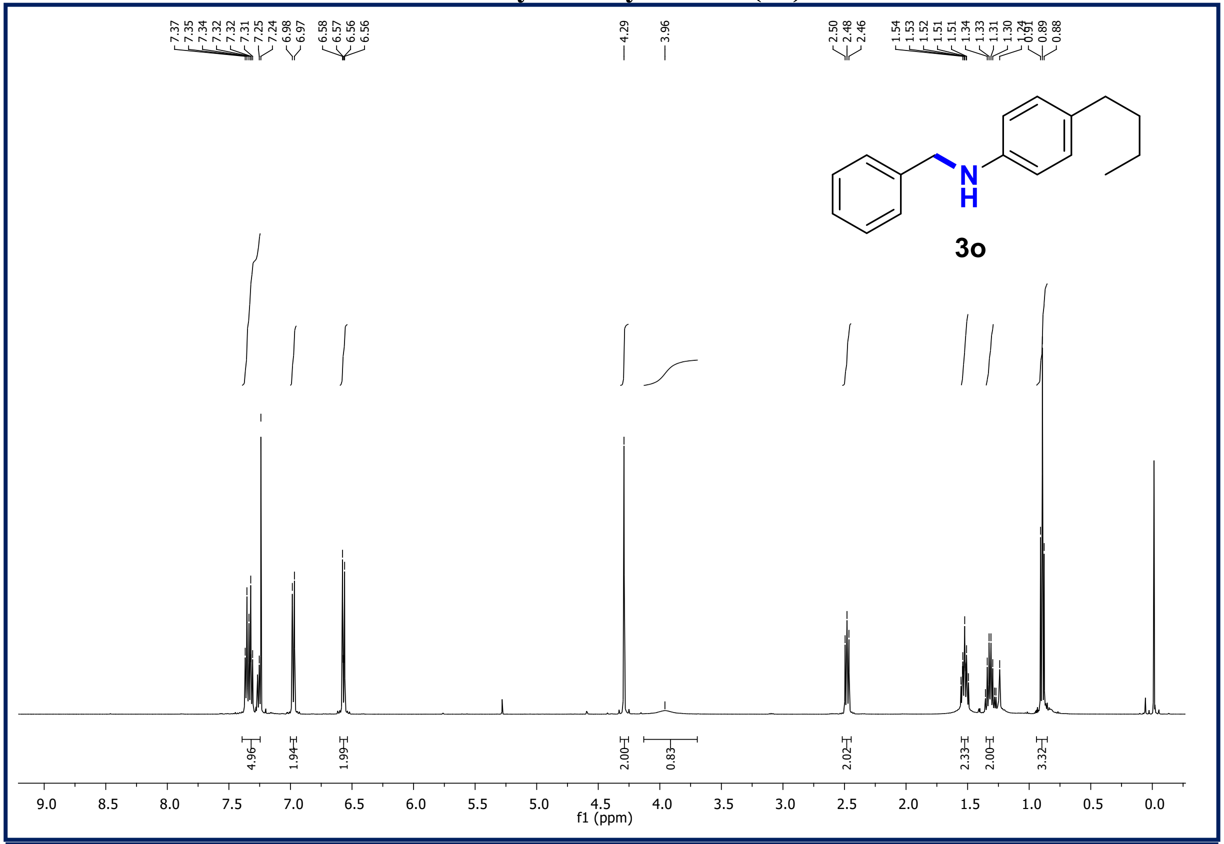

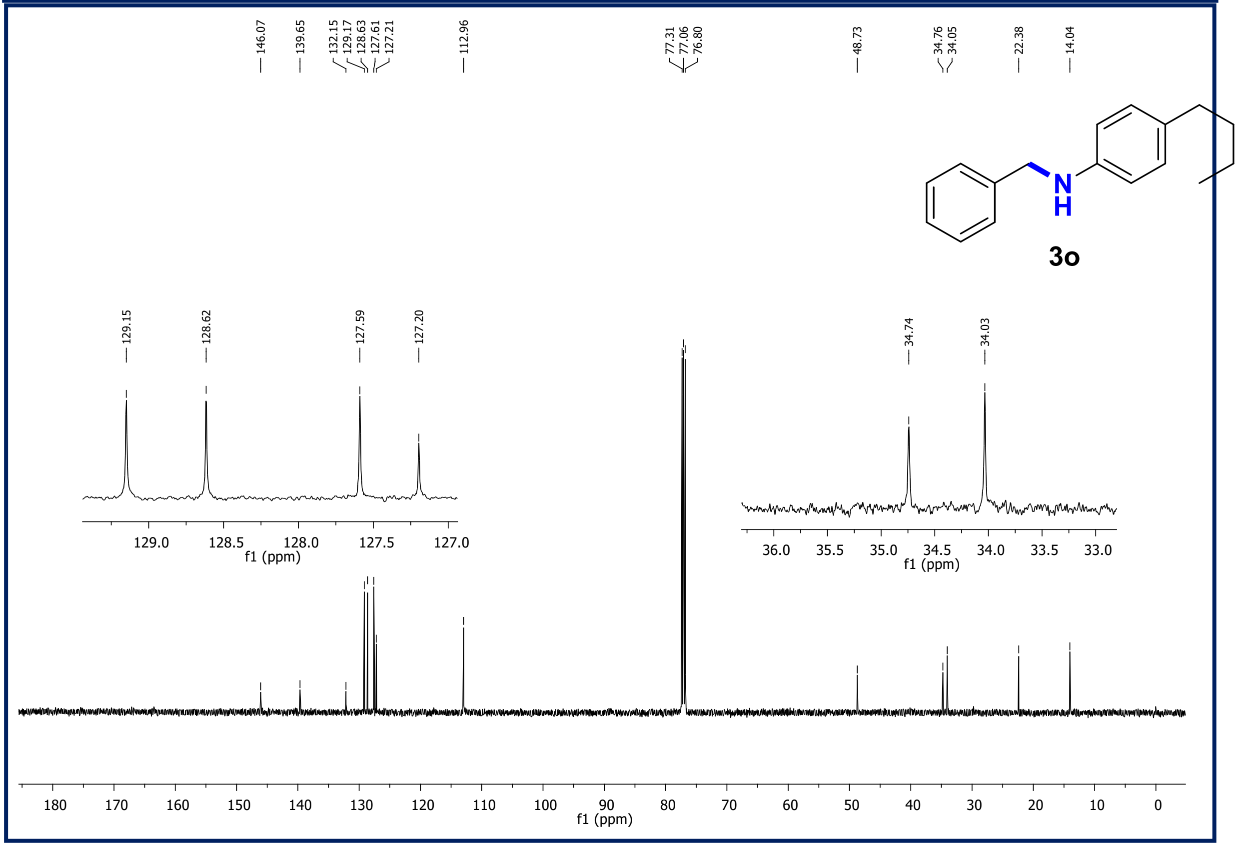

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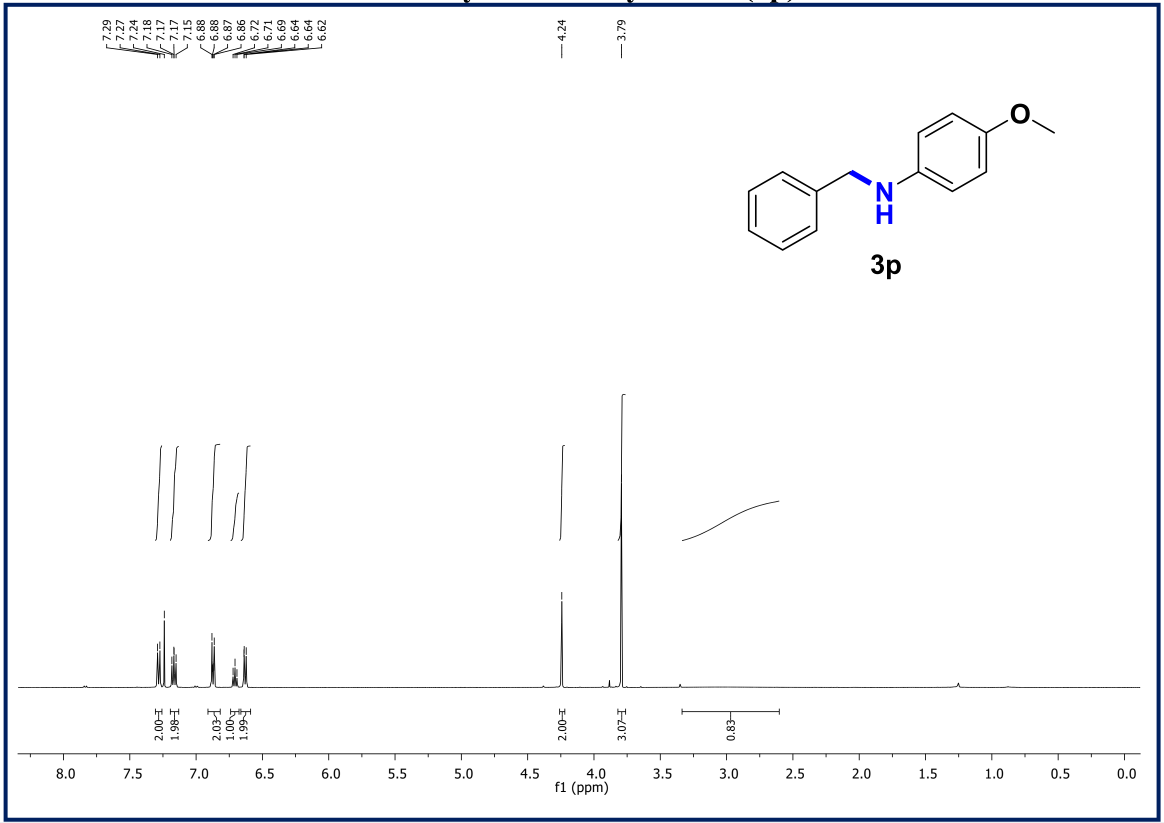

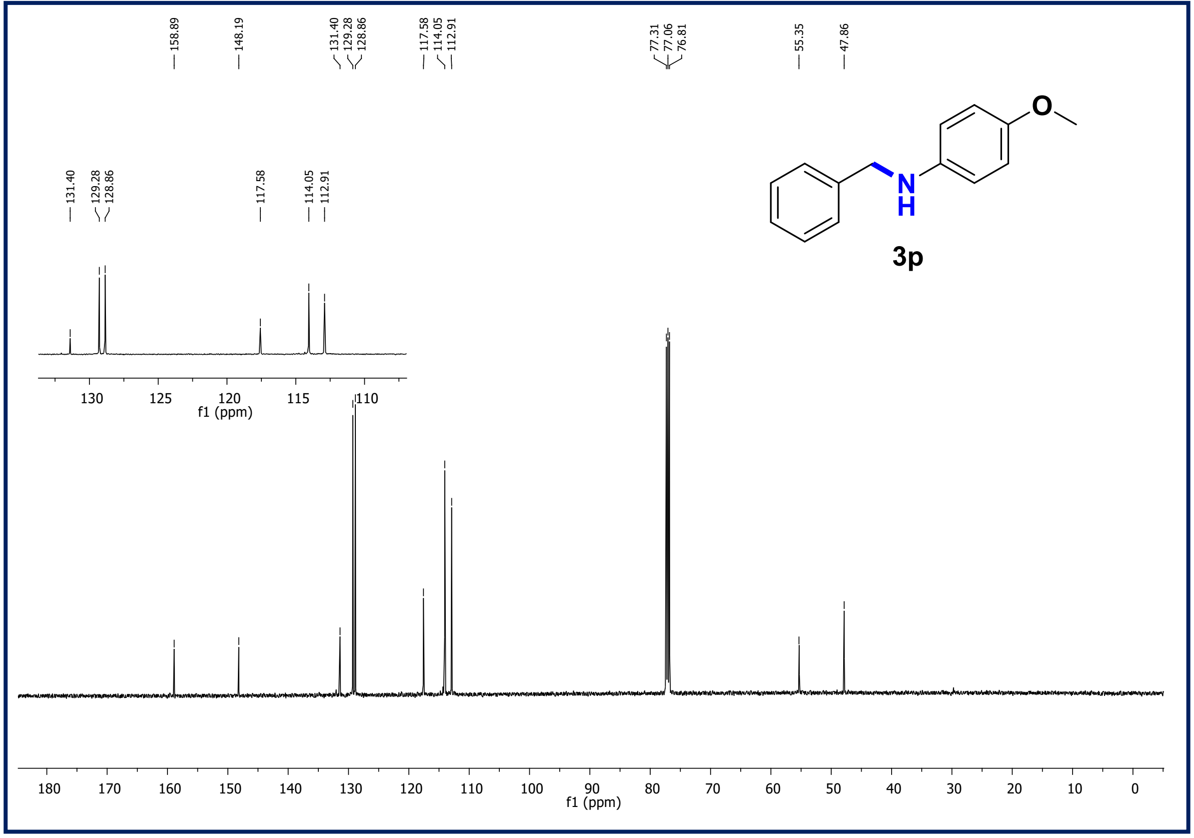

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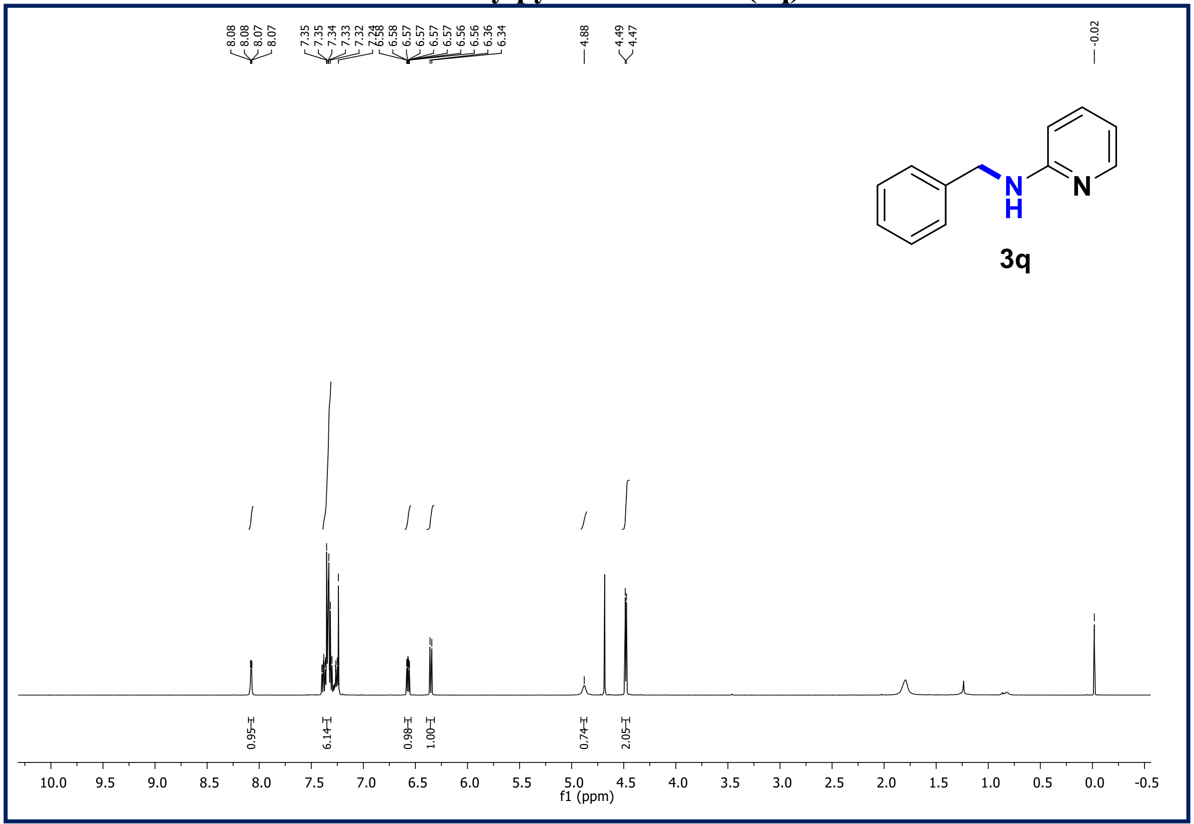

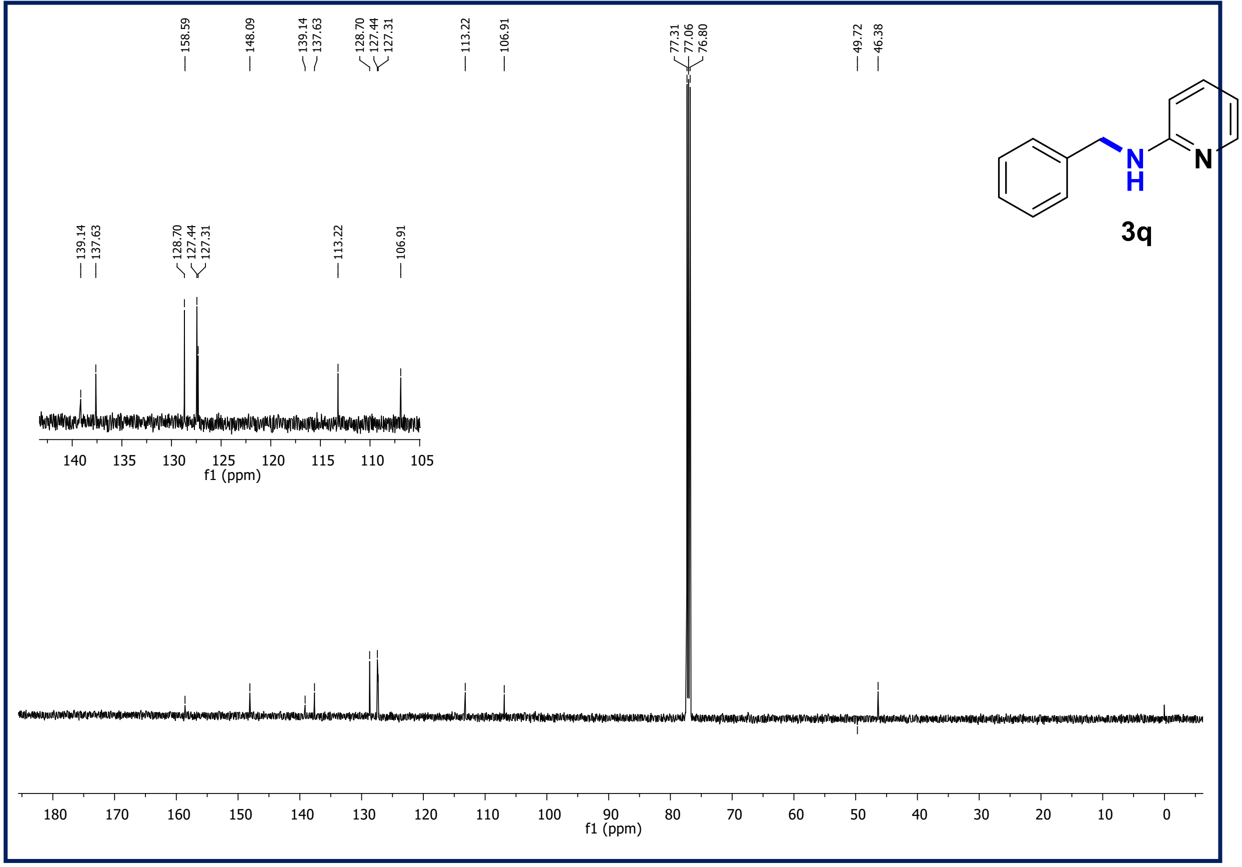

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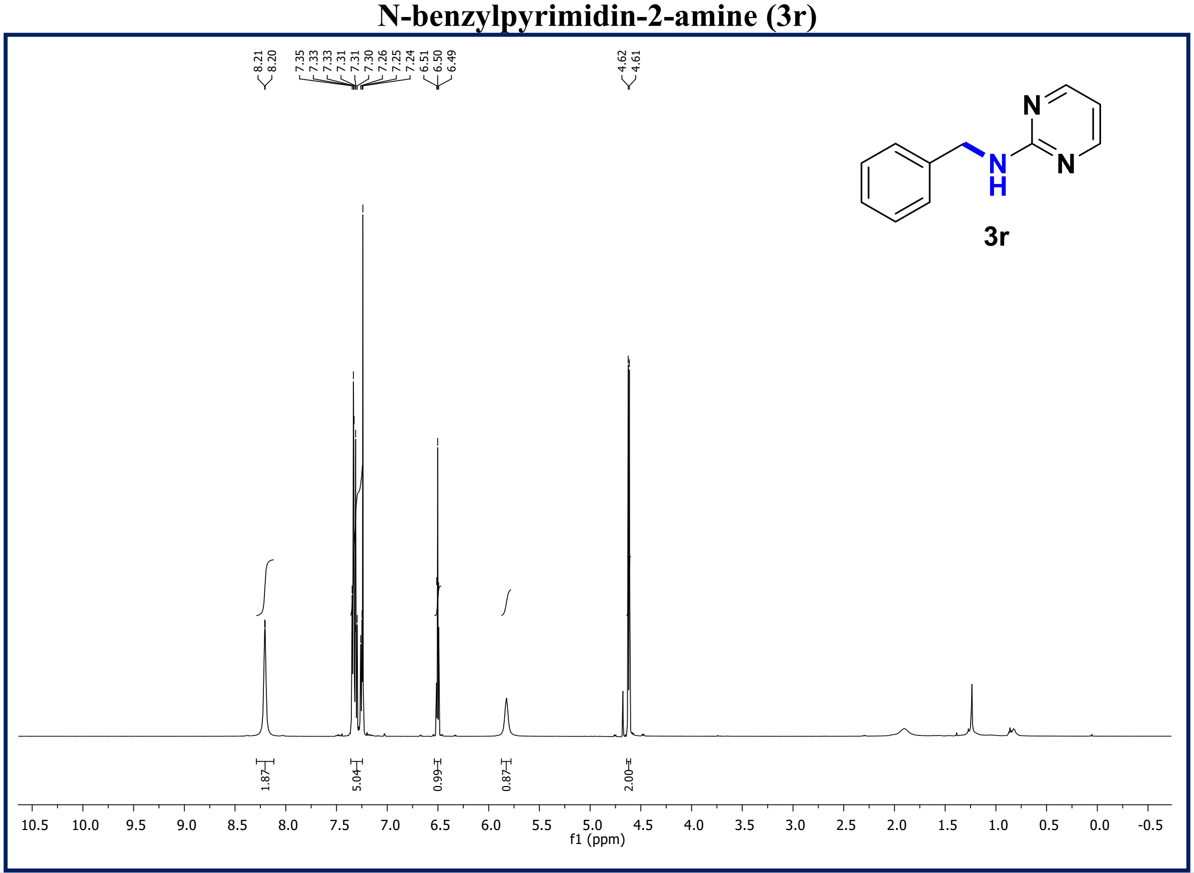

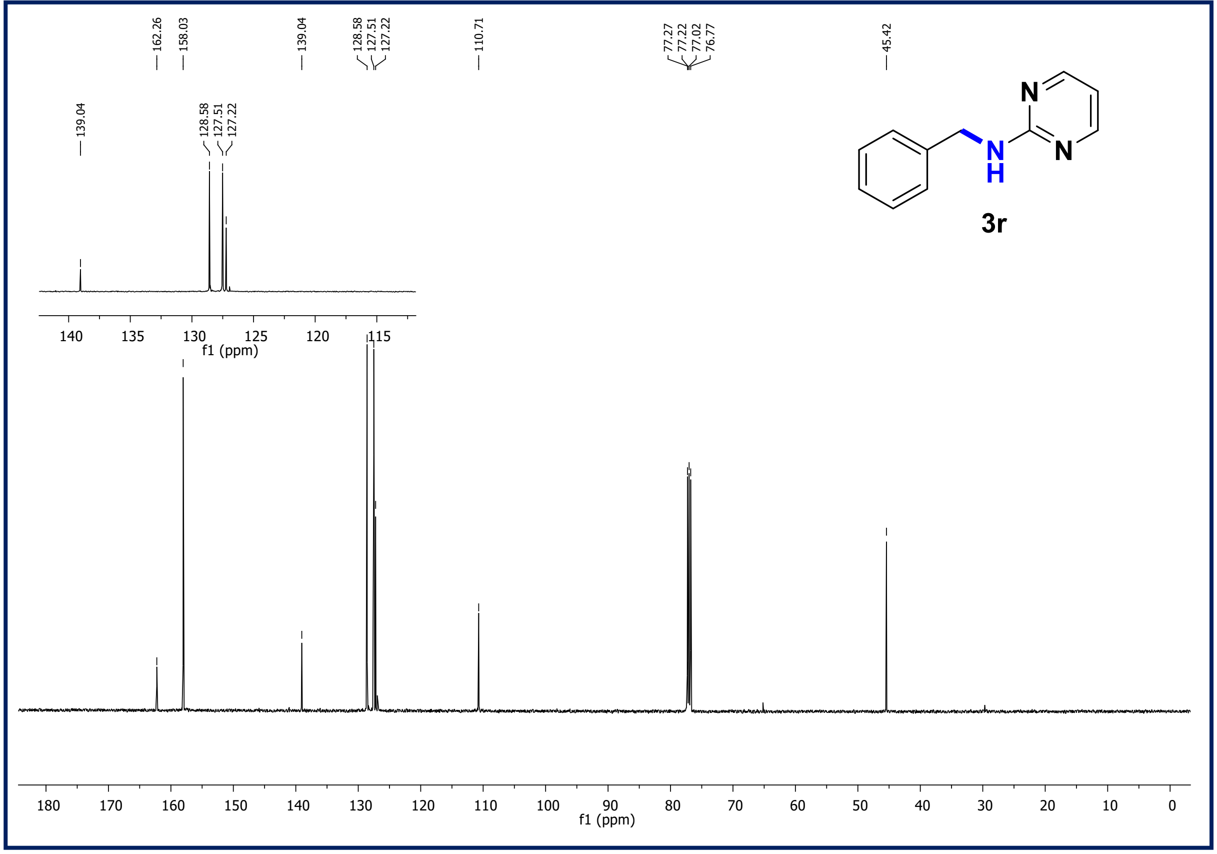

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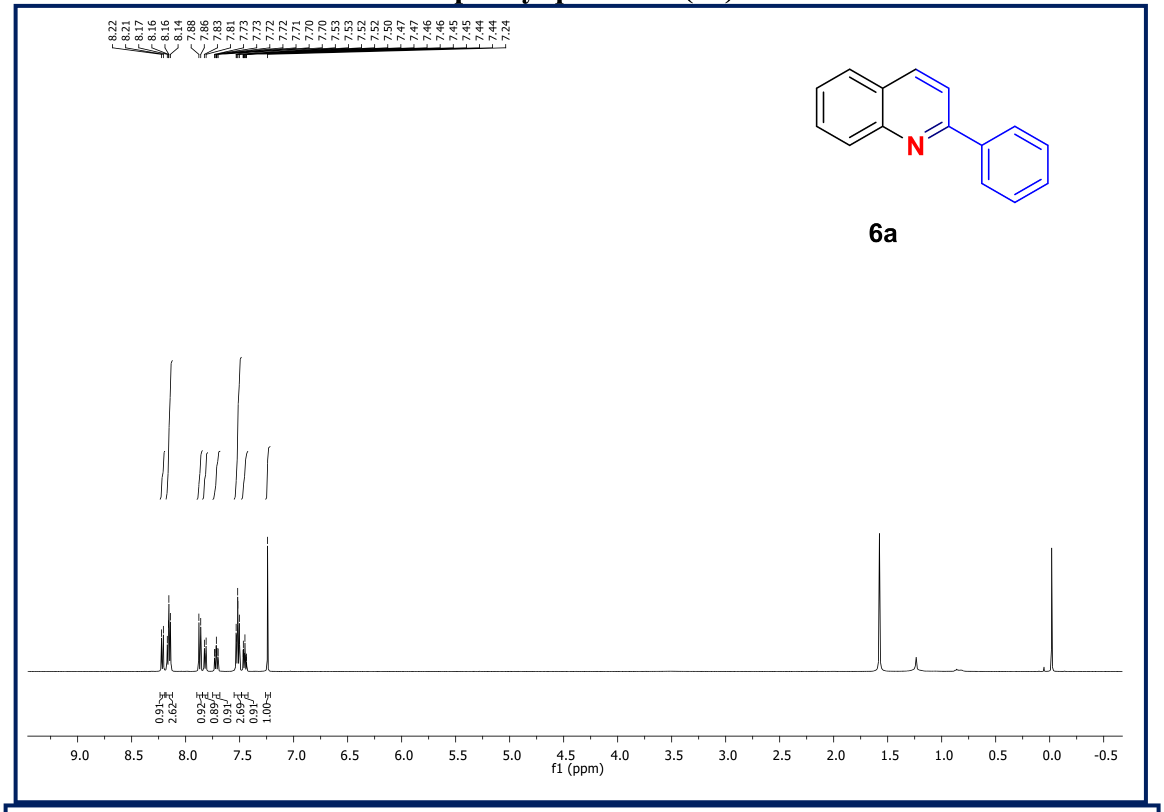

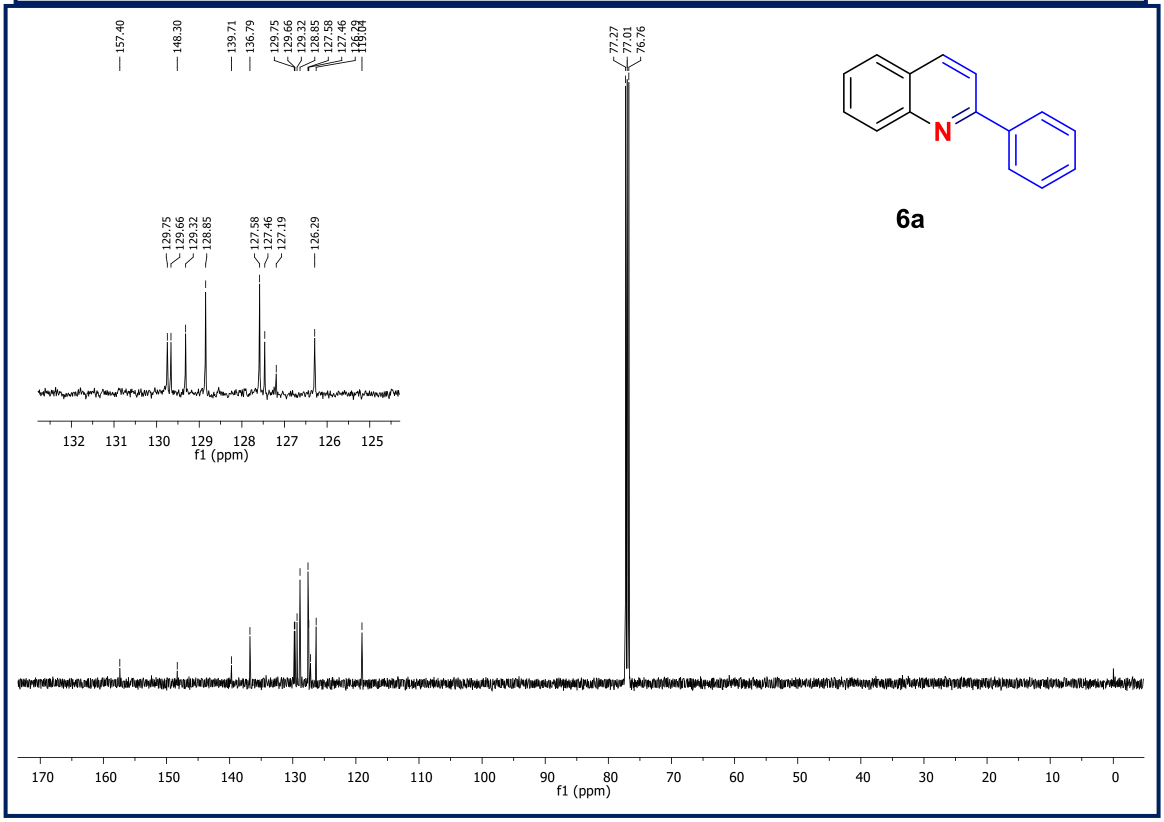

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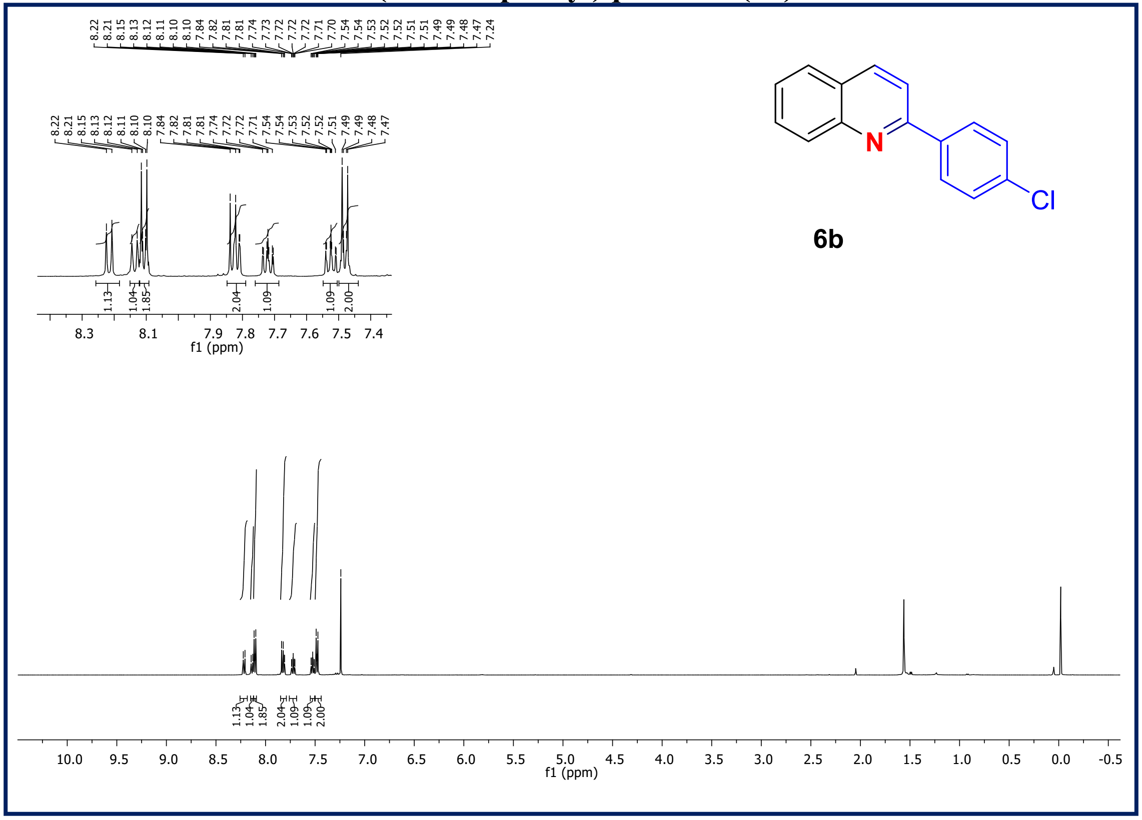

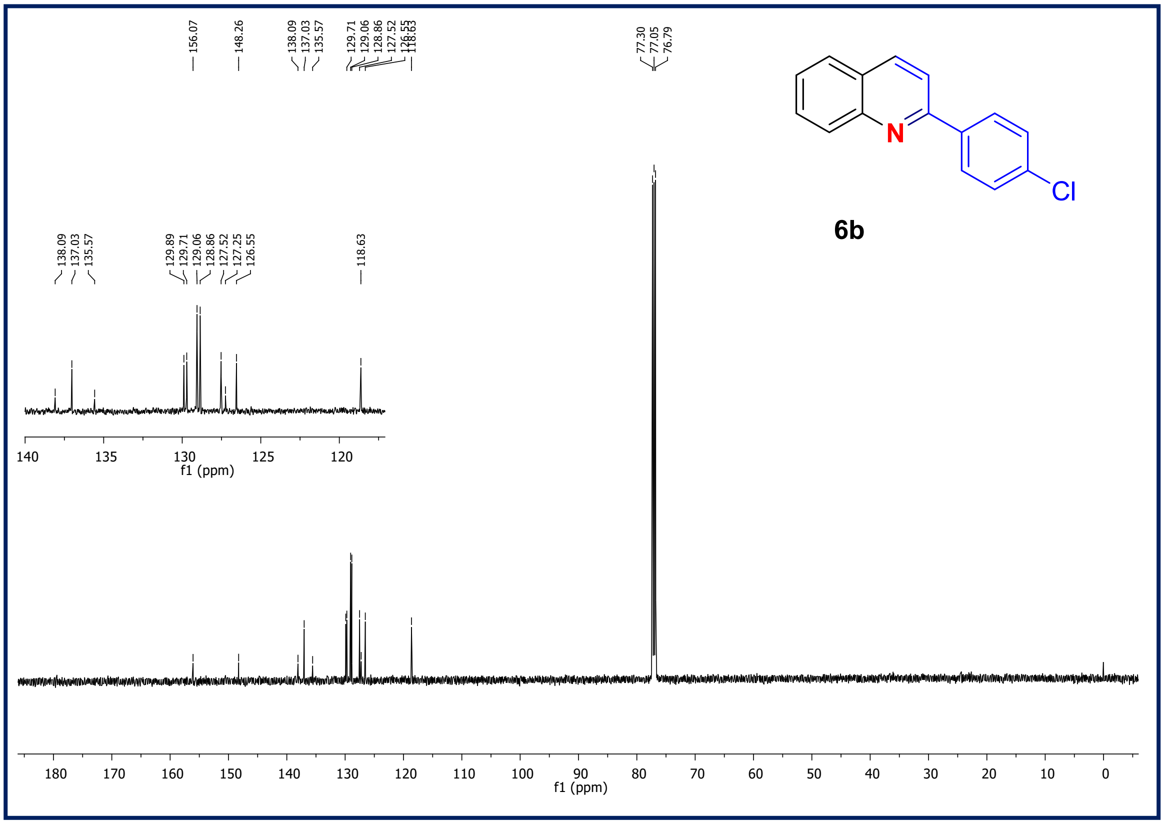

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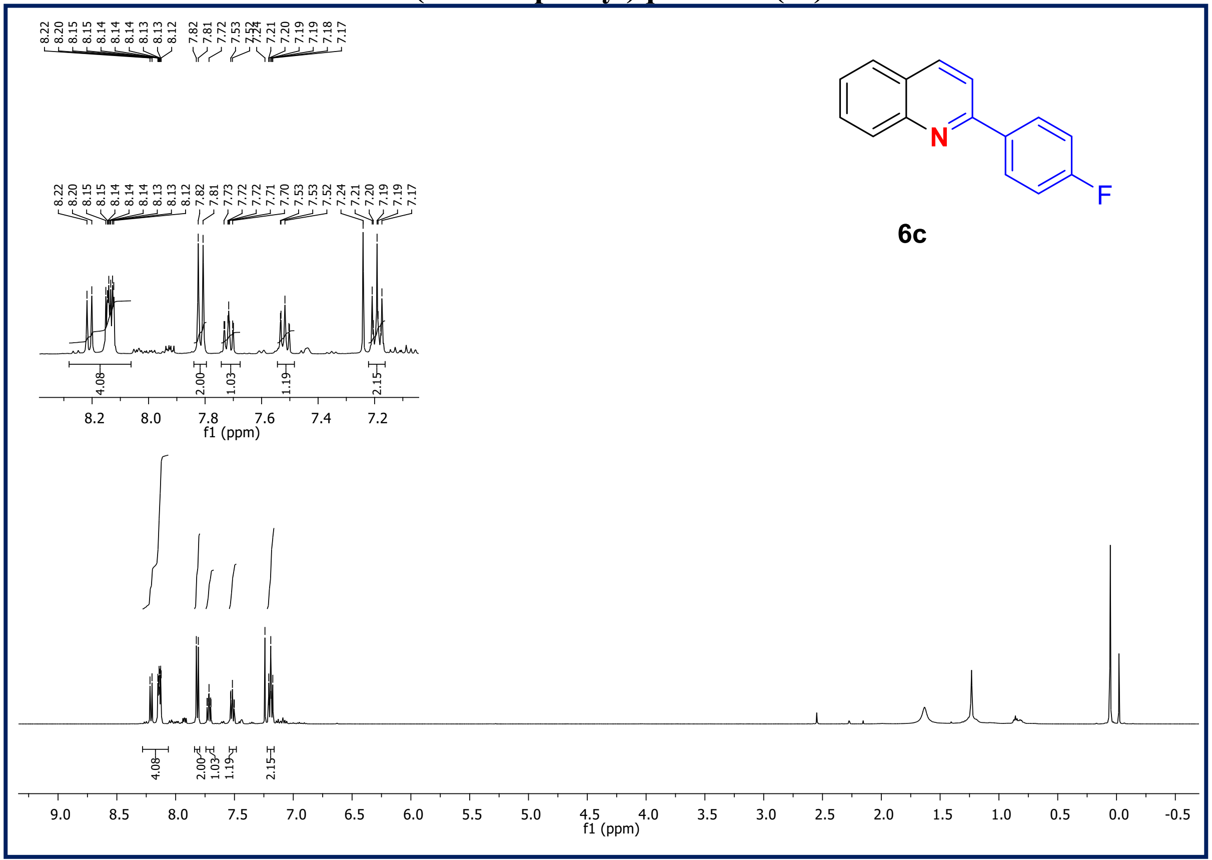

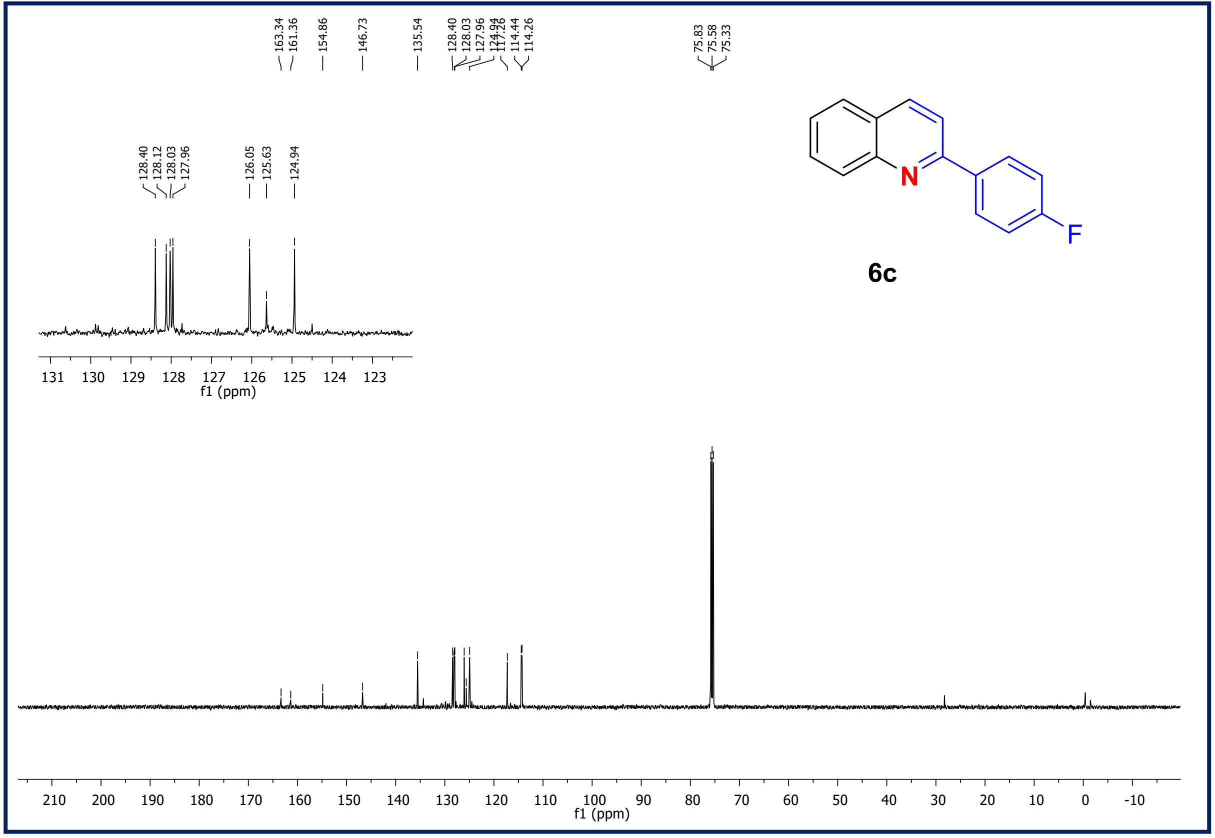

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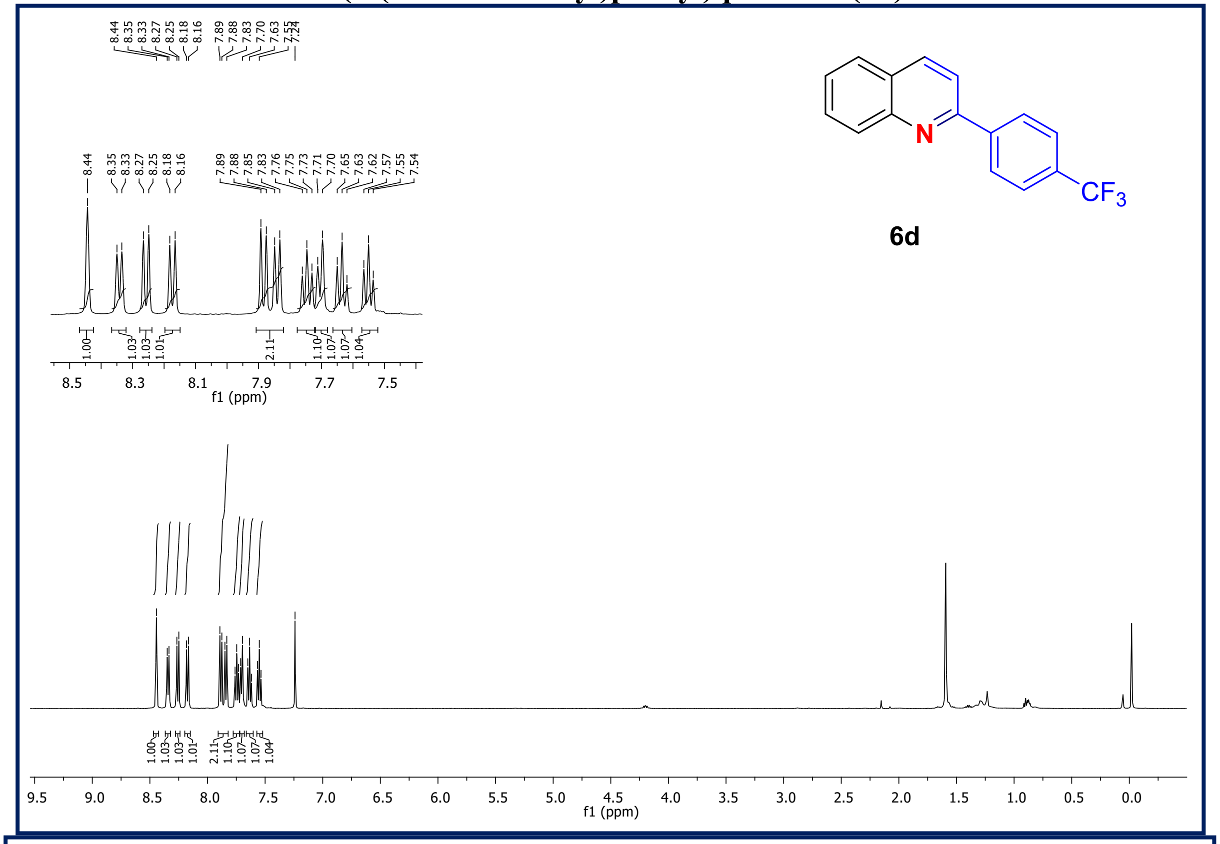

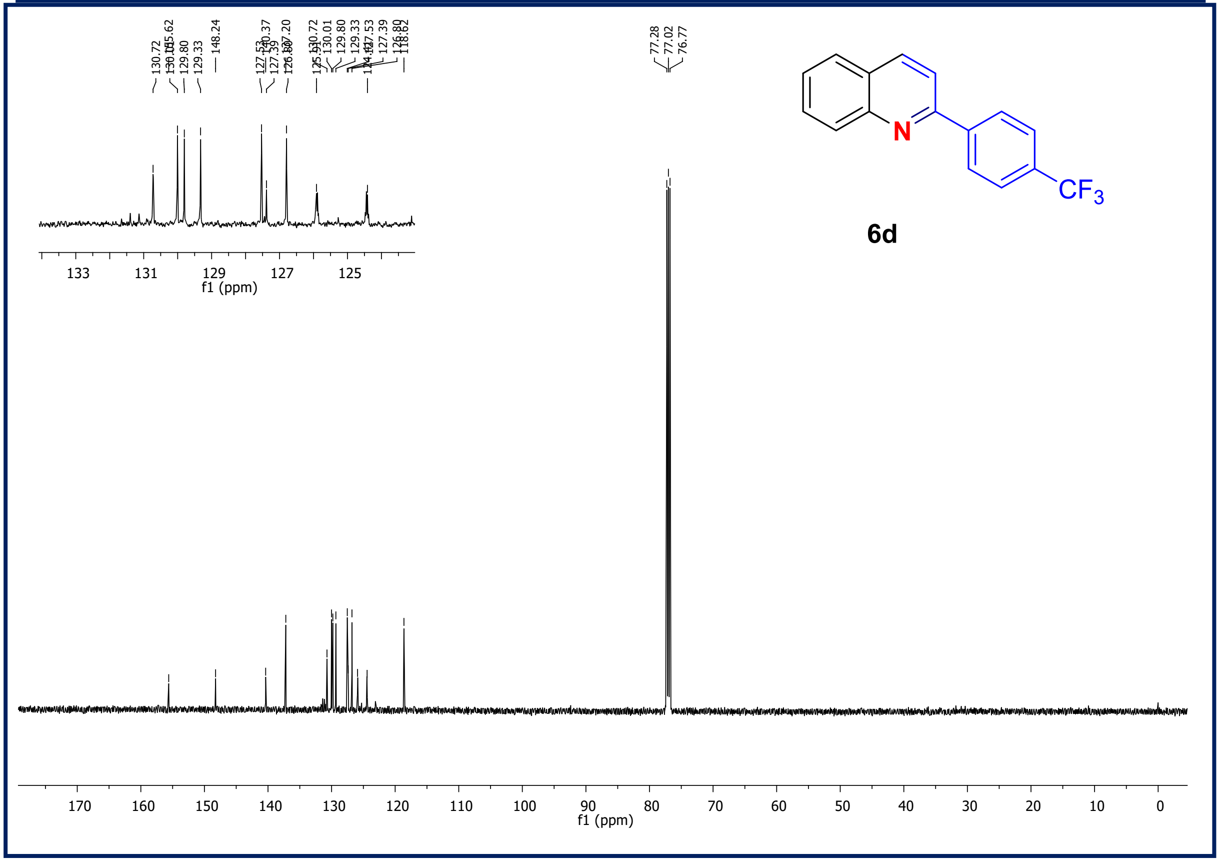

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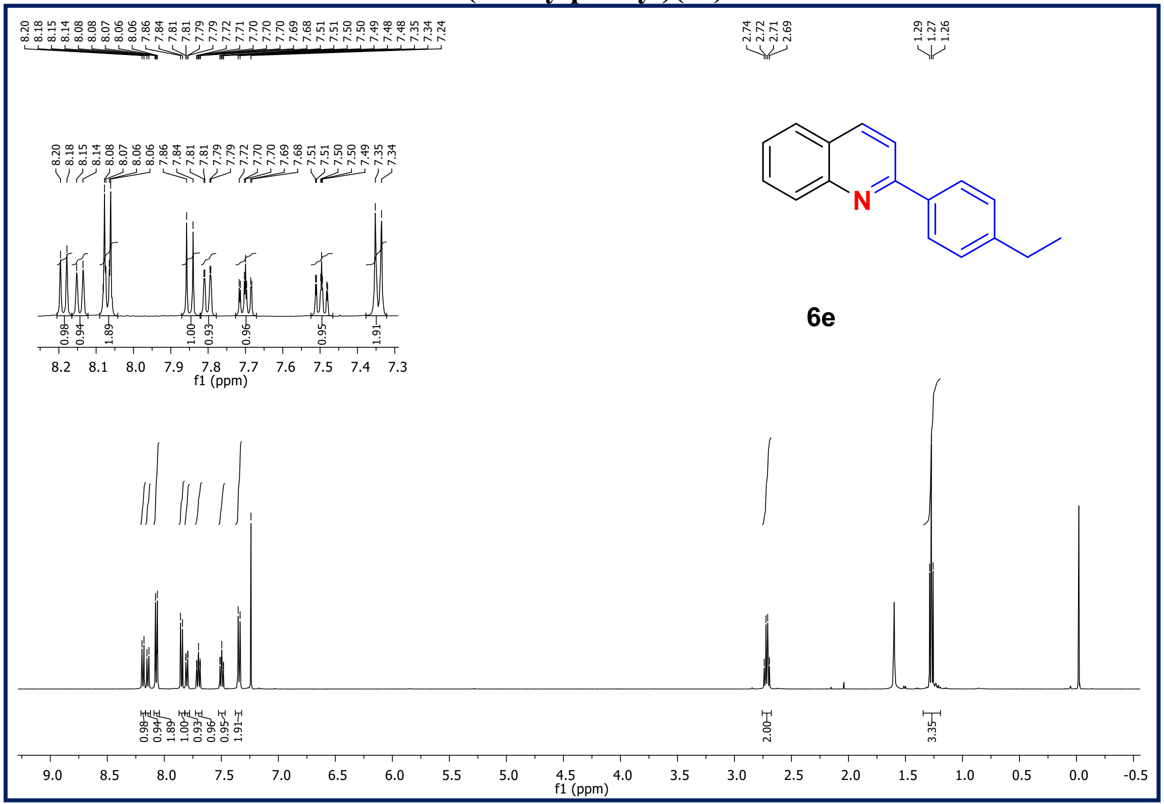

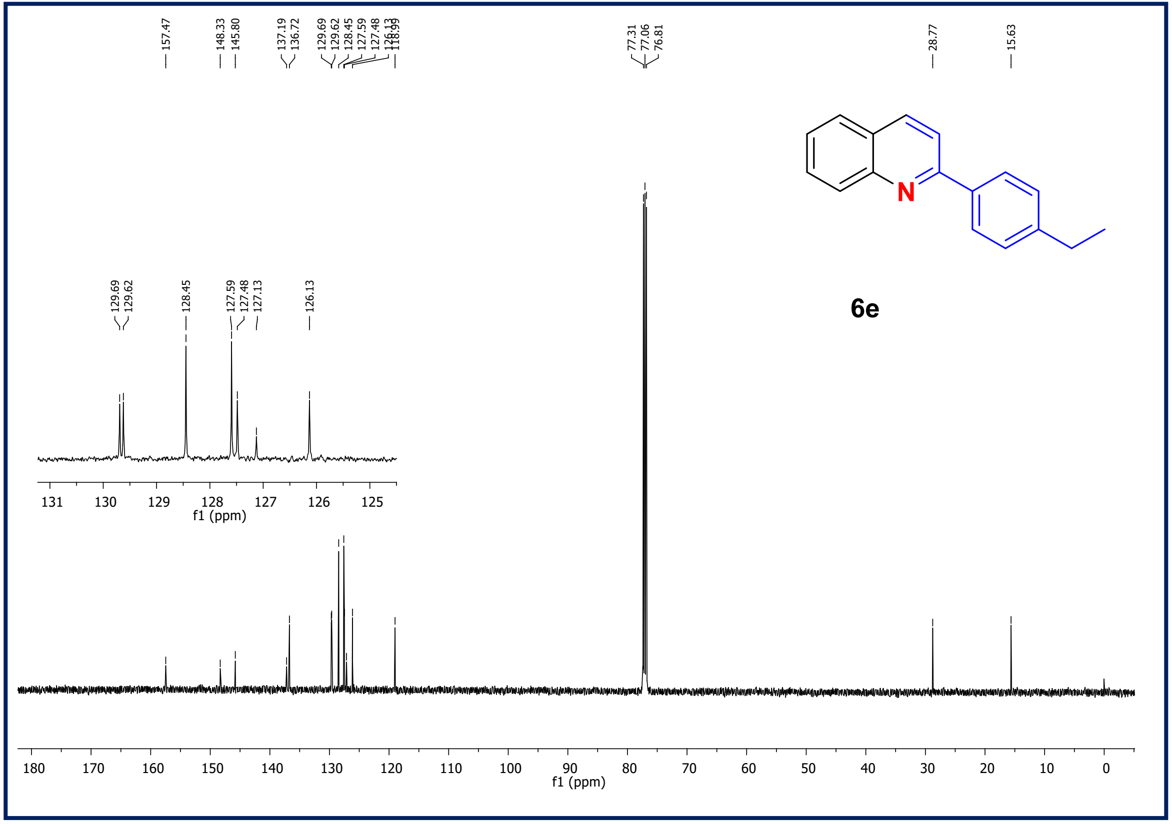

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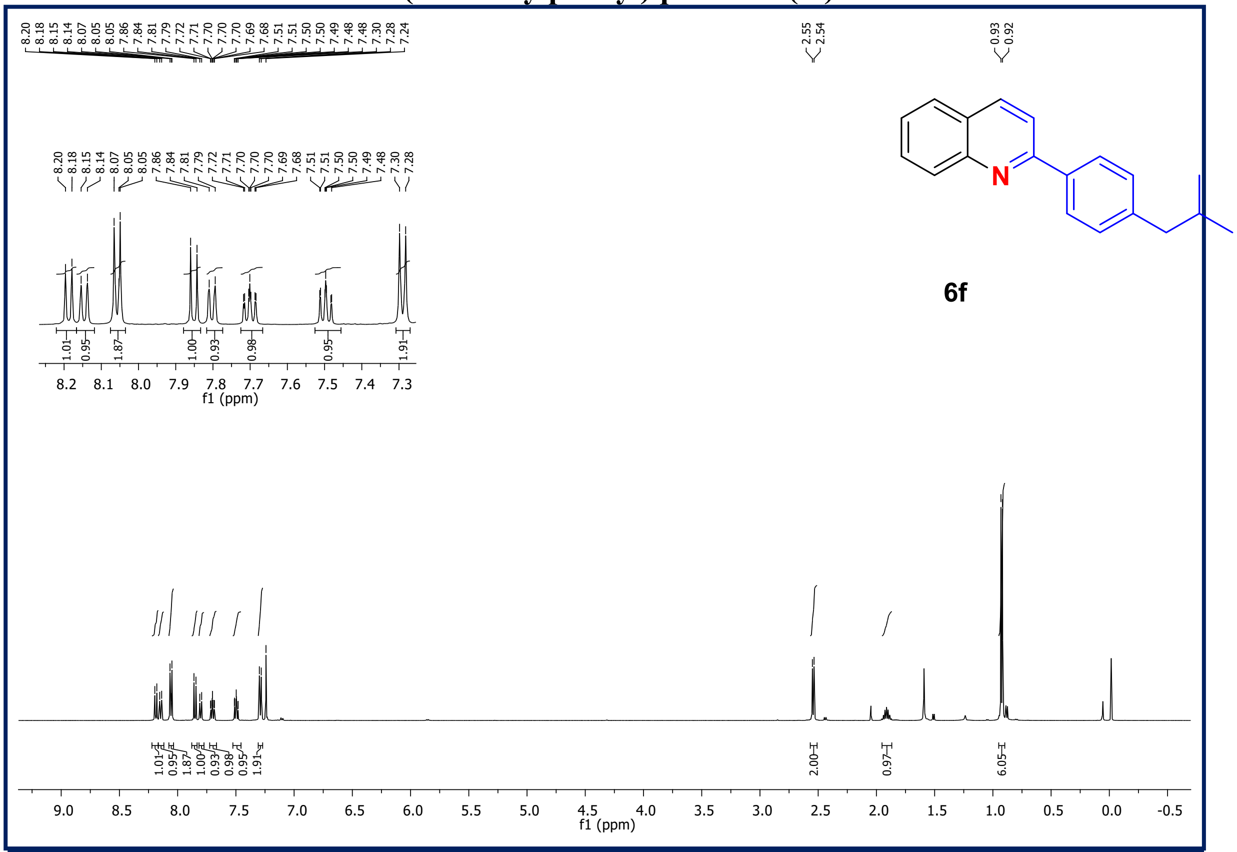

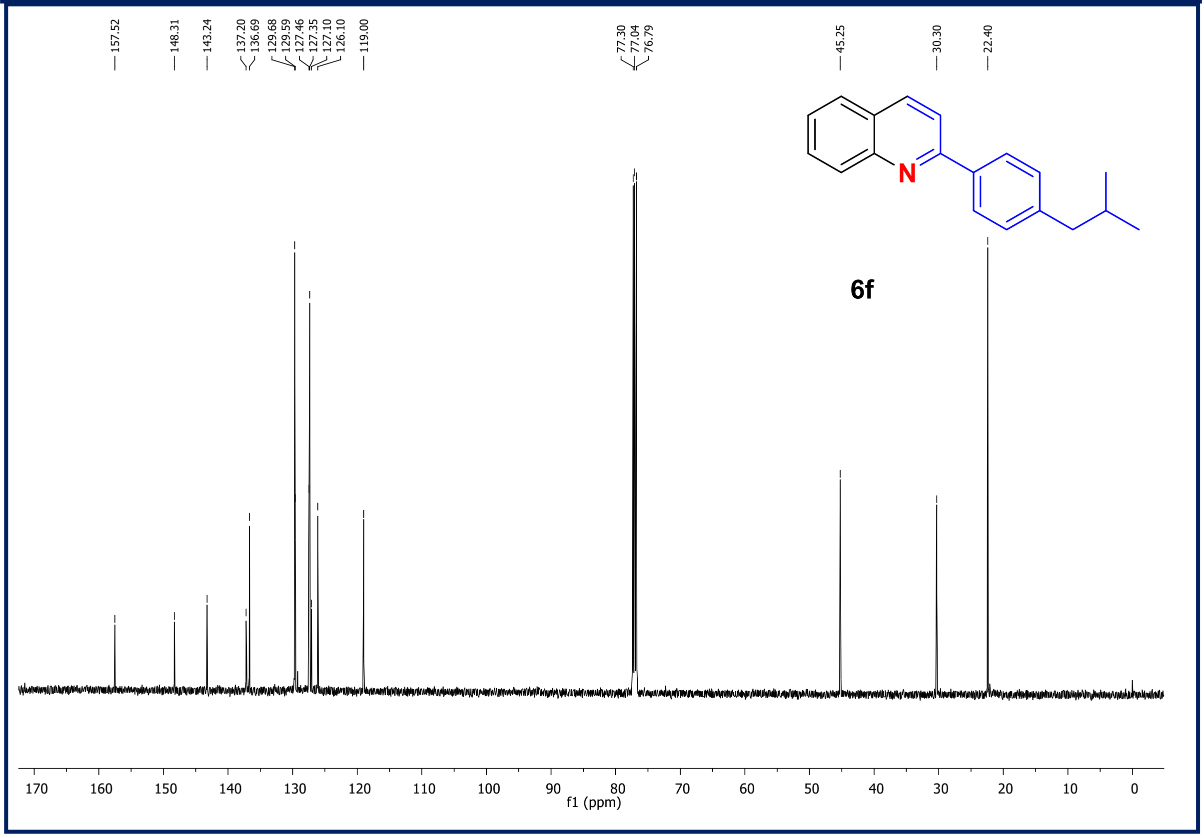

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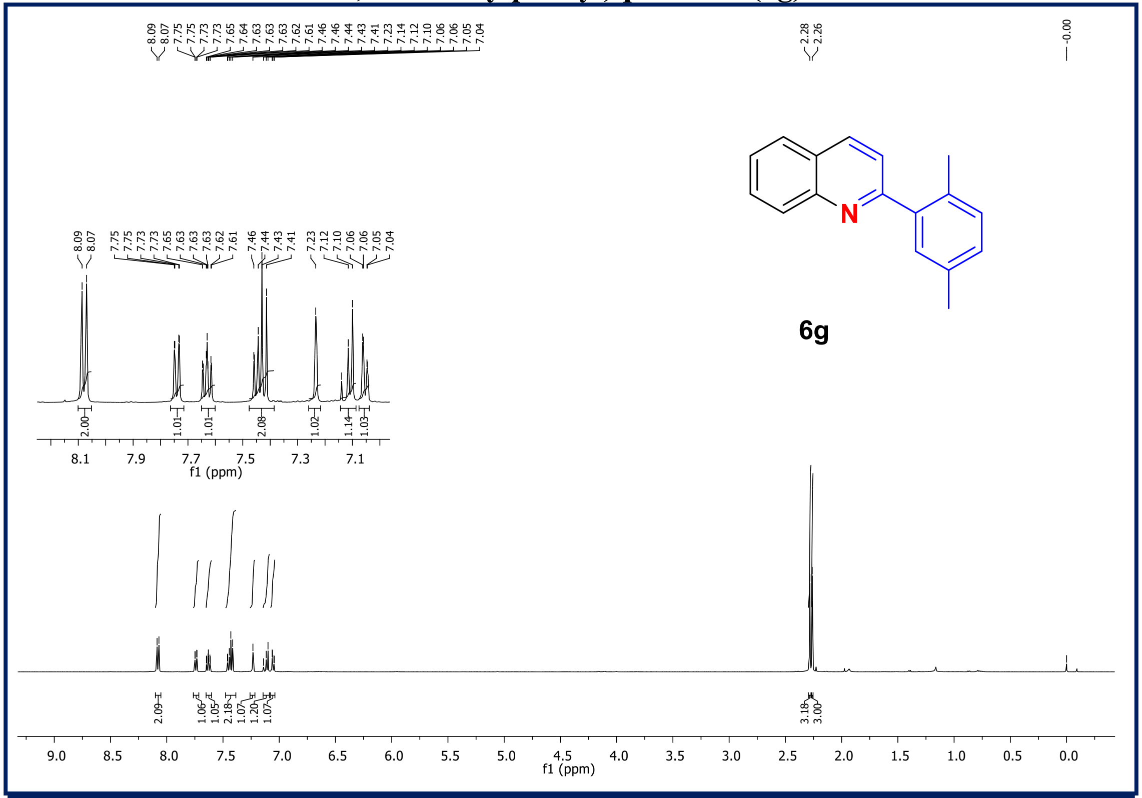

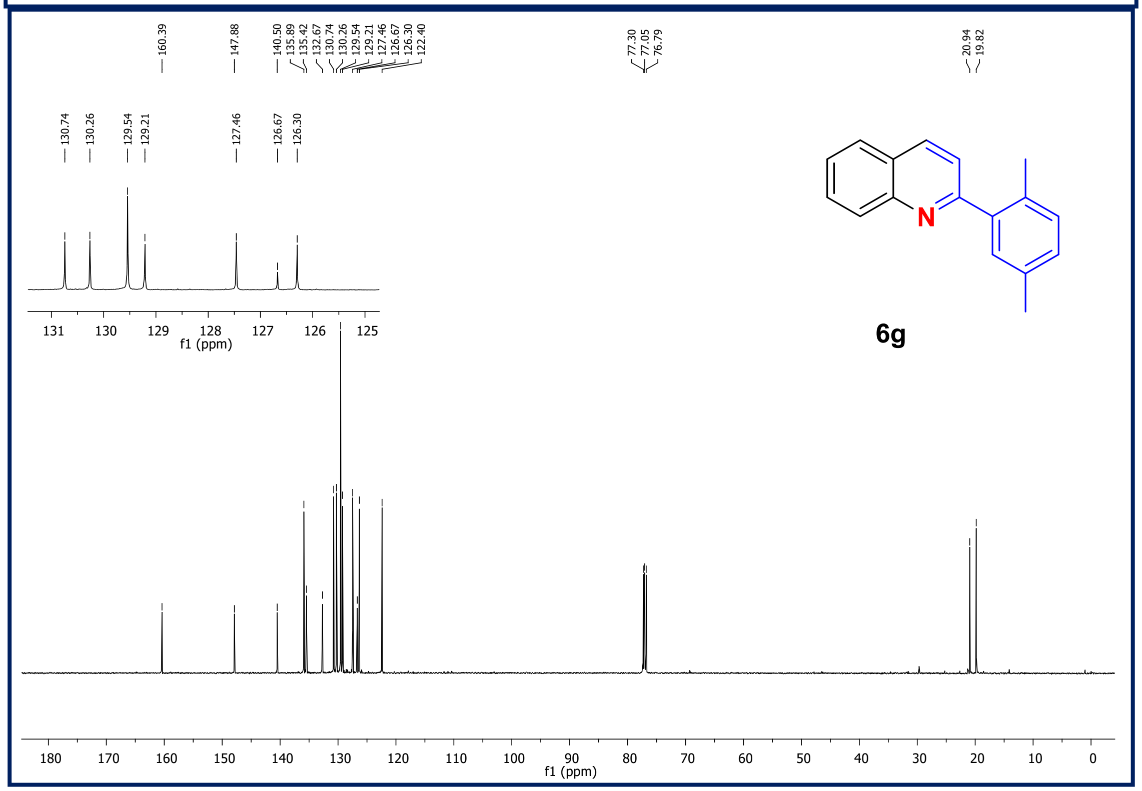

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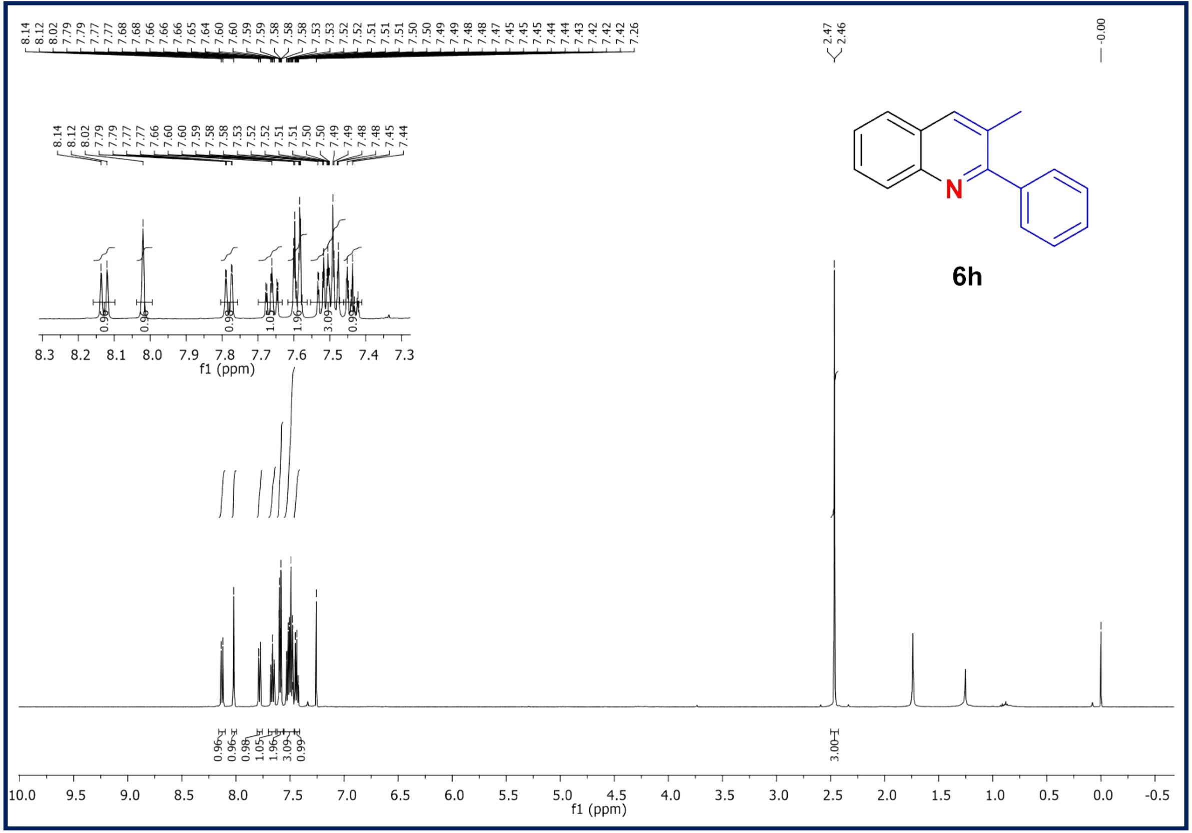

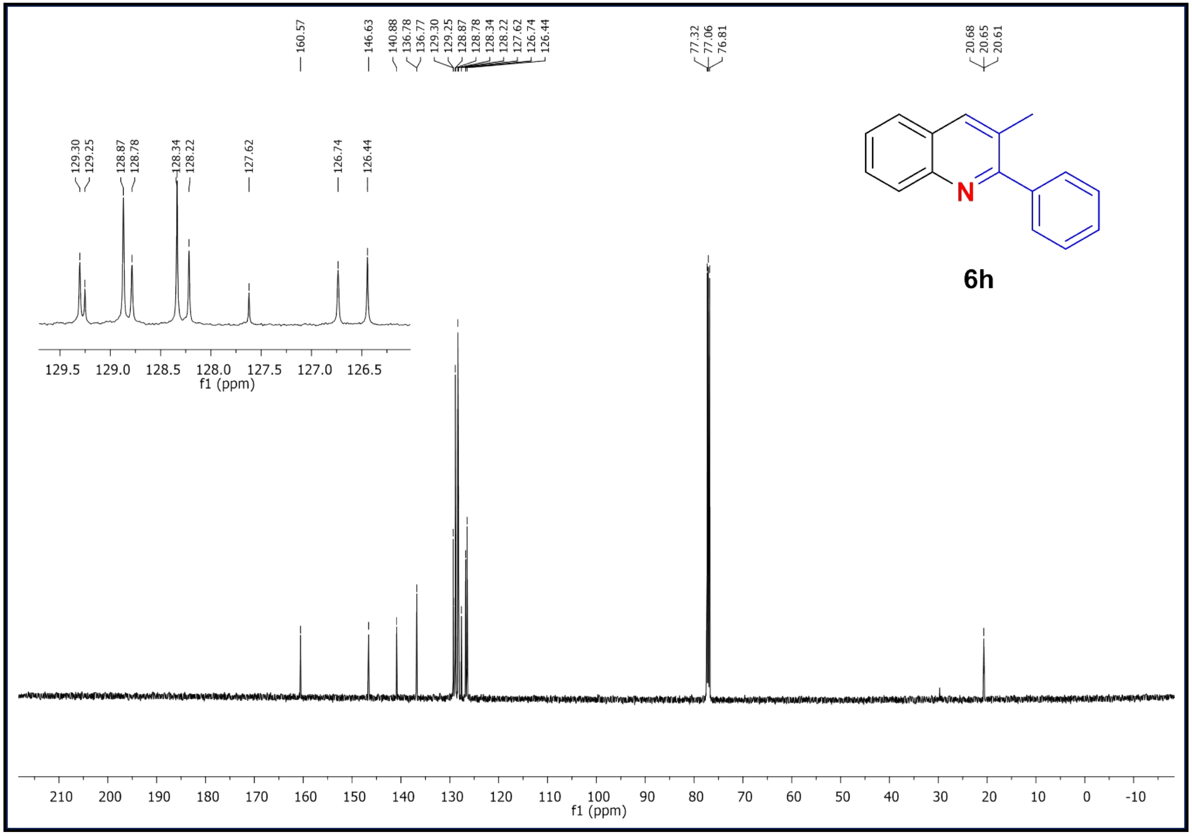

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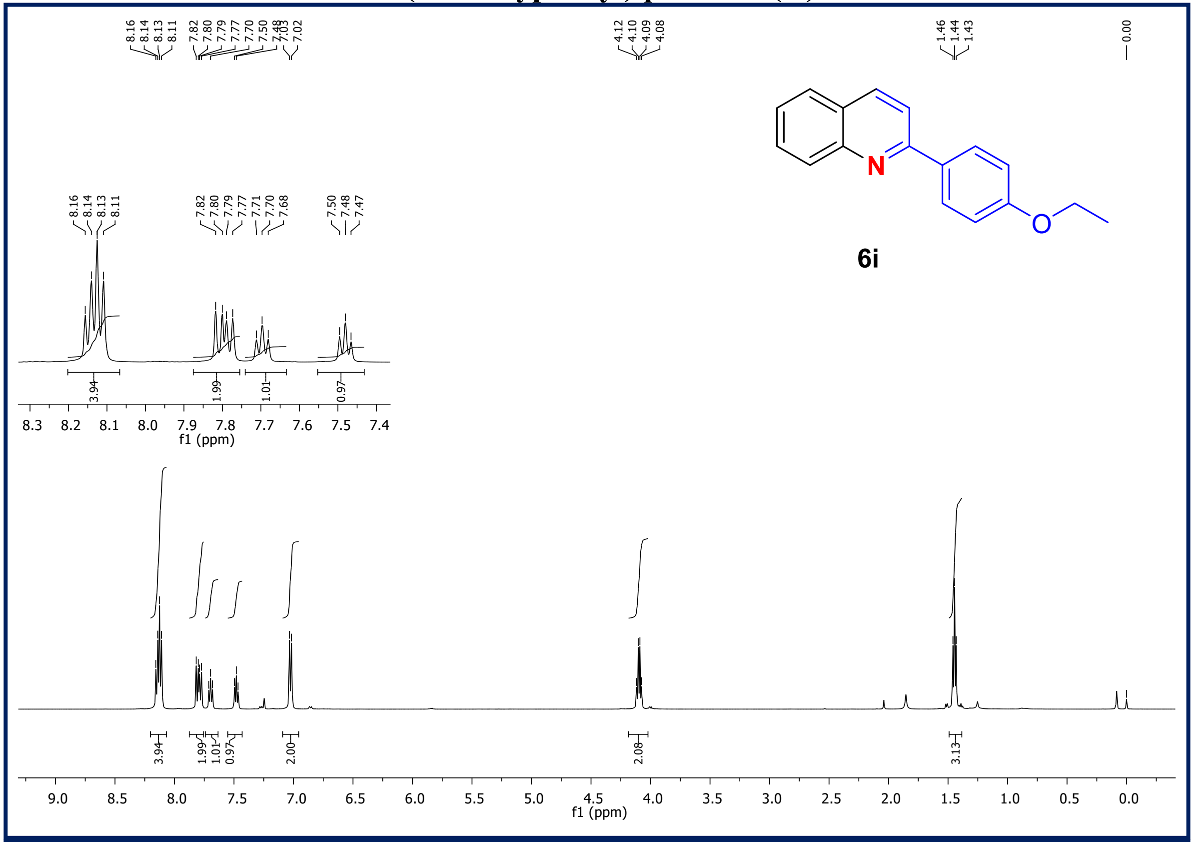
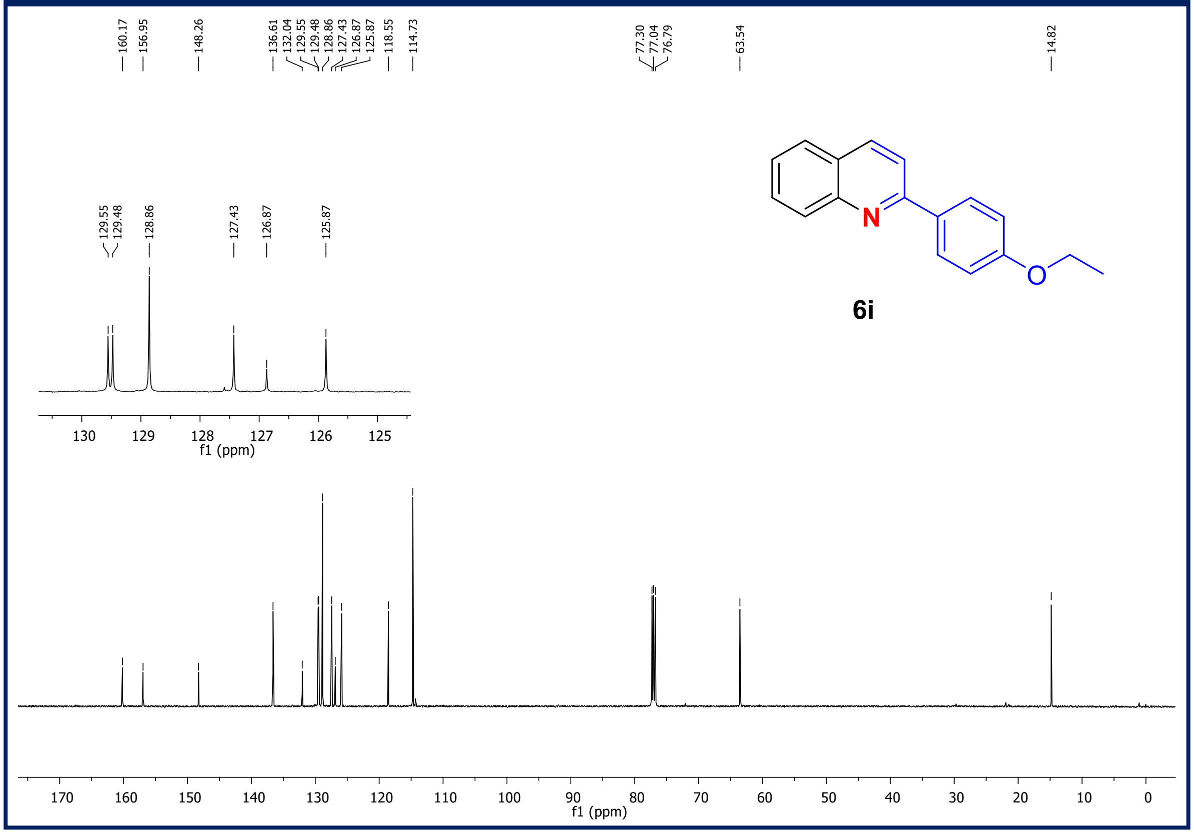
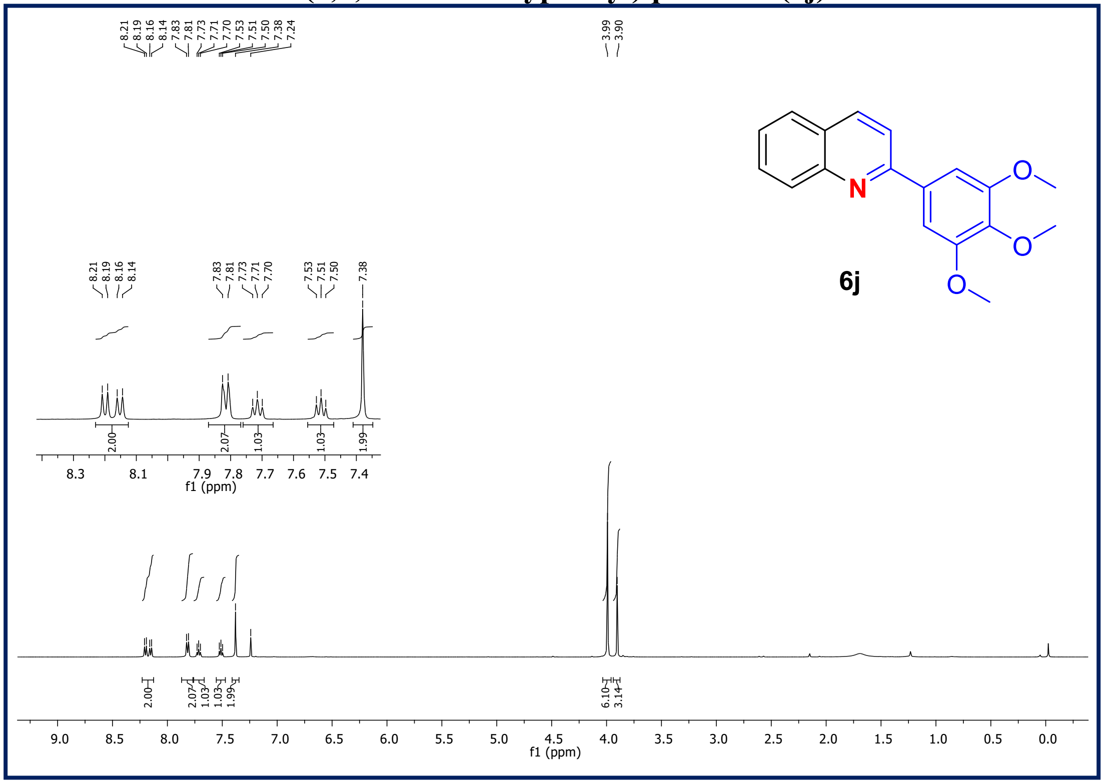
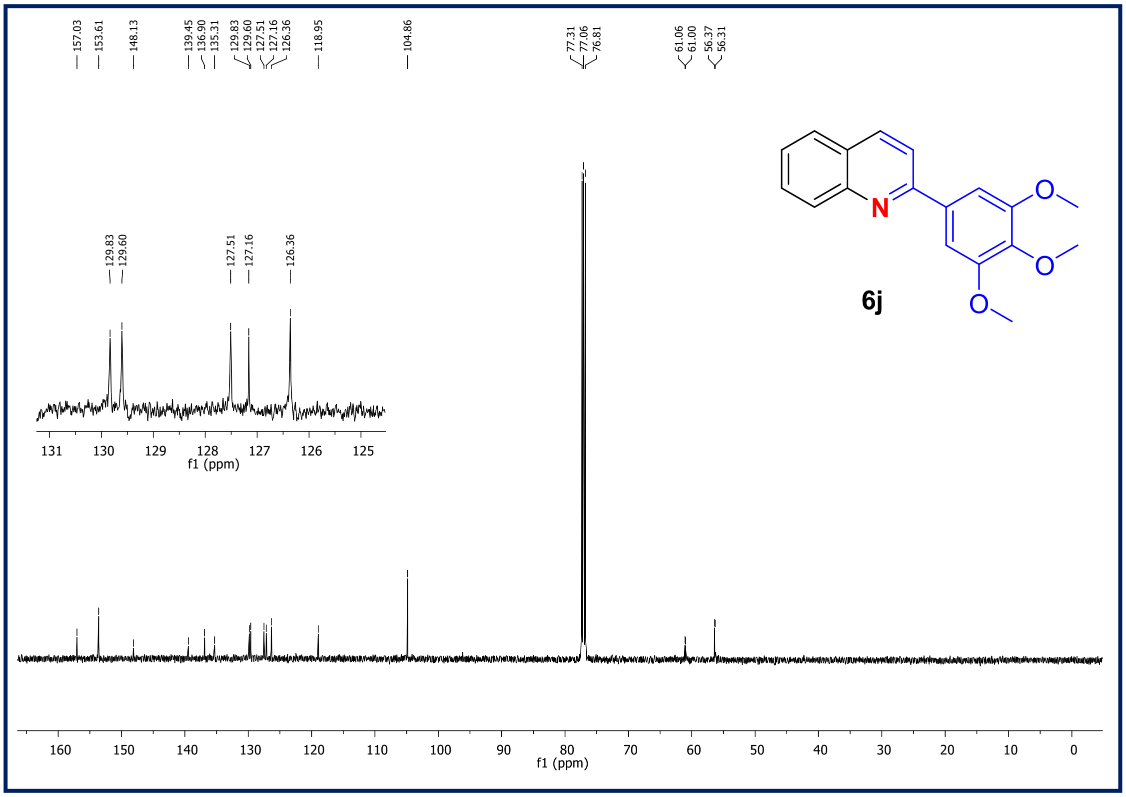




2-(3,4,5-trimethoxyphenyl)quinoline (6j)





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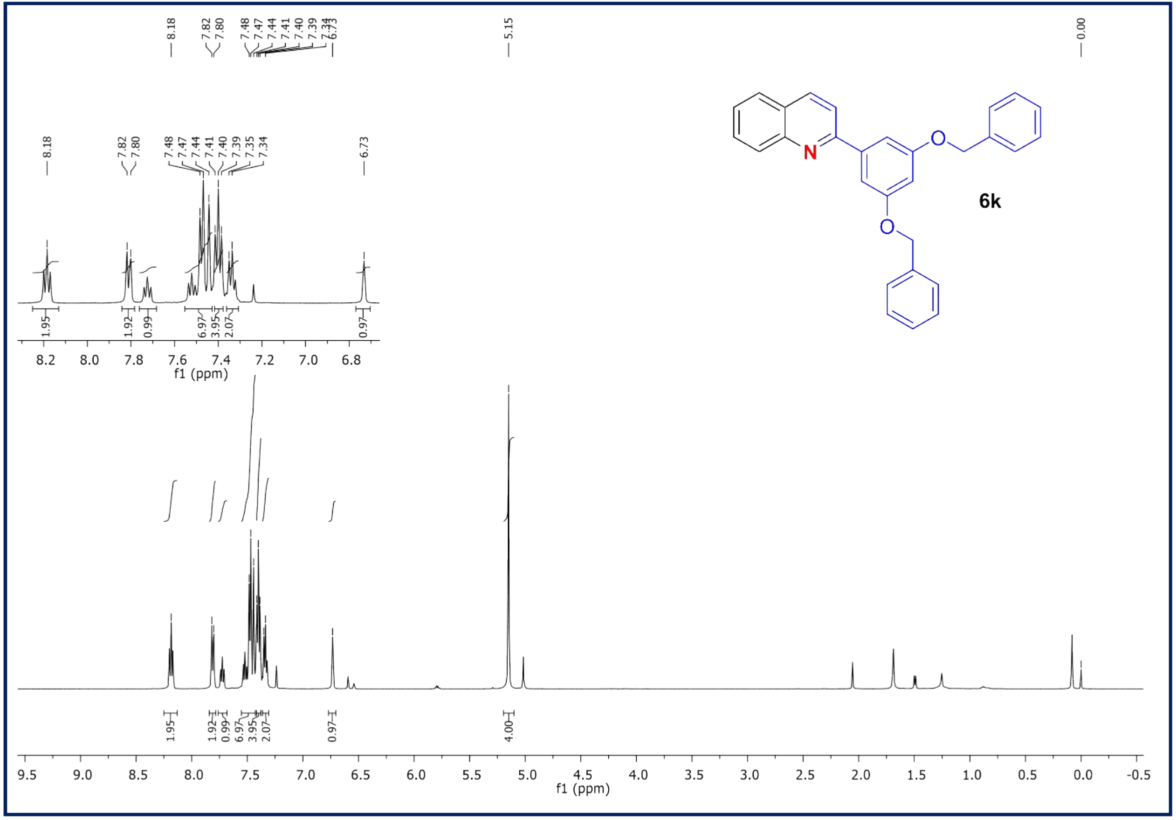

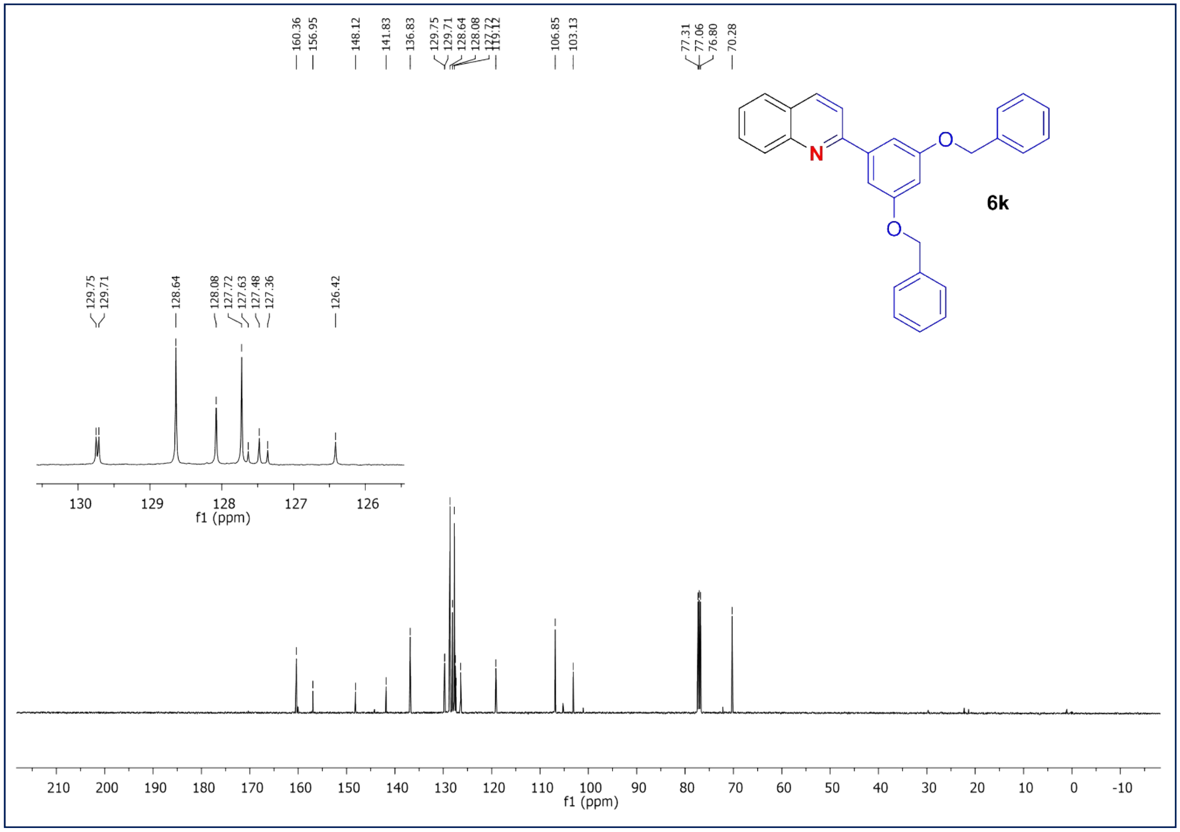

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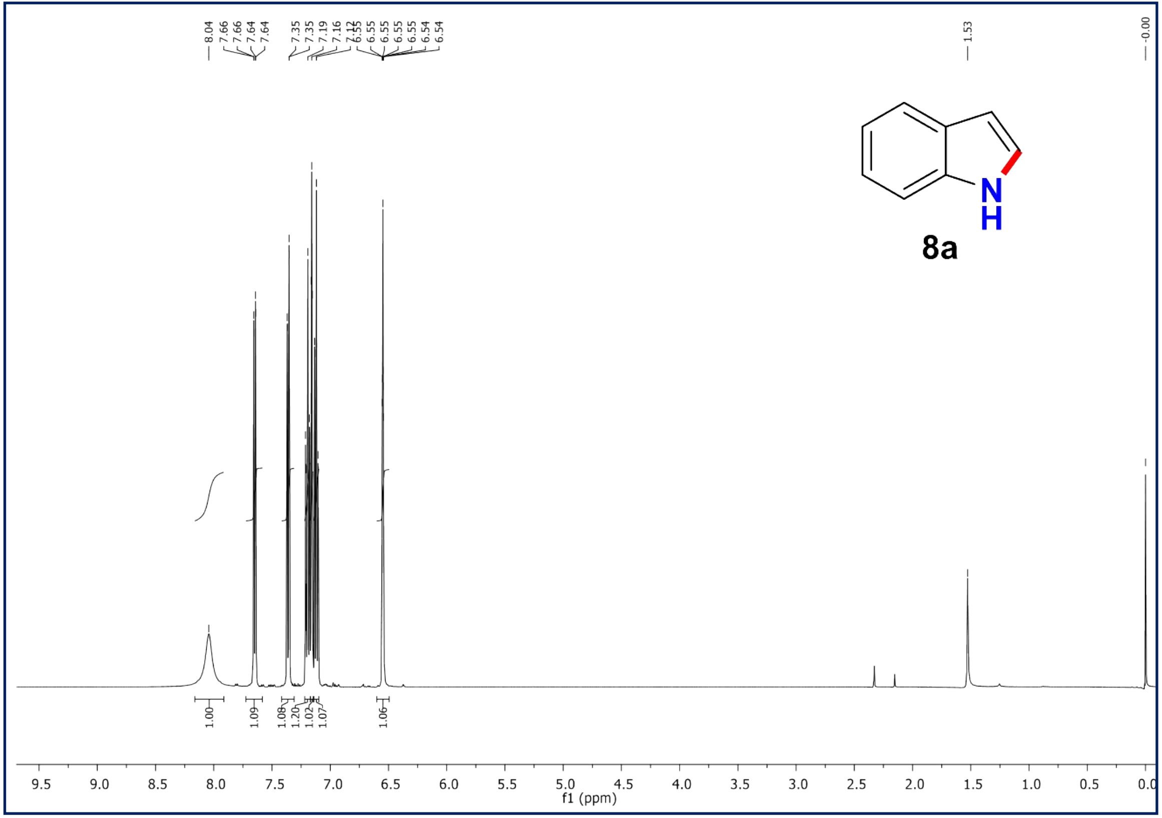
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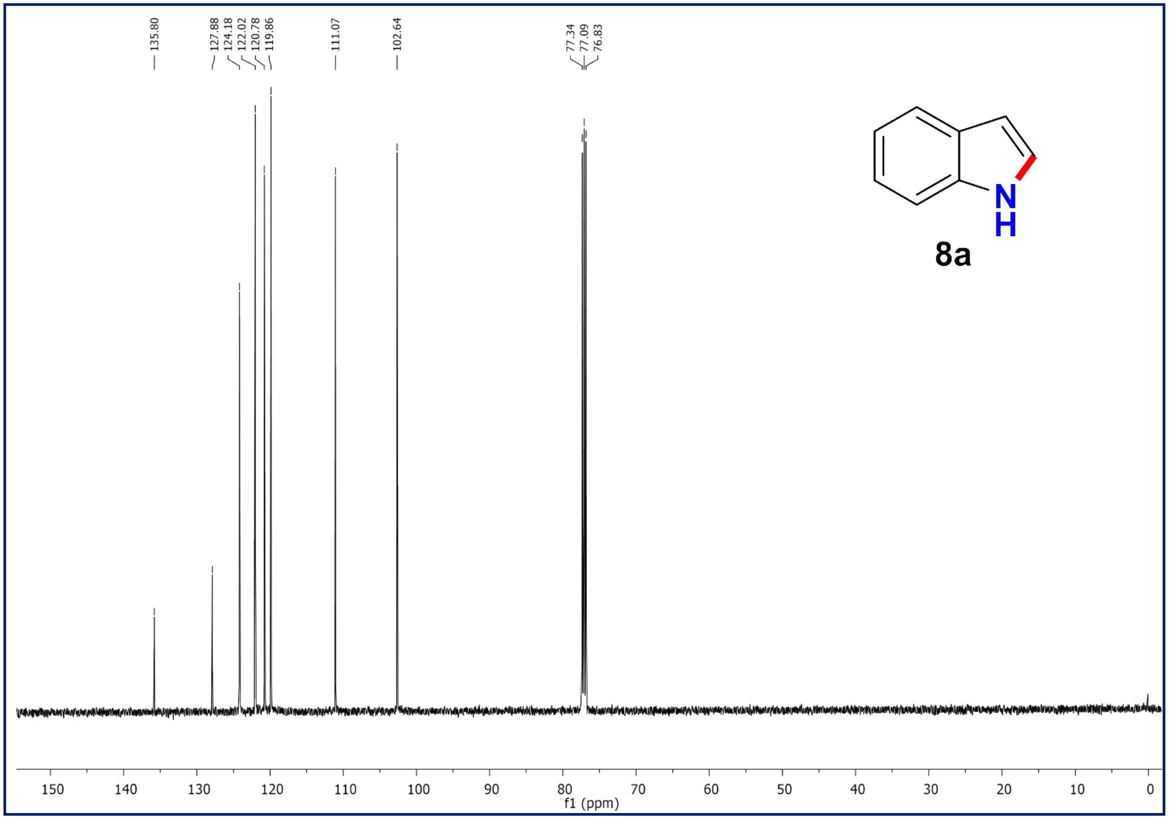
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70
60
50
40
30
20
10
0
f1 (ppm)