

Supporting Information

Copper (II) ions Supported on Functionalized Graphene Oxide: An Organometallic

Nanocatalyst for Oxidative Amination of Azoles via C–H/ C–N Bond Activation

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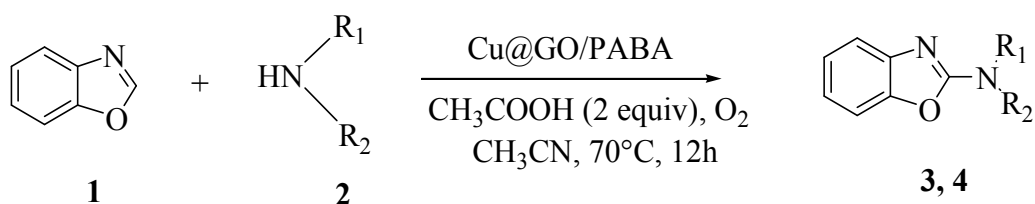
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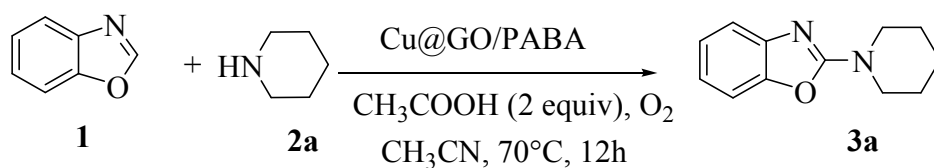
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1. Experimental Section for Synthesis of 2- amino Benzoxazole and Benzothiazole

1.1 Scheme S1: oxidative amination of azoles

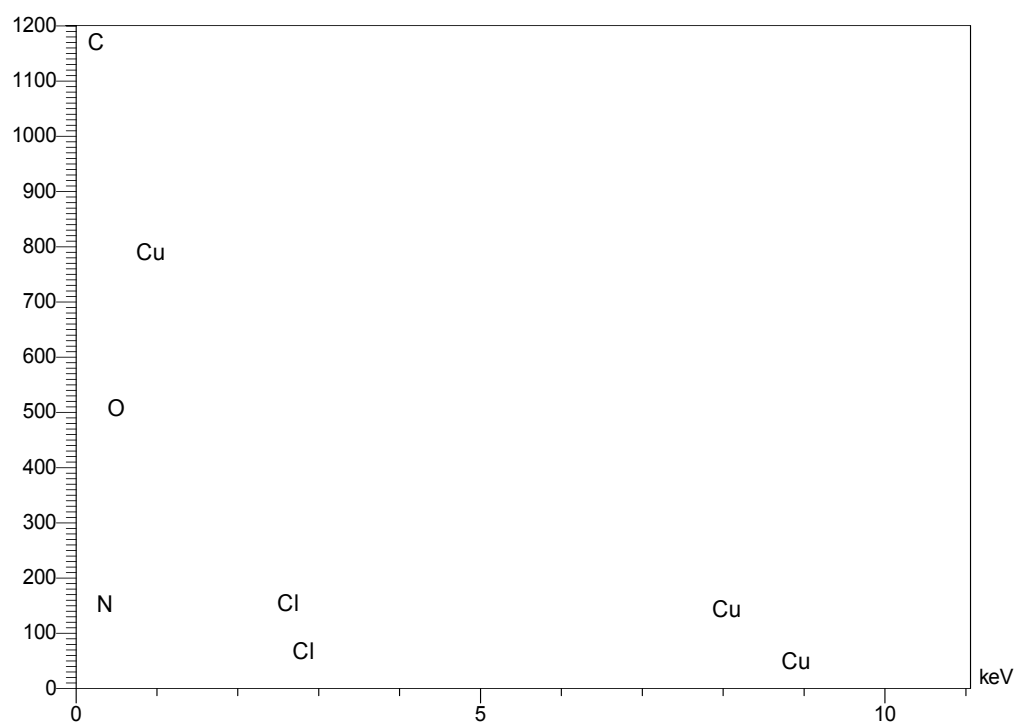


1.2 Table S1: Optimization of the Reaction Conditions of Benzoxazole and Pipyridine (Model reaction)



Entry	Additive (equiv)	Solvent (ml)	Cat. (mol %)	Oxidant (1 atm)	Time (h)	Conversion (%)	Yield (%)
1	CH ₃ COOH (2)	CH ₃ CN (2)	0.5	O ₂	12	60	31
2	CH ₃ COOH (2)	CH ₃ CN (2)	1	O ₂	12	90	52
3	CH ₃ COOH (2)	CH ₃ CN (2)	2	O ₂	12	100	84
4	CH ₃ COOH (2)	CH ₃ CN (2)	3	O ₂	12	95	73
5	CH ₃ COOH (2)	CH ₃ CN (2)	5	O ₂	12	95	70
6	CH ₃ COOH (2)	CH ₃ CN (2)	10	O ₂	12	80	70
7	CH ₃ COOH (2)	CH ₃ CN (2)	Optimized amount	air	12	trace	18
8	CH ₃ COOH (2)	CH ₃ CN (2)	-	O ₂	12	N.R	N.R

2. Characterization Data for synthesis of nano organometallic catalyst Cu⁺²@GO/PABA

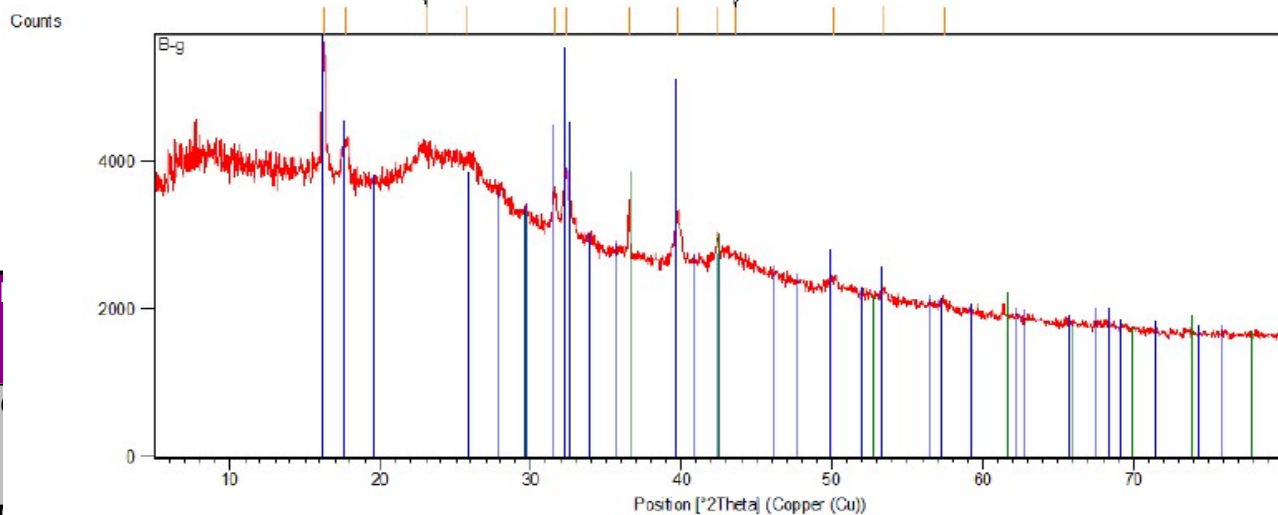
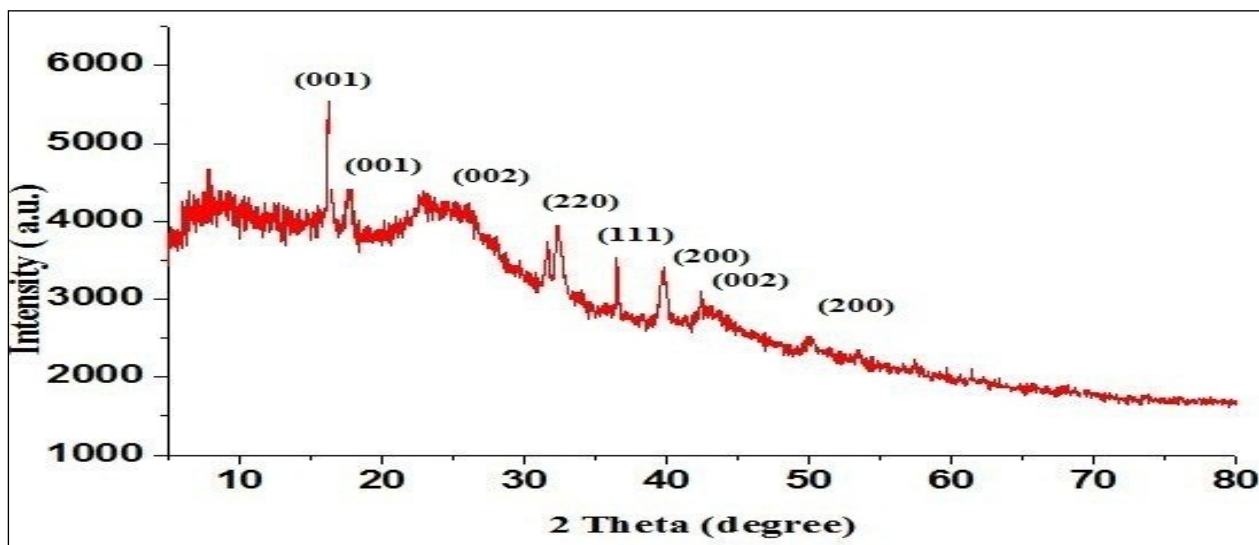


2.1 SEM-EDX

Figure S1. EDX images and quantitative result of the Cu@GO-PABA catalysts.

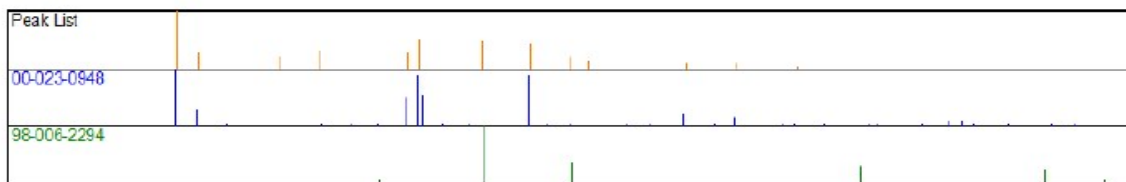
Quantitative Results

2.2 XRD



HConf	Cat#
57.18	0.00

4.69 0.00



28.59 0.00

1.19 0.00

9 1 3 3

Cu	Ka	54.6	0.554	0.199	0.083	11.45	2.62	0.731	0.00	12.90	A	10.83	12.07	0.00
			4	6	8			9						
				1.000	0.419	100.0	100.0		0.00					0.00
				0	9	0	0							

Figure S2. XRD patterns of Cu@GO-PABA.

3. Characterized data for amination of benzoxazole and benzothiazole

2-(N, N-Diethyl amino) benzoxazole (**3a**):³⁴ Yellow liquid in 80% isolated yield; ¹HNMR (500 MHz, CDCl₃) δ (ppm) 7.93 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 10 Hz, 1H), 7.55 (t, *J* = 15.0 Hz, 1H), 7.50 (t, *J* = 15.0 Hz, 1H), 4.23 (q, *J* = 6.6 Hz, 4H), 3.62 (t, *J* = 5 Hz, 6H); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 160.5, 145.2, 140.5, 127.5, 125.7, 121.5, 111.4, 61.6, 48.1; GC-MS (EI) *m/z* = 190 [M].

2- (N, N-Dipropylamino) benzoxazole (**3b**): Isolated yield 40%; ¹HNMR (500 MHz, CDCl₃) δ (ppm) 7.36 (d, *J* = 10.0 Hz, 1H), 7.26 (t, *J* = 10.0 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 3.50 (hextet, 4H), 1.74 (t, *J* = 7.2 Hz, 4H), 0.99 (t, 6H); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 162.7, 148.7, 143.7, 123.7, 119.8, 115.7, 50.3, 22.2, 11.1; GC-MS (EI) *m/z* = 218 [M].

2-(N, N-Diisopropylamino) benzoxazole (**3c**): Isolated yield 30%; ¹HNMR (500 MHz, CDCl₃) δ (ppm) 7.72-7.74 (m, *J* = 10.0 Hz, 2H), 7.55-7.57 (m, *J* = 10.0 Hz, 2H), 4.24 (heptet, 2H), 1.31 (d, *J* = 7.2 Hz, 12H); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 164.5, 157.0, 128.8, 118.9, 116.0, 110.5, 106.5, 42.1, 29.7; GC-MS (EI) *m/z* = 218 [M].

2-(Piperidin-1-yl) benzoxazole (**3d**):³⁴ Yellow solid in 84% isolated yield; ¹HNMR (500 MHz, CDCl₃) δ (ppm) 7.36 (d, *J* = 5.0 Hz, 1H), 7.25 (d, *J* = 5.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 3.69 (br, 4H), 1.71 (br, 6H); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 148.7, 143.3, 128.7, 123.8, 120.2, 116.0, 108.5, 46.6, 25.5, 24.0; GC-MS (EI) *m/z* = 202 [M].

2-(Morpholin-1-yl) benzoxazole (**3e**):³⁴ Yellow solid in 53% isolated yield; ¹HNMR (500 MHz, CDCl₃) δ (ppm) 7.37 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 3.80 (br, *J* = 4.4 Hz, 4H), 3.67 (br, *J* = 4.4 Hz, 4H); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 162.0, 148.7, 142.8, 124.0, 120.9, 116.4, 108.8, 66.1, 45.7; GC-MS (EI) *m/z* = 204 [M].

2-(Pipirazin-i-yl) benzoxazole (**3f**): Yellow solid in 75% isolated yield; ¹HNMR (500 MHz, CDCl₃) δ (ppm) 7.42 (d, *J* = 10.0 Hz, 1H), 7.31 (d, *J* = 10.0 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 3.89 (br, 4H), 3.69 (br, 4H), 1.59 (br, 1H, NH); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 164.6, 155.1, 137.7, 124.2, 121.1, 118.5, 117.3, 45.8, 45.0; GC-MS (EI) *m/z* = 203 [M].

2-(4-Methyl-piperazine-1-yl) benzoxazole (**3g**): Yellow solid in 70% isolated yield; ¹HNMR (500 MHz, CDCl₃) δ (ppm) 7.38 (d, *J* = 5.0 Hz, 1H), 7.27 (d, *J* = 5 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 3.75 (s, 3H, N-CH₃), 2.55 (br, 4H), 2.37 (br, 4H); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 163.8, 152.6, 143.1, 123.9, 120.6, 116.3, 108.7, 54.2, 46.2, 45.5; GC-MS (EI) *m/z* = 217 [M].

2-(4-Phenyl-piperazine-1-yl) benzoxazole (**3h**): Yellow solid in 50% isolated yield; ¹HNMR (500 MHz, CDCl₃) δ (ppm) 7.40-6.97 (m, *J* = 8 Hz, 9H of aromatic ring), 3.95 (m, 4H, N-CH₂), 3.31 (m, *J* = 4.4, 4H of piperazine ring), 2.20-2.17 (m, *J* = 4.4, 2H of piperazine ring); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 159.1, 156.2, 147.8, 129.2, 124.0, 120.8, 117.3, 116, 9, 108.7, 104.8, 49.1, 45.6.

2-(Pyrrolidin-1-yl) benzoxazole (**3i**):³⁴ White solid in 32% isolated yield; ¹HNMR (500 MHz, CDCl₃) δ (ppm) 7.37 (d, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 9.1 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.7 Hz, 1H), 3.68 (t, *J* = 6.6 Hz, 4H), 2.07 (t, *J* = 6.7 Hz, 4H); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 153.8, 143.6, 132.0, 123.7, 120.0, 115.9, 108.5, 47.3, 25.5; GC-MS (EI) *m/z*=188 [M].

2-(N, N-Diethyl amino) benzothiazole (**4a**): Yellow liquid in 94% isolated yield, ¹HNMR (500 MHz, CDCl₃) δ (ppm) 7.92 (br, *J* = 7.2 Hz, 1H), 7.83 (br, *J* = 8.0 Hz, 1H), 7.57 (br, *J* = 8.0 Hz, 1H), 7.07 (br, *J* = 8.0 Hz, 1H), 3.19 (m, *J*₁ = 7.2 Hz, *J*₂ = 14.4 Hz, 4H), 2.09 (t, *J* = 7.2 Hz, 6H); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 151.4, 135.1, 132.4, 131.5, 128.4, 126.2, 123.4, 117.2, 49.6, 11.07; GC-MS (EI) *m/z* = 206 [M].

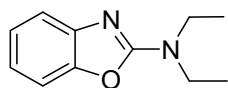
2-(N, N-Dipropylamino) benzothiazole (**4b**): 45% Isolated yield, ¹HNMR (500 MHz, CDCl₃) δ (ppm) 7.97-7.99 (d, *J* = 10.0 Hz, 1H), 7.92-7.93 (d, *J* = 5.0 Hz, 1H), 7.73-7.75 (t, *J* = 7.5 Hz, 1H), 7.68-7.64 (t, *J* = 7.5 Hz, 1H), 4.33 (t, 4H), 3.58-3.65 (hextet, *J* = 7.2 Hz, 2H), 1.47-1.73 (t, 6H); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 158.1, 143.8, 127.6, 125.4, 124.6, 116.1, 103.1, 62.1, 26.3, 15.8; GC-MS (EI) *m/z* = 234 [M].

2-(Piperidin-1-yl) benzothiazole (**4d**). Yellow solid in 94% isolated yield; ¹HNMR (500 MHz, CDCl₃) δ (ppm) 8.57-7.26 (m, 4H), 3.6 (t, 4H), 3.05 (m, 4H), 2.09 (impurity, NH), 1.70-1.26 (m, 6H); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 158.8, 141.3, 143.1, 130.9, 129.7, 116.7, 112.3, 46.6, 29.6, 25.0; GC-MS (EI) *m/z* = 218 [M].

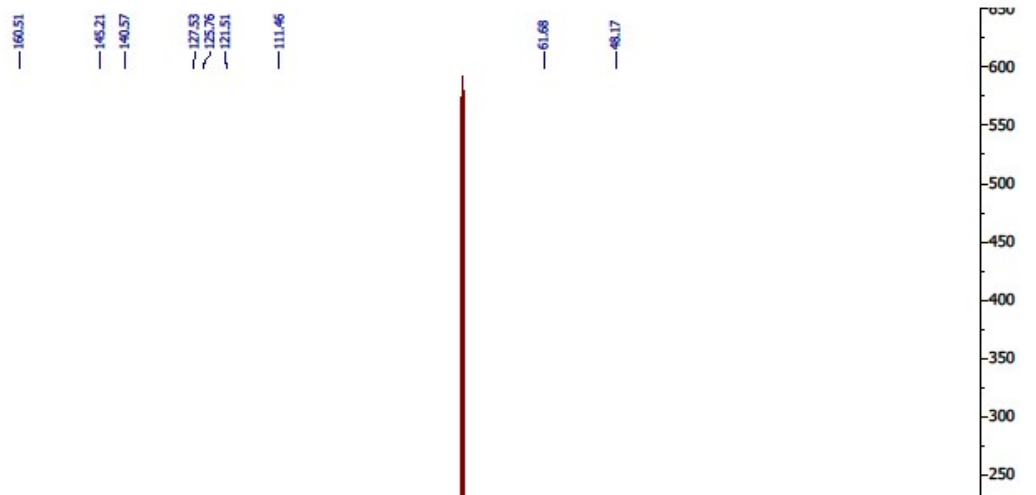
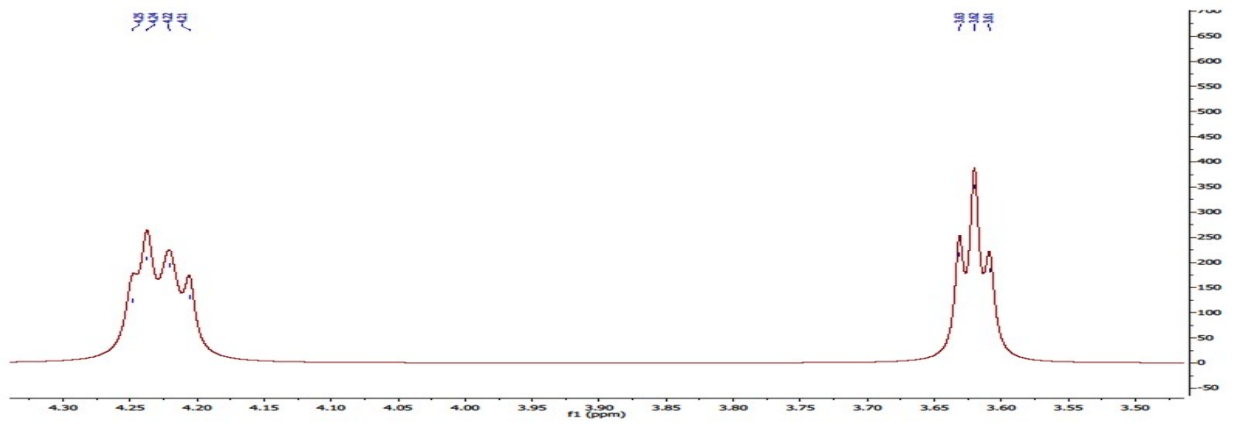
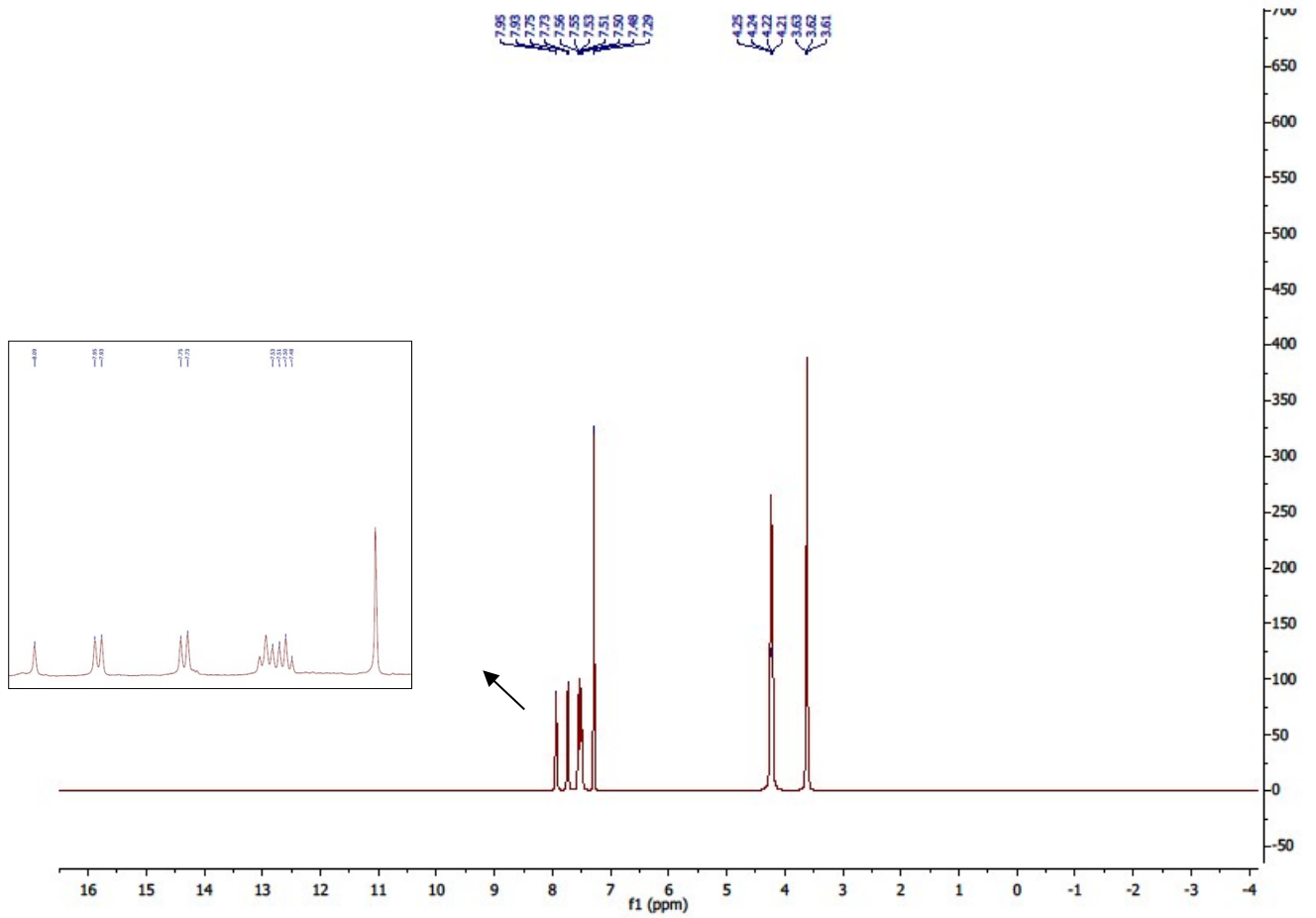
2-(Morpholin-1-yl) benzothiazole (**4e**). Yellow solid in 90% isolated yield; ¹HNMR (500 MHz, CDCl₃) δ (ppm) 7.76 (d, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.33 (m, *J* = 7.0 Hz, 1H), 3.73 (br, 4H), 3.13 (br, 4H); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 176.5, 146.5, 141.9, 134.4, 130.4, 117.7, 117.2, 66.1, 45.9; GC-MS (EI) *m/z* = 220 [M].

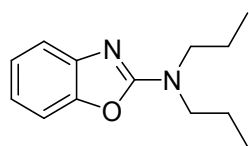
2-(Pyrrolidin-1-yl) benzoxazole (**4i**): White solid in 40% isolated yield; ¹HNMR (500 MHz, CDCl₃) δ (ppm) 7.96 (t, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 6.3 Hz, 1H), 7.29 (t, *J* = 8.8 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 3.06 (m, *J* = 5.6 Hz, 4H), 2.10 (m, *J* = 5.9 Hz, 4H); ¹³CNMR (125 MHz, CDCl₃) δ (ppm) 164.7 (2C), 151.3, 125.8, 120.6 (2C), 118.7, 49.4, 25.6; GC-MS (EI) *m/z* = 204 [M].

4. Copies of ^1H NMR and ^{13}C NMR of prepared materials

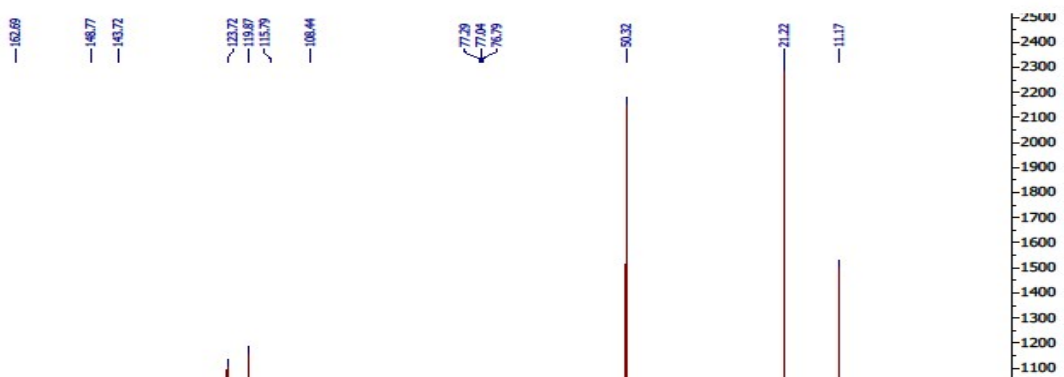
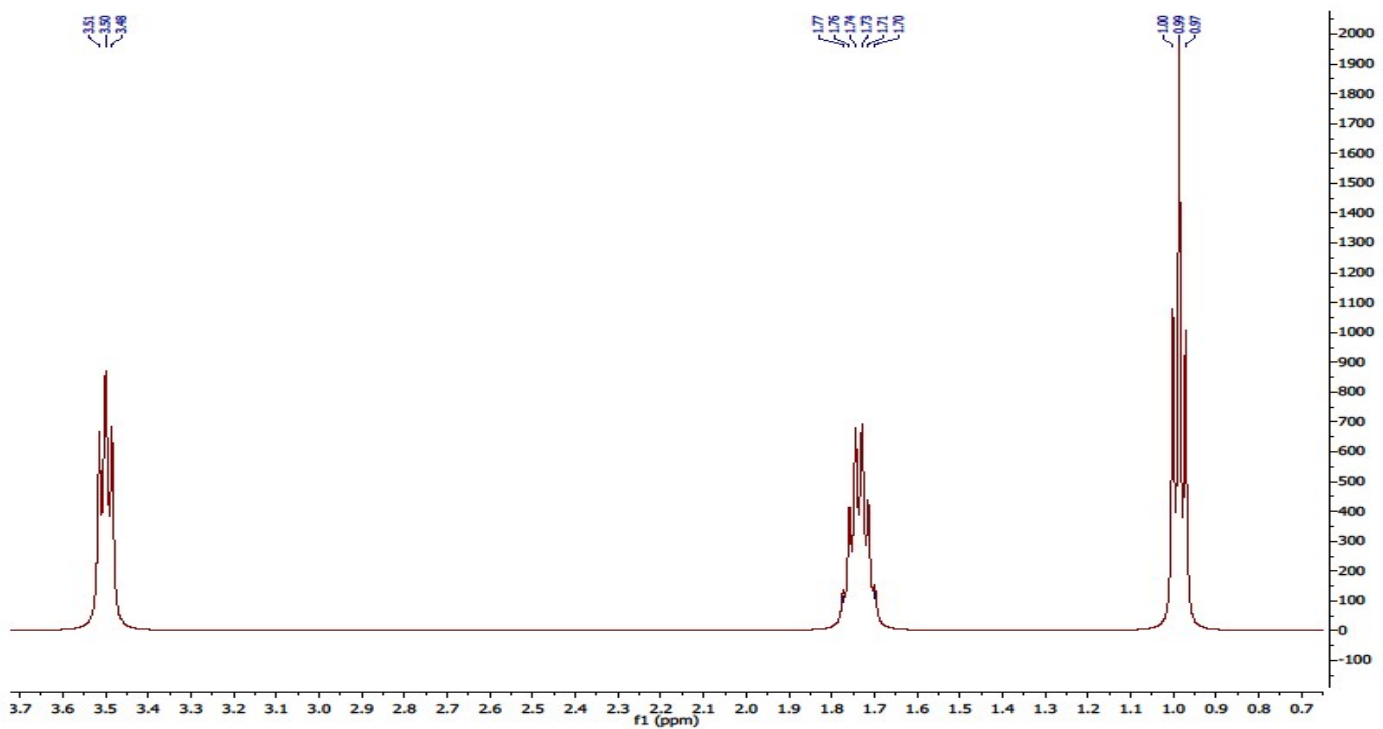
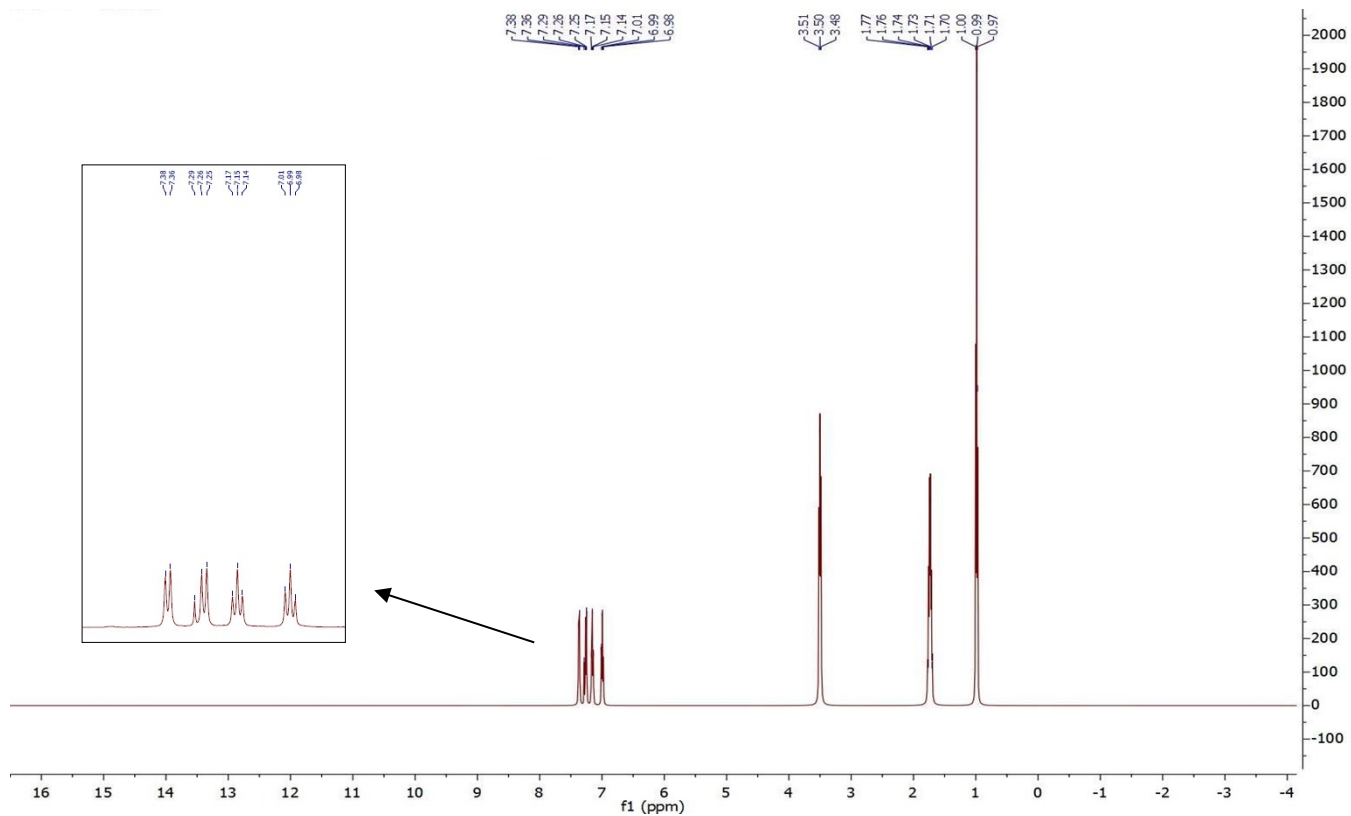


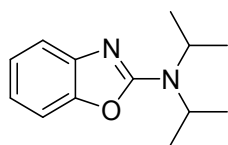
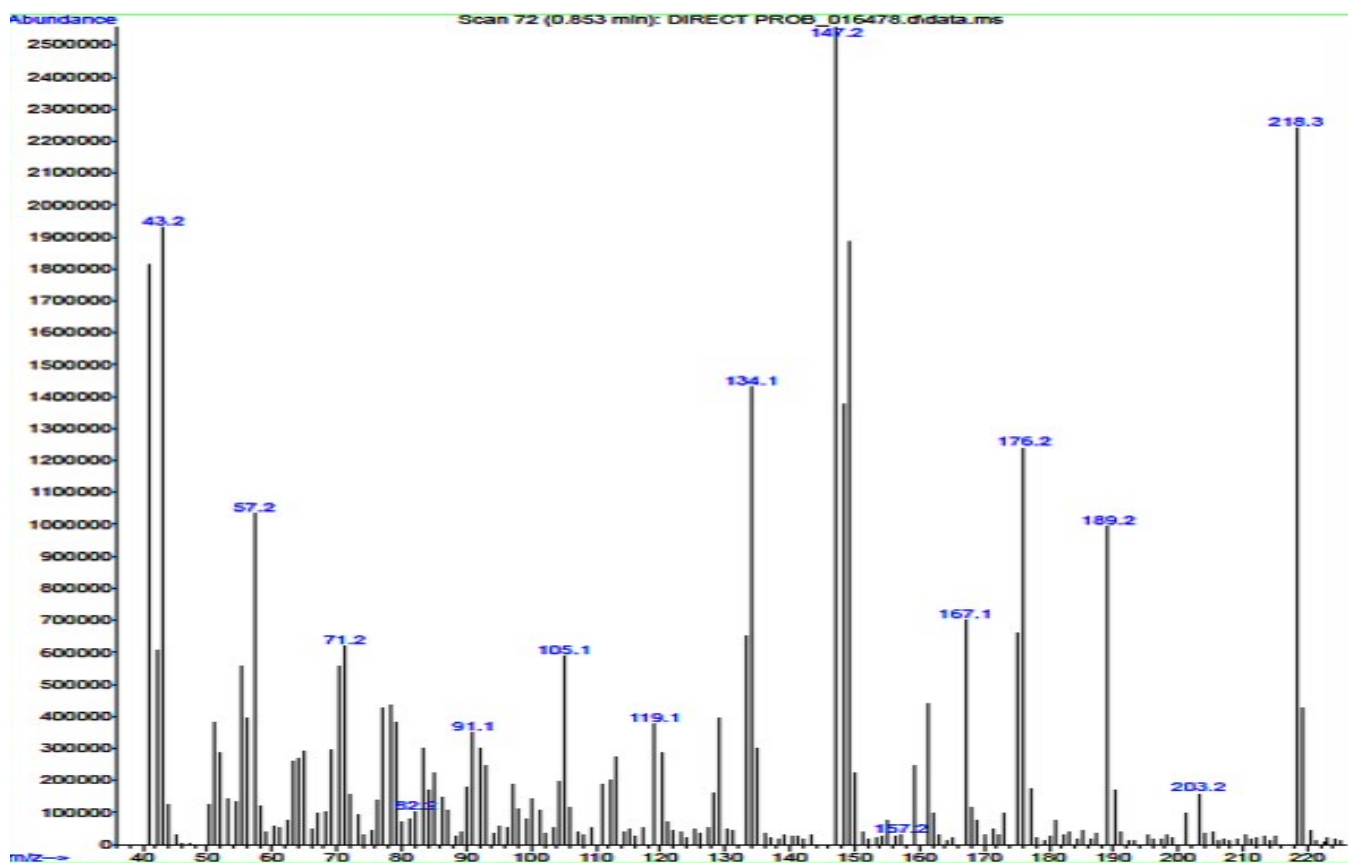
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3b





3c

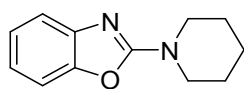
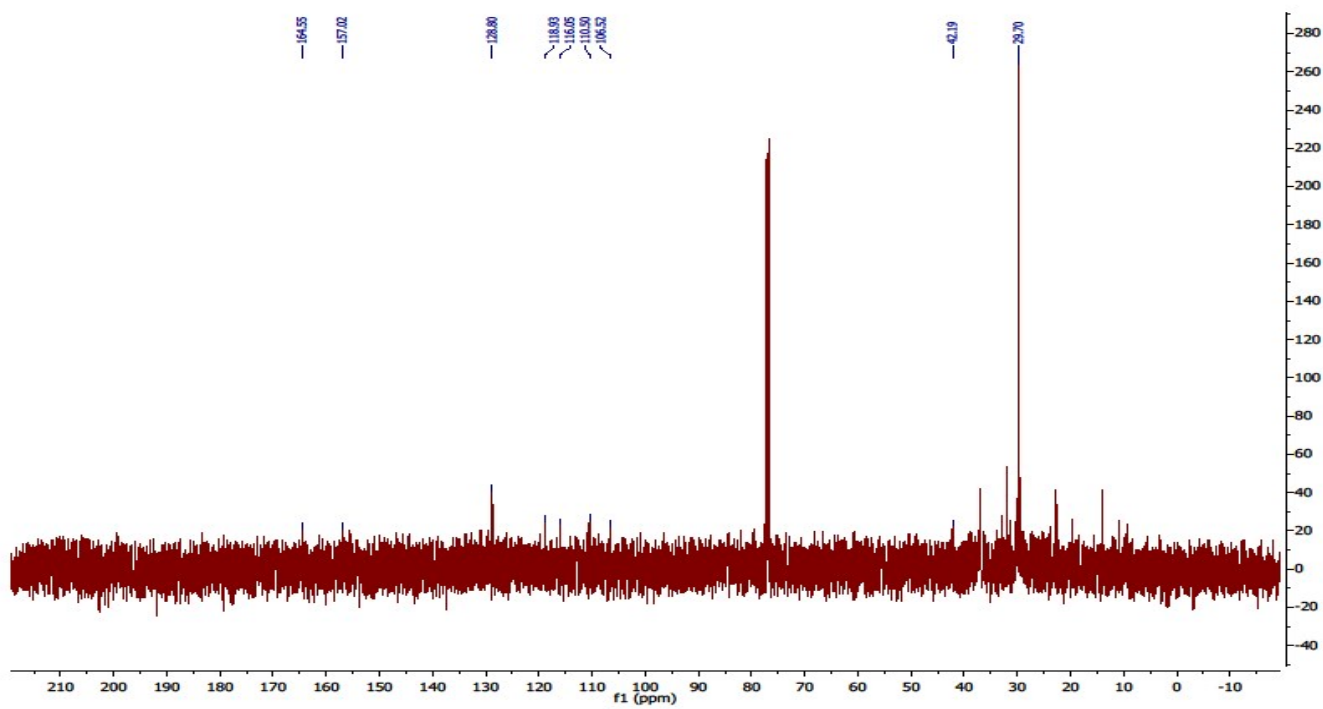
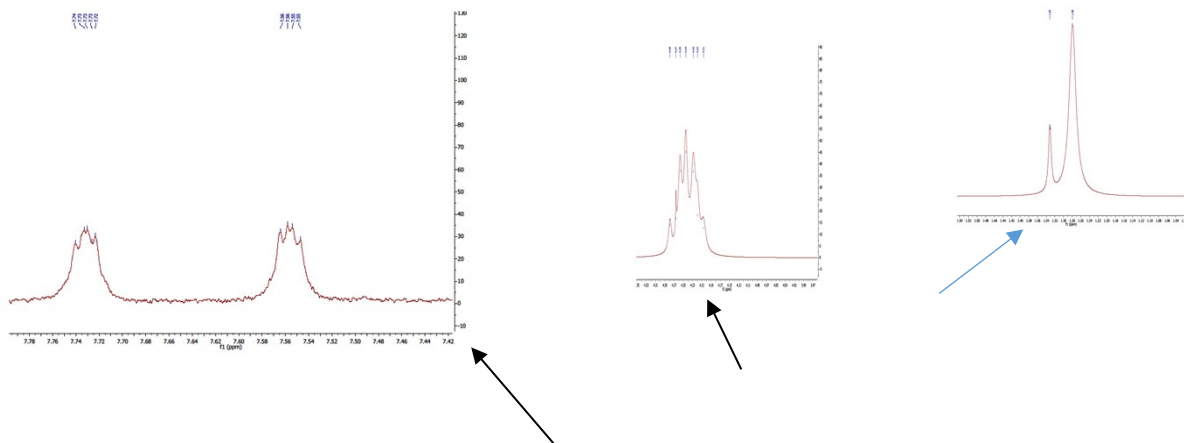
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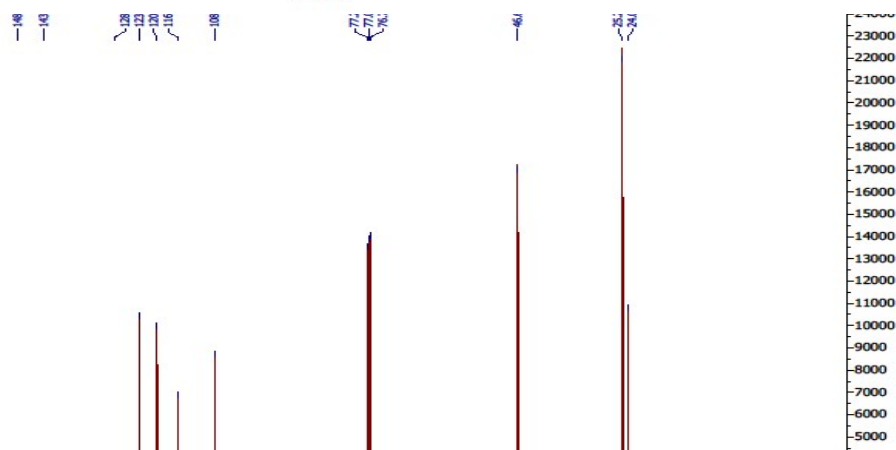
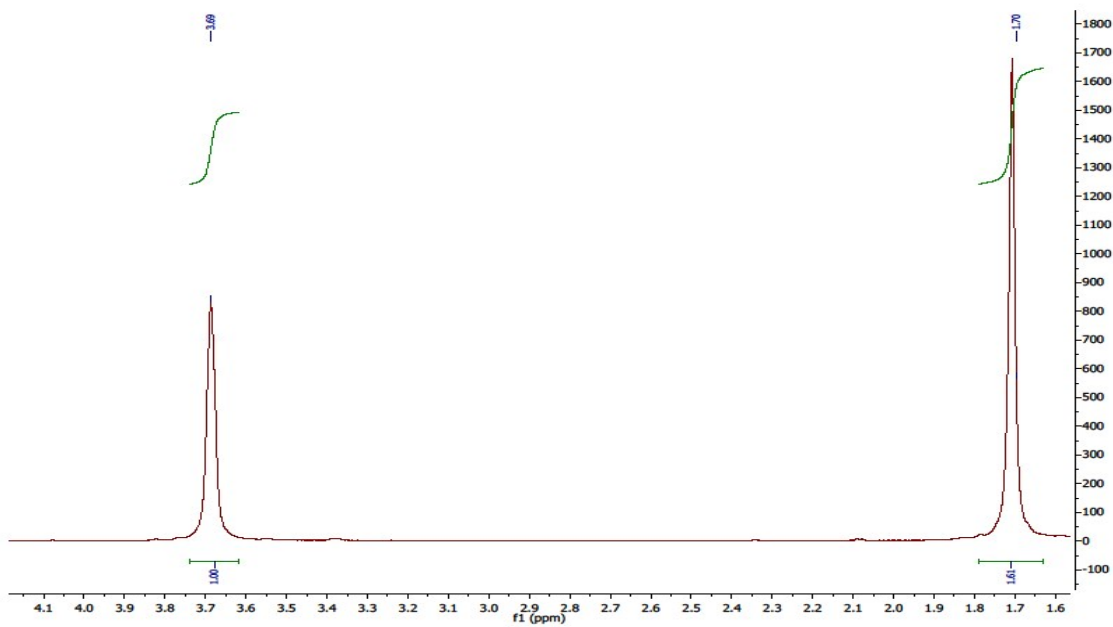
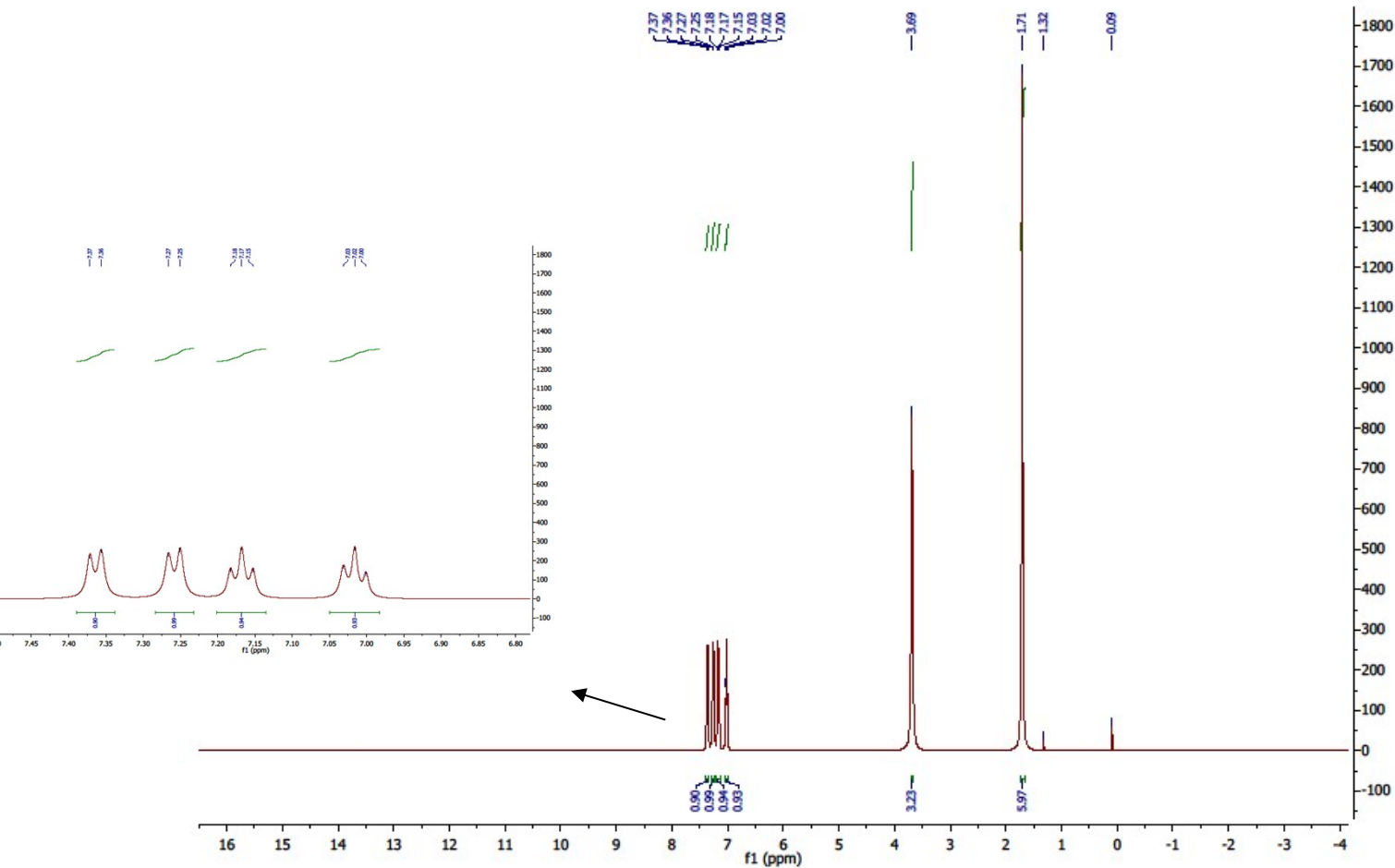
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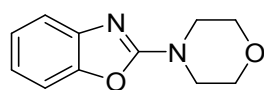
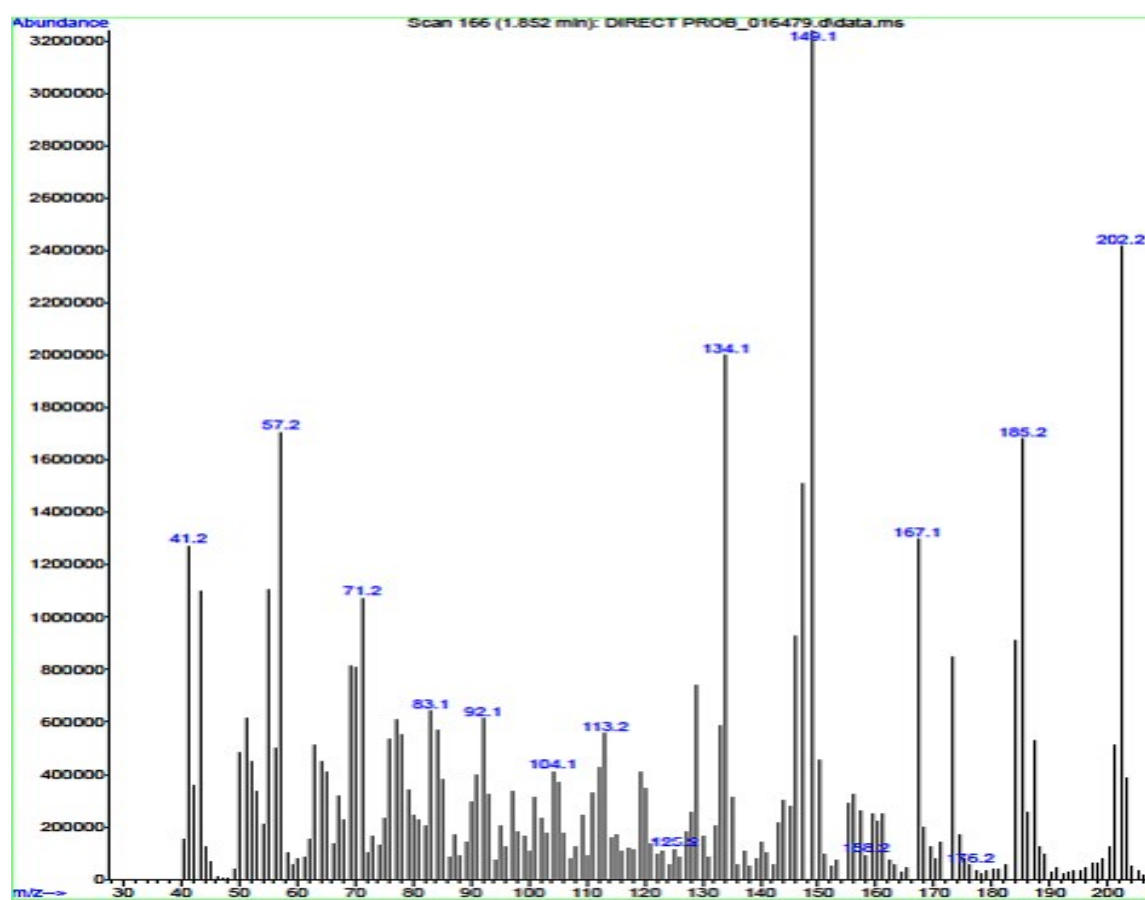
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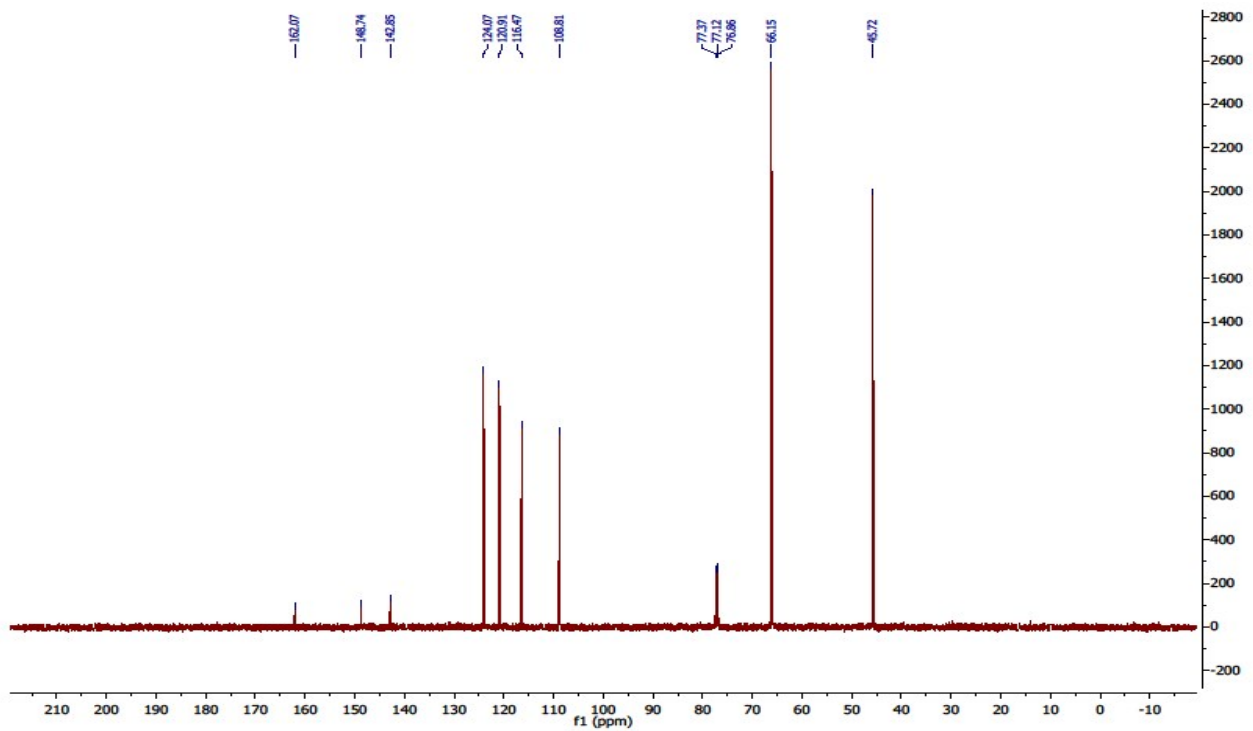
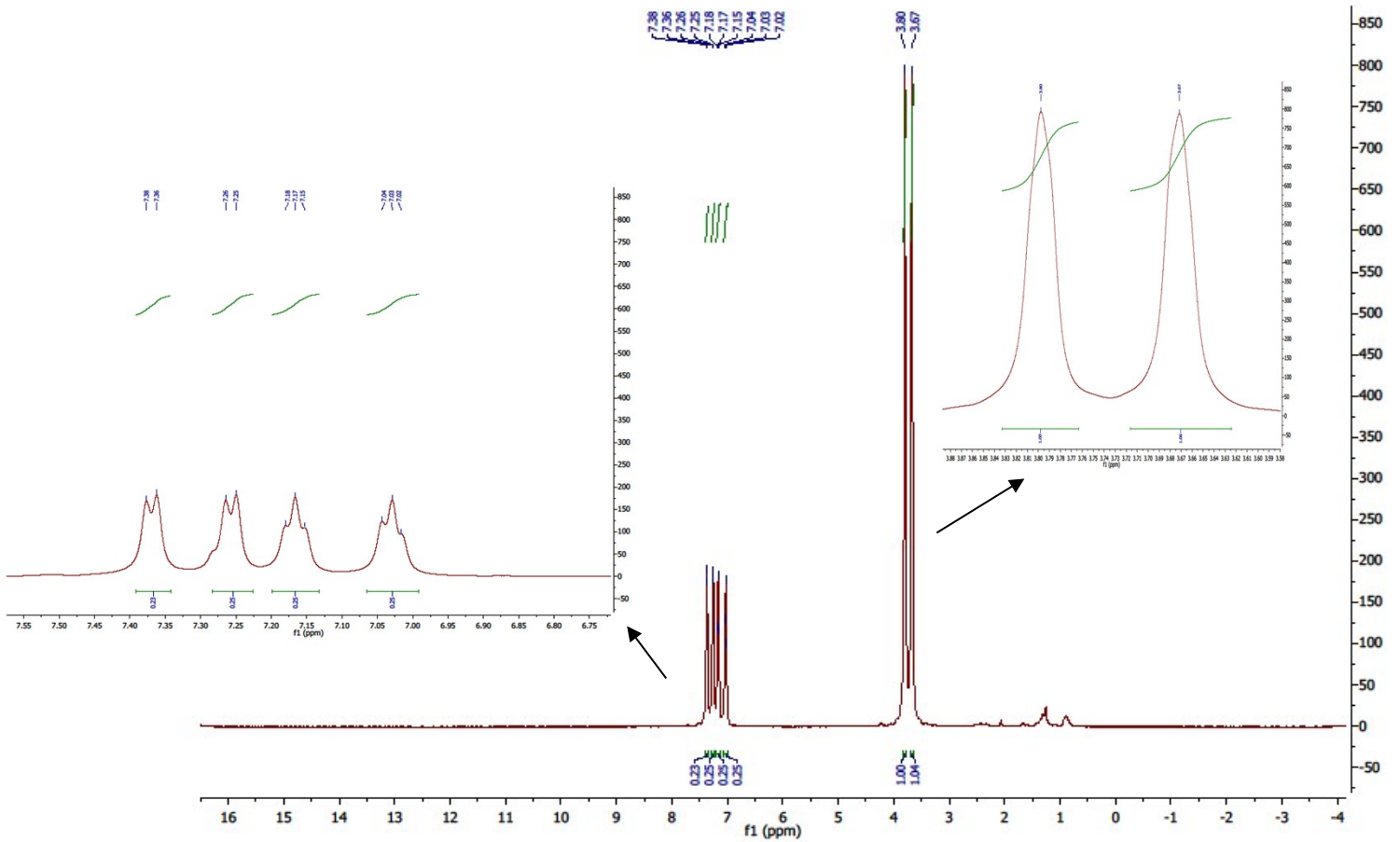


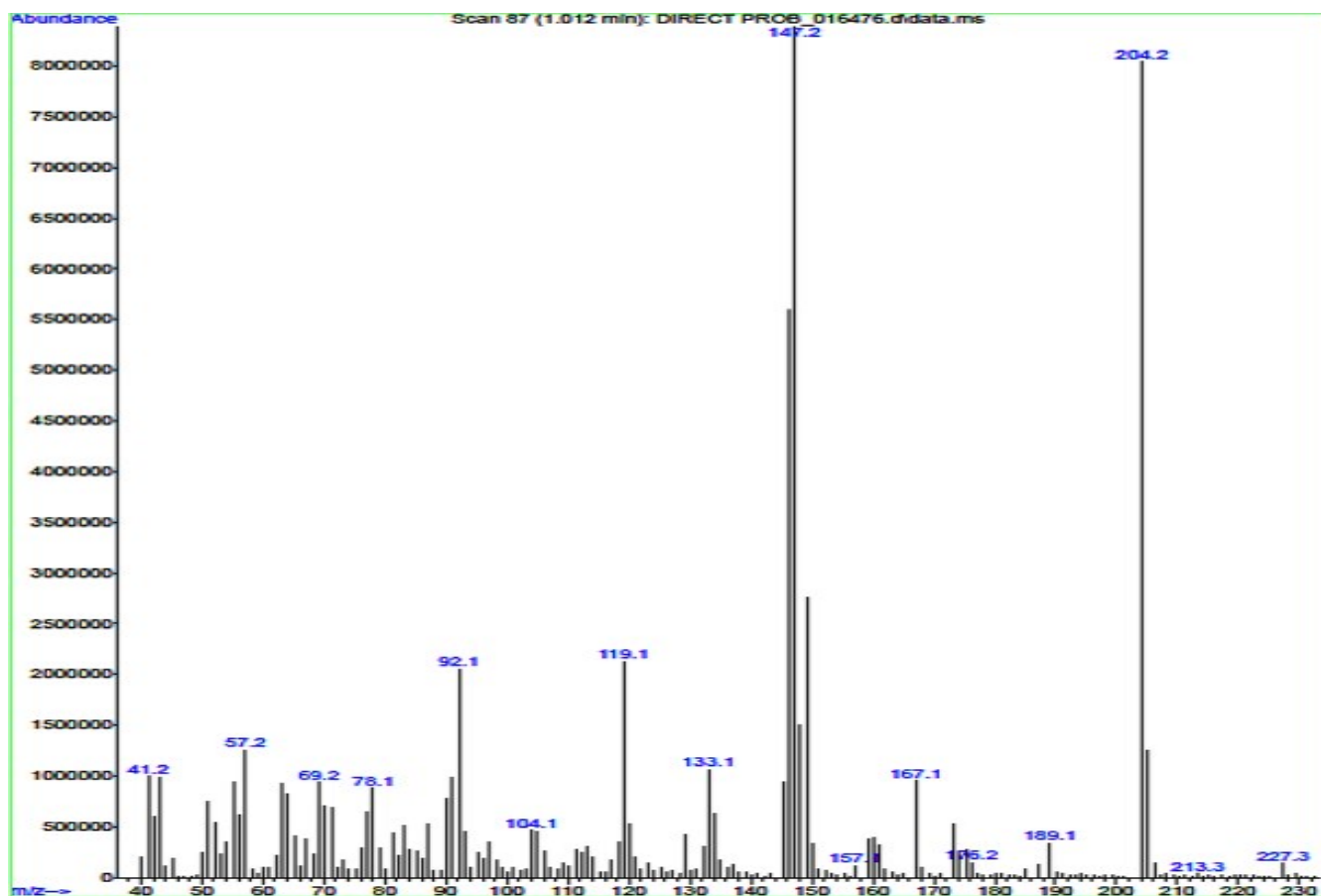
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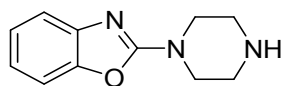




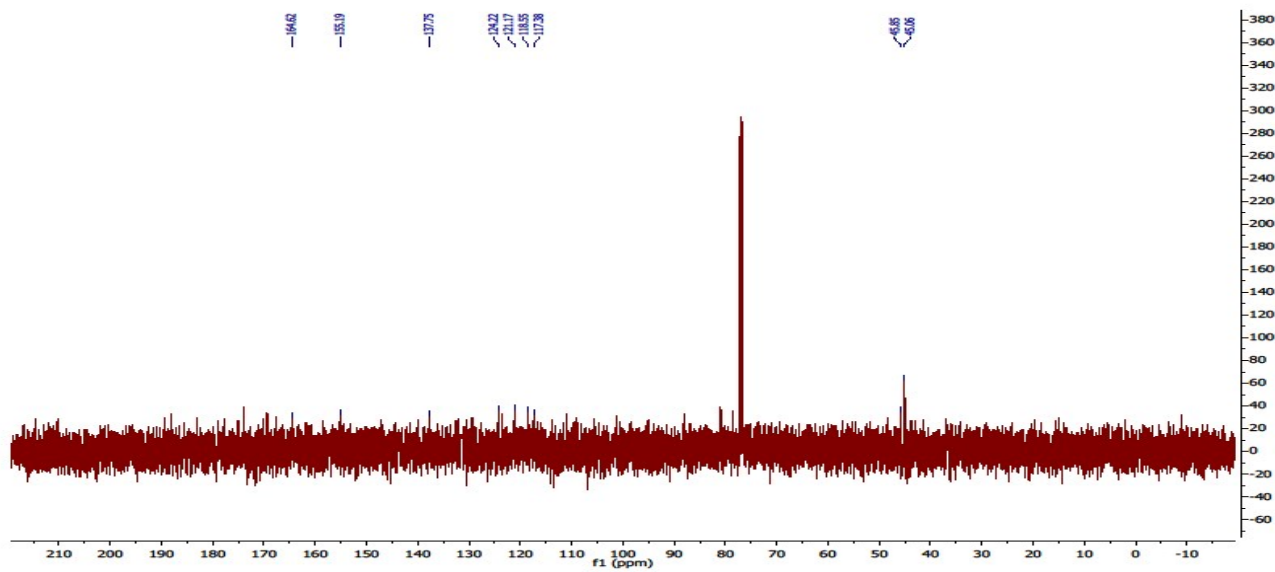
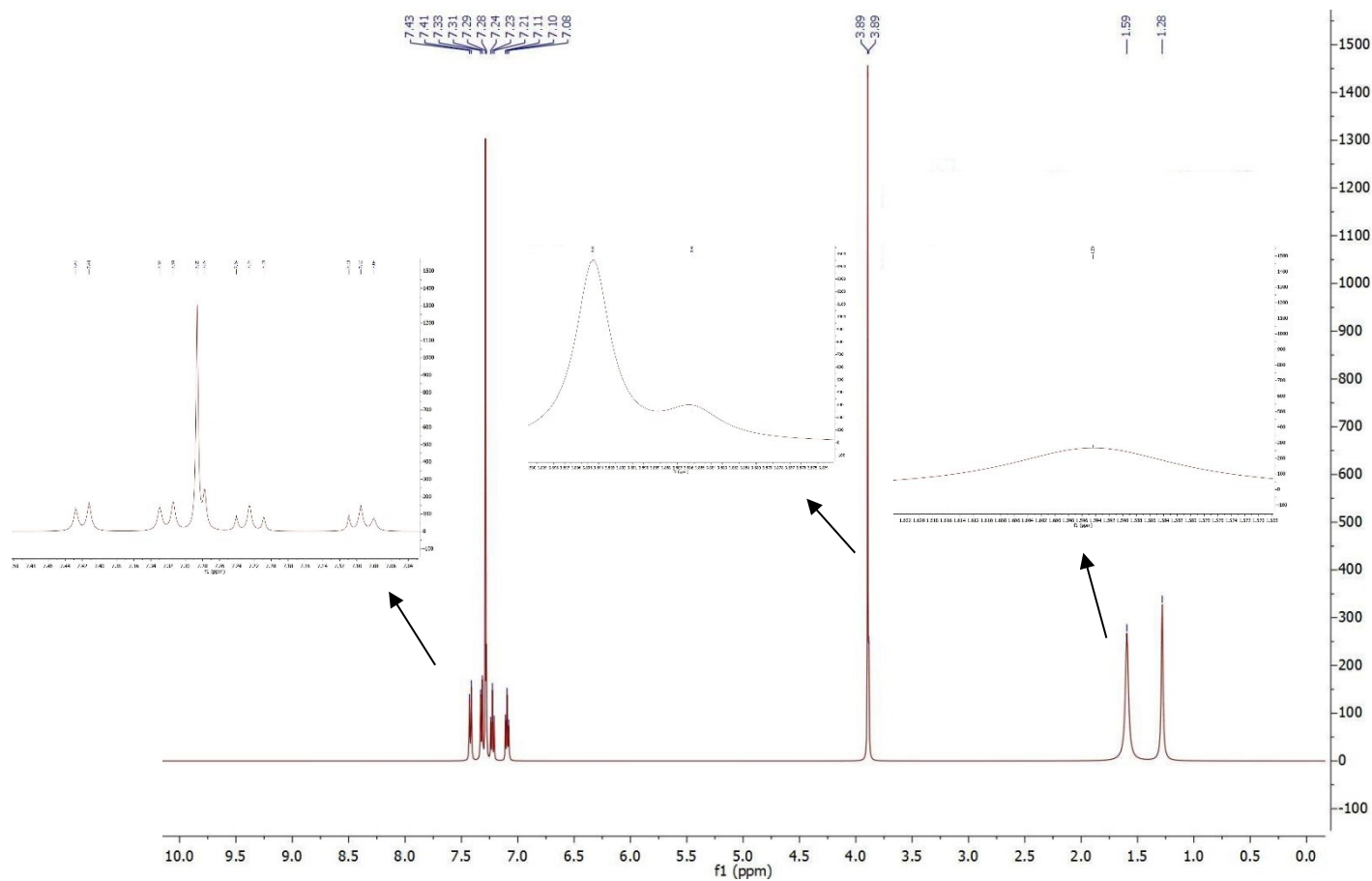
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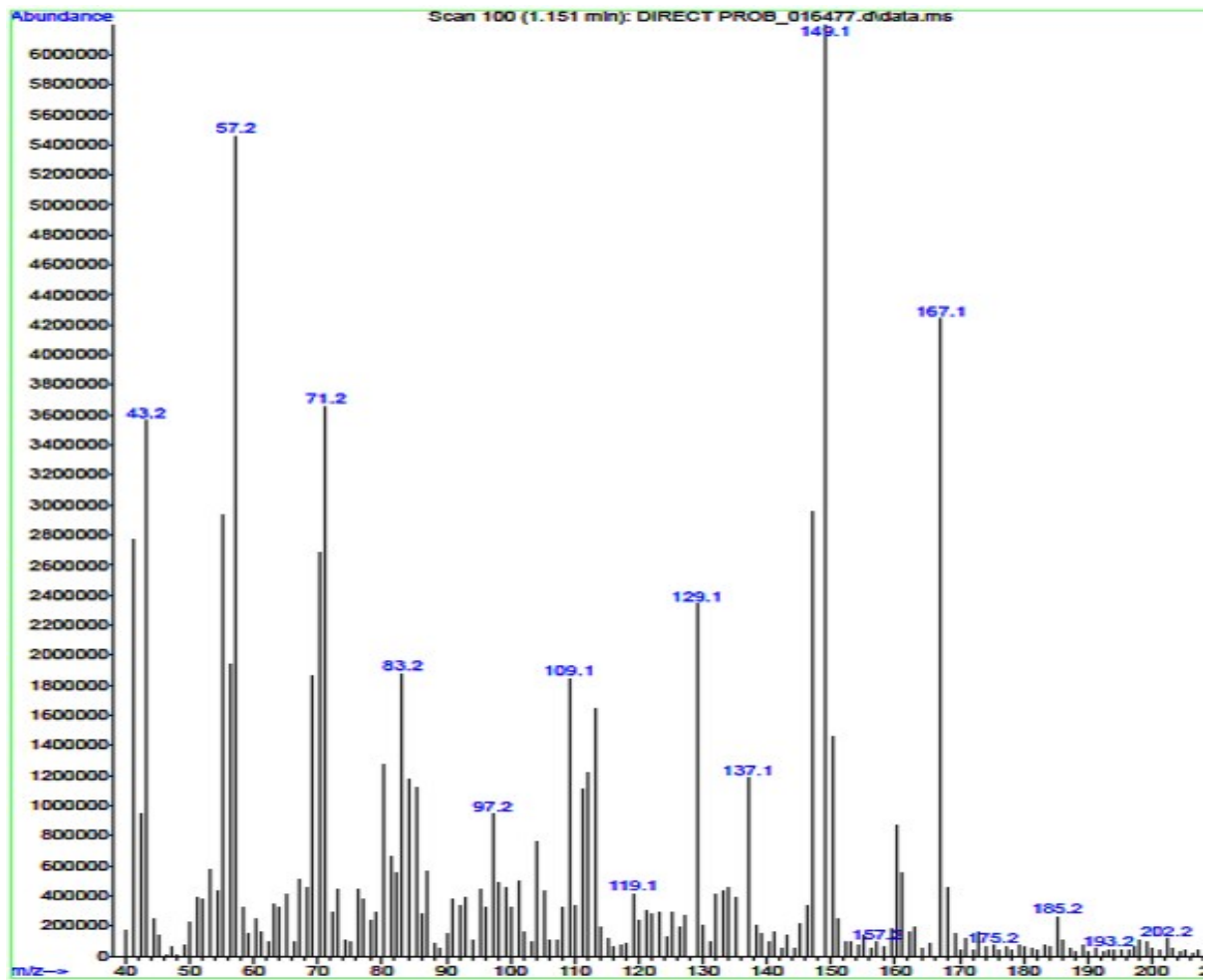


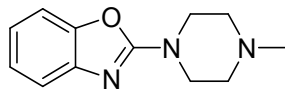




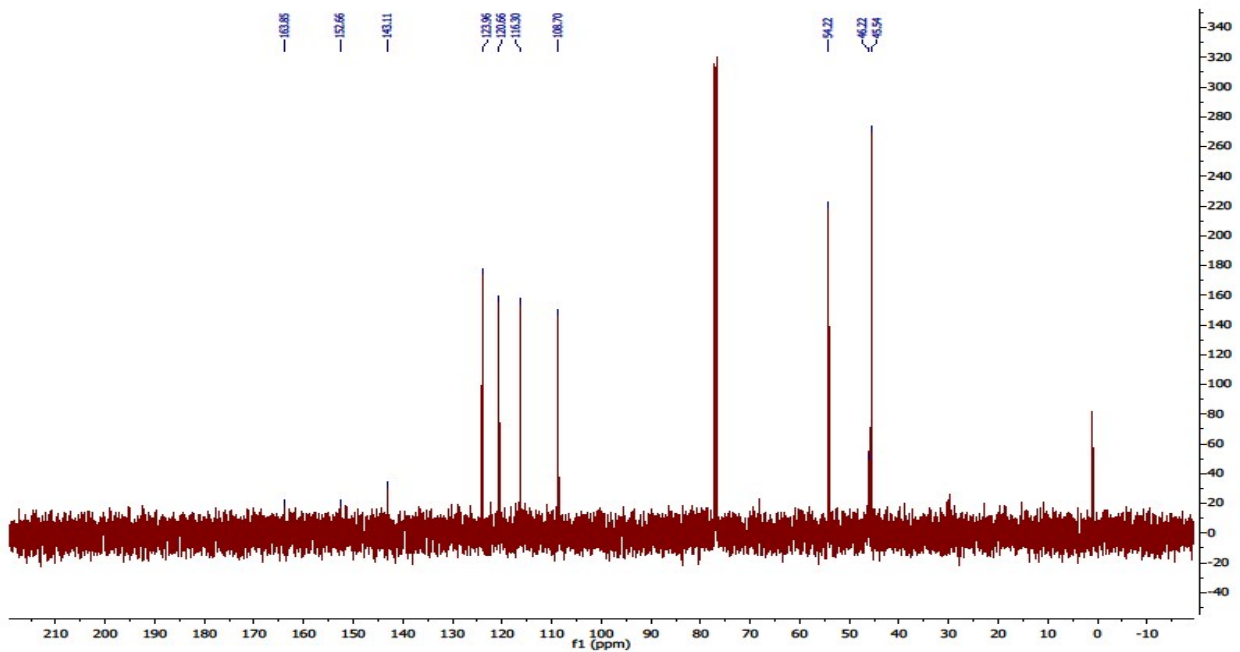
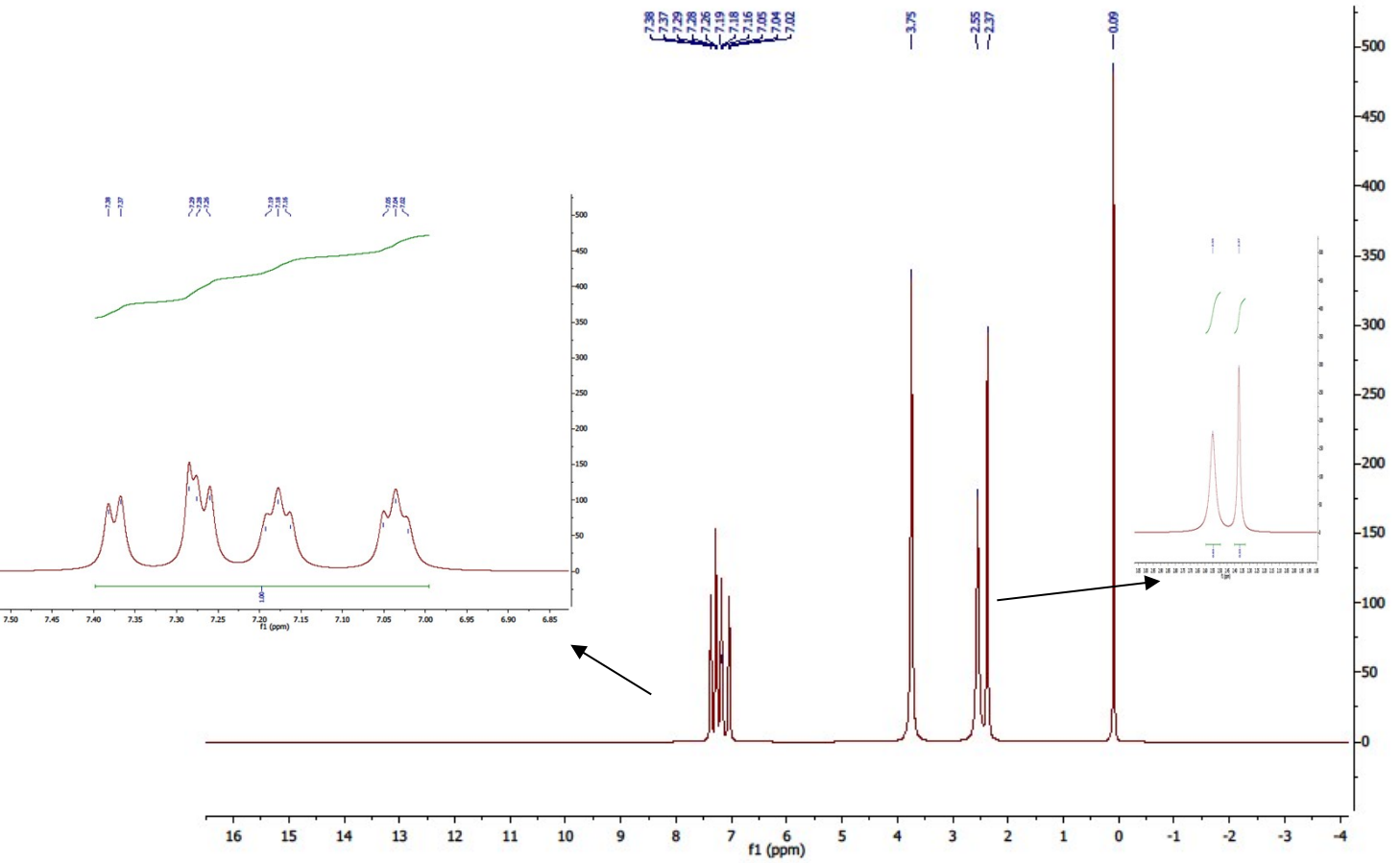
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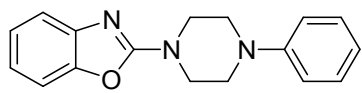




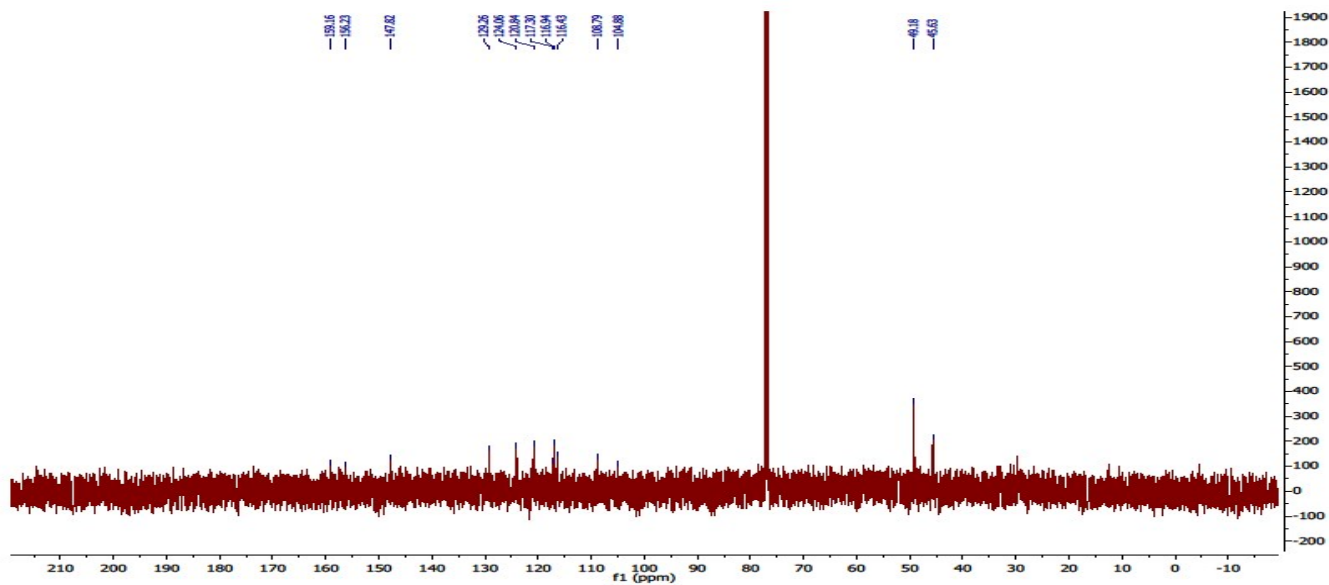
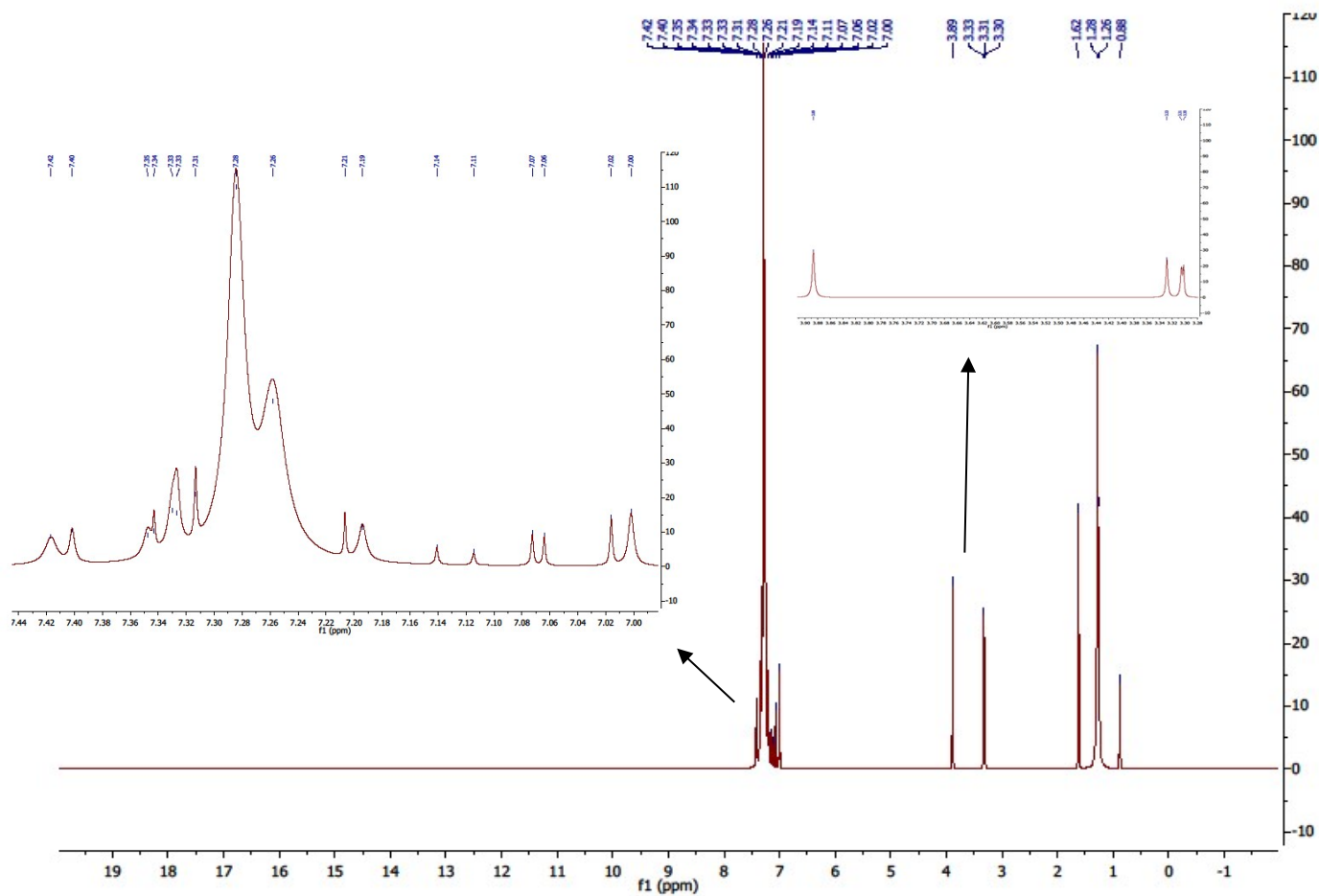


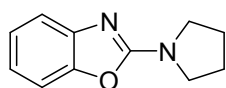
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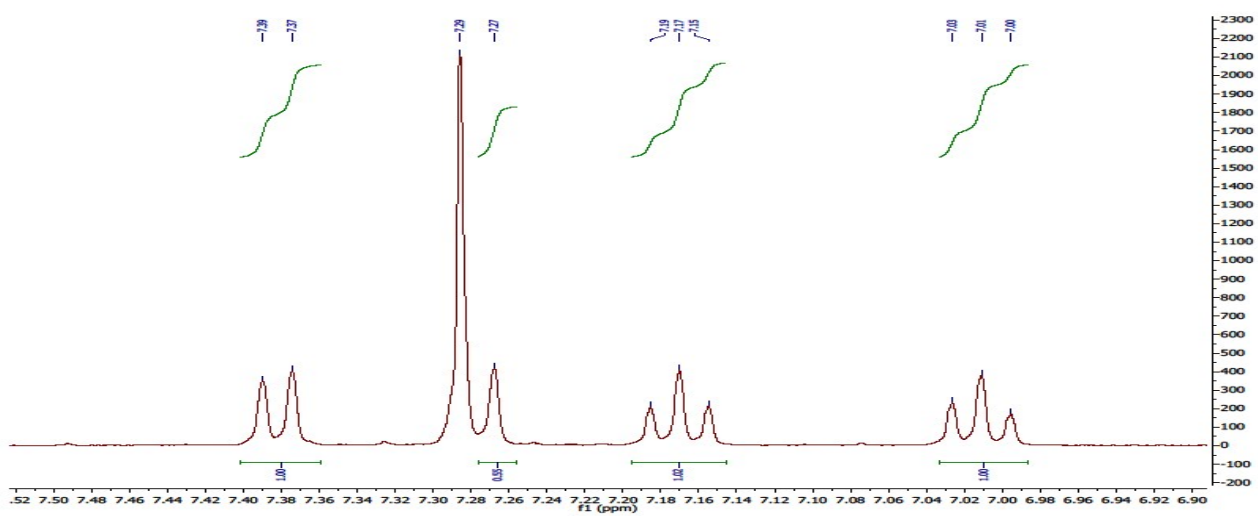
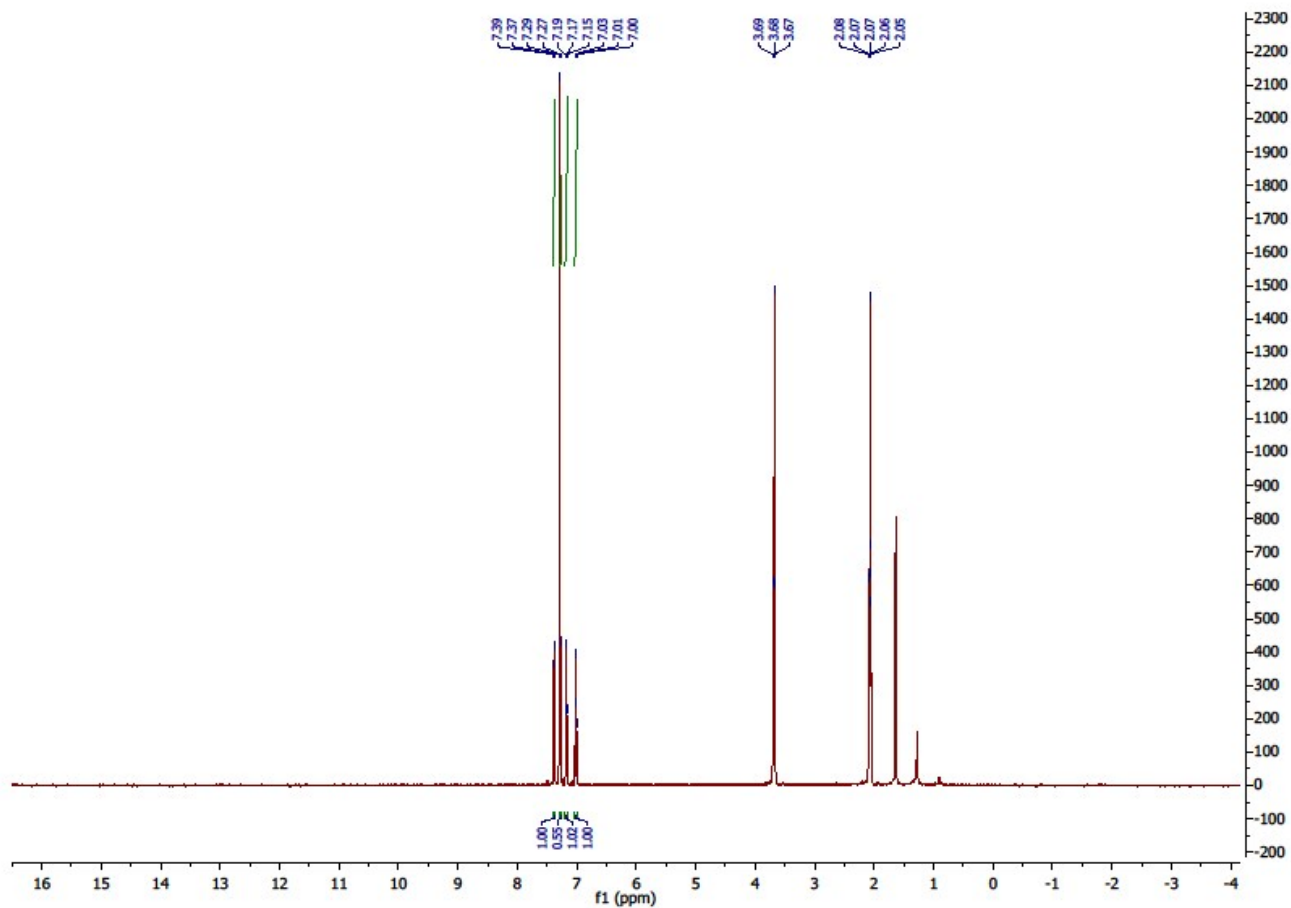


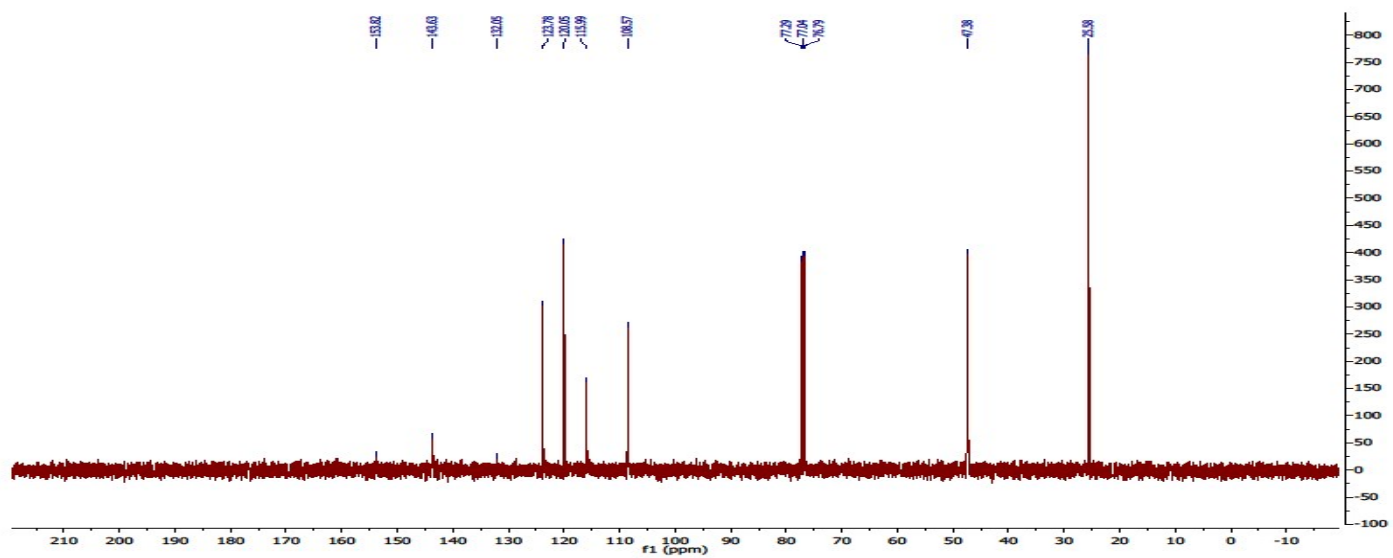
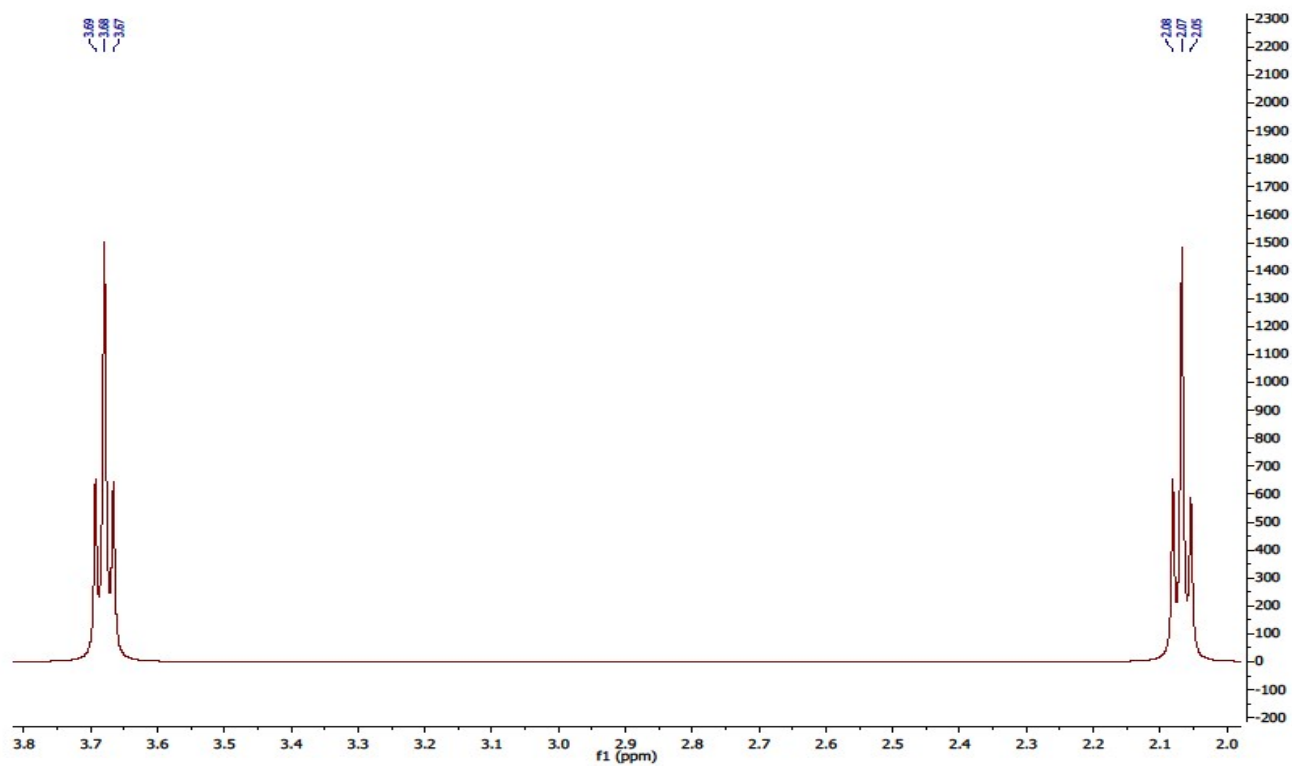
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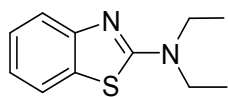




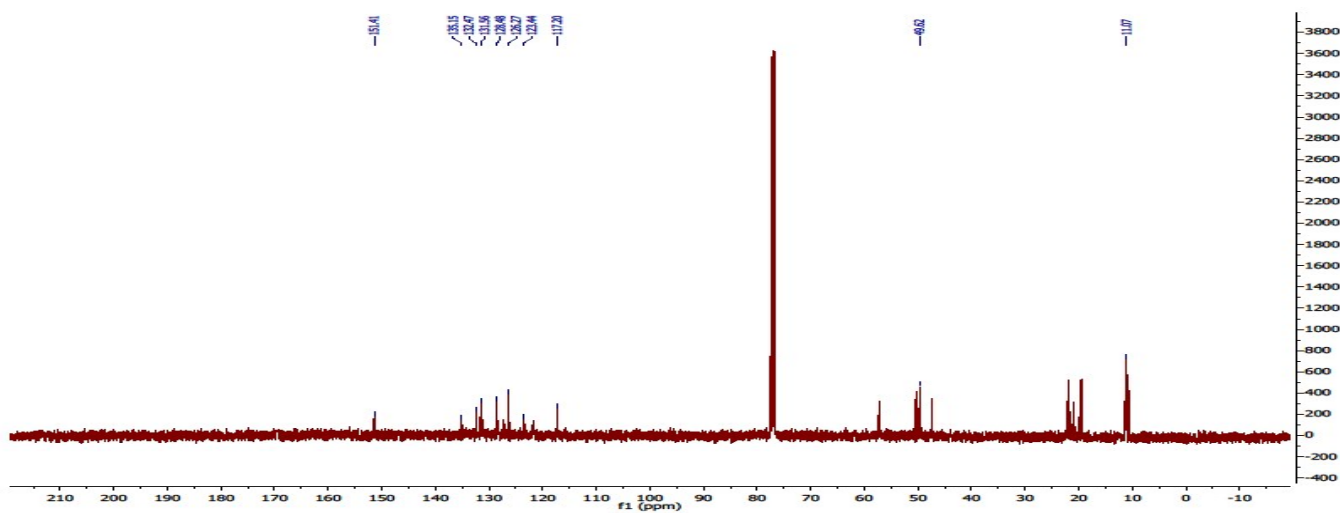
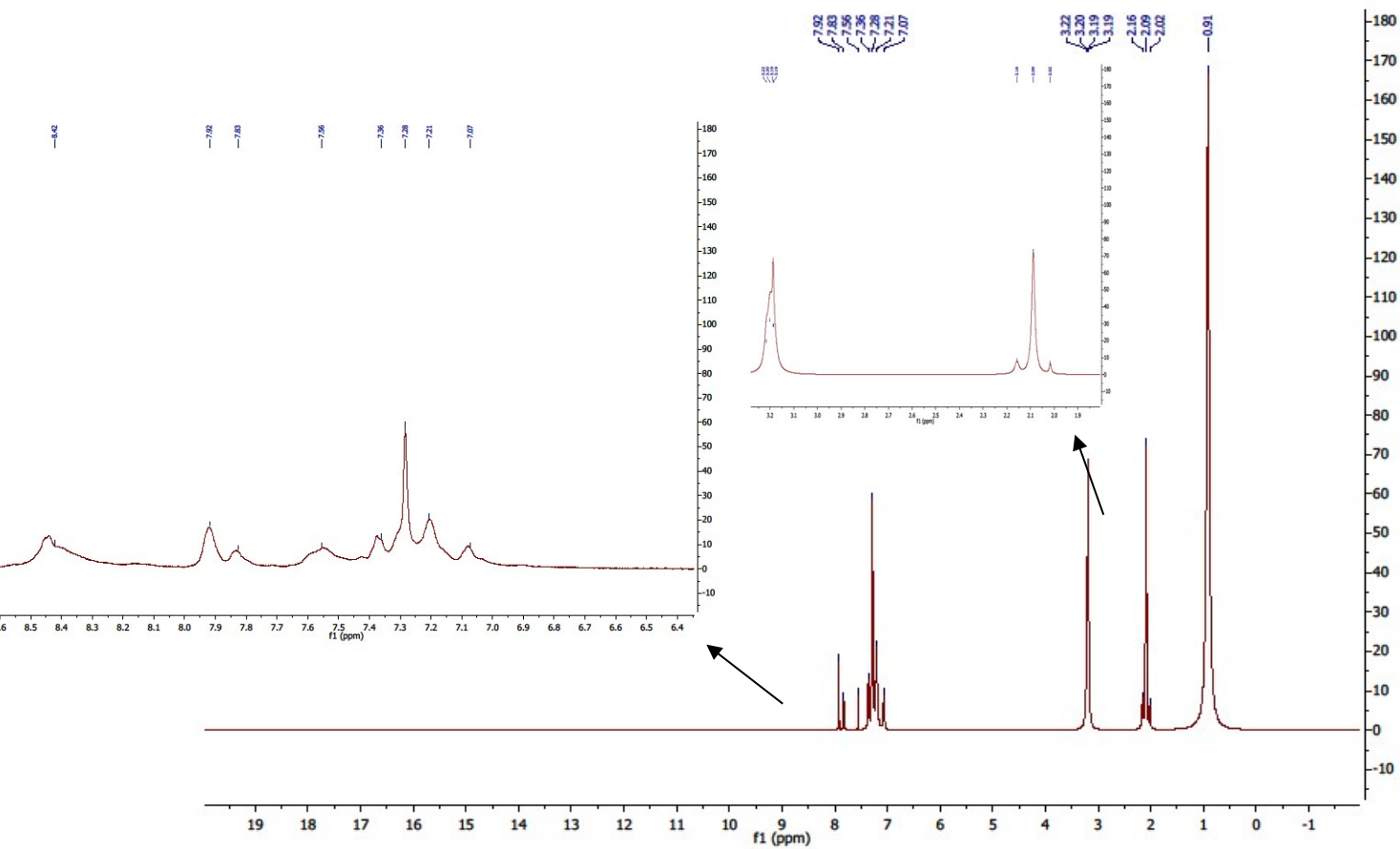
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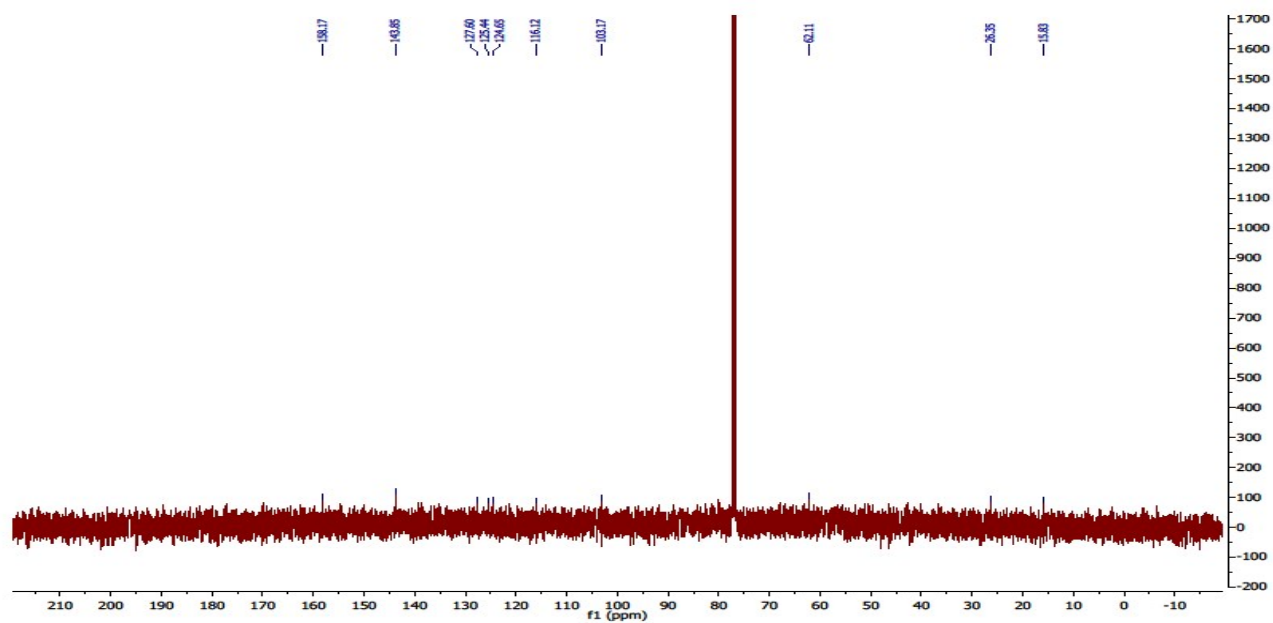
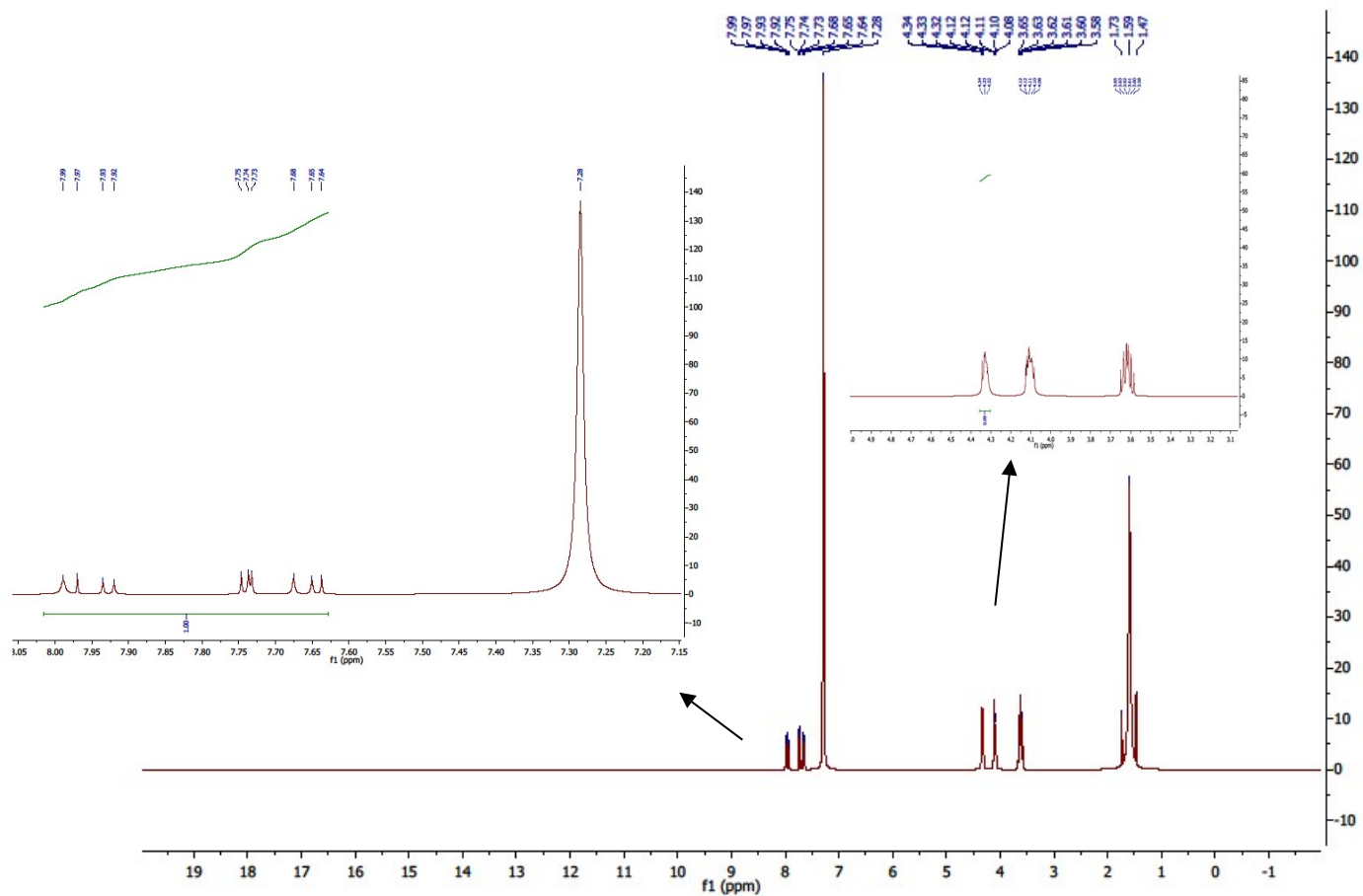
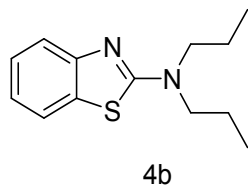


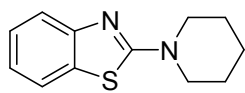




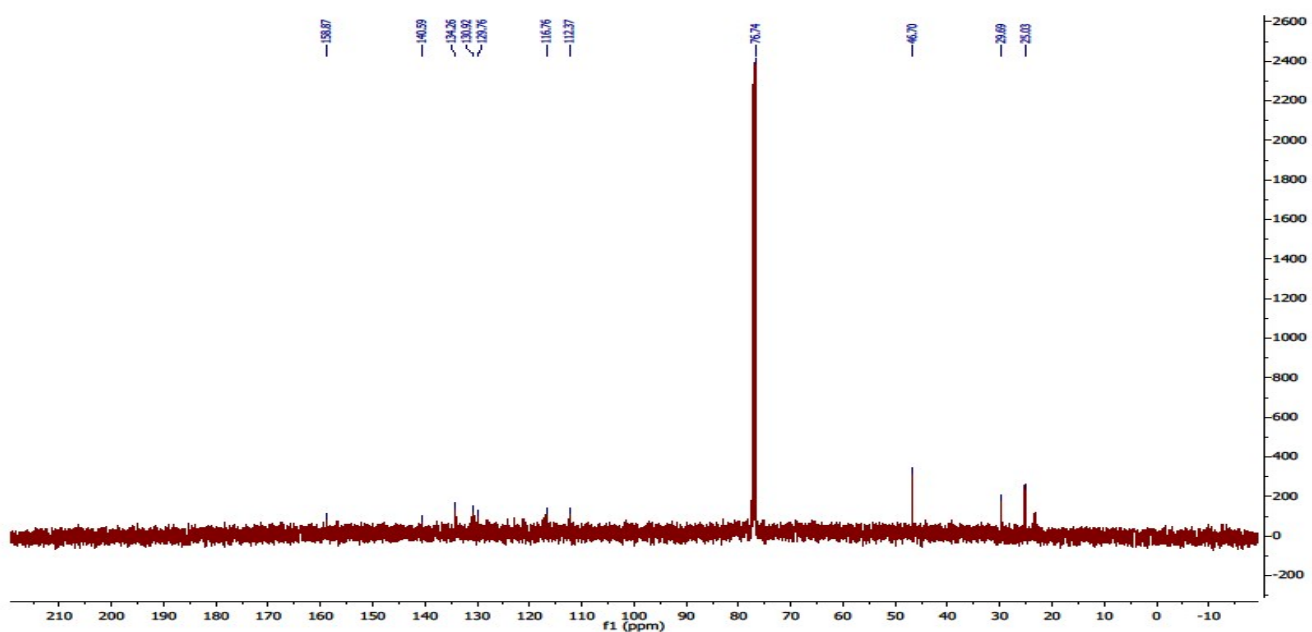
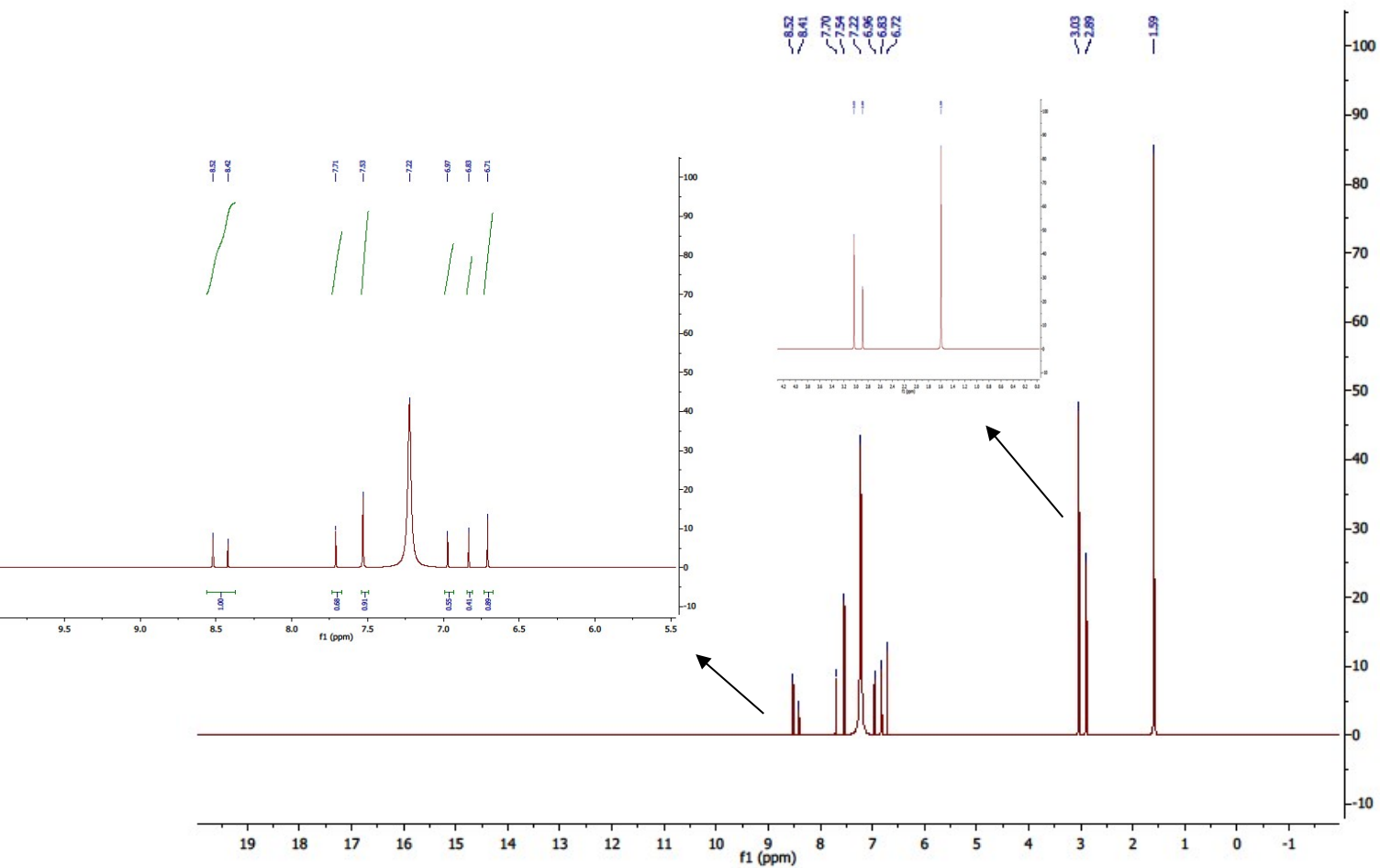
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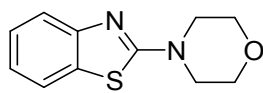




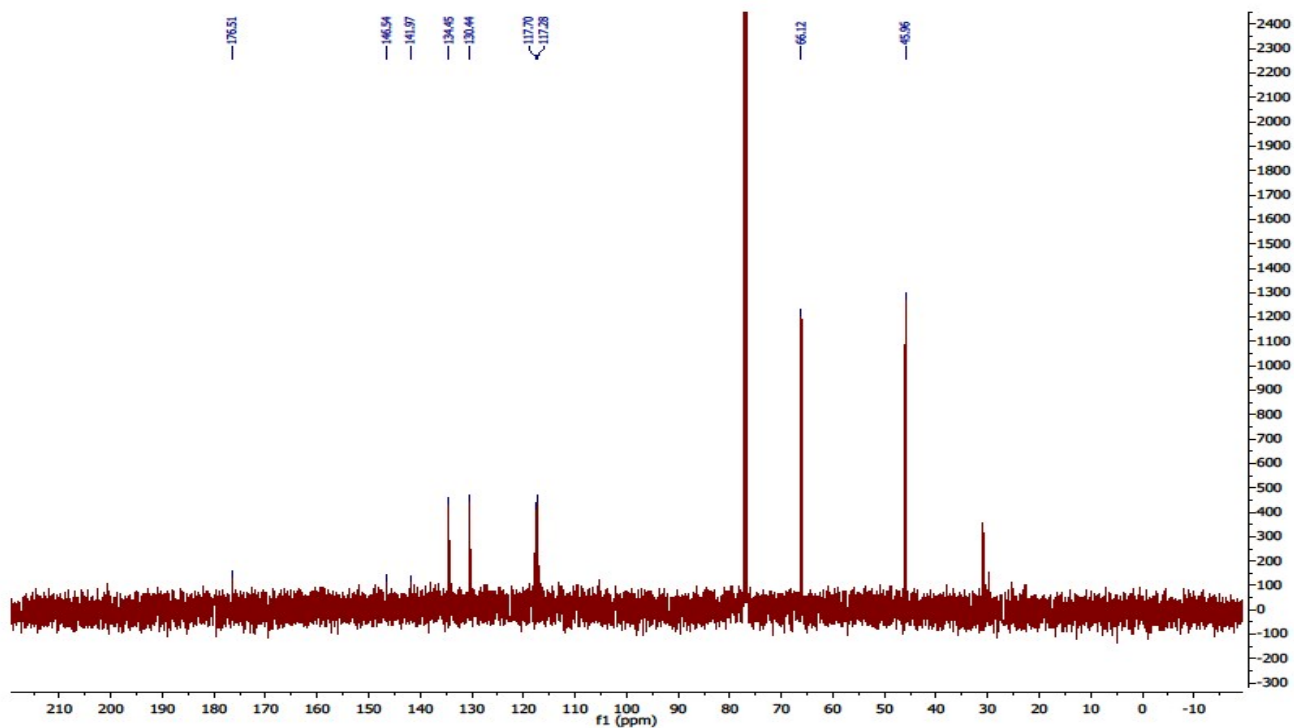
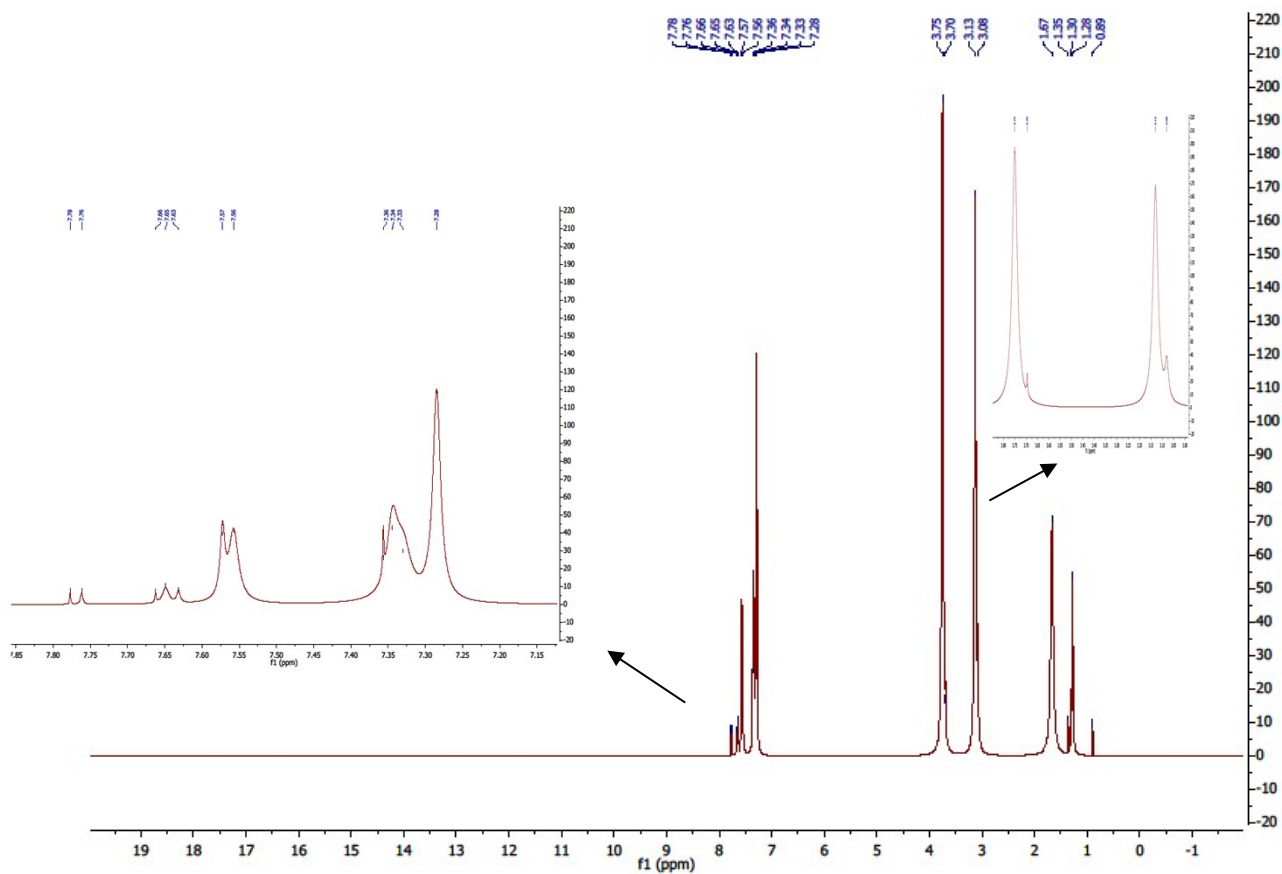


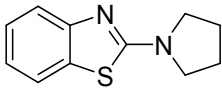
4d





4e





4i

