Electronic Supporting Information

$SnCl_2$ Catalyzed Multicomponent Coupling: Synthesis of 1,3-Oxazolidine Derivates Using Paraformaldehyde as a C1 Feedstock

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1. General Information

All reagents, compounds, and solvents were obtained from commercially accessible sources such as Aldrich, Merck, SRL, and Spectrochem. Distillation was performed as necessary. The transition metal catalysts were synthesized in the presence of an inert Argon environment. The solvents employed in the processes have undergone a process of dehydration and distillation. The reactions were monitored using $60F_{254}$ thin-layer chromatography (TLC) plates, and column chromatography was performed using silica gel with particle sizes of 60-120 mesh and 100-200 mesh.

The Bruker-AC 400 MHz Spectrometer was used to record the ^{1}H and ^{13}C NMR spectra. The standard for reporting chemical shifts is tetramethyl silane (TMS), with values given in parts per million (ppm). The chemical shift value (δ) for the proton (H) in the ^{1}H NMR spectrum of $CDCl_3$ is 7.26 parts per million (ppm), whereas the chemical shift value (δ) for the carbon (C) in the ^{13}C NMR spectrum is 77.23 ppm. ^{1}H NMR data is presented as chemical shift values, indicating the displacement of a proton's resonance frequency with a reference compound. The data also includes information about the multiplicity, which describes the splitting pattern observed in the spectrum (s = singlet, d = doublet, t = triplet, br = broad, and m = multiplet). Additionally, the coupling constant is provided in hertz (Hz), representing the strength of the magnetic interaction between neighboring protons.

High-resolution mass spectral analysis (HRMS) was performed on a Thermoscintific Exactive Plus ORBITRAP mass spectrometer using MeOH as a solvent with an electrospray ionization (ESI) positive method. Gas chromatograms were recorded using Centurion Scientific Gas chromatograph.

General Procedure for Synthesis of 1,3-Oxazolidone using Paraformaldehyde as the Methylene Source

To an oven-dried sealed tube, was loaded with aniline (1 mmol, 92 µL), styrene oxide (1.5 mmol, 172 µL), paraformaldehyde (3 mmol, 90 mg), and $SnCl_2$ catalyst (1 mol%, 1.9 mg). To it, toluene (2mL) was added and the reaction mixture was heated in an oil bath at a temperature of 85 ℃ for four hours with vigorous stirring. The completion of the reaction was monitored using TLC. Then the stirring was stopped and the reaction mixture was brought to room temperature, 20 mL of ethyl acetate was added, and inorganic impurities were removed with

water in a separating funnel. The organic layer was collected and dried with Na_2SO_4, and the solvent was removed in vacuo. The pure product was isolated using column chromatography.

General Procedure for Synthesis of Benzothiazole using Paraformaldehyde as the Methylene Source

An oven-dried sealed tube with a tiny magnetic bar was charged with $SnCl_2$ (1 mol%, 1.9 mg), paraformaldehyde (3 mmol, 90 mg), 2-aminothiophenol (1 mmol, 92 µL), and toluene (2 mL). The reaction mixture was heated in an oil bath at a temperature of 90 ℃ for 6 hours while being stirred. Following the conclusion of the reaction, the stirring was stopped and the reaction mixture was brought to room temperature, 20 mL of ethyl acetate was added, and inorganic impurities were removed with water in a separating funnel. The organic layer was collected and dried with Na_2SO_4, and the solvent was removed in vacuo. The pure product was isolated using column chromatography the solvent was extracted in reduced pressure and the pure product was isolated using column chromatography**.**

General Procedure for the Synthesis of Diarylmethane using Paraformaldehyde as Methylene Source

An oven-dried sealed tube with a small magnetic bar was charged with $SnCl_2$ (2 mol%, 1.9 mg), paraformaldehyde (0.5 mmol, 15 mg), N, N dimethylaniline (0.5 mmol, 64 µL), and toluene (2 mL). The reaction mixture was heated in an oil bath at a temperature of 90 ℃ for 6 hours while being stirred. Then the stirring was stopped and the reaction mixture was brought to room temperature, 20 mL of ethyl acetate was added, and inorganic impurities were removed with water in a separating funnel. The organic layer was collected and dried with Na_2SO_4, and the solvent was removed in vacuo. The pure product was isolated using column chromatography.

General procedure for Gas Chromatographic analysis

GC analysis was done using a flame ionization detector (fid) using heliflex GC capillary columns

(30 m * 0.25 mm * 0.50 µm) with stationary phase AT-WAX+

The parameters for analysis were set as follows;

Injector temperature: 230 ºC

Detector temperature: 240 ºC

Career gas (N2) flow: 0.2 bar

Oven temperature: 60 ºC-5 min, 5 ºC / min- 90 ºC -0 min, 10 ºC /min- 240 ºC - 20 min

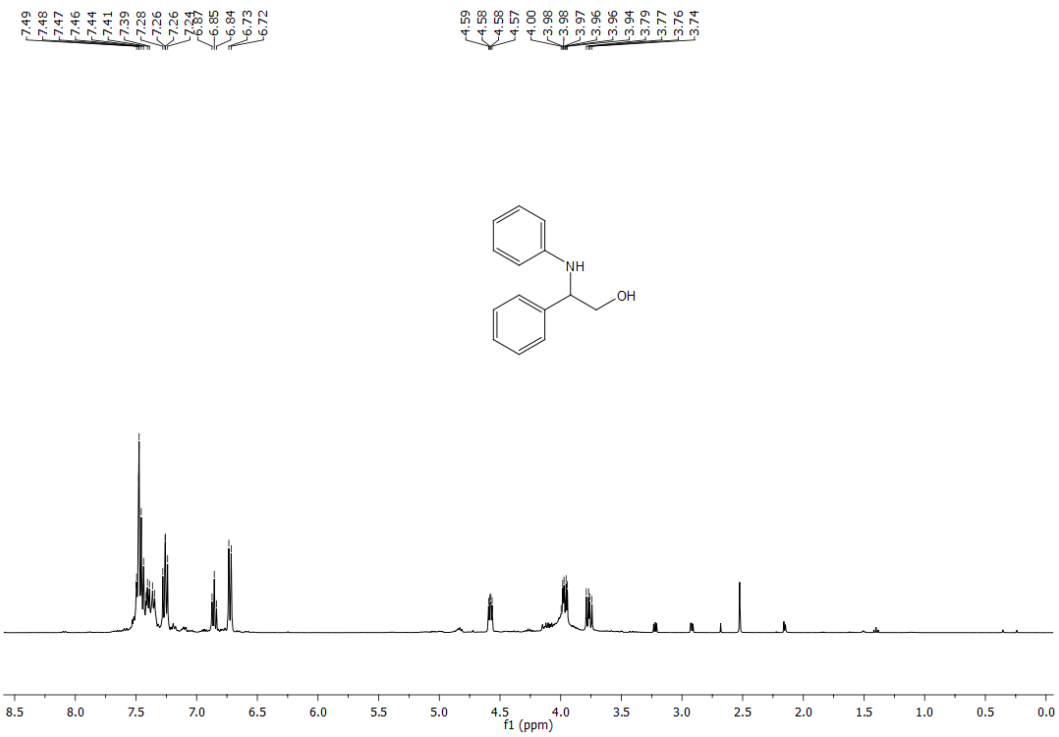


Figure S1. Formation of β-amino alcohol from the reaction of **1a** and **2a** in presence of $SnCl_2$

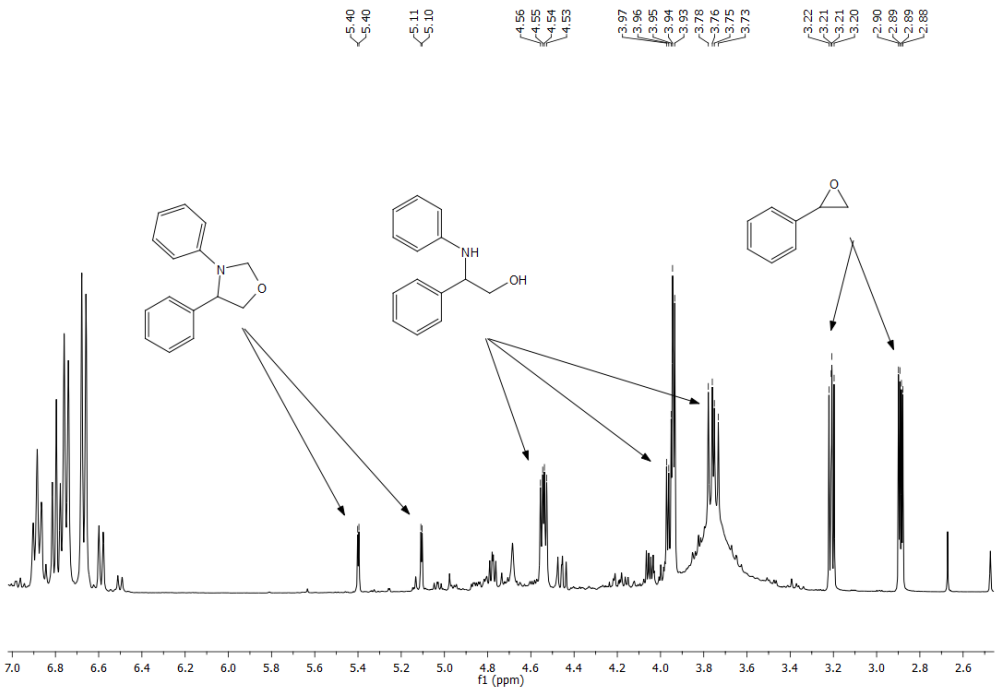
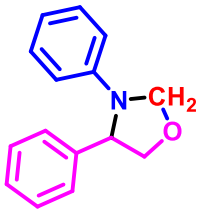


Figure S2. In situ NMR of reaction mixture after 15 minutes

Spectral Data of Products

3,4-Diphenyloxazolidine (4a)

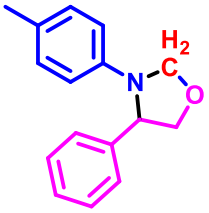


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 5H), 7.28 – 7.15 (m, 2H), 6.78 (s, 1H), 6.56 – 6.49 (m, 2H), 5.36 (d, *J* = 2.3 Hz, 1H), 5.06 (d, *J* = 2.3 Hz, 1H), 4.73 (dd, *J* = 6.8, 4.4 Hz, 1H), 4.43 (dd, *J* = 8.3, 6.9 Hz, 1H), 4.01 (dd, *J* = 8.4, 4.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.06, 141.50, 129.29, 128.89, 127.61, 126.24, 117.72, 112.81, 82.83, 75.76, 61.72.

HRMS (ESI-ORBITRAP): m/z $[M + H]^+$ calculated for $C_{15}H_{15}NO$ 226.1231, found 226.1221

4-Phenyl-3-(*p*-tolyl)oxazolidine (4b)[1]

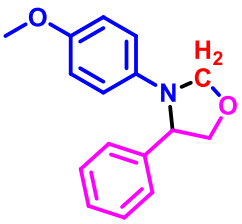


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 5H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.44 (d, 2H), 5.34 (d, *J* = 2.3 Hz, 1H), 5.03 (d, *J* = 2.3 Hz, 1H), 4.69 (dd, *J* = 6.8, 4.7 Hz, 1H), 4.42 (dd, *J* = 8.3, 6.9 Hz, 1H), 3.98 (dd, *J* = 8.4, 4.7 Hz, 1H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.06, 141.60, 129.78, 128.84, 127.53, 126.92, 126.25, 112.93, 83.16, 75.73, 61.94, 20.35.

HRMS (ESI-ORBITRAP): m/z $[M + H]^+$ calculated for $C_{16}H_{17}NO$ 240.1388, found 240.1386 and m/z $[M – (HCHO) + H]^+$ calculated for $C_{16}H_{17}NO$ 210.1282,found 210.1282

3-(4-Methoxyphenyl)-4-phenyloxazolidine (4c)

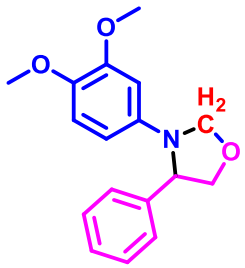


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 5H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.46 (d, *J* = 9.0 Hz, 2H), 5.30 (d, *J* = 2.2 Hz, 1H), 4.96 (d, *J* = 2.2 Hz, 1H), 4.62 (dd, *J* = 6.9, 5.1 Hz, 1H), 4.41 (dd, *J* = 8.3, 7.0 Hz, 1H), 3.94 (dd, *J* = 8.3, 5.0 Hz, 1H), 3.72 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.24, 141.53, 139.92, 128.83, 127.54, 126.28, 114.90, 114.02, 83.65, 75.71, 62.44, 55.76.

HRMS (ESI-ORBITRAP): m/z $[M + H]^+$ calculated for $C_{16}H_{17}NO_2$ 256.1337, found 256.1317 and m/z $[M – (HCHO) + H]^+$ calculated for $C_{16}H_{17}NO_2$ 226.1231,found 226.1211

3-(3,4-Dimethoxyphenyl)-4-phenyloxazolidine (4d)

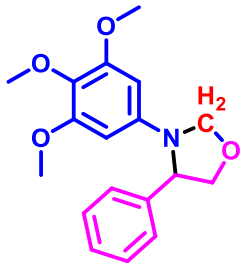


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.30 (m, 5H), 6.73 (d, *J* = 8.7 Hz, 1H), 6.10 (d, *J* = 2.7 Hz, 1H), 6.01 (dd, *J* = 8.7, 2.7 Hz, 1H), 5.30 (d, *J* = 2.2 Hz, 1H), 4.98 (d, *J* = 2.2 Hz, 1H), 4.62 (dd, *J* = 6.8, 5.2 Hz, 1H), 4.42 (dd, *J* = 8.3, 7.0 Hz, 1H), 3.95 (dd, *J* = 8.4, 5.1 Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.82, 141.72, 141.47, 128.87, 127.62, 126.31, 113.23, 104.17, 98.78, 83.48, 75.74, 62.54, 56.65, 55.68.

HRMS (ESI-ORBITRAP): m/z $[M + H]^+$ calculated for $C_{17}H_{19}NO_3$ 286.1443, found 286.1431

3-(3,4,5-Methoxyphenyl)-4-phenyloxazolidine (4e)

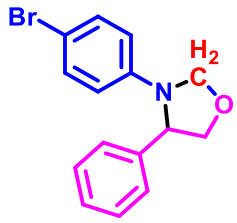


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dt, *J* = 19.7, 10.2 Hz, 5H), 5.68 (s, 2H), 5.30 (d, *J* = 2.2 Hz, 1H), 5.01 (d, *J* = 2.2 Hz, 1H), 4.64 (dd, *J* = 6.8, 5.0 Hz, 1H), 4.42 (dd, *J* = 8.4, 6.9 Hz, 1H), 3.97 (dd, *J* = 8.4, 4.9 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.78, 141.92, 141.40, 128.92, 127.72, 126.27, 90.76, 83.05, 75.80, 62.37, 61.04, 55.90.

HRMS (ESI-ORBITRAP): m/z [M + H]+ calculated for $C_{18}H_{21}NO_4$ 316.1549, found 316.1545

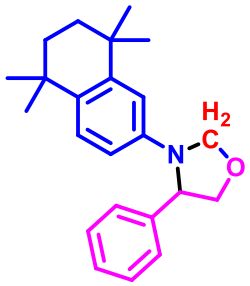
3-(4-Bromophenyl)-4-phenyloxazolidine (4f)[1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 7.24 (d, *J* = 9.0 Hz, 2H), 6.37 – 6.26 (m, 2H), 5.28 (d, *J* = 2.4 Hz, 1H), 4.99 (d, *J* = 2.4 Hz, 1H), 4.65 (dd, *J* = 6.7, 4.5 Hz, 1H), 4.42 (dd, *J* = 8.4, 6.9 Hz, 1H), 3.97 (dd, *J* = 8.5, 4.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.81, 140.73, 131.92, 128.92, 127.75, 126.12, 114.30, 82.63, 75.76, 61.68.

4-Phenyl-3-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronapthalen-2-yl)oxazolidine (4g)

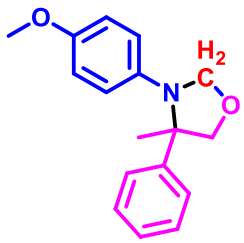


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dt, *J* = 31.7, 12.2 Hz, 5H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 6.52 – 6.11 (m, 2H), 6.41 – 6.31 (m, 2H), 5.32 (s, 1H), 5.32 (s, 1H), 5.00 (s, 1H), 5.00 (s, 1H), 4.68 – 4.58 (m, 1H), 4.72 – 4.57 (m, 1H), 4.37 (t, *J* = 7.6 Hz, 1H), 4.37 (t, *J* = 7.6 Hz, 1H), 3.96 (dd, *J* = 8.3, 4.7 Hz, 1H), 3.96 (dd, *J* = 8.3, 4.7 Hz, 1H), 1.62 (s, 4H), 1.62 (s, 4H), 1.29 – 1.18 (m, 10H), 1.23 (dd, *J* = 14.5, 5.3 Hz, 9H), 1.07 (s, 4H), 1.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.62, 142.99, 134.42, 128.77, 127.47, 127.24, 126.39, 111.17, 110.51, 83.06, 75.68, 62.26, 35.22, 35.17, 33.45, 31.94, 31.90, 31.84, 31.74.

HRMS (ESI-ORBITRAP): m/z $[M + H]^+$ calculated for $C_{23}H_{29}NO$ 336.2327, found 336.2309

3-(4-Methoxyphenyl)-4-methyl-4-phenyloxazolidine (4h)

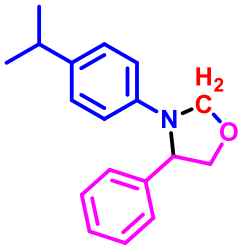


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.3, 1.3 Hz, 2H), 7.36 (dd, *J* = 8.3, 6.9 Hz, 3H), 6.71 (d, *J* = 9.1 Hz, 2H), 6.33 (d, *J* = 9.1 Hz, 2H), 5.24 (d, *J* = 2.2 Hz, 1H), 5.08 (d, *J* = 2.2 Hz, 1H), 4.02 (s, 2H), 3.71 (s, 3H), 1.71 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.93, 144.26, 137.36, 128.70, 128.46, 128.40, 127.03, 126.05, 124.73, 124.56, 115.52, 114.99, 114.58, 113.72, 83.38, 83.10, 64.17, 55.65, 19.75.

HRMS (ESI-ORBITRAP): m/z $[M + H]^+$ calculated for $C_{17}H_{19}NO_2$ 270.1494,found 270.1487 and m/z $[M – (HCHO) + H]^+$ calculated for $C_{16}H_{17}NO_2$ 240.1388,found 240.1360.

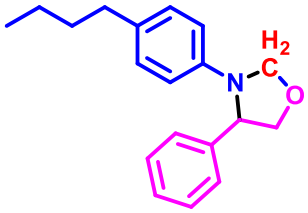
3-(4-Isopropylphenyl)-4-phenyloxazolidine (4i)[1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 5H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.60 (d, *J* = 8.6 Hz, 2H), 5.45 (d, *J* = 2.3 Hz, 1H), 5.13 (d, *J* = 2.3 Hz, 1H), 4.78 (dd, *J* = 6.8, 4.6 Hz, 1H), 4.49 (dd, *J* = 8.3, 7.0 Hz, 1H), 4.08 (dd, *J* = 8.4, 4.5 Hz, 1H), 2.98 – 2.87 (m, 1H), 1.35 (dd, *J* = 6.9, 1.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.52, 141.91, 138.23, 128.94, 128.65, 127.64, 127.27, 126.39, 125.66, 83.23, 75.82, 62.16, 52.47, 51.30, 33.28, 24.38.

3-(4-Butylphenyl)-4-phenyloxazolidine (4j)

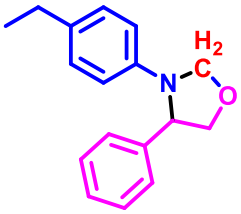


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 5H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.47 (d, *J* = 7.8 Hz, 2H), 5.36 (d, *J* = 1.9 Hz, 1H), 5.05 (d, *J* = 1.8 Hz, 1H), 4.70 (dd, *J* = 6.7, 4.7 Hz, 1H), 4.47 – 4.37 (m, 1H), 4.00 (dd, *J* = 8.3, 4.5 Hz, 1H), 2.54 (t, *J* = 7.7 Hz, 2H), 1.58 (dt, *J* = 15.5, 7.9 Hz, 2H), 1.38 (dd, *J* = 14.8, 7.4 Hz, 2H), 0.96 (dd, *J* = 7.9, 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.25, 141.74, 132.16, 129.17, 128.85, 126.28, 112.83, 83.15, 75.75, 62.01, 34.70, 34.01, 22.41, 14.06.

HRMS (ESI-ORBITRAP): m/z [M + H]+ calculated for $C_{19}H_{23}NO$ 282.1857, found 282.1854 and m/z $[M – (HCHO) + H]^+$ calculated for $C_{19}H_{23}NO$ 252.1752, found 252.1743

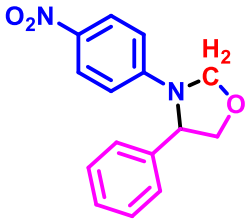
3-(4-ethylphenyl)-4-phenyloxazolidine (4k)[1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 4H), 7.36 – 7.29 (m, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.49 (d, *J* = 8.5 Hz, 2H), 5.37 (d, *J* = 2.3 Hz, 1H), 5.05 (d, *J* = 2.3 Hz, 1H), 4.71 (dd, *J* = 6.8, 4.6 Hz, 1H), 4.43 (dd, *J* = 8.3, 7.0 Hz, 1H), 4.01 (dd, *J* = 8.4, 4.6 Hz, 1H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.31, 141.71, 133.55, 128.86, 128.63, 127.56, 126.29, 112.95, 83.17, 75.75, 62.02, 27.92, 15.95.

3-(4-nitrophenyl)-4-phenyloxazolidine (4l)

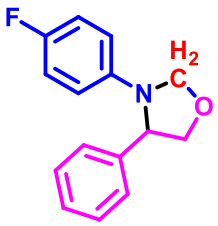


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 9.3 Hz, 2H), 7.43 – 7.24 (m, 5H), 6.40 (d, *J* = 9.3 Hz, 2H), 5.35 (d, *J* = 3.1 Hz, 1H), 5.11 (d, *J* = 3.1 Hz, 1H), 4.84 (dd, *J* = 6.5, 3.8 Hz, 1H), 4.46 (dd, *J* = 8.6, 6.6 Hz, 1H), 4.05 (dd, *J* = 8.6, 3.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.80, 139.60, 138.38, 129.18, 128.60, 128.21, 126.36, 126.11, 126.04, 125.84, 113.92, 111.49, 81.77, 75.80, 61.34.

HRMS (ESI-ORBITRAP): m/z $[M + H]^+$ calculated for $C_{15}H_{14}N_2O_3$ 271.1082, found 271.1081

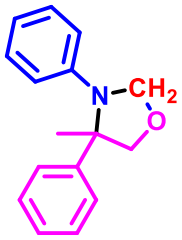
3-(4-Fluorophenyl)-4-phenyloxazolidine (4m)[1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 4.4 Hz, 4H), 7.32 (dd, *J* = 9.1, 4.2 Hz, 1H), 6.91 (t, *J* = 8.8 Hz, 2H), 6.47 – 6.40 (m, 2H), 5.32 (d, *J* = 2.3 Hz, 1H), 5.00 (d, *J* = 2.3 Hz, 1H), 4.66 (dd, *J* = 6.8, 4.8 Hz, 1H), 4.44 (dd, *J* = 8.3, 7.0 Hz, 1H), 3.98 (dd, *J* = 8.4, 4.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.15, 154.80, 141.78, 141.76, 141.18, 128.94, 127.72, 126.24, 115.86, 115.63, 113.62, 113.55, 83.28, 75.80, 62.25.

4-Methyl-3,4-diphenyloxazolidine (4n)

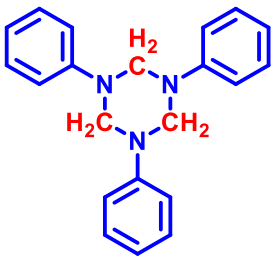


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 5H), 7.17 – 7.04 (m, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.32 (d, *J* = 7.9 Hz, 2H), 5.31 (d, *J* = 2.2 Hz, 1H), 5.16 (d, *J* = 2.2 Hz, 1H), 4.06 (d, *J* = 8.2 Hz, 1H), 4.01 (d, *J* = 8.2 Hz, 1H), 1.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.71, 142.68, 128.91, 128.74, 127.09, 126.00, 116.97, 113.72, 83.92, 82.62, 63.83, 19.79.

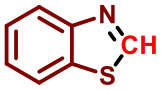
HRMS (ESI-ORBITRAP): m/z $[M + H]^+$ calculated for $C_{16}H_{17}NO$ 240.1388, found 240.1383 and m/z $[M – HCHO]^+$ calculated for $C_{16}H_{17}NO$ 210.1282, found 210.1285.

1,3,5-Triphenyl-1,3,5-triazinane (5)[2]



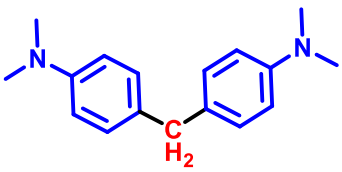
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.92 (t, *J* = 7.3 Hz, 1H), 4.94 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.69, 129.24, 120.98, 117.73, 68.62. 114.14, 67.35, 60.17.

Benzothiazole (9)[3]



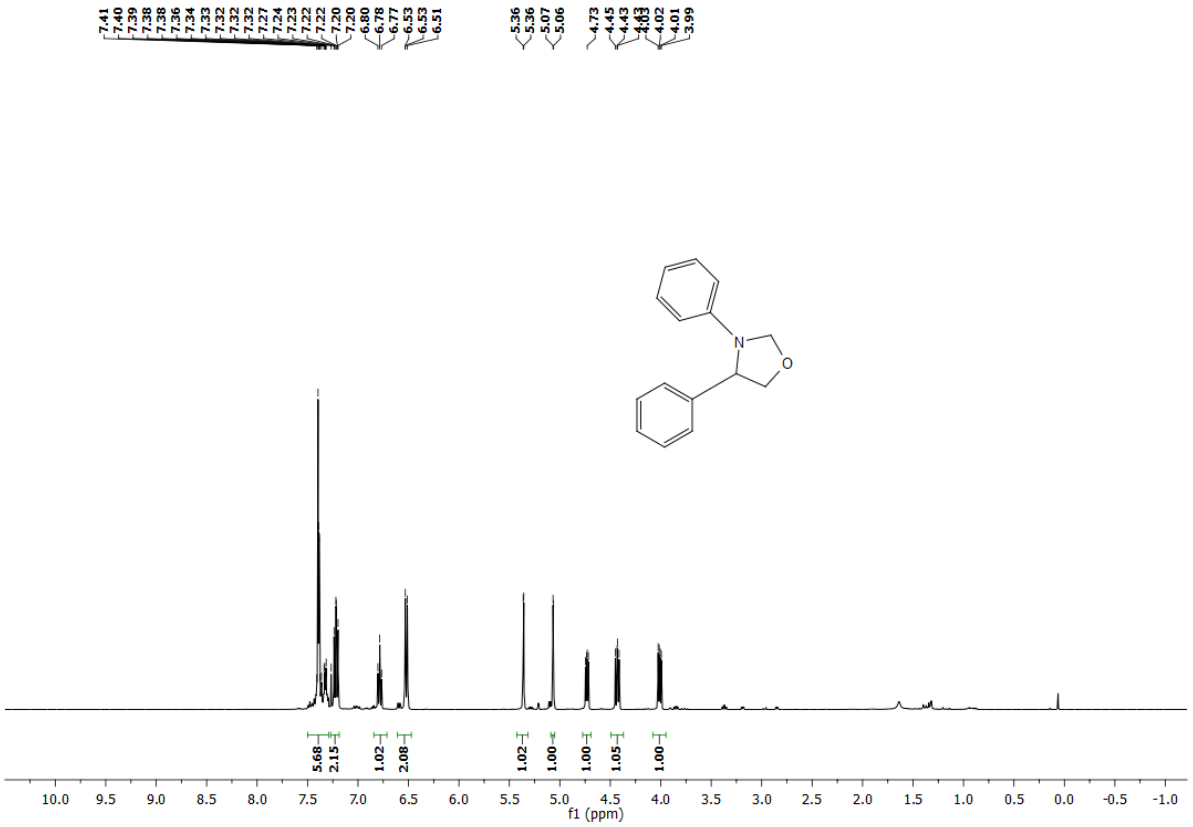
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.49 – 7.43 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.92, 153.25, 133.71, 126.19, 125.56, 123.65, 121.90.

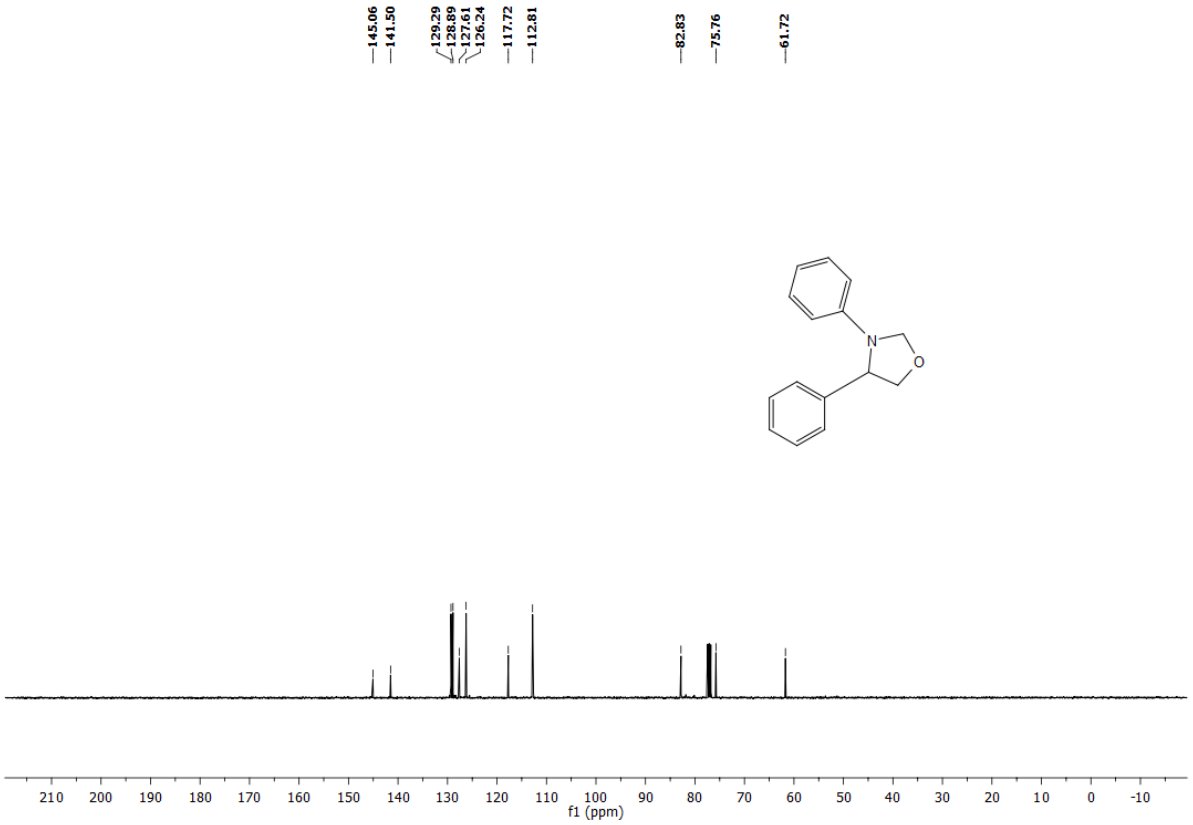
4,4'-Methylenebis(N,N-dimethylaniline) (11)[4]

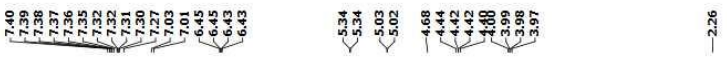


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.7 Hz, 4H), 6.72 (d, *J* = 8.7 Hz, 4H), 3.84 (s, 2H), 2.93 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.10, 130.39, 129.44, 113.10, 40.97, 39.91.

NMR spectra of products



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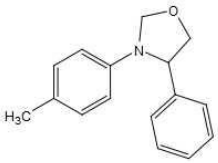
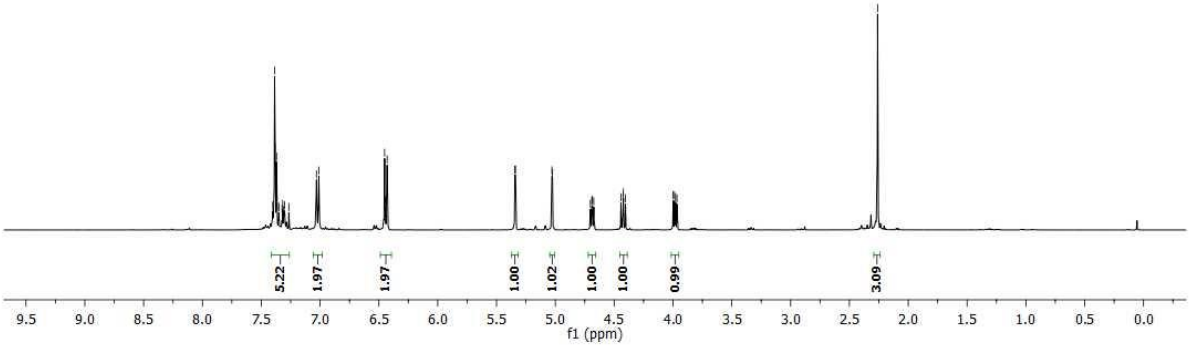
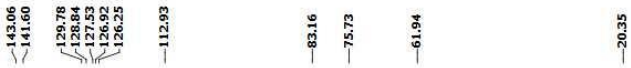
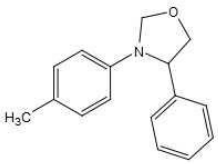
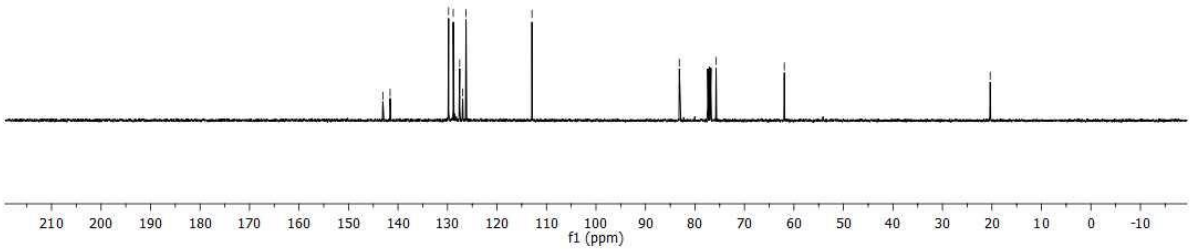
7.39
7.38
7.37
7.36
7.35
7.32
7.32
7.31
7.30
7.27
7.03
7.01
6.45
6.43
6.43
5.34
5.34
5.03
5.02
4.68
4.44
4.42
4.42
4.00
3.99
3.98
3.97
2.26


O
N
H3C


5.22
1.97
1.97
1.00
1.02
1.00
1.00
0.99
3.09
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)


143.06
141.60
129.78
128.84
127.53
126.92
126.25
112.93
83.16
75.73
61.94
20.35


O
N
H3C


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.35
7.33
7.32
7.31
7.30
7.27
7.25
7.23
6.35
6.34
6.34
6.33
6.32
5.28
5.27
4.99
4.98
4.66
4.65
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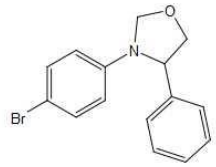
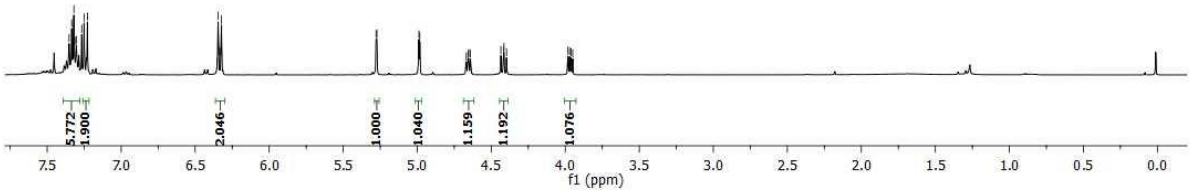
4.42
4.41
4.40
3.97
3.96
3.95


O
N
Br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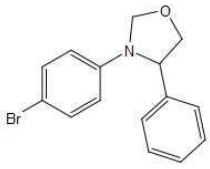
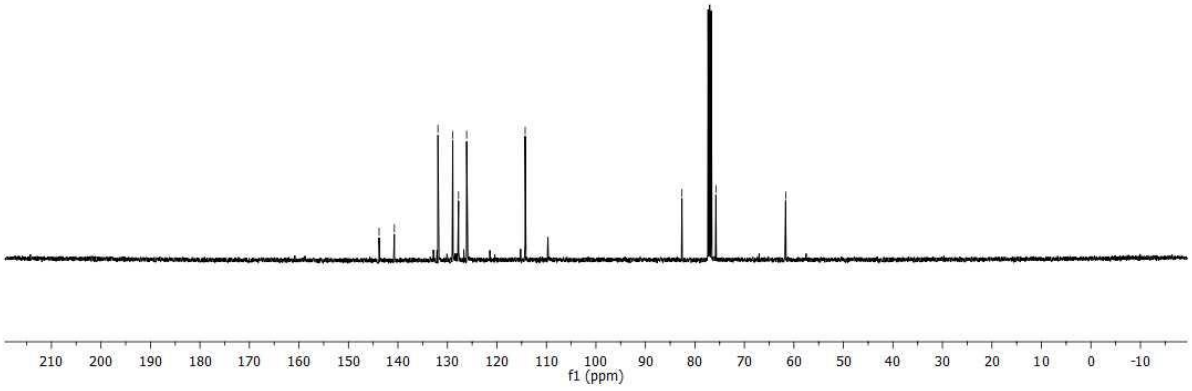
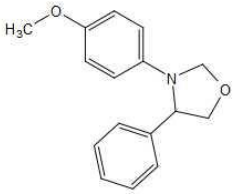
2.046
1.000
1.040
1.159
1.192
1.076
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

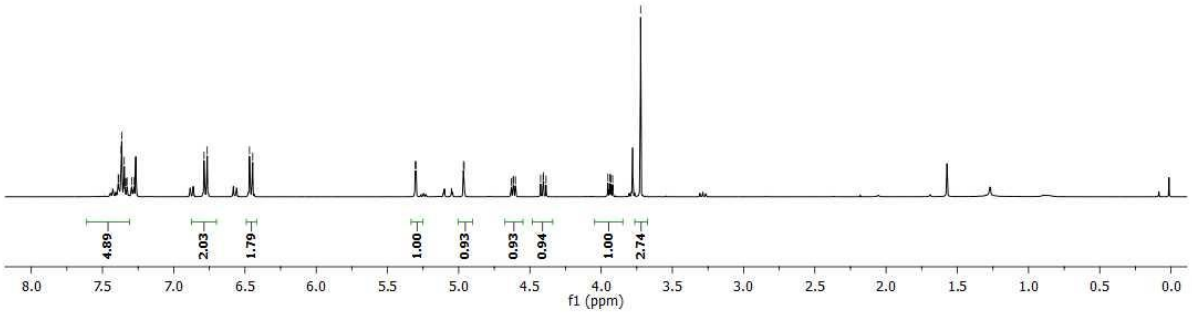

143.81
140.73
131.92
128.92
127.75
126.12
114.30
82.63
75.76
61.68

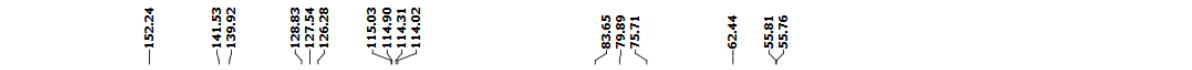

O
N
Br

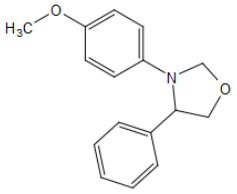

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

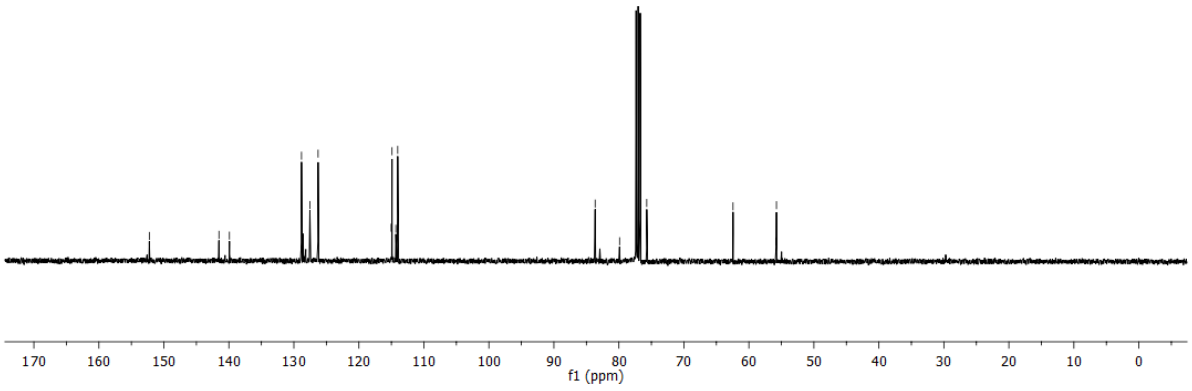

7.39
7.39
7.37
7.37
7.35
7.34
7.33
7.33
7.29
7.28
6.79
6.76
6.47
6.45
5.30
5.30
4.97
4.96
4.62
4.61
4.60
4.42
4.41
4.40
3.94
3.93
3.92
3.72

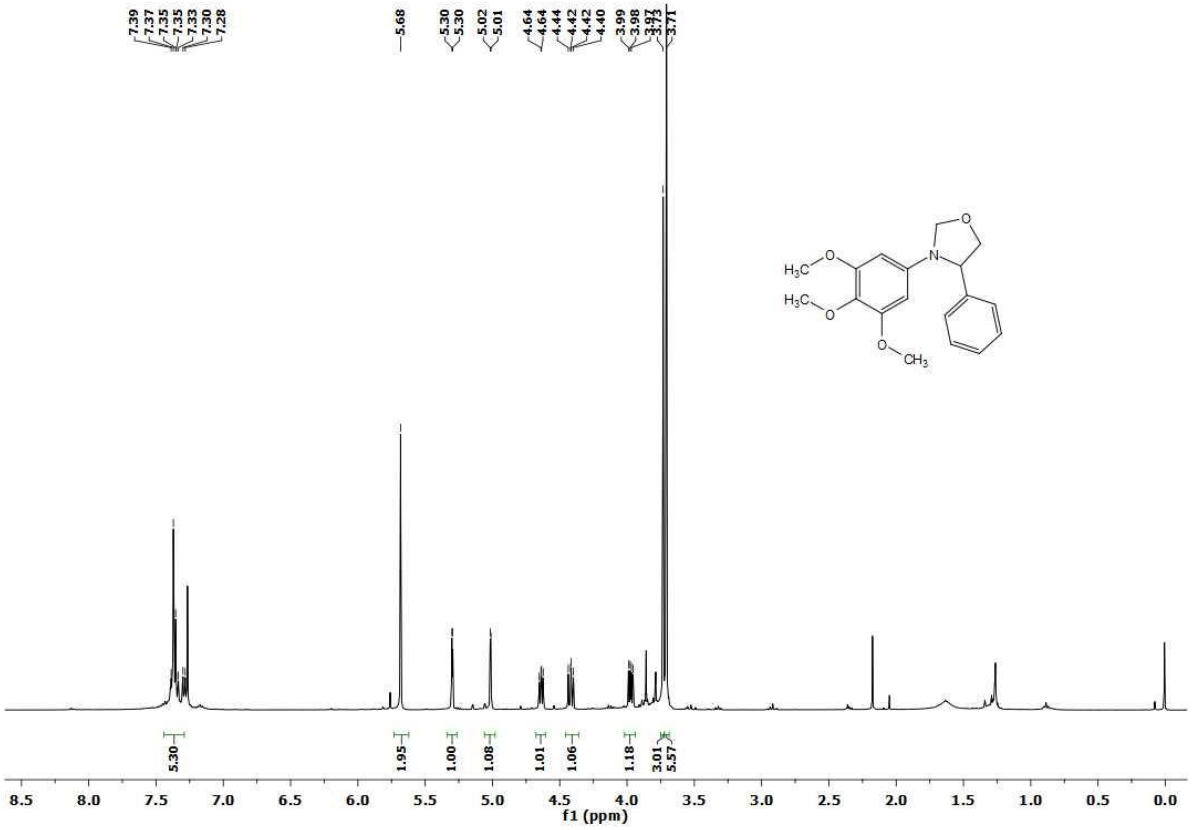

H3C
O
N
O

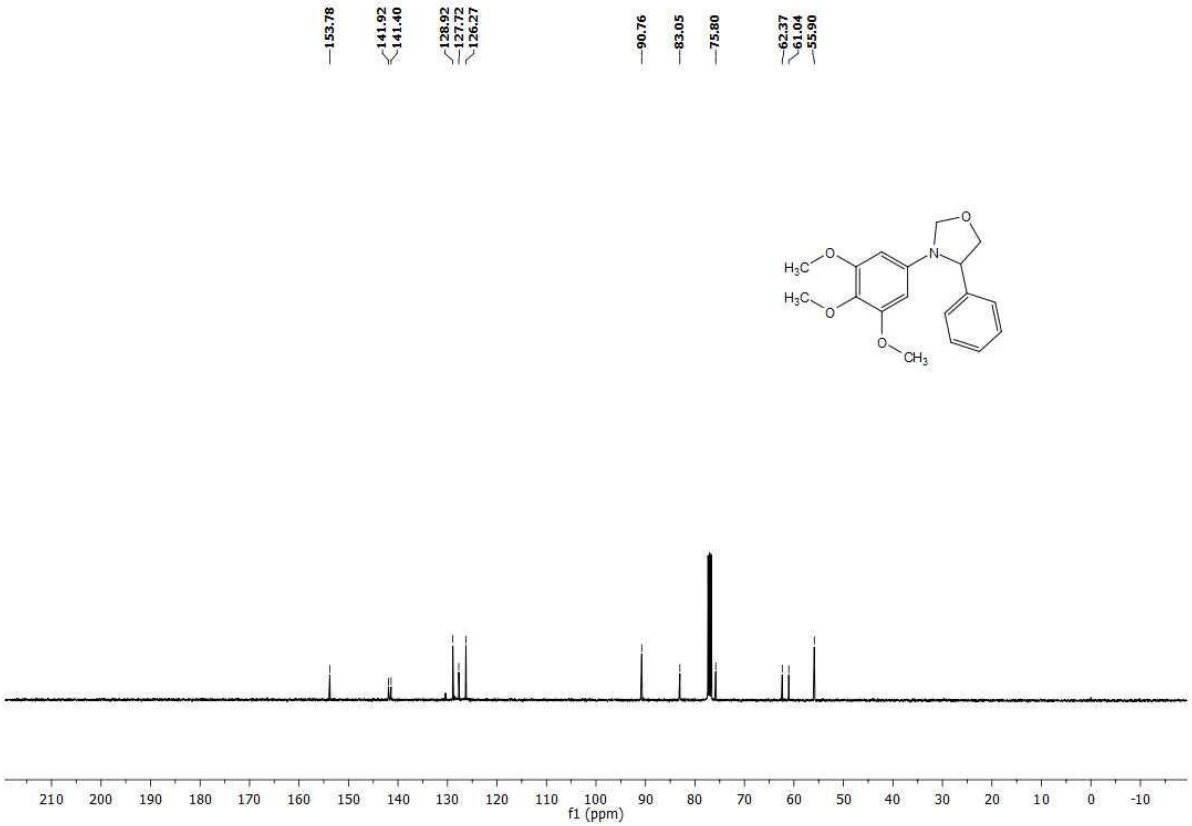

4.89
2.03
1.79
1.00
0.93
0.93
0.94
1.00
2.74
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


152.24
141.53
139.92
128.83
127.54
126.28
115.03
114.90
114.31
114.02
83.65
79.89
75.71
62.44
55.81
55.76


H3C
O
N
O


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.39
7.37
7.35
7.35
7.33
7.30
7.28
5.68
5.30
5.30
5.02
5.01
4.64
4.64
4.44
4.42
4.42
4.40
3.99
3.98
3.97
3.73
3.71
5.30
1.95
1.00
1.08
1.01
1.06
1.18
3.01
5.57
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)
H3C
O
H3C
O
O
CH3
N
O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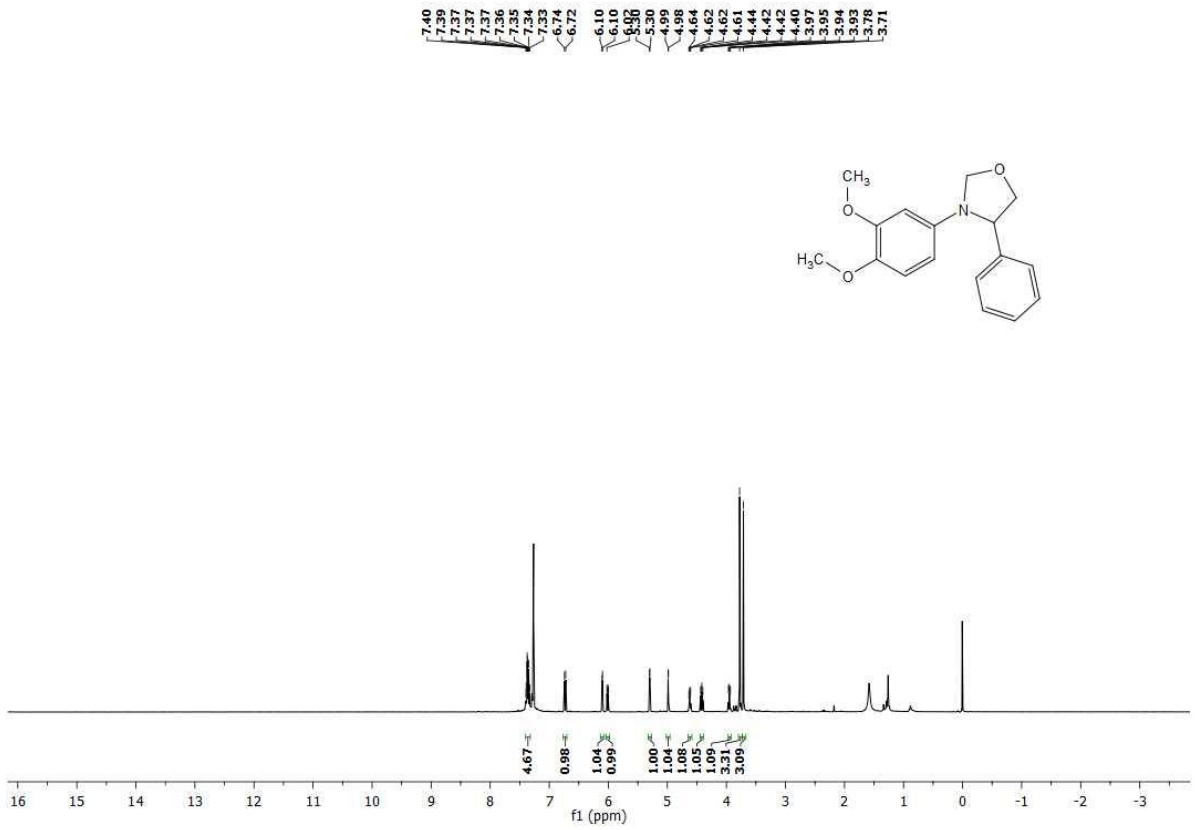
141.40
128.92
127.72
126.27
90.76
83.05
75.80
62.37
61.04
55.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
H3C
O
H3C
O
O
CH3
N
O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7.34
7.33
6.74
6.72
6.10
6.10
6.02
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5.30
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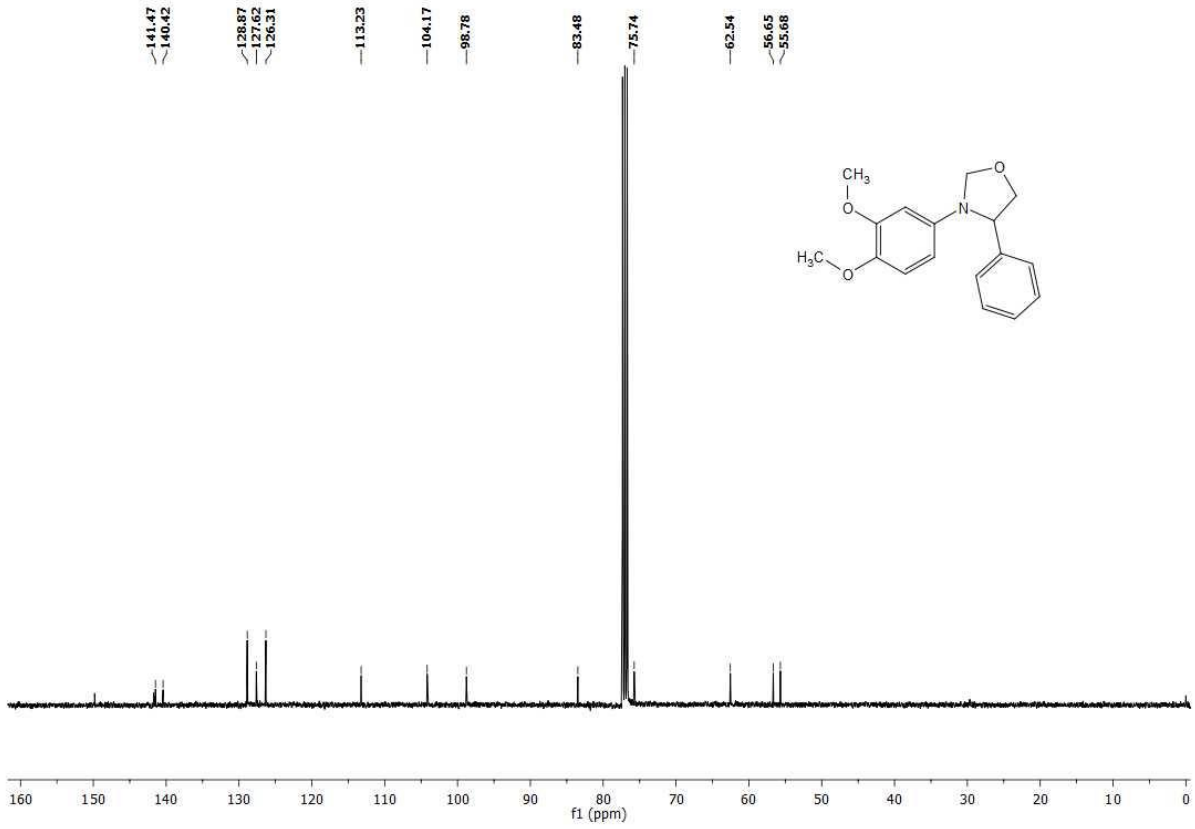
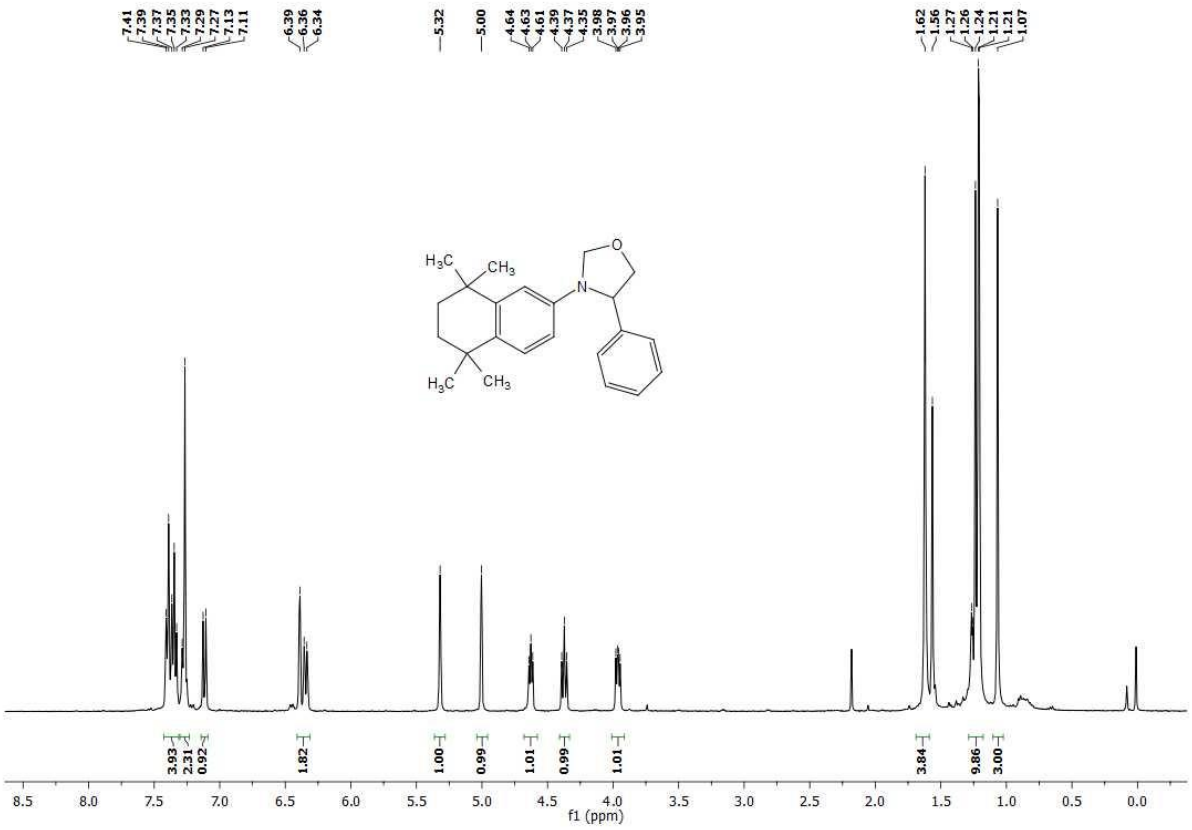
4.98
4.64
4.62
4.62
4.61
4.44
4.42
4.42
4.40
3.97
3.95
3.94
3.93
3.78
3.71
CH3
O
H3C
O
O
N
4.67
0.98
1.04
0.99
1.00
1.04
1.08
1.05
1.09
3.31
3.09
f1 (ppm)


141.47
140.42
128.87
127.62
126.31
113.23
104.17
98.78
83.48
75.74
62.54
56.65
55.68
CH3
O
H3C
O
O
N
f1 (ppm)


7.41
7.39
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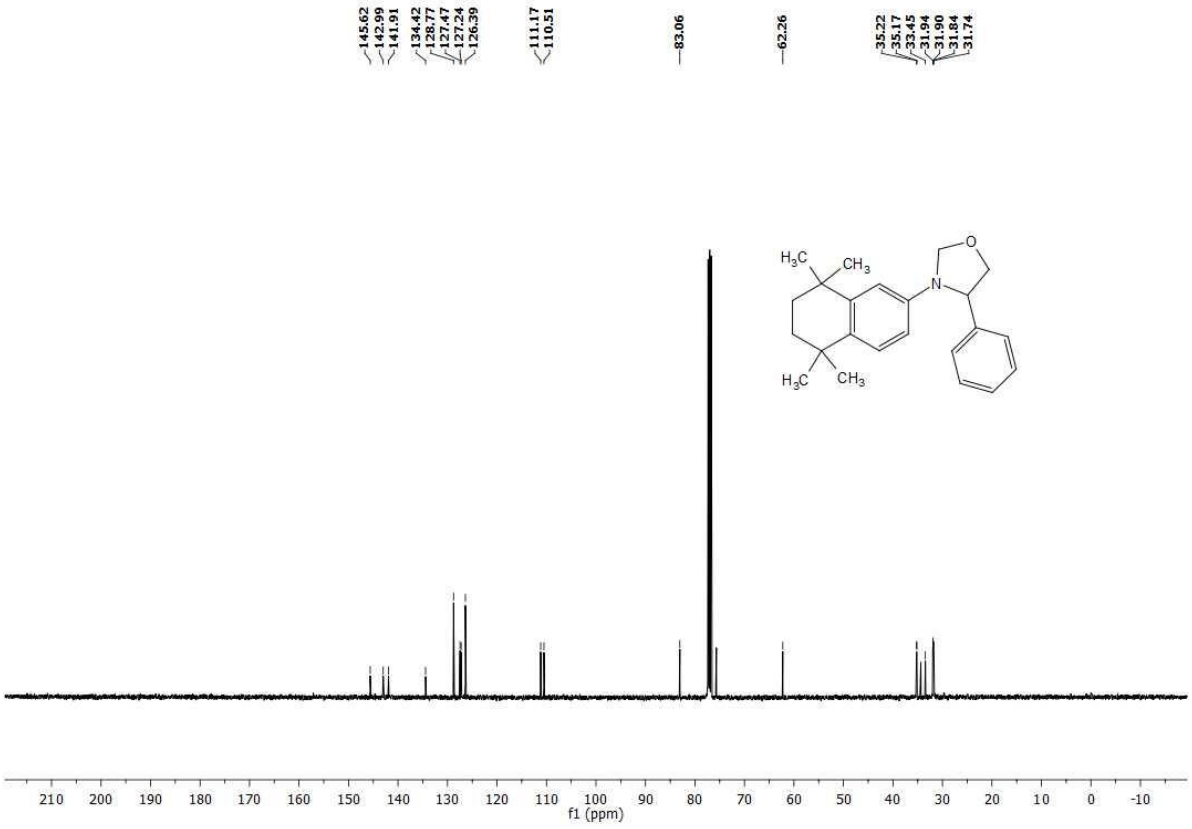
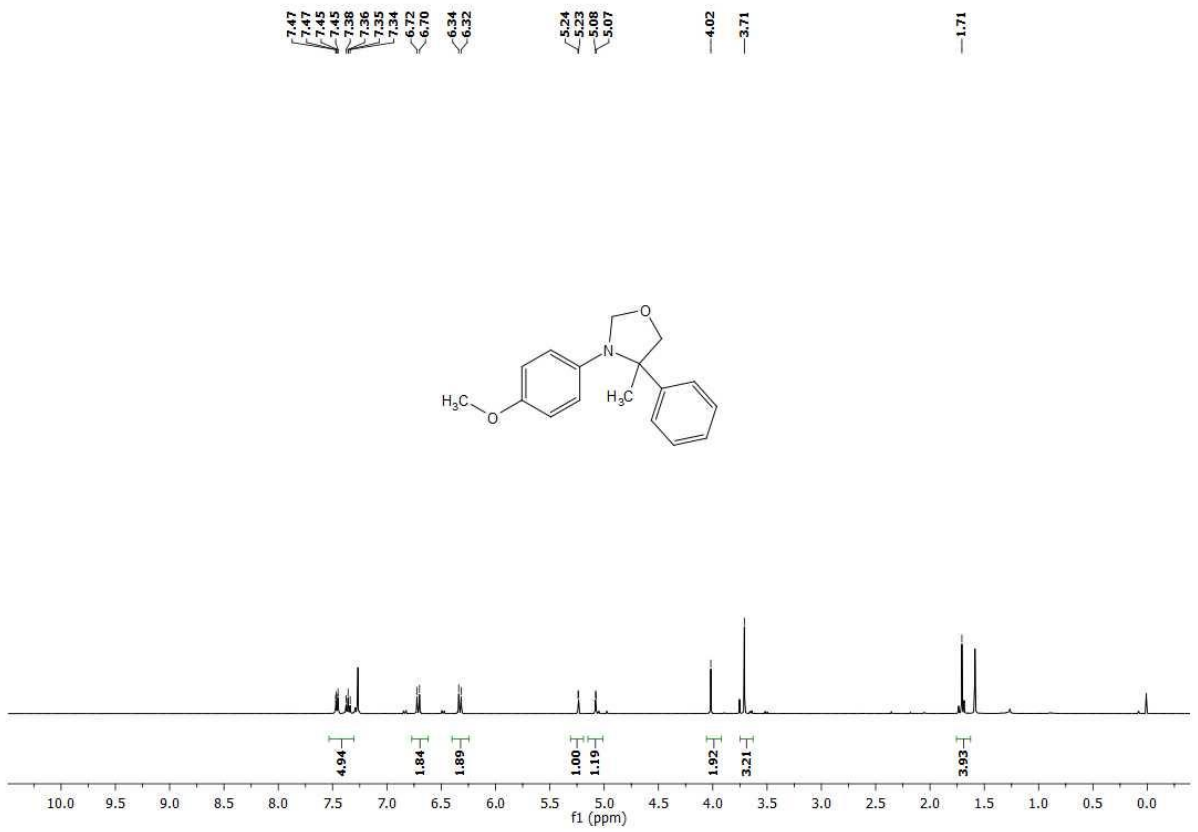
7.35
7.33
7.29
7.27
7.13
7.11
6.39
6.36
6.34
5.32
5.00
4.64
4.63
4.61
4.39
4.37
4.35
3.98
3.97
3.96
3.95
1.62
1.56
1.27
1.26
1.24
1.21
1.21
1.07
H3C
CH3
O
N
H3C
CH3
3.93
2.31
0.92
1.82
1.00
0.99
1.01
0.99
1.01
3.84
9.86
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.62
142.99
141.91
134.42
128.77
127.47
127.24
126.39
111.17
110.51
83.06
62.26
35.22
35.17
33.45
31.94
31.90
31.84
31.74
H3C
CH3
O
N
H3C
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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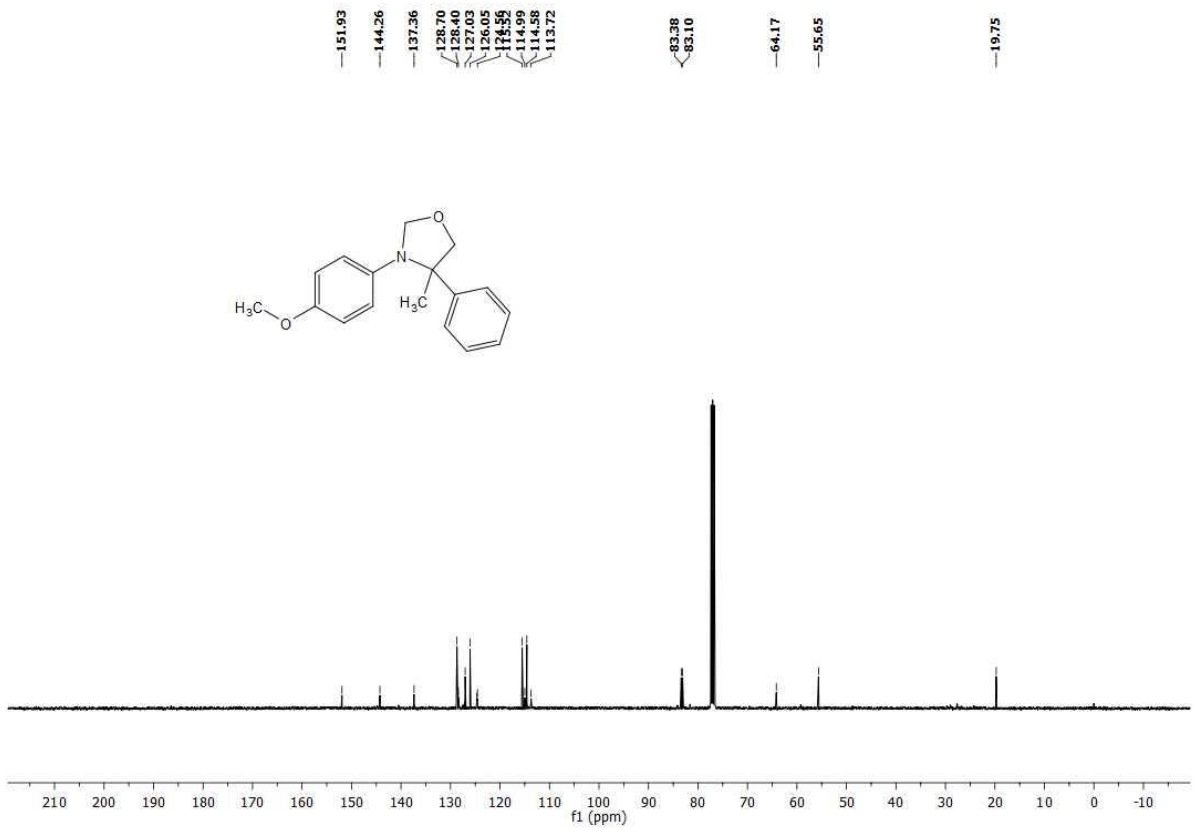
7.38
7.36
7.35
7.34
6.72
6.70
6.34
6.32
5.24
5.23
5.08
5.07
4.02
3.71
1.71
O
N
H3C
O
H3C
4.94
1.84
1.89
1.00
1.19
1.92
3.21
3.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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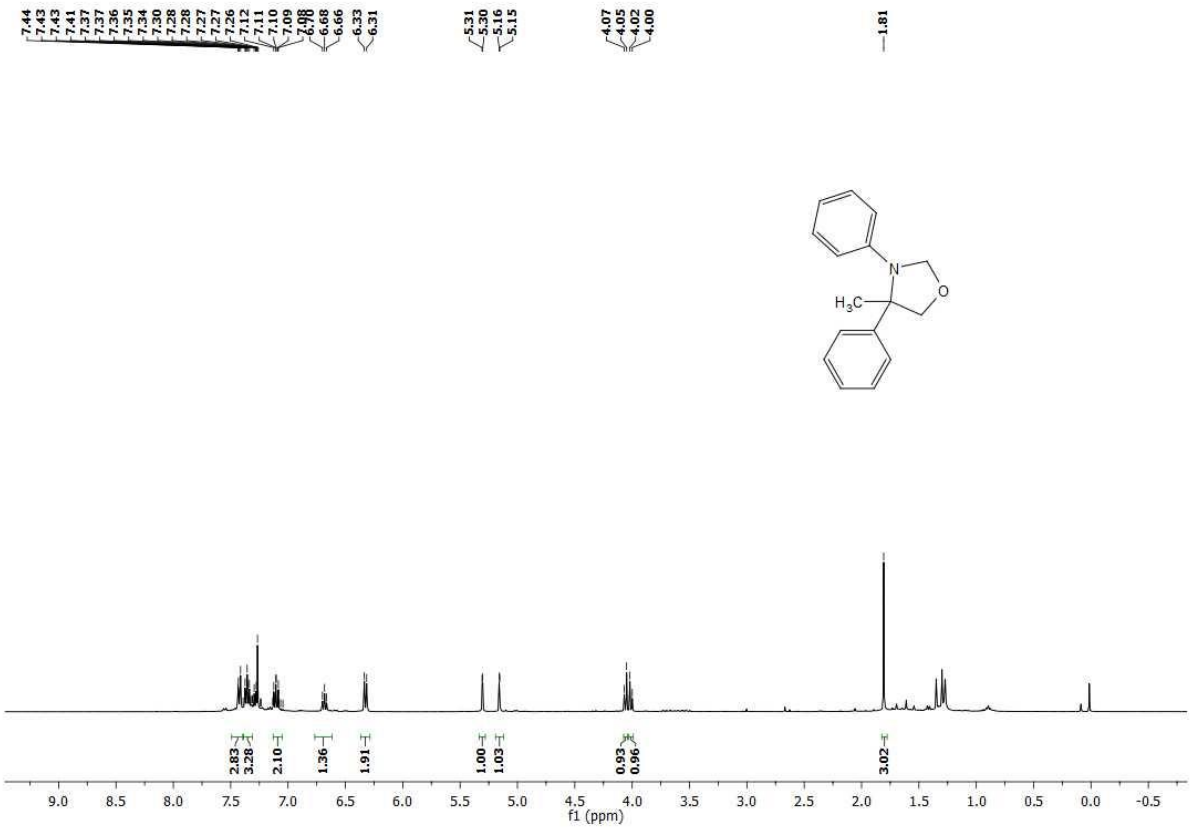
127.03
126.05
115.52
114.99
114.38
113.72
83.38
83.10
64.17
55.65
19.75
O
N
H3C
O
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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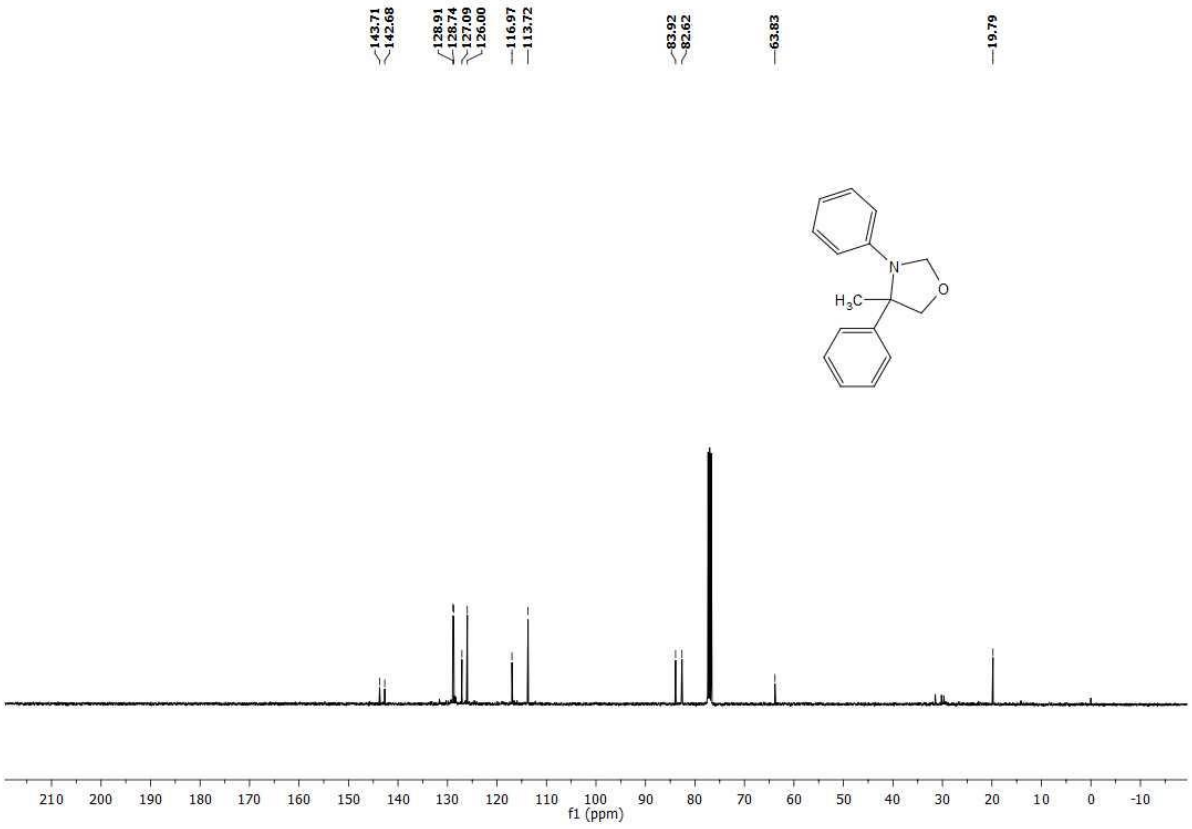
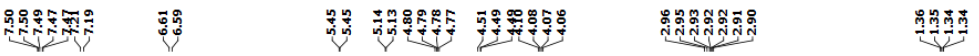
7.35
7.34
7.30
7.28
7.28
7.27
7.27
7.26
7.12
7.11
7.10
7.09
7.08
6.70
6.68
6.66
6.33
6.31
5.31
5.30
5.16
5.15
4.07
4.05
4.02
4.00
1.81
N
O
H3C
2.83
3.28
2.10
1.36
1.91
1.00
1.03
0.93
0.96
3.02
f1 (ppm)


143.71
142.68
128.91
128.74
127.09
126.00
116.97
113.72
83.92
82.62
63.83
19.79
N
O
H3C
f1 (ppm)


7.50
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7.19
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6.59
5.45
5.45
5.14
5.13
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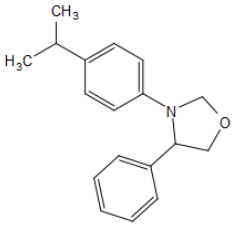
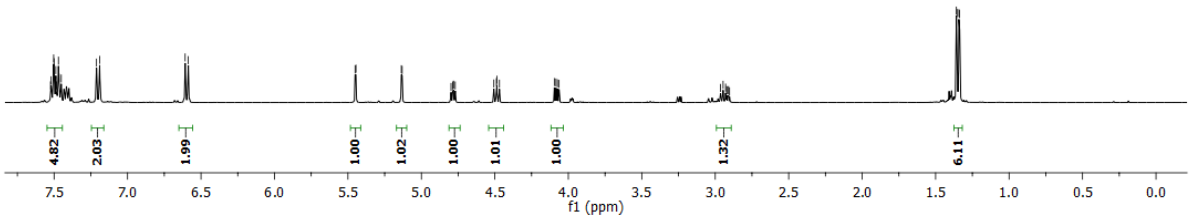
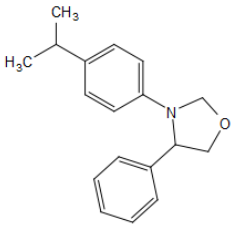
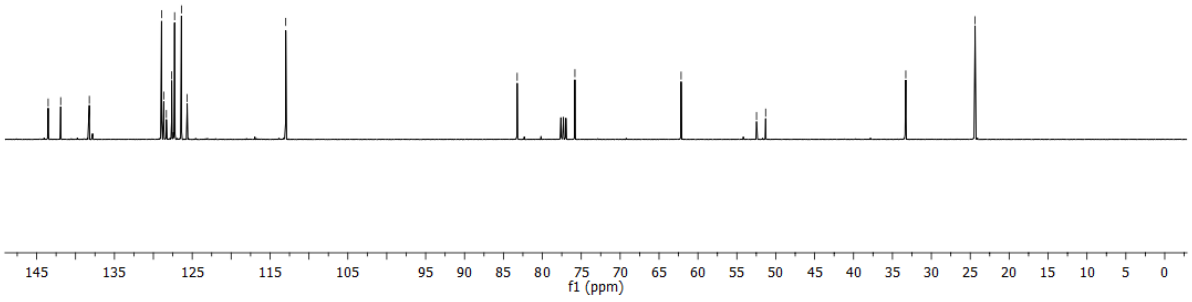
4.79
4.78
4.77
4.51
4.49
4.08
4.07
4.06
2.96
2.95
2.93
2.92
2.92
2.91
2.90
1.36
1.35
1.34
1.34

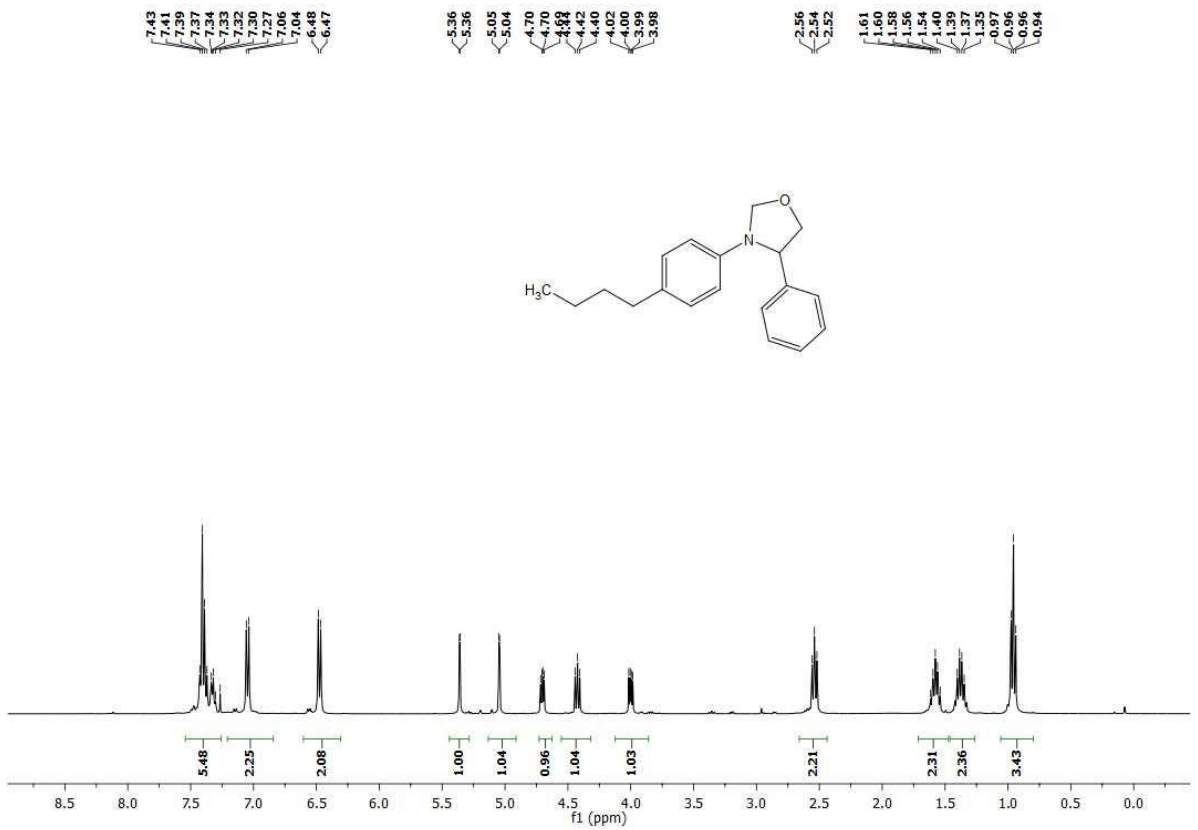

CH3
H3C
N
O

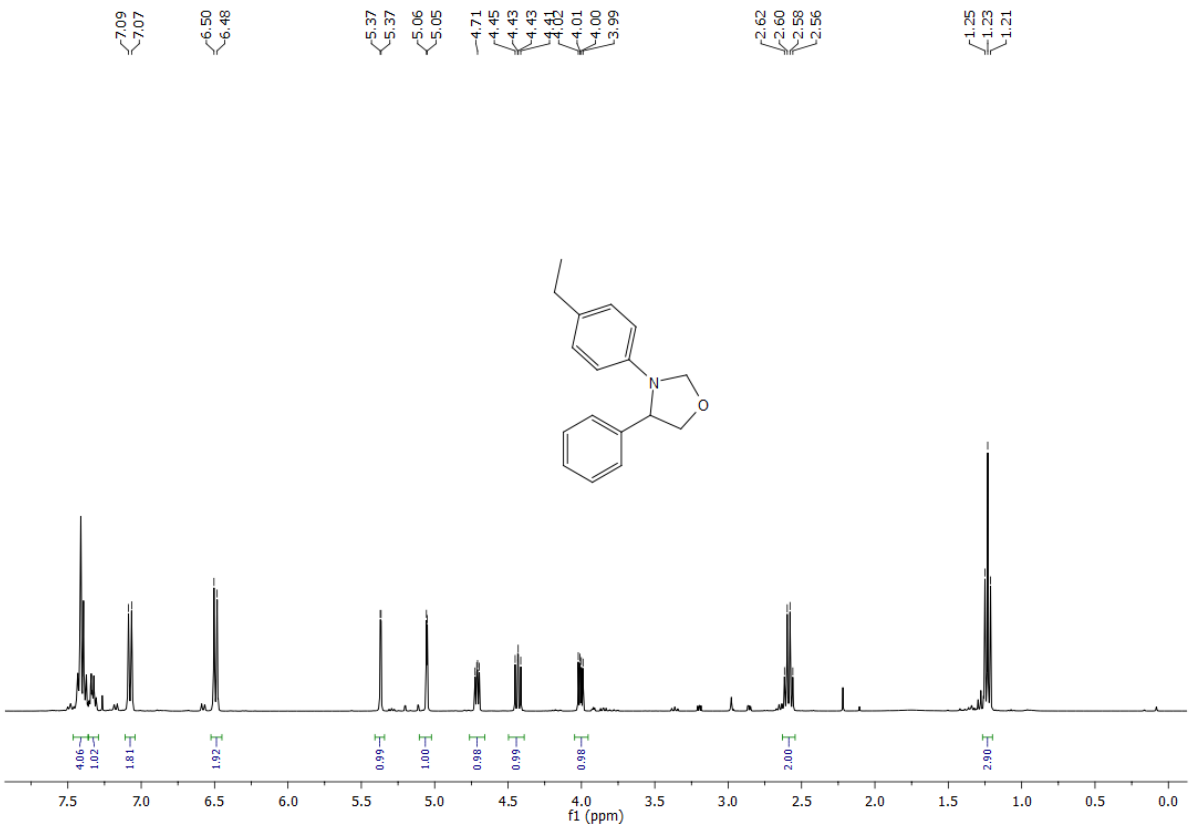

4.82
2.03
1.99
1.00
1.02
1.00
1.01
1.00
1.32
6.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

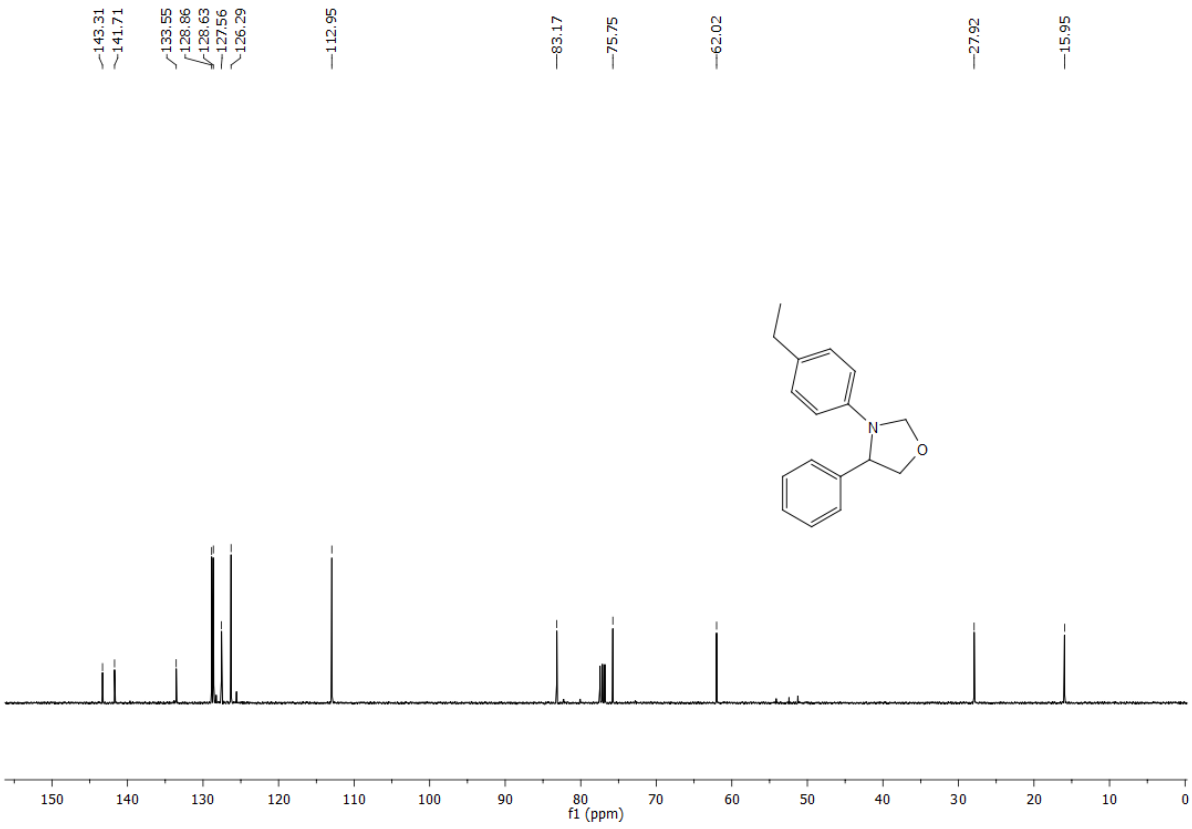

143.52
141.91
138.23
128.94
128.65
128.32
127.64
127.27
126.39
125.66
112.98
83.23
75.82
62.16
52.47
51.30
33.28
24.38


CH3
H3C
N
O

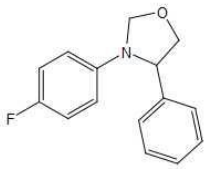

145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

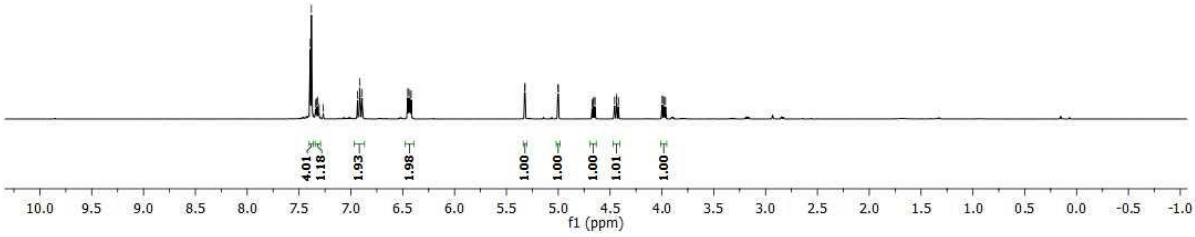

7.43
7.41
7.39
7.37
7.34
7.33
7.32
7.30
7.27
7.06
7.04
6.48
6.47
5.36
5.36
5.05
5.04
4.70
4.70
4.69
4.44
4.42
4.40
4.02
4.00
3.99
3.98
2.56
2.54
2.52
1.61
1.60
1.58
1.56
1.54
1.40
1.39
1.37
1.35
0.97
0.96
0.96
0.94
O
N
H3C
5.48
2.25
2.08
1.00
1.04
0.96
1.04
1.03
2.21
2.31
2.36
3.43
f1 (ppm)
143.25
141.74
132.16
129.17
128.85
126.28
112.83
83.15
75.75
62.01
34.70
34.01
22.41
14.06
O
N
H3C
f1 (ppm)


7.09
7.07
6.50
6.48
5.37
5.37
5.06
5.05
4.71
4.45
4.43
4.43
4.41
4.02
4.01
4.00
3.99
2.62
2.60
2.58
2.56
1.25
1.23
1.21
N
O
4.06
1.02
1.81
1.92
0.99
1.00
0.98
0.99
0.98
2.00
2.90
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)

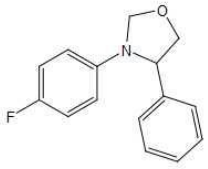

143.31
141.71
133.55
128.86
128.63
127.56
126.29
112.95
83.17
75.75
62.02
27.92
15.95
N
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

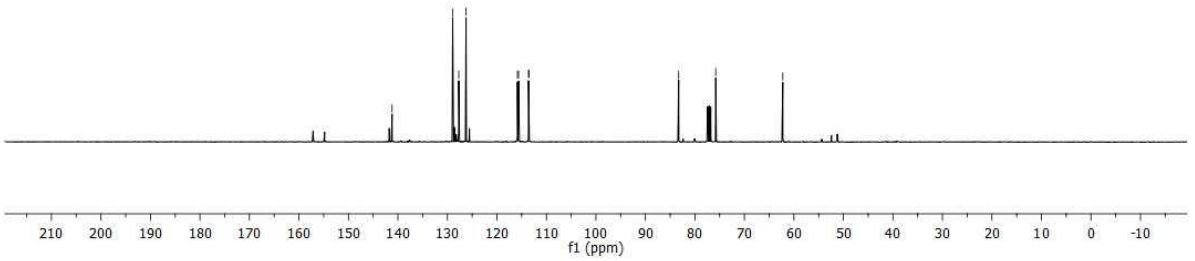

7.39
7.38
7.34
7.33
7.32
7.31
7.27
6.94
6.91
6.89
6.45
6.45
6.44
6.44
6.43
6.42
5.33
5.32
5.00
5.00
4.66
4.46
4.44
4.44
4.00
3.99
3.98
3.97


O
N
F

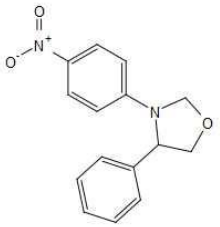

4.01
1.18
1.93
1.98
1.00
1.00
1.00
1.01
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

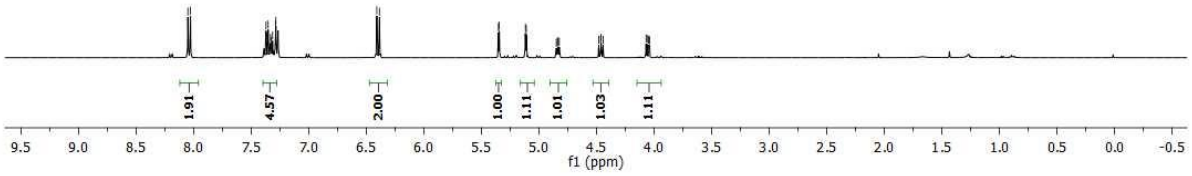

141.18
128.94
127.72
126.24
115.86
115.63
113.62
113.55
83.28
75.80
62.25


O
N
F

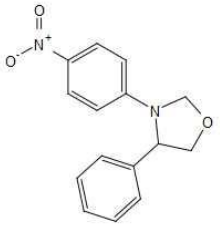

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

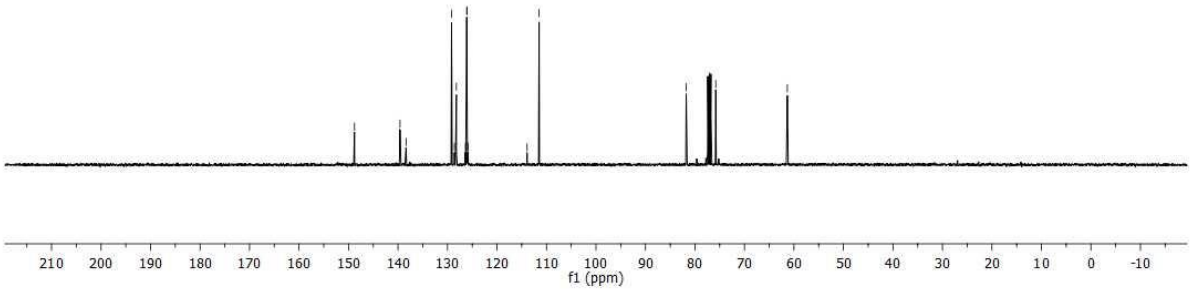

8.05
8.03
7.37
7.37
7.35
7.33
7.33
7.31
7.29
7.29
6.41
6.39
5.35
5.34
5.12
5.11
4.83
4.82
4.46
4.46
4.44
4.07
4.06
4.05
4.04



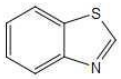

1.91
4.57
2.00
1.00
1.11
1.01
1.03
1.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

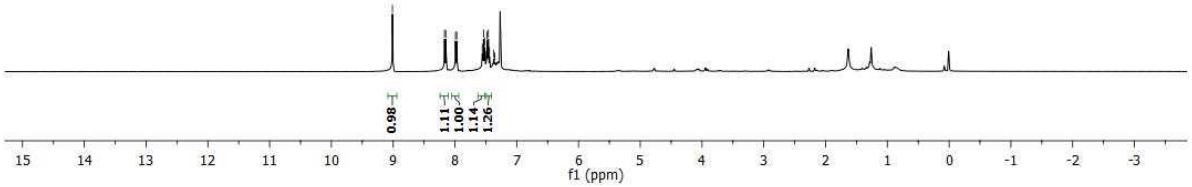

148.80
139.60
138.38
129.18
128.21
126.36
126.11
126.04
111.49
81.77
75.80
61.34



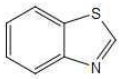

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

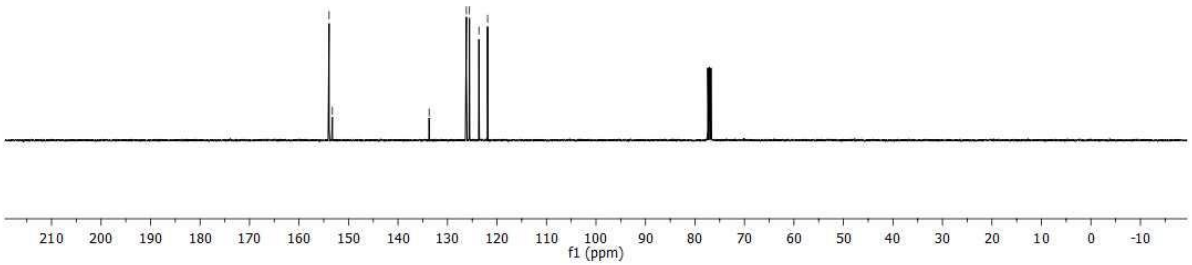

9.01
8.17
8.15
7.99
7.97
7.56
7.54
7.52
7.49
7.48
7.46
7.44
7.37
7.35

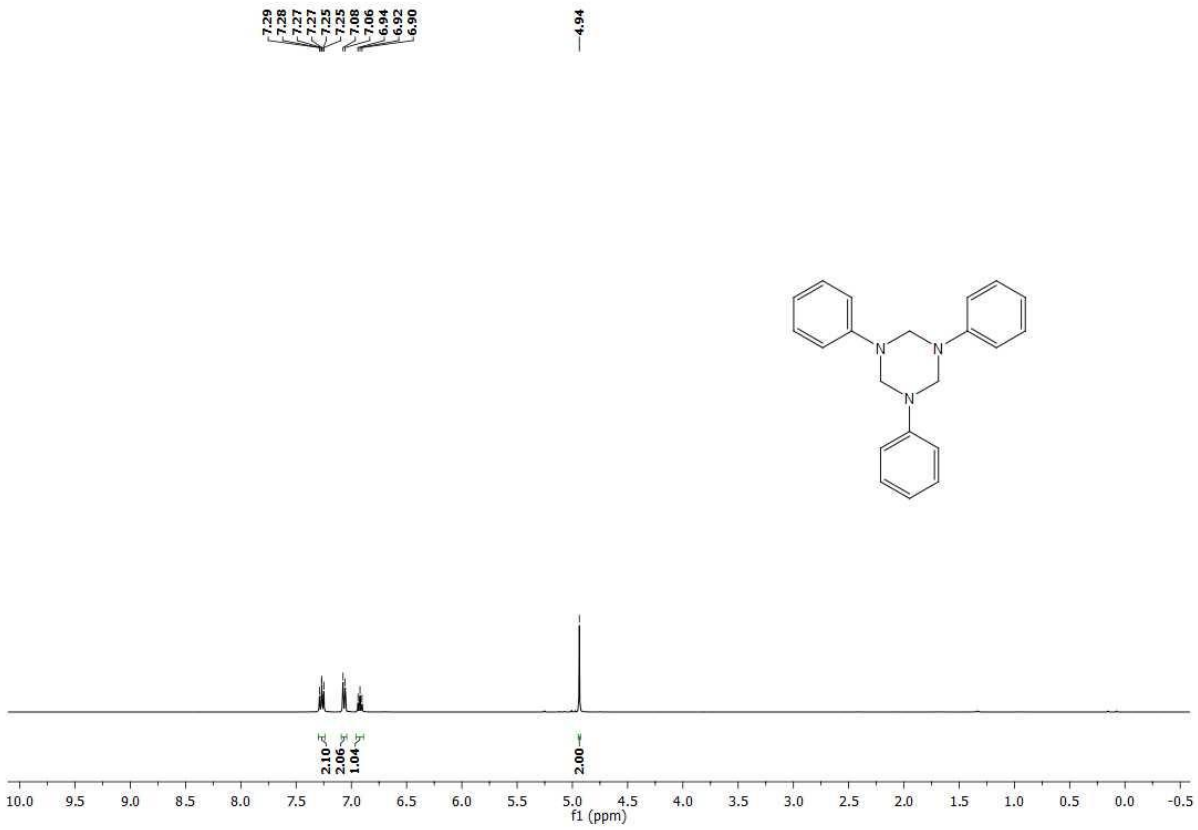

S
N

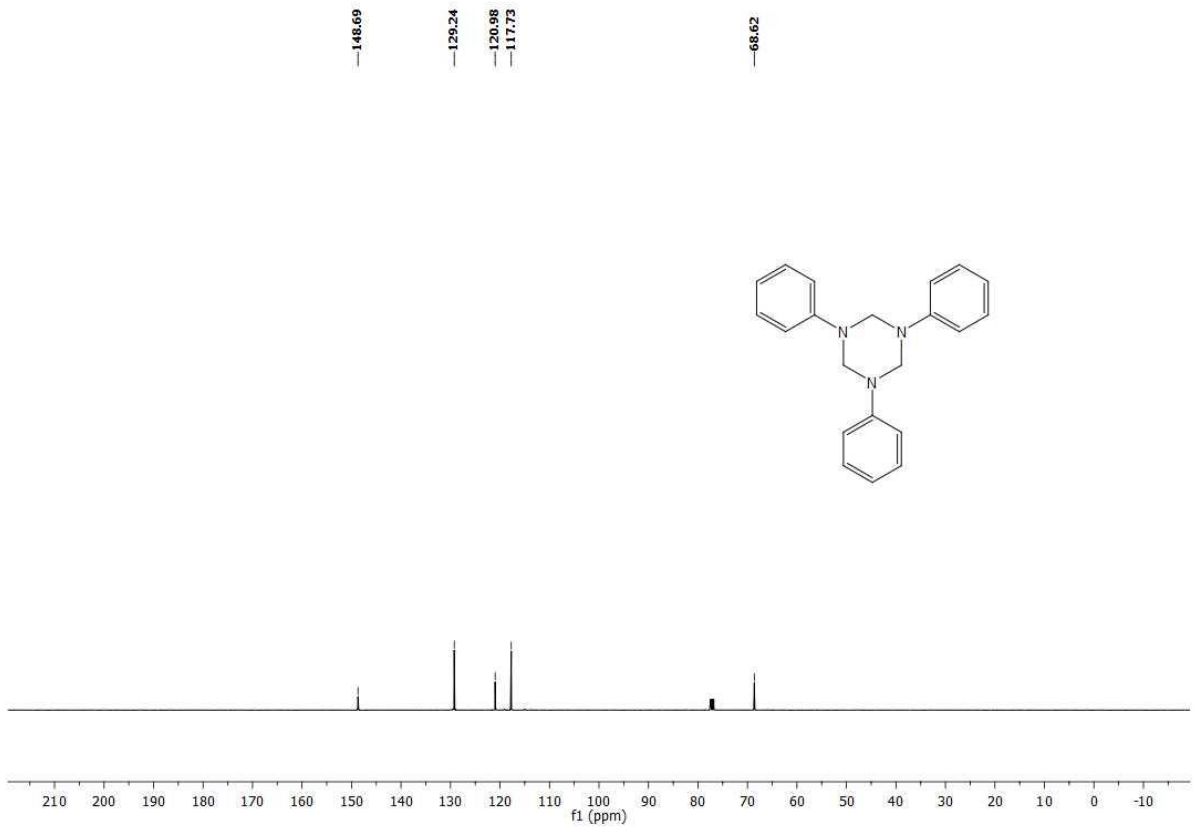

0.98
1.11
1.00
1.14
1.26
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


153.92
153.25
133.71
126.19
125.56
123.65
121.90


S
N


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.29
7.28
7.27
7.27
7.25
7.08
7.06
6.94
6.92
6.90
4.94
2.10
2.06
1.04
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


148.69
129.24
120.98
117.73
68.62
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

References

1 V. Satheesh, S. Vivek Kumar and T. Punniyamurthy, *Chem. Commun.*, 2018, **54**, 11813–11816.

2 Z. H. Wang, X. H. Fu, Q. Li, J. Q. Zhao, Y. You, Y. P. Zhang and W. C. Yuan, *Org. Lett.*, 2024, **26**, 1589–1594.

3 X. F. Song, L. J. Zhang, X. G. Zhang and H. Y. Tu, *J. Org. Chem.*, 2024, **89**, 3403–3412.

4 P. G. Dalai, S. Swain and N. Panda, *J. Org. Chem.*, 2024, **89**, 2599–2604.