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SYNTHESIS OF ^{13}C- AND ^{15}N-LABELED DNAN

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Isotopically labeled (^{13}C and ^{15}N) and unlabeled DNAN were synthesized in two steps from chlorobenzene in high purity and regioselectivity with an overall yield of 69% from readily available materials. The syntheses and full characterizations (^{1}H, ^{13}C, ^{14}N, ^{15}N NMR, IR, and HRMS) of labeled and unlabeled DNAN, as well as its synthetic precursor, 1-chloro-2,4-dinitrobenzene, are discussed. The use of isotopically labeled material and their spectra will enable the toxicity and biodegradation potential of DNAN to be more easily determined.

15. SUBJECT TERMS

DNAN, dinitroanisole, chlorodinitrobenzene, synthesis, ^{15}N-isotopically labeled DNAN, ^{13}C-isotopically labeled DNAN, ^{15}N-isotopically labeled chlorodinitrobenzene, ^{14}N NMR, ^{15}N NMR, T_1 longitudinal relaxation time

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FOREWORD

The synthetic and analytical work described herein helps address a basic understanding of the toxicity and biodegradation potential of DNAN. Using two different isotopically labeled DNAN compounds will allow bioaccumulation factors and biodegradation mechanisms for DNAN, its metabolites, and its end-products to be determined. These data can then be applied to existing fate and effects models to determine the potential environmental risk that new insensitive munitions containing DNAN pose.

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LIST OF ABBREVIATIONS AND ACRONYMS

DNAN	2,4-Dinitroanisole
Et_2O	Diethyl ether
IM	Insensitive Munitions
IMX-101	Insensitive Munition Explosive 101
IR	Infrared spectroscopy
HRMS	High resolution mass spectroscopy
NMR	Nuclear magnetic resonance spectroscopy
PAX-21	Picatinny Arsenal Explosive 21
R_f	Retention factor
T_1	Longitudinal relaxation time
T_2	Transverse relaxation time
T_2^*	Observed transverse relaxation time
TNT	2,4,6-Trinitrotoluene
TLC	Thin layer chromatography

ABSTRACT

Isotopically labeled (^{13}C and ^{15}N) and unlabeled DNAN were synthesized in two steps from chlorobenzene in high purity and regioselectivity with an overall yield of 69% from readily available materials. The syntheses and full characterizations (^{1}H, ^{13}C, ^{14}N, ^{15}N NMR, IR, and HRMS) of labeled and unlabeled DNAN, as well as its synthetic precursor, 1-chloro-2,4-dinitrobenzene, are discussed. The use of isotopically labeled material and their spectra will enable the toxicity and biodegradation potential of DNAN to be more easily determined.

INTRODUCTION

The use of DNAN (2,4-dinitroanisole) has been undergoing a renaissance over the last decade. Once considered a poor substitute for TNT in terms of performance,[1] the insensitivity of DNAN makes it attractive for use in melt-castable insensitive munitions (IM), such as PAX-21 used in the 60-mm mortar (M720A1) and IMX-101 used in 155-mm artillery munitions (M795).[2] However, the environmental impact of DNAN at manufacturing facilities and training ranges, i.e., Picatinny Arsenal and Holston Army Ammunition Plant, is unclear. Of primary concern is the bioaccumulation of the highly toxic 2,4-dinitrophenol, a breakdown product readily formed via hydrolysis of DNAN, among other degradation products of interest.

In order to assist the determination of the biological degradation mechanisms and bioaccumulation data of DNAN and its metabolites, we have synthesized two different isotopically labeled DNAN compounds: one compound labeled with a ^{13}C-methoxy group and the other labeled with two ^{15}N-nitro groups (Fig. 1). This labeling strategy will allow the potential transformations of de-methylation, de-nitration, and nitro-reduction to be easily tracked by various mass spectroscopy and nuclear magnetic resonance techniques.

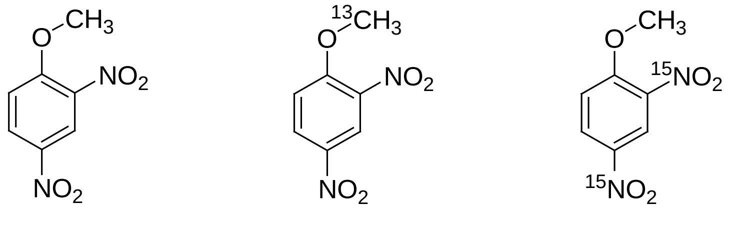

Figure 1. DNAN, ^{13}C-Labeled DNAN, and ^{15}N-Labeled DNAN

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[1] DNAN is approximately 10% less powerful than TNT (Fedoroff et al., 1960)

[2] PAX-21 (36% RDX, 34% DNAN, 30% AP, <1% *N*-methyl nitroaniline) and IMX-101 (40% nitroguanidine, 40% DNAN, 20% NTO)

DNAN is synthesized in high yield and high purity by first dinitrating chlorobenzene to yield chlorodinitrobenzene, and then displacing chloride with methoxide to form DNAN (Fig. 2). Theoretically, dinitration of chlorobenzene can produce six possible regioisomers; in practice however, only two are predominantly formed: 1-chloro-2,4-dinitrobenzene and 1-chloro-2,6-dinitrobenzene (Urbański, 1964; Fedoroff and Sheffield, 1966). Regioselective nitration is best controlled via reaction temperature, with lower temperatures favoring the desired low *ortho*-to-*para* (σ/ρ) ratio. Whereas the first nitration can be conducted at low temperatures, higher temperatures are required for the second nitration of the more deactivated chloronitrobenzene, and some loss of regioselective control is unavoidable at this step. Thus, the regioselectivity of the first nitration is critical to synthesize the desired regioisomer of chlorodinitrobenzene.

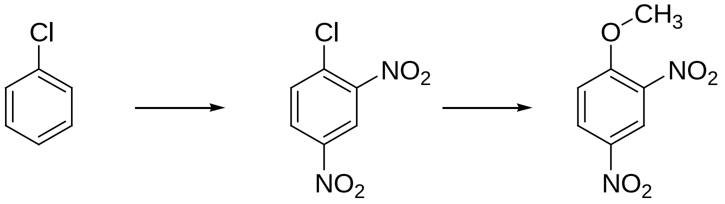

Figure 2. Synthesis of DNAN

RESULTS AND DISCUSSION

The industrial production of chlorodinitrobenzene uses 100% nitric, 96% sulfuric acid, and chlorobenzene, and has been extensively studied (Urbański, 1964; Fedoroff and Sheffield, 1966). To synthesize ^{15}N-labeled chlorodinitrobenzene in a cost effective manner, we adapted our procedure using ^{15}N-labeled sodium nitrate to generate ^{15}N-labeled nitric acid *in situ*, avoiding loses that may occur while distilling ^{15}N-labeled nitric acid. We modeled our molar ratio of sodium nitrate, sulfuric acid, and chlorobenzene on the 100-gram preparation of chlorodinitrobenzene (Davis, 1943), in which the molar ratio of sulfuric acid / nitric acid / chlorobenzene was 3.7 / 2.9 / 1. The sodium sulfate formed acted as a desiccant, absorbing the water produced during nitration (Fig. 3). Also since the sodium nitrate / sulfuric acid mixture was very heterogeneous, we decided to double the amount of sulfuric acid to improve both the mixing efficiency and the thermal control of the reaction.

$$\begin{gathered}
2\ NaNO_3 + H_2SO_4 \rightleftharpoons 2\ HNO_3 + Na_2SO_4 \\
C_6H_5Cl_1 + 2\ HNO_3 \rightleftharpoons C_6H_5N_2O_4Cl_1 + 2\ H_2O \\
Na_2SO_4 + 2\ H_2O \rightleftharpoons Na_2SO_4{\bullet}2H_2O
\end{gathered}$$

Figure 3. Dinitration of Chlorobenzene

The reaction conditions of our first trial nitration of chlorobenzene were not strong enough, as a significant amount of mono-nitro product (chloronitrobenzene) was observed in the product mixture by ^{1}H NMR analysis (Table 1). We increased the amount of sodium nitrate and sulfuric acid used in the second trial nitration, and then we increased the reaction time for the third trial nitration. ^{1}H and ^{13}C NMR analyses of the product mixture for the third trial nitration showed a mixture of the two regioisomers (1-chloro-2,4-dinitrobenzene and 1-chloro-2,6-dinitrobenzene), and failed to show any mono-nitro product. The yield of the third trial nitration was quantitative (ca. 99%).

Table 1. Initial Trial Nitrations of Chlorobenzene

Trial Nitration	Chlorobenzene	Sodium Nitrate	Sulfuric Acid	Conditions	Mono-nitro-product
1	0.51 mL (1)	1.29 g (3)	2.0 mL (7.2)	100 °C / 3 h	10%
2	0.51 mL (1)	1.72 g (4)	3.0 mL (10.8)	100 °C / 4 h	6%
3	0.51 mL (1)	1.72 g (4)	3.0 mL (10.8)	100 °C / 16 h	0%

[a] Numbers in parentheses represent the molar ratios used.

We then scaled the nitration reaction 5-fold using the same reaction conditions of our third trial nitration. We improved the regioisomeric ratio of the desired 1-chloro-2,4-dinitrobenzene versus 1-chloro-2,6-dinitrobenzene from 85:15 to 95:5 by changing the heating regimen. Instead of heating the reaction mixture to 40 °C (external temperature), and then slowly raising the temperature to 100 °C over one hour, we introduced a one hour residence time at 40 °C before raising the temperature. This low temperature residence time directed the first nitration toward *para* instead of *ortho*, thus improving the regioselectivity of the final product mixture. Mixing efficiency during the initial nitration also seems to improve the regioselectivity. Again, the yield was quantitative (ca. 99%).

We synthesized DNAN from chlorodinitrobenzene by the simple displacement of chloride using methanol and sodium hydroxide at 60 °C (Fedoroff et al., 1960). Recrystallization from methanol gave needles in good yield (ca. 70%). To improve the yield, the remaining mass balance (ca. 30%) for this reaction could have been recovered during work-up[3] and recrystallization. However our objective was to isolate DNAN in very high purity, and recrystallization improved the regioisomeric ratio of 2,4-dinitroanisole to 2,6-dinitroanisole from 95:5 to greater than 98:2, as determined by ^{1}H and ^{13}C NMR analyses. The use of ^{13}C-labeled methanol as a reagent readily allowed the synthesis of ^{13}C-labeled DNAN, and any possible scrambling of the ^{13}C-labeled carbon with the unlabeled methanol used in the recrystallization was not observed by HRMS analysis.

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3) The yield might be increased by first removing some of the reaction solvent before water addition.

Remarkably, the ^{1}H and ^{13}C NMR spectra for unlabeled chlorodinitrobenzene and unlabeled DNAN were unknown until recently (Aridoss and Laali, 2011), and are reported herein. The mono-nitro product (1-chloro-4-nitrobenzene) and 1-chloro-2,6-dinitrobenzene each possess a plane of symmetry, and were readily identified via ^{1}H NMR analysis by the presence of a pair of coupled doublets and by the presence of a triplet coupled with a doublet, respectively. The nitro carbons of chlorodinitrobenzene and DNAN were readily identified in the ^{13}C NMR spectra since these chemical shifts are broad due to quadrupolar relaxation from the directly attached ^{14}N nucleus. The chemical shifts for these same nitro carbons of the ^{15}N-labeled compounds each becomes a sharpened doublet of doublets as the quadrupolar relaxation mechanism no longer exists without an ^{14}N nucleus present, allowing the one- and three-bond coupling (^{1}J N,C and ^{3}J N,C) between the ^{13}C and ^{15}N nuclei to be readily observed.

We collected the ^{15}N NMR spectra for ^{15}N-labeled chlorodinitrobenzene and DNAN, as well as their ^{1}H and ^{13}C NMR spectra. We observed two chemical shifts in the ^{15}N NMR spectra for both compounds, each in the characteristic region (10 to -30 ppm) of an aromatic nitro group (Berger et al., 1997). The longitudinal relaxation times (T_1) for these ^{15}N nitro groups were measured to be quite long (hundreds of seconds). Since ^{15}N NMR also suffers from low sensitivity and a negative gyromagnetic ratio, knowledge of T_1 allows one to optimize ^{15}N NMR pulse sequences of chlorodinitrobenzene and DNAN at natural abundance levels of nitrogen. Since we determined the T_1 values using de-oxygenated samples, one must keep in mind that the paramagnetic oxygen present in the typically prepared NMR solution will shorten the true T_1 reported herein.

We also collected the ^{14}N NMR spectra for natural abundance chlorodinitrobenzene, natural abundance DNAN, and ^{13}C-labeled DNAN. Whereas T_1 governs ^{15}N NMR, the transverse relaxation time (T_2) dictates ^{14}N NMR. Since the observed T_2 values (T_2^*) were extremely short (milliseconds), the spectra we collected show significant line broadening, and the NMR acquisition times used were only 26 milliseconds. The two nitro groups for both compounds are indistinguishable by ^{14}N NMR, and only one chemical shift is observed. Nevertheless, these ^{14}N NMR spectra clearly show that an aromatic nitro group is present (Berger et al., 1997).

We observed strong absorption bands in all the IR spectra that are characteristic for the symmetrical (1360-1310 cm^{-1}) and asymmetrical stretches (1560-1490 cm^{-1}) of the aromatic nitro group (Pretsch et al., 2000). The effect of isotopic substitution on the nitro stretches in the IR spectra is readily apparent as we observe the expected shift to lower vibrational frequencies for the ^{15}N-labeled compounds (ca. 25 cm^{-1} shift).

CONCLUSIONS

We synthesized chlorodinitrobenzene and ^{15}N-labeled chlorodinitrobenzene in high yield (ca. 99%) and high regioselectivity (ca. 95:5) via dinitration of chlorobenzene. Using sodium nitrate and sulfuric acid, we conducted the nitration first at 40 °C, and then slowly raised the reaction temperature to 100 °C. We determined the regioselectivity by ^{1}H NMR analysis, and we did not observe any chloronitrobenzene after our procedure had been optimized. The use of ^{15}N-labeled sodium nitrate readily allows the synthesis of the ^{15}N-labeled product. We also report the ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR, as well as the IR, and HRMS spectra for labeled and unlabeled chlorodinitrobenzene, as well as the ^{15}N NMR T_1 values.

We synthesized DNAN, ^{13}C-labeled DNAN, and ^{15}N-labeled DNAN from chlorodinitrobenzene by the simple displacement of chloride using methanol and sodium hydroxide at 60 °C. Recrystallization from methanol improved the purity, with a regioisomeric ratio of 2,4-dinitroanisole to 2,6-dinitroanisole greater than 98:2, yielding needles in high yield (ca. 70%). The use of ^{13}C-labeled methanol as a reagent readily allows the synthesis of ^{13}C-labeled DNAN. We also report the ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR, as well as the IR, and HRMS spectra for labeled and unlabeled DNAN, as well as the ^{15}N NMR T_1 values. We hope the use of these selectively labeled DNAN compounds will support future work in the determination of bioaccumulation factors and biodegradation mechanisms for DNAN.

EXPERIMENTAL SECTION

Chlorobenzene, sodium nitrate, and methanol were purchased from Aldrich Chemical Co. Sulfuric acid and sodium hydroxide were purchased from Fisher Scientific. The isotopic enrichment of ^{15}N-labeled sodium nitrate was 98.2%, and the isotopic enrichment of ^{13}C-labeled methanol was 99.1%; both were purchased from Cambridge Isotope Laboratories, Inc. Chlorodinitrobenzene and DNAN are toxic, and care was taken to avoid exposure to by working with gloves in a well-ventilated hood. Chlorodinitrobenzene and DNAN are also 1.1 explosives, and the appropriate safety precautions and disposal methods were taken.

Melting points are uncorrected and were measured using a Mel-Temp apparatus. ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR analyses (300.1, 75.5, 21.7, 30.4 MHz, respectively) were performed on a Varian Mercury Plus 300 instrument and on an Agilent DD2 300 instrument in samples dissolved in $CDCl_3$. Downfield chemical shifts are recorded in positive δ units in ppm relative to TMS (δ = 0.00) for ^{1}H NMR, to the residual solvent peak in $CDCl_3$ (δ = 77.0) for ^{13}C NMR, and to external nitromethane (δ = 0.00) for ^{14}N and ^{15}N NMR. Multiplicities are described as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of doublet of doublets (ddd), multiplet (m), and broad (br). Proton decoupling (WALTZ-16) was used for acquiring the ^{13}C NMR spectra, and an inverse gated decoupling sequence was used for acquiring the ^{15}N NMR spectra. The line-widths at half height ($\Delta\nu_{½}$) reported for the ^{14}N NMR spectra were processed without exponential multiplication; T_2^*-values were determined using solutions degassed of nitrogen[4] (multiple freeze-pump-thaw cycles with J Young valves) from the equation: $\pi\Delta\nu_{½} = 1/T_2^*$. The T_1-values reported for the ^{15}N NMR spectra were determined using 150 mM solutions degassed of oxygen (multiple freeze-pump-thaw cycles with J Young valves) via the inversion recovery method at 25 °C after sample calibration of the 90° pulse width, and fitted (<2.5% error) to an exponential plot. IR spectra were recorded on a Nicolet 750 FTIR spectrometer at 2 wavenumber resolution using a Diamond ATR accessory. High resolution (<10 ppm) mass spectra were acquired on a JEOL AccuTOF (time-of-flight) mass spectrometer using DART ionization conditions (250 °C, 20 eV), calibrated to PEG 600. Retention factors (R_f) for thin layer chromatography (TLC) were performed using Sigma-Aldrich 0.20 mm silica gel pre-coated aluminum plates; spots were visualized under UV light. All glassware used was oven dried for >2 h at 120 °C. All spectra are included in the Supporting Information section.

Synthesis of 1-Chloro-2,4-dinitrobenzene

A heterogeneous mixture of sodium nitrate (99%, 8.585 g, 100 mmol, 4 equiv) and sulfuric acid (96%, 15.0 mL, 270 mmol, 10.8 equiv) was stirred in a 50-mL round bottom flask in a room temperature oil bath at 900 rpm with a 20-mm egg-shaped stir bar for 30 min. Chlorobenzene (99.8%, 2.55 mL, 25.0 mmol, 1 equiv) was added dropwise over 2 min and a condenser was attached to the reaction flask. The oil bath was heated to 40 °C over 5 min, and the yellow reaction mixture was stirred for 1 h. Then the oil bath temperature was slowly raised to 100 °C over 1 h in 10 °C increments, and the reaction mixture was stirred for 16 h.

The reaction flask was removed from heat, and the warm reaction mixture was poured via a glass funnel into a 125-mL Erlenmeyer flask containing cold water (75 mL) that was sitting in an ice bath, along with the cold water (25 mL) rinsings of the reaction flask. After allowing the diluted reaction mixture to sit at 4 °C for 30 min, the resulting solid was isolated using vacuum filtration (Whatman #1) via a handheld pump, and the solid was washed with water (25 mL). The solid was dissolved in diethyl ether (50 mL) and transferred to a 125-mL separatory funnel, along with diethyl ether (25 mL total) rinsings of the reaction flask and the Erlenmeyer flask. The organic layer was washed with saturated sodium bicarbonate (3 x 25 mL), water (2 x 25 mL), and saturated brine (25 mL), and the solution was allowed to air-dry in a conductive container in the hood to yield a yellow solid (5.013 g, 99%). TLC showed one spot, $R_f = 0.65$ (Et_2O). ^1H NMR analysis determined the isomeric ratio of 1-chloro-2,4-dinitrobenzene to 1-chloro-2,6-dinitrobenzene to be ca. 95:5.

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[4] Molecular nitrogen was removed for aesthetic reasons. ^{14}N NMR ($CDCl_3$): δ -75 ppm.

1-Chloro-2,4-dinitrobenzene

mp: 44-46 °C

^{1}H NMR (CDCl$_3$): δ 8.77 (d, 2.6Hz, 1H), 8.40 (dd, 9.0Hz, 2.7Hz, 1H), and 7.80 (d, 8.8Hz, 1H) ppm.

^{13}C NMR (CDCl$_3$): δ 147.8 (br), 146.3 (br), 133.9, 133.2, 127.3, and 121.1 ppm.

^{14}N NMR (CDCl$_3$): δ -23 ($\Delta\nu_{½}$ = 52Hz, T_2^* = 6.1 ms) ppm.

IR: 3108, 1604, 1590, 1542, 1532, 1458, 1346, 1304, 1246, 1158, 1140, 1046, 918, 902, 850, 836, 748, and 730 cm^{-1}.

HRMS: Calcd for $C_6H_4N_2O_4Cl_1$ [M+H]$^+$ 202.9854. Found 202.9853 (0.5 ppm).

1-Chloro-2,6-dinitrobenzene (^{1}H NMR chemical shift values for this isomer were determined directly from the isolated isomeric mixture.)

^{1}H NMR (CDCl$_3$): δ 8.00 (d, 8.1Hz, 2H) and 7.62 (t, 8.1Hz, 1H) ppm.

1-Chloro-4-nitrobenzene (^{1}H NMR chemical shift values were determined directly from the crude reaction mixture.)

^{1}H NMR (CDCl$_3$): δ 8.19 (d, 9.2Hz, 2H) and 7.54 (d, 9.2Hz, 2H) ppm.

1-Chloro-[2,4-$^{15}N_2$]dinitrobenzene

mp: 44-46 °C

^{1}H NMR (CDCl$_3$): δ 8.77 (dd, 4.8Hz, 2.6Hz, 1H), 8.40 (ddd, 8.8Hz, 2.6Hz, 1.8Hz, 1H), and 7.81 (d, 8.8Hz, 1H) ppm.

^{13}C NMR (CDCl$_3$): δ 147.8 (dd, 18Hz, 3Hz), 146.3 (dd, 17Hz, 3Hz), 133.9, 133.2 (t, 2Hz), 127.3 (d, 2Hz), and 121.1 (m*) ppm. *Apparent triplet with approximately 2Hz coupling.

^{15}N NMR (CDCl$_3$): δ -22.7 (T_1 = 97 s ± 2 s) and -23.6 (T_1 = 143 s ± 3 s) ppm.

IR: 3108, 1588, 1510, 1456, 1318, 1246, 1156, 1138, 1046, 914, 900, 850, 828, 748, and 720 cm^{-1}.

HRMS: Calcd for $C_6H_4{}^{15}N_2O_4Cl_1$ [M+H]$^+$ 204.9795. Found 204.9799 (2.0 ppm).

1-Chloro-[2,6-$^{15}N_2$]dinitrobenzene (^{1}H NMR chemical shift values for this isomer were determined directly from the isolated isomeric mixture.)

^{1}H NMR ($CDCl_3$): δ 8.02 (dd, 8.1Hz, 1.8Hz, 2H), and 7.63 (t, 8.1Hz, 1H) ppm.

Synthesis of 2,4-Dinitroanisole (DNAN)

A heterogeneous mixture of freshly ground sodium hydroxide (97%, 619 mg, 15.0 mmol, 1.2 equiv) and methanol (99.8%, 4.06 mL, 100 mmol, 8 equiv) was stirred in a 25-mL round bottom flask in a room temperature water bath at 600 rpm with a 20-mm egg-shaped stir bar for 30 min. 1-Chloro-2,4-dinitrobenzene (2.532 g, 12.5 mmol, 1 equiv) was added in portions via a glass funnel over 10 min, and a condenser was attached to the reaction flask. The water bath was heated to 60 °C over 15 min, and the red reaction mixture was stirred for 1 h.

After the orange reaction mixture was removed from heat, water (10 mL) was added, and the stirred reaction mixture was allowed to cool to room temperature over 30 min. The crude solid was isolated using vacuum filtration (Whatman #1) via a handheld pump, and the solid was washed with water (4 x 10 mL). Recrystallization was achieved by stirring a heterogeneous mixture of the yellow solid and methanol (45 mL) in a 125-mL Erlenmeyer flask sitting in a room temperature water bath, and then heating the water bath to 85 °C. The resulting clear solution was poured into a 250-mL beaker, and allowed to cool to room temperature over 30 min with occasional gentle swirling. The product was isolated using vacuum filtration (Whatman #1) via a handheld pump, and then allowed to air-dry in a conductive container in the hood to yield yellow needles; successive second and third recrystallization crops also yielded yellow needles (1.734 g, 70%). TLC showed one spot, $R_f = 0.38$ (Et_2O).

2,4-Dinitroanisole

mp: 86-88 °C

^{1}H NMR ($CDCl_3$): δ 8.77 (d, 2.9Hz, 1H), 8.46 (dd, 9.2Hz, 2.9Hz, 1H), 7.23 (d, 9.2Hz, 1H), and 4.10 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$): δ 157.3, 140.2 (br), 138.9 (br), 129.1, 121.9, 113.6, and 57.5 ppm.

^{14}N NMR ($CDCl_3$): δ -21 ($\Delta\nu_{½}$ = 70Hz, T_2^* = 4.5 ms) ppm.

IR: 3098, 1600, 1520, 1488, 1442, 1416, 1344, 1318, 1278, 1186, 1152, 1136, 1070, 1002, 920, 830, 792, 762, and 742 cm^{-1}.

HRMS: Calcd for $C_7H_7N_2O_5$ $[M+H]^+$ 199.0350. Found 199.0335 (7.5 ppm).

[2,4-$^{15}N_2$]Dinitroanisole

mp: 86-88 °C

^{1}H NMR ($CDCl_3$): δ 8.77 (m, 4.8Hz, 2.6Hz, 1H), 8.46 (ddd, 9.2Hz, 2.6Hz, 1.8Hz, 1H), 7.23 (d, 9.2Hz, 1H), and 4.10 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$): δ 157.3, 140.1 (dd, 17Hz, 3Hz), 138.8 (dd, 17Hz, 3Hz), 129.2 (d, 2Hz), 121.9 (t, 2Hz), 113.6 (m*), and 57.5 ppm. *Apparent triplet with approximately 2Hz coupling.

^{15}N NMR ($CDCl_3$): δ -21.1 (T_1 = 104 s ± 2 s) and -21.4 (T_1 = 135 s ± 2 s) ppm.

IR: 3114, 1602, 1498, 1442, 1414, 1328, 1310, 1276, 1186, 1152, 1136, 1068, 1002, 916, 828, 790, 750, and 730 cm^{-1}.

HRMS: Calcd for $C_7H_7{}^{15}N_2O_5$ $[M+H]^+$ 201.0290. Found 201.0302 (6.0 ppm).

[*methyl*-^{13}C]2,4-Dinitroanisole

mp: 86-88 °C

^{1}H NMR ($CDCl_3$): δ 8.77 (d, 2.9Hz, 1H), 8.46 (dd, 9.2Hz, 2.9Hz, 1H), 7.23 (d, 9.2Hz, 1H), and 4.10 (d, 147.0Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$): δ 157.3, 140.2 (br), 138.8 (br), 129.1, 121.9, 113.6 (d, 5Hz), and 57.5 ppm.

^{14}N NMR ($CDCl_3$): δ -21 ($\Delta\nu_{½}$ = 68z, T_2^* = 4.7 ms) ppm.

IR: 3098, 1600, 1522, 1488, 1438, 1416, 1344, 1318, 1278, 1180, 1150, 1136, 1068, 990, 918, 830, 790, 762, and 742 cm^{-1}.

HRMS: Calcd for $C_6{}^{13}C_1H_7N_2O_5$ $[M+H]^+$ 200.0383. Found 200.0397 (7.0 ppm).

SUPPORTING INFORMATION

1-Chloro-2,4-dinitrobenzene

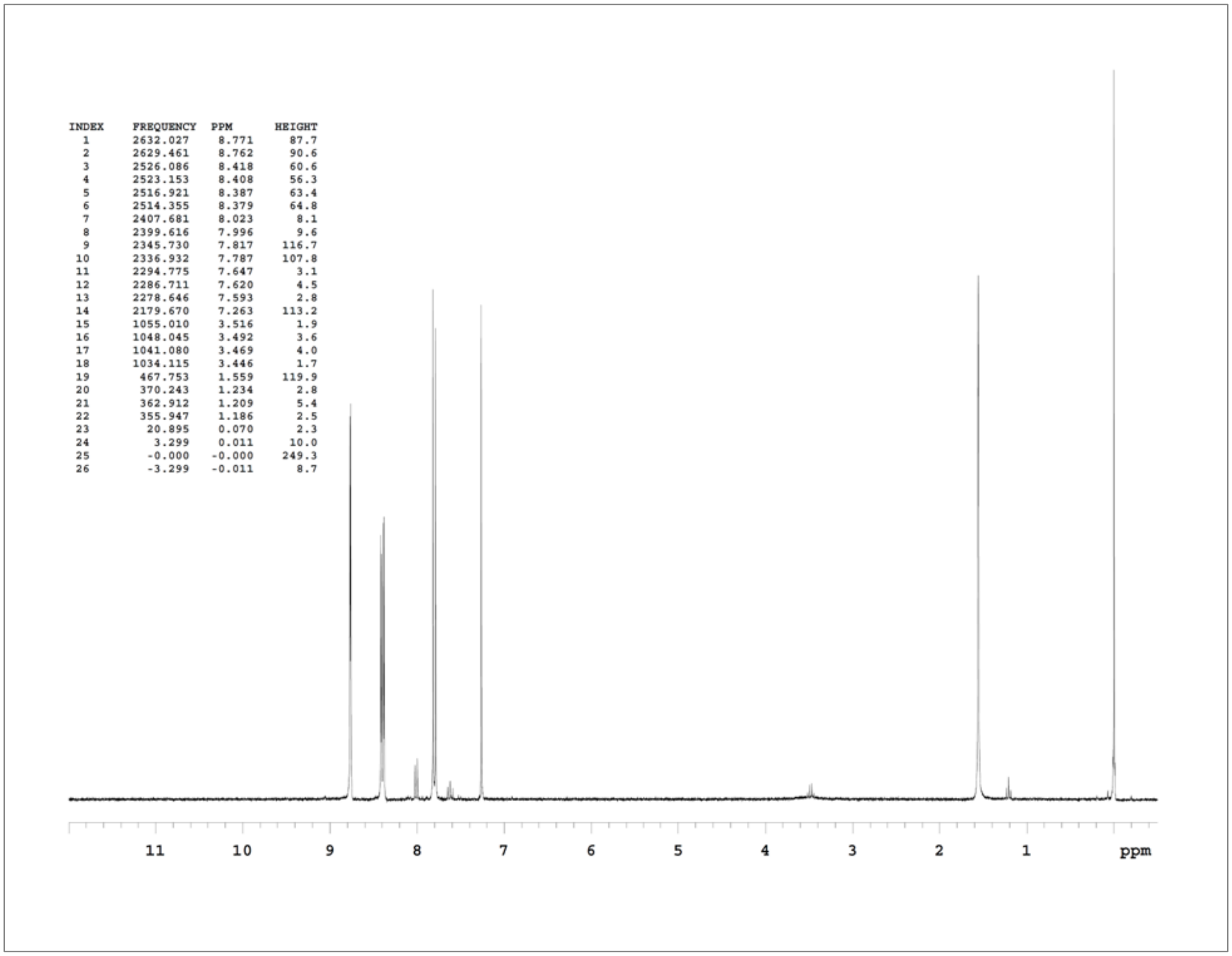
1-Chloro-[2,4-^{15}N$_2$]dinitrobenzene

2,4-Dinitroanisole

[2,4-^{15}N$_2$]Dinitroanisole

[*methyl*-^{13}C]2,4-Dinitroanisole

1-Chloro-2,4-dinitrobenzene / ^{1}H NMR



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INDEX    FREQUENCY  PPM      HEIGHT
  1      2632.027    8.771     87.7
  2      2629.461    8.762     90.6
  3      2526.086    8.418     60.6
  4      2523.153    8.408     56.3
  5      2516.921    8.387     63.4
  6      2514.355    8.379     64.8
  7      2407.681    8.023      8.1
  8      2399.616    7.996      9.6
  9      2345.730    7.817    116.7
 10      2336.932    7.787    107.8
 11      2294.775    7.647      3.1
 12      2286.711    7.620      4.5
 13      2278.646    7.593      2.8
 14      2179.670    7.263    113.2
 15      1055.010    3.516      1.9
 16      1048.045    3.492      3.6
 17      1041.080    3.469      4.0
 18      1034.115    3.446      1.7
 19       467.753    1.559    119.9
 20       370.243    1.234      2.8
 21       362.912    1.209      5.4
 22       355.947    1.186      2.5
 23        20.895    0.070      2.3
 24         3.299    0.011     10.0
 25        -0.000   -0.000    249.3
 26        -3.299   -0.011      8.7
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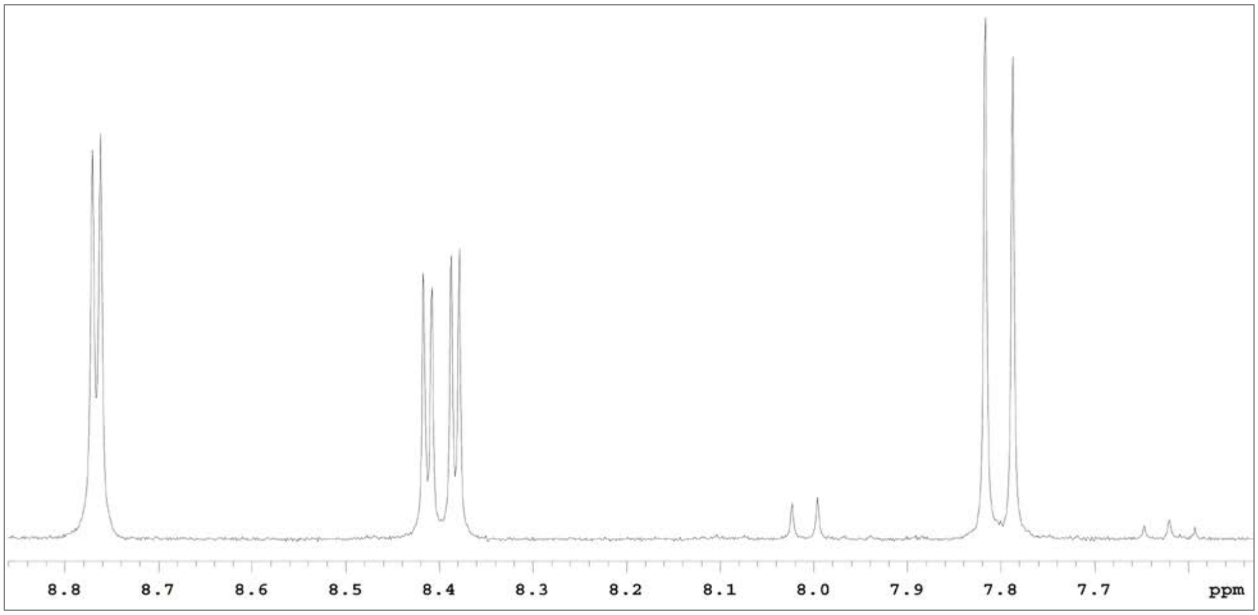
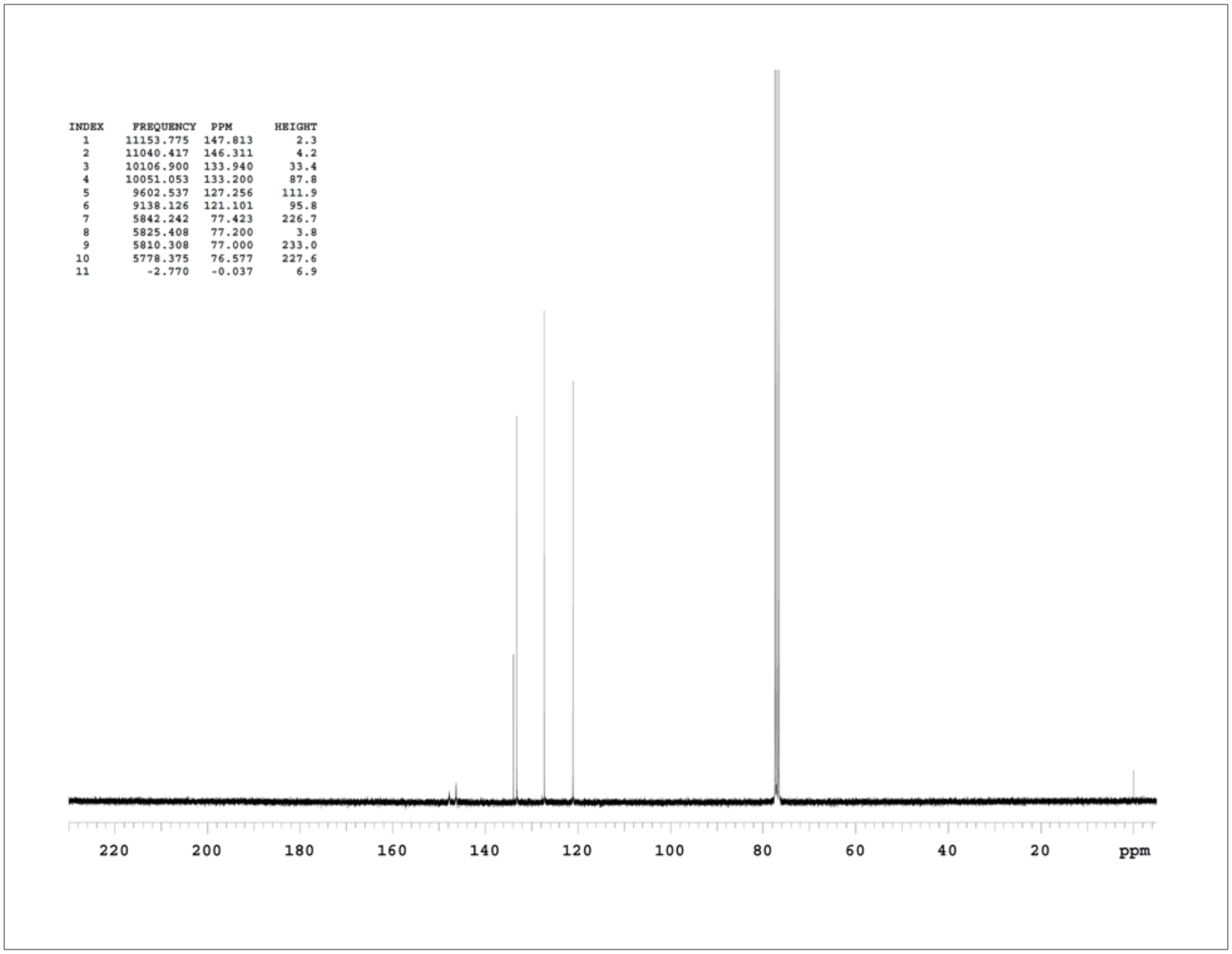


1-Chloro-2,4-dinitrobenzene / ^{13}C NMR



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INDEX    FREQUENCY  PPM       HEIGHT
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  2      11040.417  146.311      4.2
  3      10106.900  133.940     33.4
  4      10051.053  133.200     87.8
  5       9602.537  127.256    111.9
  6       9138.126  121.101     95.8
  7       5842.242   77.423    226.7
  8       5825.408   77.200      3.8
  9       5810.308   77.000    233.0
 10       5778.375   76.577    227.6
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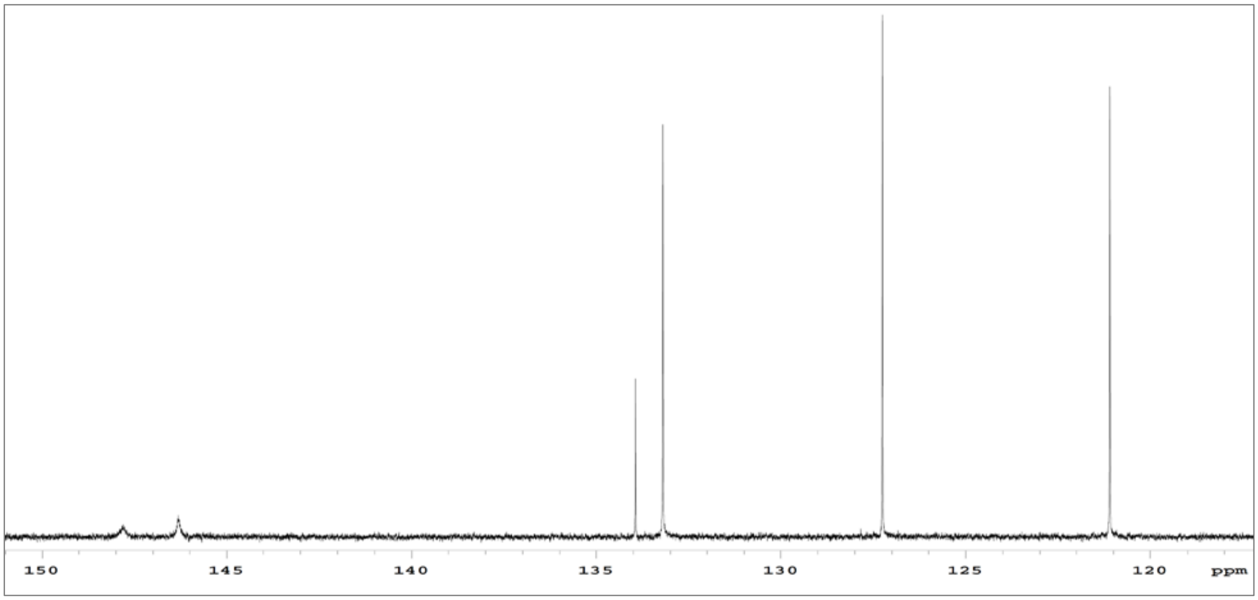
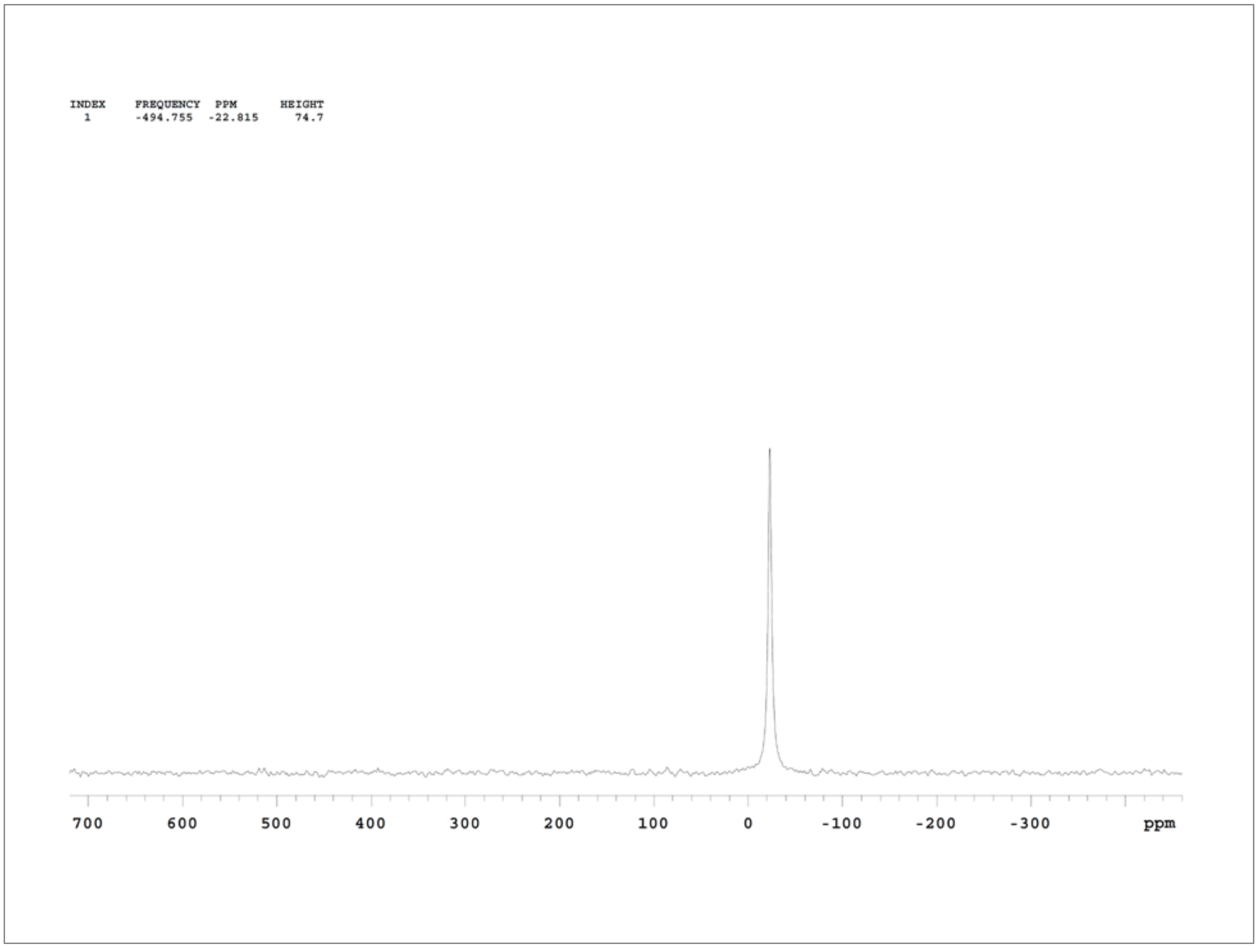
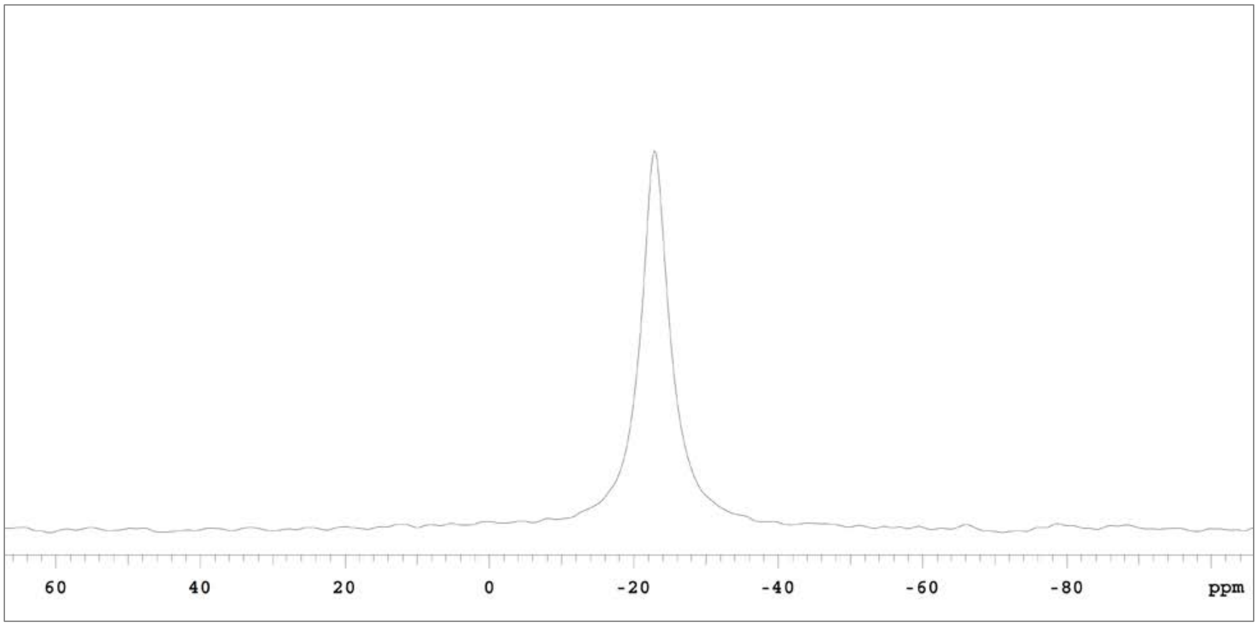
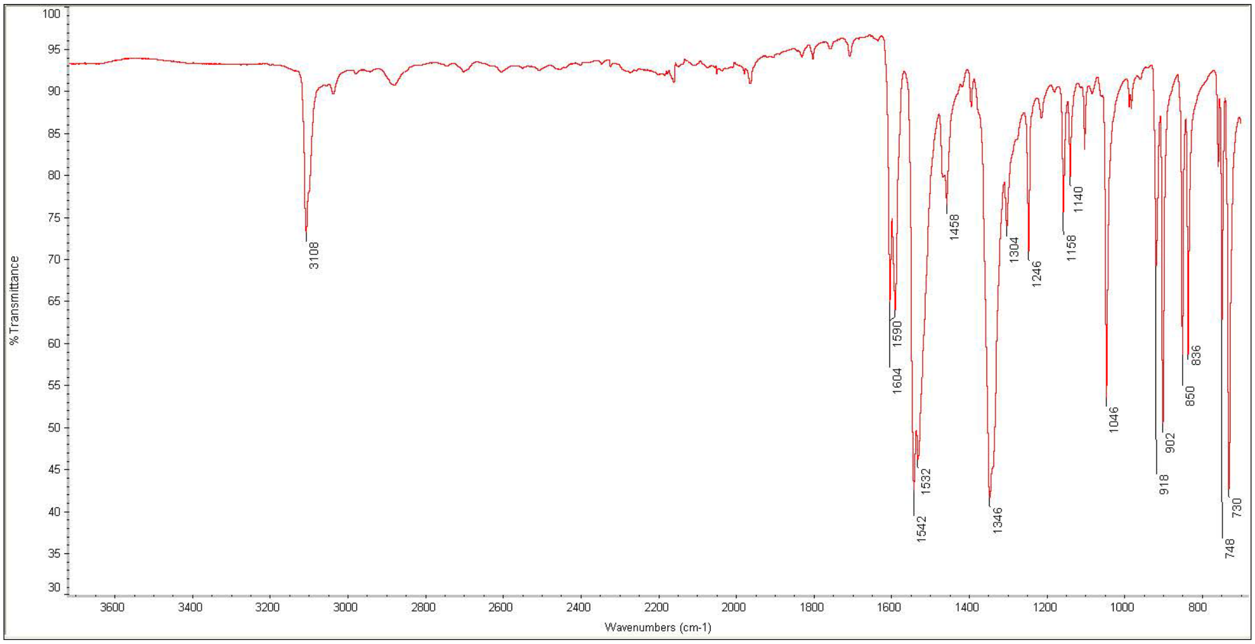


1-Chloro-2,4-dinitrobenzene / ^{14}N NMR

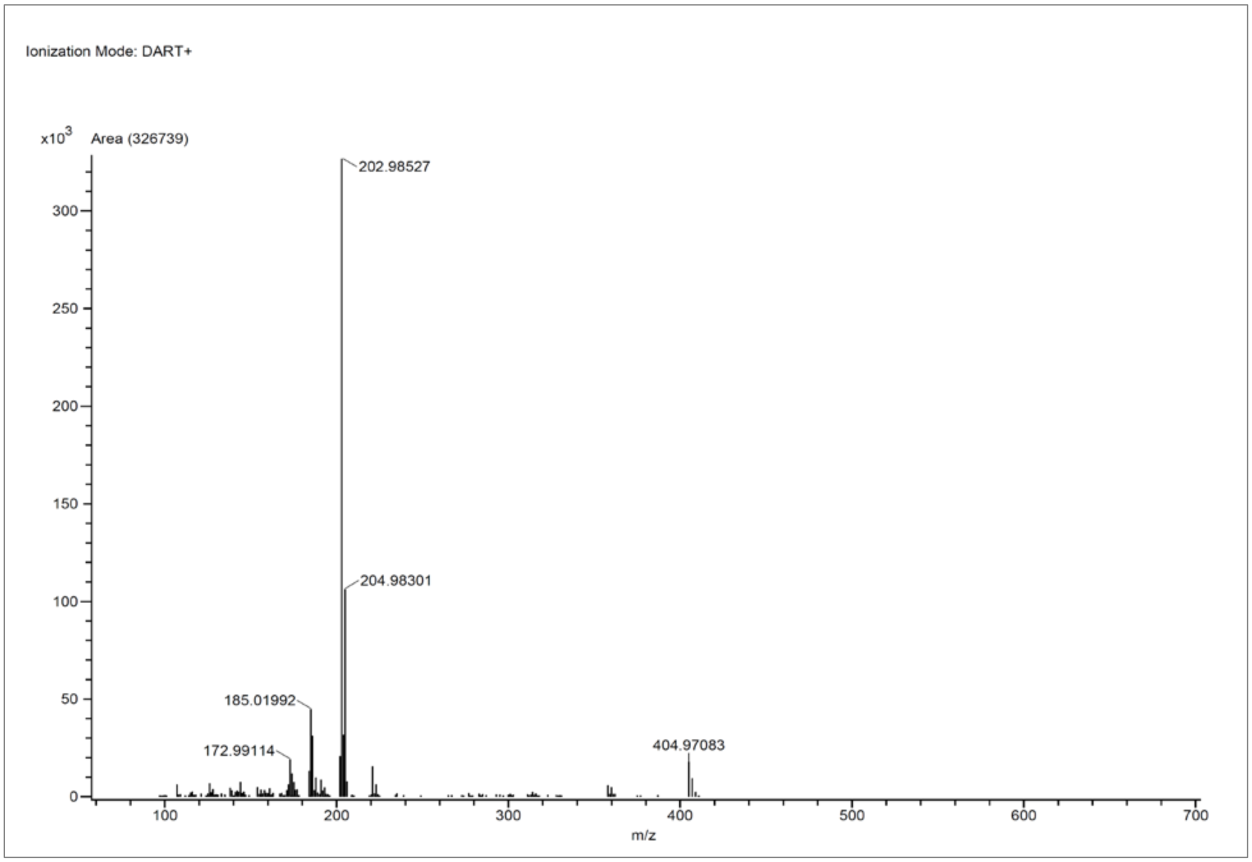




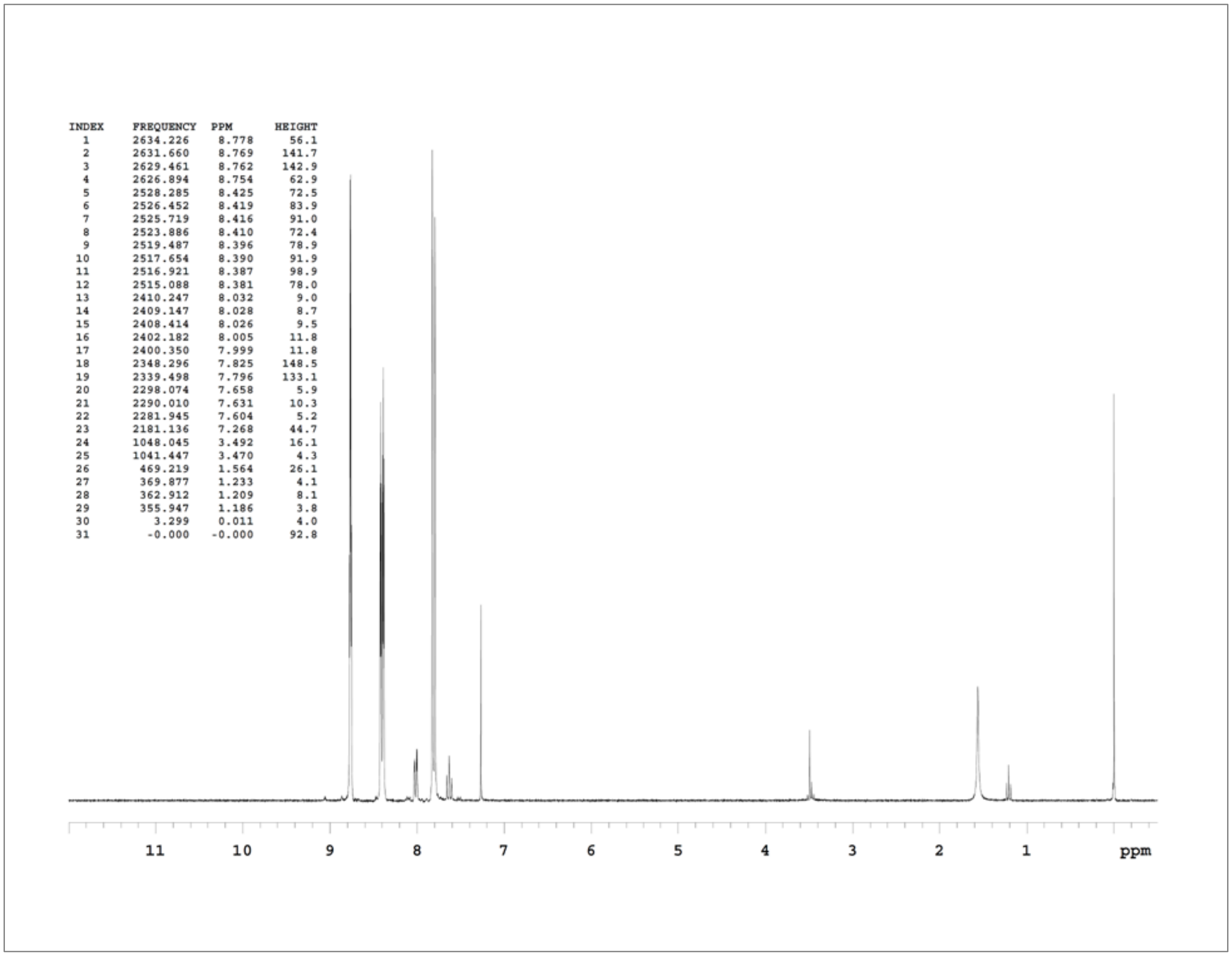
1-Chloro-2,4-dinitrobenzene / IR



1-Chloro-2,4-dinitrobenzene / HRMS



1-Chloro-[2,4-$^{15}N_2$]dinitrobenzene / ^{1}H NMR



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INDEX    FREQUENCY  PPM      HEIGHT
  1      2634.226    8.778     56.1
  2      2631.660    8.769    141.7
  3      2629.461    8.762    142.9
  4      2626.894    8.754     62.9
  5      2528.285    8.425     72.5
  6      2526.452    8.419     83.9
  7      2525.719    8.416     91.0
  8      2523.886    8.410     72.4
  9      2519.487    8.396     78.9
 10      2517.654    8.390     91.9
 11      2516.921    8.387     98.9
 12      2515.088    8.381     78.0
 13      2410.247    8.032      9.0
 14      2409.147    8.028      8.7
 15      2408.414    8.026      9.5
 16      2402.182    8.005     11.8
 17      2400.350    7.999     11.8
 18      2348.296    7.825    148.5
 19      2339.498    7.796    133.1
 20      2298.074    7.658      5.9
 21      2290.010    7.631     10.3
 22      2281.945    7.604      5.2
 23      2181.136    7.268     44.7
 24      1048.045    3.492     16.1
 25      1041.447    3.470      4.3
 26       469.219    1.564     26.1
 27       369.877    1.233      4.1
 28       362.912    1.209      8.1
 29       355.947    1.186      3.8
 30         3.299    0.011      4.0
 31        -0.000   -0.000     92.8
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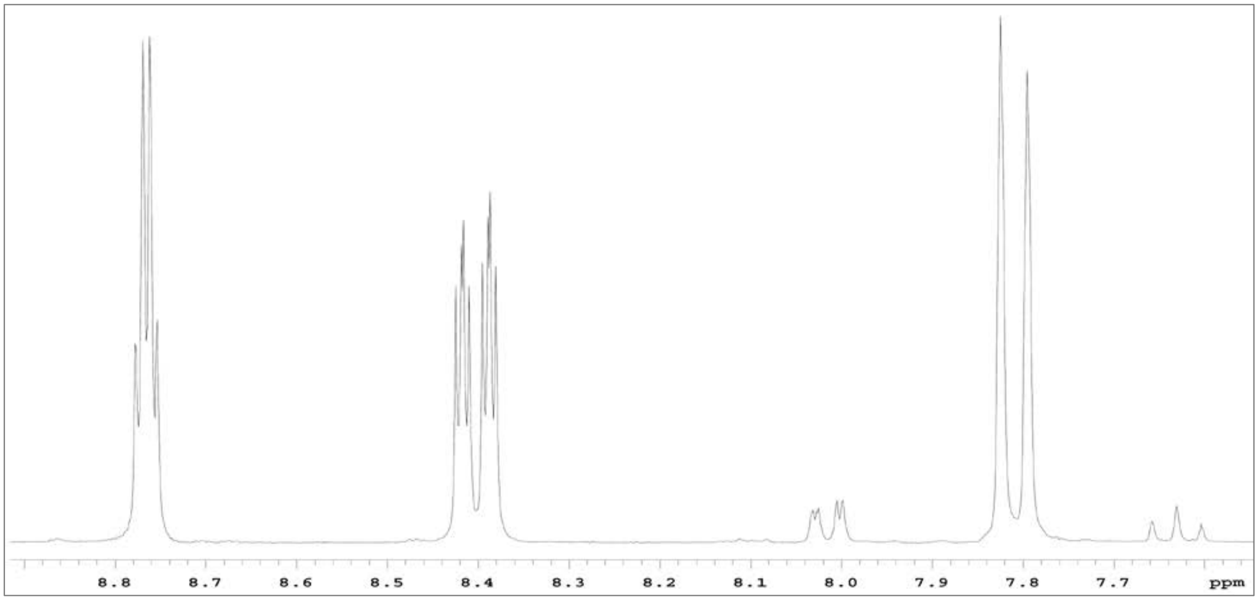
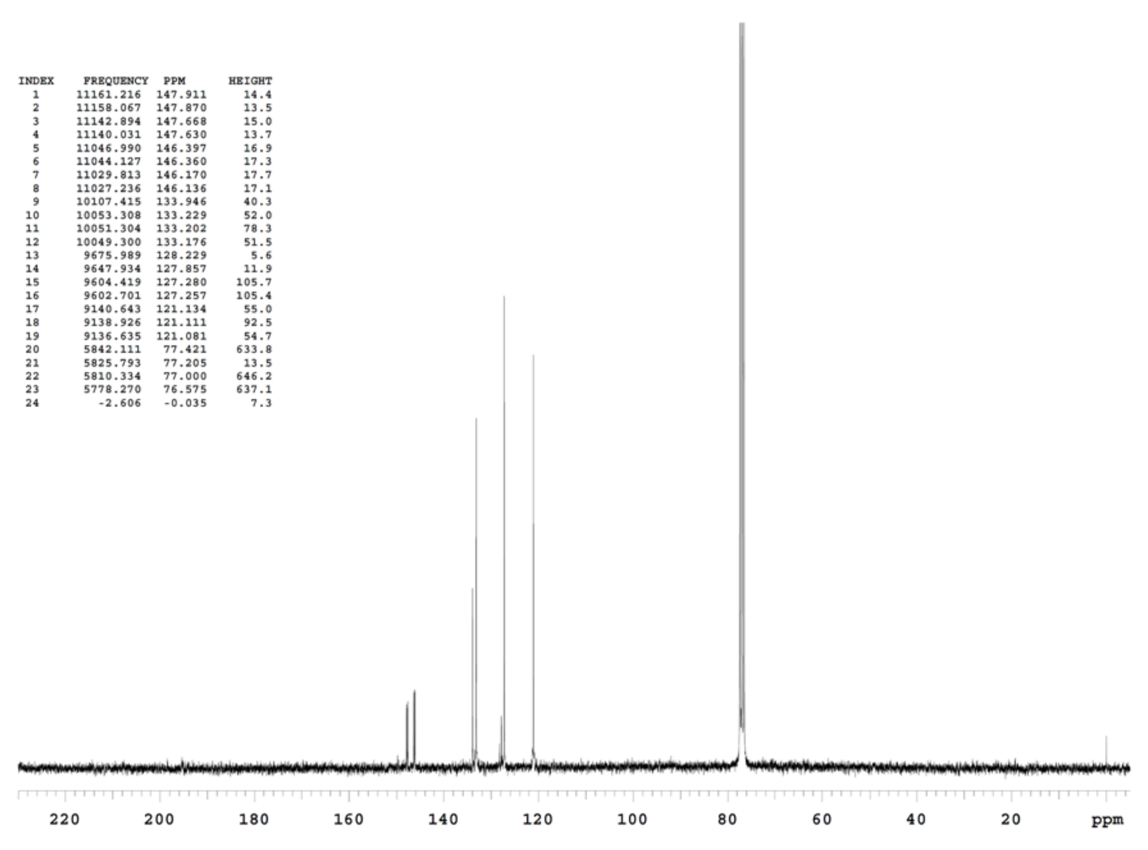


1-Chloro-[2,4-$^{15}N_2$]dinitrobenzene / ^{13}C NMR



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INDEX    FREQUENCY  PPM      HEIGHT
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  2      11158.067  147.870    13.5
  3      11142.894  147.668    15.0
  4      11140.031  147.630    13.7
  5      11046.990  146.397    16.9
  6      11044.127  146.360    17.3
  7      11029.813  146.170    17.7
  8      11027.236  146.136    17.1
  9      10107.415  133.946    40.3
 10      10053.308  133.229    52.0
 11      10051.304  133.202    78.3
 12      10049.300  133.176    51.5
 13       9675.989  128.229     5.6
 14       9647.934  127.857    11.9
 15       9604.419  127.280   105.7
 16       9602.701  127.257   105.4
 17       9140.643  121.134    55.0
 18       9138.926  121.111    92.5
 19       9136.635  121.081    54.7
 20       5842.111   77.421   633.8
 21       5825.793   77.205    13.5
 22       5810.334   77.000   646.2
 23       5778.270   76.575   637.1
 24         -2.606   -0.035     7.3
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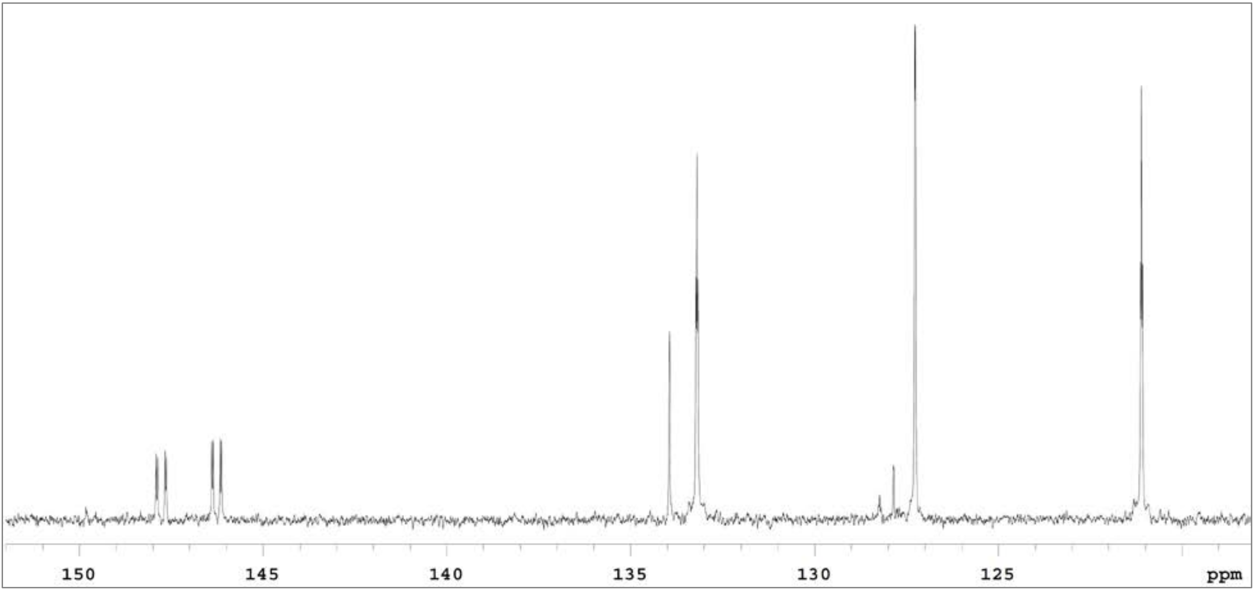
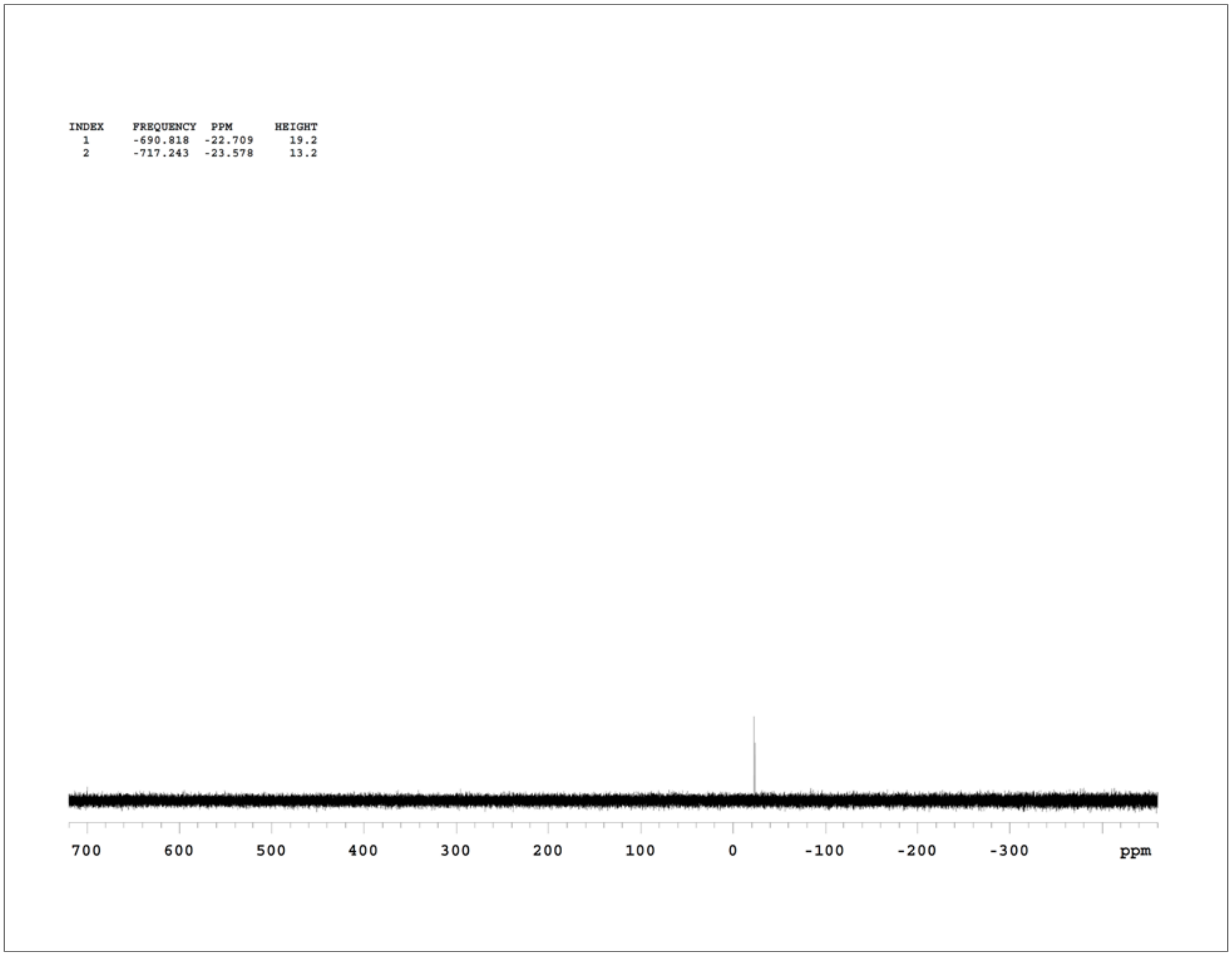


1-Chloro-[2,4-$^{15}N_2$]dinitrobenzene / ^{15}N NMR



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INDEX    FREQUENCY   PPM      HEIGHT
  1      -690.818  -22.709     19.2
  2      -717.243  -23.578     13.2
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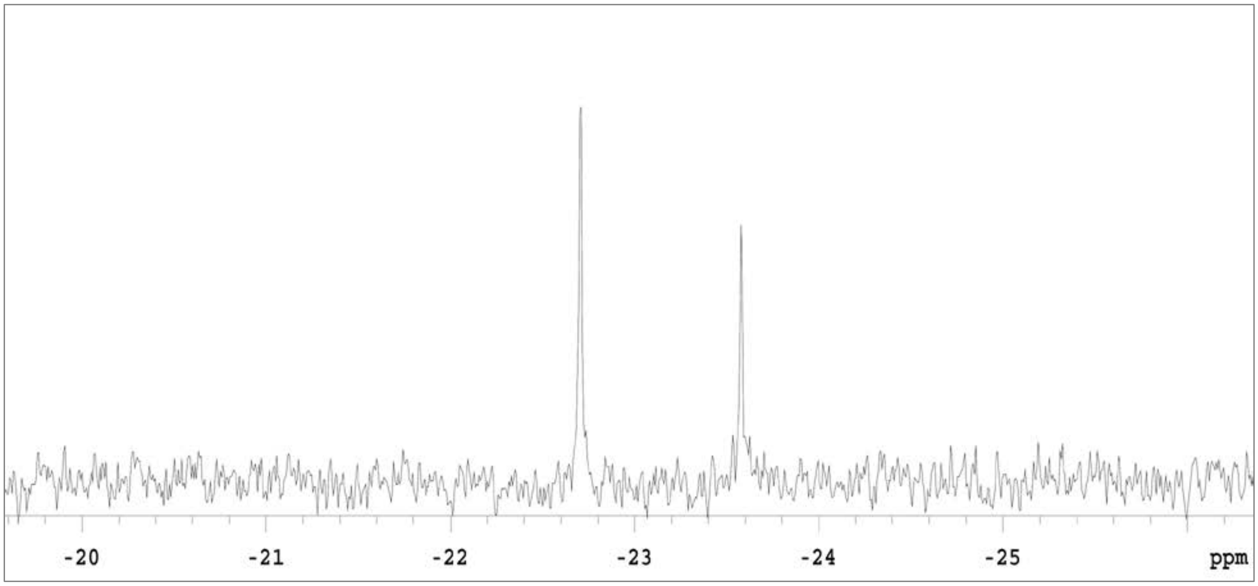
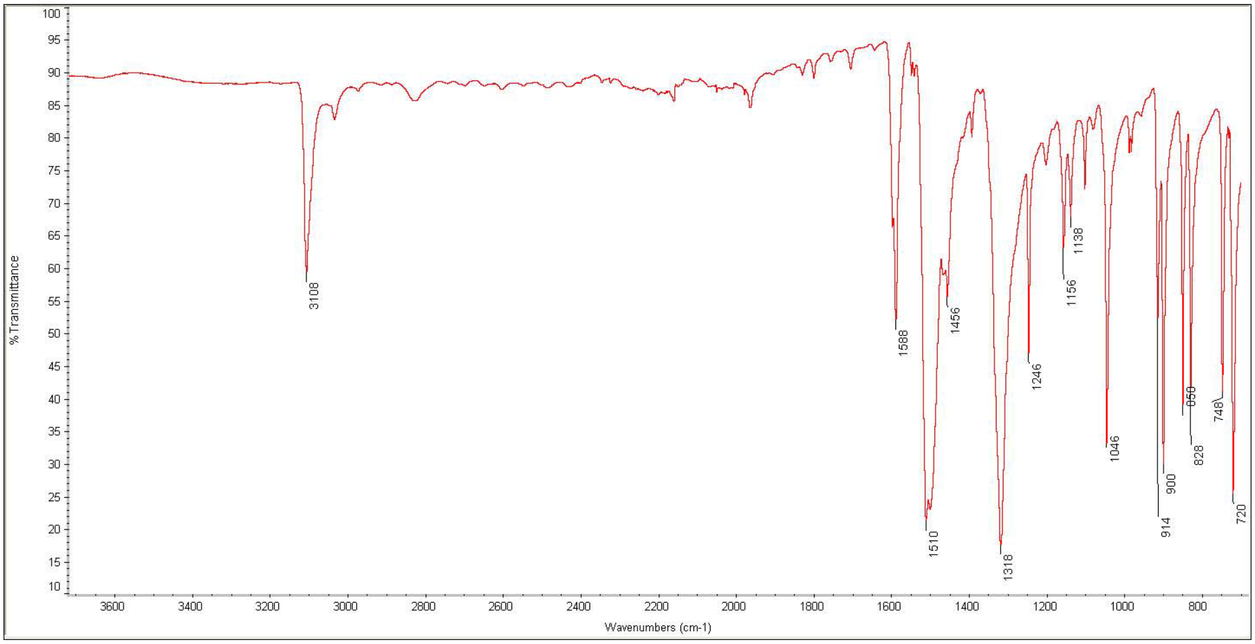
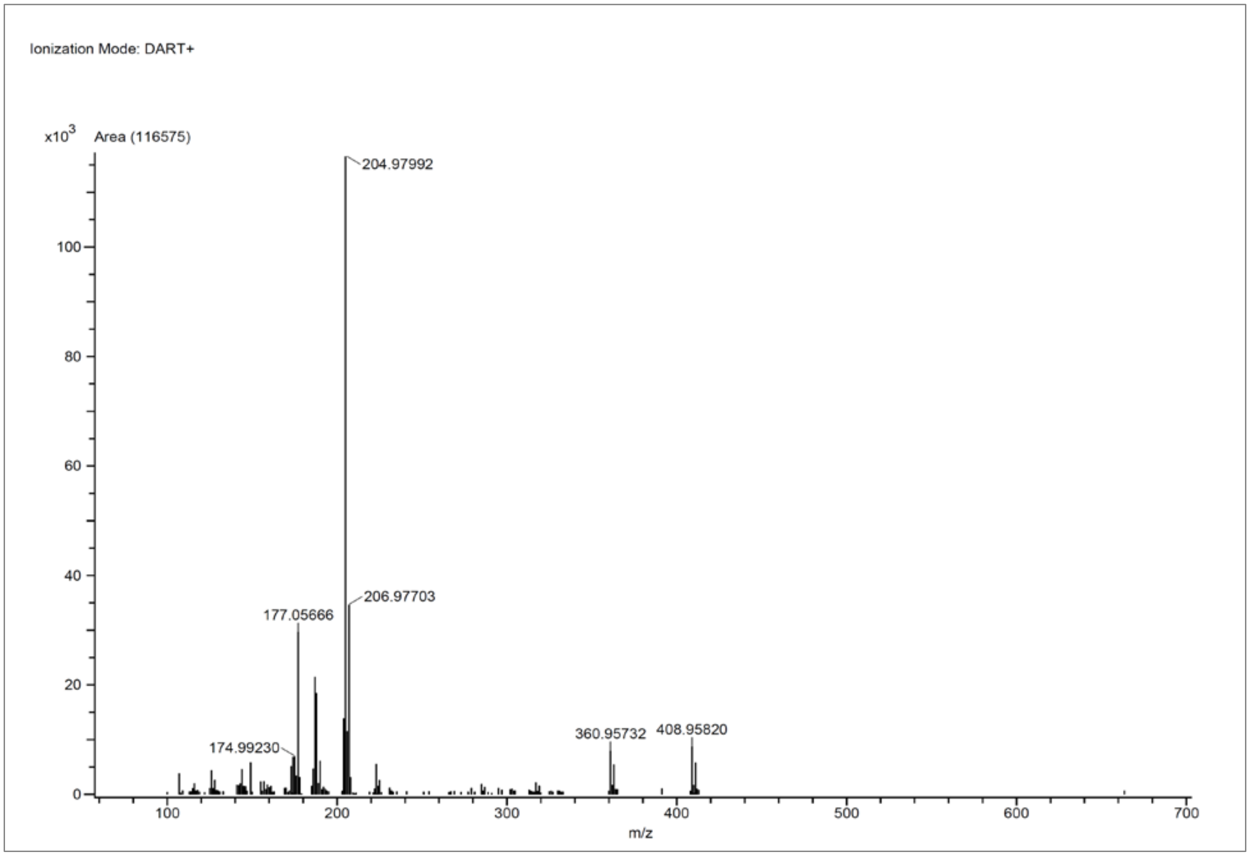


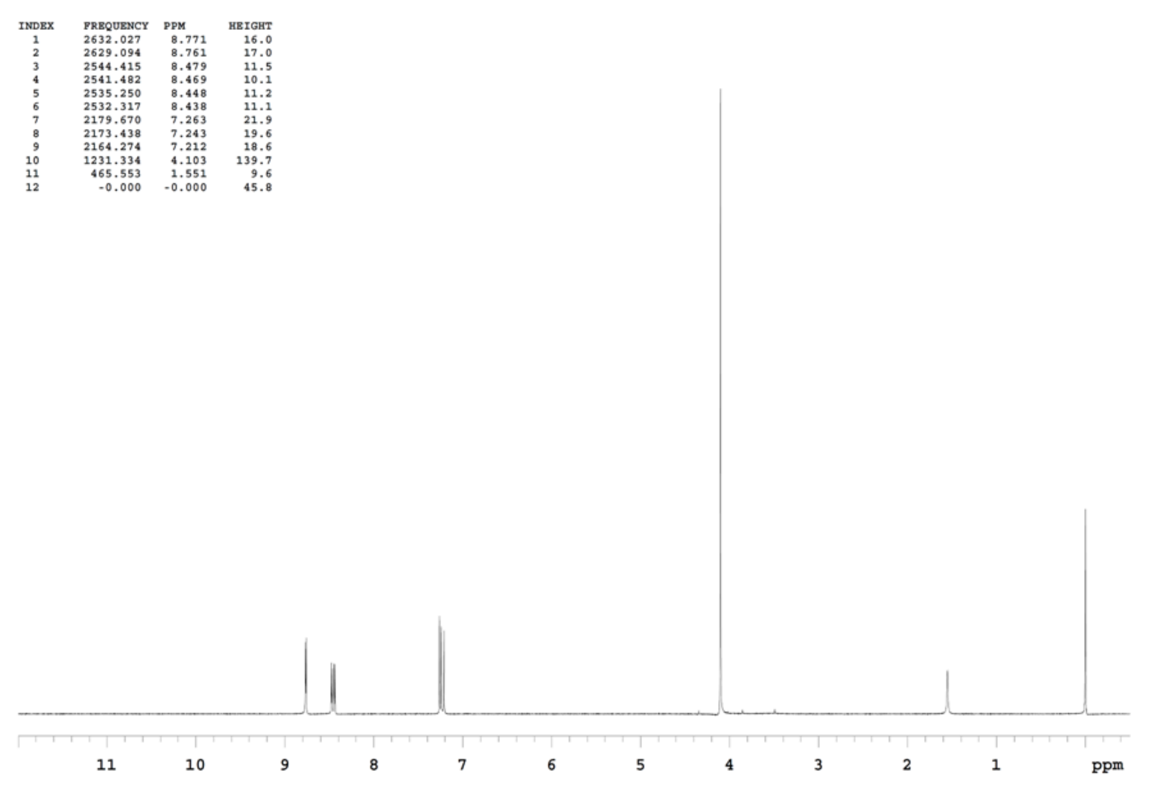
1-Chloro-[2,4-$^{15}N_2$]dinitrobenzene / IR



1-Chloro-[2,4-$^{15}N_2$]dinitrobenzene / HRMS



2,4-Dinitroanisole / ^{1}H NMR



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INDEX    FREQUENCY  PPM      HEIGHT
  1      2632.027    8.771     16.0
  2      2629.094    8.761     17.0
  3      2544.415    8.479     11.5
  4      2541.482    8.469     10.1
  5      2535.250    8.448     11.2
  6      2532.317    8.438     11.1
  7      2179.670    7.263     21.9
  8      2173.438    7.243     19.6
  9      2164.274    7.212     18.6
 10      1231.334    4.103    139.7
 11       465.553    1.551      9.6
 12        -0.000   -0.000     45.8
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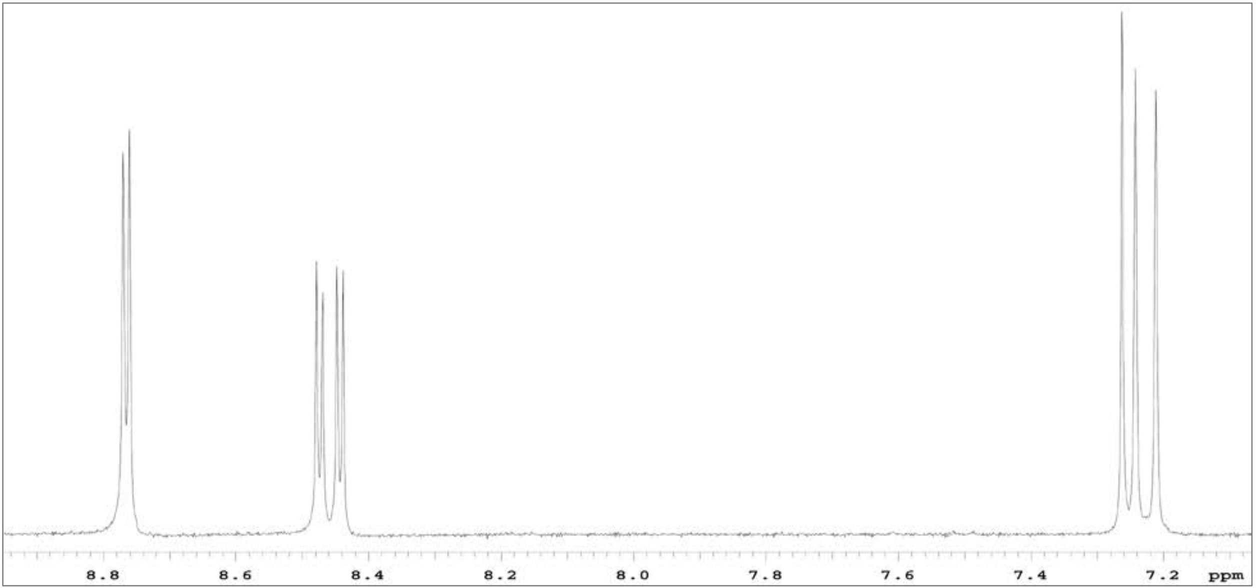
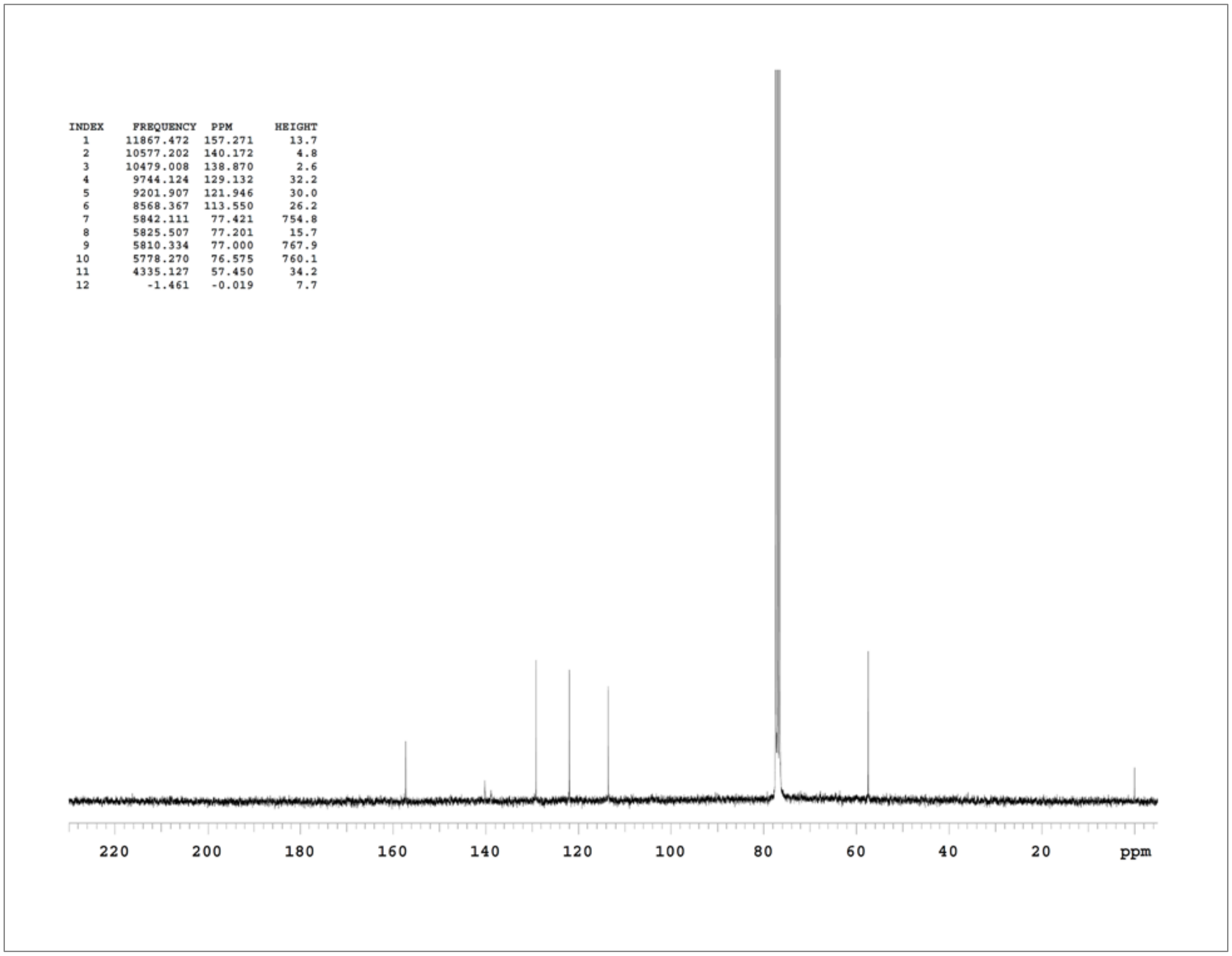


2,4-Dinitroanisole / ^{13}C NMR



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INDEX    FREQUENCY  PPM       HEIGHT
  1      11867.472  157.271     13.7
  2      10577.202  140.172      4.8
  3      10479.008  138.870      2.6
  4       9744.124  129.132     32.2
  5       9201.907  121.946     30.0
  6       8568.367  113.550     26.2
  7       5842.111   77.421    754.8
  8       5825.507   77.201     15.7
  9       5810.334   77.000    767.9
 10       5778.270   76.575    760.1
 11       4335.127   57.450     34.2
 12         -1.461   -0.019      7.7
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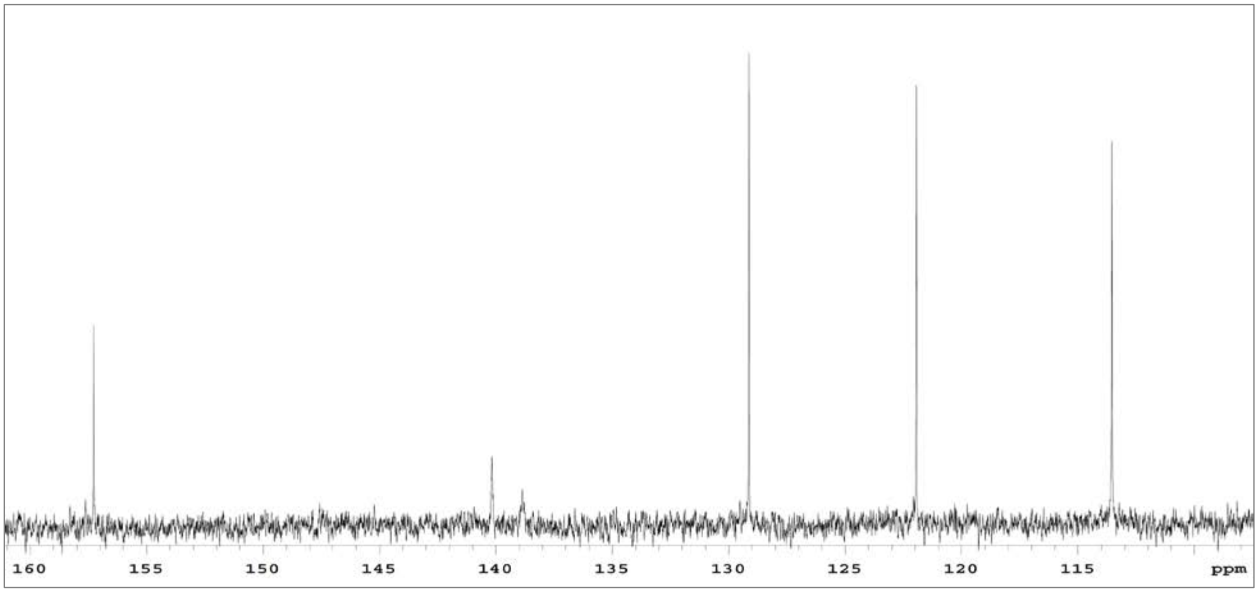
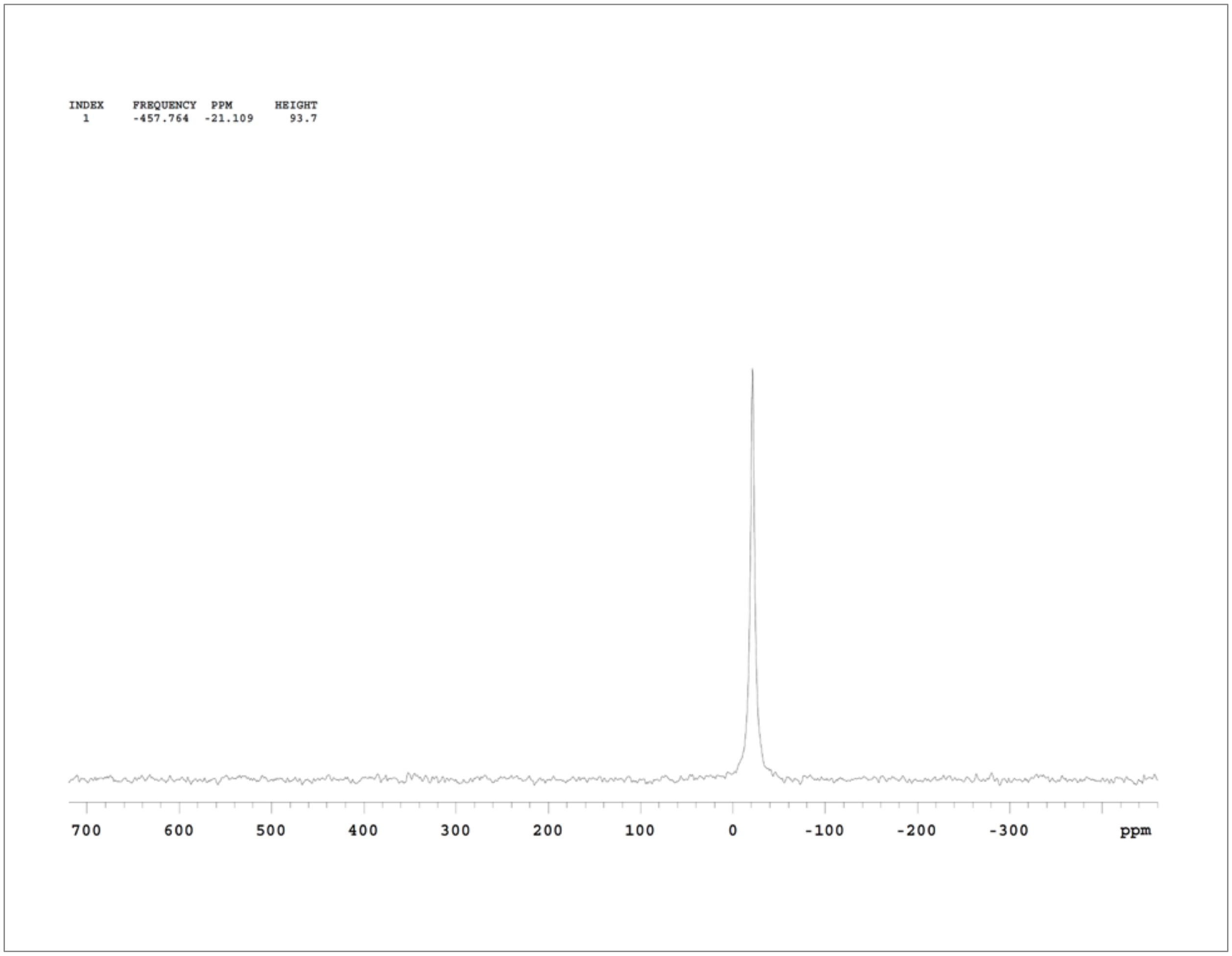


2,4-Dinitroanisole / ^{14}N NMR



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INDEX    FREQUENCY  PPM      HEIGHT
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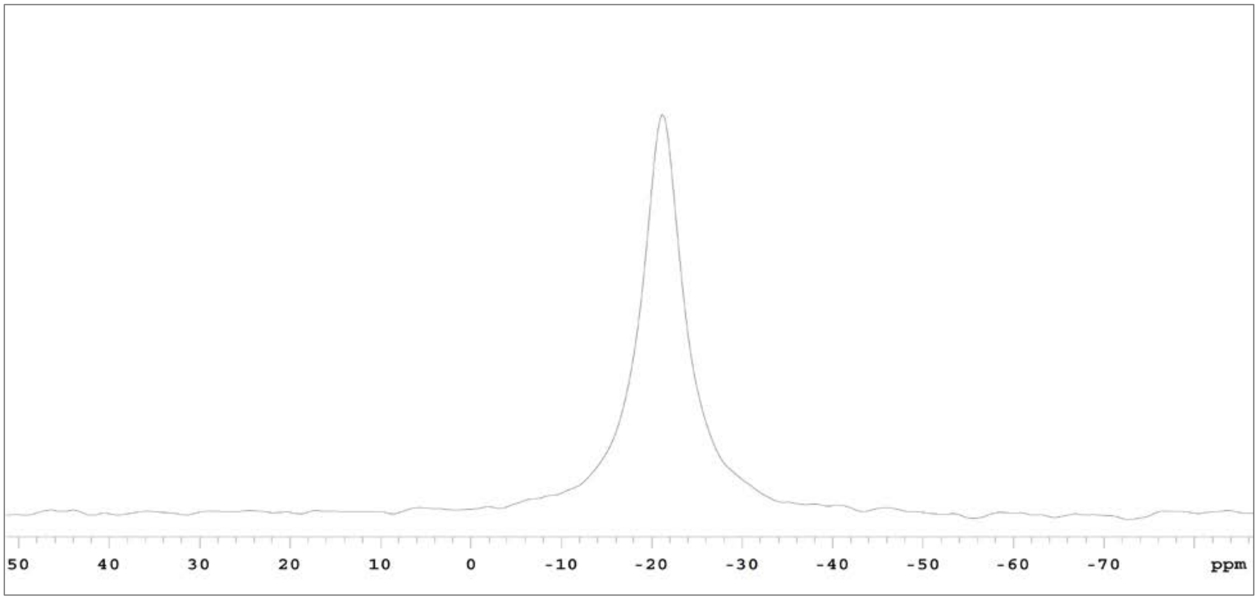
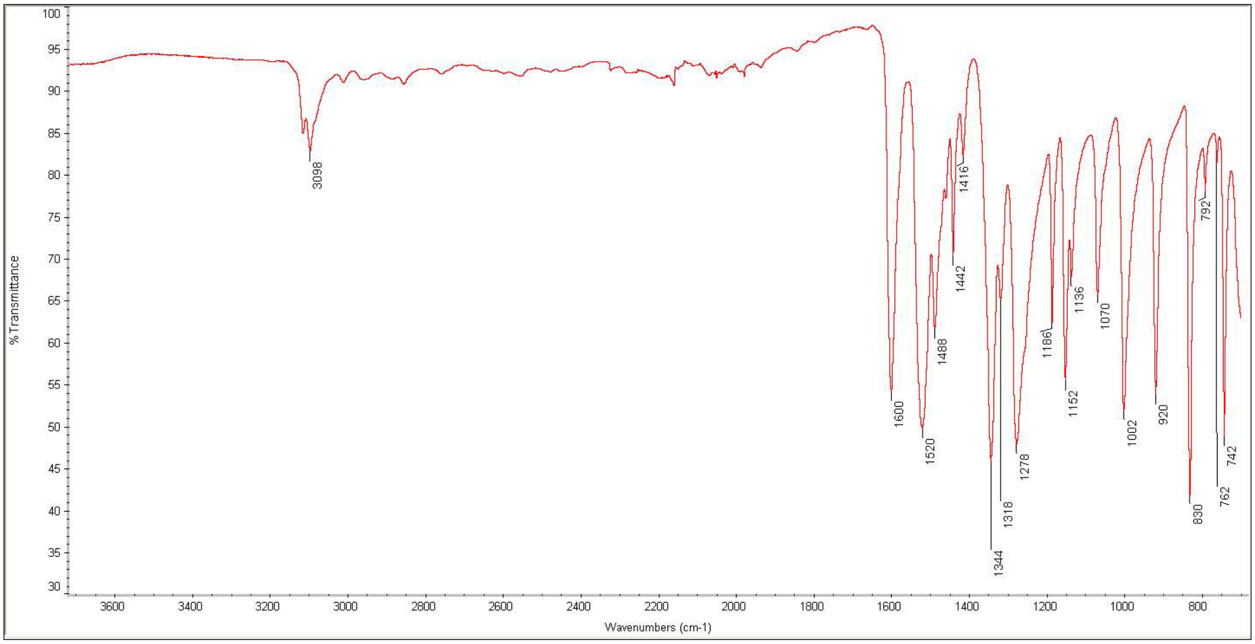
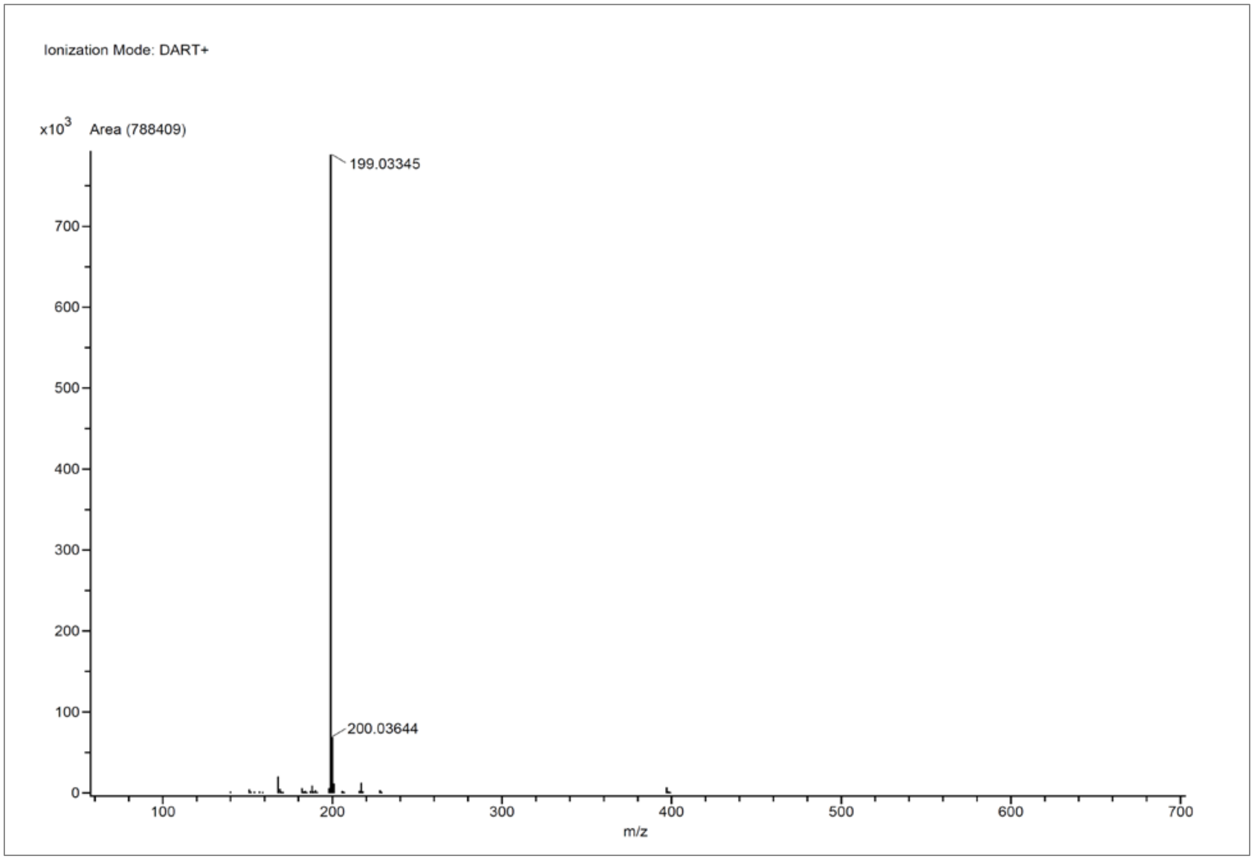


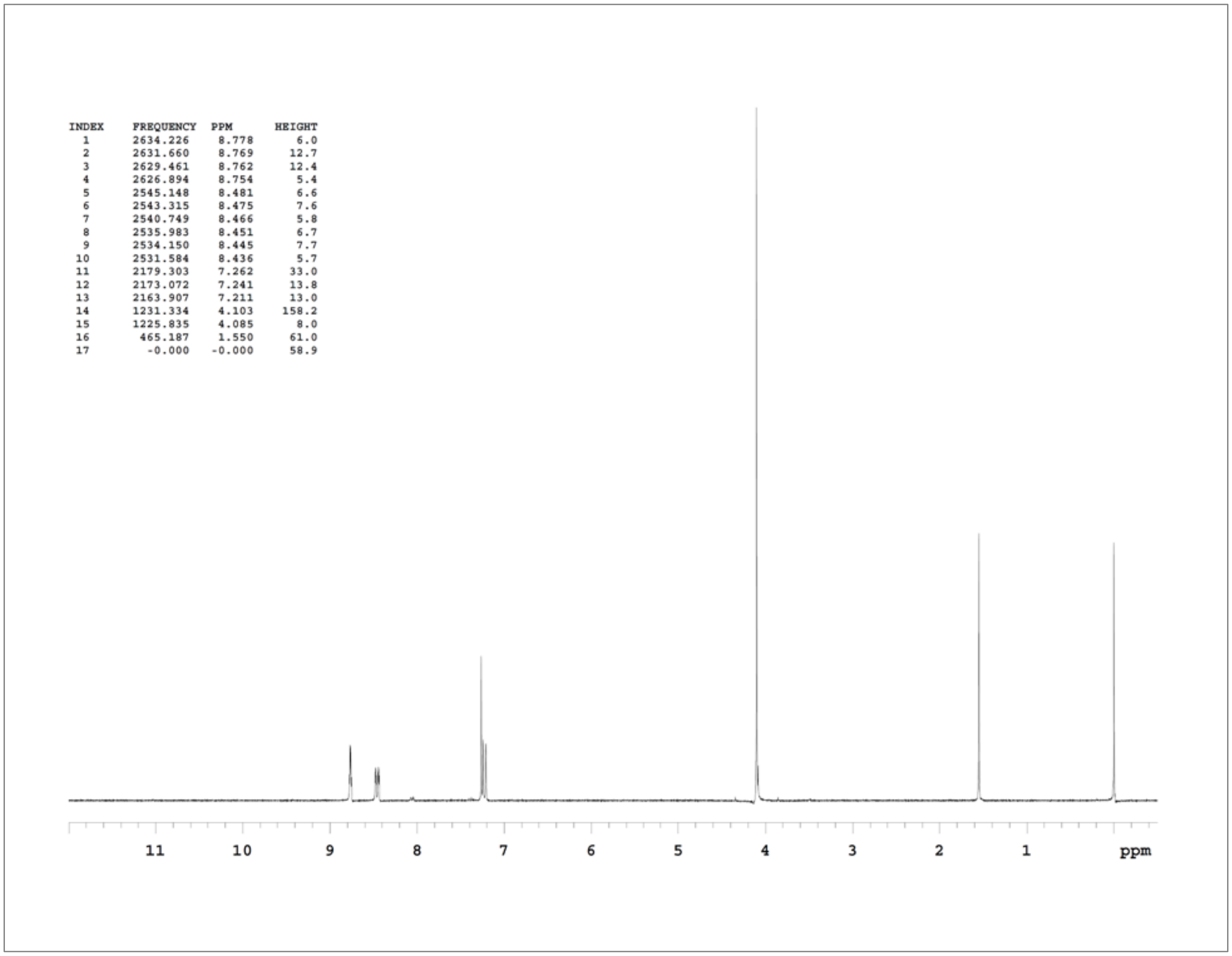
2,4-Dinitroanisole / IR



2,4-Dinitroanisole / HRMS



[2,4-$^{15}N_2$]Dinitroanisole / ^{1}H NMR



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INDEX    FREQUENCY  PPM      HEIGHT
  1      2634.226    8.778      6.0
  2      2631.660    8.769     12.7
  3      2629.461    8.762     12.4
  4      2626.894    8.754      5.4
  5      2545.148    8.481      6.6
  6      2543.315    8.475      7.6
  7      2540.749    8.466      5.8
  8      2535.983    8.451      6.7
  9      2534.150    8.445      7.7
 10      2531.584    8.436      5.7
 11      2179.303    7.262     33.0
 12      2173.072    7.241     13.8
 13      2163.907    7.211     13.0
 14      1231.334    4.103    158.2
 15      1225.835    4.085      8.0
 16       465.187    1.550     61.0
 17        -0.000   -0.000     58.9
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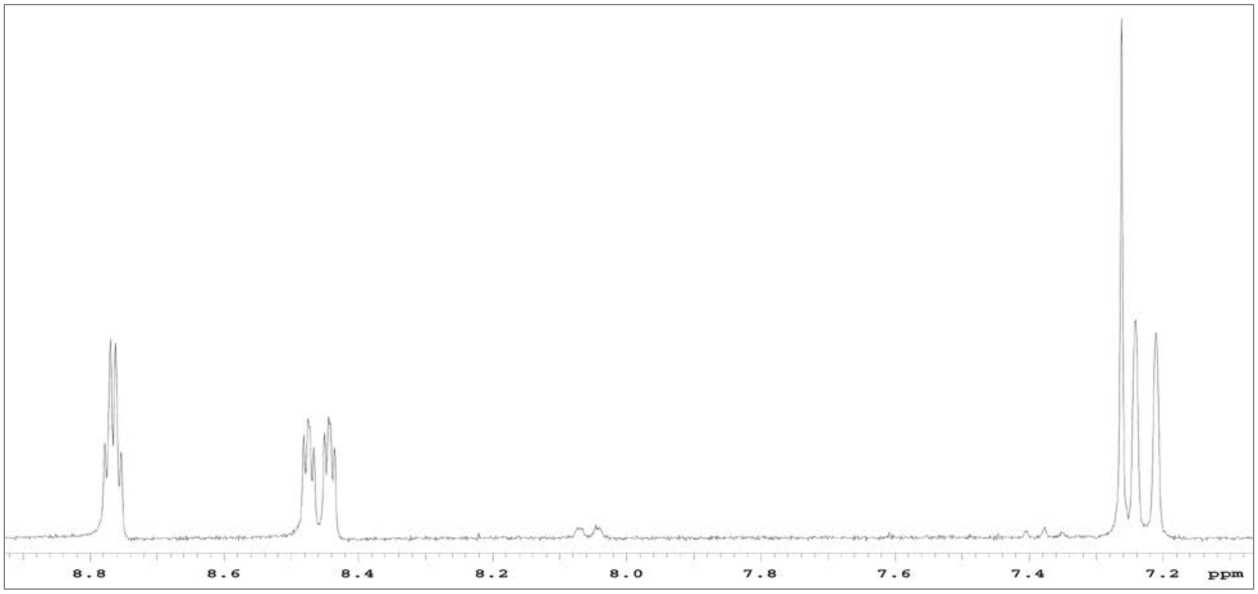
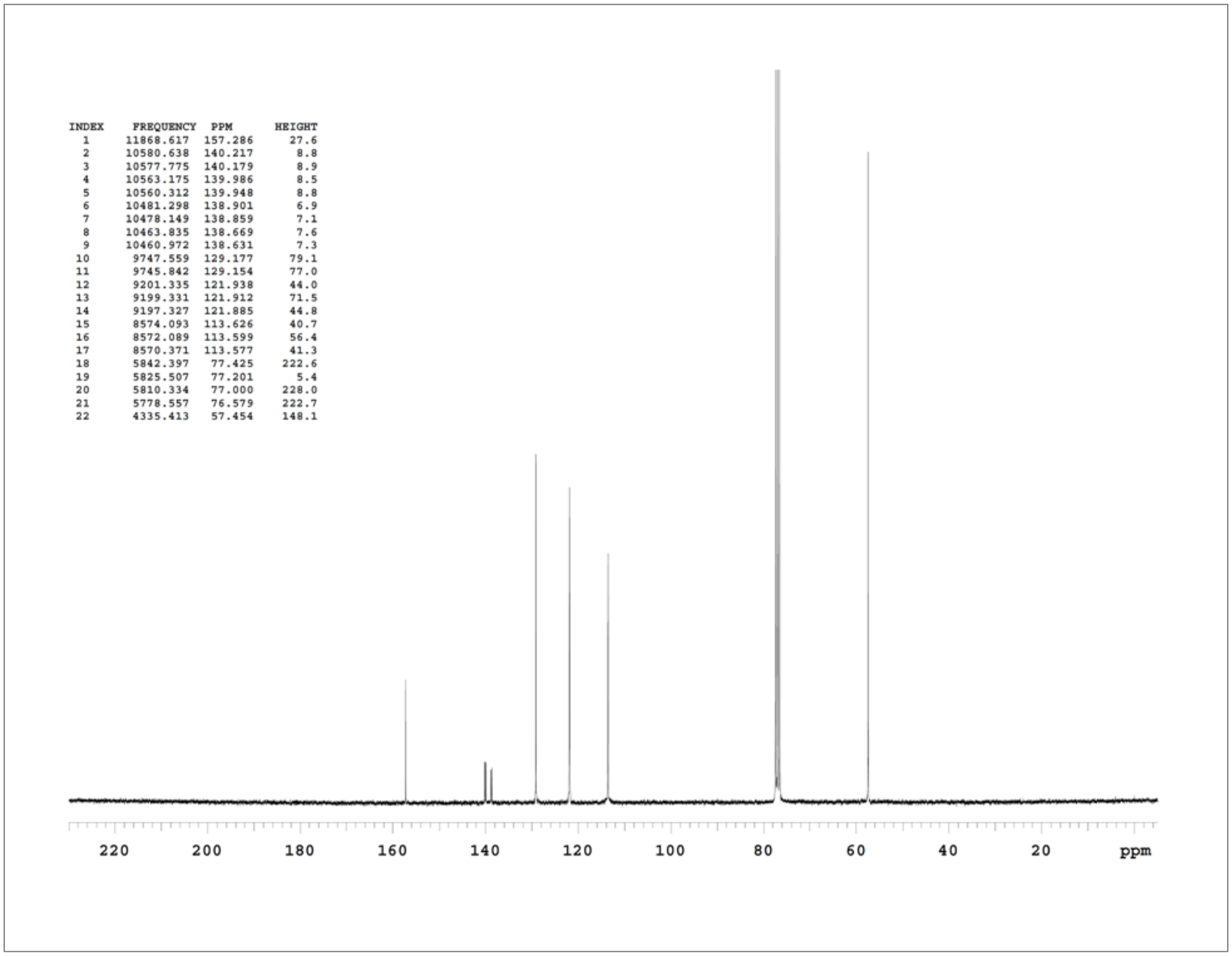


[2,4-$^{15}N_2$]Dinitroanisole / ^{13}C NMR



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INDEX    FREQUENCY  PPM      HEIGHT
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  3      10577.775  140.179     8.9
  4      10563.175  139.986     8.5
  5      10560.312  139.948     8.8
  6      10481.298  138.901     6.9
  7      10478.149  138.859     7.1
  8      10463.835  138.669     7.6
  9      10460.972  138.631     7.3
 10       9747.559  129.177    79.1
 11       9745.842  129.154    77.0
 12       9201.335  121.938    44.0
 13       9199.331  121.912    71.5
 14       9197.327  121.885    44.8
 15       8574.093  113.626    40.7
 16       8572.089  113.599    56.4
 17       8570.371  113.577    41.3
 18       5842.397   77.425   222.6
 19       5825.507   77.201     5.4
 20       5810.334   77.000   228.0
 21       5778.557   76.579   222.7
 22       4335.413   57.454   148.1
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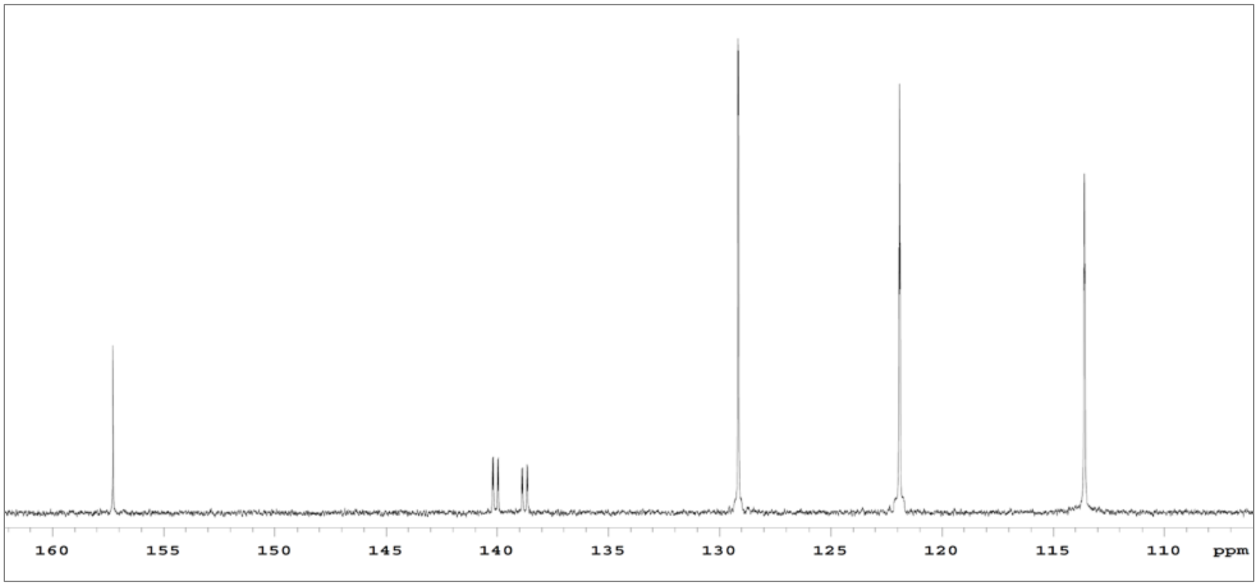
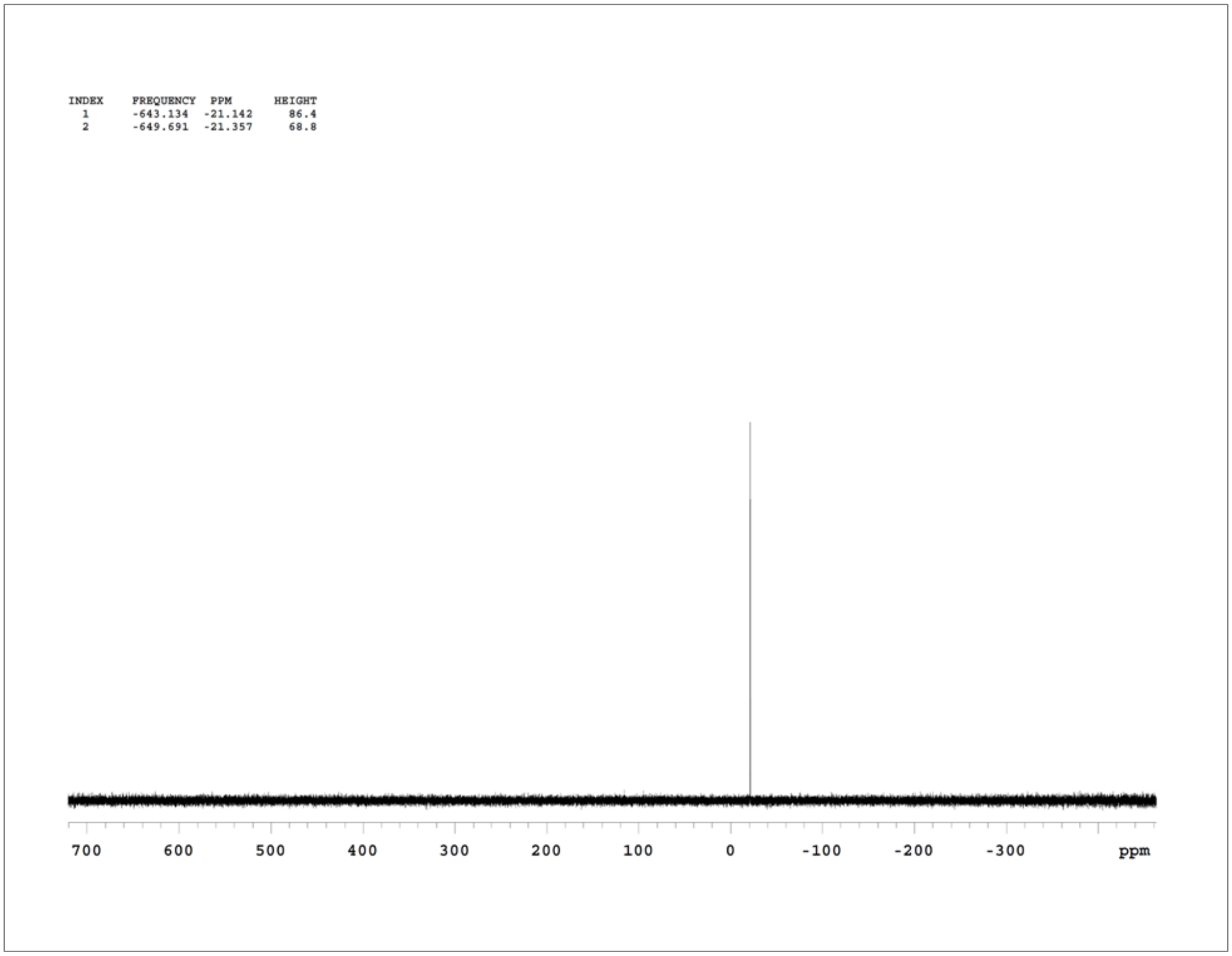


[2,4-$^{15}N_2$]Dinitroanisole / ^{15}N NMR



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INDEX    FREQUENCY  PPM      HEIGHT
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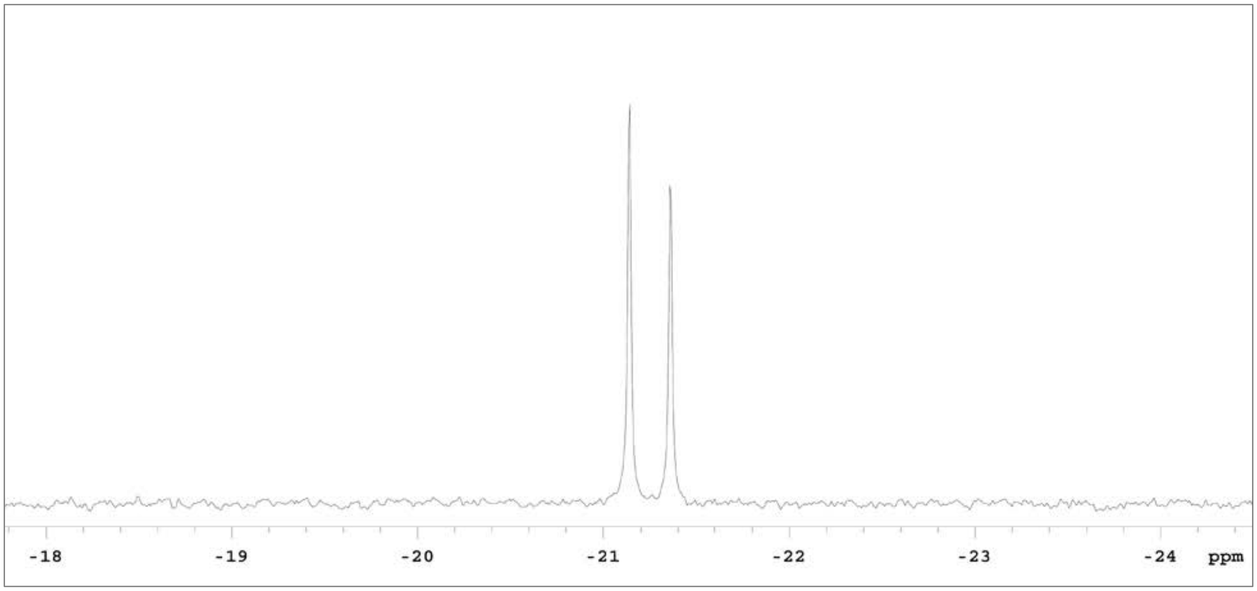
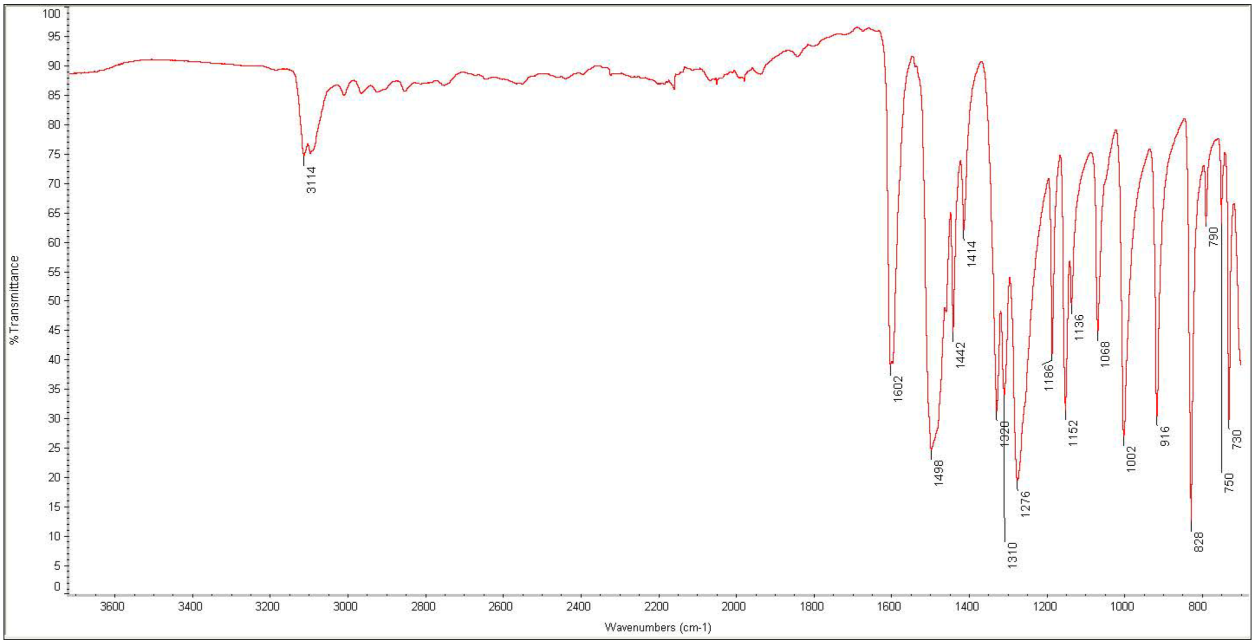
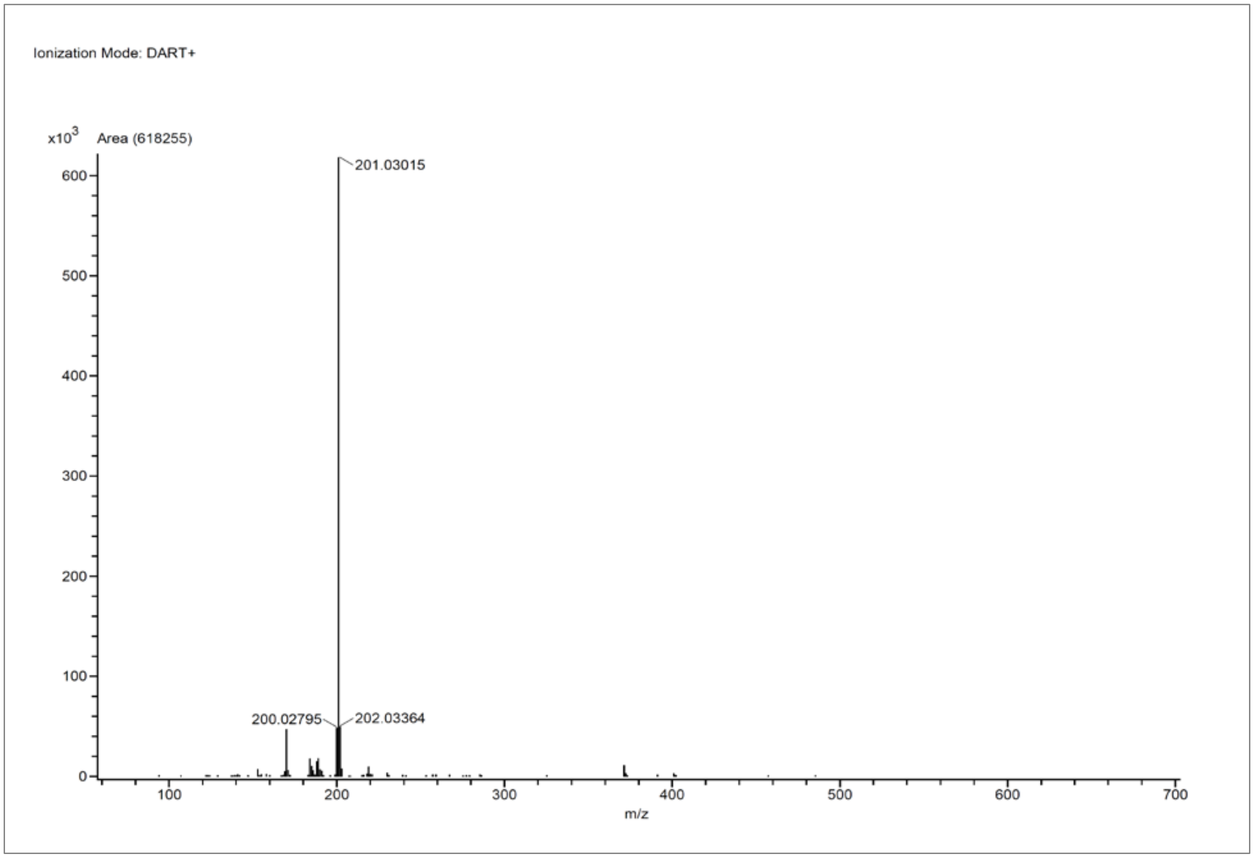


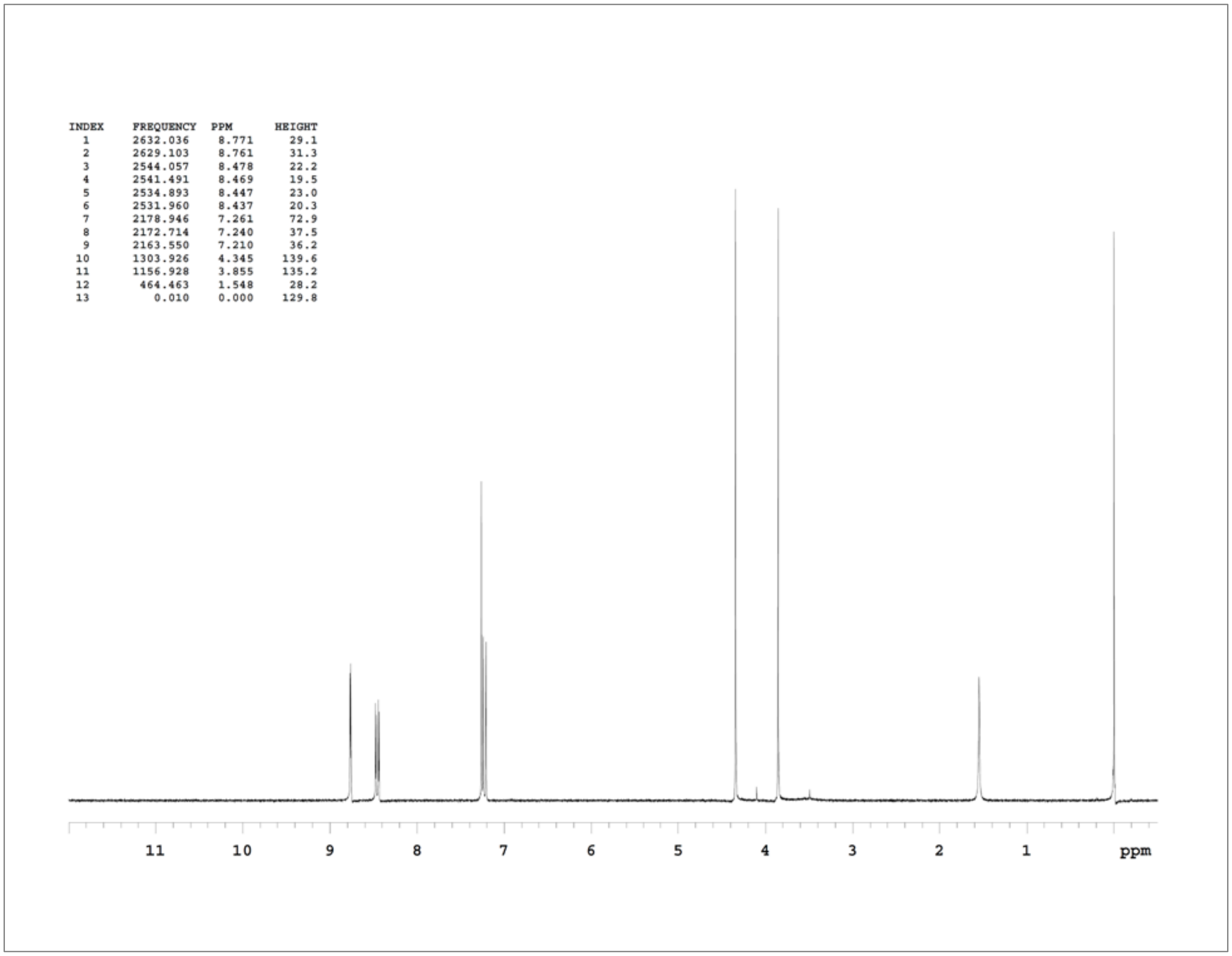
[2,4-$^{15}N_2$]Dinitroanisole / IR



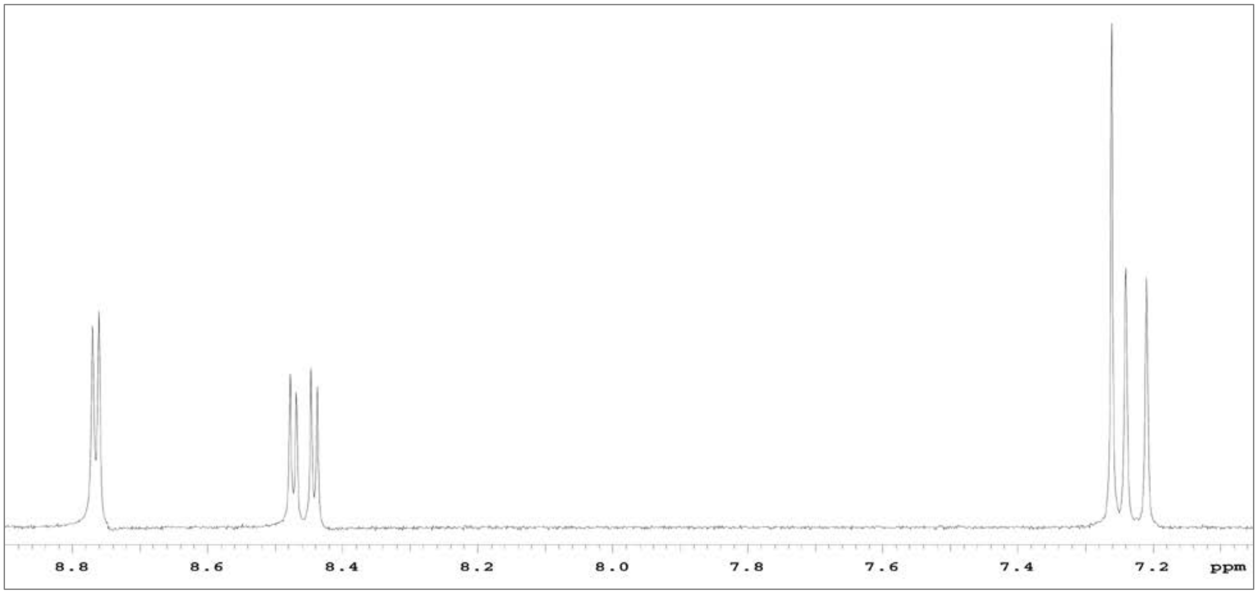
[2,4-$^{15}N_2$]Dinitroanisole / HRMS



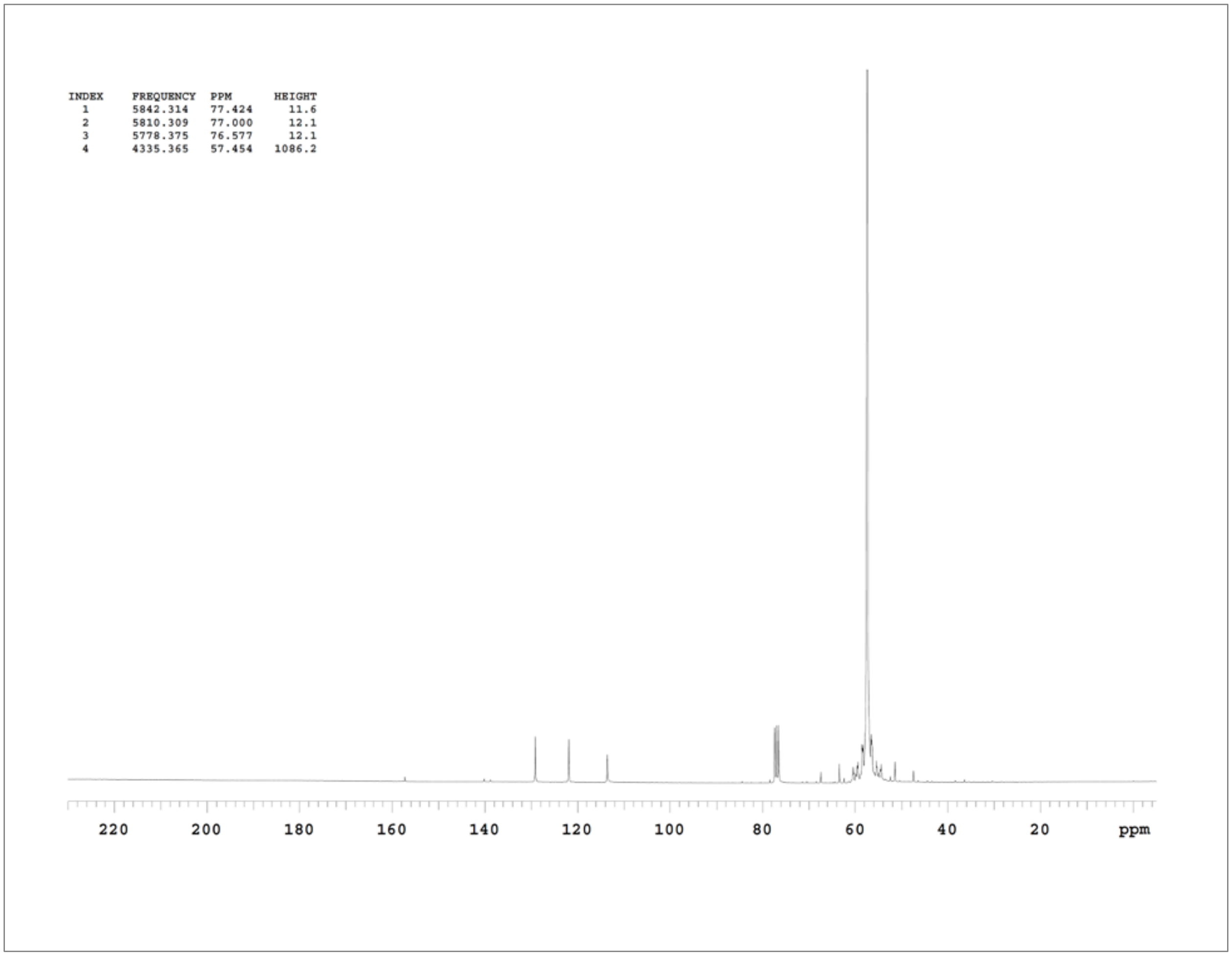
[*methyl*-^{13}C]2,4-Dinitroanisole / ^{1}H NMR



INDEX	FREQUENCY	PPM	HEIGHT
1	2632.036	8.771	29.1
2	2629.103	8.761	31.3
3	2544.057	8.478	22.2
4	2541.491	8.469	19.5
5	2534.893	8.447	23.0
6	2531.960	8.437	20.3
7	2178.946	7.261	72.9
8	2172.714	7.240	37.5
9	2163.550	7.210	36.2
10	1303.926	4.345	139.6
11	1156.928	3.855	135.2
12	464.463	1.548	28.2
13	0.010	0.000	129.8



[*methyl*-^{13}C]2,4-Dinitroanisole / ^{13}C NMR



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INDEX    FREQUENCY  PPM      HEIGHT
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  2      5810.309   77.000     12.1
  3      5778.375   76.577     12.1
  4      4335.365   57.454   1086.2
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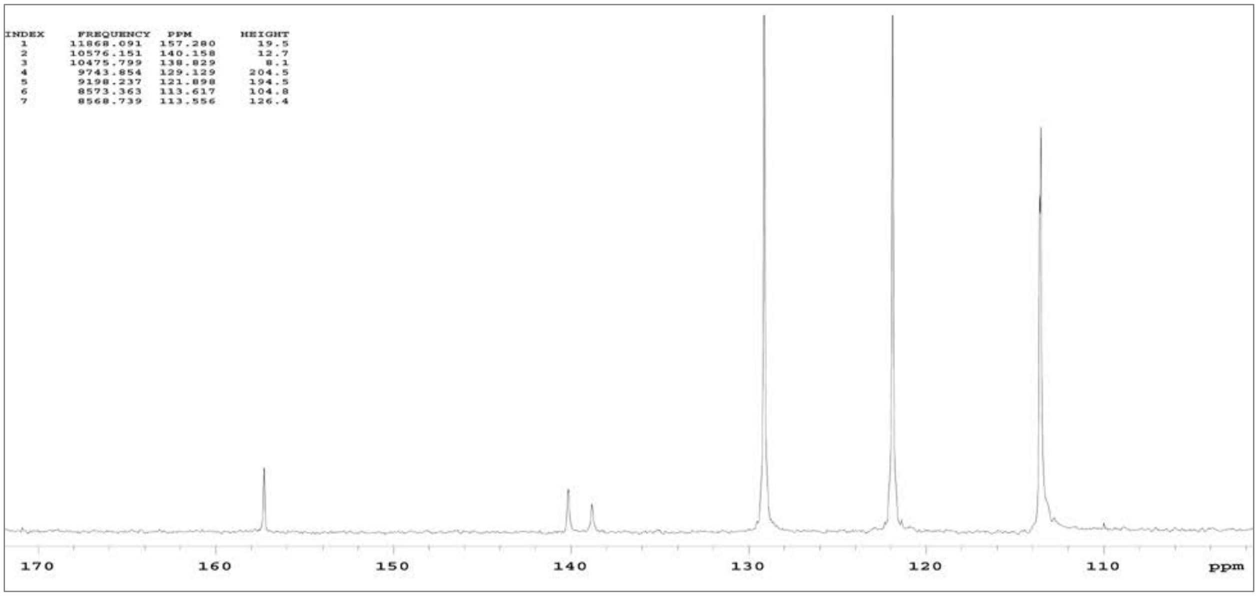

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  2      10576.151   140.158      12.7
  3      10475.799   138.829       8.1
  4       9743.854   129.129     204.5
  5       9198.237   121.898     194.5
  6       8573.363   113.617     104.8
  7       8568.739   113.556     126.4
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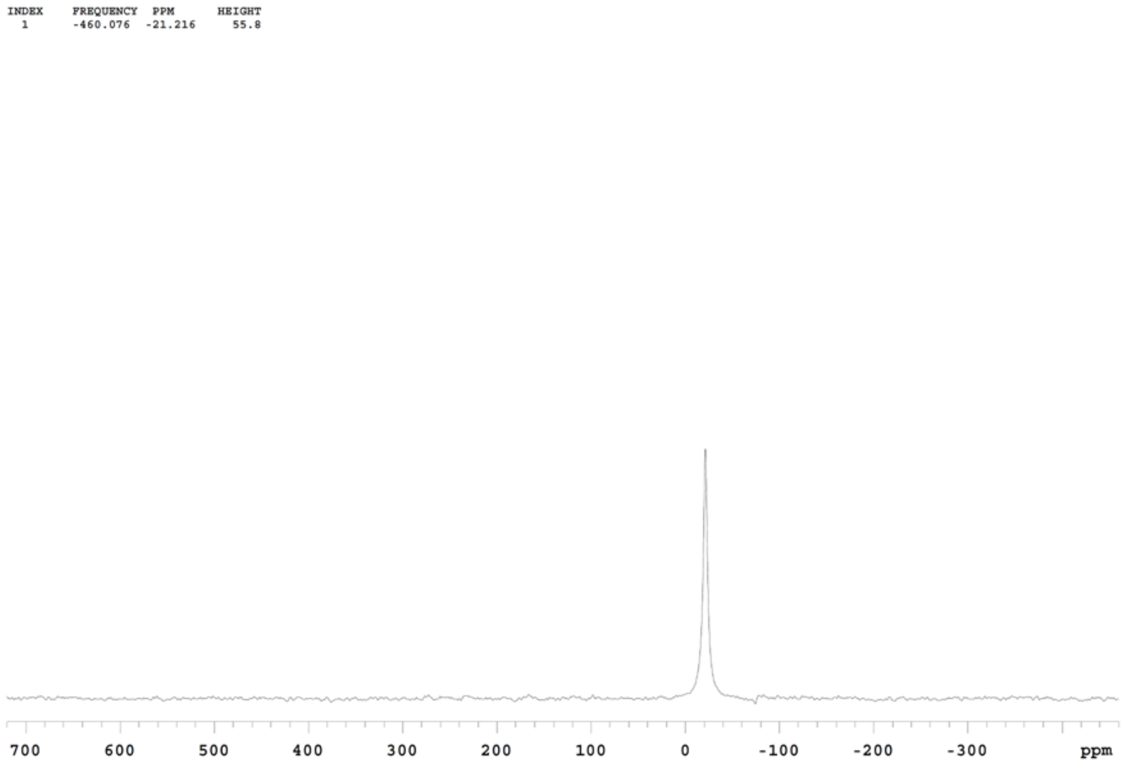
[*methyl*-^{13}C]2,4-Dinitroanisole / ^{14}N NMR



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INDEX    FREQUENCY  PPM      HEIGHT
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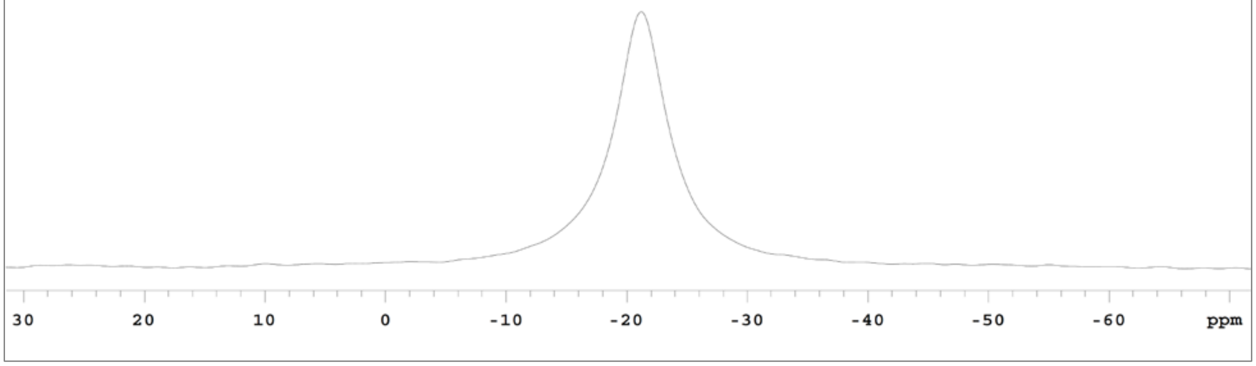
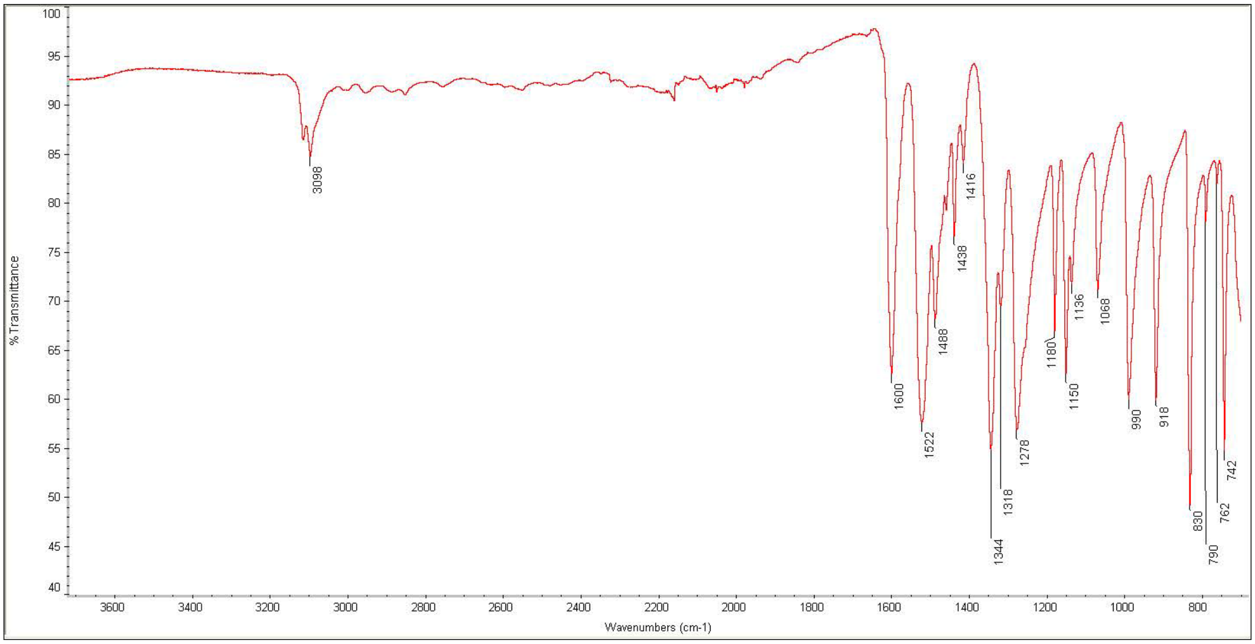
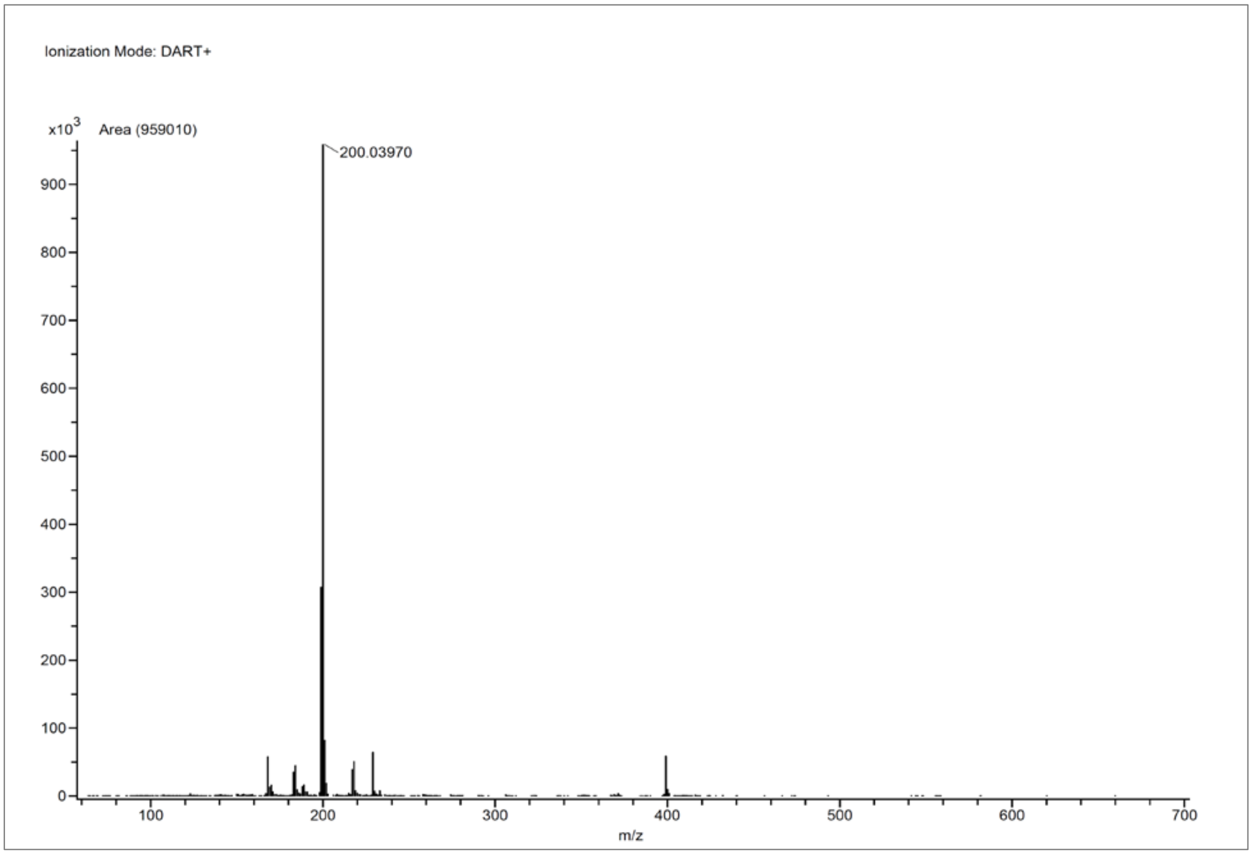


[*methyl*-^{13}C]2,4-Dinitroanisole / IR



[*methyl*-^{13}C]2,4-Dinitroanisole / HRMS



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BIBLIOGRAPHY

Aridoss, G. and Laali, K. K. *J. Org. Chem.* **2011**, 76, pp 8088-94.

Berger, S., Braun, S., and Kalinowski, H.-O. *NMR Spectroscopy of the Non-Metallic Elements*; Wiley: New York, **1997**, pp 111-318.

Davis, T. L. *The Chemistry of Powder and Explosives*; Wiley: New York, **1943**; pp 140-41.

Fedoroff, B. T., Aaronson, H. A., Sheffield, O. E., Reese, E. F., and Clift, G. D. *Encyclopedia of Explosives and Related Items*; Picatinny Arsenal: Dover, NJ, **1960**; Vol. 1, pp A448-49.

Fedoroff, B. T. and Sheffield, O. E. *Encyclopedia of Explosives and Related Items*; Picatinny Arsenal: Dover, NJ, **1966**; Vol. 3, pp C249-50.

Pretsch, E., Bühlmann, P., and Affolter, C. *Structure Determination of Organic Compounds*; Springer-Verlag: Berlin, **2000**; pp 270-72.

Urbański, T. *Chemistry and Technology of Explosives*; Pergamon Press: Oxford, **1964**; Vol. 1, pp 449-59.

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