Cross-Coupling Biarylation of Nitroaryl Chlorides Through High Speed Ball Milling

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Abstract

Solvent-free reaction using a high-speed ball milling technique has been applied to the classical Ullmann coupling reaction. Cross-coupling biarylation of several nitroaryl chlorides was achieved in good yields when performed in custom-made copper vials through continuous shaking without additional copper or solvent. Cross-coupling products were obtained almost pure and NMR-ready. These reactions were cleaner than solution phase coupling which require longer reaction time in high boiling solvents, and added catalysts as well as lengthy extraction and purification steps. Gram quantities of cross biaryl compounds have been synthesized with larger copper vials, a proof that this method can be used to reduce industrial waste and for sustainability.

Keywords: Solvent-free Reaction, Ullmann, Biarylation, Cross-coupling, High Speed, Ball Milling.

Introduction

The importance of aryl-aryl bond formation cannot be overstated. Over the last few years, hundreds of articles and several reviews addressing this issue have been published [1-5]. Crosscoupling biarylation is considered the cornerstone of medicinal chemistry and drug discovery, and usually introduced early in the synthesis of important natural products. Indeed, the presence of a C-C bond between two aryl groups is very common in many naturally occurring and biologically relevant molecules. The elaboration of this important moiety has attracted the attention of synthetic chemists since the days of Ullmann and Goldberg who used catalytic copper in both C-C, and C-Heteroatom biarylation [6-8]. Modern organometallic reactions involving metals such as nickel, tin, palladium, and ruthenium have been efficient in achieving this goal [9-11]. Given the high costs of catalysts involving these metals, the need to find simpler and less onerous reagents has, recently, turned the scientific community back to copper and Fritz Ullmann. The most cost effective method of biarylation is arguably the copper-mediated Ullmann coupling of aromatic halides. Biaryl coupling using a copper catalyst is known as the traditional Ullmann Coupling reaction of aryl halides [12]. High temperatures and lower rates of coupling in case of deactivated aromatic halides were often cited as limitations to this reaction [12b]. Over the last few years there has been a sort of renaissance for these copper-mediated biaryl forming reactions with the introduction of newer catalytic systems and reaction partners (or ligands) to improve the yields of cross-coupling biarylation. Reviews on Cu-mediated crosscoupling reactions by Beletskaya, Ley, and Lemaire have been expansive on the recent modification aimed at improving these reactions [13-15]. Notwithstanding the cost of all these metals and catalysts, and in consideration of the enormous environmental cost associated with the use and removal of waste generated from solvents and metal residues, solvent-less methods forcross-coupling biarylation offer a certain advantage for both the environment, and the economy [16]. Over the past few years, synthetic techniques relying on grinding reactants in absence of solvents have become available. The field of mechanochemistry has emerged with the assumption that mechanical force can produce new chemistries through bond processing and transformations [17-18]. Mechanochemical processes such as solvent-free grinding, milling, sonication, and/or applied pressure are fast becoming synonymous to “green” or clean, sustainable technology [19]. High Speed Ball Milling (HSBM) process has been adapted to several well-known chemical reactions including alkene bond-forming reactions, and aryl-aryl cross-coupling reactions [20-21]. We

hypothesized that a High Speed Ball Milling process applied to Ullmann cross-coupling reaction would be cost-effective if sufficiently activated haloarenes were to undergo cross-coupling, at room temperature, without solvent or added copper as catalyst. Palladium catalysts are much more expensive than copper, and the prospect of avoiding the use of solvents altogether made the HSBM process appealing [22-23]. We have previously reported on the self-coupling of nitroaryl chlorides under HSBM conditions. Herein, we report a new HSBM methodology leading to the preparation of cross-biaryl compounds **6** and **7** obtained when 2-chloronitrobenzene **1** underwent a cross-coupling reaction with 2,3dichloronitrobenzene **2**, and 2,3-dichloro-1,4-dinitrobenzene **3** respectively. We also report on the preparation of cross-triaryl compounds **8** and **9** from double cross coupling reactions between 1,5-dichloro-2,4-dinitrobenzene **4** in one hand and 2-chloronitrobenzene **1** and 2,3dichloronitrobenzene **2** respectively.

Materials and Method: The HSBM (High Speed Ball Milling) Method

Using custom-made copper vessels of variable sizes made from copper rods (McMaster-Carr Supply), and a copper shot (1/8 inch diameter of the vial's diameter), different nitroaryl chlorides (**1-6**) were milled together in different proportion overnight at high speed of 5 m/s in a Parr 2500 shaker. While most products appeared as solid cast on the inner side of the vial/cap, some products were found as powder as shown in pictures below. All crude compounds were NMRready, and did not require workup or a lengthy extraction for isolation before spectroscopic analysis.

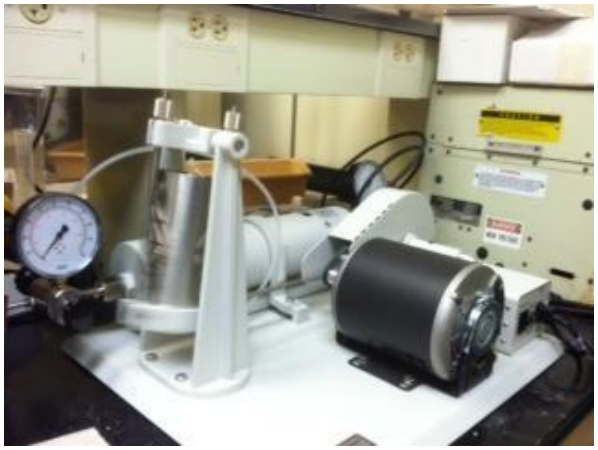


Fig 1 Shaker (*Parr 2500*)

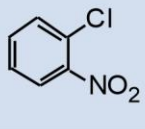
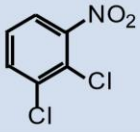
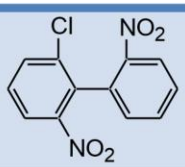
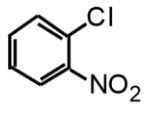
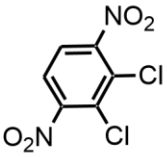
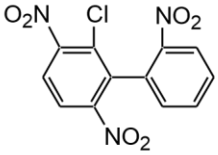
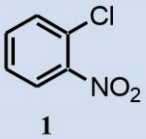
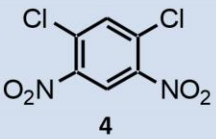
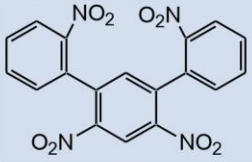
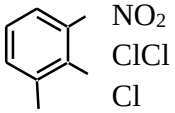
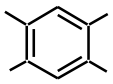
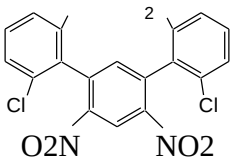
Fig 2. Reusable Custom made copper vials/caps

Ball milling of the nitroaryl chlorides between the caps of the copper vessel at high speed grinds the compounds into finite particles which react faster and cleaner in the gas phase. The use of high speed ball milling method circumvents the addition of catalyst and the use of high boiling and, often toxic solvents at elevated temperatures [24]. The feasibility of a solventless reaction in an all copper vessel and a copper ball is now an established method [25]. In our cases, Biarylation consisted of novel solvent-less Ullmann cross-coupling reactions. Typically, two different chlorinated nitroaryls were subjected to mechanical milling in custom made copper vials using a spherical copper ball for 12 hr. The resulting crude powder or liquid was generally NMR-ready as only insignificant amount of inorganic waste was generated in the process. However for the purpose of accurate melting point measurement, the crude solid was purified by recrystallization. When further purification was required to separate the products of crosscoupling of different aryl halides, flash chromatography was utilized.

Results and Discussion

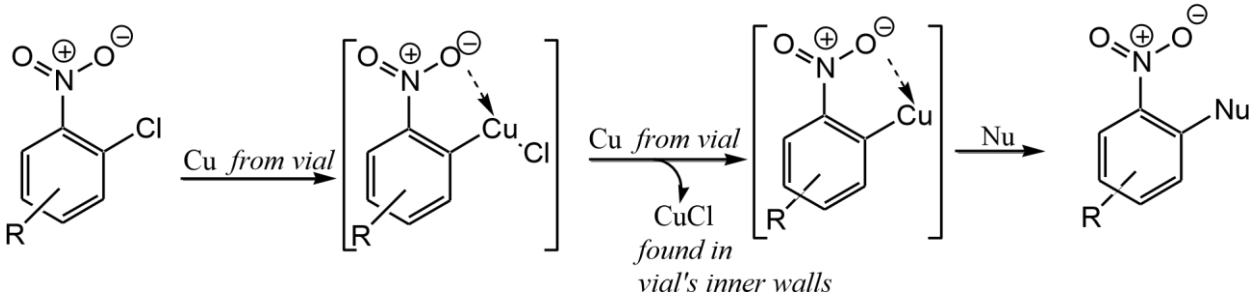
Within a custom-made copper vial and using an all copper ball, *ortho*-nitrated arylhalides **2-5** underwent Ullmann type cross-coupling with 2-chloronitrobenzene **1** and 2.3-dichloronitrobenzene **2** respectively in solvent-free conditions and at room temperature. The custom- made copper vial, and copper ball, served as sources/sites for catalysis. Coupling, under these conditions, were performed with simple and complex nitroaryl halides structures as reported below. Building on the general assumption that Ullmann coupling proceeds most rapidly with aryl halides bearing electron-withdrawing groups at *ortho* position to the leaving halogen, known as the *ortho-effect*, we selected suitably substituted nitroaryl halides, some commercially available and others prepared in our laboratory.

Table 1: Cross-coupling Biarylation of Nitroaryl Chlorides

Entry	Aryl 1	Aryl 2	Biaryl/Triaryl	Yield/notes
1.	 **1**	 **2** *Ratio: 1:1*	 **6**	65% *By product: 2,2'dinitrobiphenyl*
2.	 **1**	 **3** *Ratio: 1:1*	 **7**	50% *By product: 2,2'-dinitrobiphenyl*
3.	 **1**	 **4** *Ratio: 2:1*	 **8**	72% *By product: 2,2'-dinitrobiphenyl*
4.	 **2**	 **4** *Ratio: 2:1*	 **9**	75% *By product: 2,2'-dichloro-6,6'dinitrobiphenyl*

Adapting the classical Ullmann coupling reaction of *ortho*-halogenated nitroarenes to High Speed Ball Milling (HSBM) process, we have prepared, in good yields, cross biaryl compounds **6-9** in solvent free conditions.

Table 1 summarizes our results for the syntheses of biaryl compounds. In entry 1, HSBM cross coupling between commercially available 2,3dichloronitrobenzene **2** and 2-chloronitrobenzene **2** afforded 2-chloro-2',6-dinitrobiphenyl **6** in
65% yield and a byproduct, namely 2, 2'-dinitrobiphenyl **5** the self-coupling product of the more reactive 2-chloronitrobenzene **1**. The latter was cross coupled (Entry 2) with synthetic 1, 4dinitro-2,3-dichlorobenzene **3**, obtained by nitration of 2,3-dichloronitrobenzene **2** with potassium nitrate in warm sulfuric acid. The cross biaryl product, 2-chloro-2', 3,6trinitrobiphenyl **7** was a yellowish powder which came with **5** the dimer of **1**. In entries 3-4, we explored the possibility of simultaneous Ullmann cross coupling. Tetrasubstituted 2,4-dichloro1,5-dinitrobenzene **4** was synthesized from 1,3-dichlobenzene and subjected to HSBM cross biarylation with 2-chloronitrobenzene **1** and 2,3-dichloronitrobenzene **2**, resulting in the formation of triaryl compounds **8** and **9** respectively. It should be noted that dimerization of **1** and **2** was also observed, albeit in less proportion during these reactions. These results provide a validation of the general scope of the HSBM Ullmann biarylation reaction. Traditional Ullmann cross-coupling reactions have been unreliable until recently because of lack of selectivity. Often, the isolated yield of the desired biaryl compound did not warrant the tedious separation process. For this reason, cross-coupling biarylation has been done using other transition metals, especially palladium. Our results show that cross biarylation using solventless conditions proceed in higher yield and may be an alternative to palladium catalysts which are known to be incompatible with some functional groups. It is notable that polymerization, which occurs in reaction conducted at high temperature in solvents such as dimethyl formamide, or pyridine, was not a factor hence a markedly improved yield of biarylation. Our results also confirm that in Ullmann-type reactions, the most important factor is activation by a nitro group located *ortho* to the halo group, not solubility since coupling may, in many of the HSBM reactions, occur in a "solventless" phase. The mechanism by which the HSBM biarylation reactions proceed is yet to be elucidated. Any mechanism would be, however, intrinsically similar to what is believed to occur in the traditional Ullmann coupling reaction. The use of copper vials and copper balls provides the necessary catalyst for the reaction as it's incorporated in the hardware. The inner walls of the copper vial are the reactive sites where the exchange halogen/metal occurs, aided by the well documented *ortho*-chelating effect from the nitro group at *ortho* position (scheme 1) [26]. The nitro group, or other groups have been found to act as an intramolecular ligand in these Ullmann *coupling* reactions in the same role as external ligands which catalyze several Ullmann-Goldberg *Condensation* reactions between aryl halides and heterocyclic compounds [27].



Scheme 1. Ortho-chelation/stabilization by the nitro group.

A single electron transfer (SET) mechanism leads to the formation of an aryl radical followed by oxidative addition. The formation of an aryl radical is supported by dimerization of highly hindered haloarenes forming substituted biaryls [28]. In the cross coupling of two different aryl halides, dimerization can be minimized by a combination of electronic and steric factors. It is noteworthy that the more demanding nitroaryl chlorides were chosen in lieu of fast reacting nitroaryl iodides, or for instance highly reactive methoxyaryl iodides which form dimers at higher rates [29].

Conclusion

The goals of sustainable biarylation methods, so crucial in drug synthesis, remain the development and systematic use of "green" synthetic techniques that are both efficient (i.e. economical) and environmentally friendly. Synthetic processes done in solvent-free with no additional catalysts do cut costs and lower risks of exposure to toxic chemicals. HSBM Ullmann biarylation in general, and our application thereof on solvent-free homo and cross-coupling of less expensive, and more accessible aryl chlorides demonstrates a proof of the concept in this area. We are currently using mechanochemistry to explore related biarylation of aryl bromides, nitriles, carboxylates, sulfonates in order to broaden the scope of HSBM Ullmann biarylation reactions, which will be disclosed in the near future.

Acknowledgements

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Experimental

^{1}H and ^{13}C NMR spectra were recorded using a Varian Inova 500 MHz or a Varian Mercury 400 MHz spectrometer. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, Inc., Andover, MA. GC- and LC-MS data were recorded at Valdosta State University in Valdosta, GA or at the University of South Caroline, Columbia SC. All reagents were purchased from Sigma-Aldrich and used without further purification. Copper ball-bearings and copper vials were custom-made from copper rods purchased from McMaster-Carr Supply. Ball-milling was carried out in a modified *2500 Parr* shaker.

Typical "HSBM" procedure for the classical Ullmann Coupling of *ortho*-nitrated aryl halides: A nitro-aryl halide was measured and placed into a dry custom-made 2.0 x 0.5 inch screw-capped copper vial, along with a copper shot (1/4 in. diameter). Without adding solvent or catalyst, the vial was screw-capped and inserted into the compartment of a 2500 model of a Parr shaker (vibrational speed: 5m/s), and the compounds were milled for 12 hours. The crude product was usually a dry powder, occasionally a paste cast on the walls of the vial and caps. Preliminary ^{1}H NMR of the crude was taken to determine the purity of the sample. Inorganic biproducts collected in the inner walls of the copper vessels as seen in the lost of shine due to oxidation. Copper vessels were re-usable after cleaning the inner walls in a mixture of vinegar and salt.

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^{1} H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm): 8.56 (s, ABB'A', 2H). GC-MS: m/z, calculated: 237; found: 238

Synthesis of 2-Chloro-2',3,6-trinitrobiphenyl 7: 1,4-dinitro-2,3-dichlorobenzene **3** (3.27g~10mmol) and 2-chloronitrobenzene **1** (1.57g~10mmol) were loaded into a copper vial charged with a copper ball-bearing and subjected to high speed ball milling procedure as described above to afford a yellowish powder of 2-chloro-2',3,6-trinitrobiphenyl **7.** 1H NMR showed the presence of the cross-coupling product **7** as well as 2,2'-dinitrobiphenyl **5**, the product of self-coupling of 2-chloronitrobenzene **1**. The crude mixture was resolved by flash column chromatography with a 10% solution of ethyl acetate in petroleum ether.

Synthesis of 2-Chloro-2',6-dinitrobiphenyl 6: 2,3-dichloronitrobenzene **2** (1.92g~10mmol) and 2-chloronitrobenzene **1** (1.57g~10mmol) were loaded into a copper vial charged with a copper ball-bearing and subjected to high speed ball milling procedure as described above to afford a yellowish paste. 2-chloro-2',6-dinitrobiphenyl **6** and 2,2'-dinitrobiphenyl **5**, the product of selfcoupling of 2-chloronitrobenzene **1** were separated by flash column chromatography using a 10% solution of ethyl acetate in petroleum ether.
^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.22(d, 1H), 7.55(t, 1H), 7.65(t, 1H), 7.62(t, 1H) 7.78(d, 1H), 8.08(d, 1H), 8.35(d, 1H). ^{13}C NMR (400 MHz, $CDCl_3$, TMS): δ (ppm): 118.7, 119.8, 125.2, 128.5, 129.7, 130.2, 131.58, 131.59, 131.9, 134.3, 145.8, 146.5. LC-MS: m/z 302, calculated: 278.65; found: 301.2 – 23[Na] = 278.2

Synthesis of 2,3-dichloro-1,4-dinitrobenzene 3: 2,3-dichloronitrobenzene **2** (9.5g – 50mmol) was added into a stirring solution of potassium nitrate (10.1g – 100mmol) in concentrated sulfuric acid (50mL) in a 125 mL Erlenmeyer flask placed on a hotplate. The mixture was stirred at room temperature for 6 hr and poured into a beaker of crushed ice. The light paste was extracted with ethyl acetate, and dried over magnesium sulfate. Solvent removal under reduced pressure yielded 9.0g (95%) of 2,3-dichloro-1,4-dinitrobenzene **3** as a slow crystallizing oil.
^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.60(t, 2H), 7.81(d, 2H), 8.22(d, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 124.0, 131.0, 132.5, 133.5, 140.0, 146.0. GC-MS: m/z 322, calculated: 323; found: 323

Synthesis of 1,5-dichloro-2,4-dinitrobenzene 4: 1,3-dichlorobenzene (14.7g – 0.1mol) was added into a stirring solution of potassium nitrate (20.2g – 0.2mol) in concentrated sulfuric acid (50mL) in a 125 mL Erlenmeyer flask placed on a hotplate. The mixture was heated at 90 °C for 1hr and, then at room temperature for another hour before being poured into a beaker of crushed ice. The light yellow precipitate was vacuum filtered in a Buchner funnel, and recrystallized in not ethanol to yield 12.5g (97%) of 1,5-dichloro-2,4-dinitrobenzene **4**. Mp (137-140 °C)
^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm): 7.8 (s, 1H), 8.6 (s, 1H). GC-MS: m/z, calculated: 237; found: 238

Synthesis of 2,2',2",4'-tetranitrotriphenyl 8: 1,5-dichloro-2,4-dinitrobenzene **4** (3.27g~10mmol) and 2-chloronitrobenzene **1** (1.57g~10mmol) were loaded into a copper vial charged with a copper ball-bearing and subjected to high speed ball milling procedure as described above to afford a yellowish paste of **2,2',2",4'-tetranitrotriphenyl 8.** ^{1}H NMR showed the presence of the cross-coupling product **8** as well as 2,2'-dinitrobiphenyl **5**, the product of self-coupling of 2-chloronitrobenzene **1**. The crude mixture was resolved by flash column chromatography with a 20% solution of ethyl acetate in hexanes, and 5% ethanol.
^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.60(t, 2H), 7.81(d, 2H), 8.22(d, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 124.0, 131.0, 132.5, 133.5, 140.0, 146.0. GC-MS: m/z 322, calculated: 322; found: 323

Synthesis of 2,2"-dichloro-2',4',6,6"-tetranitrotriphenyl 9: 1,5-dichloro-2,4-dinitrobenzene **4** (3.27g~10mmol) and 2,3-dichloronitrobenzene **2** (1.57g~10mmol) were loaded into a copper vial charged with a copper ball-bearing and subjected to high speed ball milling procedure as described above to afford a yellowish paste of **2,2"-dichloro-2',4',6,6"-tetranitrotriphenyl 9.** 1H NMR showed the presence of the cross-coupling product **9** as well as 2,2'-dichloro-6,6'dinitrobiphenyl, the product of self-coupling of 2,3-dichloronitrobenzene **2**. The crude mixture was resolved by flash column chromatography with a 20% solution of ethyl acetate in hexanes, and 5% ethanol.
^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 7.60(t, 2H), 7.81(d, 2H), 8.22(d, 2H). ^{13}C NMR
(400 MHz, $CDCl_3$, TMS): δ (ppm) 124.0, 131.0, 132.5, 133.5, 140.0, 146.0. GC-MS: m/z 322, calculated: 322; found: 323

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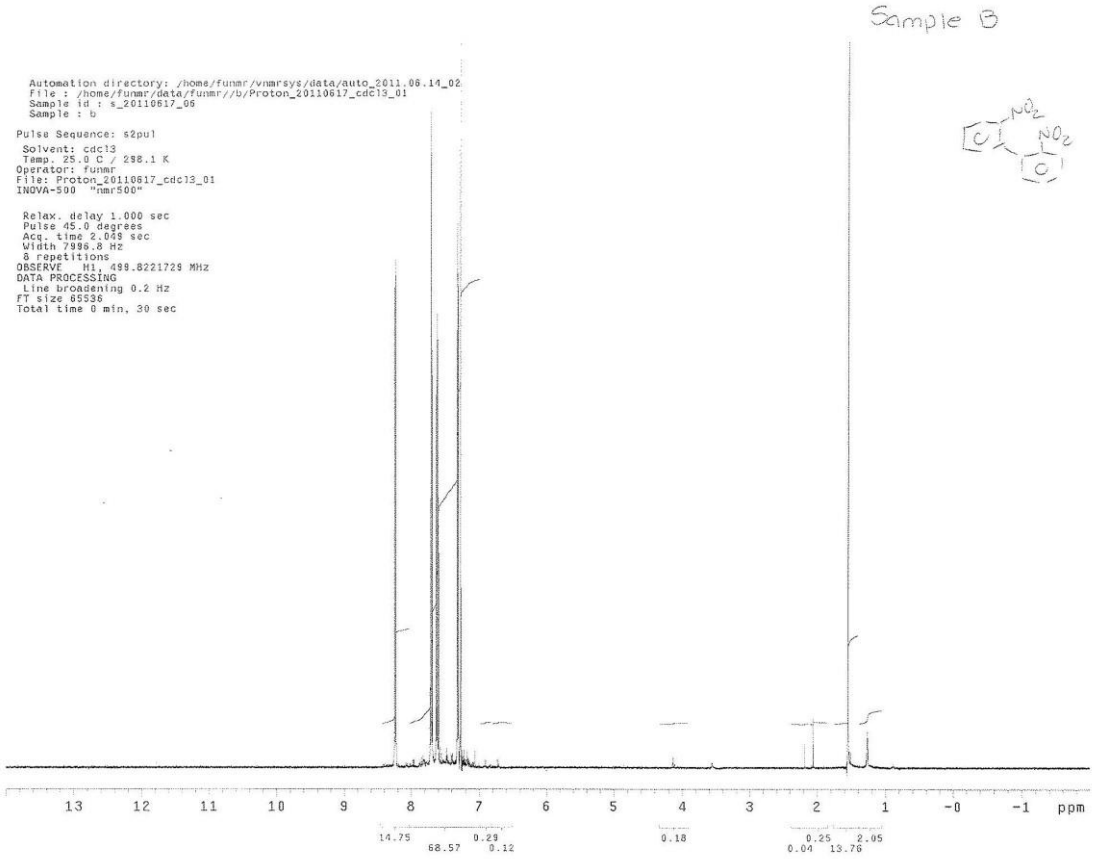
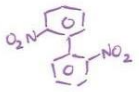
Supplemental Materials: NMR and GCMS Spectra 2,2'-dinitrobiphenyl:

$_1$H NMR (400 MHz, $CDCl_3$, TMS): □□(ppm) 7.29(d, 2H), 7.60(t, 2H), 7.68(t, 2H), 8.22(d, 2H)

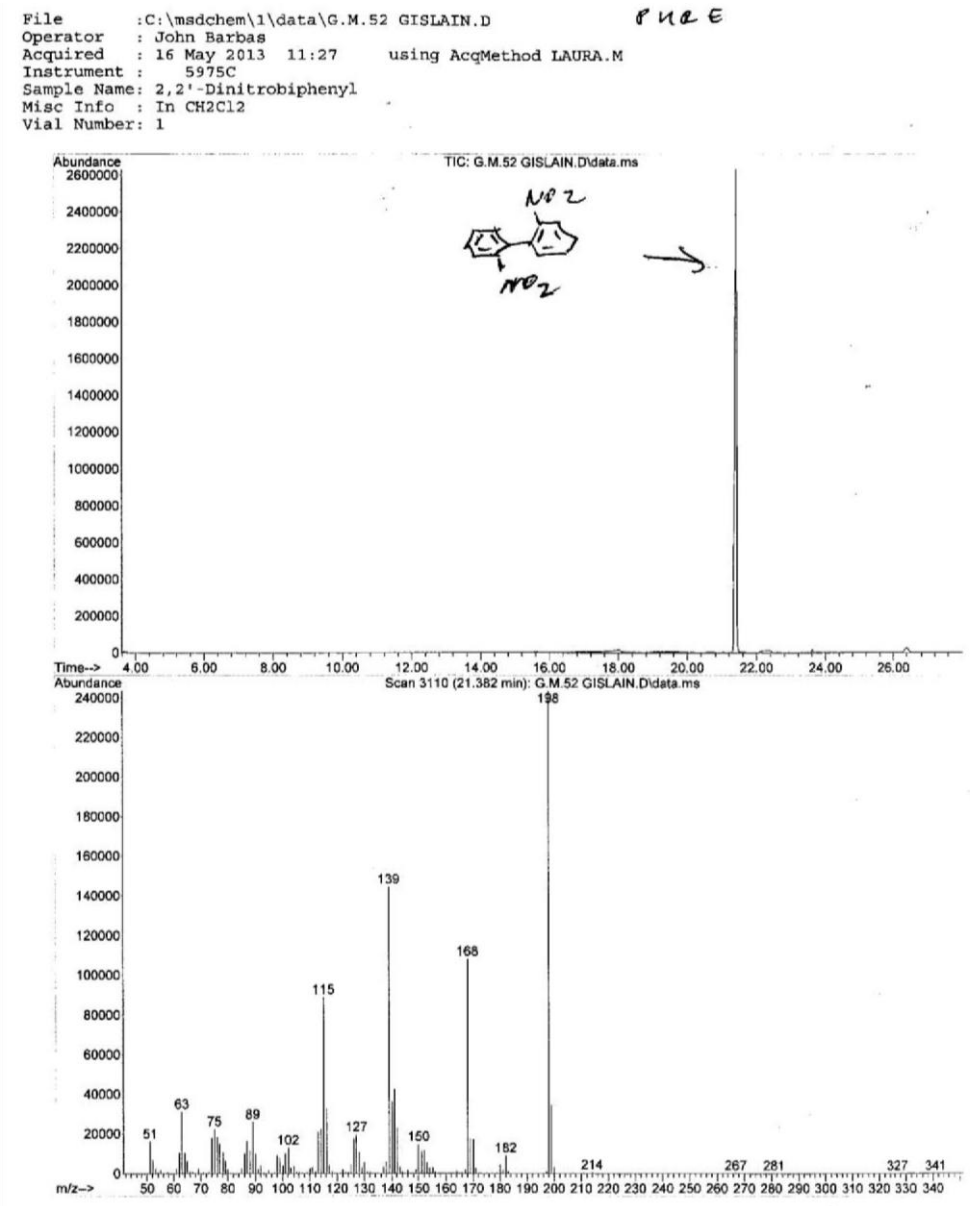


13

C NMR (400 MHz, $CDCl_3$, TMS): □□(ppm) 124.7(CH), 129.1(CH), 130.8(CH), 133.3(CH), 134.1(CC), 147.1(CNO_2)

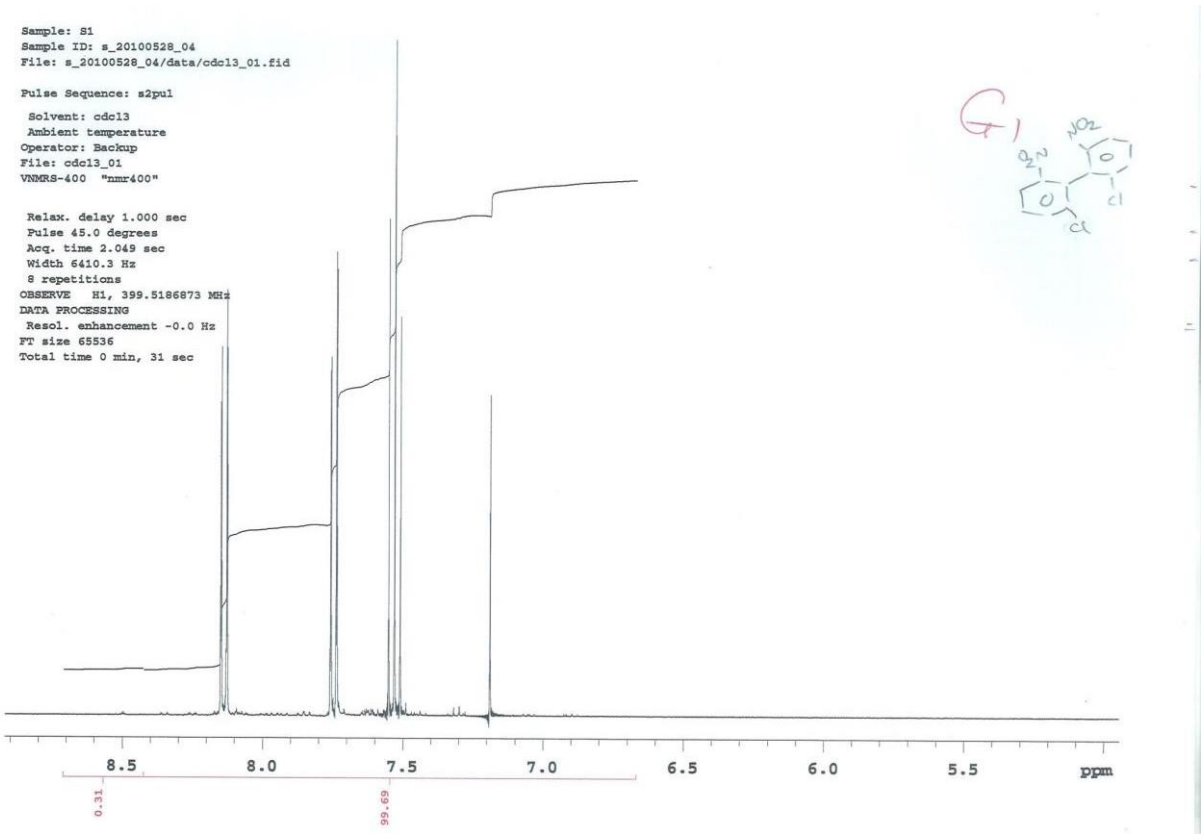


GC-MS: m/z 198, calculated: 244; found: 198 (loss of NO_2 as shown to be common for nitrated aromatic compounds by NIST).



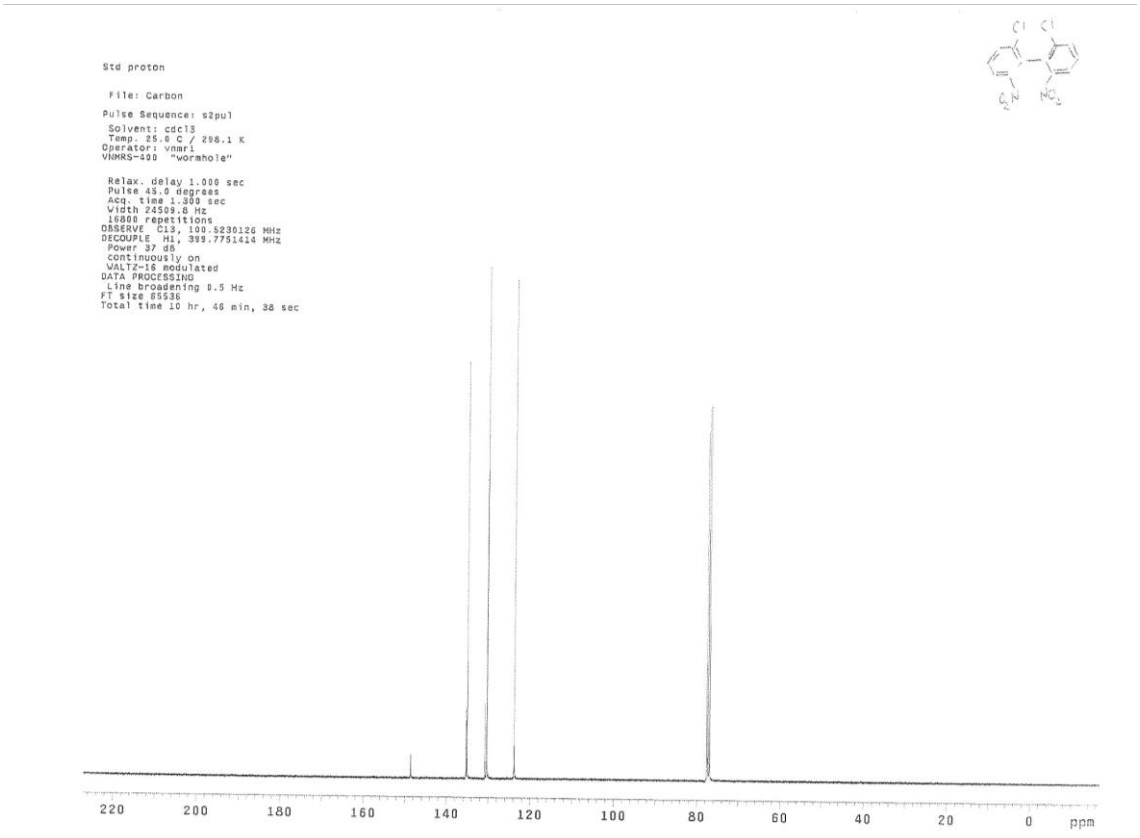
2,2'-dichloro-6,6'-dinitrobiphenyl:

^{1}H NMR (400 MHz, $CDCl_3$, TMS): □ (ppm) 7.60(t, 2H), 7.81(d, 2H), 8.22(d, 2H)

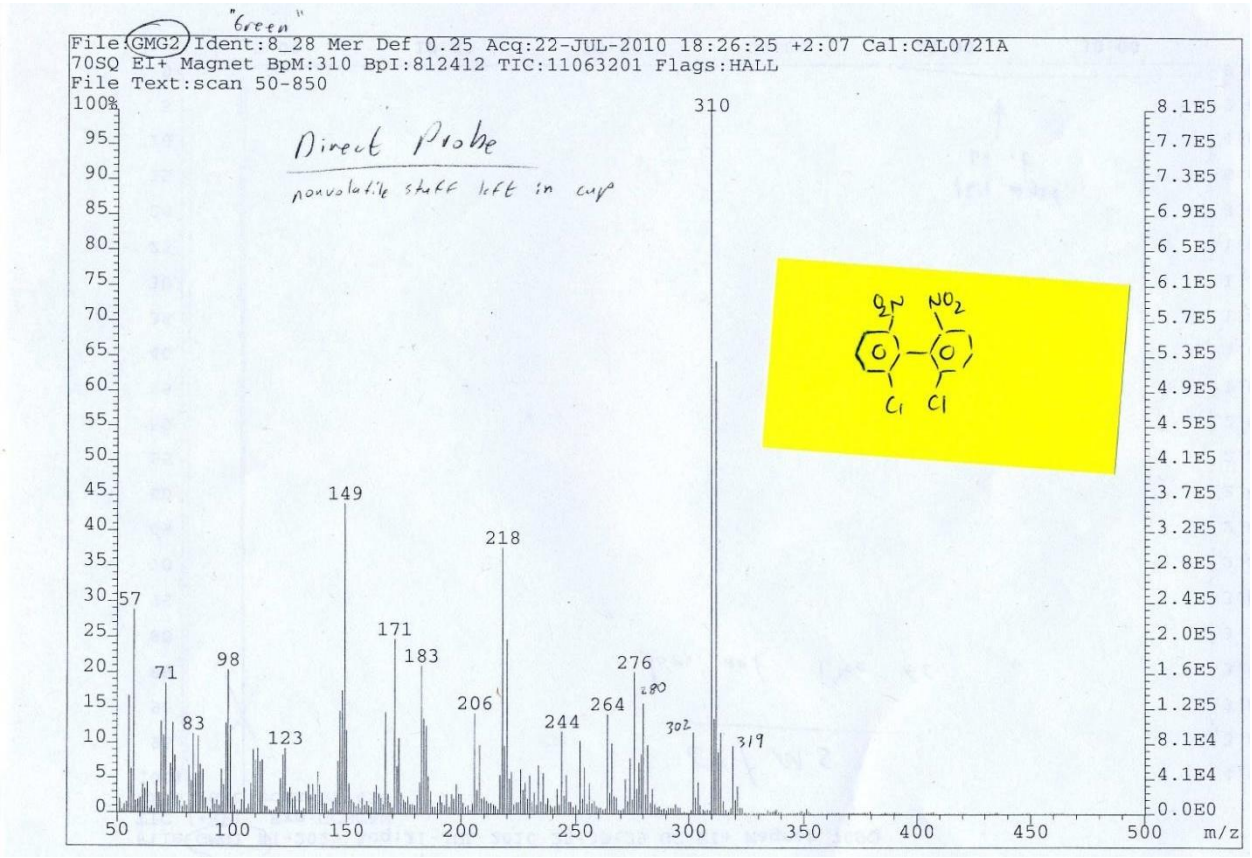


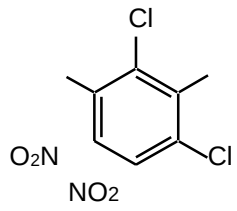
13

C NMR (400 MHz, $CDCl_3$, TMS): □ (ppm) 123.8(CH), 130.3(CH), 130.8(CAr), 135.1(CH), 135.3(CCl), 148.1(CNO_2)

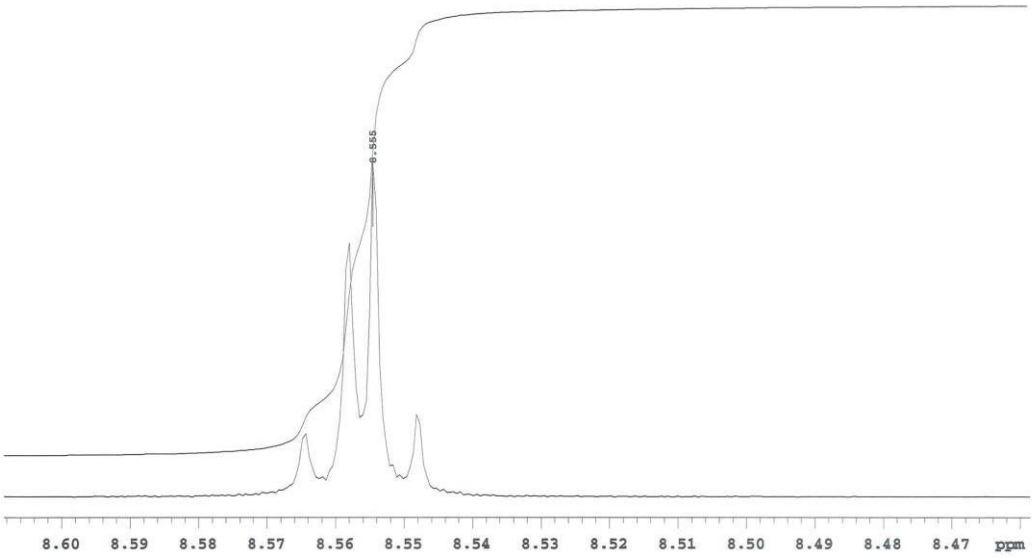


GC-MS: m/z 312, calculated: 312; found: 312

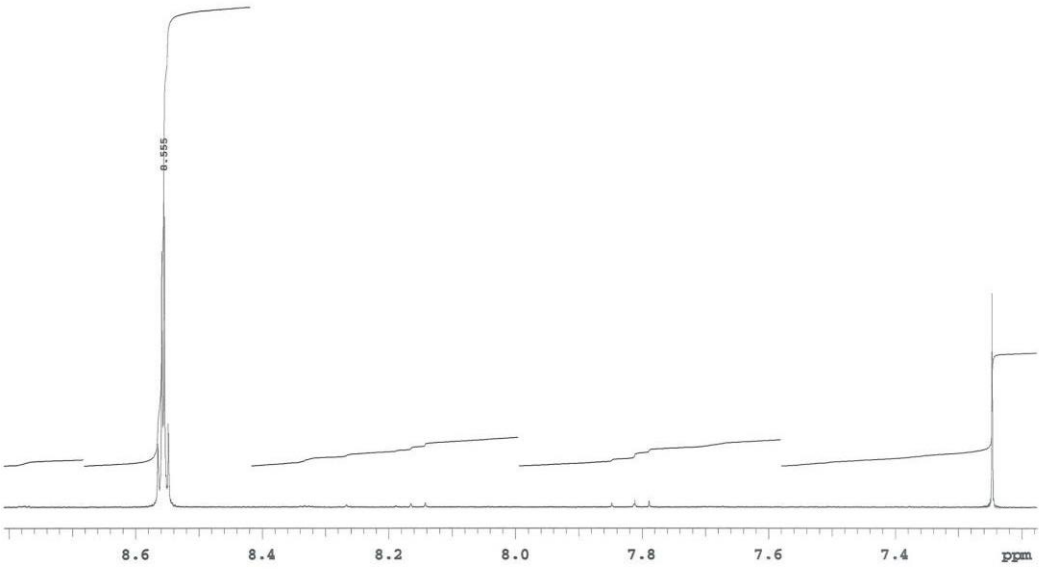




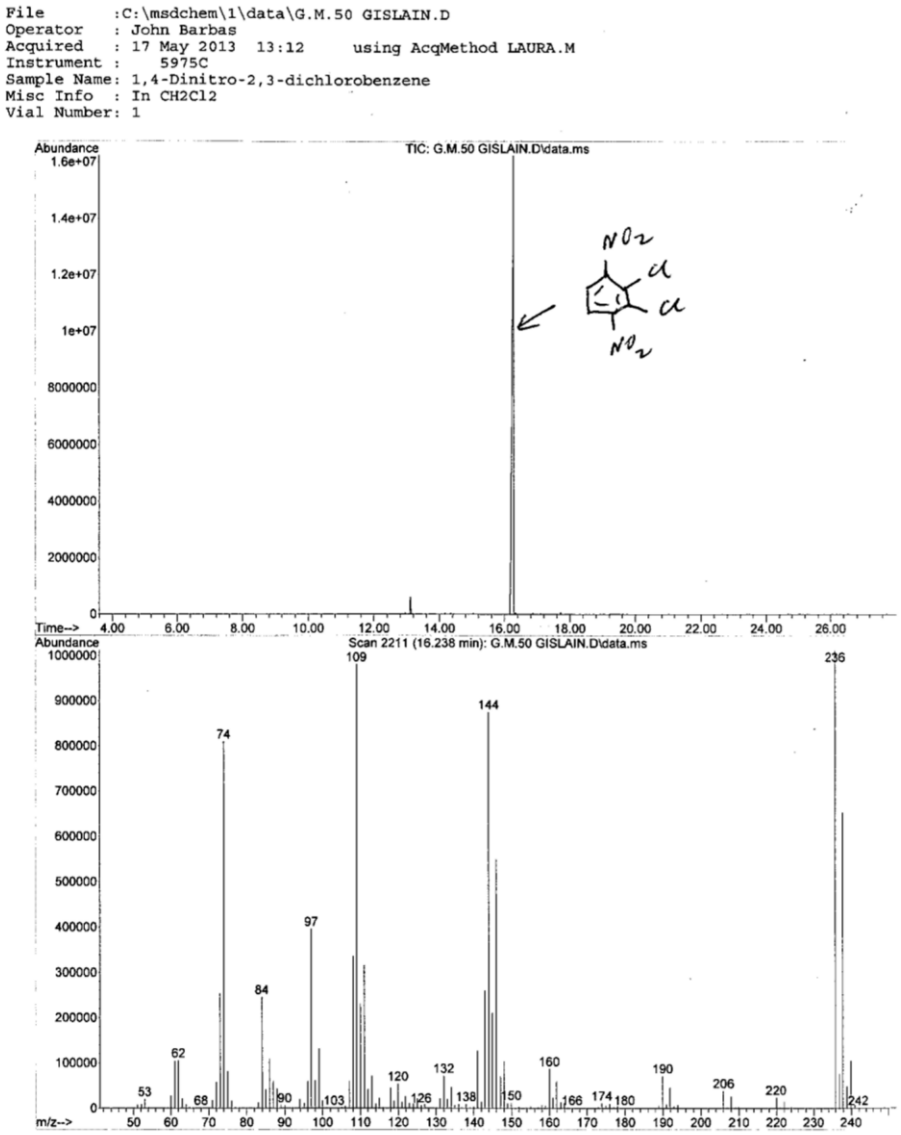
2,3-Dichloro-1,4-dinitrobenzene **3**

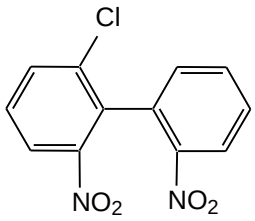


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 2.049 sec Width 6410.3 Hz 8 repetitions	OBSERVE H1, 399.5186643	DATA PROCESSING Resol. enhancement -0.0 Hz FT size 65536 Total time 1 minute	Solvent: cdcl3 Ambient temperature Operator: funmr File: Proton_20100708_cdcl3_01 VNMRS-400 "nmr400"	SAMPLE: s1 Nf2 Sample: s1 Nf2 Sample ID: s_20100708_02 File: /home/funmr/data/funmr//s1_Nf2/Pr
File: /home/funmr/data/funmr//s1_Nf2/Proton_20100708_cdcl3_01.fid				Pulse Sequence: s2pul

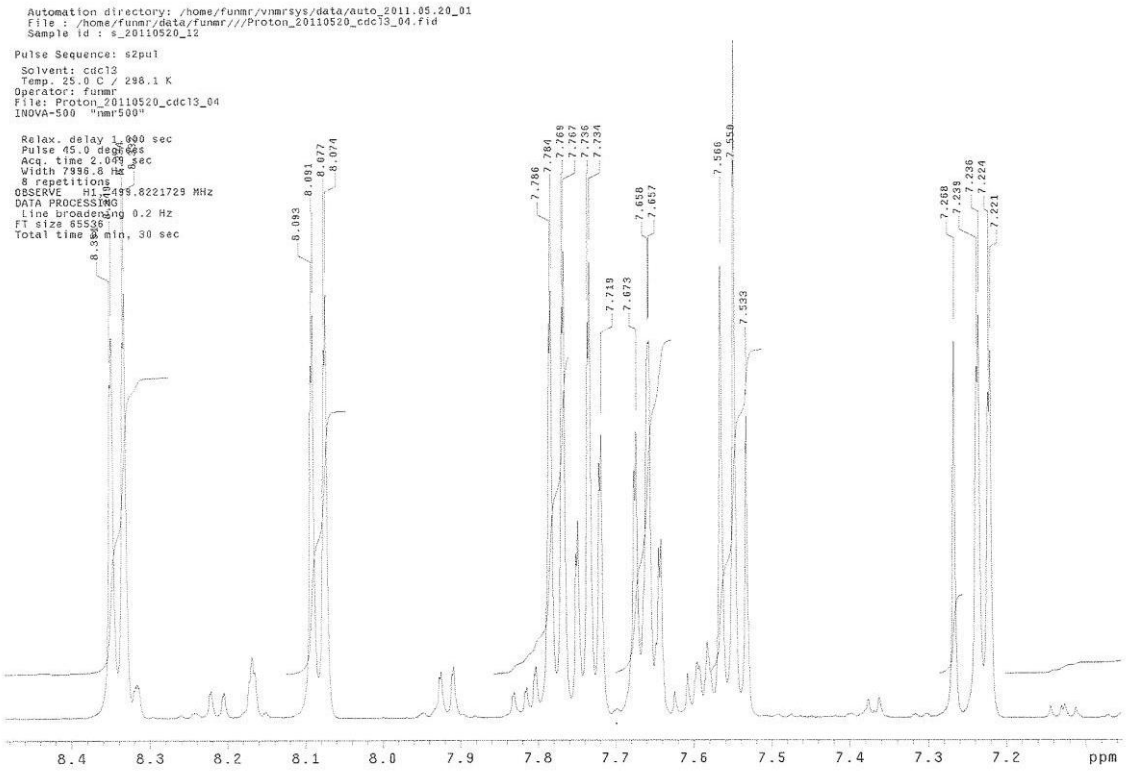


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 2.049 sec Width 6410.3 Hz 8 repetitions	OBSERVE H1, 399.5186643	DATA PROCESSING Resol. enhancement -0.0 Hz FT size 65536 Total time 1 minute	Solvent: cdcl3 Ambient temperature Operator: funmr File: Proton_20100708_cdcl3_01 VNMRS-400 "nmr400"	SAMPLE: s1 Nf2 Sample: s1 Nf2 Sample ID: s_20100708_02 File: /home/funmr/data/funmr//s1_Nf2/Pr
File: /home/funmr/data/funmr//s1_Nf2/Proton_20100708_cdcl3_01.fid				Pulse Sequence: s2pul





2-Chloro-2',6-dinitrobiphenyl **6**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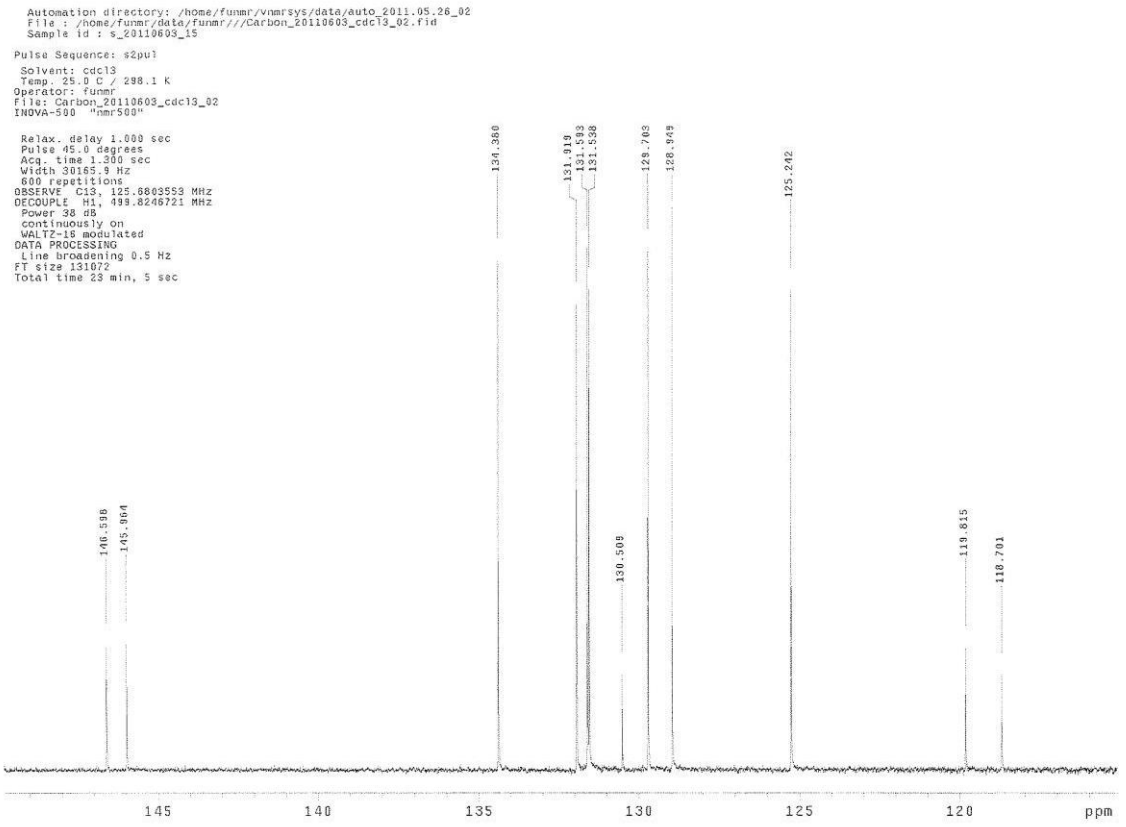
File : /home/funmr/data/funmr///Proton_20110520_cdcl3_04.fid
Sample id : s_20110520_12
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: funmr
File: Proton_20110520_cdcl3_04
INOVA-500 "nmr500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 7996.8 Hz
8 repetitions
OBSERVE H1, 499.8221729 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 30 sec
8.377
8.093
8.091
8.077
8.074
7.786
7.764
7.758
7.747
7.736
7.734
7.719
7.673
7.658
7.657
7.566
7.559
7.533
7.268
7.239
7.236
7.224
7.221
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
ppm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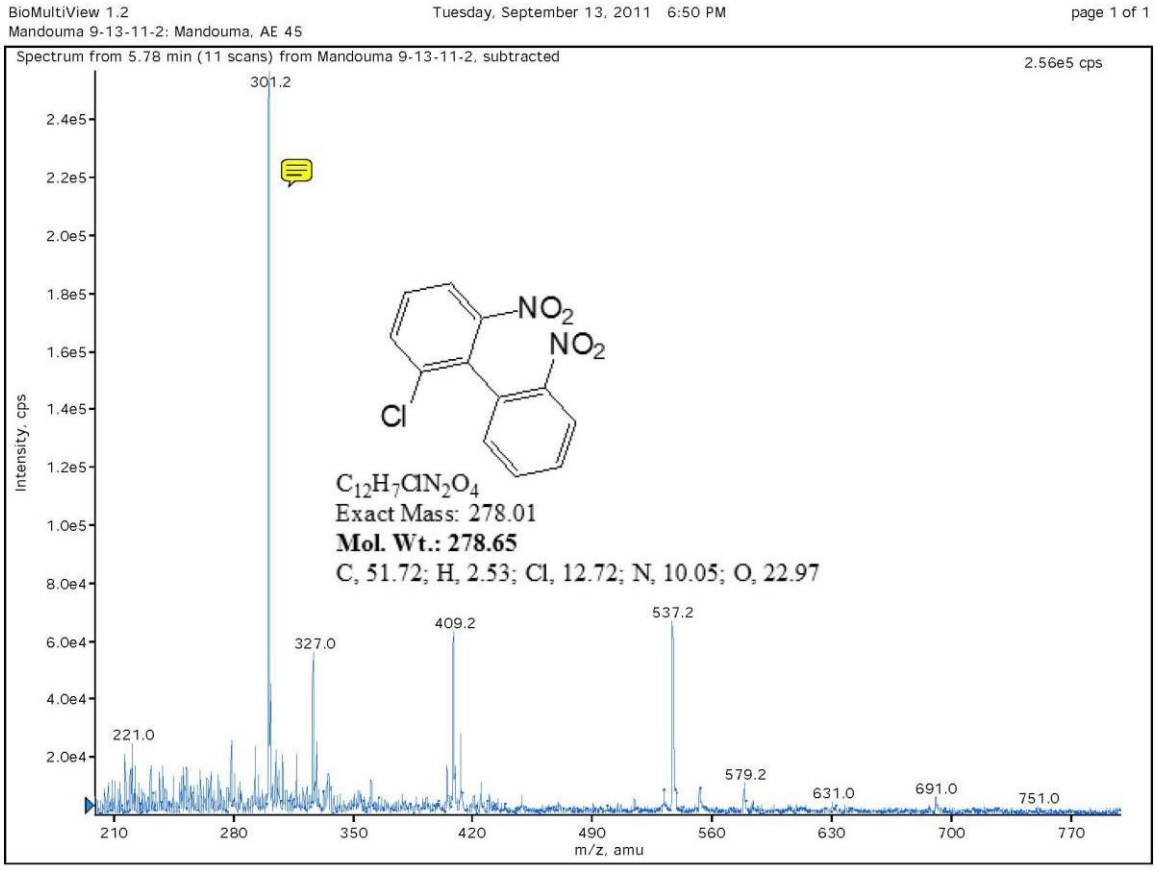
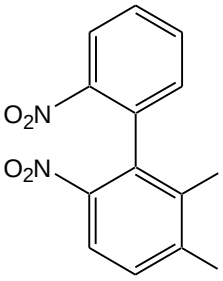
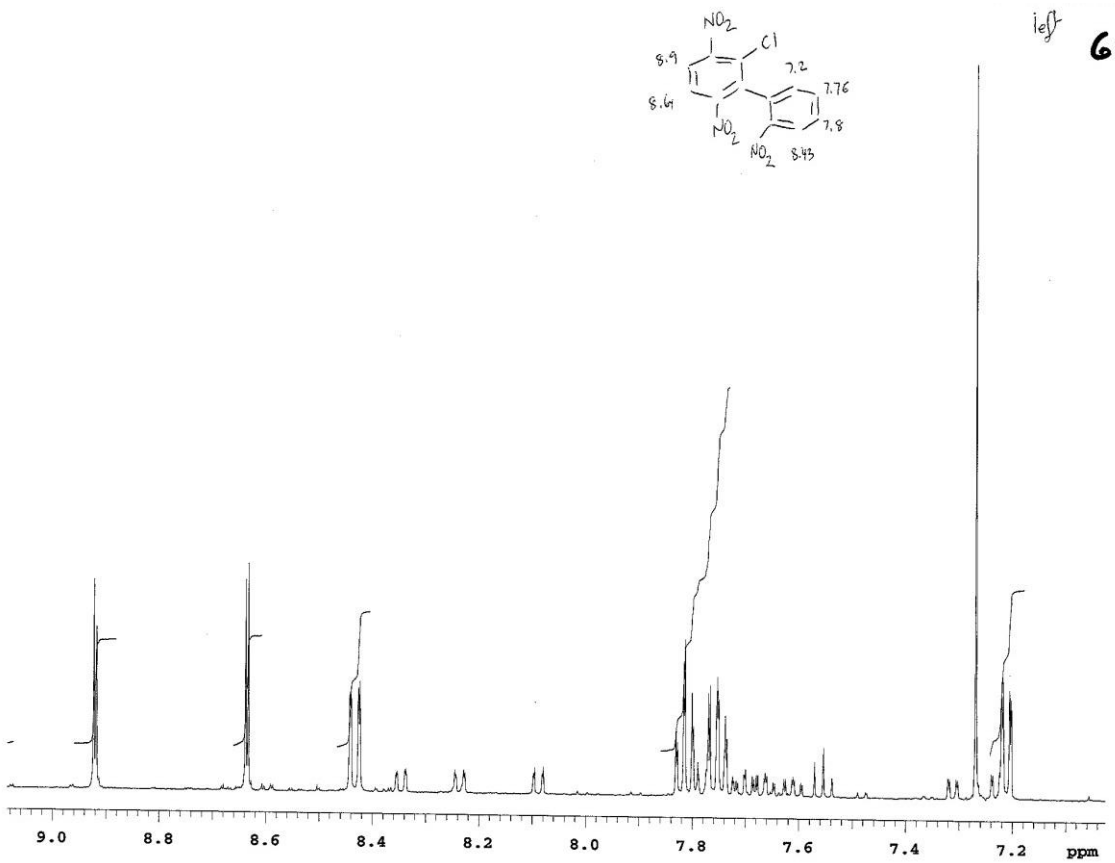
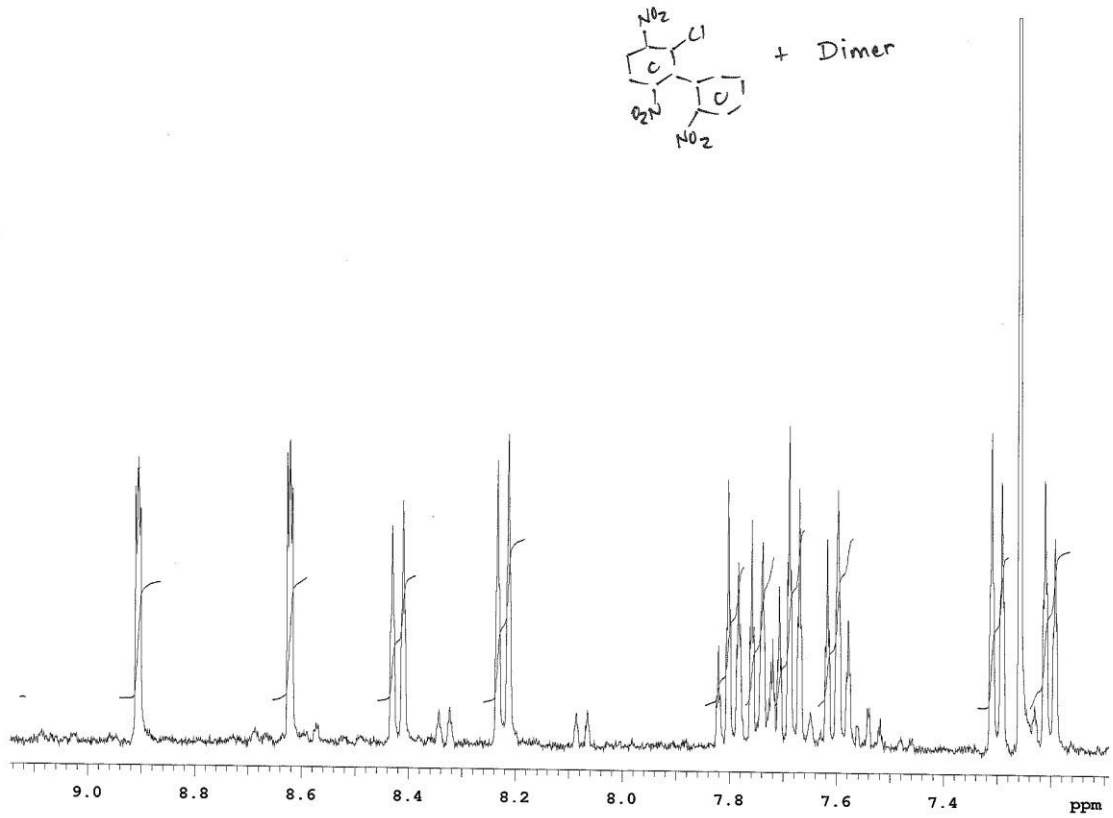
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: funmr
File: Carbon_20110603_cdcl3_02
INOVA-500 "nmr500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
600 repetitions
OBSERVE C13, 125.6803553 MHz
DECOUPLE H1, 499.8246721 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 23 min, 5 sec
146.598
145.864
134.360
131.919
131.593
131.538
130.509
129.703
128.949
125.242
119.815
118.701
145
140
135
130
125
120
ppm

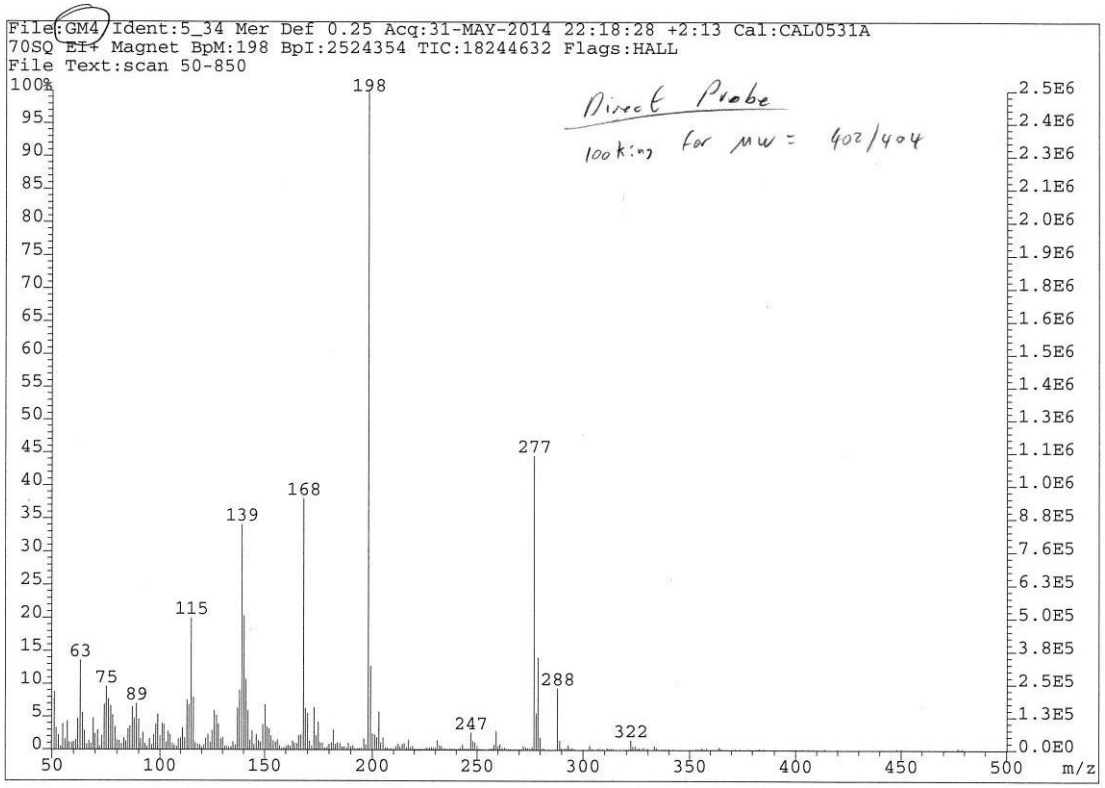


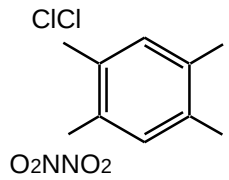


$C_{12}H_6ClN_3O_6$
Exact Mass: **322.99**
Mol. Wt.: 323.65
C, 44.53; H, 1.87; Cl, 10.95; N, 12.98; O, 29.66
Cl
NO_2
2-Chloro-2',3,6-trinitrobiphenyl **7**

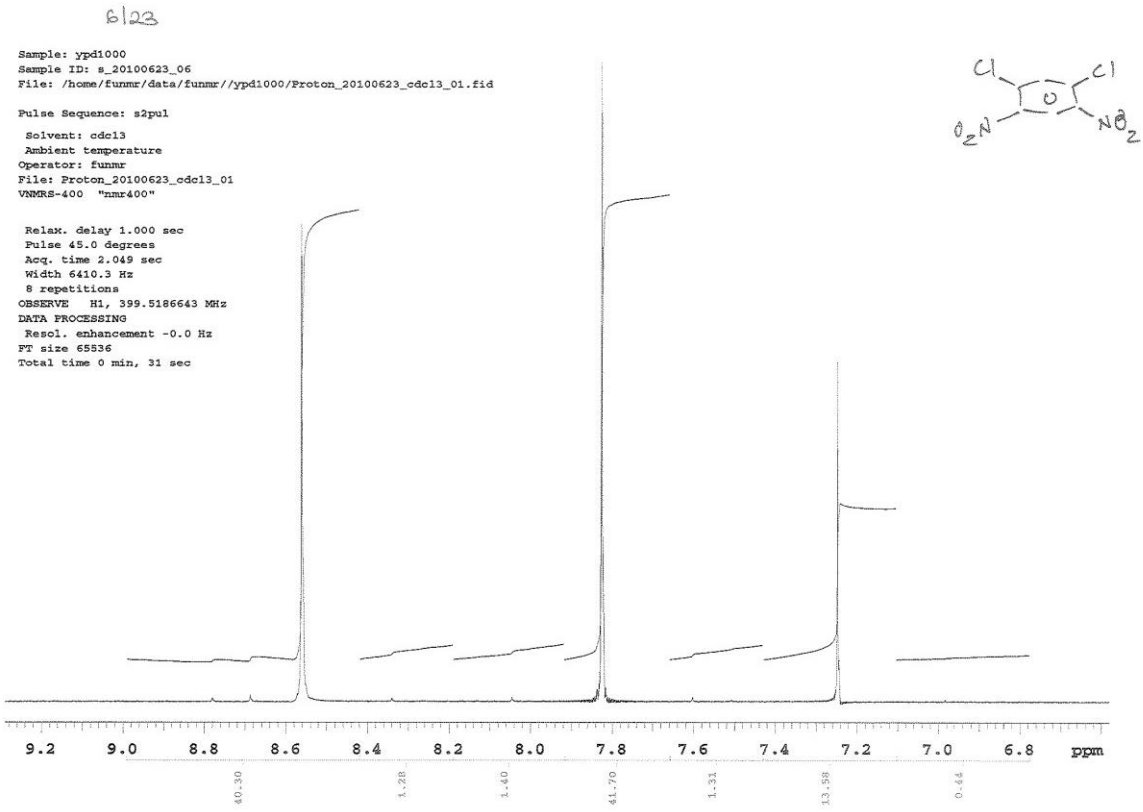

jeff
63
NO2
Cl
8.9
8.6
7.2
7.76
7.8
NO2
NO2
8.43
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm


NO2
Cl
O2N
NO2
+ Dimer
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
ppm





1,5-Dichloro-2,4-dinitrobenzene **4**


6123
Sample: ypd1000
Sample ID: s_20100623_06
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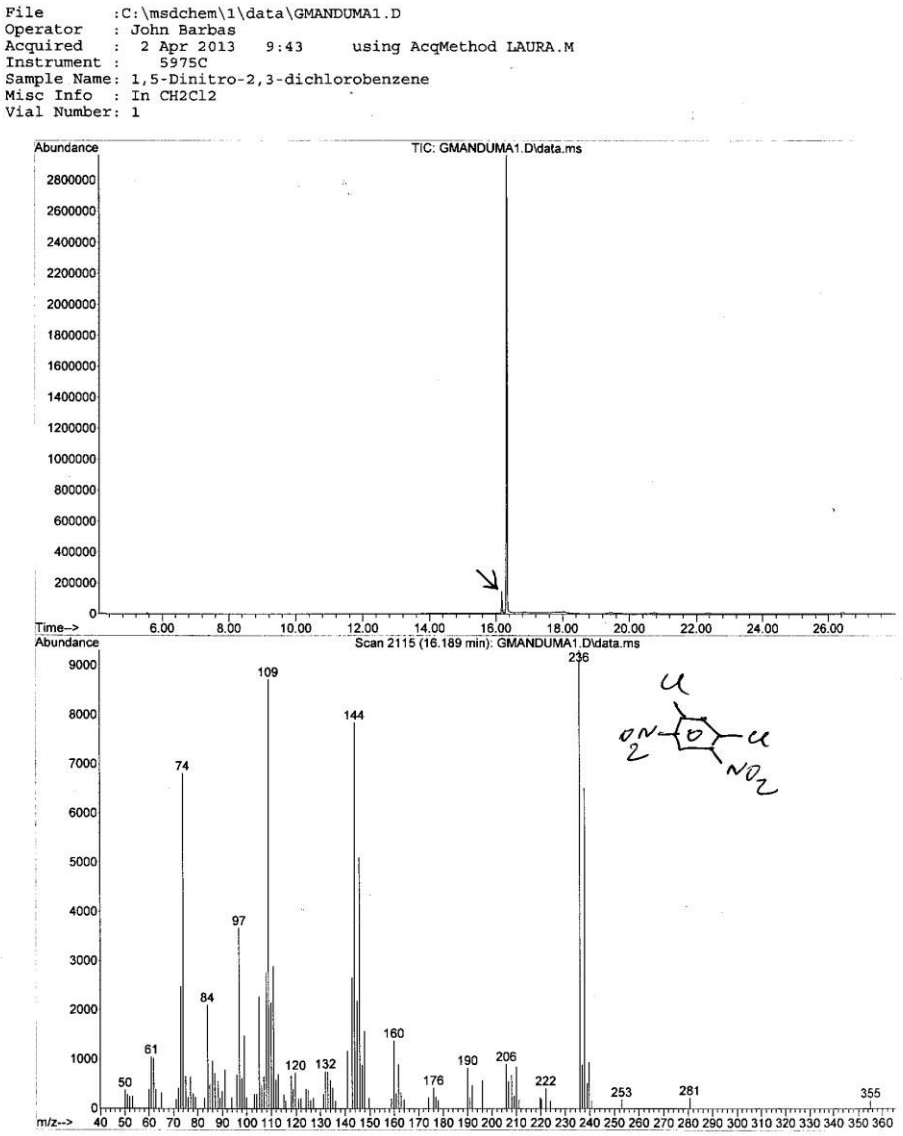
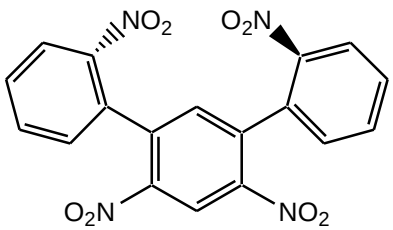
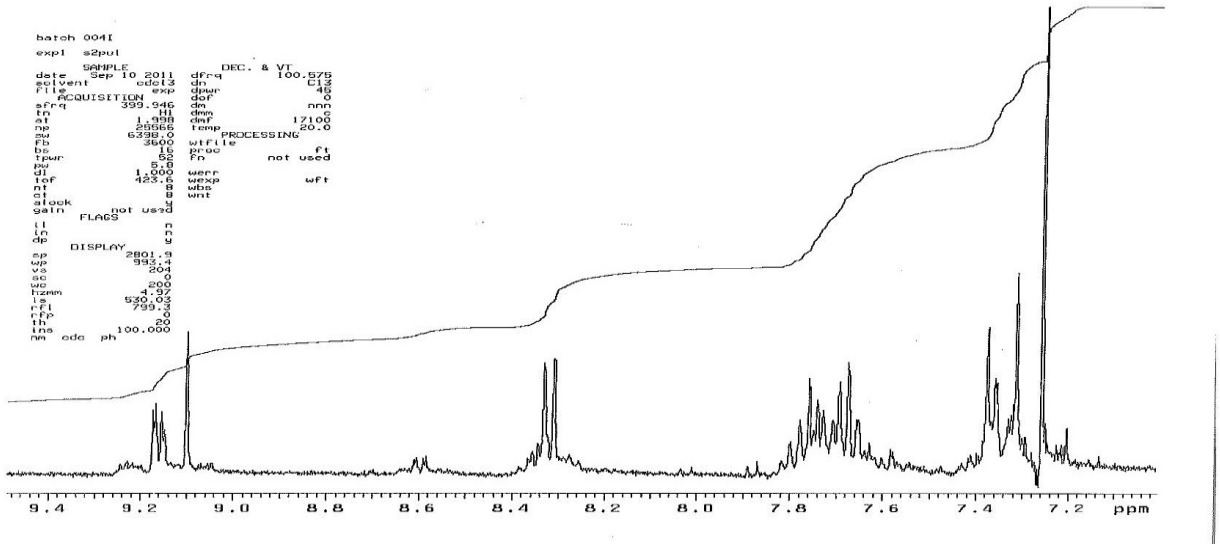
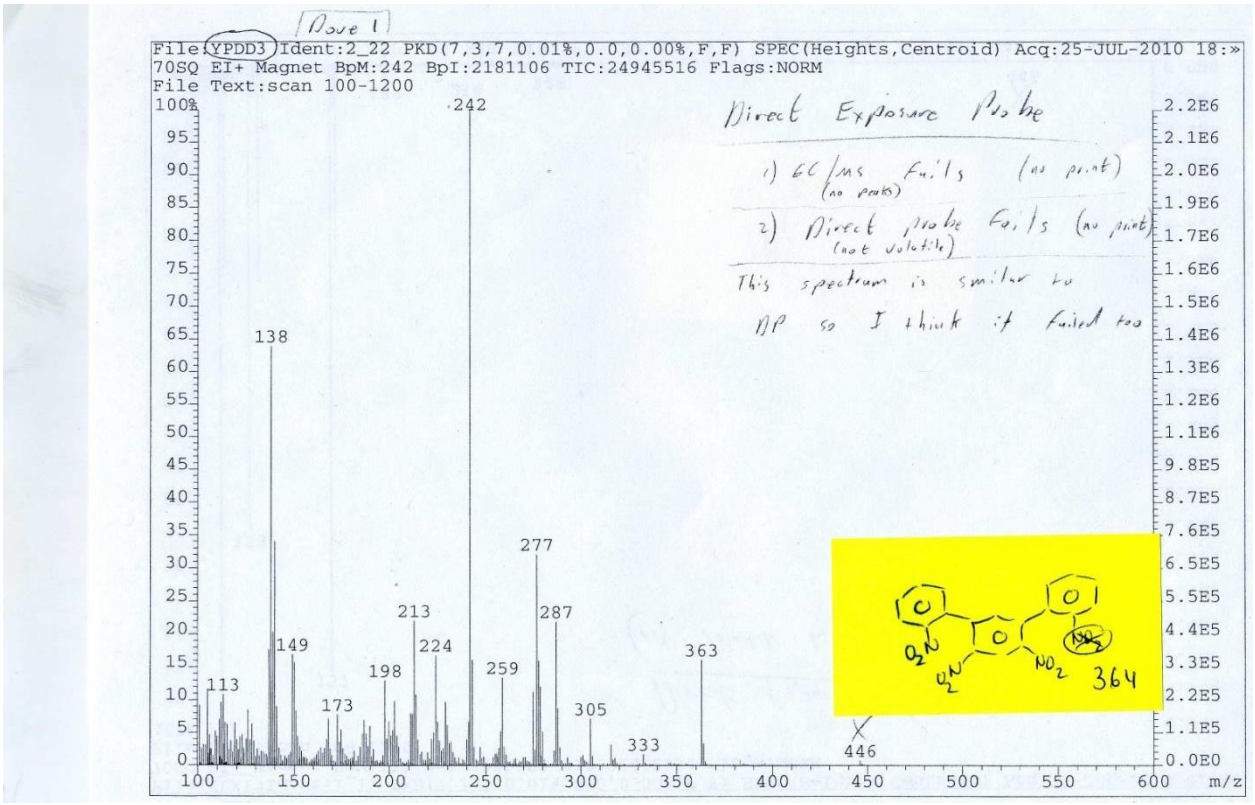
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: funmr
File: Proton_20100623_cdcl3_01
VNMRS-400 "nmr400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.5186643 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 31 sec
Cl
Cl
O
O2N
NO2
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
ppm
40.30
1.28
1.40
41.70
1.31
13.58
0.44

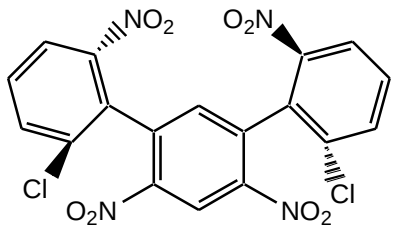




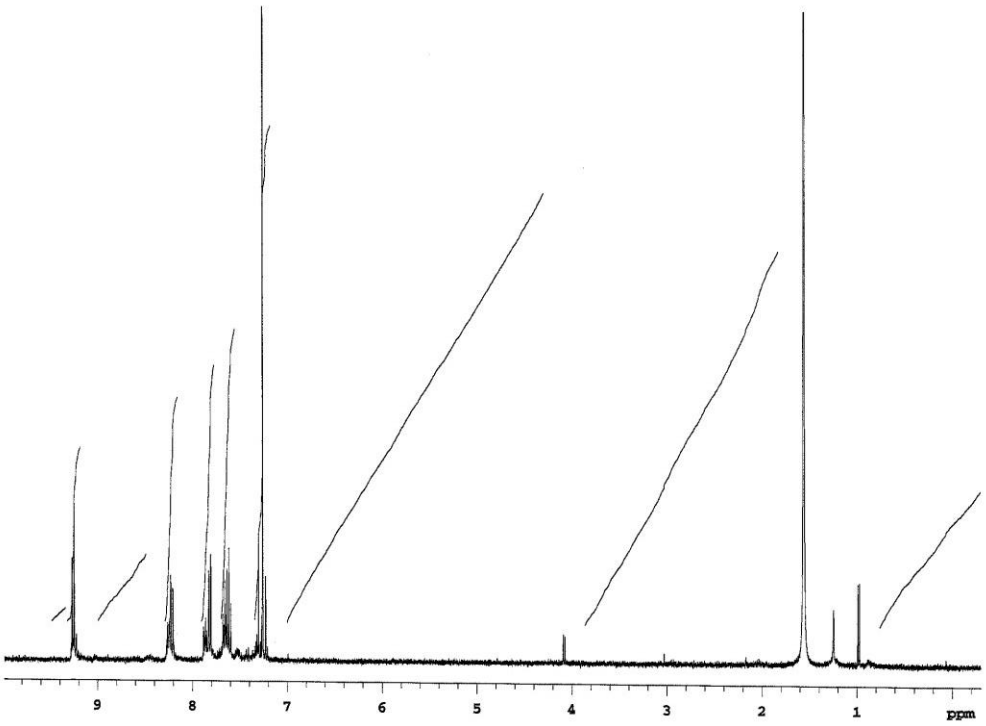
2,2',4',6"-Tetranitrotriphenyl **8**

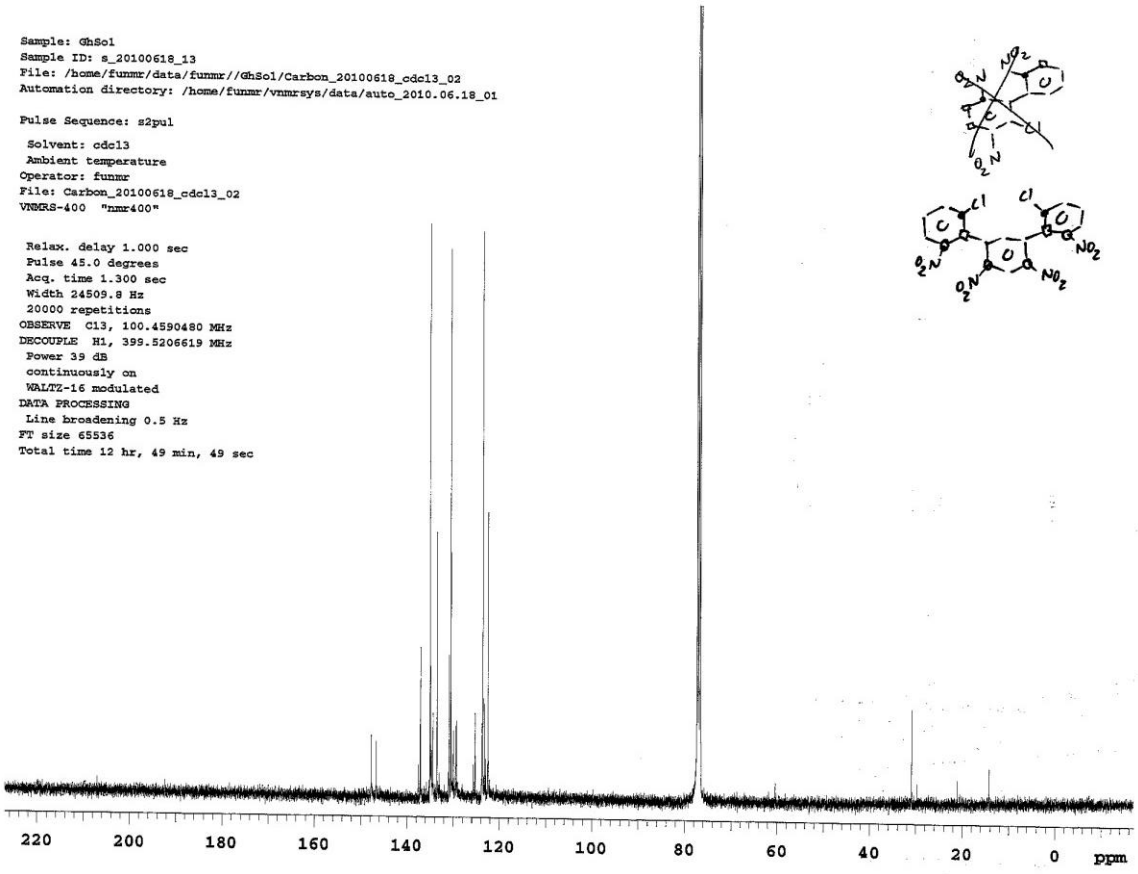






2,2''-Dichloro-2',4',6,6"-tetranitrotriphenyl **9**


9
8
7
6
5
4
3
2
1
ppm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Sample ID: s_20100618_13
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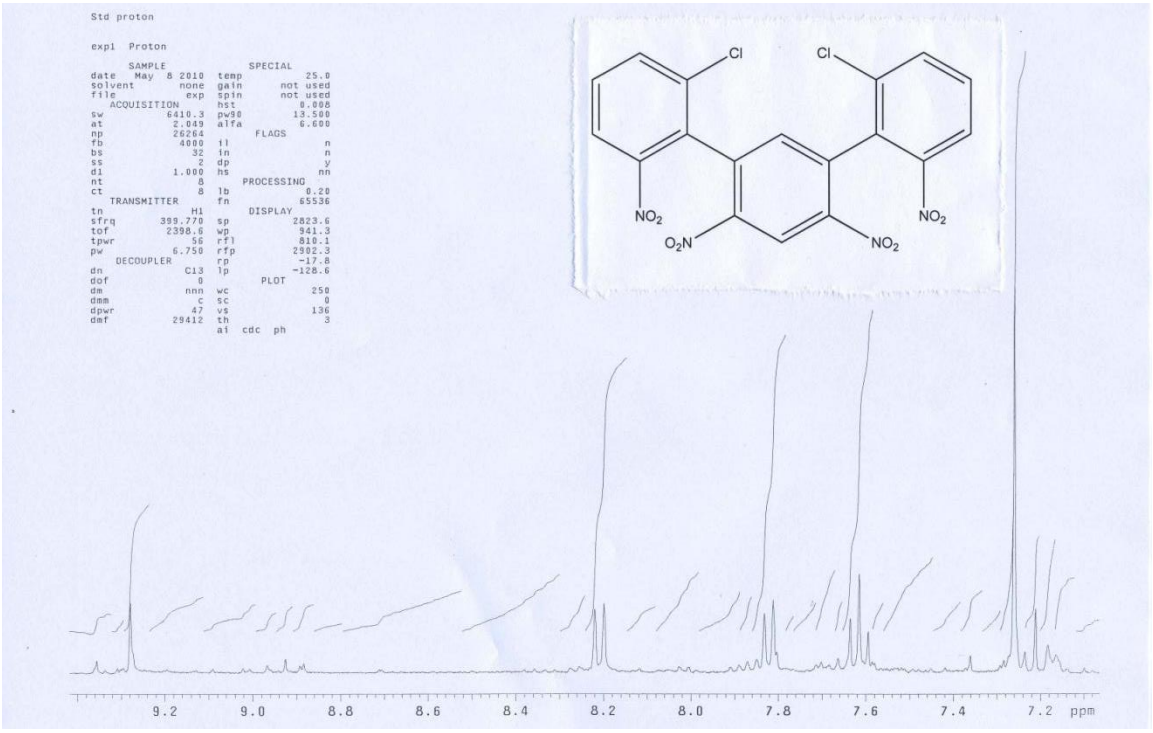
Automation directory: /home/funmr/vnmrsys/data/auto_2010.06.18_01
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: funmr
File: Carbon_20100618_cdcl3_02
VNMRS-400 "nmr400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
20000 repetitions
OBSERVE C13, 100.4590480 MHz
DECOUPLE H1, 399.5206619 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 12 hr, 49 min, 49 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Std proton
expl Proton
SAMPLE
date May 8 2010
solvent none
file exp
ACQUISITION
sw 6410.3
at 2.049
np 26264
fb 4000
bs 32
ss 2
d1 1.000
nt 8
ct 8
TRANSMITTER
tn H1
sfrq 399.770
tof 2398.6
tpwr 56
pw 6.750
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 47
dmf 29412
SPECIAL
temp 25.0
gain not used
spin not used
hst 0.008
pw90 13.500
alfa 6.600
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.20
fn 65536
DISPLAY
sp 2823.6
wp 941.3
rfl 810.1
rfp 2902.3
rp -17.8
lp -128.6
PLOT
wc 250
sc 0
vs 136
th 3
ai cdc ph
Cl
Cl
NO2
O2N
NO2
NO2
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm