AN ABSTRACT OF THE THESIS OF

Melissa Luana McIntosh for the degree of Master of Science in Chemistry presented on June 9, 2014.

Title: Synthesis, Characterization, and Analysis of Nitroaromatic Compounds

Abstract approved:

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Staci L. Massey Simonich

Nitroaromatic compounds have important chemical applications and can be found in nature as pollution sources. Synthetic nitroaromatic compounds have been used in a variety of materials including explosives, pharmaceuticals, dyes, plastics, and pesticides. These compounds can find their way into the environment through normal or improper disposal methods.

Poly-aromatic compounds are important structural motifs due to their presence in complex natural products and pharmaceutical scaffolds. Previously, the Carter laboratory has developed a Diels-Alder Approach to Biaryls (DAB), which provides access to highly functionalized poly-aromatic compounds. The extension of this methodology to the synthesis of heterocycles such as poly-aromatic triazoles and isoxazoles through the use of a [3+2] dipolar cycloaddition utilizing *o*-nitrophenylalkynes will be disclosed.

Nitro-polycyclic aromatic hydrocarbons (NPAHs) are potential carcinogenic compounds found in the atmosphere. NPAHs can be formed as byproducts of the incomplete combustion of coal, crude oil, gas, tobacco, and other organic substances. NPAHs are also formed from the reaction of the parent PAHs with atmospheric

oxidants. Due to the harmful nature of PAHs it is important to investigate the properties of the derivatized versions of these pollutants. The lack of significant quantities of NPAH's for full characterization, toxicology studies, and use as analytical standards have motivated our efforts toward the synthesis and analysis of these compounds. The direct nitration of benzo[k]fluoranthene (BKF) and benzo[ghi]perylene (BGHIP) provided separable mixtures of regioisomers. The regiochemistry and full characterization of the isolated nitrated compounds was confirmed through a variety of 1D and 2D nuclear magnetic resonance (NMR) spectroscopic techniques, infrared (IR) spectroscopy, high-resolution mass spectroscopy (HRMS), and gas chromatography mass spectroscopy (GC-MS). Prep HPLC on isolated compounds provided 99% pure samples as shown by GC-MS. These samples were submitted for Ames testing. A generalized method to access nitrated BKF derivatives employs palladium cross-coupling reactions to bring together strategically designed naphthalene components.

Synthesis, Characterization, and Analysis of Nitroaromatic Compounds

by
Melissa Luana McIntosh

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APPROVED:

Major Professor, representing Chemistry

Chair of the Department of Chemistry

Dean of the Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Melissa Luana McIntosh, Author

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CHAPTER 1: INTRODUCTION

Section 1.1. Nitroaromatic Compounds

Nitroaromatic compounds have important chemical applications and can be found in nature as pollution sources. Synthetic nitroaromatic compounds have been used in a variety of materials including explosives, pharmaceuticals, dyes, plastics, and pesticides.[1,2,3] These compounds can then find their way into the environment through normal or improper disposal methods. Contributing to nitroaromatic pollutants are nitrated polycyclic aromatic hydrocarbons (NPAHs). NPAHs are formed from incomplete combustion of natural or anthropogenic sources. Illustrative examples of a few different types of these nitroaromatics are presented in Figure 1.1.1.

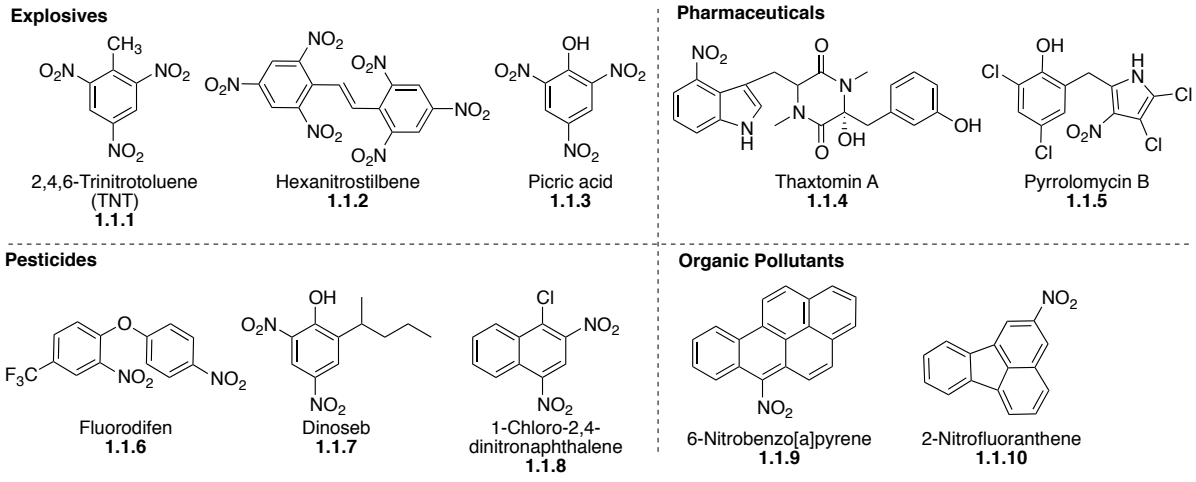
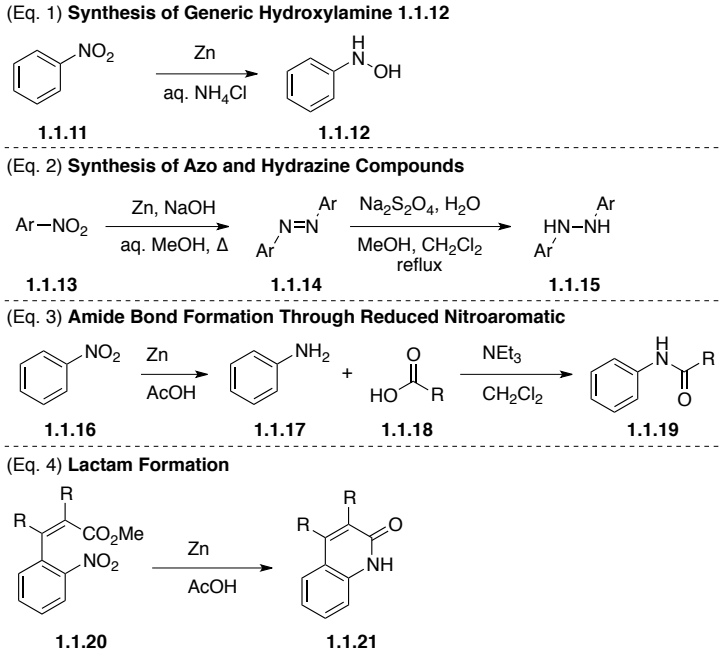


Figure 1.1.1. Examples of Nitroaromatic Compounds

Nitroaromatic compounds can also be utilized to achieve larger functionalized molecules. The nitro moiety is a useful functional handle that provides access to

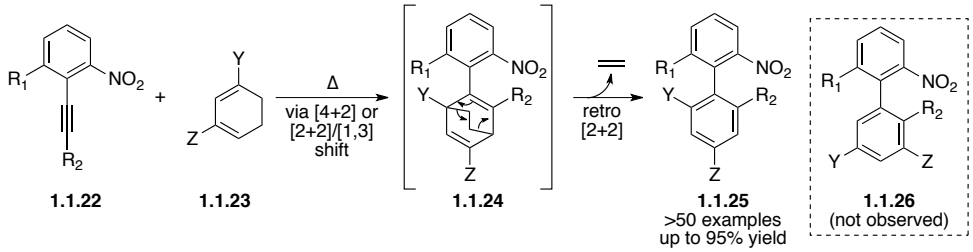
hydroxylamines, azo compounds, hydrazines, amines, amides or lactams (Scheme 1.1.1). Hydroxylamines can be formed from nitroaromatic compounds through a reaction with zinc and aqueous ammonium chloride (Scheme 1.1.1, Equation 1).[4] Nitroaromatics can also form azo compounds,[5] which can be further reduced to aryl hydrazines (Scheme 1.1.1, Equation 2).[6] Nitroaromatics can undergo reduction to produce aromatic amines (Scheme 1.1.1, Equation 3).[7] These amines can then be reacted with carboxylic acids to form amides (Scheme 1.1.1, Equation 3).[8] The formation of lactams is also possible, in one pot, from reduction of a tethered *ortho*-nitro moiety and ester moiety with zinc in acetic acid (Scheme 1.1.1, Equation 4).[9] The multiple transformations that the nitro group can participate in make it an excellent substituent for further functionalization of a molecule.

Scheme 1.1.1. Nitroaromatic Transformation Reactions



Another exciting application of the nitro moiety is shown through previous work in the Carter laboratory, which focused on a Diels-Alder approach to construct highly substituted biaryl scaffolds (Scheme 1.1.2).[10] The strategy employed an electron-deficient aryl alkyne, which included the *ortho*-nitrophenyl alkyne. This process was highly regioselective and provided access to tetra-*ortho*-substituted biaryl compounds. The *o*-nitro moiety is most likely responsible for the regioselectivity and unpredictability of this reaction sequence. The steric congestion of the *ortho* substituents on the aromatic ring was inconsequential due to the electron withdrawing nature of the *o*-nitro moiety overriding the inherent steric bias. Over 50 products were constructed through this method. Other comparative reactions, using the *para*-nitrophenyl alkyne, were also explored. Interestingly, this modification was not beneficial to the yield of the process.[10e] The mechanism of this transformation is likely via the formation of [2.2.2]-bicyclic intermediate **1.1.24** (Scheme 1.1.2) postulated by the Carter group[10] and others.[11] We hypothesized that the *ortho*-nitro moiety on the aromatic ring is critical in directing the regioselectivity of this process because of the highly regioselective outcome.

Scheme 1.1.2. Diels Alder Approach to Biaryls



Polycyclic aromatic hydrocarbons (PAHs), which are known organic pollutants, have been shown to contain nitro substituents as well. PAHs and NPAHs are formed in

the environment from partial combustion of diesel fuel or organic matter. NPAHs can also be formed through reaction of the parent PAH with environmental oxidants. [12] PAHs are an environmental concern because of their potential persistence in the environment and their ability to undergo long-range atmospheric transport.[13] PAHs have been found in remote regions, such as the Arctic,[14,15] which are nowhere near potential pollution sources. The presence of the nitro group on PAHs was shown to increase the toxicity of these compounds.[12] Our group was particularly interested in the higher molecular weight nitrated PAHs (Figure 1.1.2), since there is limited data in the literature on these compounds.

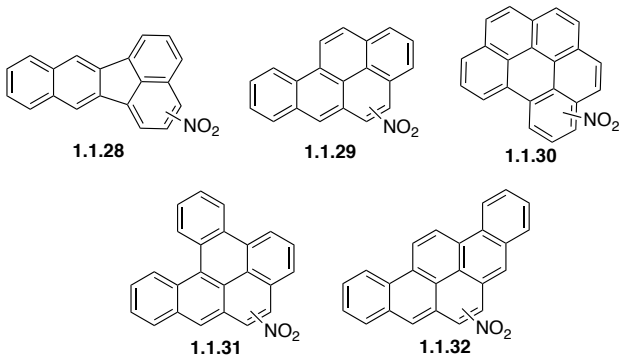


Figure 1.1.2. High Molecular Weight Nitrated Polycyclic Aromatic Hydrocarbons

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CHAPTER 2: SYNTHESIS OF DENSELY FUNCTIONALIZED TRIAZOLES USING *ORTHO*-NITROPHENYLALKYNES

Section 2.1. Triazole Background

Triazoles can be found in a variety of compounds and are very important in agriculture and medicines due to their antifungal properties. Albaconazole, fluconazole,[1] itraconazole,[1] posaconazole, ravuconazole, terconazole and voriconazole are all antifungal medicines, which contain triazoles (Figure 2.1.1).[2] The triazole functionality in these fungicides work by inhibiting the biosynthesis of ergosterol. This occurs through the nitrogen moiety of the triazole binding to cytochrome P-450 and inhibiting the α14-demethylase enzyme, which is needed to transform lanosterol into ergosterol. In agriculture, the use of triazole fungicides has been utilized to ensure the survival of important crops. These fungicides include epoxiconazole, prothioconazole, metconazole and tebuconazole (Figure 2.1.2)[3] and have been used as protection against *Fusarium* head blight in wheat caused by the fungal pathogen *Gibberella zeae* (teleomorph) also known as *Fusarium graminearum* (anamorph).[4]

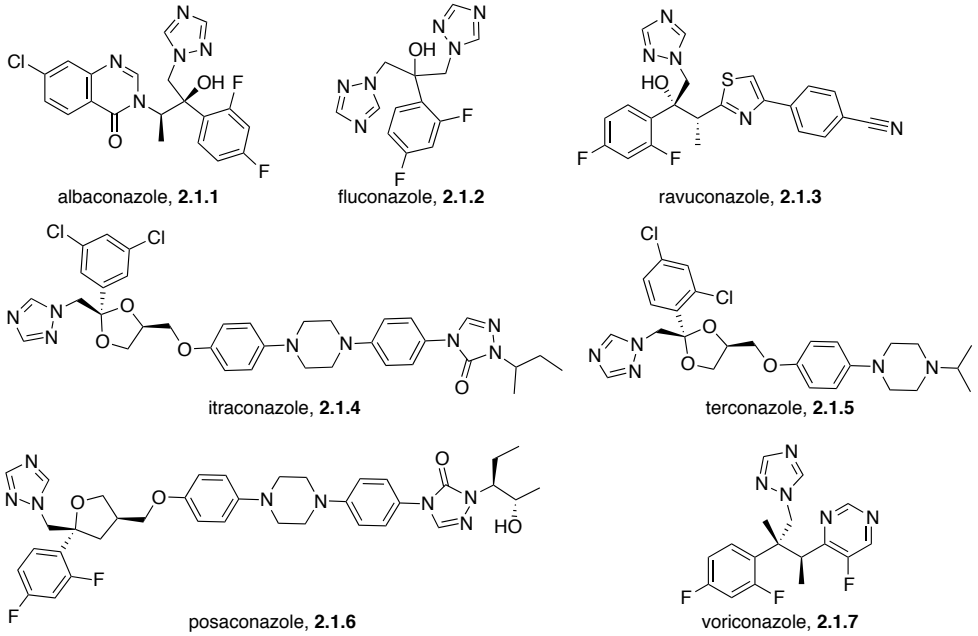


Figure 2.1.1. Antifungal Medicine

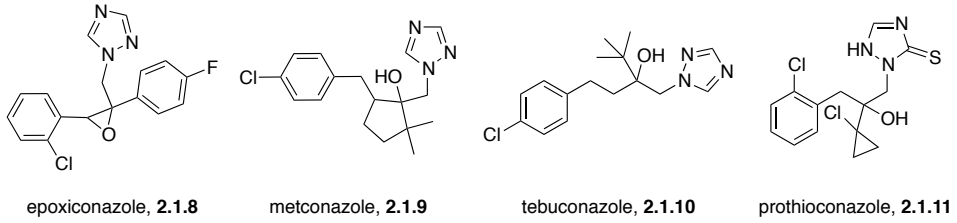
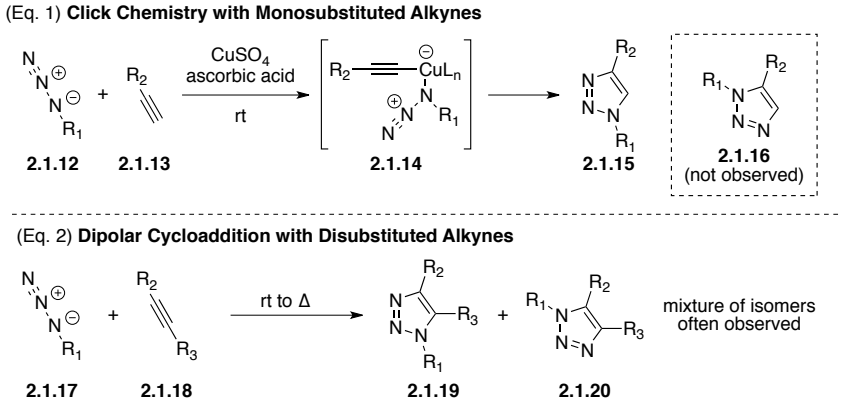


Figure 2.1.2. Fungicides Used in Agriculture

Triazoles have also gained interest in the synthetic community due to the nature of their formation through [3+2] cycloadditions. There has been interest in these dipolar cycloadditions since their discovery in the 1960's by Robert Huisgen.[5] "Click" chemistry has become the gold standard approach to access triazoles.[6] The copper catalyzed reaction of azides with terminal alkynes is shown in Scheme 2.1.1, Equation 1. Numerous research fields utilize "Click" chemistry, such as polymer chemistry, materials science,[7] chemical biology,[8] bioorthogonal synthesis,[9] and pharmacology.[10] This reaction

provides excellent regioselectivity for the 1,4-triazole. Ruthenium-based catalysis has been shown to reverse the selectivity to provide the 1,5-triazole.[11,12] These methods are generally ill-suited for disubstituted alkynes. Disubstituted alkynes can be accessed through copper free dipolar cycloadditions (Scheme 2.1.1, Equation 2). Controlling regioselectivity of the metal-free reactions, however, has remained a challenge.

Scheme 2.1.1. Alkyne/Azide Dipolar Cycloadditions

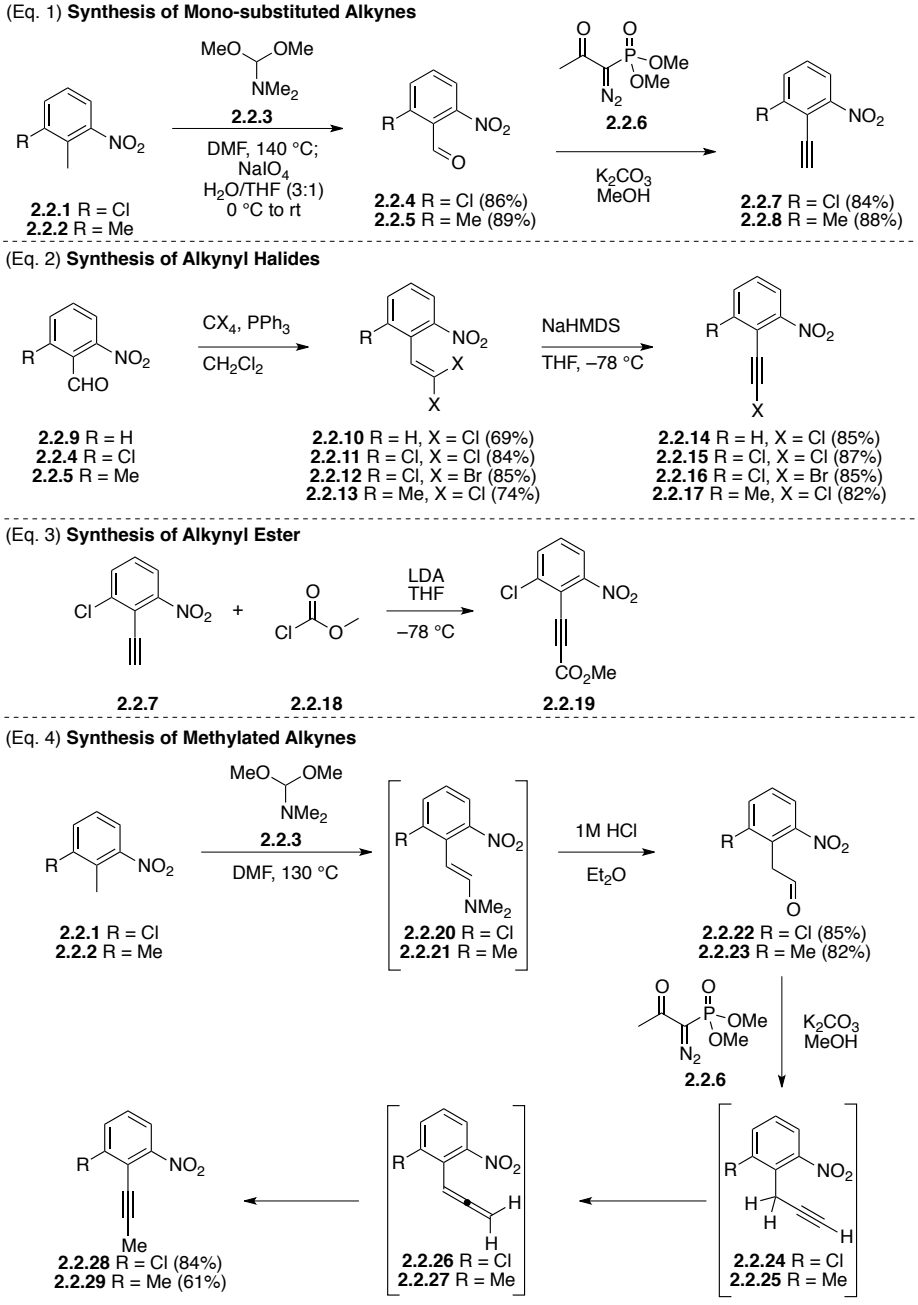


Section 2.2. Results and Discussion

In our synthetic work towards densely functionalized triazoles, the syntheses of the starting acetylenes were accomplished following standard literature procedures. Mono-substituted alkynes were obtained from the corresponding nitro-toluene using the conditions shown in Scheme 2.2.1, Equation 1.[13] The alkynyl halides were obtained using the Corey-Fuchs olefination[14] of the known aldehydes **2.2.4, 2.2.5** and **2.2.9**[13,15] followed by NaHMDS-mediated elimination of the dihalides **2.2.10-2.2.13**[16,17] in high yield (Scheme 2.2.1, Equation 2). The halogenated alkynes were stored at –30 °C and protected from light. As expected, the chloro alkynes **2.2.14**,[18] **2.2.15**, and **2.2.17** were

more stable than bromo alkyne **2.2.16**. The synthesis of the alkynyl ester is shown in Scheme 2.2.1, Equation 3. Reaction of acetylene **2.2.7** with LDA, followed by addition of methyl chloroformate **2.2.18** at –78 °C, provided alkynyl ester **2.2.19** in high yield.[13c] Synthesis of methylated acetylenes performed by previous group members followed Scheme 2.2.1, Equation 4.[19] Standard alkylation methods to obtain methylated acetylenes were unreliable, which prompted the development of a new method to access these acetylenes (Scheme 2.2.1, Equation 4) using unconjugated aldehydes. Unconjugated aldehydes **2.2.22** and **2.2.23** were obtained in high yields, upon hydrolysis of enamines **2.2.20**[20] and **2.2.21,** through divergence of our standard pathway to access aldehydes such as aldehyde **2.2.4**.[13b,21] The desired methylated compounds **2.2.28** and **2.2.29** were obtained in good yields after treatment of aldehydes with the Ohira-Bestmann reagent **2.2.6**.[22] The mechanism of this transformation most likely proceeds via the unconjugated alkynes **2.2.24** and **2.2.25**, which first undergo base catalyzed isomerization to allenes **2.2.26** and **2.2.27** before finally resting as aryl alkynes **2.2.28** and **2.2.29**.

Scheme 2.2.1. Synthesis of Alkynyl Substrates

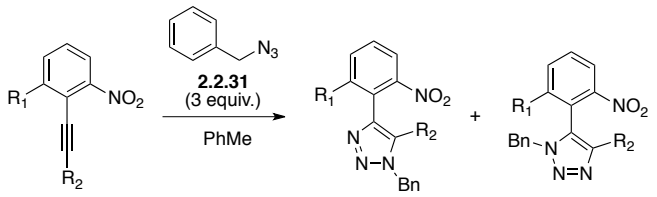


Our lab utilized the *ortho*-nitrophenylalkynes and azides in a heated [3+2] cycloaddition to access a variety of densely functionalized triazoles. The alkynes

screened in this transformation can be categorized as monosubstituted alkynes (a-c), disubstituted alkynes (d-g), and halogenated alkynes (h-k) as seen in Table 2.2.1. The exploration of the cycloadditions with the monoalkynes began with the simple *o*-nitrophenylacetylene **1.1.22**. This reaction had not been preformed previously, however, Feringa and co-workers were able to obtain triazole **2.2.32a** in 63% yield, with excellent selectivity using a phosphoramidate-accelerated copper-catalyzed reaction.[23] This group found that reactions with electron deficient alkynes, like **1.1.22**, provided low yields and sluggish reaction times. Our cycloaddition (entry a) provided a very good yield (84%) for the system, but the regioselectivity was poor (3.4:1). When utilizing "Click" conditions ($CuSO_4$, ascorbic acid, and *t*-BuOH/H_2O (1:1), rt) for the transformation, as expected, only one regioisomer (**2.2.32a**) was observed in comparable yield (79%) to the thermal transformation. Similarly, the reaction of 2-chloro-6-nitrophenylalkyne (entry b) resulted in poor regioselectivity (2:1) and only moderate yield (59%). This was contradictory to what was previously observed by our group for the thermal cycloadditions using these alkynes to form biaryl compounds.[13] Substitution of a chlorine for a methyl group on the aromatic ring provided a decrease in reaction time, with similarly low regioselectivity (2.3:1). Again, use of "Click" conditions provided a single regioisomer in excellent yield (98%). Access to the 1,4-triazole through click chemistry for the monosubstituted alkynes is by far a superior route to the thermal cycloaddition strategy employed herein. The regioselectivity of the disubstituted alkynes (entries d-g) was comparable to what was observed for monosubstituted alkynes as well. It is

important to note, however, that standard "Click" conditions cannot be explored with disubstituted alkynes due to the mechanism constraints of the reaction (Scheme 2.1.1, Equation 1). X-ray crystallography was used to confirm the structure of **2.2.33e**. Of the disubstituted alkynes, ester alkyne **2.2.19** (entry f) was the most selective, providing 3.2:1 regioselectivity (**2.2.32f** :**2.2.33f**) with an overall yield of 92%. The synthesis of tertiary alcohol **2.2.34** (entry g) was very slow and low yielding with no selectivity, which was in contrast to the observed reactivity and selectivity in the biaryl project. The final group of compounds explored in the thermal [3+2] cycloadditions was the halogenated alkynes. These halogenated compounds have the potential for rapid derivatization providing triazole templates. A concurrent computational study performed by the Cheong group[19] indicated a likely increase in selectivity with use of the halogenated alkynes. The halogenated alkynes did indeed provide higher regioselectivities for all reactions (entries h-k). Halogenated alkyne **2.2.14** provided a 5.7:1 rr with a 67% yield (entry h). The reaction required a high temperature of 120 °C and 48 h to complete, which could account for the reduced selectivity. Substitution of an *o*-methyl group for the *o*-chloro provided similar selectivity (entry i). Doubly halogenated alkynes **2.2.15** and **2.2.16** proved to be more activated and provided the highest regioselectivity (9:1), with moderate yields (64-72%) (entries j-k), for these thermal dipolar cycloadditions. Thus, the halogenated alkynes can be utilized to access high regioselectivity for these transformations.

Table 2.2.1. Scope of Azide Dipolar Cycloaddition with *o*-Nitrophenyl Acetylenes



Entry	R_1	R_2	Time (h)	Temp (°C)	Yield (%)	Ratio (**2.2.32:2.2.33**)
a	H	H	48	80	84 (79)[a]	3.4:1 (1:0)[a]
b	Cl	H	26	80	59	2:1
c	Me	H	96	80	79 (98)[a]	2.3:1 (1:0)[a]
d[b]	Me	Me	72	120	43	1:1
e[b]	Cl	Me	24	120	65	2:1
f	Cl	CO_2Me	24	80	92	3.2:1
g	Cl	$C(OH)Ph_2$	45	120	51	1:1
h	H	Cl	48	120	67	5.7:1
i[b]	Me	Cl	24	120	68	7:1
j	Cl	Cl	70	80	72	9:1
k	Br	Br	72	80	64	9:1

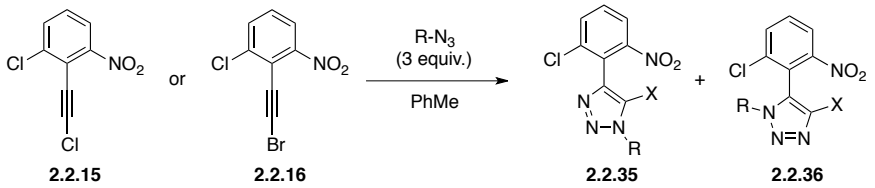
(a) reaction conditions: Cu_2SO_4, ascorbic acid, *t*-BuOH:H_2O (1:1), rt.

(b) reaction performed by previous group member

Halogenated alkynes **2.2.15** and **2.2.16** provided the highest regioselectivities of the substrates screened in the thermal dipolar cycloadditions with benzyl azide. Because

of this selectivity, they were suitable substrates for briefly exploring the scope of substituted azide reactivity (Table 2.2.2). Cinnamyl azide provided comparable regioselectivity with the chloro alkyne **2.2.15** (11:1, entry a), but regioselectivity was significantly reduced with the bromo alkyne **2.2.16** (4:1, entry b). The use of phenyl azide showed a significant decrease in yield and little regioselectivity for both bromo- and chloroalkynes. The final azide screened, *tert*-butyl azidoacetate, provided high regioselectivities (9:1) for both alkynes (entries e-f), but only provided modest yields (37-58%).

Table 2.2.2. Brief Exploration of the Scope of Azide Reactivity in the Cycloaddition

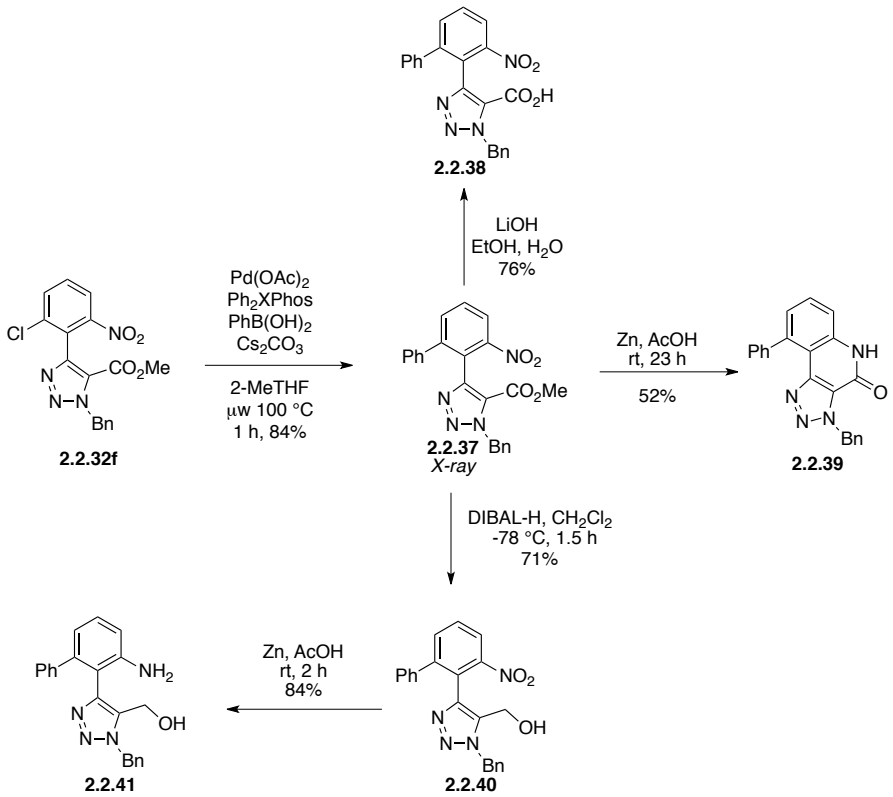


2.2.15 **2.2.16** **2.2.35** **2.2.36**

Entry	Alkyne	R	X	Time (h)	Temp (°C)	Overall yield (%)	Ratio (**2.2.35:2.2.36**)
a	**2.2.15**	(*E*)-PhCH=CHCH$_2$-	Cl	48	80	49	11:1
b	**2.2.16**	(*E*)-PhCH=CHCH$_2$-	Br	29	80	69	4:1
c	**2.2.15**	Ph	Cl	72	80	36	2:1
d	**2.2.16**	Ph	Br	53	120	24	1:1
e	**2.2.15**	*t*-BuO$_2$CCH$_2$-	Cl	48	80	37	9:1
f	**2.2.16**	*t*-BuO$_2$CCH$_2$-	Br	48	80	58	9:1

The use of aryl halides in Suzuki coupling reactions is a well-known procedure.[24] In order to explore this utility, previously reported boroxines and Organ's catalyst (PEPPSI-IPr) were examined.[13g,25] For the case of the ester containing compound **2.2.32f** Buckwald's Ph_2X-Phos ligand,[26] phenylboronic acid, and $Pd(OAc)_2$ conditions proved to be more appropriate (Scheme 2.2.2). Also, microwave irradiation provided more efficient heating for completion of the reaction. X-ray crystallography was used to confirm the Suzuki coupling product **2.2.38**. An important observation in the use of unpurified commercial "phenylboronic acid" is the significant amount of boroxine present as seen by NMR spectroscopy. One can speculate that the boroxine plays an important role in the coupling transformation. Subsequent derivatization of the highly aromatic scaffold **2.2.37** is shown in Scheme 2.2.2. The reduction of the ester **2.2.37** to the corresponding carboxylic acid **2.2.38** (76%) is reported. Nitro reduction of **2.2.37** using Zn/HOAc acid conditions provided the lactam **2.2.39** in moderate yield (52%). Alcohol **2.2.40** was obtained via reduction of the ester moiety with DIBAL-H. Subsequent reduction of the nitro group of alcohol **2.2.40** with Zn/HOAc provided the amino alcohol **2.2.41** in 60% yield over two steps.

Scheme 2.2.2. Derivativization of Triazoles



Section 2.3. Conclusion

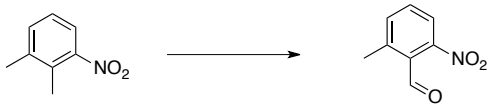
The utility of dipolar cycloadditions using *o*-nitrophenylalkynes was demonstrated on a variety of substrates. The regioselectivity of the triazole compounds was highly dependent on the dipolarophile, with the highest regioselectivities being seen for the halogenated alkynes. Concurrent computational work showed comparable regioisomeric ratios to the observed regioisomeric ratios for the cycloaddition products. The regioselectivity is thought to come from a combination of steric and electronic effects. Derivatization of the scaffolds was possible and was demonstrated to provide densely functionalized triazole templates.

Section 2.4. Experimental Section

General. Infrared spectra were recorded neat unless otherwise indicated and are reported in cm^{-1}. ^{1}H NMR spectra were recorded in deuterated solvents and are reported in ppm relative to tetramethylsilane and/or referenced internally to the residually protonated solvent. ^{13}C NMR spectra were recorded in deuterated solvents and are reported in ppm relative to tetramethylsilane and/or referenced internally to the residually protonated solvent.

Routine monitoring of reactions was performed using EM Science DC-Alufolien silica gel, aluminum-backed TLC plates. Flash chromatography was performed with the indicated eluents on EM Science Gedurian 230-400 mesh silica gel.

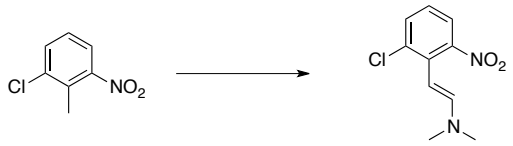
Air and/or moisture sensitive reactions were performed under usual inert atmosphere conditions. Reactions requiring anhydrous conditions were performed under a blanket of argon, in glassware dried in an oven at 120°C or by flame, then cooled under argon. Dry THF, Toluene and DCM were obtained via a solvent purification system. All other solvents and commercially available reagents were either purified via literature procedures or used without further purification.



2.2.2 **2.2.5**

Aldehyde 2.2.5: To a stirred solution of **2.2.2** (4.56 g, 4.00 mL, 30.17 mmol) in DMF (75 mL) was added *N*,*N*-dimethylformamide dimethyl acetal (DMF•DMA) (10.8 g,

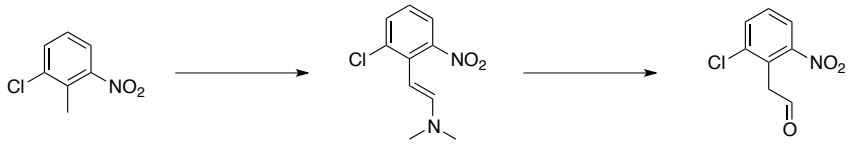
12.0 mL, 90.3 mmol). After heating at 140°C for 72 h, the dark red solution was cooled to rt and added quickly to a rapidly stirred solution of $NaIO_4$ (21.04 g, 98.37 mmol) in H_2O (74 mL) and DMF (24 mL) at 0°C. The reaction flask was washed with DMF (5 mL) at 0°C and added to $NaIO_4$ mixture. The reaction was stirred at 0°C for 2 h, before warming to rt. The orange solution was filtered and rinsed with Et_2O (200 mL). The filtrate was then washed with H_2O (3 x 25 mL) and sat. aq. NaCl (3 x 25 mL). The dried (Na_2SO_4) extract was concentrated *in vacuo* to a dark red oil and purified via flash chromatography over silica gel, eluting with 10-30% Et_2O/Hexanes gave known aldehyde **2.2.5**[15] (4.390 g, 26.58 mmol, 89%) as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.99 (dd, J = 1.5, 7.5 Hz, 1H), 7.65-7.50 (m, 2H), 2.45 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.4, 148.7, 139.2, 137.0, 131.9, 131.3, 121.9, 19.4 ppm.



2.2.4 **2.2.20**

Enamine 2.2.20: To a stirred solution of **2.2.4** (3.855 g, 22.46 mmol) in DMF (50 mL) was added *N*,*N*-dimethylformamide dimethyl acetal (DMF•DMA) (8.07 g, 9.00 mL, 67.75 mmol). After heating at 140°C for 16 h, the dark red solution was cooled to rt and diluted with Et_2O (200 mL) and washed with HCl (2 x 50 mL, 10% v/v), sat aq. $NaHCO_3$ (2 x 50 mL), and sat aq. NaCl (2 x 5 mL). The dried (Na_2SO_4) extract was concentrated *in vacuo* to give **2.2.20** (4.940 g, 111.0 mmol, 97%) as a red oil. IR (thin

film, cm^{-1}) 3081, 2847, 2808, 1634, 1585, 1524, 1378, 1101, 952, 866, 835, 774, 752, 723; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 - 7.32 (m, 2H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 13.8 Hz, 1H), 5.10 (d, *J* = 13.8 Hz, 1H), 2.86 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 145.5, 133.0, 132.1, 131.9, 123.1, 122.1, 86.9, 39.3 ppm. HRMS (EI+) calcd. for $C_{10}H_{11}N_2O_2Cl$ (M+) 226.0509, found 226.0508.

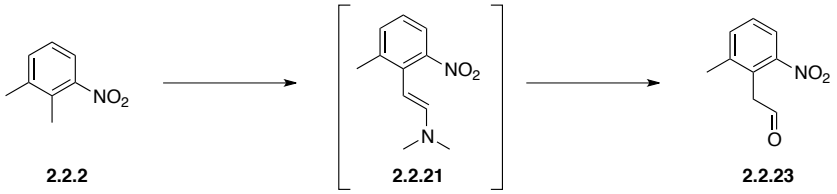


2.2.4 **2.2.20** **2.2.22**

2-(2'-Chloro-6'-nitrophenyl)acetaldehyde (**2.2.22**): A 2-L, single necked, round-bottomed flask, equipped with a powder funnel and magnetic stirring bar, was charged with DMF (1-L) and 2-chloro-6-nitrotoluene **2.2.4**, (69.74 g, 406.5 mmol, 1 equiv.). *N,N*-Dimethylformamide dimethylacetal (162 mL, 1.22 mol, 3 equiv.) was added via syringe to the yellow solution. The powder funnel was replaced by a Fredrichs condenser and the mixture was brought to 135°C in a silicon oil bath over 2 hours. The reaction was covered with aluminum foil to aid heating. After 18 hours, the reaction evolved to a brick red solution and showed complete conversion via TLC. The mixture was cooled to room temperature over 2 hours, and then carefully poured over 2 min into a rapidly, mechanically stirred, ice-cooled solution of sat. aq. $NaHCO_3$ (500 mL) and Et_2O (500 mL) in a 2-L Erlenmeyer flask. After 15 min, the solution was transferred to a separatory funnel and let settle for 15 min. A 1-L portion of the mixture was collected in an Erlenmeyer flask, and the remaining solution in the separatory funnel was washed

with 5% aq. $NaHCO_3$ (4 x 300 mL). The ethereal partition was collected and set aside. The previously collected 1-L portion was transferred to a separatory funnel and extracted with ether (3 x 400 mL) via separatory funnel. The ethereal partitions were combined and concentrated via rotary evaporation (38°C, 28 mmHg) to give enamine **2.2.20**[20] as a dark red liquid.[27]

A 2-L, three necked, round-bottomed flask, equipped with a mechanical stirrer, yellow poly-cap and powder funnel, was immersed in a ice-cold water bath, and charged with the red enamine **2.2.20** oil and diluted with Et_2O (300 mL). To the solution was added 1 M HCl (300 mL), and the powder funnel was replaced by a 90° gas inlet adapter open to the air. The mixture was allowed to warm to rt over 2.5 hours with *vigorous* stirring. The biphasic solution was transferred to a 2-L separatory funnel and the ethereal partition was collected. The aqueous partition was acidified to pH = 1 with 3M HCl and was extracted with MTBE (2 x 200 mL). The ethereal partitions were combined and washed with 10% aq. $NaHCO_3$ (2 x 50 mL), H_2O (100 mL), and brine (2 x 50 mL), dried over Na_2SO_4, filtered and concentrated via rotary evaporation (38°C, 28 mmHg) and then under high vacuum (50°C, 0.50 mmHg) to provide aldehyde **2.2.22** as a red oil (69.34 g 347.4 mmol, 85%). IR (thin film) 3432, 2844, 2733, 1731, 1580, 1351, 1109, 1019, 876, 802, 730, 667 cm^{-1}; 1H NMR (300 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.97 (dd, J = 8.4, 1.2 Hz, 1H), 7.74 (dd, J = 8.4, 1.2 Hz, 1H), 7.46 (t, J = 8.4, 1H), 4.31 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.5, 150.8, 137.1, 134.3, 129.0, 126.8, 123.5, 44.5 ppm; HRMS (EI+) calcd. for $C_8H_7NO_3Cl$ (M+) 200.0114, found 200.0117.

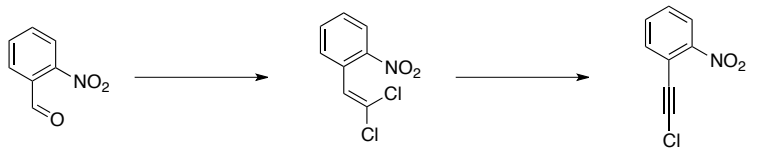


2.2.2 2.2.21 2.2.23

Aldehyde 2.2.23: To a stirred solution containing **2.2.2** (5.26 g, 6.00 mL, 34.8 mmol) and DMF (80 mL), was added *N,N*-dimethylformamide dimethylacetal (14.0 mL, 12.6 g, 105.7 mmol) was added via syringe to the yellow solution and heated to 140°C. After 24 hours, the reaction evolved to a brick red solution and cooled to room temperature, and quenched with aq. $NaHCO_3$ (200 mL, 5% w/v) and extracted with Et_2O (3 x 150 mL). The ethereal partition were combined and concentrated *in vacuo* to give enamine **2.2.21** as a dark red liquid (ca. 200 mL).

To a mechanically stirred solution of the dark red enamine **2.2.21** and Et_2O (250 mL), was added aq. HCl (250 mL, 10% v/v). After 2.5 hours of *vigorous* stirring, the biphasic solution was extracted with Et_2O (3 x 100 mL). The ethereal partitions were combined and washed with aq. $NaHCO_3$ (2 x 100 mL, 10% w/v), and sat aq. NaCl (2 x 100 mL). The dried (Na_2SO_4) extract was *in vacuo* to provide crude **2.2.23** as a red oil. Purification via flash chromatography over silica gel, eluting with PhMe gave known **2.2.23**[28] (5.121 g, 28.58 mmol, 82%) as dark orange oil. IR (thin film) 3430, 2842, 2732, 1724, 1610, 1524, 1348, 935, 803, 731, 672 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.86 (t, J = 0.9 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.51 (d, J = 7.4 Hz, 1H), 7.37 (t, J = 7.9 Hz, 1H), 4.02 (s, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 150.5, 140.3,

135.1, 128.0, 126.5, 122.7, 43.9, 20.4 ppm; HRMS (CI+) calcd. for $C_8H_5NO_2Cl$ (M+) 180.0661, found 180.0666.

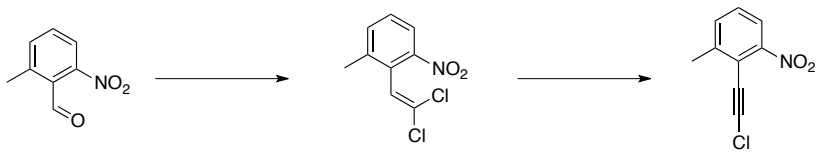


2.2.9 **2.2.10** **2.2.14**

Chloroacetylene 2.2.14: To a stirred solution of **2.2.9** (4.584 g, 30.33 mmol) and CH_2Cl_2 (500 mL), was added CCl_4 (8.61 g, 5.40 mL, 56.0 mmol), and PPh_3 (23.94 g, 91.27 mmol) at rt. After 6 h, the black solution was concentrated *in vacuo* until ca. 100 mL of mixture remained. The residue was then purified via flash chromatography over silica gel, eluting with 10-30% EtOAc/Hexanes to give known **2.2.10**[16] (4.567 g, 20.95 mmol, 69%) as a crude yellow solid.

To a stirred solution of impure **2.2.10** (4.567 g, 20.95 mmol) and THF (50 mL) was added NaHMDS (21.0 mL, 21.0 mmol, 1M in THF) at -78°C over 10 min. After 1 h, the reaction was warmed to 0°C and quenched with sat. aq. NH_4Cl (50 mL). The solution was diluted with H_2O, extracted with Et_2O (3 x 50 mL), washed with sat. aq. NaCl (1 x 100 mL) and brine (2 x 50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* to give known **2.2.14**[18] (3.218 g, 17.82 mmol, 85%) as a beige solid. MP 79-81 °C; IR (neat) 3103, 2845, 2220, 1569, 1519, 1341, 786, 742 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 1.0, 8.3 Hz, 1H), 7.68 (dd, *J* = 1.2, 7.8 Hz, 1H), 7.61 (td, *J* = 1.3, 7.6 Hz, 1H), 7.51 (td, *J* = 1.5, 7.4 Hz, 1H) ppm ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2,

135.3, 132.9, 129.0, 124.8, 117.7, 76.3, 64.8 ppm; HRMS (CI+) calcd. for $C_8H_5ClNO_2$ (M+H) 182.0009, found 182.0005.

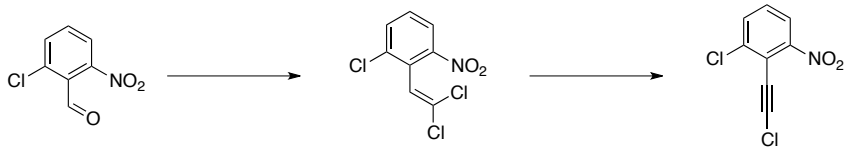


2.2.5 **2.2.13** **2.2.17**

Chloroacetylene 2.2.17: To a stirred solution of **2.2.5** (5.828 g, 33.29 mmol) and CH_2Cl_2 (350 mL), was added CCl_4 (8.29 g, 5.20 mL, 52.93 mmol), and PPh_3 (27.77 g, 105.9 mmol) at rt. After 30 h, the black solution was concentrated *in vacuo* until ca. 100 mL of mixture remained. The residue was then purified via flash chromatography over silica gel, eluting with 0-10% EtOAc/Hexanes to give impure **2.2.13** (6.038 g) as a yellow oil.

To a stirred solution of impure **2.2.13** (3.316 g, 14.29 mmol) and THF (36.0 mL) was added NaHMDS (15.0 mL, 15.0 mmol, 1M in THF) at -78°C over 10 min turning from an orange to darks brown solution. After 1 h, the reaction was warmed to 0°C and quenched with sat. aq. NH_4Cl (50 mL). After 5 min, the orange-brown solution was extracted with Et_2O (3 x 50 mL), and washed with sat. aq. NaCl (2 x 20 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica, eluting with 35% Hexanes/PhMe to give **2.2.17** (2.372 g, 12.13 mmol, 85%) as a yellow solid. MP 93-94 °C; IR (thin film) 2213, 1526, 1456, 1381, 802, 740, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.2, 1H), 7.51(d, J = 7.6 Hz, 1H), 7.37 (t, J = 8.0,

1H), 2.55 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 144.2, 133.9, 128.2, 122.0, 116.9, 80.3, 63.4, 21.2 ppm; HRMS (CI+) calcd. for $C_9H_7NO_2Cl$ (M+H) 196.0165, found 196.0154.

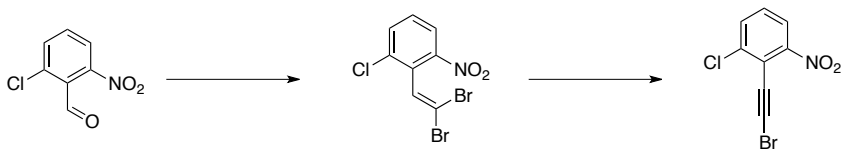


2.2.4 **2.2.11** **2.2.15**

Chloroacetylene 2.2.15: To a stirred solution of **2.2.4** (3.118 g, 16.80 mmol) and CH_2Cl_2 (170 mL), was added CCl_4 (3.98 g, 2.50 mL, 25.9 mmol), and PPh_3 (13.36 g, 50.93 mmol) at rt. After 30 h, the black solution was concentrated *in vacuo* until ca. 50 mL of mixture remained. The residue was then purified via flash chromatography over silica gel, eluting with 10-30% EtOAc / Hexanes to give **2.2.11** (3.567 g) as an impure yellow oil.

To a stirred solution of impure **2.2.11** (3.567 g, 14.12 mmol) and THF (35.0 mL) was added NaHMDS (14.30 mL, 14.30 mmol, 1 M in THF) at -78°C. After 1 h, the dark brown solution was quenched with sat. aq. NH_4Cl (20 mL), extracted with EtOAc (3 x 50 mL), and washed with sat. aq. NaCl (2 x 10 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 20-50 % EtOAc / Hexanes to give **2.2.15** (2.954 g, 13.67 mmol, 97%) as a bright yellow crystalline solid. MP 93-94 °C; IR (thin film) 2217, 1526, 1338, 1118, 797, 750, 737 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.1, 1.2 Hz, 1H), 7.72 (dd, J = 8.1, 1.2 Hz, 1H), 7.43 (t, J = 8.2 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 139.5, 13.7,

128.9, 122.7, 117.3, 82.3, 61.8 ppm; HRMS (EI+) calcd. for $C_8H_3NO_2Cl_2$ 214.9541, found 214.9539.

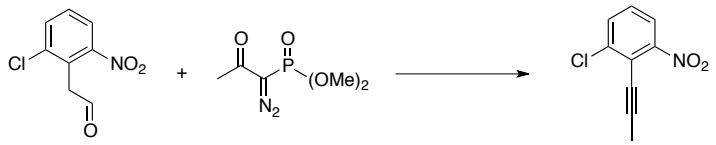


2.2.4 **2.2.12** **2.2.16**

Bromoacetylene 2.2.16: To a stirred solution of **2.2.4** (2.628 g, 14.16 mmol) and CH_2Cl_2 (94 mL), was added CBr_4 (7.10 g, 2.08 mL, 21.42 mmol), and PPh_3 (11.23 g, 42.81 mmol, 0.4 M in CH_2Cl_2) at 0 ˚C. After 15 h, the black solution was concentrated *in vacuo* until ca. 60 mL of mixture remained. The residue was then purifed via flash chromatography over silica gel, eluting with 0-20% EtOAc / hexanes gave crude **2.2.12** (4.117 g) as an orange solid.

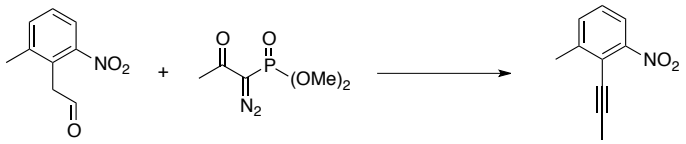
To a stirred solution of impure **2.2.12** (3.051 g, 8.937 mmol) and THF (22 mL) was added NaHMDS (9.00 mL, 9.00 mmol, 1 M in THF) at -78°C over 5 min. The reaction was warmed to 0°C. After 2 h, the dark brown mixture was quenched with sat. aq. NH_4Cl (20 mL). The solution was extracted with EtOAc (3 x 20 mL) and washed with H_2O (2 x 10 mL) and sat. aq. NaCl (2 x 10 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica gel, eluting with PhMe to give **2.2.16** (1.971 g, 7.567 mmol, 85%) as a yellow solid. MP 86-88 °C; IR (thin film) 2220, 1527, 1340, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 8.1, 1.2 Hz, 1H), 7.51 (dd, J = 8.1, 1.2, 1H), 7.37 (t, J = 8.2 Hz, 1H) ppm; ^{13}C NMR (75 MHz,

$CDCl_3$) δ 151.7, 139.6, 133.7, 128.9, 122.8, 117.7, 72.2, 65.3 ppm; HRMS (EI+) calcd. for $C_8H_3NO_2ClBr$ 258.9036, found 258.9035.



2.2.22 **2.2.6** **2.2.28**

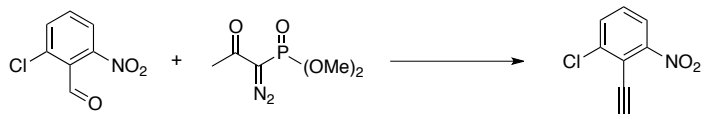
Propyne 2.2.28: To a stirred solution of **2.2.22** (5.412 g, 27.11 mmol) and MeOH (385 mL) was added K_2CO_3 (7.635 g, 55.24 mmol), and **2.2.6**[22] (6.253 g, 32.55) dropwise via syringe at rt. After 4 h, the dark red mixture was quenched with pH 7 buffer (350 mL), concentrated *in vacuo*, and filtered. The orange solid was washed with H_2O (20 mL), dissolved in EtOAc (100 mL) and washed with sat. aq. NaCl (2 x 15 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* to give **2.2.28** (4.467 g, 22.84 mmol, 84%) as an orange solid. MP 100-102 °C; IR (thin film) 3086, 2249, 2208, 1519, 1346, 881, 809, 742 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (dd, J = 8.1, 1.0 Hz, 1H), 7.64 (dd, J = 8.1, 1.0 Hz, 1H), 7.32 (t, J = 8.2 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8, 138.6, 133.2, 127.7, 122.4, 118.8, 101.5, 71.8, 5.0; HRMS (EI+) calcd. for $C_9H_6NO_2Cl$ (M+) 195.0087, found 195.0088.



2.2.23 **2.2.6** **2.2.29**

Propyne 2.2.29: To a stirred solution of **2.2.23** (4.786 g, 26.71 mmol) and MeOH (480 mL) was added K_2CO_3 (7.322 g, 52.98 mmol), and **2.2.6**[22] (6.208 g, 32.31 mmol)

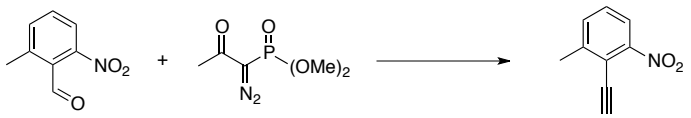
dropwise via syringe at rt. After 15 h, the dark red mixture was quenched with pH 7 buffer (480 mL), concentrated *in vacuo*, and filtered. The orange solid was washed with H_2O (20 mL), dissolved in EtOAc (100 mL) and washed with sat. aq. NaCl (2 x 25 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified via flash chromatography over silica gel, eluting with 0-15% EtOAc/Hexanes to give **2.2.29** (2.845 g, 16.34 mmol, 61%) as an orange solid. MP 42-44 °C; IR (thin film) 2251, 2208, 1607, 1528, 804, 743, 710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 8.1 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 7.12 (t, J = 7.9 Hz, 1H), 2.48 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8, 143.2, 133.3, 127.0, 121.3, 118.1, 99.12, 73.3, 20.9, 4.5; HRMS (EI+) calcd. for $C_{10}H_9NO_2$ (M+) 175.0633, found 175.0633.



2.2.4 **2.2.6** **2.2.7**

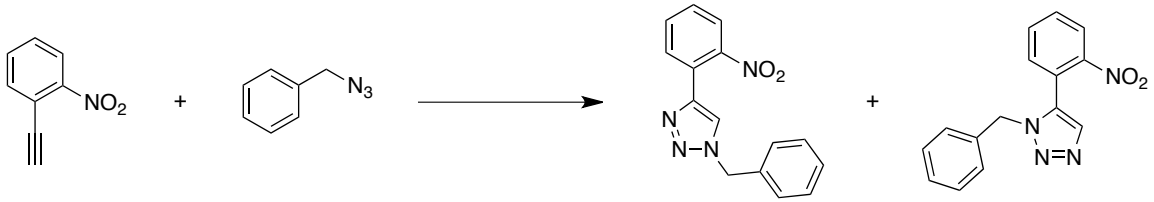
Acetylene 2.2.7: To a stirred solution of **2.2.4** (16.64 g, 89.67 mmol), K_2CO_3 (25.14 g, 181.9 mmol), and MeOH (1.34 L) was added diazophosphonate **33**[22] (24.33 g, 208.7 mmol) at rt. After 4 h, the solution was quenched with sat. aq. $NaHCO_3$ (500 mL) and concentrated *in vacuo* to remove the MeOH. The solution was diluted with EtOAc (700 mL) and washed with H_2O (3 x 200 mL), and sat. aq. NaCl (2 x 150 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 1% EtOAc / Hexanes, to give **2.2.7** (13.84 g, 76.22 mmol, 85%) as a pale yellow solid. MP 94-95 °C; IR (thin film) 3286, 1521, 1351, 808, 756, 736, 681; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.2, 1.1 Hz, 1H), 7.74 (dd, J = 8.2, 1.1 Hz,

1H), 7.47 (t, *J* = 8.2, 1H), 3.86 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 134.0, 129.6, 123.1, 117.6, 109.9, 91.7, 75.3 ppm; HRMS (CI+) calcd. for $C_8H_5NO_2Cl$ (M+H) 182.0009, found 182.0005.



2.2.5 **2.2.6** **2.2.8**

Acetylene 2.2.8: To a stirred solution of **2.2.5** (1.655 g, 10.00 mmol), K_2CO_3 (3.620 g, 26.20 mmol), and MeOH (140 mL) was added diazophosphonate **2.2.6**[22] (2.350 g, 12.23 mmol) slowly, at rt, in ca. 0.2 mL portions over 1 hour. After 3 h, the solution was quenched with pH 7 buffer (200 mL) and concentrated *in vacuo* to remove the MeOH and give crude **2.2.8** as an orange solid (1.387 g). The solid was filtered, and the mother liquor was diluted with EtOAc (150 mL) and washed with sat. aq. NaCl (2 x 50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo*, and purified by flash chromatography over silica gel, eluting with 1% EtOAc/Hexanes, to give crude **2.2.8** (138.5 mg). The crude material isolated from recrystalization and column chromatography were combined and recrystalized with hexane to give **2.2.8** as a pale yellow solid (1.422 g, 8.823 mmol, 88%). MP 58-59 °C; IR (thin film) 3284, 2108, 1529, 1349, 797, 778, 736, 645 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 3.75 (s, 1H), 2.56 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 144.2, 133.8, 128.5, 121.8, 116.7, 89.7, 76.7, 21.2; HRMS (EI+) calcd. for $C_9H_7NO_2$ (M+) 161.0477, found 161.0467.

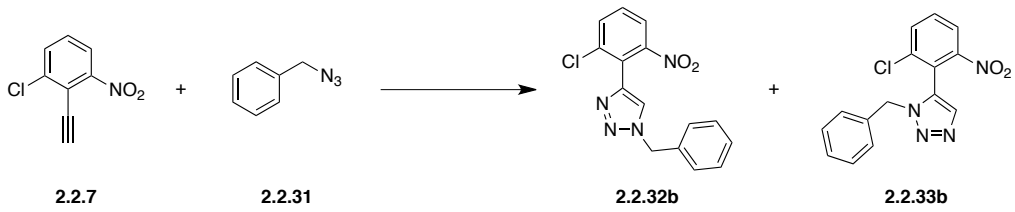


2.2.30 **2.2.31** **2.2.32a** **2.2.33a**

Triazole 2.2.32a and 2.2.33a. To a pressure vessel containing **2.2.30** (73.5 mg, 0.500 mmol) was added PhMe (1 mL) and azide **2.2.31** (199.5 mg, 1.5 mmol) sequentially at rt. The reaction mixture was sealed under Ar and heated to 80 °C. After 48 h, the crude mixture was cooled to rt, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 20-40% EtOAc/Hexanes to give sequentially **2.2.32a** (91.5 mg, 327 μmol, 65%, 2.7:1) as a white solid followed by **2.2.33a** (26.1 mg, 93.2 μmol, 18.6%) as a pale yellow solid. Major regioisomer **2.2.32a**:[23] Mp 103-105 °C; IR (neat) 1528, 1359 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.74 (s, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.38-7.41 (m, 3H), 7.33 (d, *J* = 6.5 Hz, 2H), 5.61 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 142.4 134.3, 132.5, 131.1, 129.2, 128.9, 128.9, 128.0, 124.7, 124.0, 122.9, 54.3 ppm; HRMS (ES+) calcd. for $C_{15}H_{13}N_4O_2$ (M+H) 281.1039, found 281.1029. Minor regioisomer **2.2.33a**: Mp 73-75 °C; IR (neat) 1528, 1350 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.9 Hz, 1H), 7.66 (s, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.18-7.24 (m, 3H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 6.8 Hz, 2H), 5.43 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 134.4, 133.9, 133.2, 133.1, 133.08,

131.0, 128.7, 128.4, 127.8, 124.9, 122.2, 52.8 ppm; HRMS (ES+) calcd. for $C_{15}H_{13}N_4O_2$ (M+H) 281.1039, found 281.1029.

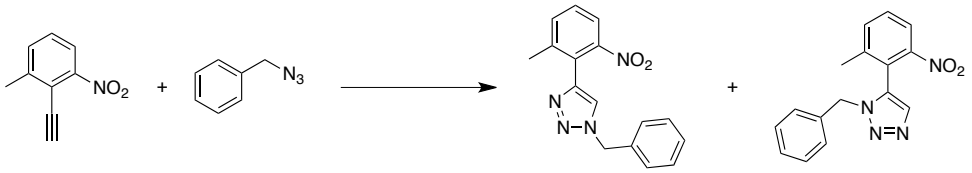
Triazole 2.2.32a: To a stirred solution of **2.2.30** (73.5 mg, 500 μmol) and H_2O / *t*-BuOH (3.00 mL, 1:1) was added ascorbic acid (14.5 mg, 82.5 μmol), Cu_2SO_4•$5H_2O$ (6.5 mg, 26 μmol) and azide **2.2.31** (199.5 mg, 1.5 mmol) sequentially at rt. After 19 h, the mixture was filtered and washed with hexanes to give the sole regioisomer **2.2.32a**[23] (110.1 mg, 393 μmol, 79%) as a beige solid.



2.2.7 **2.2.31** **2.2.32b** **2.2.33b**

Triazoles 2.2.32b and 2.2.33b: To a pressure vessel containing **2.2.7**[13a,b] (45.6 mg, 0.251 mmol) was added PhMe (500 μL) and azide **2.2.31** (100 mg, 750 μmol) at rt. The reaction mixture was sealed under Ar and heated to 80 °C. After 26 h, the crude mixture was cooled to rt, filtered through celite eluting with 100% EtOAc and concentrated *in vacuo* to give an inseparable mixture of regioisomers (46.6 mg, 0.148 mmol, 59%, 2:1 (**2.2.32b:2.2.33b**)). Mp 174-175 °C; IR (thin film) 3077, 2879, 1527, 1362, 1229, 1089, 760, 729 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 7.95 (d, J = 8.2 Hz, 1H of minor), 7.80 (dd, J = 8.1, 1.2 Hz, 1H of major), 7.75 (s, 1H of major), 7.72 (dd, J = 8.1, 1.2 Hz, 1H of major), 7.71 (d, J = 8.2 Hz, 1H of minor), 7.69 (s, 1H of minor), 7.61 (t, J = 8.2 Hz, 1H of minor), 7.49 (t, J = 8.1 Hz, 1H of major), 7.45-7.35 (m, 3H of

major), 7.35-7.25 (m, 2H of major), 7.25 (t, J = 7.3 Hz, 1H of minor), 7.20 (t, J = 7.5 Hz, 2H of minor), 7.03 (d, J = 7.5 Hz, 2H of minor), 5.67 (s, 2H of major), 5.45 (dd, J = 15.0 Hz, 2H of minor) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 151.4, 139.6, 135.9, 134.4, 134.1, 133.4, 131.6, 129.9, 129.2, 128.8, 128.7, 128.6, 128.3, 127.8, 124.5, 124.2, 123.1, 122.6, 54.3, 53.4; HRMS (EI+) calcd. for $C_{15}H_{11}N_4O_2Cl$ (M+H) 314.0570, found 314.0581.

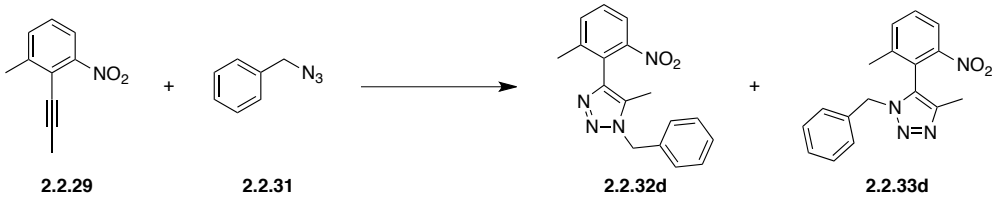


2.2.8 **2.2.31** **2.2.32c** **2.2.33c**

Triazoles 2.2.32c and 2.2.33c: To a pressure vessel containing **2.2.8** (39.9 mg, 0.248 mmol) was added PhMe (500 μL) and azide **2.2.31** (133 mg, 1 mmol) at rt. The reaction mixture was sealed under Ar and heated to 80 °C. After 96 h, the crude mixture was cooled to rt, concentrated *in vacuo* to give an inseparable mixture of regioisomers (70.2 mg, 0.197 mmol, 79%, 2.3:1 (**2.2.32c:2.2.33c**)). Regioisomer mixture: Mp 152-153 °C; IR (neat) 3077, 1529, 1362, 807 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.94 (d, J = Hz, 1H of minor), 7.70 (d, J = 7.8 Hz, 1H of major), 7.60 (s, 1H of minor), 5.64 (s, 2H of major), 7.56 (t, J = 7.9 Hz, 1H of minor), 7.52 (d, J = 7.5 Hz, 1H of minor), 7.59-7.18 (m, 8H of major), 7.21 (t, J = 7.5 Hz, 2H of minor), 7.00 (d, J = 7.4 Hz, 2H of minor), 5.65 (d, 1H of minor), 5.13 (d, J = 15.0 Hz, 1H of minor), 2.26 (s, 3H of major). ^{13}C NMR (175 MHz, $CDCl_3$) δ 150.8, 149.7, 142.1, 141.5, 140.7, 134.8, 134.6, 134.1, 133.8, 133.7, 131.4, 130.7, 129.2, 129.1, 128.8, 128.7, 128.6, 128.5, 127.8, 124.4, 123.2, 122.3, 121.4,

121.1, 54.2, 53.0, 20.7, 19.6 ppm. HRMS (ES+) calcd. for $C_{16}H_{15}N_4O_2$ (M+H) 295.1195, found 295.1208.

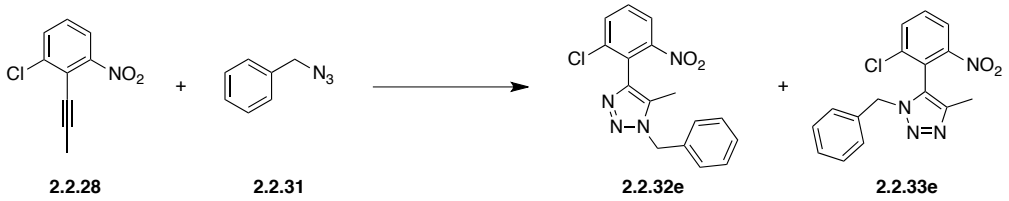
Triazole 2.2.32c: To a stirred solution of **2.2.8** (111.6 mg, 692.3 μmol) and H_2O / *t*-BuOH (3.00 mL, 1:1) was added ascorbic acid (20.1 mg, 114 μmol), Cu_2SO_4•$5H_2O$ (9.0 mg, 36 μmol) and azide **2.2.31** (293.4 mg, 2.196 mmol) sequentially at rt. Upon addition of azide **2.2.31** a white ppt formed. After 12 h, the mixture was filtered and washed with hexanes to give the sole regioisomer **2.2.32c** (199.6 mg, 678.3 μmol, 98%) as a pure white solid.



2.2.29 2.2.31 2.2.32d 2.2.33d

Triazole 2.2.32d and Triazole 2.3.33d: To a pressure vessel containing **2.2.29** (69.2 mg, 390.5 μmol) was added PhMe (800 μL) and azide **2.2.31** (174.3 mg, 1.309 mmol) at rt. The reaction mixture was sealed under Ar and heated to 120˚C. After 72 h, the reaction was cooled to rt, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 20-40% EtOAc/Hexanes to give an inseparable mixture of regioisomers (50.3 mg, 168 μmol, 43%, 1:1 (**2.2.32d:2.3.33d**)) as a yellow oil. Regioisomer mixture: IR (neat) 1529, 1496, 1455, 1353, 1016, 914, 804, 754, 731 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.58-7.47 (m, 2H), 7.46-7.39 (m, 2H), 7.38-7.27 (m, 3H), 7.26-7.09 (m, 5H),

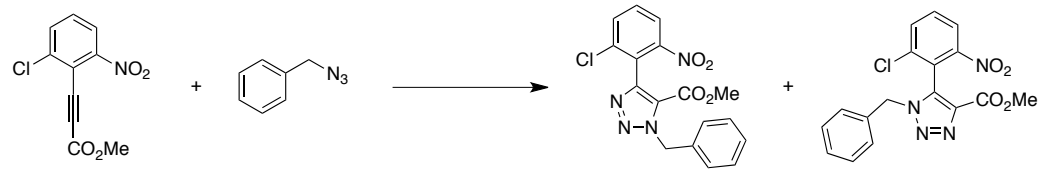
6.92 (d, J = 7.3 Hz, 2H), 5.56 (s, 2H), 5.49 (d, J = 14.9 Hz, 1H), 5.05 (d, J = 14.9 Hz, 1H), 2.15 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.50 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 149.8, 142.5, 142.1, 141.5, 140.2, 134.8, 134.7, 134.3, 134.0, 132.0, 130.7, 129.4, 129.1, 128.6, 128.6, 128.5, 128.3, 128.3, 126.7, 124.9, 122.2, 121.7, 121.0, 53.2, 52.0, 20.2, 19.1, 10.2, 8.2 ppm; HRMS (EI+) calcd. for $C_{17}H_{16}N_4O_2$ (M+) 308.1273, found 308.1288.



2.2.28 **2.2.31** **2.2.32e** **2.2.33e**

Triazole 2.2.32e and Triazole 2.2.33e: To a pressure vessel containing **2.2.28** (316.2 mg, 1.909 mmol) was added PhMe (2.00 mL) and azide **2.2.31** (1.066 mg, 8.006 mmol) at rt. The reaction mixture was sealed under Ar and heated to 120˚C. After 24 h, the reaction was cooled to rt, concentrated *in vacuo* and purified via flash chromatography over silica gel, eluting with 20-40% EtOAc/Hexanes to give an inseparable mixture of regioisomers (405.4 mg, 1.233 mmol, 65%, 2:1 (**2.2.32e:2.2.33e**)) as a yellow oil. Regioisomer mixture: IR (neat) 1733, 1533, 1455, 1437, 1359, 1122, 883, 806, 728 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.1, 1.3 Hz, 1H of minor), 7.90 (dd, J = 8.1, 1.2 Hz, 1H of major), 7.76 (dd, J = 8.1, 1.2 Hz, 1H of major), 7.69 (dd, J = 8.1, 1.3 Hz, 1H of minor), 7.59 (t, J = 8.1 Hz, 1H of minor), 7.55 (t, J = 8.1 Hz, 1H of major), 7.48-7.34 (m, 3H of major/minor), 7.24-7.14 (m, 2H of major/minor), 6.99-6.94 (m, 1H of minor), 5.40 (d, J = 12.7 Hz, 1H of minor), 5.62 (s, 2H of major), 5.32 (d, J =

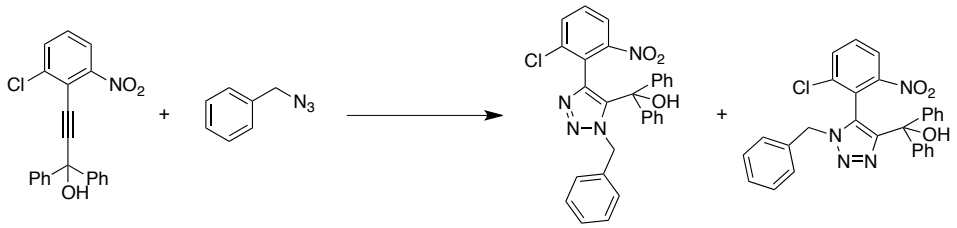
12.7 Hz, 1H of minor), 2.16 (s, 3H of minor), 2.12 (s, 3H of major) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 138.7, 137.9, 134.6, 134.2, 133.6, 132.8, 132.6, 131.5, 130.4, 129.1, 128.6, 128.4, 128.34, 128.31, 128.1, 126.7, 125.2, 123.1, 122.7, 52.1, 53.5, 10.3, 8.5 ppm. HRMS (EI+) calcd. for $C_{16}H_{13}N_4O_2Cl$ (M+) 328.0727, found 328.0723.



2.2.19 **2.2.31** **2.2.32f** **2.2.33f**

Triazole 2.2.32f and 2.2.33f. To a pressure vessel containing **2.2.19** (220 mg, 917 μmol) was added PhMe (2 mL) and azide **2.2.31** (366 mg, 2.75 mmol) sequentially at rt. The reaction mixture was sealed under Ar and heated to 80 °C. After 24 h, the crude mixture was cooled to rt, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 30-40% EtOAc/Hexanes to give a separable mixture of regioisomers **2.2.32f** / **2.2.33f** (315.3 mg, 845 μmol, 92% yield, 3.2:1). Major regioisomer **2.2.32f**: IR (neat) 1731, 1536, 1479, 1347, 1260, 1212, 1158, 1101 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 0.6, 8.3 Hz, 1H), 7.79 (dd, *J* = 0.6, 8.1 Hz, 1H), 7.61 (t, *J* = 8.2 Hz, 1H), 7.33-7.38 (m, 3H), 7.29 (d, *J* = 6.4 Hz, 2H), 6.02 (s, 2H), 3.66 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 150.2, 144.4, 137.0, 135.0, 134.2, 130.6, 128.9, 128.4, 127.3, 125.9, 125.6, 123.0, 54.3, 52.6 ppm; HRMS (EI+) calcd. for $C_{17}H_{13}N_4O_4Cl$ (M+) 372.0625, found 372.0637. Minor regioisomer **2.2.33f**: Mp 125-129 °C; IR (neat) 1733, 1536, 1474, 1355, 1209, 1063 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 1.0, 8.2 Hz, 1H), 7.76 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.65 (t, *J* = 8.2 Hz, 1H),

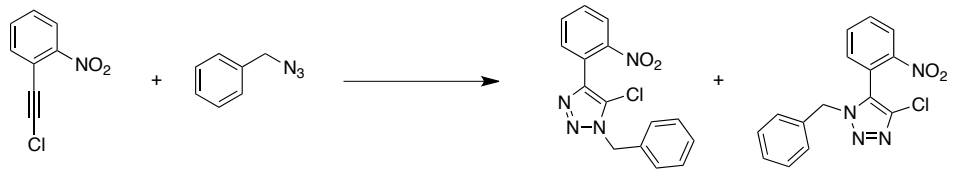
7.24-7.27 (m, 1H), 7.20 (t, J = 7.3 Hz, 2H), 7.02 (d, J = 7.4 Hz, 2H), 5.52 (d, J = 15.0 Hz, 1H), 5.39 (d, J = 14.9 Hz, 1H), 3.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 149.0, 137.6, 136.8, 135.1, 134.7, 132.4, 131.9, 128.9, 128.7, 128.5, 123.6, 121.7, 53.9, 52.2 ppm; HRMS (EI+) calcd. for $C_{17}H_{13}N_4O_4Cl$ (M+) 372.0625, found 372.0621.



2.2.34 **2.2.31** **2.2.32g** **2.2.33g**

Triazole 2.2.32g and 2.2.33g. To a pressure vessel containing **2.2.34** (10 mg, 27.5 μmol) was added PhMe (60 μL) and azide **2.2.31** (11 mg, 82.5 μmol) sequentially at rt. The reaction mixture was sealed under Ar and heated to 120 °C. After 45 h, the crude mixture was cooled to rt, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-40% EtOAc/Hexanes to give a mixture of regioisomers (7.0 mg, 2.00 μmol, 51%, 1:1 (**2.2.32g:2.2.33g)**). Analytical samples of the individual isomers could be obtained by preparative thin layer chromatography over silica gel, eluting with 30% EtOAc/Hexanes to give sequentially **2.2.33g** then **2.2.32g**. Regioisomer **2.2.32g**: IR (neat) 3286, 2919, 1531, 1447, 1346, 1025, 737 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.76 (dd, J = 1.0, 8.3 Hz, 1H), 7.45 (dd, J = 1.0, 8.0 Hz, 1H), 7.31 (m, 4H), 7.27 (m, 3H), 7.15 (m, 4H), 7.11 (m, 2H), 7.07 (m, 3H) 5.41 (s, 2H), 3.04 (s, 1H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.1, 142.9, 142.6, 140.0, 138.1, 137.7, 135.5, 134.0, 129.5, 128.7, 128.23, 128.16, 128.13, 128.07, 127.9, 127.5, 126.5, 126.2, 123.1, 53.8 ppm; HRMS (ES+) calcd.

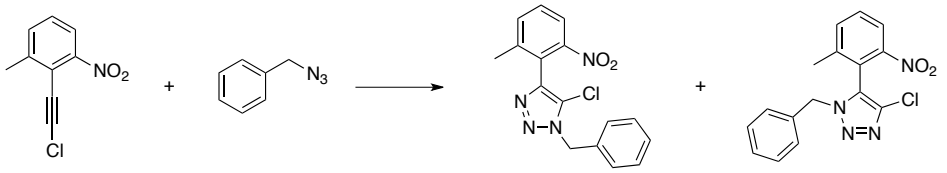
for $C_{27}H_{19}ClN_4NaO_3$ (M+Na) 505.1043, found 505.1047. Regioisomer **2.2.33g**: IR (neat) 3401, 3062, 2925, 1724, 1532, 1448, 1347, 758 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 1.0, 8.3 Hz, 1H), 7.46 (dd, *J* = 1.1, 8.0 Hz, 1H), 7.37 (t, *J* = 8.2 Hz, 1H), 7.24 (m, 3H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.13 (m, 4H), 6.98 (d, *J* = 7.6 Hz, 1H), 5.36 (d, *J* = 15.0 Hz, 1H), 5.24 (d, *J* = 14.9 Hz, 1H), 3.29 (s, 1H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 150.0, 149.1, 144.73, 144.68, 137.6, 134.0, 133.0, 130.8, 128.8, 128.64, 128.56, 128.5, 127.8, 127.7, 127.5, 127.4, 127.2, 123.3, 123.2, 53.5 ppm; HRMS (ES+) calcd. for $C_{27}H_{19}ClN_4NaO_3$ (M+Na) 505.1043, found 505.1047.



2.2.14 **2.2.31** **2.2.32h** **2.2.33h**

Triazole 2.2.32h and 2.2.33h. To a pressure vessel containing **2.2.14** (90.5 mg, 0.500 mmol) was added PhMe (1 mL) and azide **2.2.31** (199.5 mg, 1.5 mmol) sequentially at rt. The reaction mixture was sealed under Ar and heated to 120 °C. After 24 h, the crude mixture was cooled to rt, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 10-30% EtOAc/Hexanes to give sequentially **2.2.32h** (87.9 mg, 280 μmol, 56%, 5.7:1) as an orange oil followed by **2.2.33h** (16 mg, 50.9 μmol, 10%) as a pale yellow solid. Major regioisomer **2.2.32h**: IR (neat) 1533, 1352 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.70-7.72 (m, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.35 (m, 5H), 5.61 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ

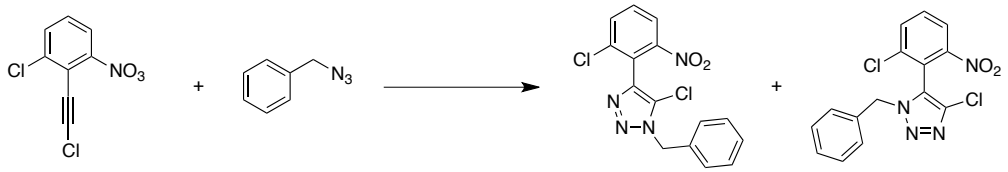
148.5, 139.9, 133.6, 133.0, 132.2, 130.0, 129.1, 128.8, 128.7, 127.7, 124.9, 124.1, 123.7, 52.4 ppm; HRMS (ES+) calcd. for $C_{15}H_{12}N_4O_2Cl$ (M+H) 315.0649, found 315.0649. Minor regioisomer **2.2.33h**: Mp 100-102 °C; IR (neat) 1528, 1346, 1284 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.20-7.25 (m, 3H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.2, 2H), 5.60 (d, *J* = 15.1 Hz, 1H), 5.23 (d, *J* = 15.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 134.8, 133.6, 133.5, 133.1, 131.6, 130.0, 128.8, 128.7, 127.9, 125.4, 120.4, 54.2 ppm; HRMS (EI+) calcd. for $C_{15}H_{11}N_4O_2Cl$ (M+) 314.0571, found 314.0567.



2.2.17 **2.2.31** **2.2.32i** **2.2.33i**

Triazole 2.2.32i and Triazole 2.2.33i: To a pressure vessel containing **2.2.17** (639.2 mg, 3.268 mmol) was added PhMe (6.00 mL) and azide **2.2.31** (1.531 mg, 11.50 mmol) at rt. The reaction mixture was heated to 120˚C. After 24 h, the reaction was cooled to rt, concentrated *in vacuo* and purified via flash chromatography over silica gel, eluting with 20-40% EtOAc/Hexanes to give an inseparable mixture of regioisomers (733.6 mg, 2.23 mmol, 68%, 7:1 (**2.2.32i**:**2.2.33i**)) as a yellow oil. Regioisomer mixture: IR (neat) 1534, 1459, 1369 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 1H for minor), 7.90 (d, *J* = 8.0 Hz, 1H for major), 7.61-7.59 (m, 1H for minor), 7.58 (d, *J* = 8.0 Hz, 1H for major), 7.51 (t, *J* = 8.0 Hz, 1H for major), 7.48 (d, *J* = 8.1 Hz, 1H for minor), 7.44-7.32 (m, 3H for major/minor), 7.31-7.25 (m, 2H for major), 7.19 (t, *J* = 7.2

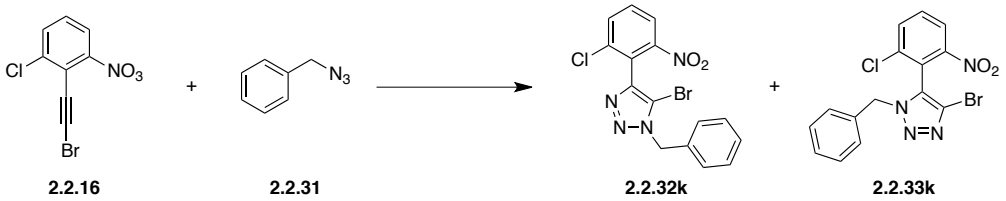
Hz, 2H for minor), 6.96 (d, J = 7.4 Hz, 2H for minor), 5.89 (d, J = 14.8 Hz, 1H for minor), 5.65 (s, 2H for major), 5.09 (d, J = 14.8 Hz, 1H for minor), 2.24 (s, 3H for major), 1.59 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 149.1, 142.4, 141.5, 139.1, 135.4, 134.8, 133.8, 133.0, 131.4, 130.0, 129.1, 128.9, 128.8, 128.6, 128.5, 127.3, 124.6, 122.8, 122.8, 122.3, 119.0, 54.4, 52.3, 20.1, 19.1 ppm; HRMS (CI+) calcd. for $C_{16}H_{14}N_4O_2Cl$ (M+) 329.0805, found 329.0791.



2.2.15 **2.2.31** **2.2.32j** **2.2.33j**

Triazole 2.2.32j and Triazole 2.2.33j: To a pressure vessel containing **2.2.15** (54.2 mg, 253 μmol) was added PhMe (500 μL) and azide **2.2.31** (100 mg, 750 μmol) at rt. The reaction mixture was sealed under Ar and heated to 80˚C. After 70 h, the reaction was cooled to rt, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-30% EtOAc / Hexanes to give to give a separable mix of regioisomers **2.2.32j** / **2.2.33j** (63.3 mg, 181 μmol, 72 %, 9:1). Major regioisomer **2.2.32j**: IR (neat) 1608, 1533, 1355, 1226, 991, 883, 808, 759, 727, 704 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.99 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.61 (t, J = 8.1 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.29 (d, J = 7.1 Hz, 2H), 5.66 (s, 2H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 151.0, 137.5, 134.1, 133.7, 131.1, 129.1, 128.6, 127.2, 125.5, 123.2, 123.1, 52.4 ppm; HRMS (ES+) calcd. for $C_{15}H_{11}N_4O_2Cl_2$ (M+H) 349.0259, found 349.0270. Minor regioisomer **2.2.33j**: IR (neat) 3090, 2920,

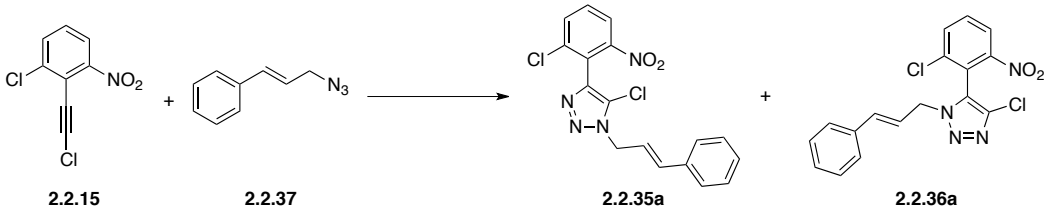
1533, 1345, 1285, 804, 745 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 1.1, 8.3 Hz, 1H), 7.75 (dd, *J* = 1.2, 8.1 Hz, 1H), 7.66 (t, *J* = 8.2 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.1 Hz, 2H), 5.44 (d, *J* = 14.9, 1H), 5.40 (d, *J* = 14.9, 1H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.6, 138.0, 134.7, 132.5, 132.3, 129.2, 128.9, 128.8, 128.4, 127.8, 123.6, 120.0 ppm; HRMS (ES+) calcd. for $C_{15}H_{11}N_4O_2Cl_2$ (M+H) 349.0259, found 349.0245.



2.2.16 **2.2.31** **2.2.32k** **2.2.33k**

Triazole 2.2.32k and Triazole 2.2.33k: To a pressure vessel containing **2.2.16** (21 mg, 80.7 μmol) was added PhMe (160 μL) and azide **2.2.31** (32 mg, 240 μmol) at rt. The reaction mixture was sealed under Ar and and heated to 80˚C. After 72 h, the reaction was cooled to rt, concentrated *in vacuo* and purified via flash chromatography over silica gel, eluting with 0-40% EtOAc / Hexanes to give a separable mixture of regioisomers **2.2.32k** / **2.2.33k** (20.2 mg, 51.6 μmol, 64%, 9:1) as a red-orange solid. Major regioisomer **2.2.32k**; MP 126-128 ^oC; IR (neat) 3088, 3034, 2924, 1533, 1455, 1353, 988, 759 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.42-7.38 (m, 3H), 7.27 (m, 2H), 5.70 (s, 2H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 150.9, 140.8, 137.6, 134.1, 133.9, 131.0, 129.1, 128.6, 127.2, 123.8, 123.1, 112.2, 53.2 ppm; HRMS (ES+) calcd. for $C_{15}H_{11}N_4O_2ClBr$ (M+H) 392.9754, found 392.9770. Minor regioisomer **2.2.33k**; IR (neat) 3096, 2922, 1532,

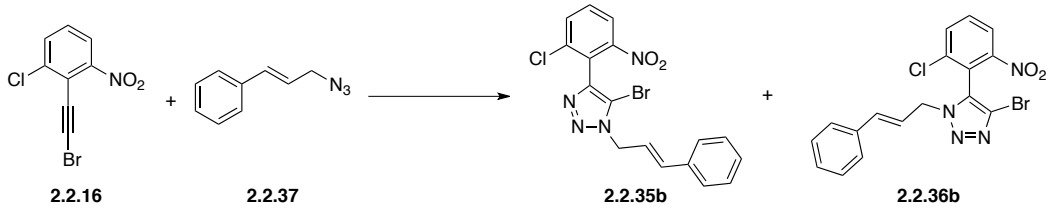
1455, 1347, 1263, 743 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 5.46 (d, *J* = 15.0 Hz, 1H) 5.42 (d, *J* = 15.2 Hz, 1H) ppm; HRMS (ES+) calcd. for $C_{15}H_{11}N_4O_2ClBr$ (M+H) 392.9754, found 392.9753.



2.2.15 **2.2.37** **2.2.35a** **2.2.36a**

Triazole 2.2.35a and 2.2.36a. To a pressure vessel containing **2.2.15** (17.8 mg, 83.2 μmol) was added PhMe (190 μL) and azide **2.2.37** (45.8 mg, 288 μmol) sequentially at rt. The reaction mixture was sealed under Ar and heated to 80 °C. After 48 h, the crude mixture was cooled to rt, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-30% EtOAc/Hexanes to give a mixture of regioisomers (15.2 mg, 40.5 μmol, 49%, 11:1 (**2.2.35a:2.2.36a**)). Analytical samples of the individual isomers could be obtained by preparative thin layer chromatography over silica gel, eluting with 30% EtOAc/Hexanes to give sequentially **2.2.35a** then **2.2.36a**. Major regioisomer **2.2.35a**; IR (neat) 3083, 3028, 2926, 1533, 1449, 1355, 1266, 966, 760 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.40 (tt, *J* = 5.8, 15.8 Hz, 1H), 5.24 (d, *J* = 5.6 Hz, 2H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 151.1, 137.5, 137.4, 135.5, 134.7, 134.1,

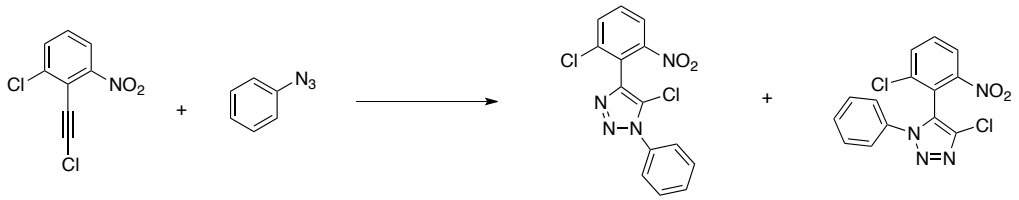
131.1, 128.7, 128.5, 126.8, 125.3, 123.3, 123.1, 120.7, 50.7 ppm; HRMS (ES+) calcd. for $C_{17}H_{13}N_4O_2Cl_2$ (M+H) 375.0416, found 375.0410. Minor regioisomer **2.2.36a**; IR (neat) 2921, 2849, 1533, 1450, 1348, 1046, 733 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 8.2 Hz, 1H), 7.30-7.28 (m, 3H), 7.19 (d, *J* = 5.8 Hz, 2H), 6.28 (d, *J* = 15.3 Hz, 1H), 6.21 (m, 1H), 5.06 (qd, *J* = 5.8, 14.6 Hz, 2H) ppm; HRMS (ES+) calcd. for $C_{17}H_{13}N_4O_2Cl_2$ (M+H) 375.0416, found 375.0397.



2.2.16 **2.2.37** **2.2.35b** **2.2.36b**

Triazole 2.2.35b and 2.2.36b. To a pressure vessel containing **2.2.16** (21.0 mg, 80.7 μmol) was added PhMe (160 μL) and azide **2.2.37** (39.3 mg, 247 μmol) sequentially at rt. The reaction mixture was sealed under Ar and heated to 80 °C. After 29 h, the crude mixture was cooled to rt, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-40% EtOAc/Hexanes to give a mixture of regioisomers (22.3 mg, 53.1 μmol, 69%, 4:1 (**2.2.35b:2.2.36b**)). Analytical samples of the individual isomers could be obtained by preparative thin layer chromatography over silica gel, eluting with 30% EtOAc/Hexanes to give sequentially **2.2.35b** then **2.2.36b**. Major regioisomer **2.2.35b**: Mp 133-136 °C; IR (neat) 3083, 3028, 2925, 1532, 1449, 1355, 1222, 760, 737 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 1.0, 8.2 Hz, 1H), 7.81 (dd, *J* = 1.0, 8.1 Hz, 1H), 7.61 (t, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J*

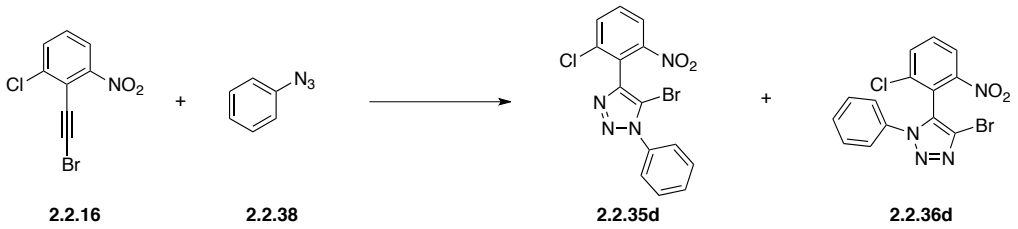
= 7.4 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.40 (tt, *J* = 5.7, 15.9 Hz, 1H), 5.28 (d, *J* = 5.7 Hz, 2H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 151.0, 140.6, 137.6, 135.6, 134.7, 134.1, 131.0, 128.7, 128.4, 126.8, 123.8, 123.1, 120.9, 112.0, 51.6 ppm; HRMS (ES+) calcd. for $C_{17}H_{13}BrClN_4O_2$ (M+H) 418.9832, found 418.9930. Minor regioisomer **2.2.36b**: IR (neat) 2919, 2851, 1532, 1449, 1351, 1263, 732 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.78 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.28 (m, 3H), 7.19 (dd, *J* = 1.4, 7.3 Hz, 2H), 6.29 (d, *J* = 15.9 Hz, 1H), 6.40 (tt, *J* = 5.7, 15.9 Hz, 1H), 5.28 (d, *J* = 5.7 Hz, 2H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 150.0, 137.8, 135.9, 135.2, 134.7, 132.2, 130.0, 128.6, 126.6, 123.6, 121.7, 120.7, 120.3, 53.1 ppm; HRMS (ES+) calcd. for $C_{17}H_{13}BrClN_4O_2$ (M+H) 418.9910, found 418.9916.



2.2.15 **2.2.38** **2.2.35c** **2.2.36c**

Triazole 2.2.35c and 2.2.36c. To a pressure vessel containing **2.2.15** (19 mg, 88.8 μmol) was added PhMe (190 μL) and azide **2.2.38** (33 mg, 277 μmol) sequentially at rt. The reaction mixture was sealed under Ar and heated to 80 °C. After 72 h, the crude mixture was cooled to rt, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-40% EtOAc/Hexanes to give a mixture of regioisomers (11.5 mg, 34.3 μmol, 36%, 2:1 (**2.2.35c:2.2.36c**)). Analytical samples of the

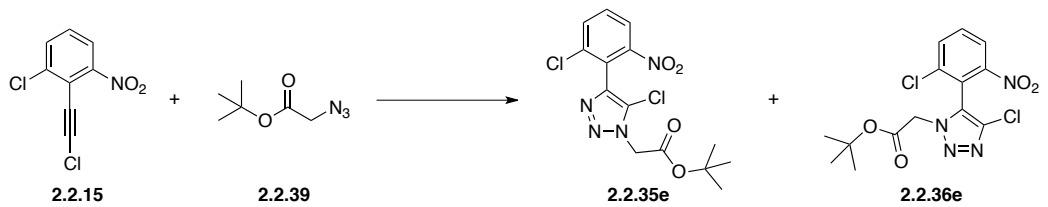
individual isomers could be obtained by preparative thin layer chromatography over silica gel, eluting with 30% EtOAc/Hexanes to give sequentially **2.2.35c** then **2.2.36c**. Major regioisomer **2.2.35c**; IR (neat) 3082, 2919, 1533, 1501, 1351, 1242, 983, 760, 746 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 1.0, 8.3 Hz, 1H), 7.85 (dd, *J* = 1.1, 8.1 Hz, 1H), 7.73 (m, 2 H), 7.63 (m, 4H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 151.1, 137.8, 137.6, 134.9, 134.2, 131.2, 130.2, 129.6, 125.6, 125.4, 125.0, 123.1 ppm; HRMS (ES+) calcd. for $C_{14}H_9Cl_2N_4O_2$ (M+H) 335.0103, found 335.0110. Minor regioisomer **2.2.36c**; IR (neat) 3084, 2924, 2854, 1717, 1537, 1498, 1348, 1307, 1262, 1098, 994, 759 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$) δ 8.10 (dd, *J* = 1.0, 8.3 Hz, 1H), 7.81 (dd, *J* = 1.0, 8.1 Hz, 1H), 7.68 (t, *J* = 8.2 Hz, 2H), 7.43 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 137.8, 136.2, 135.3, 135.0, 132.4, 130.0, 129.9, 127.7, 124.0, 123.8, 120.7, 120.4 ppm; HRMS (ES+) calcd. for $C_{14}H_9Cl_2N_4O_2$ (M+H) 335.0103, found 335.0098.



2.2.16 **2.2.38** **2.2.35d** **2.2.36d**

Triazole 2.2.35d and 2.2.36d. To a pressure vessel containing **2.2.16** (19.8 mg, 76.1 μmol) was added PhMe (160 μL) and azide **2.2.38** (29.1 mg, 244 μmol) sequentially at rt. The reaction mixture was sealed under Ar and heated to 80 °C. After 53 h, the crude mixture was cooled to rt, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-40% EtOAc/Hexanes to give a mixture of

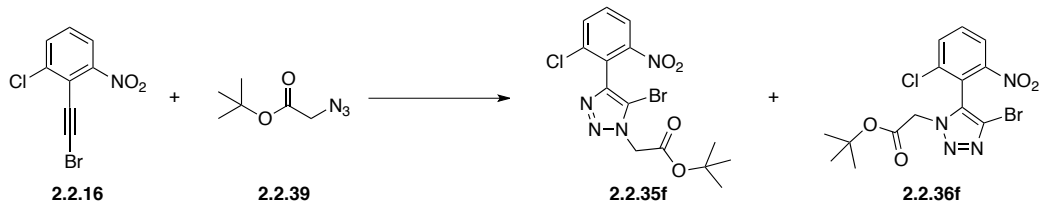
regioisomers (mg, μmol, 24%, 1:1 (**2.2.35d**:**2.2.36d**)). Analytical samples of the individual isomers could be obtained by preparative thin layer chromatography over silica gel, eluting with 30% EtOAc/Hexanes to give sequentially **2.2.35d** then **2.2.36d**. Major regioisomer **2.2.35d**: IR (neat) 2920, 1533, 1499, 1350, 808, 759, 745 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 2 H), 7.65 (t, *J* = 8.3 Hz, 1 H), 7.64 (m, 3H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 151.0, 141.0, 137.7, 135.6, 134.2, 131.1, 130.3, 129.5, 125.5, 123.7, 123.1, 112.2 ppm; HRMS (ES+) calcd. for $C_{14}H_9BrClN_4O_2$ (M+H) 378.9597, found 378.9612. Minor regioisomer **2.2.36d**: IR (neat) 3083, 2922, 2851, 1535, 1497, 1347, 1292, 1092, 992, 758 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.68 (t, *J* = 8.2 Hz, 1 H), 7.45 (m, 4 H), 7.28 (m, 1H) ppm; HRMS (ES+) calcd. for $C_{14}H_9BrClN_4O_2$ (M+H) 378.9597, found 378.9587.



2.2.15 **2.2.39** **2.2.35e** **2.2.36e**

Triazole 2.2.35e and 2.2.36e. To a pressure vessel containing **2.2.15** (19.9 mg, 93.0 μmol) was added PhMe (190 μL) and azide **2.2.39** (46.8 mg, 298 μmol) sequentially at rt. The reaction mixture was sealed under Ar and heated to 80 °C. After 48 h, the crude mixture was cooled to rt, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-40% EtOAc/Hexanes to give a mixture of

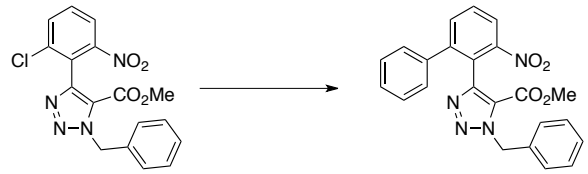
regioisomers (12.8 mg, 34.3 μmol, 37%, 9:1 (**2.2.35e:2.2.36e**)). Analytical samples of the individual isomers could be obtained by preparative thin layer chromatography over silica gel, eluting with 30% EtOAc/Hexanes to give sequentially **2.2.35e** then **2.2.36e**. Major regioisomer **2.2.35e**; Mp 95-97 °C; IR (neat) 3086, 2982, 2932, 1747, 1536, 1354, 1238, 1156, 993, 760 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 1.1, 8.2 Hz, 1H), 7.82 (dd, *J* = 1.2, 8.1 Hz, 1H), 7.63 (t, *J* = 8.2 Hz, 1H), 5.14 (s, 2H), 1.52 (s, 9H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.7, 151.0, 137.6, 137.2, 134.1, 131.1, 126.2, 123.0, 84.4, 50.3, 27.9 ppm; HRMS (ES+) calcd. for $C_{14}H_{15}Cl_2N_4O_4$ (M+H) 373.0470, found 373.0472. Minor regioisomer **2.2.36e**; IR (neat) 2923, 2852, 1748, 1538, 1369, 1239, 1156, 757 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 1.0, 8.3 Hz, 1H), 7.90 (dd, *J* = 1.1, 8.1 Hz, 1H), 7.76 (t, *J* = 8.3 Hz, 1H), 4.91 (d, *J* = 17.3 Hz, 1H), 4.81 (d, *J* = 17.3 Hz, 1H), 1.28 (s, 9H) ppm; HRMS (ES+) calcd. for $C_{14}H_{15}Cl_2N_4O_4$ (M+H) 373.0470, found 373.0487.



2.2.16 **2.2.39** **2.2.35f** **2.2.36f**

Triazole 2.2.35f and 2.2.36f. To a pressure vessel containing **2.2.16** (26.1 mg, 100 μmol) was added PhMe (200 μL) and azide **2.2.39** (47.2 mg, 300 μmol) sequentially at rt. The reaction mixture was sealed under Ar and heated to 80 °C. After 48 h, the crude mixture was cooled to rt, concentrated *in vacuo*, and purified via flash

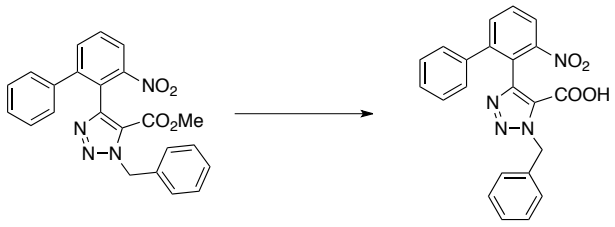
chromatography over silica gel, eluting with 0-35% EtOAc/Hexanes to give a mixture of regioisomers (24.5 mg, 58.7 μmol, 58%, 9:1 (**2.2.35f:2.2.36f**)). Analytical samples of the individual isomers could be obtained by preparative thin layer chromatography over silica gel, eluting with 30% EtOAc/Hexanes to give sequentially **2.2.35f** then **2.2.36f**. Major regioisomer **2.2.35f**: Mp 140-142 °C; IR (neat) 3084, 2981, 2934, 1748, 1534, 1455, 1370, 1236, 990, 760 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 8.2 Hz, 1H), 5.17 (d, *J* = 18.2 Hz, 2H), 1.51 (s, 9H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 161.8, 151.0, 140.5, 137.6, 134.1, 131.1, 123.6, 123.0, 113.0, 84.3, 51.2, 27.9 ppm; HRMS (ES+) calcd. for $C_{14}H_{15}BrClN_4O_4$ (M+H) 416.9965, found 416.9977. Minor regioisomer **2.2.36f**: IR (neat) 3087, 2982, 2929, 1748, 1537, 1353, 1238, 1156, 858, 758, 744 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 1.0, 8.3 Hz, 1H), 7.90 (dd, *J* = 1.0, 8.1 Hz, 1H), 7.75 (t, *J* = 8.3 Hz, 1H), 4.92 (d, *J* = 17.2 Hz, 1H), 4.83 (d, *J* = 17.2 Hz, 1H), 1.40 (s, 9H) ppm; HRMS (ES+) calcd. for $C_{14}H_{15}BrClN_4O_4$ (M+H) 416.9965, found 416.9973.



2.2.32f **2.2.37**

Triazole 2.2.37: To a microwave vessel containing **2.2.32f** (25 mg, 80 μmol) was added sequentially $PhB(OH)_2$ (45.6 mg, 240 μmol), Cs_2CO_3 (79.9 mg, 240 μmol), Ph_2XPhos (7.4 mg, 16 μmol), $Pd(OAc)_2$ (1.8 mg, 8 μmol) and 2-MeTHF (400 μL). The

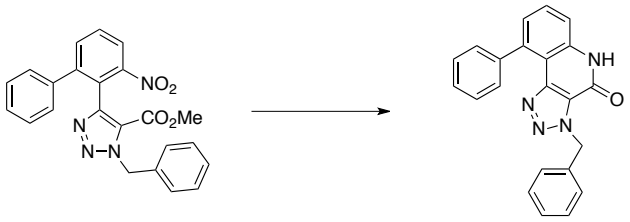
solution was sealed under argon and heated to 100 °C in a microwave. After 1 hour, the mixture was filtered over a pad of Celite®, eluting with Et_2O and concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting 0-30% EtOAc/hexanes, to give **2.2.37** (27.8 mg, 67 μmol, 84%) as a pale yellow solid. Mp 110-113 °C; IR (neat) 3062, 3034, 2955, 1732, 1540, 1479, 1355, 1266, 1218, 1105, 820, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = Hz, 1H), 7.69 (m, 2H), 7.30 (m, 3H), 7.21 (t, *J* = 7.30 Hz, 1H), 7.16 (t, *J* = 7.36 Hz, 2H), 6.99 (m, 4H), 5.84 (q, *J* = 14.81, 34.16 Hz, 2H), 3.57 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 149.6, 146.1, 145.4, 138.7, 135.2, 134.4, 129.8, 129.1, 128.7, 128.1,128.0, 127.6, 126.9, 125.7, 124.6, 123.4, 54.0, 52.3 ppm; HRMS (EI+) calcd. for $C_{23}H_{18}N_4O_4$ (M+) 414.1328, found 414.1331.



2.2.37 **2.2.38**

Carboxylic Acid 2.2.38: To a vial containing triazole **2.2.37** (88 mg, 212 μmol) stirring in EtOH (1 mL) was added $LiOH \cdot H_2O$ (36 mg, 848 μmol) at rt. After 9 h, the reaction was quenched with 6N HCl (3 mL) and concentrated *in vacuo*. The reaction solid was taken up in EtOAc (5 mL) and DI water (5 mL). The aqueous layer was extracted with EtOAc (2 X 5 mL). The organic layer was washed with brine (2 X 5 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The solid was purified by flash chromatography

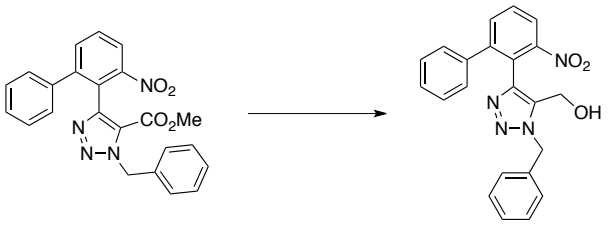
over silica gel, eluting 0-10% MeOH/DCM, to give **2.2.38** (64.7 mg, 161 μmol, 76%) as a white solid. IR (neat) 3381, 2924, 1607, 1530, 1497, 1356, 764 cm^{-1}; ^{1}H NMR (400 MHz, MeOD) δ 8.10 (m, 1H), 7.2 (d, *J* = 5.2 Hz, 2H), 7.14-7.27 (m, 8H), 6.96 (m, 2H), 6.08 (d, *J* = 14.8 Hz, 1H), 5.81 (d, *J* = 14.8 Hz, 1H) 4.88 (s, 1H) ppm; ^{13}C NMR (100 MHz, MeOD) δ 152.0, 145.5, 139.2, 136.5, 134.2, 129.3, 129.0, 128.2, 127.5, 127.3, 127.0, 126.5, 125.1, 122.8, 121.9, 52.7 ppm.



2.2.37 **2.2.39**

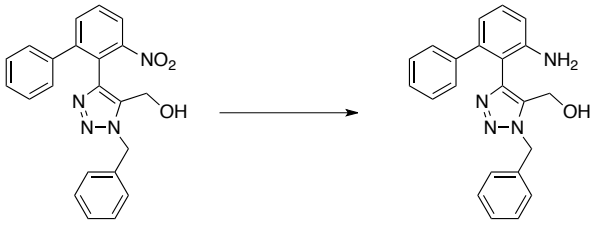
Lactam 2.2.39: To a flask containing triazole **2.2.37** (25.3 mg, 61 μmol) stirring in glacial acetic acid (240 μL) at rt was added Zn dust (12.1 mg, 185 μmol). After 20 h, a second portion of Zn dust (16.8 mg, 0.257 mmol) was added. After 3 h, the reaction was quenched with sat. aq. $NaHCO_3$ (15 mL). The reaction mixture was diluted with EtOAc (15 mL) and the organic layer was washed with sat. aq.$NaHCO_3$ (15 mL), DI water (15 mL), and sat. NaCl (15 mL). The organic layer was then dried over $MgSO_4$ and concentrated *in vacuo*. The pink solid was purified by trituration with EtOAc to give **2.2.39** (11.0 mg, 31 μmol, 52%) as a white solid. MP 257-258 °C; IR (neat) 3060, 2923, 1695, 1664, 1675, 1558, 1373, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.57 (m, 3H), 7.51 (m, 5H), 7.40 (m, 1H), 7.32 (m, 8H), 6.12 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 147.7, 140.4, 140.2, 136.6, 135.2, 129.5, 128.9, 128.8, 128.6,

128.0, 127.9, 126.7, 123.6, 115.4, 112.6, 53.4 ppm; HRMS (ES+) calcd. for $C_{22}H_{17}N_4O_4$ (M+H) 353.1404, found 353.1385.



2.2.37 **2.2.40**

Alcohol 2.2.40: To a flask containing triazole **2.2.37** (25mg, 60 μmol) stirring in DCM (600 μL) at – 78 °C was added DIBAL-H (180 mL, 18 μmol). After 1.5 h, the reaction was warmed to 0 °C and quenched with Rochelle's salt. The reaction mixture was diluted with DCM (10 ml) and the aqueous layer was extracted with DCM (3 x 10 mL ea.). The combined organics were washed with brine (2 x 10 mL ea.), dried over $MgSO_4$ and concentrated *in vacuo*. The solid was purified by flash chromatography over silica gel, eluting 0-30% EtOAc/hexanes, to give **2.2.40** (16.5 mg, 43 μmol, 71%) as a beige solid. MP 148-150 °C; IR (neat) 3315, 3063, 2927, 1532, 1359, 732, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 7.55. 1.81 Hz, 1H), 7.69 (m, 2H), 7.31 (m, 6H), 7.14 (dd, J = 7.91, 1.54 Hz, 2H), 7.01 (m, 2H) 5.58 (s, 2H), 4.02 (m, 2H), 0.49 (t, J = 7.00 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 144.5, 140.5, 138.8, 134.7, 133.8, 133.2, 130.0, 129.5, 128.9, 128.5, 128.2, 128.0, 126.9, 123.6, 123.5, 52.7, 52.4 ppm; HRMS (CI+) calcd. for $C_{22}H_{19}N_4O_4$ (M+H) 387.1458, found 387.1243.



2.2.40 2.2.41

Amino alcohol 2.2.41: To a flask containing triazole **2.2.40** (10.9 mg, 28 μmol) stirring in glacial acetic acid (120 μL) at rt was added Zn dust (5.5 mg, 84 μmol). After 2 h, the reaction was quenched with sat. aq. $NaHCO_3$ (3 mL). The reaction mixture was diluted with EtOAc (5 mL) and the organic layer was washed with sat. aq. $NaHCO_3$ (3 mL), DI water (3 mL). The aqueous layer was extracted with EtOAc (5 mL). The organic layer was washed with sat. NaCl (5 mL). The organic layer was then dried over $MgSO_4$ and concentrated *in vacuo*. The solid was purified by flash chromatography over silica gel, eluting 0-100% EtOAc/hexanes, to give **2.2.41** (8.4 mg, 24 μmol, 84%) as a pale yellow solid. IR (neat) 3361, 1616, 1462, 1004, 761, 729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.12 (overlapping m, 13H), 7.12 (d, J = 7.5 Hz, 1H), 6.87 (d, J = 8.03 Hz, 1H), 5.54 (d, J = 8.59 Hz, 2H), 4.32 (bs, 2H), 3.98 (d, J = 13.83 Hz, 1H), 3.77 (d, J = 13.78, 1H), 0.53 (bs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 143.0, 142.4, 141.4, 134.8, 132.9, 130.0, 129.8, 128.8, 128.3, 128.2, 127.5, 126.9, 120.2, 115.5, 114.0, 52.9, 52.4 ppm; HRMS (CI+) calcd. for $C_{22}H_{21}N_4O$ (M+H) 357.1715, found 357.1716.

Section 2.5. References

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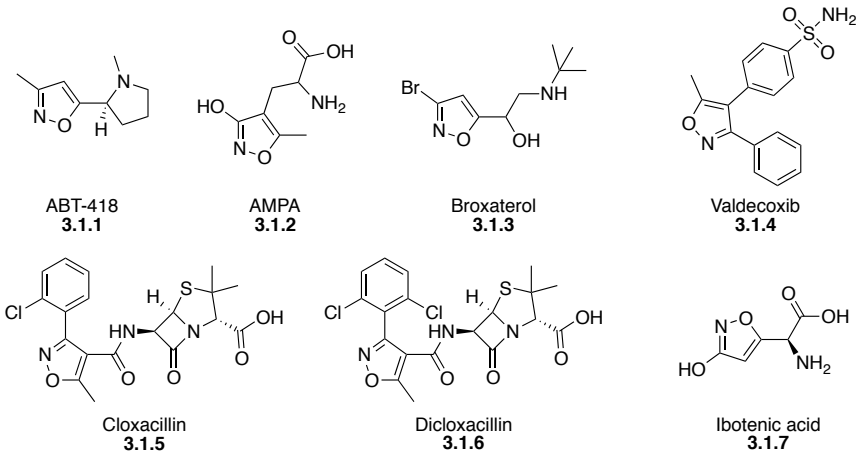
CHAPTER 3: REGIOSELECTIVE SYNTHESIS OF ISOXAZOLES THROUGH [3+2] CYCLOADDITIONS OF NITRILE OXIDES WITH *ORTHO*-NITROPHENYLALKYNES

Section 3.1. Isoxazole Background

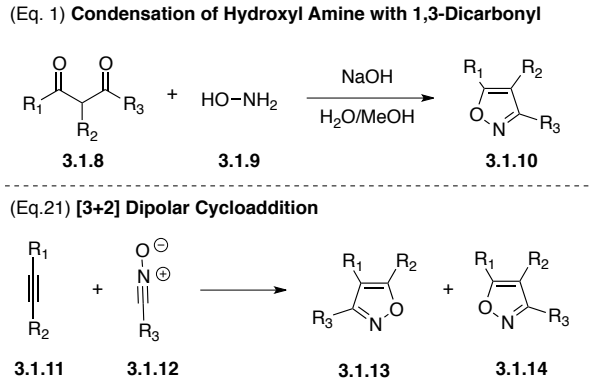
Isoxazoles are an important class of compounds that are found in natural products and medicinally relevant compounds. The scaffold has been found in medicines used to help patients with COPD (chronic obstructive pulmonary disease), such as broxaterol (Figure 3.1).[1] It is present in valdecoxib,[2] an NSAID medication formerly used for the treatment of rheumatoid arthritis. This medication was taken off the market in 2005 because of the increased risk of heart attack and stroke.[3] Isoxazoles are part of antibiotic penicillin derivatives such as cloxacillin and dicloxacillin (Figure 3.1).[4,5] Isoxazole moieties can also be found in natural products such as ibotenic acid, which is a neurotoxin (Figure 3.1.1).[6]

Figure 3.1.1. Medicinally Relevant Compounds and Natural Products, Which Contain Isoxazoles



The synthesis and reactivity of isoxazoles was recently reviewed by Pinho e Melo.[7] Two methods are generally used to synthesize isoxazoles. They include the condensation of hydroxylamine with a 1,3-dicarbonyl substrate (Scheme 3.1.1, Equation 1) and the cycloaddition of an alkyne with a nitrile oxide (Scheme 3.1.1, Equation 2).[8] Our research efforts focused on the cycloaddition reaction.[9,10]

Scheme 3.1.1. Formation of Isoxazole Scaffolds



Previous regioselective syntheses of isoxazoles using [3+2] cycloaddition methodology have been reported. A copper(I) catalyzed route was used by Fokin and co-workers[11] to access 3,5-disubstituted isoxazoles regioselectively. A computational study suggested that thermal, uncatalyzed conditions would favor the 3,5-regioisomer in a 100:1 ratio over the 3,4-regioisomer.[12] Instead of the predicted selectivity, Fokin observed a mixture of regioisomers in the absence of the catalyst. A ruthenium-catalyzed reaction to access 3,5-disubstituted, 3,4-disubstituted, and 3,4,5-trisubstituted isoxazoles was explored by Grecian and Fokin.[13] The complexation of the different dipoles to the ruthenium catalyst controlled the regioselectivity. Cycloaddition of an alkynyldimethylsilyl ether with an aryl or alkyl nitrile oxide was accomplished to provide

3,4,5-trisubstituted isoxazoles.[14] The inherent bias of the dipolarophile and dipole are employed to control regioselectivity in these reactions. Access to 3,4,5-trisubstituted isoxazoles by exploiting haloalkynes has been underutilized. The cycloaddition of aryl alkynes with alkyl and THP ether nitrile oxides was used by Ohlmeyer and co-workers[15] to access 5-aryl-4-bromo-3-carboxyisoxazoles in modest yields. The reaction of alkynyliodide with nitrile oxides to provide 3,4,5-trisubstituted isoxazoles was utilized in a separate study.[16] Dimerization pathways often occur in these [3+2] cycloadditions, but can be avoided if the nitrile oxides are formed *in situ*.[11,14,15]

Section 3.2. Results and Discussion

Densely functionalized isoxazoles were accessed using our highly regioselective methodology of dipolar cycloadditions.[17] As discussed in Chapter 2, our group was able to utilize the *o*-nitro moiety of the phenylalkyne in the thermal, dipolar cycloaddition with azides to form triazoles with up to an 11:1 regioisomeric ratio.[10] Similar thermal conditions were explored in the reactions of *o*-nitrophenylalkynes with nitrile oxides. We are aware of only one other study utilizing *ortho*-nitrophenylalkynes in [3+2] cycloadditions to access isoxazoles.[18]

Exploration into the reactivity and selectivity of the cycloaddition process for isoxazoles began with *o*-nitrophenylalkyne **2.2.7** being reacted with oximal acid chloride **3.2.1**[19] (Scheme 3.2.1). This reaction resulted in high yield and excellent regioselectivity. However, the more sterically encumbered alkyne (**2.2.28**) was not amendable to the cycloaddition reaction, which provided the dimerization product (**3.2.4**). In this case, *in*

situ formation of the nitrile oxide did not eliminate dimerization.[11,14,15] This result suggests that when a disubstituted alkyne is employed, the increased steric effect causes the rate of formation of the cycloaddition product to be slower than the formation of the dimerization product. X-ray crystallography was used to confirm the structure of the dimer (Figure 3.2.1). We speculated that the dimerization pathway could be circumvented if a bulkier nitrile oxide is used. Using a bulkier nitrile oxide would cause a reduction in the rate of formation of the dimer, most likely due to steric effects.

Scheme 3.2.1. Initial Exploration of Nitrile Dipolar Cycloadditions

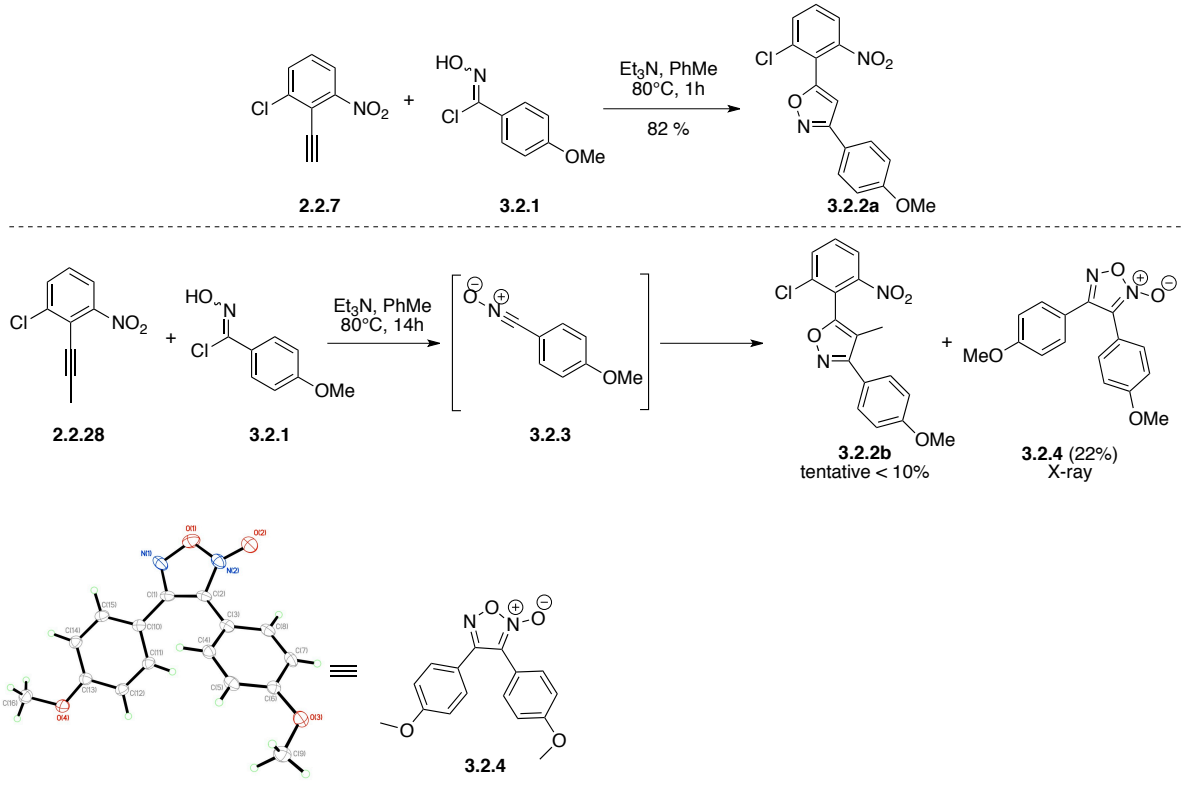
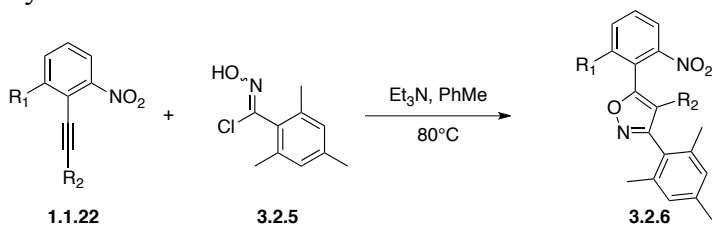


Figure 3.2.1. ORTEP Representation of Isolated Dimer **3.2.4**

Our strategy for accessing isoxazoles then focused on the *in situ* formation of the bulky nitrile oxide to adequately suppress dimer formation. The more sterically hindered mesityl derivative **3.2.5**[20] was selected, since it had been shown to minimize dimerization pathways in the past.[21] Nitrile oxide **3.2.5** was then screened with alkyne **2.2.7** (entry a), resulting in excellent chemical yield (88%) and only a single regioisomer (**3.2.6a**). Fortunately, the steric encumbrance experienced previously (Scheme 3.2.1) with alkyne **2.2.28** was no longer an issue in this reaction, which provided excellent yield (87%) and a single regioisomer (**3.2.6b**). High chemical yields and excellent regioselectivities were observed for all mono- and di-substituted alkynes[9] screened (entries c-j). X-ray crystallographic analyses of compounds **3.2.6b**, **3.2.6d**, **3.2.6g**, and **3.2.6h** (Figure 3.2.2) were used to determine the regiochemistry of the reactions. The excellent regiochemistry (shown in Table 3.2.1) was distinctly different from what was observed in the azide series from Chapter 2, where the R_2 substituent influenced the regiochemical outcome. The isoxazole regiochemical outcome is speculated to arise from the dipole of the nitrile oxide.

Table 3.2.1. Exploration of Alkyne Scope in Nitrile Oxide/Alkyne Dipolar Cycloadditions



1.1.22 3.2.5 3.2.6

Entry	R_1	R_2	Yield[a] (%)
a[b]	Cl	H	88
b[b]	Cl	Me	87
c	Cl	CO_2Me	83
d[b]	Cl	Br	68
e[b]	Cl	Cl	70
f	H	Cl	69
g[b]	Me	Cl	73
h	H	H	90
i[b]	Me	H	92
j[b]	Me	Me	74

(a) Regioselectivity in each case was >20:1 as determined by crude ^{1}H NMR.

(b) Reactions performed by previous group members.

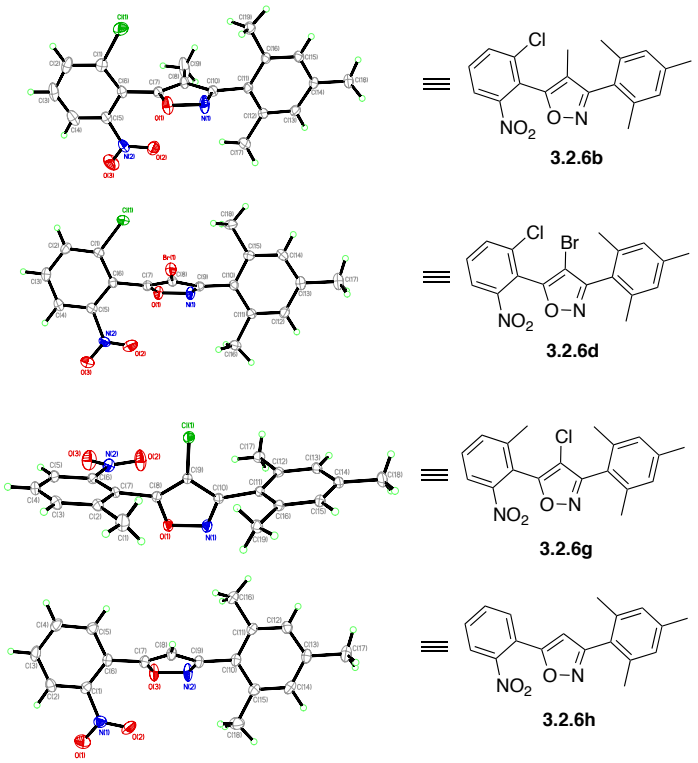
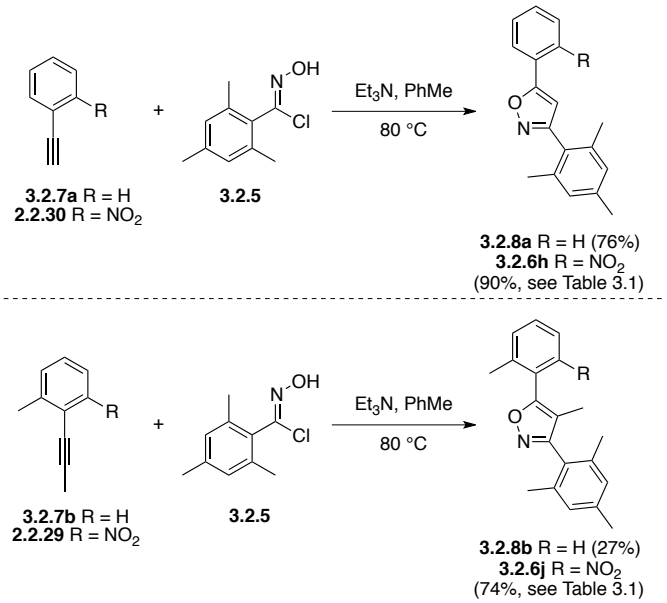


Figure 3.2.2. ORTEP Representation of Isoxazoles **3.2.6b**, **3.2.6d**, **3.2.6g**, and **3.2.6h**

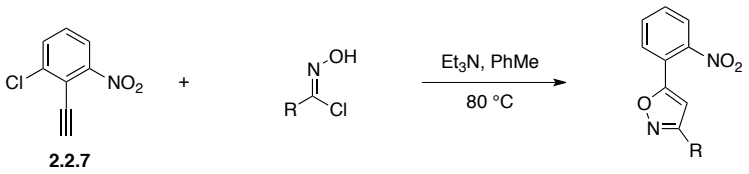
Scheme 3.2.2 shows the important role the *ortho*-nitro moiety plays in the overall yield of the reaction. The *o*-nitro moiety is important in activating the cycloaddition, which leads to improved yields. Alkynes **3.2.7a** and **3.2.7b** provided only 76% and 27% yields, respectively. The corresponding nitro substrates provided higher yields in both cases, demonstrating that the electronic benefits of the ortho-nitro substituent clearly out weigh the steric penalty of its presence.

Scheme 3.2.2. Important Effect of *ortho*-Nitro Moiety in Cycloadditions

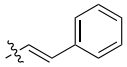
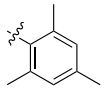


A brief exploration of the oximal acid chloride scope is shown in Table 3.2.2. Variation of the dipole component led to varying yields. Surprisingly, the cycloaddition of alkyne **2.2.7** with nitrile oxide precursor **3.2.9b** provided a much higher yield of cycloaddition product **3.2.10b** (75 %) than the cycloaddition of the more sterically hindered precursor **3.2.9a** with **2.2.7** (**3.2.10a**, 29%). We had witnessed the opposite effect when switching from nitrile oxide precursor **3.2.1** to the more bulky **3.2.5**. More experimentation into the oxime scope is needed to determine a plausible reason for this occurrence. The use of nitrile oxide precursor **3.2.9c** with **2.2.7** provided a 39% yield of the cycloaddition product **3.2.10c**. All yields of the variant oximes were lower than the parent mesityl oximal acid chloride **3.2.5** (88%, Table 3.2.1).

Table 3.2.2. Brief Exploration of the Scope of Nitrile Oxide Reactivity

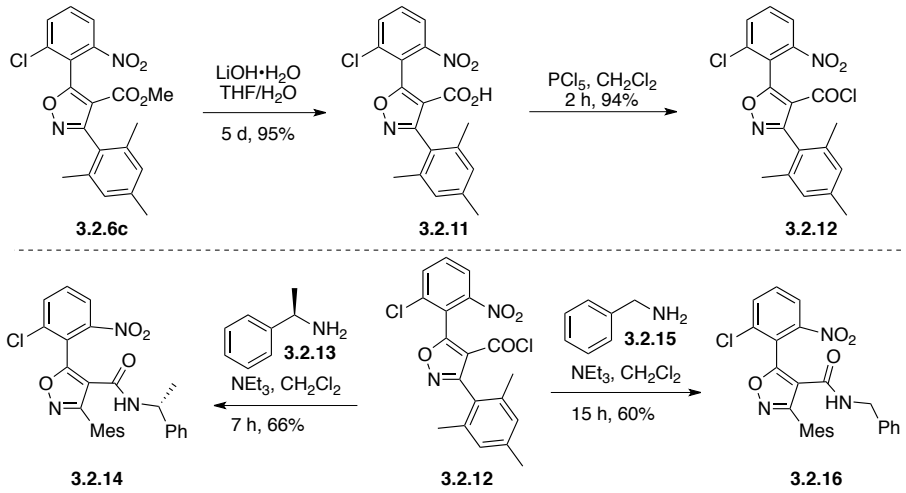


2.2.7

Entry	Time (h)	Oximal Acid Chlcoride	R	Product	Yield (%)
a	15	**3.2.9a**		**3.2.10a**	29
b	15	**3.2.9b**		**3.2.10b**	75
c	14	**3.2.9c**		**3.2.10c**	39
d	10	**3.2.5**		**3.2.6a**	88

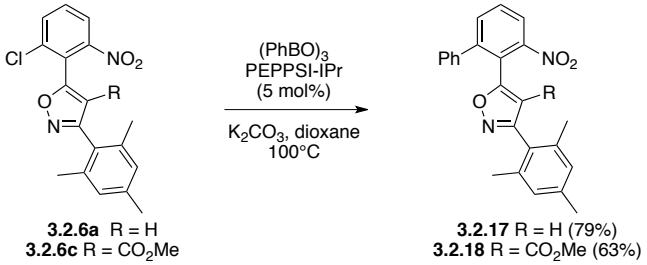
Derivatization of selected isoxazoles was demonstrated as shown in Scheme 3.2.3. The halogen and ester moieties were the targets for modification. The ester functionality of **3.2.6c** could be reacted under optimized LiOH conditions to provide acid **3.2.11** in 95% yield. The acid could be further functionalized to the acid chloride **3.2.12**. The acid chloride **3.2.12** could then be reacted with (R)-(+)-α-methyl benzylamine **3.2.13** or benzyl amine **3.2.15** to form the desired amides, **3.2.14** (66 %) and **3.2.16** (60 %), in moderate yields. The chiral amide **3.2.14** showed doubling of *ortho*-methyl and *meta*-aryl protons in the ^{1}H NMR spectrum, indicating restricted rotation around the mesityl group on the NMR time scale.

Scheme 3.2.3. Derivatization of Selected Isoxazoles



Isoxazoles **3.2.6a** and **3.2.6c** were cross-coupled using the *ortho*-chloro functional handle on the phenyl ring. Previously reported reaction conditions using PEPPSI-IPr[22] and boroxine were utilized to provide biaryls **3.2.17** and **3.2.18** in good yield (Scheme 3.2.4). Attempts to synthesize a variety of biaryls using different boroxines was also attempted; however, these reactions were low yielding and provided reaction products with inseparable impurities.

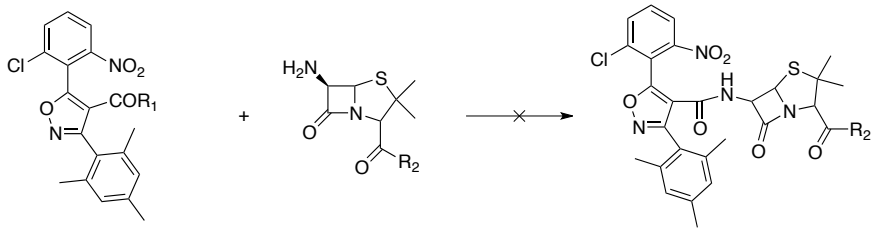
Scheme 3.2.4. Suzuki Coupling Reactions of Selected Isoxazoles



Penicillin type antibiotics containing isoxazole scaffolds have been utilized for antibiotic medicines,[4,5] making them a desirable target to pursue. Table 3.2.3, entries a-f,

show our efforts towards the synthesis of penicillin compounds. The possible isoxazole coupling partners included carboxylic acid **3.2.11**, acid chloride **3.2.12**, and mixed anhydride **3.2.19**. The penicillin derivative was either 6-aminopenicillanic acid **3.2.20** or the methyl ester variant **3.2.21**. A variety of conditions were attempted to access new penicillin compounds, however, only decomposition products and starting material were obtained.

Table 3.2.3. Attempted Synthesis of Penicillin Derivative



R_1 = OH **3.2.11**
R_1 = Cl **3.2.12**
R_1 = $OCOCH_2CH(CH_3)_2$ **3.2.19**

R_2 = OH **3.2.20**
R_2 = OMe **3.2.21**

R_2 = OH **3.2.22**
R_2 = OMe **3.2.23**

Entry	Isoxazole	Penicillin Target	Conditions
a	**3.2.12**	**3.2.20**	NEt_3, DMAP, THF, 0 °C - rt
b	**3.2.12**	**3.2.20**	NEt_3, DMAP, THF, rt
c	**3.2.11**	**3.2.21**	EDC, DMAP, CH_3CN
d	**3.2.12**	**3.2.21**	NEt_3, DMF, DCM
e	**3.2.19**	**3.2.21**	NEt_3, DMF, THF, then DMAP
f	**3.2.11**	**3.2.21**	Hünig's base, HATU, DMF

Section 3.3. Conclusion

A highly regioselective method for the production of densely functionalized isoxazoles utilizing a dipolar cycloaddition of nitrile oxides (*in situ* generated) and *o*-nitrophenylalkynes has been reported. Substituents on the alkyne dipolarophile are inconsequential to regioselectivity and a wide range of substituents is tolerated. The R group on the nitrile oxide precursor was of great importance to the chemical yield of the reaction (Scheme 3.2.2). Derivatization of two selected isoxazoles was accomplished.

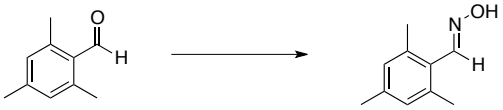
Section 3.4. Experimental Section

General. Infrared spectra were recorded neat unless otherwise indicated and are reported in cm^{-1}. ^{1}H NMR spectra were recorded in deuterated solvents and are reported in ppm relative to tetramethylsilane and/or referenced internally to the residually protonated solvent. ^{13}C NMR spectra were recorded in deuterated solvents and are reported in ppm relative to tetramethylsilane and/or referenced internally to the residually protonated solvent.

Routine monitoring of reactions was performed using EM Science DC-Alufolien silica gel, aluminum-backed TLC plates. Flash chromatography was performed with the indicated eluents on EM Science Gedurian 230-400 mesh silica gel.

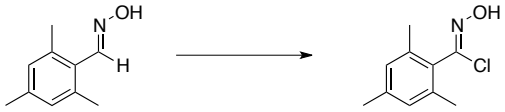
Air and/or moisture sensitive reactions were performed under usual inert atmosphere conditions. Reactions requiring anhydrous conditions were performed under a blanket of argon, in glassware dried in an oven at 120°C or by flame, then cooled under argon. Dry THF, Et_2O, Toluene and DCM were obtained via a solvent purification

system. All other solvents and commercially available reagents were either purified via literature procedures or used without further purification.



3.2.20 3.2.19

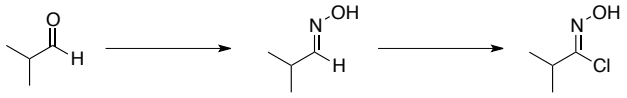
Oxime 3.2.19: To a stirred solution of ice (46 g) in H_2O/Ethanol (40 mL, 1:1) was added mesitylaldehyde **3.2.20** (6 mL, 40.7 mmol), hydroxylamine hydrochloride (4.2 g, 61.0 mmol) and NaOH (17 mL, 100 mmol, 6.0 M in H_2O). After 2 h, the reaction was quenched with 1 M HCl (50 mL), extracted with Et_2O (3 X 30 mL), and washed with brine (30 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* and purified by recrystallization with Et_2O and Hexanes to give known oxime **3.2.19**[20] (6.05 g, 37.1 mmol, 91%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 6.91 (s, 2H), 2.39 (s, 6H), 2.30 (s, 3H) ppm.



3.2.19 3.2.5

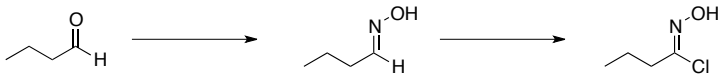
Oximyl Acid Chloride 3.2.5: To a stirred solution of oxime **3.2.19** (3.0 g, 18.4 mmol) in DMF (18.5 mL) at 0 °C, was added 4 portions of NCS (0.75 g X 4, 20 min apart). Upon warming to rt over 4 h, the reaction was quenched with H_2O/Ice (50 mL), extracted with Et_2O (4 X 25 mL), and washed with brine (2 X 10 mL). The dried (Na_2SO_4) extract was

concentrated *in vacuo* to give known **3.2.5**[20] (3.6 g, 18.4 mmol, 99%) as a white semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 2H), 2.27 (s, 9H) ppm.



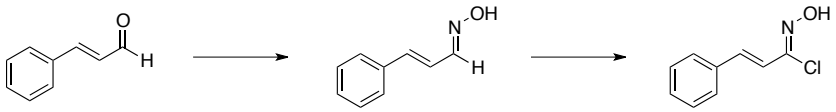
3.2.21 **3.2.22** **3.2.9a**

Oximyl Acid Chloride 3.2.9a: To a stirred solution of ice (15 g) in H_2O/Ethanol (14 mL, 1:1) was added aldehyde **3.2.21** (1.3 mL, 14 mmol), hydroxylamine hydrochloride (1.5 g, 21 mmol) and NaOH (5.8 mL, 35 mmol, 6.0 M in H_2O). After 21 h, the reaction was quenched with 1 M HCl (10 mL), extracted with DCM (3 X 25 mL), and washed with brine (50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* to give crude oxime **3.2.22** as a yellow liquid which was used without further purification. To a stirred solution of oxime **3.2.22** (1.2 g, 14 mmol) in DMF (14 mL) at 0 °C, was added 4 portions of NCS (0.49 g X 4, 20 min apart). After 18 h at rt, the reaction was diluted with H_2O (20 mL), extracted with Et_2O (3 X 20 mL), and washed with brine (1 X 50 mL). The dried (Na_2SO_4) extract was concentrated *in vacuo* to give known **3.2.9a**[23] (1.63 g, 13.4 mmol, 96%) as a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (bs, 1H), 2.82 (septet, J = 6.8 Hz, 1H), 1.23 (d, J = 6.8 Hz, 6H) ppm.



3.2.23 3.2.24 3.2.9b

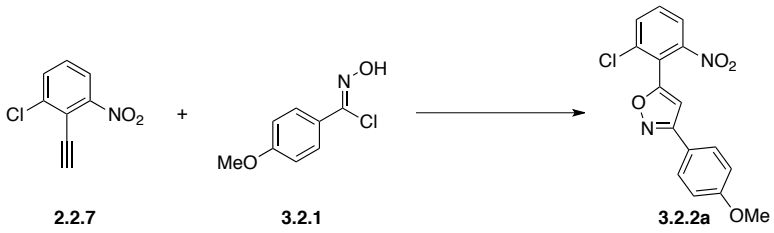
Oximyl Acid Chloride 3.2.9b: To a stirred solution of ice (15 g) in H_2O/Ethanol (14 mL, 1:1) was added aldehyde **3.2.23** (1.3 mL, 14 mmol), hydroxylamine hydrochloride (1.5 g, 21 mmol) and NaOH (5.8 mL, 35 mmol, 6.0 M in H_2O). After 2.5 h, the reaction was quenched with 2 M HCl (10 mL), extracted with Et_2O (3 X 20 mL), and washed with brine (50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* to give crude oxime **3.2.24** as a colorless liquid which was used without further purification. To a stirred solution of oxime **3.2.24** (1.2 g, 14 mmol) in DMF (14 mL) at 0 °C, was added 4 portions of NCS (0.49 g X 4, 20 min apart). After 18.5 h at rt, the reaction was diluted with H_2O (20 mL), extracted with Et_2O (3 X 20 mL), and washed with brine (1 X 50 mL). The dried (Na_2SO_4) extract was concentrated *in vacuo* to give known **3.2.9b**[24] (1.7 g, 14 mmol, 99%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (bs, 1H), 2.50 (t, J = 7.3 Hz, 2H), 1.70 (sextet, J = 7.4 Hz, 6H), 0.98 (t, J = 7.3, 3H) ppm.



3.2.25 3.2.26 3.2.9c

Oximyl Acid Chloride 3.2.9c: To a stirred solution of ice (15 g) in H_2O/Ethanol (14 mL, 1:1) was added aldehyde **3.2.25** (1.8 mL, 14 mmol), hydroxylamine hydrochloride (1.5 g, 21 mmol) and NaOH (5.8 mL, 35 mmol, 6.0 M in H_2O). After 4.5 h, the reaction was quenched with 1 M HCl (12 mL), extracted with Et_2O (3 X 20 mL), and washed with

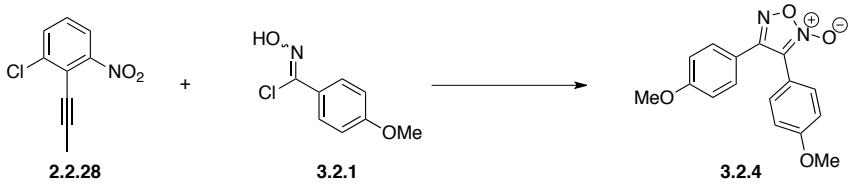
brine (50 mL). The dried ($MgSO_4$) extract was concentrated *in vacuo* to give crude oxime **3.2.26** as a yellow solid which was used without further purification. To a stirred solution of oxime **3.2.26** (2.06 g, 14 mmol) in DMF (14 mL) at 0 °C, was added 4 portions of NCS (0.49 g X 4, 20 min apart). After 11 h at rt, the reaction was diluted with H_2O (50 mL), extracted with Et_2O (2 X 40 mL), and washed with H_2O (3 X 60 mL). The dried (Na_2SO_4) extract was concentrated *in vacuo* to give known **3.2.9c**[23] (2.49 g, 13.7 mmol, 98%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (bs, 1H), 7.51 (d, J = 7.6 Hz, 2H), 7.48-7.31 (overlapping m, 4H), 6.88 (d, J = 15.6, 1H) ppm.



2.2.7 3.2.1 3.2.2a

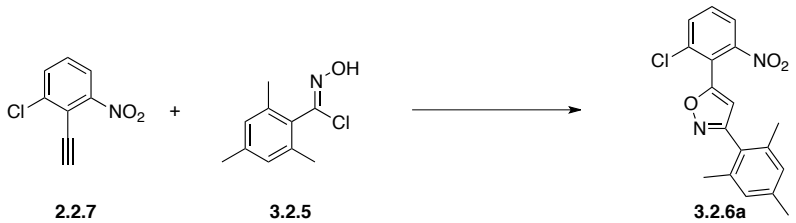
Isoxazole 3.2.2a: To a pressure vessel containing **2.2.7**[9c] (63.2 mg, 348 µmol) was added dry PhMe (600 µL), NEt_3 (150 µL, 109 mg, 1.08 mmol) and **3.2.1**[8,19] (208.5 mg, 1.123 mmol) sequentially, and heated to 80 °C. Immediately after addition of **3.2.1**, a white solid formed along with a mild exotherm. After 1 h, the reaction was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 10-25% EtOAc / Hexanes to give **3.2.2a** (101.4 mg, 306.6 µmol, 82%) as a yellow solid. Mp 82-84 °C; IR (neat) 3087, 2839, 1612, 1534, 1434, 1255, 1029, 809, 738 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 8.2 Hz, 1H), 7.82 (m, 3H), 7.64 (t, J = 8.2 Hz, 1H), 7.02 (m, 2H), 6.82 (s, 1H), 3.89 (s, 3H) ppm; ^{13}C NMR (100 MHz,

$CDCl_3$) δ 162.3, 162.2, 161.2, 150.4, 136.2, 134.3, 131.6, 128.4, 123.0, 122.2, 121.0, 114.4, 104.0, 55.4 ppm; HRMS (ES+) calcd. for $C_{16}H_{12}N_2O_4Cl$ (M+H) 331.0486, found 331.0476.



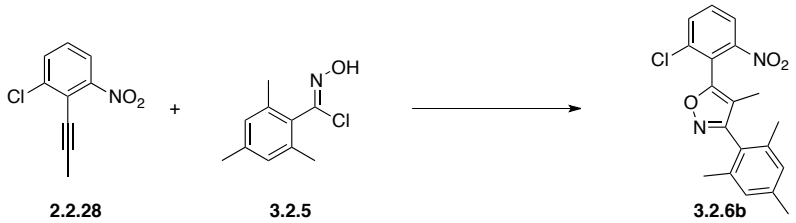
2.2.28 3.2.1 3.2.4

Dimer 3.2.4: To a stirred solution of **2.2.28**[10] (19.4 mg, 99 μmol) and **3.2.1**[8,19] (184 mg, 990 μmol) in PhMe (500 μL) at 80 °C was added NEt_3 (800 μL, 1.19 mmol, 1.50 M in PhMe) via syringe pump over 5 hours. After 14 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-50 % EtOAc / Hexanes to give undesired dimer **3.2.4** (64.6 mg, 216 μmol, 22%) as a yellow solid. Mp 105-107 °C; IR (neat) 2938, 2840, 1611, 1591, 1574, 1520, 1450, 1258, 1179, 835 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (t, J = 8.34 Hz, 4H), 6.97 (dd, J = 9.04, 2.64 Hz, 4H), m, 3H), 3.88 (s, 3H), 3.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 161.1, 155.9, 130.2, 129.8, 199.0, 114.9, 114.5, 55.4 ppm; HRMS (EI+) calcd. for $C_{16}H_{14}N_2O_4$ (M+) 298.0953, found 298.0952.



2.2.7 3.2.5 3.2.6a

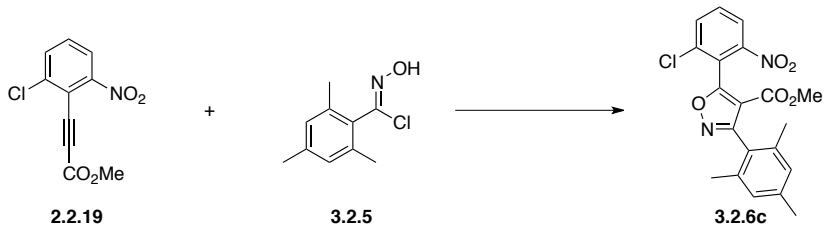
Isoxazole 3.2.6a: To a stirred solution of **2.2.7**[9c] (63.8 mg, 351 μmol) and NEt_3 (500 μL, 363 mg, 3.59 mmol) in PhMe (700 μL) at 80 °C was added **3.2.5**[20] (15.4 mL, 3.846 mmol, 250 mM in PhMe) via syringe pump over 5 hours. After 10 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 2-8% EtOAc / Hexanes gave pure **3.2.6a** (105.9 mg, 309.0 μmol, 88%) as a yellow oil. IR (thin film) 1750, 1613, 1536, 1464, 1439, 1382, 1353, 906, 882, 808, 757, 737 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.2, 1.2 Hz, 1H), 7.83 (dd, J = 8.2, 1.2 Hz, 1H), 7.65 (t, J = 8.2 Hz, 1H), 7.00 (s, 2H), 6.49 (s, 1H), 2.36 (s, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 162.2, 150.2, 139.1, 137.3, 136.3, 134.4, 131.7, 128.4, 125.5, 123.1, 122.4, 107.6, 21.8, 20.2 ppm; HRMS (EI+) calcd. for $C_{18}H_{15}N_2O_3Cl$ (M+) 342.0771, found 342.0759.).



2.2.28 3.2.5 3.2.6b

Isoxazole 3.2.6b: To a stirred solution of **2.2.28**[10] (41.4 mg, 212 μmol) and **3.2.5**[20] (446.3 mg, 2.258 mmol) in PhMe (1.00 mL) at 80 °C was added NEt_3 (1.72 mL, 2.58 mmol,

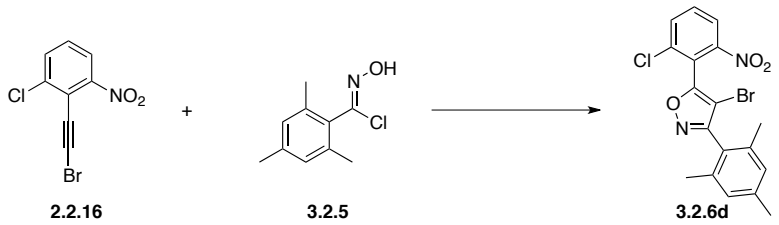
1.50 M in PhMe) via syringe pump over 5 hours. After 10 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 5-15 % EtOAc / Hexanes to give impure **3.2.6b** as a yellow oil. The impure oil was triturated and recrystallized from hexanes / methanol to give pure **3.2.6b** (65.6 mg, 184 μmol, 87%) as a pale yellow solid. Mp 151-153 °C; IR (thin film) 1609, 1535, 1456, 1437, 1348, 901, 852, 808, 759, 735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.85 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.68 (t, *J* = 8.2 Hz, 1H), 7.00 (s, 2H), 2.37 (s, 3H), 2.18 (s, 6H), 1.75 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 159.0, 150.3, 139.0, 137.5, 137.0, 134.5, 131.8, 128.3, 124.8, 123.3, 122.8, 114.8, 21.2, 19.7, 7.1 ppm; HRMS (EI+) calcd. for $C_{19}H_{17}N_2O_3Cl$ (M+) 356.0928, found 356.0926.



2.2.19 **3.2.5** **3.2.6c**

Isoxazole 3.2.6c: To a stirred solution of **2.2.19**[9c] (50 mg, 208 μmol) and **3.2.5**[20] (411 mg, 2.08 mmol) in PhMe (1.5 mL) at 80 °C, was added NEt_3 (1.7 mL, 2.55 mmol, 1.5 M in PhMe) via syringe pump over 5 hours. After 14 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 10-20% EtOAc/Hexanes to give impure **3.2.6c** as a yellow solid. Repurification via trituration with hexanes gave impure **3.2.6c** as a pale yellow solid.

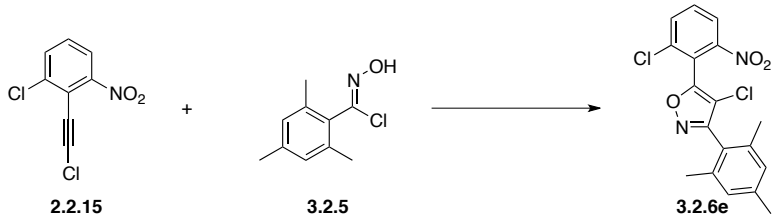
Repurification via flash chromatography over silica gel, eluting 20-40% EtOAc/Hexanes gave impure **3.2.6c**. Repurification via trituration with hexanes and EtOAc gave **3.2.6c** (69.5 mg, 173 μmol, 83%) as a white solid. Mp 177-178 °C; IR (neat) 1730, 1534, 1456, 1400, 1348, 1310, 1120 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 0.8, 8.3 Hz, 1H), 7.89 (dd, *J* = 0.8, 8.1 Hz, 1H), 7.75 (t, *J* = 8.2 Hz, 1H), 6.98 (s, 2H), 3.51 (s, 3H), 2.37 (s, 3H), 2.81 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 162.0, 160.7, 149.2, 139.1, 136.6, 134.9, 132.2, 128.1, 124.2, 123.4, 123.0, 111.9, 51.9, 21.3, 19.9 ppm; HRMS (EI+) calcd. for $C_{20}H_{17}N_2O_5Cl$ (M+) 400.0826, found 400.0838.



2.2.16 **3.2.5** **3.2.6d**

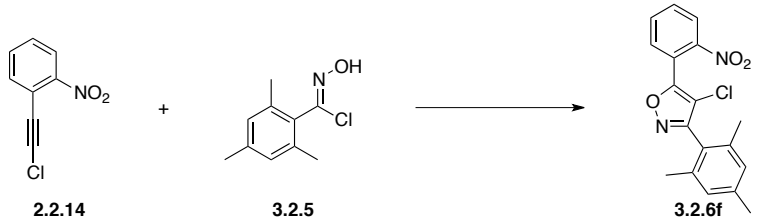
Isoxazole 3.2.6d: To a stirred solution of **2.2.16**[10] (42.8 mg, 164 μmol) and **3.2.5**[20] (353.8 mg, 1.790 mmol) in PhMe (1.00 mL) at 80 °C was added NEt_3 (1.43 mL, 2.15 mmol, 1.50 M in PhMe) via syringe pump over 5 hours. After 10 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 2-10 % EtOAc / Hexanes to give impure **3.2.6d** as a yellow solid. The impure solid was recrystalized from methanol to give pure **3.2.6d** (46.8 mg, 111 μmol, 68%) as a light brown oil. IR (thin film) 1527, 1356, 1116 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.74 (t, *J* = 8.2 Hz, 1H), 7.02 (s, 2H), 2.38 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H) ppm; ^{13}C NMR (100 MHz,

$CDCl_3$) δ 162.9, 161.7, 149.6, 139.8, 138.0, 137.3, 135.0, 132.6, 128.4, 128.3, 123.6, 121.4, 97.3, 21.3, 19.7 ppm; HRMS (EI+) calcd. for $C_{18}H_{14}N_2O_3ClBr$ (M+) 419.9876, found 419.9880.



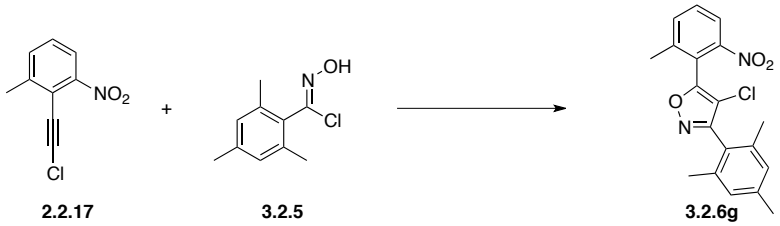
2.2.15 **3.2.5** **3.2.6e**

Isoxazole 3.2.6e: To a stirred solution of **2.2.15**[10] (41.1 mg, 190 μmol) and **3.2.5**[20] (386.8 mg, 1.957 mmol) in PhMe (1.00 mL) at 80 °C was added NEt_3 (1.67 mL, 2.51 mmol, 1.50 M in PhMe) via syringe pump over 5 hours. After 10 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 10-30 % EtOAc / Hexanes to give impure **3.2.6e** as a yellow solid. The impure solid was recrystallized from methanol to give pure **3.2.6e** (50.2 mg, 133 μmol, 70%) as a light brown oil. IR (thin film) 1528, 1353 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 8.2, 1.2 Hz, 1H), 7.90 (dd, J = 8.2, 1.2 Hz, 1H), 7.74 (t, J = 8.2 Hz, 1H), 7.02 (s, 2H), 2.38 (s, 3H), 2.23 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 159.4, 149.7, 139.8, 137.9, 137.4, 134.9, 132.6, 128.4, 123.6, 122.6, 120.9 111.2, 21.2, 19.7 ppm; HRMS (EI+) calcd. for $C_{18}H_{14}N_2O_3Cl_2$ (M+) 376.0382, found 376.0400.

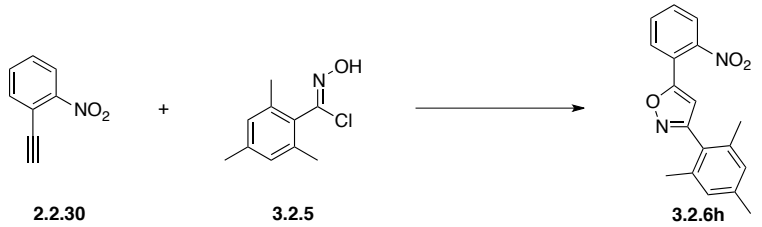


2.2.14 3.2.5 3.2.6f

Isoxazole 3.2.6f: To a stirred solution of **2.2.14**[10] (50 mg, 0.276 mmol) and **3.2.5**[20] (545 mg, 2.76 mmol) in PhMe (1.5 mL) at 80 °C, was added NEt_3 (2.2 mL, 3.30 mmol, 1.5 M in PhMe) via syringe pump over 5 hours. After 16.5 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 5-10% EtOAc/Hexanes to give impure **3.2.6f** as a yellow oil. Purification via flash chromatography over silica gel, eluting 10% EtOAc/Hexanes gave impure **3.2.6f** as a yellow oil. Repurification via flash chromatography over silica gel, eluting 20% Et_2O/Pentane gave **3.13f** (66 mg, 0.193 mmol, 69%) as a beige solid. Mp 89-92 °C; IR (neat) 1534, 1351, 1129, 852 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 1H), 7.76-7.86 (m, 3H), 7.01 (s, 2H), 2.37 (s, 3H), 2.21 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 161.5, 148.2, 139.8, 137.8, 133.4, 131.8, 131.6, 128.4, 125.3, 122.7, 121.0, 109.6, 21.3, 19.8 ppm; HRMS (EI+) calcd. for $C_{18}H_{15}N_2O_3Cl$ (M+) 342.0771, found 342.0772.

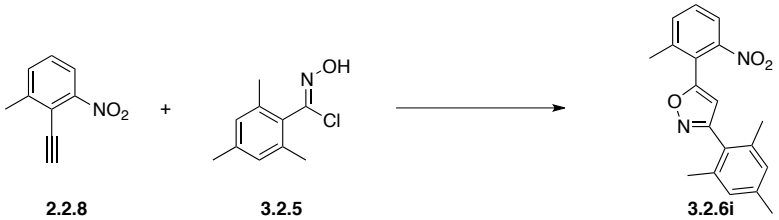


Isoxazole 3.2.6g: To a stirred solution of **2.2.17**[10] (240.9 mg, 1.231 mmol) and **3.2.5**[20] (2.369 g, 11.98 mmol) in PhMe (6.10 mL) at 80 °C was added NEt_3 (10.1 mL, 15.1 mmol, 1.50 M in PhMe) via syringe pump over 5 hours. After 10 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 10-30 % EtOAc / Hexanes to give impure **3.2.6g** as a yellow solid. The impure solid was recrystallized from methanol to give pure **3.2.6g** (346.8 mg, 977.5 μmol, 73%) as a yellow solid. Mp 178-180 °C; IR (thin film) 1538, 1455, 1384, 1339, 912, 880, 854, 803, 748, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.11 (dd, J = 7.4, 2.0 Hz, 1H), 7.70 (d, J = 5.7 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.02 (s, 2H), 2.39 (s, 3H), 2.38 (s, 3H), 2.23 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7, 161.4, 149.0, 141.5, 139.8, 135.5, 131.5, 128.4, 122.8, 122.8, 120.4, 110.0, 21.3, 19.7, 19.5 ppm; HRMS (EI+) calcd. for $C_{19}H_{17}N_2O_3Cl$(M+) 356.0928, found 356.0913.



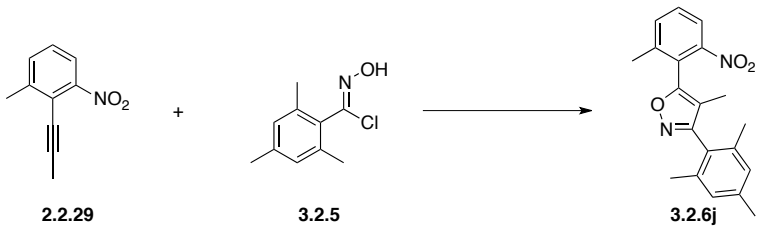
2.2.30 3.2.5 3.2.6h

Isoxazole 3.2.6h: To a stirred solution of **2.2.30** (50 mg, 0.340 mmol) and **3.2.5**[20] (672 mg, 3.40 mmol) in PhMe (1.5 mL) at 80 °C, was added NEt_3 (2.7 mL, 4.05 mmol, 1.5 M in PhMe) via syringe pump over 5 hours. After 11.5 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 10% EtOAc/Hexanes to give impure **3.2.6h** as a yellow solid. Repurification via flash chromatography over silica gel, eluting 20% EtOAc/Hexanes gave impure **3.2.6h**. Repurification via trituration with hexanes gave **3.2.6h** (94.4 mg, 0.306 mmol, 90%) as a white solid. Mp 122-123 °C; IR (neat) 1534, 1353 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (td, J = 1.2, 8.1 Hz, 2H), 7.75 (td, J = 1.2, 7.6 Hz, 1H), 7.66 (td, J = 1.3, 7.7 Hz, 1H), 6.98 (s, 2H), 6.46 (s, 1H), 2.35 (s, 3H), 2.12 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 162.7, 148.2, 139.1, 137.3, 132.6, 131.0, 130.4, 128.4, 125.5, 124.4, 121.8, 105.4, 21.2, 20.3 ppm; HRMS (EI+) calcd. for $C_{18}H_{16}N_2O_3$ (M+) 308.1161, found 308.1162.



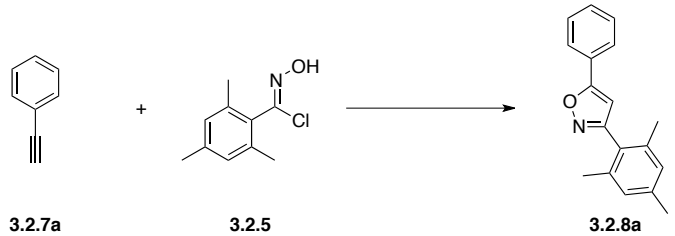
2.2.8 3.2.5 3.2.6i

Isoxazole 3.2.6i: To a stirred solution of **2.2.8**[10] (47.2 mg, 293 μmol) and **3.2.5**[20] (519.9 mg, 2.630 mmol) in PhMe (1.50 mL) at 80 °C was added NEt_3 (2.40 mL, 3.60 mmol, 1.50 M in PhMe) via syringe pump over 5 hours. After 10 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and was purified via flash chromatography over silica gel, eluting with 10-25 % EtOAc / Hexanes to give impure **3.2.6i** as a solid. The impure solid was recrystalized from Hexanes / methanol to give pure **3.2.6i** (87.1 mg, 269 μmol, 92%) as a pale yellow oil. IR (thin film) 1613, 1528, 1457, 1381, 1354, 906, 855, 832, 802, 707 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.7, 1.0 Hz, 1H), 7.63 (d, J = 6.5 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 6.99 (s, 2H), 6.29 (s, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 2.24 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 162.3, 149.6, 140.8, 139.0, 137.2, 134.9, 130.8, 128.4, 125.7, 122.3, 122.1, 106.1, 21.2, 20.2, 20.0 ppm; HRMS (EI+) calcd. for $C_{19}H_{18}N_2O_3$ (M+) 322.1317, found 322.1304.



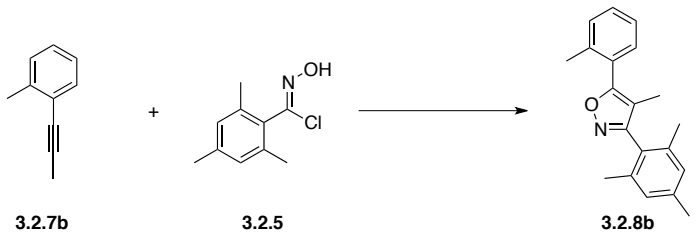
2.2.29 3.2.5 3.2.6j

Isoxazole 3.2.6j: To a stirred solution of **2.2.29**[10] (80.9 mg, 462 μmol) and **3.2.5**[20] (845.6 mg, 4.278 mmol) in PhMe (2.30 mL) at 80 °C was added NEt_3 (3.70 mL, 5.55 mmol, 1.50 M in PhMe) via syringe pump over 5 hours. After 10 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 2-10 % EtOAc / Hexanes to give impure **3.2.6j** as a yellow solid. The impure solid was recrystalized from methanol to give pure **3.2.6j** (115.7 mg, 349.3 μmol, 74%) as a light brown solid. Mp 133-135 °C; IR (thin film) 1643, 1613, 1533, 1457, 1347, 914, 853, 804, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 8.4, 1.3 Hz, 1H), 7.65 (dd, J = 7.7, 1.9 Hz, 1H), 7.60 (t, J = 7.9 Hz, 1H), 7.00 (s, 2H), 2.36 (s, 3H), 2.33 (s, 3H), 2.18 (s, 6H), 1.67 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 161.3, 149.6, 141.4, 138.9, 137.3, 135.0, 130.7, 128.2, 125.0, 122.5, 122.3, 113.4, 21.2, 19.7, 19.6, 6.9 ppm; HRMS (EI+) calcd. for $C_{20}H_{20}N_2O_3$ (M+) 336.1470, found 336.1462.



3.2.7a 3.2.5 3.2.8a

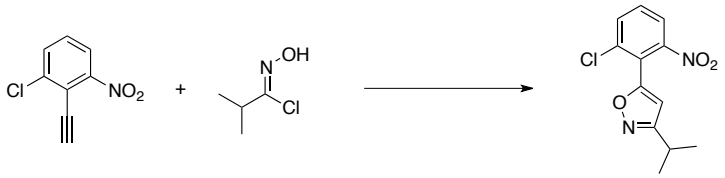
Isoxazole 3.2.8a: To a stirred solution of **3.2.7a** (50 µL, 455 µmol) and **3.2.5**[20] (900 mg, 4.55 mmol) in PhMe (3.0 mL) at 80 °C was added NEt_3 (3.6 mL, 5.46 mmol, 1.5 M in PhMe) via syringe pump over 5 hours. After 20 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-10 % EtOAc / Hexanes to give impure **3.2.8a** as a yellow solid. The impure solid was recrystallized from EtOAc/Hex to give known **3.2.8a**[16] (89.4 mg, 340 µmol, 75%) as a white solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.88 (d, J = 7.1 Hz, 2H), 7.53 (t, J = 7.1 Hz, 2H), 7.48 (t, J = 7.1 Hz, 1H), 6.99 (s, 2H), 6.50 (s, 1H), 2.36 (s, 3H), 2.22 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 162.7, 138.8, 137.2, 130.1, 129.0, 128.4, 127.6, 126.2, 125.9, 100.9, 21.1, 20.2 ppm.



3.2.7b 3.2.5 3.2.8b

Isoxazole 3.2.8b: To a stirred solution of **3.2.7b**[25] (50.0 mg, 384 µmol) and **3.2.5**[20] (759 mg, 3.84 mmol) in PhMe (1.5 mL) at 80 °C was added NEt_3 (3.1 mL, 4.61 mmol, 1.5 M in PhMe) via syringe pump over 5 hours. After 15 h, the crude mixture was cooled to rt,

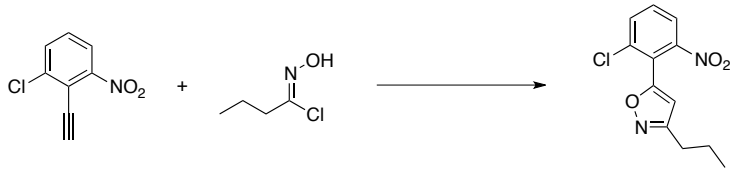
filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-20 % EtOAc / Hexanes to give impure **3.2.8b**. Repurification via trituration with Hexanes and EtOAc gave **3.2.8b** (29.9 mg, 103 μmol, 27%) as a white solid. Mp 96-99 °C; IR (neat) 2923, 1614, 1450, 1145, 1006, 898, 852, 766, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.31 (overlapping m, 4H), 6.99 (s, 2H), 2.41 (s, 3H), 2.37 (s, 3H), 2.16 (s, 6H), 1.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 163.4, 138.7, 137.8, 137.3, 130.8, 129.8, 129.6, 128.2, 128.0, 125.7, 111.4, 21.2, 20.1, 19.8, 7.6 ppm. HRMS (ES+) calcd. for $C_{20}H_{22}NO$ (M+H) 292.1701, found 292.1689.



2.2.7 **3.2.9a** **3.2.10a**

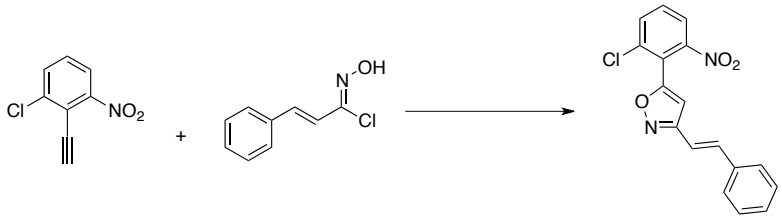
Isoxazole 3.2.10a: To a stirred solution of **2.2.7**[9c] (69.7 mg, 384 μmol) and **3.2.9a**[23] (467 mg, 3.84 mmol) in PhMe (1.5 mL) at 80 °C was added NEt_3 (3.1 mL, 4.61 mmol, 1.5 M in PhMe) via syringe pump over 5 hours. After 15 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-30 % EtOAc / Hexanes to give impure **3.2.10a**. Repurification via flash chromatography over silica gel, eluting with 0-10 % EtOAc / Hexanes gave **3.2.10a** (29.5 mg, 111 μmol, 29%) as a yellow oil with 10% inseparable impurity. IR (neat) 3089, 2970, 1537, 1352, 1124, 950, 883, 759, 739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 8.2, 1.0 Hz, 1H), 7.78 (dd, J = 8.2, 1.1 Hz, 1H), 7.60 (t, J = 8.2 Hz, 1H),

6.42 (s, 1H), 3.16 (septet, J = 7.1 Hz, 1H), 1.37 (d, J = 7.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 161.5, 150.4, 136.0, 134.2, 131.4, 122.9, 122.4, 104.4, 26.7, 21.6 ppm. HRMS (EI+) calcd. for $C_{12}H_{11}N_2O_3Cl$ (M+) 266.0458, found 266.0462.



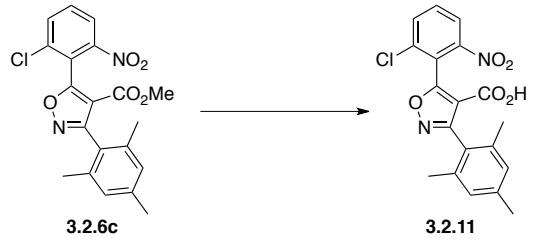
2.2.7 **3.2.9b** **3.2.10b**

Isoxazole 3.2.10b: To a stirred solution of **2.2.7**[9c] (69.7 mg, 384 μmol) and **3.2.9b**[24] (467 mg, 3.84 mmol) in PhMe (1.5 mL) at 80 °C was added NEt_3 (3.1 mL, 4.61 mmol, 1.5 M in PhMe) via syringe pump over 5 hours. After 15 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-30 % EtOAc / Hexanes to give impure **3.2.10b**. Repurification via flash chromatography over silica gel, eluting with 0-10 % EtOAc / Hexanes gave **3.2.10b** (76.8 mg, 288 μmol, 75%) as a yellow oil. IR (neat) 3090, 2964, 2875, 1538, 1417, 1354, 1125, 950, 883, 808, 738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.60 (t, J = 8.1 Hz, 1H), 6.40 (s, 1H), 2.75 (t, J = 7.3 Hz, 2H), 1.77 (sextet, J = 7.4 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 161.6, 150.3, 136.0, 134.2, 131.5, 122.9, 122.4, 105.8, 28.0, 21.5, 13.6 ppm. HRMS (EI+) calcd. for $C_{12}H_{11}N_2O_3Cl$ (M+) 266.0458, found 266.0469.

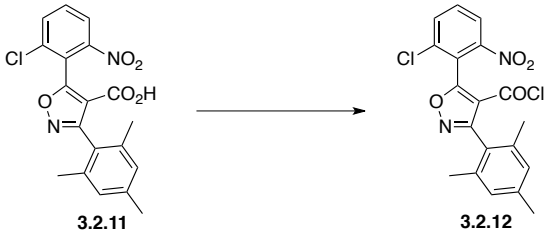


2.2.7 3.2.9c 3.2.10c

Isoxazole 3.2.10c: To a stirred solution of **2.2.7**[9c] (69.7 mg, 384 μmol) and **3.2.9c**[23] (697 mg, 3.84 mmol) in PhMe (1.5 mL) at 80 °C was added NEt_3 (3.1 mL, 4.61 mmol, 1.5 M in PhMe) via syringe pump over 5 hours. After 14 h, the crude mixture was cooled to rt, filtered, concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-20 % EtOAc / Hexanes to give impure **3.2.10c**. Repurification via trituration with Hexanes and EtOAc gave **3.2.10c** (49.4mg, 151 μmol, 39%) as a yellow solid with 10% inseparable impurities. Mp 117-120°C; IR (neat) 1535, 1425, 1353, 965, 884, 755, 737, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.64 (t, J = 8.2 Hz, 1H), 7.57 (d, J = 7.1 Hz, 2H), 7.44-7.33 (overlapping multiplets, 3H), 7.27, 7.20 (ABq, J = 16.5 Hz, 2H), 6.80 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 161.9, 150.4, 136.6, 136.3, 135.7, 134.3, 131.7, 129.1, 128.9, 127.1, 123.0, 122.1, 155.6, 103.3 ppm. HRMS (ES+) calcd. for $C_{17}H_{11}N_2O_3Cl$ (M+H) 327.0536, found 327.0543.

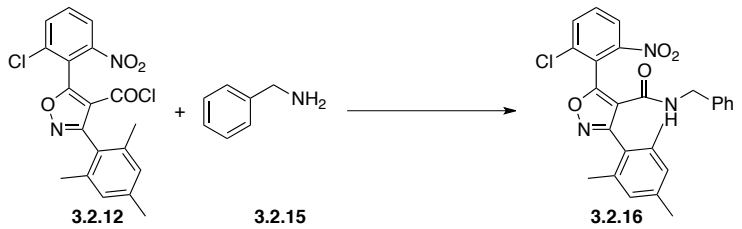


Carboxylic Acid 3.2.11: To a stirred solution of **3.2.6c** (100 mg, 249 μmol) stirring in THF/H_2O (2:1, 0.2 M, 1.2 mL) was added LiOH•H_2O (36.2 mg, 863 μmol). After 5 days the reaction mixture was quenched with 6 M HCl (1.5 mL) and the aqueous layer extracted with EtOAc (3 x 10 mL ea.). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$ and concentrated *in vacuo* to yield **3.2.11** as a beige solid (91.9 mg, 238 μmol, 95%). Mp 195-197 °C; IR (neat) 2919, 1691, 1536, 1348, 1139, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 8.4 Hz, 1H), 6.98 (s, 2H), 2.36 (s, 3H), 2.18 (s, 6H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.7, 162.9, 161.9, 148.8, 139.3, 137.4, 137.1, 136.6, 135.1, 132.4, 128.3, 128.1, 123.9, 123.6, 122.8, 111.2, 21.3, 19.9 ppm; HRMS (ES+) calcd. for $C_{19}H_{16}ClN_2O_5$ (M+H) 387.0762, found 387.0748.



Acid Chloride 3.2.12: To a stirred solution of **3.2.11** (10 mg, 25.8 μmol) in CH_2Cl_2 (100 μL) was added PCl_5 (6.4 mg, 30.7 μmol). After 2 h at reflux the crude mixture was

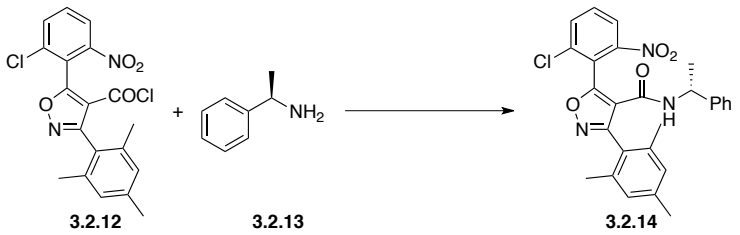
cooled to rt and concentrated *in vacuo* to give **3.2.12** as a beige solid (9.8 mg, 24.2 μmol, 94%). Crude materials were used without further purification. Mp 132-136 °C; IR (neat) 2925, 1733, 1536, 1315, 1124, 737 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.82 (t, *J* = 8.4 Hz, 1H), 7.02 (m, 2H), 2.83 (s, 3H), 2.22 (s, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.8, 161.6, 157.9, 148.5, 139.9, 137.4, 137.1, 136.6, 135.5, 133.0, 128.5, 128.4, 123.9, 123.0, 122.4, 116.5, 21.1, 19.9 ppm; HRMS (EI+) calcd. for $C_{19}H_{14}Cl_2N_2O_4$ (M+) 404.0331, found 404.0330.



3.2.12 3.2.15 3.2.16

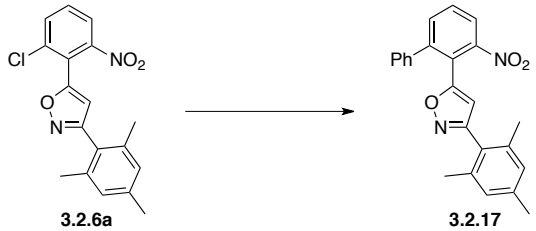
Amide 3.2.16: To a stirred solution of **3.2.12** (14.5 mg, 35.8 μmol) in CH_2Cl_2 (360 μL) was added NEt_3 (10 μL, 71.6 μmol) and benzylamine **3.2.15** (8 μL, 73.2 μmmol) at rt. After 15 h the crude materials were concentrated *in vacuo* and purified via flash chromatography over silica gel, eluting 0-40% EtOAc/Hexanes to give **3.2.16** as a beige solid (10.2 mg, 21.4 μmol, 60%). Mp 139-141 °C; IR (neat) 3400, 2922, 1666, 1531, 1350, 1150, 738 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.70 (t, *J* = 8.4 Hz, 1H), 7.23 (m, 3H), 6.93 (s, 2H), 6.86 (m, 2H), 5.52 (s, 1H), 4.25 (d, *J* = 4.6 Hz, 1H), 4.18 (d, *J* = 4.1 Hz, 1H), 2.30 (s, 3H), 2.17 (s, 6H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.2, 159.2, 159.1, 149.2, 140.7, 138.0, 137.3, 136.8, 136.6, 134.8, 131.9, 129.2, 129.0, 128.5, 127.5, 127.2, 123.6, 123.4, 123.3, 113.6, 43.2,

21.2, 19.7 ppm; HRMS (ES+) calcd. for $C_{26}H_{23}ClN_3O_4$ (M+H) 476.1377, found 476.1358.



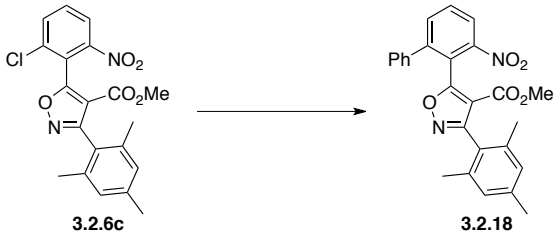
3.2.12 3.2.13 3.2.14

Amide 3.2.14: To a stirred solution of **3.2.12** (4.8 mg, 11.8 μmol) in CH_2Cl_2 (120 μL) was added NEt_3 (3.3 μL, 23.6 μmol) and (R)-(+)-α-methyl benzylamine **3.2.13** (3 μL, 23.6 μmmol) at rt. After 7 h the crude materials were concentrated *in vacuo* and purified via flash chromatography over silica gel, eluting 0-30% EtOAc/Hexanes to give **3.2.14** as a beige solid (3.8 mg, 7.75 μmol, 66%). Mp 51-53 °C; IR (neat) 3388, 2924, 1667, 1534, 1351, 757, 699 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.24 (bs, 1H), 7.85 (dd, J = 7.6, 14.8 Hz, 1H), 7.68 (t, J = 8.2 Hz, 1H), 7.22 (m, 3H), 7.13 (s, 1H of rotamer), 7.10 (s, 1H of rotamer), 6.96 (s, 1H of rotamer), 6.94 (s, 1H of rotamer), 6.80 (m, 2H), 5.65 (bs, 1H), 4.89 (s, 1H), 2.39 (s, 3H), 2.28 (s, 3H of a rotamer), 2.26 (s, 3H of a rotamer), 2.09 (s, 3H), 1.16 (m, 3H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.0, 159.1, 158.3, 149.2, 142.4, 142.2, 140.8, 138.3, 138.1, 137.7, 137.4, 136.6, 134.8, 131.8, 129.4, 129.2, 128.9, 128.5, 127.3, 125.4, 123.6, 123.4, 113.7, 48.6, 22.2, 21.3, 19.8, 19.7 ppm; HRMS (ES+) calcd. for $C_{27}H_{25}ClN_3O_4$ (M+H) 490.1534, found 490.1524.



3.2.6a 3.2.17

Isoxazole 3.2.17: To a pressure vessel containing **3.2.6a** (83.4 mg, 243 μmol) and dioxane (1.00 mL), was sequentially added PEPPSI-IPr (16.8 mg, 24.7 μmol), $(PhBO)_3$ (124.3 mg, 340 μmol), K_2CO_3 (127.6 mg, 923 μmol). The solution was sealed under Ar and heated to 80 °C. After 48 h, the reaction was cooled to rt, and filtered through a Celite pad with CH_2Cl_2 (40 mL). The elutant was concentrated *in vacuo*, and purified via flash chromatography over silica gel, eluting with 0-15% EtOAc / hexanes to give **3.2.17** (74.1 mg, 19.3 μmol, 79%) as a pale yellow solid. Mp 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, J = 2.1, 7.3 Hz, 1H), 7.76 (m, 2H), 7.35 (m, 3H), 7.24 (m, 2H), 6.92 (s, 2H), 5.85 (s, 1H), 2.32 (s, 3H), 2.02 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 162.0, 149.5, 145.3, 138.8, 138.4, 137.3, 134.6, 130.9, 128.9, 128.4, 128.21, 128.20, 125.7, 123.6, 121.7, 107.0, 21.1, 20.0 ppm; HRMS (EI+) calcd. for $C_{24}H_{20}N_2O_3$ (M+) 384.1474, found 384.1465.



3.2.6c 3.2.18

Isoxazole 3.2.18: To a seal tube containing **3.2.6c** (50 mg, 125 μmol) was added sequentially K_2CO_3 (52 mg, 374 μmol), $(PhBO)_3$ (117 mg, 374 μmol), and PEPPSI-IPr (3.8 mg, 5.6 μmol). The vessel was evacuated and backfilled with argon 3 times. Dioxane was added and the reaction was let stir at 100 °C. After 15 h, the crude material was cooled to rt, filtered through Celite and concentrated *in vacuo*. Purification via flash chromatography over silica gel, eluting 5-20% EtOAc/Hexanes gave **3.2.18** as a yellow solid (37.4 mg, 84.5 μmol, 63%). Mp 175-178 °C; IR (neat) 2953, 1732, 1534, 1123, 737, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (t, J = 4.8 Hz, 1H), 7.82 (d, J = 4.8 Hz, 2H), 7.32 (m, 3H), 7.21 (m, 2H), 6.92 (s, 1H), 6.86 (s, 1H), 3.41 (s, 3H), 2.31 (s, 3H), 2.13 (s, 3H) 1.76 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 161.8, 160.6, 148.3, 145.6, 138.8, 137.9, 137.1, 136.9, 135.1, 131.3, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 124.4, 123.9, 122.1, 111.7, 51.6, 21.2, 19.8, 19.7 ppm; HRMS (EI+) calcd. for $C_{26}H_{22}N_2O_5$ (M+) 442.1529, found 442.1531.

Section 3.5. References

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CHAPTER 4. SYNTHESIS, CHARACTERIZATION, AND ANALYSIS OF NOVEL NITRO-POLYCYCLIC AROMATIC HYDROCARBONS (NPAHS)

Section 4.1. Introduction

Nitro polycyclic aromatic hydrocarbons (NPAHs) are ubiquitous pollutants found in the environment.[1] NPAHs are formed through partial combustion of organic materials or from the parent PAH reacting with photochemical oxidants in the atmosphere.[2] The sources of NPAHs include natural sources, such as forest fires, or anthropogenic sources, such as diesel exhaust. Many PAH compounds are known carcinogens and the NPAHs can be more mutagenic than the parent PAH.[3,4] It is important to understand whether NPAHs are present in the environment and their toxicity.

Previously, our investigated at the formation of novel NPAHs using heterogeneous chamber reactions of parent PAHs with NO_2, NO_3/N_2O_5 and OH radicals.[5] The NPAHs anticipated to be formed in this study are shown in Figure 4.1.1. This research showed how parent PAHs could be transformed into nitrated PAHs through atmospheric photochemical reactions, an especially important phenomenon in the long-range atmospheric transport of these pollutants. Gaussian modeling was used to predict the reactive sites of the parent PAHs and dipole moment calculations were used to estimate their elution order.[5] This work also included the resultant Ames assays which provided confirmation of substantially higher mutagenicity of these nitrated PAHs as compared to the corresponding parent PAH.[5]

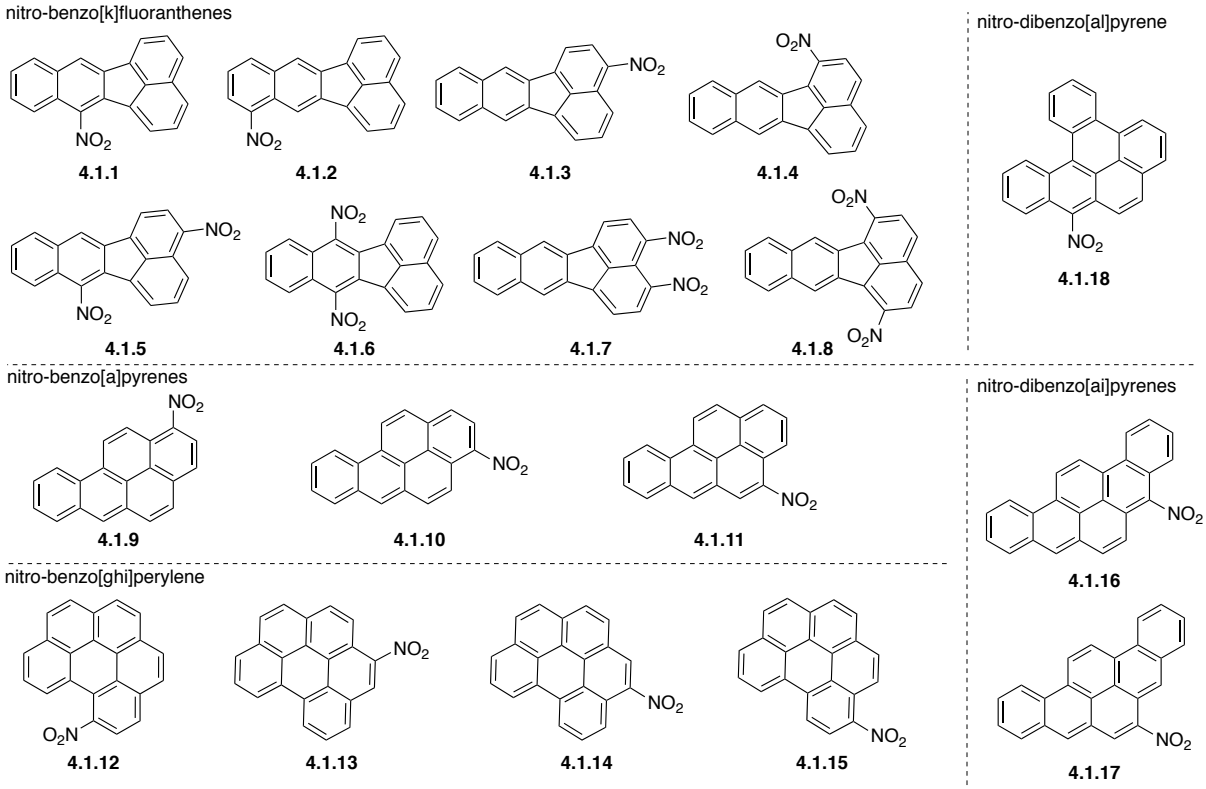


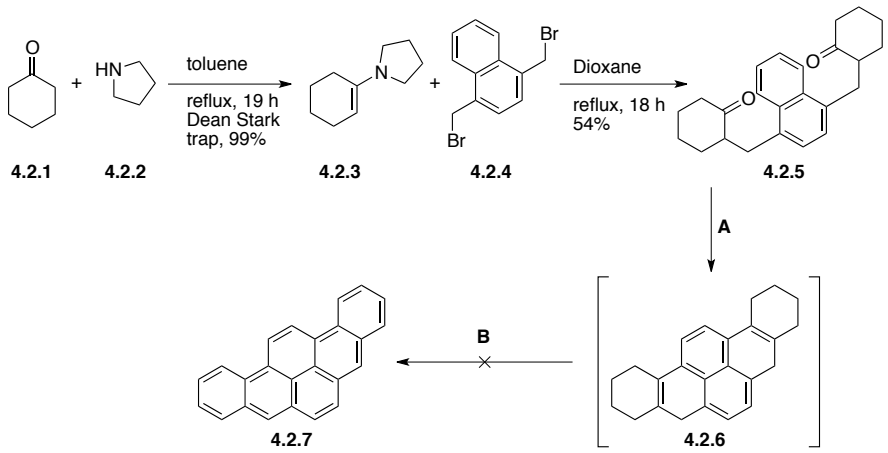
Figure 4.1.1. Structures of Novel NPAHs Predicted From Chamber Reactions[5]

Section 4.2. Results and Discussion

In order to confirm the structures of the NPAHs formed in the chamber study, these novel NPAHs needed to be synthesized. In some cases, the parent PAH could be subjected to a simple nitration to form the NPAH. Computational calculations showed the possible sites of electrophilic aromatic substitution (EAS) on the parent PAH. Direct nitration of the parent PAH should proceed via this mechanism to provide the expected NPAH. Some parent PAHs are not available in large enough quantities to nitrate, thus the synthesis of these parent PAHs was necessary.

Dibenzo[a,i]pyrene (DBAIP, **4.2.7**) was only commercially available in solution form, or in milligram quantities, at high costs, prompting our group to attempt its synthesis. Attempted synthesis of DBAIP, using a known procedure (Table 4.2.1),[6] began with the synthesis of enamine **4.2.3** through condensation of cyclohexanone **4.2.1** with pyrrolidine **4.2.2**. The enamine was then coupled with dibromonaphthalene **4.2.4** to form compound **4.2.5**. Synthesis of cyclized compound **4.2.6** was attempted using multiple conditions (Table 4.2.1, entries 1-4), but provided a complex mixture of products. Our inability to reproduce the anhydrous HF conditions in the known literature procedure proved detrimental to the reaction. The subsequent aromatization step was attempted with the unpurified complex mixture using the conditions listed in Table 4.2.1, entries 5-7. However, formation of compound **4.2.7** was not observed. Because of the difficulties in synthesizing **4.2.6**, and ultimately DBAIP (**4.2.7**), we decided to abandon this synthesis and focus on direct nitration of the parent PAHs we had on hand.

Table 4.2.1. Attempted Synthesis of Dibenzo[ai]pyrene

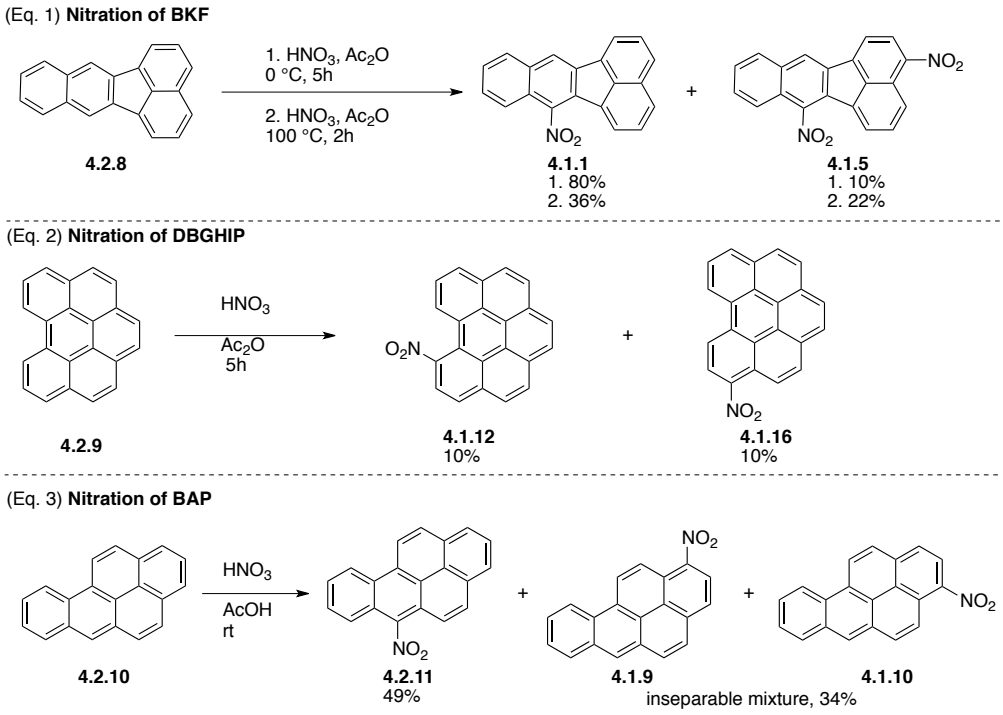


Entry	Reaction	Conditions	Result
1	**A**	H_3CSO_2OH, $CHCl_3$, 2.5 d	Complex mixture
2	**A**	PPA, 110 °C, 3 h	Complex mixture
3	**A**	HF 48% aq. 72 h	Complex mixture
4	**A**	HBr, HOAc, reflux, 4 d	Complex mixture
5	**B**	Pd/C, triglyme, reflux, 18 h	No product observed
6	**B**	Pd/C, triglyme, μW, 220 °C, 30 m	No product observed
7	**B**	DDQ, benzene, reflux, 1 h	No product observed

Benzo[k]fluoranthene (BKF, **4.2.8**), benzo[ghi]perylene (BGHIP, **4.2.9**), and benzo[a]pyrene (BAP, **4.2.10**) were available for direct nitration (Scheme 4.2.1). Following known procedures,[7] benzo[k]fluoranthene was nitrated to provide 7-nitrobenzo[k]fluoranthene **4.1.1**[8] and 3,7-dinitrobenzo[k]fluoranthene **4.1.5**. The known nitration of BKF was accomplished under controlled conditions so that 7-NBKF (**4.1.1**)

was the only product observed.[8] Interestingly, through our nitration procedure, we found that, at higher temperatures, a higher yield of the di-nitro **4.1.5** was observed, although the yield of the mono-nitrated **4.1.1** decreased significantly (Scheme 4.2.1, Equation 1). Nitration of BGHIP[9] provided known nitration products 5-NBGHIP **4.1.12** and 7-NBGHIP **4.1.16** in 10% yield each (Scheme 4.2.1, Equation 2). This was lower than what was observed in the original paper.[9] Purification by preparatory HPLC gave analytically pure samples of the 7-NBKF (**4.1.1**), 3,7-NBKF (**4.1.5**), 5-NBGHIP (**4.1.12**), and 7-NBGHIP (**4.1.16**). Nitration of BAP[9] **4.2.10** provided commercially available 6-NBAP **4.2.11** and an inseparable mixture of 1-NBAP **4.1.9** and 3-NBAP **4.1.10** (Scheme 4.2.1, Equation 3).

Scheme 4.2.1. Direct Nitration of Parent PAHs



Pure NPAHs were structurally confirmed by 1D and 2D NMR spectroscopy. The ^{1}H NMR spectrum for 7-NBKF (**4.1.1**) showed a variety of multiplets, but only one singlet at δ 8.47, suggesting that the nitro substituent was on ring B and carbon position 7 (Figure 4.2.1). Computed values of BKF suggested the most reactive site would provide the 3-NBKF (**4.1.3**). Analysis of the splitting patterns and COSY spectrum for 7-NBKF **4.1.1** was in agreement with this assignment. NMR data correlation tables for 3,7-NBKF **4.1.5**, 7-NBGHIP **4.1.12**, and 5-NBGHIP **4.1.13** are shown in Chapter 6. The ^{1}H NMR spectrum for 3,7-NBKF (**4.1.5**) shows a characteristic singlet at δ 8.49 (carbon 12) implying one nitro substituent was on carbon 7 (Figure 4.2.1). Due to the chemical shifts and limited ^{1}H-^{1}H correlations in the COSY NMR spectrum, the other nitro substituent was determined to be on the ring corresponding with proton signals at δ 8.12 (d) and δ 8.70 (d). These data suggested that the nitro substituent would be on ring D or E. NOE experiments were used to determine through space correlations between ^{1}H signals at δ 8.49 (position 12) and signals at δ 8.12 (d) and δ 8.03 (dd). As the signal at δ 8.12 was on the second nitrated ring, the nitro substituent must be on ring D. Because of the observed ^{1}H-^{1}H correlation, carbon position 1 must be protonated; therefore, the nitrated position must be carbon 3. Analysis of HSQC and HMBC ^{1}H-^{13}C correlation data supported this structural assignment. Analysis of the ^{1}H NMR spectrum for 7-NBGHIP (**4.1.12**) showed the presence of only doublet and triplet proton splitting patterns suggesting that the nitro substitution position must be on rings A or E (Figure 4.2.1) and that the substituent must be on carbon 5 or 7. The symmetry in the molecule makes the

distinction between ring A and E arbitrary. The ^{13}C signal at δ 146.4 did not show a correlation in the HSQC data suggesting that this was a quaternary carbon and the chemical shift was consistent with a carbon bearing a nitro substituent. HMBC spectroscopy provides ^{1}H-^{13}C correlations between 2-4 bonds away from each other. The HMBC spectra obtained for 7-NBGHIP **4.1.12**, showed correlations from two proton signals, δ 8.25 and δ 8.10, to the ^{13}C resonance at δ 146.4. This suggested that the nitro substituent was in carbon position 7. The NMR analysis of 5-NBGHIP (**4.1.16**) also provided only doublet and triplet proton splitting patterns leading to a similar possible structure as determined for 7-NBGHIP. The nitro substituent was predicted to be on the A or E ring in position 5 or 7. In this case, the nitro-carbon signal at δ 144.2 showed correlations to 3 proton signals (δ 9.06, δ 8.94, δ 8.73), suggesting that the nitro group was at carbon position 5. Examination of the 2D NMR data supported this assignment.

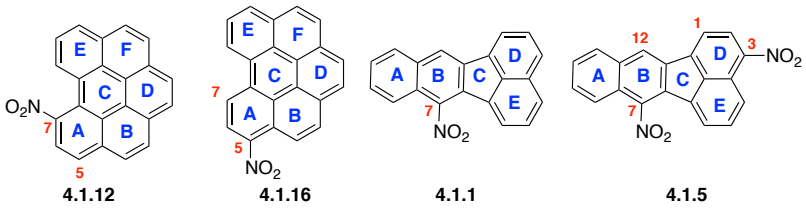


Figure 4.2.1. Ring Assignments

During the synthesis process, a universal approach was envisioned to access a wide range of nitrated BKF derivatives. The retrosynthetic strategy shown in Figure 4.2.2 employed a palladium-catalyzed cross-coupling reaction of nitrated naphthalene derivatives to access a variety of nitrated BKF compounds. Based on work by Hiyama and coworkers,[10] in the synthesis of phenanthrenes and dibenzo[g,p]chrysenes, a Suzuki

coupling strategy, employing a dihalogenated naphthalene and a diboronic acid naphthalene was envisioned. In order to utilize this exciting strategy, the synthesis of the coupling partners was needed.

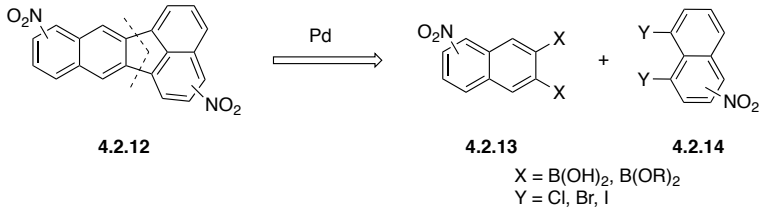
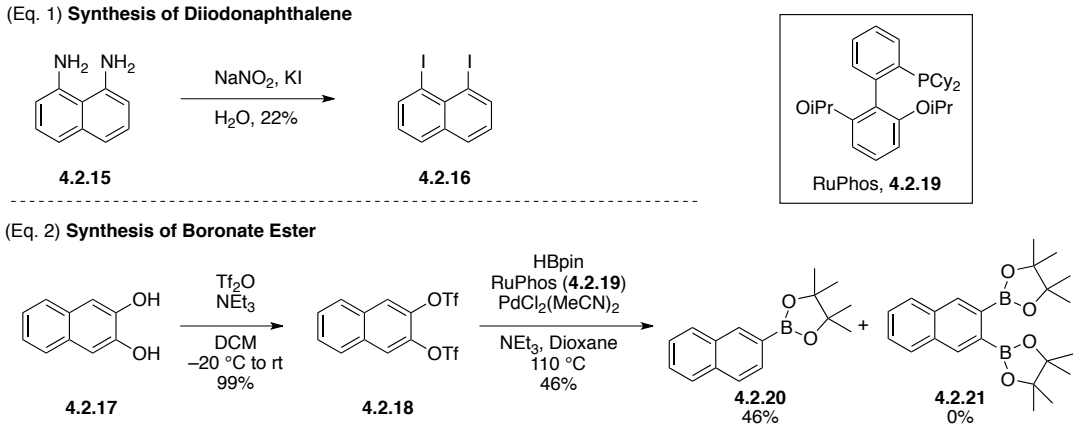


Figure 4.2.2. Retrosynthetic Strategy for Access to Nitrated Benzo[k]fluoranthenes

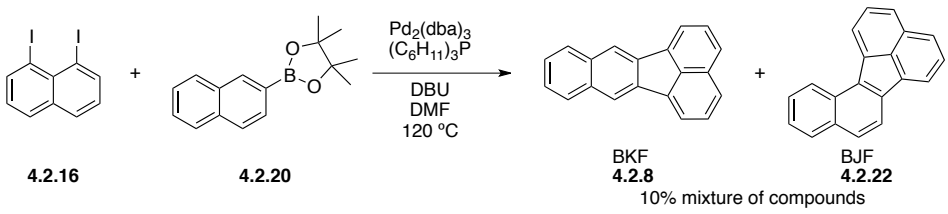
The sythesis of naphthalene coupling reagents was explored and the non-nitrated system was used as a model system. The synthesis of 1,8-diiodonaphthalene **4.2.16**[11] was accomplished in poor yield (22%) from the corresponding diaminonaphthalene **4.2.15** (Scheme 4.2.2, Equation 1). Standard triflation[12] of the diol **4.2.17** provided known ditriflate **4.2.18** in quantitative yield (Scheme 4.2.2, Equation 2). The synthesis of the diboronate ester was attempted from the corresponding ditriflate **4.2.18**.[13] However, the mono-boronate ester **4.2.20**[14] was obtained. In this case, it is speculated that proto-deborylation was occurring with the use of pinacol borane. In order to circumvent the proto-deborylation, a coupling reaction using bis(pinacolato)diboron was attempted. Unfortunately, the desired coupling partner **4.2.21** was not formed and only starting material was recovered.

Scheme 4.2.2. Synthesis of Non-nitrated Coupling Partners



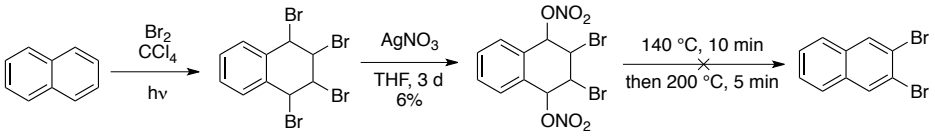
Through a literature search, a method employing a Suzuki-Heck coupling reaction was found.[15] We envisioned using this method to couple mono-boronate **4.2.20** and diiodonaphthalene **4.2.16**. To our delight, this coupling was accomplished using the un-optimized conditions[16] shown in Scheme 4.2.3. What was even more exciting was the fact that this reaction also provided benzo[j]fluoranthene (BJF, **4.2.22**). Due to time constraints, the resolution of the two fluoranthene isomers **4.2.8** and **4.2.22**[17] was not attempted, nor was the reaction optimized. These preliminary results, using mono-boronated naphthalene **4.2.20**, offer the possibility of accessing a wide variety of nitrated BKF and BJF compounds.

Scheme 4.2.3. Preliminary Suzuki-Heck Coupling



Before the use of diol **4.2.17** as a coupling partner precursor was realized, a strategy to access 2,3-dibromonaphthalene was attempted. The synthesis began with the photochemical reaction shown in Scheme 4.2.4. Literature precedent reported that a complex mixture of products would be obtained due to the multiple stereoiosomers possible.[18] Our photochemical reaction used a modified apparatus from what was described in the paper and we obtained a complex mixture of what we speculated was comprised of stereoisomers **4.2.24**. This complex mixture was then reacted with $AgNO_3$ in THF to provide what appeared to be the di-nitroso compound **4.2.25** (^{1}H NMR) in very low yield (6%).[19] The final elimination-aromatization step was attempted; however, none of the desired product (**4.2.26**) was obtained. The scrupulous reaction conditions needed and lack of appropriate equipment likely contributed to the irreproducibility of the reaction.

Scheme 4.2.4. Attempted Synthesis of 2,3-Dibromonaphthalene



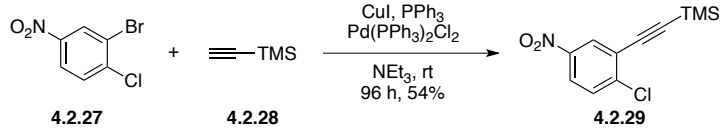
4.2.23 **4.2.24** **4.2.25** **4.2.26**

An alternate route to obtain 2,3-dibromonaphthalene was possible through acetylation of 2,3-dibromobenzene,[20] followed by bromination and cycloaromatization.[21] We attempted this synthesis as a nitrated version (Scheme 4.2.5). The synthesis began with the Sonagashira coupling reaction of commercially available 3-bromo-4-chloronitrobenzene **4.2.27** with TMS acetylene **4.2.28**. The reaction conditions could be modulated to provide either what we believe to be the 2-trimethylsilylethynyl-3-

chloronitrobenzene **4.2.29** (Scheme 4.2.5, Equation 1) or to provide known 3,4-bis(trimethylsilylethynl)nitrobenzene **4.2.30** (Scheme 4.2.5, Equation 2) by varying the palladium catalyst. The TMS groups in compound **4.2.30** were then substituted with bromines using N-bromosuccinimide to provide **4.2.31** in 57% yield. While literature precedent showed that the non-nitrated dibromoethynylbenzene would undergo cycloaromatization in 1,4-cyclohexadiene at 180 °C in a steel bomb reactor to form 2,3-dibromonaphthalene,[21] we were unable to repeat the cycloaromatization with nitrated substrate **4.2.31**, most likely due to the thermal instability of nitroaromatic compounds at high pressures.

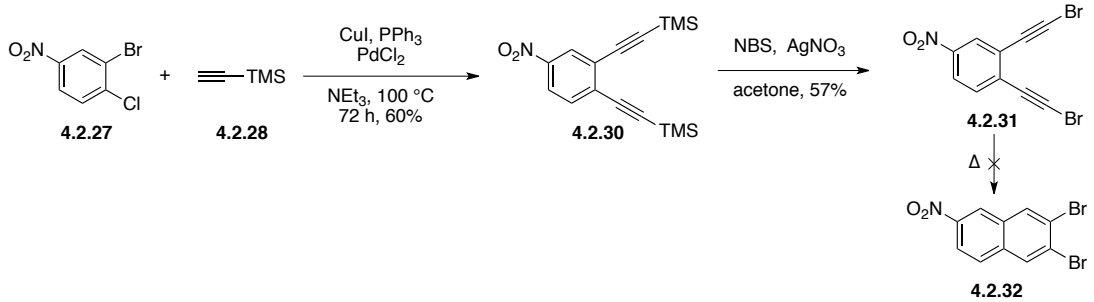
Scheme 4.2.5. Synthetic Progress Towards 2,3-Dibromo-6-nitronaphthalene **4.2.32**

(Eq. 1) **Sonagashira Couping of TMS-acetylene and 2-Bromo-3-chloronitronaphthalene**



4.2.27 **4.2.28** **4.2.29**

(Eq. 2) **Optimized Sonagashira Coupling and Progress Towards 2,3-Dibromo-6-nitronaphthalene**

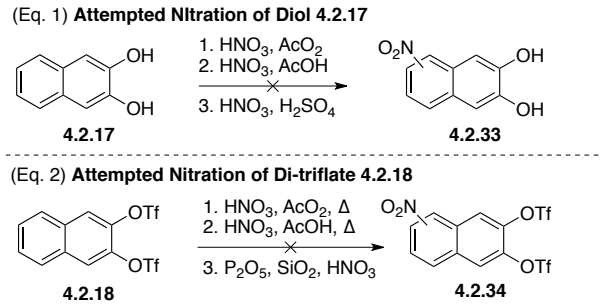


4.2.27 **4.2.28** **4.2.30** **4.2.31** **4.2.32**

Without access to dibromines **4.2.24** and **4.2.32**, a new strategy to access coupling partners using 2,3-dihydroxynaphthalene **4.2.17** was developed. Direct nitration of diol **4.2.17** was attempted using the conditions provided in Scheme 4.2.6, Equation 1, but produced only insoluble oils. Direct nitration of the previously obtained 2,3-

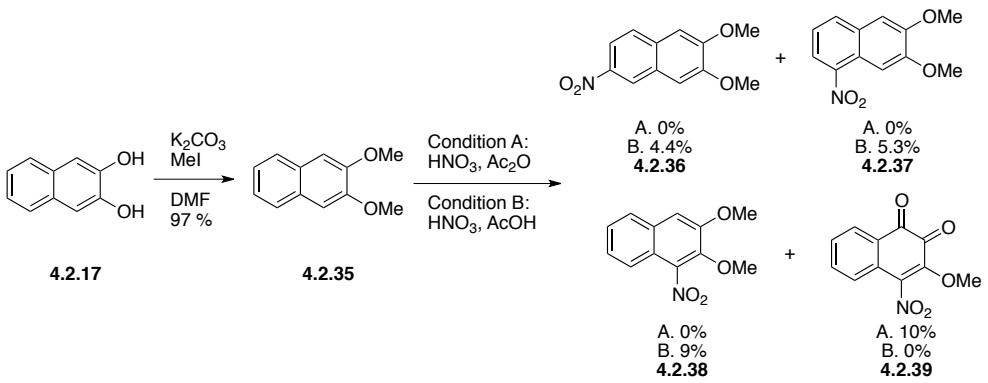
bis(trifluoromethanesulfonyl)naphthalene **4.2.18** (Scheme 4.2.2, Equation 2) was attempted using the reaction conditions in Scheme 4.2.6, Equation 2. In all cases, starting material was recovered proving this substrate to be too robust to undergo nitration even in harsh conditions such as $P_2O_5/SiO_2/HNO_3$.[22]

Scheme 4.2.6. Attempted Nitration of Diol **4.2.17** and Ditriflate **4.2.18**



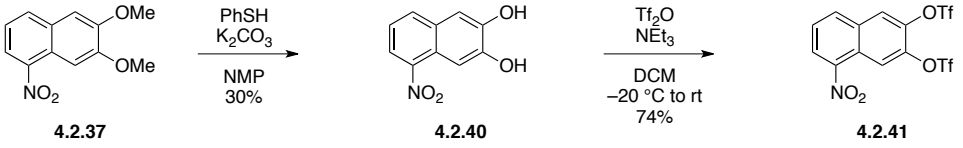
A known procedure for the nitration of 2,3-dimethoxynaphthalene was then explored.[23] The transformation of diol **4.2.17** to the 2,3-dimethoxynaphthalene **4.2.35** was facile,[24] providing a 97% yield of the desired compound (Scheme 4.2.7). Variation of conditions for the nitration of **4.2.35** provided a complex mixture of compounds, including suspected dinitrated naphthalenes (inseparable), three separable nitrated regioisomers **4.2.36**, **4.2.37**, and **4.2.38** and an undesired quinone **4.2.39** (Scheme 4.2.7).

Scheme 4.2.7. Synthesis of Nitrated 2,3-Dimethoxynaphthalenes



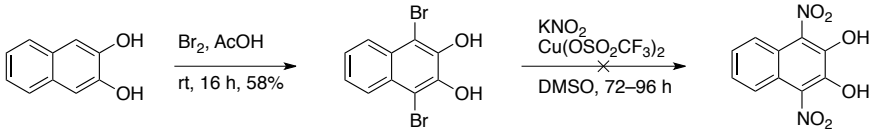
Manipulation of dimethoxy regiosomer **4.2.37** has been accomplished (Scheme 4.2.8). Common de-methylation conditions[25] using BBr_3 at –78 °C proved ineffective with compound **4.2.37**; however, thiophenol conditions[26] (Scheme 4.2.8) provided the desired compound in modest yield. Subsequent triflation[12] of **4.2.40** provided the desired product in high yield. The next step in this sequence will be to form the boronate ester coupling partner from triflate **4.2.41**.

Scheme 4.2.8. Synthesis of Ditriflate **4.2.41**



The synthesis of a dinitro coupling partner was also attempted (Scheme 4.2.9). Diol **4.2.17** underwent bromination in moderate yield (58%) to provide 1,4-dibromo-2,3-hydroxynaphthalene **4.2.42**.[27] The subsequent *ipso*-nitration substitution reaction provided decomposition products.[28] We suspect the presence of a small amount of water interfered with the reaction.

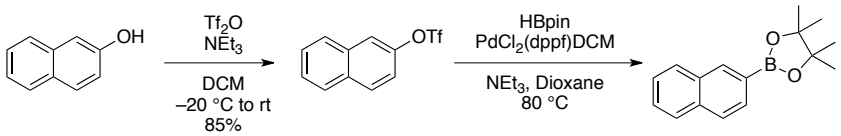
Scheme 4.2.9. Attempted Synthesis of 2,3-Dihydroxy-1,4-dinitronaphthalene



4.2.17 **4.2.42** **4.2.43**

Due to the utility of mono-boronated naphthalene **4.2.20**, a route to obtain coupling partners using 2-hydroxynaphthalene was envisioned (Scheme 4.2.10). Triflation of 2-hydroxynaphthalene **4.2.44** proceeded in 85% yield to provide compound **4.2.45**.[29] Subsequent boronation of triflate **4.2.45** could be accomplished using $PdCl_2$(dppf) complexed with dichloromethane.[30]

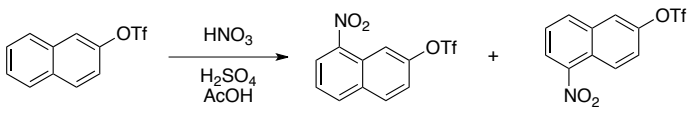
Scheme 4.2.10. Synthesis of Boronate Ester **4.2.20**



4.2.44 **4.2.45** **4.2.20**

Direct nitration of triflate **4.2.45** was accomplished using the usual conditions (Scheme 4.2.11). To our delight, this nitration provided the products **4.2.46** in 43% and **4.2.47** in 48% yield. This was an extremely different result than the attempted nitration of di-triflate **4.2.18**. We hypothesize that the second triflate electronically deactivates the naphthalene, so nitration does not occur.

Scheme 4.2.11. Nitration of Triflate **4.2.45**

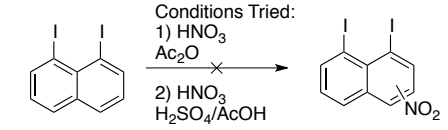


4.2.45 **4.2.46** 43% **4.2.47** 48%

Manipulation of 1,8-diiodonaphthalene was briefly explored (Scheme 4.2.12). Nitration of **4.2.16** was attempted, but only provided suspected dimerization products, unsubstituted naphthalene and recovered starting material (Scheme 4.2.12, Equation 1). Transformation of diiodide **4.2.16** into a diboronate ester or diboronic acid coupling partner was also attempted (Scheme 4.2.12, Equation 2). The attempted synthesis of boronic acid **4.2.49,** using trimethoxy borate, provided a complex mixture of products.[31] This route was postponed while other coupling partners were synthesized. Attempts to synthesize the diboronate ester provided what we believe to be monoboronated naphthalene **4.2.50** in 11 % yield (Scheme 4.2.12, Equation 2), along with a complex mixture of suspected dimerization and decomposition products. After these preliminary results, it was reasoned that it would be advantageous to keep the diiodonaphthalene as the halogenated coupling partner.

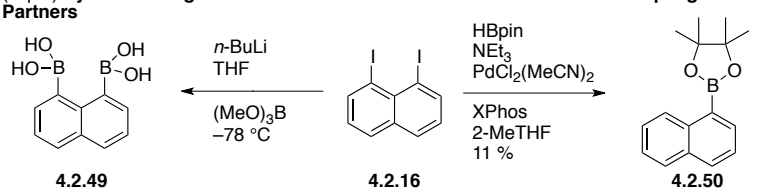
Scheme 4.2.12. Manipulation of 1,8-Diiodonaphthalene

(Eq. 1) **Attempted Nitration of 1,8-Diiodonaphthalene**



4.2.16 **4.2.48**

(Eq. 2) **Synthetic Progress Towards Boronic Acid and Boronate Ester Coupling Partners**



4.2.49 **4.2.16** **4.2.50**

Section 4.3. Analysis of Synthesized NPAHs

The synthesized NPAHs were run on the gas chromatography mass spectrometer (GC/MS) to determine purity and to confirm the identity of the predicted NPAHs formed in the chamber reactions. The mass spectrometer (MS) was in electron ionization (EI) mode to confirm the purity of the synthesized compound. The GC retention times for the NPAHs that were synthesized were in good agreement with what was predicted from the chamber studies, Gaussian modeling, and dipole moment calculations.[5] Figure 4.3.1 shows the gas chromatogram for 7-NBKF (**4.1.1**) in EI mode to prove purity. The corresponding mass spectrum of that peak is shown. This spectrum provides information about the molecular ion, which is at m/z 297 and fragment ions at m/z 267 (loss of NO), 251 (loss of NO_2), 250 (loss of HNO_2), and 239 (loss of NO and CO) shown in Table 4.3.1. See Chapter 6, section 6.4 for GC chromatograms and mass spectrometric data for 3,7-NBKF, 5-NBGHIP, and 7-NBGHIP. Table 4.3.1 presents the MS data for the 4 purified NPAHs.

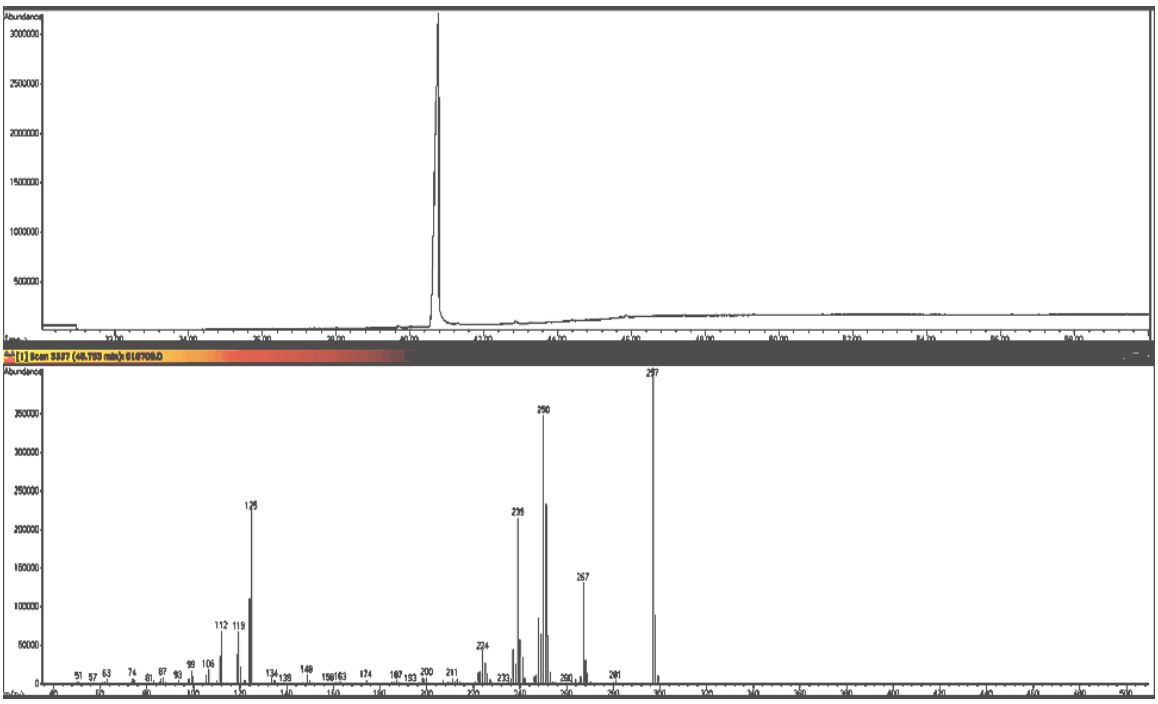


Figure 4.3.1. Gas Chromatogram and Mass Spectrum of 7-NBKF

Table 4.3.1. MS Data for Purified Compounds

7-NBKF		3,7-NBKF		7-NBGHIP		5-NBGHIP	
m/z	**loss**	**m/z**	**loss**	**m/z**	**loss**	**m/z**	**loss**
297	Molecular Ion	342	Molecular Ion	321	Molecular Ion	321	Molecular Ion
267	NO	312	NO	291	NO	291	NO
251	NO_2	266	NO_2, NO	275	NO_2	275	NO_2
250	HNO_2	250	NO_2, NO_2	274	HNO_2	274	HNO_2
239	NO, CO	238	NO, NO_2, CO	236	NO, CO	236	NO, CO

The Ames assay is a widely used reverse mutation assay, which detects a range of chemical compounds that are mutagenic.[32] During the assay, histidine-dependent bacteria are plated on glucose minimal agar containing trace amounts of histidine. The bacteria then grow to colony size when an added substance, such as a NPAH, promotes reversion to histidine independence (His+). The revertant colonies per plate are then used to quantify the mutagenicity of a compound. Our synthesized NPAHs were tested in the Ames assay using *Salmonella* strain T98 with and without metabolic activation (±S9) (Figure 4.3.2).[5] Testing the assay with and without metabolic activation is important because some carcinogenic PAHs are inactive unless they are metabolized. The study showed that the dinitro compound 3,7-NBKF (**4.1.5**) exhibited both indirect- (513 rev/nmol) and direct- (96 rev/nmol) (Table 4.3.2, Entry 2) acting mutagenicity, whereas the mono-nitro compound 7-NBKF (**4.1.1**) showed neither direct- nor indirect-acting mutagenicity.[5] For the perylene PAHs, the 5-NBGHIP (**4.1.16**) showed indirect acting mutagenicity (27 rev/nmol) (Table 4.3.2, Entry 3), while the 7-NBGHIP (**4.1.12**) was not mutagenic in either assay.

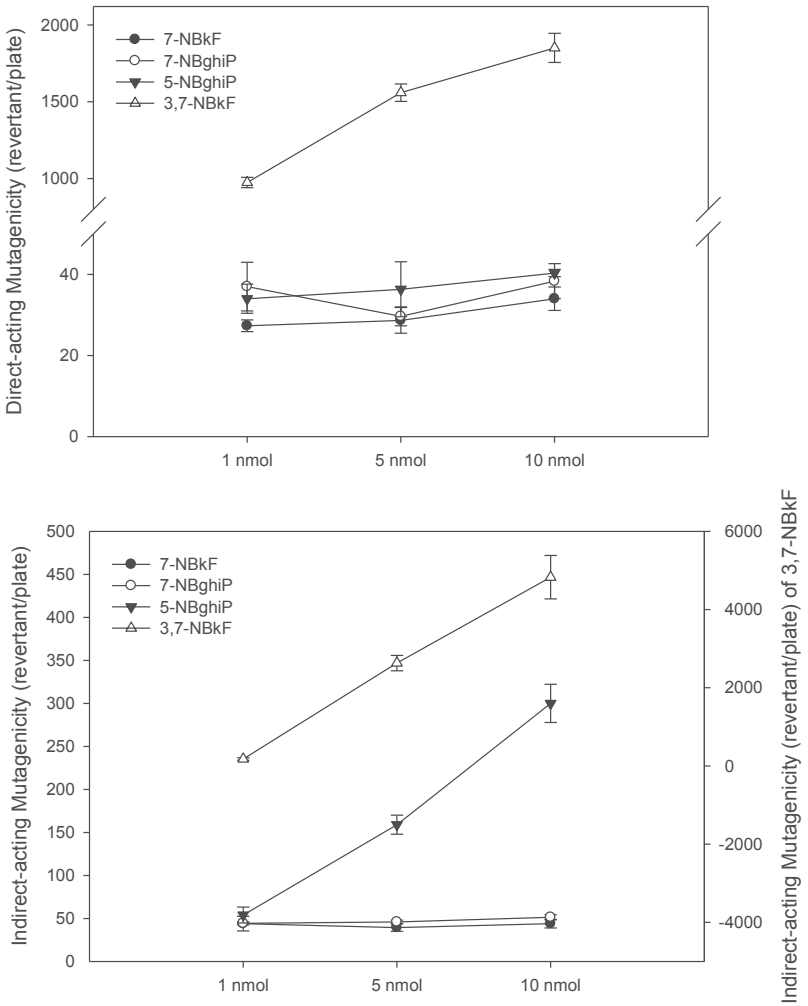


Figure 4.3.2. Dose Response Profiles for 7-NBKF, 3,7-NBKF, 5-NBGHIP and 7-NBGHIP[5]

Table 4.3.2. Ames Assay[5]

Entry	Compound	Direct Acting Mutagenicity (-S9) rev/nmol	Indirect Acting Mutagenic (+S9) rev/nmol
1	7-NBKF (**4.1.1**)	<1	<1
2	3,7-DNBKF (**4.1.5**)	96	513
3	5-NBGHIP (**4.1.16**)	<1	27
4	7-NBGHIP (**4.1.12**)	<1	<1

Section 4.4. Conclusion

The synthesis and synthetic progress towards novel NPAHs was accomplished. The model reaction shows promise for the coupling with nitrated naphthalene derivatives. The synthesis, characterization and purification of 7-NBKF, 3,7-NBKF, 5-NBGHIP, and 7-NBGHIP were accomplished. The comparison of these fully characterized NPAHs with the chamber reaction samples, in the mass spectrometer (MS) in chemical ionization (CI) mode, confirmed the presence of these compounds. This comparison also showed the accuracy in the methods used by our group in predicting which compounds would form and where they would elute in the GC relative to one another.

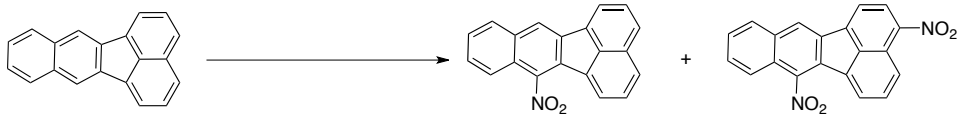
Section 4.5. Experimental Section

General. Infrared spectra were recorded neat unless otherwise indicated and are reported in cm^{-1}. ^{1}H NMR spectra were recorded in deuterated solvents and are reported in ppm and referenced internally to the residually protonated solvent. ^{13}C NMR

spectra were recorded in deuterated solvents and are reported in ppm and referenced internally to the residually protonated solvent. Gas chromatography mass spectrometry (GC/MS) data was obtained on an Agilent 6890 GC coupled to a 5793 MS in electron impact ionization (EI). High resolution mass spectrometry (HRMS) was performed by the Mass Spectrometry Facility at OSU.

Routine monitoring of reactions was performed using EM Science DC-Alufolien silica gel, aluminum-backed TLC plates. Flash chromatography was performed with the indicated eluents on EM Science Gedurian 230-400 mesh silica gel.

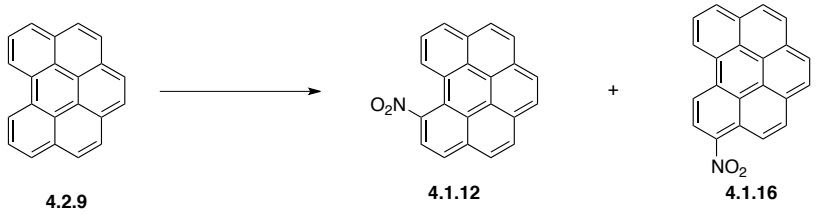
Air and/or moisture sensitive reactions were performed under usual inert atmosphere conditions. Reactions requiring anhydrous conditions were performed under a blanket of argon, in glassware dried in an oven at 120 °C or by flame, then cooled under argon. Dry THF, Toluene and DCM were obtained via a solvent purification system. All other solvents and commercially available reagents were either purified via literature procedures or used without further purification.



4.2.8 4.1.1 4.1.5

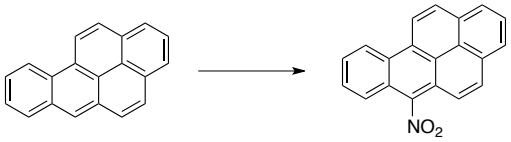
7-Nitrobenzo(k)fluornanthene 4.1.1 and **3,7-Dinitrobenzo(k)fluornathene 4.1.5**: To a stirred solution of benzo(k)fluoranthene **4.2.8** (20 mg, 0.079 mmol) in Ac_2O (1 mL) was added HNO_3 (600 µL, 0.395 mmol, 0.68 M in Ac_2O) at rt, then cooled to 0 °C. After 5 h, the reaction was quenched with ice and concentrated HCl (0.8 mL) for 3 h.

The crude material was then extracted with DCM (3 X 10 mL), and washed with sat. aq. $NaHCO_3$ (1 X 20 mL) and brine (10 mL). The dried ($MgSO_4$) extract was concentrated in vacuo and purified via flash chromatography over silica gel, eluting with 0-50% EtOAc/Hexanes to give known nitration product **4.1.1** and nitration product **4.1.5** (18.9 mg, 63.6 μmol, 80%). mono-nitro **4.1.1**: Mp 198-201 °C; IR (neat) 3059, 1521, 1325, 823, 771, 744 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.08 (d, *J* = 4.0 Hz, 1H), 8.04 (d, *J* = 4.8 Hz, 2H), 8.00 (d, *J* = 4.8 Hz, 1H), 7.94 (t, *J* = 4.8 Hz, 2H), 7.67 (apparent pentet, *J* = 4.8 Hz, 2H), 7.65 (m, 2H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 142.3, 137.8, 135.2, 134.5, 133.4, 131.7, 130.4, 128.9, 128.7, 128.6, 128.5, 128.34, 128.26, 127.4, 127.3, 124.3, 123.2, 122.6, 122.4, 120.2 ppm; HRMS (EI+) calcd. for $C_{20}H_{11}NO_2$ (M+) 297.07898, found 297.07957. di-nitro **4.1.5**: (2.6 mg, 7.6 μmol, 9.6%): Mp 236-240 °C; IR (neat) 2921, 2851, 1519, 1329, 813, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.4 Hz, 1H), 8.7 (d, *J* = 7.7 Hz, 1H), 8.49 (s, 1H), 8.12 (d, *J* = 7.7 Hz, 1H), 8.03 (dd, *J* = 7.0, 8.4 Hz, 2H), 7.90 (m, 2H), 7.73 (t, *J* = 7.0 Hz, 1H), 7.68 (t, *J* = 7.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 142.6, 141.4, 135.9, 135.4, 133.6, 132.3, 132.2, 129.6, 129.4, 128.5, 128.3, 127.6, 126.3, 125.1, 124.7, 124.5, 123.6, 122.6, 118.4 ppm; HRMS (ES+) calcd. for $C_{20}H_{10}N_2O_4$ (M+) 342.06406, found 342.06437.



7-Nitrobenzo(ghi)perylene (**4.1.12**) and **5-Nitrobenzo(ghi)perylene** (**4.1.16**):[9] To a stirred solution of benzo(ghi)perylene **4.2.9** (23.4 mg, 8.5 μmol) in Ac_2O (700 μL) was added HNO_3 (715 μL, 362 μmol, 0.51 M in Ac_2O) at rt. After 16 h, the reaction was quenched with ice and aq. HCl (10 mL, 6M) for 1 h. The crude material was then extracted with DCM (3 X 10 mL), and washed with sat. aq. $NaHCO_3$ (1 X 30 mL) and brine (30 mL). The dried ($MgSO_4$) extract was concentrated in vacuo and purified via flash chromatography over silica gel, eluting with 0-15% EtOAc/Hexanes to give a mixture of products. Prep plate chromatography with toluene gave known nitration products **4.1.12** (2 mg, 6.2 μmol, 10 %) and **4.1.16** (2 mg, 6.2 μmol, 10 %). 7-nitrobenzo(ghi)perylene **4.1.12**: IR (neat) 2918, 1515, 1366, 844, 728, 615 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.63 (d, J = 7.9 Hz, 1H), 8.46 (dd, *J* = 8.1, 8.1 Hz, 2H), 8.33 (d, *J* = 7.6 Hz, 1H), 8.31 (d, *J* = 8.7 Hz, 1H), 8.25 (d, *J* = 8.7 Hz, 1H), 8.21 (dd, *J* = 8.6, 8.7 Hz, 2H), 8.16 (d, *J* = 8.6 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 8.00 (t, *J* = 7.8 Hz, 1H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 146.4, 133.5, 131.9, 129.9, 129.8, 129.3, 128.7, 128.1, 127.3, 126.9, 126.62, 126.57, 126.5, 126.34, 126.30, 126.0, 125.3, 125.1, 123.4, 123.3, 122.2, 121.6 ppm; HRMS (EI+) calcd. for $C_{22}H_{11}NO_2$ (M+) 321.0790, found 321.0788. 5-nitrobenzo(ghi)perylene **4.1.16**: IR (neat) 2918, 2850, 1509, 1493, 1325, 1297, 843, 807, 744, 646 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 9.11 (d, *J* = 7.8 Hz, 1H), 9.06 (d, *J* = 8.7

Hz, 2H), 8.94 (d, *J* = 9.0 Hz, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 8.49 (dd, J = 8.0, 8.1 Hz, 1H), 8.43 (d, *J* = 9.1 Hz, 2H), 8.23 (dd, *J* = 8.5, 8.7 Hz, 1H), 8.14 (t, *J* = 7.6 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 135.4, 131.9 131.4, 130.6, 128.9, 128.8, 128.5, 128.1, 127.8, 127.0, 126.7, 126.5, 126.4, 125.4, 125.3, 123.6, 123.4, 123.0, 122.7, 121.4, 119.6 ppm; HRMS (ES+) calcd. for $C_{22}H_{11}NO_2$ (M+) 321.0790, found 321.0781.

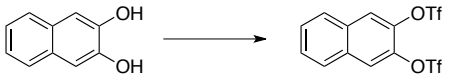


4.2.10 4.2.11

6-Nitrobenzo(a)pyrene (4.2.11):[9] To a stirred solution of benzo(a)pyrene (10 mg, 0.0396 mmol) in Ac_2O (7.9 mL) was added HNO_3 (172 µL, 0.158 mmol, 0.96 M in Ac_2O) at 0 °C. After 17.5 h, the reaction was quenched with DI water (9 mL) and concentrated H_2SO_4 (50 µL) for 9 h. The crude material was then extracted with DCM (3 X 10 mL) and washed with sat. aq. $NaHCO_3$ (1 X 20 mL). The dried ($MgSO_4$) extract was concentrated in vacuo and purified via flash chromatography over silica gel, eluting with 0-20% EtOAc/Hexanes to give known nitration product **4.2.11** as a yellow solid (29 mg, 9.8 µmol, 49%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.12 (d, *J* = 7.4 Hz, 1H), 9.08 (d, *J* = 9.0 Hz, 1H), 8.47 (d, *J* = 9.0 Hz, 1H), 8.38 (d, *J* = 7.7 Hz, 1H), 8.23 (d, *J* = 7.3 Hz, 1H), 8.19-8.20 (m, 1H), 8.14 (d, *J* = 9.3 Hz, 1H), 8.10 (t, *J* = 7.6 Hz, 1H), 7.93-7.96 (m, 3H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 143.0, 132.4, 131.6, 131.1, 130.9, 130.3, 129.9, 129.1, 128.8, 128.4, 127.8, 127.7, 127.1, 127.0, 124.5, 123.3, 122.3, 122.0, 121.1, 120.6 ppm.

4.2.15 4.2.16

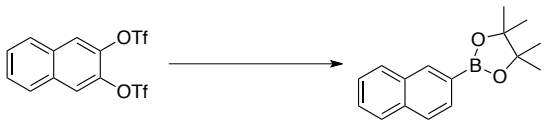
1,8-Diiodonaphthalene 4.2.16:[11] To a stirred solution of diamine **4.2.15** (1.02g, 6.32 mmol) in H_2SO_4 (11.6 mL, 6.9M), was added a solution of $NaNO_2$ (1.32 g, 19.0 mmol) in DI water (5 mL) dropwise (30 min) at –20 °C, followed by addition of a solution of KI (6.3 g, 37.9 mmol) in DI water (5 mL) with H_2SO_4 (2 mL, 6.9M) to facilitate stirring. After 10 min at 80 °C, the reaction was quenched with NaOH pellets to provided a black solid. Soxhlet extraction with Et_2O provided a black solid. Recrystallization with hexane to give known diiodide **4.2.16** as a dark brown solid (529 mg, 1.4 mmol, 22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 1.2, 7.6 Hz, 2H), 7.85 (dd, *J* = 1.2, 8,4 Hz, 2H), 7.09 (t, *J* = 8.0 Hz, 2H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 144.1, 135.8, 132.1, 131.1, 127.0, 96.0 ppm.



4.2.17 4.2.18

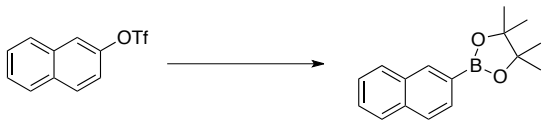
2,3-bis(trifluoromethanesulfonyl)naphthalene (4.2.18):[12] To a stirred solution of triflic anhydride (649 mg, 390 µL, 2.3 mmol) in DCM (1.5 mL) was added diol **4.2.17** (1.32 mL, 1 mmol, 0.76 M sln in DCM/NEt_3 3:1) at –38 °C. After 17 h at rt, the reaction was quenched with ice, extracted with DCM (3 X 5 mL), washed with brine (15 mL), dried over $MgSO_4$, and concentrated *in vacuo* to give known ditriflate **4.2.18** as a yellow solid (420.8 mg, 992 µmol, 99%). The solid was used without further purification. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.93 (m, 2H), 7.69 (m, 2H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 138.0, 131.8, 128.8, 128.1, 122.3, 118.6 (q, J = 319 Hz) ppm.



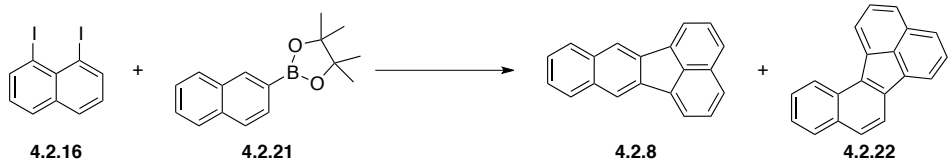
4.2.18 **4.2.20**

2-pinacolotoboronaphthalene (4.2.20): A pressure vessel containing **4.2.18** (119.6 mg, 0.282 mmol), RuPhos **4.2.19** (10.8 mg, 0.0226 mmol), and $PdCl_2(MeCN)_2$ (1.6 mg, 0.00564 mmol) was evacuated and backfilled with argon three times. Dioxane (340 μL), NEt_3 (171 mg, 240 μL, 1.69 mmol), and H-Bpin (108 mg, 123 μL, 0.846 mmol) were then added sequentially. The tube was sealed under Argon and heated to 110 °C. After 23.5 h, the reaction was cooled to rt and filtered through celite with DCM (5 mL) to give a brown oil. The oil was dissolved in DCM (5 mL) and washed with water (3 X 5 mL) and brine (1 X 10 mL). The aqueous washes were extracted with DCM (1 X 10 mL). The organic extracts were then dried over $MgSO_4$ and concentrated *in vacuo* to give a yellow oil. Recrystallization from hexanes at –20 °C gave known **4.2.20** as a yellow oil (32.9 mg, 130 μmol, 46 %). ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.90-7.85 (m, 4H), 7.52 (m, 2H), 1.42 (s, 12H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 136.3, 135.0, 132.8, 130.4, 128.7, 127.7, 127.0, 125.8, 84.0, 24.9 ppm.



4.2.45 4.2.20

2-pinacolotoboronaphthalene (4.2.20): To a vial containing $PdCl_2$(dppf)•DCM (4.4 mg, 5.43 μmol) stirring in dioxane (325 μL), was added a solution of triflate **4.2.45** (50 mg, 0.181 mmol) in dioxane (325 μL), followed by NEt_3 (55.1 mg, 75μL, 0.543 mmol) and HBpin (34.8 mg, 40 μL, 0.272 mmol) at rt. After 6 h at 80 °C, the reaction was cooled to rt, quenched with water (1 mL), extracted with benzene (3 X 4 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give a brown solid. Recrystallization from hexanes at –20 °C gave known boronate **4.2.20** as an oil (8.7 mg, 34 μmol, 19 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.90-7.85 (m, 4H), 7.52 (m, 2H), 1.42 (s, 12H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 136.3, 135.0, 132.8, 130.4, 128.7, 127.7, 127.0, 125.8, 84.0, 24.9 ppm.



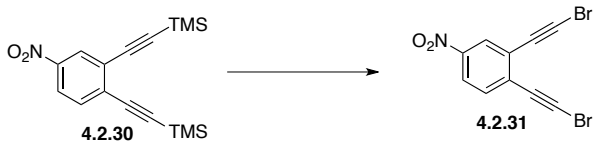
4.2.16 4.2.21 4.2.8 4.2.22

Benzo(k)fluoranthene (4.2.8) and Benzo(j)fluoranthene (4.2.22): To a stirred solution of **4.2.21** (30 mg, 0.118 mmol), $Pd_2(dba)_3$ (12 mg, 0.0118 mmol), PCy_3 (10 mg, 0.0354 mmol) and **4.2.16** (54 mg, 0.142 mmol) was added DMF (590 μL) and DBU (90 μL). After 16.5 h at 120 °C, the reaction was cooled to rt, diluted with DCM (2 mL), washed with water (2 X 10 mL) and brine (1 X 10 mL), dried over $MgSO_4$, concentrated

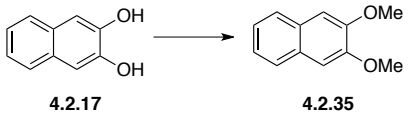
in vacuo and purified by column chromatography on silica gel eluting 0-5% EtOAc/Hexane to give a complex mixture of compounds (8.9 mg, 30 %) and a mixture of known BKF **4.2.8** and known BJF **4.2.22** (2:1, 1.7 mg, 6.7 μmol, 5.7%). **4.2.8** and **4.2.22** mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.70 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 7.0 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 6.9 Hz, 1H), 7.95(m, 1H), 7.86 (d, *J* = 7.4, 2H), 7.72-7.59 (m, 3H), 7.51 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H) ppm.

4.2.27 4.2.28 4.2.30

2,3-bis(trimethylsilylethynyl)nitrobenzene (4.2.30): To a pressure vessel containing 1-bromo-2-chloro-5-nitrobenzene **4.2.27** (100 mg, 0.423 mmol), PPh_3 (11 mg, 0.042 mmol), $PdCl_2$ (15 mg, 0.021 mmol), and CuI (8 mg, 0.042 mmol) was added NEt_3 (3.3 mL, 0.08M) and TMS acetylene **4.2.28** (119 mg, 150 μL, 1.06 mmol). The tube was sealed under Argon and heated to 100 °C. After 72 h, the reaction was cooled to rt and filtered through celite with DCM (5 mL) to give a brown solid. The solid was recrystallized from EtOAc/Hexanes twice to give known alkyne **4.2.30** as a brown solid (102.1 mg, 324 μmol, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 2.0 Hz, 1H), 8.09 (dd, J = 2.2, 8.6 Hz, 1H), 7.62 (d, J = 8.6 Hz), 0.31 (s, 18H) ppm; ^{13}C NMR (MHz, $CDCl_3$) δ 146.7, 133.1, 131.9, 128.6, 127.2, 122.6, 104.9, 101.8, 101.4, 100.9, -0.17, -0.21 ppm.

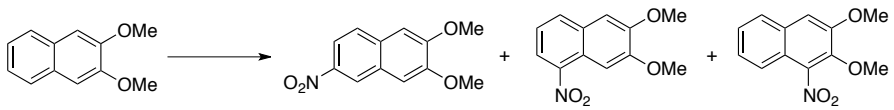


3,4-bis(dibromoethynyl)nitrobenzene (4.2.31): To a stirred solution of 3,4-bis(trimethylsilylethynyl)nitrobenzene **4.2.30** (10.3 mg, 0.032 mmol) in acetone (150 μL) was added NBS (18.9 mg, 0.096 mmol) and $AgNO_3$ (1.8 mg, 0.0096 mmol) at rt. After 4 h, the reaction was filtered through silica with hexane/EtOAc (9:1) and concentrated in vacuo to give alkyne **4.2.31** as a yellow solid (6.0 mg, 18 μmol, 57%). IR (neat) 3105, 2924, 2851, 2192, 1732, 1569, 1516, 1345, 1082, 898, 837, 744 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.32 (d, *J* = 2.1 Hz, 1H), 8.15 (dd, *J* = 2.1, 8.4 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 146.9, 133.3, 131.9, 127.33, 127.27, 123.0, 76.6, 60.6, 57.8 ppm; HRMS (EI+) calcd. for $C_{10}H_3Br_2NO_2$ (M+) 326.8531, found 326.8531.



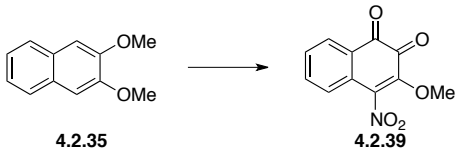
2,3-dimethoxynaphthalene (4.2.35):[24] To a stirred solution of diol **4.2.17** (2 g, 12.5 mmol) and K_2CO_3 (8.6 g, 62.5 mmol) in DMF (8 mL) was added MeI (2.3 mL, 37.5 mmol) at 0 °C over 1 h. After 19.5 h at rt, the reaction was quenched with DI water. The precipitate was filtered, rinsed with water (20 mL), and dried to give known **4.2.35** as a beige solid (2.29 g, 12.2 mmol, 97%). The solid was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.93 (m, 2H), 7.69 (m, 2H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.4, 129.2, 126.3, 124.2, 106.3, 55.9 ppm.



2,3-dimethoxy-6-nitronaphthalene (4.2.36), 2,3-dimethoxy-5-nitronaphthalene (4.2.37) 2,3-dimethoxy-1-nitronaphthalene (4.2.38): To a stirred solution of 2,3-dimethoxynaphthalene **4.3.35** (1.0g mg, 5.31 mmol) in AcOH (5.3 mL) was added HNO_3 (2.7 mL, 26.6 mmol, 10 M in AcOH) at rt. After 10 min the precipitate was filtered off, rinsed with water and recrystallized with EtOH to provide an impure yellow solid (73.4 mg). The water rinse was extracted with DCM (3 X 10 mL). The dried ($MgSO_4$) extract was concentrated in vacuo to give a red solid (347 mg). The red solid was purified via flash chromatography over silica gel, eluting with 0-10% EtOAc/Hexanes up to1:1:0 ratio EtOAc:Hexanes:DCM to give nitration products 2,3-dimethoxy-6-nitronaphthalene (**4.2.36**, 54.8 mg, 235 μmol, 4%), 2,3-dimethoxy-5-nitronaphthalene (**4.2.37**, 65.6 mg, 281 μmol, 5%), and 2,3-dimethoxy-1-nitronaphthalene (**4.2.38**, 111 mg, 476 μmol, 9%). 2,3-dimethoxy-6-nitronaphthalene **4.2.36**: Mp 152-154 °C; IR (neat) 2966, 1607, 1525, 1484, 1339, 1267, 1167, 1002, 855, 751, 735, 473 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.68 (d, J = 2.2 Hz, 1H), 8.14 (dd, J = 2.3, 8.9 Hz, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.28 (s, 1H), 7.22 (s, 1H), 4.08 (s, 3H), 4.07 (s, 3H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 152.5, 151.0, 144.4, 132.7, 127.9, 127.4, 122.9,

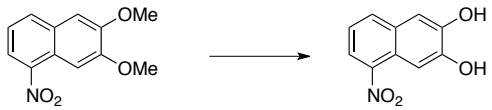
118.0, 107.7, 106.2, 56.2, 56.1 ppm; HRMS (TOF MS ES+) calcd. for $C_{12}H_{12}NO_4$ (M+H) 234.722, found 234.0766. 2,3-dimethoxy-5-nitronaphthalene **4.2.37**: Mp 154-156 °C; IR (neat) 2838, 1623, 1606, 1520, 1314, 1269, 1137, 1016, 864, 738 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 1.2, 7.8 Hz, 1H), 8.08 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0, 1H), 7.23 (s, 1H), 4.09 (s, 3H), 4.07 (s, 3H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 152.4, 150.2, 145.0, 133.1, 130.9, 122.8, 122.5, 121.7, 106.8, 102.2, 56.2, 56.0 ppm; HRMS (TOF MS ES+) calcd. for $C_{12}H_{12}NO_4$ (M+) 234.0766, found 234.0766. 2,3-dimethoxy-1-nitronaphthalene **4.2.38**. Mp 82-83 °C; IR (neat) 2945, 2836, 1530, 1483, 1280, 1264, 1123, 1049, 953, 770, 744, 633, 453 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.1 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.48 (m, 2H), 7.29 (s, 1H), 4.06 (s, 3H), 4.04 (s, 3H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 151.5, 141.9, 141.6, 130.3, 126.8, 126.7, 126.3, 120.8, 120.2, 109.6, 62.5, 56.2 ppm; HRMS (TOF MS ES+) calcd. for $C_{12}H_{12}NO_4$ (M+H) 234.0780, found 234.0766.



4.2.35 **4.2.39**

Quinone 4.2.39: To a stirred solution of 2,3-dimethoxynaphthalene **4.2.35** (100 mg, 0.531 mmol) in Ac_2O (9.9 mL) was added HNO_3 (110 µL, 2.65 mmol, 0.54 M in Ac_2O) at rt. After 19 h, the reaction was quenched with ice and HCl (2 mL, 6M) for 3 h. The crude material was then extracted with DCM (3 X 10 mL), and washed with sat. aq. $NaHCO_3$ (1 X 30 mL) and brine (30 mL). The dried ($MgSO_4$) extract was concentrated in

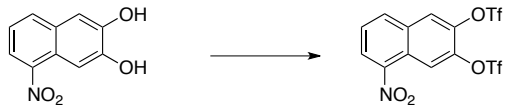
vacuo and purified via flash chromatography over silica gel, eluting with 0-30% EtOAc/Hexanes to give inseparable nitration products and undesired quinone **4.2.39** (12.9 mg, 55 μmol, 10%). Mp 116-122 °C; IR (neat) 2954, 2918, 1689, 1537, 1332, 1302, 1274, 1077, 884, 785, 761 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 0.98, 7.63 Hz, 1H), 7.72 (td, *J* = 1.4, 7.77 Hz, 1H), 7.56 (dd, *J* = 0.98, 7.63 Hz, 1H), 7.14 (d, *J* = 7.84 Hz, 1H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 177.6, 176.2, 147.0, 141.8, 136.6, 131.5, 130.7, 128.2, 127.6, 124.3, 61.8 ppm. HRMS (EI+) calcd. for $C_{11}H_7NO_5$ (M+) 233.0324, found 233.0327.



4.2.37 **4.2.40**

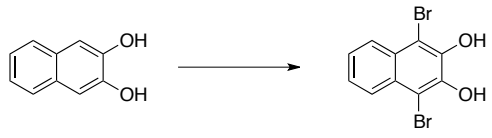
2,3-dihydroxy-5-nitronaphthalene (4.2.40): A stirred solution of dimethoxynitronaphthalene **4.2.37** (11.4 mg, 49 μmol), K_2CO_3 (1.0 mg, 4.8 μmol), and PhSH (11 mg, 10 μL, 98 μmol) in NMP (50 μL) was heated by heat gun for 15 min. The solution was cooled to rt, quenched with NaOH (5 mL, 5% sln in DI H_2O), extracted with Et_2O (2 X 10 mL). The aqueous layer was acidified with HCl (6M), extracted with Et_2O (4 x 10 mL), dried over Na_2SO_4, concentrated in vacuo, and purified by flash column chromatography on silica gel eluting 0-50% EtOAc/Hexane to give diol **4.2.40** as a yellow solid (3.0 mg, 14.6 μmol, 30%). IR (neat) 3437, 2921, 2856, 1520, 1467, 1318, 1261, 1054, 855, 736, 714 cm^{-1}; ^{1}H NMR (700 MHz, MeOD) δ 8.05 (d, J = 7.6 Hz, 1H), 7.93 (m, 2H), 7.33 (t, J = 7.9 Hz, 1H), 7.29 (s, 1H), 7.24 (s, 1H) ppm; ^{13}C NMR (175

MHz, MeOD) δ 150.0, 147.6, 144.8, 132.3, 131.2, 121.2, 121.15, 121.07, 110.0, 104.8 ppm.



4.2.40 **4.2.41**

2,3-bis(trifluoromethanesulfonyl)5-nitronaphthalene (4.2.41): To a stirred solution of triflic anhydride (9.5 mg, 6.0 µL, 33.6 µmol) in DCM (25 µL) was added diol **4.2.40** (20 µL, 15 µmol, 0.75 M sln in DCM/NEt_3 3:1) at –20 °C. After 24 h at rt, the reaction was quenched with ice, extracted with DCM (3 X 1 mL), washed with brine (1 X 3 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give ditriflate **4.2.41** as a yellow solid (5.1 mg, 10.9 µmol, 74%). IR (neat) 3468, 2924, 2851, 1525, 1422, 1351, 1216, 1134, 983, 816, 611 cm^{-1}. ^1H NMR (700 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.57 (d, J = 7.5 Hz, 1H), 8.28 (d, J = 8.3 Hz, 1H), 8.13 (s, 1H), 7.84 (t, J = 8.1 Hz, 1H) ppm. ^{13}C (175 MHz, $CDCl_3$) δ 145.8, 140.7, 139.4, 134.9, 133.1, 127.6, 127.1, 124.2, 122.8, 119.5, 118.6 (q, J = 318 Hz) ppm. HRMS (EI+) calcd. for $C_{12}H_5F_6NO_8S_2$ (M+) 468.9361, found 468.9364.



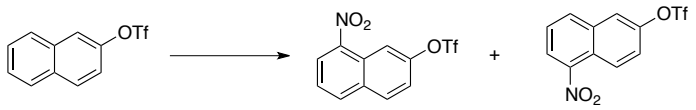
4.2.17 **4.2.42**

1,4-dibromo-2,3-dihydroxnaphthalene 4.2.42:[27] To a stirred solution of diol **4.2.17** (160.2 mg, 1.0 mmol) in AcOH (1.2 mL) was added bromine (160 mg, 52 µL, 1.0

mL) dropwise at rt. After 18 h, the reaction was filtered with DI water. The solid was dissolved in DCM, filtered, washed with water (5 mL), dried over $MgSO_4$ and concentrated in vacuo to give known phenol **4.2.42** as a yellow solid (185 mg, 582 µmol, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 3.2, 6.4 Hz, 2H), 7.54 (dd, *J* = 3.6, 6.8 Hz, 2H), 6.19 (s, 2H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$) δ 141.5, 127.7, 126.3, 126.0, 105.6 ppm.

4.2.44 **4.2.45**

2-Naphthyltrifluoromethanesulfonate (4.2.45):[29] To a stirred solution of triflic anhydride (677 mg, 400 µL, 2.4 mmol) in DCM (2 mL) was added at –40 °C, a solution of alcohol **4.2.44** (288.4 mg, 2 mmol) in NEt_3 (243 mg, 340 µL, 2.4 mmol) and DCM (1.6 mL). After 15 h at rt, the reaction was quenched with ice, extracted with DCM (3 X 10 mL), washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated down to give a brown oil. The oil was purified by column chromatography over silica gel eluting 0-15% EtOAc/Hexanes to give known triflate **4.2.45** as a colorless oil (476.3 mg, 1.7 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 9.1 Hz, 1H), 7.92 (t, *J* = 8.7 Hz, 2H), 7.78 (d, *J* = 2.4 Hz, 1H), 7.61 (m, 2H), 7.41 (dd, *J* = 2.5, 9.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 133.4, 132.3, 130.6, 128.1, 127.9, 127.6, 127.2, 119.6, 119.2, 118.8 (q, *J* = 318 Hz) ppm.



4.2.45 4.2.46 4.2.47

3-Trifluoromethanesulfonyl-3-nitronaphthalene (4.2.46) and 4-Trifluoromethanesulfonyl-1-nitronaphthalene (4.2.47): To a stirred solution of triflate **4.2.45** (27.6 mg, 0.10 mmol) in AcOH (1 mL) was added a solution of HNO_3 (4 ml, 0.50 mmol) and H_2SO_4 (27 μL, 0.50 mmol) at rt. After 29 h at 110 °C, the reaction was cooled to rt, diluted with water (3 mL), extracted with EtOAc (3 X 3 mL), washed with sat. aq. $NaHCO_3$ (2 X 5 mL), washed with brine (1 X 5 mL), dried over $MgSO_4$ and concentrated in vacuo to give a colorless oil. The oil was purified by column chromatography eluting 0-20% EtOAc/Hexanes to give triflates **4.2.46** (15.3 mg, 47.6 μmol, 48%) and **4.2.47** (13.8 mg, 43.0 μmol, 43%). 3-Trifluoromethanesulfonyl-3-nitronaphthalene **4.2.46**: IR (neat) 3088, 2922, 2856, 1604, 1527, 1425, 1341, 1213, 1138, 880, 823, 799, 606 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.69 (d, J = 2.3 Hz, 1H), 8.48 (dd, J = 0.9, 7.6 Hz, 1H), 8.25 (d, J = 8.2 Hz, 8.12 (d, J = 9.0 Hz, 1H), 7.72 (t, J = 7.9 Hz, 1H), 7.59 (dd, J = 2.4, 9.0 Hz, 1H) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.7, 146.0, 135.0, 133.2, 131.5, 126.2, 125.8, 125.6, 121.6, 118.8 (q, J = 318 Hz), 116.1 ppm; HRMS (EI+) calcd. for $C_{11}H_6F_3NO_5S$ (M+) 320.9919, found 320.9925. 4-Trifluoromethanesulfonyl-1-nitronaphthalene **4.2.47**: IR (neat) 3114, 2921, 2849, 1634, 1572, 1527, 1425, 1336, 1211, 1138, 921, 841, 742, 609 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 8.77 (d, J = 9.6 Hz, 1H), 8.37 (d, J = 7.6 Hz, 1H), 8.20 (d, J = 8.2 Hz, 1H), 7.93 (s, 1H), 7.72 (t, J = 7.9 Hz, 1H), 7.65 (dd, J = 2.5, 9.6 Hz, 1H) ppm; ^{13}C NMR (175

MHz, $CDCl_3$) δ 147.8, 146.5, 134.7, 126.7, 126.3, 125.3, 124.2, 123.0, 119.9, 118.8 (q, *J* = 321 Hz) ppm; HRMS (EI+) calcd. for $C_{11}H_6F_3NO_5S$ (M+) 320.9919, found 320.9907.

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CHAPTER 5: CONCLUSION

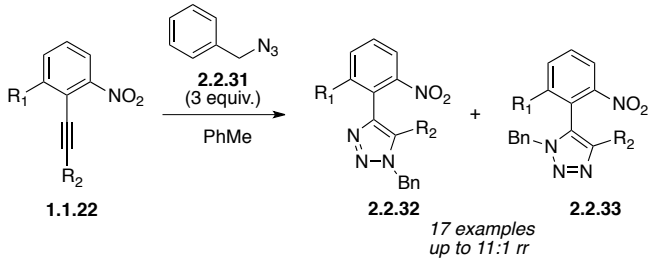
Section 5.1. Background

Nitroaromatic scaffolds are found in a variety of compounds including pharmaceuticals, pesticides, and organic pollutants making them interesting targets to pursue. The potential for nitroaromatic compounds to be prevalent pollutants in the environment also makes them desirable compounds to synthesize. We ventured to make a variety of nitrated triazoles, isoxazoles and nitro-polycyclic aromatic hydrocarbons (NPAHs).

Section 5.2. Accomplished Work

Previous work accomplished by the Carter group using a Diels-Alder approach to biaryls[1] caused us to expand our biaryl project to include triazoles. This work showed the power of the *ortho*-nitro moiety in increasing yields and regioselectivity. This work showed 17 examples of cyclized products with up to 11:1 regioisomeric ratio (Scheme 5.2.1).[2] Derivitization was also explored, showing the utility of these scaffolds in larger aromatic compounds.

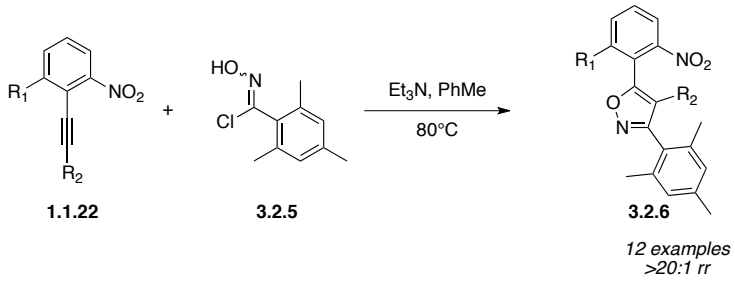
Scheme 5.2.1. Synthesis of Triazoles Using *o*-Nitrophenylalkynes



The excellent results of the Diel-Alder approach to biaryls also prompted the synthetic efforts of [3+2] cycloadditions to provide isoxazoles. Isoxazole regioselectivity

was excellent and yields were greatly improved by the *ortho*-nitro functionality. These molecules could be built up using the halogen or the nitro moiety as functional handles. This project provided 12 examples of cyclized products with >20:1 regioisomeric ratio (rr) (Scheme 5.2.2.).[3] The scope of the nitrile oxide was briefly explored showing the importance of the nitrile oxide in reaction yield.

Scheme 5.2.2. [3+2] Cycloadditions of Nitrile Oxides to *o*-Nitrophenylalkynes to Provide Isoxazoles



Chamber reactions performed by our group provided insight into which NPAHs would be formed by environmental oxidants.[4] Seven NPAHs were synthesized through direct nitration (Figure 5.2.1). Four of these were purified and tested in the Ames assay for toxicity. 3,7-NBKF showed a substantially higher mutagenicity than most. 5-NBGHIP also showed mutagenicity, suggesting that the position on the ring is important in mutagenicity. Gas chromatogram mass spectroscopy data shows that these NPAHs were in good agreement with what was predicted in the chamber studies.

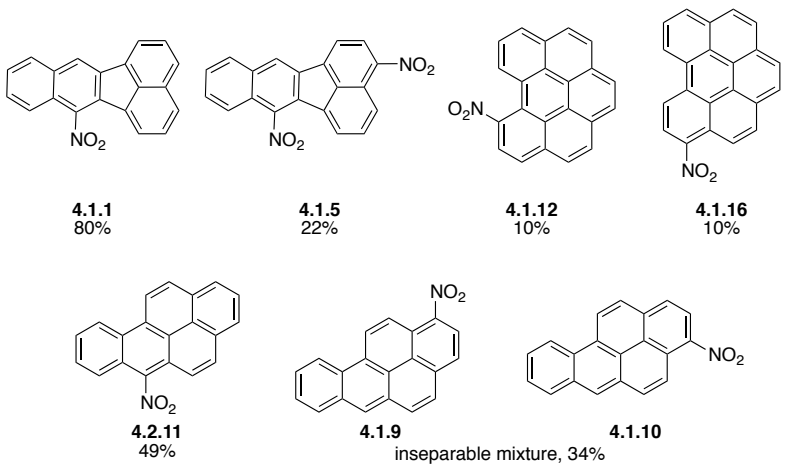


Figure 5.2.1. NPAH Products Formed From Direct Nitration

Synthetic progress towards naphthalene coupling partners is shown in Figure 5.2.2. Nitration of the 2,3-dimethoxynaphthalene provided multiple nitrated products including the separate regioisomers **4.2.36**, **4.2.37**, and **4.2.38**. Nitrated di- and mono-triflates **4.2.43**, **4.2.42**, **4.2.48**, and **4.2.49** were also obtained. Naphthalene coupling partner **4.2.20** could be obtained from both the non-nitrated di- and mono-triflated naphthalenes.

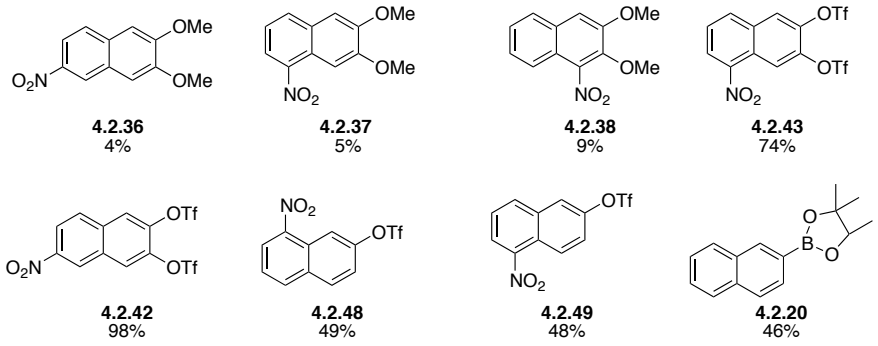
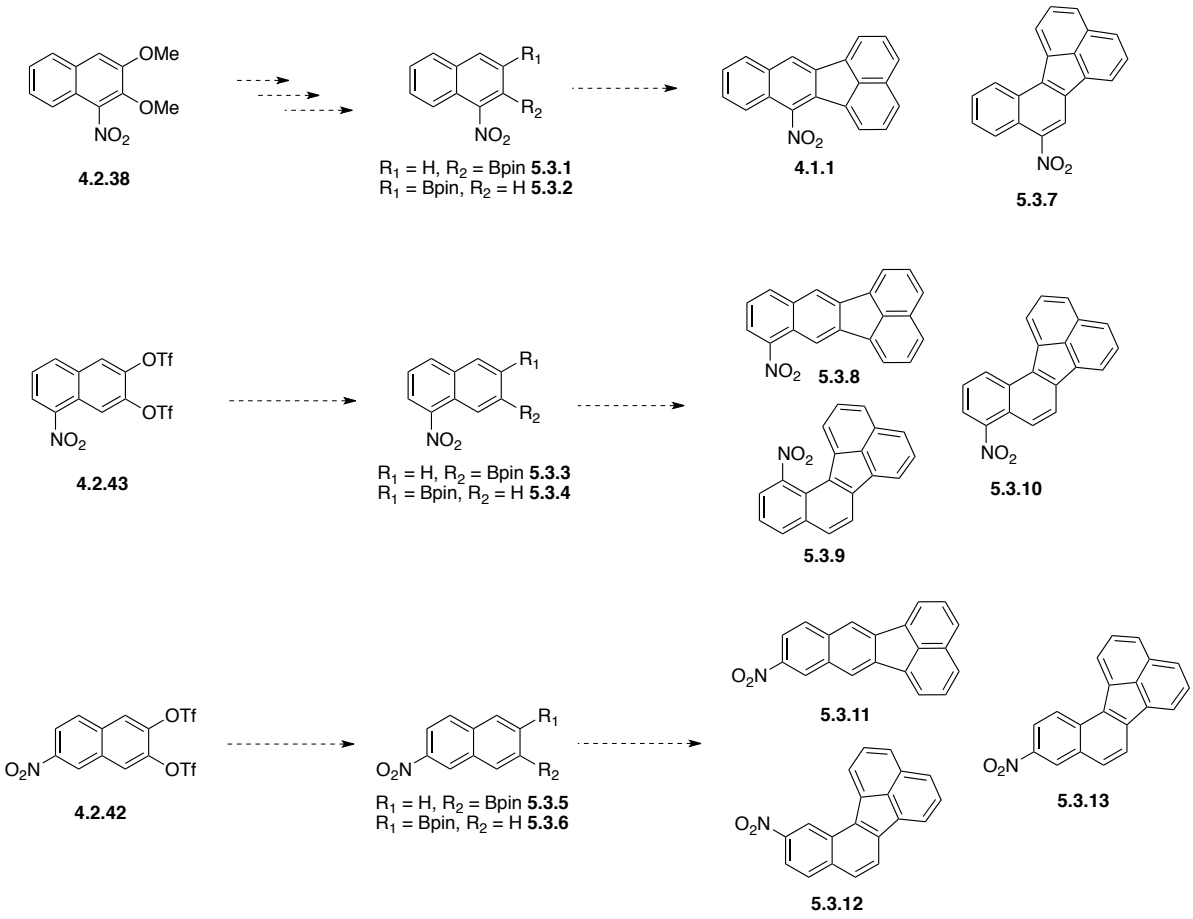


Figure 5.2.2. Naphthalene Substrates

Section 5.3. Future Plans

Future work will include optimization of the BKF and BJF coupling reaction and modification of the nitro naphthalenes, to provide the necessary coupling partners to access NBKF and NBJF derivatives. Scheme 5.3.1 shows the possible NBKF and NBJF products that are possible. Nitrated mono-triflate **4.2.48** and **4.2.49** are not shown, but could provide products **5.3.8**, **5.3.9** and **5.3.10**.

Scheme 5.3.1. Potential NBKF and NBJF Products From Synthesized Naphthalenes



Section 5.4. References

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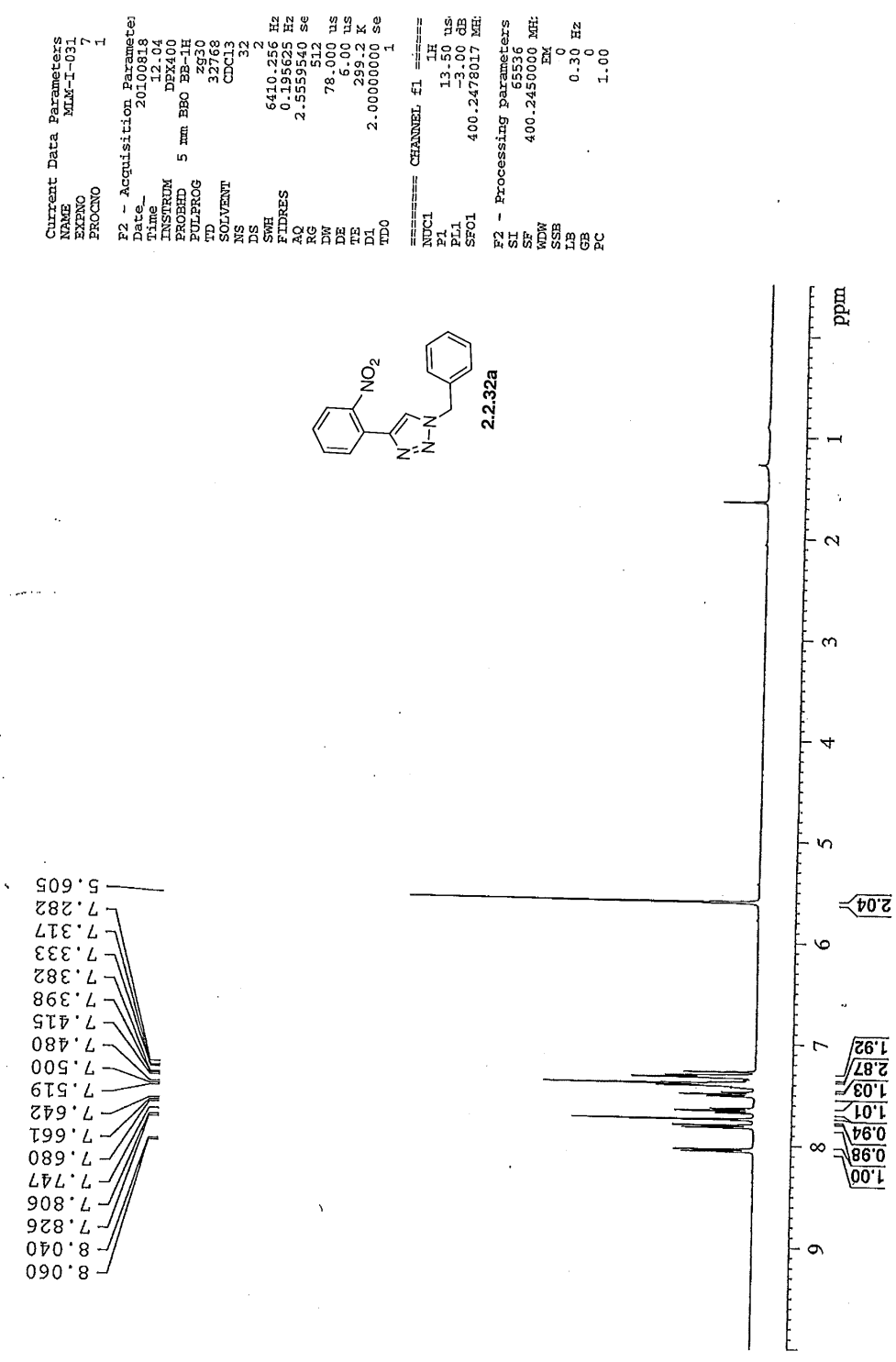
CHAPTER 6: SUPPLEMENTAL MATERIAL

Section 6.1. Triazole NMR Spectra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FIDRES 0.195625 Hz
AQ 2.5559540 se
RG 512
DW 78.000 us
DE 6.00 us
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P1 13.50 us
PL1 -3.00 dB
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LB 0.30 Hz
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7.398
7.382
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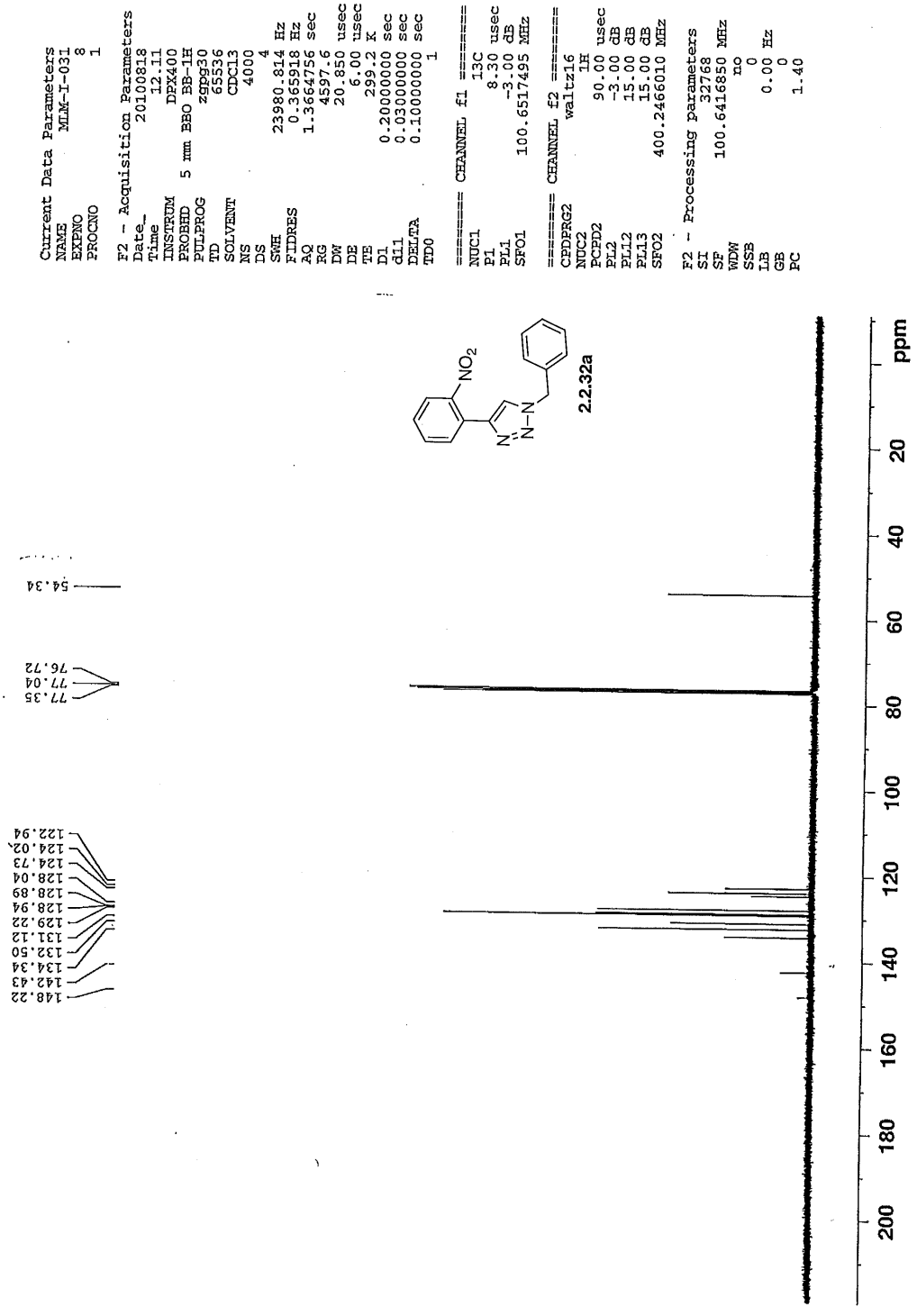
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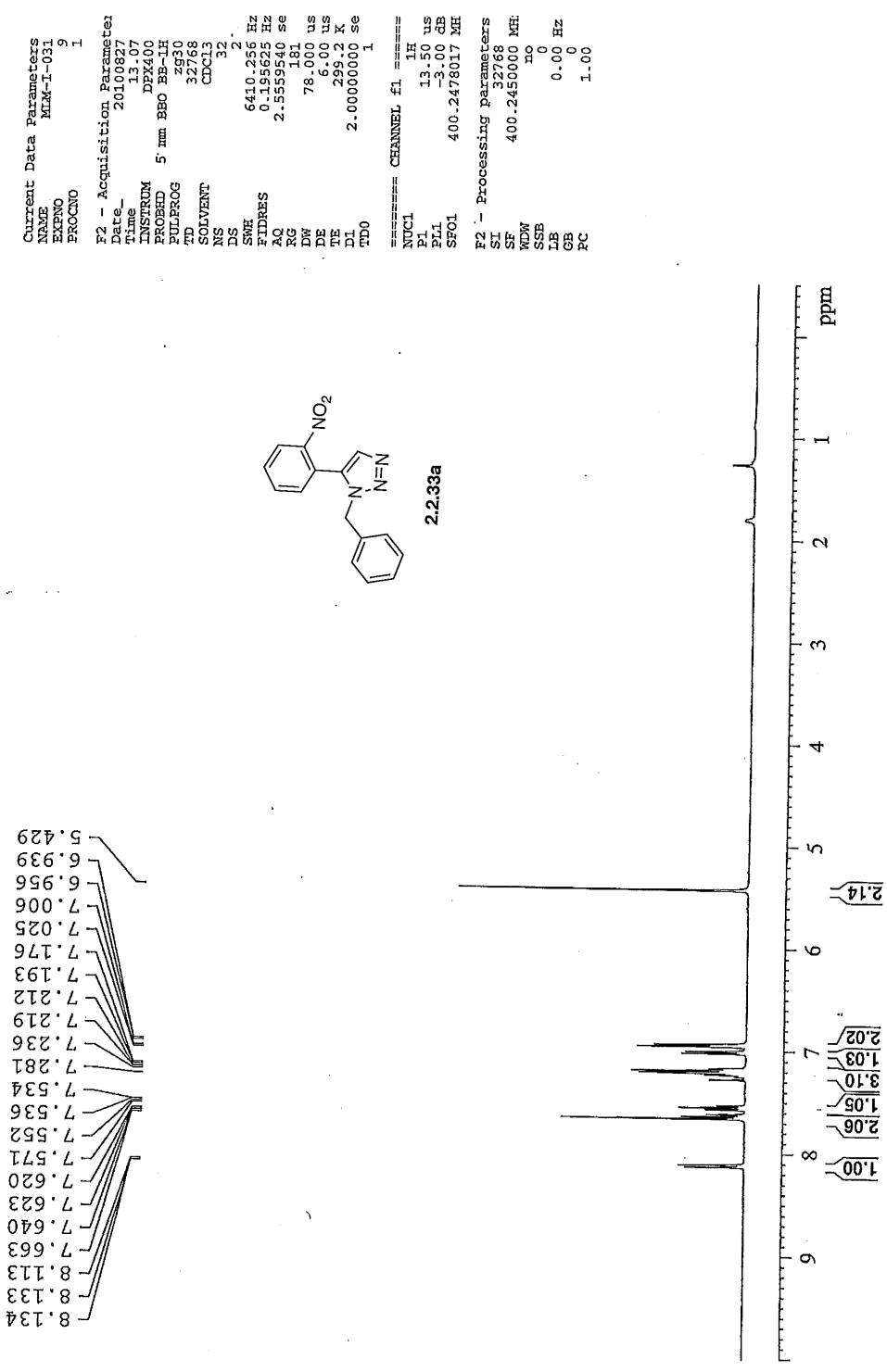
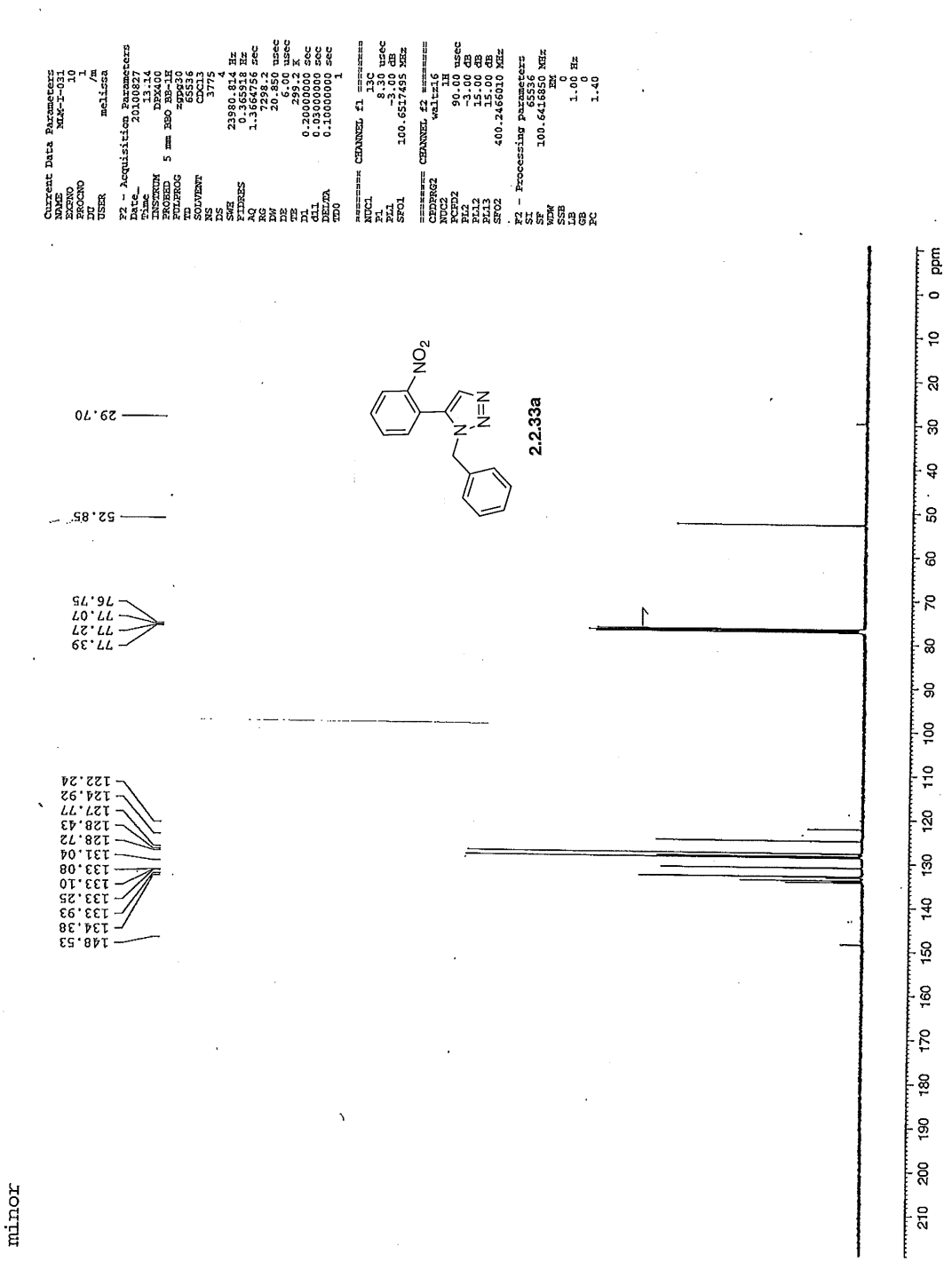
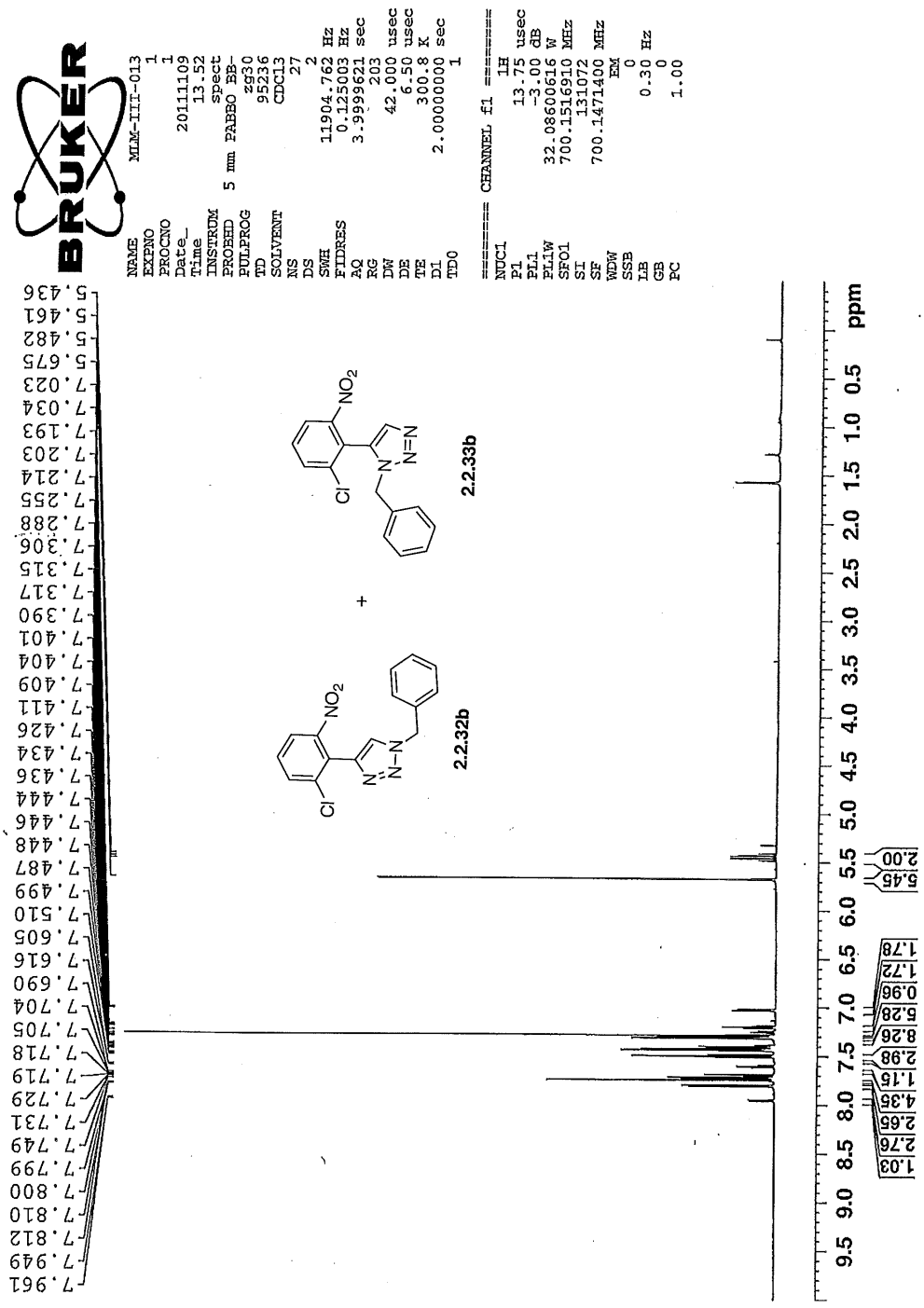
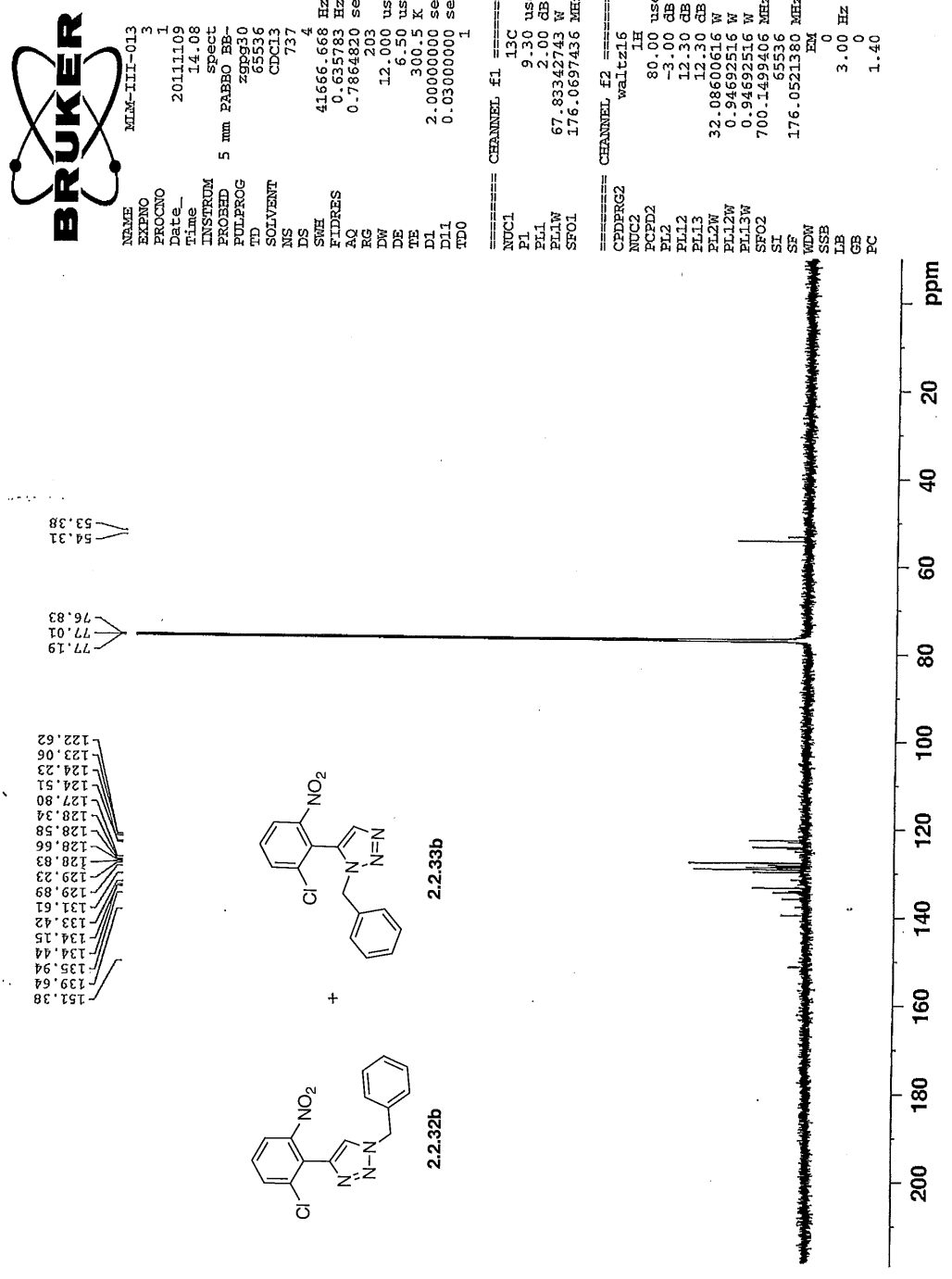
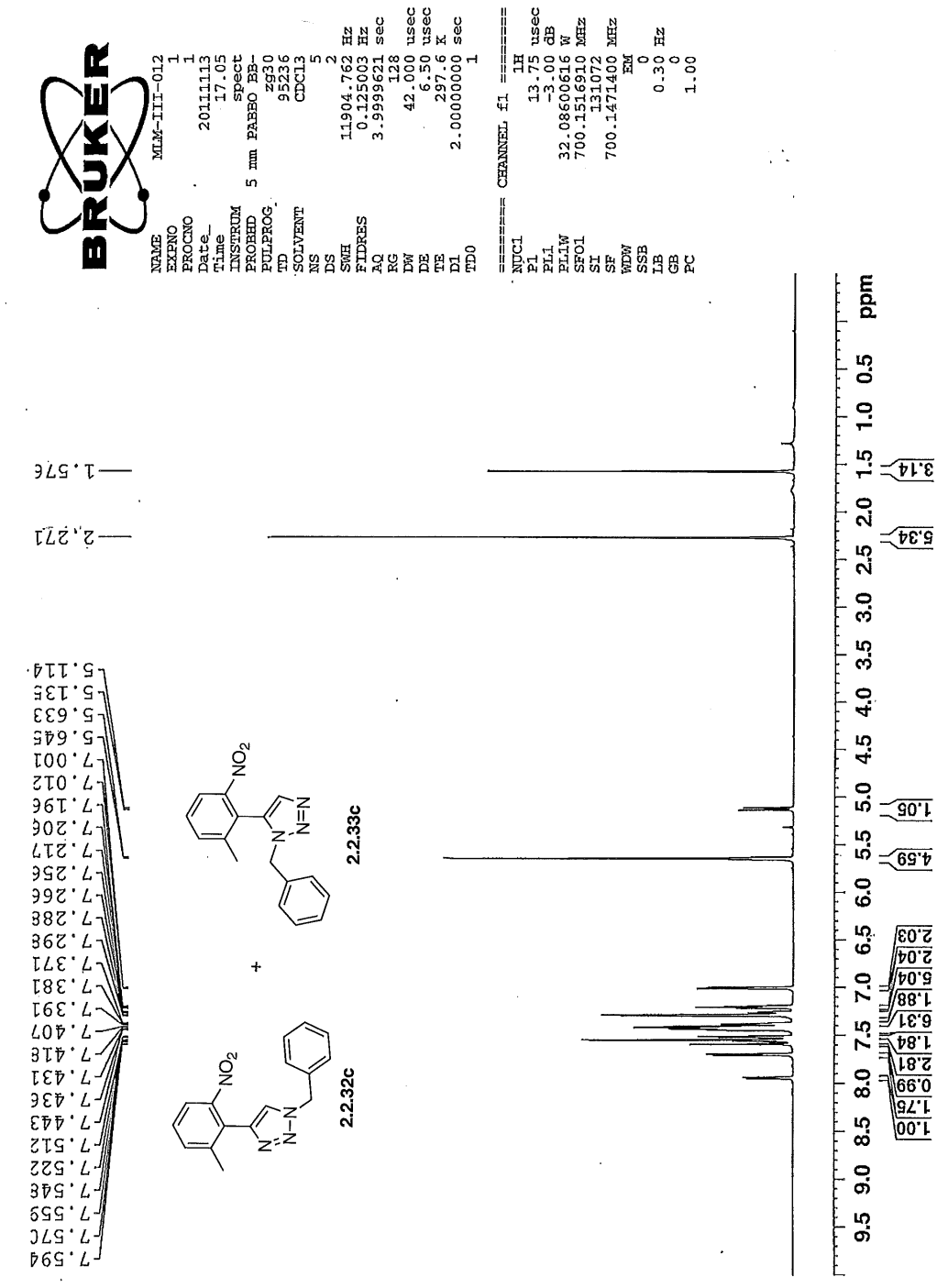
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 32768
SF 100.6416850 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
NO2
2.2.32a
54.34
77.35
77.04
76.72
148.22
142.43
134.34
132.50
131.12
129.22
128.94
128.89
128.04
124.73
124.02
122.94
200
180
160
140
120
100
80
60
40
20
ppm

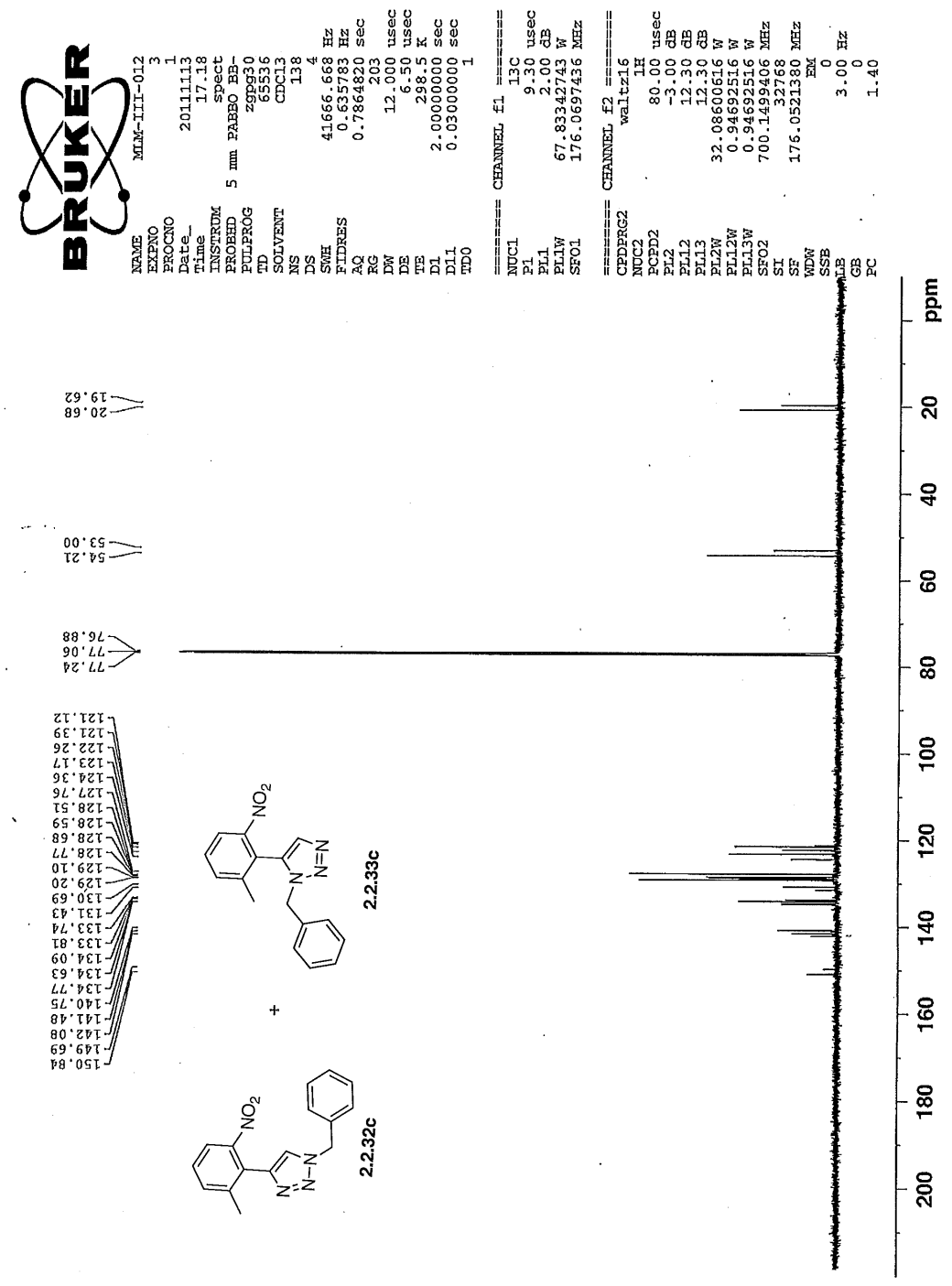

Current Data Parameters
NAME MIM-I-031
EXPNO 9
PROCNO 1
F2 - Acquisition Parameter
Date_ 20100827
Time 13.07
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.55599540 se
RG 181
DW 78.000 us
DE 6.00 us
TE 299.2 K
D1 2.00000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 13.50 us
PL1 -3.00 dB
SFO1 400.2478017 MH
F2 - Processing parameters
SI 32768
SF 400.2450000 MH
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
NO2
N=N
2.2.33a
5.429
6.939
6.956
7.006
7.025
7.176
7.193
7.212
7.219
7.236
7.281
7.534
7.536
7.552
7.571
7.620
7.623
7.640
7.663
8.113
8.133
8.134
2.14
1.00
2.06
1.05
3.10
1.03
2.02
ppm

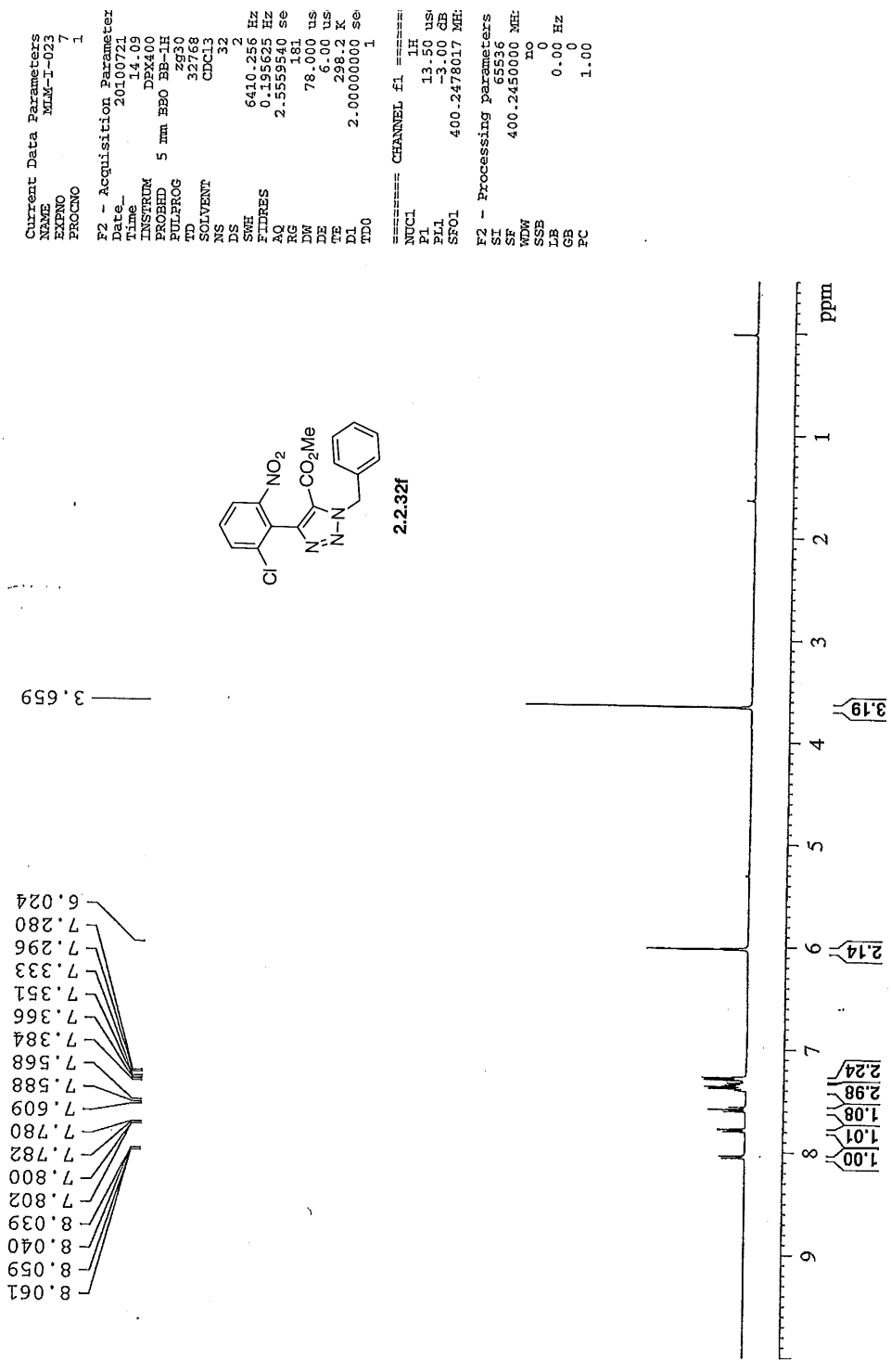

Current Data Parameters
NAME MAC-I-031
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100827
Time 13.14
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3775
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 7298.2
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
D11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 65536
SF 100.6416850 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
29.70
52.85
76.75
77.07
77.27
77.39
122.24
124.92
127.77
128.43
128.72
131.04
133.08
133.10
133.25
133.93
134.38
148.53
minor
2.2.33a
ppm

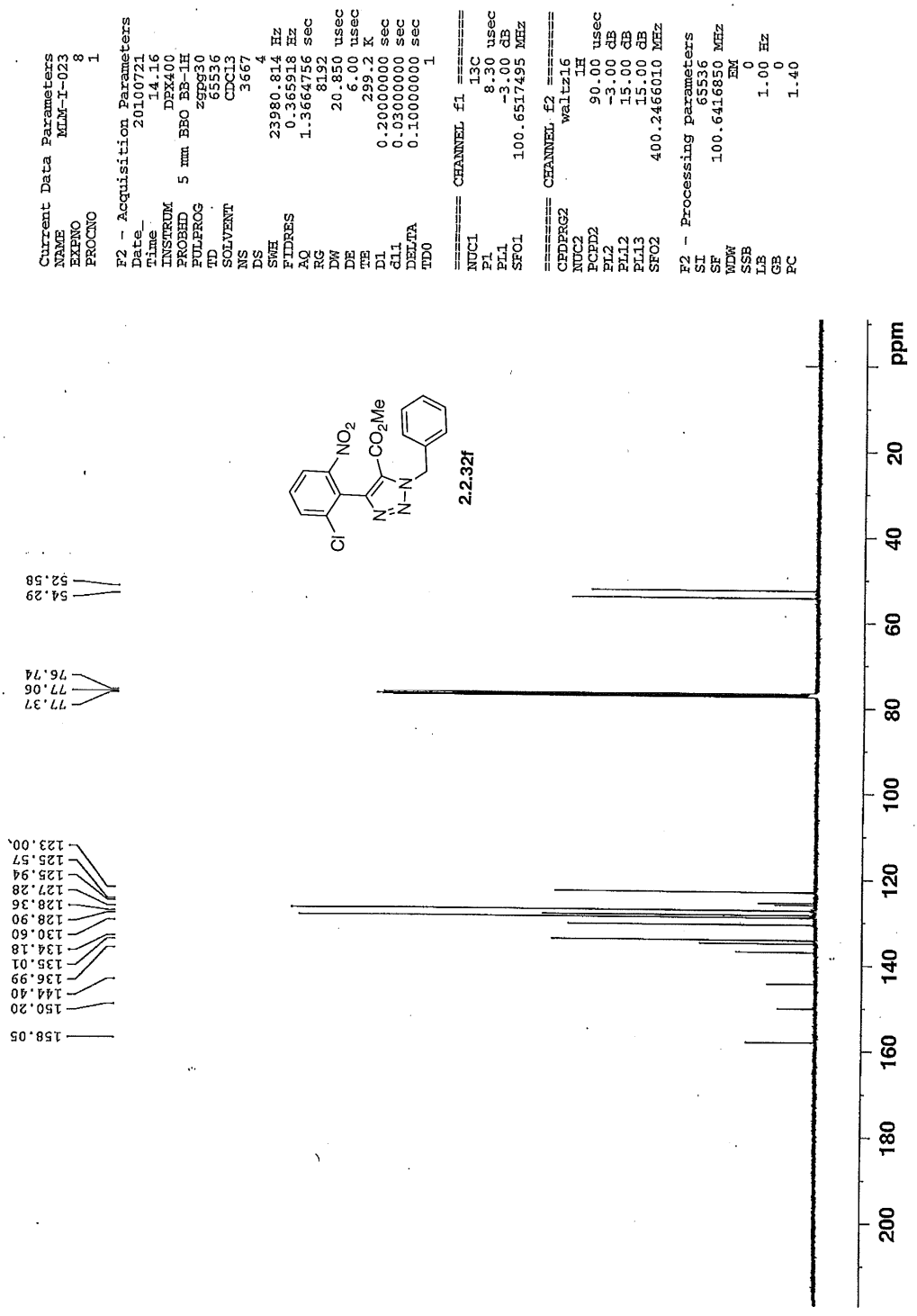

BRUKER
NAME MLM-III-013
EXPNO 1
PROCNO 1
Date_ 20111109
Time_ 13.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 27
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.99999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 300.8 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.2.33b
2.2.32b
ppm

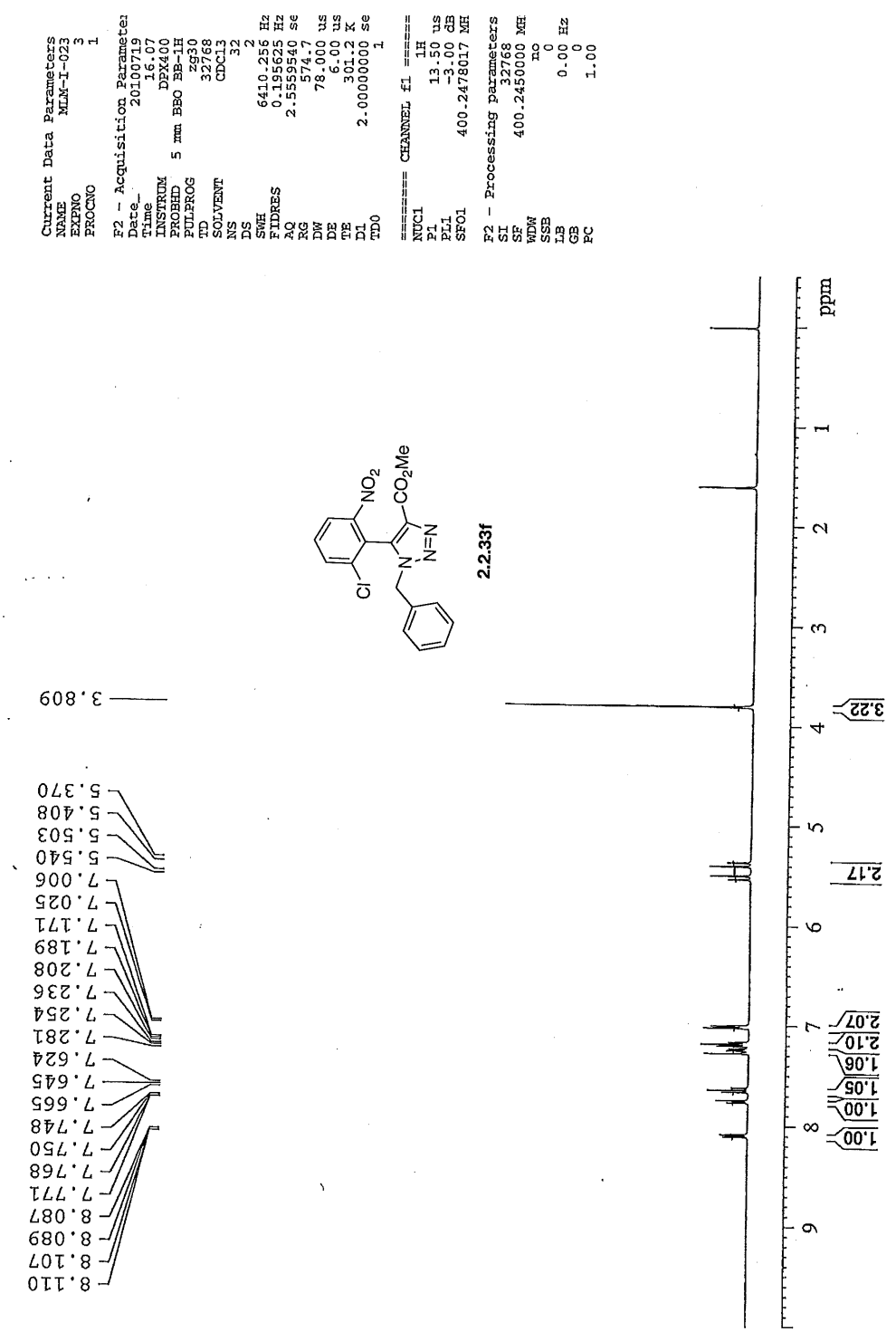

BRUKER
NAME MLM-III-013
EXPNO 3
PROCNO 1
Date_ 20111109
Time 14.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 737
DS 4
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 6.50 usec
TE 300.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 2.00 dB
PL1W 67.83342743 W
SFO1 176.0697436 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.30 dB
PL13 12.30 dB
PL2W 32.08600616 W
PL12W 0.946925516 W
PL13W 0.946925516 W
SFO2 700.1499406 MHz
SI 65536
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
151.38
139.64
135.94
134.44
134.15
133.42
131.61
129.89
129.23
128.83
128.66
128.58
128.34
127.80
124.51
124.23
123.06
122.62
77.19
77.01
76.83
54.31
53.38
ppm
200
180
160
140
120
100
80
60
40
20
2.2.33b
+
2.2.32b

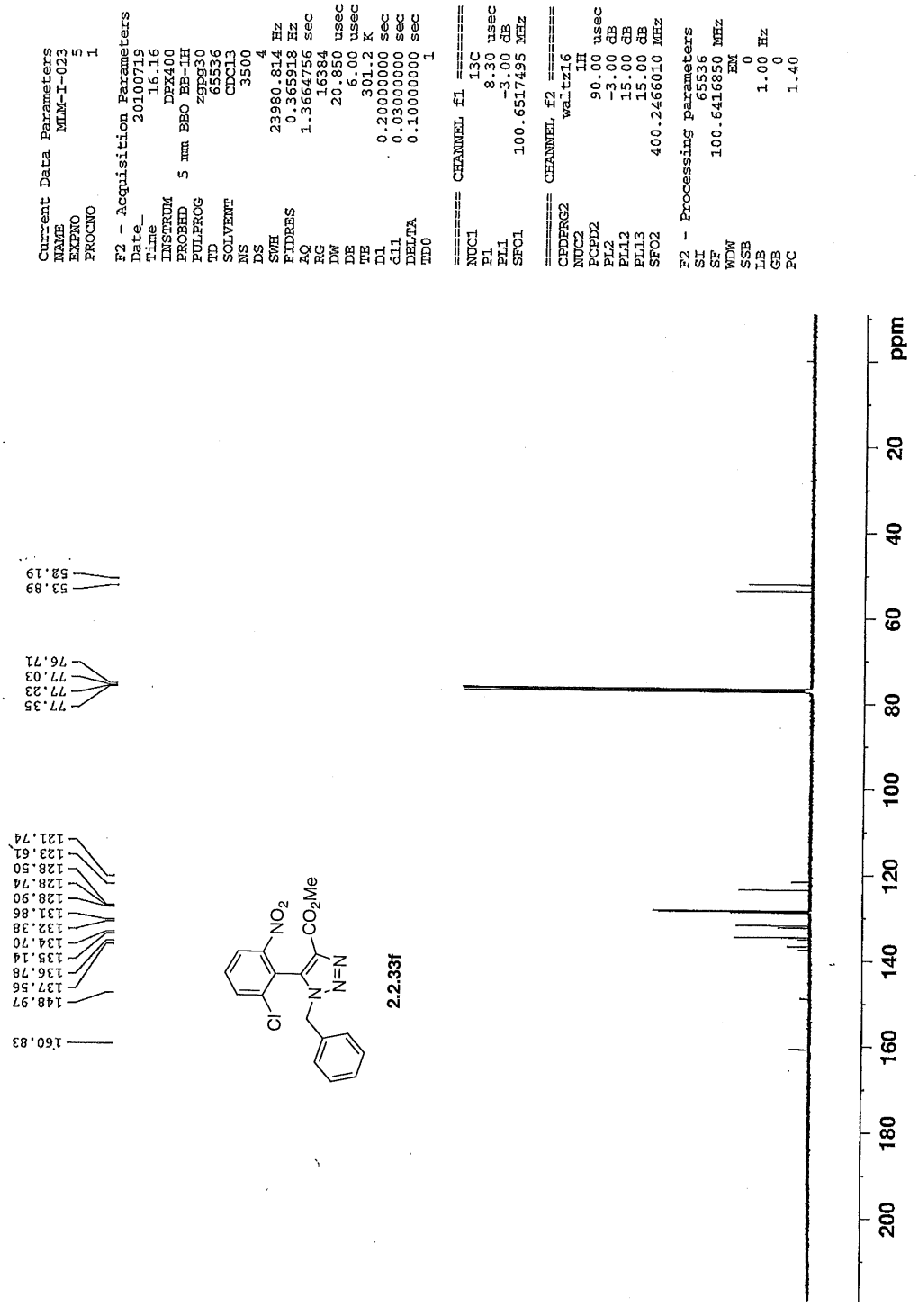

BRUKER
NAME MLM-III-012
EXPNO 1
PROCNO 1
Date_ 20111113
Time 17.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 5
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 128
DW 42.000 usec
DE 6.50 usec
TE 297.6 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.576
2.271
7.594 7.570 7.559 7.548 7.522 7.512 7.443 7.436 7.431 7.418 7.407 7.391 7.381 7.371 7.298 7.288 7.266 7.256 7.217 7.206 7.196 7.012 7.001 5.645 5.633 5.135 5.114
NO2
N=N
2.2.33c
+
NO2
N=N
2.2.32c
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 ppm
1.00 1.76 0.99 2.81 1.84 6.31 1.88 5.04 2.04 2.03
4.59
1.05
5.34
3.14

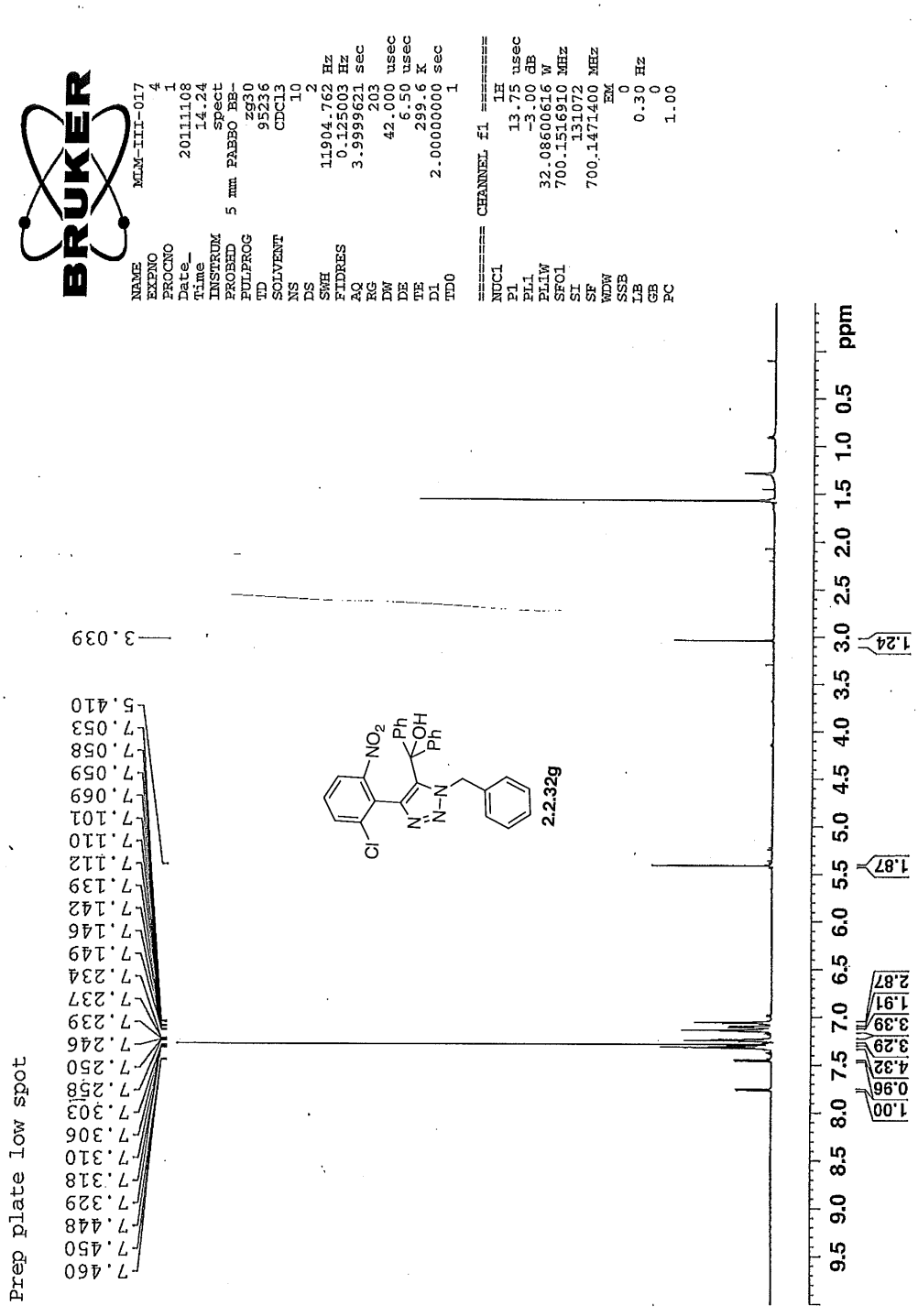

BRUKER
NAME MLM-III-012
EXPNO 3
PROCNO 1
Date_ 20111113
Time 17.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 138
DS 4
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 6.50 usec
TE 298.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 2.00 dB
PL1W 67.83342743 W
SFO1 176.0697436 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.30 dB
PL13 12.30 dB
PL2W 32.08600616 W
PL12W 0.94692516 W
PL13W 0.94692516 W
SFO2 700.1499406 MHz
SI 32768
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
20.68
19.62
54.21
53.00
77.24
77.06
76.88
121.12
121.39
122.26
123.17
124.36
127.76
128.51
128.59
128.68
128.77
129.10
129.20
130.69
131.43
133.74
133.81
134.09
134.63
134.77
140.75
141.48
142.08
149.69
150.84
NO2
N=N
2.2.33c
+
NO2
N=N
2.2.32c
ppm
200
180
160
140
120
100
80
60
40
20

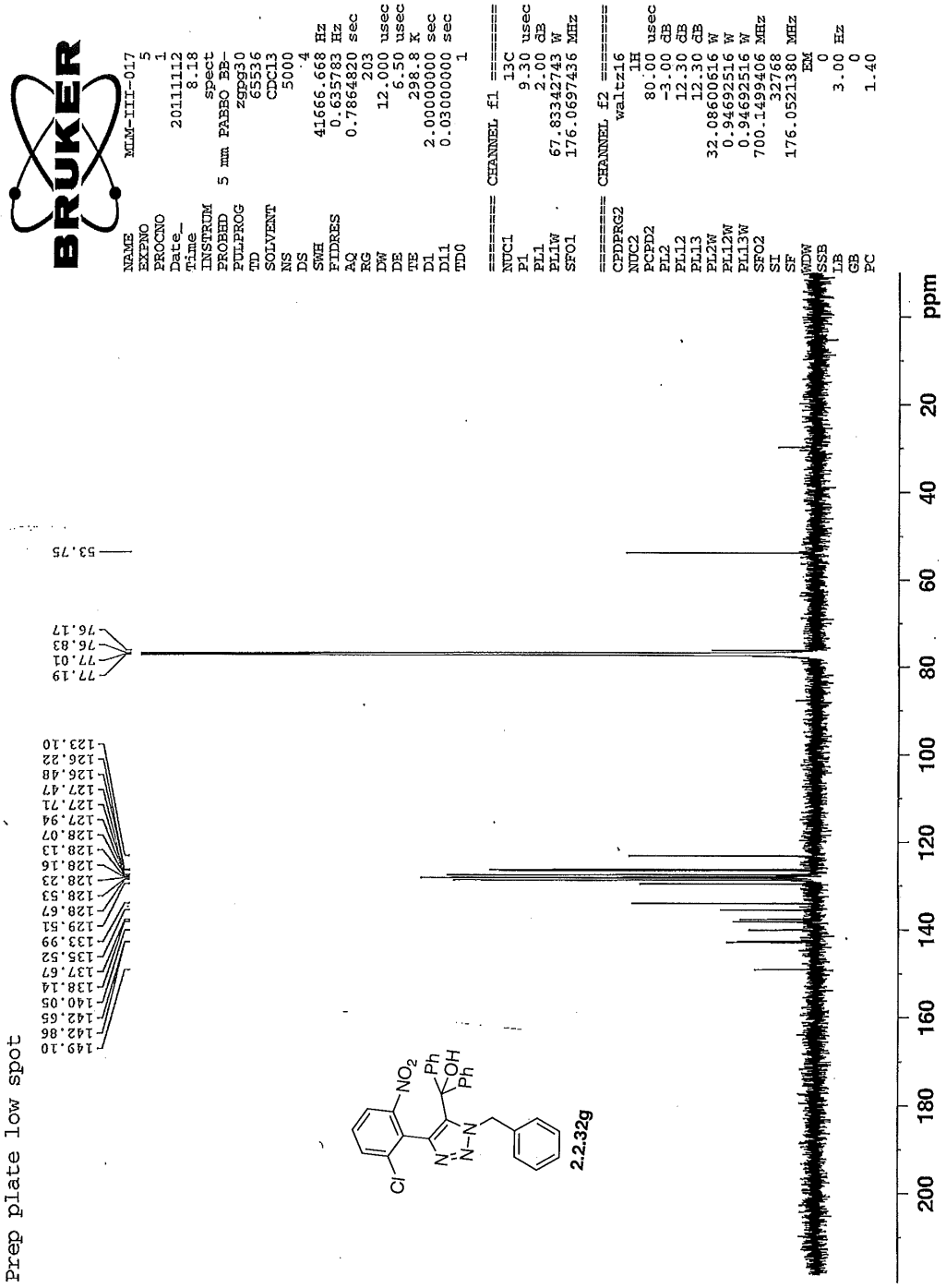

Current Data Parameters
NAME MLM-I-023
EXPNO 7
PROCNO 1
F2 - Acquisition Parameter
Date_ 20100721
Time 14.09
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 se
RG 181
DW 78.000 us
DE 6.00 us
TE 298.2 K
D1 2.00000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 13.50 us
PL1 -3.00 dB
SFO1 400.2478017 MH
F2 - Processing parameters
SI 65536
SF 400.2450000 MH
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
NO2
CO2Me
Cl
N
N-N
2.2.32f
3.659
6.024
7.280
7.296
7.333
7.351
7.366
7.384
7.568
7.588
7.609
7.780
7.782
7.800
7.802
8.039
8.040
8.059
8.061
ppm
1
2
3
4
5
6
7
8
9
3.19
2.14
1.00
1.01
1.08
2.98
2.24

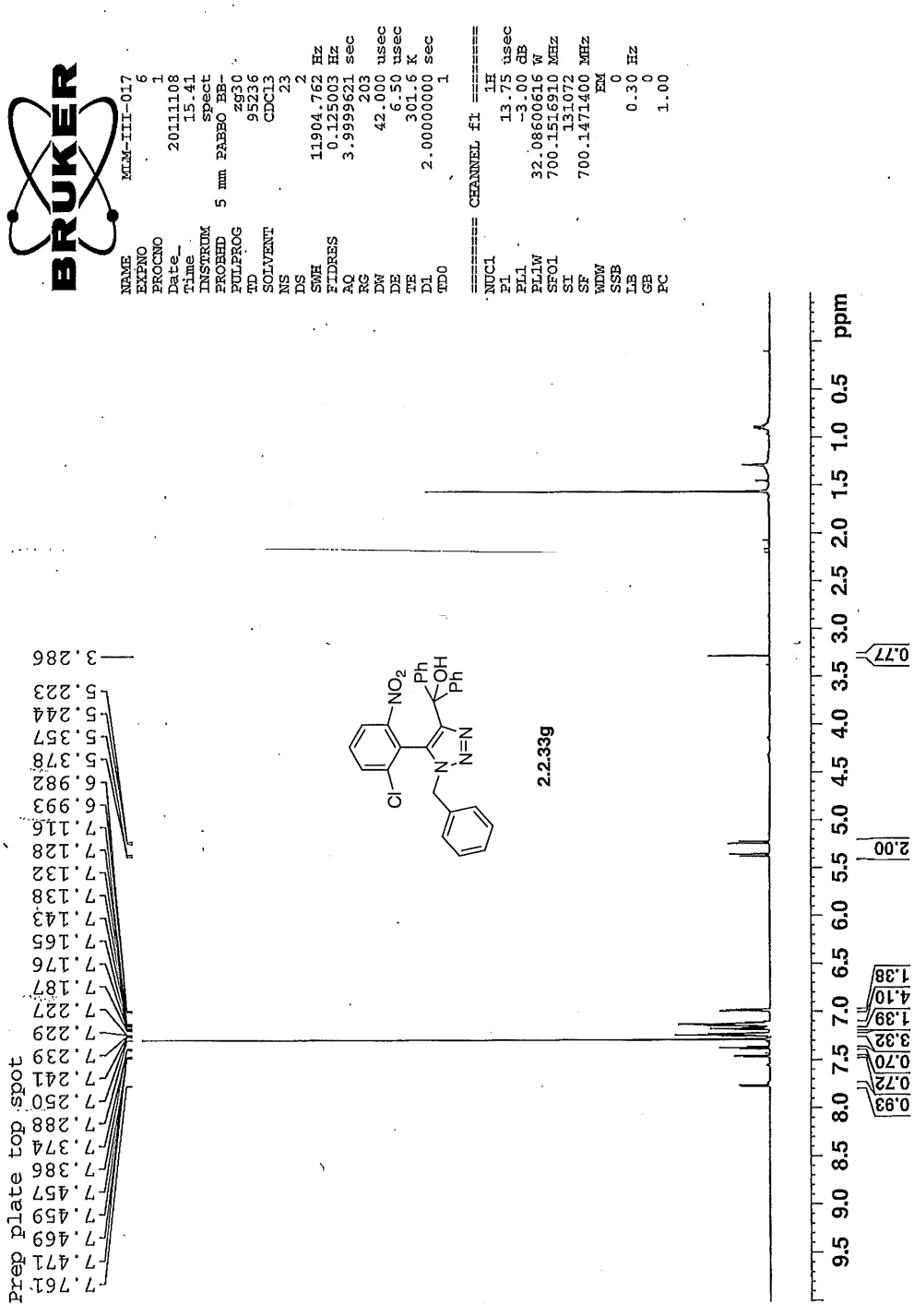

Current Data Parameters
NAME MLM-I-023
EXPNO 8
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100721
Time 14.16
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3667
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.36647556 sec
RG 8192
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 65536
SF 100.6416850 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
NO2
CO2Me
Cl
N
N
2.2.32f
52.58
54.29
76.74
77.06
77.37
123.00
125.57
125.94
127.28
128.36
128.90
130.60
134.18
135.01
136.99
144.40
150.20
158.05
200
180
160
140
120
100
80
60
40
20
ppm

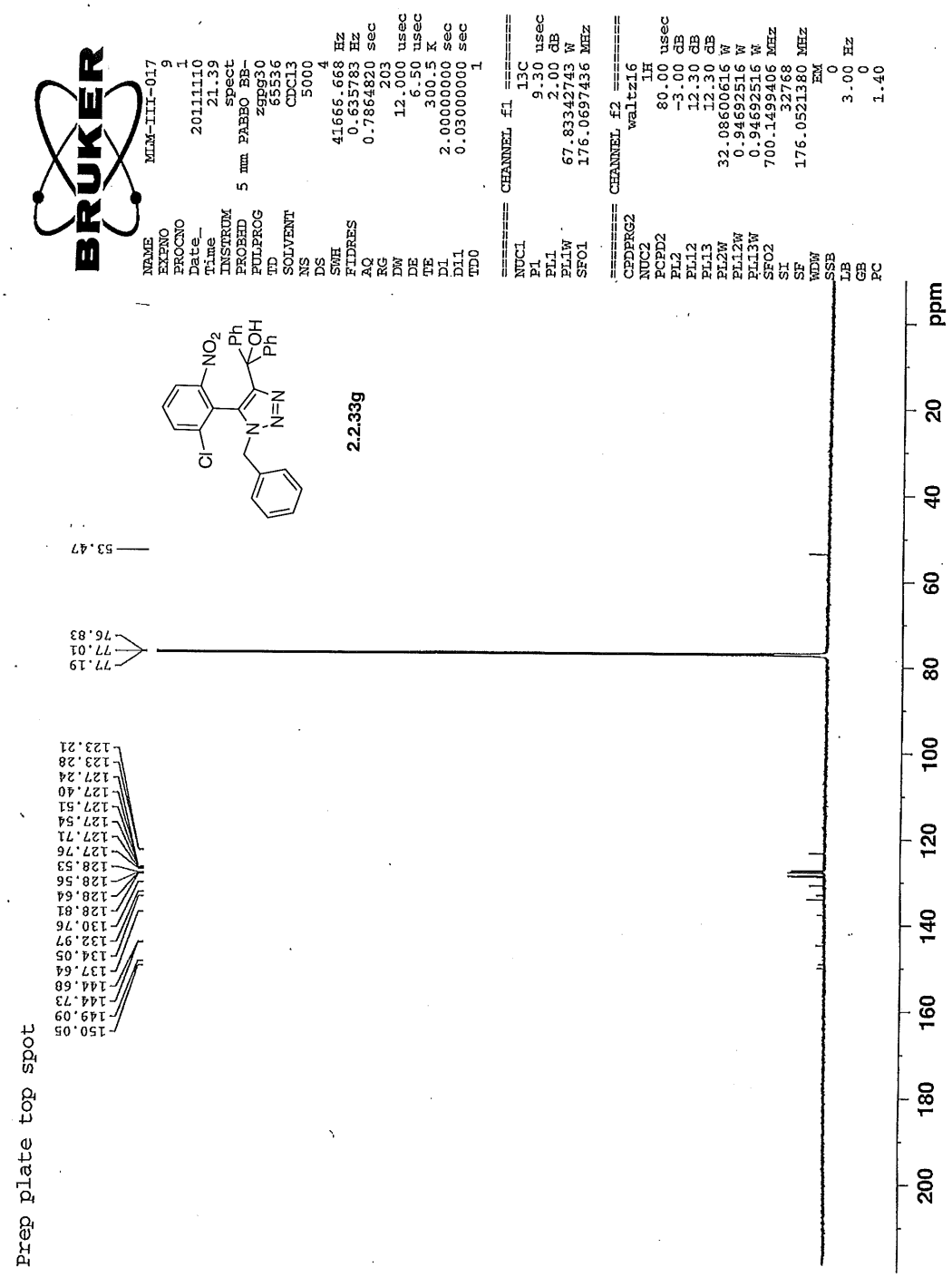

Current Data Parameters
NAME MLM-I-023
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100719
Time 16.07
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 se
RG 574.7
DW 78.000 us
DE 6.00 us
TE 301.2 K
D1 2.00000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 13.50 us
PL1 -3.00 dB
SFO1 400.2478017 MH
F2 - Processing parameters
SI 32768
SF 400.2450000 MH
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
NO2
CO2Me
Cl
N=N
2.2.33f
3.809
5.370
5.408
5.503
5.540
7.006
7.025
7.171
7.189
7.208
7.236
7.254
7.281
7.624
7.645
7.665
7.748
7.750
7.768
7.771
8.087
8.089
8.107
8.110
3.22
2.17
1.00
1.00
1.05
1.06
2.10
2.07
ppm

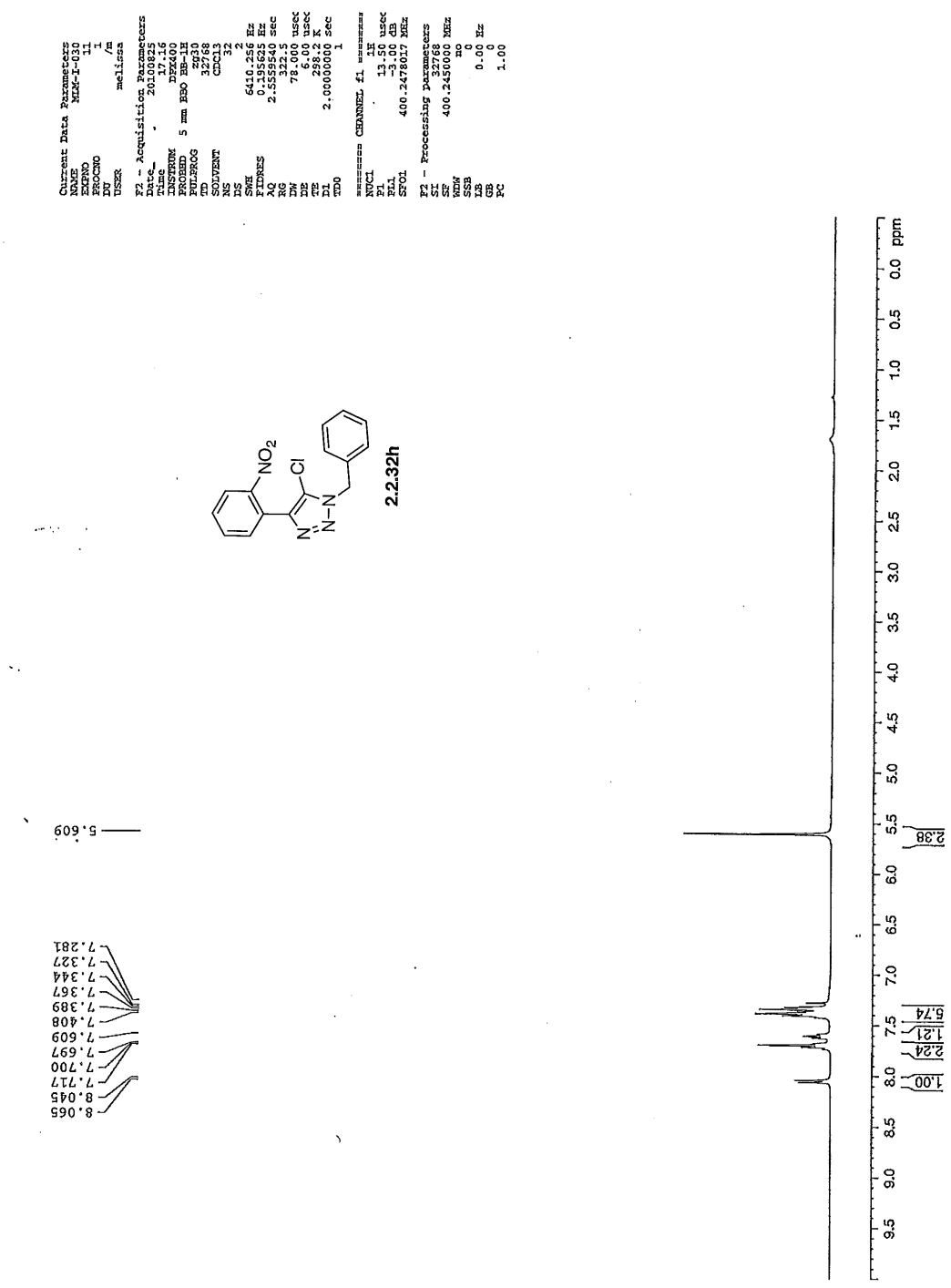

Current Data Parameters
NAME MIM-I-023
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100719
Time 16.16
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3500
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.36647568 sec
RG 16384
DW 20.850 usec
DE 6.00 usec
TE 301.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 65536
SF 100.6416850 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160.83
148.97
137.56
136.78
135.14
134.70
132.38
131.86
128.90
128.74
128.50
123.61
121.74
77.35
77.23
77.03
76.71
53.89
52.19
NO2
CO2Me
Cl
N
N=N
2.2.33f
200
180
160
140
120
100
80
60
40
20
ppm

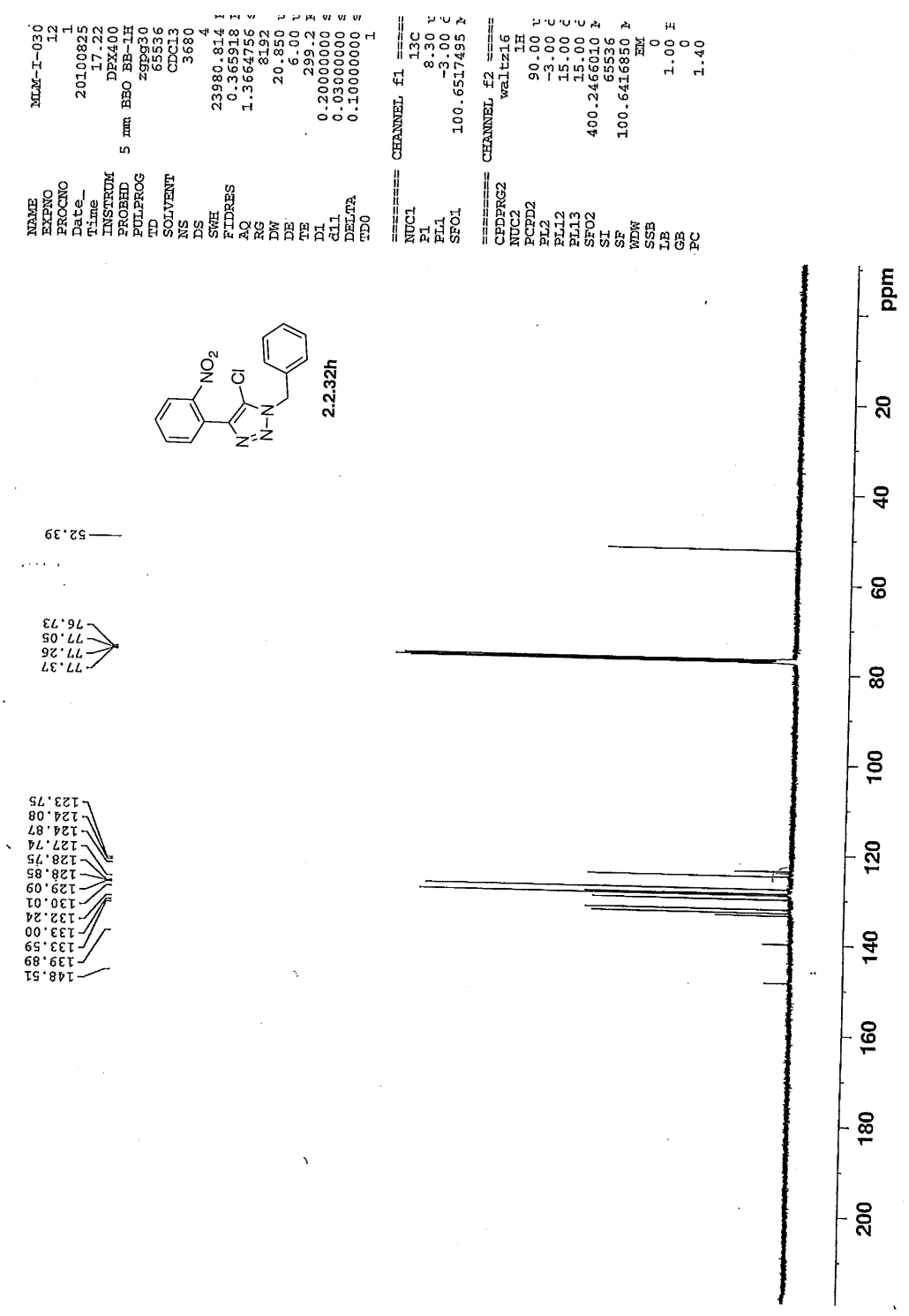

BRUKER
NAME MLM-III-017
EXPNO 4
PROCNO 1
Date_ 20111108
Time 14.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 10
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 299.6 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Prep plate low spot
7.460
7.450
7.448
7.329
7.318
7.310
7.306
7.303
7.258
7.250
7.246
7.239
7.237
7.234
7.149
7.146
7.142
7.139
7.112
7.110
7.101
7.069
7.059
7.058
7.053
5.410
3.039
NO2
Ph
OH
Ph
Cl
N
N
2.2.32g
ppm
1.24
1.87
1.00
0.96
4.32
3.29
3.39
1.91
2.87

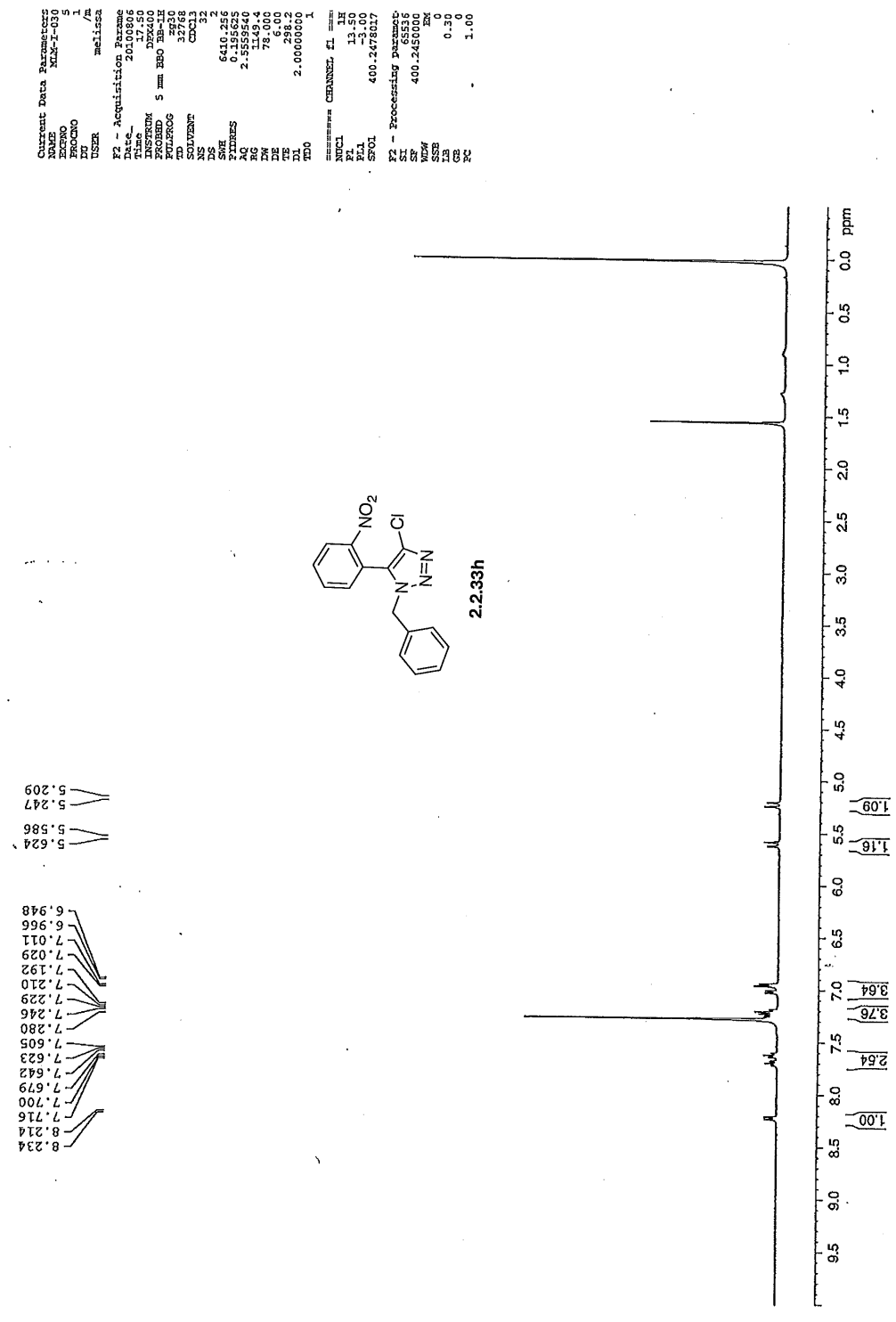

Prep plate low spot
BRUKER
NAME MLM-III-017
EXPNO 5
PROCNO 1
Date_ 20111112
Time 8.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 5000
DS 4
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 6.50 usec
TE 298.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 2.00 dB
PL1W 67.83342743 W
SFO1 176.0697436 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.30 dB
PL13 12.30 dB
PL2W 32.08600616 W
PL12W 0.94692516 W
PL13W 0.94692516 W
SFO2 700.14999406 MHz
SI 32768
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
53.75
76.17
76.83
77.01
77.19
123.10
126.22
126.48
127.47
127.71
127.94
128.07
128.13
128.16
128.23
128.53
128.67
129.51
133.99
135.52
137.67
138.14
140.05
142.65
142.86
149.10
NO2
Ph
OH
Ph
Cl
N
N
2.2.32g
200
180
160
140
120
100
80
60
40
20
ppm

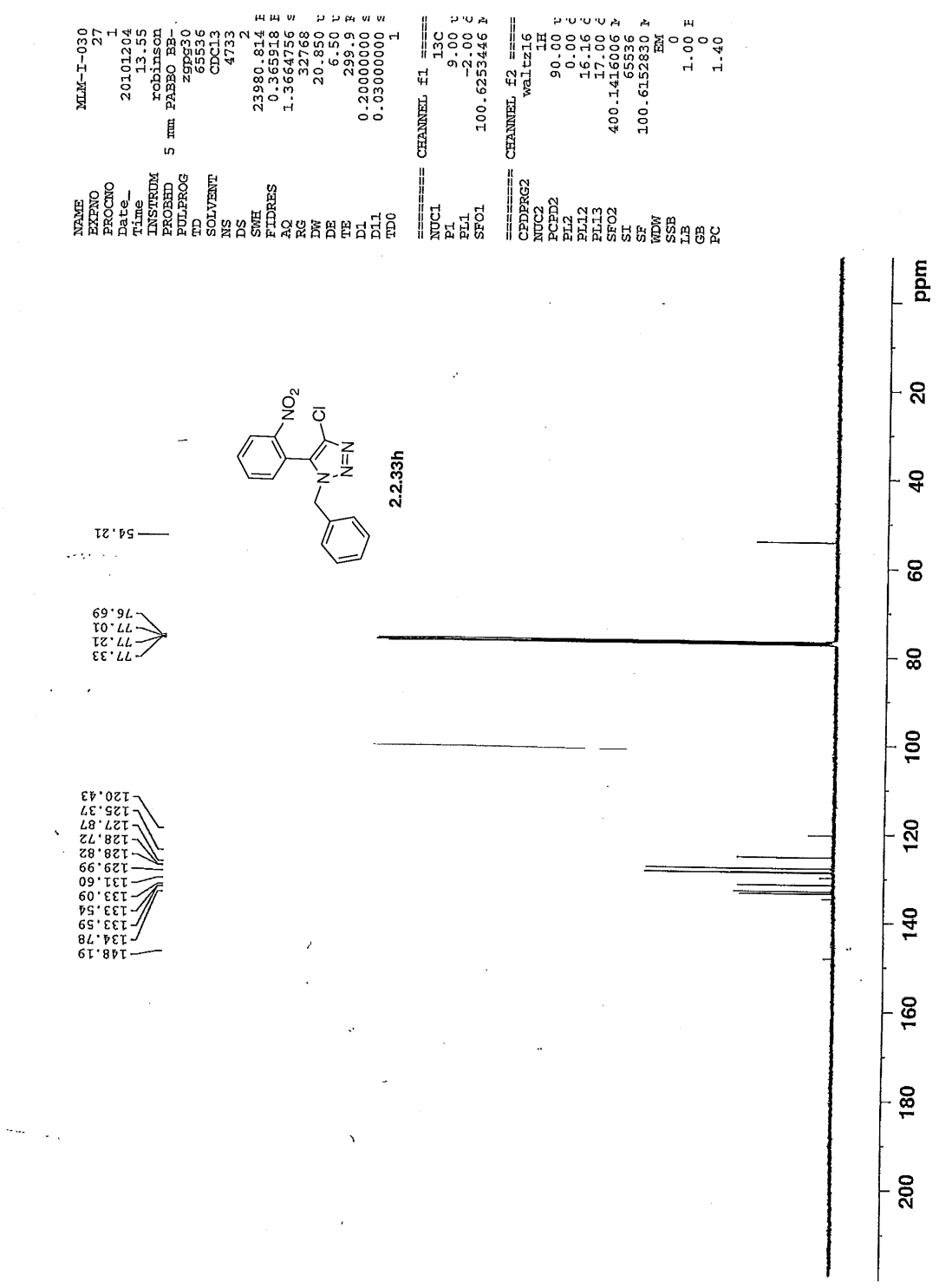

BRUKER
NAME MLM-III-017
EXPNO 6
PROCNO 1
Date_ 20111108
Time 15.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 23
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 301.6 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Prep plate top spot
7.761
7.471
7.469
7.459
7.457
7.386
7.374
7.288
7.250
7.241
7.239
7.229
7.227
7.187
7.176
7.165
7.143
7.138
7.132
7.128
7.116
6.993
6.982
5.378
5.357
5.244
5.223
3.286
NO2
Ph
OH
Ph
Cl
N
N
2.2.33g
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 ppm
0.93
0.72
0.70
3.32
1.39
4.10
1.38
2.00
0.77

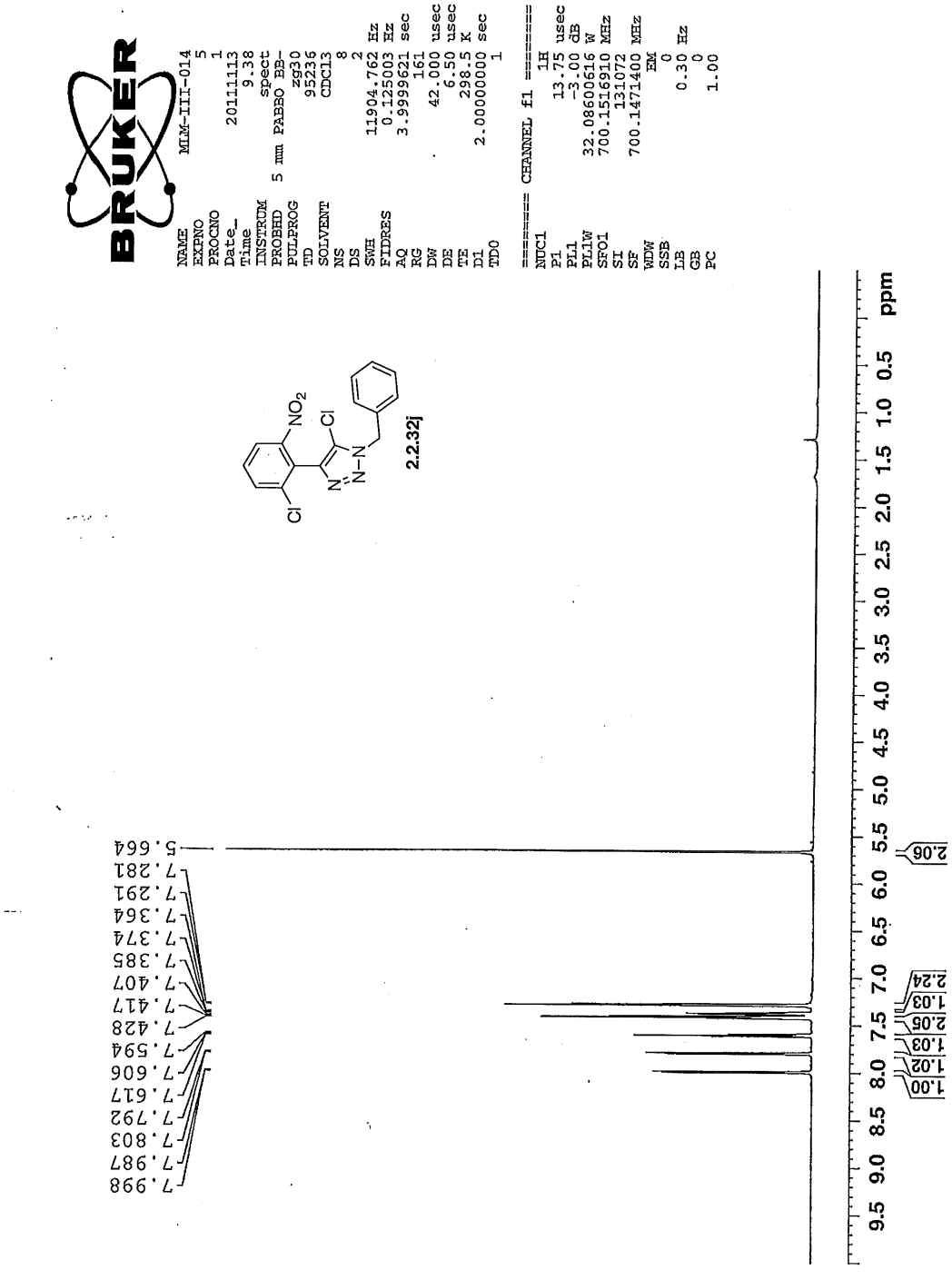

Prep plate top spot
2.2.33g
NAME MLM-III-017
EXPNO 9
PROCNO 1
Date_ 20111110
Time 21.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 5000
DS 4
SWH 41665.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 6.50 usec
TE 300.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 9.30 usec
PL1 2.00 dB
PL1W 67.83342743 W
SFO1 176.0697436 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.30 dB
PL13 12.30 dB
PL2W 32.08600616 W
PL12W 0.94692516 W
PL13W 0.94692516 W
SFO2 700.1499406 MHz
SI 32768
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
77.19
77.01
76.83
53.47
150.05
149.09
144.73
144.68
137.64
134.05
132.97
130.76
128.81
128.64
128.56
128.53
127.76
127.71
127.54
127.51
127.40
127.24
123.28
123.21
200
180
160
140
120
100
80
60
40
20
ppm

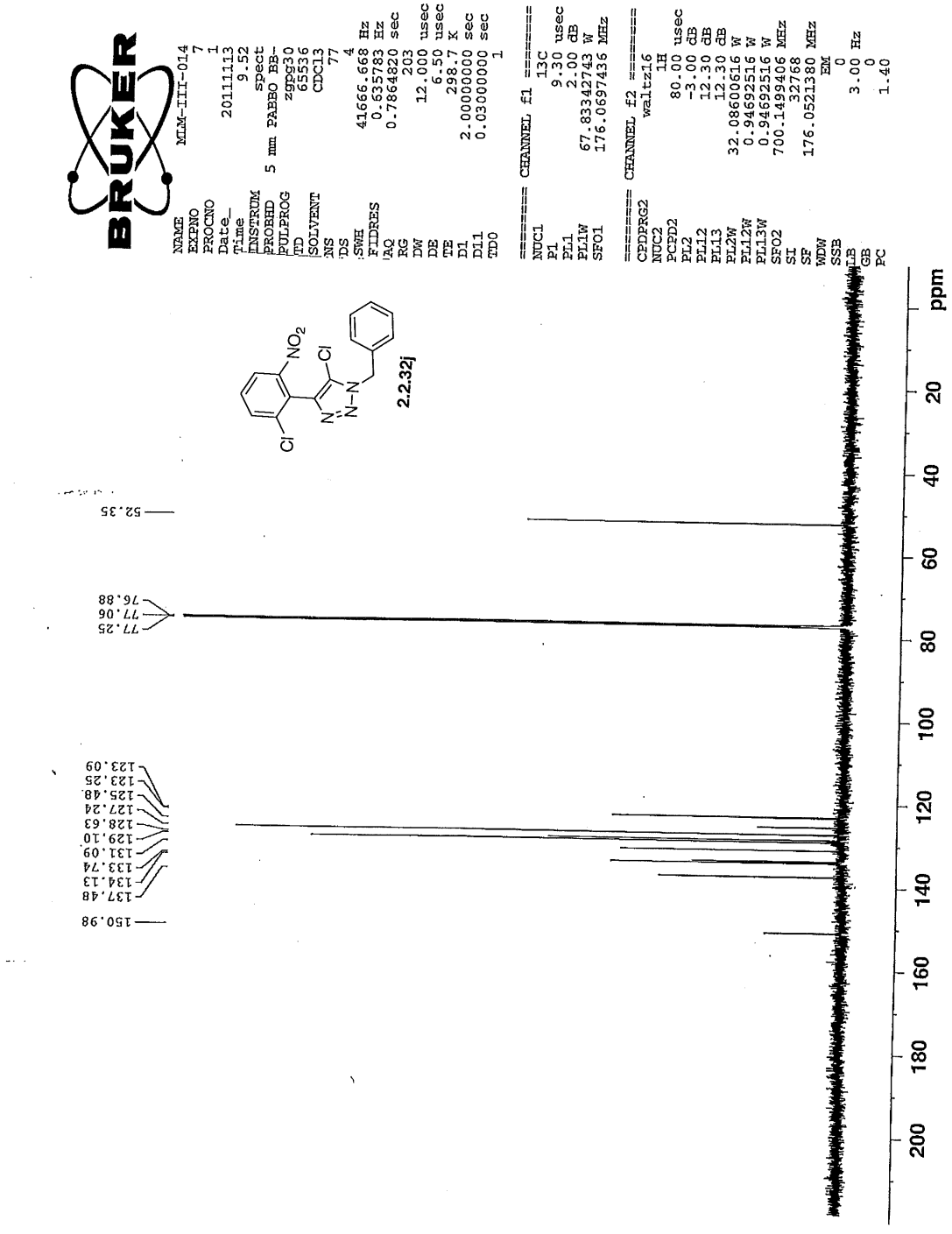

Current Data Parameters
NAME MIK-I-030
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100825
Time 17.16
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 228.5
DW 78.001 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 13.50 usec
PL1 -3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 32768
SF 400.2450000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
2.2.32h
5.609
7.281
7.327
7.344
7.367
7.389
7.408
7.609
7.697
7.700
7.717
8.045
8.065
2.38
6.74
1.21
2.24
1.00
ppm

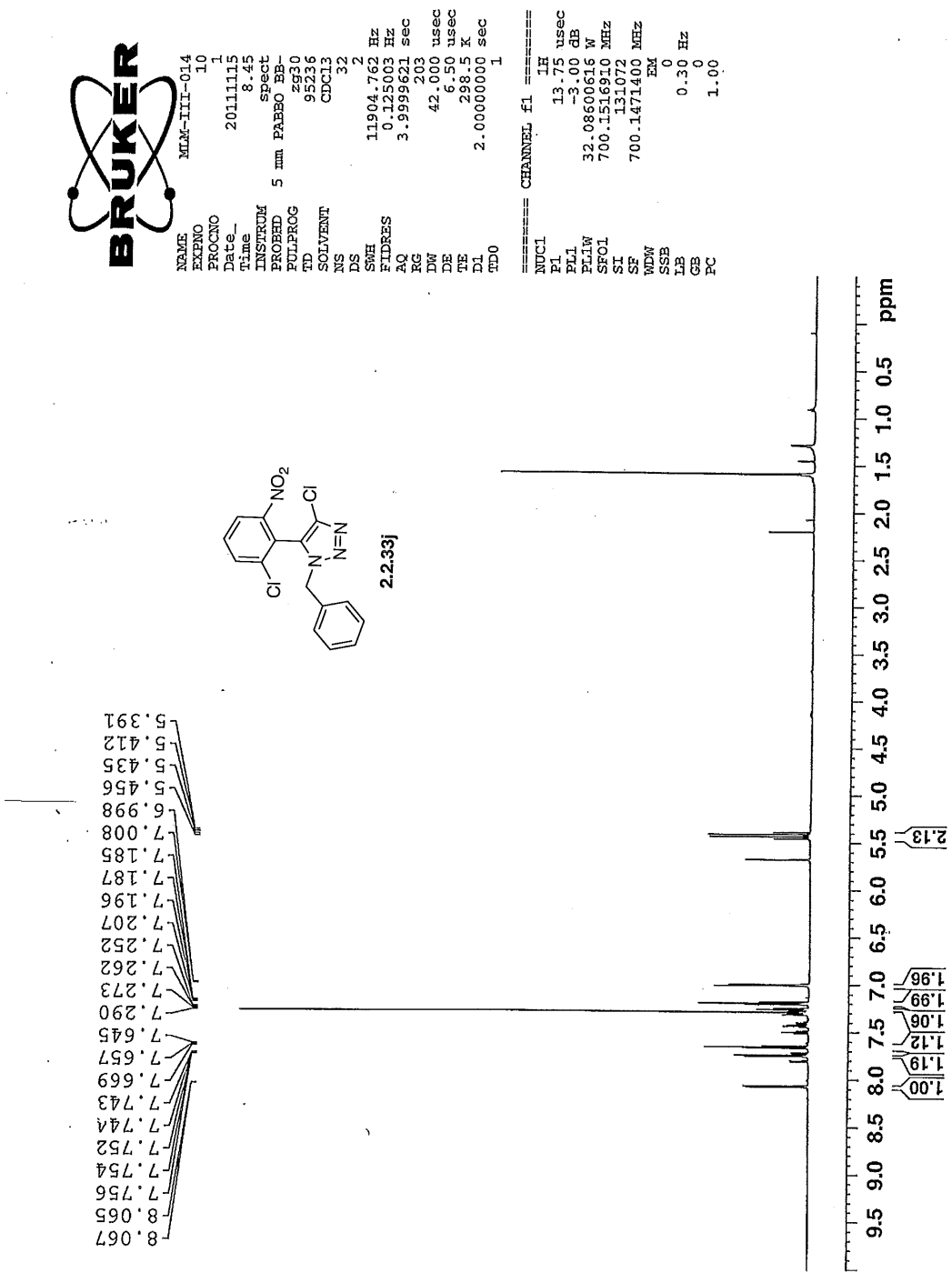

NAME MLM-I-030
EXPNO 12
PROCNO 1
Date_ 20100825
Time 17.22
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3680
DS 4
SWH 23980.814
FIDRES 0.365918
AQ 1.3664756
RG 8192
DW 20.850
DE 6.00
TE 299.2
D1 0.20000000
d11 0.03000000
DELTA 0.10000000
TD0 1
CHANNEL f1 13C
P1 8.30
PL1 -3.00
SFO1 100.6517495
CHANNEL f2 waltz16
NUC2 1H
PCPD2 90.00
PL2 -3.00
PL12 15.00
PL13 15.00
SFO2 400.2466010
SI 65536
SF 100.6416850
WDW EM
SSB 0
LB 1.00
GB 0
PC 1.40
NO2
Cl
N
N
2.2.32h
52.39
76.73
77.05
77.26
77.37
123.75
124.08
124.87
127.74
128.75
128.85
129.09
130.01
132.24
133.00
133.59
139.89
148.51
ppm
200
180
160
140
120
100
80
60
40
20

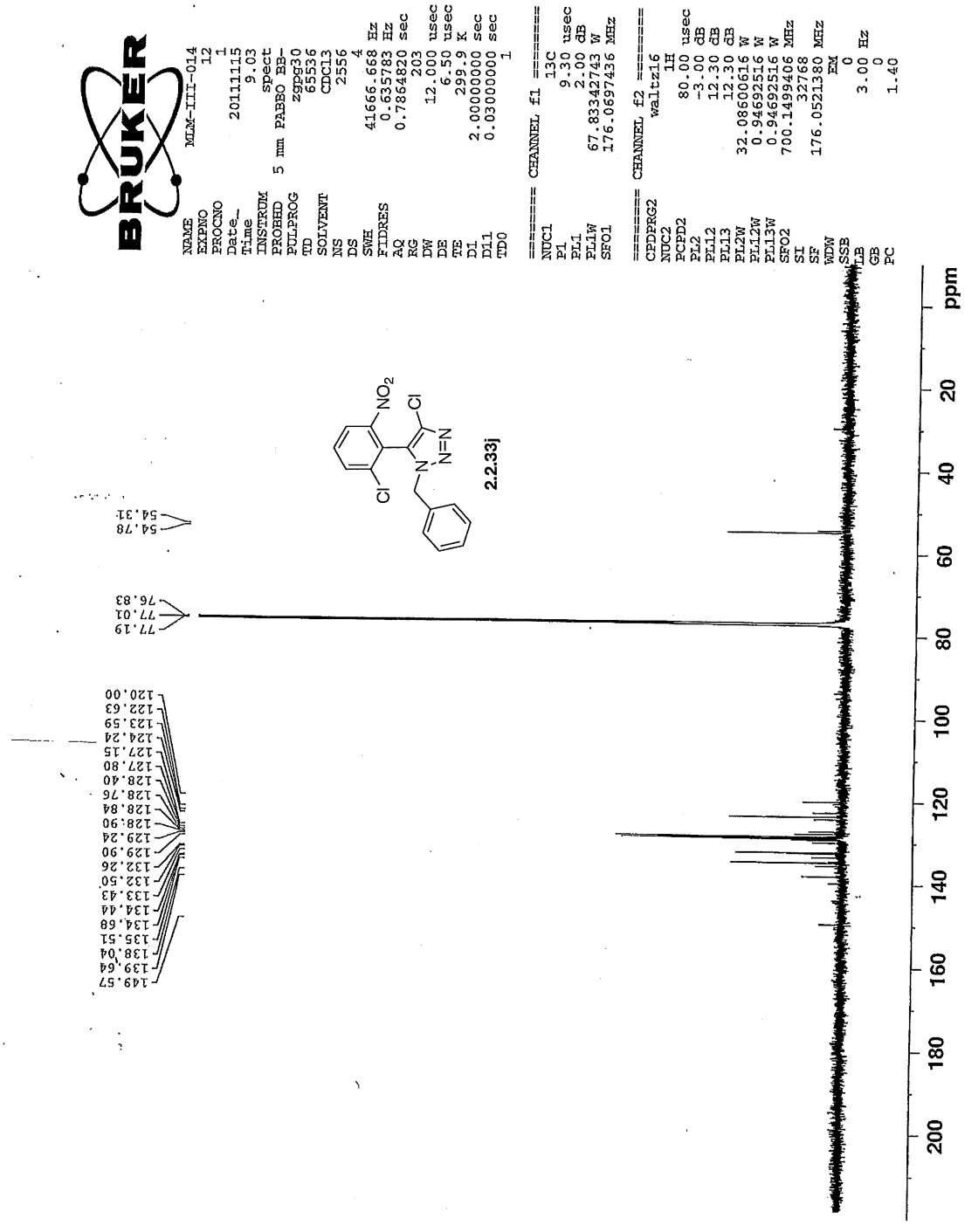

Current Data Parameters
NAME MAK-I-030
EXPNO 5
PROCNO 1
F2 - Acquisition Parame
Date_ 20100806
Time 17.50
INSTRUM DPX400
PROBHD 5 mm BBO BB-IF
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256
FIDRES 0.195625
AQ 2.5559040
RG 1149.4
DW 78.000
DE 6.00
TE 298.2
D1 2.00000000
TD0 1
CHANNEL f1
NUC1 1H
P1 13.50
PL1 -3.00
SFO1 400.2478017
F2 - Processing parmeter
SI 65536
SF 400.2450000
WDW EM
SSB 0
LB 0.30
GB 0
PC 1.00
2.2.33h
5.209
5.247
5.586
5.624
6.948
6.966
7.011
7.029
7.192
7.210
7.229
7.246
7.280
7.605
7.623
7.642
7.679
7.700
7.716
8.214
8.234
1.09
1.16
3.64
3.76
2.64
1.00
ppm

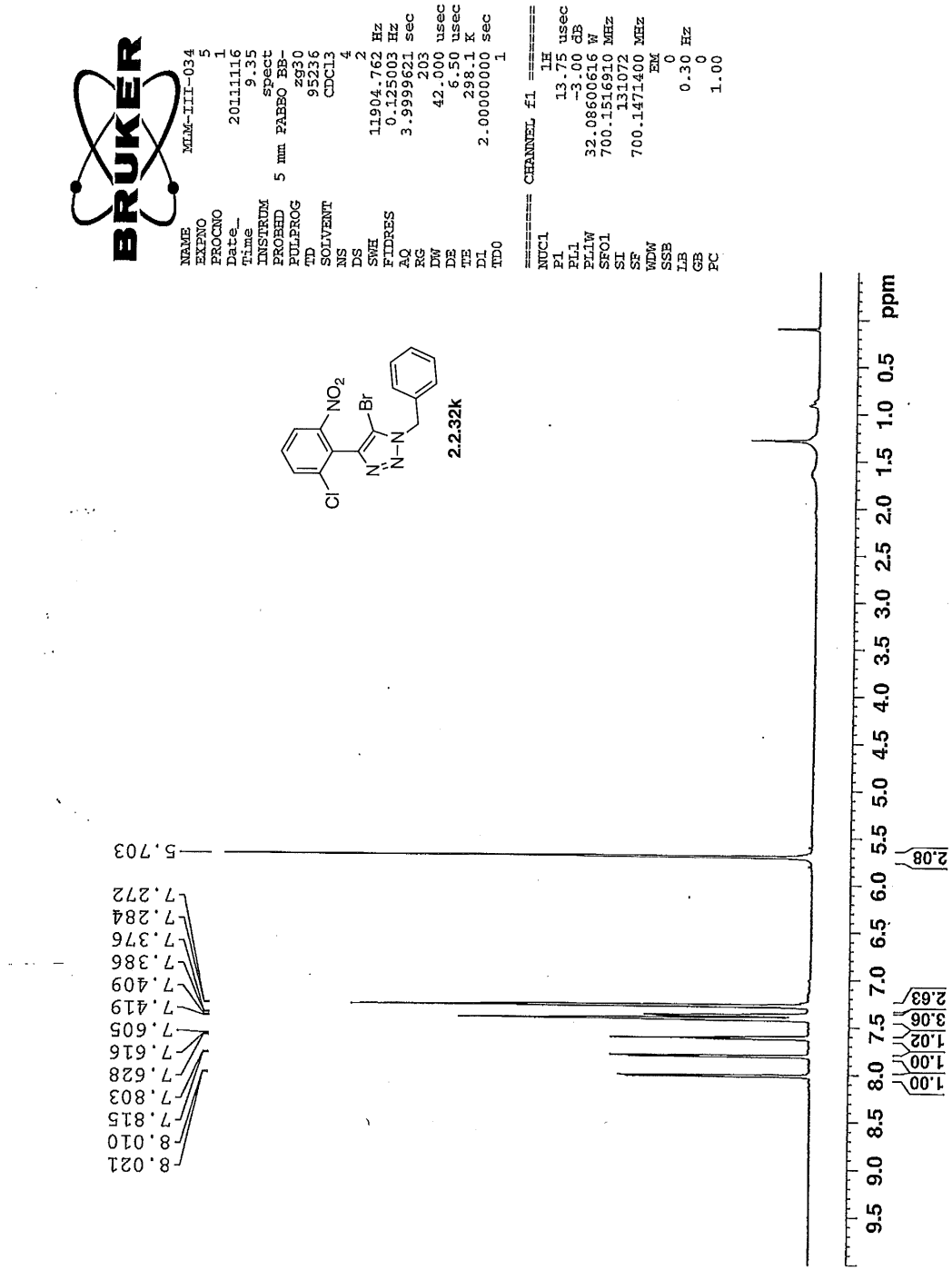

NAME MLM-T-030
EXPNO 27
PROCNO 1
Date_ 20101204
Time 13.55
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4733
DS 2
SWH 23980.814 H
FIDRES 0.365918 H
AQ 1.3664756 s
RG 32768
DW 20.850 u
DE 6.50 u
TE 299.9 K
D1 0.20000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 9.00 u
PL1 -2.00 d
SFO1 100.6253446 M
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 u
PL2 0.00 d
PL12 16.16 d
PL13 17.00 d
SFO2 400.1416006 M
SI 65536
SF 100.6152830 M
WDW EM
SSB 0
LB 1.00 H
GB 0
PC 1.40
NO2
Cl
N=N
2.2.33h
54.21
76.69
77.01
77.21
77.33
120.43
125.37
127.87
128.72
128.82
129.99
131.60
133.09
133.54
133.59
134.78
148.19
200
180
160
140
120
100
80
60
40
20
ppm

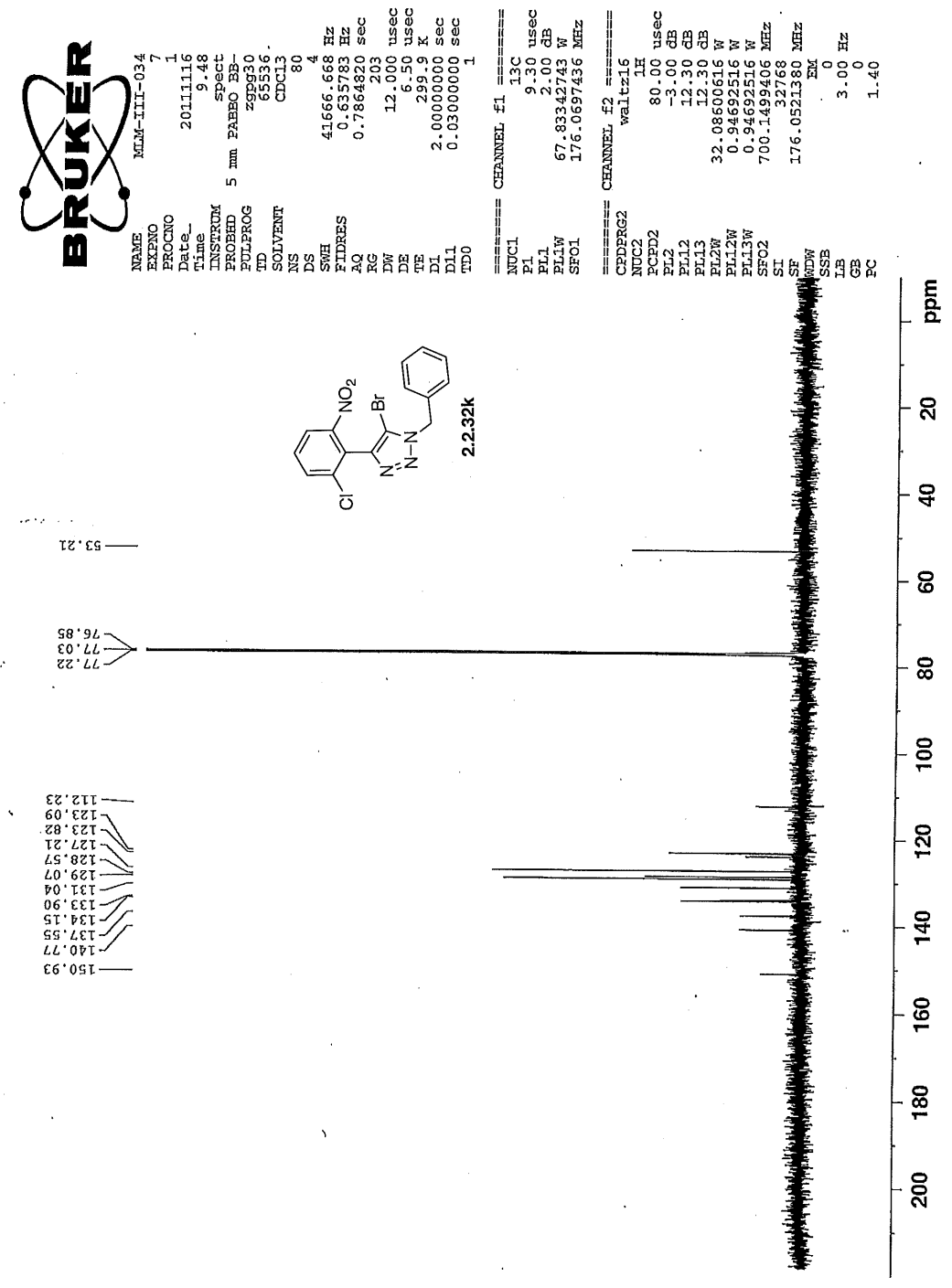

BRUKER
NAME MLM-III-014
EXPNO 5
PROCNO 1
Date_ 20111113
Time 9.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 8
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 161
DW 42.000 usec
DE 6.50 usec
TE 298.5 K
D1 2.00000000 sec
TDO 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.2.32j
5.664
7.281
7.291
7.364
7.374
7.385
7.407
7.417
7.428
7.594
7.606
7.617
7.792
7.803
7.987
7.998
2.06
1.00
1.02
1.08
2.05
1.03
2.24
ppm

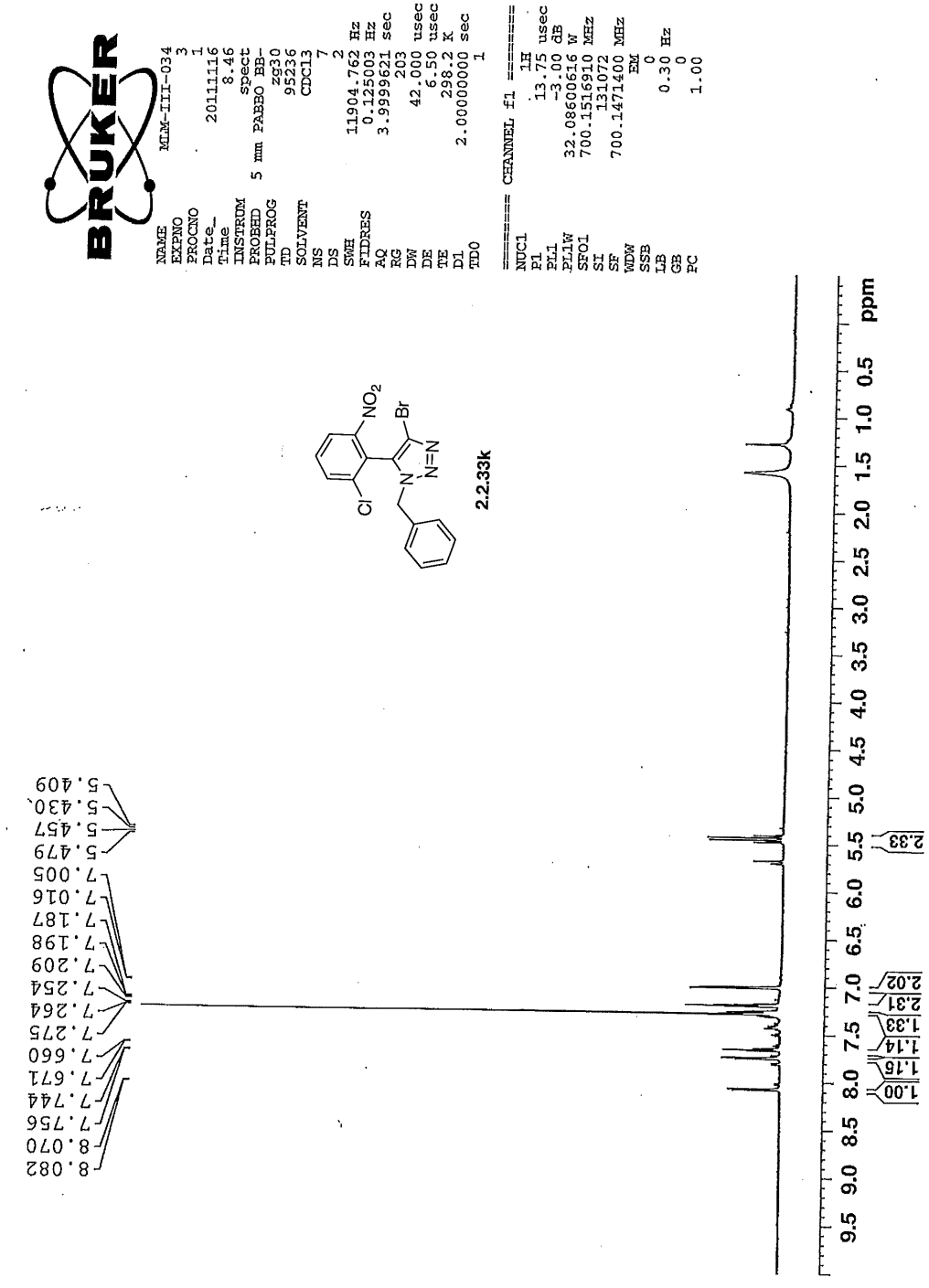

BRUKER
NAME MLM-III-014
EXPNO 7
PROCNO 1
Date_ 20111113
Time 9.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 77
DS 4
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 6.50 usec
TE 298.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 2.00 dB
PL1W 67.83342743 W
SFO1 176.0697436 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.30 dB
PL13 12.30 dB
PL2W 32.08600616 W
PL12W 0.94692516 W
PL13W 0.94692516 W
SFO2 700.1499406 MHz
SI 32768
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
2.2.32j
52.35
76.88
77.06
77.25
123.09
123.25
125.48
127.24
128.63
129.10
131.09
133.74
134.13
137.48
150.98
ppm

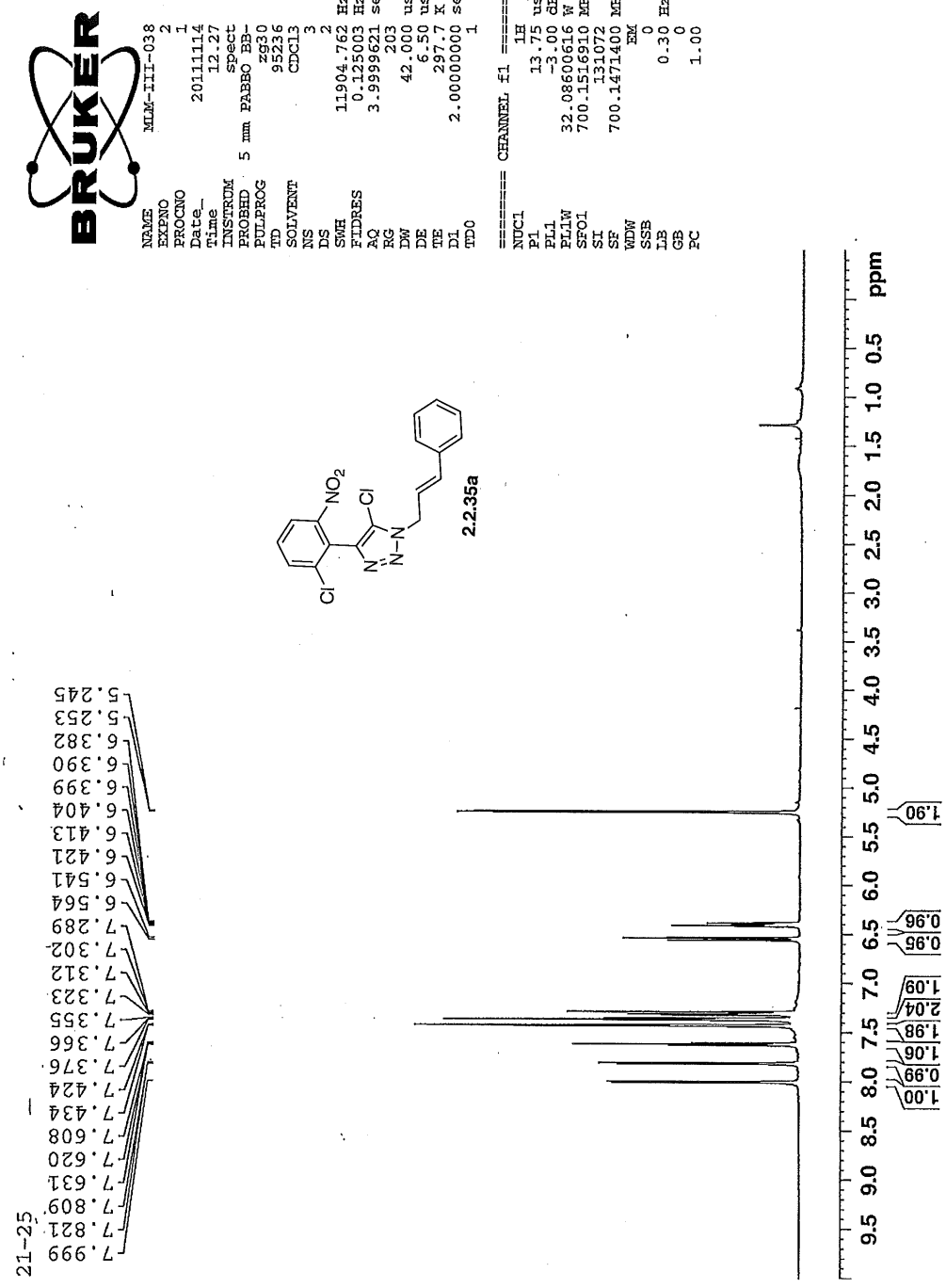

BRUKER
NAME MLM-III-014
EXPNO 10
PROCNO 1
Date_ 20111115
Time 8.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 32
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 298.5 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PLW 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.2.33j
8.067
8.065
7.756
7.754
7.752
7.744
7.743
7.669
7.657
7.645
7.290
7.273
7.262
7.252
7.207
7.196
7.187
7.185
7.008
6.998
5.456
5.435
5.412
5.391
1.00
1.19
1.12
1.06
1.99
1.96
2.13
ppm

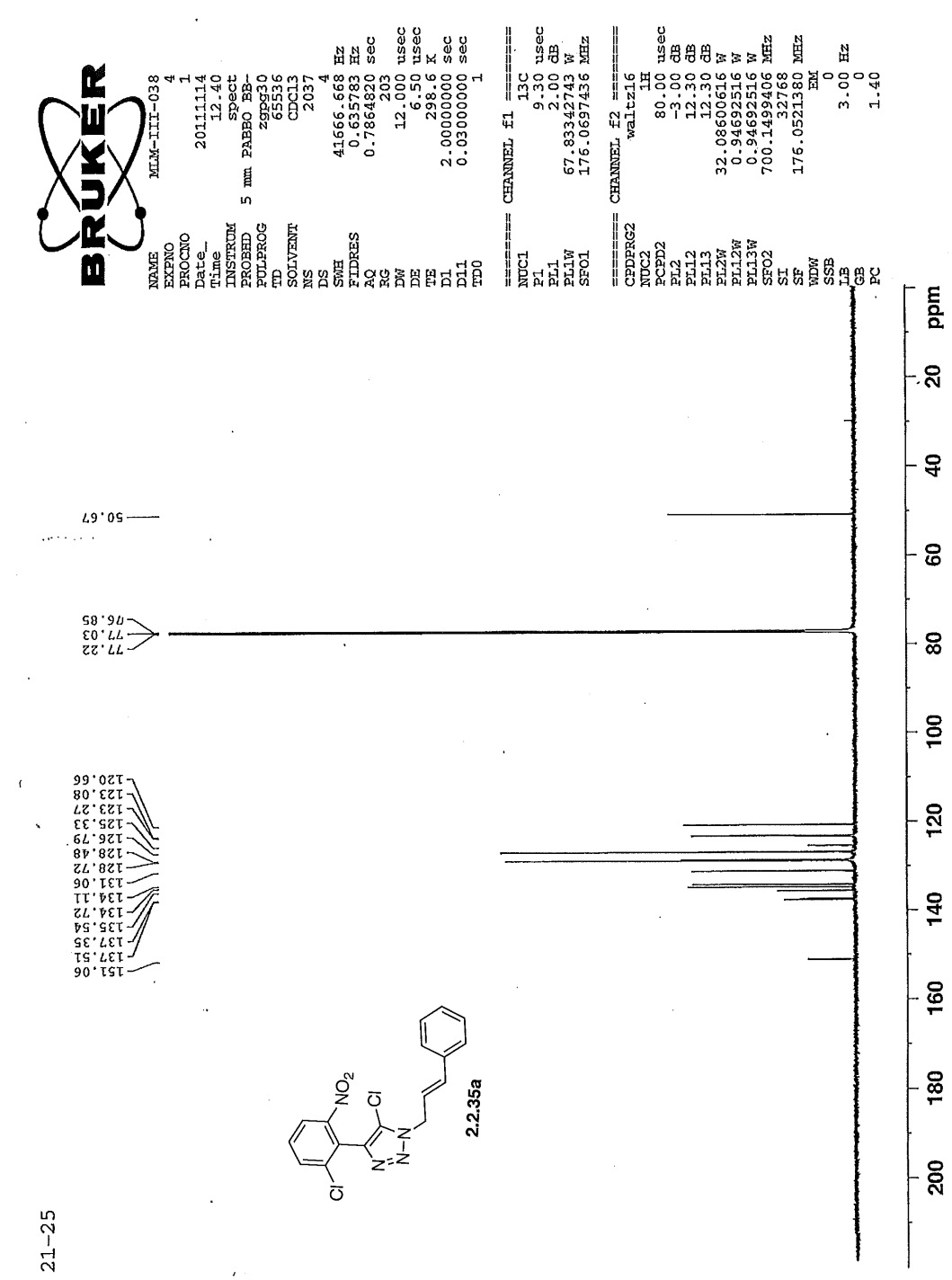

BRUKER
NAME MLM-III-014
EXPNO 12
PROCNO 1
Date_ 20111115
Time_ 9.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2556
DS 4
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 2.00 dB
PL1W 67.83342743 W
SFO1 176.0697436 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.30 dB
PL13 12.30 dB
PL2W 32.08600616 W
PL12W 0.94692516 W
PL13W 0.94692516 W
SFO2 700.1499406 MHz
SI 32768
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
NO2
Cl
Cl
N=N
2.2.33j
54.31
54.78
76.83
77.01
77.19
120.00
122.63
123.59
124.24
127.15
127.80
128.40
128.76
128.84
128.90
129.24
129.90
132.26
132.50
133.43
134.44
134.68
135.51
138.04
139.64
149.57
200
180
160
140
120
100
80
60
40
20
ppm

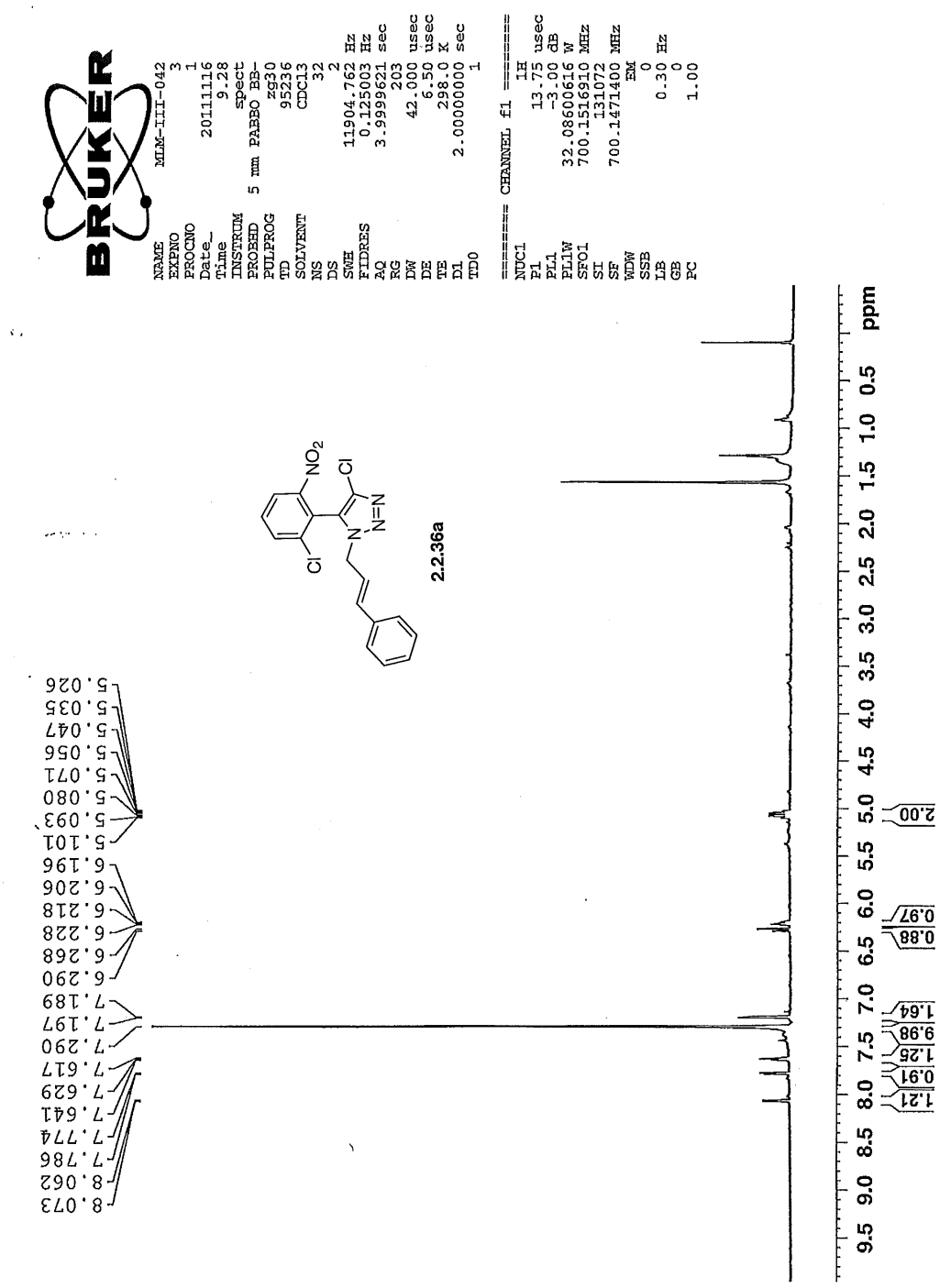

NAME MLM-III-034
EXPNO 5
PROCNO 1
Date_ 20111116
Time 9.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 4
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.2.32k
NO2
Br
Cl
N
N
5.703
8.021
8.010
7.815
7.803
7.628
7.616
7.605
7.419
7.409
7.386
7.376
7.284
7.272
2.08
1.00
1.00
1.02
3.06
2.63
ppm

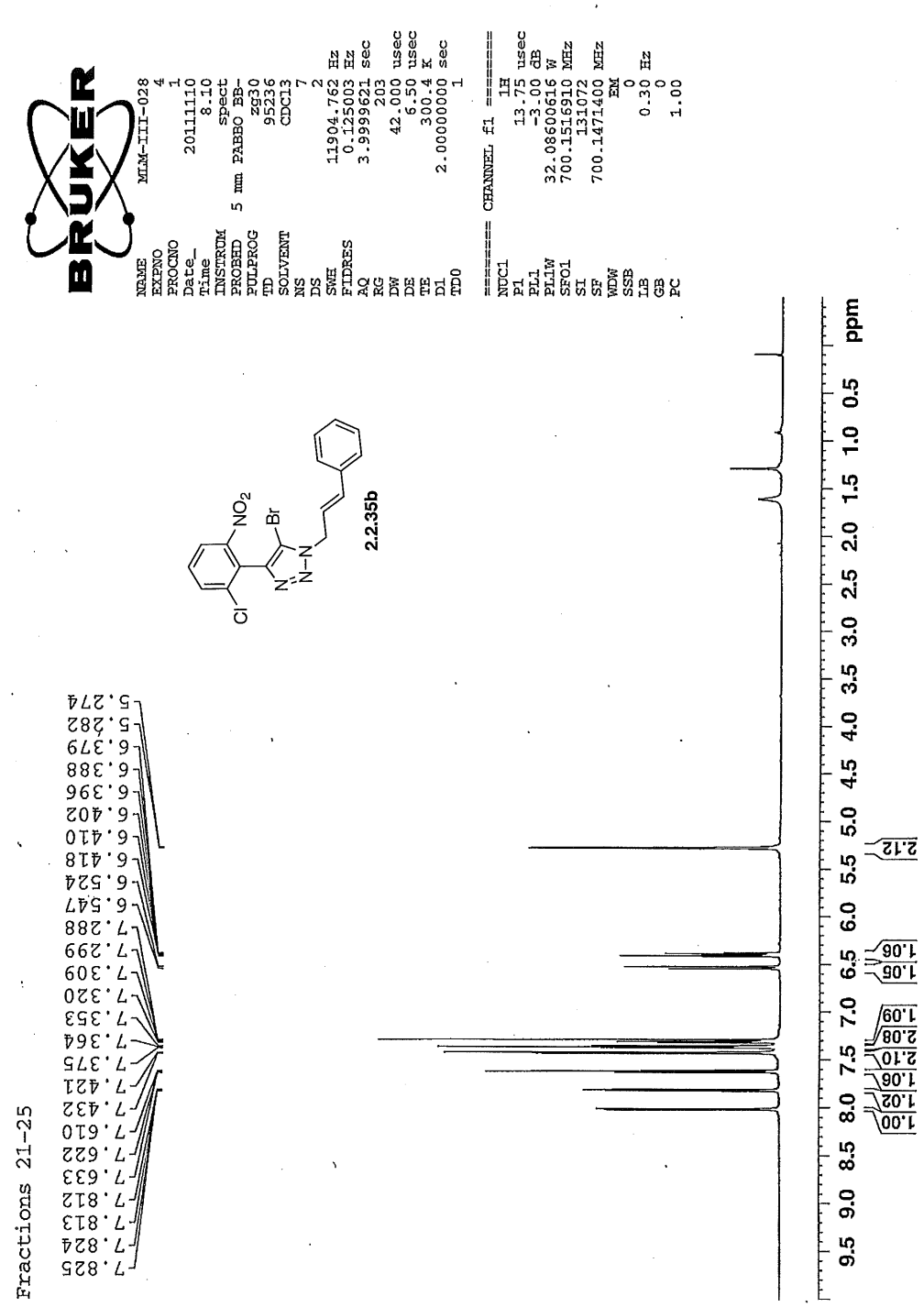

BRUKER
NAME MLM-III-034
EXPNO 7
PROCNO 1
Date_ 20111116
Time 9.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 80
DS 4
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 2.00 dB
PL1W 67.83342743 W
SFO1 176.0697436 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.30 dB
PL13 12.30 dB
PL2W 32.08600616 W
PL12W 0.94692516 W
PL13W 0.94692516 W
SFO2 700.1499406 MHz
SI 32768
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
2.2.32k
53.21
76.85
77.03
77.22
112.23
123.09
123.82
127.21
128.57
129.07
131.04
133.90
134.15
137.55
140.77
150.93
200
180
160
140
120
100
80
60
40
20
ppm

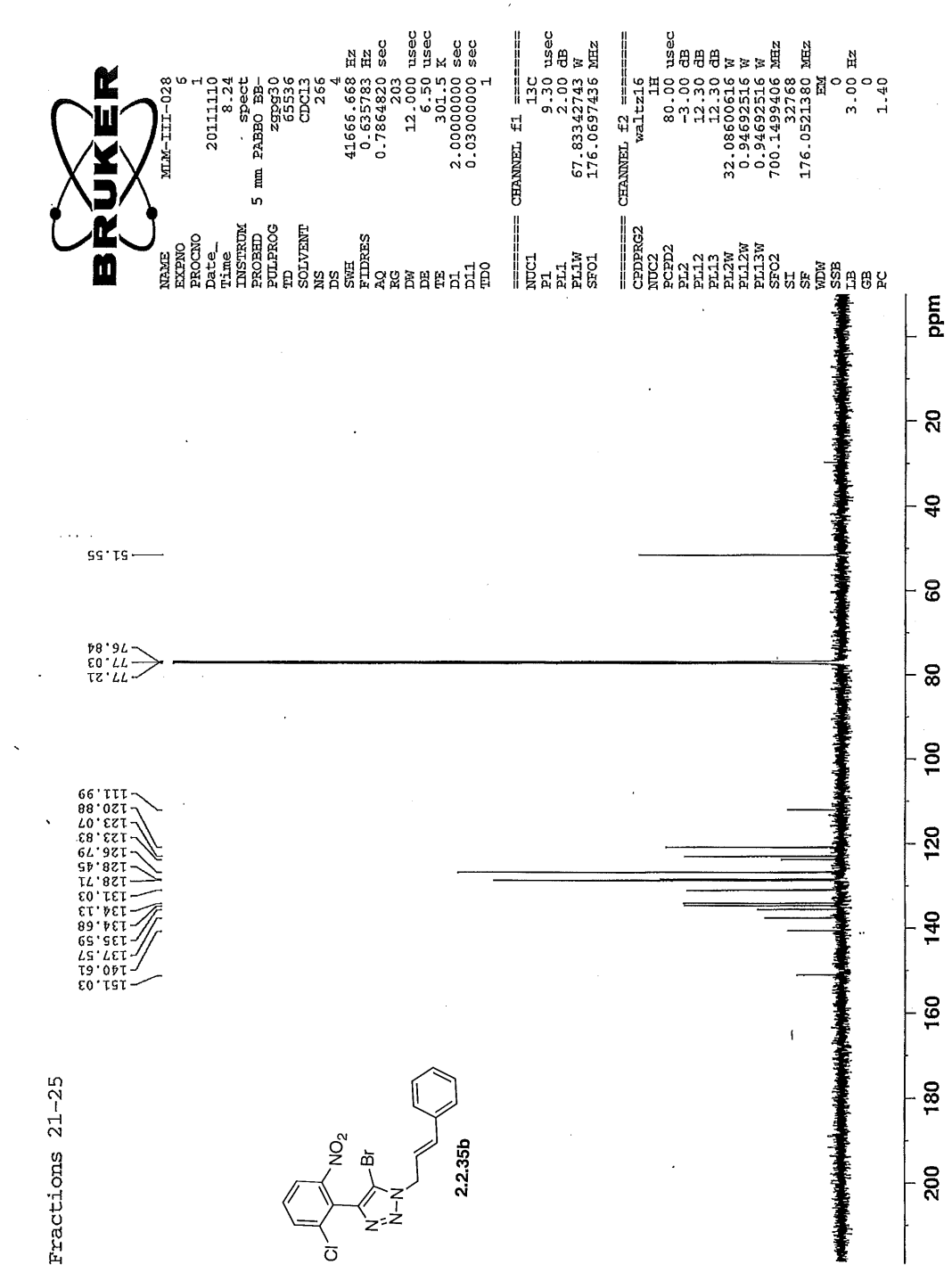

BRUKER
NAME MLM-III-034
EXPNO 3
PROCNO 1
Date_ 20111116
Time 8.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 7
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NO2
Br
Cl
N=N
2.2.33k
8.082
8.070
7.756
7.744
7.671
7.660
7.275
7.264
7.254
7.209
7.198
7.187
7.016
7.005
5.479
5.457
5.430
5.409
1.00
1.16
1.14
1.33
2.31
2.02
2.33
ppm

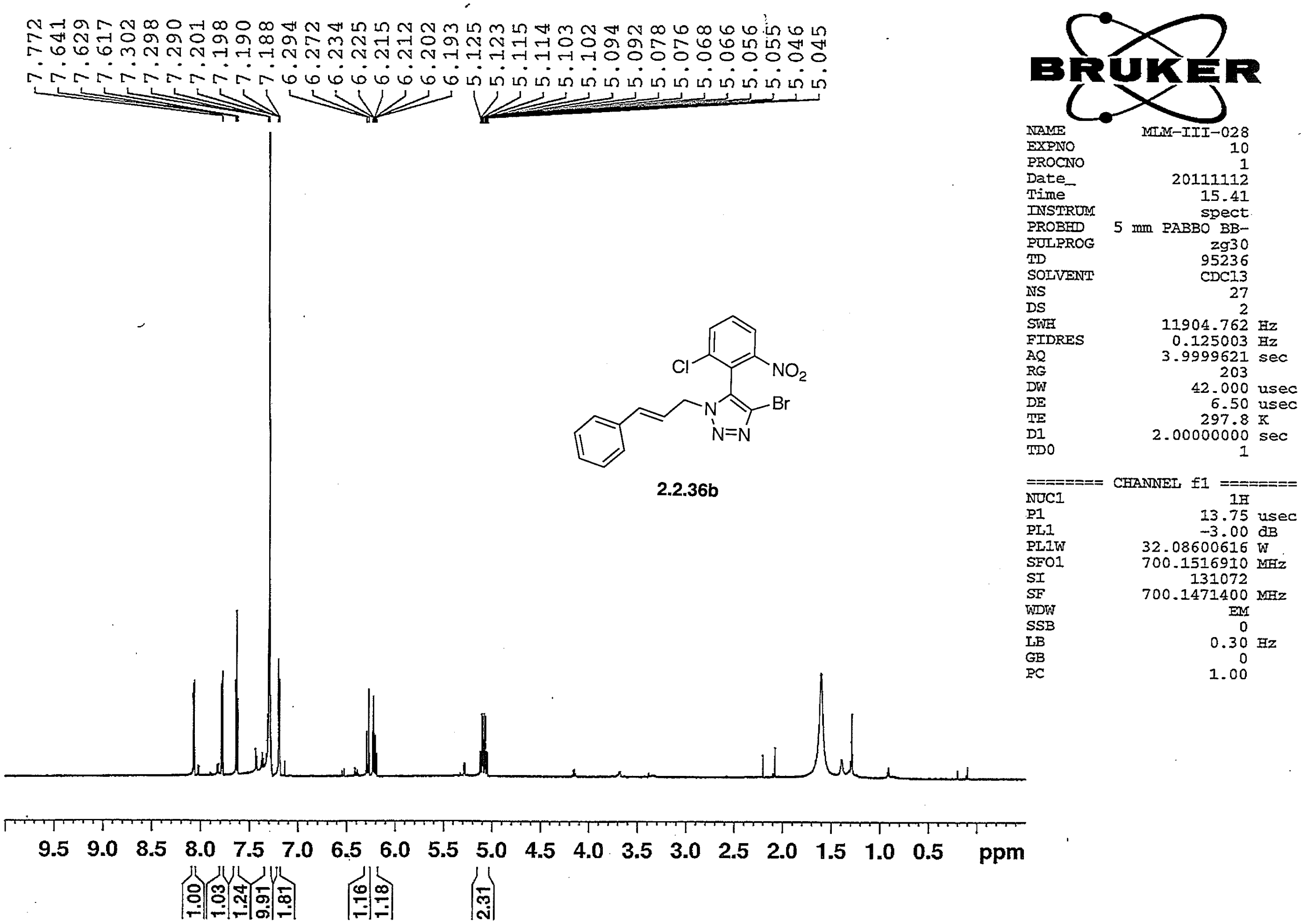

BRUKER
NAME MLM-III-038
EXPNO 2
PROCNO 1
Date_ 20111114
Time 12.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 3
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 297.7 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.2.35a
21-25
7.999
7.821
7.809
7.631
7.620
7.608
7.434
7.424
7.376
7.366
7.355
7.323
7.312
7.302
7.289
6.564
6.541
6.421
6.413
6.404
6.399
6.390
6.382
5.253
5.245
1.90
0.96
0.96
1.09
2.04
1.98
1.06
0.99
1.00
ppm

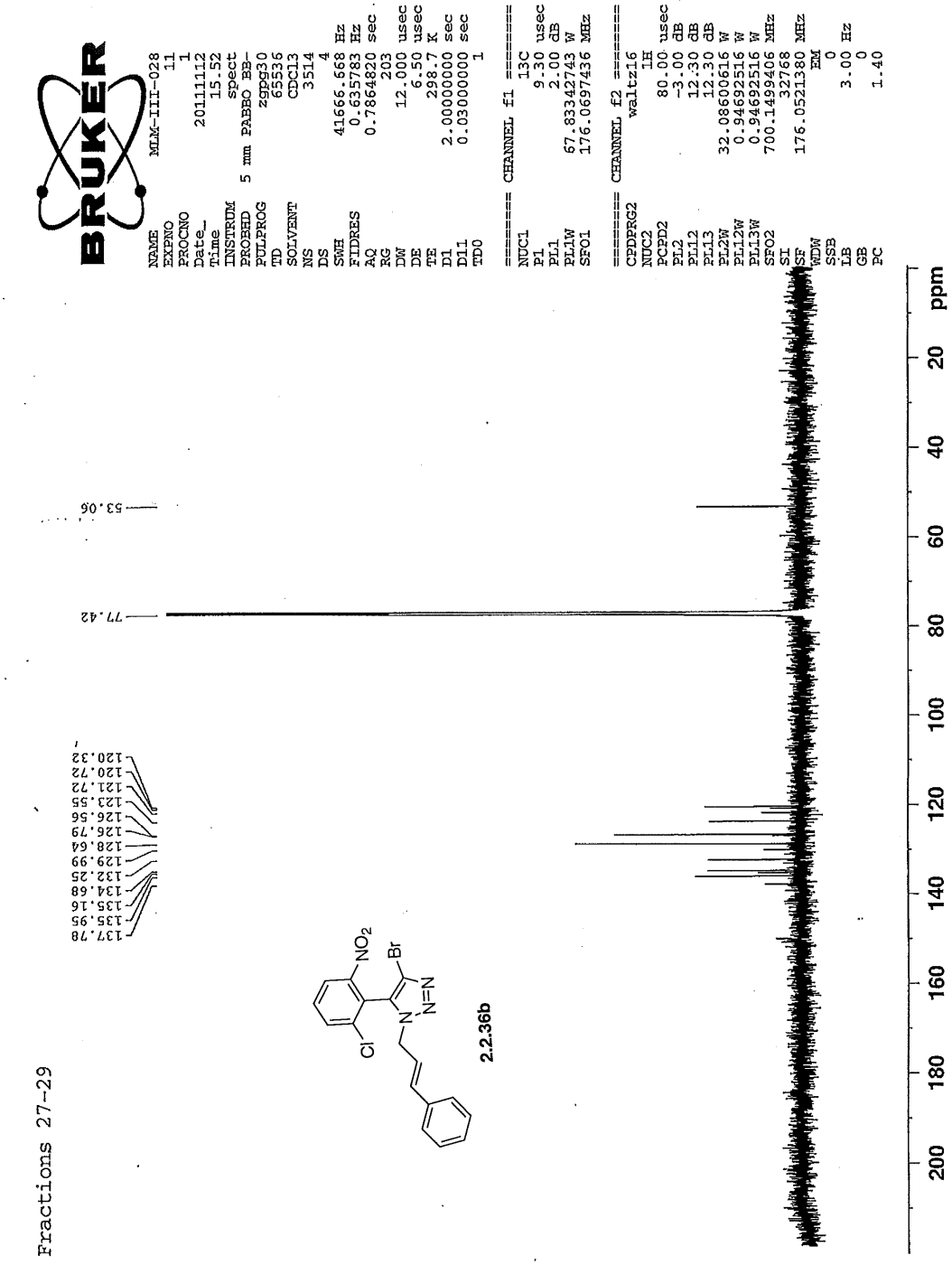

BRUKER
NAME MLM-III-038
EXPNO 4
PROCNO 1
Date_ 20111114
Time 12.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2037
DS 4
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 6.50 usec
TE 298.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 9.30 usec
PL1 2.00 dB
PL1W 67.83342743 W
SFO1 176.0697436 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.30 dB
PL13 12.30 dB
PL2W 32.08600616 W
PL12W 0.94692516 W
PL13W 0.94692516 W
SFO2 700.1499406 MHz
SI 32768
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
77.22
77.03
76.85
50.67
151.06
137.51
137.35
135.54
134.72
134.11
131.06
128.72
128.48
126.79
125.33
123.27
123.08
120.66
Cl
NO2
Cl
N
N
N
2.2.35a
21-25
200
180
160
140
120
100
80
60
40
20
ppm

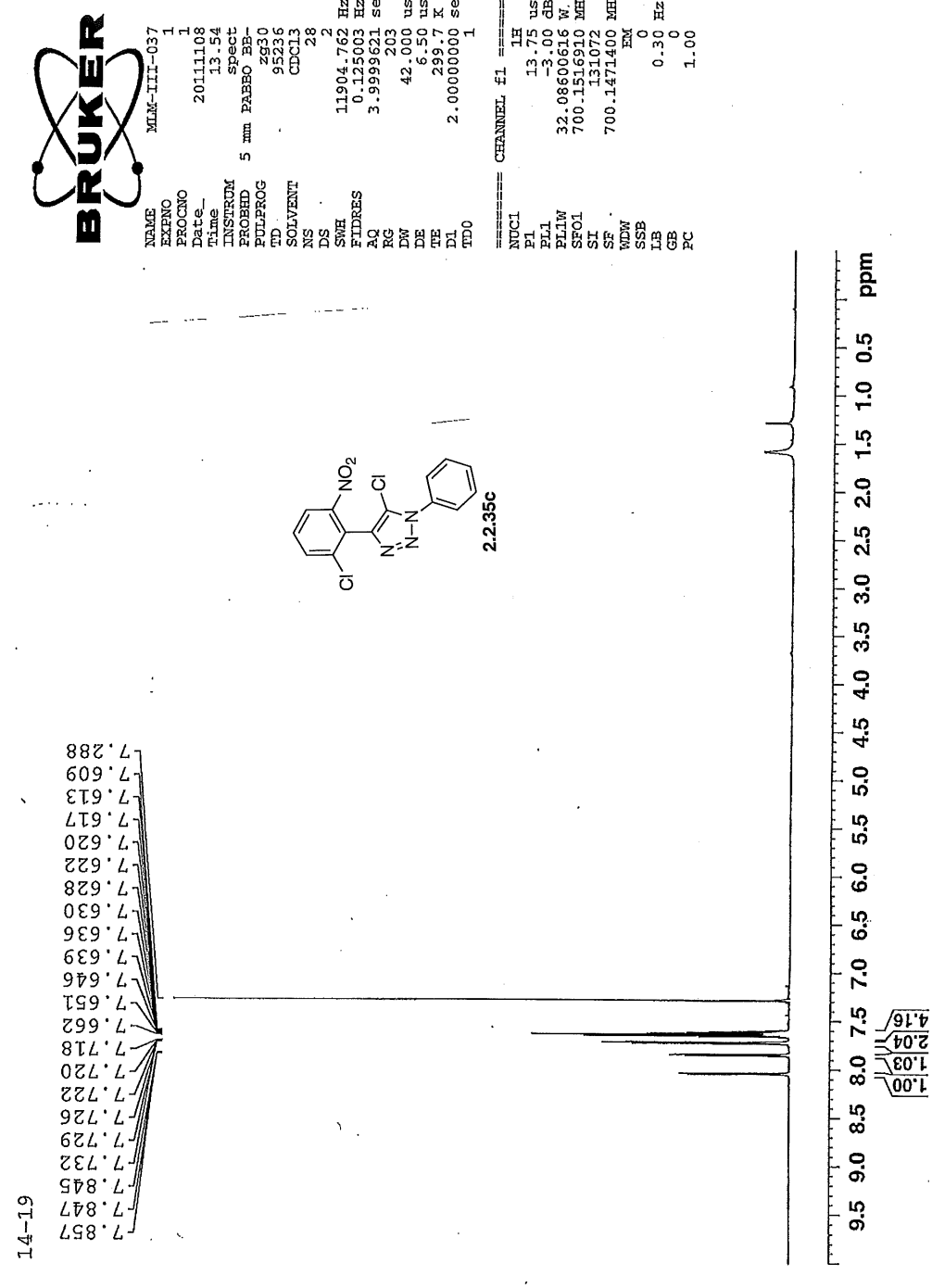

NAME MIM-III-042
EXPNO 3
PROCNO 1
Date_ 20111116
Time 9.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 32
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.2.36a
8.073
8.062
7.786
7.774
7.641
7.629
7.617
7.290
7.197
7.189
6.290
6.268
6.228
6.218
6.206
6.196
5.101
5.093
5.080
5.071
5.056
5.047
5.035
5.026
1.21
0.91
1.25
9.98
1.64
0.88
0.97
2.00
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 ppm

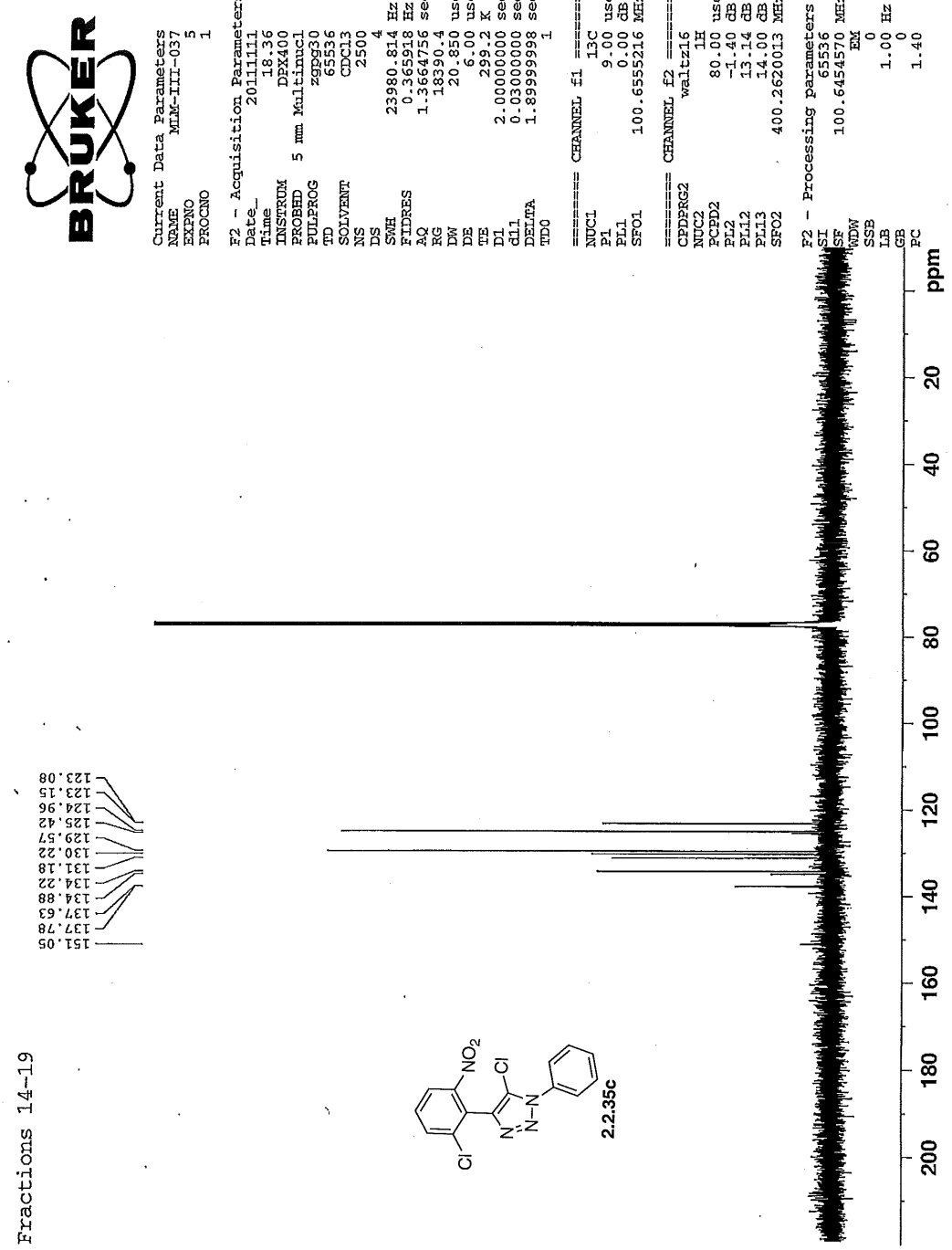

BRUKER
NAME MLM-III-028
EXPNO 4
PROCNO 1
Date_ 20111110
Time 8.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 7
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.99999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 300.4 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.2.35b
Fractions 21-25
7.825
7.824
7.813
7.812
7.633
7.622
7.610
7.432
7.421
7.375
7.364
7.353
7.320
7.309
7.299
7.288
6.547
6.524
6.418
6.410
6.402
6.396
6.388
6.379
5.282
5.274
1.00
1.02
1.06
2.10
2.08
1.09
1.06
1.06
2.12
ppm

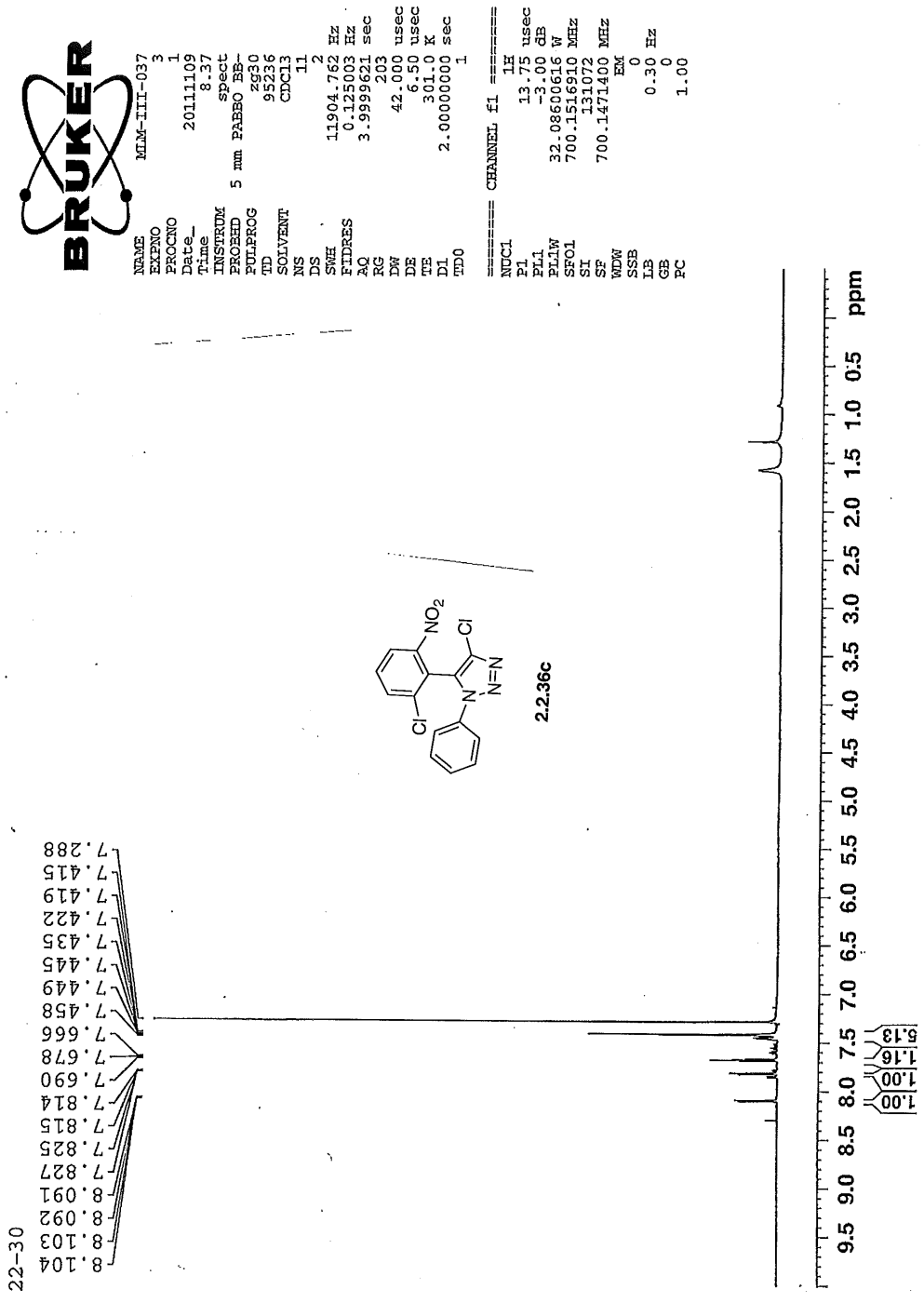

Fractions 21-25
2.2.35b
51.55
76.84
77.03
77.21
111.99
120.88
123.07
123.83
126.79
128.45
128.71
131.03
134.13
134.68
135.59
137.57
140.61
151.03
ppm
200
180
160
140
120
100
80
60
40
20
NAME MLM-III-028
EXPNO 6
PROCNO 1
Date_ 20111110
Time 8.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 266
DS 4
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 6.50 usec
TE 301.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 9.30 usec
PL1 2.00 dB
PL1W 67.83342743 W
SFO1 176.0697436 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.30 dB
PL13 12.30 dB
PL2W 32.08600616 W
PL12W 0.94692516 W
PL13W 0.94692516 W
SFO2 700.1499406 MHz
SI 32768
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

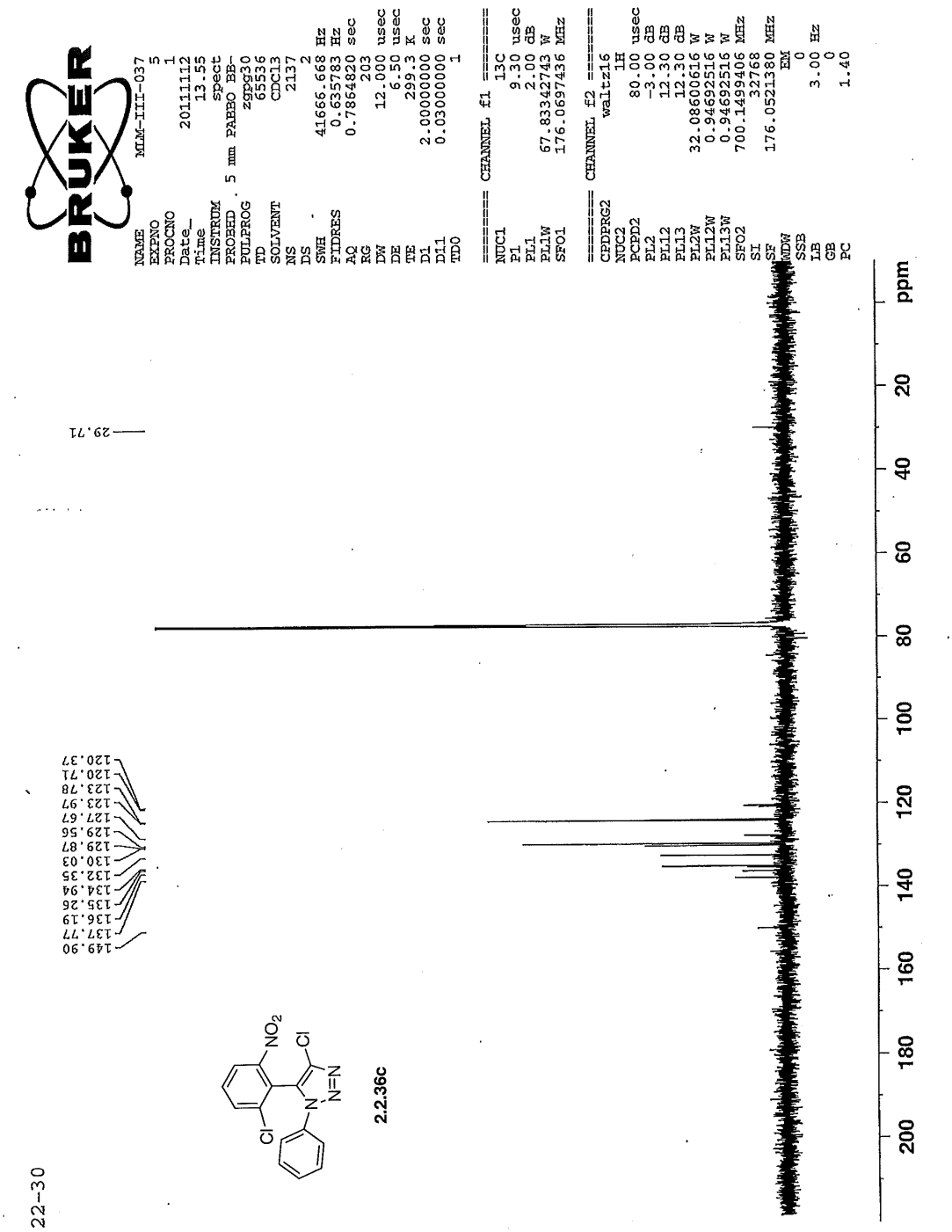

7.772
7.641
7.629
7.617
7.302
7.298
7.290
7.201
7.198
7.190
7.188
6.294
6.272
6.234
6.225
6.215
6.212
6.202
6.193
5.125
5.123
5.115
5.114
5.103
5.102
5.094
5.092
5.078
5.076
5.068
5.066
5.056
5.055
5.046
5.045
BRUKER
NAME MLM-III-028
EXPNO 10
PROCNO 1
Date_ 20111112
Time 15.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 27
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 297.8 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Cl
NO2
Br
N
N=N
2.2.36b
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 ppm
1.00
1.03
1.24
9.91
1.81
1.16
1.18
2.31

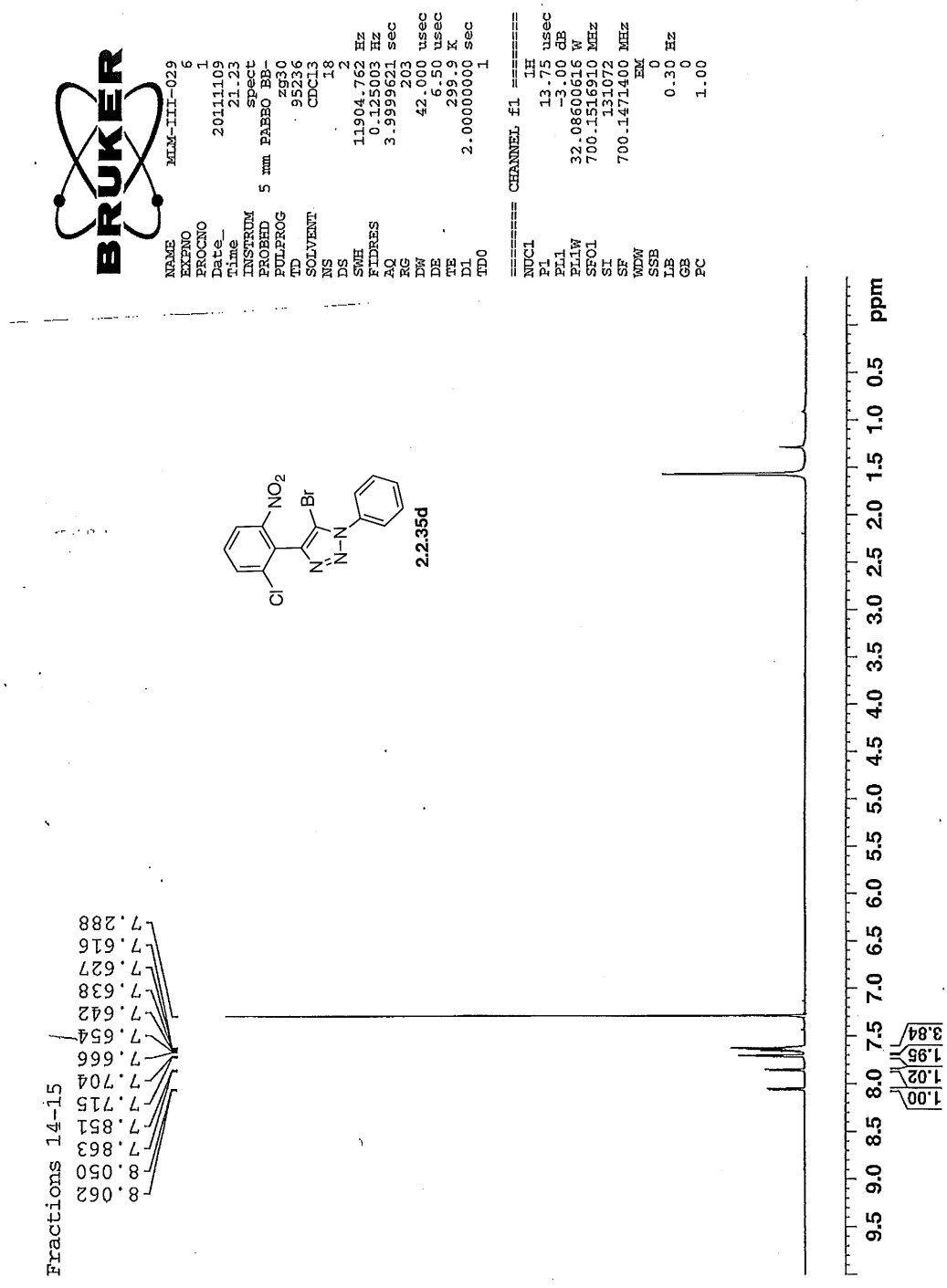

Fractions 27-29
BRUKER
NAME MLM-III-028
EXPNO 11
PROCNO 1
Date_ 20111112
Time 15.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3514
DS 4
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 6.50 usec
TE 298.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 2.00 dB
PL1W 67.83342743 W
SFO1 176.0697436 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.30 dB
PL13 12.30 dB
PL2W 32.08600616 W
PL12W 0.94692516 W
PL13W 0.94692516 W
SFO2 700.1499406 MHz
SI 32768
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
53.06
77.42
120.32
120.72
121.72
123.55
126.56
126.79
128.64
129.99
132.25
134.68
135.16
135.95
137.78
NO2
Br
Cl
N
N=N
2.2.36b
200
180
160
140
120
100
80
60
40
20
ppm

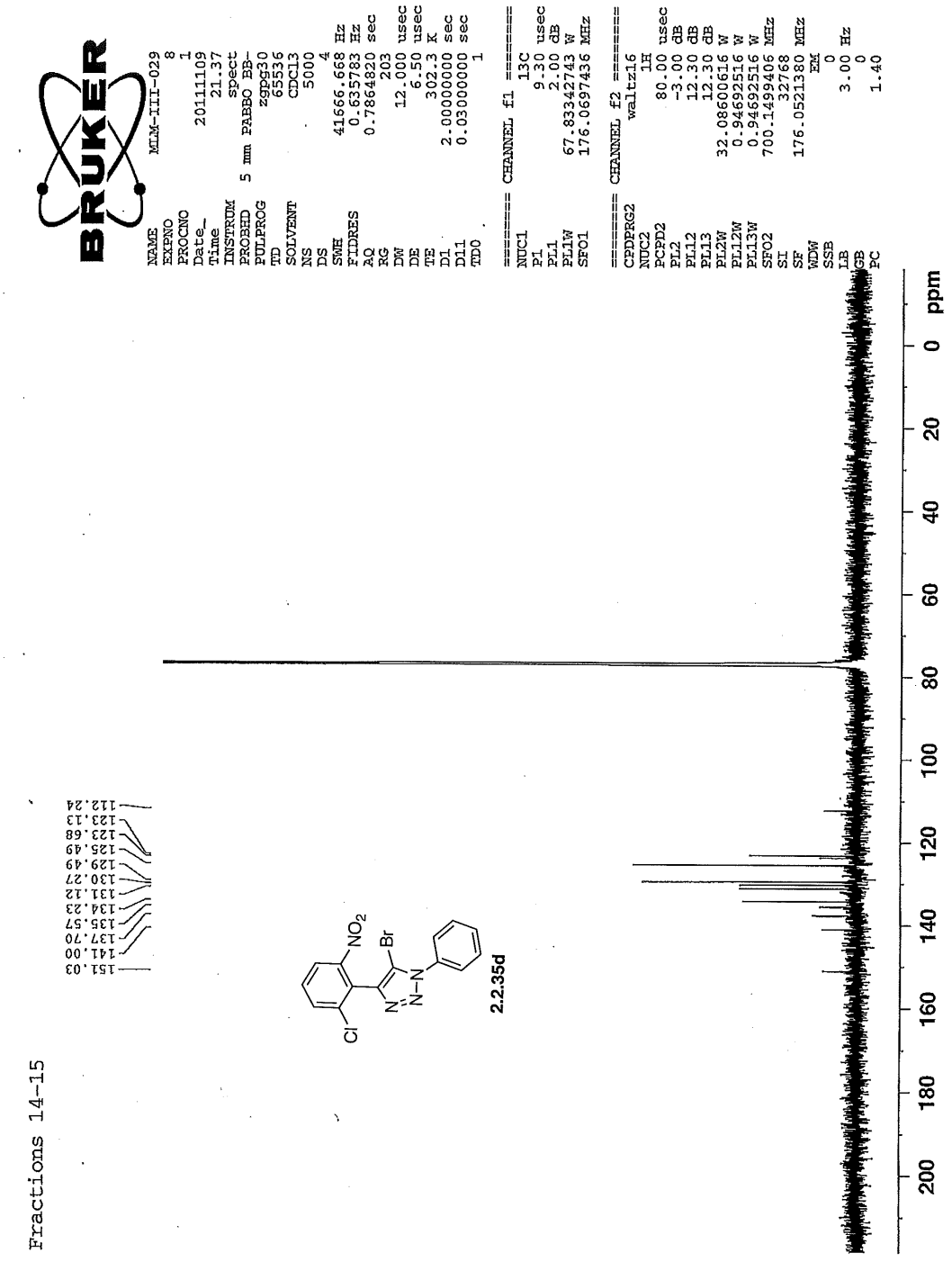

BRUKER
NAME MLM-III-037
EXPNO 1
PROCNO 1
Date_ 20111108
Time 13.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 28
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 299.7 K
D1 2.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PLIW 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.2.35c
14-1.9
7.857
7.847
7.845
7.732
7.729
7.726
7.722
7.720
7.718
7.662
7.651
7.646
7.639
7.636
7.630
7.628
7.622
7.620
7.617
7.613
7.609
7.288
1.00
1.03
2.04
4.16
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 ppm

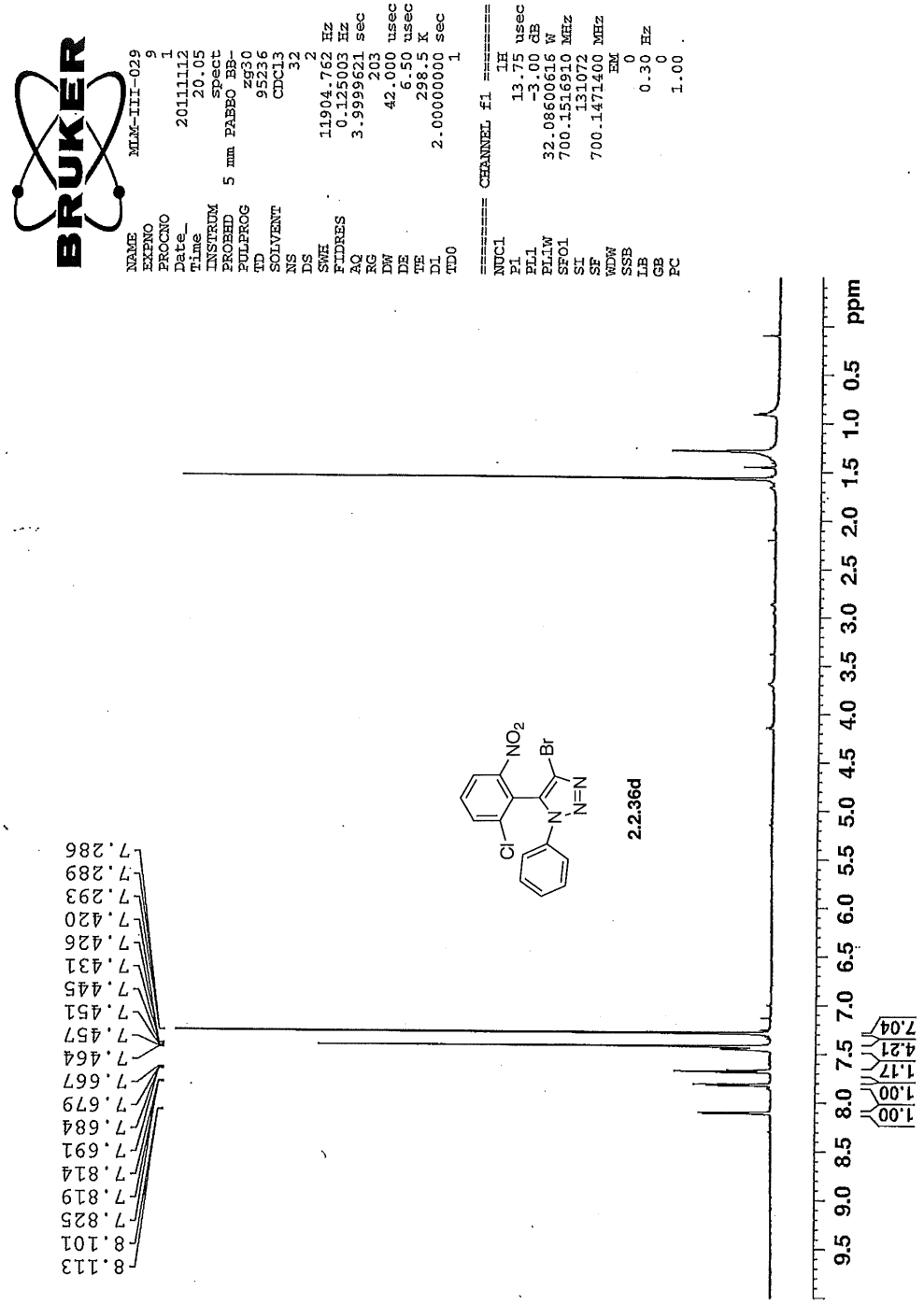

Fractions 14-19
151.05
137.78
137.63
134.88
134.22
131.18
130.22
129.57
125.42
124.96
123.15
123.08
2.2.35c
Current Data Parameters
NAME MLM-III-037
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111111
Time 18.36
INSTRUM DPX400
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2500
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.36647556 sec
RG 18390.4
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 0.00 dB
SFO1 100.6555216 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.40 dB
PL12 13.14 dB
PL13 14.00 dB
SFO2 400.2620013 MHz
F2 - Processing parameters
SI 65536
SF 100.6454570 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
ppm

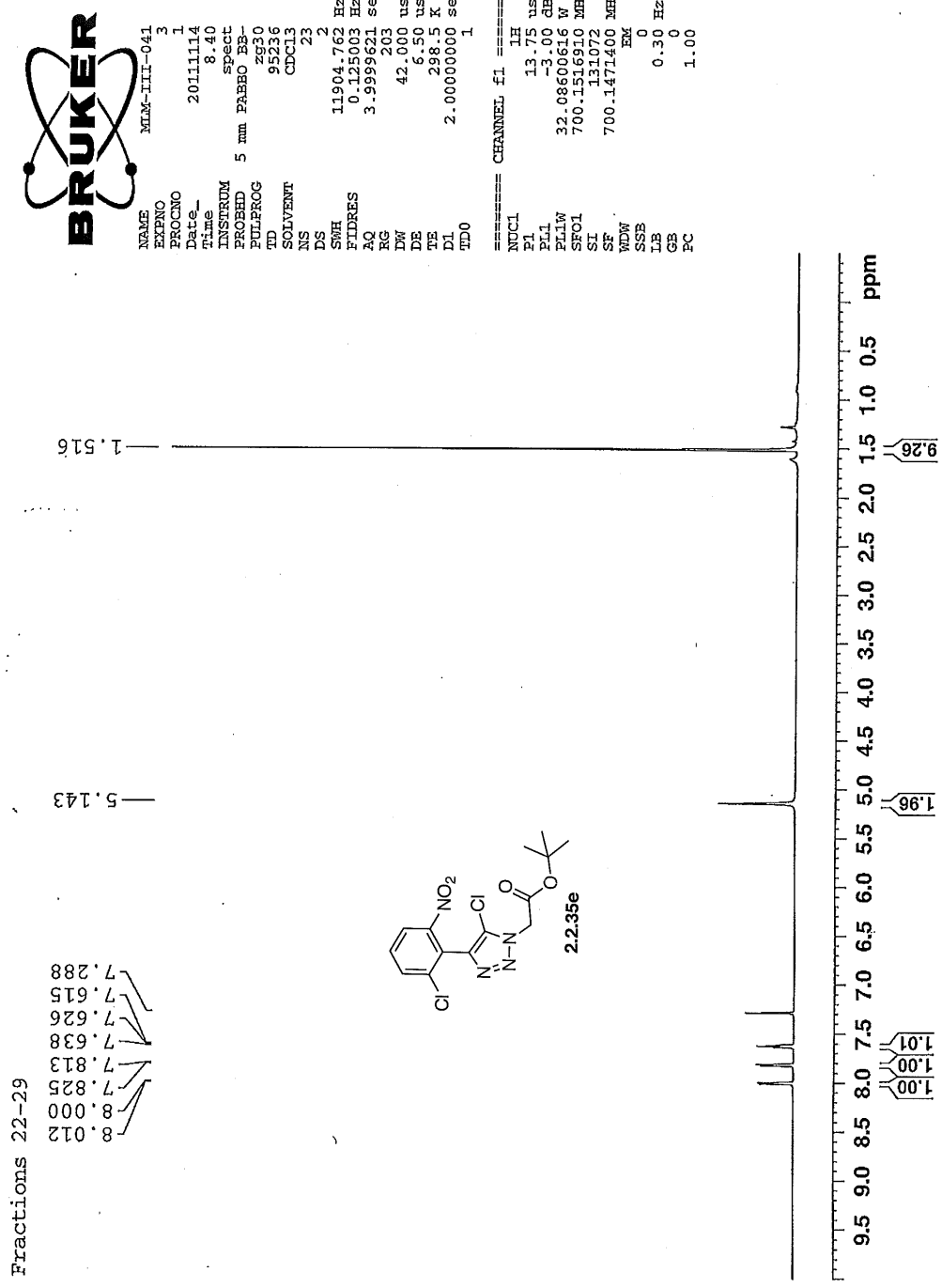

BRUKER
NAME MIM-III-037
EXPNO 3
PROCNO 1
Date_ 20111109
Time 8.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 11
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 301.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NO2
Cl
N=N
N
Cl
2.2.36c
22-30
8.104
8.103
8.092
8.091
7.827
7.825
7.815
7.814
7.690
7.678
7.666
7.458
7.449
7.445
7.435
7.422
7.419
7.415
7.288
1.00
1.00
1.16
5.13
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 ppm

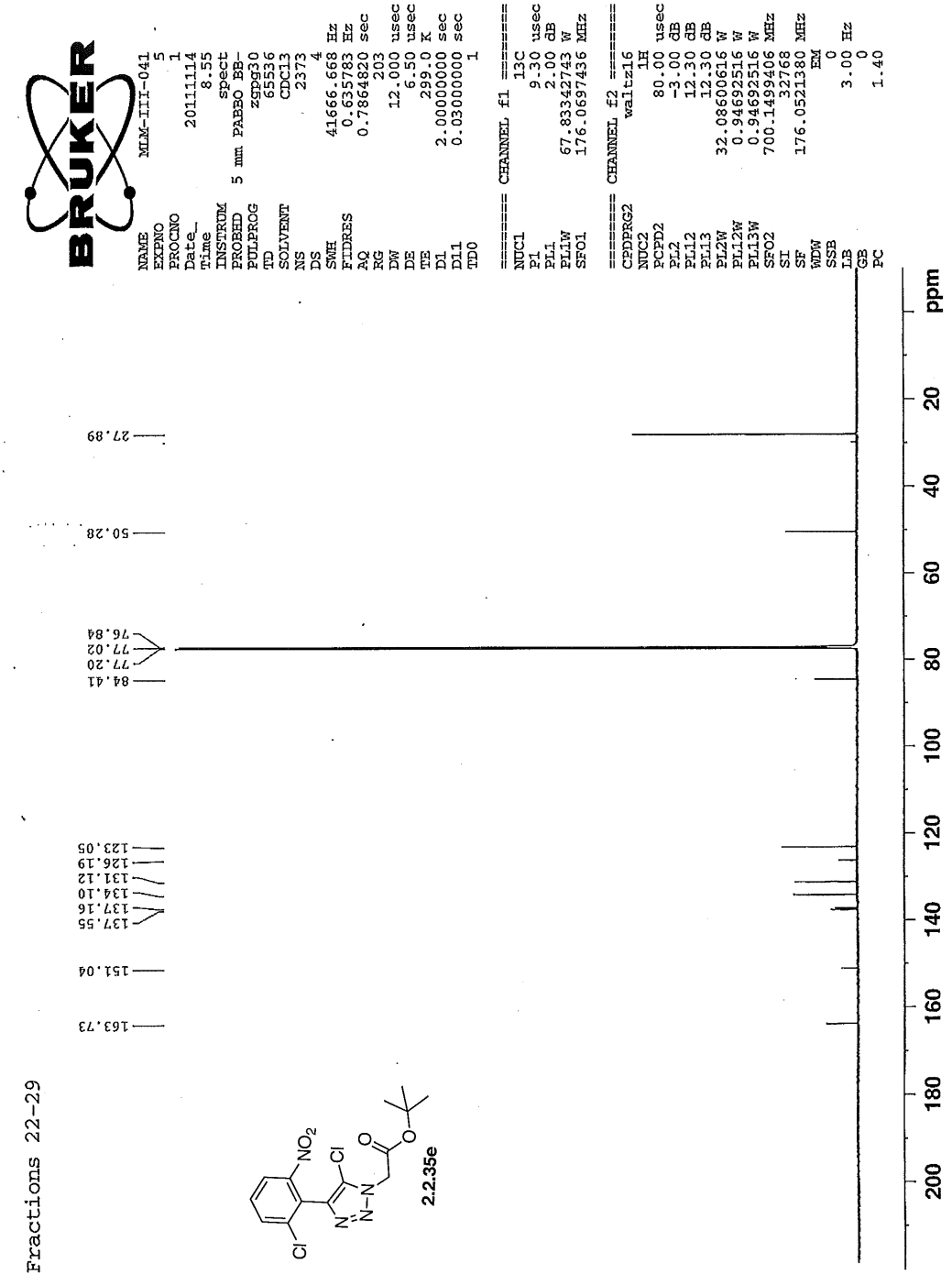

22-30
2.2.36c
29.71
149.90
137.77
136.19
135.26
134.94
132.35
130.03
129.87
129.56
127.67
123.97
123.78
120.71
120.37
NAME MLM-III-037
EXPNO 5
PROCNO 1
Date_ 20111112
Time 13.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2137
DS 2
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 6.50 usec
TE 299.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 2.00 dB
PL1W 67.83342743 W
SFO1 176.0697436 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.30 dB
PL13 12.30 dB
PL2W 32.08600616 W
PL12W 0.94692516 W
PL13W 0.94692516 W
SFO2 700.1499406 MHz
SI 32768
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 ppm

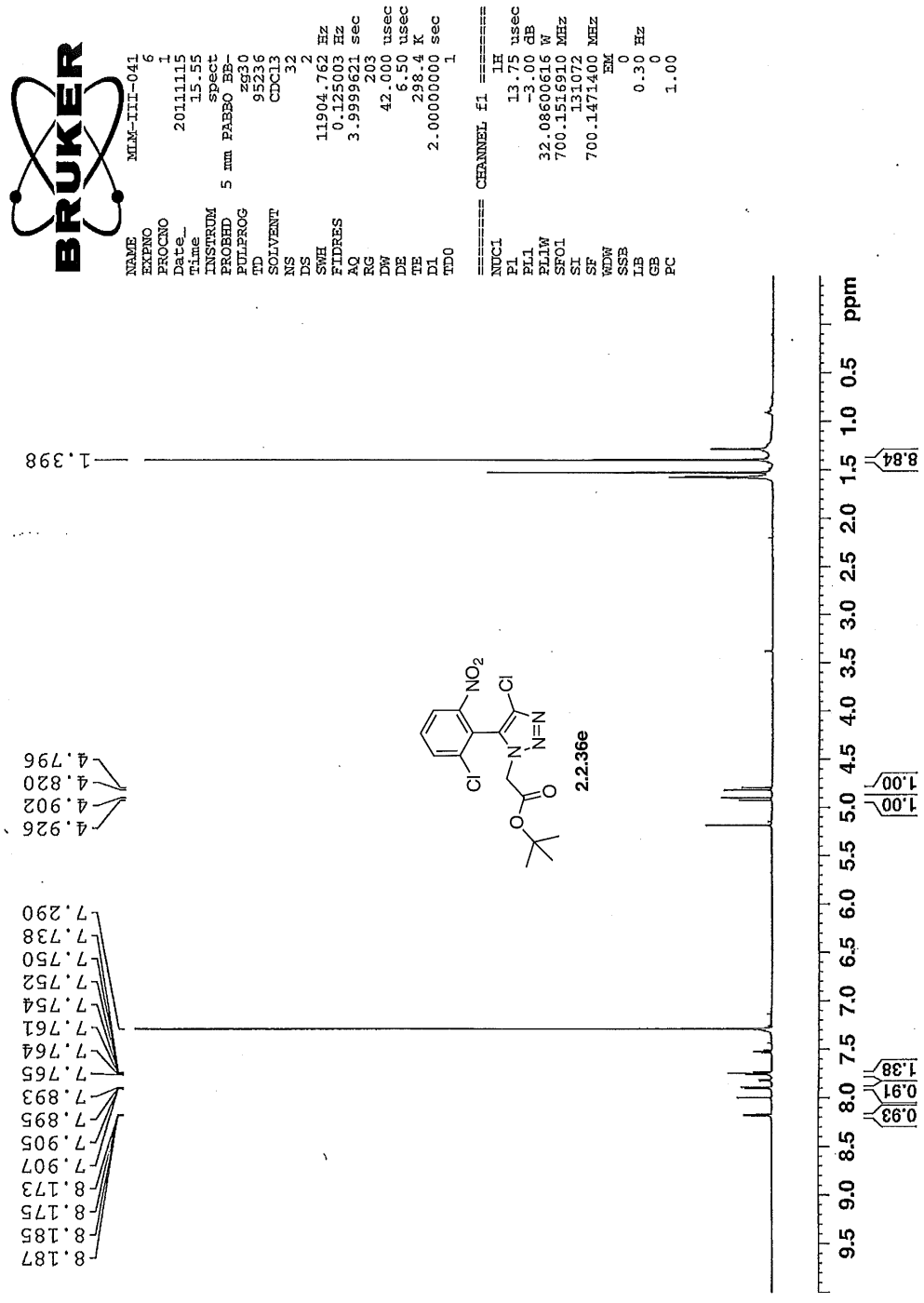

BRUKER
NAME MLM-III-029
EXPNO 6
PROCNO 1
Date_ 20111109
Time 21.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 18
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.2.35d
Fractions 14-15
8.062
8.050
7.863
7.851
7.715
7.704
7.666
7.654
7.642
7.638
7.627
7.616
7.288
1.00
1.02
1.95
3.84
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 ppm

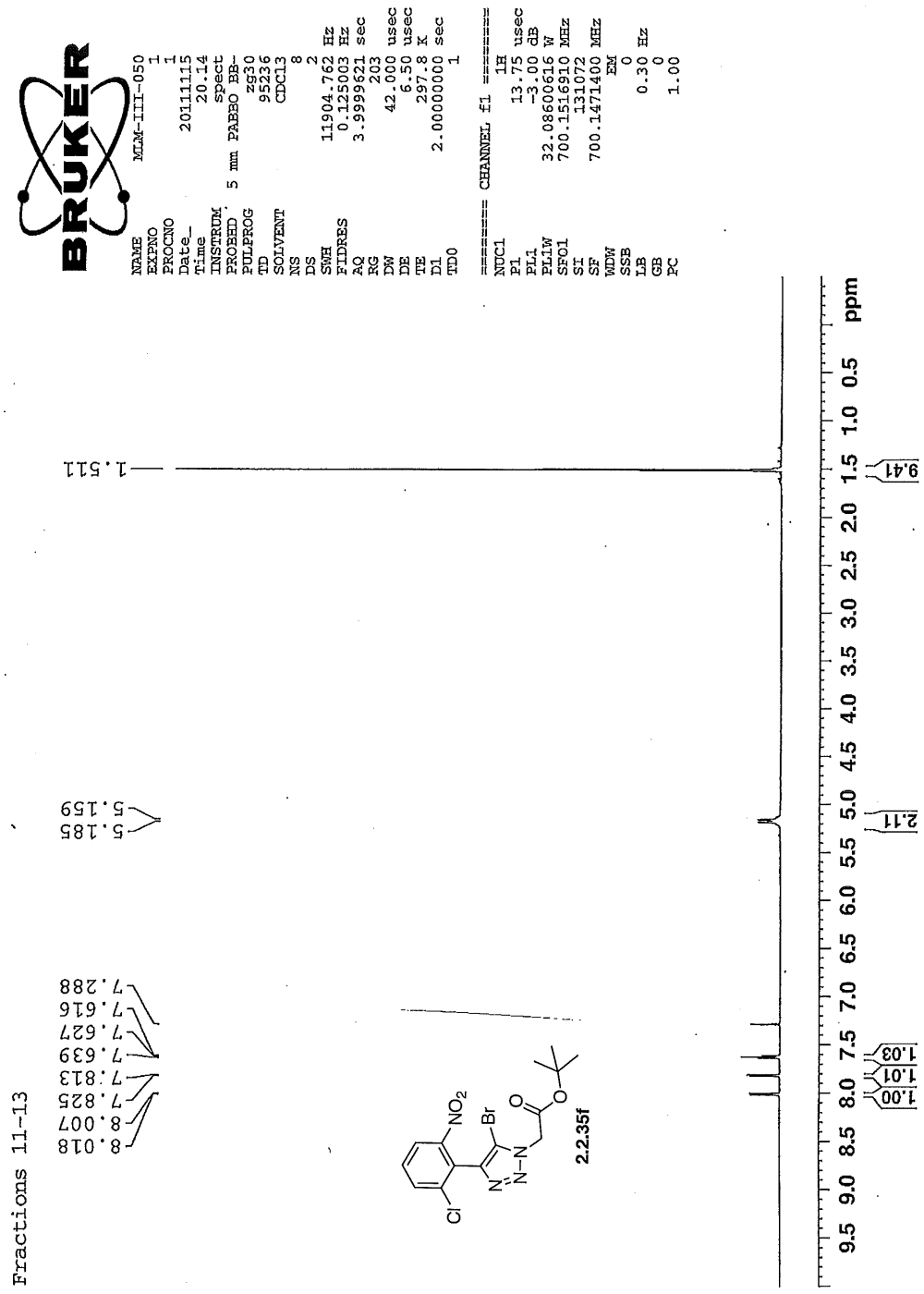

Fractions 14-15
151.03
141.00
137.70
135.57
134.23
131.12
130.27
129.49
125.49
123.68
123.13
112.24
NAME MLM-III-029
EXPNO 8
PROCNO 1
Date_ 20111109
Time 21.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 5000
DS 4
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 6.50 usec
TE 302.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 2.00 dB
PL1W 67.83342743 W
SFO1 176.0697436 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.30 dB
PL13 12.30 dB
PL2W 32.08600616 W
PL12W 0.94692516 W
PL13W 0.94692516 W
SFO2 700.1499406 MHz
SI 32768
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm
2.2.35d

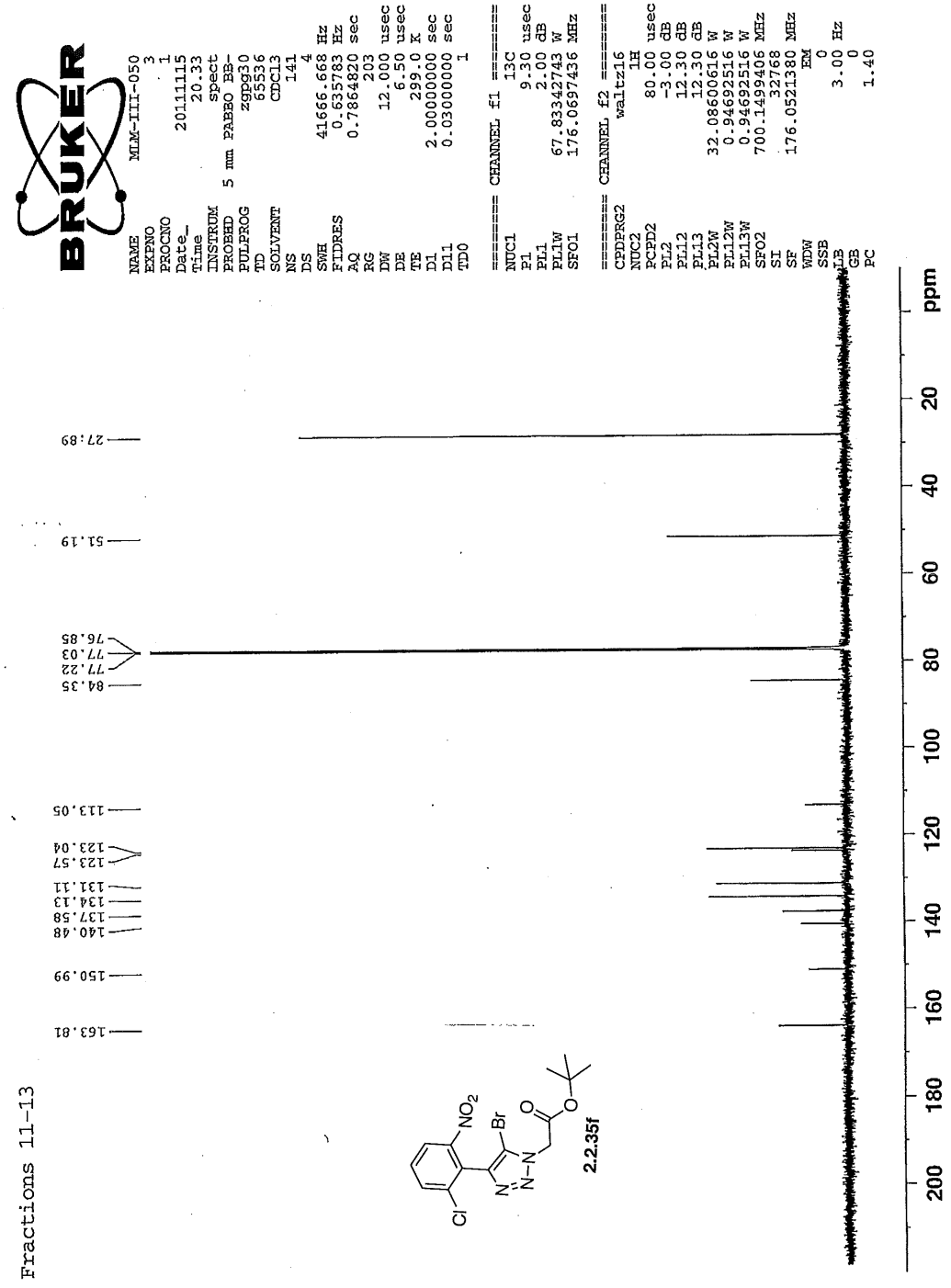

BRUKER
NAME MLM-III-029
EXPNO 9
PROCNO 1
Date_ 20111112
Time 20.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 32
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 298.5 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NO2
Br
Cl
N=N
2.2.36d
8.113
8.101
7.825
7.819
7.814
7.691
7.684
7.679
7.667
7.464
7.457
7.451
7.445
7.431
7.426
7.420
7.293
7.289
7.286
1.00
1.00
1.17
4.21
7.04
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 ppm

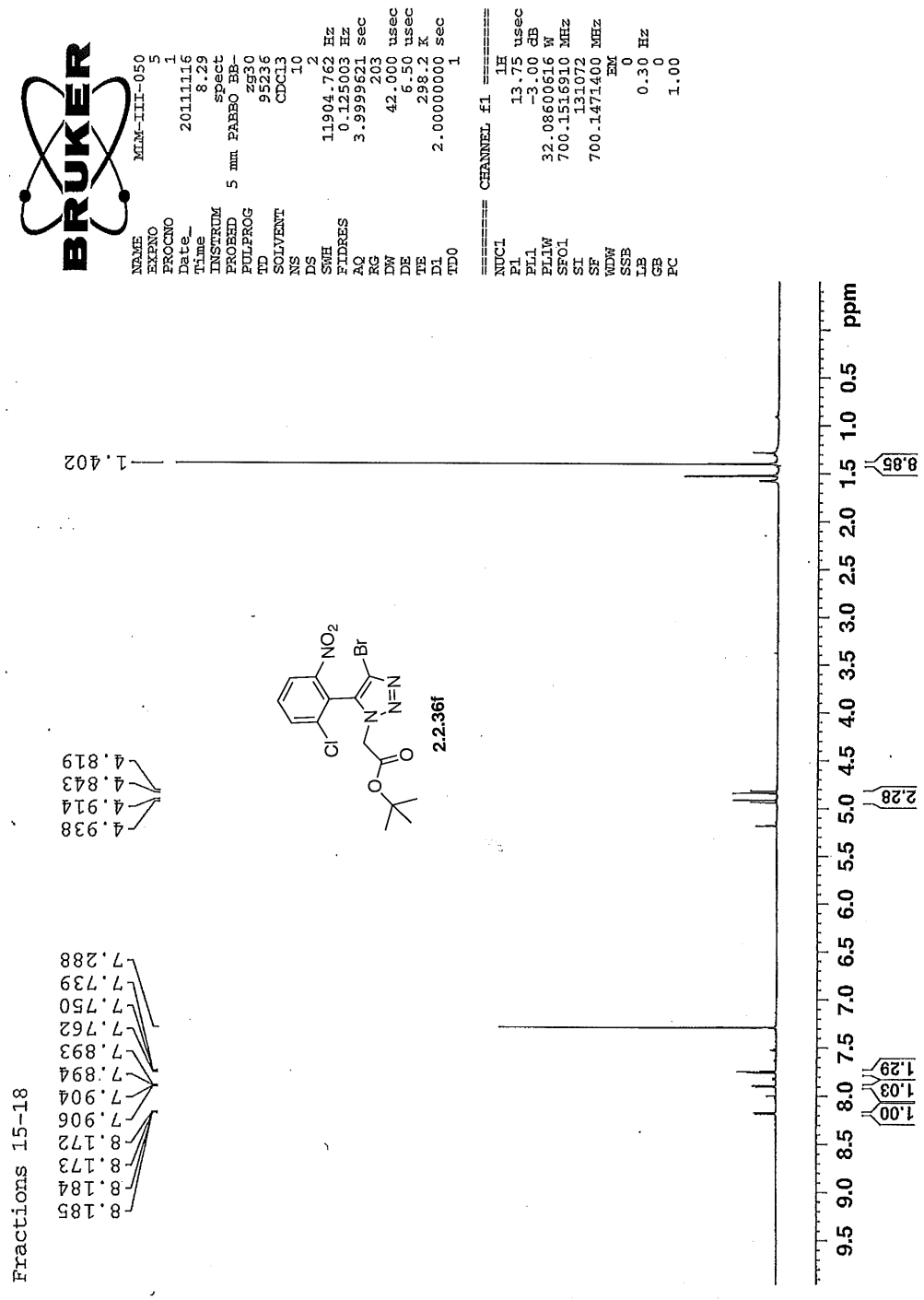

BRUKER
NAME MIM-III-041
EXPNO 3
PROCNO 1
Date_ 20111114
Time 8.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 23
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 298.5 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Fractions 22-29
8.012
8.000
7.825
7.813
7.638
7.626
7.615
7.288
5.143
1.516
2.2.35e
9.26
1.96
1.00
1.00
1.01
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 ppm

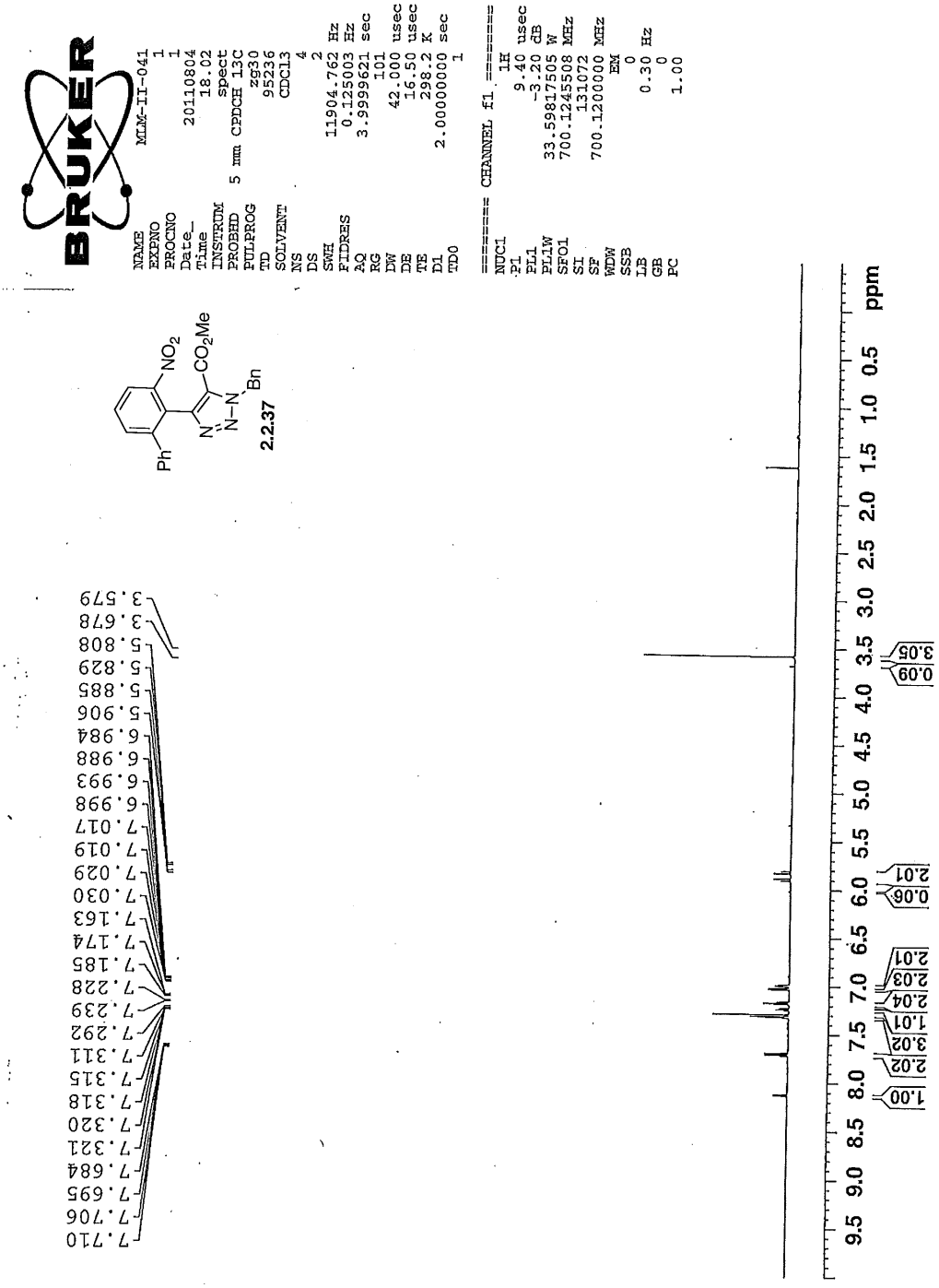

Fractions 22-29
2.2.35e
27.89
50.28
76.84
77.02
77.20
84.41
123.05
126.19
131.12
134.10
137.16
137.55
151.04
163.73
200
180
160
140
120
100
80
60
40
20
ppm

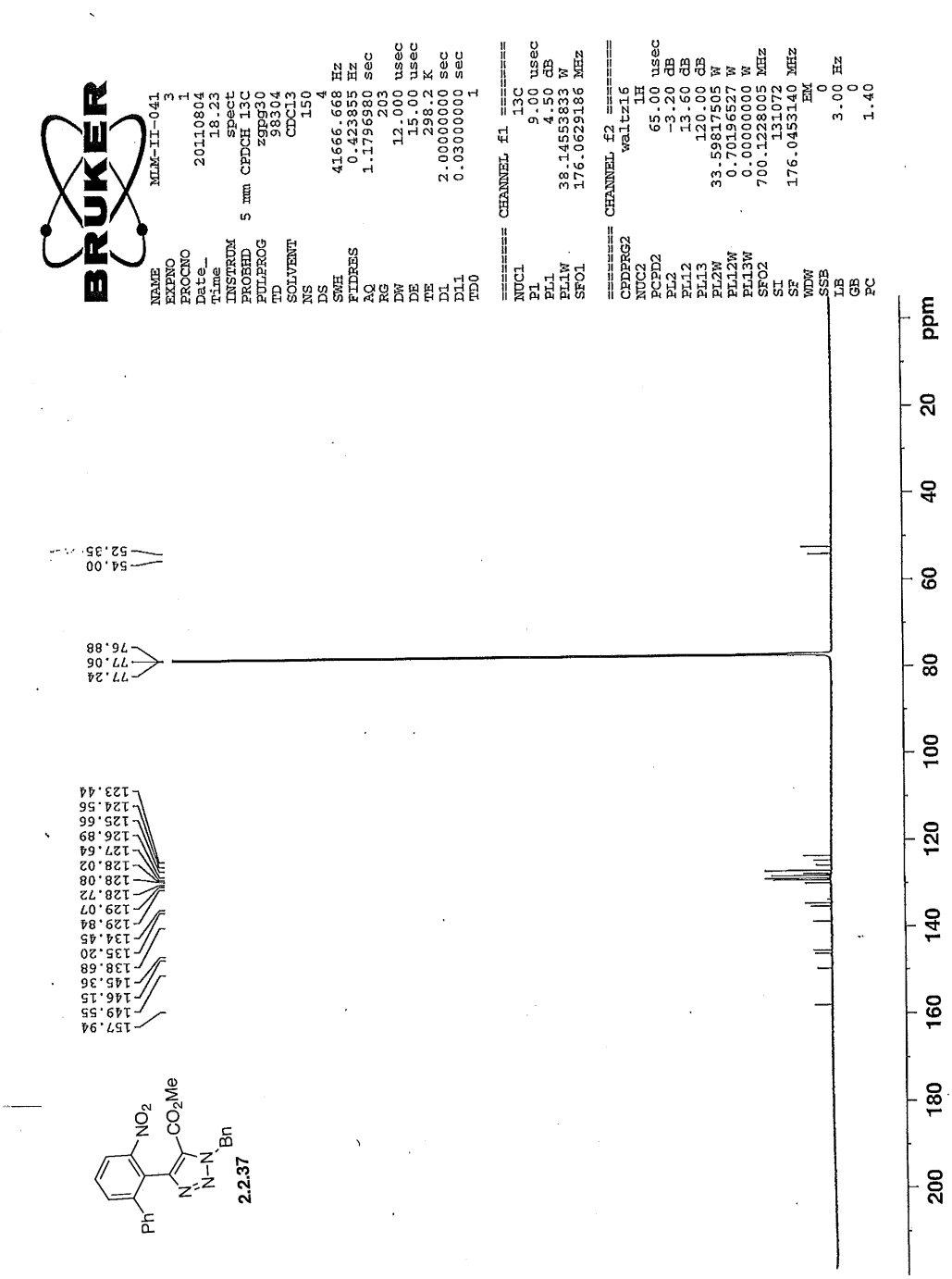

BRUKER
NAME MLM-III-041
EXPNO 6
PROCNO 1
Date_ 20111115
Time_ 15.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 32
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 298.4 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.398
4.796
4.820
4.902
4.926
7.290
7.738
7.750
7.752
7.754
7.761
7.764
7.765
7.893
7.895
7.905
7.907
8.173
8.175
8.185
8.187
2.2.36e
8.84
1.00
1.00
0.93
0.91
1.38
ppm

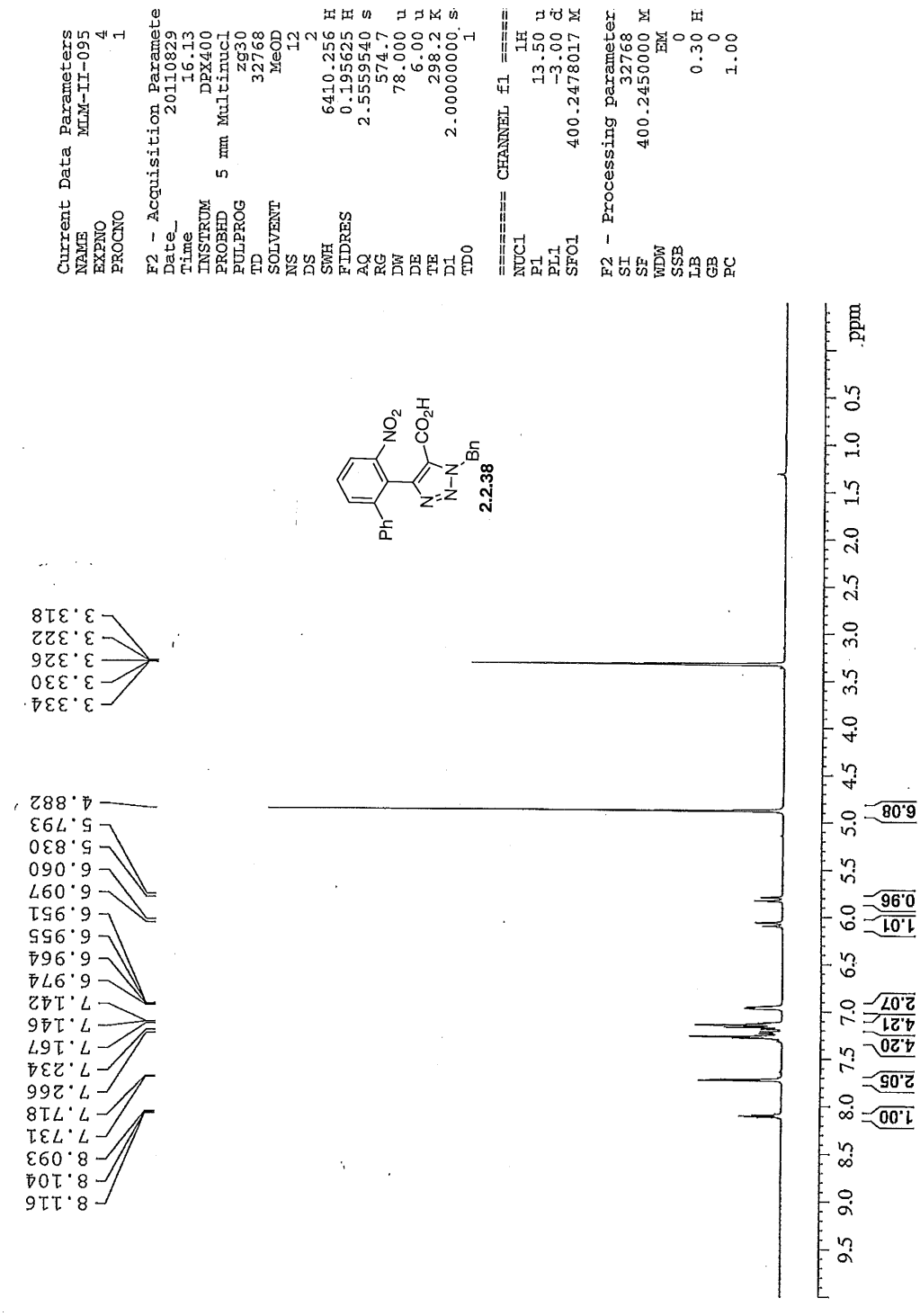

BRUKER
NAME MLM-III-050
EXPNO 1
PROCNO 1
Date_ 20111115
Time 20.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 8
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.99999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 297.8 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Fractions 11-13
8.018
8.007
7.825
7.813
7.639
7.627
7.616
7.288
5.185
5.159
1.511
NO2
Br
Cl
O
N-N
2.2.35f
9.41
2.11
1.03
1.01
1.00
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 ppm

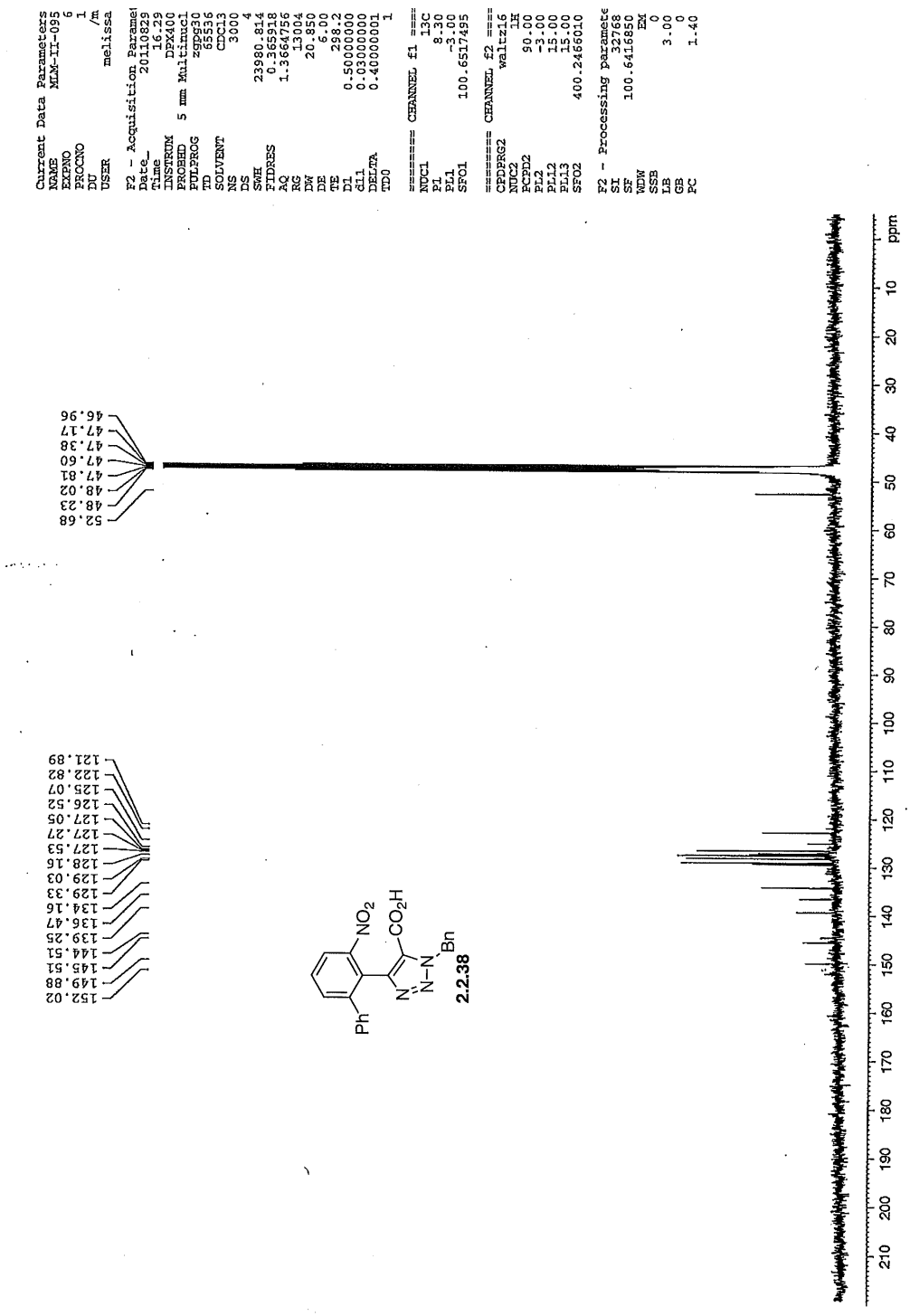

Fractions 11-13
BRUKER
NAME MLM-III-050
EXPNO 3
PROCNO 1
Date_ 20111115
Time 20.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 141
DS 4
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.30 usec
PL1 2.00 dB
PL1W 67.83342743 W
SFO1 176.0697436 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 12.30 dB
PL13 12.30 dB
PL2W 32.08600616 W
PL12W 0.94692516 W
PL13W 0.94692516 W
SFO2 700.1499406 MHz
SI 32768
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
27.89
51.19
76.85
77.03
77.22
84.35
113.05
123.04
123.57
131.11
134.13
137.58
140.48
150.99
163.81
NO2
Br
Cl
O
O
N
N
2.2.35f
200
180
160
140
120
100
80
60
40
20
ppm

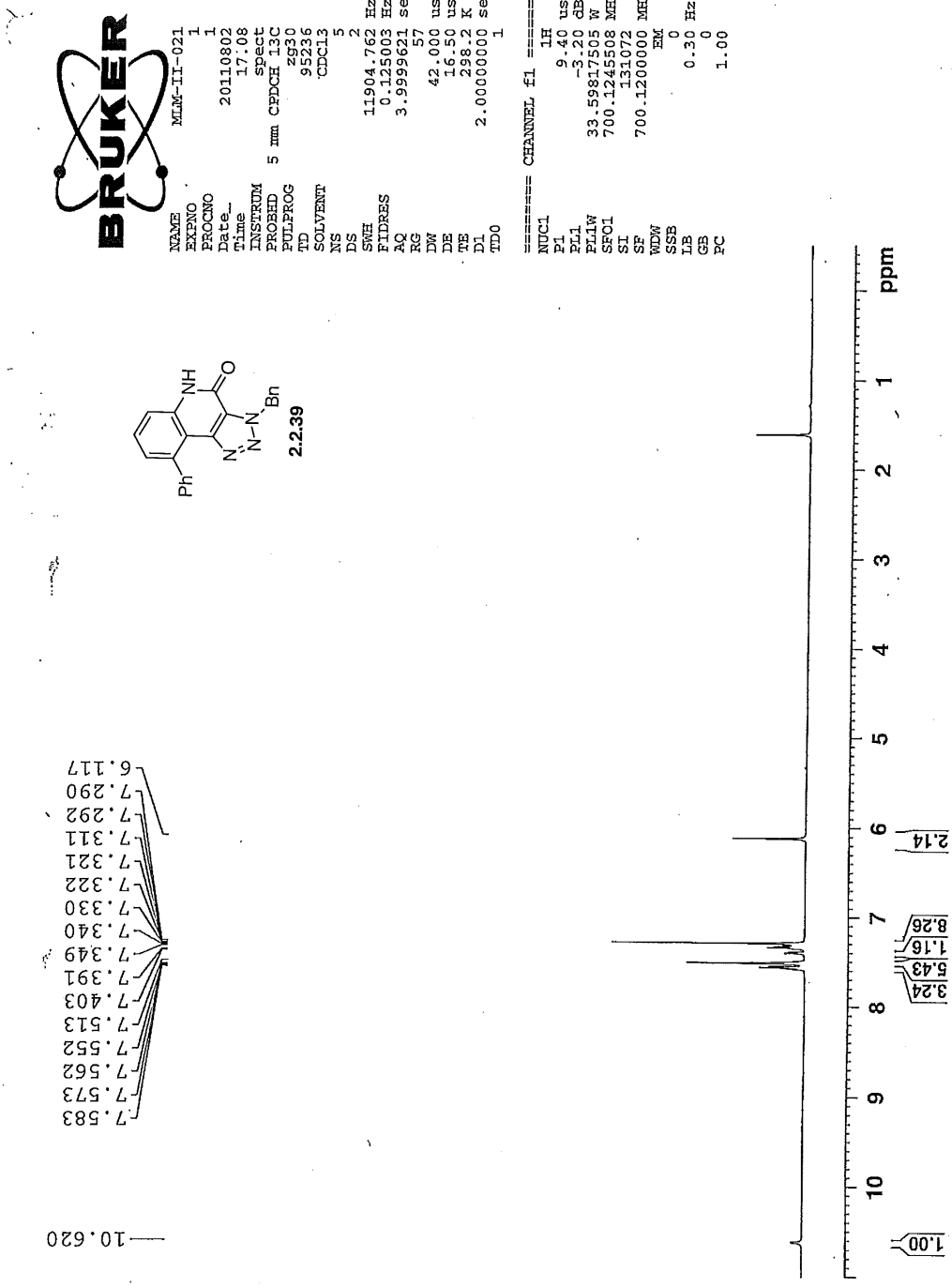

BRUKER
NAME MIM-III-050
EXPNO 5
PROCNO 1
Date_ 20111116
Time 8.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 10
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 203
DW 42.000 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.75 usec
PL1 -3.00 dB
PL1W 32.08600616 W
SFO1 700.1516910 MHz
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Fractions 15-18
8.185
8.184
8.173
8.172
7.906
7.904
7.894
7.893
7.762
7.750
7.739
7.288
4.938
4.914
4.843
4.819
1.402
2.2.36f
8.85
2.28
1.29
1.03
1.00
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 ppm

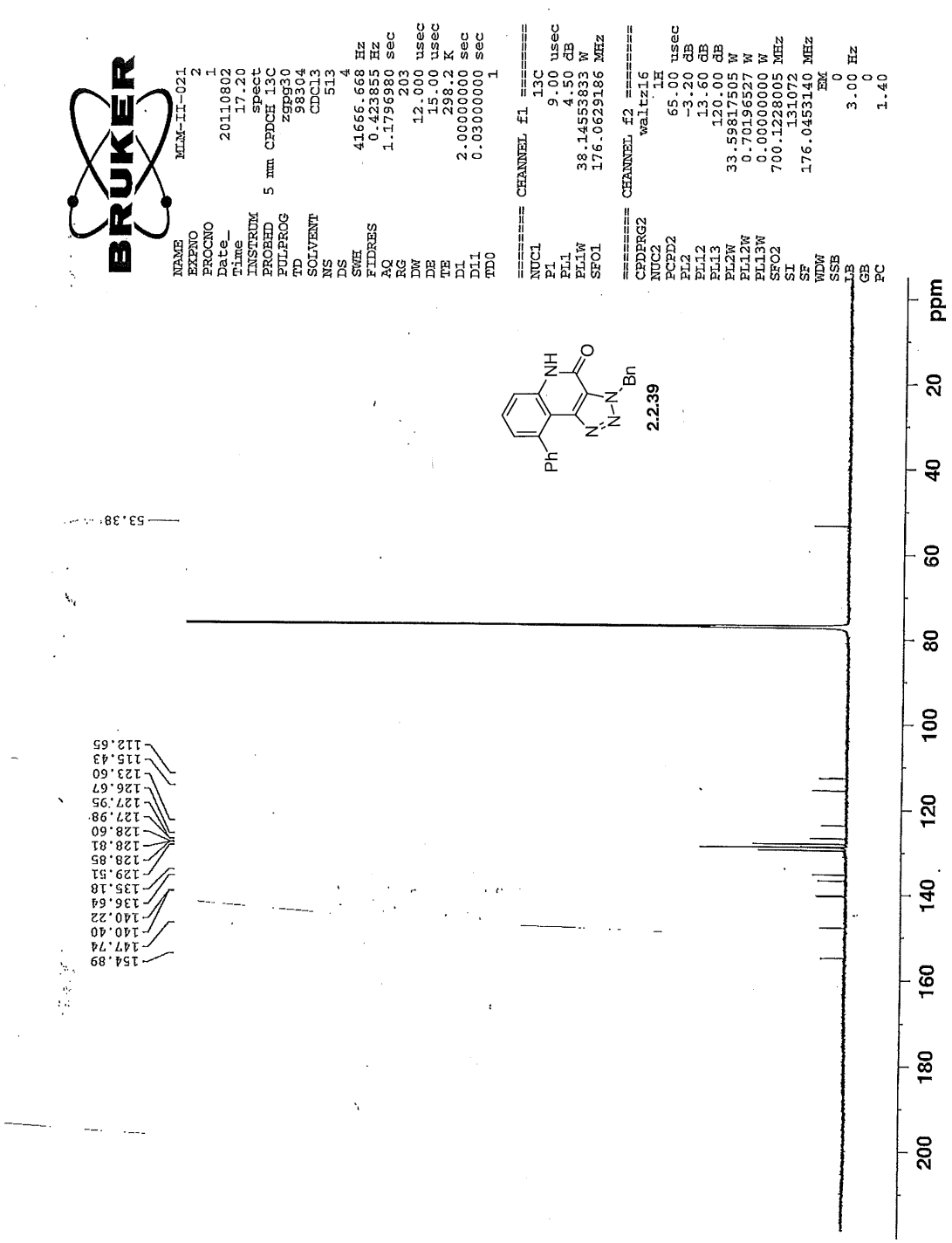

BRUKER
NAME MLM-II-041
EXPNO 1
PROCNO 1
Date_ 20110804
Time 18.02
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 4
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 101
DW 42.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 -3.20 dB
PL1W 33.59817505 W
SFO1 700.1245508 MHz
SI 131072
SF 700.1200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NO2
CO2Me
Ph
Bn
2.2.37
7.710
7.706
7.695
7.684
7.321
7.320
7.318
7.315
7.311
7.292
7.239
7.228
7.185
7.174
7.163
7.030
7.029
7.019
7.017
6.998
6.993
6.988
6.984
5.906
5.885
5.829
5.808
3.678
3.579
1.00
2.02
3.02
1.01
2.04
2.03
2.01
0.06
2.01
0.09
3.05
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 ppm

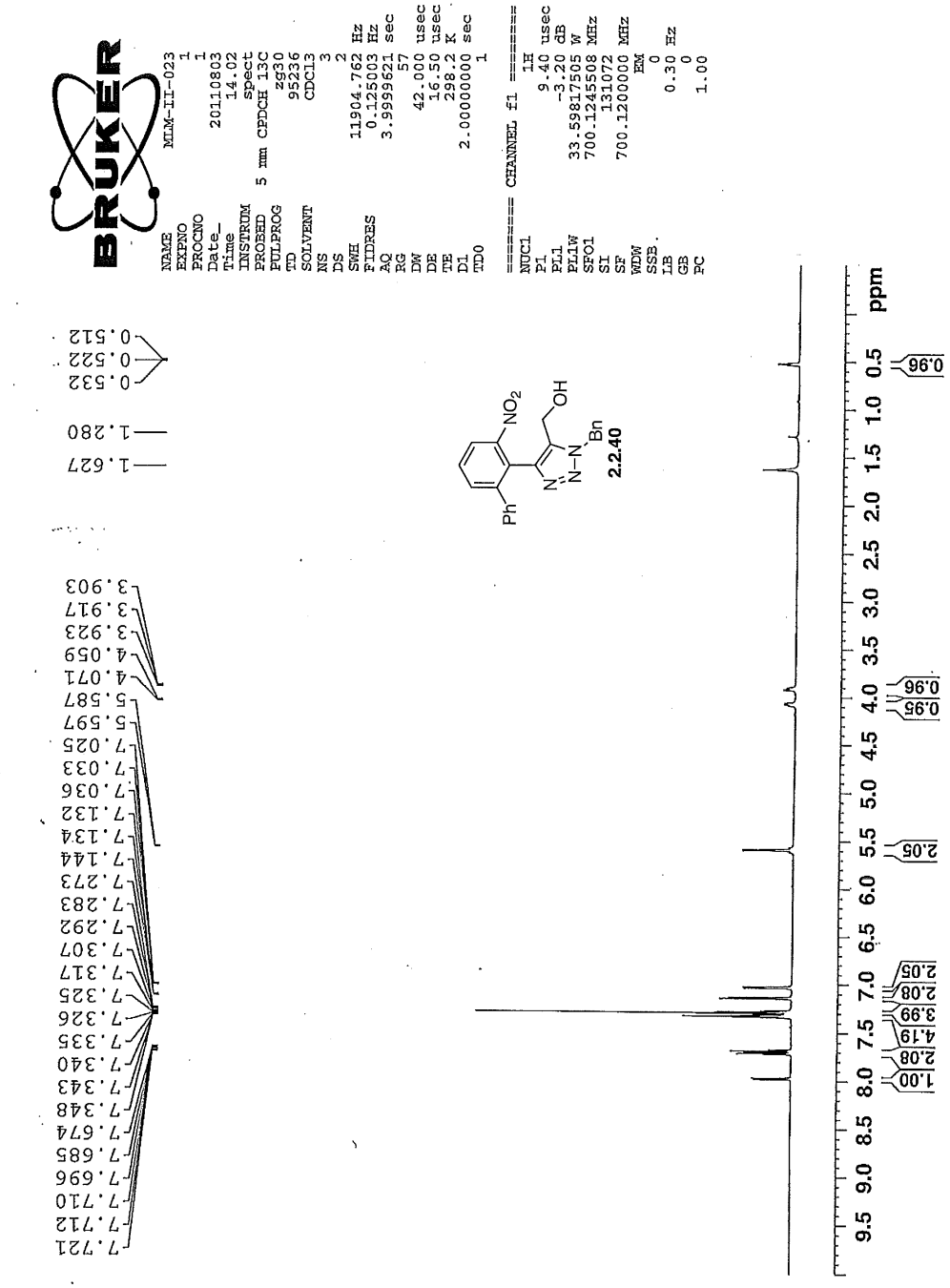

BRUKER
NAME MLM-II-041
EXPNO 3
PROCNO 1
Date_ 20110804
Time 18.23
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 98304
SOLVENT CDCl3
NS 150
DS 4
SWH 41666.668 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 203
DW 12.000 usec
DE 15.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 4.50 dB
PL1W 38.14553833 W
SFO1 176.0629186 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 usec
PL2 -3.20 dB
PL12 13.60 dB
PL13 120.00 dB
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1228005 MHz
SI 131072
SF 176.0453140 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
52.35
54.00
76.88
77.06
77.24
123.44
124.56
125.66
126.89
127.64
128.02
128.08
128.72
129.07
129.84
134.45
135.20
138.68
145.36
146.15
149.55
157.94
Ph
NO2
CO2Me
N-N
Bn
2.2.37
200
180
160
140
120
100
80
60
40
20
ppm

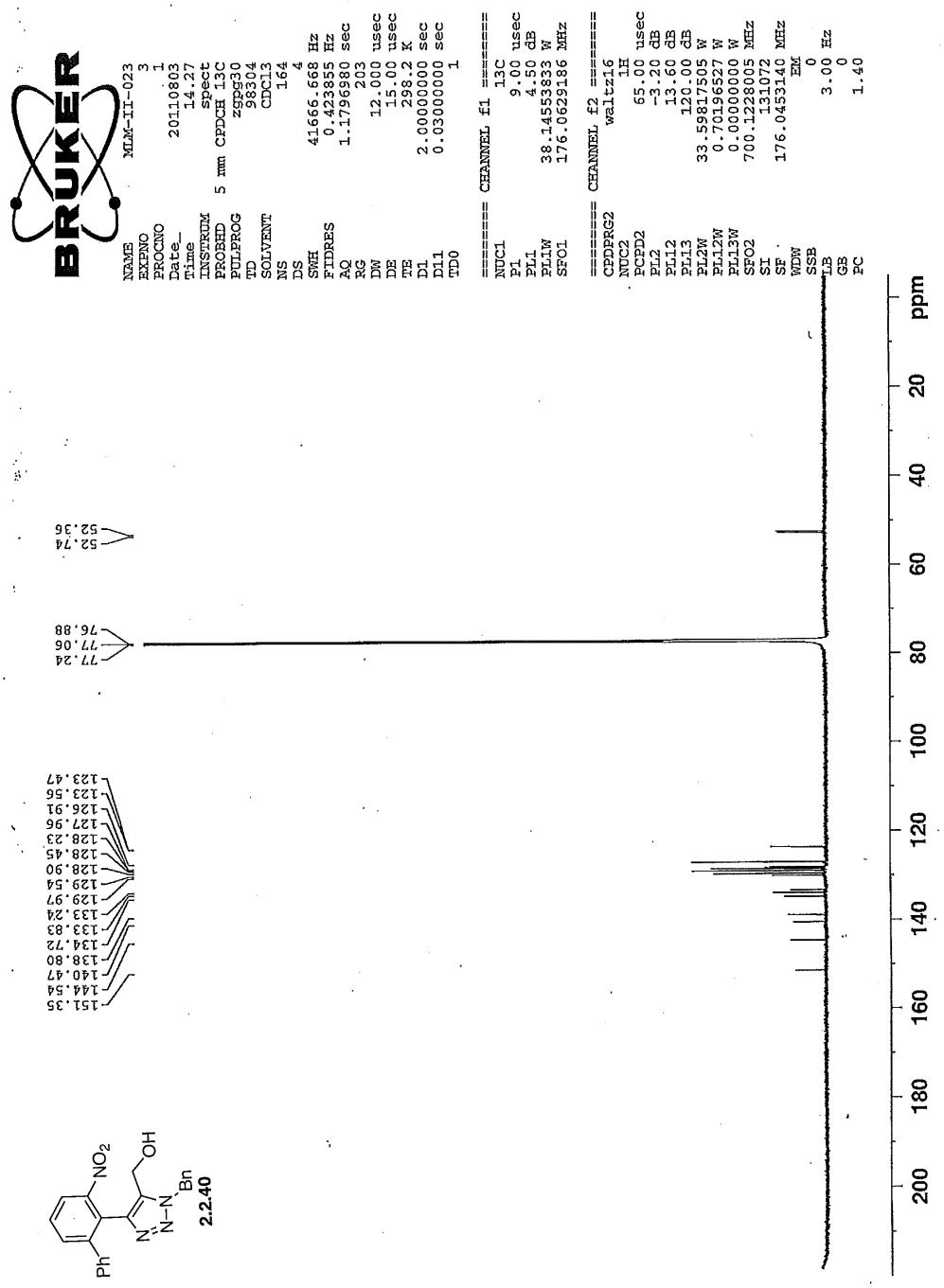

Current Data Parameters
NAME MLM-II-095
EXPNO 4
PROCNO 1
F2 - Acquisition Paramete
Date_ 20110829
Time 16.13
INSTRUM DPX400
PROBHD 5 mm Multinucl
PULPROG zg30
TD 32768
SOLVENT MeOD
NS 12
DS 2
SWH 6410.256 H
FIDRES 0.195625 H
AQ 2.5559540 s
RG 574.7
DW 78.000 u
DE 6.00 u
TE 298.2 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 =====
NUC1 1H
P1 13.50 u
PL1 -3.00 d
SFO1 400.2478017 M
F2 - Processing parameter
SI 32768
SF 400.2450000 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
NO2
CO2H
Ph
N-N
Bn
2.2.38
3.318
3.322
3.326
3.330
3.334
4.882
5.793
5.830
6.060
6.097
6.951
6.955
6.964
6.974
7.142
7.146
7.167
7.234
7.266
7.718
7.731
8.093
8.104
8.116
1.00
2.05
4.20
4.21
2.07
1.01
0.96
6.08
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
ppm

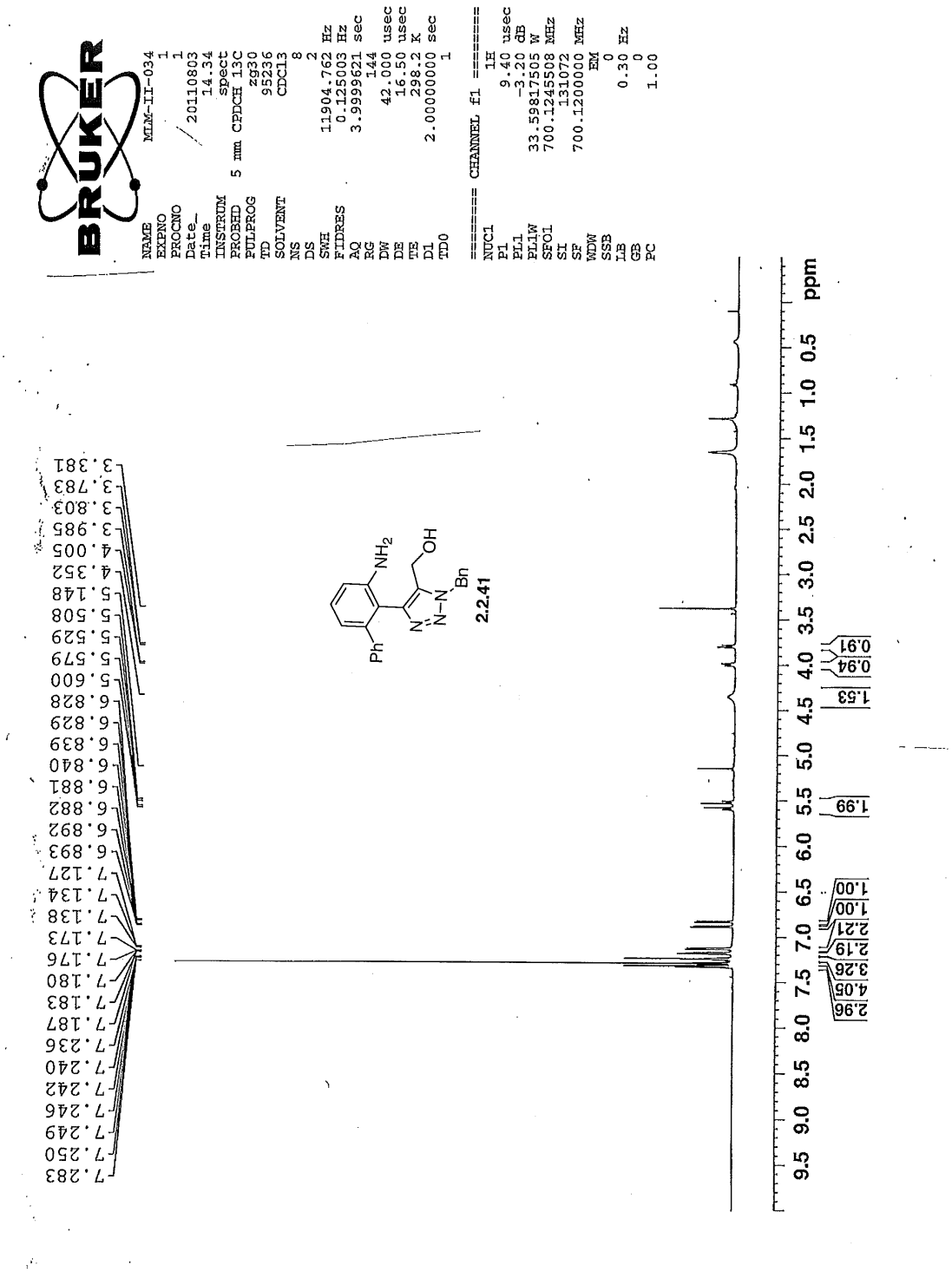

Current Data Parameters
NAME MKM-II-095
EXPNO 6
PROCNO 1
DU /m
USER melissa
F2 - Acquisition Parame
Date_ 20110829
Time 16.29
INSTRUM DPX400
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3000
DS 4
SWH 23980.814
FIDRES 0.365918
AQ 1.3664756
RG 13004
DW 20.850
DE 6.00
TE 298.2
D1 0.50000000
d11 0.03000000
DELTA 0.40000001
TD0 1
======== CHANNEL f1 ====
NUC1 13C
P1 8.30
PL1 -3.00
SFO1 100.6517495
======== CHANNEL f2 ====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00
PL2 13.00
PL12 15.00
PL13 15.00
SFO2 400.2466010
F2 - Processing parameter
SI 32768
SF 100.6416850
WDW EM
SSB 0
LB 3.00
GB 0
PC 1.40
46.96
47.17
47.38
47.60
47.81
48.02
48.23
52.68
121.89
122.82
125.07
126.52
127.05
127.27
127.53
128.16
129.03
129.33
134.16
136.47
139.25
144.51
145.51
149.88
152.02
NO2
CO2H
N
N
Bn
Ph
2.2.38
ppm

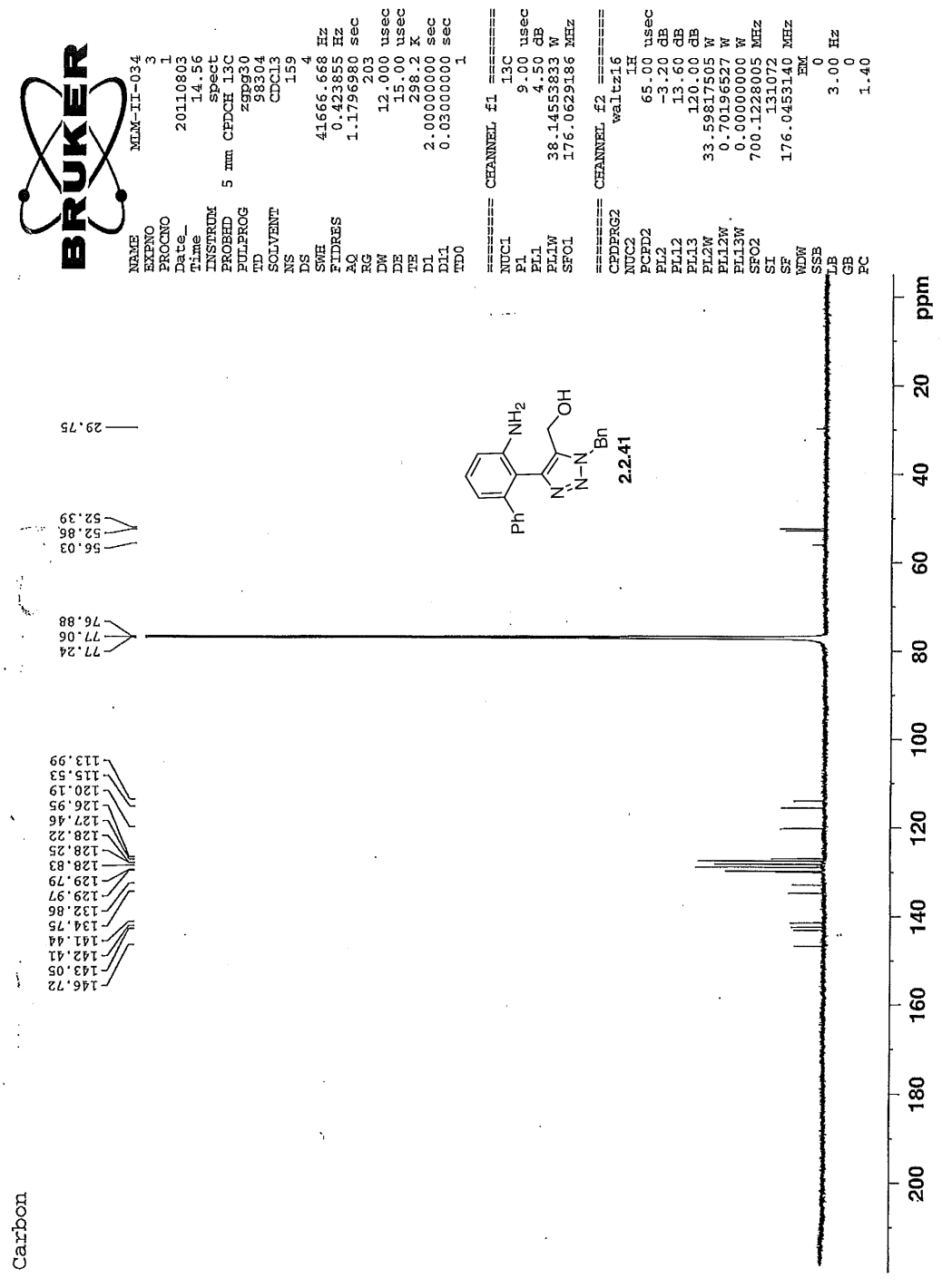

BRUKER
NAME MLM-II-021
EXPNO 1
PROCNO 1
Date_ 20110802
Time 17:08
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 5
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 57
DW 42.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 -3.20 dB
PL1W 33.59817505 W
SFO1 700.1245508 MHz
SI 131072
SF 700.1200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NH
O
N
N
N
Bn
Ph
2.2.39
10.620
7.583
7.573
7.562
7.552
7.513
7.403
7.391
7.349
7.340
7.330
7.322
7.321
7.311
7.292
7.290
6.117
ppm
1.00
2.14
3.24
5.43
1.16
8.26


BRUKER
NAME MLM-II-021
EXPNO 2
PROCNO 1
Date_ 20110802
Time 17.20
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 98304
SOLVENT CDCl3
NS 513
DS 4
SWH 41666.668 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 203
DW 12.000 usec
DE 15.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
NUC1 13C
P1 9.00 usec
PL1 4.50 dB
PL1W 38.14553833 W
SFO1 176.0629186 MHz
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 usec
PL2 -3.20 dB
PL12 13.60 dB
PL13 120.00 dB
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1228005 MHz
SI 131072
SF 176.0453140 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
NH
O
N
N
N
Bn
Ph
2.2.39
53.38
112.65
115.43
123.60
126.67
127.95
127.98
128.60
128.81
128.85
129.51
135.18
136.64
140.22
140.40
147.74
154.89
ppm
200
180
160
140
120
100
80
60
40
20

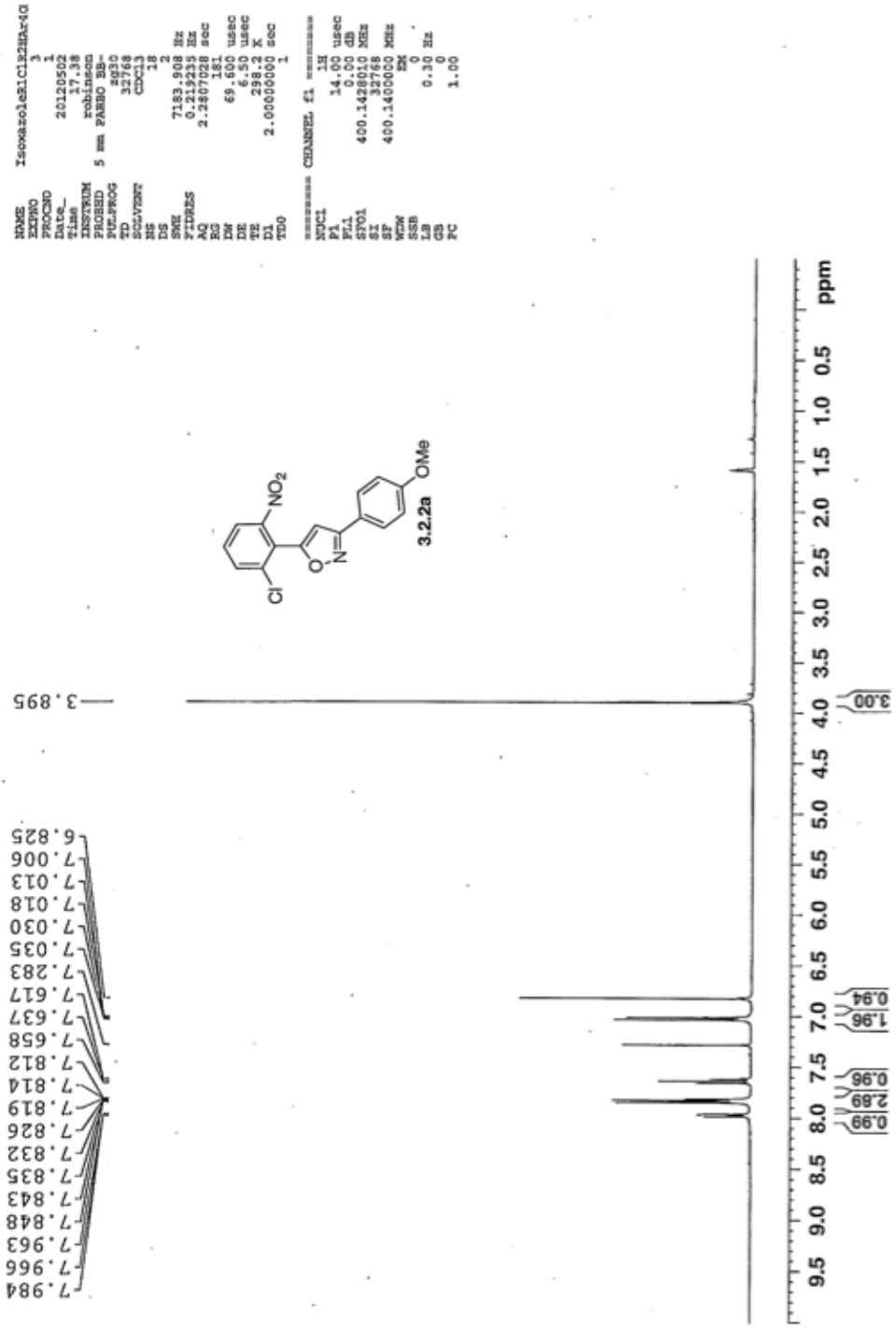

BRUKER
NAME MLM-II-023
EXPNO 1
PROCNO 1
Date_ 20110803
Time 14.02
INSTRUM spect
PROBED 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 3
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 57
DW 42.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 -3.20 dB
PL1W 33.59817505 W
SFO1 700.1245508 MHz
SI 131072
SF 700.1200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NO2
OH
Ph
N
N
Bn
2.2.40
0.512
0.522
0.532
1.280
1.627
3.903
3.917
3.923
4.059
4.071
5.587
5.597
7.025
7.033
7.036
7.132
7.134
7.144
7.273
7.283
7.292
7.307
7.317
7.325
7.326
7.335
7.340
7.343
7.348
7.674
7.685
7.696
7.710
7.712
7.721
ppm
0.96
0.95
0.96
2.05
1.00
2.08
4.19
3.99
2.08
2.05

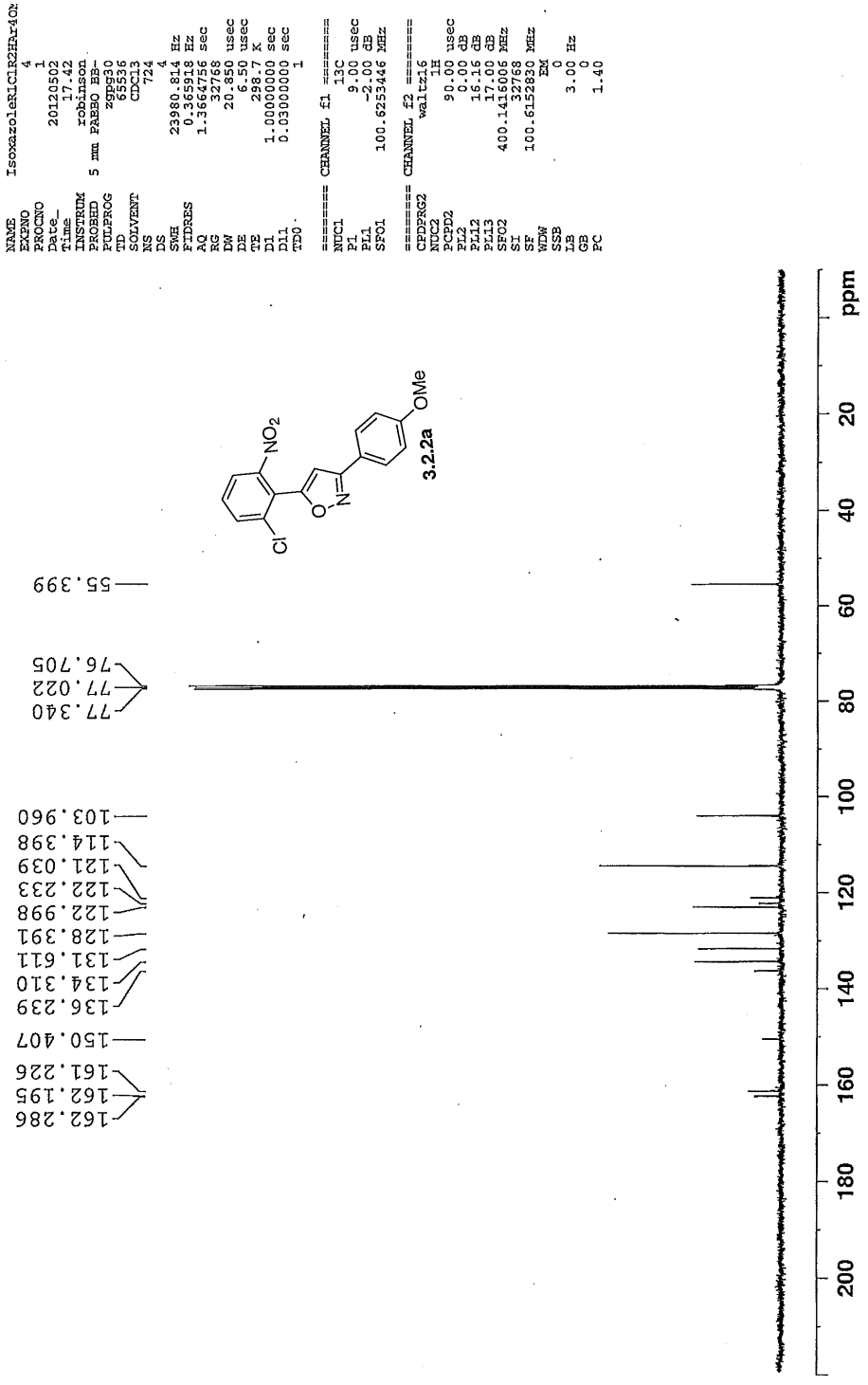

BRUKER
NAME MLM-II-023
EXPNO 3
PROCNO 1
Date_ 20110803
Time 14.27
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 98304
SOLVENT CDCl3
NS 164
DS 4
SWH 41666.668 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 203
DW 12.000 usec
DE 15.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 4.50 dB
PL1W 38.14553833 W
SFO1 176.0629186 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 usec
PL2 -3.20 dB
PL12 13.60 dB
PL13 120.00 dB
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1228005 MHz
SI 131072
SF 176.0453140 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
52.36
52.74
76.88
77.06
77.24
123.47
123.56
126.91
127.96
128.23
128.45
128.90
129.54
129.97
133.24
133.83
134.72
138.80
140.47
144.54
151.35
200
180
160
140
120
100
80
60
40
20
ppm
Ph
NO2
N
N
Bn
OH
2.2.40

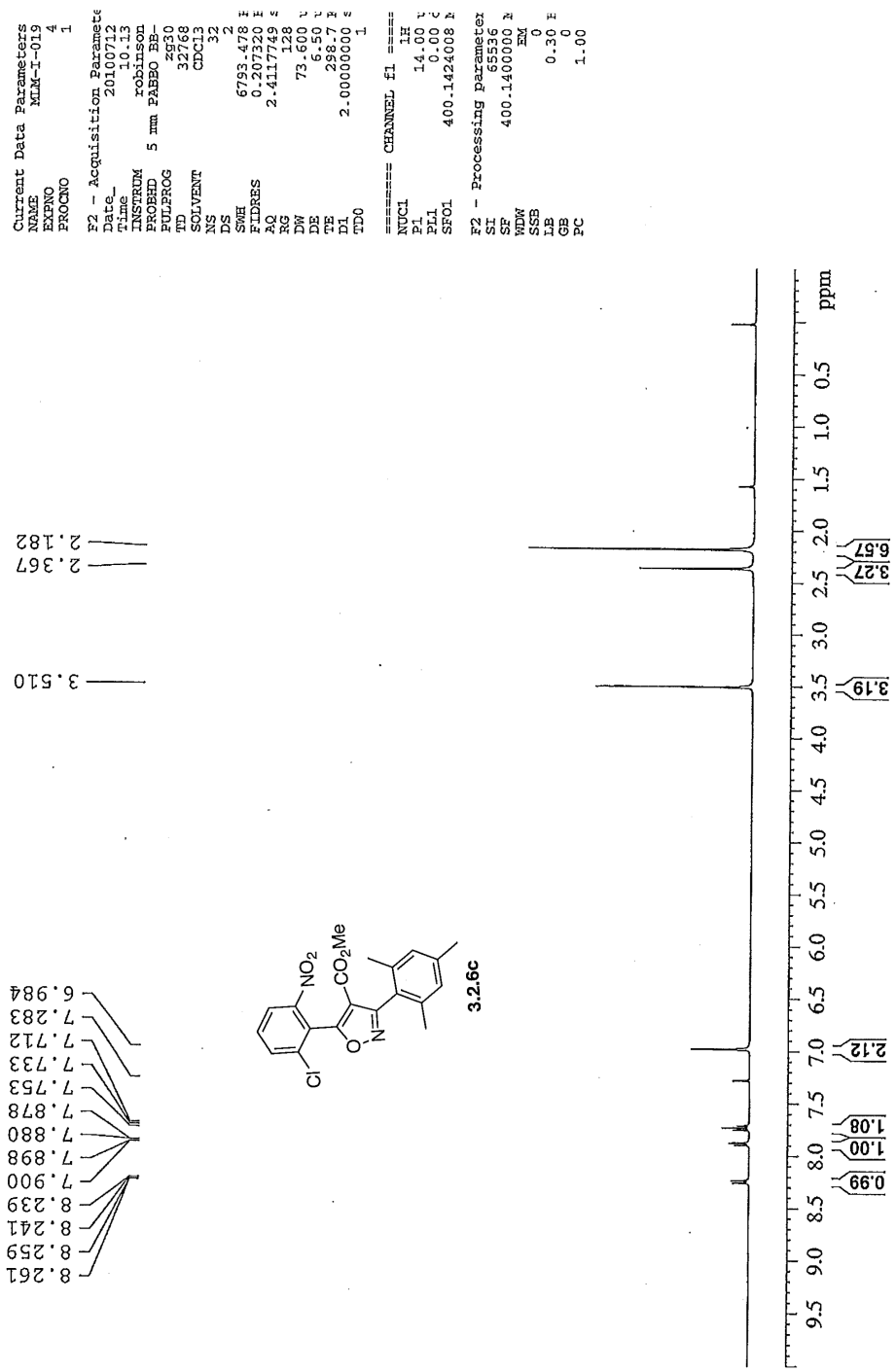

BRUKER
NAME MLM-LI-034
EXPNO 1
PROCNO 1
Date_ 20110803
Time 14.34
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 8
DS 2
SWH 11904.762 Hz
FIDRES 0.125003 Hz
AQ 3.9999621 sec
RG 144
DW 42.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 -3.20 dB
PL1W 33.59817505 W
SFO1 700.1245508 MHz
SI 131072
SF 700.1200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NH2
OH
Ph
N
N
Bn
2.2.41
7.283
7.250
7.249
7.246
7.242
7.240
7.236
7.187
7.183
7.180
7.176
7.173
7.138
7.134
7.127
6.893
6.892
6.882
6.881
6.840
6.839
6.829
6.828
5.600
5.579
5.529
5.508
5.148
4.352
4.005
3.985
3.803
3.783
3.381
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 ppm
2.96
4.05
3.26
2.19
2.21
1.00
1.00
1.99
1.53
0.94
0.91

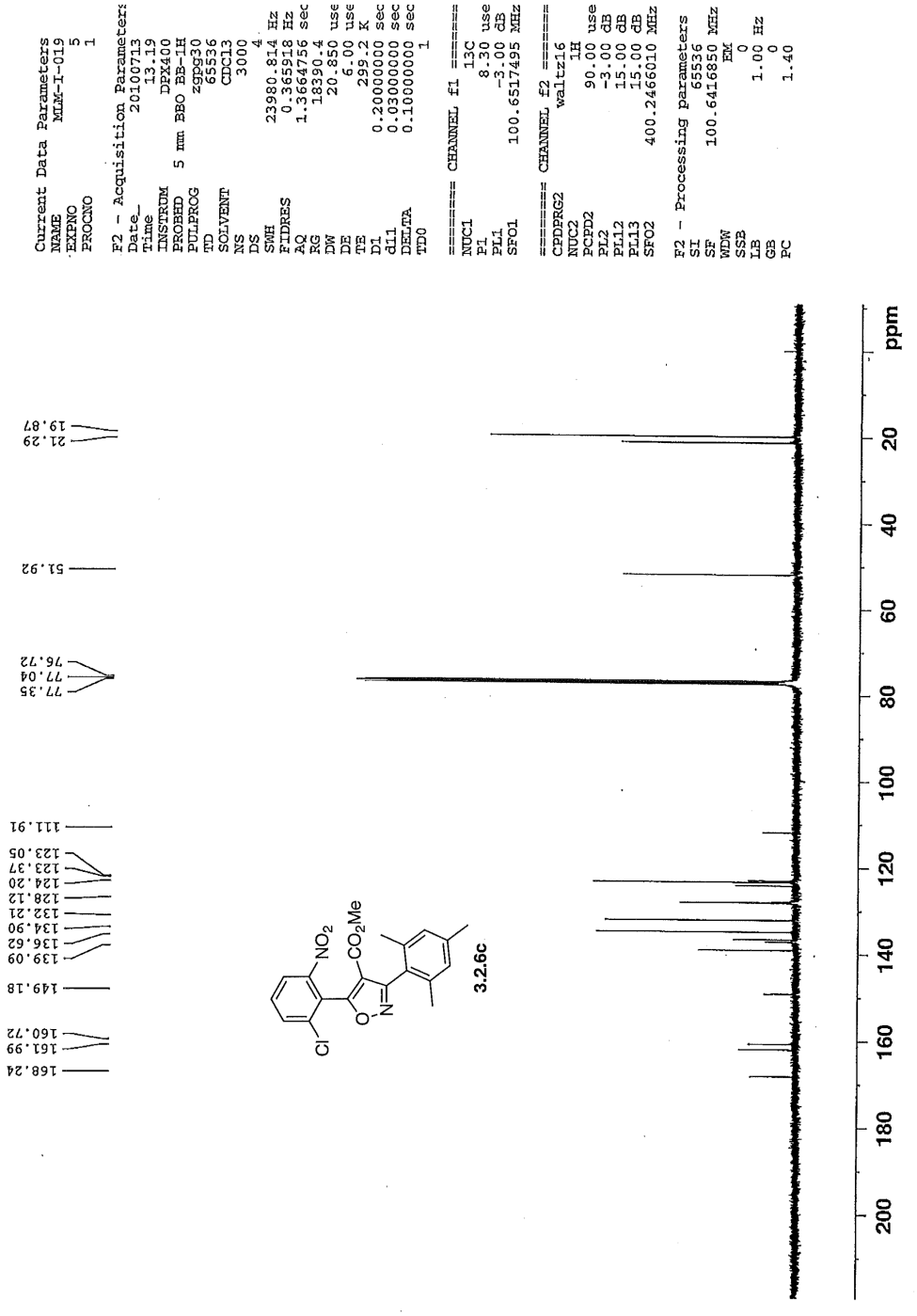

BRUKER
NAME MLM-II-034
EXPNO 3
PROCNO 1
Date_ 20110803
Time 14.56
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 98304
SOLVENT CDCl3
NS 159
DS 4
SWH 41666.668 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 203
DW 12.000 usec
DE 15.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 4.50 dB
PL1W 38.14553833 W
SFO1 176.0629186 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 usec
PL2 -3.20 dB
PL12 13.60 dB
PL13 120.00 dB
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1228005 MHz
SI 131072
SF 176.0453140 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
Carbon
29.75
52.39
52.86
56.03
76.88
77.06
77.24
113.99
115.53
120.19
126.95
127.46
128.22
128.25
128.83
129.79
129.97
132.86
134.75
141.44
142.41
143.05
146.72
NH2
OH
Bn
N
N
Ph
2.2.41
200
180
160
140
120
100
80
60
40
20
ppm

Section 6.2. Isoxazole NMR Spectra

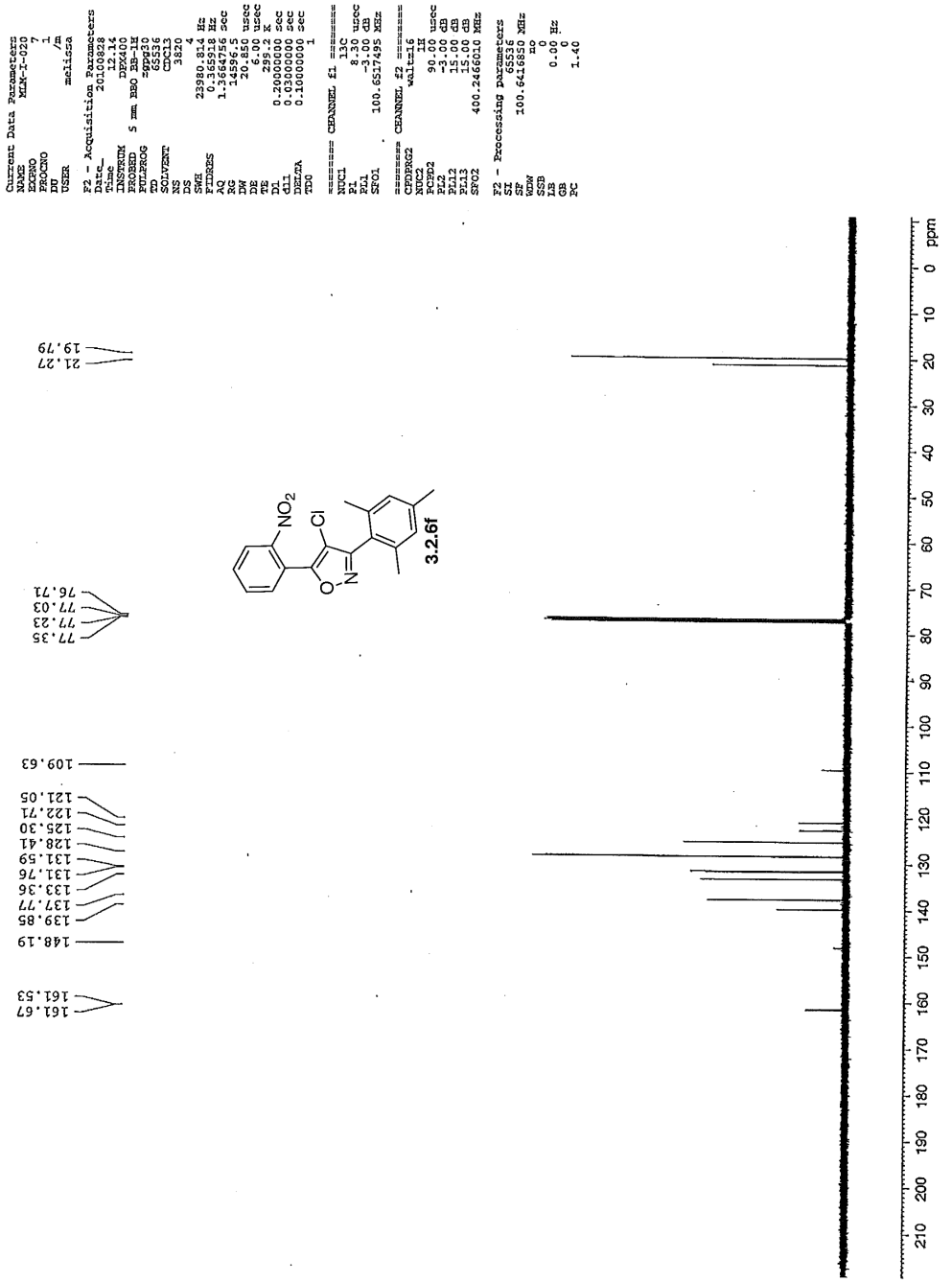

NAME IsoxazoleS1C1N2Ha-4Cl
EXPNO 3
PROCNO 1
Date_ 20120502
Time 17.38
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 7183.908 Hz
FIDRES 0.219235 Hz
AQ 2.2807028 sec
RG 181
DW 69.600 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1428010 MHz
SI 32768
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
3.2.2a
3.895
7.984
7.966
7.963
7.848
7.843
7.835
7.832
7.826
7.819
7.814
7.812
7.658
7.637
7.617
7.283
7.035
7.030
7.018
7.013
7.006
6.825
3.00
1.96
0.94
0.96
2.69
0.99
ppm

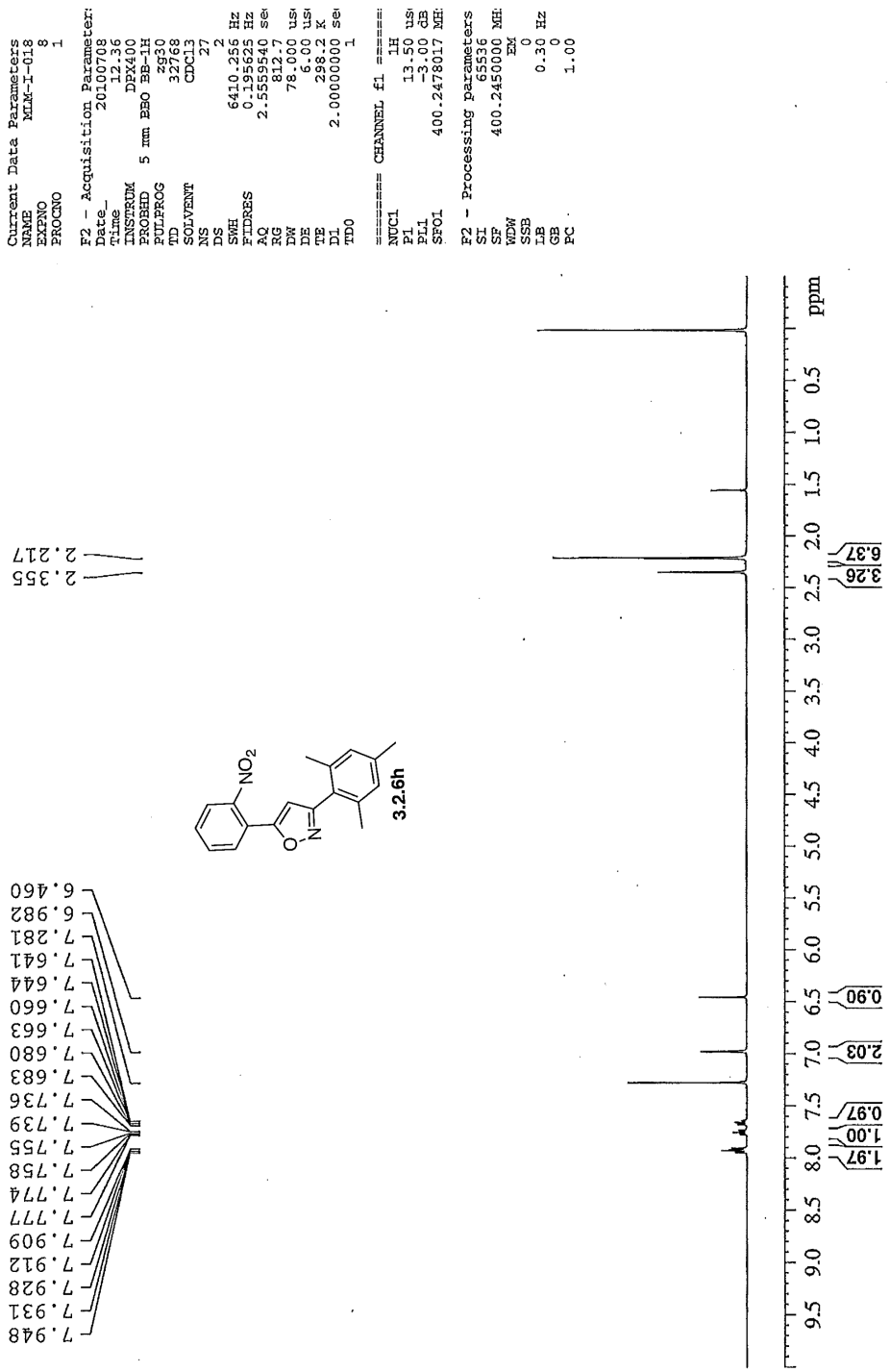

NAME IsoxazoleR1ClR2HAr4OMe
EXPNO 4
PROCNO 1
Date_ 20120502
Time 17.42
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 724
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 32768
DW 20.850 usec
DE 6.50 usec
TE 298.7 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -2.00 dB
SFO1 100.6253446 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 16.16 dB
PL13 17.00 dB
SFO2 400.1416006 MHz
SI 32768
SF 100.6152830 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
NO2
Cl
O
N
OMe
3.2.2a
55.399
76.705
77.022
77.340
103.960
114.398
121.039
122.233
122.998
128.391
131.611
134.310
136.239
150.407
161.226
162.195
162.286
200
180
160
140
120
100
80
60
40
20
ppm

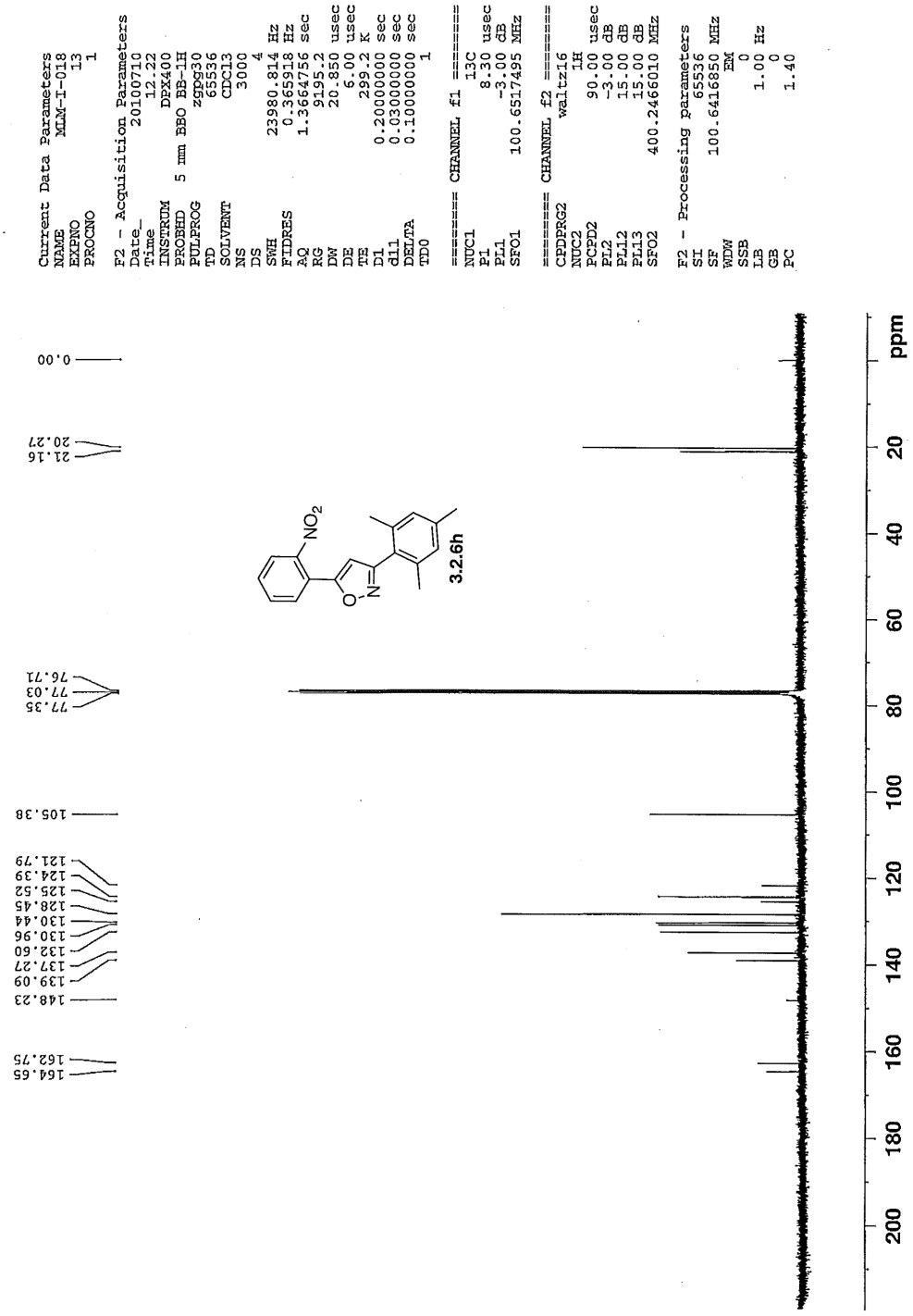

Current Data Parameters
NAME MIM-I-019
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100712
Time 10.13
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6793.478 Hz
FIDRES 0.207320 Hz
AQ 2.4117749 sec
RG 128
DW 73.600 usec
DE 6.50 usec
TE 298.7 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1424008 MHz
F2 - Processing parameters
SI 65536
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.182
2.367
3.510
6.984
7.283
7.712
7.733
7.753
7.878
7.880
7.898
7.900
8.239
8.241
8.259
8.261
NO2
CO2Me
Cl
O
N
3.2.6c
ppm
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
0.99
1.00
1.08
2.12
3.19
3.27
6.57

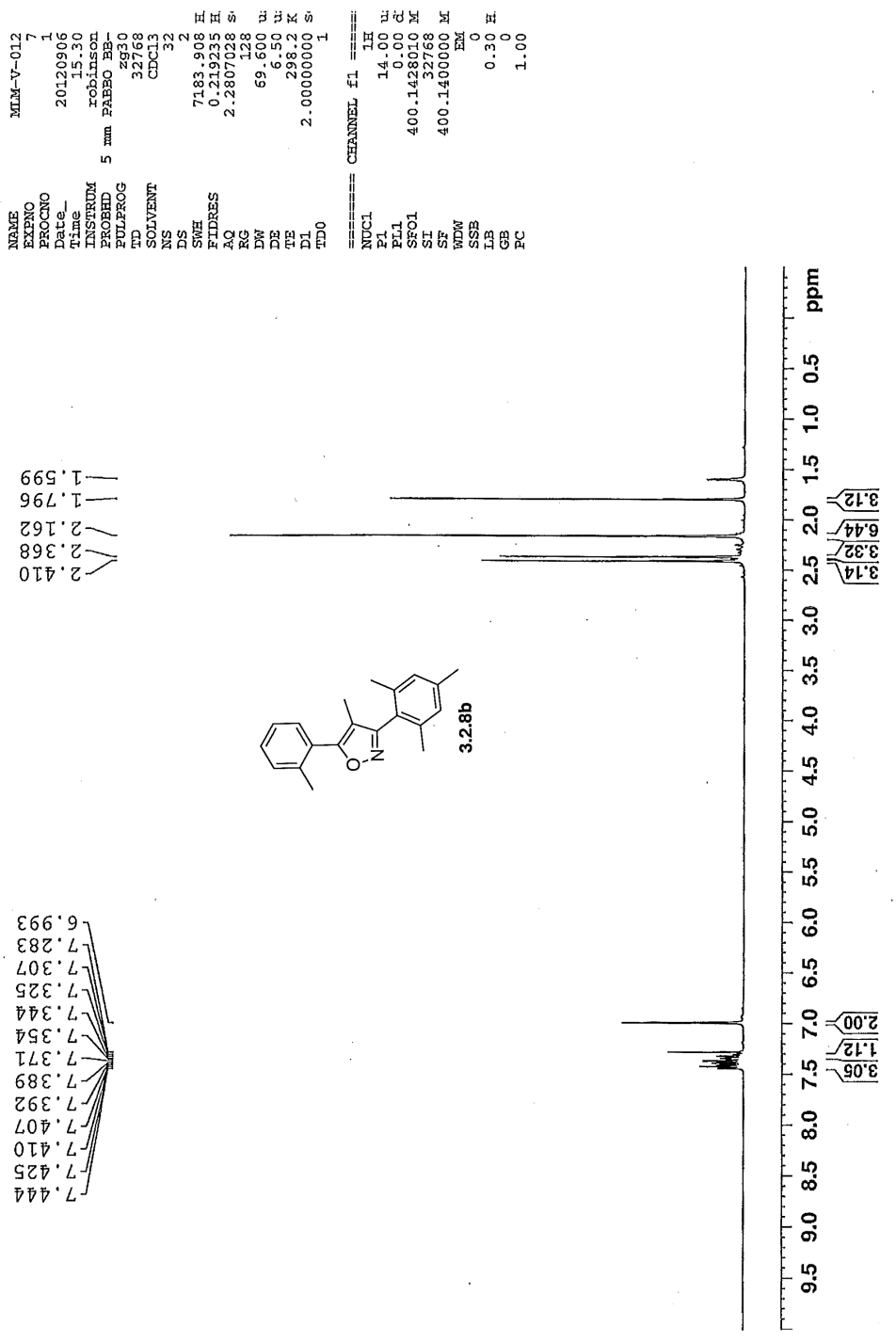

Current Data Parameters
NAME MLM-I-019
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100713
Time 13.19
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3000
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 18390.4
DW 20.850 use
DE 6.00 use
TE 299.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 use
PL1 -2.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 use
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 65536
SF 100.6416850 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
21.29
19.87
51.92
77.35
77.04
76.72
111.91
123.05
123.37
124.20
128.12
132.21
134.90
136.62
139.09
149.18
160.72
161.99
168.24
NO2
CO2Me
Cl
N
O
3.2.6c
200
180
160
140
120
100
80
60
40
20
ppm

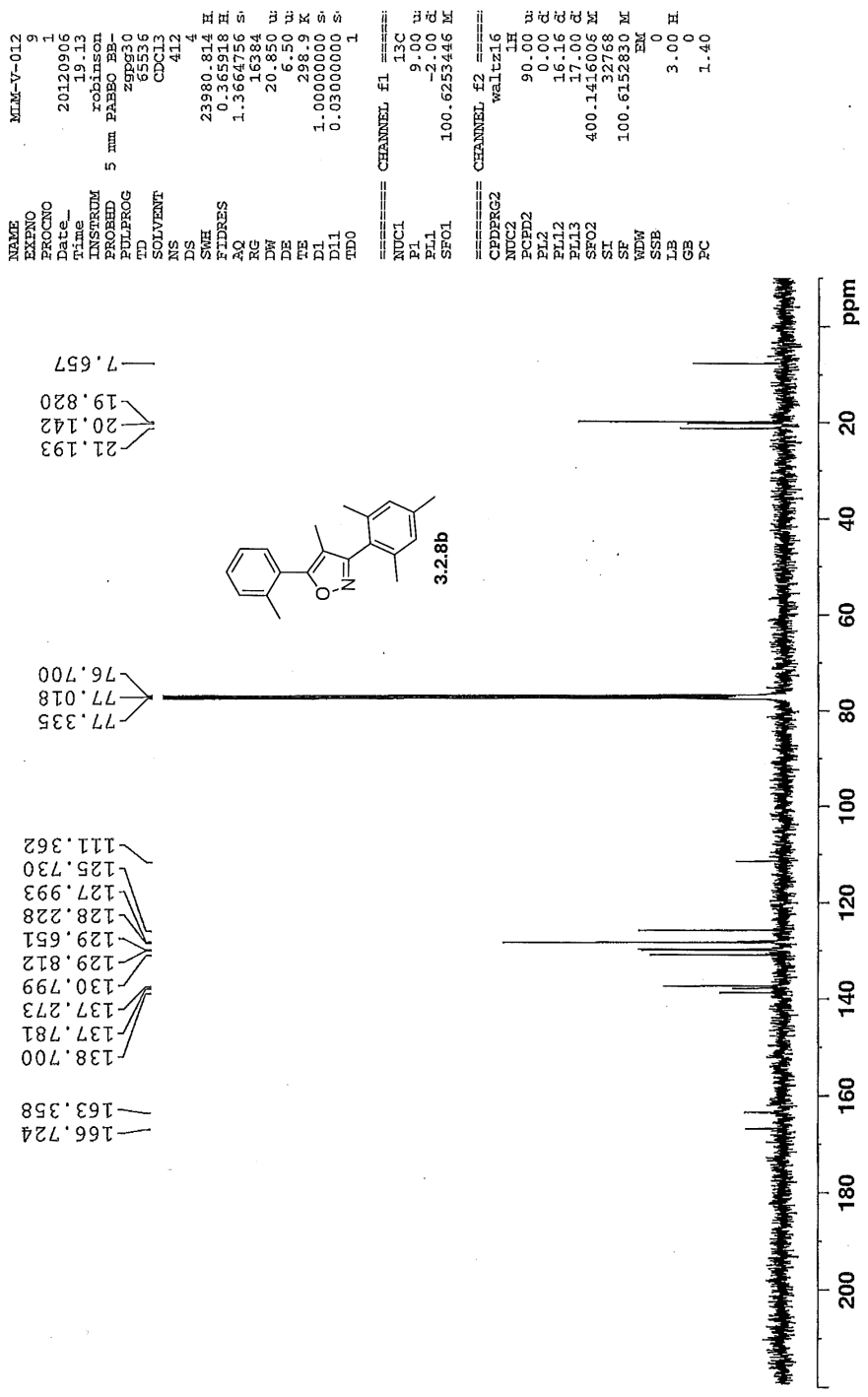

Current Data Parameters
NAME MIM-I-020
EXPNO 6
PROCNO 1
DU /m
USER melissa
F2 - Acquisition Parameters
Date_ 20100828
Time 12.06
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 406.4
DW 78.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -3.00 dB
SFO1 400.2478017 MHz
F2 - Processing parameters
SI 65536
SF 400.2450000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
2.374
2.215
7.012
7.281
7.760
7.821
7.823
7.825
7.841
8.187
8.207
6.39
3.20
2.12
3.22
1.00
ppm
3.2.6f

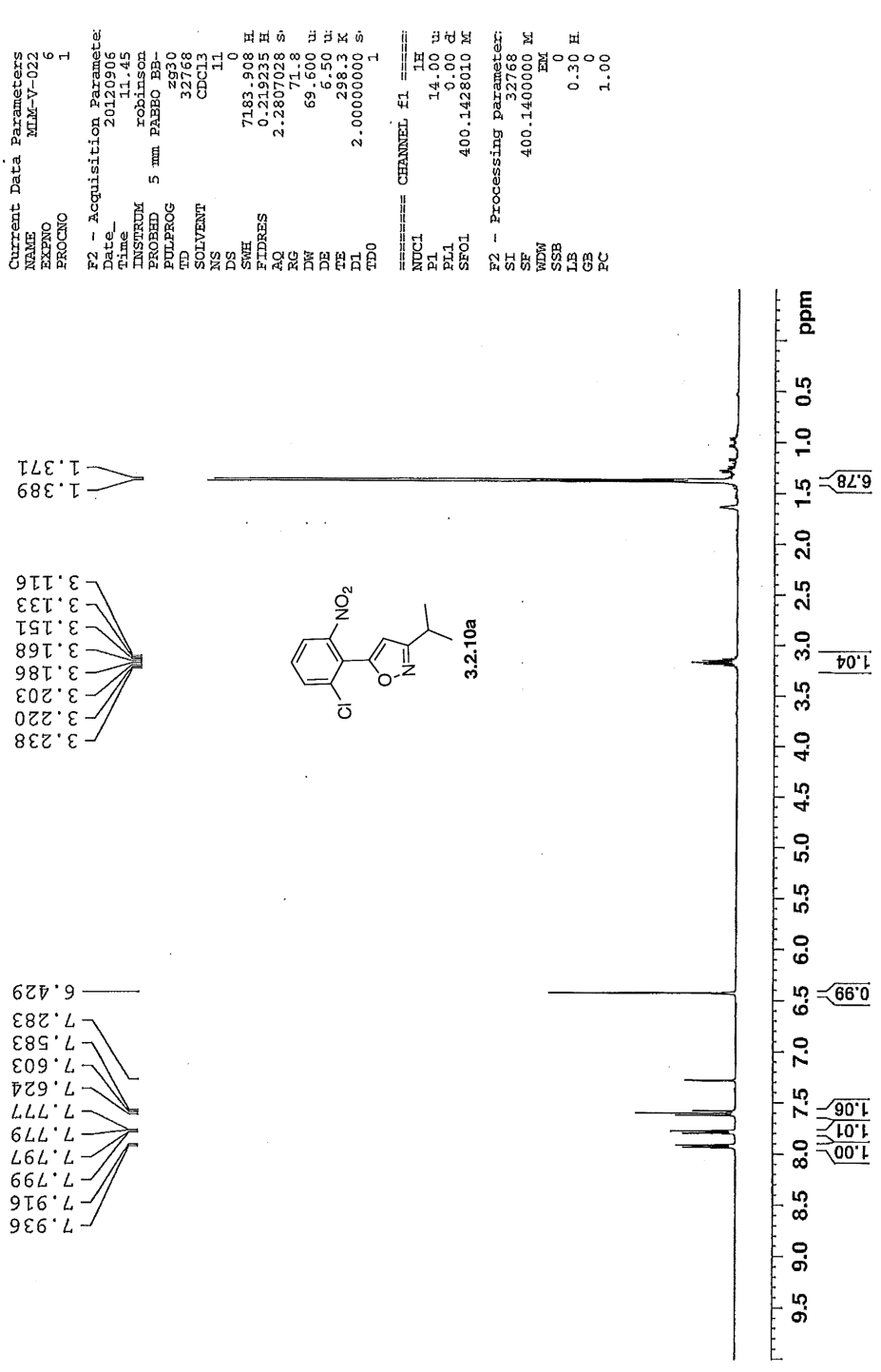

Current Data Parameters
NAME MAK-F-020
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100828
Time 22.14
INSTRUM DRX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3820
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 14596.5
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
D11 0.03000000 sec
D12 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 65536
SF 100.6416850 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
21.27
19.79
77.35
77.23
77.03
76.71
109.63
121.05
122.71
125.30
128.41
131.59
131.76
133.36
137.77
139.85
148.19
161.53
161.67
3.2.6f
ppm

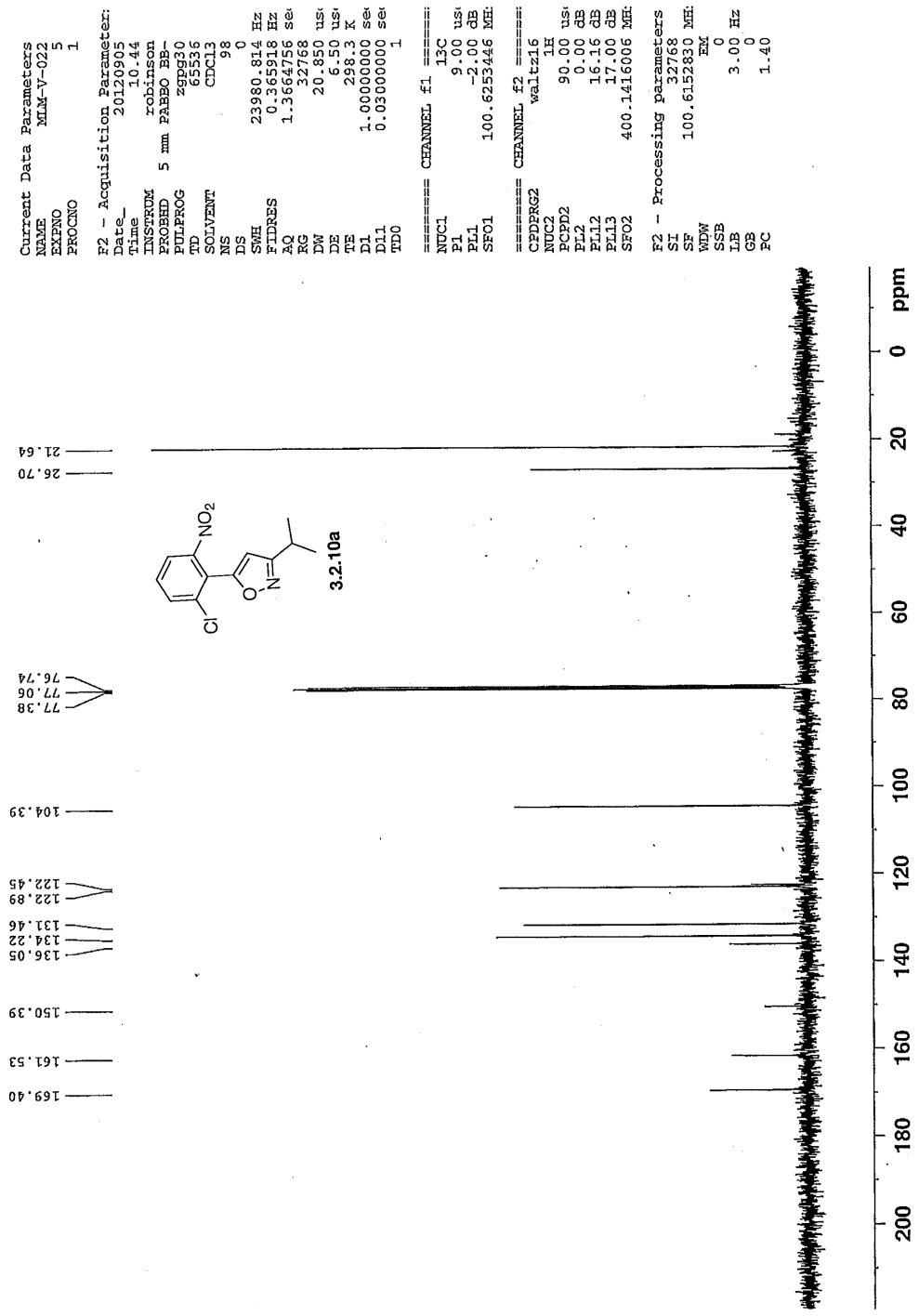

Current Data Parameters
NAME MAM-I-018
EXPNO 8
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100708
Time 12.36
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 27
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 se
RG 812.7
DW 78.000 us
DE 6.00 us
TE 298.2 K
D1 2.00000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 13.50 us
PL1 -3.00 dB
SFO1 400.2478017 MH
F2 - Processing parameters
SI 65536
SF 400.2450000 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.355
2.217
7.948
7.931
7.928
7.912
7.909
7.777
7.774
7.758
7.755
7.739
7.736
7.683
7.680
7.663
7.660
7.644
7.641
7.281
6.982
6.460
NO2
O
N
3.2.6h
6.37
3.26
0.90
2.03
0.97
1.00
1.97
ppm

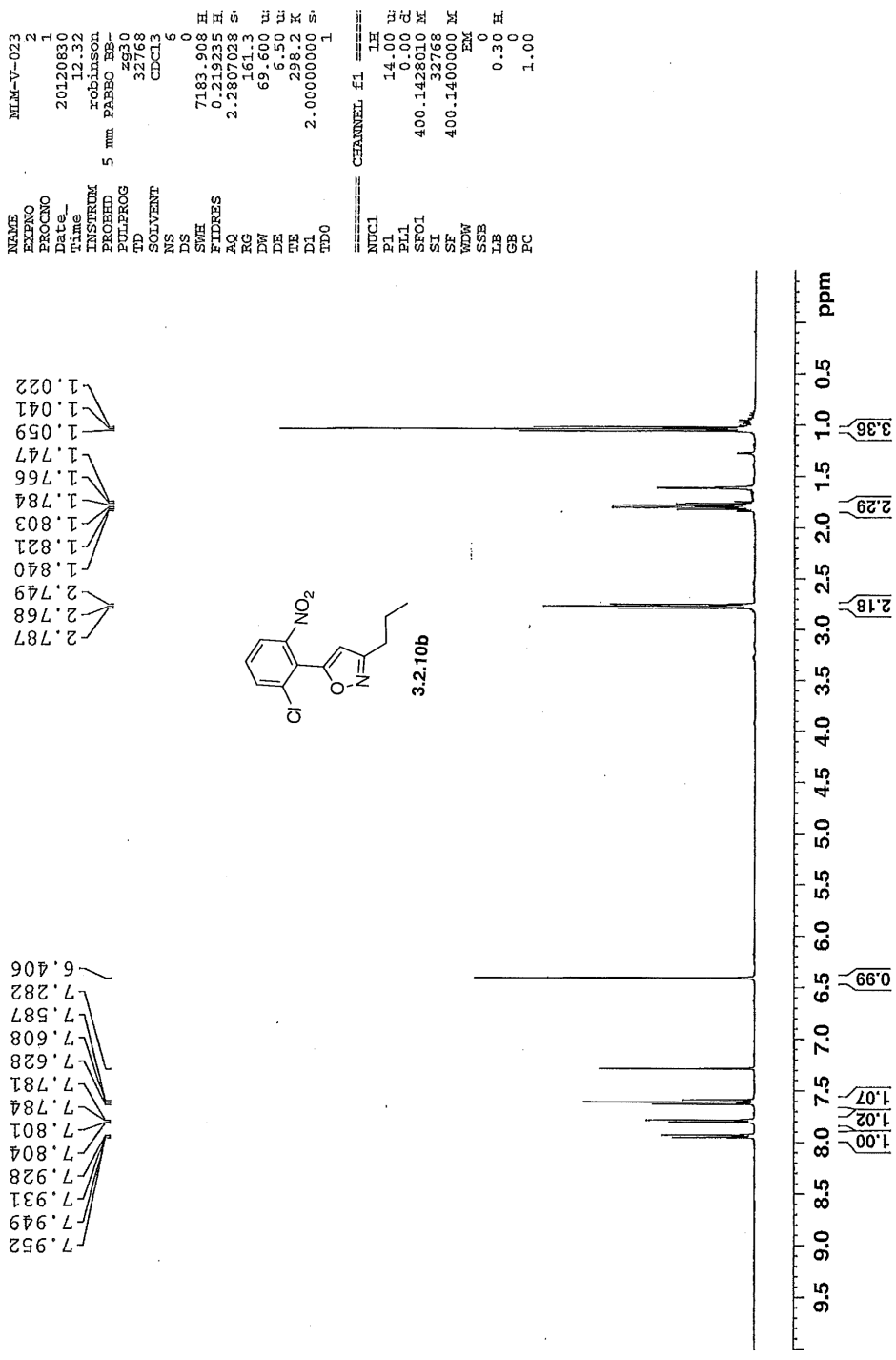

Current Data Parameters
NAME MLM-I-018
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100710
Time 12.22
INSTRUM DPX400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3000
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 9195.2
DW 20.850 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 usec
PL1 -3.00 dB
SFO1 100.6517495 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2466010 MHz
F2 - Processing parameters
SI 65536
SF 100.6416850 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
NO2
3.2.6h
0.00
20.27
21.16
76.71
77.03
77.35
105.38
121.79
124.39
125.52
128.45
130.44
130.96
132.60
137.27
139.09
148.23
162.75
164.65
200
180
160
140
120
100
80
60
40
20
ppm

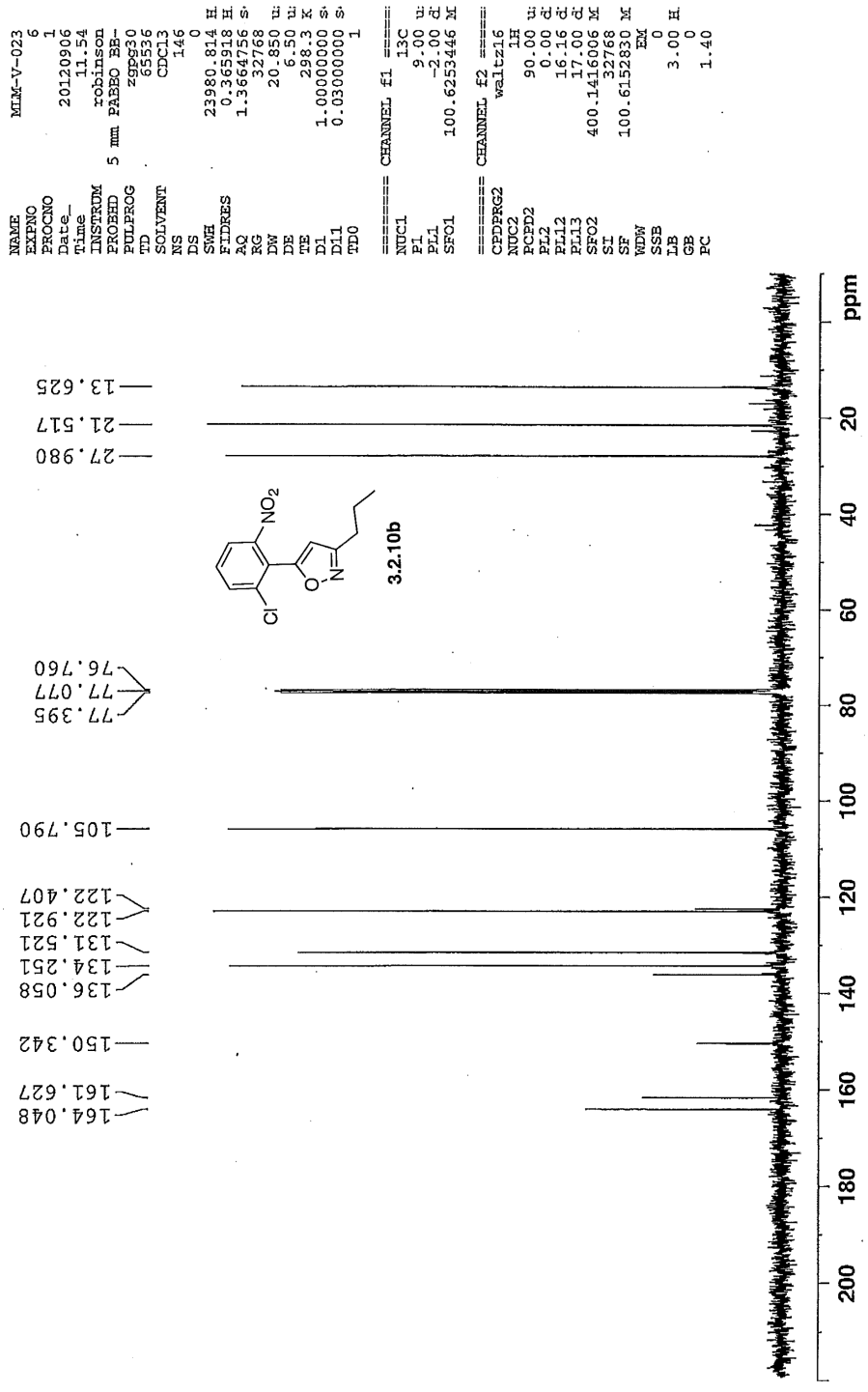

NAME MIM-V-012
EXPNO 7
PROCNO 1
Date_ 20120906
Time 15.30
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 7183.908 H
FIDRES 0.219235 H
AQ 2.2807028 s
RG 128
DW 69.600 u
DE 6.50 u
TE 298.2 K
D1 2.00000000 s
TD0 1
CHANNEL f1
NUC1 1H
P1 14.00 u
PL1 0.00 d
SFO1 400.1428010 M
SI 32768
SF 400.1400000 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
1.599
1.796
2.162
2.368
2.410
6.993
7.283
7.307
7.325
7.344
7.354
7.371
7.389
7.392
7.407
7.410
7.425
7.444
3.2.8b
3.12
6.44
3.32
3.14
3.05
1.12
2.00
ppm

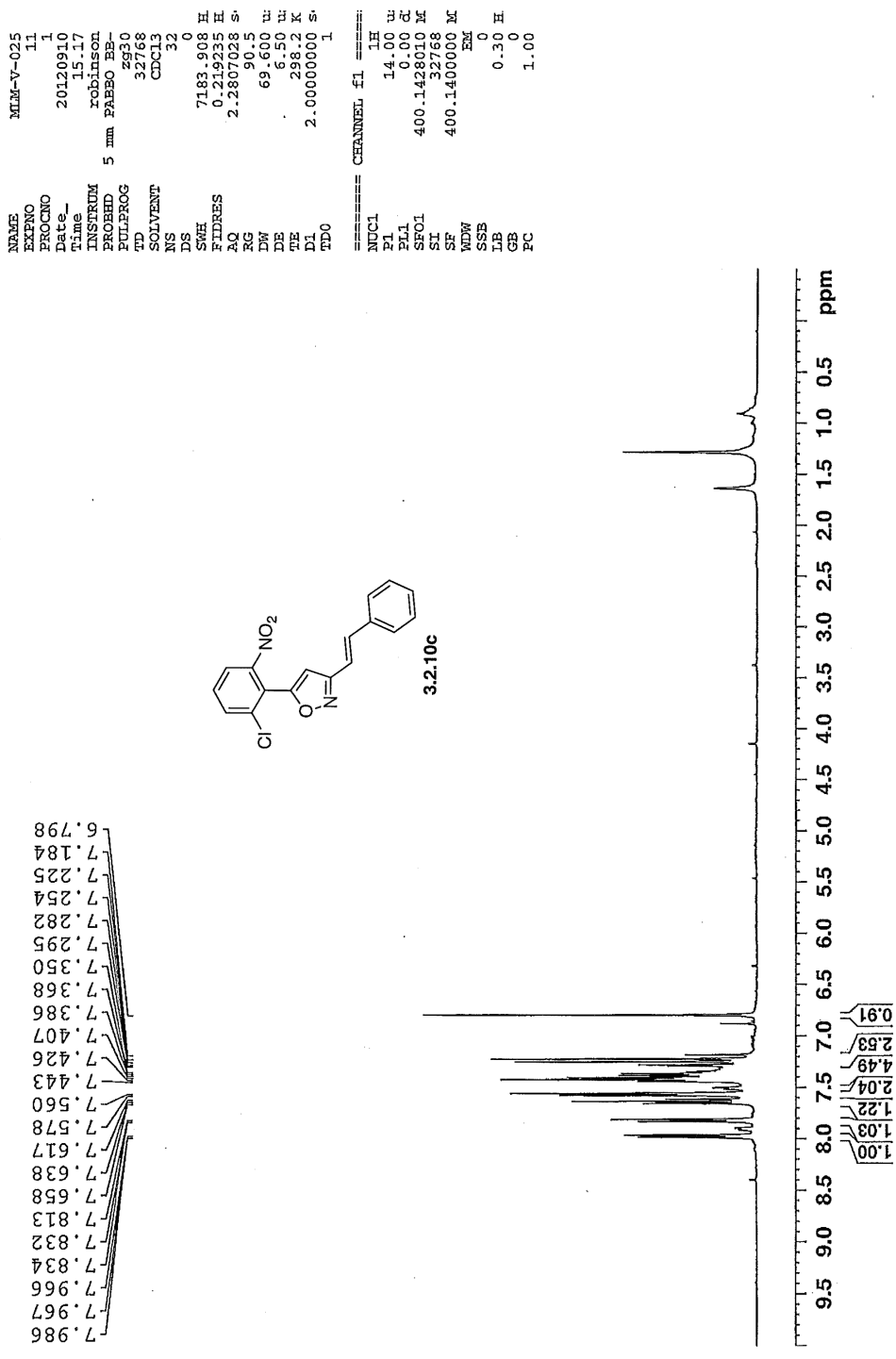

NAME MLM-V-012
EXPNO 9
PROCNO 1
Date_ 20120906
Time 19.13
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 412
DS 4
SWH 23980.814 H
FIDRES 0.365918 H
AQ 1.3664756 s
RG 16384
DW 20.850 u
DE 6.50 u
TE 298.9 K
D1 1.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 u
PL1 -2.00 d
SFO1 100.6253446 M
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 u
PL2 0.00 d
PL12 16.16 d
PL13 17.00 d
SFO2 400.1416006 M
SI 32768
SF 100.6152830 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
3.2.8b
7.657
19.820
20.142
21.193
76.700
77.018
77.335
111.362
125.730
127.993
128.228
129.651
129.812
130.799
137.273
137.781
138.700
163.358
166.724
ppm
200
180
160
140
120
100
80
60
40
20

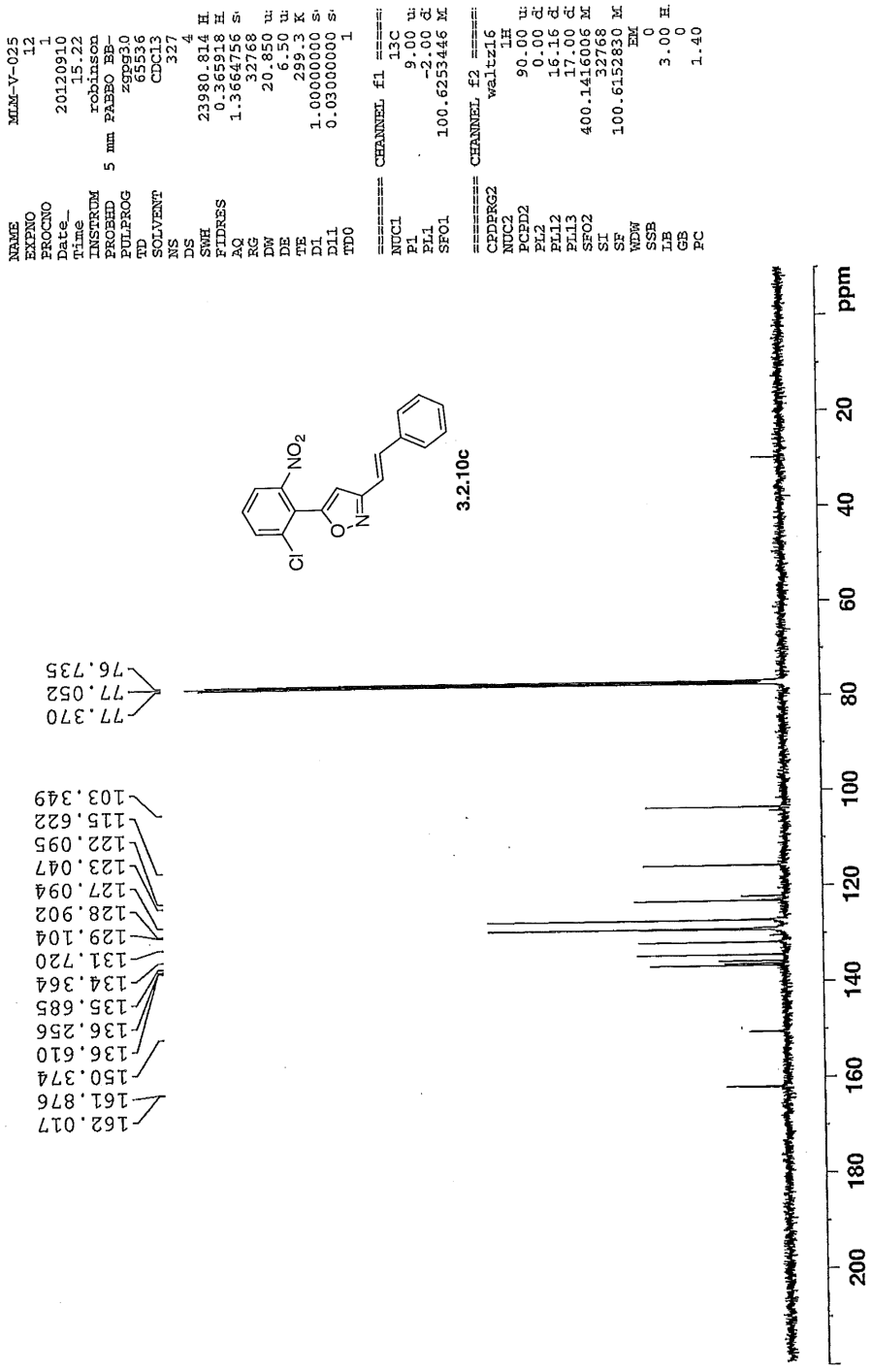

Current Data Parameters
NAME MIM-V-022
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120906
Time 11.45
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 11
DS 0
SWH 7183.908 Hz
FIDRES 0.219235 Hz
AQ 2.2807028 sec
RG 71.8
DW 69.600 usec
DE 6.50 usec
TE 298.3 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
SFO1 400.1428010 MHz
F2 - Processing parameters
SI 32768
SF 400.1400000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.371
1.389
3.116
3.133
3.151
3.168
3.186
3.203
3.220
3.238
6.429
7.283
7.583
7.603
7.624
7.777
7.779
7.797
7.799
7.916
7.936
NO2
Cl
O
N
3.2.10a
6.78
1.04
0.99
1.06
1.01
1.00
ppm

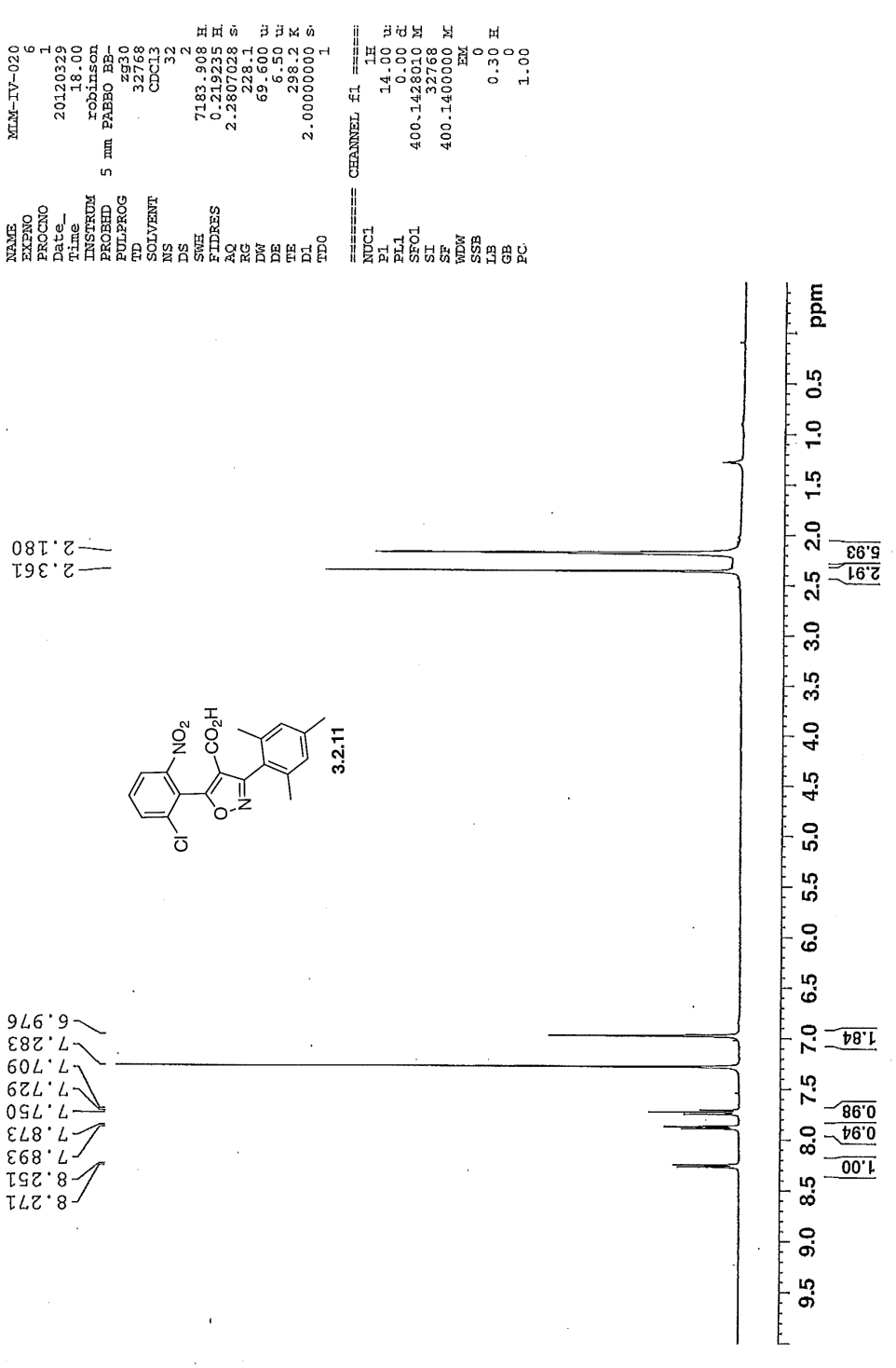

Current Data Parameters
NAME MIM-V-022
EXPNO 5
PROCNO 1
F2 - Acquisition Parameter
Date_ 20120905
Time 10.44
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 98
DS 0
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.36664756 se
RG 32768
DW 20.850 us
DE 6.50 us
TE 298.3 K
D1 1.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 9.00 us
PL1 -2.00 dB
SFO1 100.6253446 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 us
PL2 0.00 dB
PL12 16.16 dB
PL13 17.00 dB
SFO2 400.1416006 MH
F2 - Processing parameters
SI 32768
SF 100.6152830 MH
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
NO2
Cl
O
N
3.2.10a
21.64
26.70
76.74
77.06
77.38
104.39
122.45
122.89
131.46
134.22
136.05
150.39
161.53
169.40
200
180
160
140
120
100
80
60
40
20
0
ppm

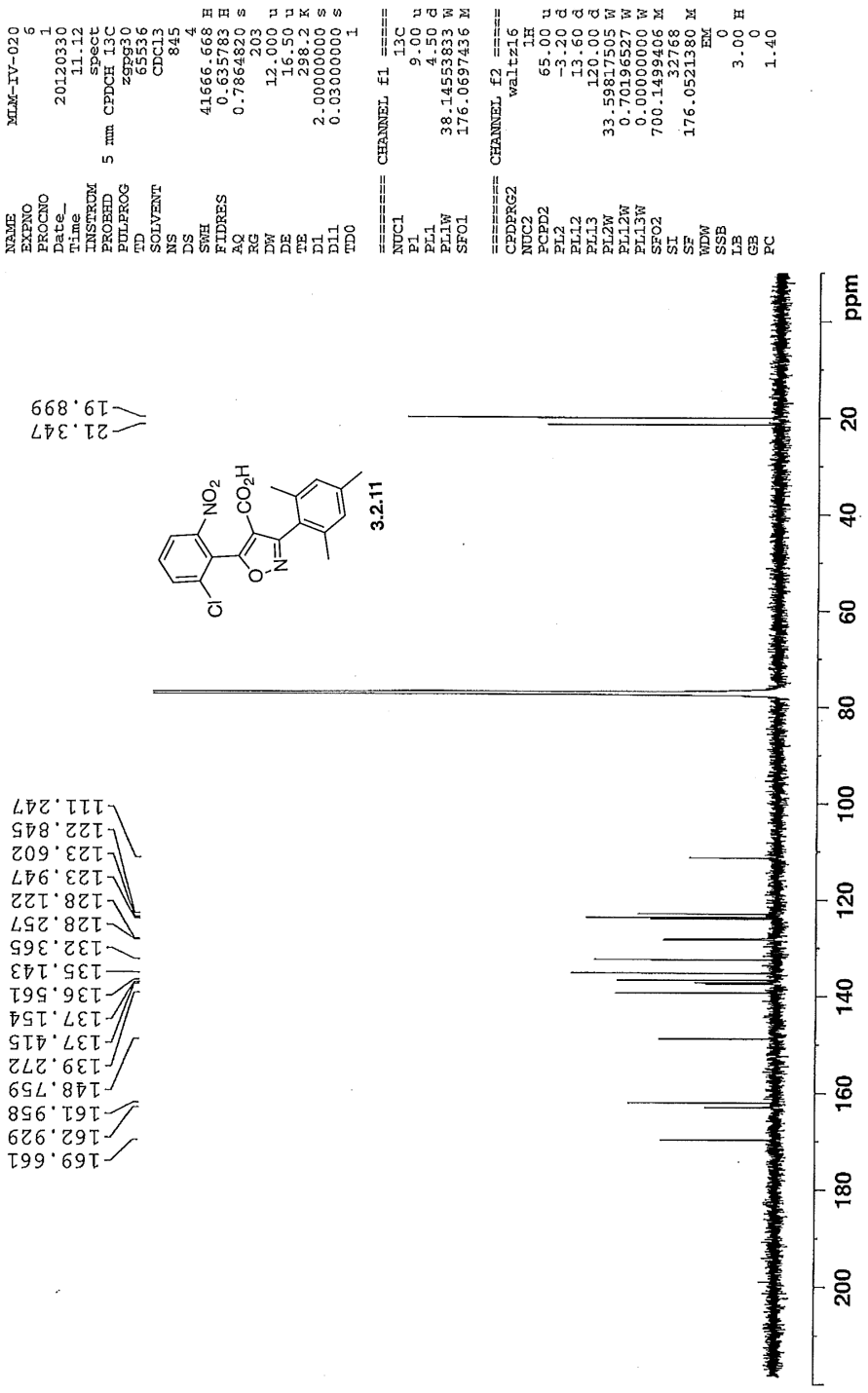

NAME MLM-V-023
EXPNO 2
PROCNO 1
Date_ 20120830
Time 12.32
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 6
DS 0
SWH 7183.908 H
FIDRES 0.219235 H
AQ 2.2807028 s
RG 161.3
DW 69.600 u
DE 6.50 u
TE 298.2 K
D1 2.00000000 s
TD0 1
CHANNEL f1
NUC1 1H
P1 14.00 u
PL1 0.00 d
SFO1 400.1428010 M
SI 32768
SF 400.1400000 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
1.022
1.041
1.059
1.747
1.766
1.784
1.803
1.821
1.840
2.749
2.768
2.787
6.406
7.282
7.587
7.608
7.628
7.781
7.784
7.801
7.804
7.928
7.931
7.949
7.952
3.2.10b
Cl
NO2
O
N
3.36
2.29
2.18
0.99
1.07
1.02
1.00
ppm

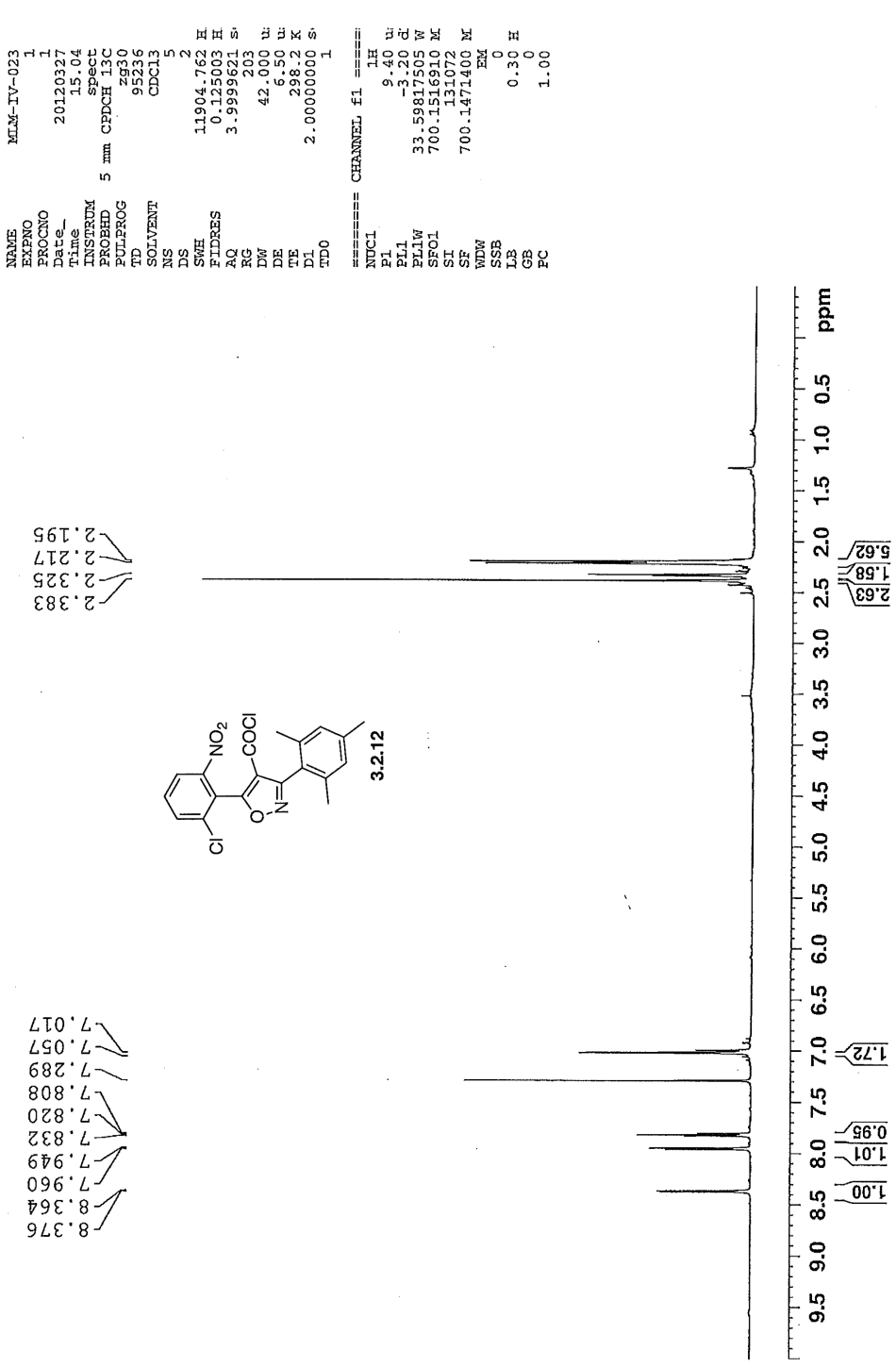

NAME MLM-V-023
EXPNO 6
PROCNO 1
Date_ 20120906
Time 11.54
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 146
DS 0
SWH 23980.814 H
FIDRES 0.365918 H
AQ 1.3664756 s
RG 32768
DW 20.850 u
DE 6.50 u
TE 298.3 K
D1 1.00000000 s
D11 0.03000000 s
TD0 1
CHANNEL f1 13C
NUC1 13C
P1 9.00 u
PL1 -2.00 d
SFO1 100.6253446 M
CHANNEL f2 1H
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 u
PL2 0.00 d
PL12 16.16 d
PL13 17.00 d
SFO2 400.1416006 M
SI 32768
SF 100.6152830 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
13.625
21.517
27.980
76.760
77.077
77.395
105.790
122.407
122.921
131.521
134.251
136.058
150.342
161.627
164.048
3.2.10b
ppm

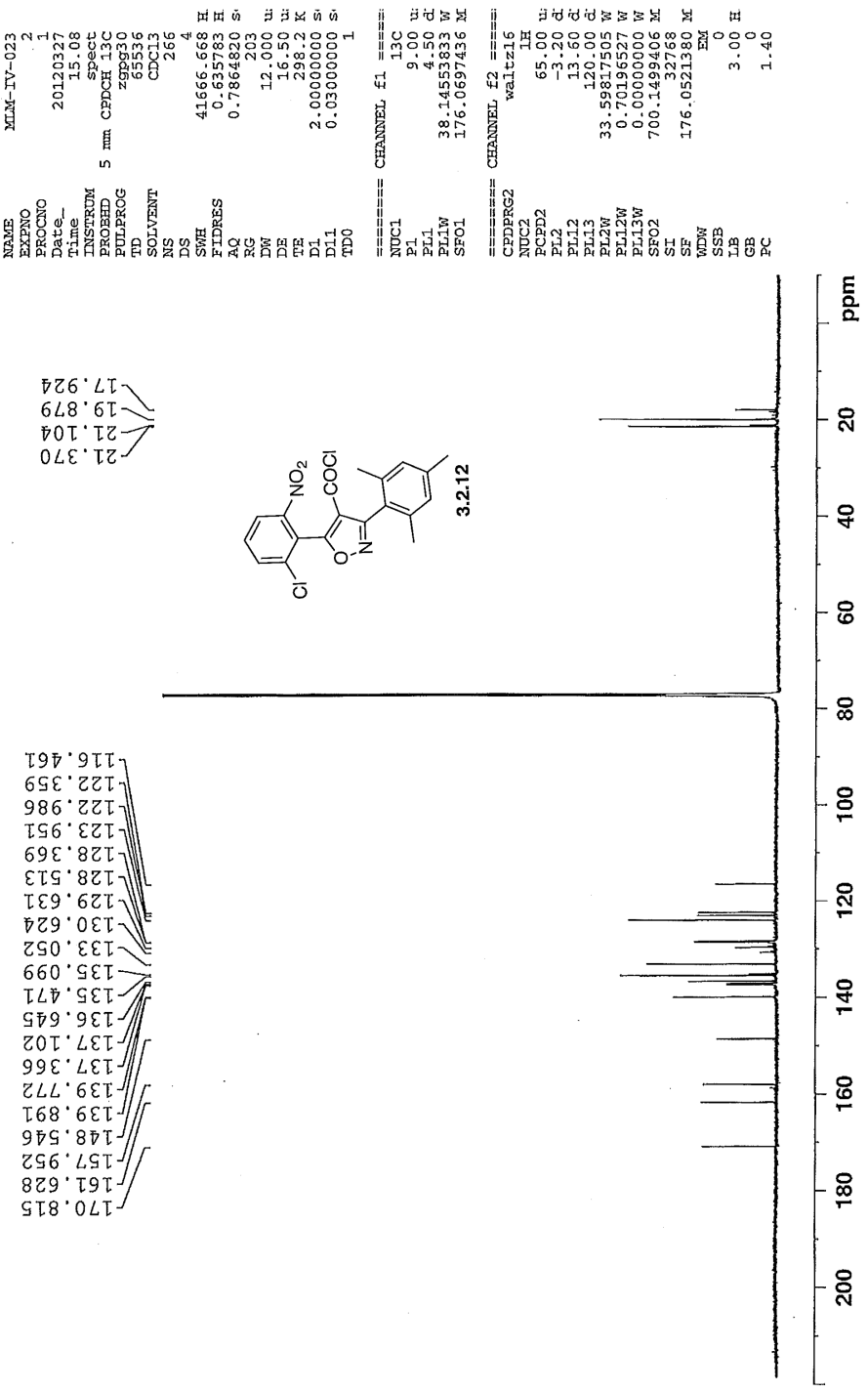

NAME MLM-V-025
EXPNO 11
PROCNO 1
Date_ 20120910
Time 15.17
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 7183.908 H
FIDRES 0.219235 H
AQ 2.2807028 s
RG 90.5
DW 69.600 u
DE 6.50 u
TE 298.2 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 14.00 u
PL1 0.00 d
SFO1 400.1428010 M
SI 32768
SF 400.1400000 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
NO2
Cl
O
N
3.2.10c
7.986
7.967
7.966
7.834
7.832
7.813
7.658
7.638
7.617
7.578
7.560
7.443
7.426
7.407
7.386
7.368
7.350
7.295
7.282
7.254
7.225
7.184
6.798
1.00
1.03
1.22
2.04
4.49
2.53
0.91
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 ppm

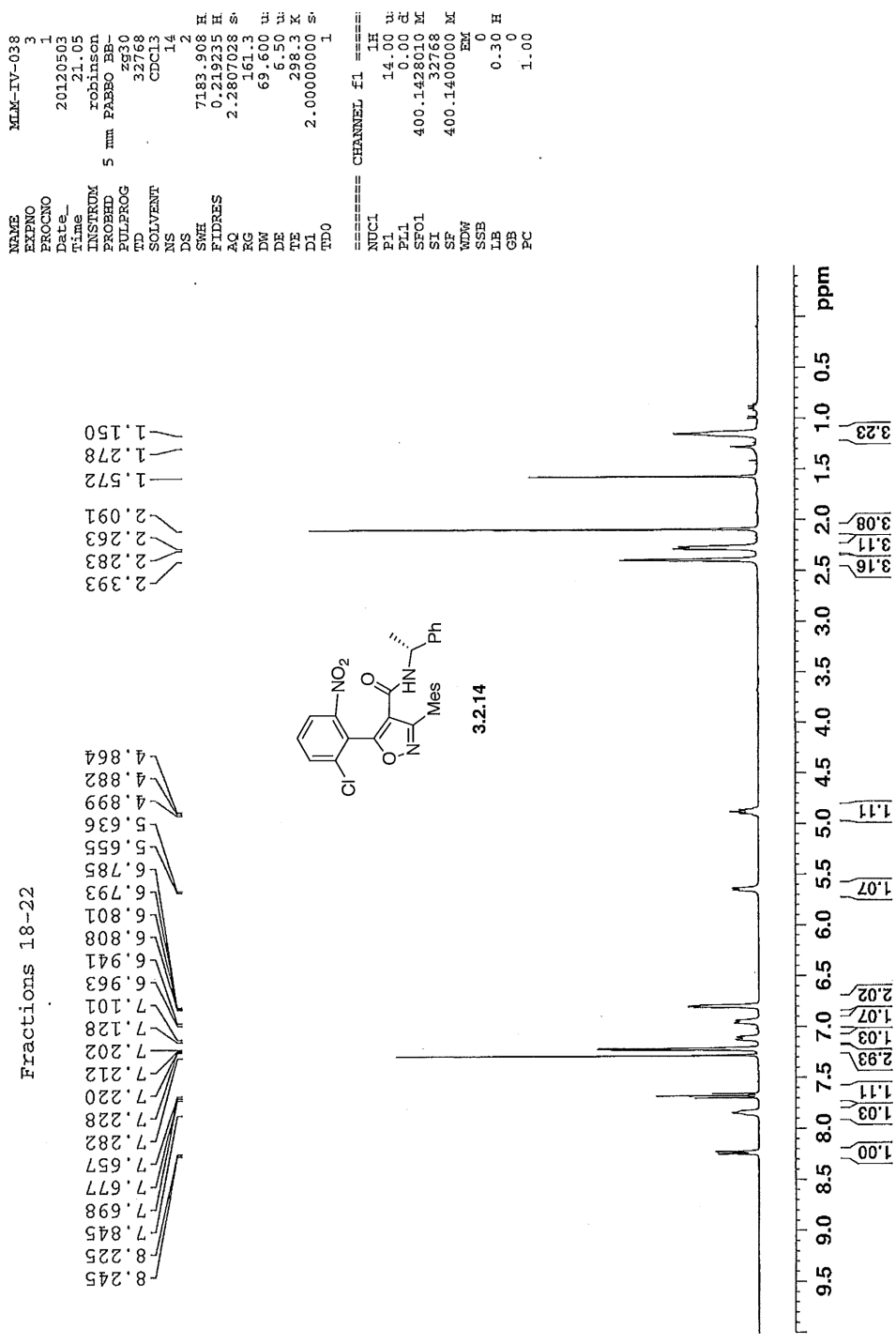

NAME MJM-V-025
EXPNO 12
PROCNO 1
Date_ 20120910
Time 15.22
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 327
DS 4
SWH 23980.814 H
FIDRES 0.365918 H
AQ 1.3664756 s
RG 32768
DW 20.850 u
DE 6.50 u
TE 299.3 K
D1 1.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 9.00 u
PL1 -2.00 d
SFO1 100.6253446 M
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 u
PL2 0.00 d
PL12 16.16 d
PL13 17.00 d
SFO2 400.1416006 M
SI 32768
SF 100.6152830 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
3.2.10c
162.017
161.876
150.374
136.610
136.256
135.685
134.364
131.720
129.104
128.902
127.094
123.047
122.095
115.622
103.349
77.370
77.052
76.735
ppm

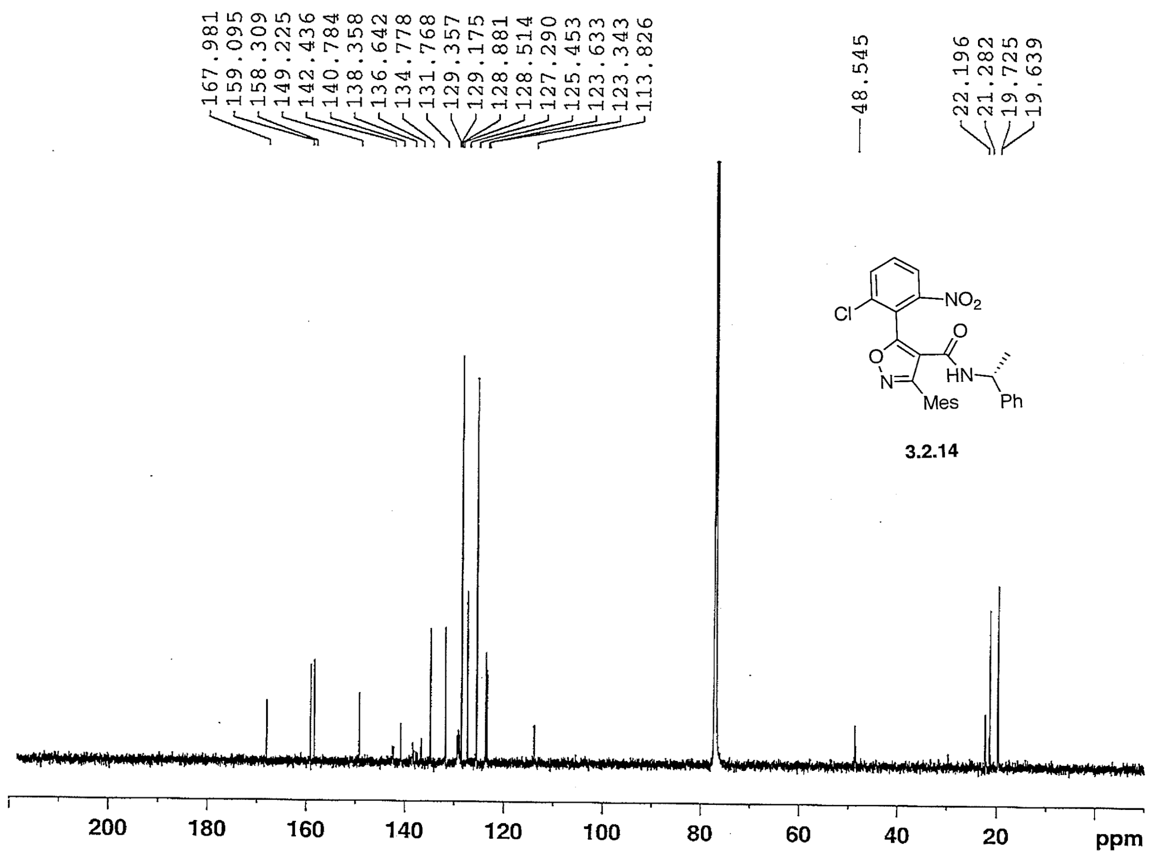

NAME MLM-IV-020
EXPNO 6
PROCNO 1
Date_ 20120329
Time 18.00
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 7183.908 H
FIDRES 0.219235 H
AQ 2.2807028 s
RG 228.1
DW 69.600 u
DE 6.50 u
TE 298.2 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 14.00 u
PL1 0.00 d
SFO1 400.1428010 M
SI 32768
SF 400.1400000 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
2.180
2.361
6.976
7.283
7.709
7.729
7.750
7.873
7.893
8.251
8.271
5.93
2.91
1.84
0.98
0.94
1.00
ppm
3.2.11


NAME MLM-IV-020
EXPNO 6
PROCNO 1
Date_ 20120330
Time 11.12
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 845
DS 4
SWH 41666.668 H
FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.2 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 =====
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0697436 M
======== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
3.2.11
21.347
19.899
111.247
122.845
123.602
123.947
128.122
128.257
132.365
135.143
136.561
137.154
137.415
139.272
148.759
161.958
162.929
169.661
ppm


NAME MLM-IV-023
EXPNO 1
PROCNO 1
Date_ 20120327
Time 15.04
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 5
DS 2
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 203
DW 42.000 u
DE 6.50 u
TE 298.2 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
NO2
COCl
Cl
3.2.12
2.383
2.325
2.217
2.195
8.376
8.364
7.960
7.949
7.832
7.820
7.808
7.289
7.057
7.017
1.00
1.01
0.95
1.72
2.63
1.58
5.62
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 ppm


NAME MLM-IV-023
EXPNO 2
PROCNO 1
Date_ 20120327
Time 15.08
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 266
DS 4
SWH 41666.668 H
FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.2 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0697436 M
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
NO2
COCl
Cl
O
N
3.2.12
21.370
21.104
19.879
17.924
116.461
122.359
122.986
123.951
128.369
128.513
129.631
130.624
133.052
135.099
135.471
136.645
137.102
137.366
139.772
139.891
148.546
157.952
161.628
170.815
ppm
200
180
160
140
120
100
80
60
40
20


NAME MLM-IV-038
EXPNO 3
PROCNO 1
Date_ 20120503
Time 21.05
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 14
DS 2
SWH 7183.908 H
FIDRES 0.219235 H
AQ 2.2807028 s
RG 161.3
DW 69.600 u
DE 6.50 u
TE 298.3 K
D1 2.00000000 s
TD0 1
CHANNEL f1 1H
NUC1 1H
P1 14.00 u
PL1 0.00 d
SFO1 400.1428010 M
SI 32768
SF 400.1400000 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
Fractions 18-22
8.245
8.225
7.845
7.698
7.677
7.657
7.282
7.228
7.220
7.212
7.202
7.128
7.101
6.963
6.941
6.808
6.801
6.793
6.785
5.655
5.636
4.899
4.882
4.864
2.393
2.283
2.263
2.091
1.572
1.278
1.150
NO2
Cl
O
HN
Ph
Mes
N
O
3.2.14
ppm
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
1.00
1.03
1.11
2.93
1.03
1.07
2.02
1.07
1.11
3.23
3.08
3.11
3.16



3.2.14

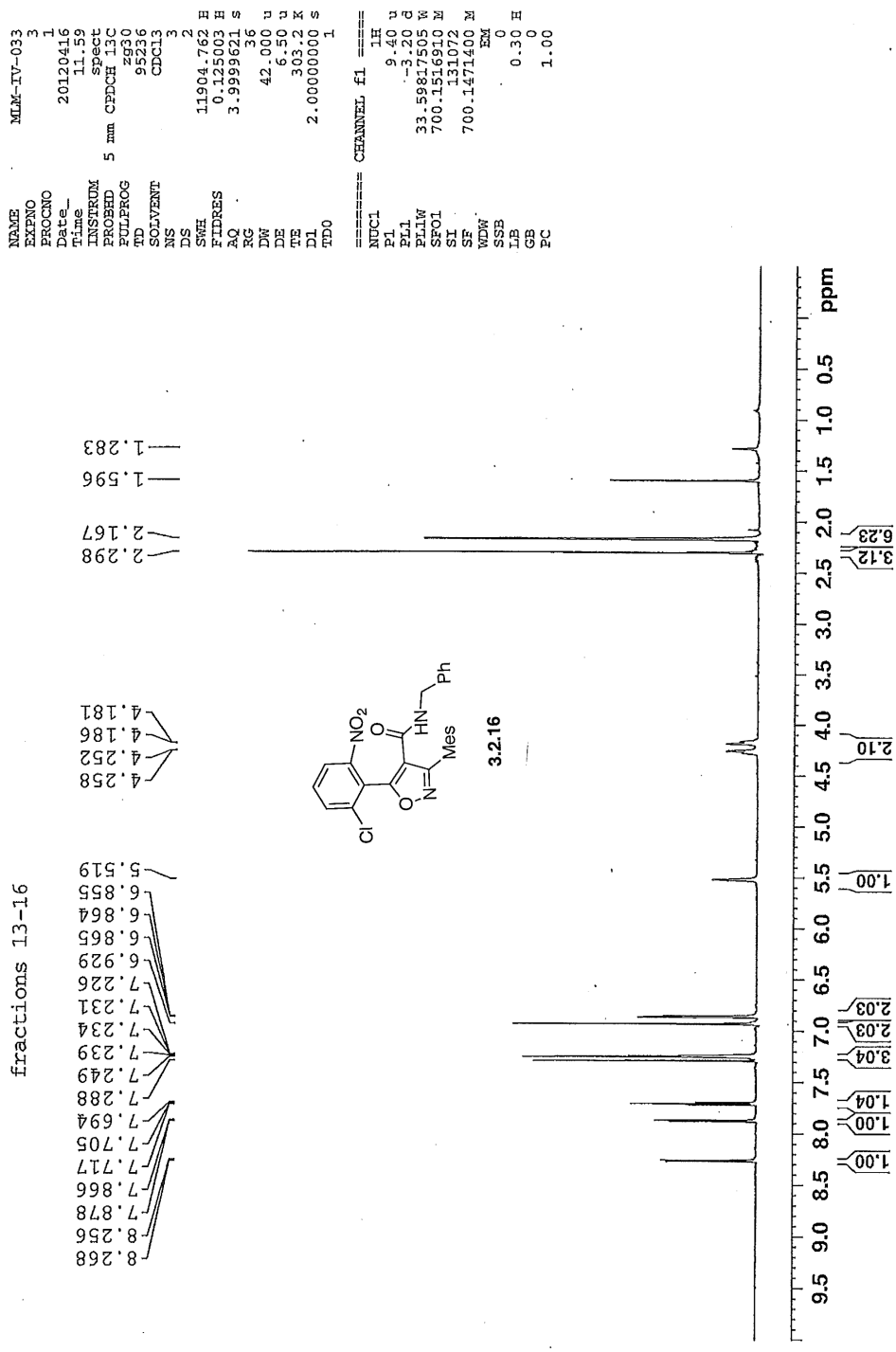
NAME	MLM-IV-038
EXPNO	6
PROCNO	1
Date_	20120503
Time	21.36
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	239
DS	4
SWH	41666.668 H
FIDRES	0.635783 H
AQ	0.7864820 s
RG	203
DW	12.000 u
DE	16.50 u
TE	298.2 K
D1	2.00000000 s
D11	0.03000000 s
TD0	1

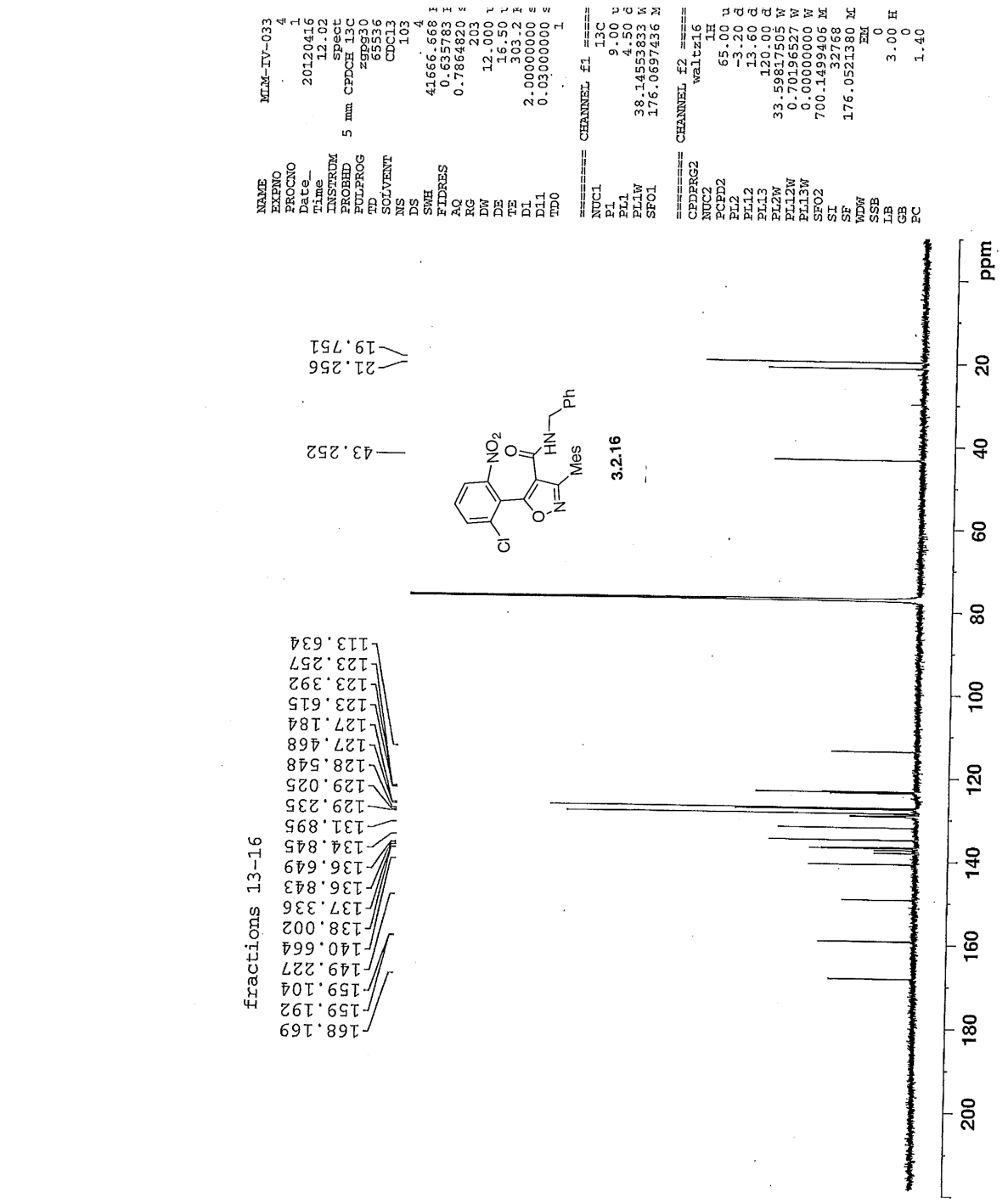
======== CHANNEL f1 =====

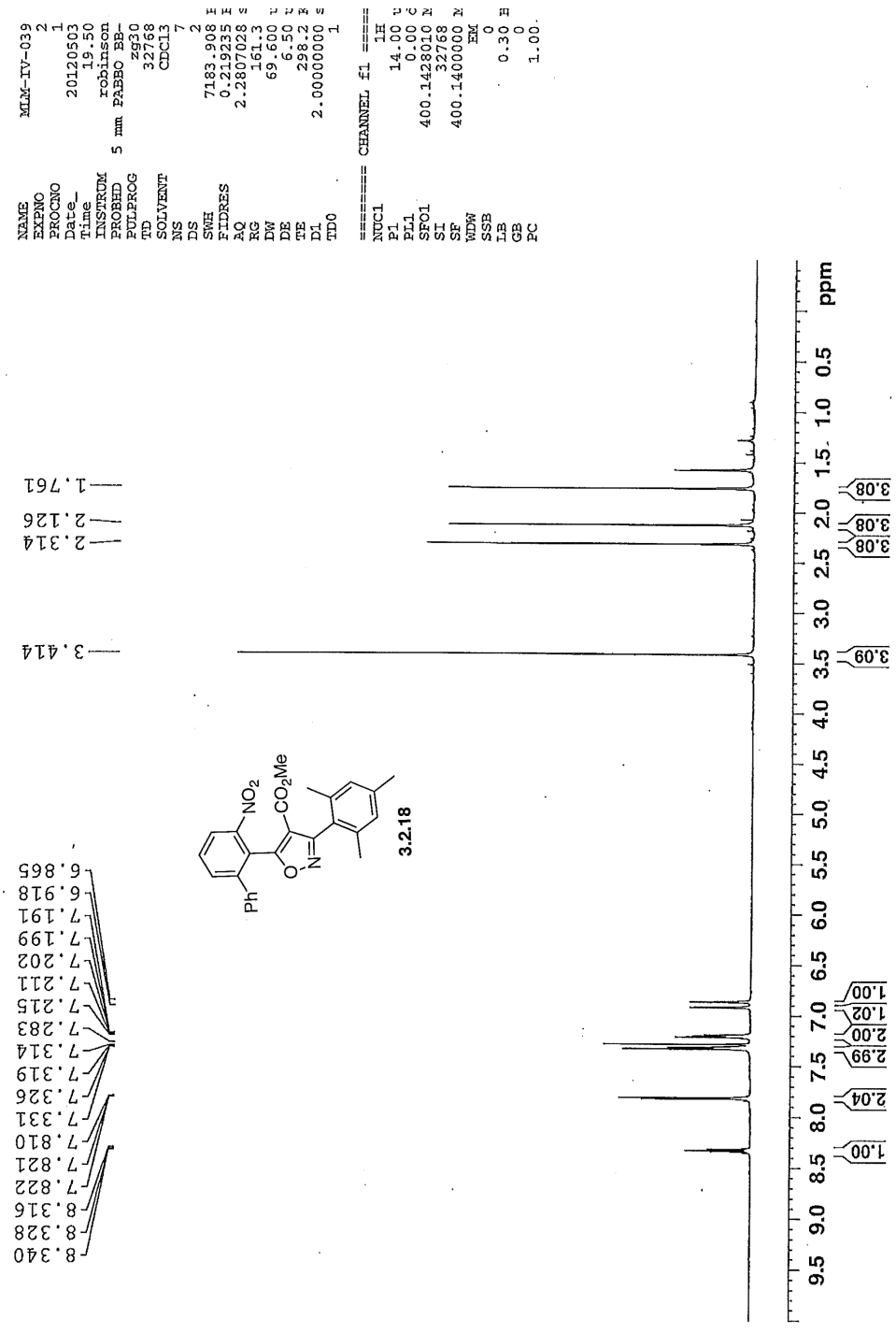
NUC1	13C
P1	9.00 u
PL1	4.50 d
PL1W	38.14553833 W
SFO1	176.0697436 M

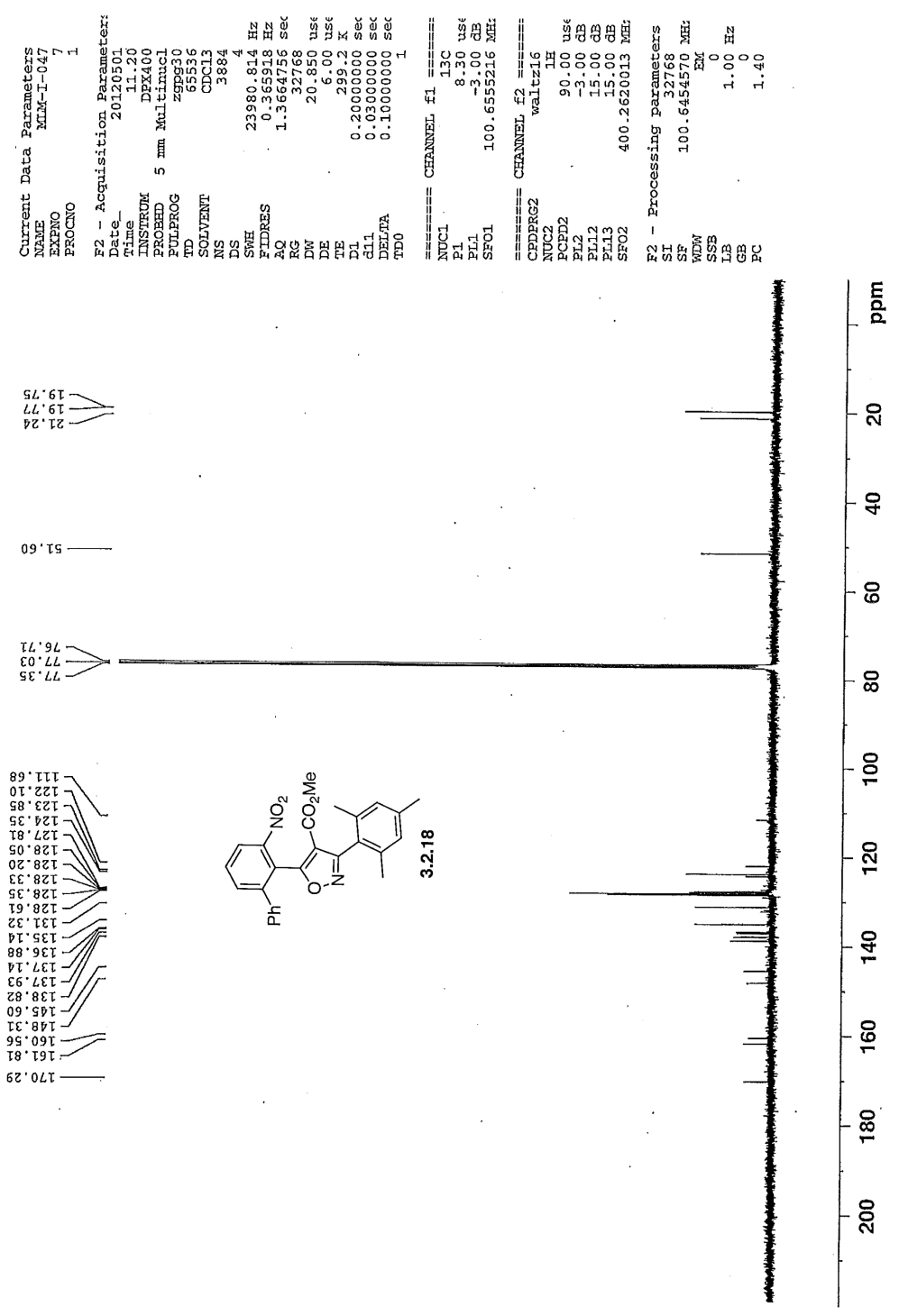
======== CHANNEL f2 =====

CPDPRG2	waltz16
NUC2	1H
PCPD2	65.00 u
PL2	-3.20 d
PL12	13.60 d
PL13	120.00 d
PL2W	33.59817505 W
PL12W	0.70196527 W
PL13W	0.00000000 W
SFO2	700.1499406 M
SI	32768
SF	176.0521380 M
WDW	EM
SSB	0
LB	3.00 H
GB	0
PC	1.40

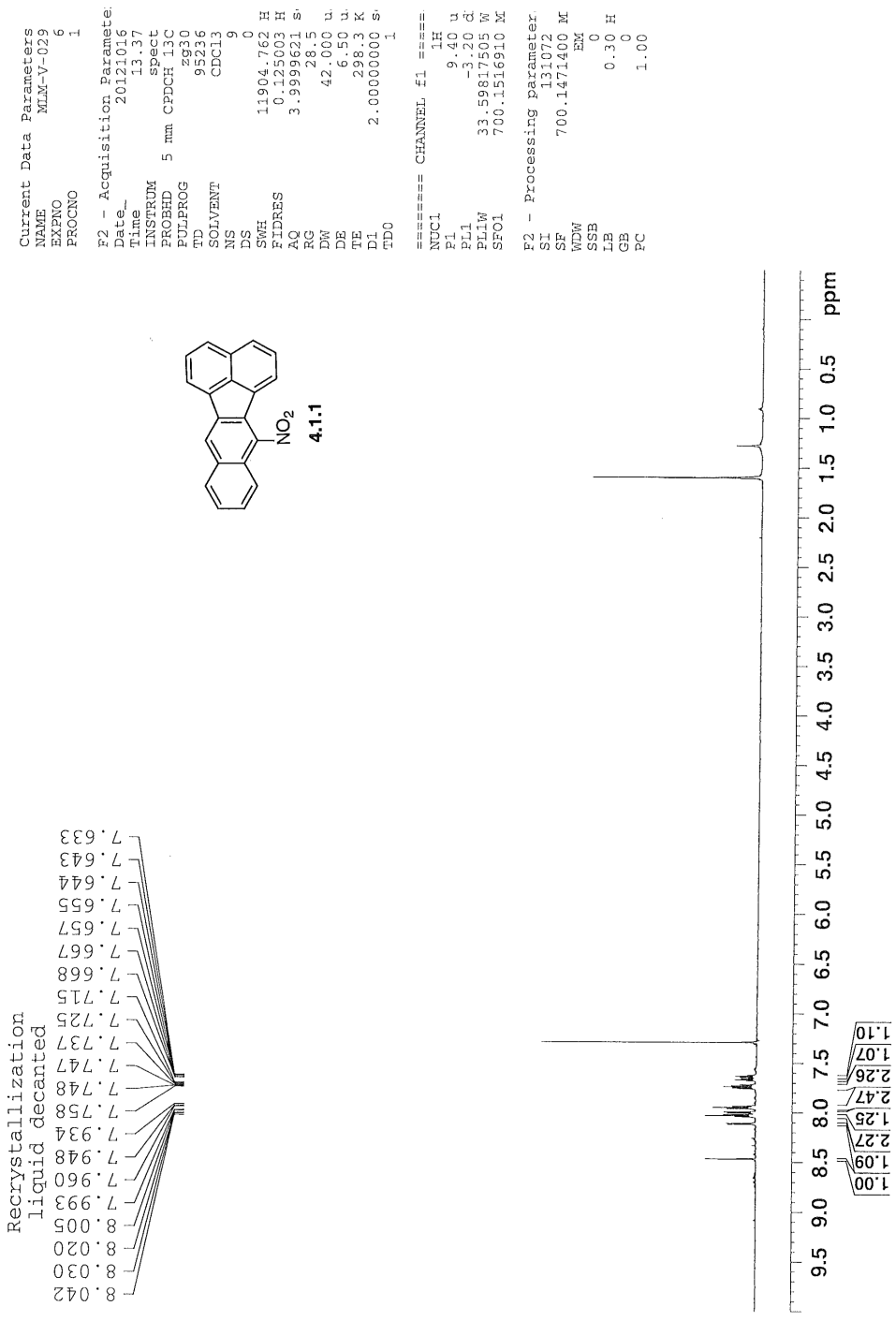

NAME MIM-IV-033
EXPNO 3
PROCNO 1
Date_ 20120416
Time 11.59
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 3
DS 2
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 36
DW 42.000 u
DE 6.50 u
TE 303.2 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PLlW 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
fractions 13-16
8.268
8.256
7.878
7.866
7.717
7.705
7.694
7.288
7.249
7.239
7.234
7.231
7.226
6.929
6.865
6.864
6.855
5.519
4.258
4.252
4.186
4.181
2.298
2.167
1.596
1.283
3.2.16
Ph
HN
Mes
N
O
O
NO2
Cl
ppm
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
1.00
1.00
1.04
2.03
2.03
3.04
1.00
2.10
3.12
6.23

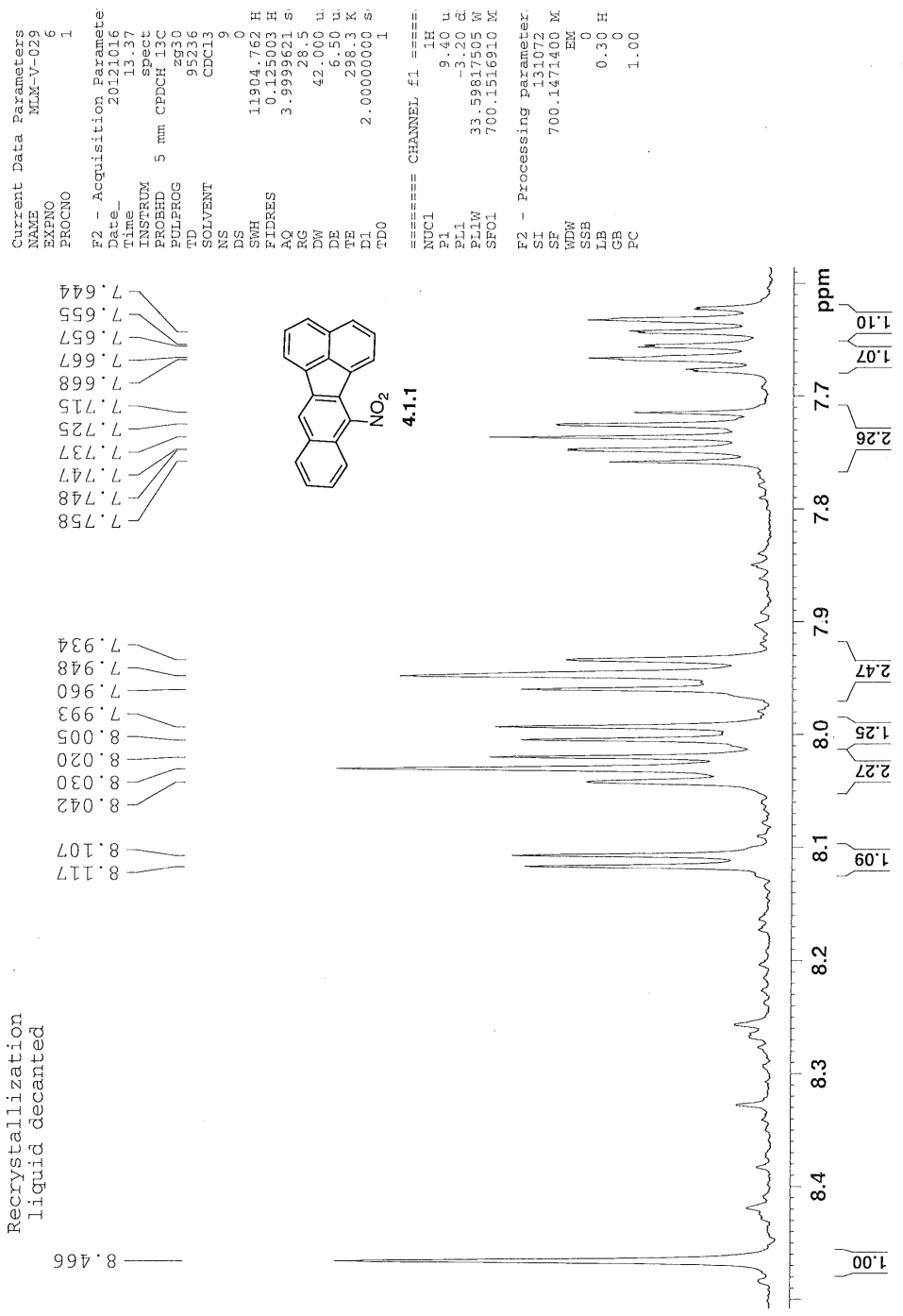

fractions 13-16
168.169
159.192
159.104
149.227
140.664
138.002
137.336
136.843
136.649
134.845
131.895
129.235
129.025
128.548
127.468
127.184
123.615
123.392
123.257
113.634
43.252
21.256
19.751
3.2.16
ppm
20
40
60
80
100
120
140
160
180
200


NAME MLM-IV-039
EXPNO 2
PROCNO 1
Date_ 20120503
Time 19.50
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 7
DS 2
SWH 7183.908 H
FIDRES 0.219235 H
AQ 2.2807028 s
RG 161.3
DW 69.600 u
DE 6.50 u
TE 298.2 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 14.00 u
PL1 0.00 d
SFO1 400.1428010 M
SI 32768
SF 400.1400000 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
1.761
2.126
2.314
3.414
8.340
8.328
8.316
7.822
7.821
7.810
7.331
7.326
7.319
7.314
7.283
7.215
7.211
7.202
7.199
7.191
6.918
6.865
NO2
CO2Me
Ph
3.2.18
ppm
3.08
3.08
3.08
3.09
1.00
2.04
2.99
2.00
1.02
1.00

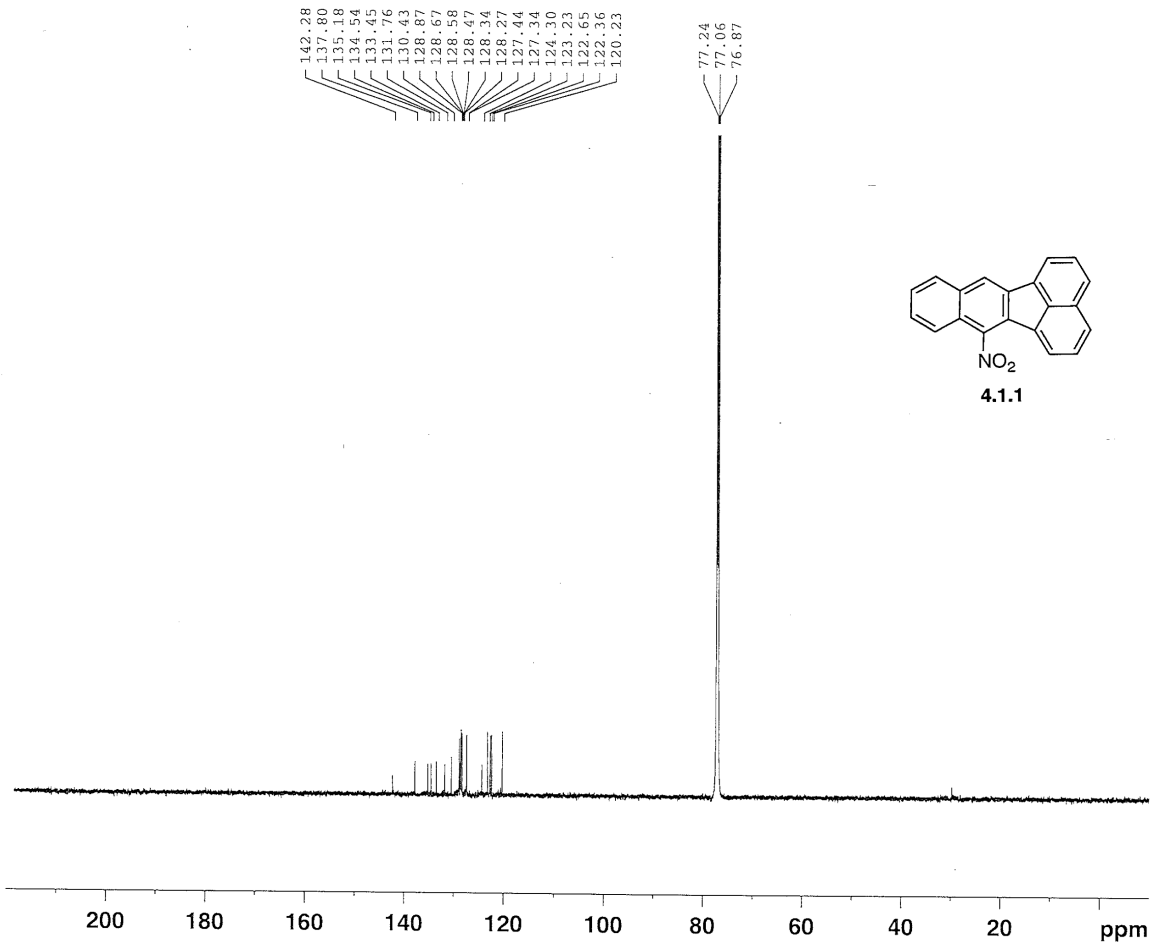

Current Data Parameters
NAME MIM-I-047
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20120501
Time 11.20
INSTRUM DPX400
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3884
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.36664756 sec
RG 32768
DW 20.850 use
DE 6.00 use
TE 299.2 K
D1 0.20000000 sec
d11 0.03000000 sec
DELTA 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.30 use
PL1 -3.00 dB
SFO1 100.6555216 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 use
PL2 -3.00 dB
PL12 15.00 dB
PL13 15.00 dB
SFO2 400.2620013 MHz
F2 - Processing parameters
SI 32768
SF 100.6454570 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
21.24
19.77
19.75
51.60
77.35
77.03
76.71
111.68
122.10
123.85
124.35
127.81
128.05
128.20
128.33
128.35
128.61
131.32
135.14
136.88
137.14
137.93
138.82
145.60
148.31
160.56
161.81
170.29
NO2
CO2Me
Ph
3.2.18
200
180
160
140
120
100
80
60
40
20
ppm

Section 6.3. NPAH NMR Spectra




Current Data Parameters
NAME MLM-V-029
EXPNO 6
PROCNO 1
F2 - Acquisition Parameter
Date_ 20121016
Time_ 13.37
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDC13
NS 9
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 28.5
DW 42.000 u
DE 6.50 u
TE 298.3 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
F2 - Processing parameter
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
Recrystallization
liquid decanted
8.466
8.117
8.107
8.042
8.030
8.020
8.005
7.993
7.960
7.948
7.934
7.758
7.748
7.747
7.737
7.725
7.715
7.668
7.667
7.657
7.655
7.644
NO2
4.1.1
ppm
1.00
1.09
2.27
1.25
2.47
7.9
8.0
8.1
8.2
8.3
8.4
2.26
1.07
1.10
7.7
7.8

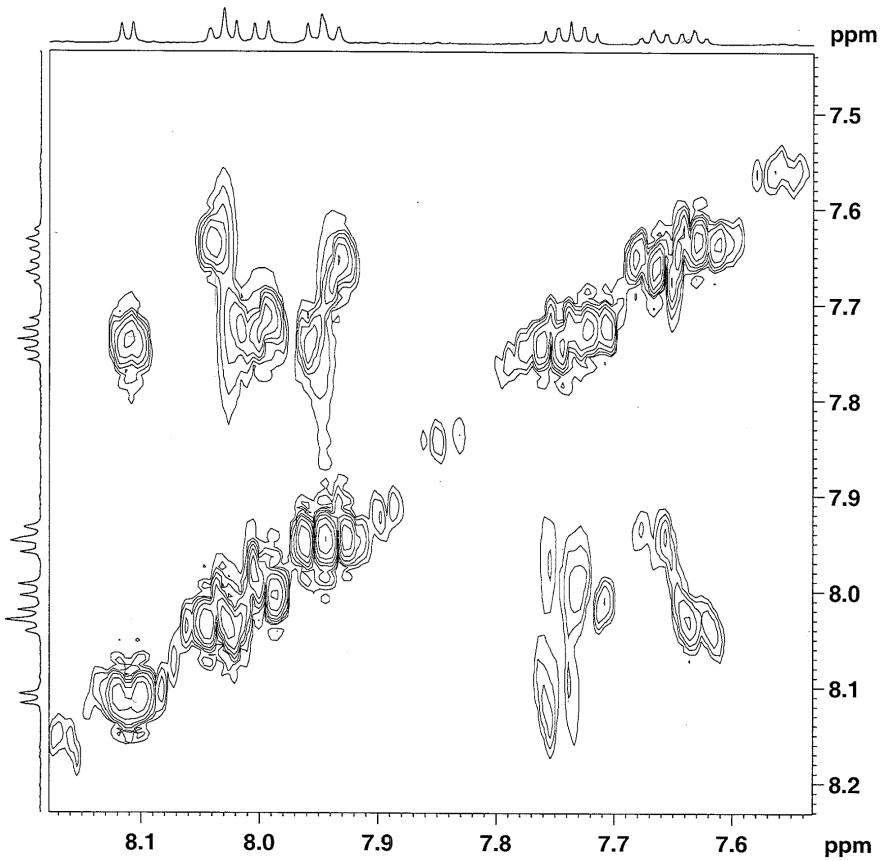
Recrystallization
liquid decanted



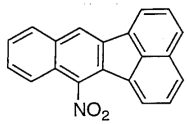
4.1.1

```
Current Data Parameters
NAME                  MLM-V-029
EXPNO                         7
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20121016
Time                      13.40
INSTRUM                   spect
PROBHD    5 mm CPDCH 13C
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         320
DS                           0
SWH                  41666.668 Hz
FIDRES                0.635783 Hz
AQ                    0.7864820 sec
RG                         203
DW                      12.000 usec
DE                      16.50 usec
TE                      298.2 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                        9.00 usec
PL1                       4.50 dB
PL1W                38.14553833 W
SFO1               176.0697436 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    65.00 usec
PL2                      -3.20 dB
PL12                     13.60 dB
PL13                    120.00 dB
PL2W                33.59817505 W
PL12W                0.70196527 W
PL13W                0.00000000 W
SFO2               700.1499406 MHz

F2 - Processing parameters
SI                         32768
SF                 176.0521380 MHz
WDW                           EM
SSB                           0
LB                         3.00 Hz
GB                            0
PC                         1.40
```

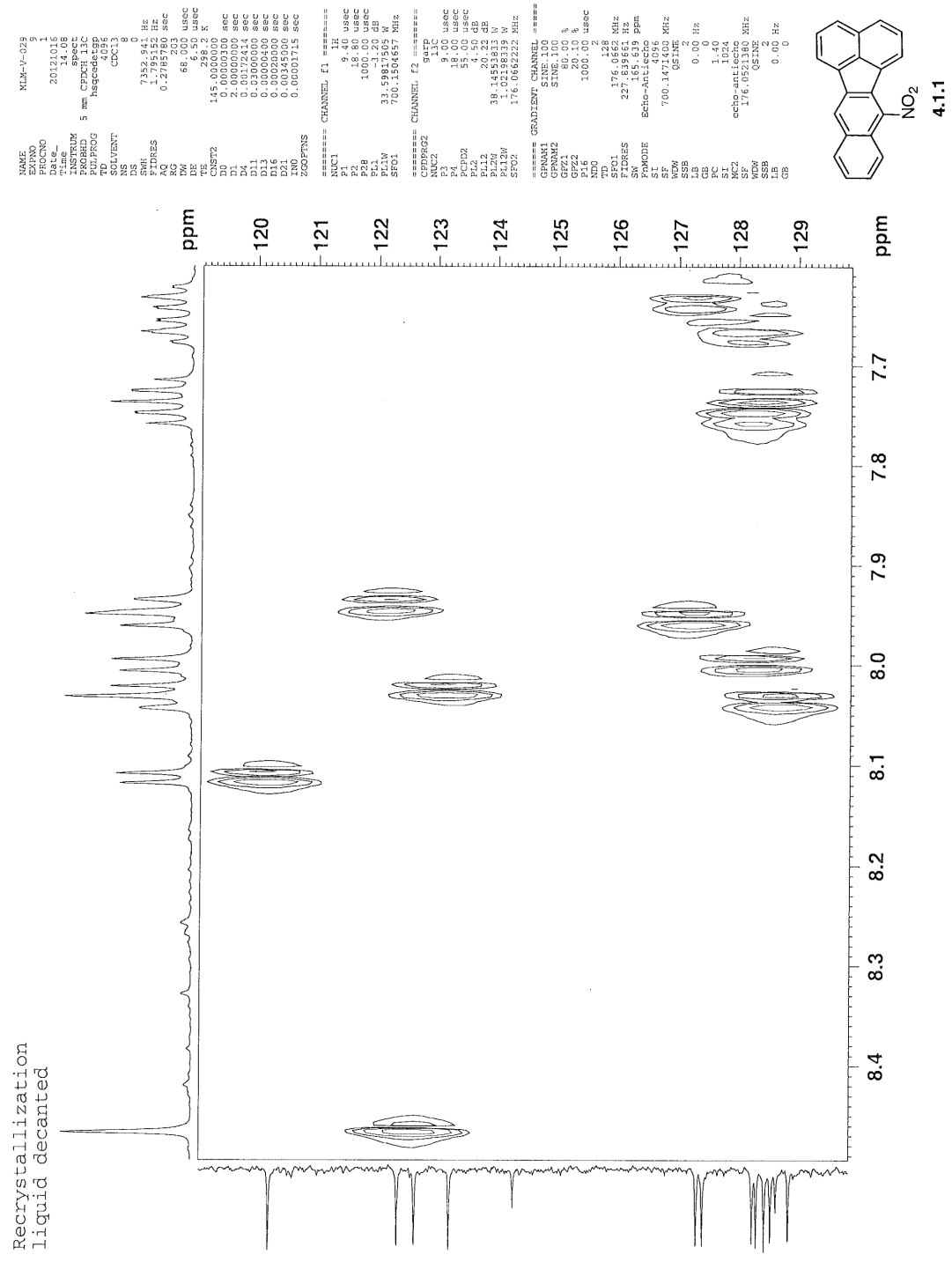
Recrystallization
liquid decanted

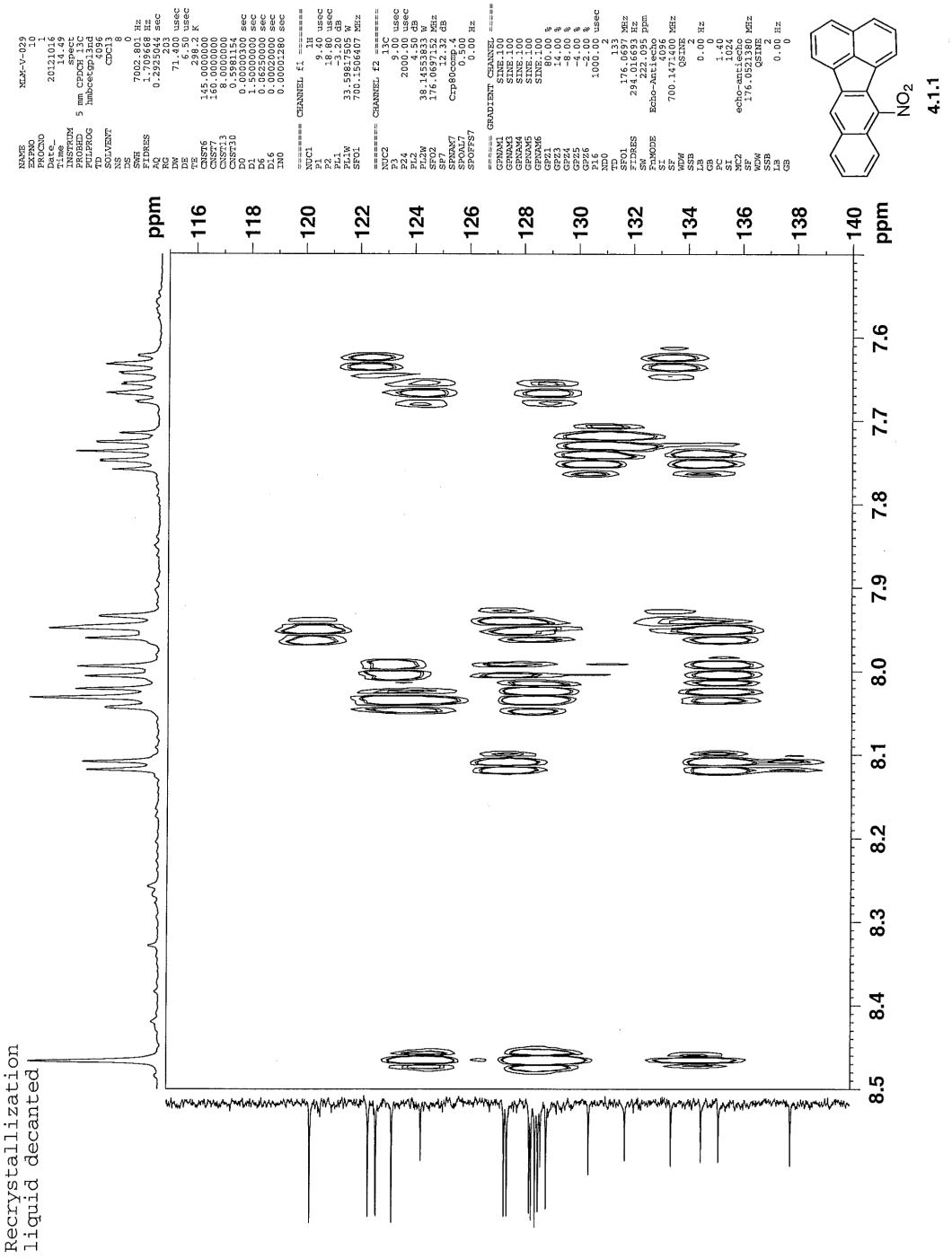


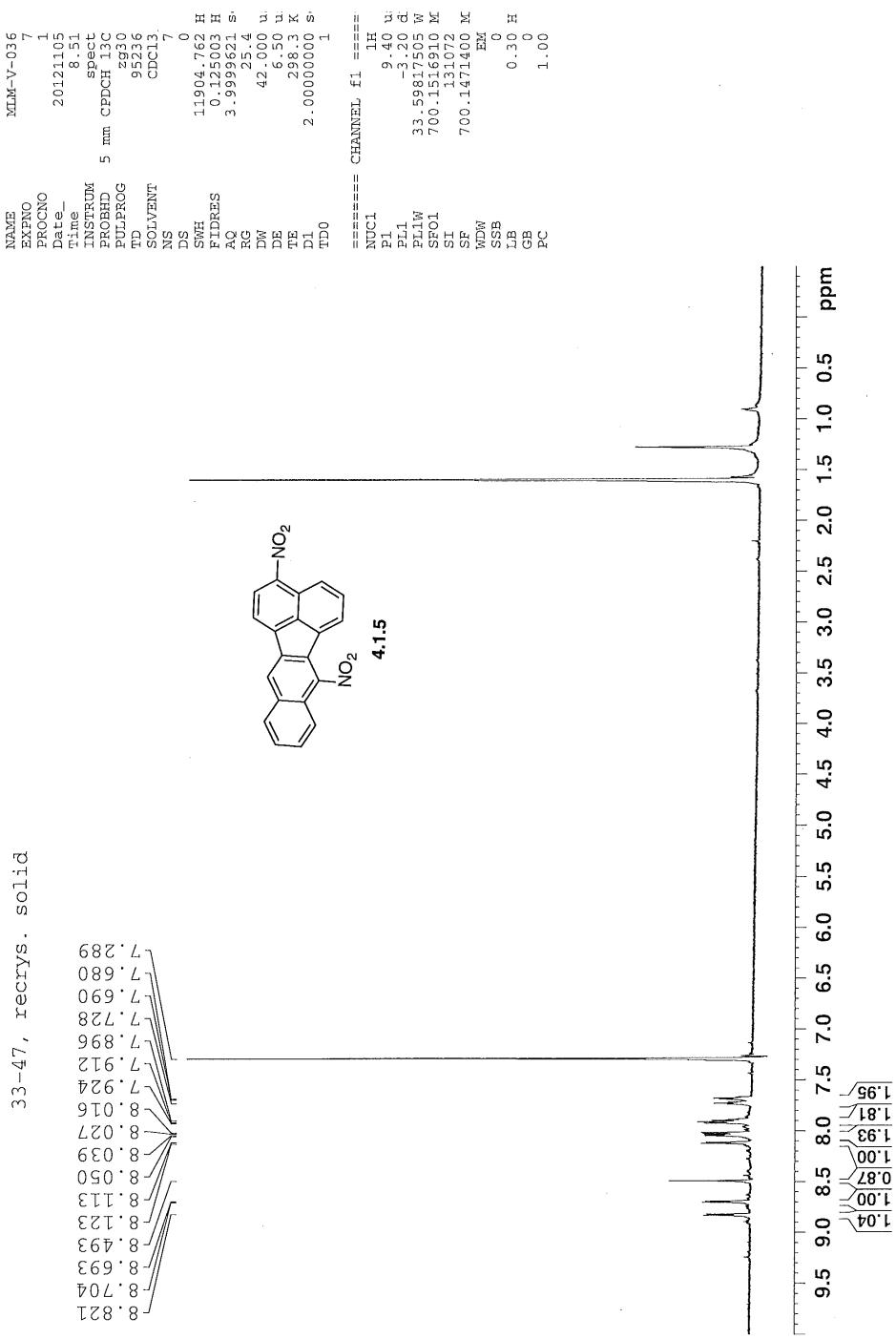
NAME	MLM-V-029	
EXPNO	8	
PROCNO	1	
Date_	20121016	
Time	13.56	
INSTRUM	spect	
PROBHD	5 mm CPDCH 13C	
PULPROG	cosygpqf	
TD	2048	
SOLVENT	CDCl3	
NS	2	
DS	4	
SWH	7352.941	Hz
FIDRES	3.590303	Hz
AQ	0.1393140	sec
RG	203	
DW	68.000	usec
DE	6.50	usec
TE	298.2	K
D0	0.00000300	sec
D1	2.00000000	sec
D13	0.00000400	sec
D16	0.00020000	sec
IN0	0.00013600	sec
======== CHANNEL f1 ========		
NUC1	1H	
P0	9.40	usec
P1	9.40	usec
PL1	-3.20	dB
PL1W	33.59817505	W
SFO1	700.1502907	MHz
====== GRADIENT CHANNEL =====		
GPNAM1	SINE.100	
GPZ1	80.00	%
P16	1000.00	usec
ND0	1	
TD	128	
SFO1	700.1503	MHz
FIDRES	57.444843	Hz
SW	10.502	ppm
FnMODE	QF	
SI	2048	
SF	700.1471400	MHz
WDW	SINE	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.40	
SI	2048	
MC2	QF	
SF	700.1471400	MHz
WDW	SINE	
SSB	0	
LB	0.00	Hz
GB	0	

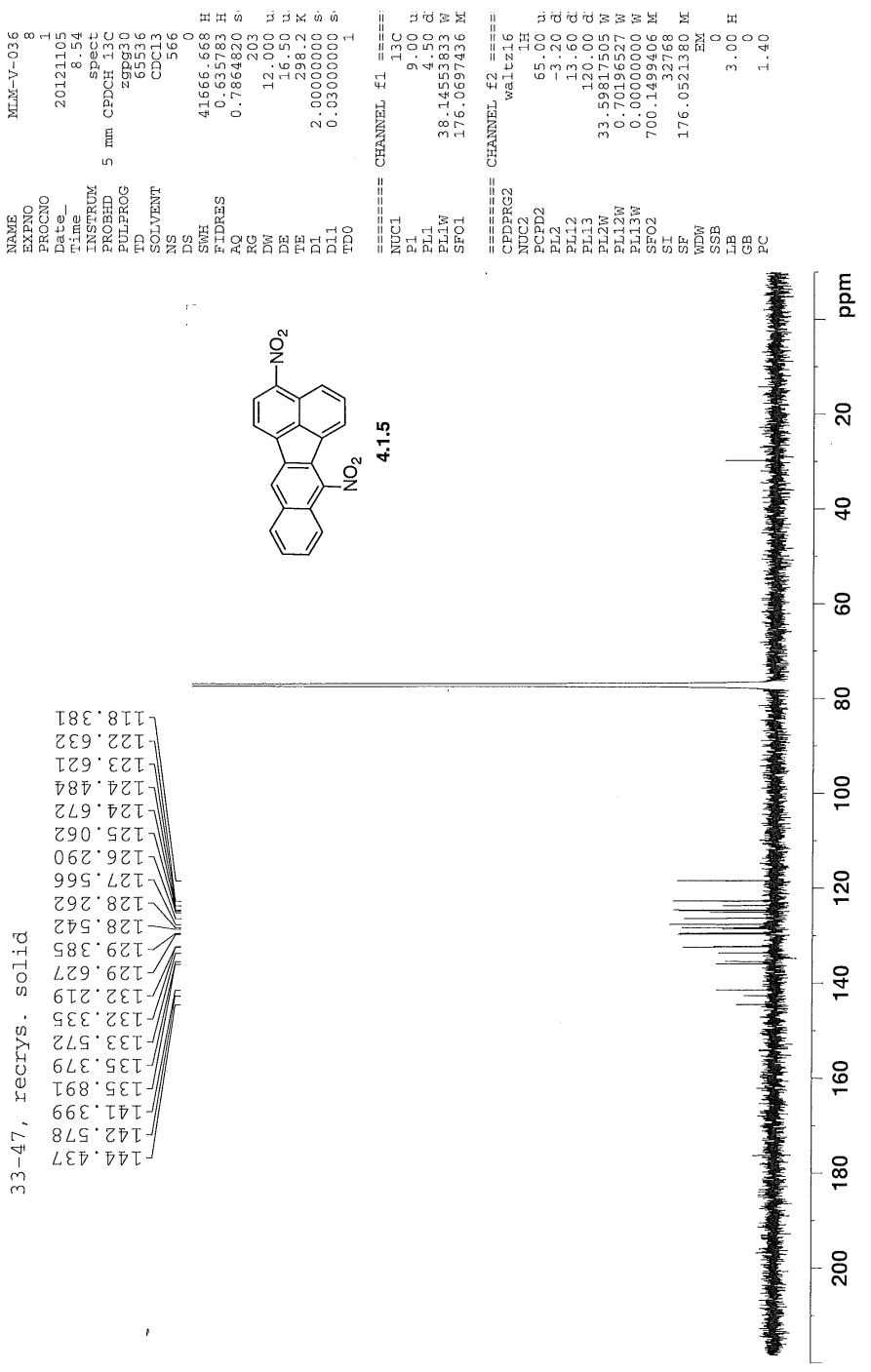


4.1.1

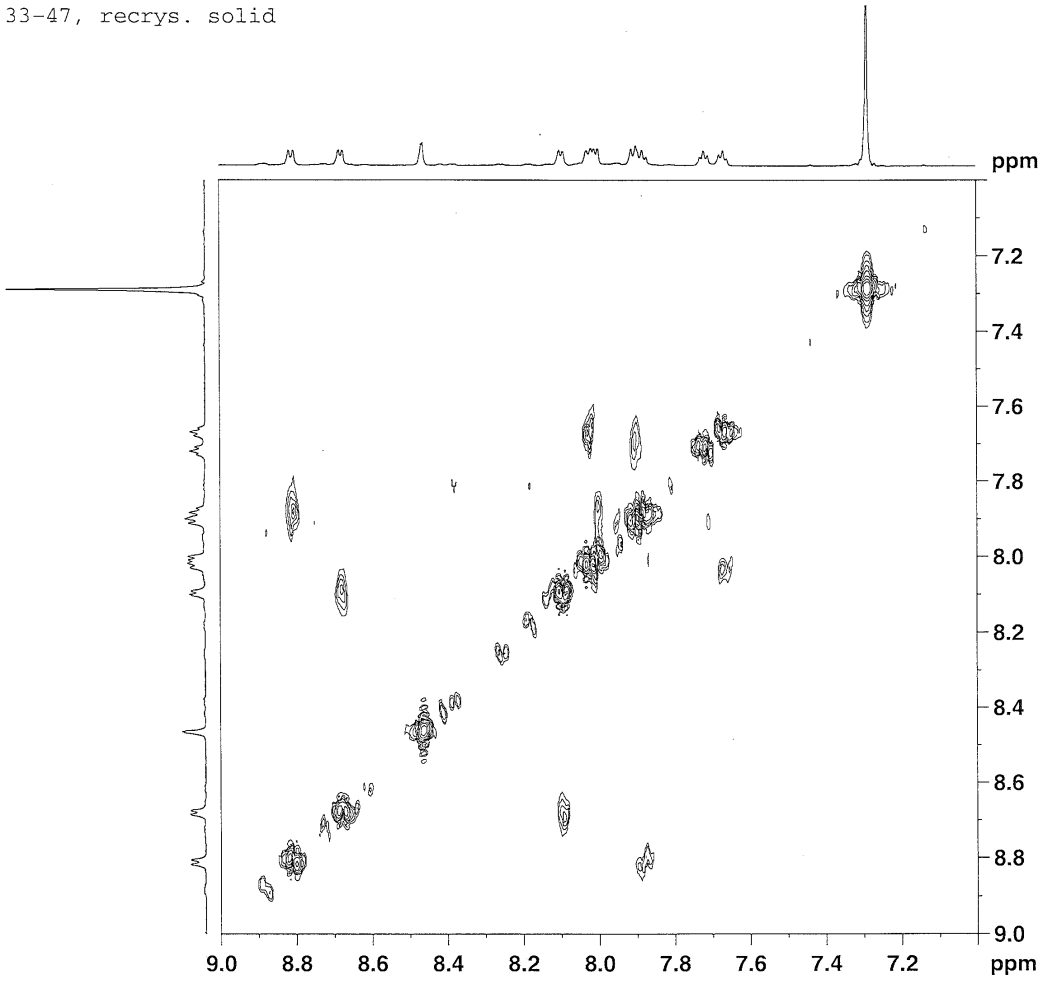

Recrystallization
liquid decanted
ppm
120
121
122
123
124
125
126
127
128
129
7.7
7.8
7.9
8.0
8.1
8.2
8.3
8.4
NAME MLM-V-029
EXPNO 9
PROCNO 1
Date_ 20121016
Time 14.08
INSTRUM spect
PROBHD 5 mm CPPSPECIAL 13C
PULPROG hsqcedetgp
TD 4096
SOLVENT CDCl3
NS 8
DS 16
SWH 7352.941 Hz
FIDRES 1.795152 Hz
AQ 0.2785780 sec
RG 203
DW 68.000 usec
DE 6.50 usec
TE 298.2 K
CNST2 145.0000000
D0 0.00000300 sec
D1 2.00000000 sec
D4 0.00172414 sec
D11 0.03000000 sec
D13 0.00000400 sec
D16 0.00020000 sec
D21 0.00345000 sec
IN0 0.00001715 sec
ZGOPTNS
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
P21 1800.00 usec
P2B 1000.00 usec
PL1 -1.20 dB
PL1W 33.59817505 W
SFO1 700.1504657 MHz
======== CHANNEL f2 ========
CPDPRG2 garp
NUC2 13C
P3 9.00 usec
P4 18.00 usec
PCPD2 55.00 usec
PL2 4.50 dB
PL12 20.22 dB
PL2W 38.14553833 W
PL12W 1.02198839 W
SFO2 176.0662222 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 80.00 %
GPZ2 100.00 %
P16 1000.00 usec
NDO 2
TD 128
SFO1 176.0662 MHz
FIDRES 227.783951 Hz
SW 165.639 ppm
PROMODE Echo-Antiecho
SI 4096
SF 700.1471400 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.40
SI 1024
MC2 echo-antiecho
SF 176.0521380 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
NO2
4.1.1


Recrystallization
liquid decanted
ppm
116
118
120
122
124
126
128
130
132
134
136
138
140
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
NO2
4.1.1

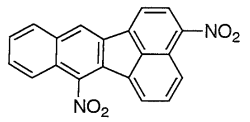

NAME MLM-V-036
EXPNO 7
PROCNO 1
Date_ 20121105
Time 8.51
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 7
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 25.4
DW 42.000 u
DE 6.50 u
TE 298.3 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
33-47, recrys. solid
8.821
8.704
8.693
8.493
8.123
8.113
8.050
8.039
8.027
8.016
7.924
7.912
7.896
7.728
7.690
7.680
7.289
NO2
NO2
4.1.5
ppm
1.04
1.00
0.87
1.00
1.93
1.81
1.95


NAME MLM-V-036
EXPNO 8
PROCNO 1
Date_ 20121105
Time 8.54
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 566
DS 0
SWH 41666.668 H
FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.2 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0697436 M
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
NO2
NO2
4.1.5
33-47, recrys. solid
144.437
142.578
141.399
135.891
135.379
133.572
132.335
132.219
129.627
129.385
128.542
128.262
127.566
126.290
125.062
124.672
124.484
123.621
122.632
118.381
200
180
160
140
120
100
80
60
40
20
ppm

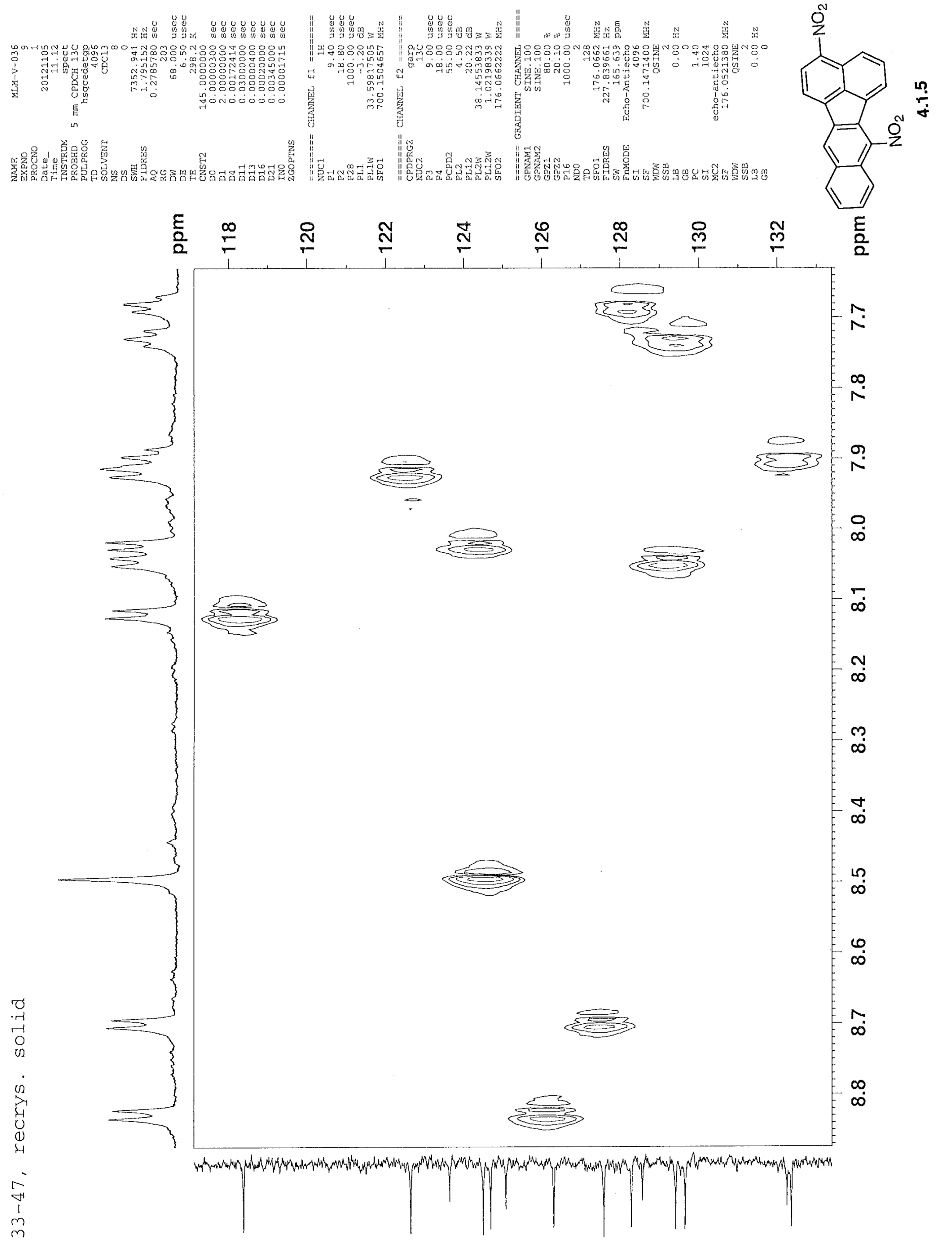
33-47, recrys. solid

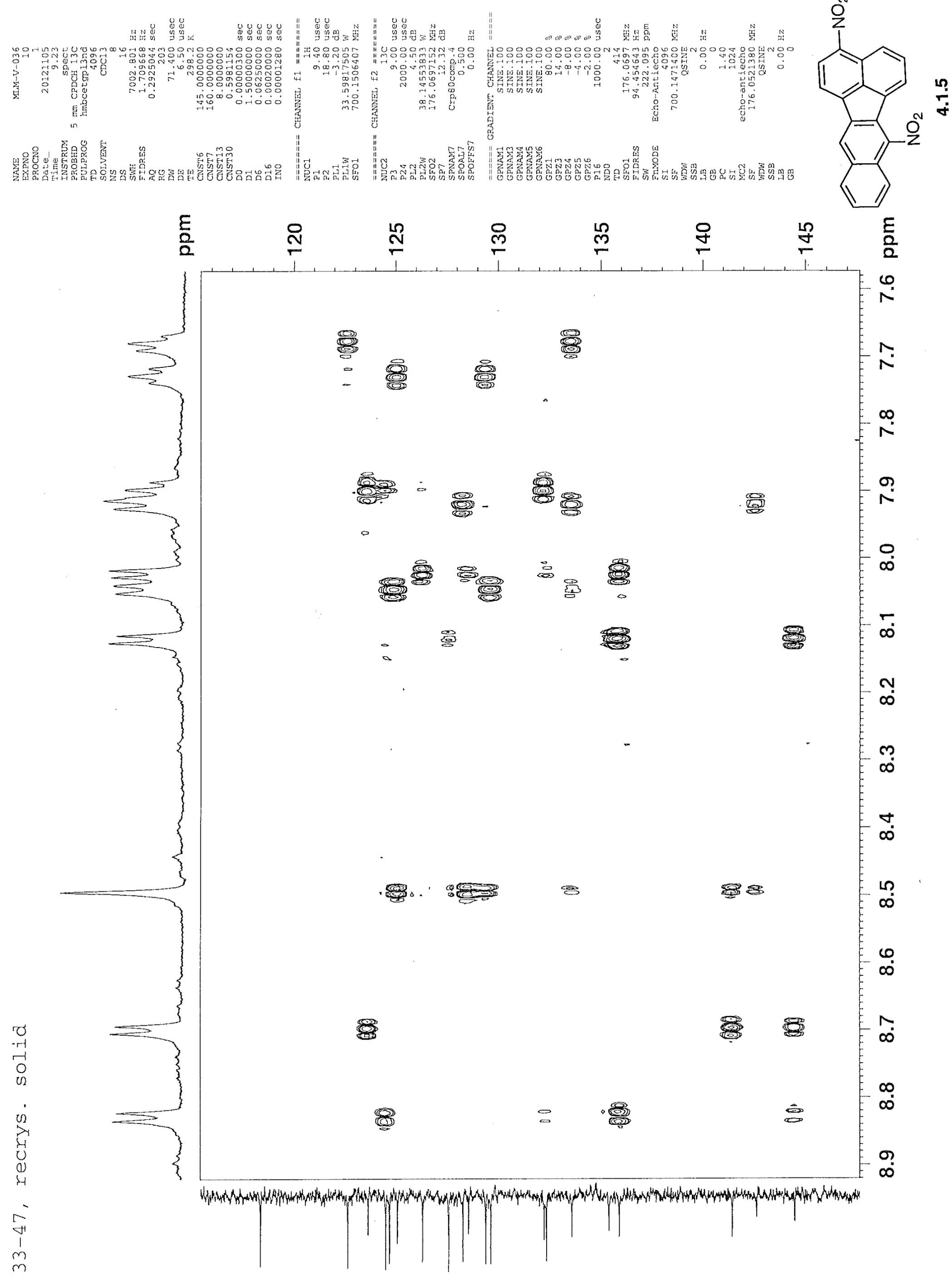


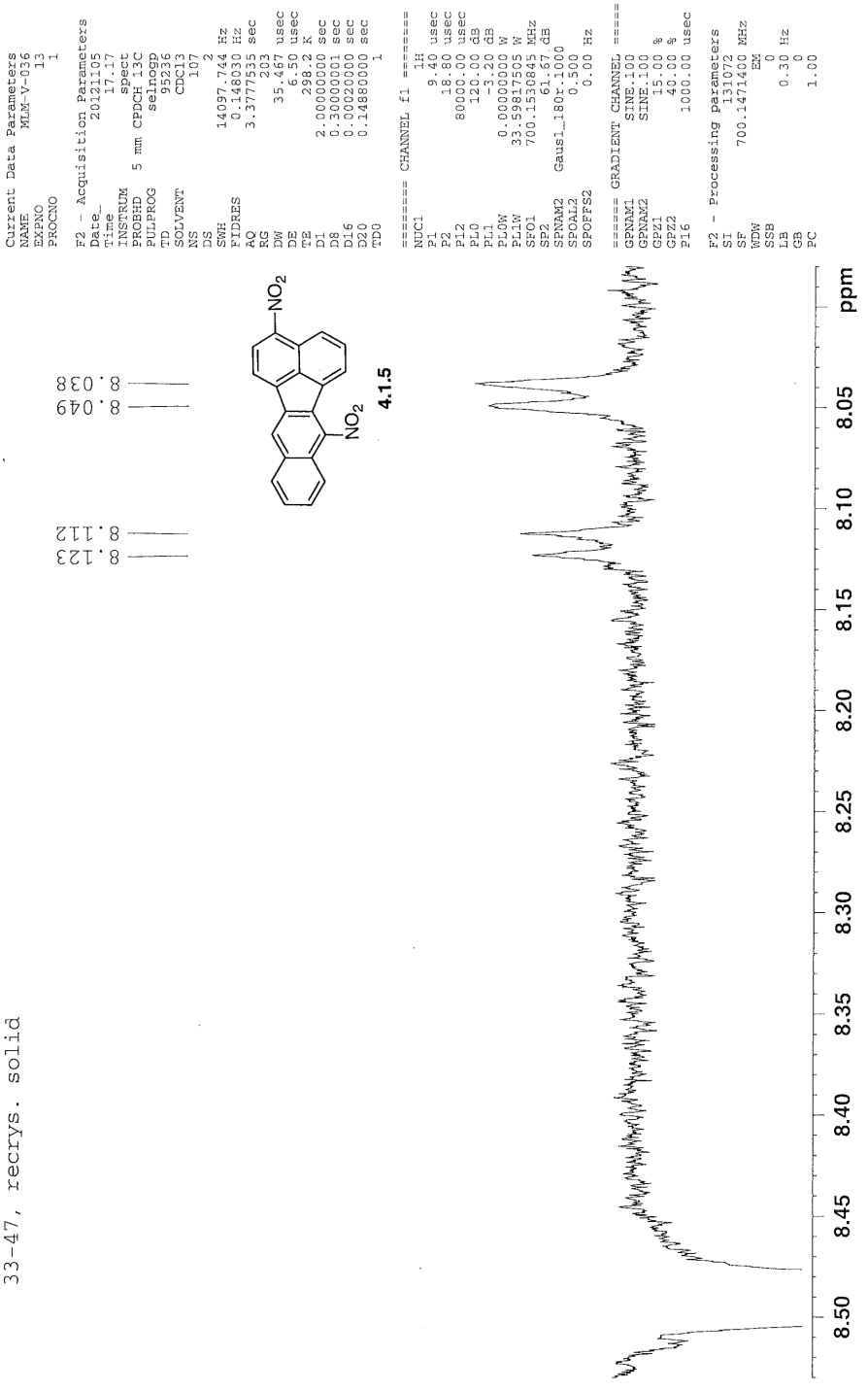
NAME	MLM-V-036	
EXPNO	1005	
PROCNO	1	
Date_	20121101	
Time	17.00	
INSTRUM	spect	
PROBHD	5 mm CPDCH 13C	
PULPROG	cosygpqf	
TD	2048	
SOLVENT	CDCl3	
NS	2	
DS	0	
SWH	7352.941	Hz
FIDRES	3.590303	Hz
AQ	0.1393140	sec
RG	203	
DW	68.000	usec
DE	6.50	usec
TE	298.2	K
D0	0.00000300	sec
D1	2.00000000	sec
D13	0.00000400	sec
D16	0.00020000	sec
IN0	0.00013600	sec
======== CHANNEL f1 ========		
NUC1	1H	
P0	9.40	usec
P1	9.40	usec
PL1	-3.20	dB
PL1W	33.59817505	W
SFO1	700.1502907	MHz
======= GRADIENT CHANNEL =====		
GPNAM1	SINE.100	
GPZ1	80.00	%
P16	1000.00	usec
ND0	1	
TD	128	
SFO1	700.1503	MHz
FIDRES	57.444843	Hz
SW	10.502	ppm
FnMODE	QF	
SI	2048	
SF	700.1471400	MHz
WDW	SINE	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.00	
SI	2048	
MC2	QF	
SF	700.1471400	MHz
WDW	SINE	
SSB	0	
LB	0.00	Hz
GB	0	

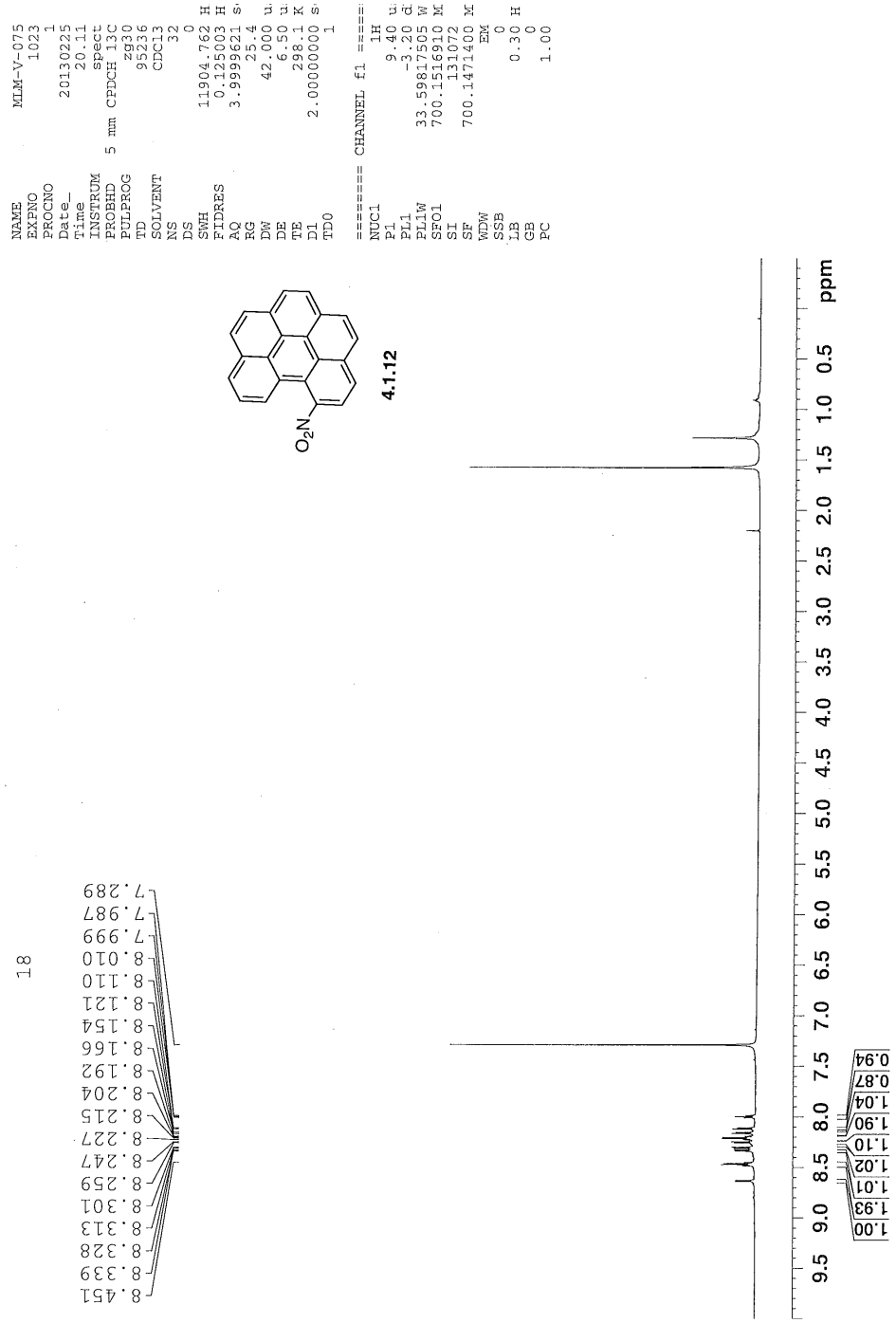


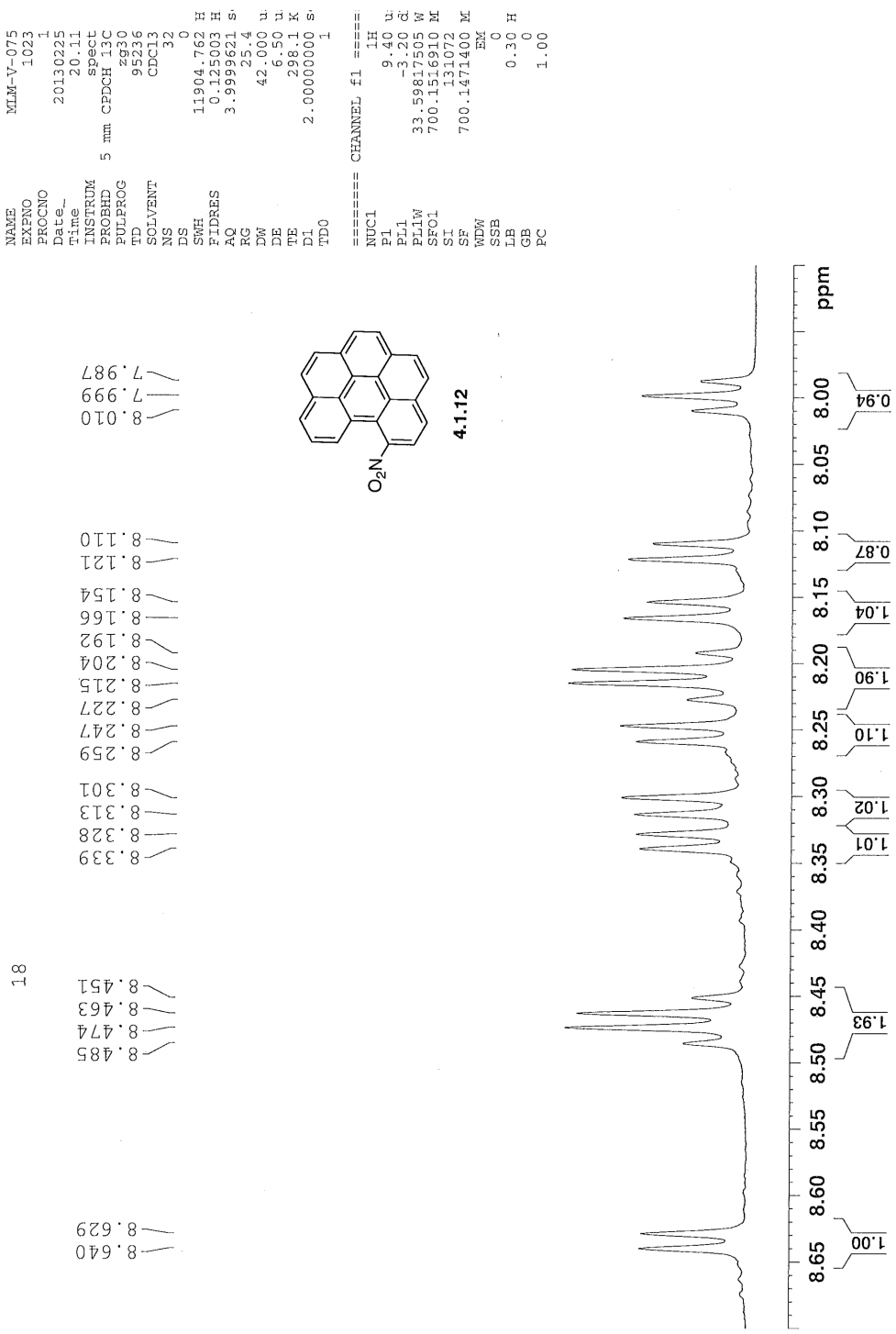
4.1.5

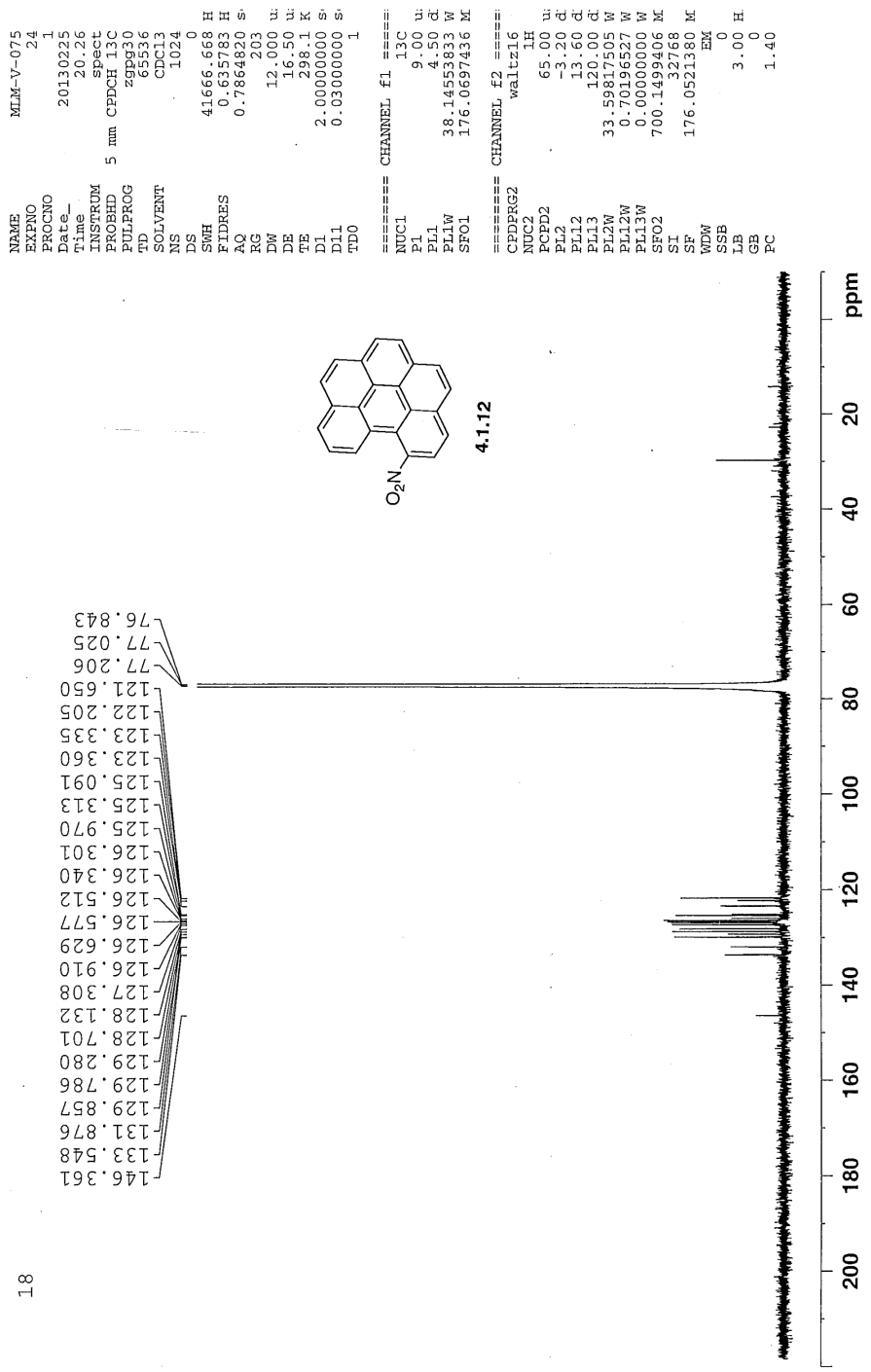

33-47, recrys. solid
ppm
4.1.5
NO2
NO2

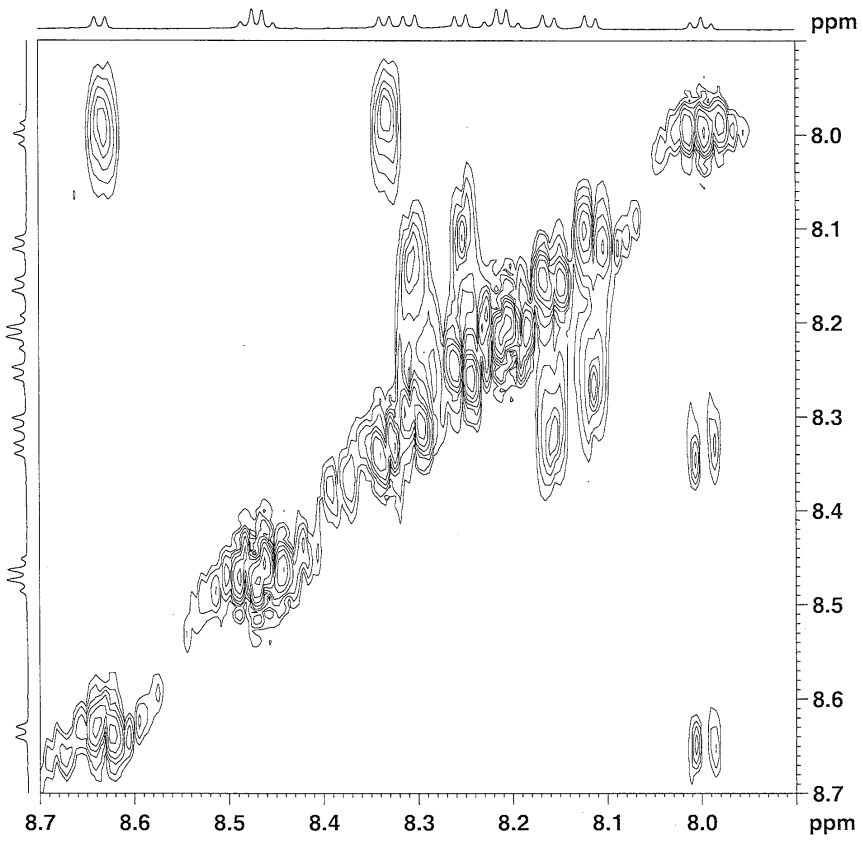

33-47, recrys. solid
ppm
NO2
NO2
4.1.5


33-47, recrys. solid
Current Data Parameters
NAME MLM-V-036
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20121105
Time 17.17
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG selnogp
TD 95236
SOLVENT CDCl3
NS 107
DS 2
SWH 14097.744 Hz
FIDRES 0.148030 Hz
AQ 3.3777535 sec
RG 203
DW 35.467 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
D8 0.30000001 sec
D16 0.00020000 sec
D20 0.14880000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
P2 18.80 usec
P12 80000.00 usec
PL0 120.00 dB
PL1 -3.20 dB
PL0W 0.00000000 W
PL1W 33.59817505 W
SFO1 700.1530845 MHz
SP2 61.67 dB
SPNAM2 Gaus1_180r.1000
SPOAL2 0.500
SPOFFS2 0.00 Hz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 15.00 %
GPZ2 40.00 %
P16 1000.00 usec
F2 - Processing parameters
SI 131072
SF 700.1471400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.123
8.112
8.049
8.038
NO2
NO2
4.1.5
8.50
8.45
8.40
8.35
8.30
8.25
8.20
8.15
8.10
8.05
ppm

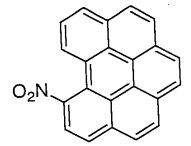

NAME MLM-V-075
EXPNO 1023
PROCNO 1
Date_ 20130225
Time 20.11
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 32
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 25.4
DW 42.000 u
DE 6.50 u
TE 298.1 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
O2N
4.1.12
18
8.451
8.339
8.328
8.313
8.301
8.259
8.247
8.227
8.215
8.204
8.192
8.166
8.154
8.121
8.110
8.010
7.999
7.987
7.289
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 ppm
1.00
1.93
1.01
1.02
1.10
1.90
1.04
0.87
0.94


NAME MLM-V-075
EXPNO 1023
PROCNO 1
Date_ 20130225
Time_ 20.11
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 32
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 25.4
DW 42.000 u
DE 6.50 u
TE 298.1 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 =====
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
4.1.12
ppm
8.65 8.60 8.55 8.50 8.45 8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00
1.00 1.93 1.01 1.02 1.10 1.90 1.04 0.87 0.94
8.640 8.629 8.485 8.474 8.463 8.451 8.339 8.328 8.313 8.301 8.259 8.247 8.227 8.215 8.204 8.192 8.166 8.154 8.121 8.110 8.010 7.999 7.987
18

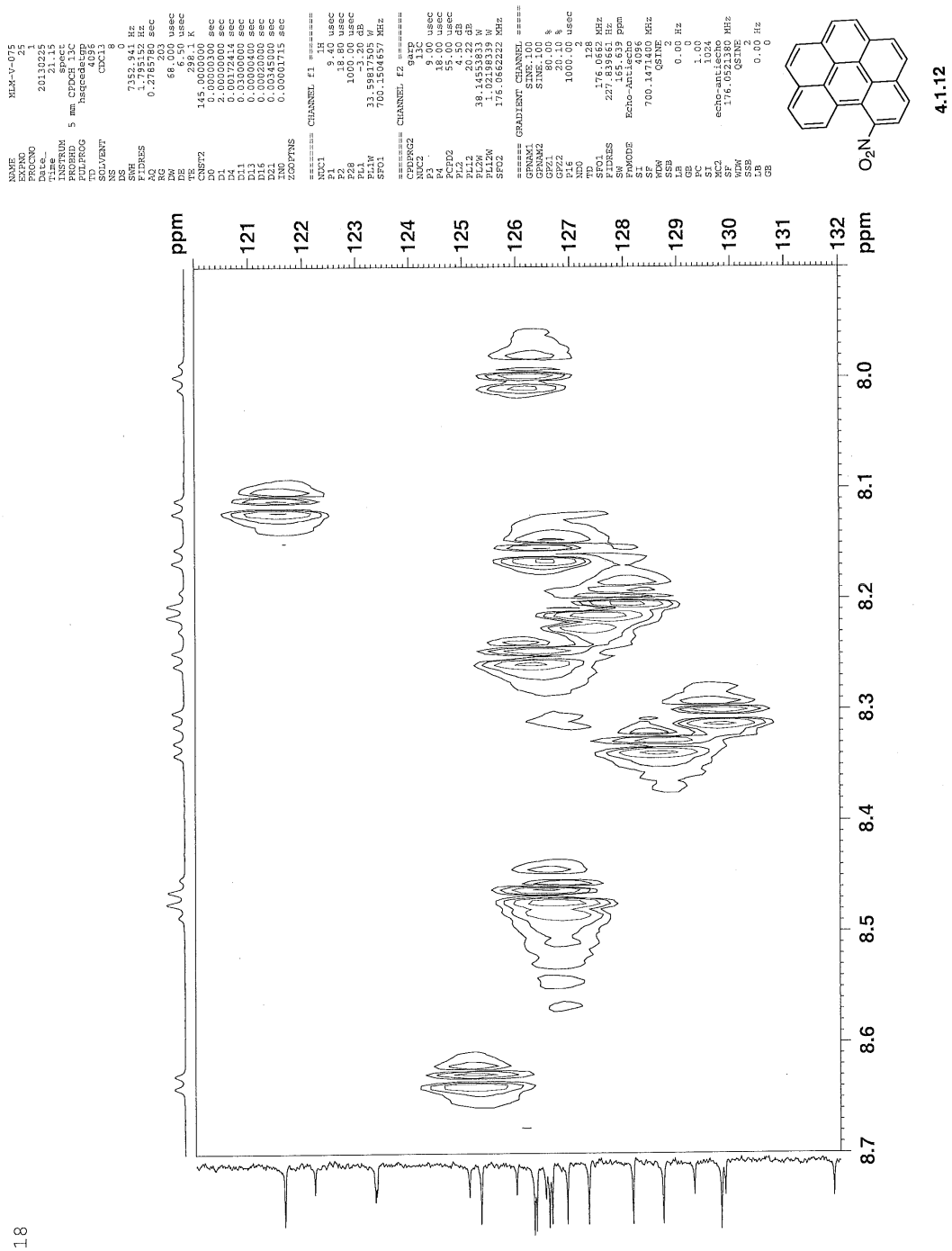

NAME MLM-V-075
EXPNO 24
PROCNO 1
Date_ 20130225
Time_ 20.26
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 0
SWH 41666.668 H
FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.1 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0697436 M
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
4.1.12
146.361
133.548
131.876
129.857
129.786
129.280
128.701
128.132
127.308
126.910
126.629
126.577
126.512
126.340
126.301
125.970
125.313
125.091
123.360
123.335
122.205
121.650
77.206
77.025
76.843
200
180
160
140
120
100
80
60
40
20
ppm
18

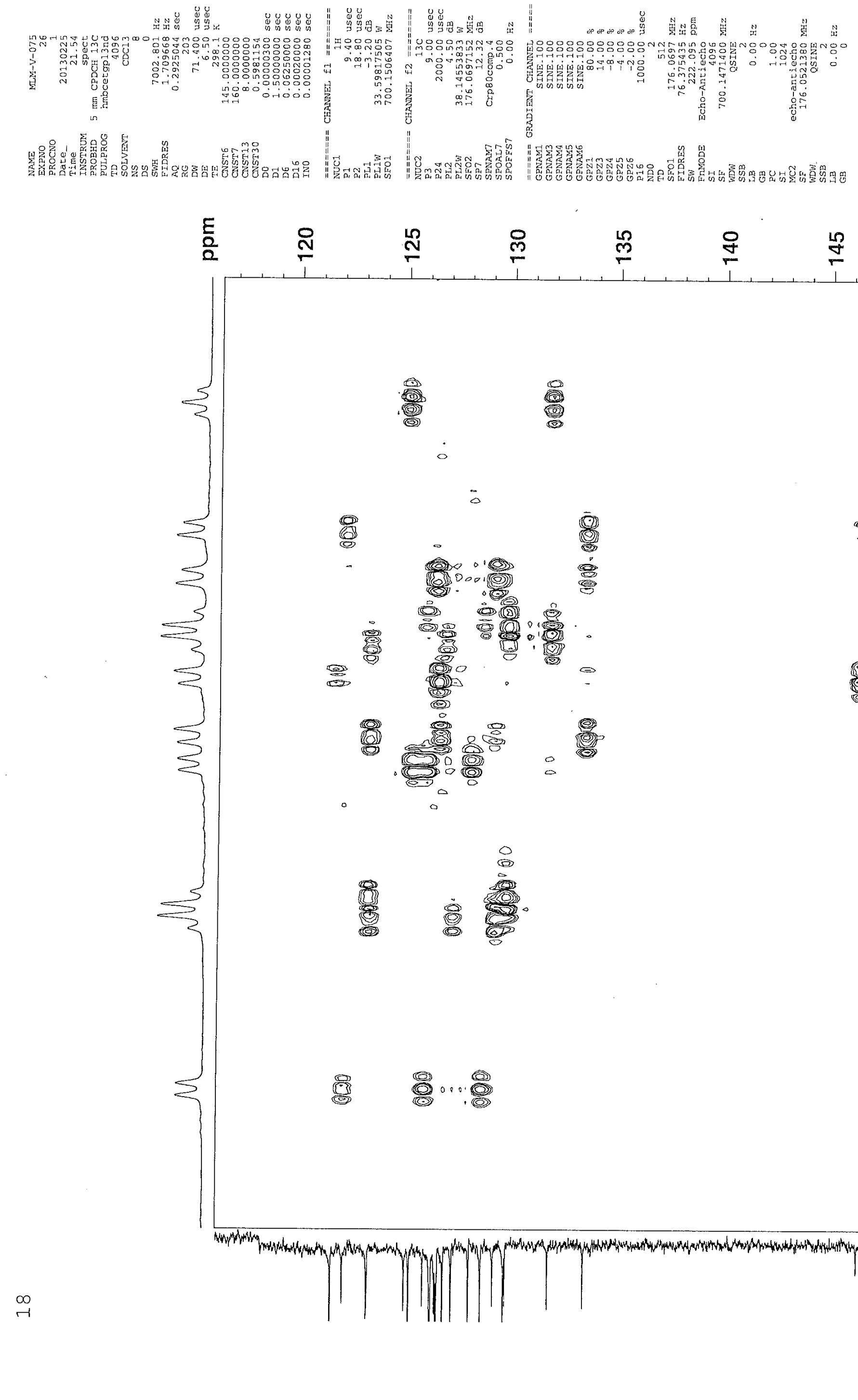


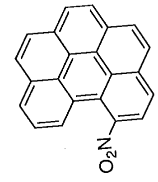
NAME	MLM-V-075
EXPNO	23
PROCNO	1
Date_	20130225
Time	20.16
INSTRUM	spect
PROBHD	5 mm CPDCH 13C
PULPROG	cosygpqf
TD	2048
SOLVENT	CDCl3
NS	2
DS	0
SWH	7352.941 Hz
FIDRES	3.590303 Hz
AQ	0.1393140 sec
RG	203
DW	68.000 usec
DE	6.50 usec
TE	298.1 K
D0	0.00000300 sec
D1	2.00000000 sec
D13	0.00000400 sec
D16	0.00020000 sec
IN0	0.00013600 sec
======== CHANNEL f1 ========	
NUC1	1H
P0	9.40 usec
P1	9.40 usec
PL1	-3.20 dB
PL1W	33.59817505 W
SFO1	700.1502907 MHz
====== GRADIENT CHANNEL =====	
GPNAM1	SINE.100
GPZ1	80.00 %
P16	1000.00 usec
ND0	1
TD	128
SFO1	700.1503 MHz
FIDRES	57.444843 Hz
SW	10.502 ppm
FnMODE	QF
SI	2048
SF	700.1471400 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00
SI	2048
MC2	QF
SF	700.1471400 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0



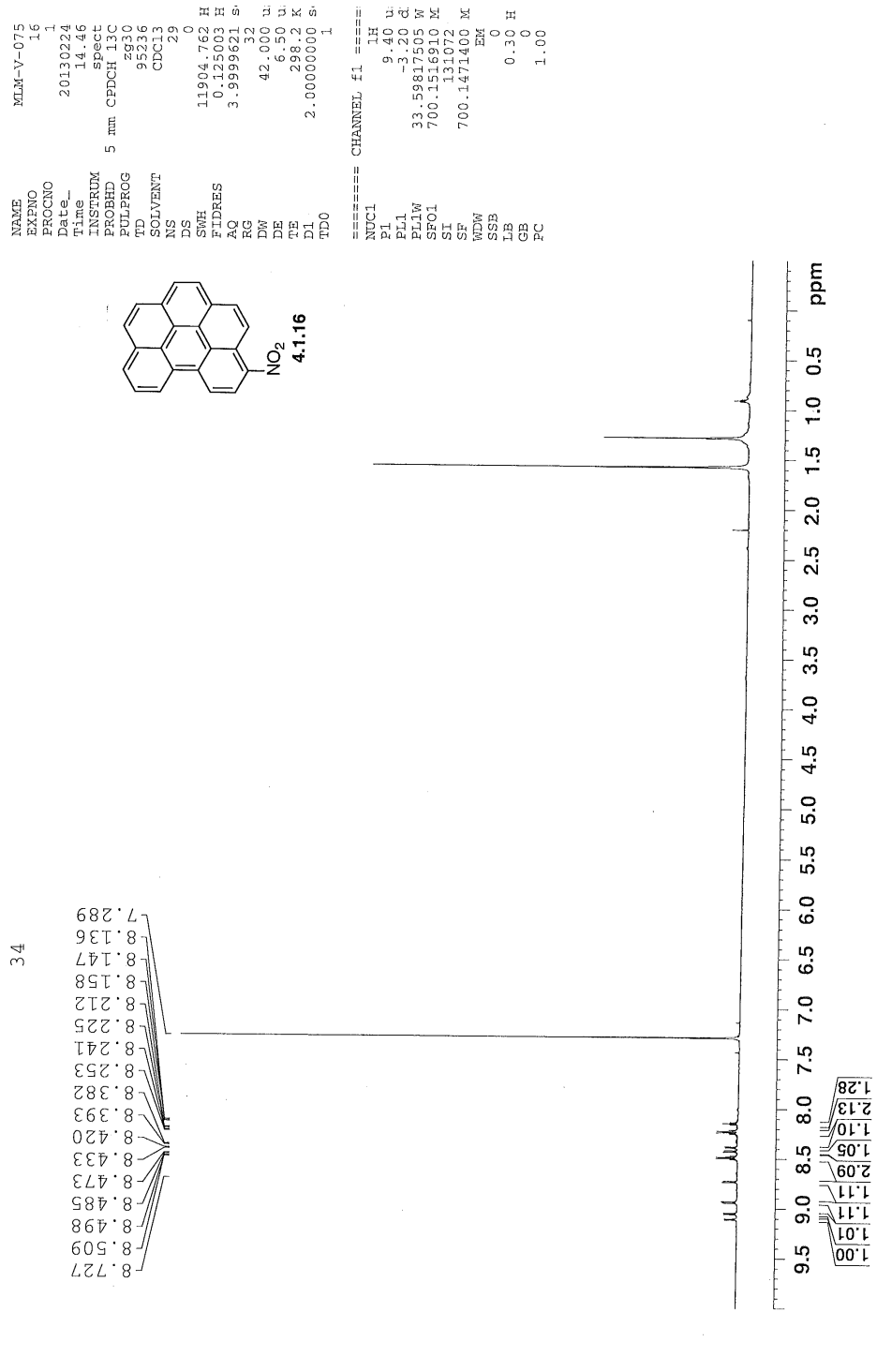
4.1.12

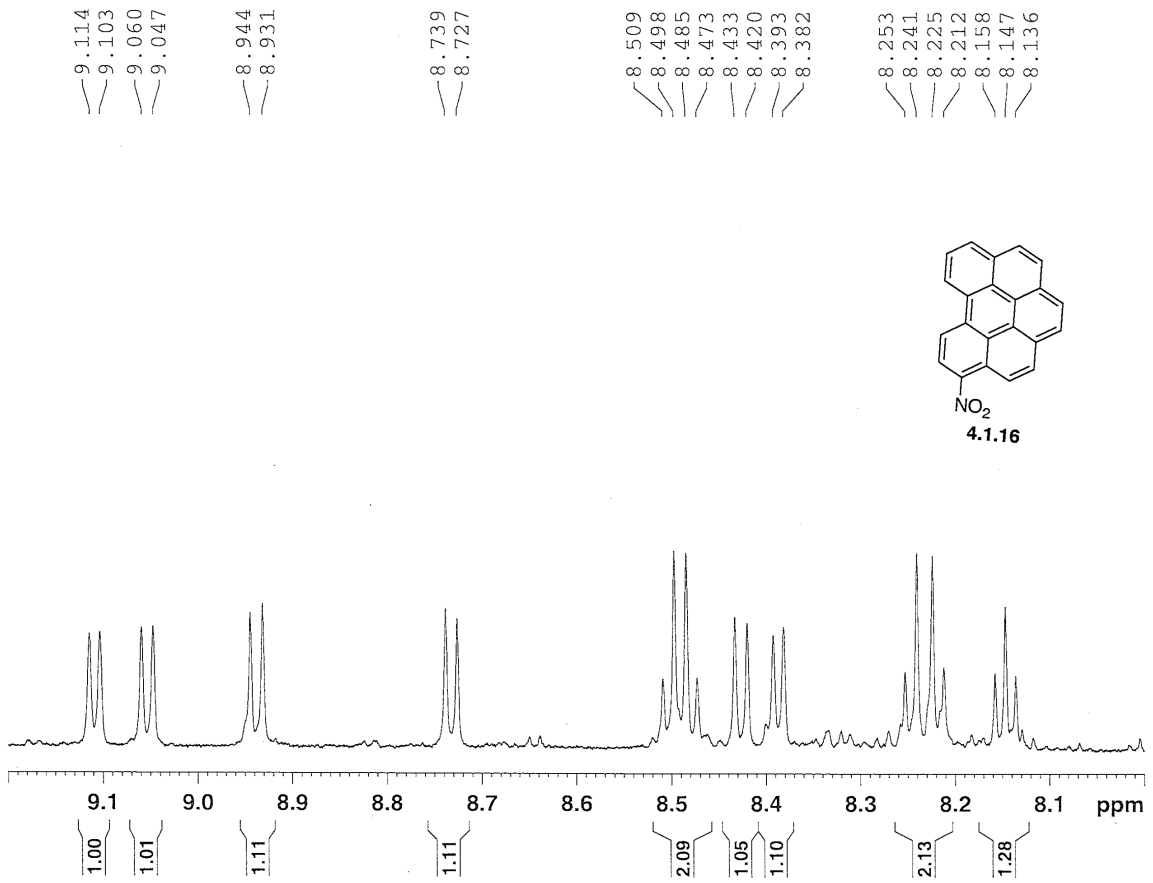

NAME MLW-V-075
EXPNO 25
PROCNO 1
Date_ 20130225
Time 21.15
INSTRUM spect
PROBHD 5 mm CPDG z SC
PULPROG hsqcedetgp
TD 4096
SOLVENT CDCl3
NS 8
DS 0
SWH 7352.941 Hz
FIDRES 1.795152 Hz
AQ 0.2785780 sec
RG 203
DW 68.000 usec
DE 6.50 usec
TE 298.1 K
CNST2 145.0000000
D0 0.00000300 sec
D1 2.00000000 sec
D4 0.00172414 sec
D11 0.03000000 sec
D13 0.00000400 sec
D16 0.00020000 sec
D21 0.00345000 sec
IN0 0.00001715 sec
ZGOPTNS
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
P2 18.80 usec
P28 1000.00 usec
PL1 -1.20 dB
PL1W 33.59817505 W
SFO1 700.1504657 MHz
======== CHANNEL f2 ========
CPDPRG2 garp
NUC2 13C
P3 9.00 usec
P4 18.00 usec
PCPD2 55.00 usec
PL2 4.50 dB
PL12 20.22 dB
PL2W 38.14553833 W
PL12W 17.06562233 W
SFO2 176.0662222 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 80.00 %
GPZ2 20.10 %
P16 1000.00 usec
NDO 1
TD0 128
SFO1 176.0662 MHz
FIDRES 227.839661 Hz
SW 165.639 ppm
FnMODE Echo-Antiecho
SF01 700.1505 MHz
SF 700.1471400 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
SI 1024
MC2 echo-antiecho
SF2 176.0551300 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
ppm
121
122
123
124
125
126
127
128
129
130
131
132
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
ppm
O_2N
4.1.12
18



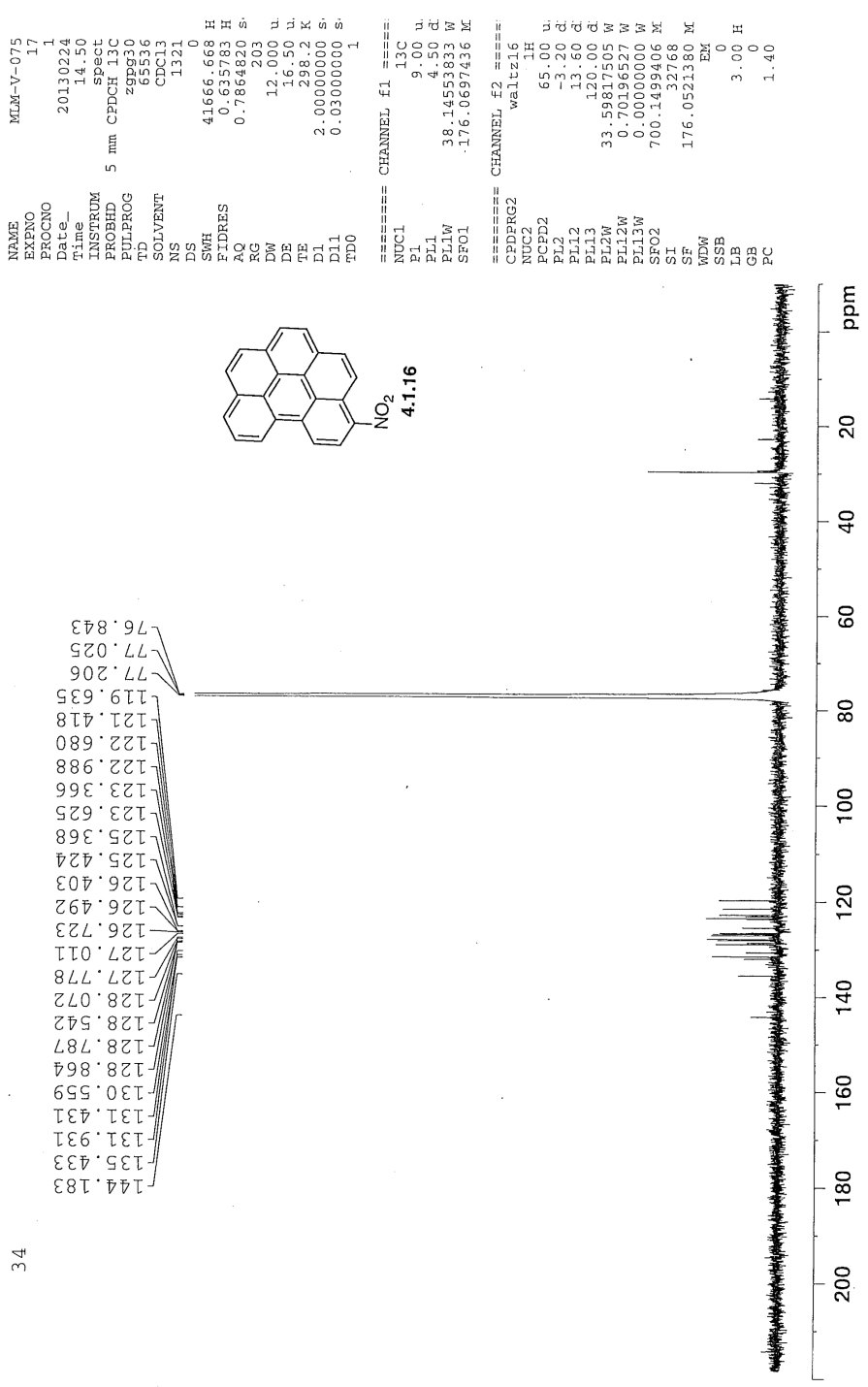


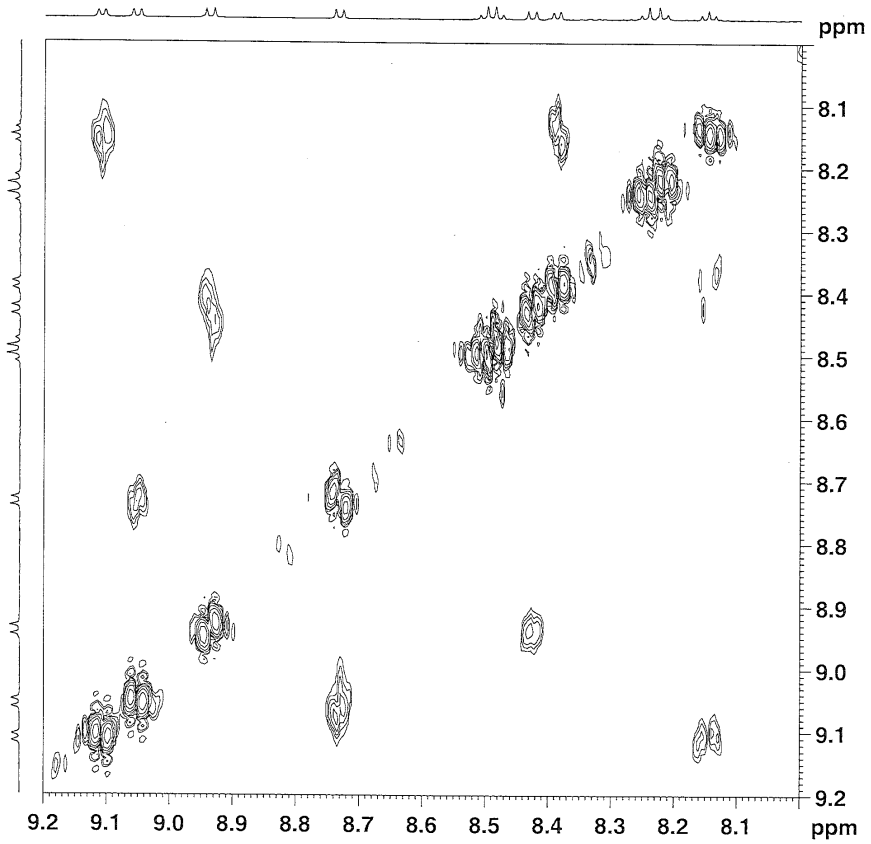
4.1.12


NAME MLM-V-075
EXPNO 16
PROCNO 1
Date_ 20130224
Time 14.46
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 29
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 32
DW 42.000 u
DE 6.50 u
TE 298.2 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ====
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
NO2
4.1.16
34
8.727
8.509
8.498
8.485
8.473
8.433
8.420
8.393
8.382
8.253
8.241
8.225
8.212
8.158
8.147
8.136
7.289
1.00
1.01
1.11
2.09
1.05
1.10
2.13
1.28
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 ppm

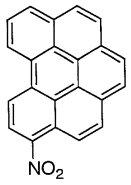


NAME	MLM-V-075	
EXPNO	16	
PROCNO	1	
Date_	20130224	
Time	14.46	
INSTRUM	spect	
PROBHD	5 mm CPDCH 13C	
PULPROG	zg30	
TD	95236	
SOLVENT	CDCl3	
NS	29	
DS	0	
SWH	11904.762	H
FIDRES	0.125003	H
AQ	3.9999621	s
RG	32	
DW	42.000	u
DE	6.50	u
TE	298.2	K
D1	2.00000000	s
TD0	1	
======== CHANNEL f1 =====		
NUC1	1H	
P1	9.40	u
PL1	-3.20	d
PL1W	33.59817505	W
SFO1	700.1516910	M
SI	131072	
SF	700.1471400	M
WDW	EM	
SSB	0	
LB	0.30	H
GB	0	
PC	1.00	

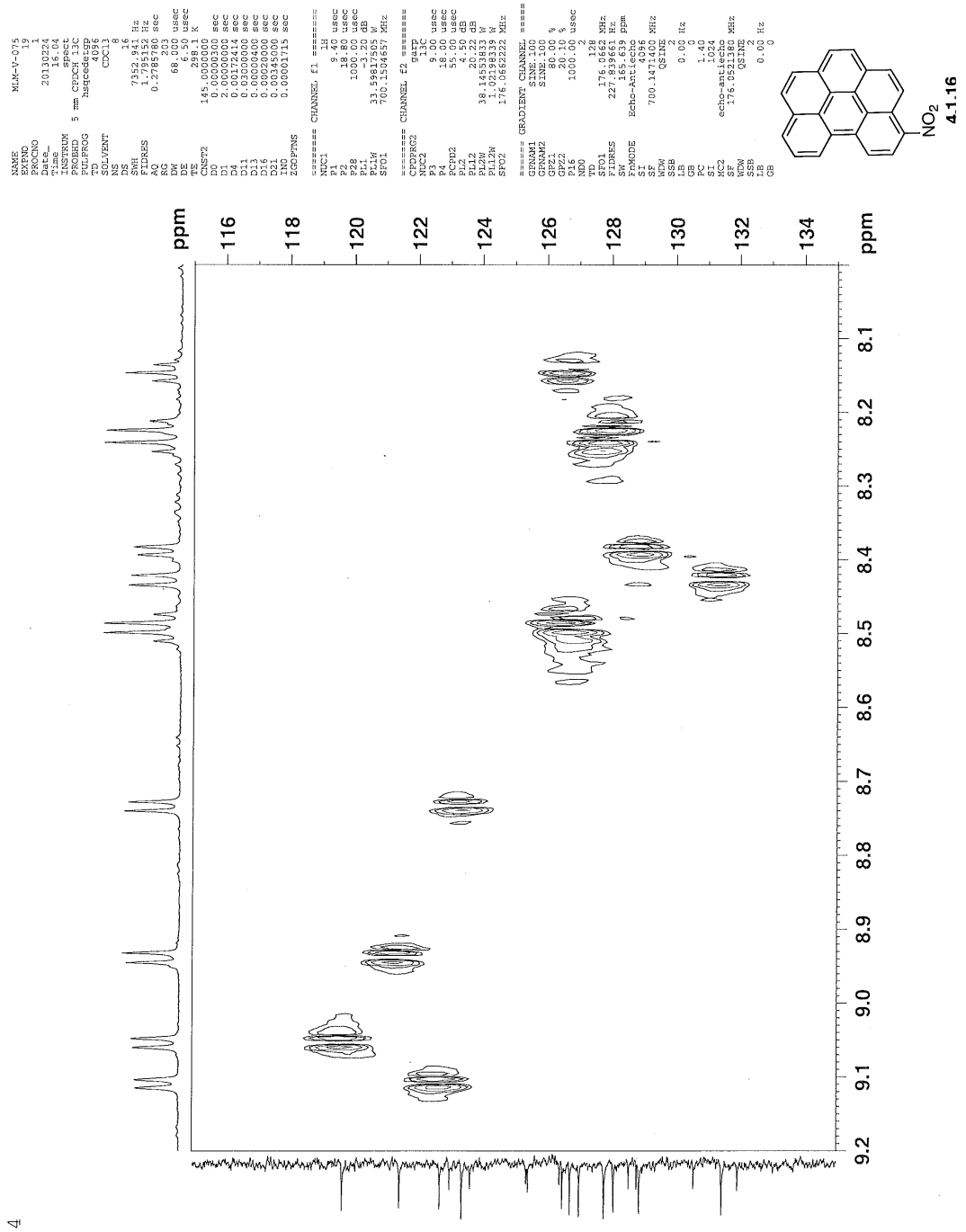

NAME MLM-V-075
EXPNO 17
PROCNO 1
Date_ 20130224
Time_ 14.50
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1321
DS 0
SWH 41666.668 H
FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.2 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 -176.0697436 M
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
NO2
4.1.16
144.183
135.433
131.931
131.431
130.559
128.864
128.787
128.542
128.072
127.778
127.011
126.723
126.492
126.403
125.424
125.368
123.625
123.366
122.988
122.680
121.418
119.635
77.206
77.025
76.843
200
180
160
140
120
100
80
60
40
20
ppm



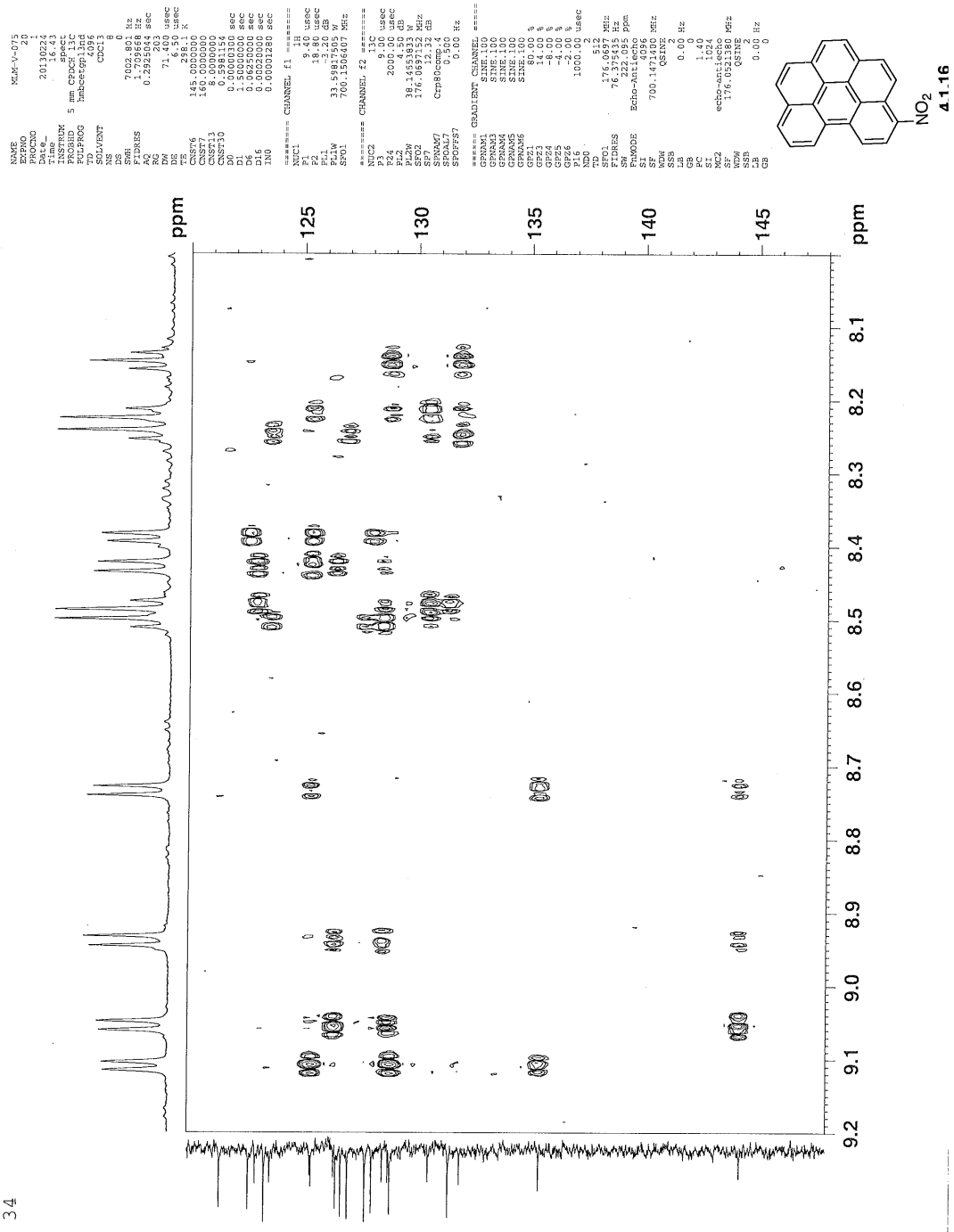
NAME	MLM-V-075	
EXPNO	18	
PROCNO	1	
Date_	20130224	
Time	15.53	
INSTRUM	spect	
PROBHD	5 mm CPDCH 13C	
PULPROG	cosygpqf	
TD	2048	
SOLVENT	CDCl3	
NS	2	
DS	4	
SWH	7352.941	Hz
FIDRES	3.590303	Hz
AQ	0.1393140	sec
RG	203	
DW	68.000	usec
DE	6.50	usec
TE	298.1	K
D0	0.00000300	sec
D1	2.00000000	sec
D13	0.00000400	sec
D16	0.00020000	sec
IN0	0.00013600	sec
======== CHANNEL f1 ========		
NUC1	1H	
P0	9.40	usec
P1	9.40	usec
PL1	-3.20	dB
PL1W	33.59817505	W
SFO1	700.1502907	MHz
====== GRADIENT CHANNEL =====		
GPNAM1	SINE.100	
GPZ1	80.00	%
P16	1000.00	usec
ND0	1	
TD	128	
SFO1	700.1503	MHz
FIDRES	57.444843	Hz
SW	10.502	ppm
FnMODE	QF	
SI	2048	
SF	700.1471400	MHz
WDW	SINE	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.40	
SI	2048	
MC2	QF	
SF	700.1471400	MHz
	SINE	
	0	
	0.00	Hz
	0	

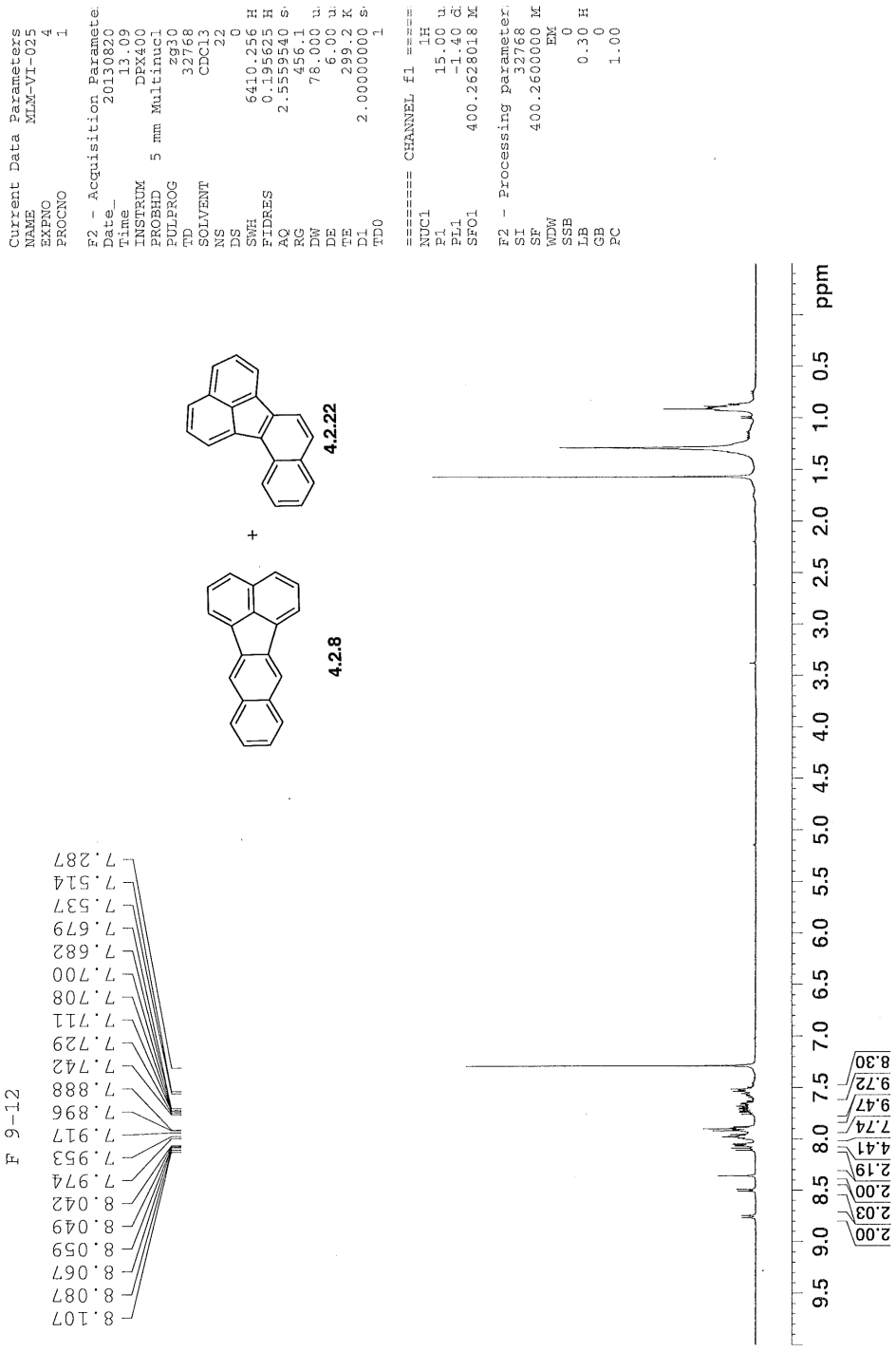


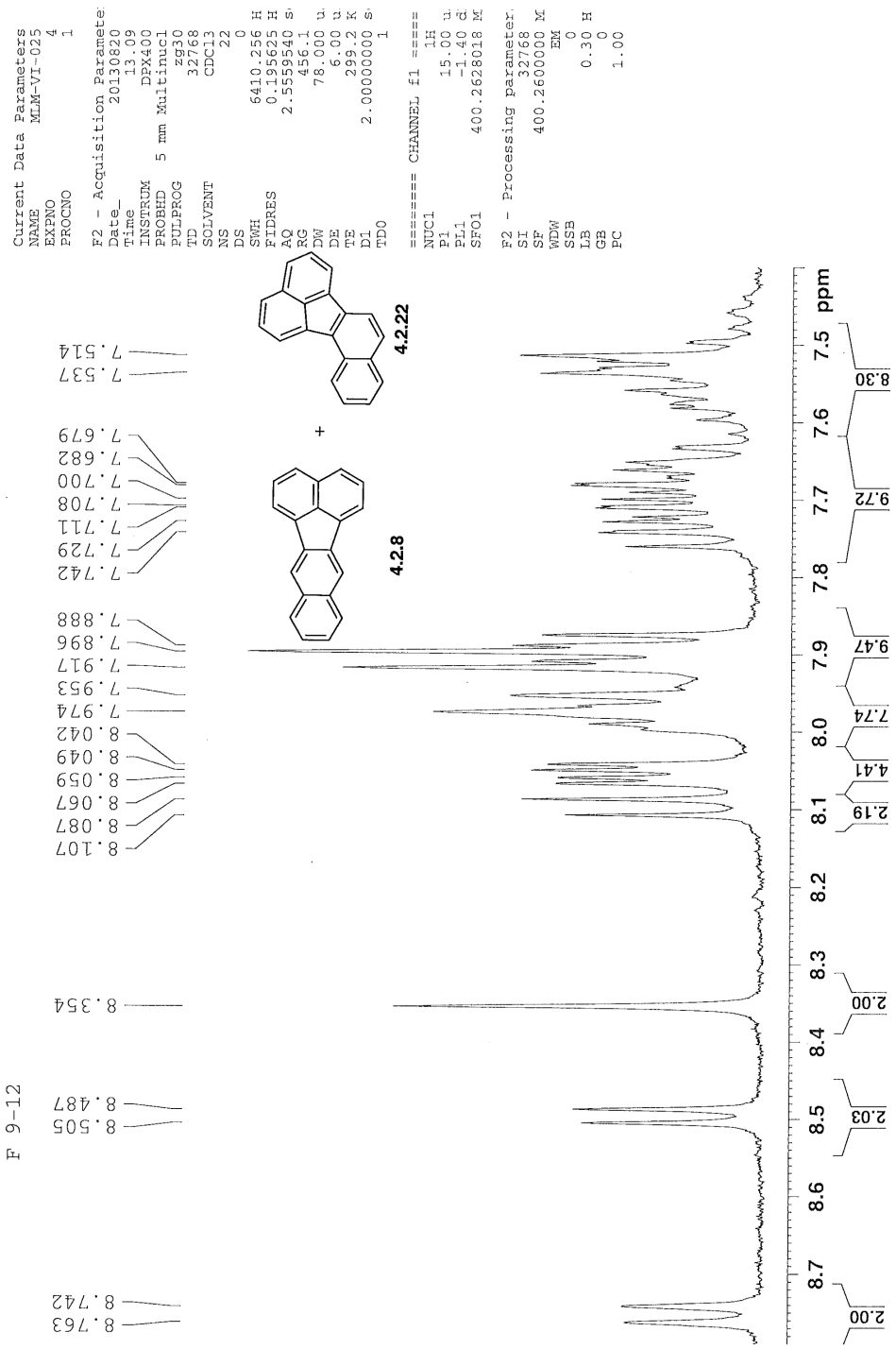
4.1.16

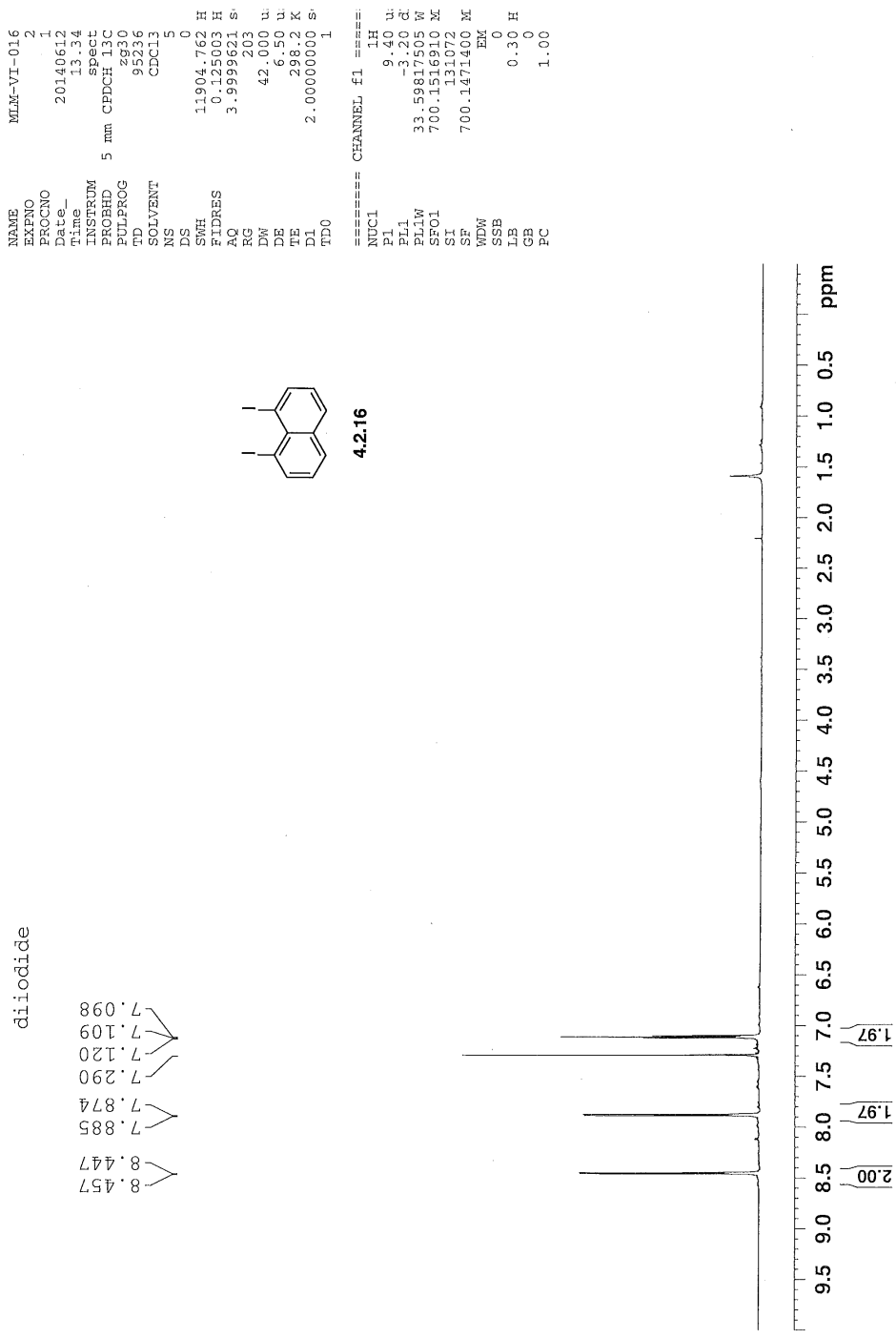

NAME MLM-V-075
EXPNO 19
PROCNO 1
Date_ 20130224
Time 16.04
INSTRUM spect
PROBHD 5 mm CPPBBO BB-1H
PULPROG hsqcedetgp
TD 4096
SOLVENT CDCl3
NS 8
DS 16
SWH 7352.941 Hz
FIDRES 1.795152 Hz
AQ 0.2785780 sec
RG 203
DW 68.000 usec
DE 6.50 usec
TE 298.1 K
CNST2 145.0000000
D0 0.00000300 sec
D1 2.00000000 sec
D4 0.00172414 sec
D11 0.03000000 sec
D13 0.00000400 sec
D16 0.00124000 sec
D21 0.00344000 sec
ING 0.00001715 sec
ZGCPPRG
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
P2 18.80 usec
P28 1000.00 usec
PL1 3.20 dB
PL1W 33.59817505 W
SFO1 700.1504657 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz
NUC2 13C
P3 9.00 usec
P4 18.00 usec
PCPD2 51.50 usec
PL2 dB
PL12 20.22 dB
PL2W 38.14553833 W
PL12W 1.02199339 W
SFO2 176.0562222 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 80.10 %
GPZ2 20.10 %
P16 1000.00 usec
NDO 2
TD1 128
SFO1 176.0462 MHz
FIDRES 227.839661 Hz
SW 165.639 ppm
FnMODE Echo-Antiecho
SI 1024
SF 700.1471400 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.40
SI 1024
MC2 echo-antiecho
SF 176.0521381 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
NO2
4.1.16
ppm
116
118
120
122
124
126
128
130
132
134
9.2
9.1
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
ppm

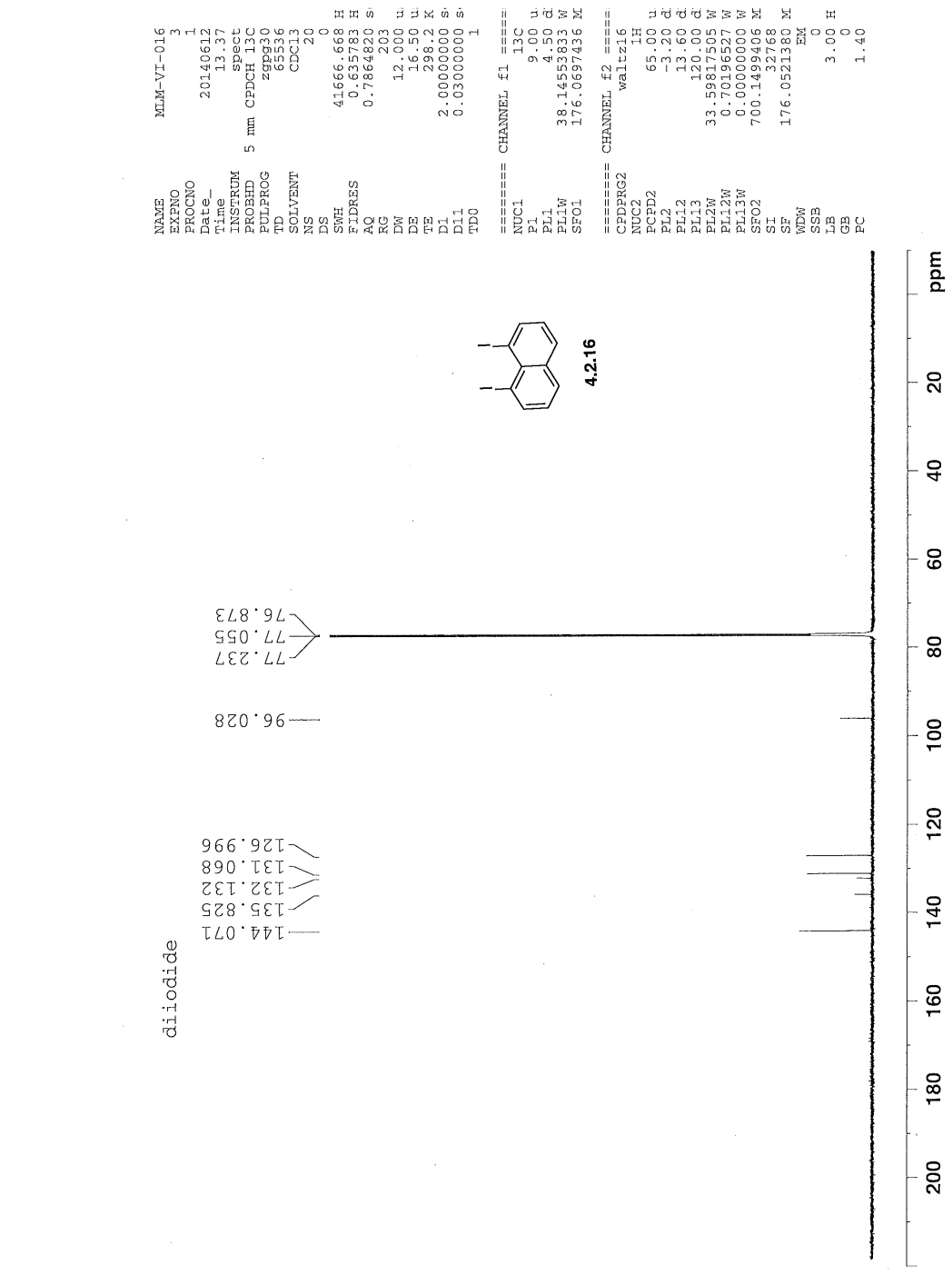
34

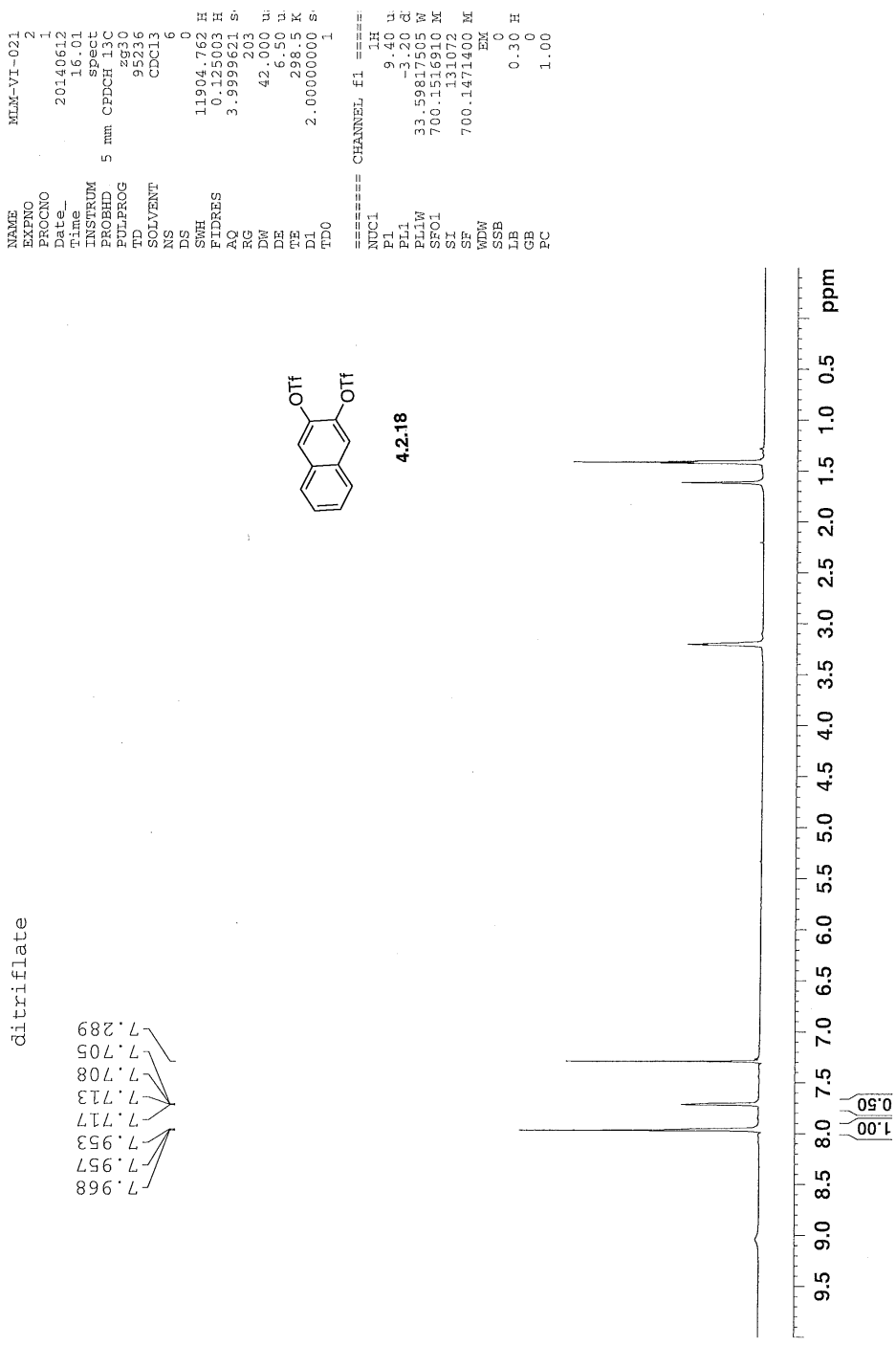

NO2
4.1.16
ppm
125
130
135
140
145
9.2
9.1
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
ppm

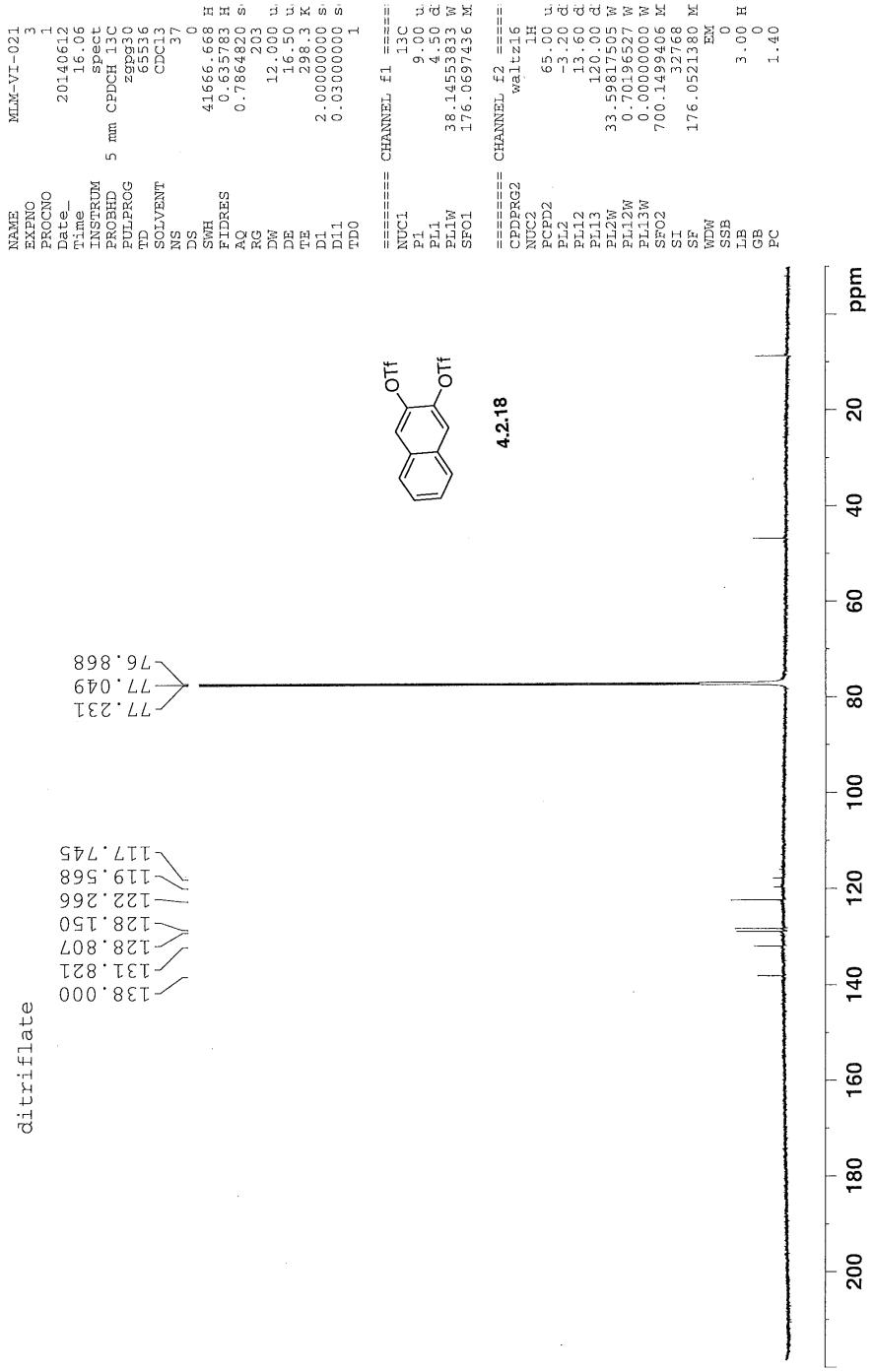

Current Data Parameters
NAME MLM-VT-025
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130820
Time 13.09
INSTRUM DPX400
PROBHD 5 mm Multinucl
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 22
DS 0
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 456.1
DW 78.000 usec
DE 6.00 usec
TE 299.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.00 usec
PL1 -1.40 dB
SFO1 400.2628018 MHz
F2 - Processing parameters
SI 32768
SF 400.2600000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F 9-12
8.107
8.087
8.067
8.059
8.049
8.042
7.974
7.953
7.917
7.896
7.888
7.742
7.729
7.711
7.708
7.700
7.682
7.679
7.537
7.514
7.287
4.2.22
4.2.8
+
2.00
2.03
2.00
2.19
4.41
7.74
9.47
9.72
8.30
ppm

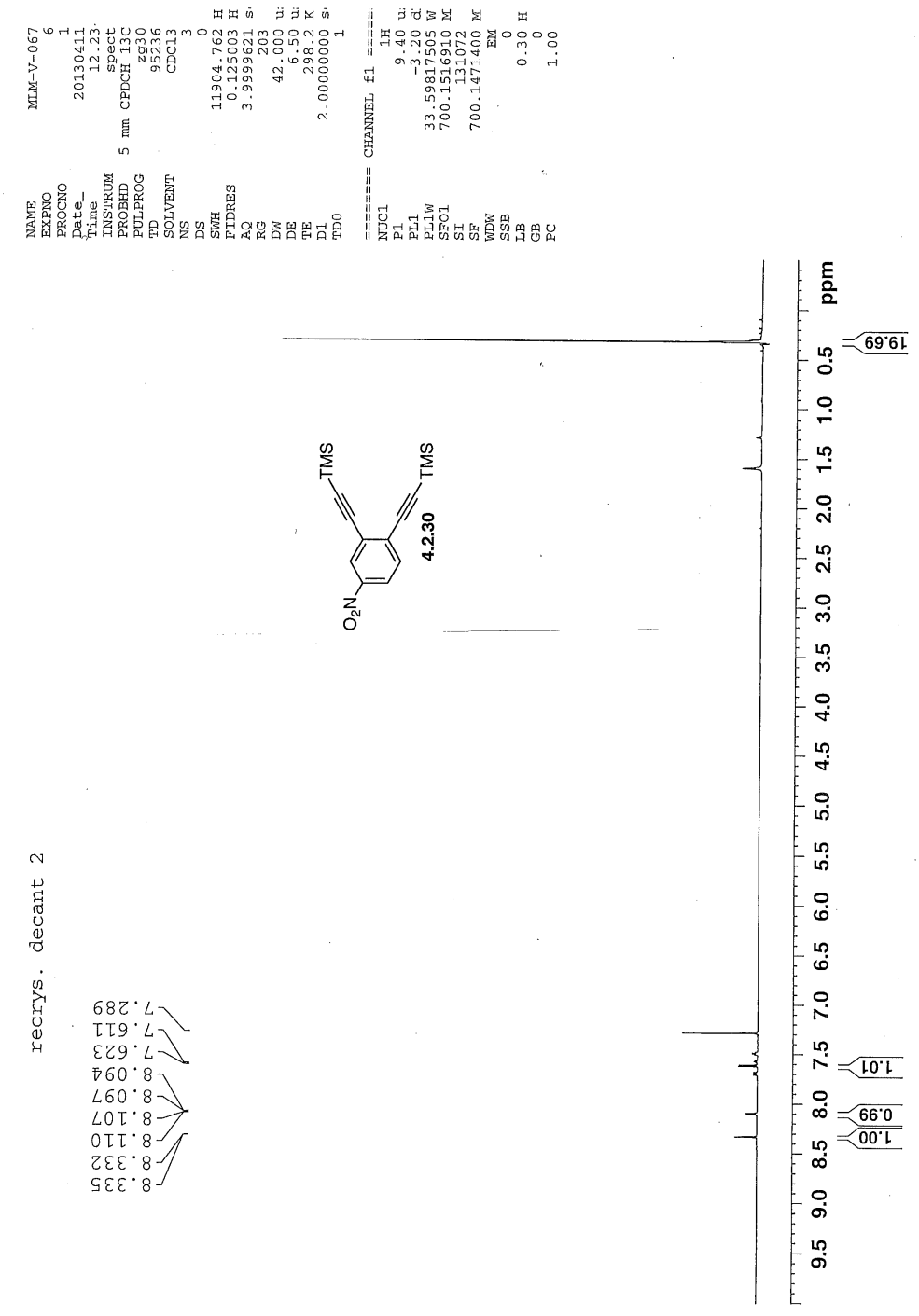

F 9-12
Current Data Parameters
NAME MLM-VI-025
EXPNO 4
PROCNO 1
F2 - Acquisition Parameter
Date_ 20130820
Time 13.09
INSTRUM DPX400
PROBHD 5 mm Multinucl
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 22
DS 0
SWH 6410.256 H
FIDRES 0.195625 H
AQ 2.5559540 s
RG 456.1
DW 78.000 u
DE 6.00 u
TE 299.2 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 =====
NUC1 1H
P1 15.00 u
PL1 -1.40 d
SFO1 400.2628018 M
F2 - Processing parameter
SI 32768
SF 400.2600000 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
4.2.22
4.2.8
+
8.763
8.742
8.505
8.487
8.354
8.107
8.087
8.067
8.059
8.049
8.042
7.974
7.953
7.917
7.896
7.888
7.742
7.729
7.711
7.708
7.700
7.682
7.679
7.537
7.514
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
ppm
2.00
2.03
2.00
2.19
4.41
7.74
9.47
9.72
8.30


diiodide
8.457
8.447
7.885
7.874
7.290
7.120
7.109
7.098
4.2.16
NAME MLM-VI-016
EXPNO 2
PROCNO 1
Date_ 20140612
Time_ 13.34
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 5
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 203
DW 42.000 u
DE 6.50 u
TE 298.2 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
2.00
1.97
1.97
1.97
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 ppm

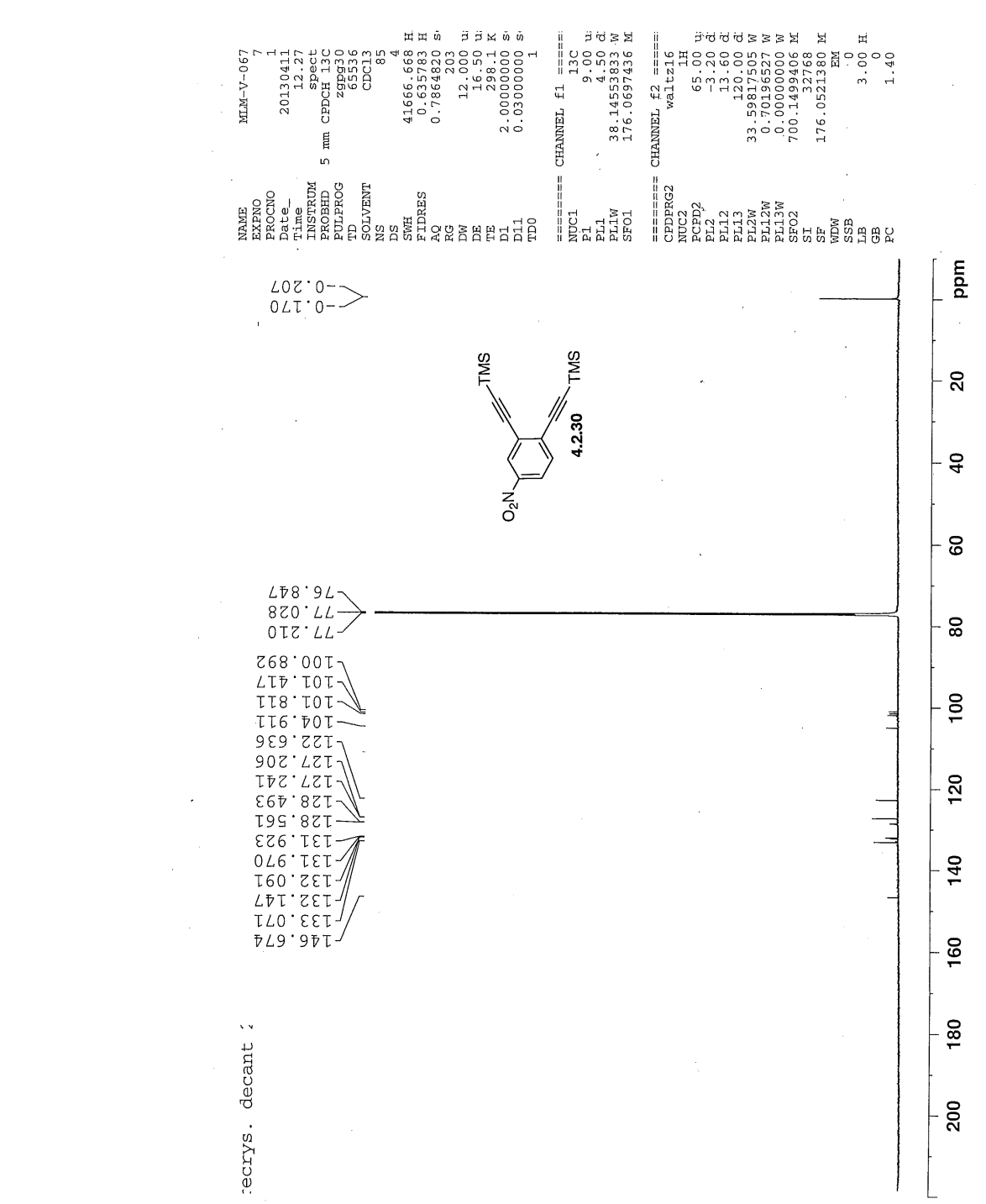

NAME MLM-VI-016
EXPNO 3
PROCNO 1
Date_ 20140612
Time 13.37
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 20
DS 0
SWH 41666.668 H
FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.2 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 =====
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0697436 M
======== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
4.2.16
diiodide
144.071
135.825
132.132
131.068
126.996
96.028
77.237
77.055
76.873
200
180
160
140
120
100
80
60
40
20
ppm

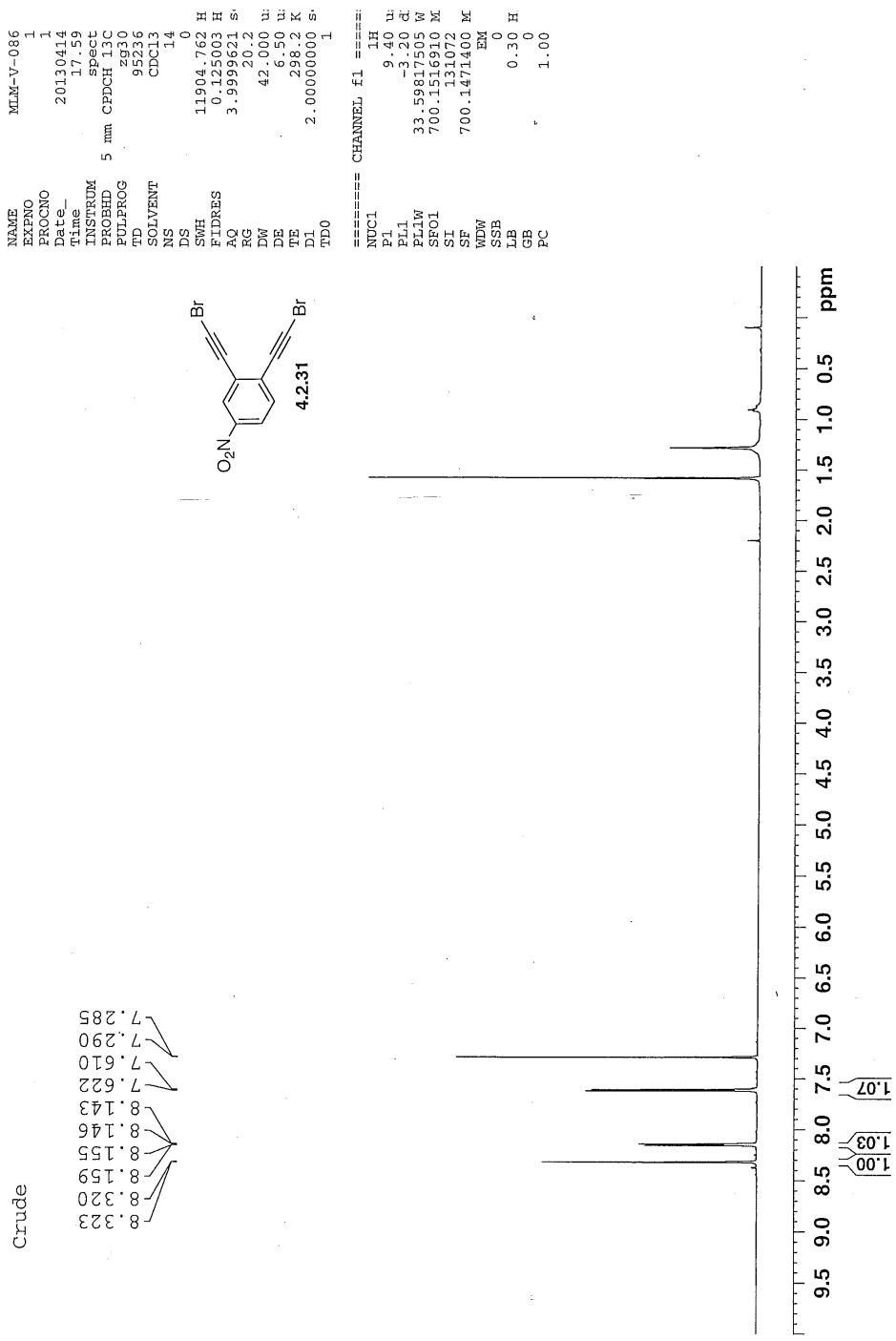

ditriflate
7.289
7.705
7.708
7.713
7.717
7.953
7.957
7.968
OTf
OTf
4.2.18
NAME MLM-VI-021
EXPNO 2
PROCNO 1
Date_ 20140612
Time 16.01
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDC13
NS 6
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 203
DW 42.000 u
DE 6.50 u
TE 298.5 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
1.00
0.50
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 ppm

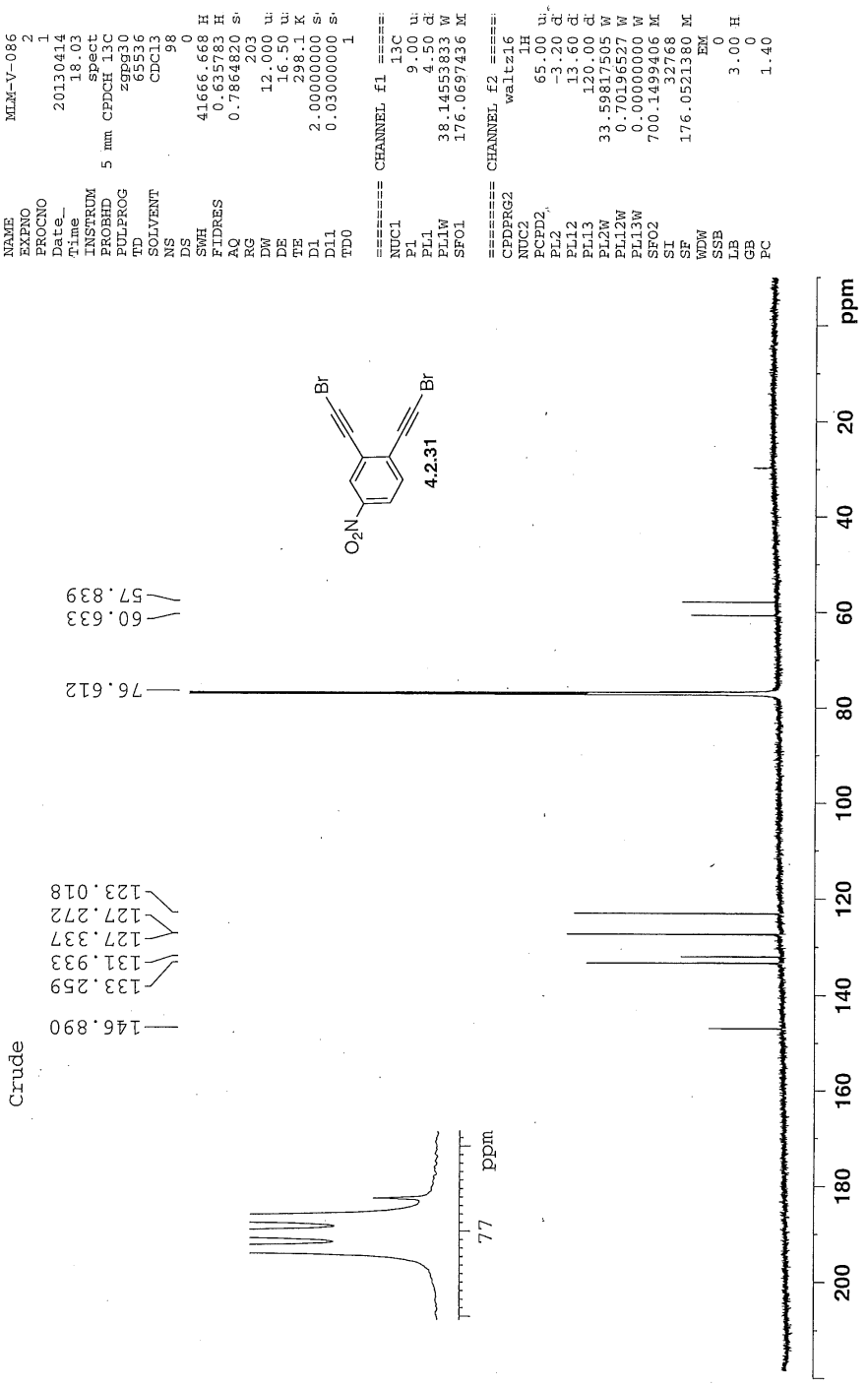

NAME MLM-VI-021
EXPNO 3
PROCNO 1
Date_ 20140612
Time 16.06
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 37
DS 0
SWH 41666.668 H
FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.3 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0697436 M
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
OTf
OTf
4.2.18
ditriflate
138.000
131.821
128.807
128.150
122.266
119.568
117.745
77.231
77.049
76.868
200
180
160
140
120
100
80
60
40
20
ppm

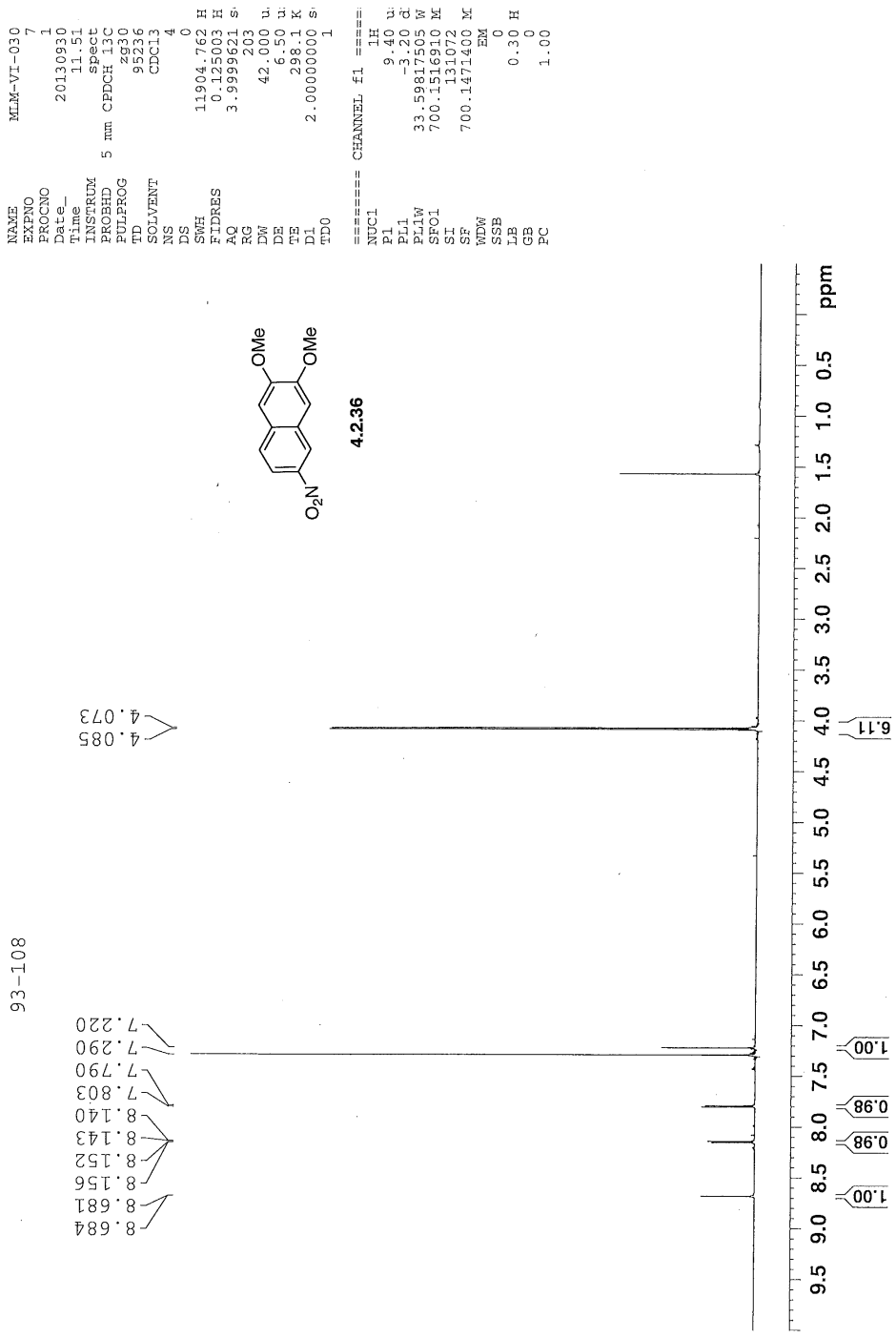


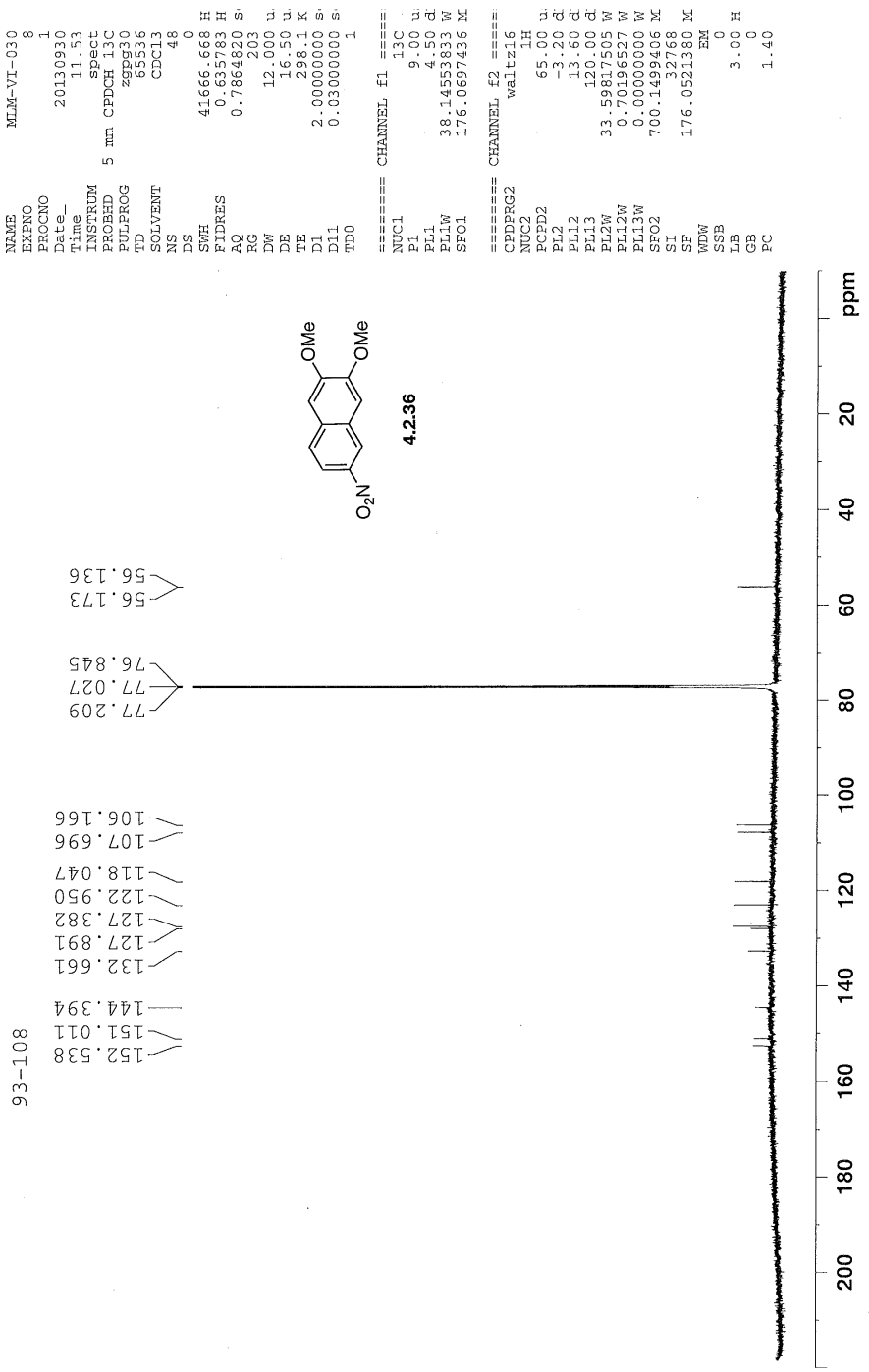

```
NAME            MLM-V-067
EXPNO                   6
PROCNO                  1
Date_            20130411
Time                12.23
INSTRUM               spect
PROBHD  5 mm CPDCH 13C
PULPROG              zg30
TD                  95236
SOLVENT             CDCl3
NS                      3
DS                      0
SWH             11904.762 H
FIDRES              0.125003 H
AQ                3.9999621 s
RG                    203
DW                 42.000 u
DE                  6.50 u
TE                298.2 K
D1                2.00000000 s
TD0                     1

======== CHANNEL f1 =====
NUC1                  1H
P1                 9.40 u
PL1               -3.20 d
PL1W        33.59817505 W
SFO1        700.1516910 M
SI                 131072
SF          700.1471400 M
WDW                   EM
SSB                    0
LB                 0.30 H
GB                     0
PC                  1.00
```

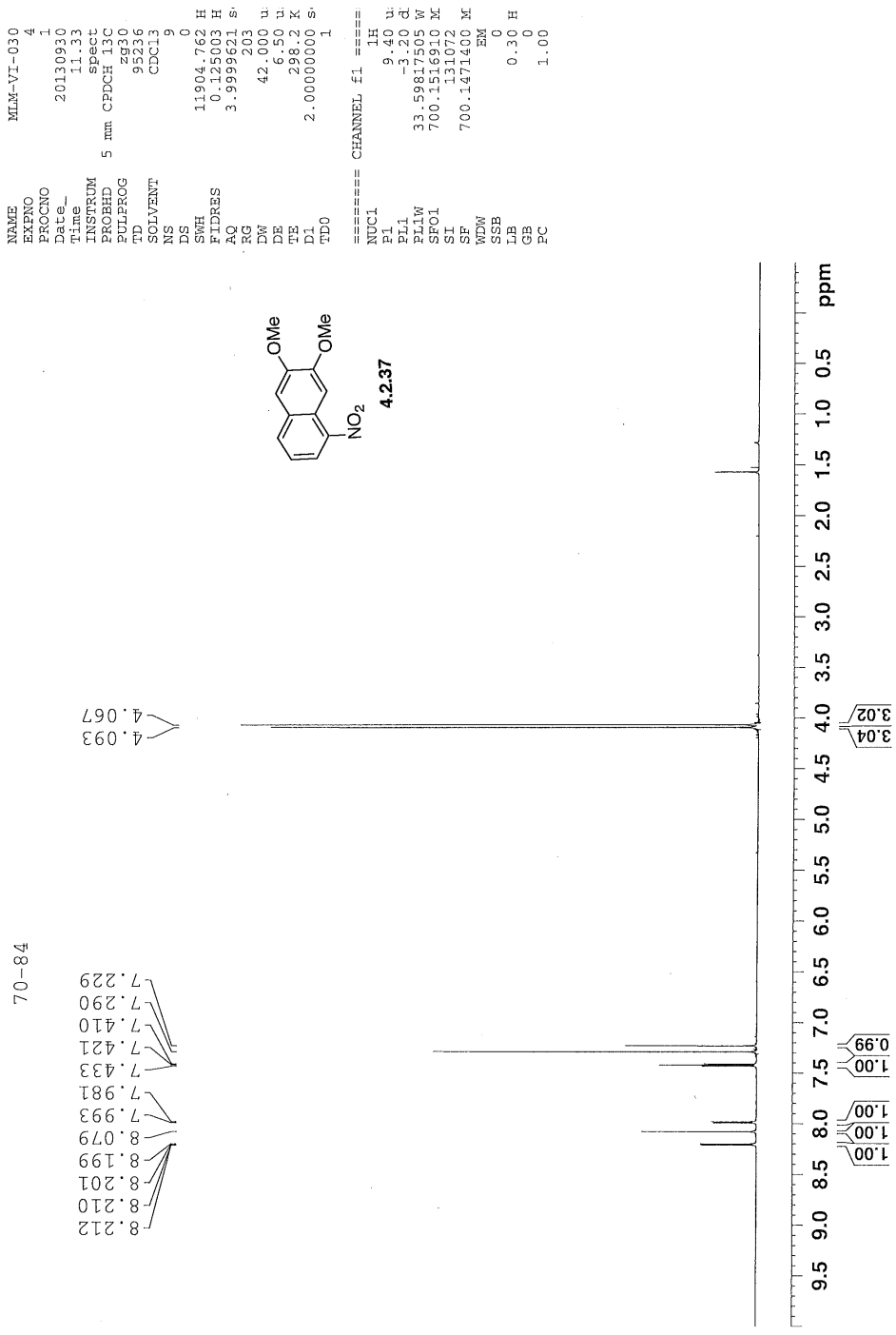

TMS
TMS
O_2N
4.2.30
ppm

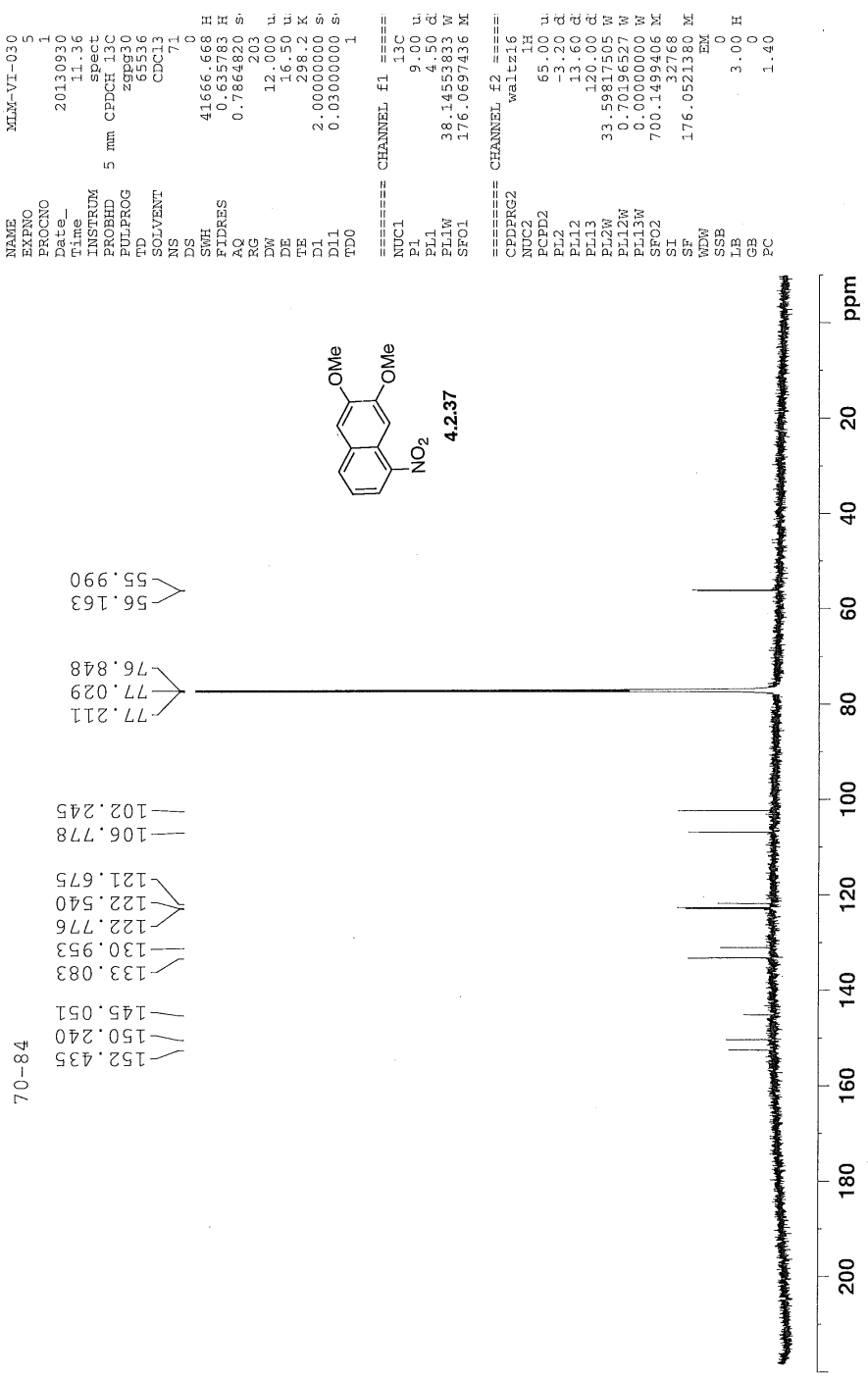

NAME MLM-V-086
EXPNO 1
PROCNO 1
Date_ 20130414
Time 17.59
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 14
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 20.2
DW 42.000 u
DE 6.50 u
TE 298.2 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 =====
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
Br
Br
O_2N
4.2.31
Crude
8.323
8.320
8.159
8.155
8.146
8.143
7.622
7.610
7.290
7.285
1.00
1.03
1.07
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 ppm

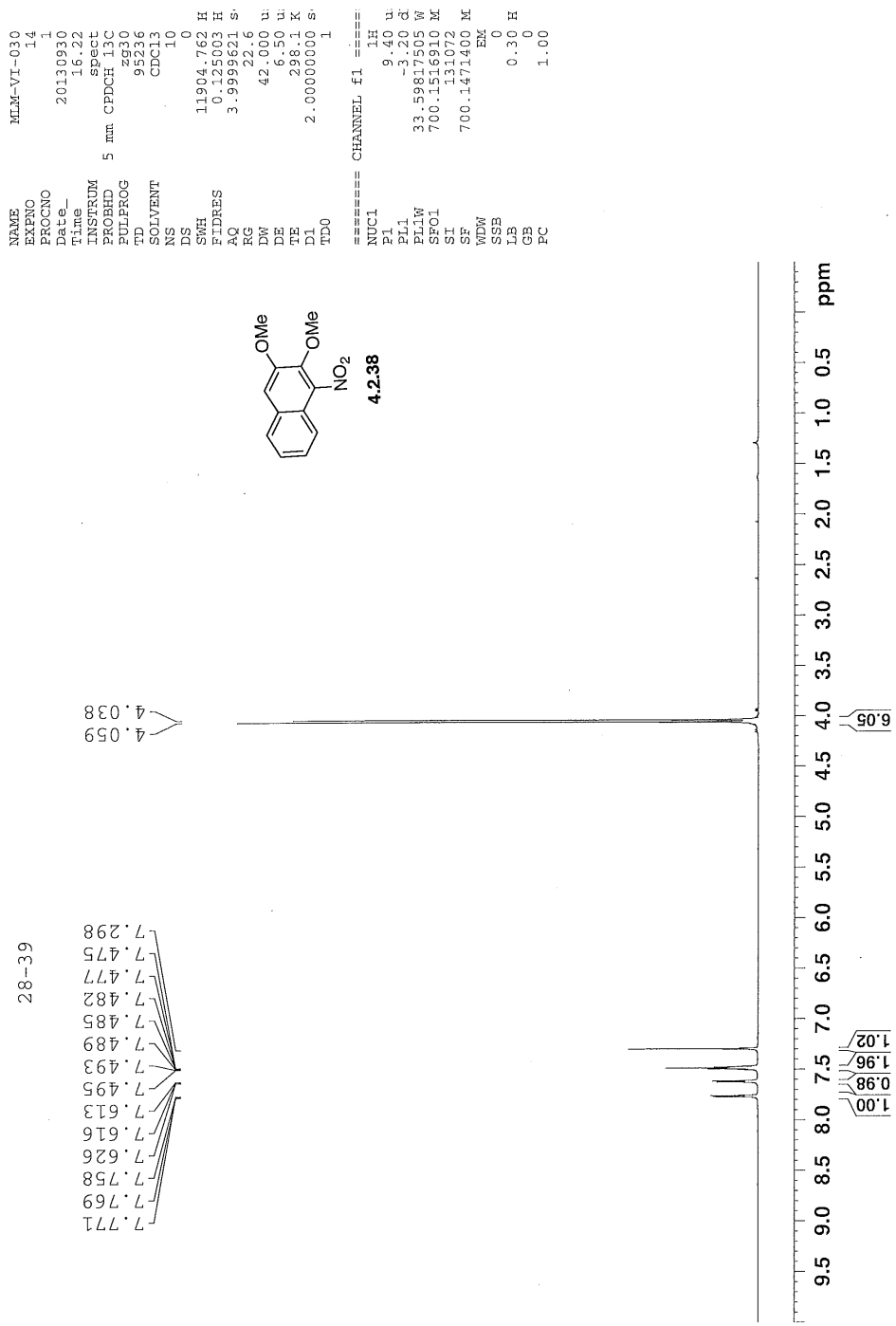

NAME MLM-V-086
EXPNO 2
PROCNO 1
Date_ 20130414
Time 18.03
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 98
DS 0
SWH 41666.668 H
FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.1 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
CHANNEL f1 13C
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0697436 M
CHANNEL f2 1H
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
Br
Br
O2N
4.2.31
Crude
146.890
133.259
131.933
127.337
127.272
123.018
76.612
60.633
57.839
ppm
77
200
180
160
140
120
100
80
60
40
20
ppm

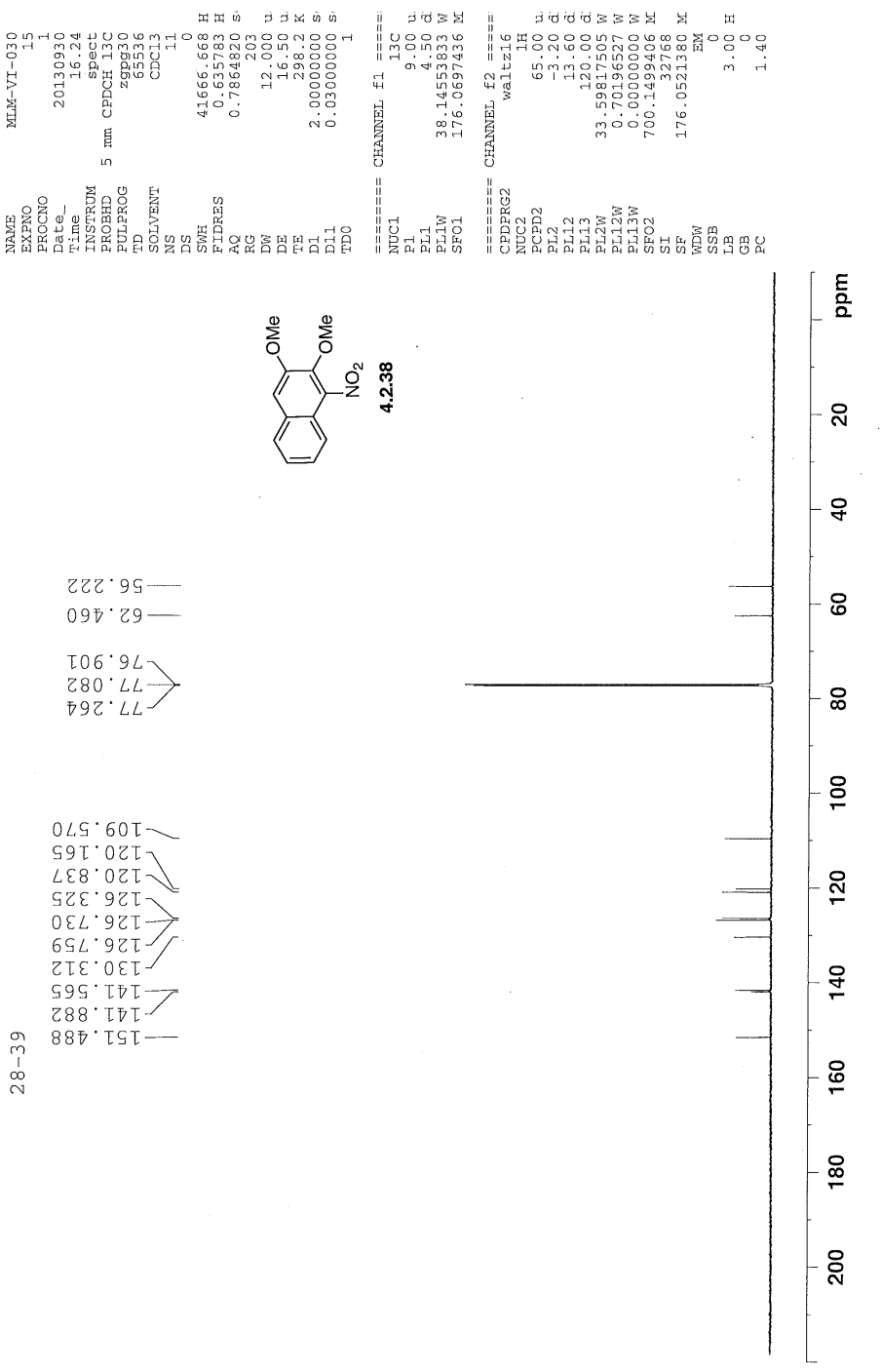

NAME MLM-VI-030
EXPNO 7
PROCNO 1
Date_ 20130930
Time 11.51
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDC13
NS 4
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 203
DW 42.000 u
DE 6.50 u
TE 298.1 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
OMe
OMe
O2N
4.2.36
93-108
8.684
8.681
8.156
8.152
8.143
8.140
7.803
7.790
7.290
7.220
4.085
4.073
6.11
1.00
0.98
0.98
1.00
ppm

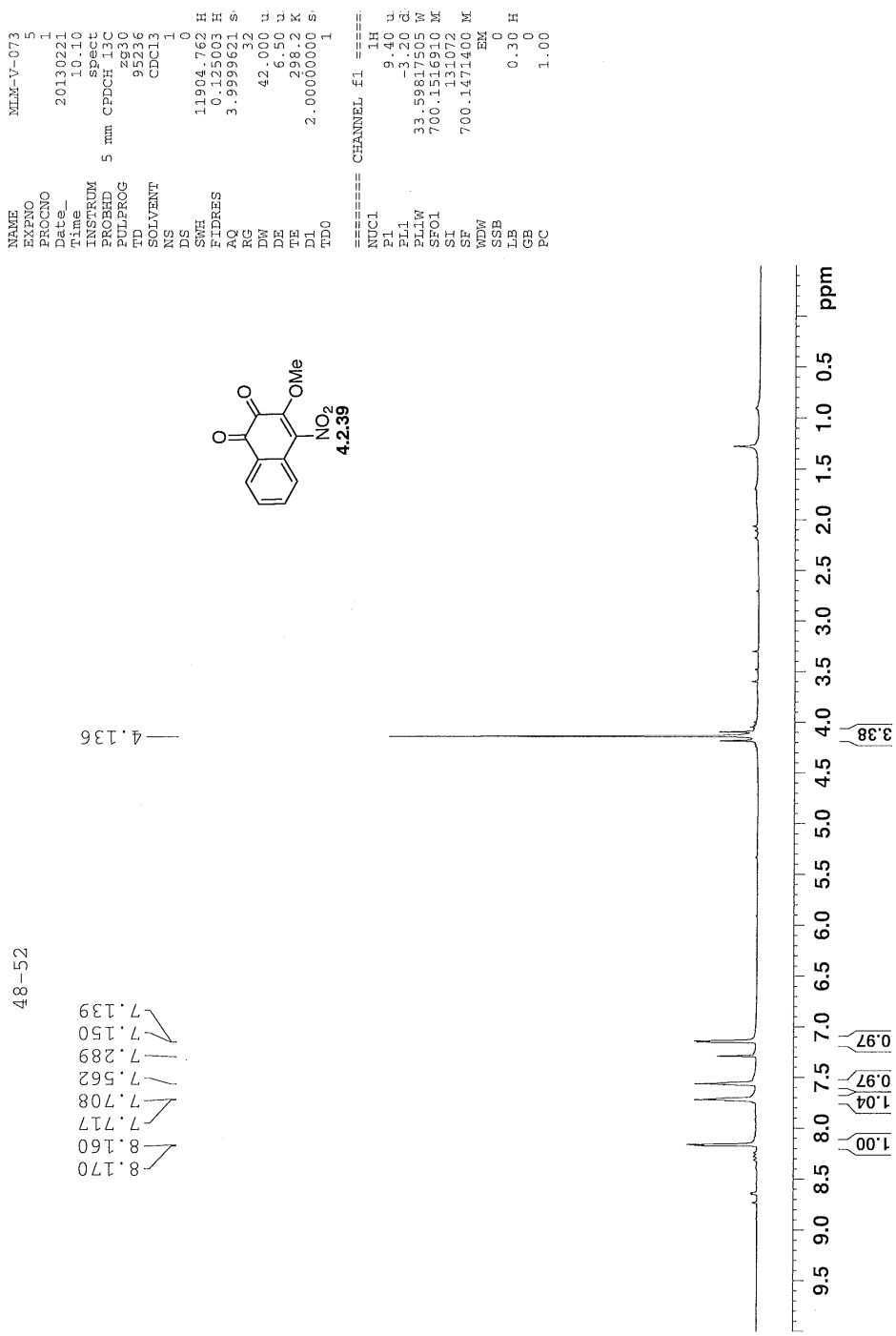

NAME MLM-VI-030
EXPNO 8
PROCNO 1
Date_ 20130930
Time 11.53
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 48
DS 0
SWH 41666.668 H
FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.1 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 =====
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0897436 M
======== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
OMe
OMe
O2N
4.2.36
93-108
152.538
151.011
144.394
132.661
127.891
127.382
122.950
118.047
107.696
106.166
77.209
77.027
76.845
56.173
56.136
200
180
160
140
120
100
80
60
40
20
ppm

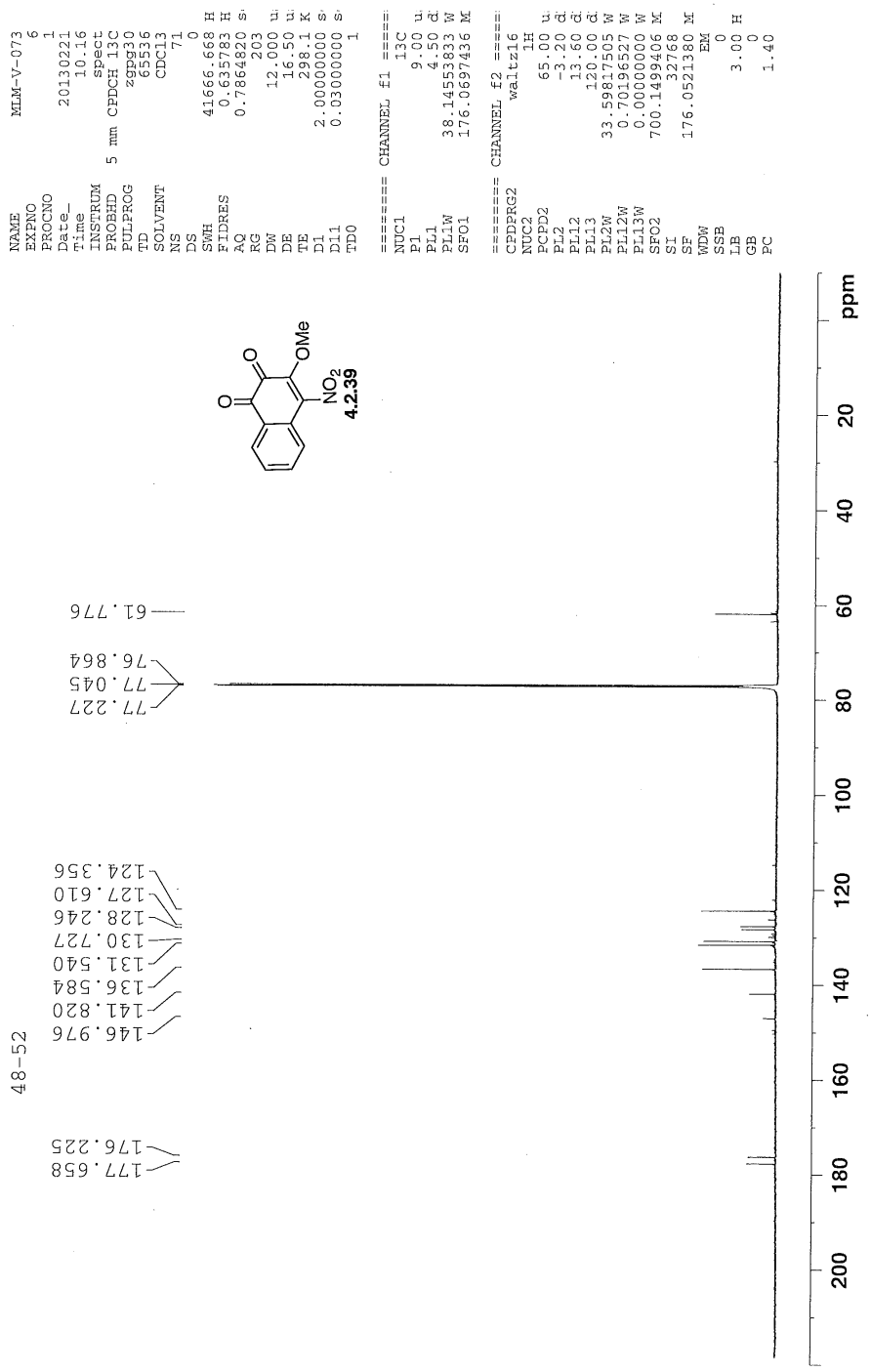

NAME MLM-VI-030
EXPNO 4
PROCNO 1
Date_ 20130930
Time_ 11.33
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 9
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 203
DW 42.000 u
DE 6.50 u
TE 298.2 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
OMe
OMe
NO2
4.2.37
70-84
8.212
8.210
8.201
8.199
8.079
7.993
7.981
7.433
7.421
7.410
7.290
7.229
4.093
4.067
3.04
3.02
1.00
0.99
1.00
1.00
1.00
ppm

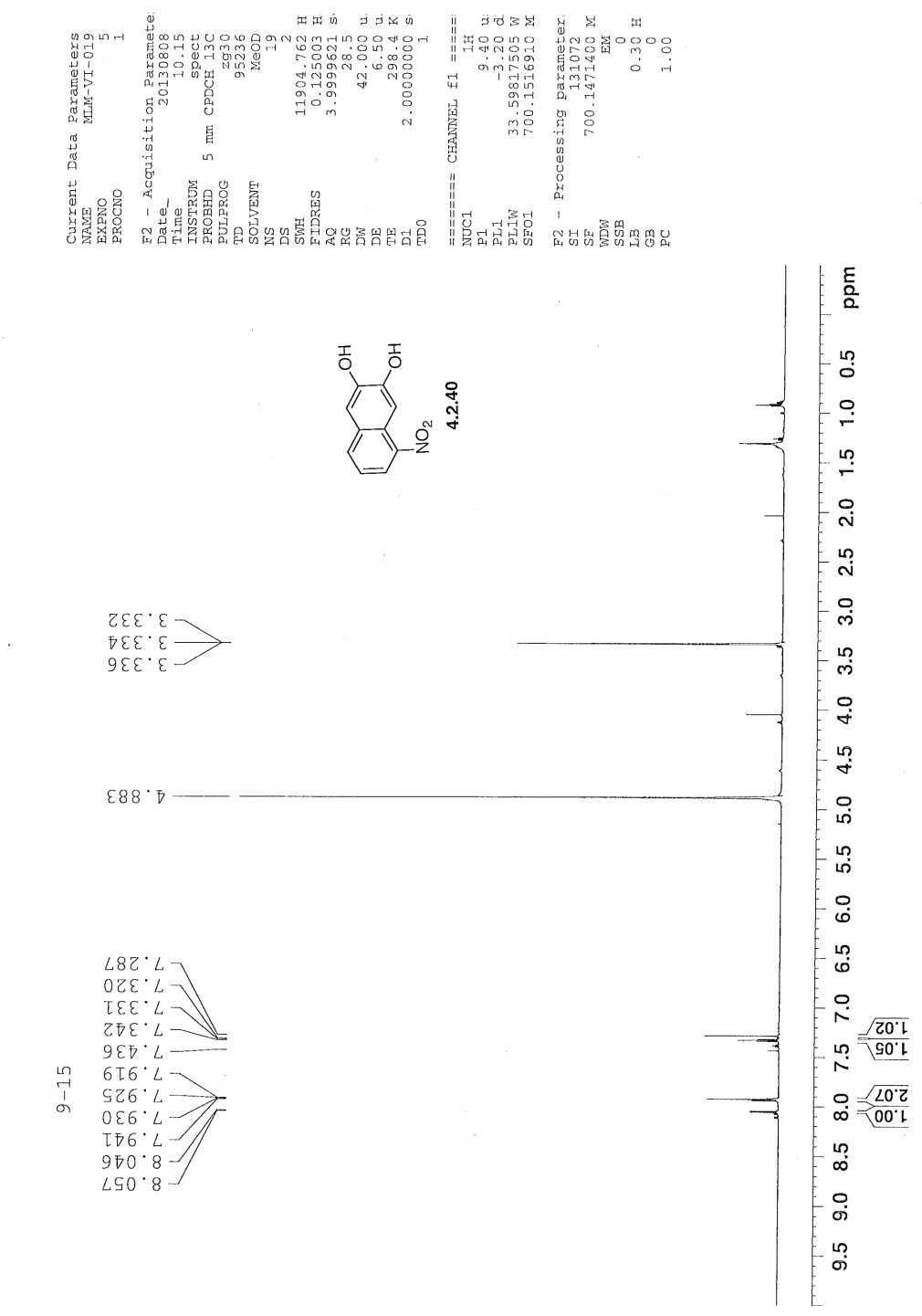

NAME MLM-VI-030
EXPNO 5
PROCNO 1
Date_ 20130930
Time 11.36
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 71
DS 0
SWH 41666.668 H
FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.2 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 =====
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0697436 M
======== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499405 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
OMe
OMe
NO2
4.2.37
70-84
152.435
150.240
145.051
133.083
130.953
122.776
122.540
121.675
106.778
102.245
77.211
77.029
76.848
56.163
55.990
200
180
160
140
120
100
80
60
40
20
ppm

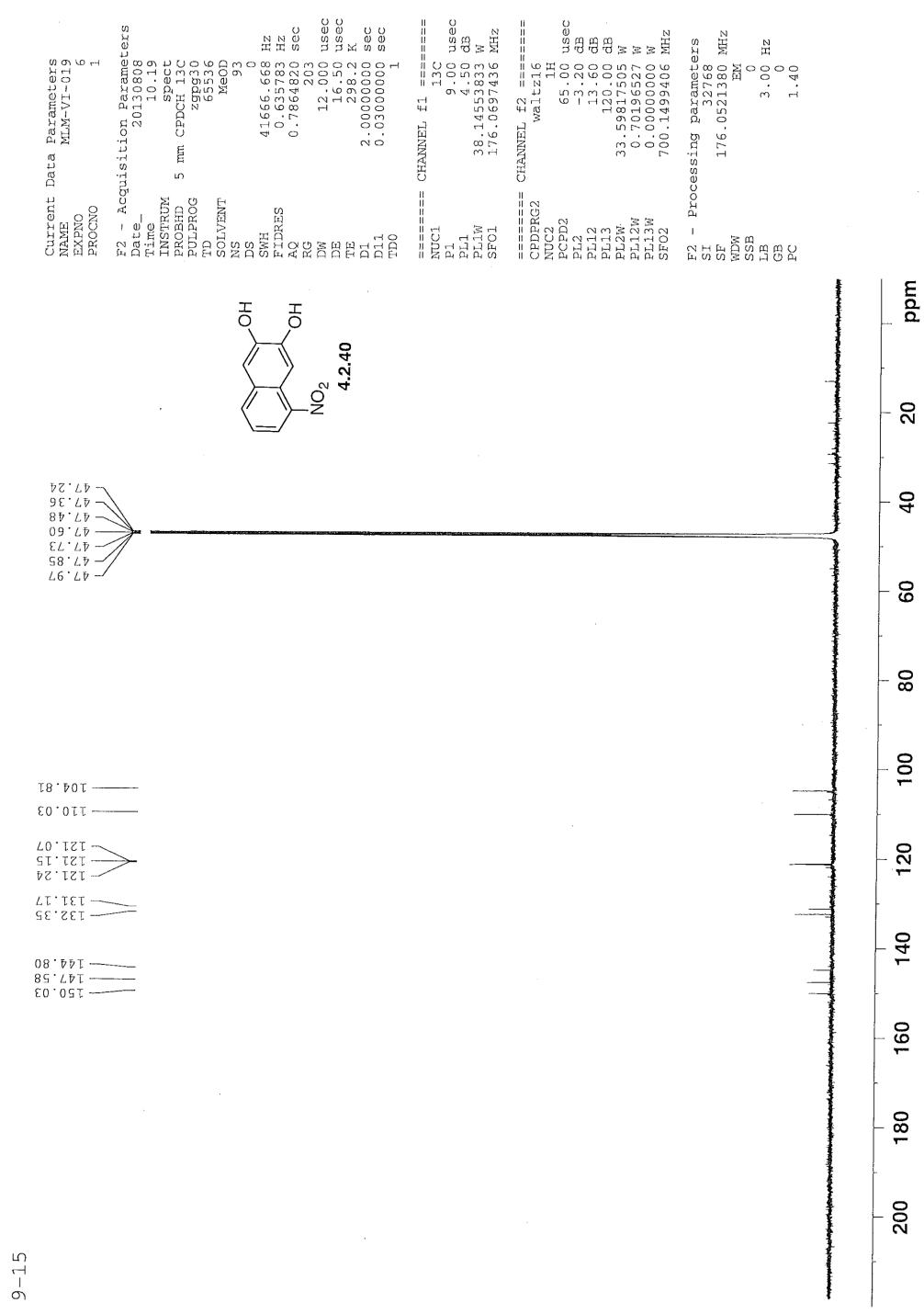

NAME MLM-VI-030
EXPNO 14
PROCNO 1
Date_ 20130930
Time_ 16.22
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 10
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 22.6
DW 42.000 u
DE 6.50 u
TE 298.1 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
OMe
OMe
NO2
4.2.38
28-39
4.059
4.038
7.771
7.769
7.758
7.626
7.616
7.613
7.495
7.493
7.489
7.485
7.482
7.477
7.475
7.298
6.05
1.00
0.98
1.96
1.02
ppm


NAME MLM-VI-030
EXPNO 15
PROCNO 1
Date_ 20130930
Time 16.24
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 11
DS 0
SWH 41666.668 H
FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.2 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0697436 M
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
OMe
OMe
NO2
4.2.38
28-39
151.488
141.882
141.565
130.312
126.759
126.730
126.325
120.837
120.165
109.570
77.264
77.082
76.901
62.460
56.222
200
180
160
140
120
100
80
60
40
20
ppm

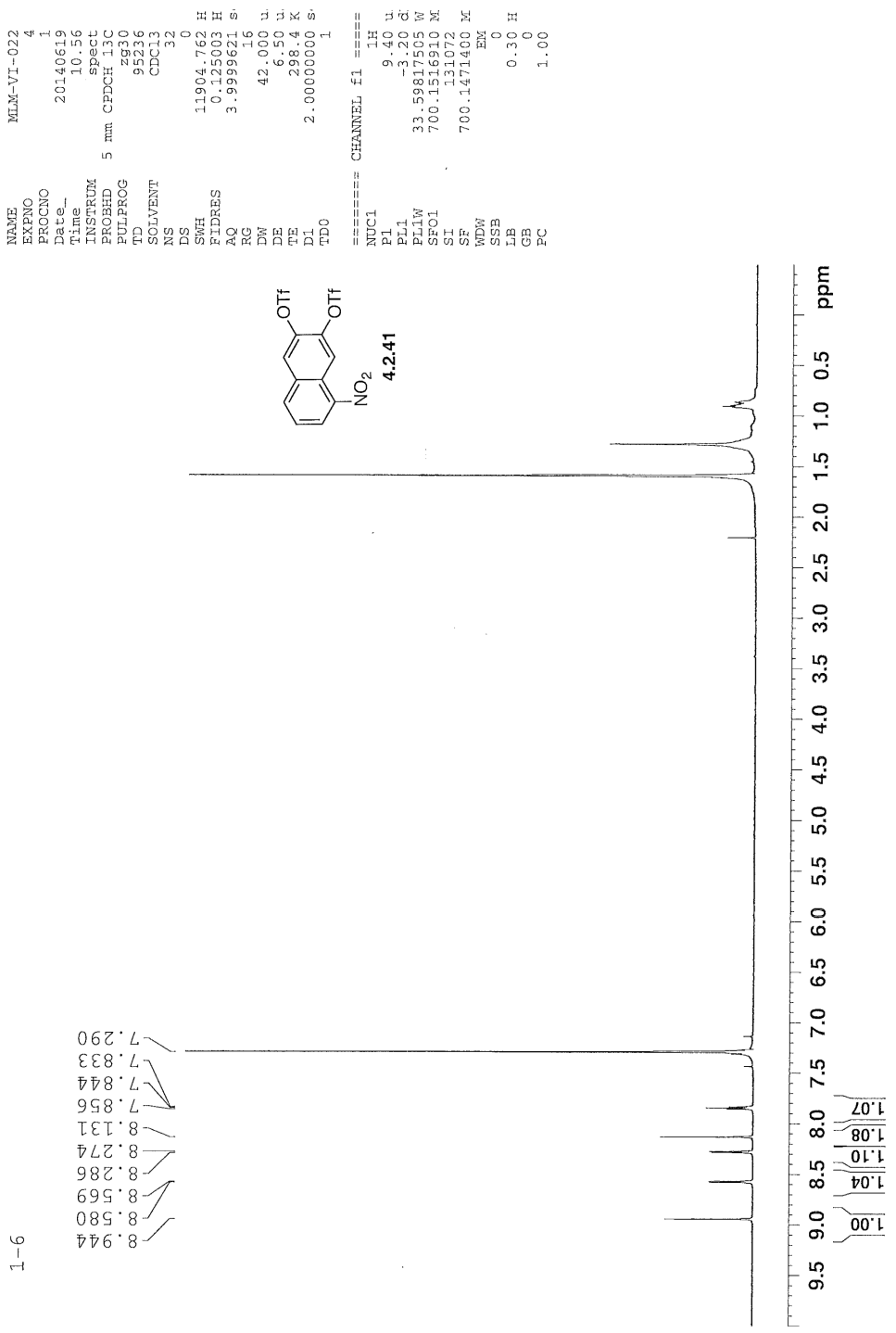

NAME MLM-V-073
EXPNO 5
PROCNO 1
Date_ 20130221
Time_ 10.10
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDCl3
NS 1
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 32
DW 42.000 u
DE 6.50 u
TE 298.2 K
D1 2.00000000 s
TDO 1
======== CHANNEL f1 ======
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
OMe
NO2
4.2.39
48-52
4.136
8.170
8.160
7.717
7.708
7.562
7.289
7.150
7.139
3.38
1.00
1.04
0.97
0.97
ppm

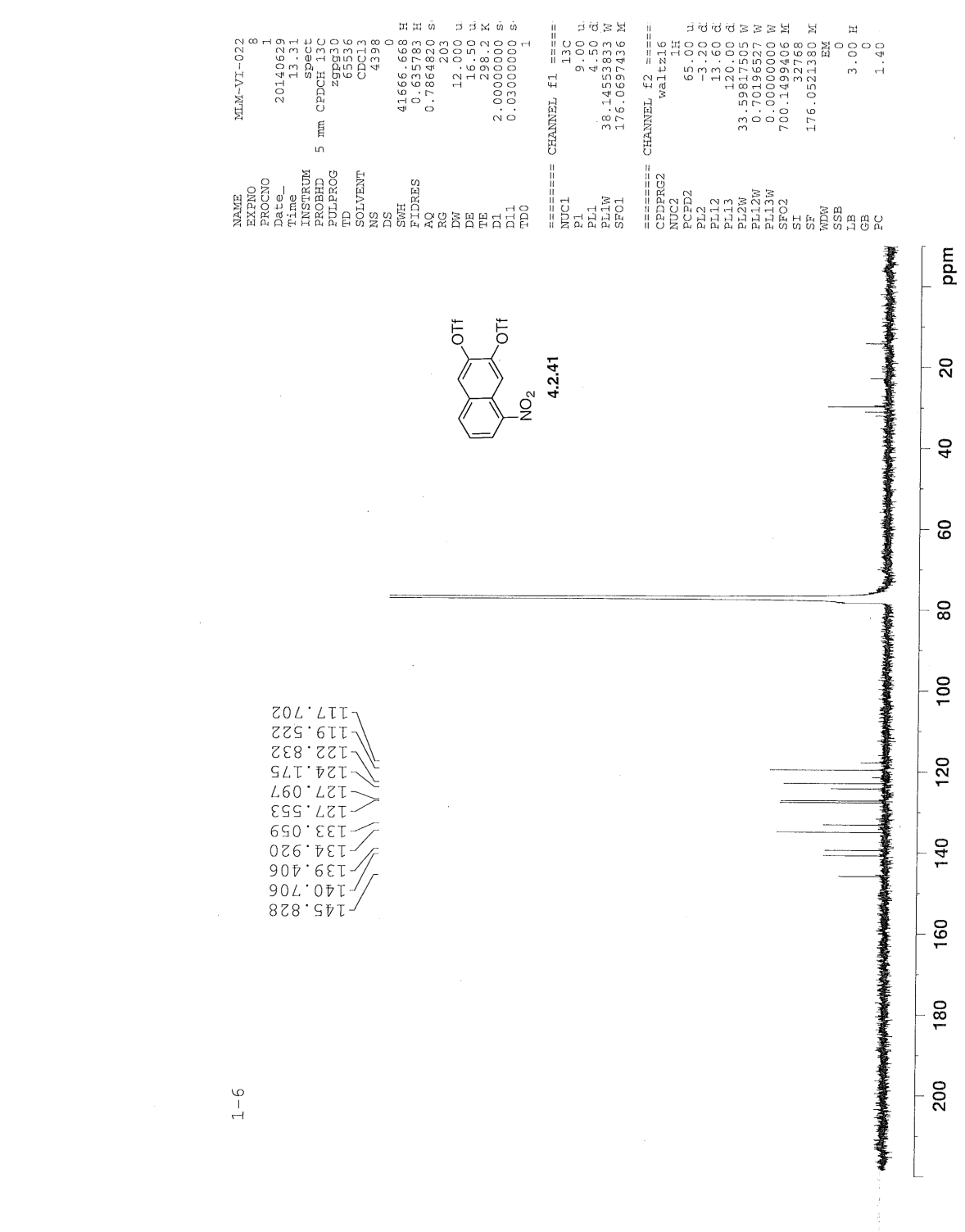

NAME MLM-V-073
EXPNO 6
PROCNO 1
Date_ 20130221
Time 10.16
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 71
DS 0
SWH 41666.668 H
FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.1 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0897436 M
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
OMe
NO2
4.2.39
48-52
61.776
76.864
77.045
77.227
124.356
127.610
128.246
130.727
131.540
136.584
141.820
146.976
176.225
177.658
ppm
200
180
160
140
120
100
80
60
40
20

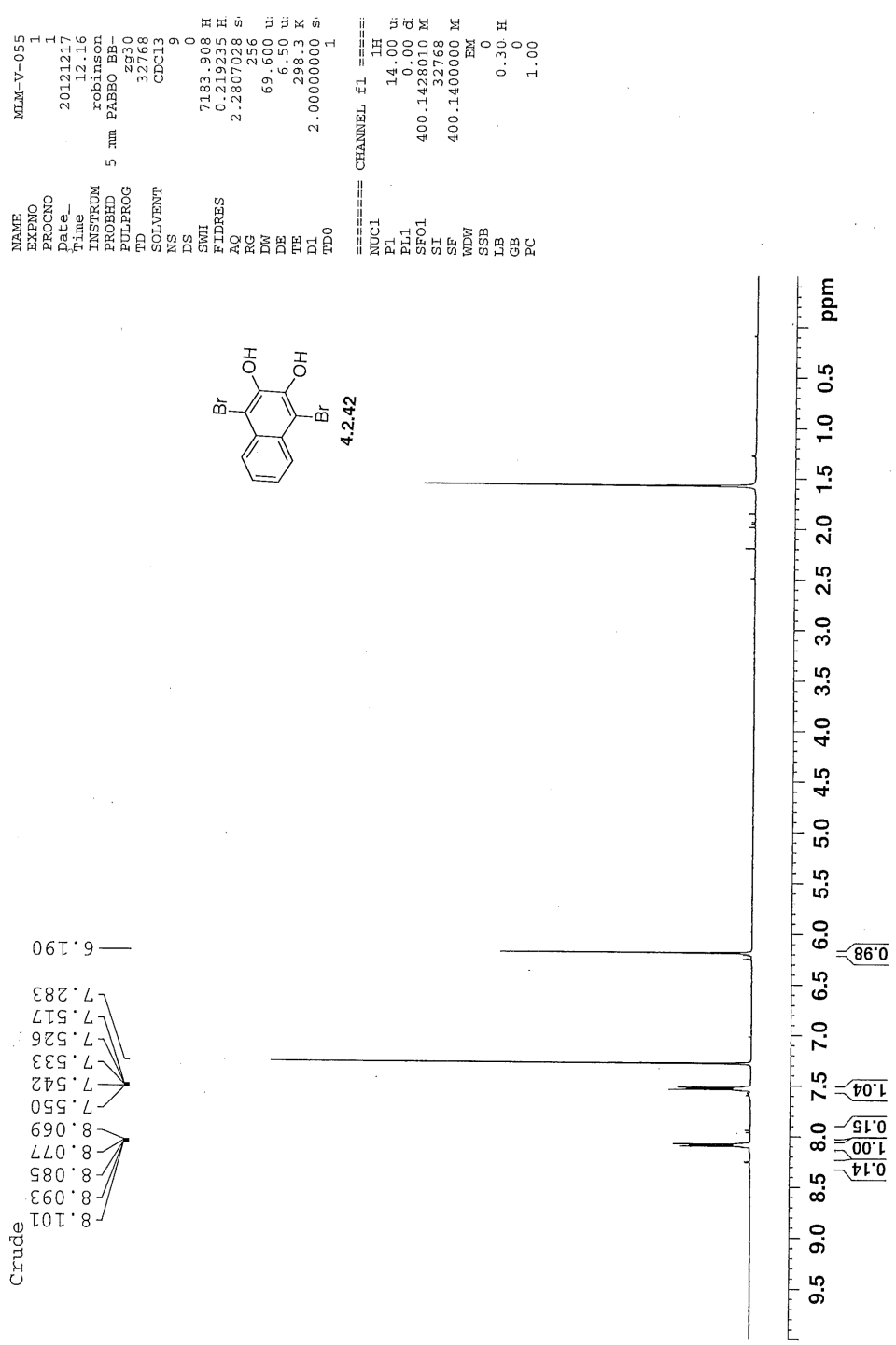

Current Data Parameters
NAME MLM-VI-019
EXPNO 5
PROCNO 1
F2 - Acquisition Parameter
Date_ 20130808
Time 10.15
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT MeOD
NS 19
DS 2
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 28.5
DW 42.000 u
DE 6.50 u
TE 298.4 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
F2 - Processing parameter
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
OH
OH
NO2
4.2.40
9-15
8.057
8.046
7.941
7.930
7.925
7.919
7.436
7.342
7.331
7.320
7.287
4.883
3.336
3.334
3.332
1.00
2.07
1.05
1.02
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 ppm

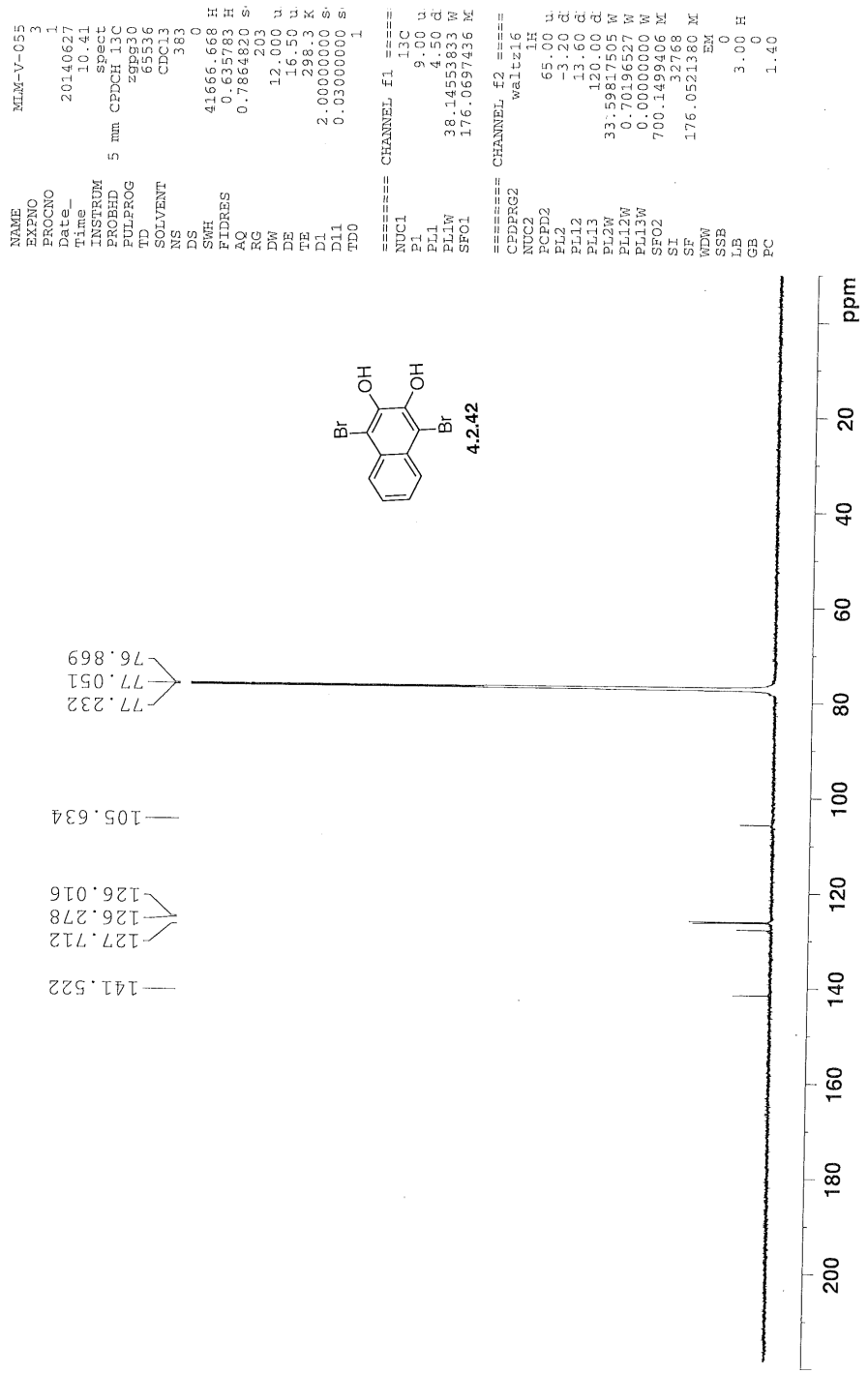

Current Data Parameters
NAME MLM-VI-019
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130808
Time_ 10.19
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 93
DS 0
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864820 sec
RG 203
DW 12.000 usec
DE 16.50 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 4.50 dB
PL1W 38.14553833 W
SFO1 176.0697436 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 usec
PL2 -3.20 dB
PL12 13.60 dB
PL13 120.00 dB
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 MHz
F2 - Processing parameters
SI 32768
SF 176.0521380 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
OH
OH
NO2
4.2.40
47.24
47.36
47.48
47.60
47.73
47.85
47.97
104.81
110.03
121.07
121.15
121.24
131.17
132.35
144.80
147.58
150.03
200
180
160
140
120
100
80
60
40
20
ppm

9-15


NAME MLM-VI-022
EXPNO 4
PROCNO 1
Date_ 20140619
Time 10.56
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 95236
SOLVENT CDC13
NS 32
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 16
DW 42.000 u
DE 6.50 u
TE 298.4 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 =====
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PL1W 33.59817505 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
OTf
OTf
NO2
4.2.41
1-6
8.944
8.580
8.569
8.286
8.274
8.131
7.856
7.844
7.833
7.290
1.00
1.04
1.10
1.08
1.07
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 ppm


NAME MLM-VI-022
EXPNO 8
PROCNO 1
Date_ 20140629
Time 13.31
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4398
DS 0
SWH 41666.668 H
FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.2 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 =====
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0697436 M
======== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
OTf
OTf
NO2
4.2.41
145.828
140.706
139.406
134.920
133.059
127.553
127.097
124.175
122.832
119.522
117.702
200
180
160
140
120
100
80
60
40
20
ppm
1-6


NAME MLM-V-055
EXPNO 1
PROCNO 1
Date_ 20121217
Time 12.16
INSTRUM robinson
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 9
DS 0
SWH 7183.908 H
FIDRES 0.219235 H
AQ 2.2807028 s
RG 256
DW 69.600 u
DE 6.50 u
TE 298.3 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 14.00 u
PL1 0.00 d
SFO1 400.1428010 M
SI 32768
SF 400.1400000 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
OH
OH
Br
Br
4.2.42
Crude
8.101
8.093
8.085
8.077
8.069
7.550
7.542
7.533
7.526
7.517
7.283
6.190
0.14
1.00
0.15
1.04
0.98
ppm


NAME MLM-V-055
EXPNO 3
PROCNO 1
Date_ 20140627
Time 10.41
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 383
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RG 203
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DE 16.50 u
TE 298.3 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
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P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0697436 M
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NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
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OH
Br
Br
4.2.42
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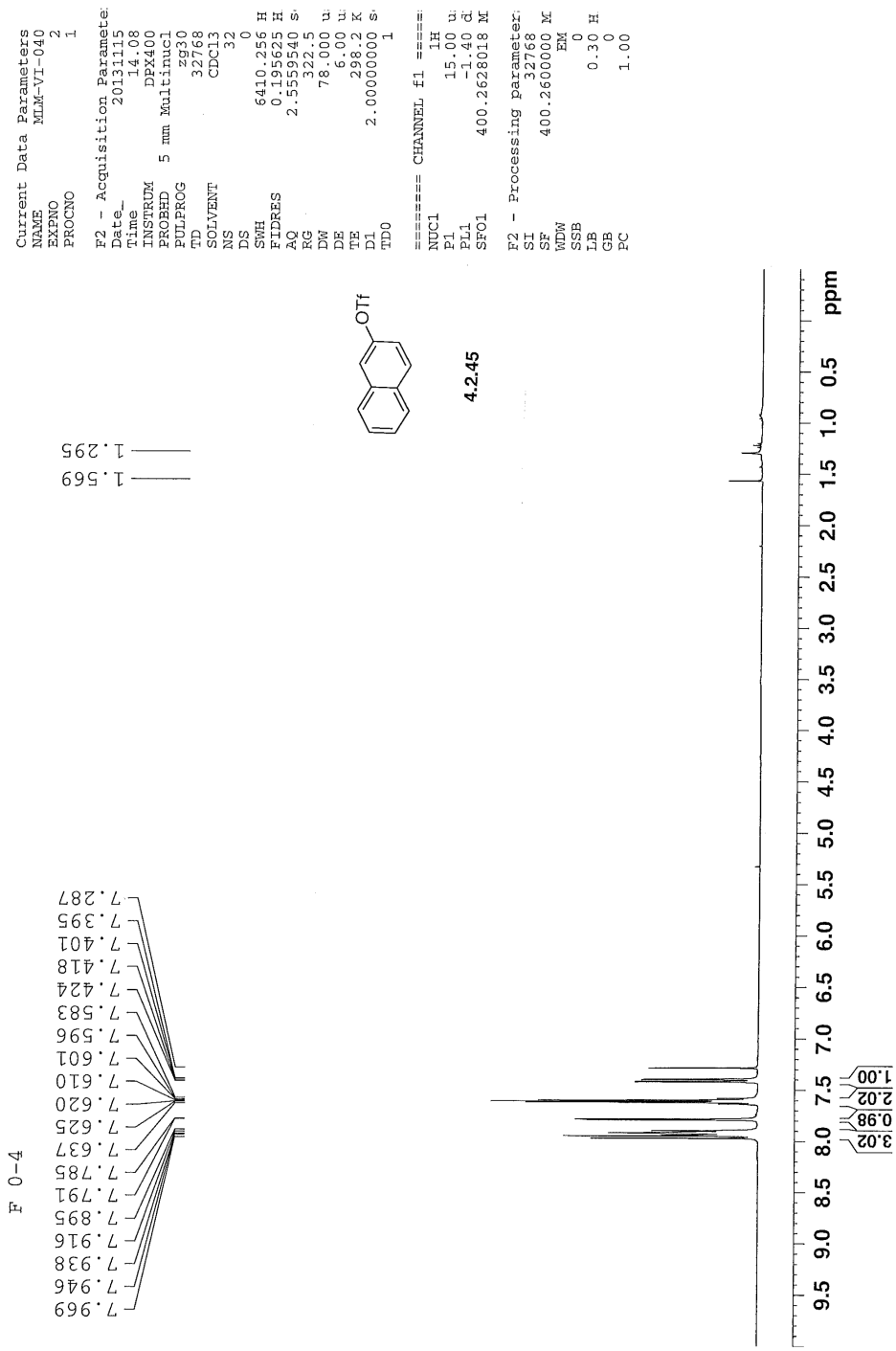
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1.295
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7.946
7.938
7.916
7.895
7.791
7.785
7.637
7.625
7.620
7.610
7.601
7.596
7.583
7.424
7.418
7.401
7.395
7.287
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0.98
2.02
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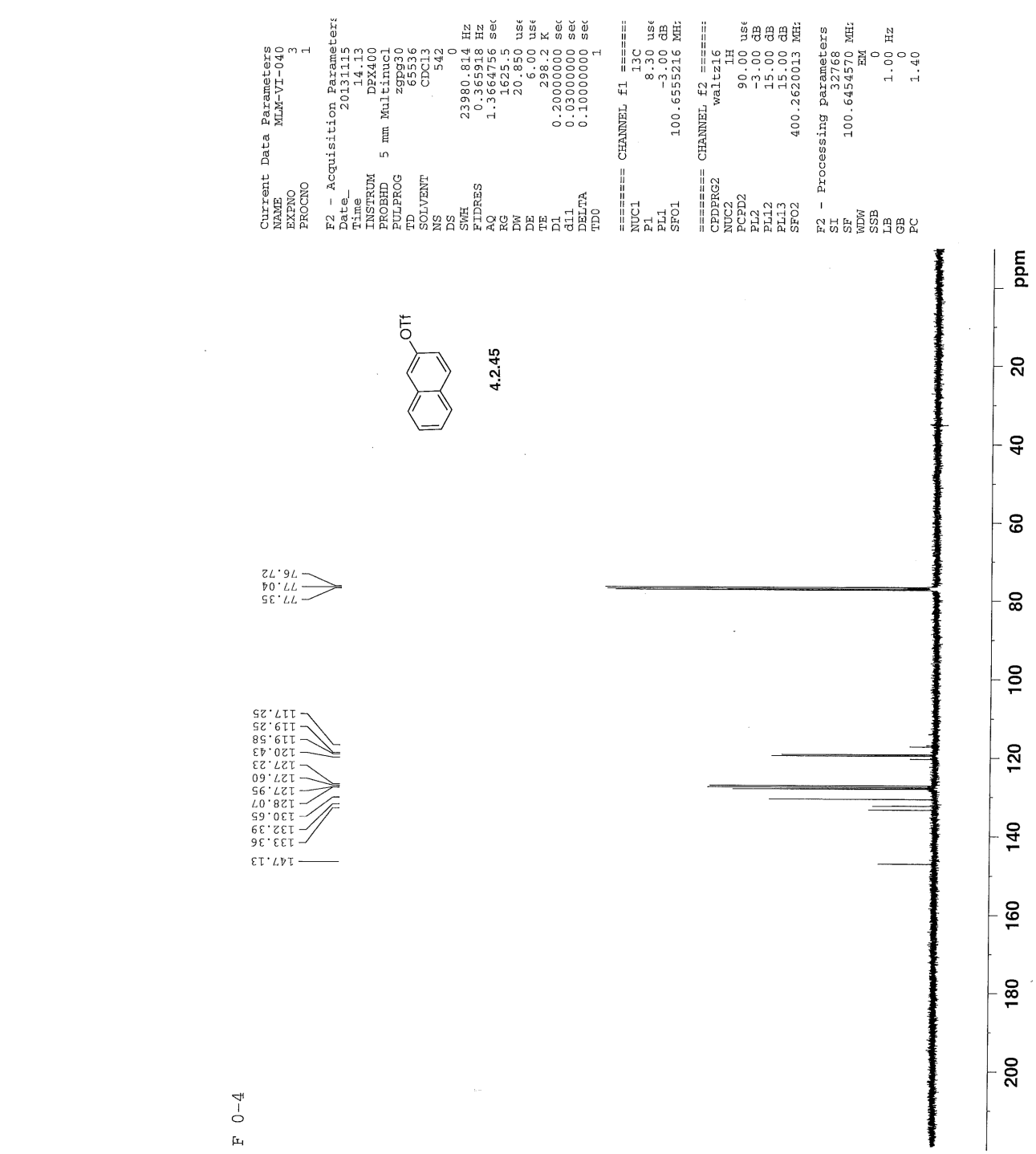
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AQ 1.3664756 sec
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d11 0.03000000 sec
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SFO1 100.6555216 MHz
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PCPD2 90.00 usec
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60
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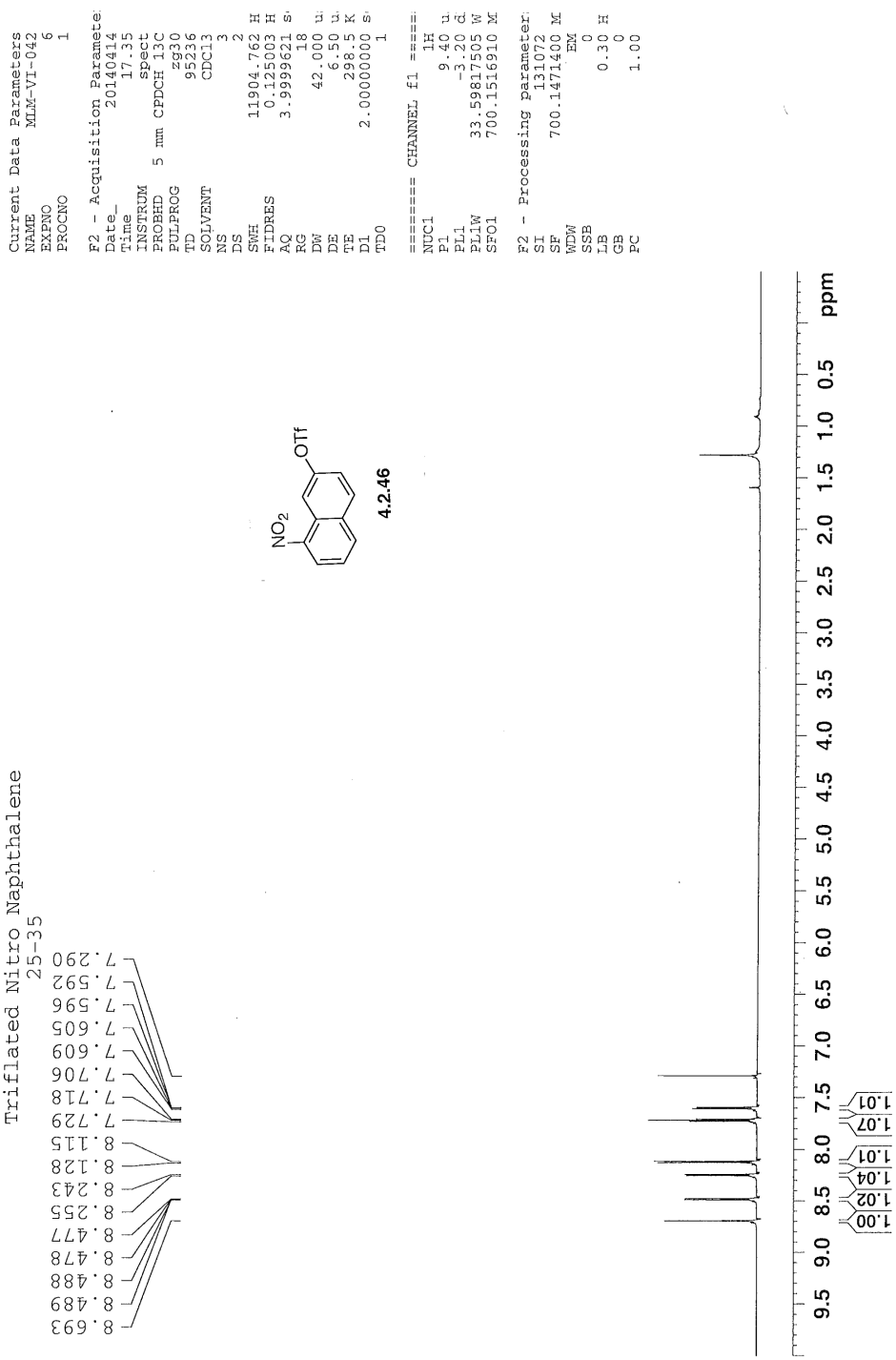
Triflated Nitro Naphthalene
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8.488
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7.609
7.605
7.596
7.592
7.290
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PROCNO 1
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TD 95236
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FIDRES 0.125003 H
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RG 18
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TE 298.5 K
D1 2.00000000 s
TD0 1
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4.2.46
1.00
1.02
1.04
1.01
1.07
1.01
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 ppm

Triflated Nitro Naphthalene
25-35

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125.61
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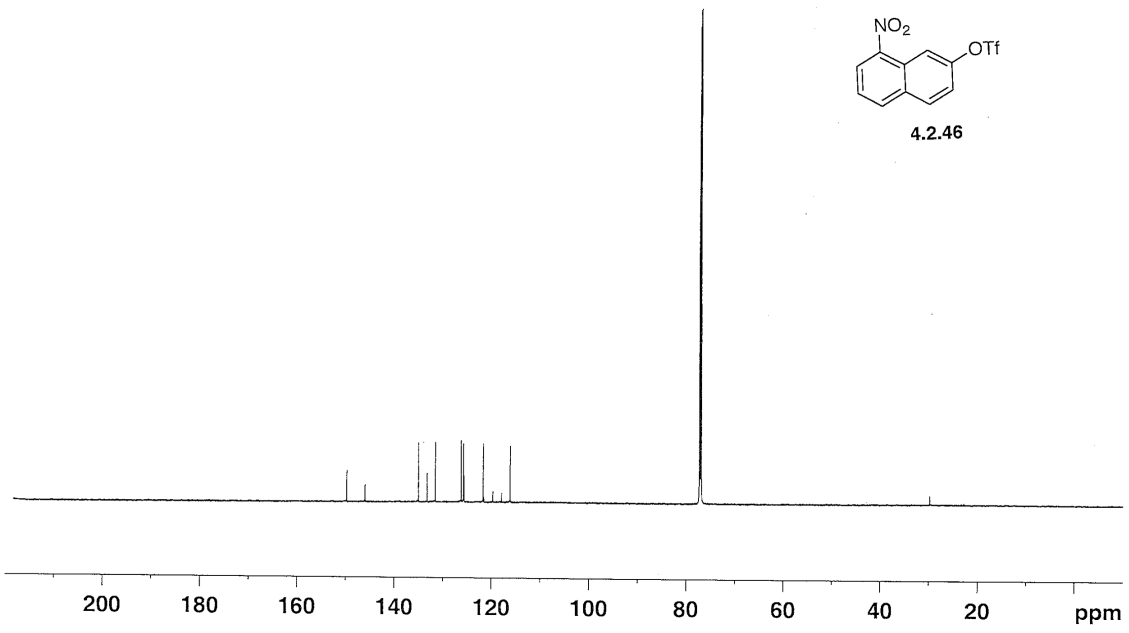

4.2.46

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PROCNO                 1

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TD                65536
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DS                    0
SWH           41666.668 Hz
FIDRES         0.635783 Hz
AQ             0.7864820 sec
RG                  203
DW                12.000 usec
DE                16.50 usec
TE                298.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 9.00 usec
PL1                4.50 dB
PL1W        38.14553833 W
SFO1       176.0697436 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             65.00 usec
PL2               -3.20 dB
PL12              13.60 dB
PL13             120.00 dB
PL2W        33.59817505 W
PL12W        0.70196527 W
PL13W        0.00000000 W
SFO2       700.1499406 MHz

F2 - Processing parameters
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WDW                   EM
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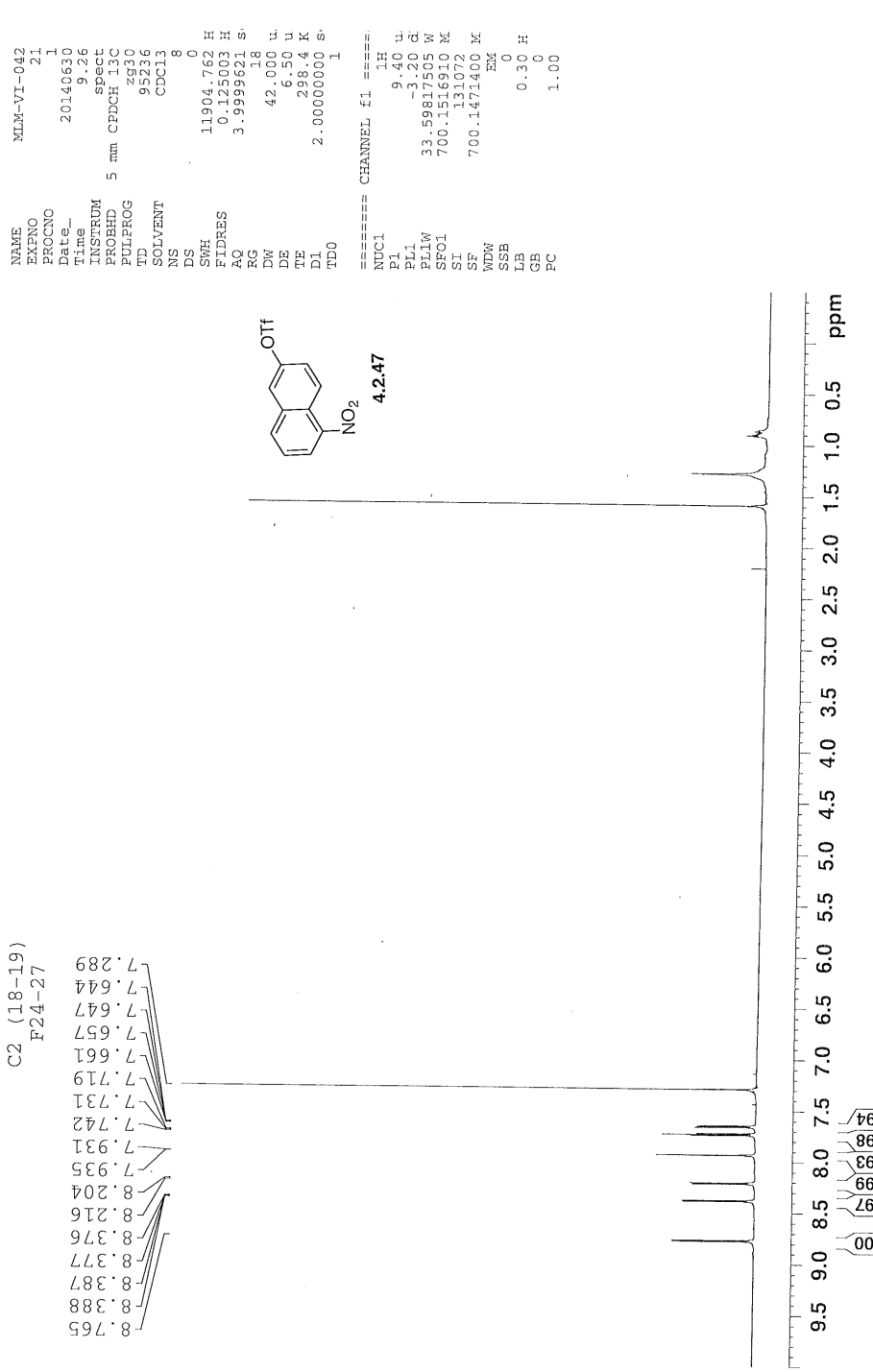
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TD 95236
SOLVENT CDCl3
NS 8
DS 0
SWH 11904.762 H
FIDRES 0.125003 H
AQ 3.9999621 s
RG 18
DW 42.000 u
DE 6.50 u
TE 298.4 K
D1 2.00000000 s
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 9.40 u
PL1 -3.20 d
PLIW 33.59817595 W
SFO1 700.1516910 M
SI 131072
SF 700.1471400 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00
OTf
NO2
4.2.47
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F24-27
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8.387
8.377
8.376
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7.931
7.742
7.731
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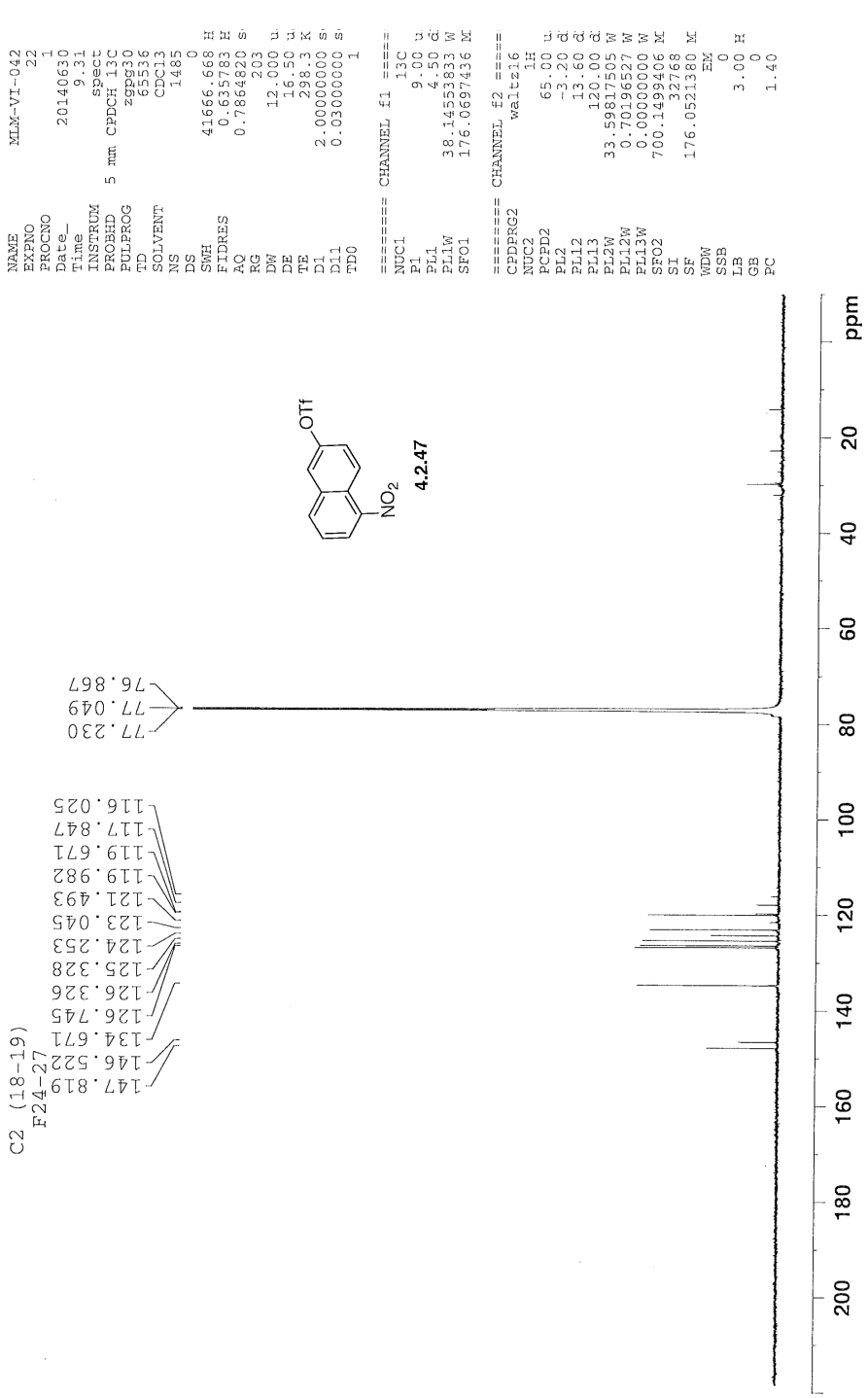
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1485
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FIDRES 0.635783 H
AQ 0.7864820 s
RG 203
DW 12.000 u
DE 16.50 u
TE 298.3 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 =====
NUC1 13C
P1 9.00 u
PL1 4.50 d
PL1W 38.14553833 W
SFO1 176.0697436 M
======== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 65.00 u
PL2 -3.20 d
PL12 13.60 d
PL13 120.00 d
PL2W 33.59817505 W
PL12W 0.70196527 W
PL13W 0.00000000 W
SFO2 700.1499406 M
SI 32768
SF 176.0521380 M
WDW EM
SSB 0
LB 3.00 H
GB 0
PC 1.40
OTf
NO2
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76.867
C2 (18-19)
F24-27
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134.671
126.745
126.326
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123.045
121.493
119.982
119.671
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ppm
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180
160
140
120
100
80
60
40
20

Section 6.4. Gas Chromatography Mass Spectrometry Data

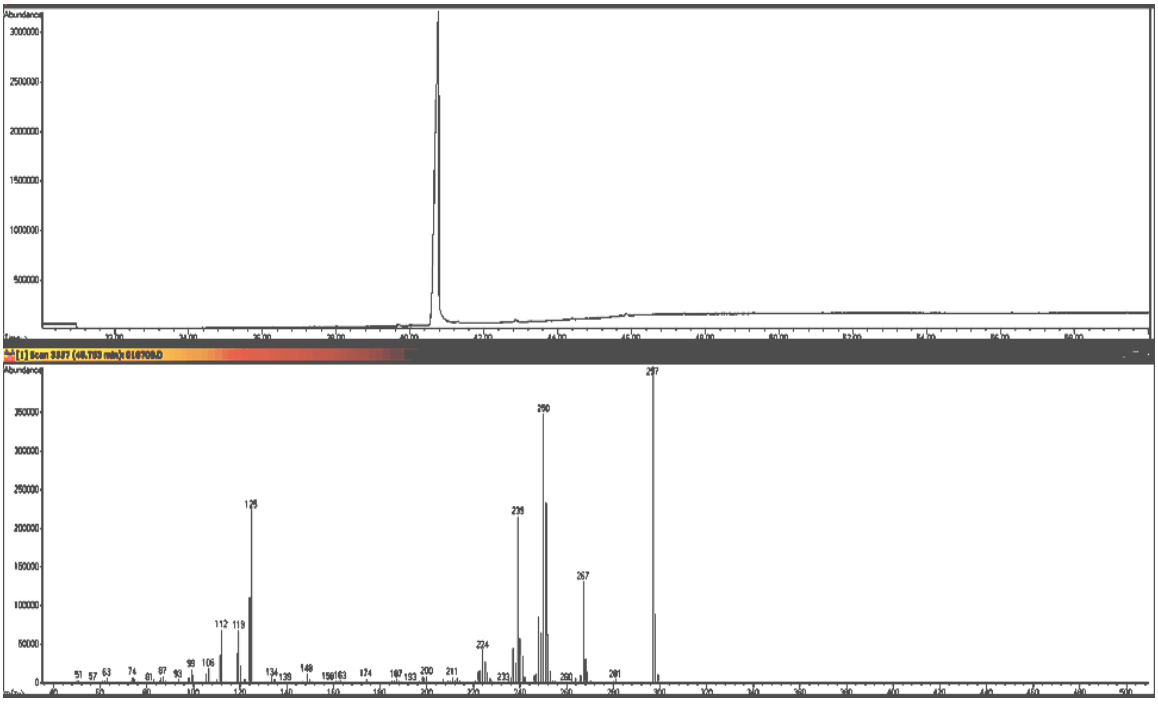

Figure 6.4.1. 7-Nitrobenzo[k]fluoranthene

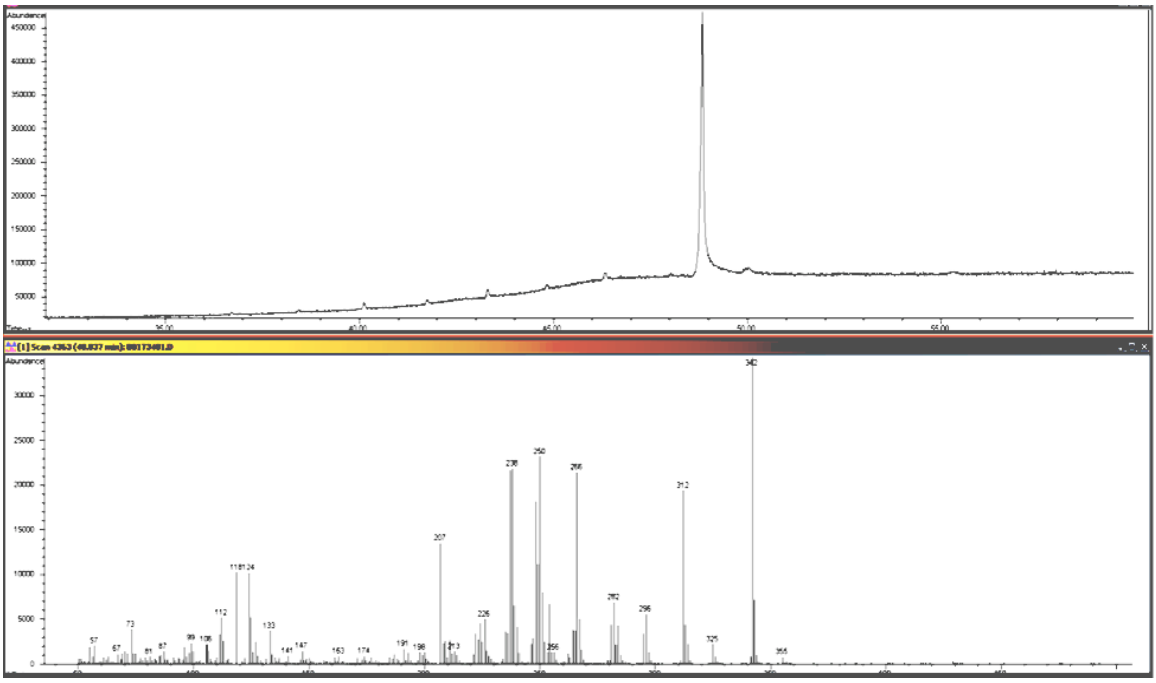

Figure 6.4.2. 3,7-Dinitrobenzo[k]fluoranthene

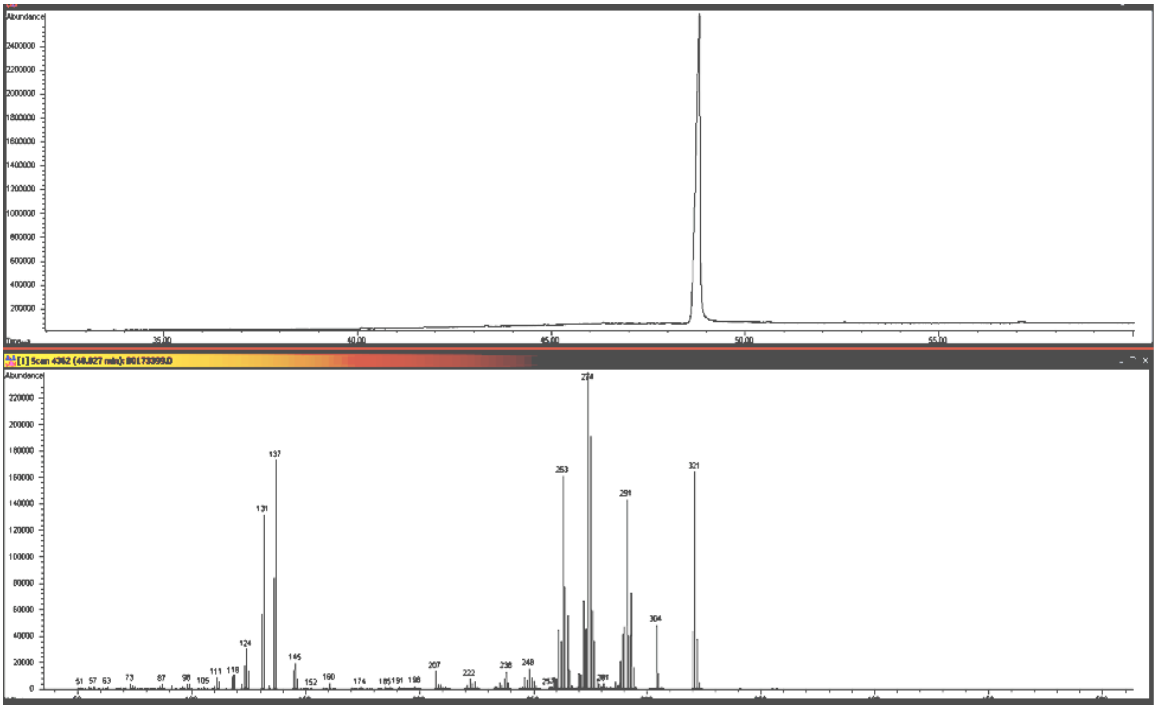

Figure 6.4.3. 7-Nitrobenzo[ghi]perylene

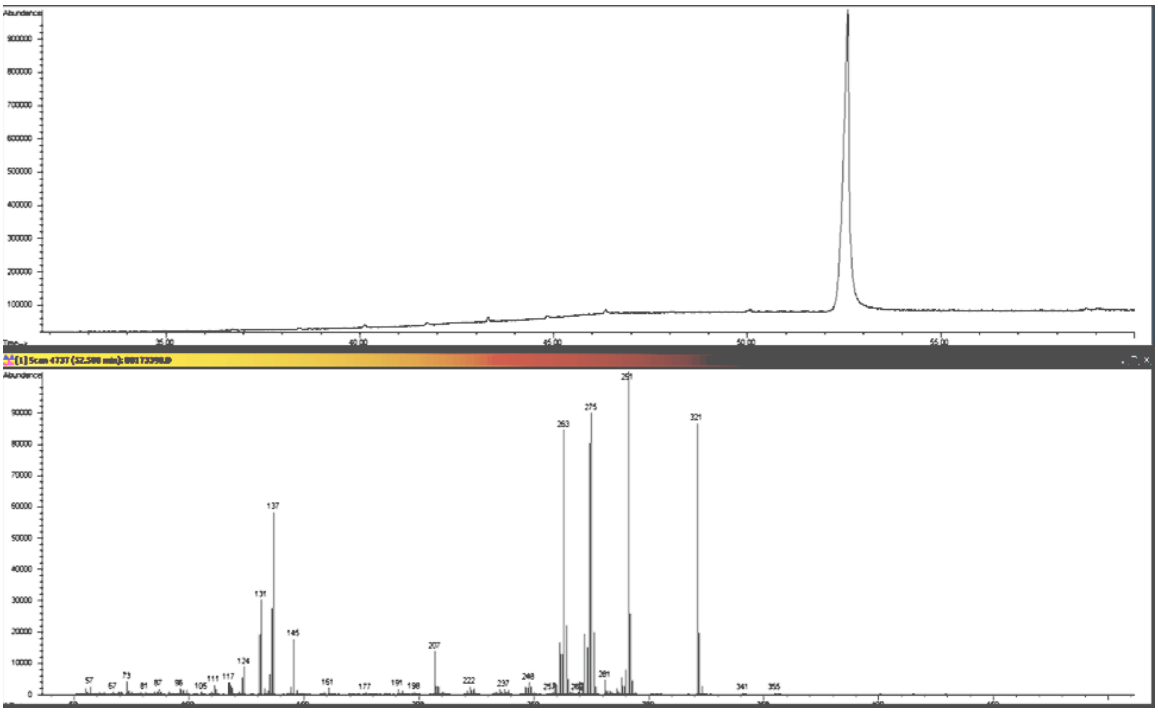

Figure 6.4.4. 5-Nitrobenzo[ghi]perylene

Section 6.5. NMR Correlation Tables

Table 6.5.1. Proton 1D and 2D NMR Data for 3,7-NBKF **4.1.5**

^{1}H shift (ppm)	Multiplicity	Integration	J values (Hz)	COSY	NOE
8.83	d	1	8.4	7.9	8.05, 7.89
8.7	d	1	7.7	8.12	8.12
8.49	s	1			8.12, 8.03
8.12	d	1	7.7	8.7	8.5, 8.7
8.03	dd	2	8.4, 7	7.68, 7.9	
7.9	m	2		7.73, 8.83	
7.73	t	1	7	7.9	
7.68	t	1	7	8.03	

Table 6.5.2. Carbon 1D and Carbon-Proton 2D NMR Correlation Data for 3,7-NBKF **4.1.5**

^{13}C shift (ppm)	HSQC	HMBC	^{13}C shift (ppm)	HSQC	HMBC
144.4	q	8.83 (w), 8.7, 8.12	128.5	q	8.02
142.6	q	8.5 (w), 7.92 (w)	128.3	7.68	8.5, 7.92
141.4	q	8.7, 8.5	127.6	8.70	
135.9	q	8.83, 8.12, 8.02	126.3	8.83	8.02
135.4	q		125.1	q	8.5, 8.05, 7.73
133.6	q	7.92, 7.68	124.7	8.50	7.89
132.3	7.9	7.89 overlap	124.5	8.03	8.83
132.2	q	7.89 overlap	123.6	q	8.7, 7.89
129.6	7.73	8.05	122.6	7.9	7.68
129.4	8.03	8.5, 7.73	118.4	8.12	none

Table 6.5.3. Proton 1D and 2D NMR Data for 5-NBGHIP **4.1.16**

^{1}H shift (ppm)	Multiplicity	Integration	J values (Hz)	COSY
9.11	d	1	7.8	8.14
9.06	d	2	8.7	8.73
8.94	d	1	9	8.43
8.73	d	1	8.4	9.06
8.49	dd	1	8.12, 7.98	
8.43	d	2	9.1	8.94
8.39	d	1	7.28	8.14
8.23	dd	1	8.54, 8.68	
8.14	t	1	7.6	8.39, 9.11

Table 6.5.4. Carbon 1D and Carbon-Proton 2D NMR Correlation Data for 5-NBGHIP **4.1.16**

^{13}C shift (ppm)	HSQC	HMBC	^{13}C shift (ppm)	HSQC	HMBC
144.2	q	9.06, 8.94 (w), 8.73(w)	126.7	8.14	
135.4	q	9.1, 8.73	126.5	8.49 (r)	8.43
131.9	q	8.23, 8.14	126.4	q	9.06, 8.94
131.4	8.43	8.69	125.4	q	9.11, 8.73, 8.43, 8.39, 8.23 overlap
130.6	q	8.69, 8.23	125.3	q	9.11, 8.73, 8.43, 8.39, 8.24 overlap
128.9	8.39	9.11	123.6	q	8.69
128.8	q	9.06	123.4	8.73	8.23
128.5	q	8.94, 8.69, 8.23, 8.14	123	q	8.69, 8.43
128.1	8.23 (r)	8.39	122.7	9.11	8.39
127.8	8.23 (l)		121.4	8.94	
127	8.49 (l)	8.23	119.6	9.06	

Table 6.5.6. Proton 1D and 2D NMR Data for 7-NBGHIP **4.1.12**

^{1}H shift (ppm)	Multiplicity	Integration	J values (Hz)	COSY
8.63	d	1	7.9	8.00
8.46	dd	2	8.1, 8.1	
8.33	d	1	7.6	8.00
8.31	d	1	8.7	8.16
8.25	d	1	8.7	8.10
8.21	dd	2	8.6, 8.7	
8.16	d	1	8.6	8.30
8.10	d	1	8.2	8.25
8.00	t	1	7.8	8.33, 8.63

Table 6.5.7. Carbon 1D and Carbon-Proton 2D NMR Correlation Data for 7-NBGHIP **4.1.12**

^{13}C shift (ppm)	HSQC	HMBC	^{13}C shift (ppm)	HSQC	HMBC
146.4	q	8.25, 8.10 (vw)	126.57	8.16	8.31, 8.25 overlap
133.5	q	8.31, 8.16, 8.10	126.5	q	8.25 overlap
131.9	q	8.21, 8.00	126.34	8	8.25, 8.16 overlap
129.9	q	8.21	126.3	8.25	8.25, 8.16 overlap
129.8	8.31	8.46	126	q	8.63, 8.33, 8.21
129.3	q	8.46, 8.31 (w), 8.16	125.3	8.63	8.33,
128.7	8.33	8.63, 8.21	125.1	q	8
128.1	8.21 (r)	8.33	123.4	q	8.46, 8.31, 8.21 overlap
127.3	8.21 (l)	8.46	123.3	q	8.46, 8.31, 8.22 overlap
126.9	8.46 (l)	8.21	122.2	q	8.63, 8.10
126.63	8.46	8.31, 8.25 overlap	121.6	8.10	8.25