Accepted Manuscript

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PII: S0040-4020(15)01059-5

DOI: 10.1016/j.tet.2015.07.022

Reference: TET 26967

To appear in: *Tetrahedron*

Received Date: 25 April 2015

Revised Date: 21 June 2015

Accepted Date: 6 July 2015

Please cite this article as: Ahadi S, Naghdiani Z, Balalaie S, Rominger F, Diastereoselective Synthesis of Polysubstituted Cyclopentanols and Cyclopentenes Containing Stereogenic Centers via Domino Michael/Cyclization Reaction, Tetrahedron (2015), doi: 10.1016/j.tet.2015.07.022.

Diastereoselective Synthesis of Polysubstituted Cyclopentanols and Cyclopentenes Containing Stereogenic Centers *via* Domino Michael/Cyclization Reaction

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Abstract

A highly efficient domino Michael/cyclization reaction was developed for the synthesis of cyclopentanols and cyclopentenes with four and three stereogenic centers that were generated in one-pot reaction conditions with high diastereoselectivity. The reactions proceeded through a one-pot three-component reaction of *β*-nitrostyrenes, malononitrile and phenacyl bromide derivatives in basic media at room temperature.

Keywords: Domino Micheal/Cyclization, Cyclopentanol, Cyclopentene, diastereoselective, *β*-Nitrostyrene

Dedicated to Dr. Mehri Seyed Hashtroudi (my wife) for all of her accompaniment

1. Introduction

The formation of carbon-carbon bonds is one of the important subjects in organic synthesis, and designing novel approaches to access this goal is the aim of organic synthesis researchers.[1] A domino reaction which includes the constitution of numerous carbon-carbon bonds and stereogenic centers in one-pot is a very significant and attractive approach due to high bond-forming efficiency and access complex molecules.[2] Polysubstituted cyclopentanes are widespread in natural products,[3] and have demonstrated extended biological activities such as treatment of viral infections including hepatitis and HIV,[4] treatment of autoimmune diseases like multiple sclerosis, rheumatoid arthritis and asthma[5] and inhibitor of both influenza A and B.[6] The structures of some bioactive compounds which contain the cyclopentane moiety are shown in Fig 1.

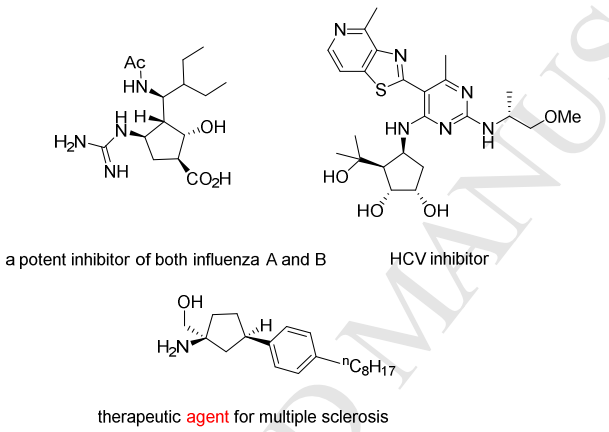
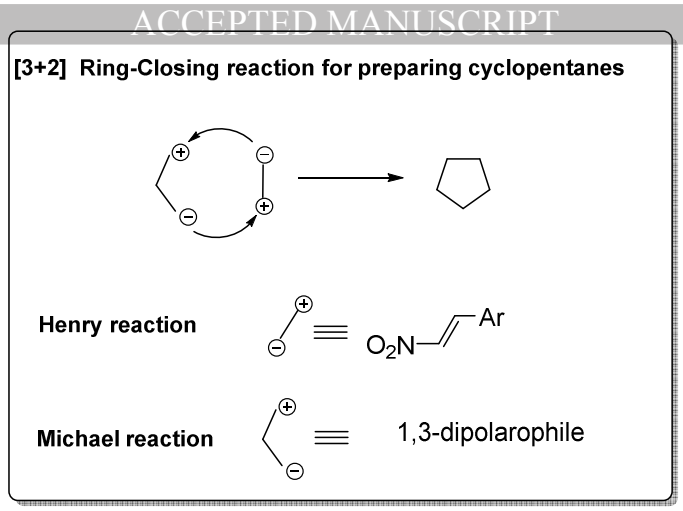


Figure 1. The structures of some cyclopentane frameworks with biological activity

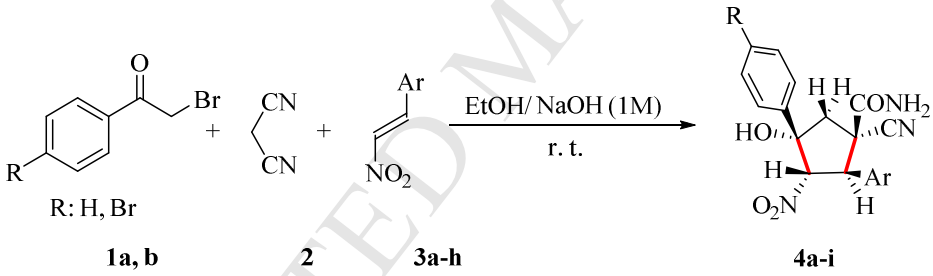
The synthesis of five-membered rings with multi-stereogenic centers in regio-, diastereo-, and enantioselective reaction conditions has been an important target for both academic and industrial researchers. There are several approaches for the synthesis of five-membered rings with multi-stereogenic centers.[7] These approaches can be classified in two categories: a) ring-closing reaction and b) using of cyclopentadiene as starting material.[8]

A domino Henry-Michael-cyclization reaction is a convenient routefor the preparation of five membered ring with multi-stereogenic centers[9] (Scheme 1). Therefore, the development of these reactions for the synthesis of functionalized cyclopentanes has always been of great interest.



Scheme 1. Sequential Henry Michael reaction to access cyclopentanes

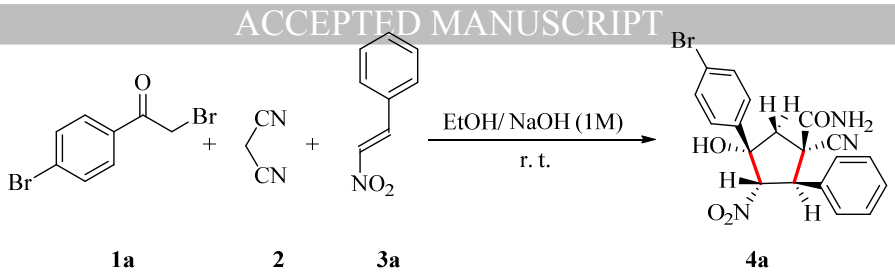
Considering the above background in the context of a Henry-Michael sequence, and in continuation of using *β*-nitrostyrene in designing multicomponent reactions,[10] we envisioned an approach to access functionalized cyclopentane derivatives through a three-component reaction of phenacyl bromide **1**, malononitrile **2** and *β*-nitrostyrene **3** based on Michael/cyclization.



Scheme 2. Three-component reaction of phenacyl bromide **1a-b**, malononitrile **2** and *β*-nitrostyrene **3a-h** to form cyclopentanol **4a-i**

At the beginning, the *β*-nitrostyrene **3** was prepared through the Henry reaction of nitromethane and benzaldehyde derivatives in the presence of sodium hydroxide.[11]

The three-component reaction of 4-bromophenacyl bromide **1a**, malononitrile **2**, and *β*-nitrostyrene **3a** in the presence of sodium hydroxide (1M) was selected as a model reaction for the screening of suitable reaction conditions. The reaction was carried out in ethanol at ambient temperature. The product **4a** was formed as a precipitate and separation was very simple (Scheme 3).



Scheme 3. The model reaction to access cyclopentanol **4a** through three-component reaction

The solvent and base played a very important role in creating the desired product. The model reaction was carried out in various solvents, such as DMF, H_2O, CH_2Cl_2, EtOH and CH_3CN in the presence of 1M NaOH as base. In water, an oily product was formed and the isolation of product was not possible and the yield of the desired product was low (25%). Only a trace of the desired product was observed in DMF and CH_2Cl_2. Since the homogenicity of the reaction mixture played an important role in the progress of the reaction, in the case of dichloromethane, *tetra*-butylammonium bromide was used as phase transfer catalyst (Table 1, entry 2). In CH_3CN, the yield of product was 50% (Table 1, entry 1). After that the reaction was carried out in ethanol in the presence of other bases, such as potassium carbonate, cesium carbonate, piperidine, triethylamine, and diisopropylethylamine DIPEA (Table 1, entry 7) and 1M NaOH. Meanwhile, *tetra*-butylammonium hydroxide (TBAH 20% in isopropyl alcohol) was used as the base in the model reaction at room temperature, although the desired product was formed (Yield= 50%), but the work-up of the reaction mixture was very difficult (Table 1, entry 8). The model reaction was investigated at room temperature. Meanwhile, the reaction mixture was heated at 50 °C, 60 °C and also at reflux conditions. However, heating led to a mixture of products. The best result was obtained with 1 M NaOH in ethanol giving 87% yield of product with high diastereoselectivity (Table 1, entry 4). The results are compiled in table 1.

Table 1. Condition screening for the three-component reaction of 4-bromo phenacyl bromide, malononitrile and *β*-nitrostyrene as model reaction to form **4a**

Entry	solvent	Base	Yield (%)
1	CH_3CN	NaOH	50
2	CH_2Cl_2	NaOH	trace
3	H_2O	NaOH	64
4	EtOH	NaOH	87
5	EtOH	K_2CO_3	52
6	EtOH	Cs_2CO_3	57

7	EtOH	piperidine	trace
8	EtOH	NEt_3	trace
9	EtOH	DIPEA	40
10	EtOH	TBAH	50

In the ^{1}H NMR spectrum, product **4a** showed four doublet peaks at δ 2.82, 3.13, 4.88 and 5.99 ppm for the geminal CH, CH-Ar and CH-NO_2 respectively. The ^{13}C NMR data shows that there is a signal in 164.0 ppm which confirms the presence of the carbonyl functional group. As a result, we proposed that the nitrile group was hydrolyzed to amide group in the alkaline reaction conditions. Based on these data, the structure of product **4a** was confirmed and it was formed through the basic hydrolysis of the nitrile group. The desired product was formed through domino Michael/Cyclization. The structure of **4a** was clarified using X-ray crystallographic data. The X-ray crystallographic data could confirm the structure and also diastereoselectivity of reaction (Fig. 2).

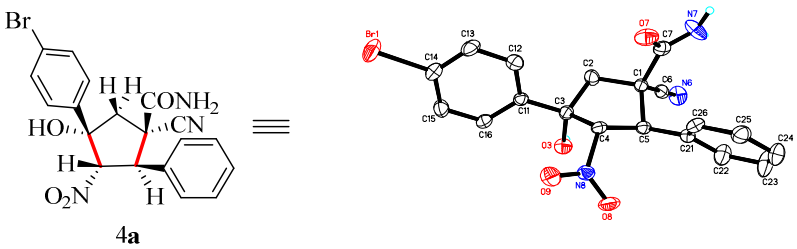


Figure 2. ORTEP structure of **4a**

The relation between the chemical shifts and also the observed coupling constants is shown in Fig 3.

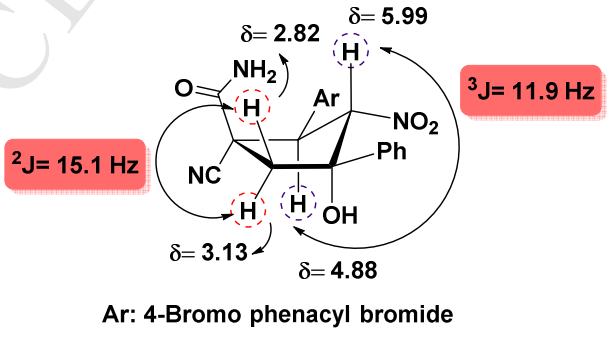
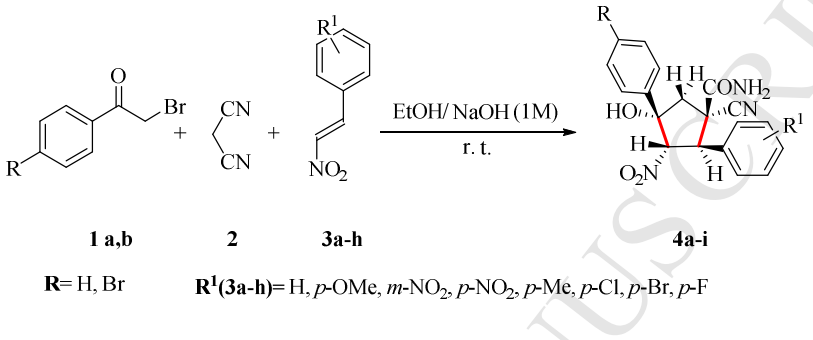


Figure 3. Structure of compound **4a** by displaying the chemical shifts and the coupling constant

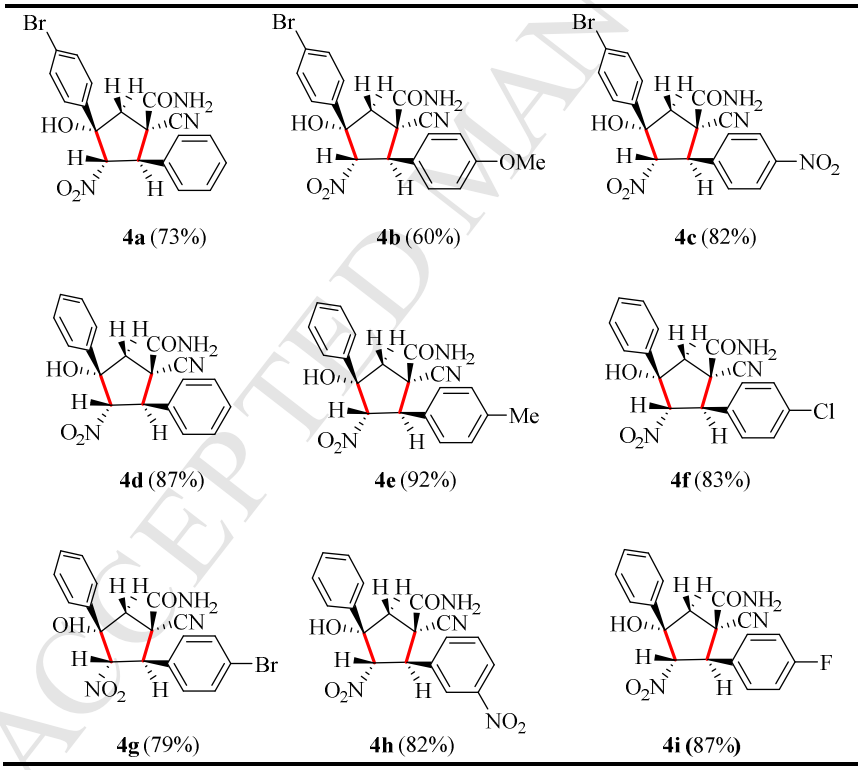
Having established the optimum reaction conditions and in order to extend the chemical library, we investigated the reaction of various *β*-nitrostyrenes **3a-h**, malononitrile **2** and different phenacyl bromides **1a,b** in the optimal reaction conditions. The results are summarized in table 2. It was observed that most of the reactions are completed within 24 h at room temperature and in all cases, leading to the formation of the desired cyclopentanols in good yields with high diastereoselectivity.

Table 2. Synthesis of functionalized cyclopentanols **4a-i** through three-component reaction of phenacyl bromides, malononitrile and *β*-nitrostyrenes



1 a,b **2** **3a-h** **4a-i**

R= H, Br **R^1(3a-h)**= H, *p*-OMe, *m*-NO_2, *p*-NO_2, *p*-Me, *p*-Cl, *p*-Br, *p*-F



4a (73%) **4b** (60%) **4c** (82%)

4d (87%) **4e** (92%) **4f** (83%)

4g (79%) **4h** (82%) **4i** (87%)

Despite the success of our procedure with phenacyl bromide **1a** and 4-bromo phenacyl bromide **1b**, we were surprised that the three-component reaction of 4-methoxy phenacyl bromide **1c**, malononitrile **2**, and *β*-nitrostyrenes **3a,e,f,i** in the same reaction conditions led to functionalized cyclopentanes **5a-d** instead of cyclopentanols with three stereogenic centers in excellent yields (table 3). The structure of the products was confirmed using spectroscopic data and also X-ray

crystallographic data. The ORTEP structure of **5a** shows the water elimination and formation of cyclopentene moiety (Fig 4).

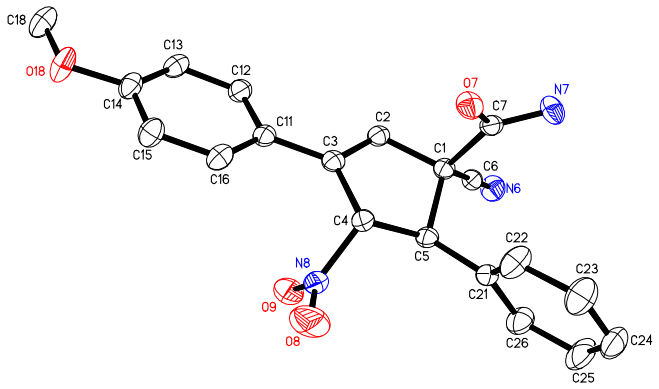
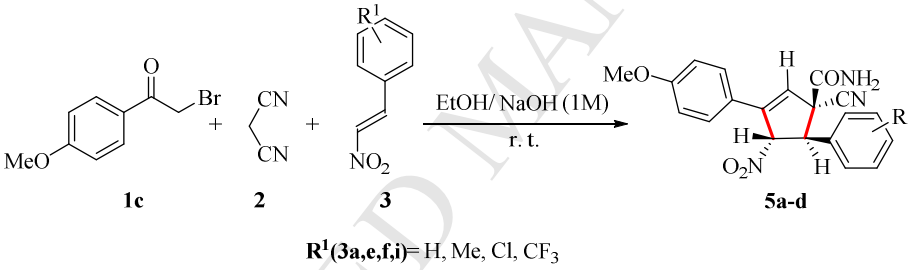
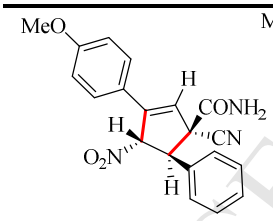
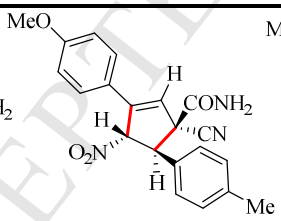
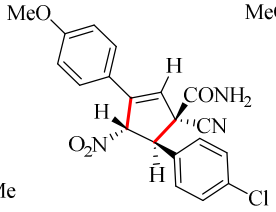
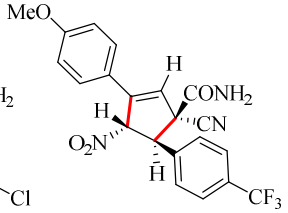


Figure 4. ORTEP structure of **5a**

Table 3. Synthesis of functionalized cyclopentene derivatives **5a-d** through three-component reaction



R[1](3a,e,f,i)= H, Me, Cl, CF_3

			
5a (97%)	**5b** (83%)	**5c** (68%)	**5d** (56%)

^{1}H-^{1}H COSY 2D-NMR was used for determination of the structure of the products. The 2D ^{1}H NMR spectra of the compounds **4b** and **5c** are provided in the supporting information.

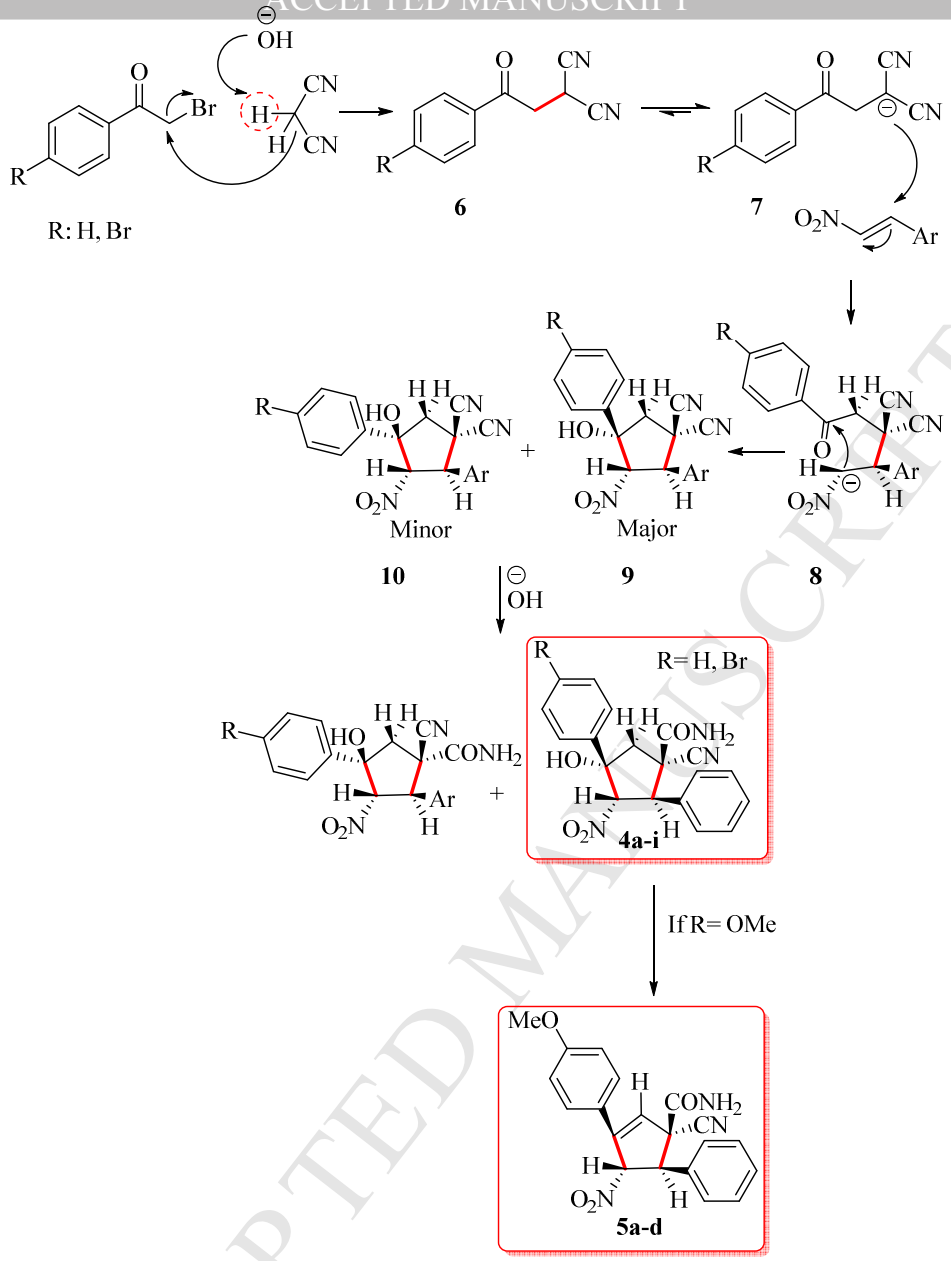
There are some exchangeable hydrogens in the structure of products **4a-i** and also **5a-d**. Investigation of H/D exchange for compound **4h** showed that a peak at δ= 8.78 ppm was removed which is related to the amidic hydrogen.

The X-ray crystallographic data of compounds **4a** and **5a** shows that there is intermolecular hydrogen bonding through amidic functional groups as donor and acceptor. The comprehensive hydrogen bond situation is shown in Fig 4.

After having these results for 4-methoxy phenacyl bromide **1c** and formation of cyclopentene skeleton **5a-d**, the mixture of reaction 4-bromo phenacyl bromide **1a**, malononitrile **2**, and *β*-nitrostyrene **3a** was heated to access the desired cyclopentene derivatives, but the reaction gave a mixture of products that was not suitable for purification.

Based on the previous results, we proposed that the reaction could proceed through domino Michael/cyclization reaction and the following mechanism could be proposed for the observed diastereoselectivity of the reaction. Besides, *β*-nitrostryrene is a common starting material used in different stereoselective reactions due to its structure and in some cases in the presence of chiral catalysts.[12]

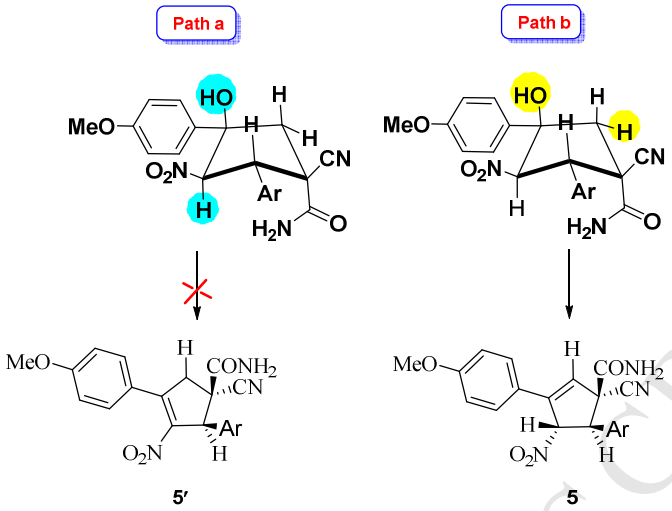
The possible mechanism of these conversions is shown in Scheme 4. This conversion involves the initial reaction of phenacyl bromide derivatives with malononitrile as active methylene compounds to form **6** and after proton abstraction, addition of the desired carbanion **7** to *β*-nitrostryrene as Michael acceptor led to **8**. The subsequent cyclization of intermediate **8** followed by the nucleophilic addition to the carbonyl moiety led to two products **9**, and **10**. In the case of using phenacyl bromide or 4-bromo-phenacyl bromide product **4** was obtained. On the other hand using 4-methoxy phenacyl bromide led to **5**. One of the nitrile groups can hydrolyze in basic media and convert to amide **4a-i**. In the case of 4-methoxy bromide, the final product is cyclopentene ring **5a-d**.



Scheme 4. Proposed mechanism for the synthesis of functionalized cyclopentanols **4a-i** and cyclopentenes **5a-d**

It seems that the existence of the 4-methoxy substituent in the structure of phenacyl bromide **1c** has an essential role in the elimination reaction and reacted as accelerator in the formation of the double bond and elimination of water to form the desired cyclopentene moiety **5**. The formation of the double bond in the cyclopentene ring could be expressed based on the stability of the formed double bond in the structure of product (Scheme 5). There are two possibilities (Paths a, b) for the water elimination in the structure of cyclopentanols. In path A, the double bond leads to steric hindrance between aryl and nitro groups. However in path B, the strong conjugation between the double bond

the aryl group and, has an essential role in the stability of product. Moreover, there is no steric hindrance.



Scheme 5. Two plausible paths for the water elimination and synthesis of **5a-d**

With this idea in mind and for expanding the reaction, alkyl cyanoacetate was used instead of malononitrile and three-component reaction of phenacyl bromide, methyl or ethyl cyanoacetate and *β*-nitrostyrene was investigated. In this case, the sole product was formed through the reaction of phenacyl bromide and alkyl cyanoacetate.

Meanwhile, domino four-component reaction of benzaldehyde, nitromethane, malononitrile and phenacyl bromide in the presence of 1M NaOH was investigated to access cyclopentanol derivatives. However, the reaction showed that a mixture of products were formed and separation of the desired product was not possible.

In conclusion, we have developed a highly efficient domino Michael/cyclization reaction to access diastereoselective functionalized cyclopentanol and cyclopentene derivatives with four and three stereogenic centers, respectively. These reactions have some advantages such as: high efficiency, high bond-forming efficiency, practical simplicity of the method, easy work-up, mild reaction conditions, and high diastereoselectivity for the synthesis of functionalized cyclopentanols **4a-i** and cyclopentenes **5a-d**. Future work in our laboratory is in progress to find a suitable basic organocatalyst to access enantioselective products.

Experimental Section:

Commercially available materials were used without further purification. Melting points were determined on an Electrothermal 9100 apparatus. IR spectra were obtained on an ABB FT-IR

FTLA 2000 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were run on Bruker DRX-300 AVANCE spectrometers at 300 MHz for ^{1}H NMR, 75 MHz for ^{13}C NMR. DMSO-d_6 and $CDCl_3$ was used as solvent. High resolution mass spectra were recorded on Mass-ESI-POS (Apex Qe-FT- ICR instrument) spectrometer. The scanning electron microscope (Hitachi 4160, Japan) was used for getting the scanning electron micrographs.

General procedure for synthesis of 4 and 5:

In a flask, a mixture of phenacyl bromide (1 mmol), malononitrile (72.6 mg, 1.1 mmol) in EtOH (3 mL) was prepared and NaOH (1M= 0.04 g in 1 mL water) was added dropwise and the solution was stirred at ambient temperature for 1h. The progress of the reaction was monitored using TLC (Eluent:*n*-hexane: EtOAc 2:1).Then, *β*-nitrostyrene (1.0 mmol) was added and the mixture was stirred for 24h at room temperature. Finally, the precipitated product was filtered and washed with methanol to afford the pure product **4a-i** or **5a-d**.

(±) 4-(4-Bromophenyl)-1-cyano-4-hydroxy-3-nitro-2-phenylcyclopentane-1-carboxamide (4a): Cream powder; yield: 314 mg (73%); Mp 218-220 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3462, 3372, 2243, 1694, 1553, 1381. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.82 (d, 1H, CH_2, J= 15.1 Hz), 3.13 (d, 1H, CH_2, J = 15.1 Hz), 4.88 (d, 1H, CH-Ph, J = 12.0 Hz), 5.99 (d, 1H, CH-NO_2, J = 12.0 Hz), 6.97 (s, 1H, OH), 7.28 (s, 1H, NH), 7.33-7.39 (m, 5H, H-Ar), 7.54 (s, 1H, NH), 7.62 (d, 2H, H-Ar, J = 8.5 Hz), 7.68 (d, 2H, H-Ar, J = 8.5 Hz).^{13}C NMR (75 MHz, DMSO-d_6): δ = 47.4, 50.6, 53.7, 80.4, 92.8, 121.0, 128.0, 128.3, 128.6, 130.9, 133.1, 141.8, 168.0. HR-MS (ESI) Calc. for $C_{19}H_{15}N_3O_3{}^{79}$ Br $[(M\text{-}OH)+H]^+$: 412.0291; found: 412.0291.

Crystallography data of 4a: colourless crystal (plate), dimensions 0.210 x 0.170 x 0.020 mm^3, crystal system monoclinic, space group $P2_1/n$, Z=4, a=7.3723(7) Å, b=6.2733(5) Å, c=38.704(3) Å, alpha=90 deg, beta=90.184(3) deg, gamma=90 deg, V=1790.0(3) Å^3, rho=1.597 g/cm^3, T=200(2) K, $Theta_{max}$= 24.415 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 2.90and a completeness of 98.4% to a resolution of 0.86 Å, 8904 reflections measured, 2918 unique (R(int)=0.0355), 2335 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS based on the Laue symmetry of the

reciprocal space, mu=2.33mm^{-1}, T_{min}=0.84, T_{max}=0.97, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL (Version 2014-3) software, 256 parameters refined, hydrogen atoms were treated using appropriate riding models, except those at hetero atoms (N7 and O3), which were refined isotropically, goodness of fit 1.16 for observed reflections, final residual values R1(F)=0.036, wR(F^2)=0.087 for observed reflections, residual electron density -0.41

to 0.43 eÅ^{-3}. CCDC 1030884 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(±) 2-(4-Bromophenyl)-1-cyano-4-hydroxy-3-nitro-4-phenylcyclopentane-1-carboxamide (4b): Cream powder; yield: 243 mg (60%); Mp 129-131 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3295, 3013, 2906, 2250, 1706, 1611, 1558, 1356. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.81 (d, 1H, C$\underline{H}_2$, J = 15.0 Hz), 3.07 (d, 1H, C$\underline{H}_2$, J = 15.0 Hz), 3.71 (s, 3H, CH_3), 4.79 (d, 1H, CH-Ph, J = 12.0 Hz), 5.87 (d, 1H, CH-NO_2, J = 12.0 Hz), 6.88 (1H, s, OH), 6.92 (d, 2H, H-Ar, J = 6.5 Hz), 7.13 (brs, 1H, NH), 7.28 (d, 2H, H-Ar, J = 8.4 Hz), 7.45 (bs, 1H, NH), 7.58 (d, 2H, H-Ar, J = 8.5 Hz), 7.64 (d, 2H, H-Ar, J = 8.6 Hz). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 47.5, 50.3, 53.2, 55.1, 80.3, 93.1, 114.0, 120.9, 121.0, 124.6, 128.1, 129.3, 130.9, 141.8, 159.1, 168.2.

(±) 4-(4-Bromophenyl)-1-cyano-4-hydroxy-3-nitro-2-(4-nitrophenyl)cyclopentane-1-carboxamide (4c): Cream powder; yield: 389 mg (82%); Mp 139-141 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3283, 3087, 3015, 2967, 1717, 1555, 1348. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 3.35(1H, OH, overlap with solvent signal), 3.42 (d, 1H, C$\underline{H}_2$, J = 11.2 Hz), 3.52 (d, 1H, C$\underline{H}_2$, J = 11.2 Hz), 5.14 (d, 1H, CH-Ph, J = 5.1 Hz), 6.42 (d, 1H, CH-NO_2, J = 5.1 Hz), 7.55-7.83 (m, 6H, H-Ar), 7.96-7.99 (d, 1H, H-Ar, J = 7.6 Hz), 8.28-8.31 (d, 1H, H-Ar, J = 8.3 Hz), 8.43 (s, 1H, NH), 8.82 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO- d_6): δ= 43.6, 48.4, 52.4, 89.1, 90.1, 114.8, 123.6, 123.9, 128.4, 129.8, 130.1, 130.2, 131.1, 131.6, 132.1, 135.1, 135.6, 147.8, 158.1. HR-MS (ESI) Calc. for $C_{19}H_{13}N_4NaO_5{}^{79}$ Br [(M-H_2O)+Na]$^+$: 478.99627; found: 478.99615, Calc. for $C_{19}H_{13}N_4NaO_5{}^{81}$ Br [(M-H_2O)+Na]$^+$: 480.9942; found: 480.9941.

(±) 1-Cyano-4-hydroxy-3-nitro-2,4-diphenylcyclopentane-1-carboxamide (4d): Cream powder; yield: 305 mg (87%); Mp 139-141 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3304, 3118, 2248, 1702, 1559, 1370. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.36 (bs, 2H, OH and C$\underline{H}_2$, overlap with solvent signal), 3.56 (d, 1H, C$\underline{H}_2$, J = 11.2 Hz), 4.80 (d, 1H, CH-Ph, J = 5.3 Hz), 6.16 (d, 1H, CH-NO_2, J = 5.3 Hz), 7.42-7.50 (m, 9H, H-Ar and NH), 7.66-7.75 (m, 2H, H-Ar), 8.66 (s, 1H, NH).^{13}C NMR (75 MHz, DMSO-d_6): δ = 44.0, 48.4, 53.6, 90.2, 90.5, 115.3, 127.9, 128.1, 128.5, 128.6, 128.8, 129.0, 130.2, 130.9, 133.0, 158.7. HR-MS (ESI) Calc. for $C_{19}H_{15}N_3NaO_3$ [(M-H_2O)+Na]$^+$: 356.1005; found: 356.1005.

(±) 1-Cyano-4-hydroxy-3-nitro-4-phenyl-2-(*p*-tolyl) cyclo peantane-1-carboxamide (4e): Cream powder; yield: 335 mg (92%); Mp 170 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3332, 3034, 2986, 2249, 1703, 1562, 1352. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.32 (s, 3H, CH_3), 3.35 (d, 1H, C$\underline{H}_2$, J = 11.1 Hz), 3.37 (1H, OH, overlap with solvent signal), 3.56 (d, 1H, C$\underline{H}_2$, J = 11.1 Hz), 4.74 (d, 1H, CH-Ph, J = 4.8 Hz), 6.11 (d, 1H, CH-NO_2, J = 4.3 Hz), 7.24 (d, 2H, H-Ar, J = 7.2 Hz), 7.44 (d, 2H, H-

Ar, 7.4 Hz), 7.48 (m, 3H, H-Ar), 7.67 (m, 2H, H-Ar), 8.64 (s, 1H, NH).^{13}C NMR (75 MHz, DMSO-d_6): δ = 20.7, 43.9, 48.5, 53.5, 90.3, 90.6, 115.3, 127.4, 128.1, 128.6, 129.1, 129.2, 129.6, 129.9, 130.2, 130.9, 138.2, 138.4, 158.8. HR-MS (ESI) Calc. for $C_{20}H_{18}N_3O_3$ $[(M-H_2O)+H]^+$: 348.1343; found: 348.1342.

(±) 2-(4-Chlorophenyl)-1-cyano-4-hydroxy-3-nitro-4-phenylcyclopentane-1-carboxamide (4f): Cream powder; yield: 319 mg (83%); Mp 145 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3487, 3319, 3034, 2911, 2247, 1704, 1559, 1366. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 3.38 (d, 1H, C$\underline{H}_2$, J = 11.1 Hz), 3.40 (1H, OH, overlap with solvent signal), 3.54 (d, 1H, C$\underline{H}_2$, J = 11.1 Hz), 4.90 (d, 1H, CH-Ph, J = 4.5 Hz), 6.17 (bs, 1H, CH-NO_2), 7.48-7.53 (m, 8H, H-Ar and NH), 7.63-7.70 (m, 2H, H-Ar), 8.67 (s, 1H, NH).^{13}C NMR (75 MHz, DMSO-d_6): δ = 43.8, 48.4, 52.7, 89.9, 90.6, 115.1, 127.5, 128.1, 128.5, 129.0, 130.2, 130.7, 130.8, 131.9, 133.8, 158.6. HR-MS (ESI) Calc. for Calc. for $C_{19}H_{14}N_3$ Na $O_3{}^{35}$Cl $[(M-H_2O)+Na]^+$:. 390.0616; found: 390.0615.

(±) 4-(4-Bromophenyl)-1-cyano-4-hydroxy-2-(4-methoxyphenyl)-3-nitrocyclopentane-1-carboxamide (4g): Cream powder; yield: 339 mg (79%); Mp 149-151 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3455, 3312, 3030, 2982, 2243, 1705, 1560, 1355.^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.35(1H, OH, overlap with solvent signal), 3.37 (d, 1H, C$\underline{H}_2$, J = 11.2 Hz), 3.53 (d, 1H, C$\underline{H}_2$, J = 11.2 Hz), 4.86 (d, 1H, CH-Ph, J = 4.98 Hz), 6.19 (d, 1H, CH-NO_2, J = 4.94 Hz), 7.46-7.48 (m, 6H, H-Ar and NH), 7.65-7.67 (m, 4H, H-Ar), 8.67 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ= 43.8, 48.3, 52.8, 89.7, 90.6, 115.1, 122.4, 127.5, 128.6, 130.2, 130.8, 131.0, 131.4, 132.4, 158.6. HR-MS (ESI) Calc. for Calc. for $C_{19}H_{16}N_3NaO_4{}^{79}$ Br $[M+Na]^+$: 452.021685; found: 452.02164, Calc. for $C_{19}H_{16}N_3NaO_4{}^{81}$ Br $[M+Na]^+$: 454.0197; found: 454.0195.

(±) 1-Cyano-4-hydroxy-3-nitro-2-(3-nitrophenyl)-4-phenylcyclopentane-1-carboxamide (4h): Cream powder; yield: 249 mg (82%); Mp 149-151 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3310, 3077, 3019, 2939, 2252, 1699, 1576, 1351. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 3.36 (1H, OH, overlap with solvent signal), 3.43 (d, 1H, C$\underline{H}_2$, J = 11.2 Hz), 3.55 (d, 1H, C$\underline{H}_2$, J = 11.2 Hz), 5.13 (d, 1H, CH-Ph, J = 5.1 Hz), 6.38 (d, 1H, CH-NO_2, J = 5.1 Hz), 7.49-7.50 (m, 4H, H-Ar), 7.68-7.71 (m, 2H, H-Ar), 7.71 (t, 1H, H-Ar, J = 7.9 Hz), 7.97 (d, 1H, H-Ar, J = 7.6 Hz), 8.29 (d, 1H, H-Ar, J = 8.1 Hz), 8.44 (s, 1H, NH), 8.78 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO- d_6): δ= 43.7, 48.4, 52.4, 89.4, 90.8, 114.9, 123.6, 123.9, 127.5, 128.6, 130.1, 130.3, 130.7, 135.1, 135.6, 147.8, 158.4. HR-MS (ESI) Calc. for $C_{19}H_{14}N_4NaO_5$ $[(M-H_2O)+Na]^+$:. 401.0858; found: 401.0856.

(±) 1-Cyano-2-(4-fluorophenyl)-4-hydroxy-3-nitro-4-phenylcyclopentane-1-carboxamide (4i): White powder; yield: 357 mg (87%); Mp 169-171 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3325, 3077, 3039, 2251, 1703, 1562, 1350. 1H NMR (300 MHz, DMSO-d6): δ = 3.36 (d, 1H, CH_2, J = 11.2 Hz), 3.37 (1H, OH, overlap with solvent signal), 3.54 (d, 1H, CH_2, J = 11.2 Hz), 4.86 (d, 1H, CHPh, J = 5.1

Hz), 6.19 (d, 1H, CH-NO_2, J = 5.1 Hz), 7.29 (t, 2H, H-Ar, J = 8.54 Hz), 7.37-7.49 (m, 3H, H-Ar and NH), 7.56-7.60 (m, 3H, H-Ar), 7.63-7.69 (m, 2H, H-Ar), 8.68 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ= 43.8, 48.5, 52.7, 89.9, 90.6, 115.2, 127.4, 128.6, 128.9, 129.0, 129.2, 129.3, 130.2, 130.8, 130.9, 131.1, 158.7. HR-MS (ESI) Calc. for $C_{19}H_{15}FN_3O_3$ $[(M-H_2O)+H]^+$: 352.1093; found: 352.1092.

(±) 1-Cyano-3-(4-methoxyphenyl)-4-nitro-5-phenylcyclopent-2-ene-1-carboxamide (5a): Cream powder; yield: 326 mg (90%); Mp 147-149 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3560, 3424, 3231, 1694, 1610, 1515, 1367. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 3.76 (s, 3H, OCH_3), 4.64 (d, 1H, CH-Ph, J= 5.3 Hz), 6.79 (s, 1H, =CH), 6.85 (d, 1H, CH-NO_2, J = 5.3 Hz), 6.98 (d, 2H, H-Ar, J = 8.2 Hz), 7.32-7.38 (m, 5H, H-Ar), 7.47 (s, 1H, NH), 7.54 (s, 1H, NH), 7.59 (d, 2H, H-Ar, J = 8.2 Hz). ^{13}C NMR (75 MHz, DMSO- d_6): δ= 55.4, 57.9, 58.7, 94.2, 114.2, 118.8, 123.7, 127.2, 128.1, 128.4, 134.1, 143.2, 160.2, 164.8. HR-MS (ESI) Calc. for Calc. for $C_{20}H_{17}N_3NaO_4$ $[M+Na]^+$ 386.1112; found: 386.1112.

Crystallography data of 5a: colourless crystal (polyhedron), dimensions 0.160 x 0.160 x 0.140 mm^3, crystal system monoclinic, space group C2/c, Z=8, a=25.9760(10) Å, b=8.4856(3) Å, c=18.9145(7) Å, alpha=90 deg, beta=121.3568(8) deg, gamma=90 deg, V=3560.2(2) $Å^3$, rho=1.356 g/cm^3, T=200(2) K, $Theta_{max}$= 25.073 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 3.33and a completeness of 99.5% to a resolution of 0.84 Å, 10816 reflections measured, 3148 unique (R(int)=0.0220), 2786 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS based on the Laue symmetry of the reciprocal space, mu=0.10mm^{-1}, T_{min}=0.90, T_{max}=0.96, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL (Version 2014-3) software, 253 parameters refined, hydrogen atoms were treated using appropriate riding models, except those of the aminde group, which were refined isotropically, goodness of fit 1.12 for observed reflections, final residual values R1(F)=0.040, wR(F^2)=0.108 for observed reflections, residual electron density -0.21 to 0.46 e$Å^{-3}$. CCDC 1030883 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(±) 1-Cyano-3-(4-methoxyphenyl)-4-nitro-5-(*p*-tolyl)cyclopent-2-ene-1-carboxamide (5b): Yellow powder; yield: 312 mg (83%); Mp 186-190 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3313, 3024, 2978, 2248, 1704, 1559, 1367. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.26 (s, 3H, CH_3),3.77 (s, 3H, OCH_3), 4.58 (d, 1H, CH-Ph, J = 5.3 Hz), 6.77 (s, 1H, =CH), 6.79 (d, 1H, CH-NO_2, J = 5.3 Hz), 6.98 (d, 2H, H-Ar, J = 8.2 Hz), 7.14 (d, 2H, H-Ar, J = 7.6 Hz), 7.27 (2H, d, H-Ar, J = 7.6 Hz), 7.44

(1H, s, NH), 7.54 (1H, s, NH), 7.58 (d, 2H, H-Ar, J = 8.3 Hz),. ^{13}C NMR (75 MHz, DMSO- d_6): δ= 55.3, 57.8, 58.6, 94.3, 114.2, 118.9, 123.8, 127.3, 128.0, 128.3, 129.0, 131.1, 137.8, 143.2, 160.2, 164.8. HR-MS (ESI) Calc. for Calc. for $C_{21}H_{19}N_3NaO_4$ $[M+Na]^+$: 400.1267; found: 400.1267.

(±) 5-(4-Chlorophenyl)-1-cyano-3-(4-methoxyphenyl)-4-nitro cyclopent-2-ene-1-carboxamide (5c): Light yellow powder; yield: 269 mg (68%); Mp 213-215 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3496, 3382, 2237, 1714, 1598, 1550, 1359. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 3.78 (s, 3H, OCH_3), 4.74 (d, 1H, CH-Ph, J = 4.9 Hz), 6.80 (s, 1H, =CH), 6.81 (d, 1H, CH-NO_2, J = 4.9 Hz), 7.00 (d, 2H, H-Ar, J = 8.4 Hz), 7.40-7.42 (m, 4H, H-Ar), 7.52 (brs, 1H, NH), 7.55-7.63 (m, 2H, H-Ar), 7.63 (brs, 1H, NH). ^{13}C NMR (75 MHz, DMSO- d_6)$^{.}$ δ= 53.3, 56.7, 58.5, 94.1, 114.3, 118.6, 123.7, 127.4, 128.1, 128.3, 130.5, 133.3, 133.5, 143.1, 160.3, 164.8. HR-MS (ESI) Calc. for $C_{20}H_{16}N_3NaO_4{}^{35}Cl$ $[M+Na]^+$: 420.07222; found: 420.07215, Calc. for $C_{20}H_{16}N_3NaO_4{}^{37}Cl$ $[M+Na]^+$: 422.0692; found: 422.0692.

(±) 1-Cyano-3-(4-methoxyphenyl)-4-nitro-5-(4-(trifluoromethyl) phenyl)cyclopent-2-ene-1-carbox amide (5d): Light yellow powder; yield: 241 mg (56%); Mp 218-220 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3506, 3393, 3010, 2924, 2238, 1716, 1552, 1366. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 3.76 (s, 3H, OCH_3), 4.83 (brs, 1H, CH-Ph), 6.83 (s, 1H, =CH), 6.89 (brs, 1H, CH-NO_2), 6.97 (d, 2H, H-Ar, J = 7.5 Hz), 7.59-7.62 (m, 5H, H-Ar and NH), 7.71 (d, 2H, H-Ar, J = 7.5 Hz). ^{13}C NMR (75 MHz, DMSO- d_6): δ= 55.4, 56.7, 58.5, 93.9, 114.2, 118.5, 122.2, 123.6, 125.1, 125.8, 127.3, 128.2, 128.6, 129.0, 129.5, 130.6, 139.2, 143.1, 160.2, 164.6. HR-MS (ESI) Calc. for $C_{21}H_{15}F_3N_3O_3$[(M-H_2O)+H]$^+$ 413.2666, found, 413.2666.

Acknowledgements

We gratefully acknowledge Iran National Science Foundation (INSF) for their financial support.

Supporting Information

Copies of ^{1}H NMR, ^{13}C NMR, HRMS spectra for compounds **4a-i** and **5a-d** and ^{1}H-^{1}H-COSY 2D NMR **4h** and **5c**; X-ray crystal data for compound **4a**, and **5b**

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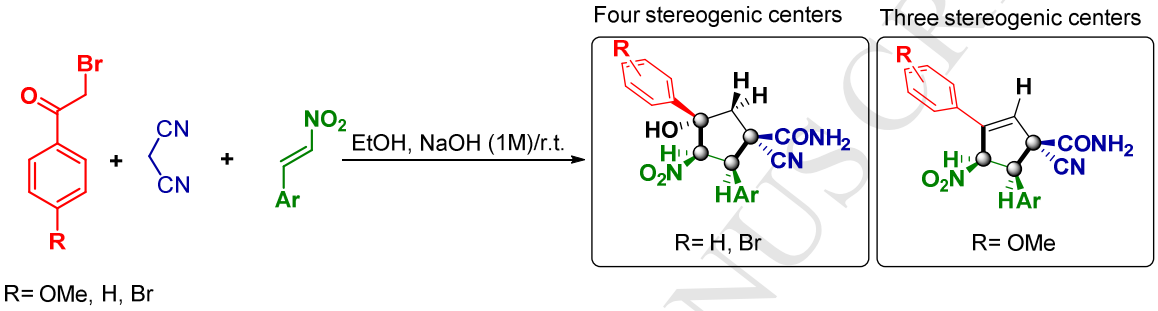
Graphical Abstract

Diastereoselective Synthesis of Polysubstituted Cyclopentanols and Cyclopentenes Containing Stereogenic Centers *via* Domino Michael/Cyclization Reaction

Somayeh Ahadi, Zeinab Naghdiani, Saeed Balalaie* and Frank Rominger



Supporting Information

Diastereoselective Synthesis of Polysubstituted Cyclopentanoles and Cyclopentenes Contained Stereogenic Centers *via* Domino Micheal-Cyclization Reaction

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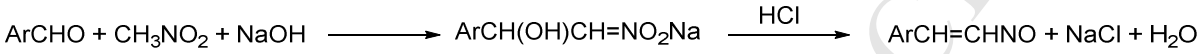
Table of Contents:

General information

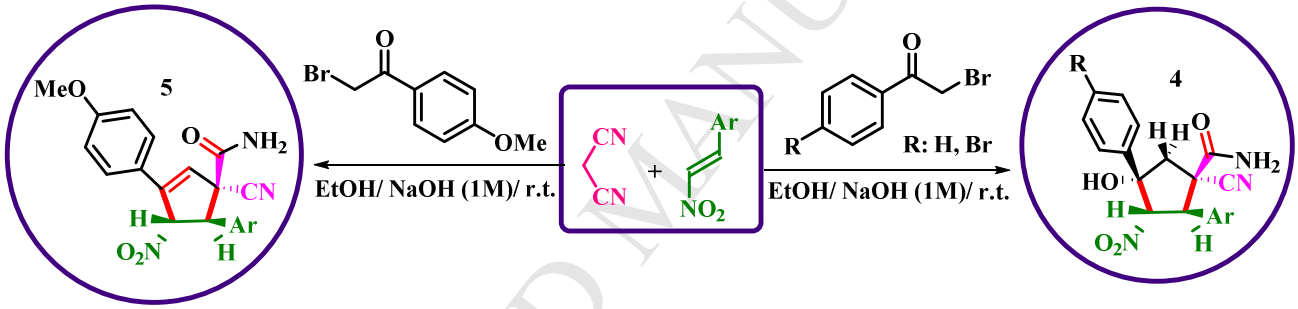
High resolution mass spectra were recorded on Mass-ESI-POS and Mass-ESI-NEG (FT-ICR) spectrometer.

Synthesis of *β*-nitro styrene derivatives 3 a-g:

The *β*-nitro styrene derivatives were synthesized based on the reported method. (*Organic Synthesis Coll. Vol. I* **1941**, 413-414)

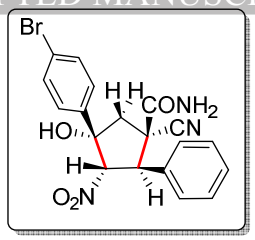


General procedure for synthesis of 4 and 5



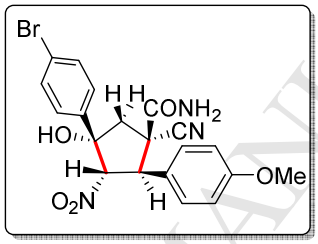
A mixture of phenacyl bromide (1 mmol), malononitrile (72.6 mg, 1.1 mmol) in EtOH (3 mL) was added dropwise NaOH (1M) and the solution was stirring at ambient temperature for 1h. The progress of the reaction was monitored using TLC (Eluent:*n*-hexane: EtOAc 2:1).Then, *β*-nitro styrene (1.0 mmol) was added and allowed the mixture to be for 24h at room temperature. Then, the precipitated product was filtered and washed with methanol to afford the pure product **4a-i** or **5a-d**.

4-(4-Bromophenyl)-1-cyano-4-hydroxy-3-nitro-2-phenylcyclopentane-1-carboxamide (4a)



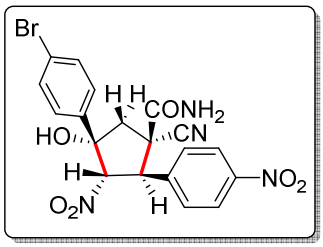
Cream powder; yield: 314 mg (73%); Mp 218-220 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3462, 3372, 1694, 1553, 1381. ^{1}H NMR (300 MHz, DMSO-d_6): δ= 2.82 (d, 1H, C<u>H</u>$_2$, J = 15.1 Hz), 3.13 (d, 1H, C<u>H</u>$_2$, J = 15.1 Hz), 4.88 (d, 1H, CH-Ph, J = 12 Hz), 5.99 (d, 1H, CH-NO$_2$, J = 12 Hz), 6.97 (s, 1H, OH), 7.28 (s, 1H, NH), 7.33-7.39 (m, 5H, H-Ar), 7.54 (s, 1H, NH), 7.62 (d, 2H, H-Ar, J = 8.5 Hz), 7.68 (d, 2H, H-Ar, J = 8.5 Hz). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 47.4, 50.6, 53.7, 80.4, 92.8, 121.0, 128.0, 128.1, 128.3, 128.7, 131.0, 133.1, 141.9, 168.1. HR-MS (ESI) Calc. for $C_{19}H_{15}N_3O_3{}^{79}$Br [(M-OH)+H]$^+$: 412.0291; found: 412.0291.

2-(4-Bromophenyl)-1-cyano-4-hydroxy-3-nitro-4-phenylcyclopentane-1-carboxamide (4b)



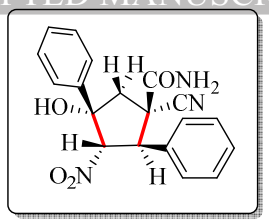
Cream powder; yield: 243 mg (60%); Mp 129-131 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3295, 3013, 2906, 2250, 1706, 1611, 1558, 1356. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.81 (d, 1H, C<u>H</u>$_2$, J = 15.0 Hz), 3.07 (d, 1H, C<u>H</u>$_2$, J = 15.0 Hz), 3.71 (s, 3H, CH$_3$), 4.79 (d, 1H, CH-Ph, J = 12.0 Hz), 5.87 (d, 1H, CH-NO$_2$, J = 12.0 Hz), 6.88 (1H, s, OH), 6.92 (d, 2H, H-Ar, J = 6.5 Hz), 7.13 (brs, 1H, NH), 7.28 (d, 2H, H-Ar, J = 8.4 Hz), 7.45 (brs, 1H, NH), 7.58 (d, 2H, H-Ar, J = 8.5 Hz), 7.64 (d, 2H, H-Ar, J = 8.6 Hz). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 47.5, 50.3, 53.2, 55.1, 80.3, 93.1, 114.1, 120.9, 121.0, 124.7, 128.1, 129.3, 130.9, 141.9, 159.2, 168.2.

4-(4-Bromophenyl)-1-cyano-4-hydroxy-3-nitro-2-(4-nitrophenyl) cyclopentane-1-carboxamide (4c):



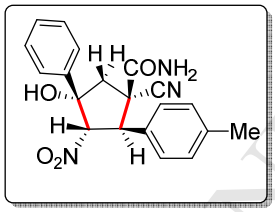
Cream powder; yield: 389 mg (82%); Mp 139-141 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3283, 3087, 3015, 2967, 1717, 1555, 1348. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.35(1H, OH, overlap with solvent signal), 3.42 (d, 1H, C<u>H</u>$_2$, J = 11.2 Hz), 3.52 (d, 1H, C<u>H</u>$_2$, J = 11.2 Hz), 5.14 (d, 1H, CH-Ph, J = 5.1 Hz), 6.42 (d, 1H, CH-NO$_2$, J = 5.1 Hz), 7.55-7.83 (m, 6H, H-Ar), 7.96-7.99 (d, 1H, H-Ar, J = 7.6 Hz), 8.28-8.31 (d, 1H, H-Ar, J = 8.3 Hz), 8.43 (s, 1H, NH), 8.82 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO- d_6): δ= 43.6, 48.4, 52.4, 89.2, 90.2, 114.8, 123.6, 123.9, 129.8, 130.1, 130.2, 131.7, 135.1, 135.6, 147.8, 158.2. HR-MS (ESI) Calc. for $C_{19}H_{13}N_4NaO_5{}^{79}$Br [(M-H$_2$O)+Na]$^+$: 478.99627; found: 478.99615, Calc. for $C_{19}H_{13}N_4NaO_5{}^{81}$Br [(M-H$_2$O)+Na]$^+$: 480.9942; found: 480.9941.

1-Cyano-4-hydroxy-3-nitro-2,4-diphenylcyclopentane-1-car boxamide (4d):



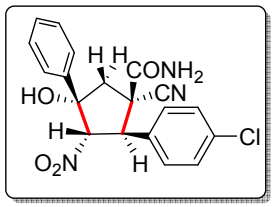
Cream powder; yield: 305 mg (87%); Mp 139-141 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3304, 3118, 2248, 1702, 1559, 1370. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.36 (brs, 2H, OH and C$\underline{H}_2$, overlap with solvent signal), 3.56 (d, 1H, C$\underline{H}_2$, J = 11.2 Hz), 4.80 (d, 1H, CH-Ph, J = 5.3 Hz), 6.16 (d, 1H, CH-NO_2, J = 5.3 Hz), 7.42-7.50 (m, 9H, H-Ar and NH), 7.66-7.75 (m, 2H, H-Ar), 8.66 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 44.0, 48.4, 53.6, 90.2, 90.5, 115.3, 127.9, 128.1, 128.5, 128.6, 128.8, 129.0, 130.2, 130.9, 133.0, 158.7. HR-MS (ESI) Calc. for $C_{19}H_{15}N_3NaO_3$ [(M-H_2O)+Na]$^+$: 356.1005; found: 356.1005.

1-Cyano-4-hydroxy-3-nitro-4-phenyl-2-(p-tolyl) cyclo peantane-1-carboxamide (4e):



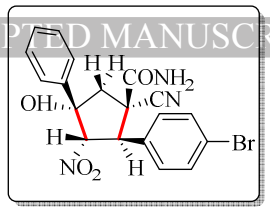
Cream powder; yield: 335 mg (92%); Mp 170 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3332, 3034, 2986, 2249, 1703, 1562, 1352. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.32 (s, 3H, CH_3), 3.35 (d, 1H, C$\underline{H}_2$, J = 11.1 Hz), 3.37 (1H, OH, overlap with solvent signal), 3.56 (d, 1H, C$\underline{H}_2$, J = 11.1 Hz), 4.74 (d, 1H, CH-Ph, J = 4.8 Hz), 6.11 (d, 1H, CH-NO_2, J = 4.3 Hz), 7.24 (d, 2H, H-Ar, J = 7.2 Hz), 7.44 (d, 2H, H-Ar, 7.4 Hz), 7.48 (m, 3H, H-Ar), 7.67 (m, 2H, H-Ar), 8.64 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 20.7, 43.9, 48.5, 53.5, 90.3, 90.6, 115.3, 127.4, 128.1, 128.6, 129.1, 129.2, 129.6, 129.9, 130.2, 130.9, 138.2, 138.4, 158.8. HR-MS (ESI) Calc. for $C_{20}H_{18}N_3O_3$ [(M-H_2O)+H]$^+$: 348.1343; found: 348.1342.

2-(4-Chlorophenyl)-1-cyano-4-hydroxy-3-nitro-4-phenyl cyclopentane-1-carboxamide (4f):



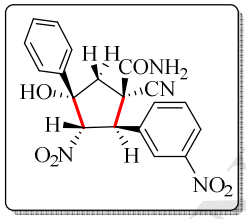
Cream powder; yield: 319 mg (83%); Mp 145 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3487, 3319, 3034, 2911, 2247, 1704, 1559, 1366. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 3.38 (d, 1H, C$\underline{H}_2$, J = 11.1 Hz), 3.40 (1H, OH, overlap with solvent signal), 3.54 (d, 1H, C$\underline{H}_2$, J = 11.1 Hz), 4.90 (d, 1H, CH-Ph, J = 4.5 Hz), 6.17 (brs, 1H, CH-NO_2), 7.48-7.53 (m, 8H, H-Ar and NH), 7.63-7.70 (m, 2H, H-Ar), 8.67 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 43.9, 48.5, 52.8, 89.9, 90.7, 115.1, 127.5, 128.5, 130.3, 130.7, 130.8, 131.9, 133.8, 158.6. HR-MS (ESI) Calc. for Calc. for $C_{19}H_{14}N_3$ Na $O_3{}^{35}Cl$ [(M-H_2O)+Na]$^+$:. 390.0616; found: 390.0615.

4-(4-Bromophenyl)-1-cyano-4-hydroxy-2-(4-methoxyphenyl)-3-nitrocyclopentane-1-carboxamide (4g):



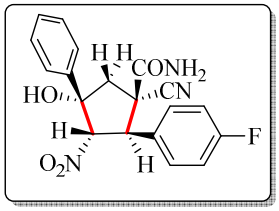
Cream powder; yield: 339 mg (79%); Mp 149-151 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3455, 3312, 3030, 2982, 2243, 1705, 1560, 1355.^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.35(1H, OH, overlap with solvent signal), 3.37 (d, 1H, C$\underline{H}_2$, J = 11.2 Hz), 3.53 (d, 1H, C$\underline{H}_2$, J = 11.2 Hz), 4.86 (d, 1H, CH-Ph, J = 4.98 Hz), 6.19 (d, 1H, CH-NO_2, J = 4.94 Hz), 7.46-7.48 (m, 6H, H-Ar and NH), 7.65-7.67 (m, 4H, H-Ar), 8.67 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ= 43.8, 48.3, 52.8, 89.7, 90.6, 115.1, 122.4, 127.5, 128.6, 130.2, 130.9, 131.0, 131.4, 132.4, 158.6. HR-MS (ESI) Calc. for Calc. for $C_{19}H_{16}N_3NaO_4^{79}$ Br $[M+Na]^+$: 452.021685; found: 452.02164, Calc. for $C_{19}H_{16}N_3NaO_4^{81}$ Br $[M+Na]^+$: 454.0197; found: 454.0195.

1-Cyano-4-hydroxy-3-nitro-2-(3-nitrophenyl)-4-phenyl cyclopentane-1-carboxamide (4h):



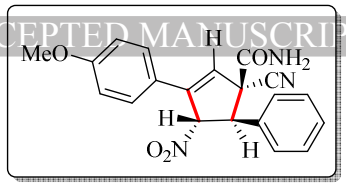
Cream powder; yield: 249 mg (82%); Mp 149-151 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3310, 3077, 3019, 2939, 2252, 1699, 1576, 1351. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 3.36 (1H, OH, overlap with solvent signal), 3.43 (d, 1H, C$\underline{H}_2$, J = 11.2 Hz), 3.55 (d, 1H, C$\underline{H}_2$, J = 11.2 Hz), 5.13 (d, 1H, CH-Ph, J = 5.1 Hz), 6.38 (d, 1H, CH-NO_2, J = 5.1 Hz), 7.49-7.50 (m, 4H, H-Ar), 7.68-7.71 (m, 2H, H-Ar), 7.71 (t, 1H, H-Ar, J = 7.9 Hz), 7.97 (d, 1H, H-Ar, J = 7.6 Hz), 8.29 (d, 1H, H-Ar, J = 8.1 Hz), 8.44 (s, 1H, NH), 8.78 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO- d_6): δ= 43.7, 48.4, 52.4, 89.4, 90.8, 114.9, 123.7, 123.9, 127.6, 128.6, 130.1, 130.3, 130.8, 135.2, 135.6, 147.8, 158.5. HR-MS (ESI) Calc. for $C_{19}H_{14}N_4NaO_5$ $[(M-H_2O)+Na]^+$:. 401.0858; found: 401.0856.

1-Cyano-2-(4-fluorophenyl)-4-hydroxy-3-nitro-4-phenylcyclopentane-1-carboxamide (4i):



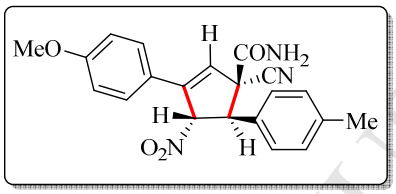
White powder; yield: 357 mg (97%); Mp 169-171 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3325, 3077, 3039, 2251, 1703, 1562, 1350. 1H NMR (300 MHz, DMSO-d6): δ = 3.36 (d, 1H, CH_2, J= 11.2 Hz), 3.37 (1H, OH, overlap with solvent signal), 3.54 (d, 1H, CH_2, J = 11.2 Hz), 4.86 (d, 1H, CHPh, J = 5.1 Hz), 6.19 (d, 1H, CH-NO_2, J = 5.1 Hz), 7.29 (t, 2H, H-Ar, J = 8.54 Hz), 7.37-7.49 (m, 3H, H-Ar and NH), 7.56-7.60 (m, 3H, H-Ar), 7.63-7.69 (m, 2H, H-Ar), 8.68 (s, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ= 43.8, 48.5, 52.7, 89.9, 90.6, 115.2, 115.6, 127.5, 128.6, 130.2, 130.9, 131.0, 131.1, 158.7, 164.0. HR-MS (ESI) Calc. for $C_{19}H_{15}FN_3O_3$ $[(M-H_2O)+H]^+$: 352.1093; found: 352.1092.

1-cyano-3-(4-methoxyphenyl)-4-nitro-5-phenylcyclopent-2-ene-1-carboxamide (5a):



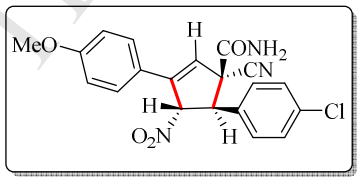
Cream powder; yield: 326 mg (90%); Mp 147-149 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3560, 3424, 3231, 1694, 1610, 1515, 1367. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 3.76 (s, 3H, OCH_3), 4.64 (d, 1H, CH-Ph, J = 5.3 Hz), 6.79 (s, 1H, =CH), 6.85 (d, 1H, CH-NO_2, J = 5.3 Hz), 6.98 (d, 2H, H-Ar, J = 8.2 Hz), 7.32-7.38 (m, 5H, H-Ar), 7.47 (s, 1H, NH), 7.54 (s, 1H, NH), 7.59 (d, 2H, H-Ar, J = 8.2 Hz). ^{13}C NMR (75 MHz, DMSO- d_6): δ= 55.4, 57.9, 58.7, 94.2, 114.2, 118.8, 123.7, 127.2, 128.1, 128.4, 134.1, 143.2, 160.2, 164.8. HR-MS (ESI) Calc. for Calc. for $C_{20}H_{17}N_3NaO_4$ $[M+Na]^+$: 386.1112; found: 386.1112.

1-Cyano-3-(4-methoxyphenyl)-4-nitro-5-(p-tolyl) cyclopent-2-ene-1-carboxamide (5b):



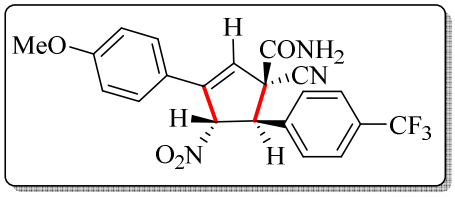
Yellow powder; yield: 312 mg (83%); Mp 186-190 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3313, 3024, 2978, 2248, 1704, 1559, 1367. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 2.26 (s, 3H, CH_3),3.77 (s, 3H, OCH_3), 4.58 (d, 1H, CH-Ph, J = 5.3 Hz), 6.77 (s, 1H, =CH), 6.79 (d, 1H, CH-NO_2, J = 5.3 Hz), 6.98 (d, 2H, H-Ar, J = 8.2 Hz), 7.14 (d, 2H, H-Ar, J = 7.6 Hz), 7.27 (2H, d, H-Ar, J = 7.6 Hz), 7.44 (1H, s, NH), 7.54 (1H, s, NH), 7.58 (d, 2H, H-Ar, J = 8.3 Hz). ^{13}C NMR (75 MHz, DMSO- d_6): δ= 20.7, 55.4, 57.8, 58.7, 94.3, 114.3, 118.9, 123.8, 127.3, 128.1, 128.4, 129.0, 131.1, 137.9, 143.2, 160.2, 164.8. HR-MS (ESI) Calc. for Calc. for $C_{21}H_{19}N_3NaO_4$ $[M+Na]^+$: 400.1267; found: 400.1267.

5-(4-Chlorophenyl)-1-cyano-3-(4-methoxyphenyl)-4-nitrocyclopent-2-ene-1-carboxamide (5c):

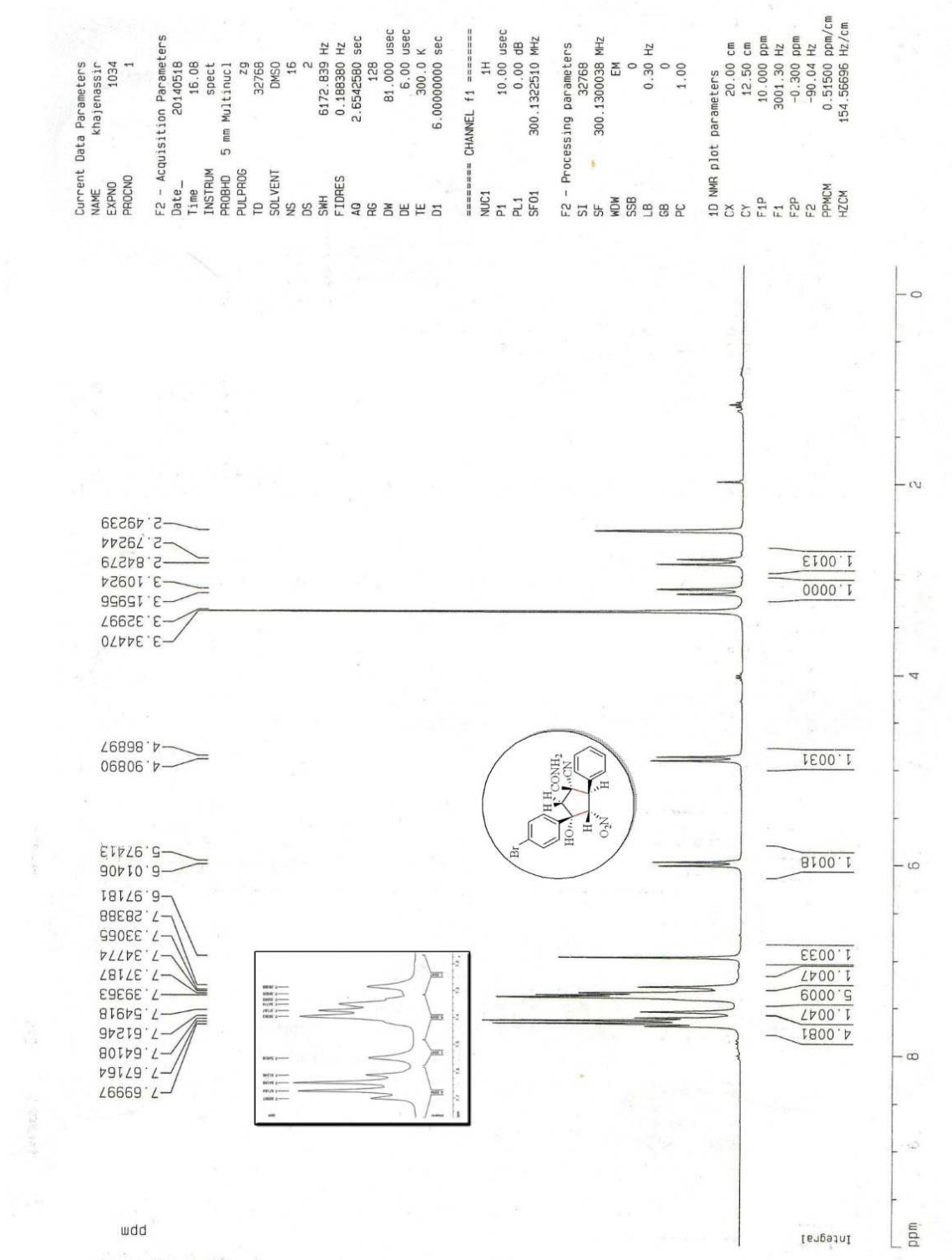


Light yellow powder; yield: 269 mg (68%); Mp 213-215 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3496, 3382, 2237, 1714, 1598, 1550, 1359. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.78 (s, 3H, OCH_3), 4.74 (d, 1H, CH-Ph, J= 4.9 Hz), 6.80 (s, 1H, =CH), 6.81 (d, 1H, CH-NO_2, J = 4.9 Hz), 7.00 (d, 2H, H-Ar, J = 8.4 Hz), 7.40-7.42 (m, 4H, H-Ar), 7.52 (brs, 1H, NH), 7.55-7.63 (m, 2H, H-Ar), 7.63 (brs, 1H, NH). ^{13}C NMR (75 MHz, DMSO- d_6): δ= 55.3, 56.7, 58.5, 94.1, 114.3, 118.7, 123.8, 127.4, 128.1, 128.4, 130.5, 133.3, 133.5, 143.2, 160.3, 164.8. HR-MS (ESI) Calc. for $C_{20}H_{16}N_3NaO_4{}^{35}Cl$ $[M+Na]^+$: 420.07222; found: 420.07215, Calc. for $C_{20}H_{16}N_3NaO_4{}^{37}Cl$ $[M+Na]^+$: 422.0692; found: 422.0692.

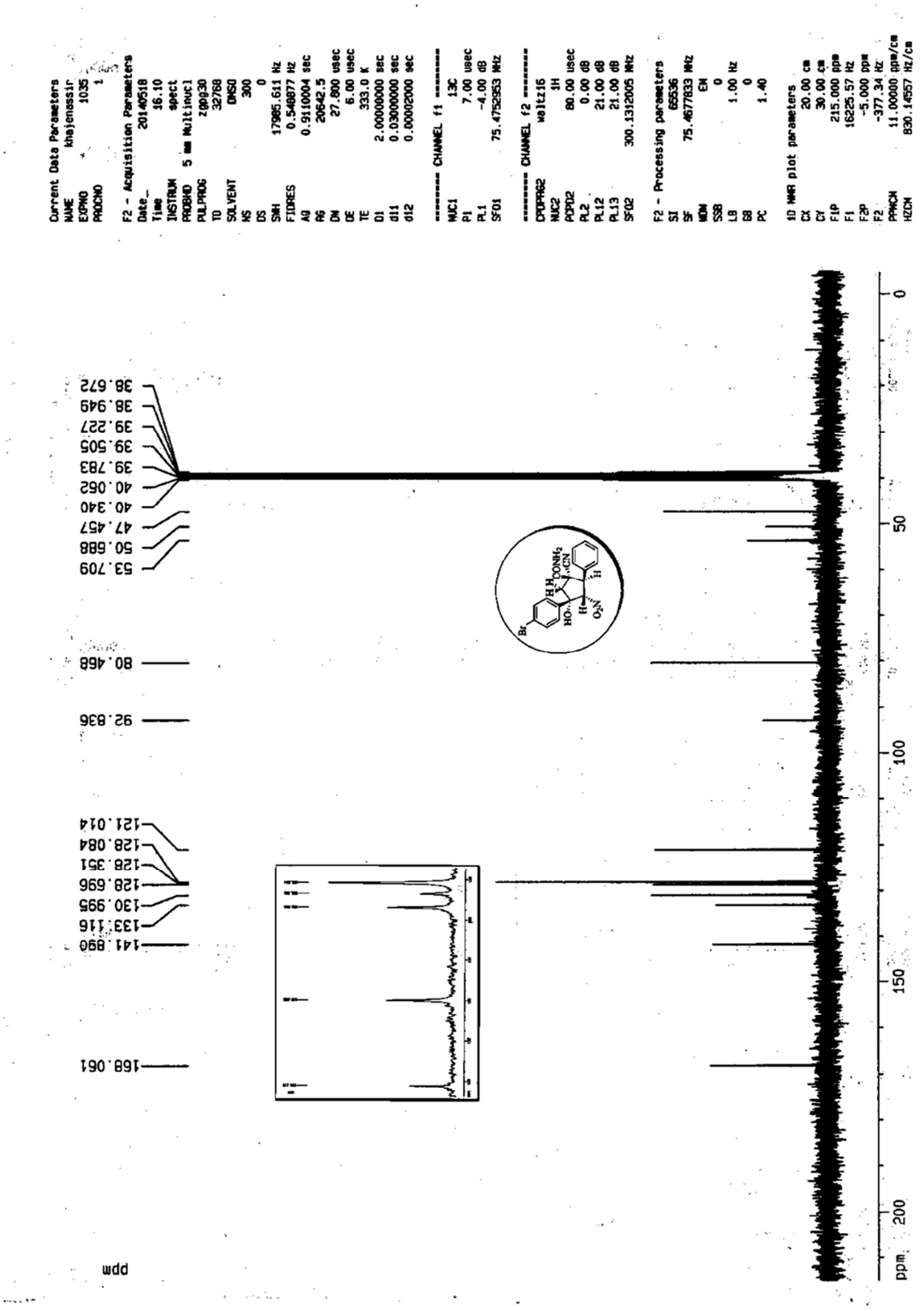
1-Cyano-3-(4-methoxyphenyl)-4-nitro-5-(4-(trifluoromethyl)phenyl)cyclopent-2-ene-1-carboxamide (5d):



Light yellow powder; yield: 241 mg (56%); Mp 218-220 ˚C. IR (KBr) (ν_{max}/ cm^{-1}): 3506, 3393, 3010, 2924, 2238, 1716, 1552, 1366. ^{1}H NMR (300 MHz, DMSO- d_6): δ = 3.76 (s, 3H, OCH_3), 4.83 (brs, 1H, CH-Ph), 6.83 (s, 1H, =CH), 6.89 (brs, 1H, CH-NO_2), 6.97 (d, 2H, H-Ar, J = 7.5 Hz), 7.59-7.62 (m, 5H, H-Ar and NH), 7.71 (d, 2H, H-Ar, J = 7.5 Hz). ^{13}C NMR (75 MHz, DMSO- d_6): δ= 55.4, 56.7, 58.5, 93.9, 114.2, 118.5, 122.2, 123.6, 125.2, 125.3, 125.8, 127.3, 128.3, 128.6, 129.1, 129.5, 130.7, 139.2, 143.2, 160.3, 164.7. HR-MS (ESI) Calc. for $C_{21}H_{15}F_3N_3O_3$[(M-H_2O)+H]$^+$ 413.2666, found, 413.2666.



^{1}H NMR (300 MHz, DMSO-d_6) 4a



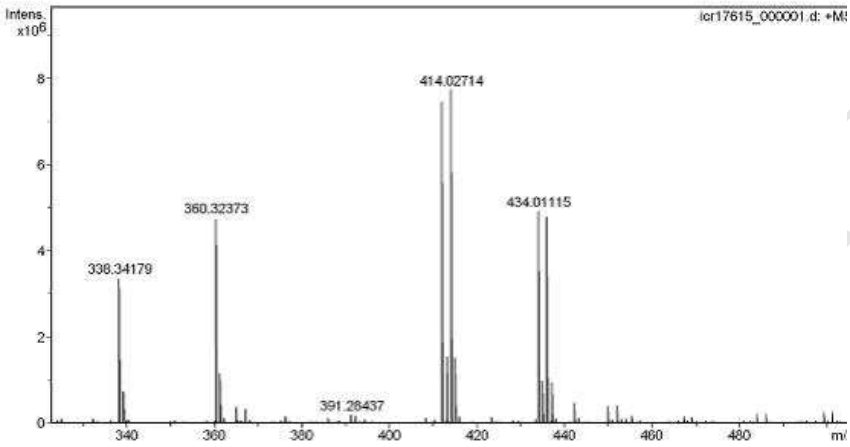
^{13}C NMR (75 MHz, DMSO-d_6) 4a

Mass Spectrum Formula Report

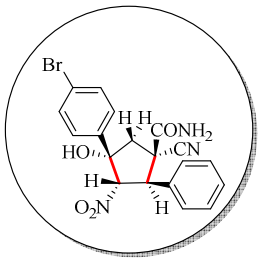
Analysis Info Acquisition Date 8/29/2014 1:23:26 PM

Analysis Name D:\Data\Balalaie\icr17615_000001.d

Comment Prof. Balalaie: SA Z30 in DCM/MeOH

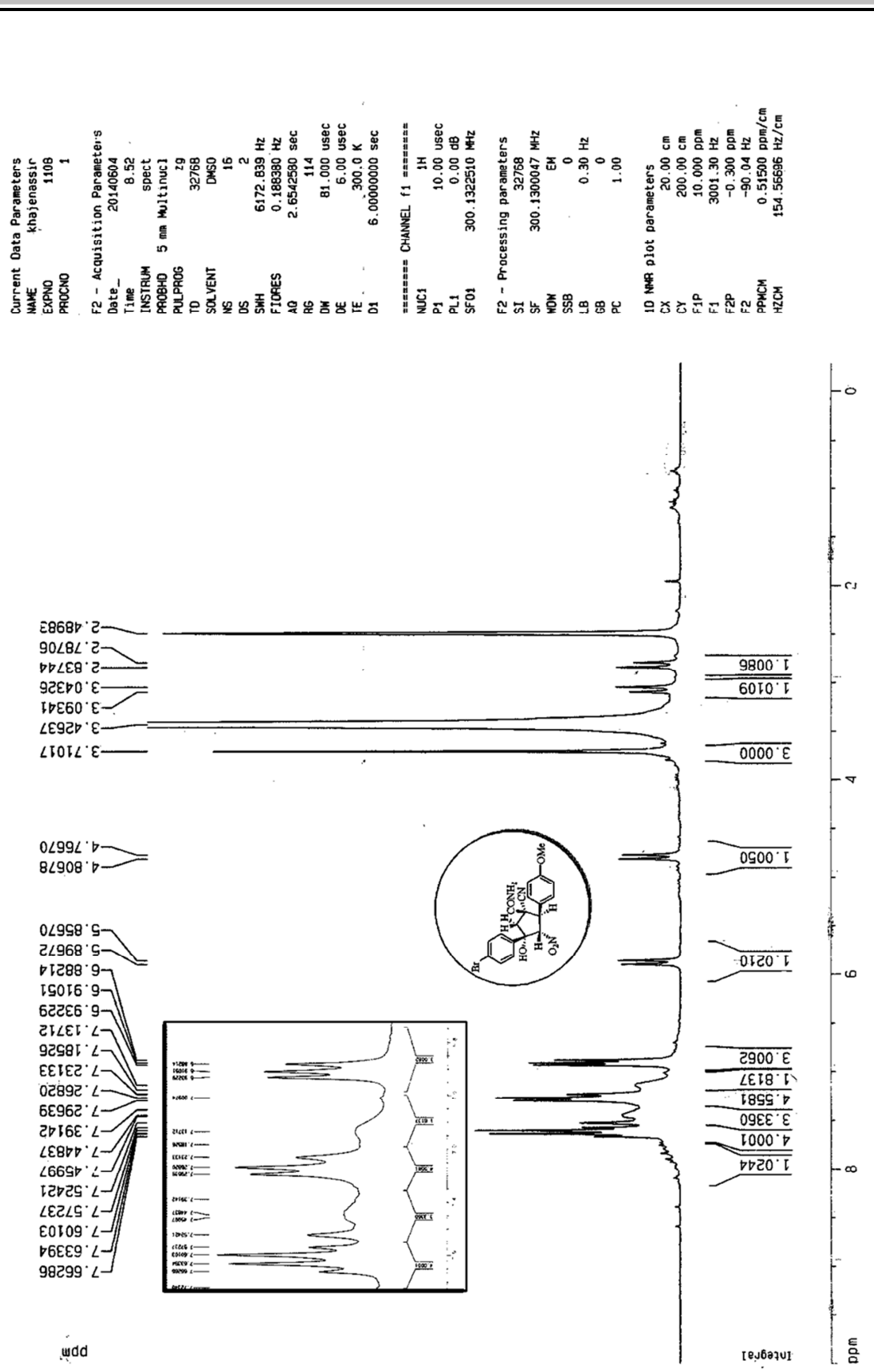


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
412.02922	C 17 H 8 N 4 O 9	412.02858	-0.6	-1.5	6.6	16.0	ok	odd
	C 16 H 2 N 11 O 4	412.02857	-0.6	-1.6	17.4	21.5	ok	even
	C 19 H 15 N 3 O 3 ^79Br	412.02913	-0.1	-0.2	17.4	13.5	ok	even
	C 19 H 10 N O 10	412.02992	0.7	1.7	21.4	15.5	ok	even
	C 18 H 4 N 8 O 5	412.02992	0.7	1.7	22.1	21.0	ok	odd
	C 13 H 24 N 4 O ^79Br ^81Br	412.02909	-0.1	-0.3	30.3	3.0	ok	odd
	C 13 H 19 N 2 O 8 ^81Br	412.02988	0.7	1.6	37.2	5.0	ok	odd
	C 25 H 15 O ^81Br	412.02803	-1.2	-2.9	42.0	18.0	ok	odd
	C 34 H 4	412.03075	-0.3	-0.7	450.6	33.0	ok	odd
	C 19 N 12 O	412.03125	0.2	0.5	569.2	26.0	ok	odd
	C 20 H 6 N 5 O 6	412.03126	0.2	0.5	576.0	20.5	ok	even
	C 21 H 17 O 4 ^79Br	412.03047	-0.6	-1.4	579.3	13.0	ok	odd
	C 16 H 12 O 13	412.02724	0.7	1.8	591.1	11.0	ok	odd
	C 14 H 15 N 6 O 4 ^81Br	412.03122	0.2	0.5	603.2	10.0	ok	odd
	C 15 H 26 N O 2 ^79Br ^81Br	412.03043	-0.6	-1.5	606.7	2.5	ok	even
	C 17 H 13 N 6 O 2 ^79Br	412.02779	1.3	3.1	669.1	14.0	ok	odd
	C 14 N 14 O 3	412.02723	0.7	1.8	670.3	22.0	ok	odd
	C 15 H 6 N 7 O 8	412.02724	0.7	1.8	679.0	16.5	ok	even
414.02714	C 19 H 15 N 3 O 3 ^81Br	414.02708	-0.1	-0.1	19.8	13.5	ok	even
	C 12 H 14 O 16	414.02764	0.5	1.2	37.2	6.0	ok	odd
	C 12 H 19 N 2 O 9 ^79Br	414.02684	-0.3	-0.7	38.2	4.0	ok	odd
	C 23 H 4 N 5 O 4	414.02578	-1.4	-3.3	47.1	24.5	ok	even
	C 25 H 6 N 2 O 5	414.02712	-0.0	-0.0	53.8	24.0	ok	odd
	C 24 N 9	414.02712	-0.0	-0.1	59.9	29.5	ok	even
	C 26 H 2 N 6 O	414.02846	-0.5	-1.3	538.6	29.0	ok	odd
	C 21 H 17 O 4 ^81Br	414.02843	-0.6	-1.3	571.9	13.0	ok	odd
	C 12 H 9 N 13 ^79Br	414.02818	-0.8	-1.9	594.2	14.5	ok	even
	C 12 H 4 N 11 O 7	414.02897	-0.0	-0.0	597.7	16.5	ok	even
	C 13 H 15 N 6 O 5 ^79Br	414.02818	-0.8	-1.9	601.2	9.0	ok	odd
	C 13 H 10 N 4 O 12	414.02897	-0.0	-0.0	602.7	11.0	ok	odd
	C 24 H 15 O 2 ^79Br	414.02499	0.6	1.6	657.5	17.0	ok	odd
	C 17 H 13 N 6 O 2 ^81Br	414.02574	1.4	3.4	677.8	14.0	ok	odd

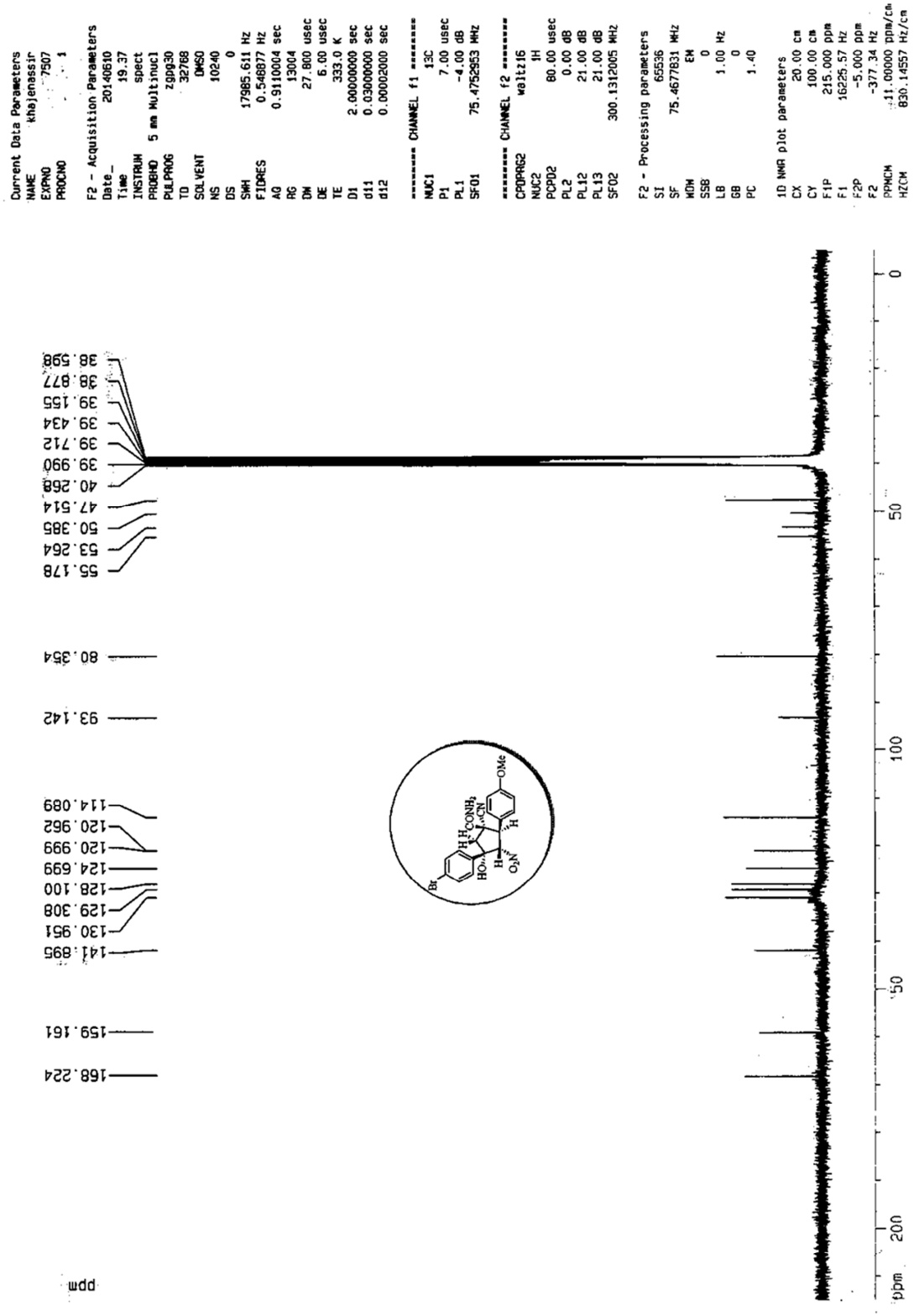


Chemical Formula: $C_{19}H_{16}BrN_3O_4$
Exact Mass: 429.03

HRMS-ESI of 4a



^{1}H NMR (300 MHz, DMSO-d_6) 4b



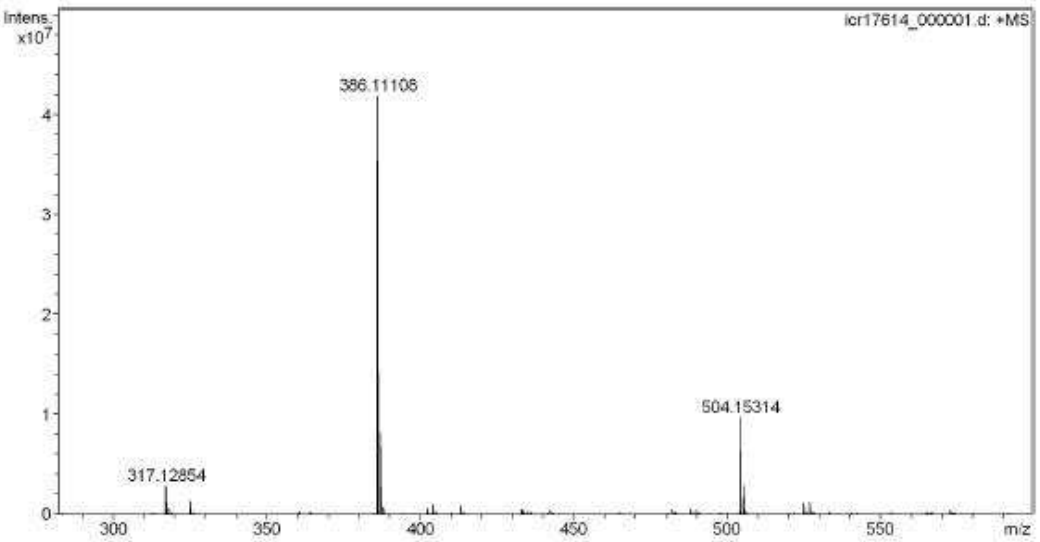
^{13}C NMR (75 MHz, DMSO-d_6) 4b

Mass Spectrum Formula Report

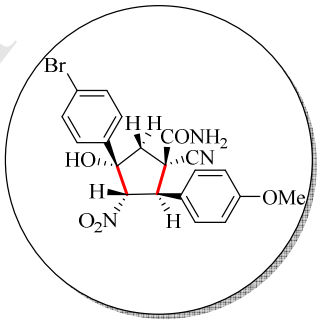
Analysis Info Acquisition Date 8/29/2014 1:11:28 PM

Analysis Name D:\Data\Balalaie\icr17614_000001.d

Comment Prof. Balalaie: SA 29 in DCM/MeOH

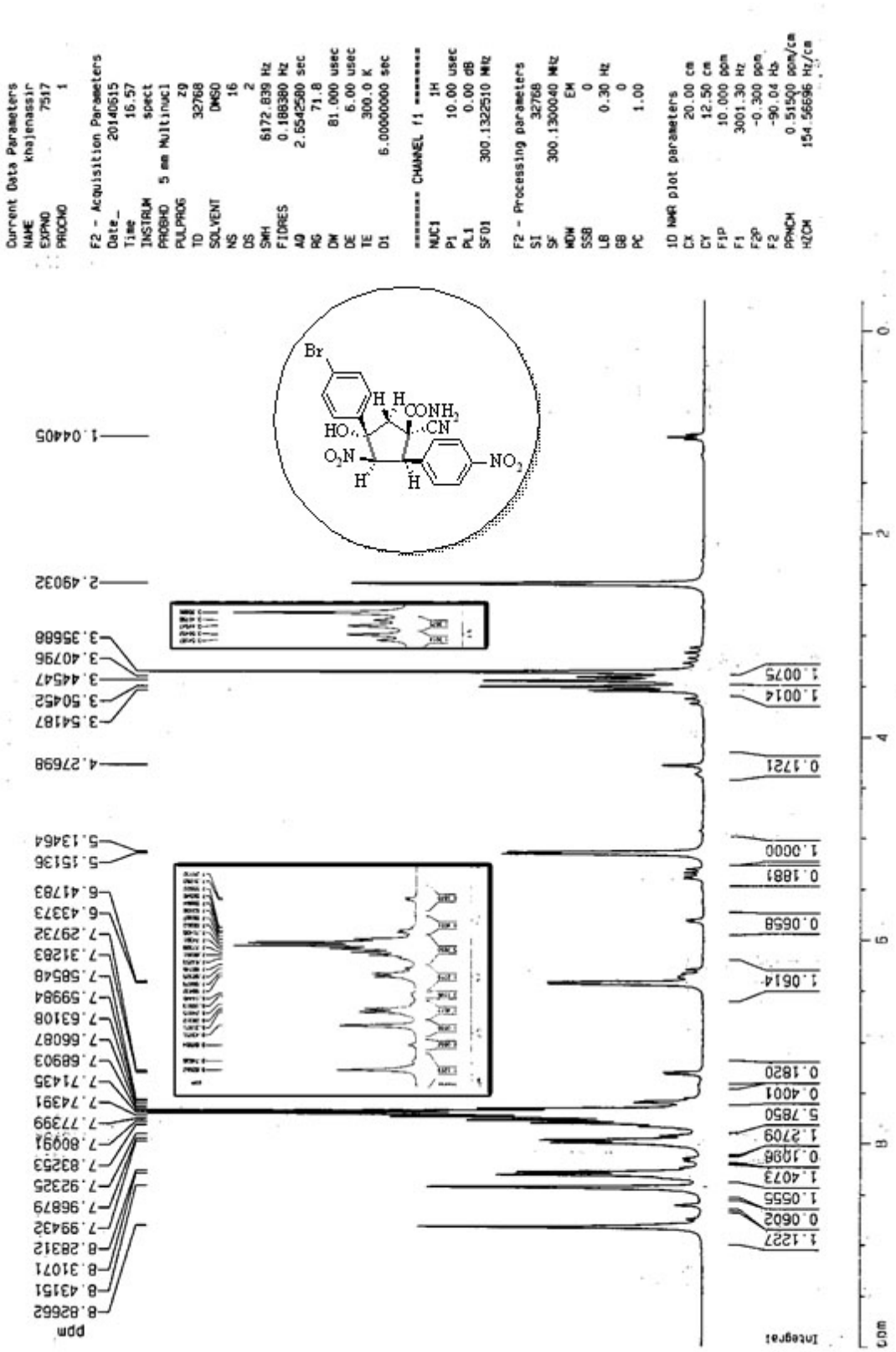


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
386.11108	C 16 H 10 N 12 O	386.10950	-1.6	-4.1	17.5	18.0	ok	odd
	C 12 H 21 N 10 ^81Br	386.11081	-0.3	-0.7	18.5	7.0	ok	odd
	C 17 H 16 N 5 O 6	386.10951	-1.6	-4.1	18.6	12.5	ok	even
	C 19 H 23 N 4 ^79Br	386.11006	-1.0	-2.6	19.2	10.0	ok	odd
	C 19 H 18 N 2 O 7	386.11085	-0.2	-0.6	22.8	12.0	ok	odd
	C 18 H 12 N 9 O 2	386.11085	-0.2	-0.6	24.6	17.5	ok	even
	C 21 H 25 N O ^79Br	386.11140	0.3	0.8	24.8	9.5	ok	even
	C 13 H 27 N 3 O 5 ^81Br	386.11081	-0.3	-0.7	28.5	1.5	ok	even
	C 31 H 14	386.10900	-2.1	-5.4	74.7	25.0	ok	odd
	C 20 H 14 N 6 O 3	386.11219	-0.5	-1.2	571.3	17.0	ok	odd
	C 14 H 23 N 7 O ^81Br	386.11215	-0.5	-1.3	598.7	6.5	ok	even
	C 15 H 29 O 6 ^81Br	386.11216	-0.5	-1.3	605.7	1.0	ok	odd

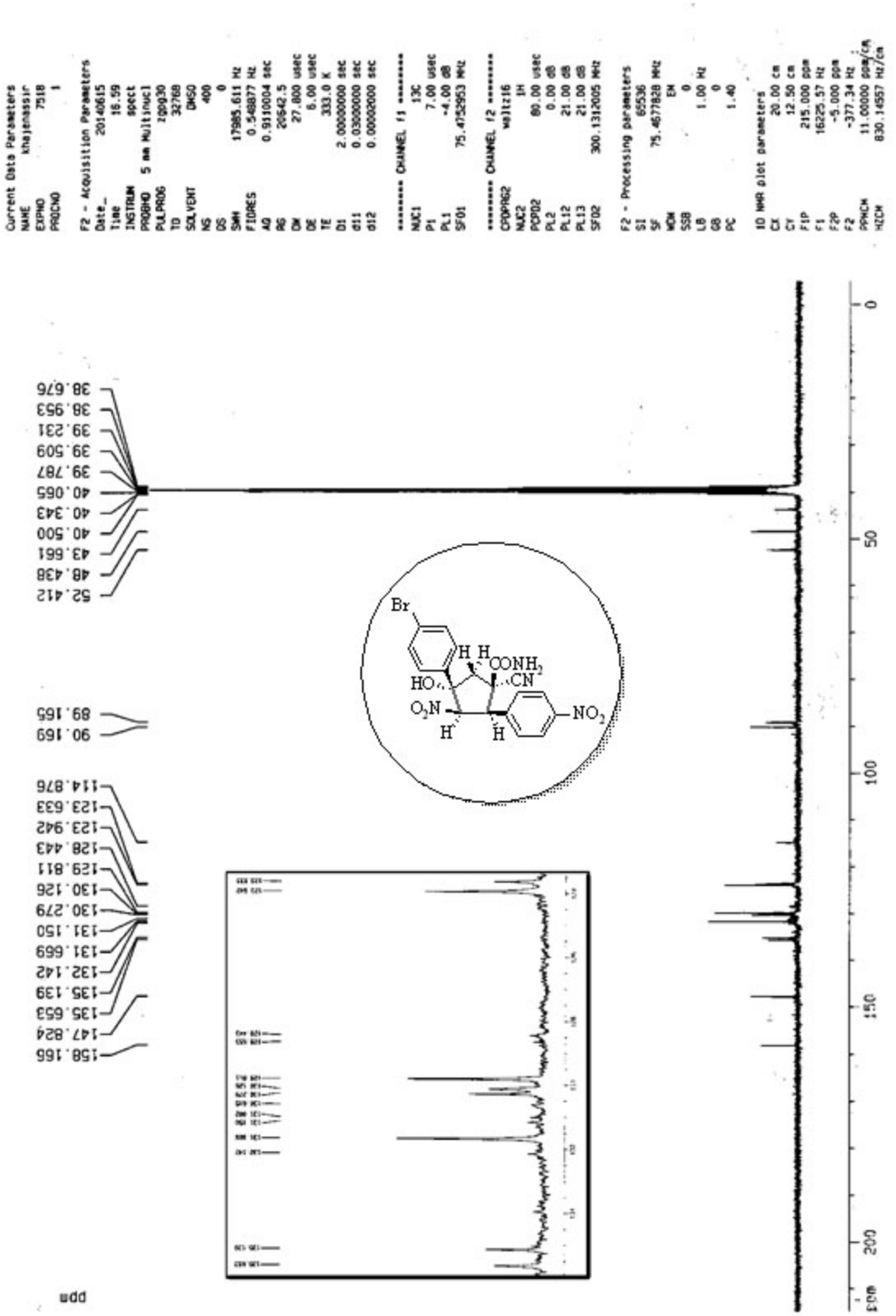


Chemical Formula: $C_{20}H_{18}BrN_3O_5$
Exact Mass: 459.04

HRMS-ESI of 4b



^{1}H NMR (300 MHz, DMSO-d_6) 4c



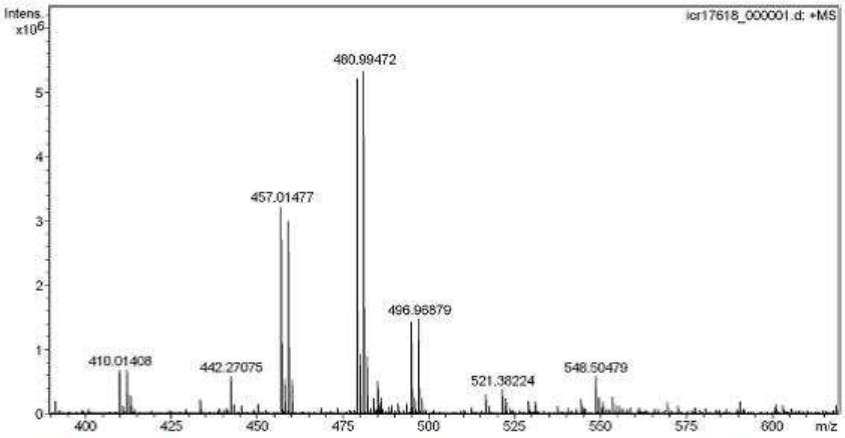
^{13}C NMR (75 MHz, DMSO-d_6) 4c

Mass Spectrum Formula Report

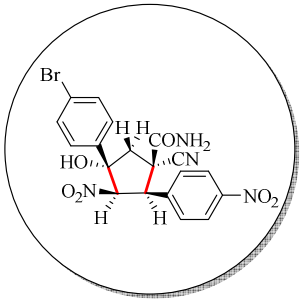
Analysis Info Acquisition Date 8/29/2014 1:51:35 PM

Analysis Name D:\Data\Balalaie\icr17618_000001.d

Comment Prof. Balalaie: SA 35 in DCM/MeOH

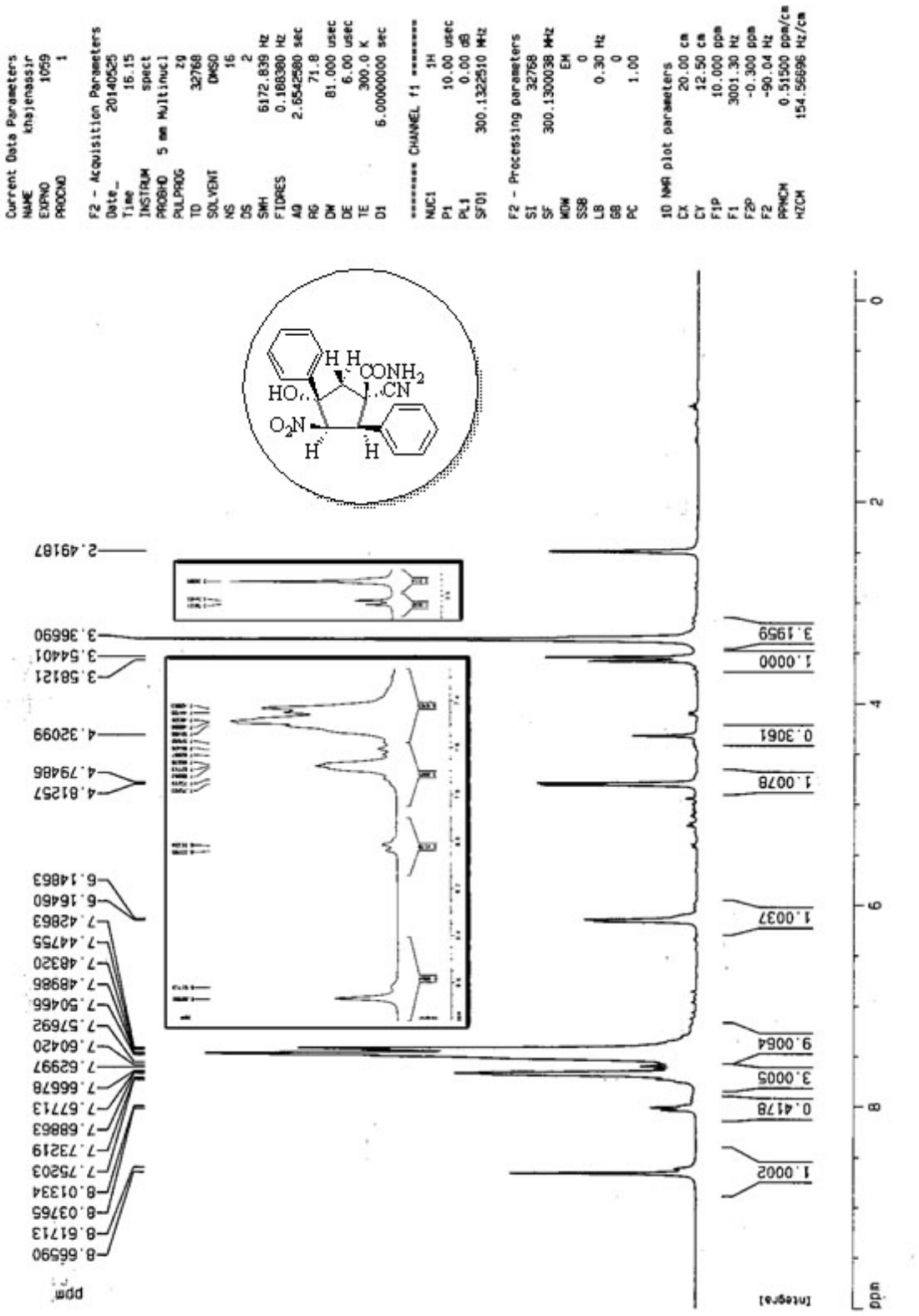


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
457.01477	C 18 H 18 O 9 ^79Br	457.01287	-1.9	-4.2	21.5	9.5	ok	even
	C 19 H 9 N 2 O 12	457.01500	0.2	0.5	32.8	16.5	ok	even
	C 19 H 14 N 4 O 5 ^79Br	457.01421	-0.6	-1.2	33.8	14.5	ok	even
	C 18 H 3 N 9 O 7	457.01499	0.2	0.5	39.2	22.0	ok	odd
	C 18 H 8 N 11 ^79Br	457.01420	-0.6	-1.2	39.4	20.0	ok	odd
	C 21 H 16 N O 6 ^79Br	457.01555	0.8	1.7	40.3	14.0	ok	odd
	C 20 H 10 N 8 O ^79Br	457.01555	0.8	1.7	45.7	19.5	ok	even
	C 25 H 14 N O 3 ^81Br	457.01311	-1.7	-3.6	63.7	19.0	ok	odd
	C 28 H 12 N 2 ^81Br	457.01579	1.0	2.2	72.9	23.5	ok	even
	C 31 H 5 O 5	457.01315	-1.6	-3.5	87.9	29.5	ok	even
	C 32 H N 4 O	457.01449	-0.3	-0.6	99.6	34.5	ok	even
	C 34 H 3 N O 2	457.01583	-1.1	-2.3	391.8	34.0	ok	odd
	C 20 H 5 N 6 O 8	457.01634	-0.5	-1.2	446.0	21.5	ok	even
	C 22 H 12 N 5 O 2 ^79Br	457.01689	0.0	0.0	506.0	19.0	ok	odd
459.01279	C 18 H 23 N 2 O 2 ^79Br ^81Br	459.01003	-2.8	-6.0	19.6	7.5	ok	even
	C 18 H 18 O 9 ^81Br	459.01082	-2.0	-4.3	20.2	9.5	ok	even
	C 19 H 14 N 4 O 5 ^81Br	459.01216	-0.6	-1.4	31.3	14.5	ok	even
	C 18 H 8 N 11 ^81Br	459.01216	-0.6	-1.4	36.5	20.0	ok	odd
	C 21 H 16 N O 6 ^81Br	459.01350	0.7	1.6	37.7	14.0	ok	odd
	C 20 H 10 N 8 O ^81Br	459.01350	0.7	1.6	42.7	19.5	ok	even
	C 23 H 23 ^79Br ^81Br	459.01406	1.3	2.8	44.5	11.5	ok	even
	C 22 H 12 N 5 O 2 ^81Br	459.01484	2.1	4.5	49.9	19.0	ok	odd
	C 24 H 14 N O 4 ^79Br	459.01007	-2.7	-5.9	55.0	18.0	ok	odd
	C 25 H 5 N 3 O 7	459.01220	-0.6	-1.3	58.2	25.0	ok	odd
	C 23 H 3 N 6 O 6	459.01086	-1.9	-4.2	60.4	25.5	ok	even
	C 27 H 7 O 8	459.01354	0.8	1.7	64.2	24.5	ok	even
	C 27 H 12 N 2 O ^79Br	459.01275	-0.0	-0.1	64.7	22.5	ok	even
	C 25 H 10 N 5 ^79Br	459.01141	-1.4	-3.0	68.3	23.0	ok	odd
	C 28 H 3 N 4 O 4	459.01488	2.1	4.6	75.7	29.5	ok	even
	C 26 H N 7 O 3	459.01354	0.8	1.6	80.4	30.0	ok	odd
	C 37 H N	459.01035	-2.4	-5.3	120.0	38.0	ok	odd

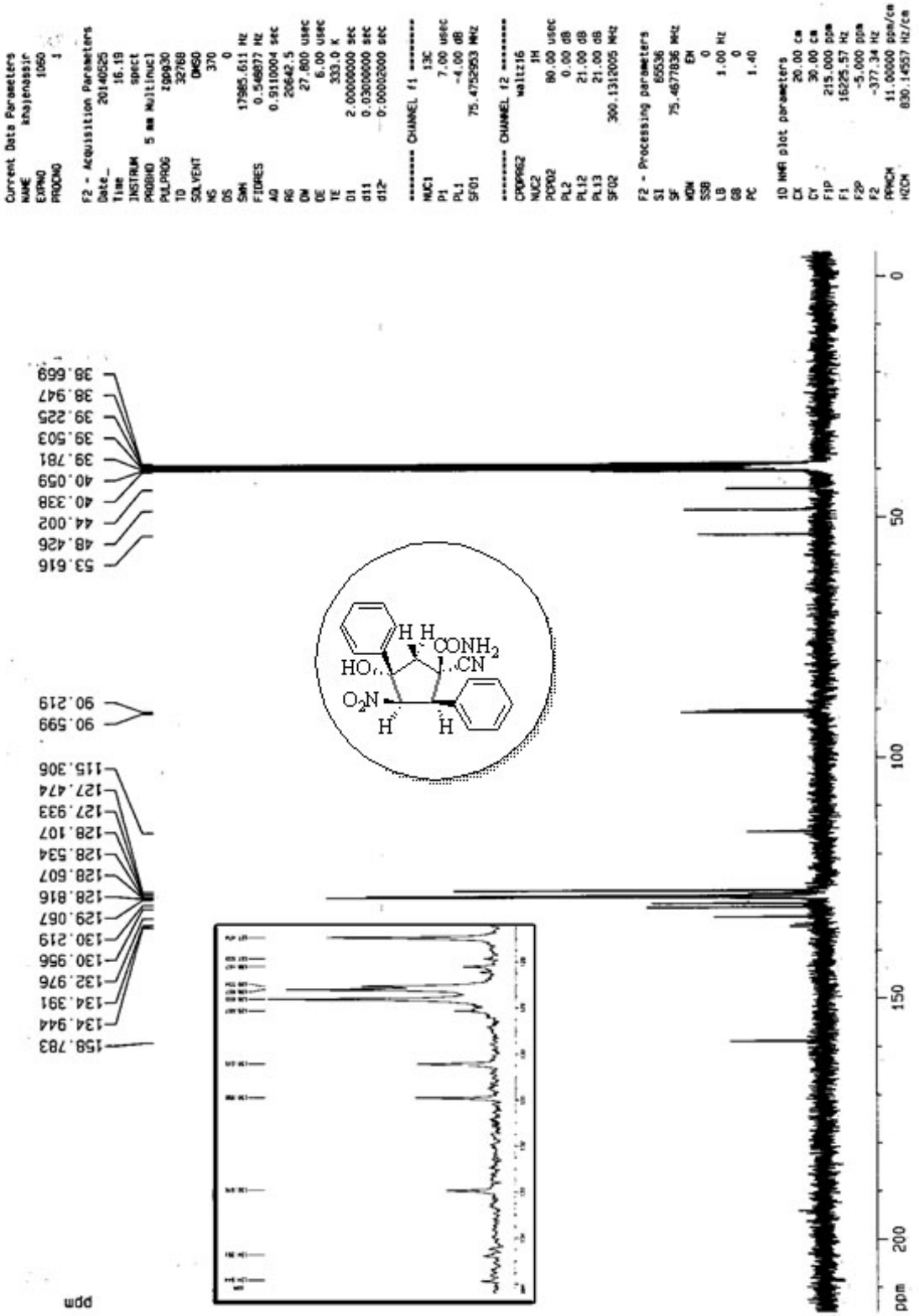


Chemical Formula: $C_{19}H_{15}BrN_4O_6$
Exact Mass: 474.02

HRMS-ESI of 4c



^{1}H NMR (300 MHz, DMSO-d_6) 4d



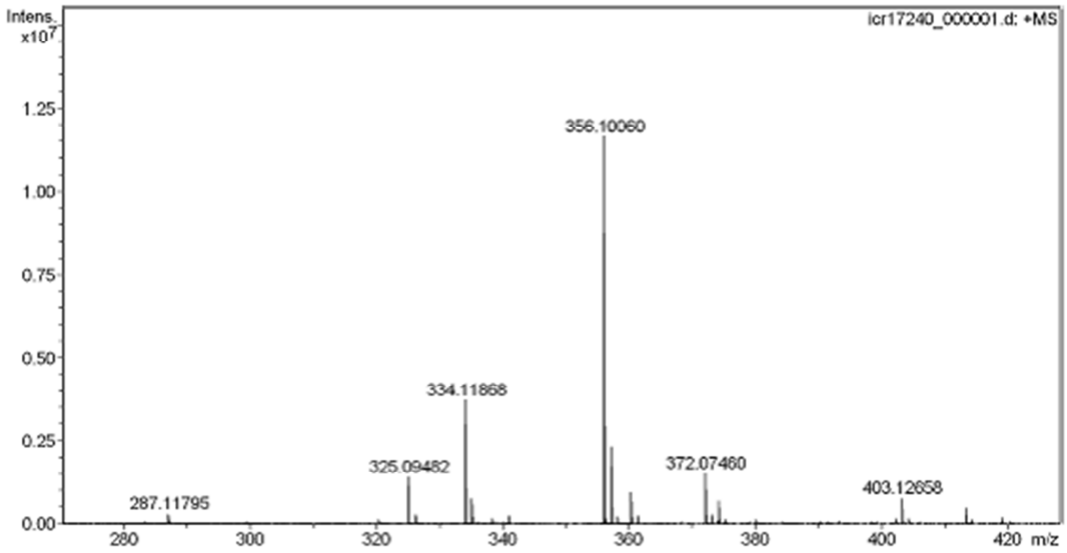
^{13}C NMR (75 MHz, DMSO-d_6) 4d

Mass Spectrum Formula Report

Analysis Info Acquisition Date 7/16/2014 4:27:05 PM

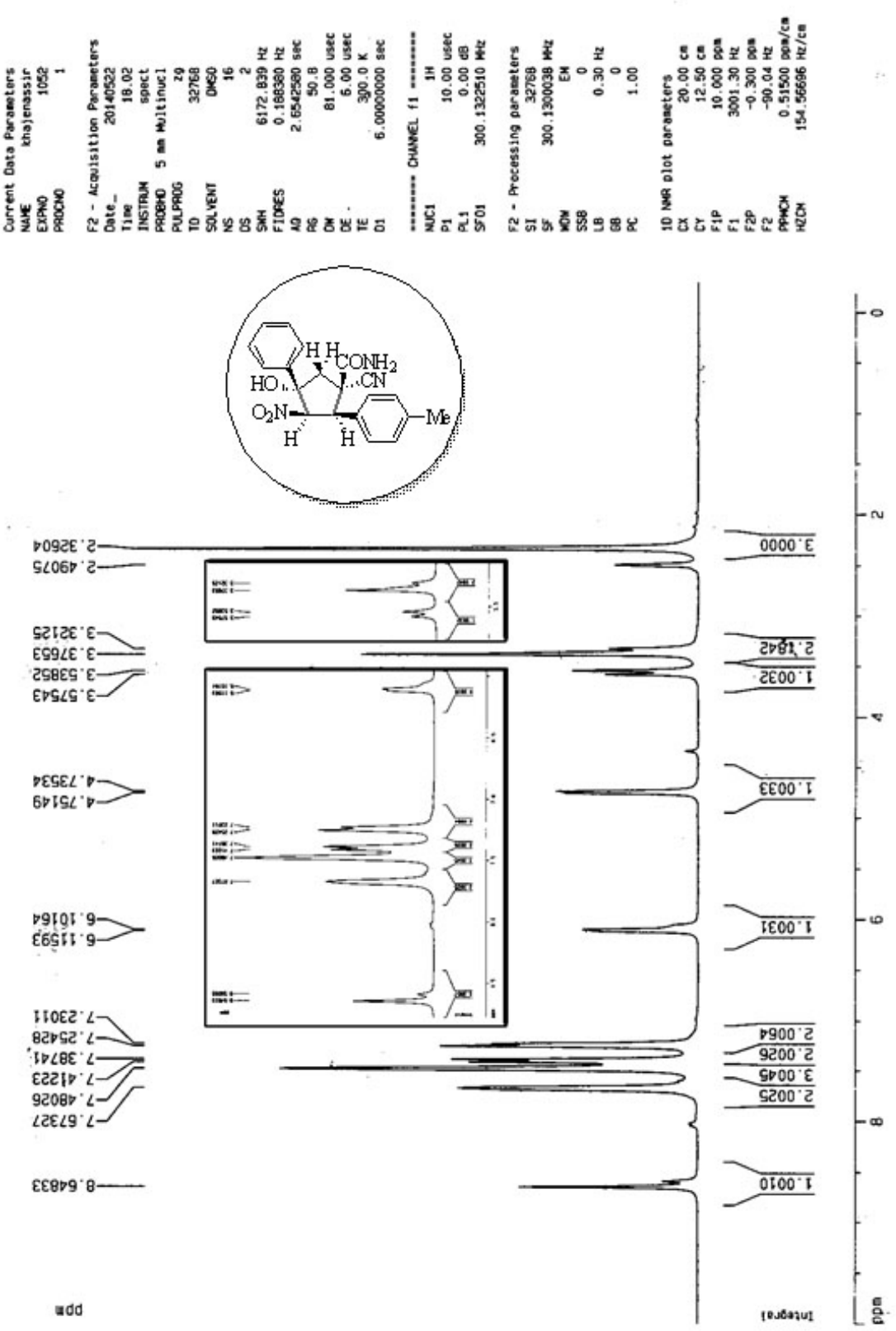
Analysis Name D:\Data\Balalaie\icr17240_000001.d

Comment Prof. Balalaie: SA 14 in DCM/MeOH

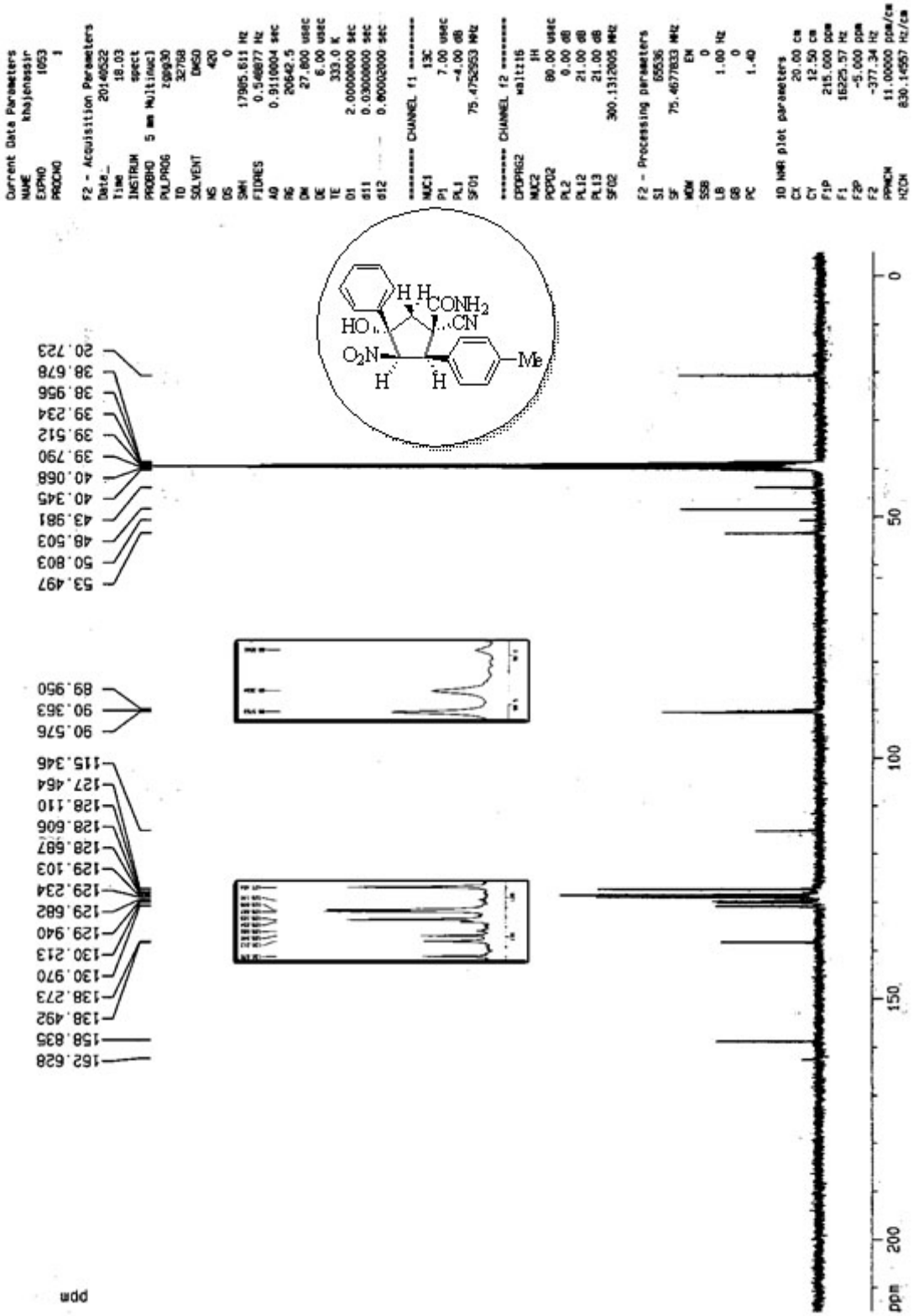


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
356.10060	C 17 H 10 N 9 O	356.10028	-0.3	-0.9	16.0	17.5	ok	even
	C 18 H 16 N 2 O 6	356.10029	-0.3	-0.9	18.3	12.0	ok	odd
	C 19 H 12 N 6 O 2	356.10163	-0.3	-0.9	597.5	17.0	ok	odd
	C 15 H 8 N 12	356.09894	-0.3	-0.9	598.2	18.0	ok	odd
	C 16 H 14 N 5 O 5	356.09895	-0.3	-0.9	605.0	12.5	ok	even

HRMS-ESI of 4d



^{1}H NMR (300 MHz, DMSO-d_6) 4e



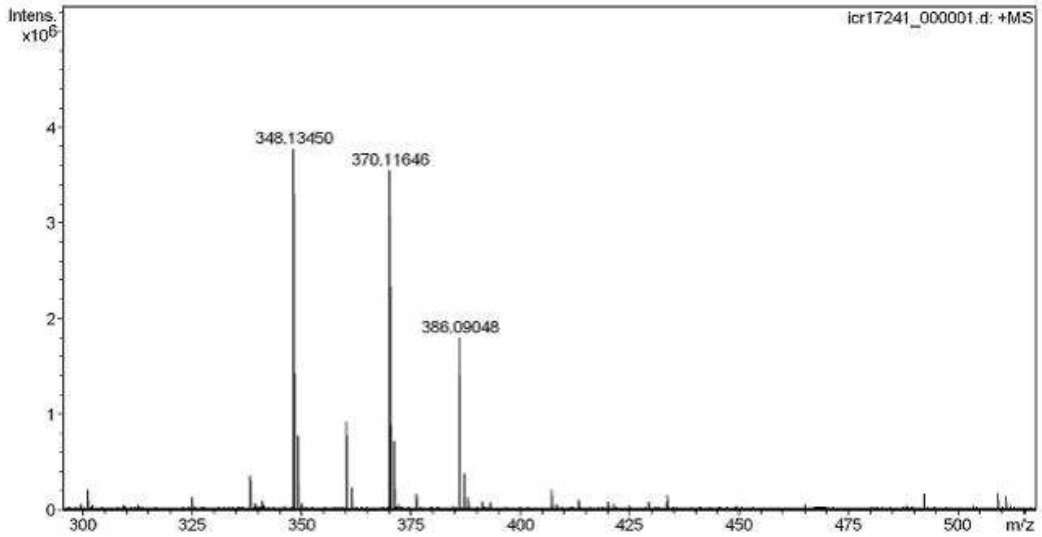
^{13}C NMR (75 MHz, DMSO-d_6) 4e

Mass Spectrum Formula Report

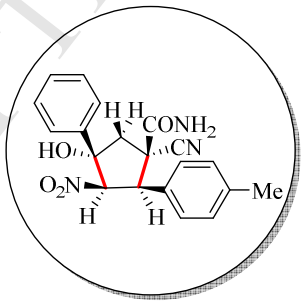
Analysis Info Acquisition Date 7/16/2014 4:41:52 PM

Analysis Name D:\Data\Balalaie\icr17241_000001.d

Comment Prof. Balalaie: SA 15 in DCM/MeOH

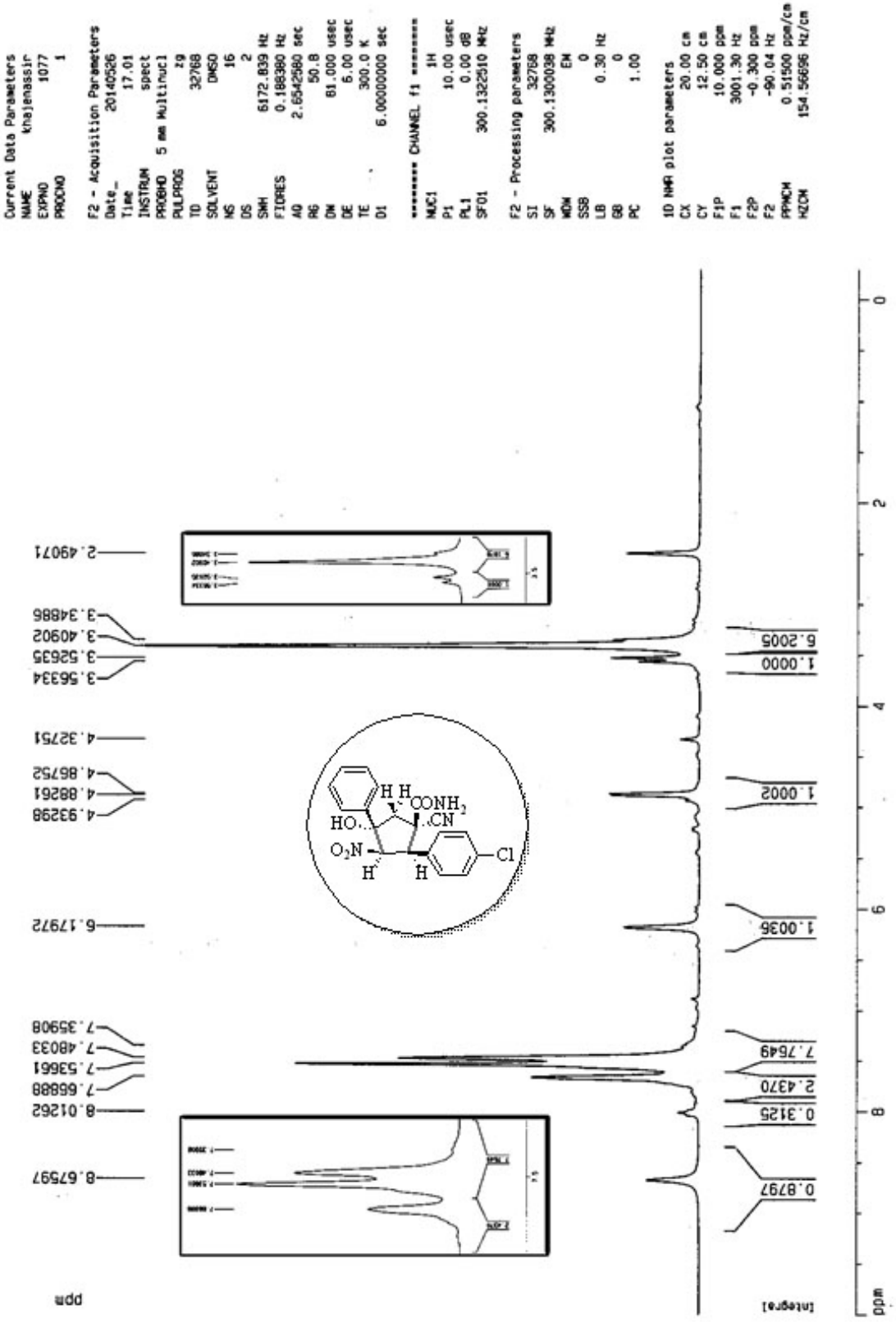


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
360.32395	C 19 H 42 N 3 O 3	360.32207	-1.9	-5.2	129.0	0.5	ok	even
	C 21 H 44 O 4	360.32341	-0.5	-1.5	135.5	0.0	ok	odd
	C 22 H 40 N 4	360.32475	0.8	2.2	149.7	5.0	ok	odd
	C 24 H 42 N O	360.32609	2.1	5.9	156.1	4.5	ok	even
370.11646	C 16 H 10 N 12	370.11459	-1.9	-5.0	14.6	18.0	ok	odd
	C 17 H 16 N 5 O 5	370.11460	-1.9	-5.0	17.1	12.5	ok	even
	C 18 H 12 N 9 O	370.11593	-0.5	-1.4	19.6	17.5	ok	even
	C 19 H 18 N 2 O 6	370.11594	-0.5	-1.4	20.2	12.0	ok	odd
	C 20 H 14 N 6 O 2	370.11728	0.8	2.2	26.7	17.0	ok	odd
	C 22 H 16 N 3 O 3	370.11862	2.2	5.8	33.1	16.5	ok	even

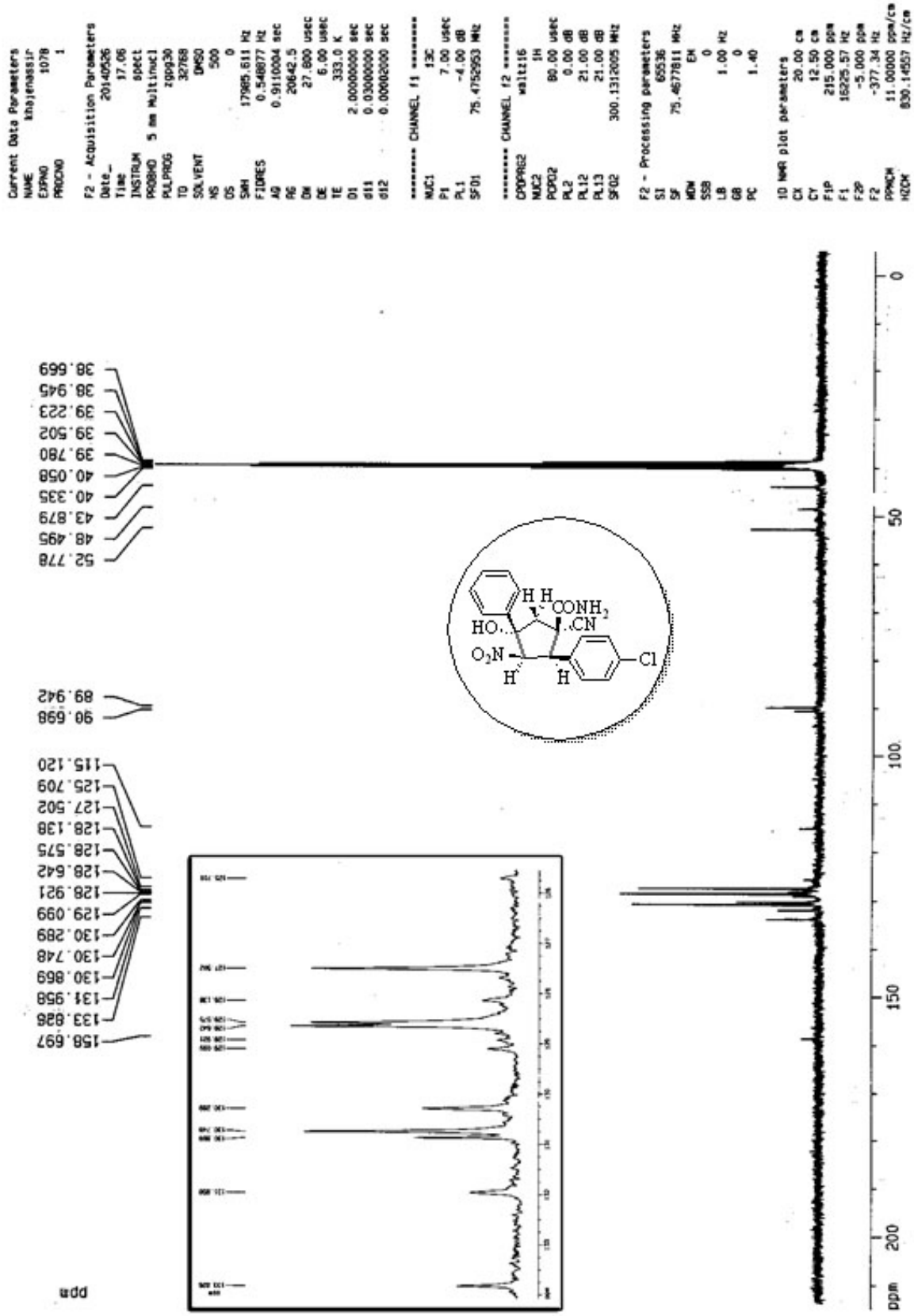


Chemical Formula: $C_{20}H_{19}N_3O_4$
Exact Mass: 365.14

HRMS-ESI of 4e



^{1}H NMR (300 MHz, DMSO-d_6) 4f



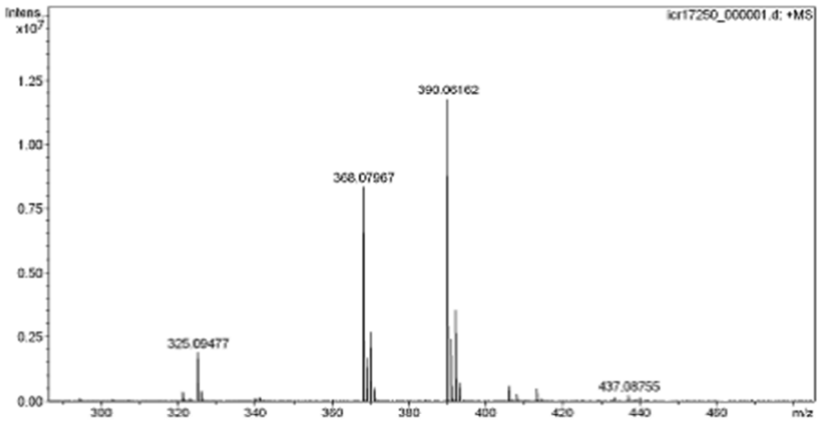
^{13}C NMR (75 MHz, DMSO-d_6) 4f

Mass Spectrum Formula Report

Analysis Info Acquisition Date 7/18/2014 11:37:48 AM

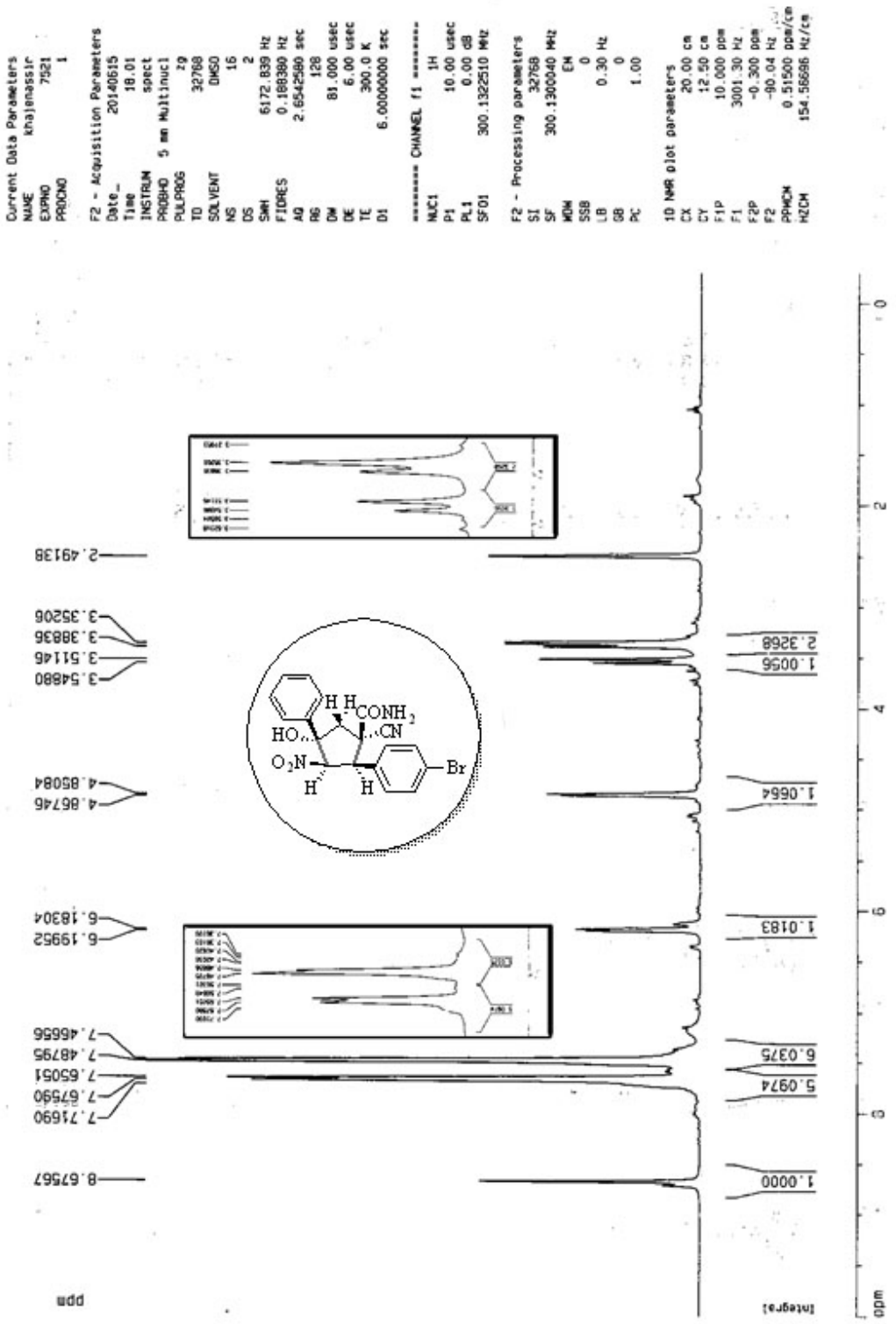
Analysis Name D:\Data\Balalaie\icr17250_000001.d

Comment Prof. Balalaie: SA 21 In DCM/MeOH

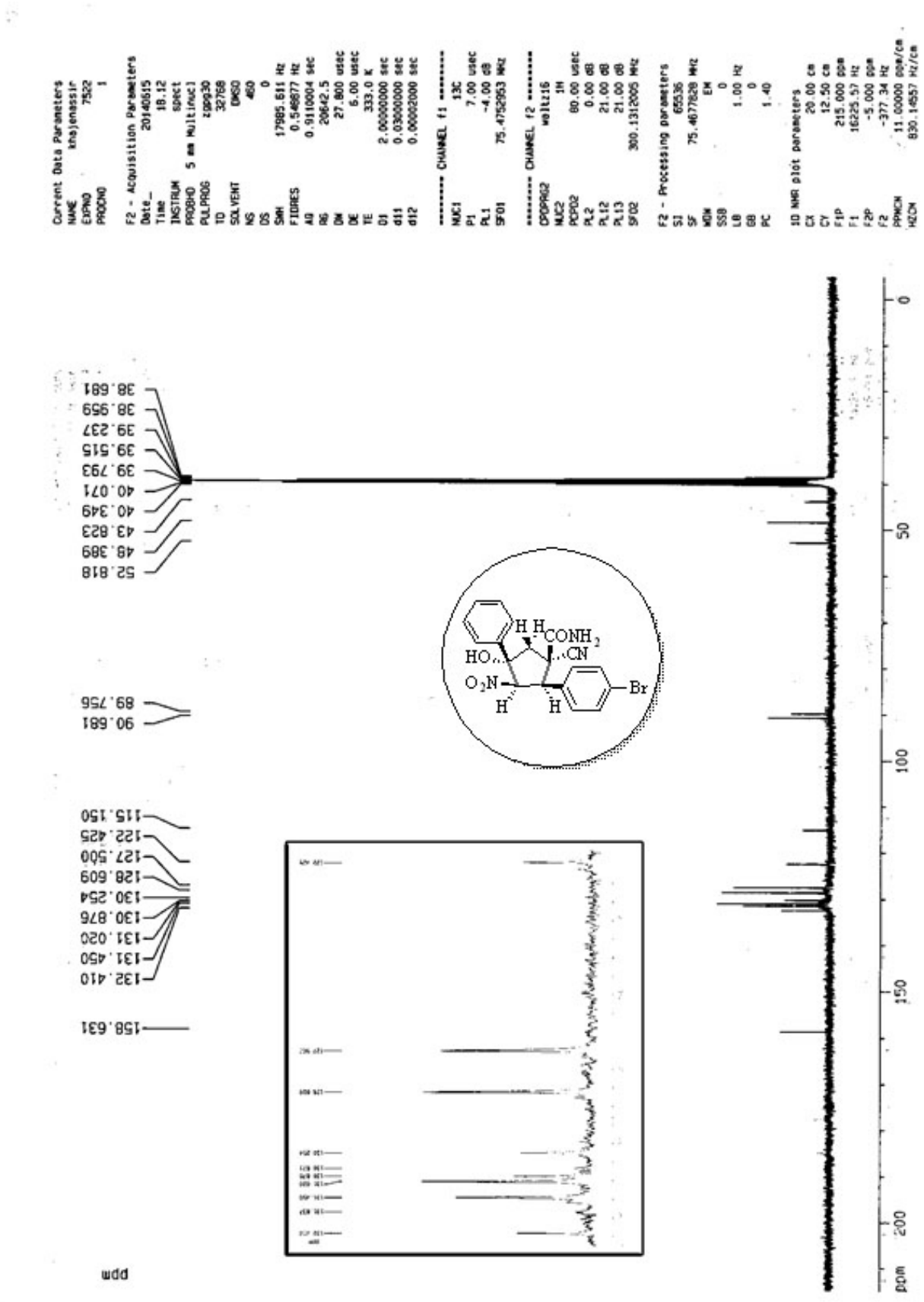


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
368.07967	C 19 H 15 N 3 O 3 ^35Cl	368.07965	-0.0	-0.1	18.6	13.5	ok	even
	C 12 H 13 N 9 O 3 ^37Cl	368.07949	-0.2	-0.5	24.5	10.5	ok	even
	C 22 H 12 N 2 O 4	368.07916	-0.5	-1.4	33.2	18.0	ok	odd
	C 13 H 19 N 2 O 8 ^37Cl	368.07949	-0.2	-0.5	34.4	5.0	ok	odd
	C 25 H 15 O ^37Cl	368.07764	-0.6	-1.7	564.3	18.0	ok	odd
	C 25 H 10 N 3 O	368.08184	0.7	1.8	572.0	22.5	ok	even
	C 23 H 8 N 6	368.08050	-0.7	-1.8	576.4	23.0	ok	odd
	C 22 H 18 N ^35Cl ^37Cl	368.07813	-0.1	-0.4	576.7	13.5	ok	even
	C 20 H 10 N 5 O 3	368.07782	-0.5	-1.3	579.8	18.5	ok	even
	C 17 H 13 N 6 O 2 ^35Cl	368.07830	0.0	0.1	592.4	14.0	ok	odd
	C 21 H 17 O 4 ^35Cl	368.08099	-0.2	-0.5	595.1	13.0	ok	odd
	C 14 H 15 N 6 O 4 ^37Cl	368.08083	-0.3	-0.9	618.4	10.0	ok	odd
	C 12 H 24 O 8 ^35Cl ^37Cl	368.08132	0.2	0.4	638.2	0.0	ok	odd
390.06162	C 19 H 14 N 3 Na O 3 ^35Cl	390.06159	-0.0	-0.1	18.2	13.5	ok	even
	C 21 H 18 O 3 ^35Cl ^37Cl	390.05980	-1.8	-4.7	22.6	12.0	ok	odd
	C 19 H 10 N 4 O 6	390.05949	-2.1	-5.5	22.8	17.0	ok	odd
	C 20 H 9 N 5 Na O 3	390.05976	-1.9	-4.8	26.3	18.5	ok	even
	C 22 H 17 N Na ^35Cl ^37Cl	390.06008	-1.5	-4.0	27.6	13.5	ok	even
	C 21 H 12 N O 7	390.06083	-0.8	-2.0	28.1	16.5	ok	even
	C 20 H 6 N 8 O 2	390.06082	-0.8	-2.0	31.2	22.0	ok	odd
	C 22 H 11 N 2 Na O 4	390.06110	-0.5	-1.3	32.5	18.0	ok	odd
	C 22 H 8 N 5 O 3	390.06217	0.5	1.4	37.8	21.5	ok	even
	C 25 H 14 Na O ^37Cl	390.05959	-2.0	-5.2	44.0	18.0	ok	odd
	C 27 H 13 O ^37Cl	390.06199	0.4	1.0	49.1	21.0	ok	odd
	C 25 H 11 N 3 ^37Cl	390.06065	-1.0	-2.5	50.4	21.5	ok	even
	C 23 H 7 N 6 Na	390.06244	-0.8	-2.1	566.2	23.0	ok	odd
	C 24 H 10 N 2 O 4	390.06351	0.3	0.7	568.1	21.0	ok	odd
	C 24 H 16 N ^35Cl ^37Cl	390.06248	-0.8	-2.0	569.5	16.5	ok	even
	C 19 H 11 N 6 O 2 ^35Cl	390.06265	-0.6	-1.5	584.9	17.0	ok	odd
	C 21 H 16 Na O 4 ^35Cl	390.06293	-0.3	-0.8	585.2	13.0	ok	odd
	C 25 H 9 N 3 Na O	390.06378	-0.4	-0.9	651.5	22.5	ok	even

HRMS-ESI of 4f



^{1}H NMR (300 MHz, DMSO-d_6) 4g



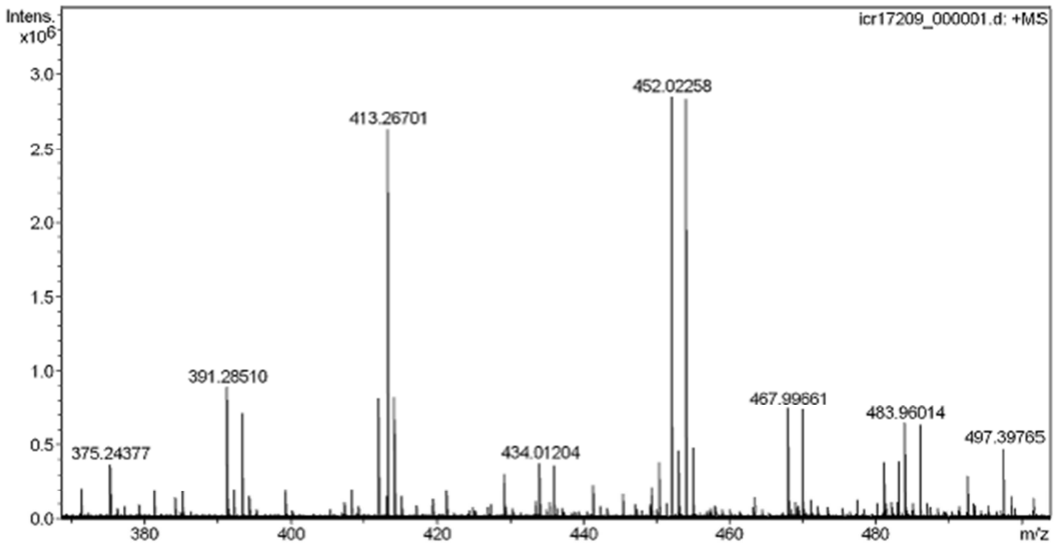
^{13}C NMR (75 MHz, DMSO-d_6) 4g

Mass Spectrum Formula Report

Analysis Info Acquisition Date 7/14/2014 4:19:21 PM

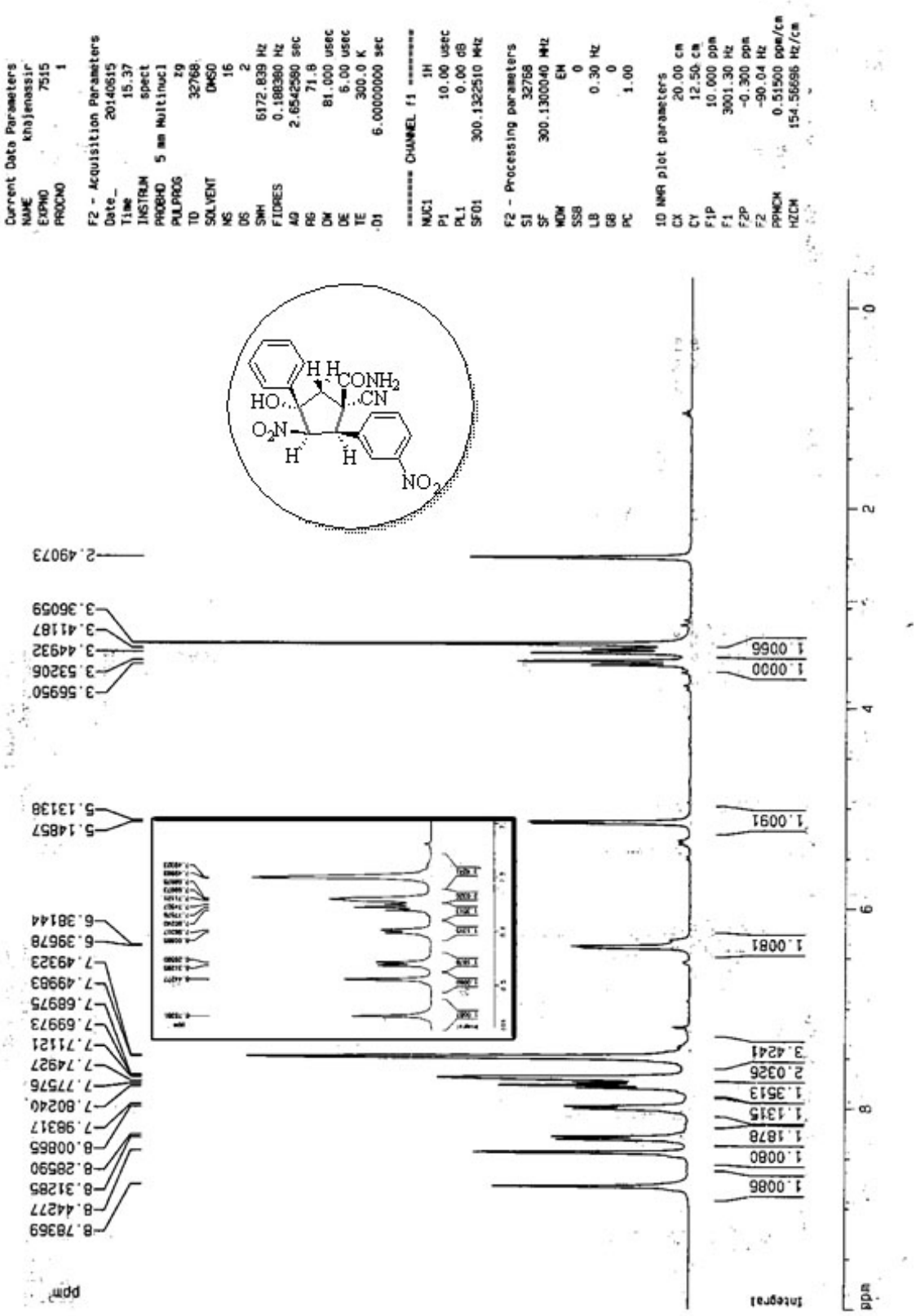
Analysis Name D:\Data\Balalaie\icr17209_000001.d

Comment Prof. Balalaie: SA 8 in DCM/MeOH

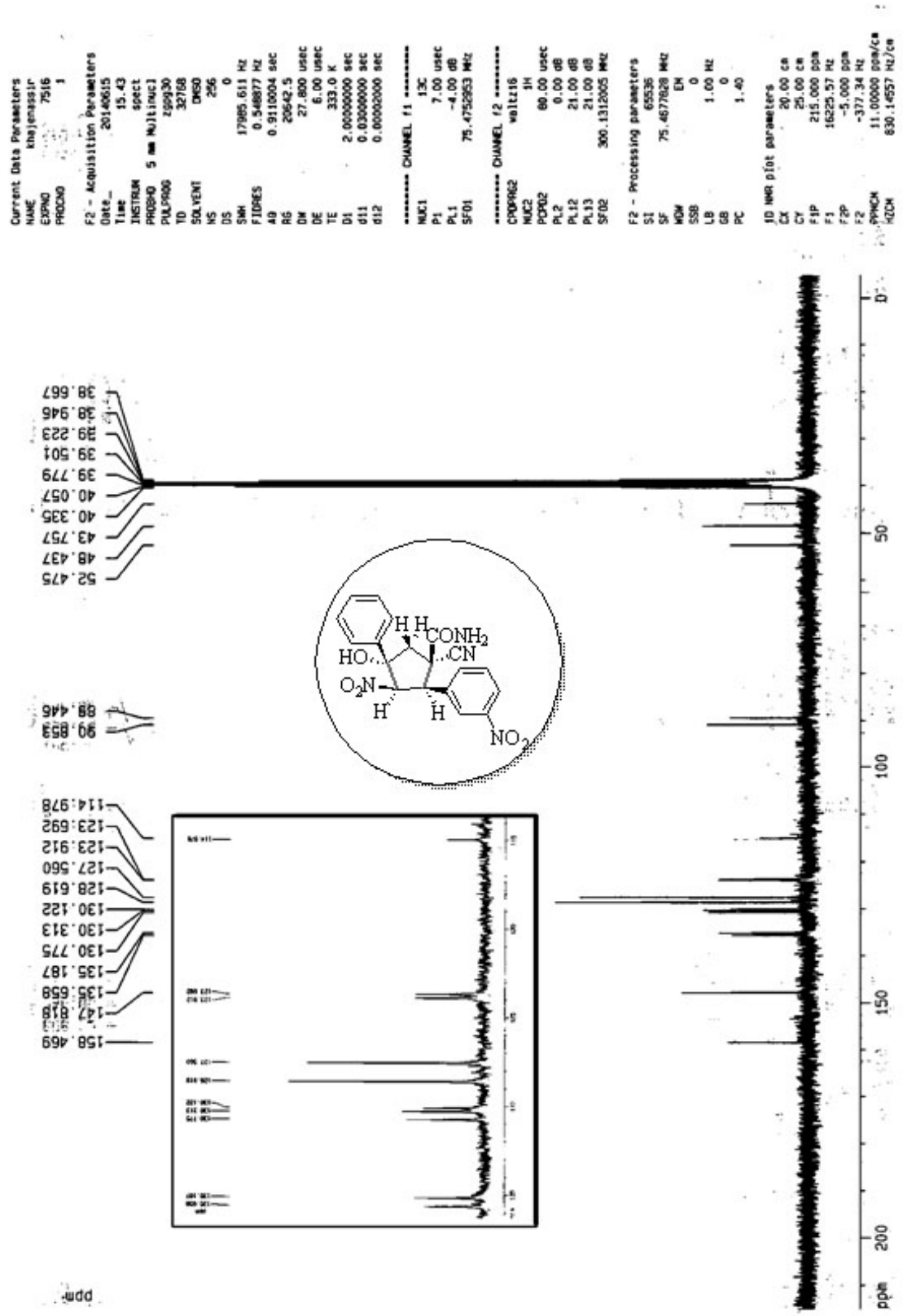


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
452.02258	C 19 H 11 N Na O 11	452.02243	-0.1	-0.3	33.1	14.5	ok	even
	C 19 H 16 N 3 Na O 4 ^79Br	452.02164	-0.9	-2.1	35.0	12.5	ok	even
	C 19 H 8 N 4 O 10	452.02349	0.9	2.0	37.3	18.0	ok	odd
	C 19 H 13 N 6 O 3 ^79Br	452.02270	0.1	0.3	40.7	16.0	ok	odd
	C 19 H N 12 Na O 2	452.02376	1.2	2.6	53.0	25.0	ok	odd
454.02049	C 19 H 16 N 3 Na O 4 ^81Br	454.01959	-0.9	-2.0	32.4	12.5	ok	even
	C 19 H 13 N 6 O 3 ^81Br	454.02066	0.2	0.4	37.9	16.0	ok	odd

HRMS-ESI of 4g



^{1}H NMR (300 MHz, DMSO-d_6) 4h



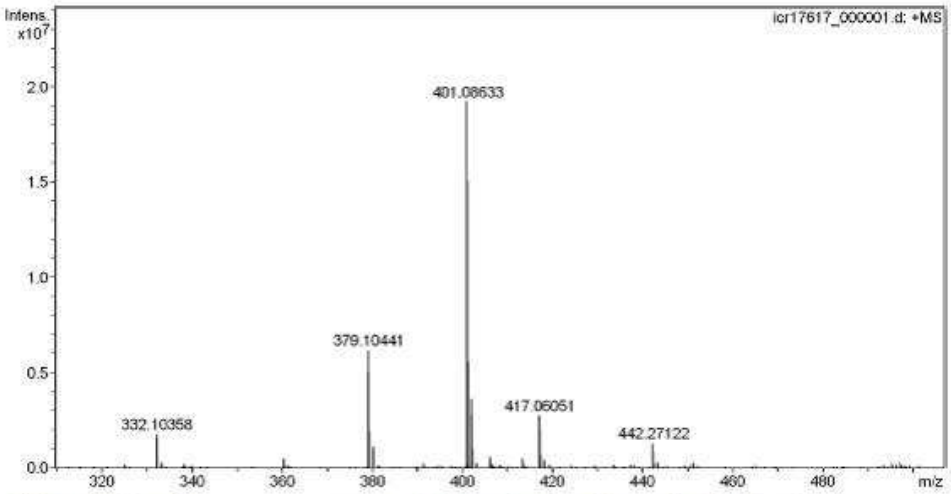
^{13}C NMR (75 MHz, DMSO-d_6) 4h

Mass Spectrum Formula Report

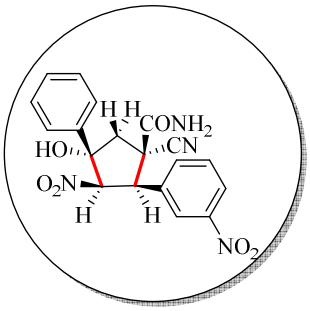
Analysis Info Acquisition Date 8/29/2014 1:42:44 PM

Analysis Name D:\Data\Balalaie\icr17617_000001.d

Comment Prof. Balalaie: SA 34 in DCM/MeOH

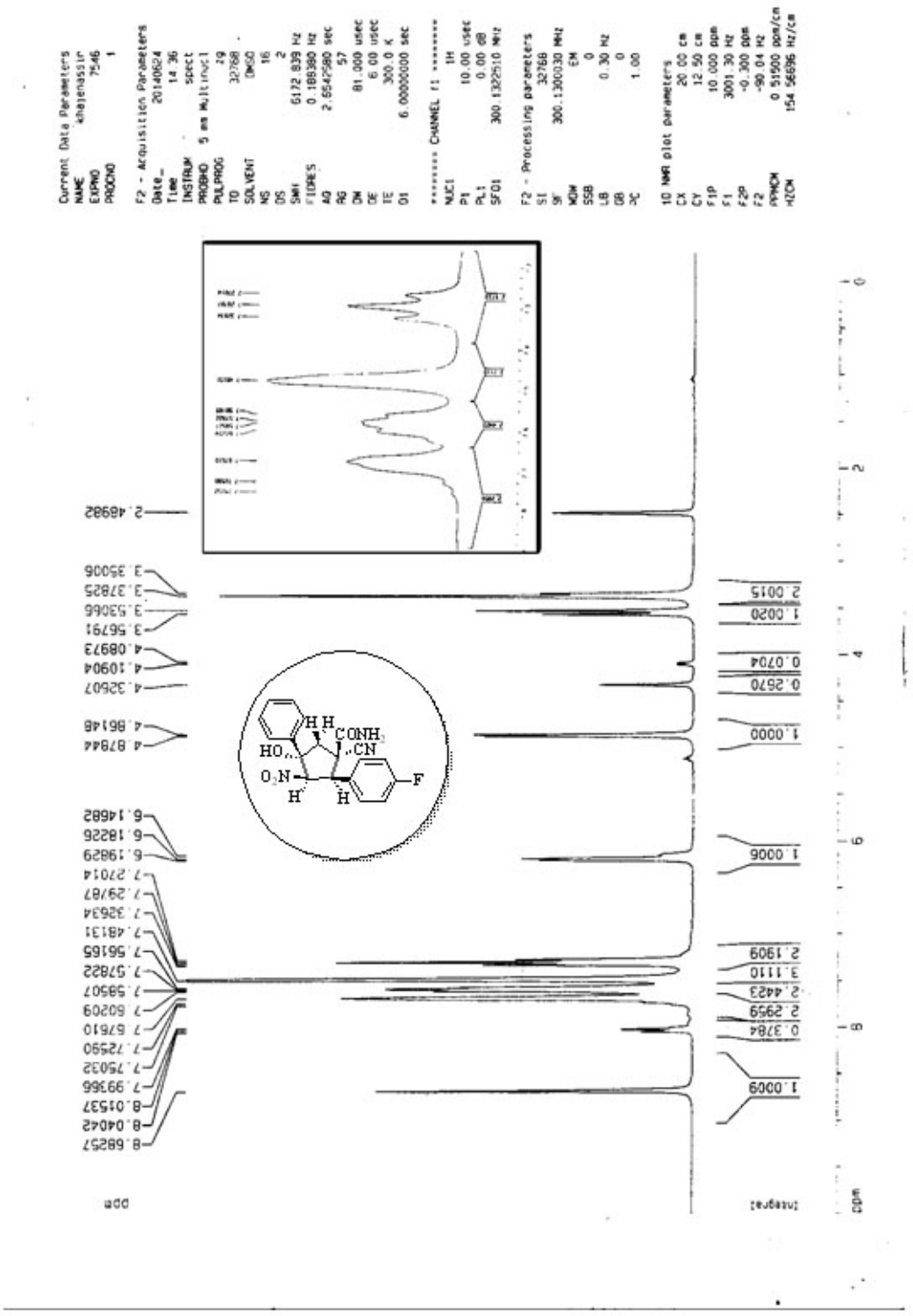


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
379.10441	C 21 H 17 N O 6	379.10504	0.6	1.7	34.4	14.0	ok	odd
	C 20 H 11 N 8 O	379.10503	0.6	1.6	39.0	19.5	ok	even
	C 22 H 13 N 5 O 2	379.10638	2.0	5.2	46.2	19.0	ok	odd
	C 18 H 19 O 9	379.10236	-0.6	-1.7	446.5	9.5	ok	even
	C 18 H 9 N 11	379.10369	0.7	1.9	494.3	20.0	ok	odd
	C 19 H 15 N 4 O 5	379.10370	0.7	1.9	502.2	14.5	ok	even
	C 17 H 13 N 7 O 4	379.10235	-0.6	-1.7	507.6	15.0	ok	odd
401.08633	C 20 H 17 O 9	401.08671	0.4	0.9	24.1	12.5	ok	even
	C 19 H 14 N 4 Na O 5	401.08564	-0.7	-1.7	25.7	14.5	ok	even
	C 18 H 8 N 11 Na	401.08564	-0.7	-1.7	29.8	20.0	ok	odd
	C 19 H 11 N 7 O 4	401.08670	0.4	0.9	30.4	18.0	ok	odd
	C 21 H 16 N Na O 6	401.08698	0.7	1.6	31.8	14.0	ok	odd
	C 20 H 10 N 8 Na O	401.08698	0.6	1.6	35.9	19.5	ok	even
	C 21 H 13 N 4 O 5	401.08805	1.7	4.3	36.9	17.5	ok	even
	C 20 H 7 N 11	401.08804	1.7	4.3	42.2	23.0	ok	odd
	C 22 H 12 N 5 Na O 2	401.08832	2.0	5.0	43.1	19.0	ok	odd
	C 18 H 18 Na O 9	401.08430	-0.4	-0.9	470.6	9.5	ok	even
	C 17 H 9 N 10 O 3	401.08536	0.7	1.7	530.4	18.5	ok	even
	C 15 H 7 N 13 O 2	401.08402	-0.6	-1.6	535.5	19.0	ok	odd
	C 17 H 12 N 7 Na O 4	401.08430	-0.4	-0.9	535.9	15.0	ok	odd
	C 18 H 15 N 3 O 8	401.08537	0.7	1.8	538.0	13.0	ok	odd
	C 16 H 13 N 6 O 7	401.08402	-0.6	-1.6	543.1	13.5	ok	even

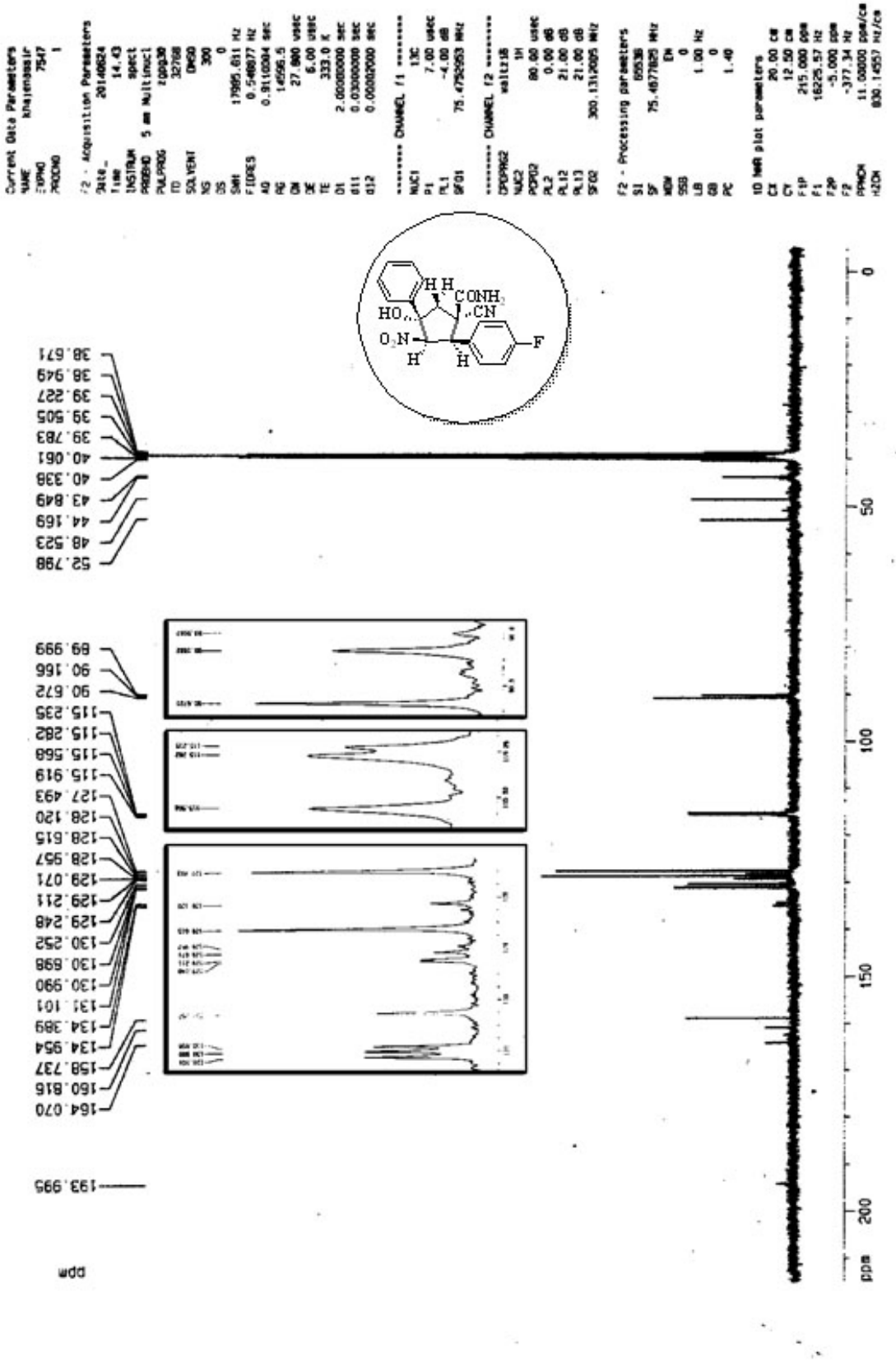


Chemical Formula: $C_{19}H_{16}N_4O_6$
Exact Mass: 396.11

HRMS-ESI of 4h



^{1}H NMR (300 MHz, DMSO-d_6) 4i



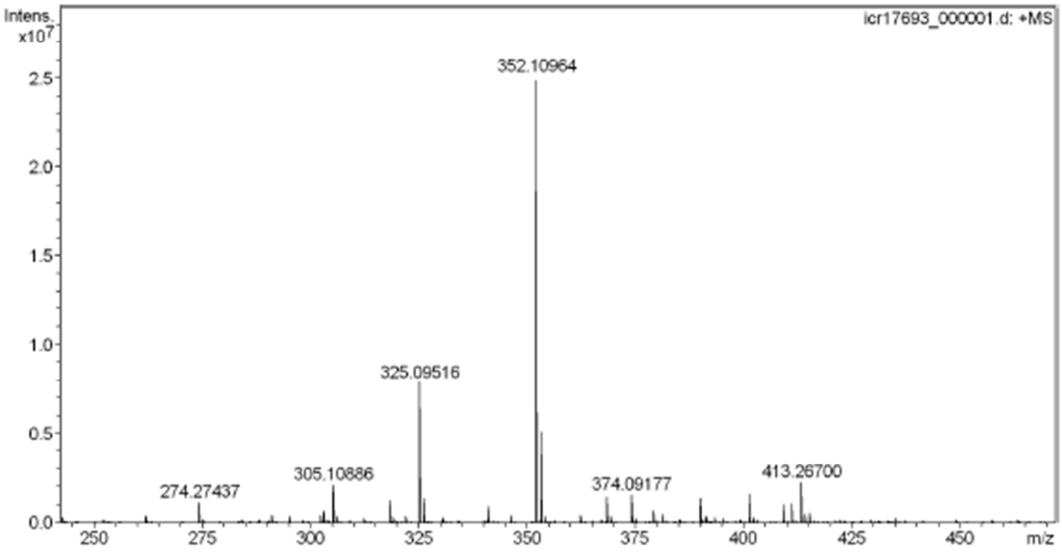
^{13}C NMR (75 MHz, DMSO-d_6) 4i +impurity of intermediate

Mass Spectrum Formula Report

Analysis Info Acquisition Date 9/10/2014 9:19:19 AM

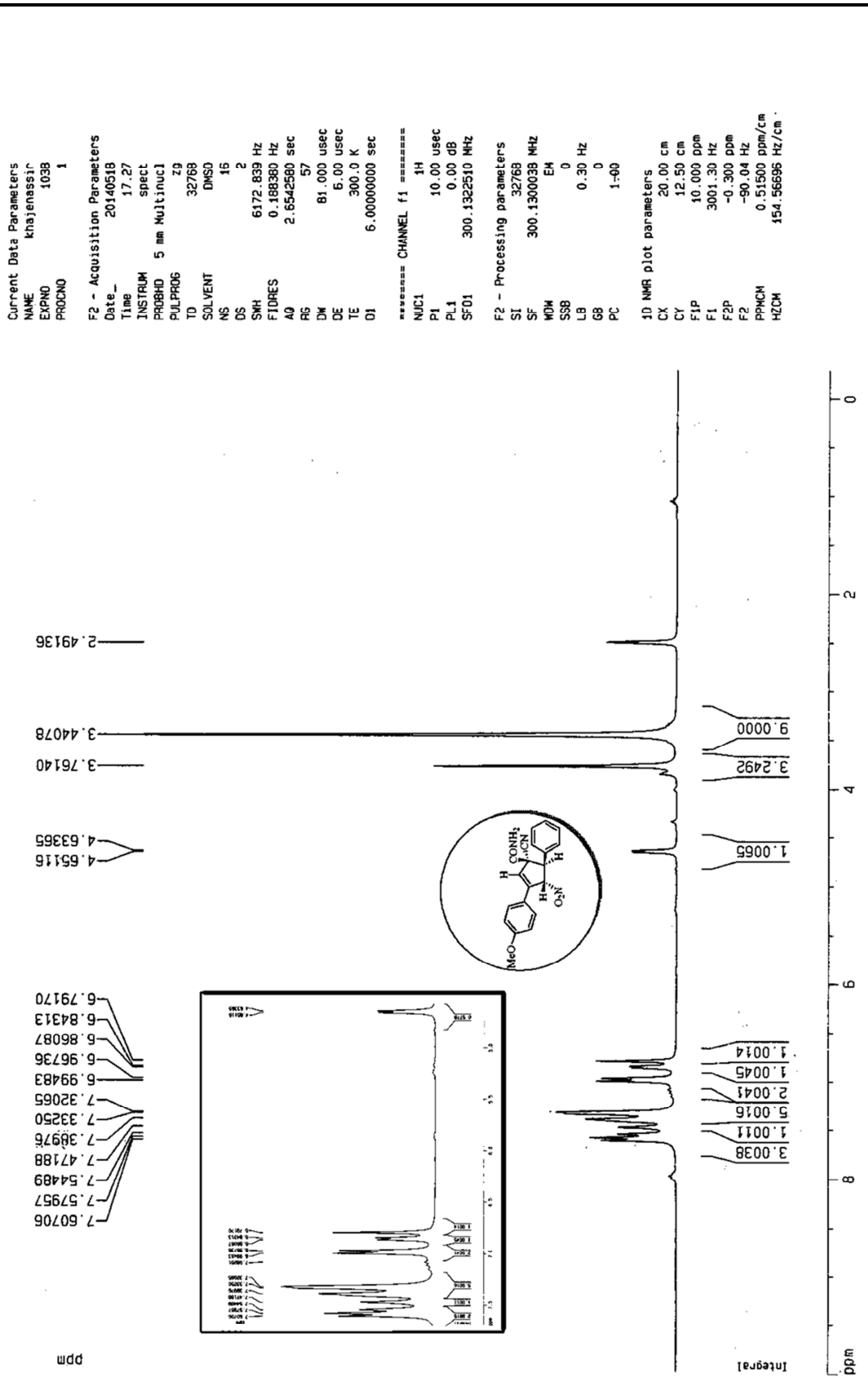
Analysis Name D:\Data\Balalaie\icr17693_000001.d

Comment Prof. Balalaie: SA 37 in DCM/MeOH

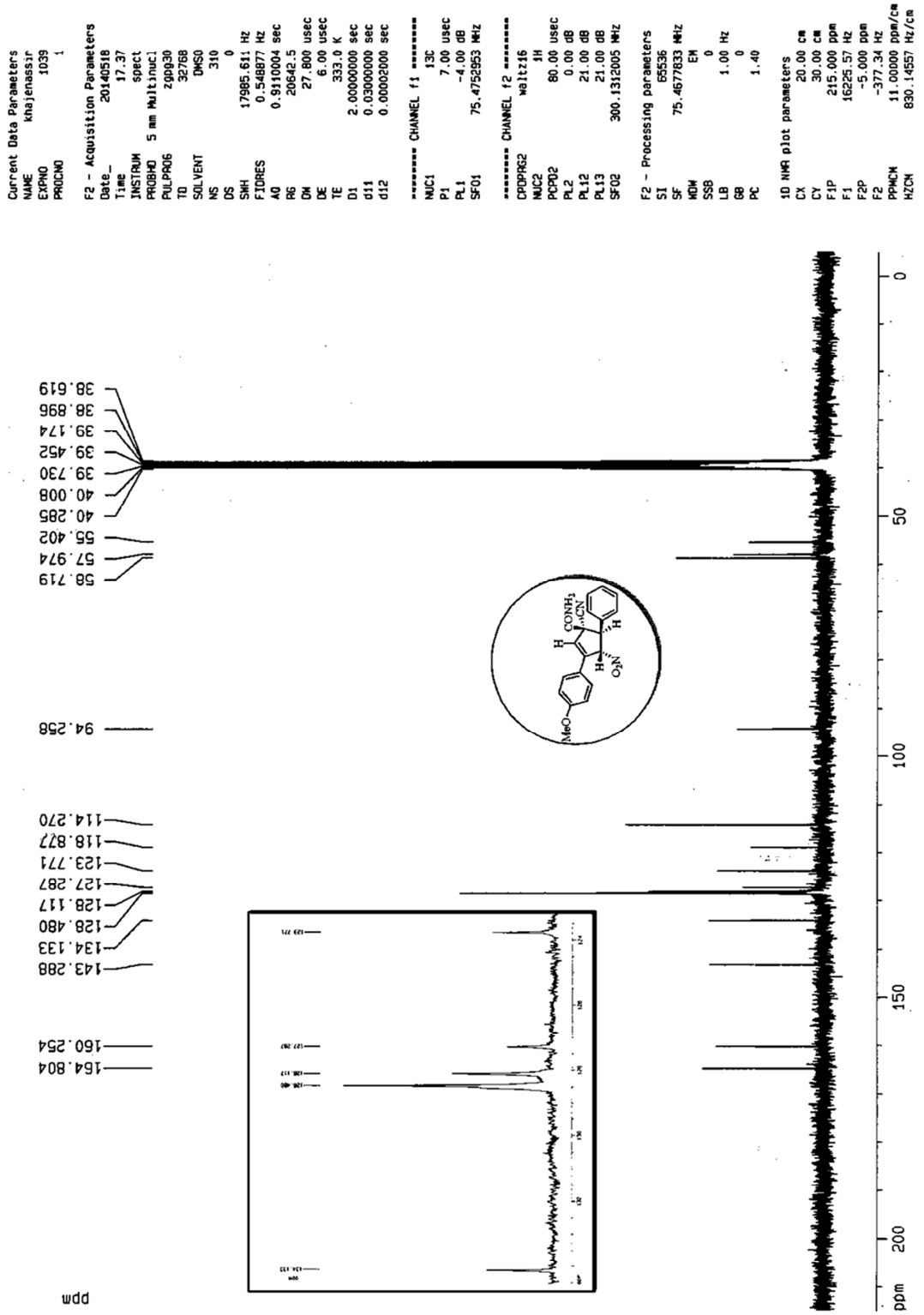


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
352.10964	C 19 H 15 F N 3 O 3	352.10920	-0.4	-1.3	17.8	13.5	ok	even
	C 24 H 16 O 3	352.10940	-0.2	-0.7	38.8	17.0	ok	odd
	C 22 H 14 N 3 O 2	352.10805	-0.3	-0.8	561.2	17.5	ok	even
	C 21 H 17 F O 4	352.11054	-0.4	-1.2	568.0	13.0	ok	odd
	C 17 H 13 F N 6 O 2	352.10785	0.3	0.8	690.9	14.0	ok	odd
368.42572	C 25 H 54 N	368.42508	-0.6	-1.8	163.3	-0.5	ok	even

HRMS-ESI of 4i



^{1}H NMR (300 MHz, DMSO-d_6) 5a



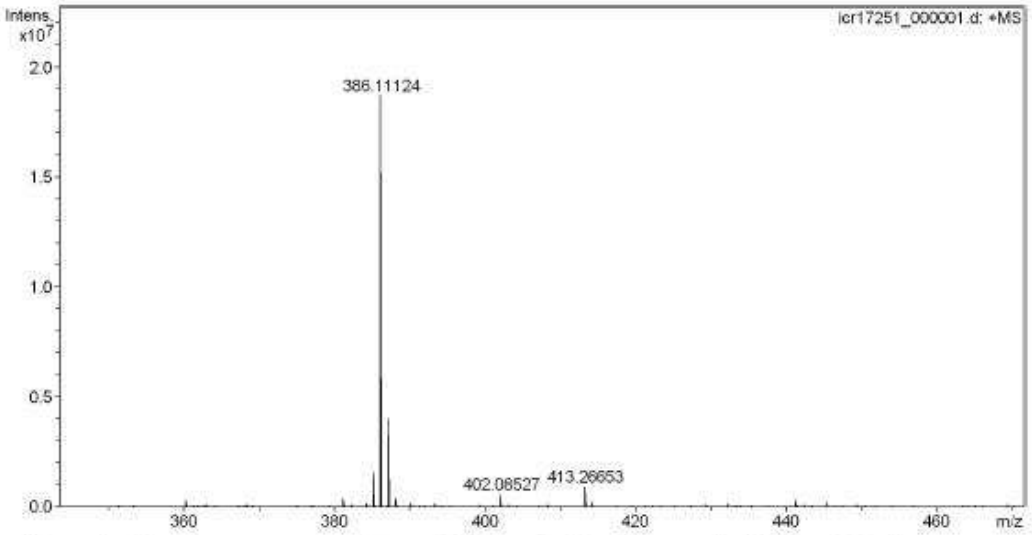
^{13}C NMR (75 MHz, DMSO-d_6) 5a

Mass Spectrum Formula Report

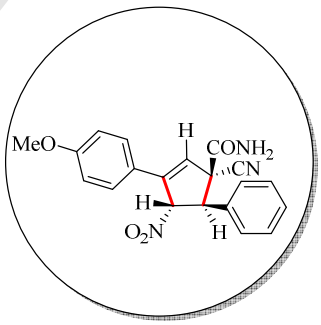
Analysis Info Acquisition Date 7/18/2014 11:49:49 AM

Analysis Name D:\Data\Balalaie\icr17251_000001.d

Comment Prof. Balalaie: SA 10 in DCM/MeOH

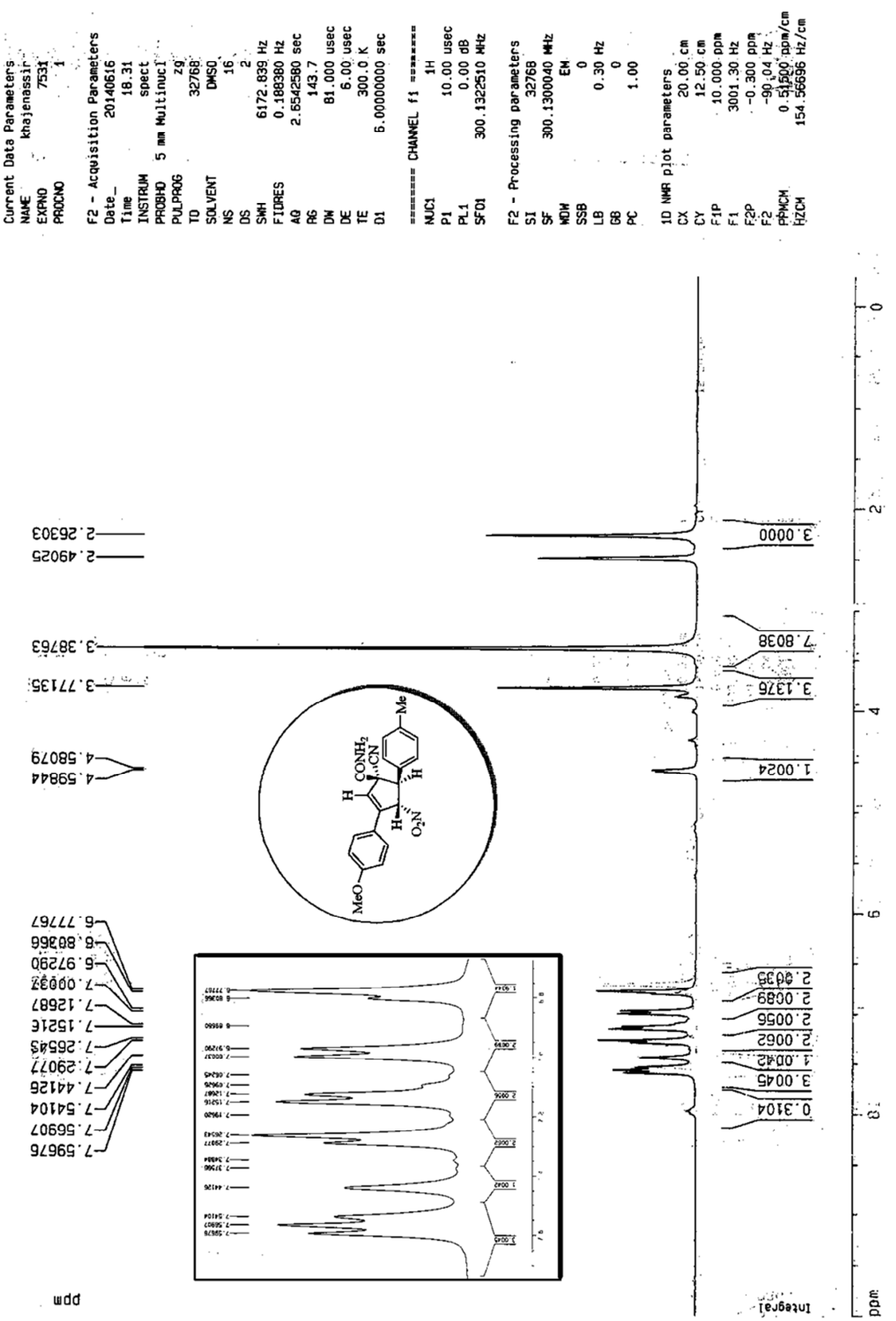


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
381.15599	C 20 H 21 N 4 O 4	381.15573	-0.3	-0.7	n.a.	12.5	ok	even
	C 21 H 17 N 8	381.15707	1.1	2.8	n.a.	17.5	ok	even
	C 22 H 23 N O 5	381.15707	1.1	2.8	n.a.	12.0	ok	odd
382.15935	C 14 H 16 N 13 O	382.15953	0.2	0.5	n.a.	13.5	ok	even
	C 15 H 22 N 6 O 6	382.15953	0.2	0.5	n.a.	8.0	ok	odd
	C 29 H 20 N	382.15903	-0.3	-0.8	n.a.	20.5	ok	even
	C 14 H 26 N 2 O 10	382.15820	-1.2	-3.0	n.a.	3.0	ok	odd
	C 13 H 20 N 9 O 5	382.15819	-1.2	-3.0	n.a.	8.5	ok	even
	C 12 H 14 N 16	382.15819	-1.2	-3.0	n.a.	14.0	ok	odd
	C 16 H 18 N 10 O 2	382.16087	1.5	4.0	n.a.	13.0	ok	odd
	C 17 H 24 N 3 O 7	382.16088	1.5	4.0	n.a.	7.5	ok	even
386.11124	C 18 H 12 N 9 O 2	386.11085	-0.4	-1.0	18.5	17.5	ok	even
	C 19 H 18 N 2 O 7	386.11085	-0.4	-1.0	20.7	12.0	ok	odd
	C 31 H 14	386.10900	0.2	0.5	544.3	25.0	ok	odd
	C 20 H 14 N 6 O 3	386.11219	-0.6	-1.6	592.4	17.0	ok	odd
	C 22 H 16 N 3 O 4	386.11353	-0.1	-0.2	662.9	16.5	ok	even
	C 16 H 10 N 12 O	386.10950	0.7	1.8	671.6	18.0	ok	odd
	C 17 H 16 N 5 O 6	386.10951	0.7	1.8	677.6	12.5	ok	even

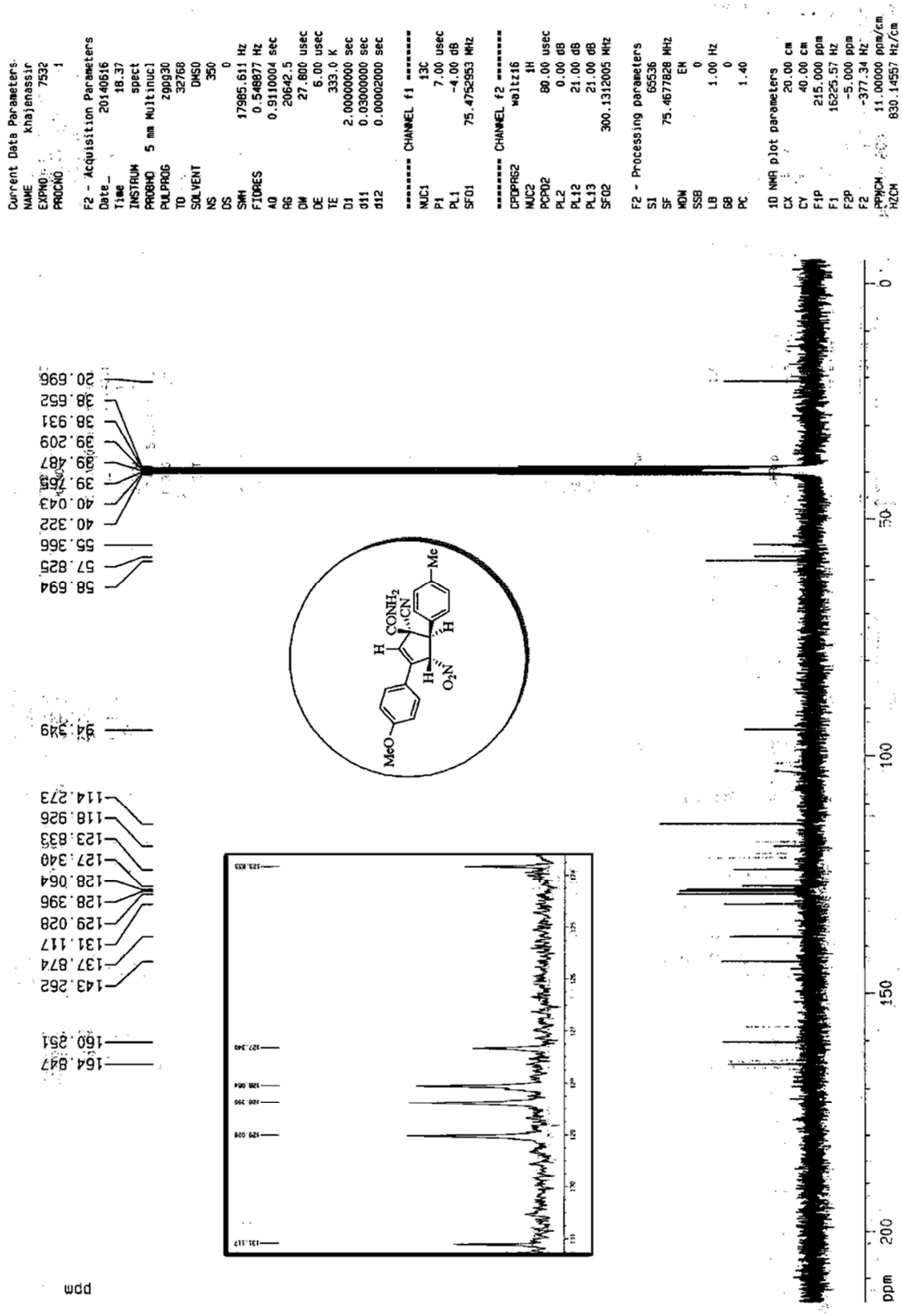


Chemical Formula: $C_{20}H_{17}N_3O_4$
Exact Mass: 363.12

HRMS-ESI of 5a



^{1}H NMR (300 MHz, DMSO-d_6) 5b



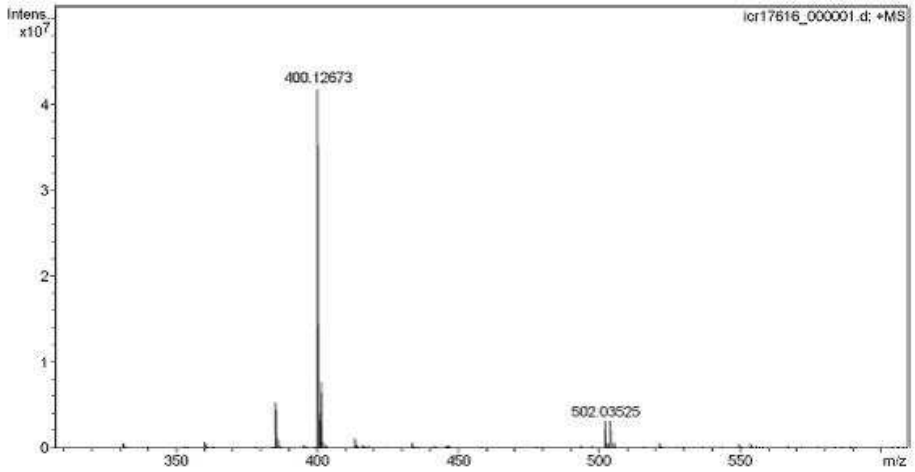
^{13}C NMR (75 MHz, DMSO-d_6) 5b

Mass Spectrum Formula Report

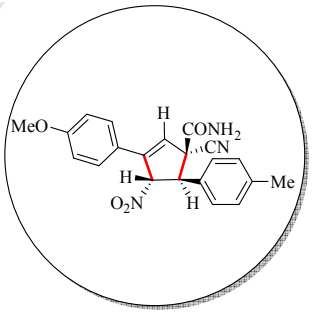
Analysis Info Acquisition Date 8/29/2014 1:33:50 PM

Analysis Name D:\Data\Balalaie\icr17616_000001.d

Comment Prof. Balalaie: SA Z33 in DCM/MeOH

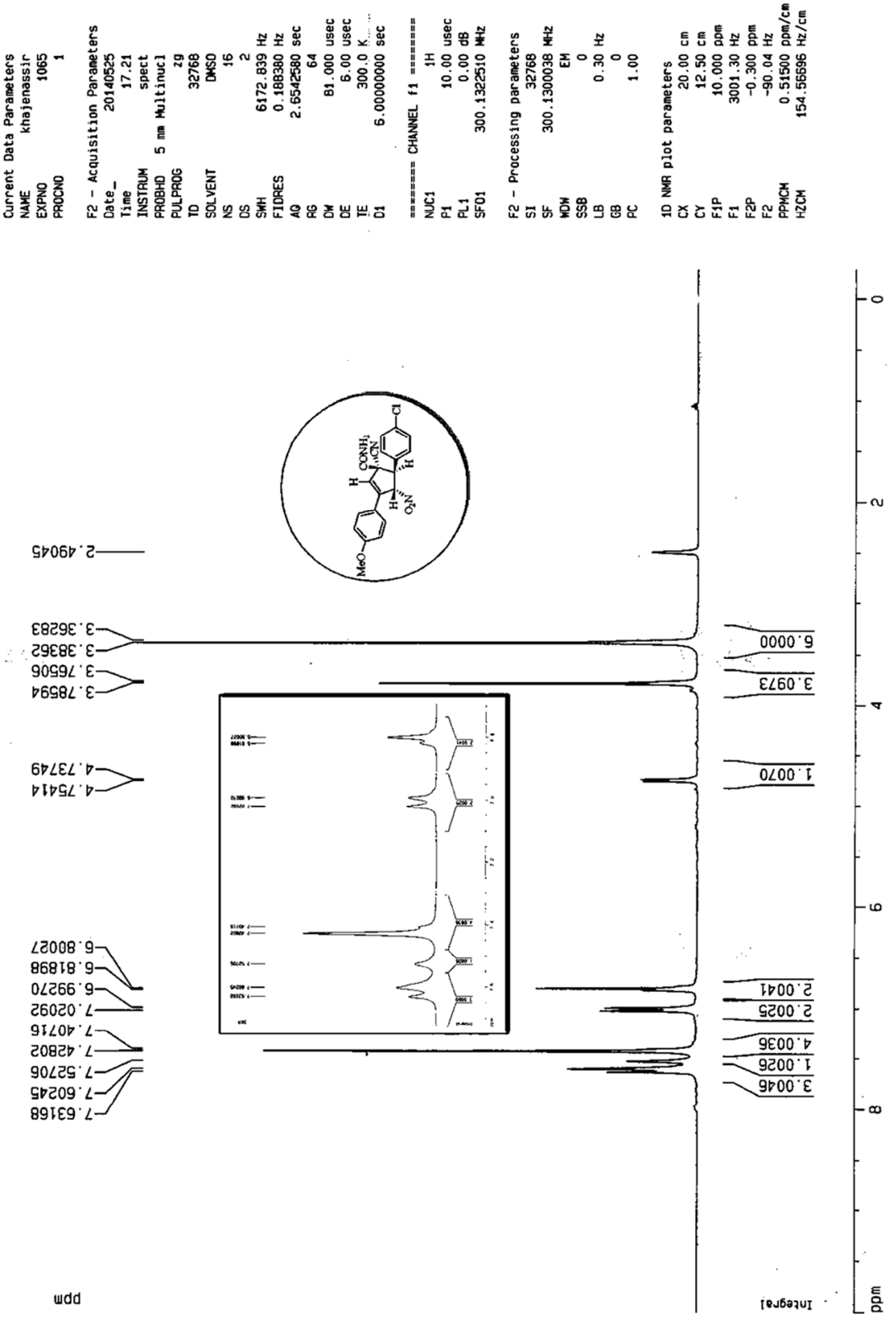


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
385.11606	C 17 H 11 N 11 O	385.11426	-1.8	-4.7	14.0	18.0	ok	odd
	C 18 H 17 N 4 O 6	385.11426	-1.8	-4.7	19.8	12.5	ok	even
	C 19 H 13 N 8 O 2	385.11560	-0.5	-1.2	20.0	17.5	ok	even
	C 20 H 19 N O 7	385.11560	-0.5	-1.2	21.6	12.0	ok	odd
	C 21 H 15 N 5 O 3	385.11694	0.9	2.3	25.7	17.0	ok	odd
	C 23 H 17 N 2 O 4	385.11828	2.2	5.8	31.7	16.5	ok	even
395.17179	C 5 H 13 N 23	395.17188	0.1	0.2	n.a.	11.0	ok	odd
	C 21 H 23 N 4 O 4	395.17138	-0.4	-1.0	n.a.	12.5	ok	even
	C 22 H 19 N 8	395.17272	0.9	2.4	n.a.	17.5	ok	even
	C 23 H 25 N O 5	395.17272	0.9	2.4	n.a.	12.0	ok	odd
	C 7 H 15 N 20 O	395.17322	1.4	3.6	n.a.	10.5	ok	even
	C 8 H 21 N 13 O 6	395.17323	1.4	3.6	n.a.	5.0	ok	odd
	C 9 H 27 N 6 O 11	395.17323	1.4	3.6	n.a.	-0.5	ok	even
	C 20 H 27 O 8	395.17004	-1.7	-4.4	n.a.	7.5	ok	even
	C 19 H 21 N 7 O 3	395.17004	-1.8	-4.4	n.a.	13.0	ok	odd
	C 24 H 21 N 5 O	395.17406	2.3	5.7	n.a.	17.0	ok	odd
400.12673	C 20 H 20 N 2 O 7	400.12650	-0.2	-0.6	32.6	12.0	ok	odd
	C 19 H 14 N 9 O 2	400.12650	-0.2	-0.6	37.3	17.5	ok	even
	C 32 H 16	400.12465	0.5	1.1	534.7	25.0	ok	odd
	C 21 H 16 N 6 O 3	400.12784	-0.6	-1.5	550.4	17.0	ok	odd
	C 17 H 12 N 12 O	400.12515	1.0	2.4	660.5	18.0	ok	odd
	C 18 H 18 N 5 O 6	400.12516	1.0	2.4	666.6	12.5	ok	even

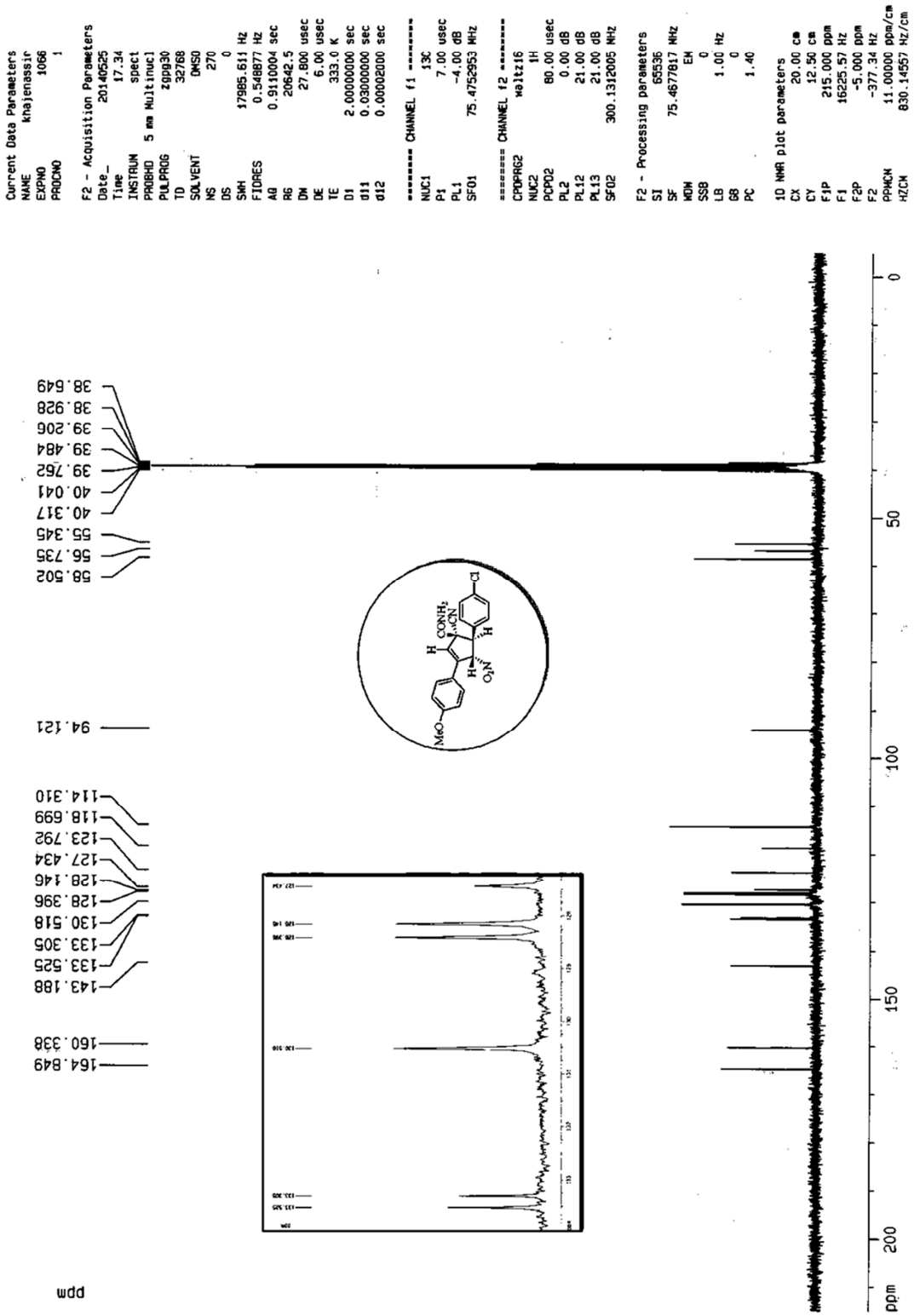


Chemical Formula: $C_{21}H_{19}N_3O_4$
Exact Mass: 377.14

HRMS-ESI of 5b



^{1}H NMR (300 MHz, DMSO-d_6) 5c



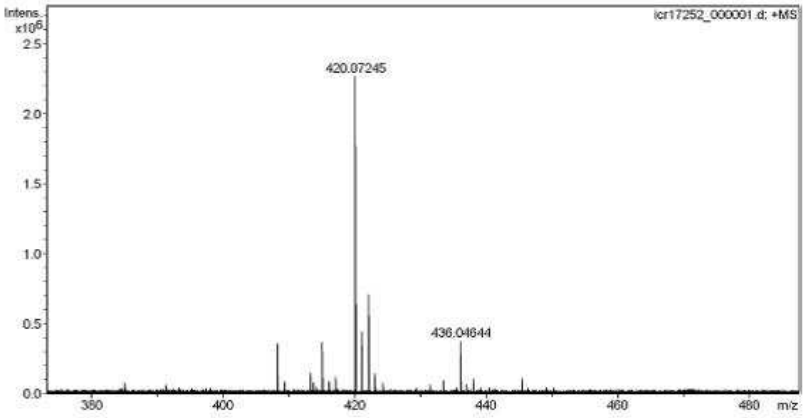
^{13}C NMR (75 MHz, DMSO-d_6) 5c

Mass Spectrum Formula Report

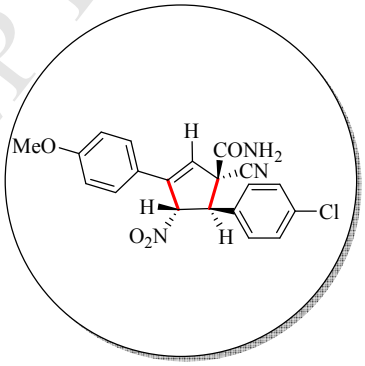
Analysis Info Acquisition Date 7/18/2014 11:59:05 AM

Analysis Name D:\Data\Balalaie\icr17252_000001.d

Comment Prof. Balalaie: SA 17 in DCM/MeOH

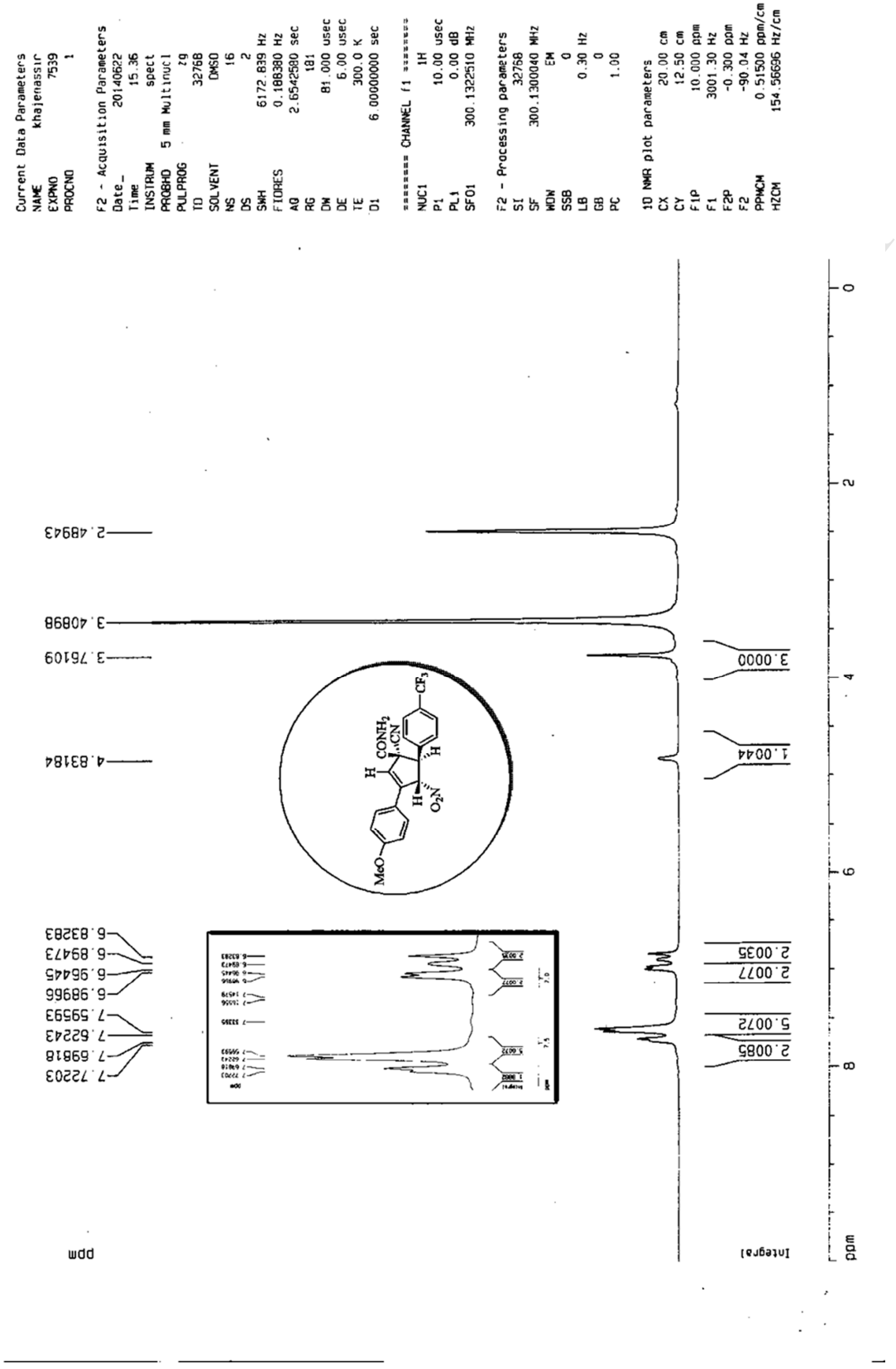


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
415.11709	C 20 H 20 N 4 O 4 ^35Cl	415.11676	-0.3	-0.8	134.8	12.5	ok	even
	C 22 H 22 N O 5 ^35Cl	415.11810	1.0	2.4	141.2	12.0	ok	odd
	C 21 H 15 N 6 O 4	415.11493	-2.2	-5.2	145.6	17.5	ok	even
	C 23 H 23 N 2 O ^35Cl ^37Cl	415.11525	-1.8	-4.4	149.0	12.5	ok	even
	C 21 H 16 N 8 ^35Cl	415.11810	1.0	2.4	149.3	17.5	ok	even
	C 23 H 17 N 3 O 5	415.11627	-0.8	-2.0	152.0	17.0	ok	odd
	C 23 H 18 N 5 O ^35Cl	415.11944	2.4	5.7	155.5	17.0	ok	odd
	C 25 H 19 O 6	415.11761	0.5	1.3	158.5	16.5	ok	even
	C 22 H 11 N 10	415.11627	-0.8	-2.0	160.0	22.5	ok	even
	C 24 H 13 N 7 O	415.11761	0.5	1.3	166.3	22.0	ok	odd
	C 26 H 20 N O 2 ^37Cl	415.11476	-2.3	-5.6	166.4	17.0	ok	odd
	C 26 H 15 N 4 O 2	415.11895	1.9	4.5	173.0	21.5	ok	even
416.12031	C 20 H 26 N O 4 ^35Cl ^37Cl	416.12039	0.1	0.2	n.a.	7.5	ok	even
	C 29 H 19 N ^35Cl	416.12005	-0.3	-0.6	n.a.	20.5	ok	even
	C 23 H 23 O 5 ^37Cl	416.11990	-0.4	-1.0	n.a.	12.0	ok	odd
	C 22 H 17 N 7 ^37Cl	416.11990	-0.4	-1.0	n.a.	17.5	ok	even
	C 32 H 16 O	416.11957	-0.7	-1.8	n.a.	25.0	ok	odd
	C 24 H 19 N 4 O ^37Cl	416.12124	0.9	2.2	n.a.	17.0	ok	odd
	C 20 H 20 N 2 O 8	416.12142	1.1	2.7	n.a.	12.0	ok	odd
	C 21 H 22 N 5 ^35Cl ^37Cl	416.12173	1.4	3.4	n.a.	12.5	ok	even
	C 21 H 21 N 3 O 4 ^37Cl	416.11856	-1.7	-4.2	n.a.	12.5	ok	even
	C 30 H 14 N 3	416.11822	-2.1	-5.0	n.a.	25.5	ok	even
	C 26 H 21 N O 2 ^37Cl	416.12258	2.3	5.5	n.a.	16.5	ok	even
	C 21 H 16 N 6 O 4	416.12275	2.4	5.9	n.a.	17.0	ok	odd
420.07245	C 20 H 12 N 4 O 7	420.07005	-2.4	-5.7	31.1	17.0	ok	odd
	C 20 H 13 N 6 O 3 ^35Cl	420.07322	0.8	1.8	31.7	17.0	ok	odd
	C 22 H 20 O 4 ^35Cl ^37Cl	420.07037	-2.1	-5.0	32.2	12.0	ok	odd
	C 22 H 14 N O 8	420.07139	-1.1	-2.5	32.3	16.5	ok	even
	C 21 H 8 N 8 O 3	420.07139	-1.1	-2.5	41.7	22.0	ok	odd
	C 23 H 16 N 4 ^35Cl ^37Cl	420.07170	-0.7	-1.8	44.1	17.0	ok	odd
	C 23 H 10 N 5 O 4	420.07273	0.3	0.7	48.4	21.5	ok	even
	C 25 H 18 N O ^35Cl ^37Cl	420.07305	0.6	1.4	50.3	16.5	ok	even

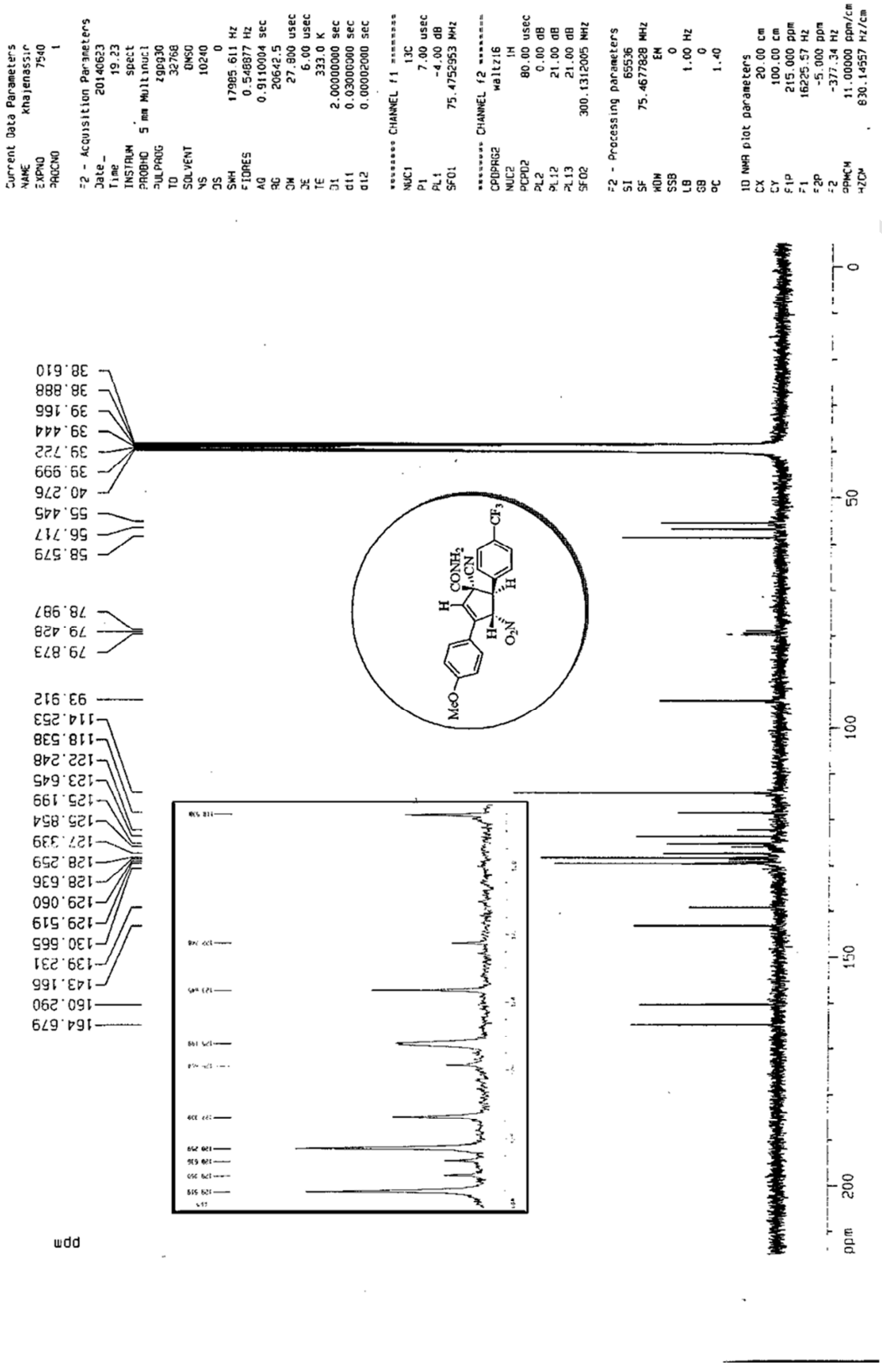


Chemical Formula: $C_{20}H_{16}ClN_3O_4$
Exact Mass: 397.08

HRMS-ESI of 5c



^{1}H NMR (300 MHz, DMSO-d_6) 5d



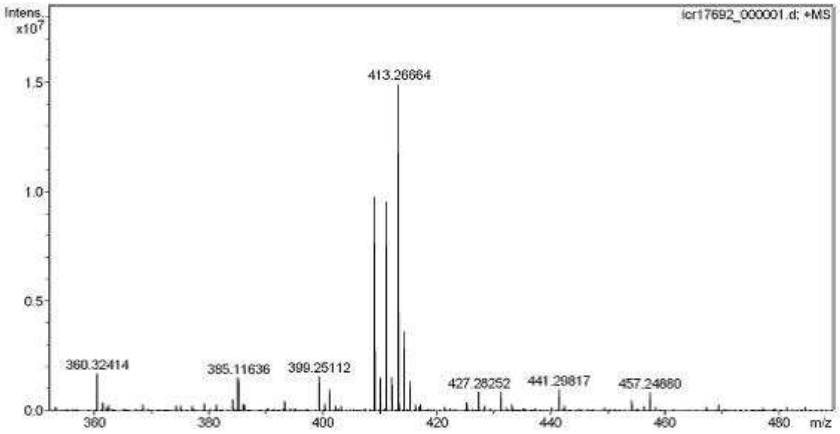
^{13}C NMR (75 MHz, DMSO-d_6) 5d

Mass Spectrum Formula Report

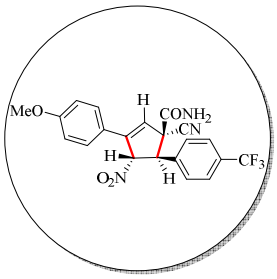
Analysis Info Acquisition Date 9/10/2014 9:03:27 AM

Analysis Name D:\Data\Balalaie\icr17692_000001.d

Comment Prof. Balalaie: SA 36 in DCM/MeOH

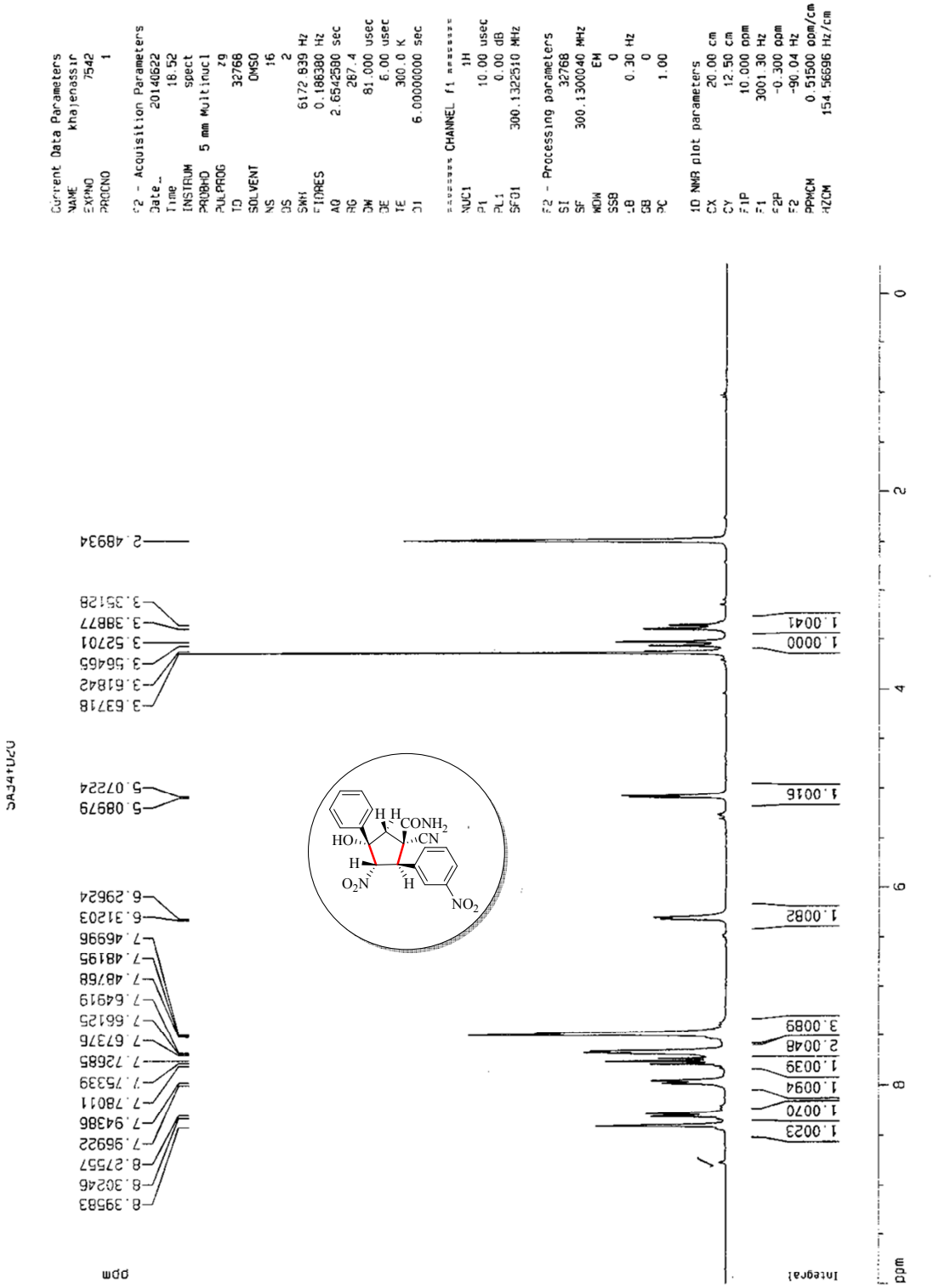


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	N-Rule	e⁻ Conf
411.07174	C 21 H 15 O 9	411.07106	-0.7	-1.7	41.0	14.5	ok	even
	C 22 H 12 F 3 N O 4	411.07129	-0.4	-1.1	52.9	16.0	ok	odd
	C 22 H 11 N 4 O 5	411.07240	0.7	1.6	59.8	19.5	ok	even
	C 23 H 8 F 3 N 5	411.07263	0.9	2.2	66.4	21.0	ok	odd
	C 21 H 5 N 11	411.07239	0.6	1.6	66.6	25.0	ok	odd
	C 28 H 9 F 2 N 2	411.07283	-0.7	-1.7	428.8	24.5	ok	even
	C 25 H 11 F 2 N O 3	411.07015	0.1	0.3	498.6	20.0	ok	odd
	C 23 H 7 N 8 O	411.07373	0.2	0.5	509.8	24.5	ok	even
	C 25 H 10 F 3 N 2 O	411.07397	0.5	1.1	510.1	20.5	ok	even
	C 24 H 13 N O 6	411.07374	0.2	0.5	517.2	19.0	ok	odd
413.26664	C 24 H 36 F 3 O 2	413.26619	-0.4	-1.1	24.5	5.5	ok	even
	C 22 H 33 N 6 O 2	413.26595	-0.7	-1.7	24.5	9.5	ok	even
	C 24 H 35 N 3 O 3	413.26729	0.7	1.6	30.3	9.0	ok	odd
	C 27 H 35 F 2 O	413.26505	0.1	0.3	485.5	9.5	ok	even
	C 26 H 37 O 4	413.26864	0.2	0.5	574.3	8.5	ok	even
	C 22 H 34 F 3 N 3 O	413.26485	-0.1	-0.2	578.6	6.0	ok	odd
	C 21 H 37 N 2 O 6	413.26461	-0.3	-0.7	584.9	4.5	ok	even
	C 21 H 36 F N 3 O 4	413.26844	0.0	0.0	592.2	5.0	ok	odd
433.08713	C 28 H 14 F O 4	433.08706	-0.1	-0.2	n.a.	21.5	ok	even
	C 23 H 13 F 2 N 3 O 4	433.08686	-0.3	-0.6	n.a.	18.0	ok	odd
	C 24 H 9 F 2 N 7	433.08820	1.1	2.5	n.a.	23.0	ok	odd
	C 25 H 15 F 2 O 5	433.08821	1.1	2.5	n.a.	17.5	ok	even
	C 31 H 13 O 3	433.08592	-1.2	-2.8	n.a.	25.5	ok	even
	C 29 H 10 F N 4	433.08840	1.3	2.9	n.a.	26.5	ok	even
	C 26 H 12 F N 3 O 3	433.08572	-1.4	-3.3	n.a.	22.0	ok	odd
	C 34 H 11 N	433.08860	1.5	3.4	n.a.	30.0	ok	odd
	C 21 H 11 F 2 N 6 O 3	433.08552	-1.6	-3.7	n.a.	18.5	ok	even
	C 21 H 10 F 3 N 7 O	433.08934	2.2	5.1	n.a.	19.0	ok	odd
	C 22 H 16 F 3 O 6	433.08935	2.2	5.1	n.a.	13.5	ok	even
	C 26 H 11 F 2 N 4 O	433.08954	2.4	5.6	n.a.	22.5	ok	even
	C 29 H 11 N 3 O 2	433.08458	-2.6	-5.9	n.a.	26.0	ok	odd
	C 31 H 12 F N O	433.08974	2.6	6.0	n.a.	26.0	ok	odd

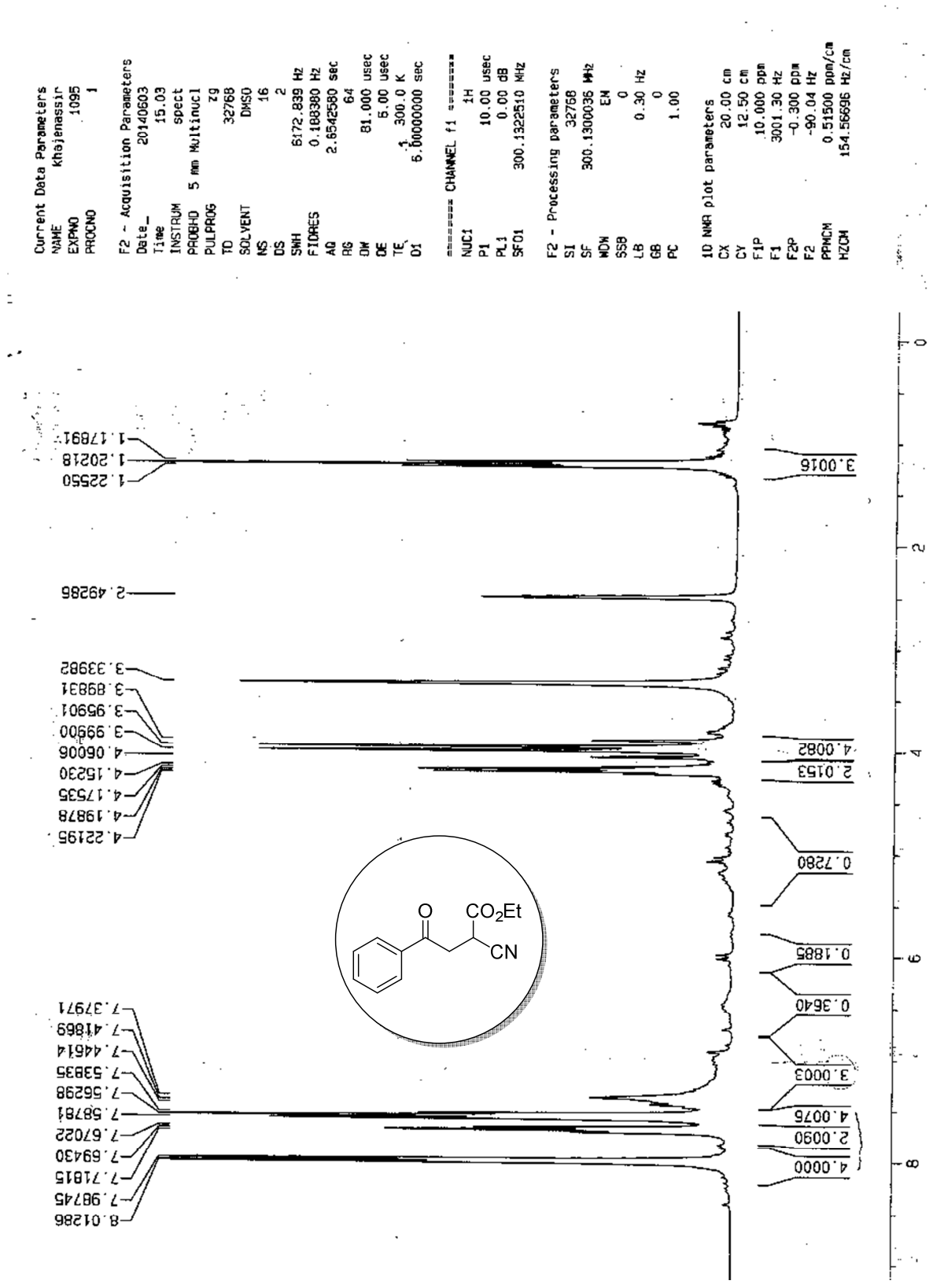


Chemical Formula: $C_{21}H_{16}F_3N_3O_4$
Exact Mass: 431.11

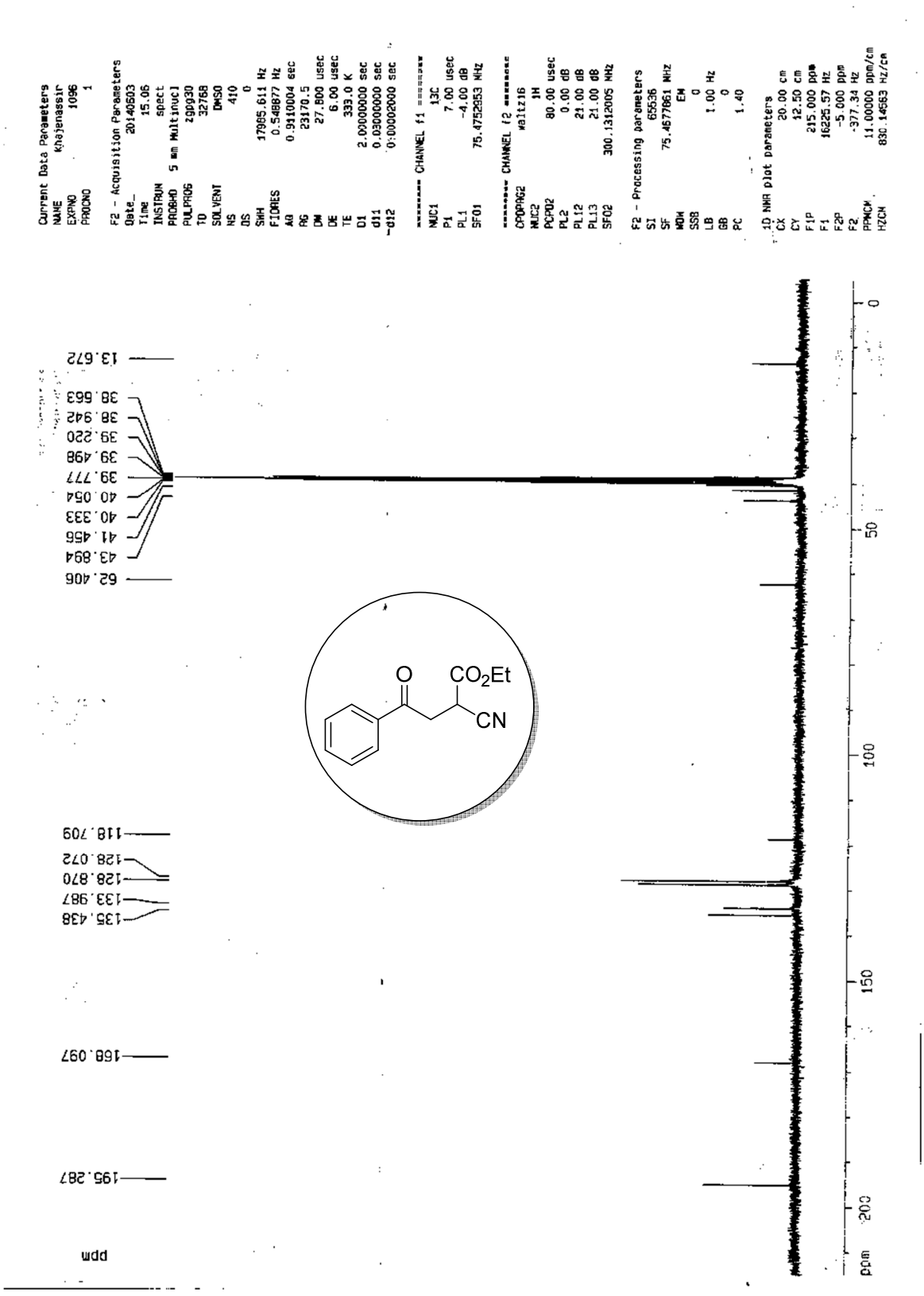
HRMS-ESI of 5d



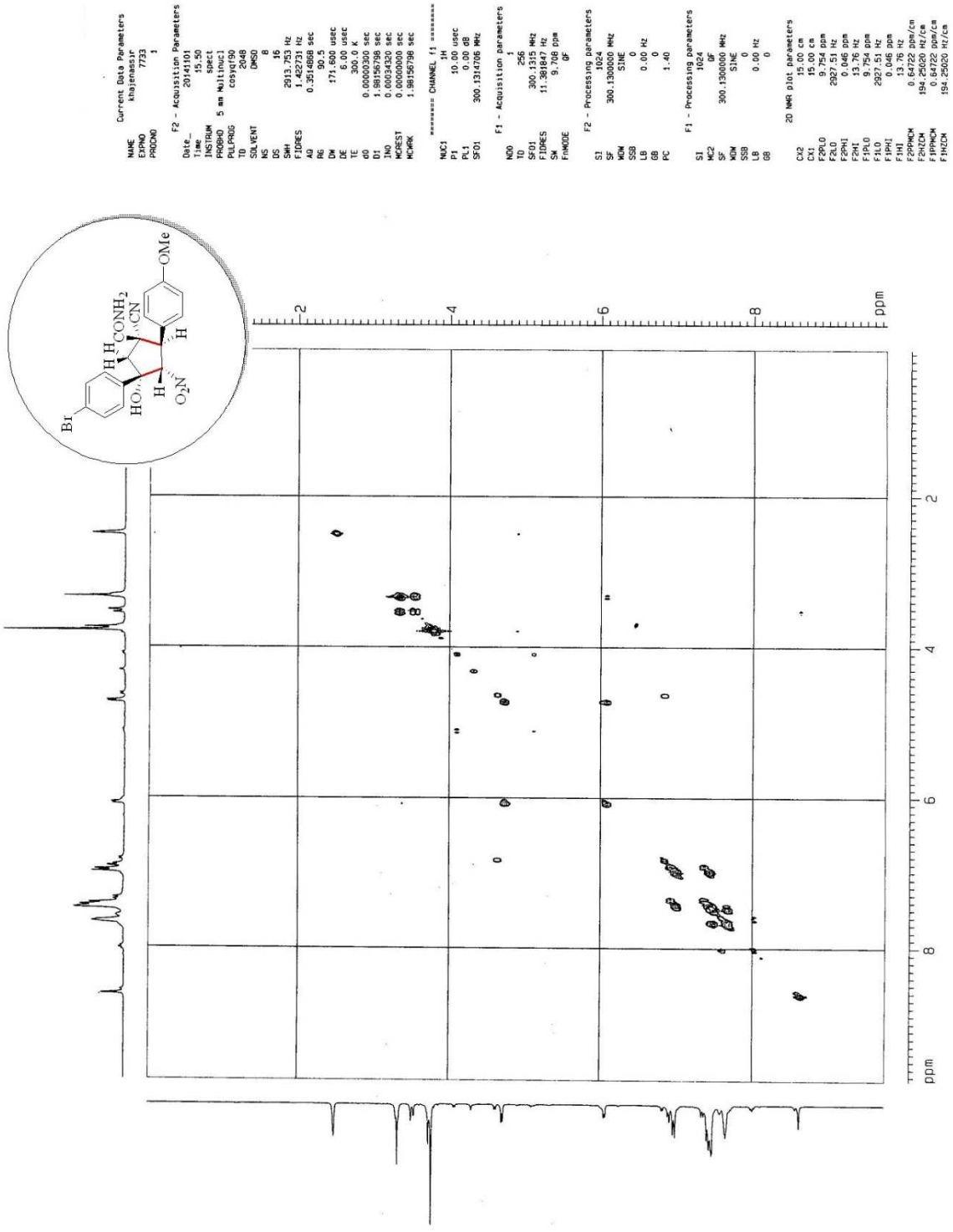
^{1}H NMR (75 MHz, DMSO-d_6+ D_2O) 5h



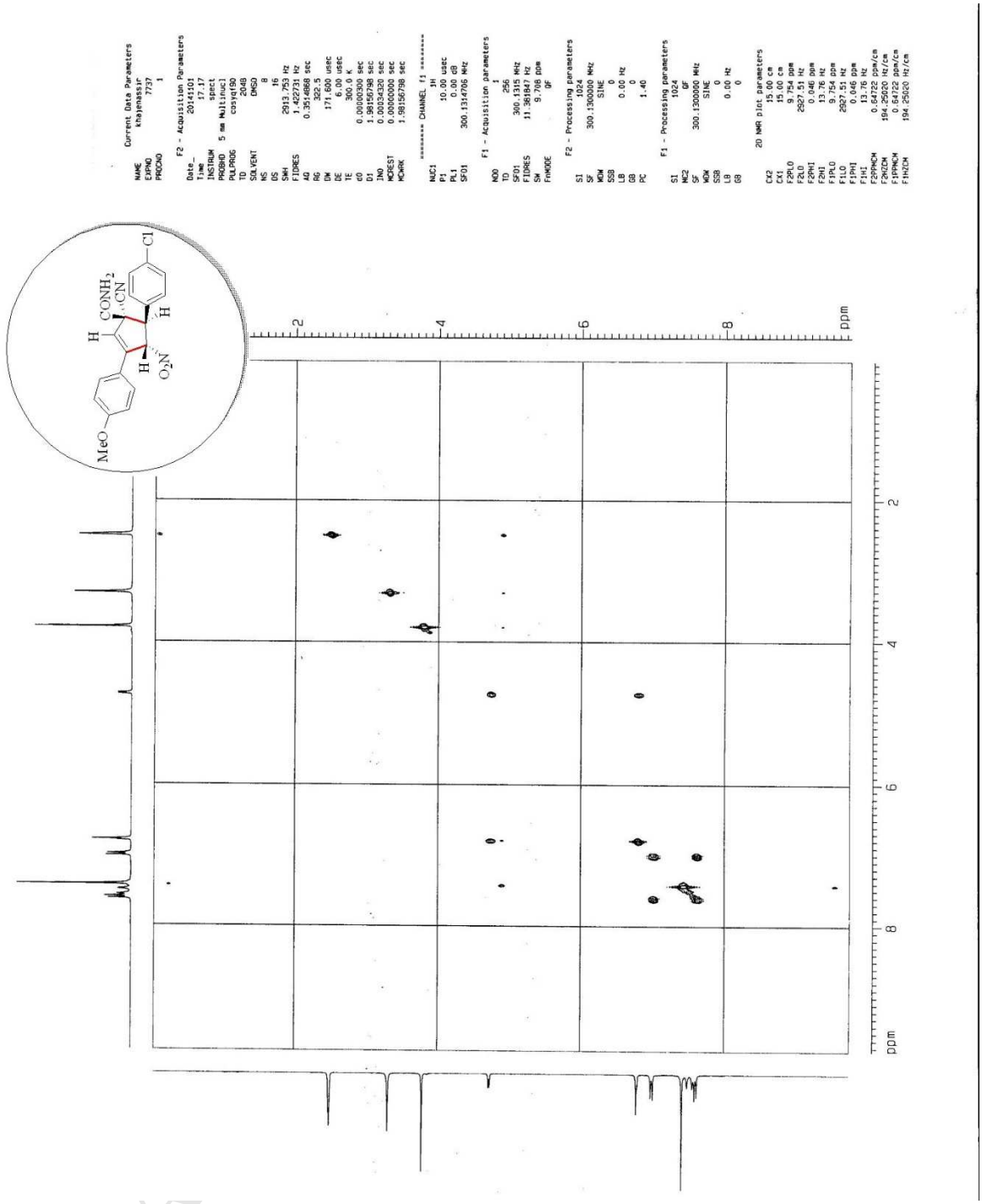
^{1}H NMR (300 MHz, DMSO-d_6) product of reaction between phenacyl bromide and ethyl cyanoacetate



^{13}C NMR (75 MHz, DMSO-d_6) product of reaction between phenacyl bromide and ethyl cyanoacetate

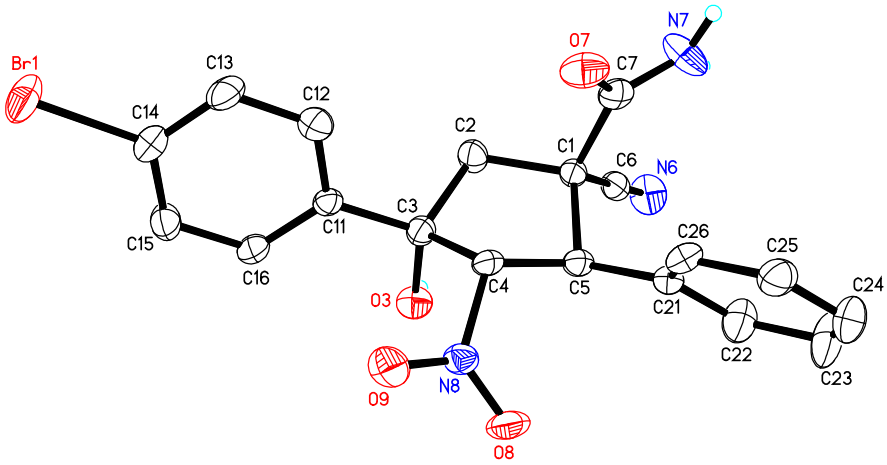


^{1}H-^{1}H-COSY 2D (300 MHz, DMSO-d_6) 4b



^{1}H-^{1}H-COSY 2D (300 MHz, DMSO-d_6) 5c

X-ray crystallographic data 6a



Chemie : Saeed Balalaie
Probe : SA8
Dateinamen : **4a**
Operateur : F. Rominger (AK Hofmann)
Gerät : Bruker APEX

Table 1: Crystal data and structure refinement for **4a**.

Identification code	sba111	
Empirical formula	$C_{19}H_{16}BrN_3O_4$	
Formula weight	430.26	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Z	4	
Unit cell dimensions	a = 7.3723(7) Å	α = 90 deg.
	b = 6.2733(5) Å	β = 90.184(3) deg.
	c = 38.704(3) Å	γ = 90 deg.
Volume	1790.0(3) $Å^3$	
Density (calculated)	1.60 g/cm^3	
Absorption coefficient	2.33 mm^{-1}	
Crystal shape	plate	
Crystal size	0.210 x 0.170 x 0.020 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.1 to 24.4 deg.	
Index ranges	-8≤h≤8, -7≤k≤6, -44≤l≤42	
Reflections collected	8904	
Independent reflections	2918 (R(int) = 0.0355)	
Observed reflections	2335 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.97 and 0.84	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2918 / 0 / 256	
Goodness-of-fit on F^2	1.16	
Final R indices (I>2sigma(I))	R1 = 0.036, wR2 = 0.087	
Largest diff. peak and hole	0.43 and -0.41 $eÅ^{-3}$	

Tabelle 2: (Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for sba111. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.)

Atom	x	y	z	U_{eq}
Br1	0.4787(1)	0.6895(1)	0.3160(1)	0.0415(2)
C1	0.3405(4)	0.7072(5)	0.1037(1)	0.0200(8)
C2	0.3066(5)	0.6190(6)	0.1410(1)	0.0253(8)
H2A	0.2407	0.7259	0.1550	0.030
H2B	0.2327	0.4874	0.1399	0.030
C3	0.4921(4)	0.5715(6)	0.1573(1)	0.0215(8)
H3	0.475(6)	0.289(6)	0.1434(10)	0.031(13)
O3	0.5540(4)	0.3646(4)	0.1485(1)	0.0266(6)
C4	0.6164(4)	0.7269(6)	0.1370(1)	0.0217(8)
H4	0.5973	0.8762	0.1453	0.026
C5	0.5536(4)	0.7057(6)	0.1000(1)	0.0212(8)
H5	0.5878	0.5588	0.0923	0.025
C6	0.2596(5)	0.5687(6)	0.0771(1)	0.0228(8)
N6	0.1967(4)	0.4672(5)	0.0558(1)	0.0355(8)
C7	0.2667(5)	0.9350(6)	0.1011(1)	0.0245(8)
H7B	0.099(7)	0.882(8)	0.0615(13)	0.065(16)
H7A	0.121(6)	1.106(9)	0.0733(12)	0.059(15)
O7	0.3209(3)	1.0667(4)	0.1221(1)	0.0347(7)
N7	0.1526(5)	0.9796(7)	0.0758(1)	0.0411(10)
N8	0.8114(4)	0.6643(5)	0.1417(1)	0.0236(7)
O8	0.8913(3)	0.5813(5)	0.1175(1)	0.0406(7)
O9	0.8794(3)	0.6979(4)	0.1698(1)	0.0351(7)
C11	0.4956(4)	0.6037(6)	0.1963(1)	0.0198(8)
C12	0.4328(5)	0.7927(6)	0.2109(1)	0.0286(9)
H12	0.3907	0.9039	0.1962	0.034
C13	0.4308(5)	0.8208(6)	0.2464(1)	0.0295(9)
H13	0.3883	0.9504	0.2561	0.035
C14	0.4916(5)	0.6576(6)	0.2673(1)	0.0265(9)
C15	0.5581(5)	0.4711(6)	0.2535(1)	0.0289(9)
H15	0.6024	0.3614	0.2682	0.035
C16	0.5595(5)	0.4452(6)	0.2180(1)	0.0263(8)
H16	0.6051	0.3167	0.2084	0.032
C21	0.6308(4)	0.8585(6)	0.0732(1)	0.0227(8)
C22	0.6454(6)	0.7895(7)	0.0392(1)	0.0363(10)
H22	0.6067	0.6499	0.0331	0.044
C23	0.7155(6)	0.9220(7)	0.0141(1)	0.0464(12)
H23	0.7239	0.8736	-0.0091	0.056
C24	0.7735(6)	1.1246(7)	0.0226(1)	0.0407(11)
H24	0.8216	1.2156	0.0053	0.049
C25	0.7615(5)	1.1938(6)	0.0560(1)	0.0312(9)
H25	0.8015	1.3331	0.0619	0.037
C26	0.6910(5)	1.0614(6)	0.0813(1)	0.0264(9)
H26	0.6839	1.1107	0.1045	0.032

Tabelle 3: (Hydrogen coordinates and isotropic displacement parameters (Å^2) for **6a**)

Atom	x	y	z	U_{eq}
H2A	0.2407	0.7259	0.1550	0.030
H2B	0.2327	0.4874	0.1399	0.030
H3	0.475(6)	0.289(6)	0.1434(10)	0.031(13)
H4	0.5973	0.8762	0.1453	0.026
H5	0.5878	0.5588	0.0923	0.025

H7B	0.099(7)	0.882(8)	0.0615(13)	0.065(16)
H7A	0.121(6)	1.106(9)	0.0733(12)	0.059(15)
H12	0.3907	0.9039	0.1962	0.034
H13	0.3883	0.9504	0.2561	0.035
H15	0.6024	0.3614	0.2682	0.035
H16	0.6051	0.3167	0.2084	0.032
H22	0.6067	0.6499	0.0331	0.044
H23	0.7239	0.8736	-0.0091	0.056
H24	0.8216	1.2156	0.0053	0.049
H25	0.8015	1.3331	0.0619	0.037
H26	0.6839	1.1107	0.1045	0.032

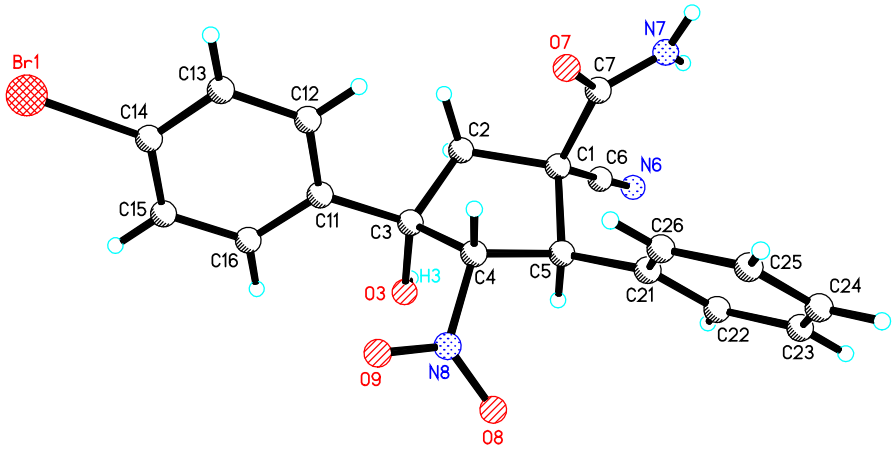
Tabelle 4: (Anisotropic displacement parameters ($Å^2$) for sba111. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ (h^2\ a^{*2}\ U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12})$)

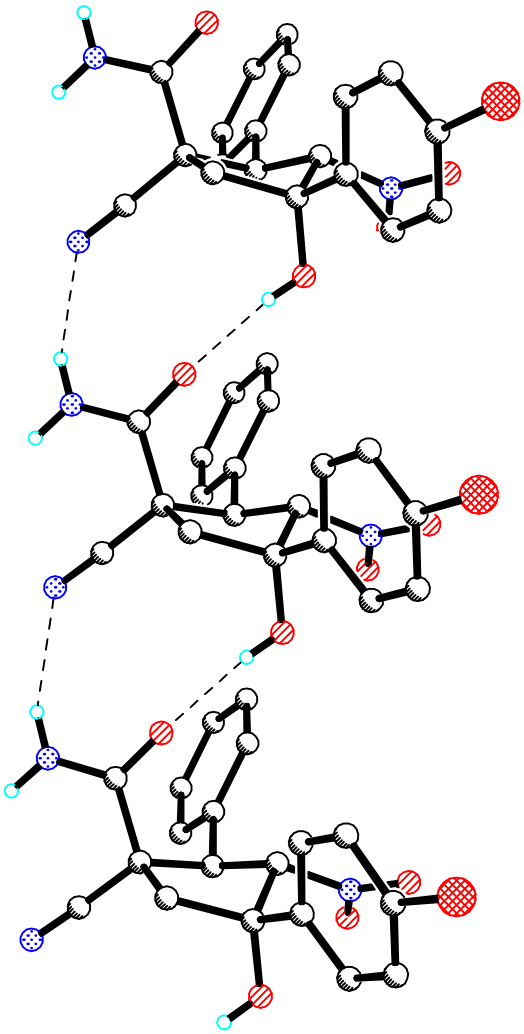
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	0.0620(3)	0.0410(3)	0.0214(3)	-0.0067(2)	0.0069(2)	0.0003(2)
C1	0.0168(17)	0.0247(19)	0.0185(19)	0.0015(16)	-0.0004(14)	0.0003(15)
C2	0.0191(18)	0.033(2)	0.024(2)	0.0039(17)	-0.0024(15)	-0.0022(16)
C3	0.0209(18)	0.024(2)	0.0198(19)	0.0004(16)	0.0008(15)	-0.0005(15)
O3	0.0273(14)	0.0222(14)	0.0301(15)	-0.0054(12)	-0.0007(12)	-0.0012(12)
C4	0.0157(17)	0.028(2)	0.0214(19)	-0.0010(16)	0.0030(15)	0.0038(15)
C5	0.0167(17)	0.025(2)	0.0220(19)	-0.0005(16)	0.0009(15)	0.0021(15)
C6	0.0193(18)	0.023(2)	0.027(2)	0.0051(18)	0.0007(16)	-0.0005(15)
N6	0.040(2)	0.0306(19)	0.0355(19)	-0.0034(17)	-0.0050(16)	-0.0068(16)
C7	0.0181(18)	0.024(2)	0.031(2)	0.0018(18)	0.0062(16)	-0.0035(15)
O7	0.0314(15)	0.0290(15)	0.0436(17)	-0.0147(14)	0.0008(13)	0.0006(12)
N7	0.045(2)	0.024(2)	0.054(3)	0.0041(19)	-0.0182(19)	0.0070(17)
N8	0.0177(15)	0.0266(17)	0.0264(18)	-0.0006(14)	0.0001(14)	-0.0004(13)
O8	0.0219(14)	0.068(2)	0.0321(16)	-0.0094(15)	0.0032(12)	0.0146(14)
O9	0.0250(14)	0.0491(18)	0.0312(16)	-0.0080(13)	-0.0105(12)	-0.0009(12)
C11	0.0153(16)	0.0246(19)	0.0196(18)	-0.0015(16)	0.0011(14)	0.0000(15)
C12	0.030(2)	0.027(2)	0.029(2)	0.0026(18)	0.0018(17)	0.0053(17)
C13	0.036(2)	0.025(2)	0.027(2)	-0.0069(18)	0.0075(17)	0.0038(17)
C14	0.029(2)	0.028(2)	0.022(2)	-0.0034(17)	0.0050(16)	-0.0030(16)
C15	0.038(2)	0.026(2)	0.022(2)	0.0024(17)	-0.0022(17)	0.0045(17)
C16	0.031(2)	0.026(2)	0.022(2)	-0.0046(17)	0.0036(16)	0.0076(16)
C21	0.0189(18)	0.027(2)	0.022(2)	0.0034(16)	0.0017(15)	0.0043(15)
C22	0.046(3)	0.036(2)	0.027(2)	0.0008(19)	0.0039(19)	-0.002(2)
C23	0.071(3)	0.047(3)	0.021(2)	0.004(2)	0.008(2)	-0.007(2)
C24	0.043(2)	0.043(3)	0.036(3)	0.017(2)	0.012(2)	-0.001(2)
C25	0.028(2)	0.029(2)	0.037(2)	0.005(2)	0.0080(18)	0.0010(17)
C26	0.0244(19)	0.031(2)	0.024(2)	-0.0020(17)	0.0078(16)	0.0050(16)

Tabelle 5: Bindungslängen (Å) und -winkel (°) für sba111.
(Bond lengths (Å) and angles (deg) for sba111.)

Br1-C14	1.896(4)	O3-H3	0.78(4)
C1-C6	1.471(5)	C4-N8	1.501(4)
C1-C7	1.532(5)	C4-C5	1.512(5)
C1-C2	1.567(5)	C4-H4	1.0000
C1-C5	1.579(4)	C5-C21	1.522(5)
C2-C3	1.534(5)	C5-H5	1.0000
C2-H2A	0.9900	C6-N6	1.138(4)
C2-H2B	0.9900	C7-O7	1.223(4)
C3-O3	1.418(4)	C7-N7	1.321(5)
C3-C11	1.524(5)	N7-H7B	0.91(5)
C3-C4	1.552(5)	N7-H7A	0.83(5)

N8-O9	1.217(4)	C16-C11-C12	118.7(3)
N8-O8	1.222(4)	C16-C11-C3	120.7(3)
C11-C16	1.383(5)	C12-C11-C3	120.6(3)
C11-C12	1.392(5)	C13-C12-C11	120.9(3)
C12-C13	1.386(5)	C13-C12-H12	119.6
C12-H12	0.9500	C11-C12-H12	119.6
C13-C14	1.379(5)	C14-C13-C12	118.9(3)
C13-H13	0.9500	C14-C13-H13	120.5
C14-C15	1.377(5)	C12-C13-H13	120.5
C15-C16	1.384(5)	C15-C14-C13	121.3(3)
C15-H15	0.9500	C15-C14-Br1	119.5(3)
C16-H16	0.9500	C13-C14-Br1	119.2(3)
C21-C26	1.383(5)	C14-C15-C16	119.2(3)
C21-C22	1.392(5)	C14-C15-H15	120.4
C22-C23	1.380(6)	C16-C15-H15	120.4
C22-H22	0.9500	C11-C16-C15	121.0(3)
C23-C24	1.380(6)	C11-C16-H16	119.5
C23-H23	0.9500	C15-C16-H16	119.5
C24-C25	1.367(6)	C26-C21-C22	118.3(3)
C24-H24	0.9500	C26-C21-C5	123.1(3)
C25-C26	1.388(5)	C22-C21-C5	118.6(3)
C25-H25	0.9500	C23-C22-C21	120.6(4)
C26-H26	0.9500	C23-C22-H22	119.7
C6-C1-C7	111.3(3)	C21-C22-H22	119.7
C6-C1-C2	111.7(3)	C22-C23-C24	120.3(4)
C7-C1-C2	109.3(3)	C22-C23-H23	119.9
C6-C1-C5	109.5(3)	C24-C23-H23	119.9
C7-C1-C5	110.7(3)	C25-C24-C23	119.8(4)
C2-C1-C5	104.1(3)	C25-C24-H24	120.1
C3-C2-C1	107.7(3)	C23-C24-H24	120.1
C3-C2-H2A	110.2	C24-C25-C26	120.3(4)
C1-C2-H2A	110.2	C24-C25-H25	119.9
C3-C2-H2B	110.2	C26-C25-H25	119.9
C1-C2-H2B	110.2	C21-C26-C25	120.8(4)
H2A-C2-H2B	108.5	C21-C26-H26	119.6
O3-C3-C11	110.8(3)	C25-C26-H26	119.6
O3-C3-C2	111.5(3)		
C11-C3-C2	113.3(3)		
O3-C3-C4	105.2(3)		
C11-C3-C4	114.2(3)		
C2-C3-C4	101.4(3)		
C3-O3-H3	112(3)		
N8-C4-C5	112.3(3)		
N8-C4-C3	110.0(3)		
C5-C4-C3	104.2(3)		
N8-C4-H4	110.0		
C5-C4-H4	110.0		
C3-C4-H4	110.0		
C4-C5-C21	118.4(3)		
C4-C5-C1	102.4(3)		
C21-C5-C1	115.6(3)		
C4-C5-H5	106.5		
C21-C5-H5	106.5		
C1-C5-H5	106.5		
N6-C6-C1	177.7(4)		
O7-C7-N7	123.7(4)		
O7-C7-C1	118.2(3)		
N7-C7-C1	118.1(3)		
C7-N7-H7B	125(3)		
C7-N7-H7A	118(3)		
H7B-N7-H7A	117(5)		
O9-N8-O8	124.1(3)		
O9-N8-C4	117.0(3)		
O8-N8-C4	119.0(3)		





Vorschlag für eine stichwortartige Experimentbeschreibung (suggestion for a short experimental part):

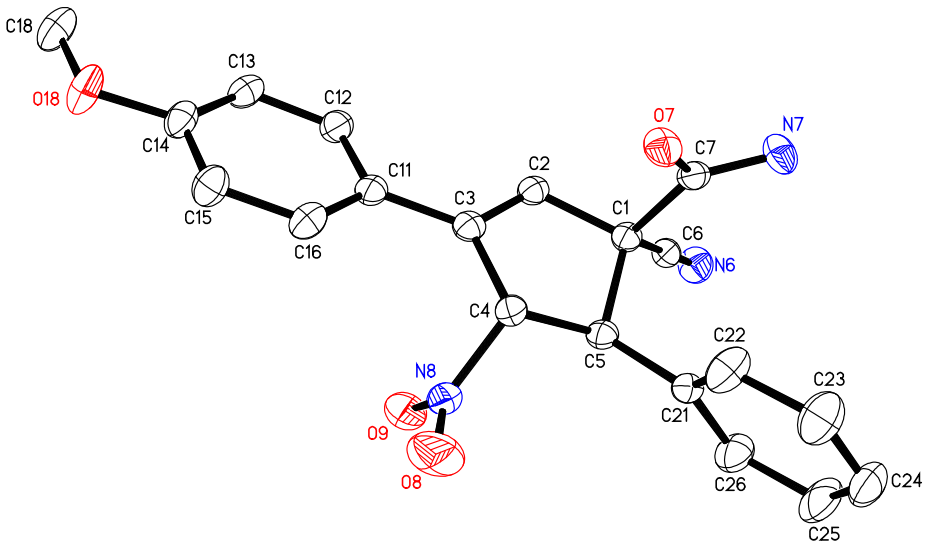
4a: colourless crystal (plate), dimensions 0.210 x 0.170 x 0.020 mm^3, crystal system monoclinic, space group $P2_1/n$, Z=4, a=7.3723(7) Å, b=6.2733(5) Å, c=38.704(3) Å, alpha=90 deg, beta=90.184(3) deg, gamma=90 deg, V=1790.0(3) $Å^3$, rho=1.597 g/cm^3, T=200(2) K, $Theta_{max}$= 24.415 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 2.90and a completeness of 98.4% to a resolution of 0.86 Å, 8904 reflections measured, 2918 unique (R(int)=0.0355), 2335 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=2.33mm^{-1}, T_{min}=0.84, T_{max}=0.97, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL (Version 2014-3) software [2], 256 parameters refined, hydrogen atoms were treated using appropriate riding models, except those at hetero atoms (N7 and O3), which were refined isotropically, goodness of fit 1.16 for observed reflections, final residual values R1(F)=0.036, $wR(F^2)$=0.087 for observed reflections, residual electron density -0.41 to 0.43 $eÅ^{-3}$. CCDC 1030884 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Lit. 1: (program SADABS 2012/1 for absorption correction) G. M. Sheldrick, Bruker Analytical X-ray-Division, Madison, Wisconsin 2012

Lit. 2: (program SHELXL 2014-3 for structure refinement) Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Lit. APEX, APEX2, SMART, SAINT, SAINT-Plus: Bruker (2007). "Program name(s)". Bruker AXS Inc., Madison, Wisconsin, USA.

X-ray crystallographic data 5a



Chemie : Saeed Balalaie
Probe : SA10
Dateinamen : **5a**
Operateur : F. Rominger (AK Hofmann)
Gerät : Bruker APEX-II Quazar

Table 1: Crystal data and structure refinement for sba110.

Identification code	sba110	
Empirical formula	$C_{20}H_{17}N_3O_4$	
Formula weight	363.36	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C2/c	
Z	8	
Unit cell dimensions	a = 25.9760(10) Å	α = 90 deg.
	b = 8.4856(3) Å	β =121.3568(8) deg.
	c = 18.9145(7) Å	γ = 90 deg.
Volume	3560.2(2) $Å^3$	
Density (calculated)	1.36 g/cm^3	
Absorption coefficient	0.10 mm^{-1}	
Crystal shape	polyhedron	
Crystal size	0.160 x 0.160 x 0.140 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.8 to 25.1 deg.	
Index ranges	-30≤h≤30, -7≤k≤10, -17≤l≤22	
Reflections collected	10816	
Independent reflections	3148 (R(int) = 0.0220)	
Observed reflections	2786 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.90	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3148 / 0 / 253	
Goodness-of-fit on F^2	1.12	
Final R indices (I>2sigma(I))	R1 = 0.040, wR2 = 0.108	

Largest diff. peak and hole	0.46 and -0.21 eÅ^{-3}

Tabelle 2: (Hydrogen coordinates and isotropic displacement parameters (Å^2) for sba110.)

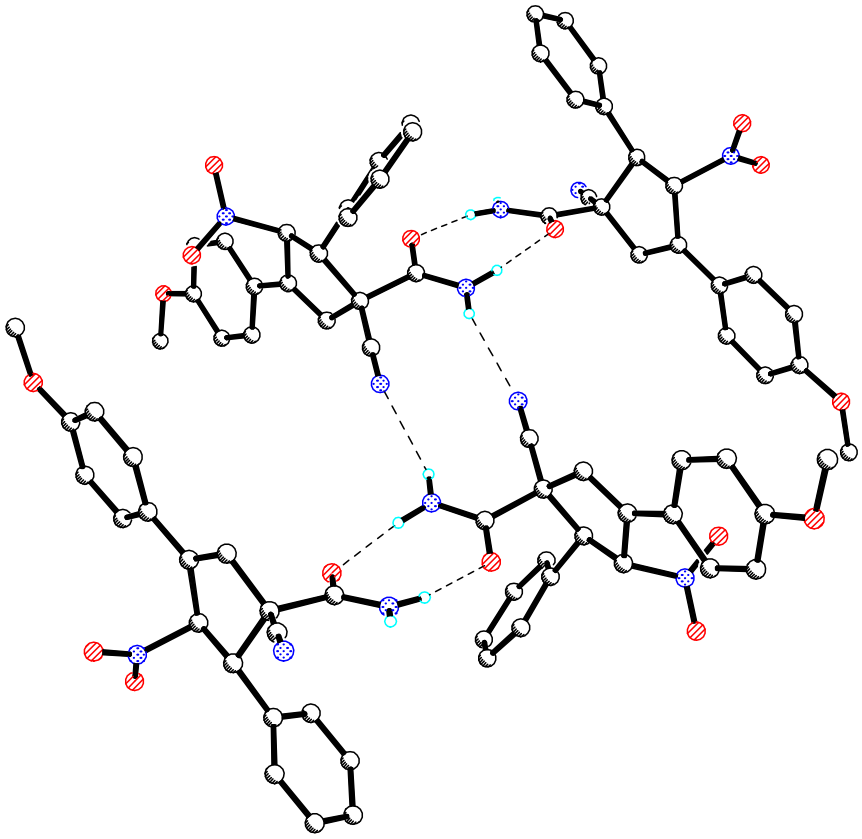
Atom	x	y	z	U_{eq}
H2	0.8477	0.3981	0.2474	0.024
H4	0.8173	0.8136	0.1633	0.025
H5	0.8276	0.7632	0.3199	0.024
H7A	1.0062(10)	0.611(3)	0.4000(15)	0.032(6)
H7B	1.0251(11)	0.655(3)	0.3384(14)	0.039(6)
H12	0.7663	0.2862	0.1441	0.029
H13	0.6902	0.1688	0.0231	0.031
H15	0.6364	0.6008	-0.0820	0.034
H16	0.7141	0.7158	0.0377	0.030
H18A	0.6345	0.0969	-0.1132	0.054
H18B	0.5637	0.1256	-0.1735	0.054
H18C	0.5923	0.1176	-0.0754	0.054
H22	0.8995	0.9728	0.2279	0.040
H23	0.9639	1.1855	0.2903	0.048
H24	0.9884	1.2709	0.4206	0.047
H25	0.9461	1.1459	0.4882	0.052
H26	0.8836	0.9288	0.4281	0.039

Tabelle 3: (Anisotropic displacement parameters (Å^2) for sba110. The anisotropic displacement factor exponent takes the form: -2 pi^2 (h^2 a^{*2} U_{11} + ... + 2 h k a* b* U_{12}))

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0206(8)	0.0210(9)	0.0192(9)	-0.0008(7)	0.0120(7)	-0.0010(7)
C2	0.0222(9)	0.0194(9)	0.0228(9)	-0.0022(7)	0.0146(8)	-0.0024(7)
C3	0.0218(9)	0.0223(10)	0.0221(9)	-0.0010(7)	0.0155(8)	-0.0017(7)
C4	0.0205(9)	0.0222(10)	0.0204(9)	-0.0026(7)	0.0109(7)	-0.0005(7)
C5	0.0217(9)	0.0221(9)	0.0197(9)	-0.0019(7)	0.0131(7)	-0.0002(7)
C6	0.0200(9)	0.0229(10)	0.0235(10)	-0.0026(8)	0.0125(8)	-0.0015(7)
N6	0.0307(9)	0.0359(10)	0.0238(9)	0.0009(8)	0.0132(7)	0.0005(7)
C7	0.0234(9)	0.0182(9)	0.0246(10)	-0.0031(8)	0.0148(8)	-0.0008(7)
O7	0.0255(7)	0.0371(8)	0.0236(7)	0.0007(6)	0.0162(6)	-0.0006(6)
N7	0.0207(8)	0.0394(10)	0.0262(9)	0.0031(8)	0.0136(7)	-0.0001(7)
N8	0.0263(8)	0.0288(9)	0.0252(8)	-0.0073(7)	0.0096(7)	0.0039(7)
O8	0.0549(10)	0.0377(10)	0.0554(11)	0.0122(8)	0.0212(9)	0.0230(8)
O9	0.0314(8)	0.0478(10)	0.0490(9)	-0.0096(8)	0.0268(7)	0.0000(7)
C11	0.0216(9)	0.0248(10)	0.0218(9)	-0.0032(8)	0.0146(8)	-0.0023(7)
C12	0.0254(9)	0.0236(10)	0.0234(9)	-0.0016(8)	0.0127(8)	-0.0001(8)
C13	0.0318(10)	0.0215(10)	0.0265(10)	-0.0054(8)	0.0172(8)	-0.0051(8)
C14	0.0273(10)	0.0314(11)	0.0206(9)	-0.0058(8)	0.0138(8)	-0.0071(8)
C15	0.0319(10)	0.0295(11)	0.0201(9)	-0.0002(8)	0.0115(8)	-0.0025(8)
C16	0.0313(10)	0.0225(10)	0.0238(10)	-0.0032(8)	0.0159(8)	-0.0051(8)
O18	0.0417(8)	0.0328(8)	0.0226(7)	-0.0064(6)	0.0085(6)	-0.0120(7)
C18	0.0424(12)	0.0342(12)	0.0299(11)	-0.0117(9)	0.0171(10)	-0.0137(10)
C21	0.0201(9)	0.0207(9)	0.0226(9)	-0.0027(7)	0.0095(7)	0.0021(7)
C22	0.0459(12)	0.0290(11)	0.0271(10)	-0.0046(9)	0.0204(9)	-0.0096(9)
C23	0.0483(13)	0.0301(12)	0.0418(13)	0.0004(10)	0.0236(11)	-0.0117(10)
C24	0.0361(11)	0.0257(11)	0.0444(13)	-0.0096(10)	0.0132(10)	-0.0081(9)
C25	0.0498(14)	0.0455(14)	0.0362(12)	-0.0225(11)	0.0225(11)	-0.0134(11)
C26	0.0367(11)	0.0367(12)	0.0305(11)	-0.0098(9)	0.0217(9)	-0.0066(9)

Tabelle 4: Bond lengths (Å) and angles (deg) for sba110.

C1-C6	1.477(2)	C5-C4-H4	110.8
C1-C2	1.506(2)	C21-C5-C4	119.30(15)
C1-C7	1.557(2)	C21-C5-C1	115.13(14)
C1-C5	1.573(2)	C4-C5-C1	102.26(13)
C2-C3	1.333(3)	C21-C5-H5	106.4
C2-H2	0.9500	C4-C5-H5	106.4
C3-C11	1.469(2)	C1-C5-H5	106.4
C3-C4	1.511(3)	N6-C6-C1	178.9(2)
C4-N8	1.516(2)	O7-C7-N7	123.50(17)
C4-C5	1.545(2)	O7-C7-C1	117.39(15)
C4-H4	1.0000	N7-C7-C1	119.11(16)
C5-C21	1.510(3)	C7-N7-H7A	122.2(15)
C5-H5	1.0000	C7-N7-H7B	116.2(15)
C6-N6	1.141(2)	H7A-N7-H7B	122(2)
C7-O7	1.230(2)	O9-N8-O8	124.74(18)
C7-N7	1.328(2)	O9-N8-C4	117.81(16)
N7-H7A	0.84(2)	O8-N8-C4	117.45(17)
N7-H7B	0.91(3)	C12-C11-C16	117.54(17)
N8-O9	1.215(2)	C12-C11-C3	120.35(17)
N8-O8	1.224(2)	C16-C11-C3	122.11(17)
C11-C12	1.396(3)	C13-C12-C11	121.68(18)
C11-C16	1.398(3)	C13-C12-H12	119.2
C12-C13	1.388(3)	C11-C12-H12	119.2
C12-H12	0.9500	C12-C13-C14	119.46(18)
C13-C14	1.391(3)	C12-C13-H13	120.3
C13-H13	0.9500	C14-C13-H13	120.3
C14-O18	1.366(2)	O18-C14-C15	115.84(18)
C14-C15	1.389(3)	O18-C14-C13	124.23(18)
C15-C16	1.382(3)	C15-C14-C13	119.93(17)
C15-H15	0.9500	C16-C15-C14	119.88(18)
C16-H16	0.9500	C16-C15-H15	120.1
O18-C18	1.423(3)	C14-C15-H15	120.1
C18-H18A	0.9800	C15-C16-C11	121.50(18)
C18-H18B	0.9800	C15-C16-H16	119.2
C18-H18C	0.9800	C11-C16-H16	119.2
C21-C26	1.386(3)	C14-O18-C18	117.06(16)
C21-C22	1.388(3)	O18-C18-H18A	109.5
C22-C23	1.381(3)	O18-C18-H18B	109.5
C22-H22	0.9500	H18A-C18-H18B	109.5
C23-C24	1.370(3)	O18-C18-H18C	109.5
C23-H23	0.9500	H18A-C18-H18C	109.5
C24-C25	1.378(3)	H18B-C18-H18C	109.5
C24-H24	0.9500	C26-C21-C22	118.31(18)
C25-C26	1.382(3)	C26-C21-C5	118.32(17)
C25-H25	0.9500	C22-C21-C5	123.22(17)
C26-H26	0.9500	C23-C22-C21	120.40(19)
C6-C1-C2	113.44(15)	C23-C22-H22	119.8
C6-C1-C7	112.41(14)	C21-C22-H22	119.8
C2-C1-C7	107.94(14)	C24-C23-C22	120.8(2)
C6-C1-C5	110.09(14)	C24-C23-H23	119.6
C2-C1-C5	102.16(14)	C22-C23-H23	119.6
C7-C1-C5	110.31(14)	C23-C24-C25	119.4(2)
C3-C2-C1	112.46(16)	C23-C24-H24	120.3
C3-C2-H2	123.8	C25-C24-H24	120.3
C1-C2-H2	123.8	C24-C25-C26	120.1(2)
C2-C3-C11	126.71(17)	C24-C25-H25	119.9
C2-C3-C4	110.06(16)	C26-C25-H25	119.9
C11-C3-C4	123.10(16)	C25-C26-C21	120.9(2)
C3-C4-N8	111.97(15)	C25-C26-H26	119.5
C3-C4-C5	104.36(14)	C21-C26-H26	119.
N8-C4-C5	108.06(14)		
C3-C4-H4	110.8		
N8-C4-H4	110.7		



5a: colourless crystal (polyhedron), dimensions 0.160 x 0.160 x 0.140 mm^3, crystal system monoclinic, space group C2/c, Z=8, a=25.9760(10) Å, b=8.4856(3) Å, c=18.9145(7) Å, alpha=90 deg, beta=121.3568(8) deg, gamma=90 deg, V=3560.2(2) $Å^3$, rho=1.356 g/cm^3, T=200(2) K, $Theta_{max}$= 25.073 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 3.33and a completeness of 99.5% to a resolution of 0.84 Å, 10816 reflections measured, 3148 unique (R(int)=0.0220), 2786 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.10mm^{-1}, T_{min}=0.90, T_{max}=0.96, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL (Version 2014-3) software [2], 253 parameters refined, hydrogen atoms were treated using appropriate riding models, except those of the aminde group, which were refined isotropically, goodness of fit 1.12 for observed reflections, final residual values R1(F)=0.040, $wR(F^2)$=0.108 for observed reflections, residual electron density -0.21 to 0.46 $eÅ^{-3}$. CCDC 1030883 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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