

Synthesis of 2-Amino-imidazoles, Purines, and Benzoxazolamines Through DIB Oxidation

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SUPPORTING INFORMATION

General:

All chemicals were purchased from commercial suppliers as noted in the procedures and were used without further purification. Diacetoxy-iodobenzene was purchased from TCI and oxalyl chloride from Aldrich. All reactions were performed under a nitrogen atmosphere unless stated otherwise.

The following instrumentation was used in this study unless otherwise noted. 1D-NMR, proton and ¹³C NMR spectra were conducted either on a Bruker Avance spectrometer at 400 MHz and 100 MHz, respectively, or on a Bruker Avance II spectrometer with cryoprobe at 600 MHz and 150 MHz, respectively. Chemical shifts are reported in ppm on the δ scale. Multiplicities are described as s (singlet), d (doublet), st (sextuplet), sp (septuplet), dd, ddd, etc. (doublet of doublets, doublet of doublets of doublets, etc.), t (triplet), q (quartet), m (multiplet), and further qualified as br (broad). Coupling constants, J, are reported in Hz. The infrared spectra were recorded on a Perkin Elmer 1710 Infrared Fourier Transform spectrometer. The low resolution mass spectra were recorded by using an Agilent HP 1090 LC equipped with a VG Fisons Micromass Quattro I mass spectrometer. High resolution mass spectroscopy was run on a Waters Q-ToF apparatus. TLC solvents were the same as those used for flash chromatography with $R_{f \approx_{es}} 0.25$

General procedure for formamides synthesis:

Formamides were prepared according to a slightly modified procedure described by Moffat et al. (Moffat, J.; Newton, M.V.; Papenmeier, G.J. *J. Org.Chem.* **1962**, *27*, 4058): the secondary amine was dissolved in EtOH/ethyl formate (1/1) ([c]= ca. 1 M) and refluxed for 10 hours. A fractional distillation gave the desired formamide as a clear oil. Alternatively, the distillation can be skipped by simply pumping off the ethanol and the excess of ethyl formate at the end of the reaction. Although this procedure yielded generally a yellow oil, both procedures were equivalent in term of yield for the subsequent reactions.

General procedure for 2-amino-imidazoles synthesis:

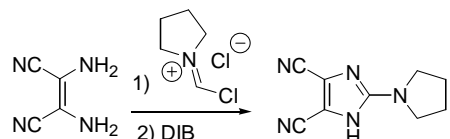
The 1,2-diamine (1 mmol) was dissolved in acetonitrile ([c]= ca. 0.2 M). In another flask, the formamide (1.2 equiv.) was dissolved in DCM ([c]= ca. 0.4 M) at 5°C and oxalyl chloride (1.2 equiv.) was then added drop-wise. Once the evolution of gas stopped (usually after 5 min) the content of this flask was added slowly (~ 2 mL/min) to the 1,2-diamine solution with vigorous stirring. The HCl salt of the formamidine intermediate precipitated immediately, and LCMS analysis showed completion of the reaction 5 min after the end of the addition. Water (2 mL) was then added followed by diacetoxy-iodobenzene (1.1 equiv.). After 5-10 min, LCMS analysis showed total formation of the 2-amino-imidazole. Aqueous NaHCO₃ (saturated, 5 mL) was added to the reaction mixture and the solution was extracted with DCM. The organic layers were dried over MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography using elution gradient mentioned in the text.

General procedure for 2-amino-benzoxazolamines synthesis:

The 2-amino-phenol (1 mmol) was dissolved in 1,4-dioxane ([c]= ca. 0.2 M). In another flask, the formamide (1.2 equiv.) was dissolved in DCM ([c]= ca. 0.4 M) at 5°C and oxalyl chloride (1.2 equiv.) was then added drop-wise. Once the evolution of gas stopped (usually after 5 min) the content of this flask was added slowly (~ 2 mL/min) to the 2-amino-phenol solution with vigorous stirring. The HCl salt of the formamidine intermediate precipitated and LCMS analysis showed completion of the reaction 5 min after the end of the addition. NaOH 2M (2 mL) was

then added followed by diacetoxy-iodobenzene (1.1 equiv.). After 5-10 min, LCMS analysis showed total formation of the 2-amino-benzoxazolamine. Water (15 mL) was added to the reaction mixture and the solution was extracted with DCM. The organic layers were dried over MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography using elution gradient mentioned in the text.

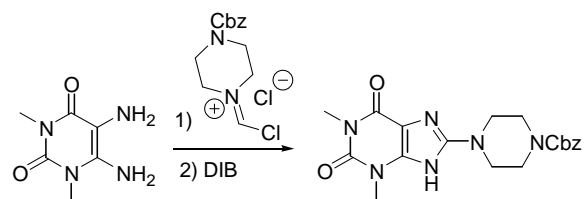
2-Pyrrolidine-imidazole-4,5-dicarbonitrile. Compound 11 (Table 1, entry 1):



According to the general procedure for the formation of 2-amino-imidazoles and starting from 1 mmol of diaminomaleonitrile, compound **5** was obtained as a solid (162 mg, 86%) after column chromatography using Hexanes/EtOAc with an elution gradient (EtOAc 0% → 100%).

Mp: 82-84°C (Ethyl acetate / hexanes); **NMR** ¹H (400 MHz, CD₃OD) δ: 5.07 (s, 1H), 3.44 (s, 4H), 2.05 (s, 4H); **NMR** ¹³C (100 MHz, CD₃OD) δ: 154.4, 114.7, 113.2, 49.5, 27.3; **IR** (neat): 2231, 1655, 1620, 1555, 1358 cm⁻¹; **MS** (ESI⁺): 188.3 (M+H⁺); **HRMS** Calc. for C₉H₁₀N₅ (M+H⁺): 188.0936; found: 188.0938.

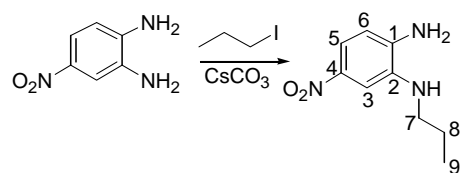
Compound 12 (Table 1, entry 2):



According to the general procedure for the formation of 2-amino-imidazoles and starting from 1 mmol of 5,6-diamino-1,3-dimethyluracil hydrate, dried under high vacuum at 50°C for 24 hours, compound **6** was obtained as a solid (346 mg, 87%) after column chromatography using Hexanes/EtOAc with an elution gradient (EtOAc 0% → 100%).

Mp: 292-296°C (Ethyl acetate / hexanes); **NMR** ¹H (400 MHz, DMSO d₆) δ: 11.82 (br, 1H), 7.40-7.29 (m, 5H), 5.11 (s, 2H), 3.51 (br, 6H), 3.36-3.32 (br, 6H), 3.20 (br, 2H); **NMR** ¹³C (100 MHz, DMSO d₆) δ: 155.4, 155.2, 153.6, 152.1, 149.5, 137.7, 129.3, 128.8, 128.5, 103.2, 100.4, 67.3, 46.2, 43.6, 30.5, 28.4; **IR** (neat): 3089, 1698, 1658, 1537, 1272 cm⁻¹; **MS** (ESI⁺): 399.3 (M+H⁺); **HRMS** Calc. for C₁₉H₂₃N₆O₄ (M+H⁺): 399.1781; found: 399.1791.

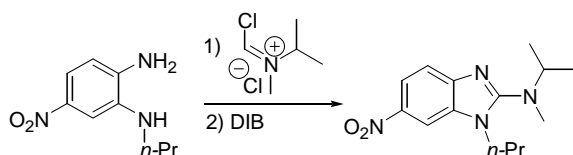
Synthesis of starting material for compound 13:



The starting material 2-(*n*-propyl)-amino-4-nitroaniline was prepared in 77% yield by a modified procedure used to describe the synthesis of 2-ethylamino-4-nitroaniline.¹ 2-Amino-4-nitroaniline (3 mmol) was dissolved in 6 mL of DMF and cesium carbonate (6 mmol) and 1-iodo-propane (4 mmol) were added. After stirring for 2 days, water (10 mL) was added and the product was extracted with EtOAc. The organic layers were combined, washed with water (3 x 15 mL) and brine and then dried over MgSO₄, filtered and concentrated. The crude product was further purified by column chromatography using Hexanes/EtOAc (3/2) to give 2-(*n*-propyl)-amino-4-nitroaniline (450 mg, 77%) as a red solid.²

Mp: 80-82°C (Ethyl acetate / hexanes); **NMR** ¹H (600 MHz, CDCl₃) δ: 7.66 (dd, J = 8.6; 2.5 Hz, 1H), 7.50 (d, J = 2.5 Hz, 1H), 6.66 (d, J = 8.6 Hz, 1H), 4.10 (br, 2H), 3.24 (br, 1H), 3.12 (t, J = 7.1 Hz, 2H), 1.72 (m, 2 H), 1.05 (t, J = 7.4 Hz, 3H); **NMR** ¹³C (150 MHz, CDCl₃) δ: 142.0, 140.8, 136.3, 116.4, 113.4, 107.0, 46.1, 22.6, 11.7; **MS** (ESI⁺): 196.3 (M+H⁺).

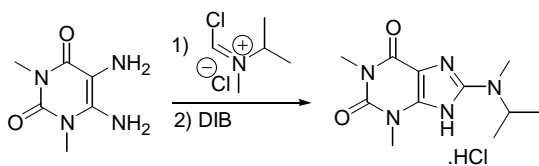
Compound 13 (Table 1, entry 3):



According to the general procedure for the formation of 2-amino-imidazoles and starting from 1 mmol of 2-(*n*-propyl)-amino-4-nitroaniline, imidazole **7** was obtained as a solid (201 mg, 73%) after column chromatography using Hexanes/EtOAc with an elution gradient (EtOAc 30% → 100%).

Mp: 44-49°C (Ethyl acetate / hexanes); **NMR** ¹H (400 MHz, CD₃OD) δ: 8.11 (d, J = 2.2 Hz, 1H), 7.99 (dd, J = 8.9; 2.2 Hz, 1H), 7.36 (d, J = 8.9 Hz, 1H), 4.07 (t, J = 7.59 Hz, 2H), 4.05 (m, 1H), 2.94 (s, 3H), 1.82 (st, J = 7.6 Hz, 2H), 1.28 (d, J = 6.2 Hz, 6H), 0.89 (t, J = 7.6 Hz, 3H); **NMR** ¹³C (100 MHz, CD₃OD) δ: 164.3, 149.0, 143.7, 136.9, 120.0, 117.3, 107.4, 54.8, 48.7, 32.6, 23.9, 20.4, 12.2; **IR** (neat): 2979, 2875, 1544, 1471, 1298 cm⁻¹; **MS** (ESI⁺): 277.3 (M+H⁺); **HRMS** Calc. for C₁₄H₂₁N₄O₂ (M+H⁺): 277.1665; found: 277.1671.

Compound 14 (Table 1, entry 4):



A slightly different procedure³ was used to prepare compound **8**. The formamide (1.2 equiv.) was dissolved in DCM ([c] = ca. 0.2 M) at 5°C under nitrogen and oxalyl chloride (1.2 equiv.) was then added drop-wise. Once the gas evolution was finished (usually after 5 min), the 1,2-diamine (5 mmol) was added slowly. After 10 min, diacetoxy-iodobenzene (1.0 equiv.) was

¹ Carella, A.; Centore, R.; Fort, A.; Peluso, A.; Sirigu, A.; Tuzi, A. *Eur. J. Org. Chem.* **2004**, 2620.

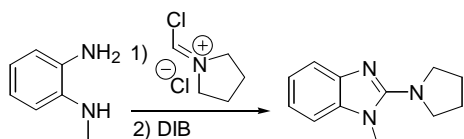
² The regioselectivity of the alkylation has been unambiguously determined by HMBC correlation between C₂ and H₇.

³ No water was added after the formation of the formamidine. It resulted in heterogeneous reaction with DIB and consequently longer reaction time was required for the reaction to go to completion. Because of this, this procedure was not used for the other substrates. The heterogeneity of the reaction was also a concern for future scale-up.

added and the solution was stirred for 10 hours. The solvents were concentrated and the residue was directly purified by flash chromatography using DCM/MeOH 9/1 to give the xanthine **8** as a solid (1.250 g, 97%).

Mp: 258-260°C (Ethanol); **NMR** ¹H (400 MHz, DMSO d₆) δ: 11.48 (s, 1H), 4.46 (sp, J= 6.8 Hz, 1H), 3.34 (s, 3H), 3.18 (s, 3H), 2.84 (s, 3H) 1.11 (d, J= 6.8 Hz, 6H); **NMR** ¹³C (100 MHz, DMSO d₆) δ: 154.5, 151.9, 150.8, 148.8, 101.3, 47.3, 29.1, 27.9, 27.0, 18.7; **IR** (neat): 3148, 2980, 1704, 1658, 1620, 1532, 1404 cm⁻¹; **MS** (ESI⁺): 252.3 (M+H⁺); **HRMS** Calc. for C₁₁H₁₈N₅O₂ (M+H⁺): 252.1460; found: 252.1453.

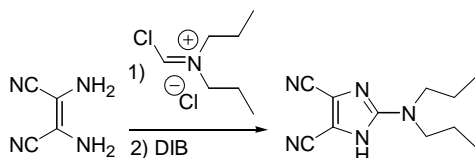
Compound 15 (Table 1, entry 5)⁴:



According to the general procedure for the formation of 2-amino-imidazoles and starting from 2 mmol of N-methyl-1,2-phenylenediamine, compound **9** was obtained as an oil (260 mg, 65%) after column chromatography using Hexanes/EtOAc with an elution gradient (EtOAc 0% → 100%).

NMR ¹H (400 MHz, CD₃OD) δ: 7.31 (dd, J= 7.0; 1.2 Hz, 1H), 7.14 (dd, J= 7.0; 1.2 Hz, 1H), 7.09-7.00 (m, 2H), 3.62 (s, 3H), 3.61-3.56 (m, 4H), 2.01-1.94 (m, 4H); **NMR** ¹³C (100 MHz, CD₃OD) δ: 156.8, 141.3, 136.0, 121.2, 119.8, 115.0, 107.7, 49.9, 30.4, 25.3; **IR** (neat): 2974, 2867, 1615, 1600, 1567, 1468, 1397 cm⁻¹; **MS** (ESI⁺): 202.4 (M+H⁺); **HRMS** Calc. for C₁₂H₁₆N₃ (M+H⁺): 202.1344; found: 202.1344.

Compound 16 (Table 1, entry 6):

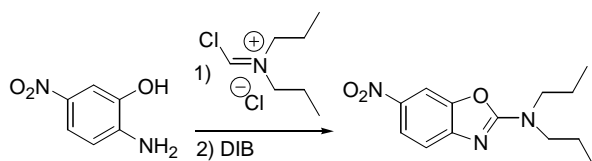


According to the general procedure for the formation of 2-amino-imidazoles and starting from 1 mmol of diaminomaleonitrile, compound **10** was obtained as a solid (178 mg, 82%) after column chromatography using Hexanes/EtOAc with an elution gradient (EtOAc 0% → 100%).

Mp: 79-81°C (Ethyl acetate / hexanes); **NMR** ¹H (400 MHz, CD₃OD) δ: 4.98 (br, 1H), 3.31 (t, J= 7.5 Hz, 4H), 1.61 (st, J= 7.5 Hz, 4H), 0.91 (t, J= 7.5 Hz, 6H); **NMR** ¹³C (100 MHz, CD₃OD) δ: 154.9, 112.6, 51.9, 21.9, 11.4; **IR** (neat): 2967, 2233, 1601, 1322 cm⁻¹; **MS** (ESI⁺): 218.4 (M+H⁺); **HRMS** Calc. for C₁₁H₁₆N₅ (M+H⁺): 218.1406; found: 218.1408.

Compound 17 (Table 1, entry 7):

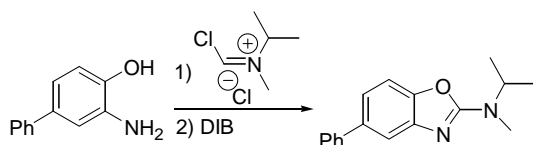
⁴ C. T. Brain, S. A. Brunton, *Tet. Lett.*, 2002, **43**, 1893 (compound isolated as the formate salt).



According to the general procedure for the formation of 2-amino-benzoxazolamines and starting from 1 mmol of 2-amino-5-nitrophenol, compound **11** was obtained as a solid (176 mg, 67%) after column chromatography using Hexanes/EtOAc with an elution gradient (EtOAc 0% → 100%).

Mp: 65-67°C (Ethyl acetate / hexanes); **NMR** ^1H (400 MHz, CDCl_3) δ : 8.15 (dd, J = 5.8; 1.2 Hz, 1H), 8.11 (d, J = 1.2 Hz, 1H), 7.29 (d, J = 5.8 Hz, 1H), 3.53 (t, J = 7.6 Hz, 4H), 1.74 (m, 4H), 0.99 (t, J = 7.6 Hz, 6H); **NMR** ^{13}C (100 MHz, CDCl_3) δ : 165.6, 150.8, 148.0, 141.1, 121.6, 114.5, 105.0, 50.8, 21.3, 11.3; **IR** (neat): 2966, 1651, 1586, 1323, 1283 cm^{-1} ; **MS** (ESI^+): 264.3 ($\text{M}+\text{H}^+$); **HRMS** Calc. for $\text{C}_{13}\text{H}_{18}\text{N}_3\text{O}_3$ ($\text{M}+\text{H}^+$): 264.1348; found: 264.1346.

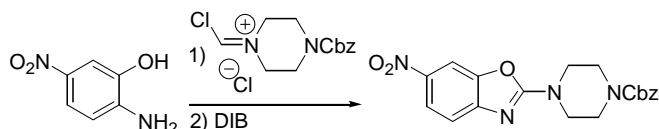
Compound 18 (Table 1, entry 8):



According to the general procedure for the formation of 2-amino-benzoxazolamines and starting from 1 mmol of 2-amino-4-phenylphenol, compound **12** was obtained as an oil (215 mg, 81%) after column chromatography using Hexanes/EtOAc with an elution gradient (EtOAc 0% → 100%).

NMR ^1H (600 MHz, CDCl_3) δ : 7.65-7.60 (m, 3H), 7.45 (t, J = 7.2 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.24 (dd, J = 8.4; 1.8 Hz, 1H), 4.63 (sp, J = 7.2 Hz, 1H), 3.06 (s, 3H), 1.28 (d, J = 7.2 Hz, 6H); **NMR** ^{13}C (150 MHz, CDCl_3) δ : 163.2, 148.4, 144.2, 141.8, 137.6, 128.8, 127.3, 126.9, 119.5, 114.6, 108.5, 48.8, 28.4, 19.6; **IR** (neat): 3031, 2976, 1646, 1586, 1469, 1425, 1133 cm^{-1} ; **MS** (ESI^+): 267.3 ($\text{M}+\text{H}^+$); **HRMS** Calc. for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}$ ($\text{M}+\text{H}^+$): 267.1497; found: 267.1501.

Compound 19 (Table 1, entry 9)⁵:



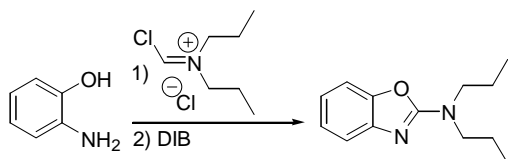
According to the general procedure for the formation of 2-amino-benzoxazolamines and starting from 1 mmol of 2-amino-5-nitrophenol, compound **13** was obtained as a solid (214 mg, 56%)

⁵ K. G. Liua, J. R. Loa, T. A. Comeryb, G. M. Zhangb, J. Y. Zhangb, D. M. Kowalb, D. L. Smithb, L. Dia, E. H. Kernsa, L. E. Schechterb and A. J. Robichauda, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 1115. Compound **19** was not isolated and characterized but instead reduced directly to the corresponding aniline.

after column chromatography using Hexanes/EtOAc with an elution gradient (EtOAc 0% → 100%).

Mp: 142-144°C (Ethyl acetate / hexanes); **NMR** ^1H (600 MHz, DMSO d_6) δ : 8.28 (d, J = 2.4 Hz, 1H), 8.13 (dd, J = 8.4; 2.4 Hz, 1H), 7.42-7.29 (m, 6H), 5.12 (s, 2H), 3.75-3.66 (br, 4H), 3.64-3.53 (br, 4H); **NMR** ^{13}C (150 MHz, DMSO d_6) δ : 165.1, 155.0, 150.7, 148.2, 141.2, 137.3, 129.1, 128.6, 128.4, 122.1, 115.4, 105.7, 67.2, 45.6, 43.3; **IR** (neat): 2931, 1703, 1646, 1586, 1332, 1242 cm^{-1} ; **MS** (ESI^+): 383.1 ($\text{M}+\text{H}^+$); **HRMS** Calc. for $\text{C}_{19}\text{H}_{19}\text{N}_4\text{O}_5$ ($\text{M}+\text{H}^+$): 383.1355; found: 383.1340.

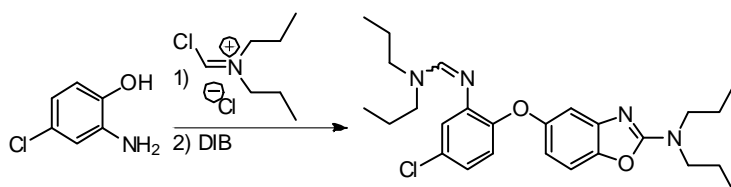
Compound 20 (Table 1, entry 10)⁶:



According to the general procedure for the formation of 2-amino-benzoxazolamines and starting from 1 mmol of 2-aminophenol, compound **14** was obtained as an oil (161 mg, 74%) after column chromatography using Hexanes/EtOAc with an elution gradient (EtOAc 0% → 100%).

NMR ^1H (600 MHz, CDCl_3) δ : 7.36 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.14 (td, J = 7.8; 0.6 Hz, 1H), 6.97 (td, J = 7.8; 1.2 Hz, 1H), 3.47 (t, J = 7.8 Hz, 4H), 1.71 (st, J = 7.8 Hz, 4H), 0.97 (t, J = 7.8 Hz, 6H); **NMR** ^{13}C (150 MHz, CDCl_3) δ : 162.9, 148.9, 143.9, 123.9, 120.1, 116.0, 108.6, 50.5, 24.4, 11.4; **IR** (neat): 2964, 1646, 1582, 1461, 1245 cm^{-1} ; **MS** (ESI^+): 219.4 ($\text{M}+\text{H}^+$); **HRMS** Calc. for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{O}$ ($\text{M}+\text{H}^+$): 219.1497; found: 219.1498.

Compound 22.

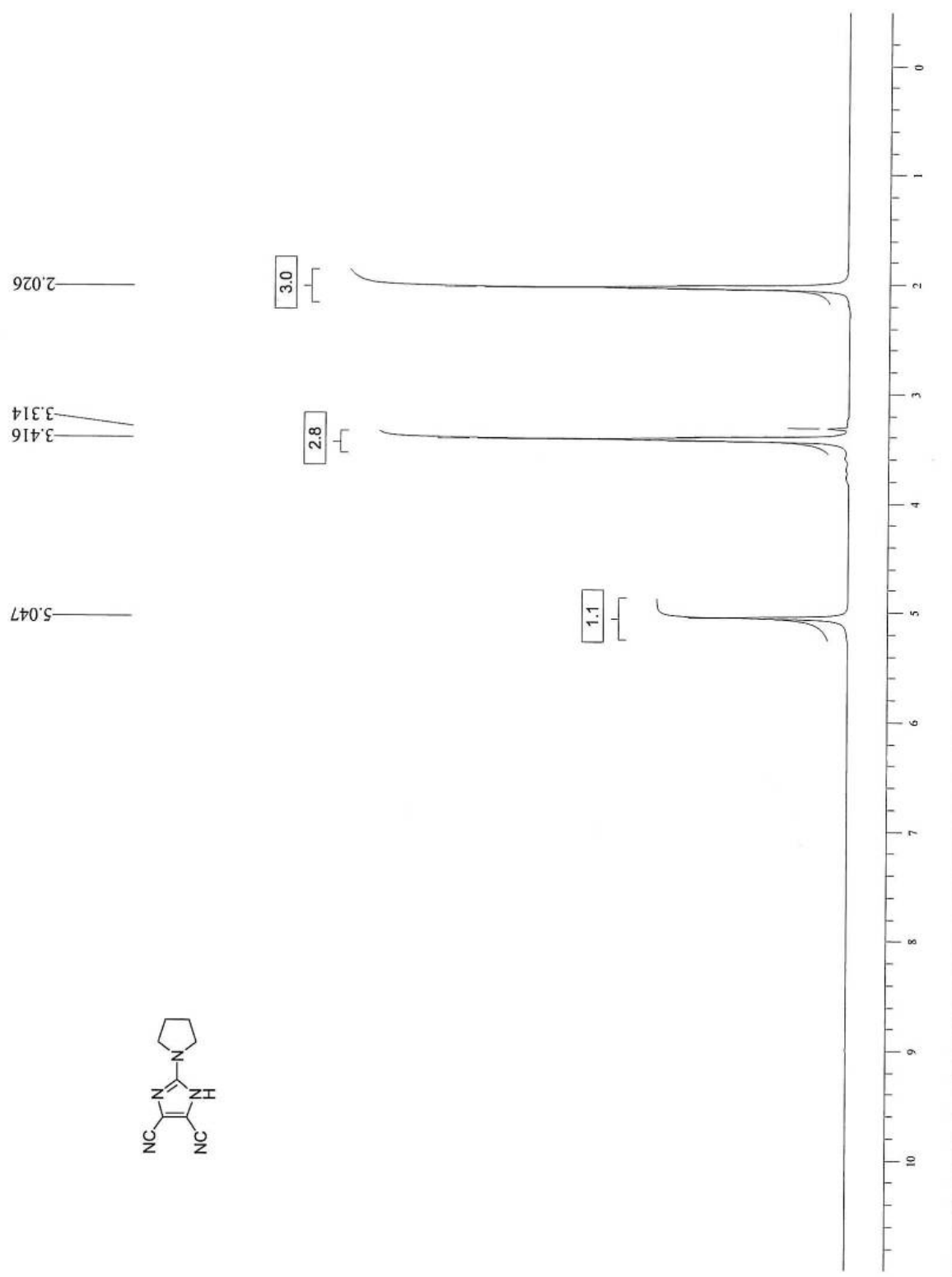


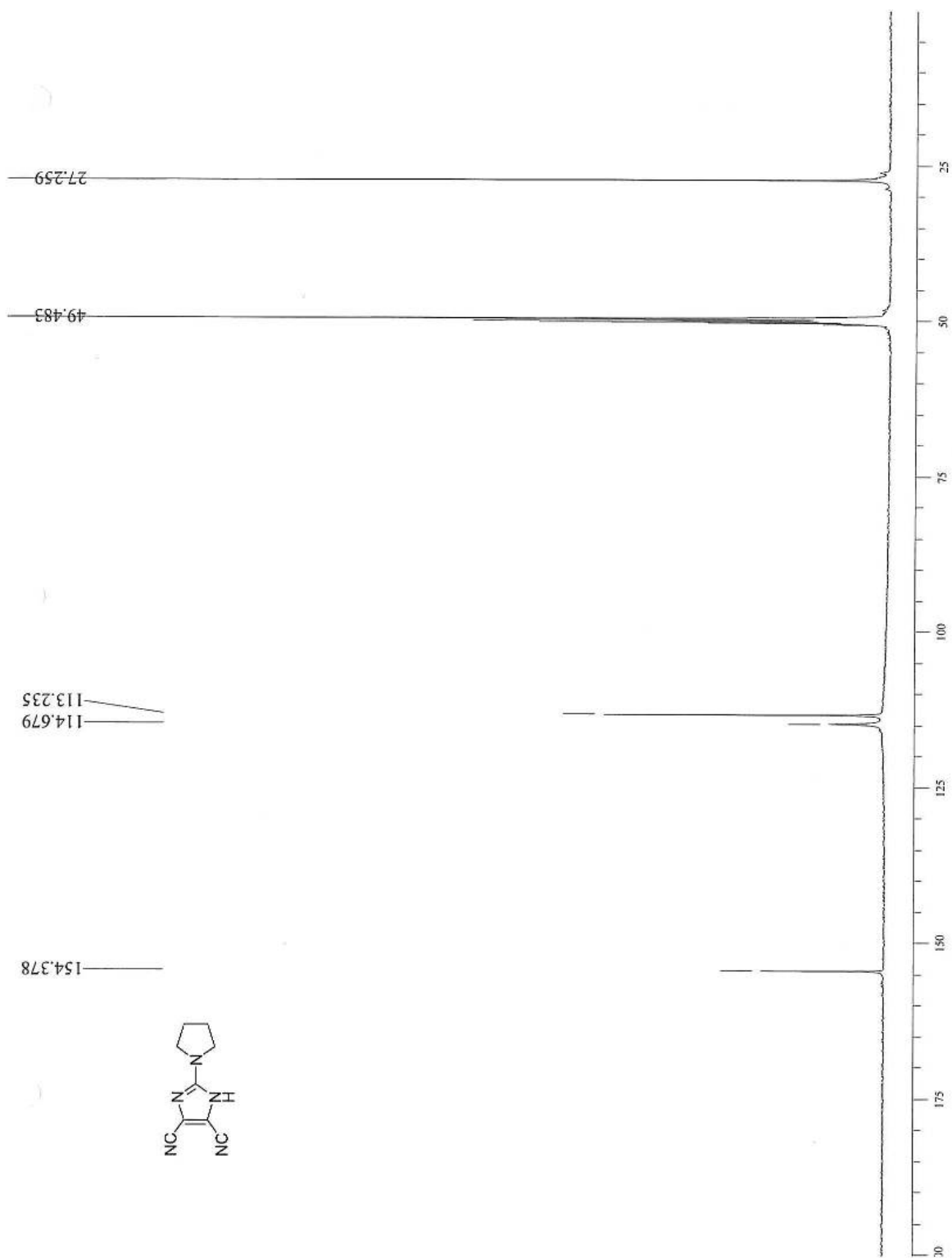
According to the general procedure for the formation of 2-amino-benzoxazolamines and starting from 1 mmol of 2-amino-4-chlorophenol, compound **16** was obtained as an oil (263 mg, 56%) after column chromatography using Hexanes/EtOAc with an elution gradient (EtOAc 0% → 100%).

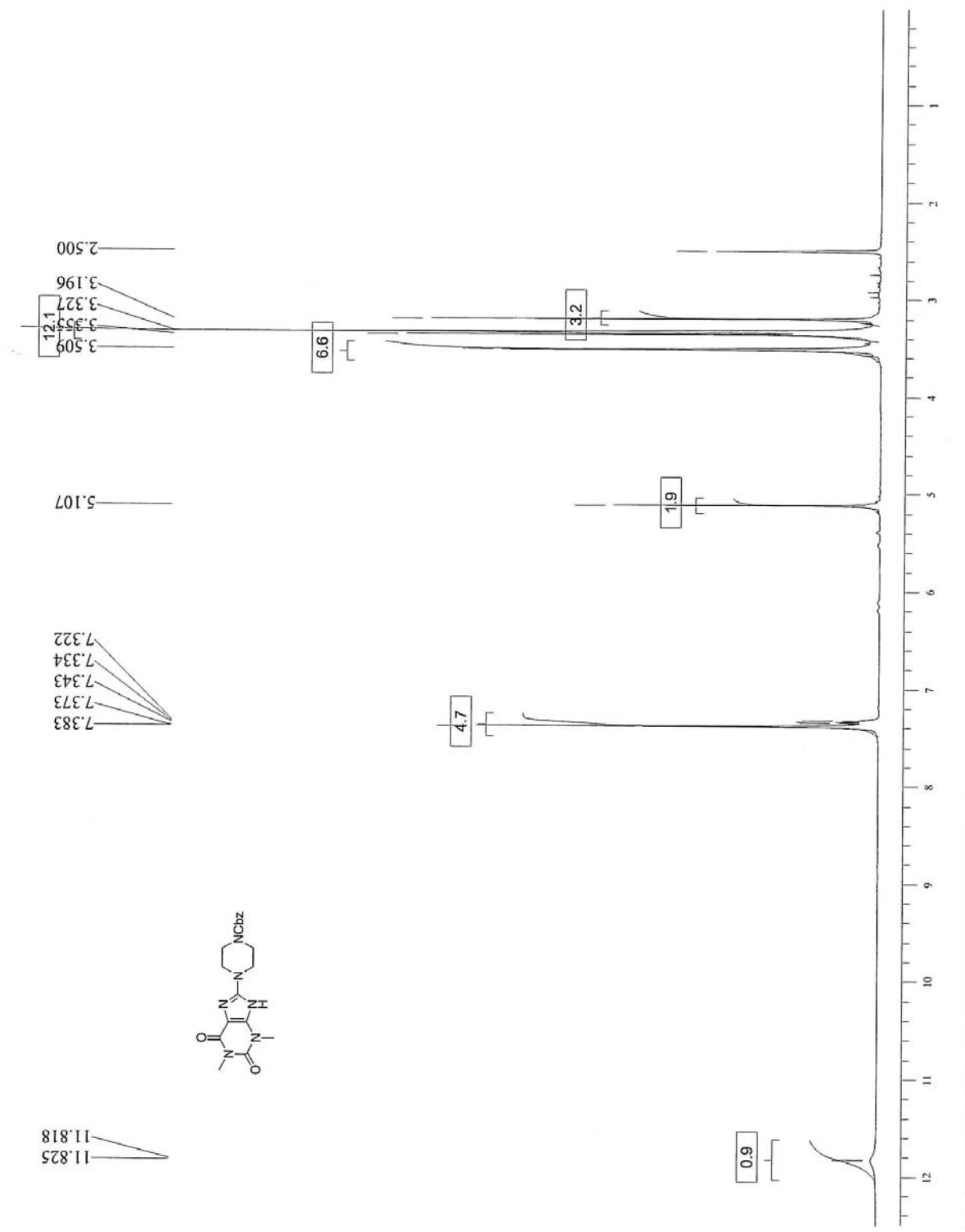
NMR ^1H (600 MHz, CDCl_3) δ : 7.48 (s, 1H), 7.06 (d, J = 8.5 Hz, 1H), 6.92-6.91 (m, 2H), 6.88 (dd, J = 8.5; 2.4 Hz, 1H), 6.84 (d, J = 2.4 Hz, 1H), 6.53 (dd, J = 8.6; 2.5 Hz, 1H), 3.45 (t, J = 7.5 Hz, 4H), 3.2 (br, 2H), 3.06 (br, 2H), 1.70 (st, J = 7.5 Hz, 4H), 1.51-1.36 (br, 4H), 0.96 (t, J = 7.5 Hz, 6H), 0.83-0.70 (br, 6H); **NMR** ^{13}C (150 MHz, CDCl_3) δ : 163.4, 155.6, 153.7, 147.6, 146.0, 144.5, 144.1, 129.3, 122.5, 122.4, 122.2, 108.6, 108.0, 104.7, 53.1, 50.3, 46.6, 22.3, 21.2, 20.0,

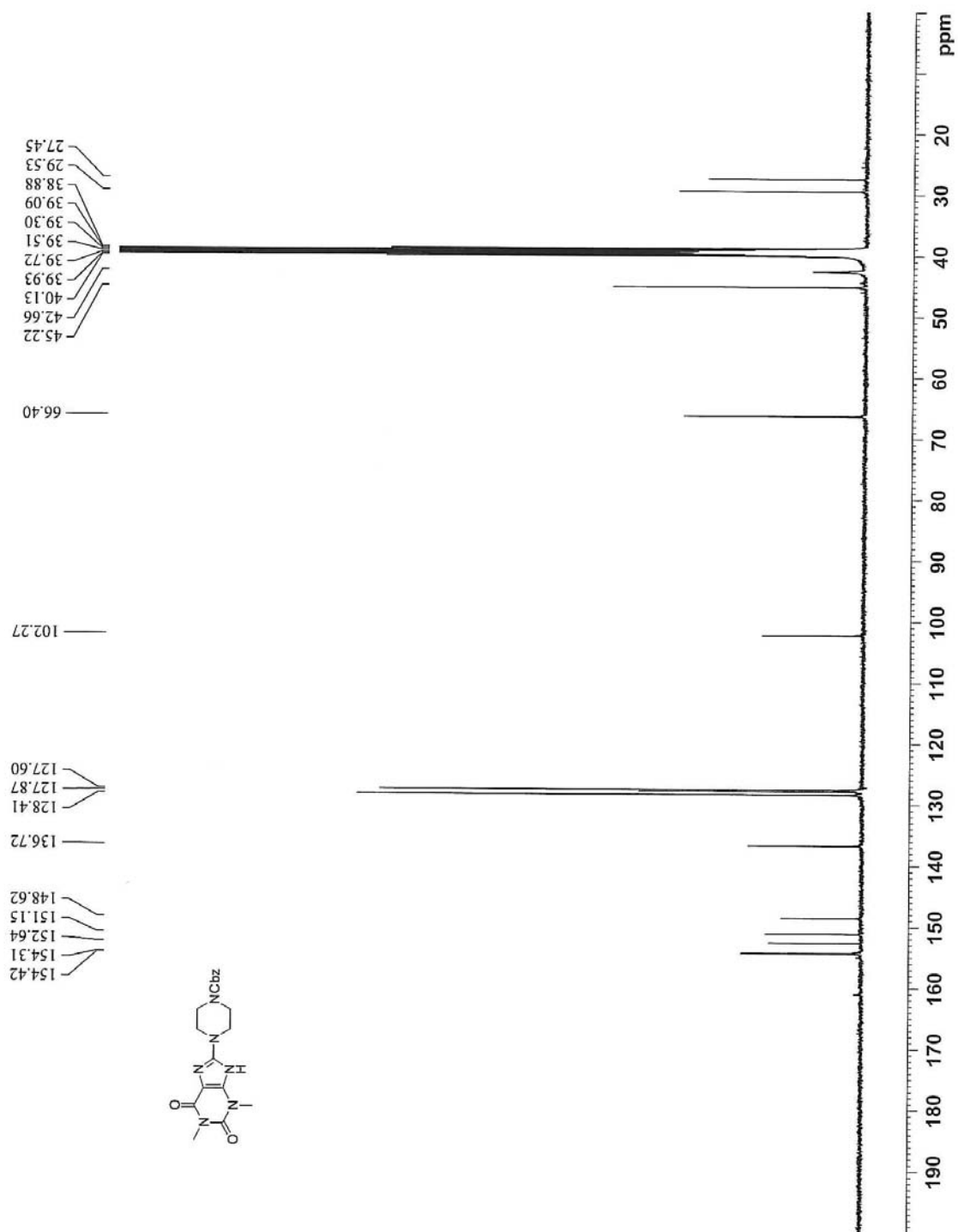
⁶ S. Guo, B. Qian, Y. Xie, C. Xia and H. Huang, *Org. Lett.*, 2011, **13**, 522.

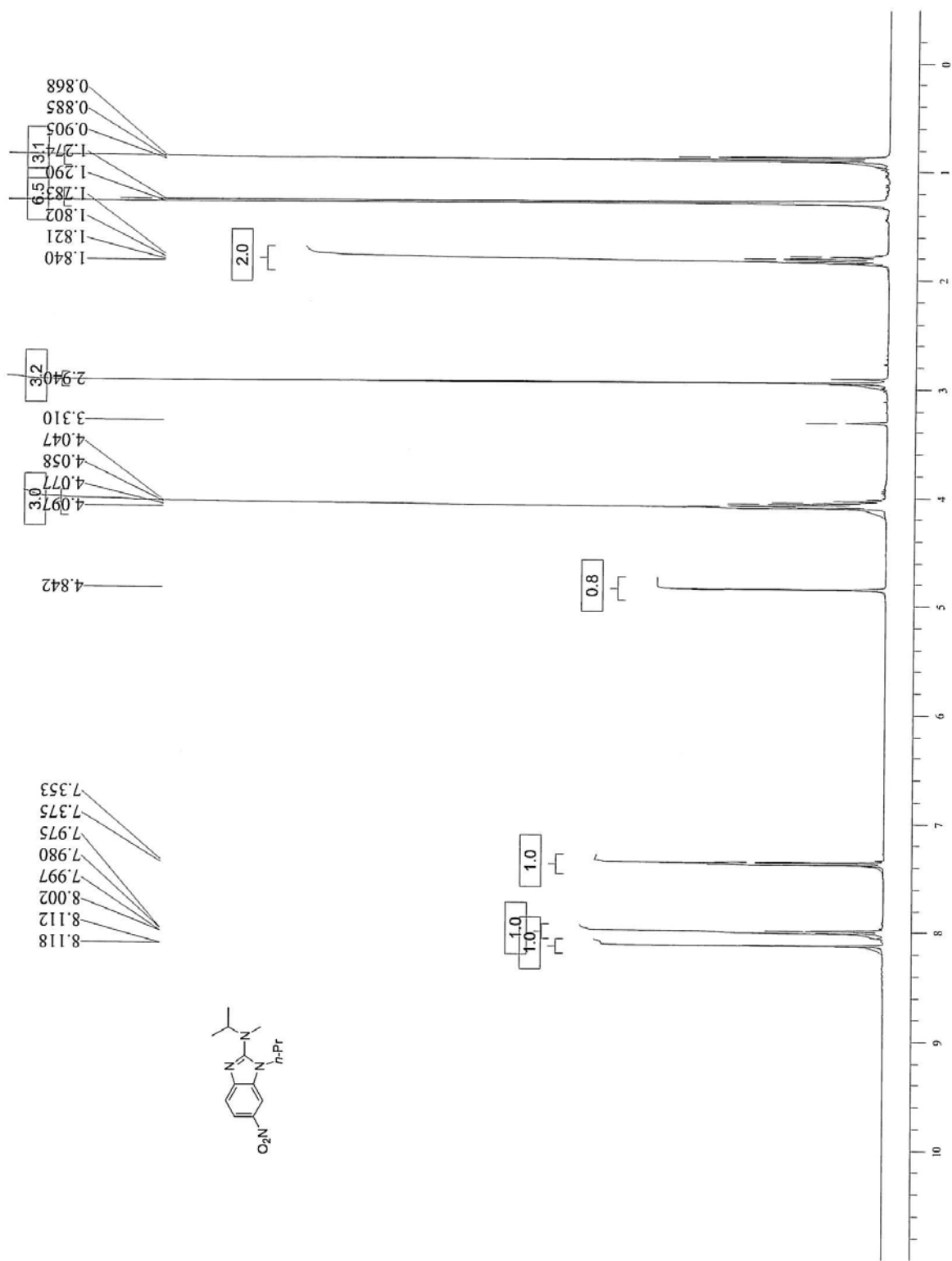
11.2, 11.1, 11.0; **IR** (neat): 2964, 1633, 1582, 1465 cm^{-1} ; **MS** (ESI^+): 471 ($\text{M}+\text{H}^+$); **HRMS** Calc. for $\text{C}_{26}\text{H}_{36}\text{N}_4\text{O}_2\text{Cl}$ ($\text{M}+\text{H}^+$): 471.2527; found: 471.2530.

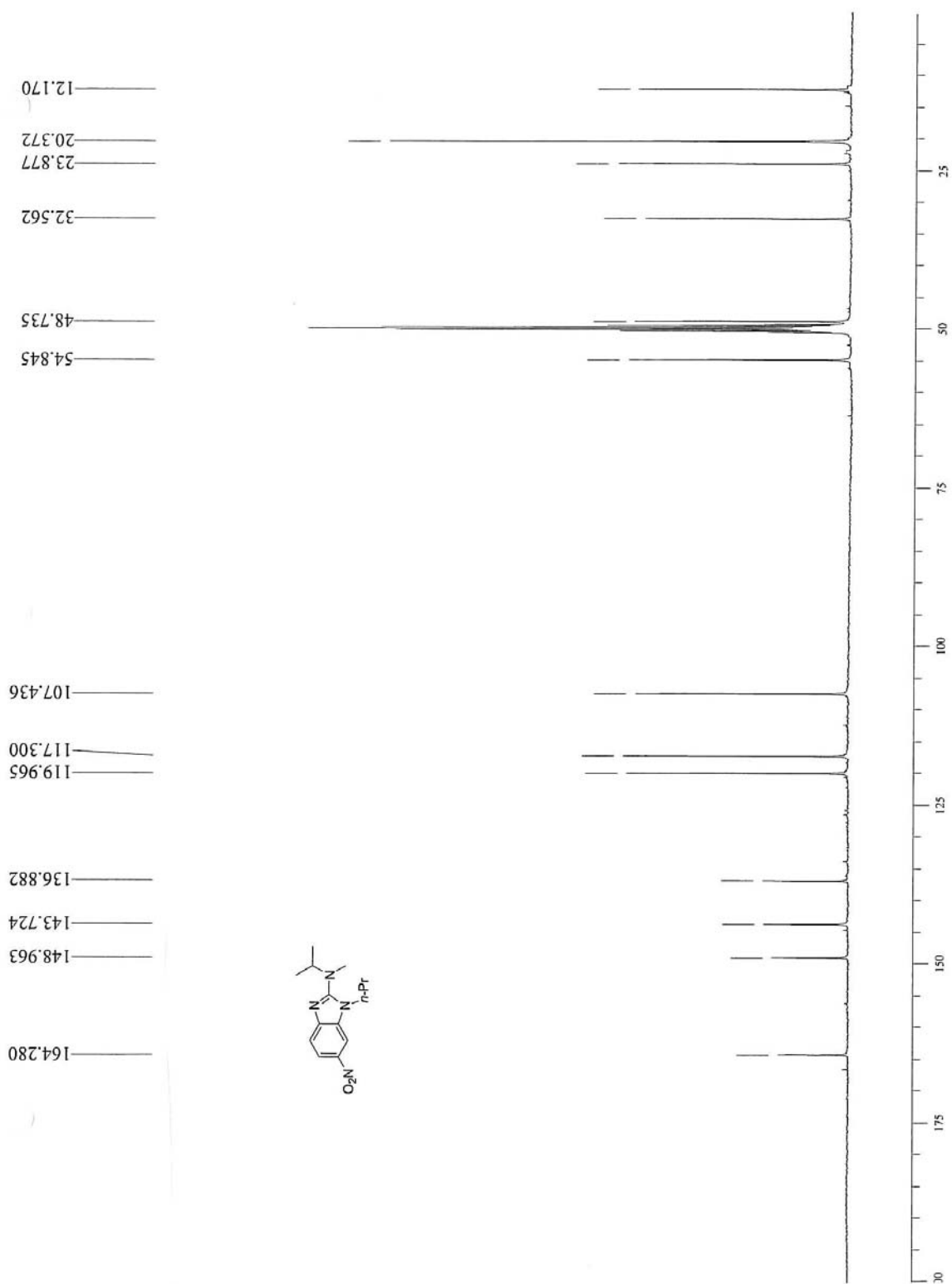


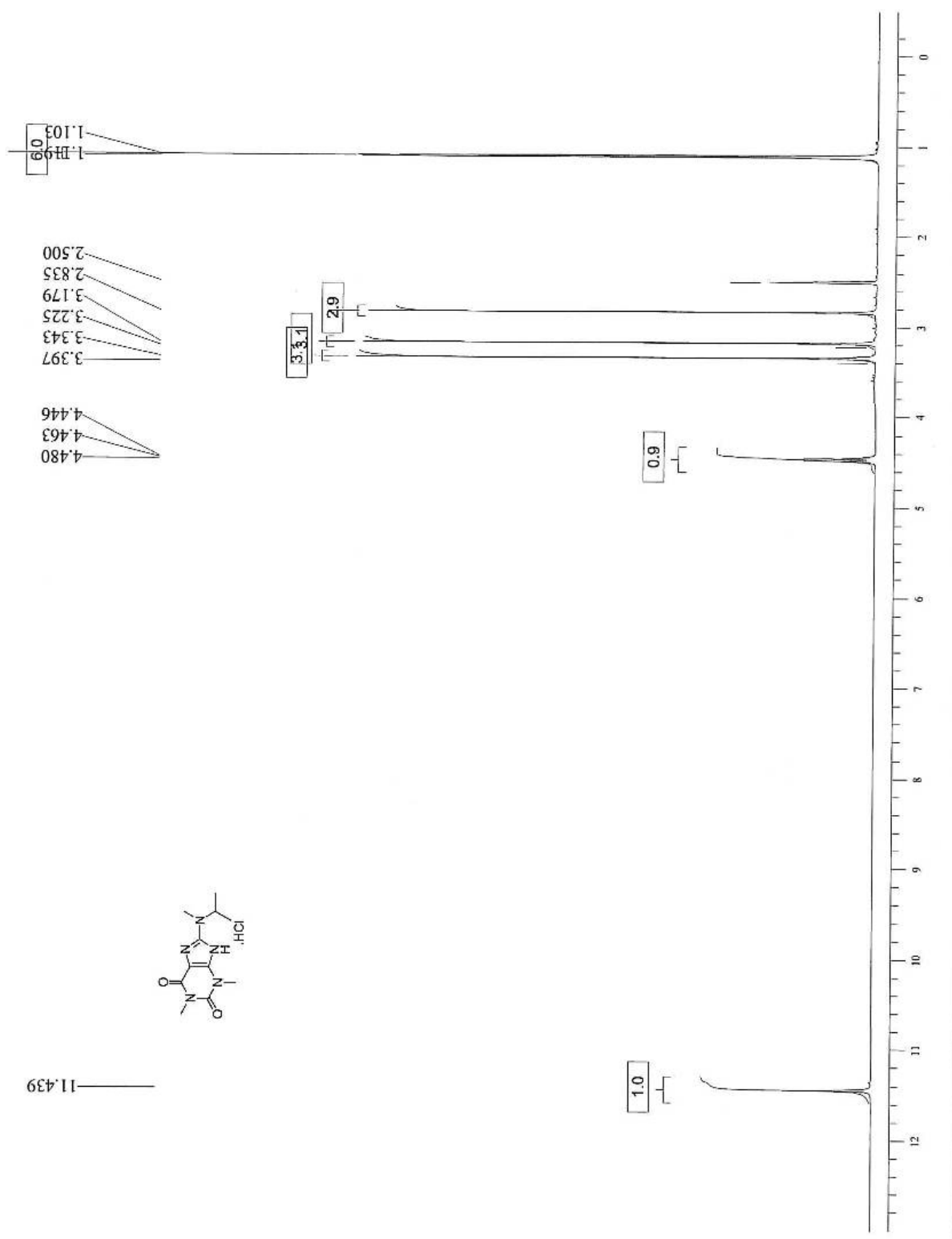


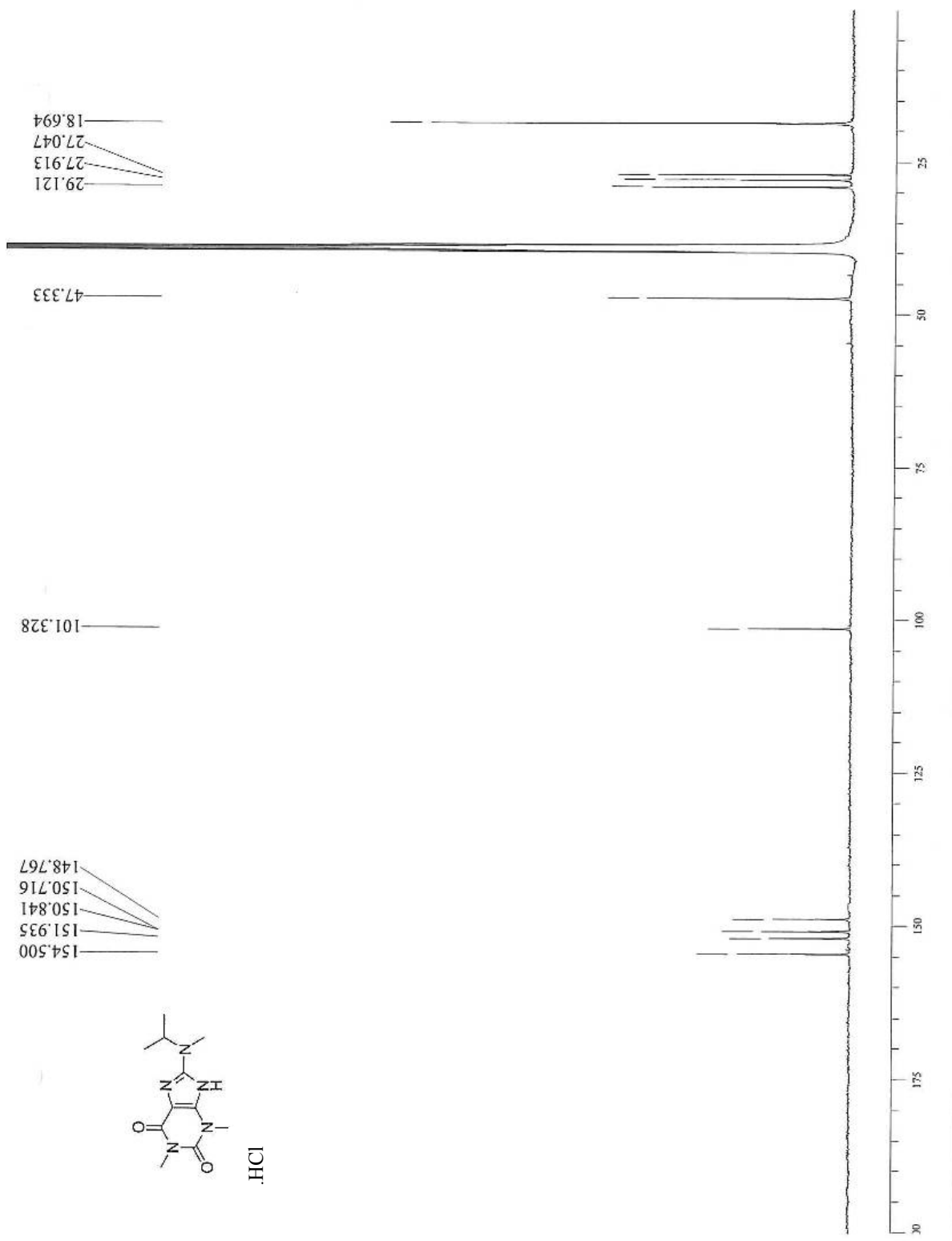


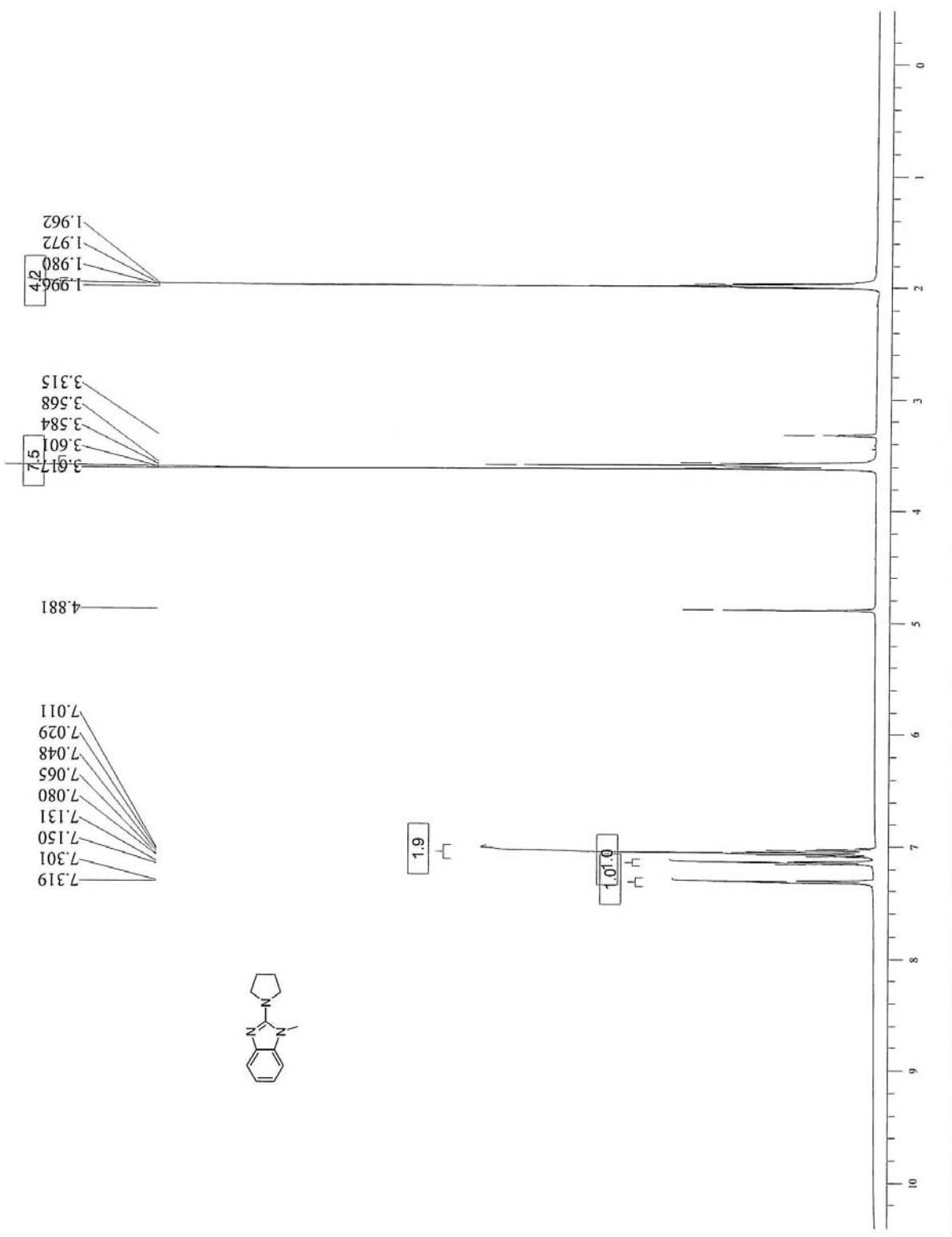


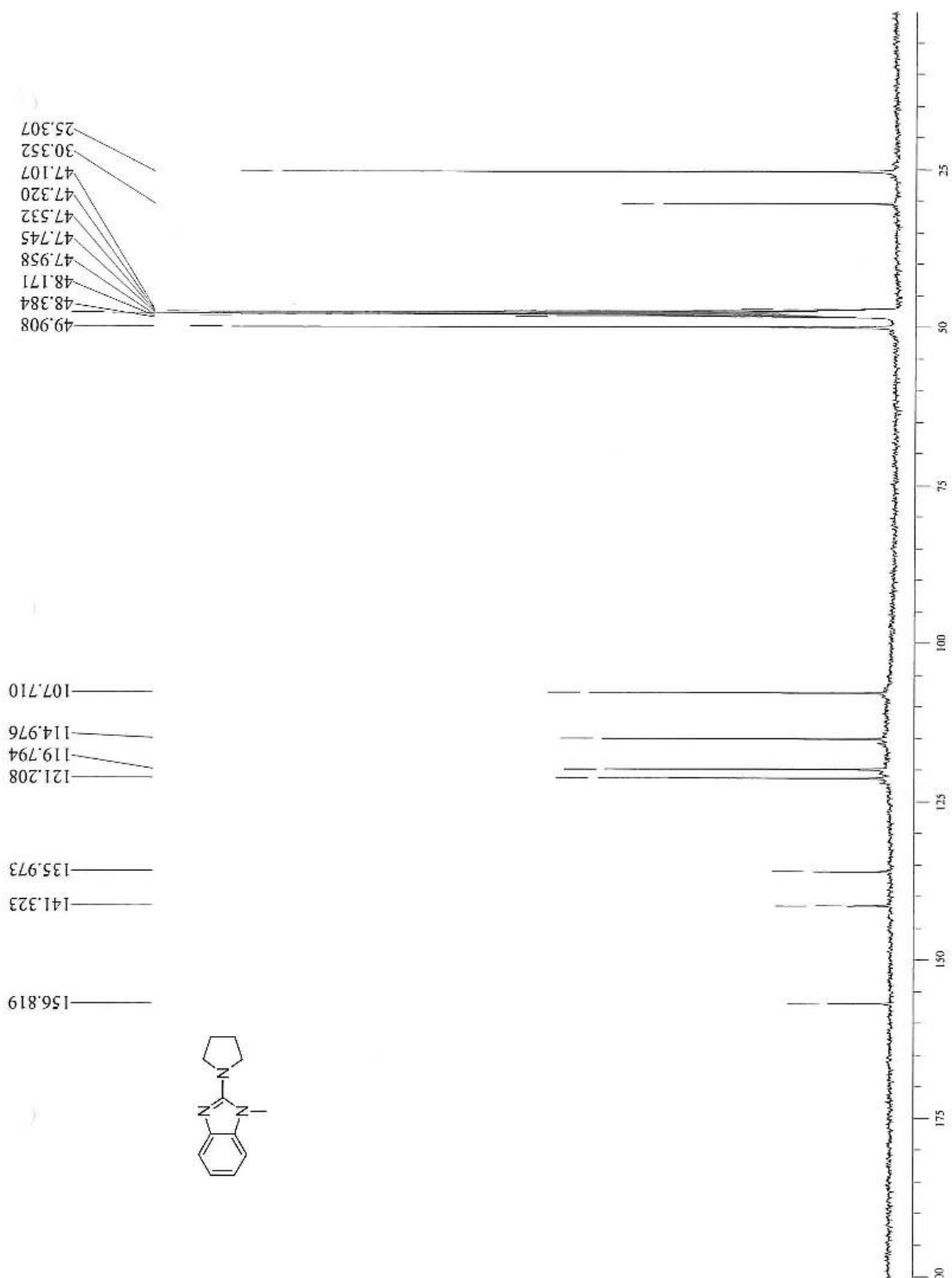


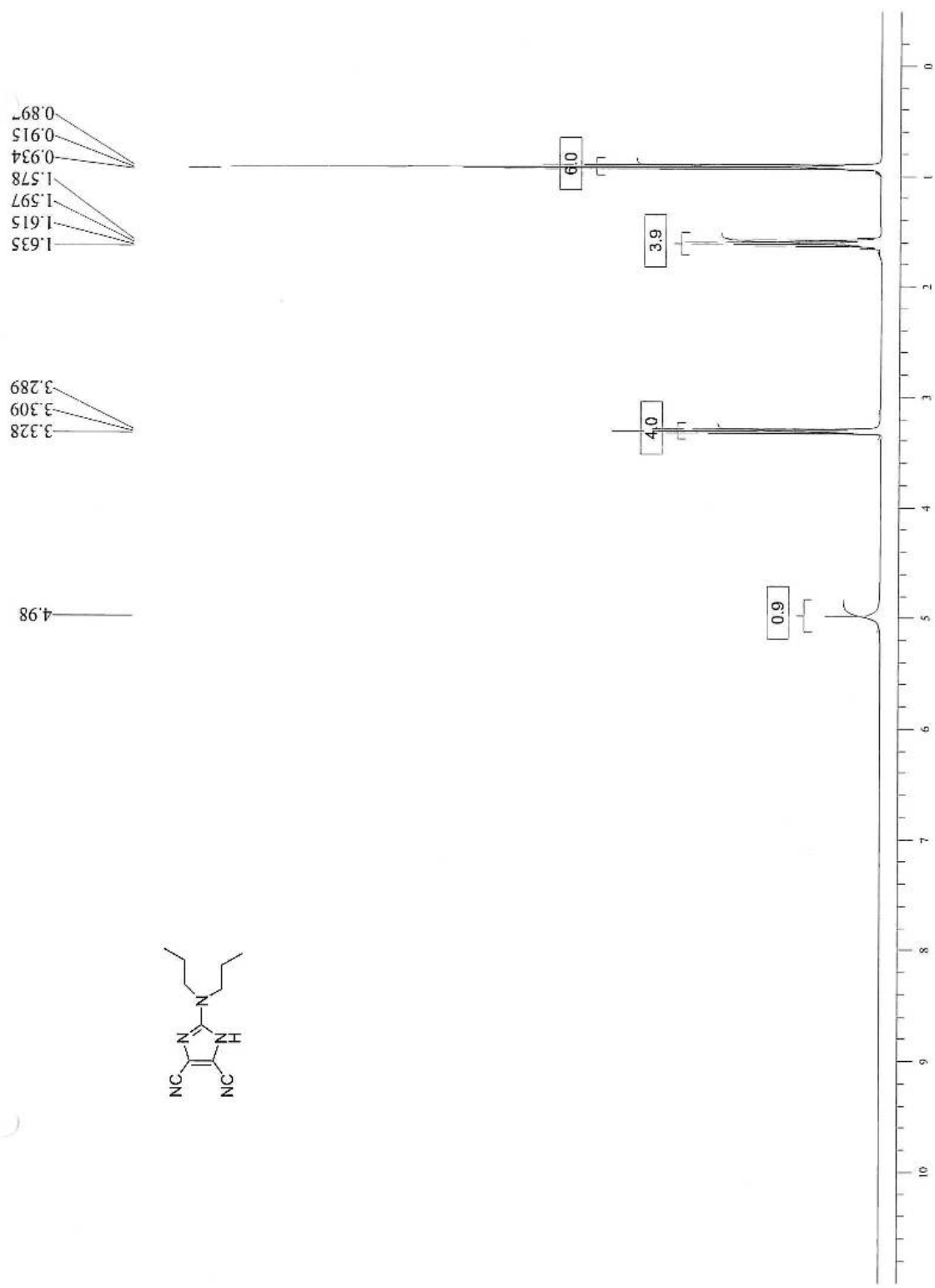


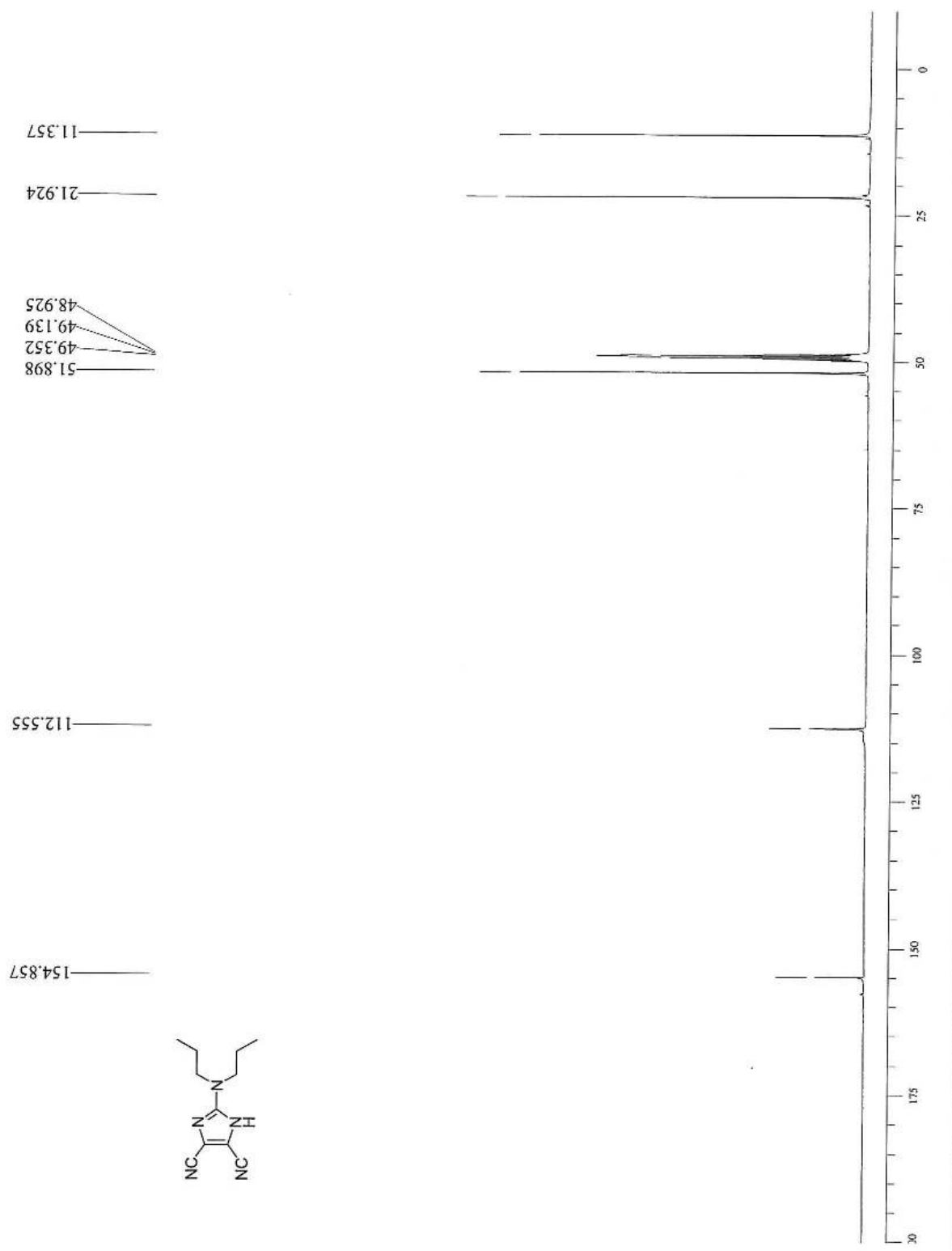






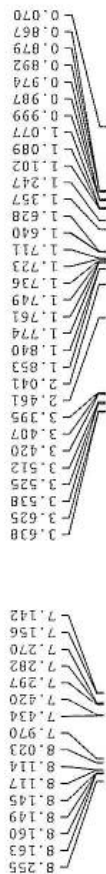






JOB NO: 11573
 ja11573 1 1

Andrez jean-Christophe JA-1068-41
 1D proton (sw=15ppm) cryoprobe

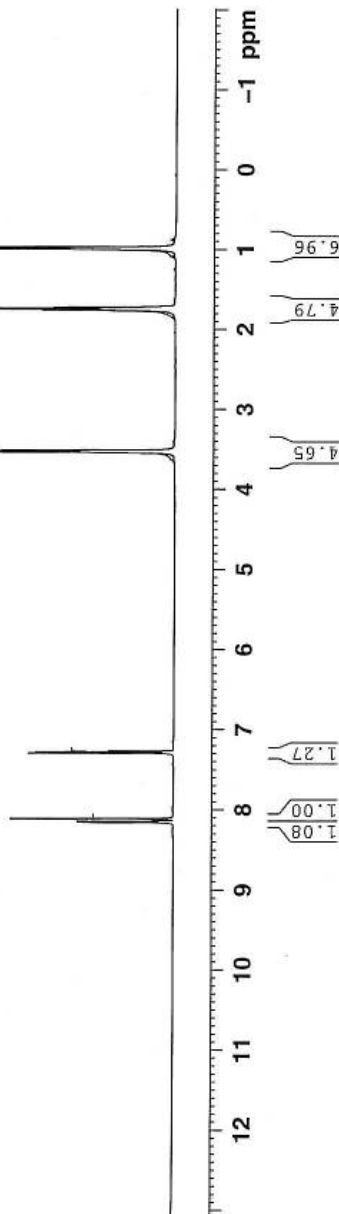


Current Data Parameters
 NAME aj11573
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080227
 Time 16:05
 INSTRUM av6002p
 PROHD 5 mm CPDCL 1H
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 34
 DS 4
 SFO1 600.153330 MHz
 FIDRES 0.276427 Hz
 AQ 1.8088988 sec
 RG 14.3
 DW 55.200 us
 DE 6.00 us
 TE 298.0 K
 T1 0.000000 sec
 T2 0.000000 sec
 MCREST 0.01500000 sec
 MCMRK 0.01500000 sec

***** CHANNEL F1 *****
 NUC1 1H
 P1 9.20 us
 PL1 3.50 dB
 SFO1 600.153330 MHz

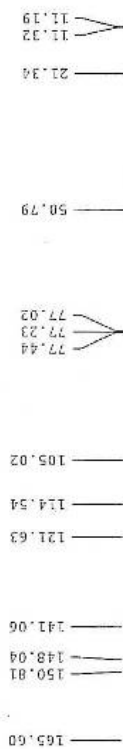
F2 - Processing parameters
 SI 32768
 SF 600.1500101 MHz
 MDW 0
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





JOB NO:11573
 aj11573 1 1

Andrez Jean-Christophe JA-1068-41
 1D C13SE(H) SW=250ppm D1=1s



```

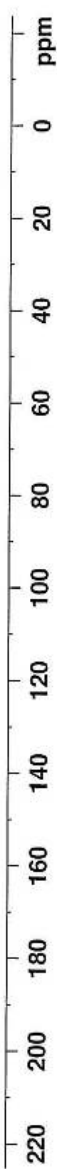
Current Data Parameters
NAME      aj11573
EXPNO    2
PROCNO   1

F1 - Acquisition Parameters
Date_    20080227
Time     18.30
PULPROG zgpg30
PROBHD   5 mm CPXI 1H
PULPROG2 carbon_90lineho_sp
TD       65536
SOLVENT  CDCl3
DS       324
SWH      37591.984 Hz
FIDRES   0.573619 Hz
AQ       0.8716921 sec
RG        317.500
SWH2     21779.000 Hz
DE       131.25 uSec
TE       298.0 K
D1       1.00000000 sec
d11      0.00000000 sec
d12      0.00000000 sec
d13      0.00000000 sec
d21      0.00081500 sec
DELTA    0.89999998 sec
INSTR    spect
PROCT    0.00000000 sec
HWDW    0.01500000 sec

===== CHANNEL f1 =====
NUC1     13C
P1       12.00 uSec
PL1      0.00 dB
PL12     -1.90 dB
SFO1     150.9239115 MHz
SFO2     600.1510000 MHz
SFOF13   0.00 Hz
SFOF13   0.00 Hz

===== CHANNEL f2 =====
CHRG2    wait=15
NUC2     13C
P2       12.00 uSec
PL2      0.00 dB
PL22     -1.90 dB
SFO2     150.9239115 MHz
SFOF13   0.00 Hz
SFOF13   0.00 Hz

===== Processing parameters
SI       32768
SF       150.9078150 MHz
RG        317.500
SSB      0
L3       0
GB       0
PC       1.40
    
```

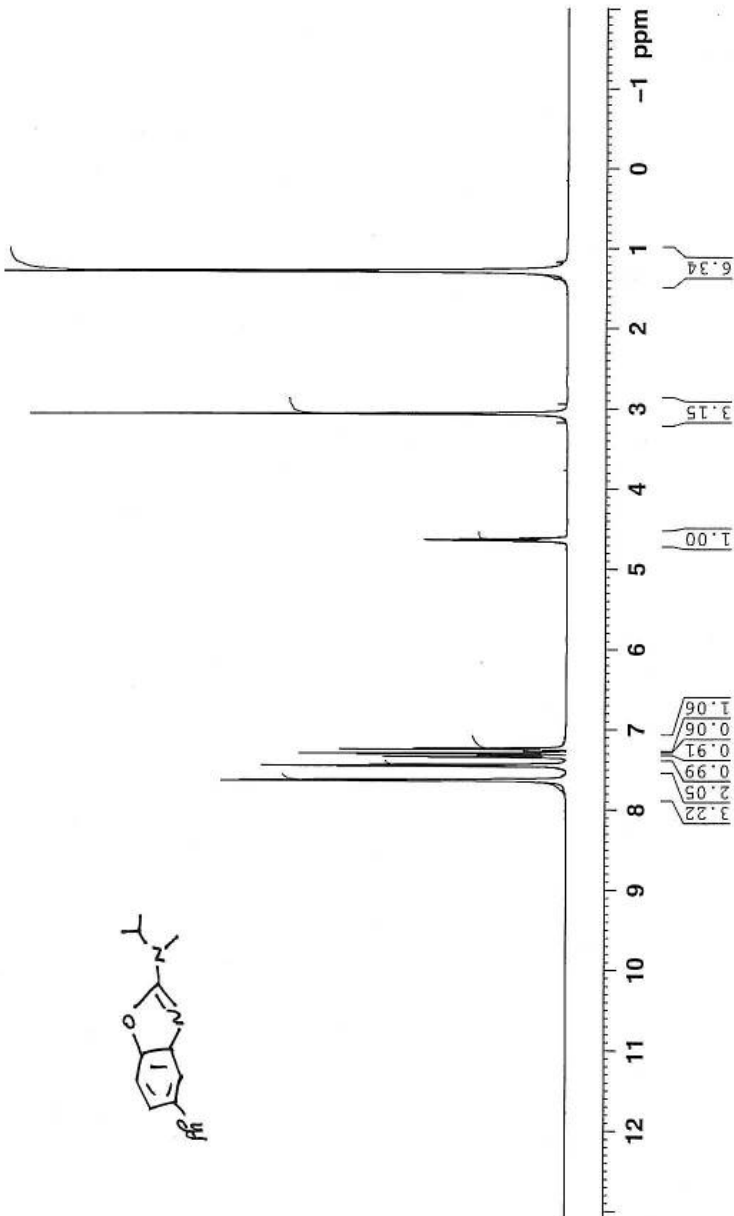




JOB NO: 11576 Andrez jean-Christophe JA-1068-42
 ja11576 1 1 1D proton (sw=15ppm) cryoprobe

7.759
7.756
7.751
7.636
7.634
7.627
7.625
7.622
7.588
7.573
7.501
7.499
7.489
7.486
7.457
7.445
7.431
7.375
7.347
7.335
7.323
7.307
7.294
7.270
7.264
7.263
7.245
7.242
7.231
7.228
7.203
7.200
7.188
7.167
4.667
4.656
4.645
4.634
4.622
4.611
4.600
3.171
3.059
3.009
2.939
1.437
1.385
1.373
1.283
1.271
1.174
1.162

Current Data Parameters
 NAME ej11576
 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameter
 Date_ 20080228
 Time 12:15
 INSTRUM av600
 PROBH 5 mm CPTCI LH
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 32
 DS 2
 SWH 8067.87 Hz
 FWHZ 0.276437 Hz
 AQ 1.806888 s
 RG 3.6
 DW 55.200 us
 DE 6.00 us
 TE 298.0 K
 D1 0.50000000 s
 DELT 0.10000000 s
 ACQRES 0.01500000 s
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 9.20 us
 PL1 3.50 dB
 SFO1 600.1533330 MHz
 F2 - Processing parameters
 SI 32768
 SF 600.1500101 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

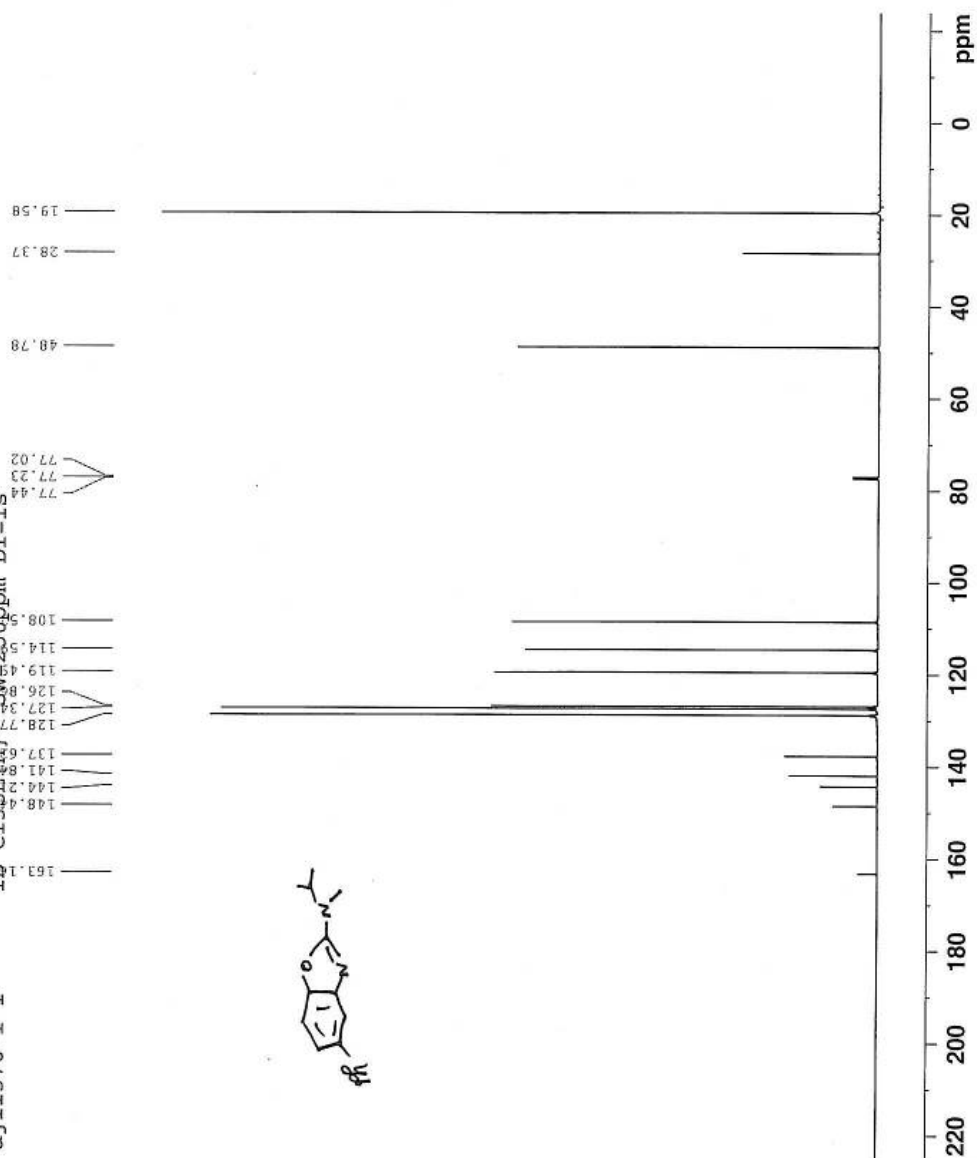




JOB NO: 11576
 aj11576 1 1

Andrez Jean-Christophe
 1D C13SE(H) SW=250ppm D1=1s

JA-1068-42



Current Data Parameters
 NAME aj11576
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080228
 Time 12.33
 Date_ 20080228
 PROBHD 5 mm CPXI 1H
 PULPROG carbon_spinnecho_dp
 TD 65536
 SOLVENT ccl13
 DS 32
 SC 4
 SWH 37593.984 Hz
 FIDRES 0.572639 Hz
 AQ 0.871621 sec
 R2 0.999999
 DM 13.300 usec
 DE 33.25 usec
 TE 298.0 K
 D1 0.000000 sec
 d11 0.0300000 sec
 D20 0.00000000 sec
 D21 0.00001500 sec
 DELTA 0.89999998 sec
 ACQOFF 0.00000000 sec
 KWPRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 13C
 PU 15.00 usec
 PB 2000.00 usec
 PL1 -1.90 dB
 SFO1 150.9230115 MHz
 SF 150.9230115 MHz
 SHAM13 Ctp60cmh14
 SFOFF13 0.00 Hz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 FCFD2 100.00 usec
 PL2 3.50 dB
 PL12 24.22 dB
 PL13 14.00 dB
 SFO2 600.1530000 MHz

F2 - Processing parameters
 SI 32768
 SF 150.9078072 MHz
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.40

JOB NO: 11575
 ja11575 I 1

Andrez jean-Christophe JA-1068-39
 1D proton (sw=15ppm) cryoprobe



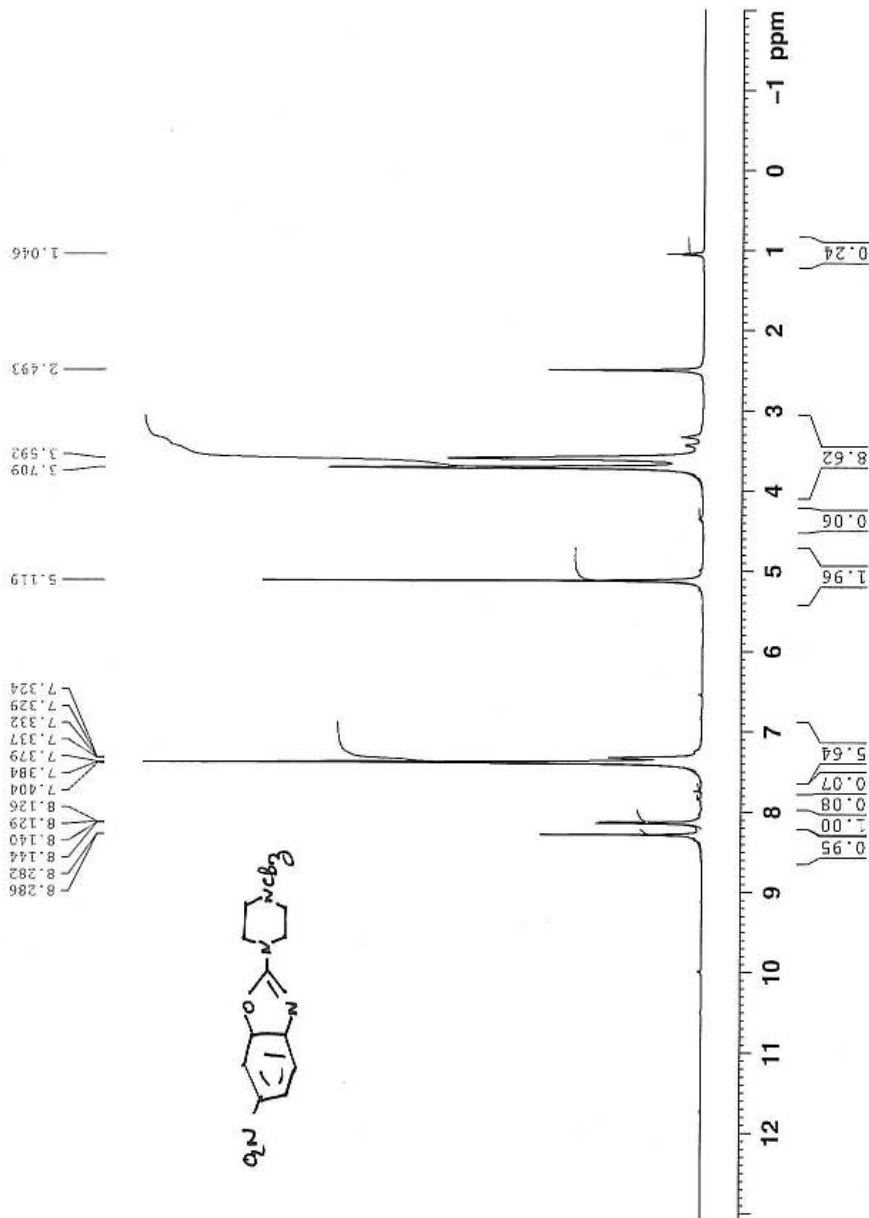
```

Current Data Parameters
NAME      aj11575
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20080228
Time     11:30
INSTRUM  spect
PROBHD   5 mm CPYCI 1H
PULPROG  zg30
TD       32768
SOLVENT  DMSO
NS       32
DS       2
DE       0.05791 Hz
AQ       0.276427 Hz
RG       1.868866 ss
RG       55.200 us
DE       6.00 us
TE       298.0 K
D1       0.50000000 ss
DELTA    0.10000000 ss
MCWEEK   0.01500000 ss

===== CHANNEL f1 =====
NUC1     1H
P1       9.20 us
PL1     -3.50 dB
SFO1    600.1533330 MHz

F2 - Processing Parameters
SI       32768
SF       600.1500101 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00
    
```

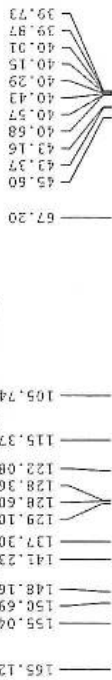




JOB NO: 11575
 aj11575 1 1

Andrez Jean-Christophe
 1D C13SE(H) SW=250ppm D1=1s

JJA-1068-39



```

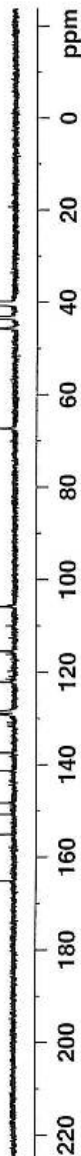
Current Data Parameters
NAME      aj11575
EXPNO    2
PROCNO   1

F2 - Acquisition Parameters
Date_    20080228
Time     12.03
INSTRUM  spect
PROBHD   5 mm CPYCI 1H
PULPROG  carbon_splanecho_sp
TD        65536
SOLVENT  CDCl3
NS        1000
DS        4
SWH       37593.964 Hz
FIDRES    0.573639 Hz
AQ         0.8775803 sec
RG         13.300 usec
DM         13.300 usec
DE         33.25 usec
TE         298.0 K
NUC1       13C
NUC2       15N
PCP002    0.0300000 sec
d11        0.0300000 sec
D20        0.0000000 sec
D21        0.00001500 sec
MELPA     0.6999998 sec
SFOFF1    0.0000000 sec
MCW001    0.0150000 sec
MCW002    0.0150000 sec

===== CHANNEL f1 =====
NUC1      13C
PCP001    15.00 usec
P8         2000.00 usec
PL1        -1.90 dB
SFO1      100.626115 MHz
SFO2      150.9230115 MHz
SFO3      150.9230115 MHz
SFO4      150.9230115 MHz
SFO5      150.9230115 MHz
SFO6      150.9230115 MHz
SFO7      150.9230115 MHz
SFO8      150.9230115 MHz
SFO9      150.9230115 MHz
SFO10     150.9230115 MHz
SFO11     150.9230115 MHz
SFO12     150.9230115 MHz
SFO13     150.9230115 MHz
SFOFF13   0.00 Hz

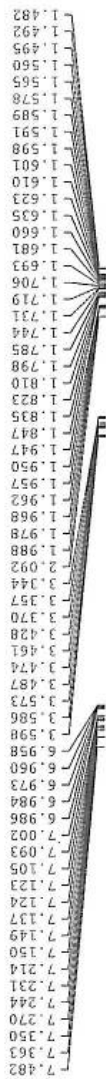
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       15N
PCP002    100.00 usec
PCPD2     3.50 dB
PL2        -1.90 dB
PL3        -1.90 dB
PL4        -1.90 dB
PL5        -1.90 dB
PL6        -1.90 dB
PL7        -1.90 dB
PL8        -1.90 dB
PL9        -1.90 dB
PL10       -1.90 dB
PL11       -1.90 dB
PL12       -1.90 dB
PL13       -1.90 dB
SFO2      600.15130000 MHz

F2 - Processing parameters
SI         32768
SF         150.9078127 MHz
WDW        EM
SSB        0
LB         2.00 Hz
GB         0
PC         1.40
    
```





JOB NO: 11574 Andrez jean-Christophe JA-1068-48
 ja11574 1 1 1D proton (sw=15ppm) cryoprobe



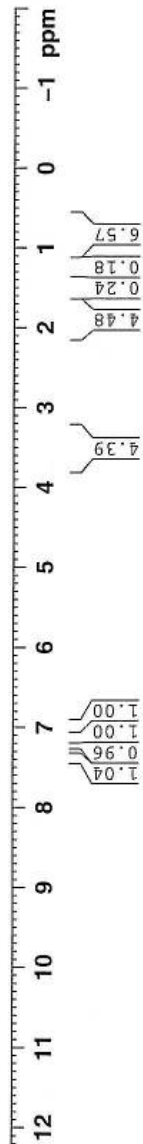
```

Current Data Parameters
NAME      aj11574
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20080227
Time      19:57
INSTRUM   av600cp
PROBHD    5 mm CPTCI 1H-
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         40
DS         4
SWH        9067.971 Hz
FIDRES     0.276627 Hz
AQ         1.8088988 s
RG         5.7
DE         55.200 us
TE         6.00 us
TD         298.0 K
MCREST     0.0000000 s
MCWEK      0.01500000 s

===== CHANNEL f1 =====
NUC1       1H
P1         9.20 us
PL1        3.50 dB
SFO1       600.1533330 MHz

F2 - Processing parameters
SI         32768
SF         600.1500101 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```

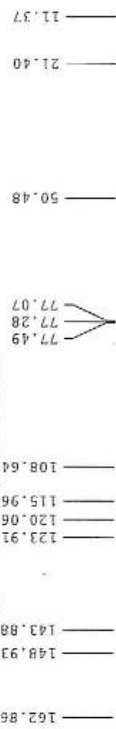




JA-1068-48

Andrez Jean-Christophe
 1D C13SE(H) SW=250ppm D1=1s

JOB NO:11574
 aj11574 1 1



```

Current Data Parameters
NAME      aj11574
EXPNO    2
PROCNO   1

F2 - Acquisition Parameters
Date_    20080227
Time     18.58
PROBHD   5 mm CPVT 1H
PULPROG  carbon_90incho_90
TD        65536
SOLVENT  CDCl3
DS        4
SWH       37593.984 Hz
FIDRES    0.573619 Hz
AQ         0.8716921 sec
RG         327.500
DW         13.100 usec
DE         13.25 usec
TE         298.0 K
NUC1       13C
NUC2       1H
P1         15.00 usec
P2         15.00 usec
P3         2000.00 usec
PL1        -1.90 dB
PL2        -1.90 dB
SFO1       150.9230115 MHz
SFO2       600.1510000 MHz
SPNAM13   Crp60cmz
SFOFF13    0.00 Hz

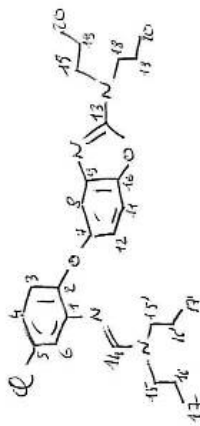
===== CHANNEL f1 =====
NUC1       13C
NUC2       1H
P1         15.00 usec
P2         15.00 usec
P3         2000.00 usec
PL1        -1.90 dB
PL2        -1.90 dB
SFO1       150.9230115 MHz
SFO2       600.1510000 MHz
SPNAM13   Crp60cmz
SFOFF13    0.00 Hz

===== CHANNEL f2 =====
NUC1       13C
NUC2       1H
P1         15.00 usec
P2         15.00 usec
P3         2000.00 usec
PL1        -1.90 dB
PL2        -1.90 dB
SFO1       150.9230115 MHz
SFO2       600.1510000 MHz
SPNAM13   Crp60cmz
SFOFF13    0.00 Hz

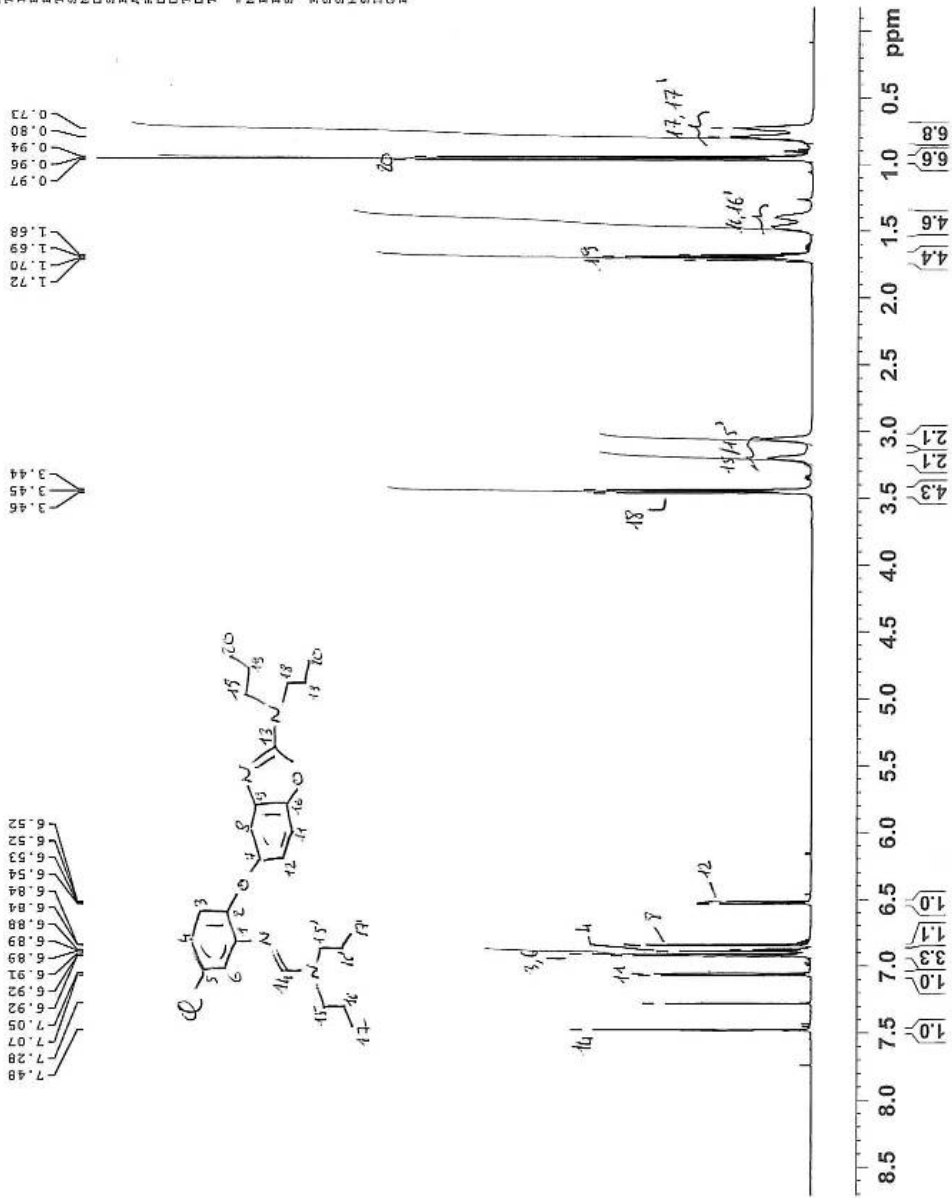
F2 - Processing parameters
SI         32768
SF         150.9078122 MHz
WDW        EM
SSB        0
LB         2.00 Hz
GB         0
PC         1.40
    
```

1H JA-1068-45-2 in l3
 T=298K
 SFU Bruker AvanceII 600 Cryoprobe QNP
 26 Feb 2008

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7.12
7.10
7.08
7.06
7.04
7.02
7.00
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6.96
6.94
6.92
6.90
6.88
6.86
6.84
6.82
6.80
6.78
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6.74
6.72
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1.00
0.98
0.96
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0.26
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0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00



Current Data Parameters
 NAME JA-1068-45-2
 EXPR0 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20080226
 Time_ 15:34
 INSTRUM spect
 PROBR0 5 mm CPQNP SWH
 PFR000 9930
 TD0 65536
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 8417.650 Hz
 FIDRES 0.124602 Hz
 AQ 3.8571296 sec
 RG 11.3
 DW 59.400 usec
 DE 2.00 usec
 TE 298.2 K
 D1 10.0000000 sec
 TD0 1
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 15.30 usec
 PL 0.00 dB
 SFO1 600.1336000 MHz
 F2 - Processing parameters
 SI 32768
 SF 600.1300000 MHz
 EQ EM
 NR 3
 SSB 0
 GB 0
 PC 1.00





13C of JA-1068-45-2 in CDCl3
 T=298K
 SFU Bruker Avance 600 MHz QNP Cryoprobe
 26 Feb 2008

Current Data Parameters
 NAME JA-1068-45-2
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080227
 Time 17.47
 INSTRUM spect
 PROBHD 5 mm CPQNP Swi
 PULPROG zgpg
 TD 131072
 SOLVENT CDCl3
 NS 2048
 DS 0
 SWH 36057.691 Hz
 FIDRES 0.275098 Hz
 AQ 1.8175818 sec
 RG 256
 DW 13.867 usec
 DE 20.14 usec
 TE 298.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 11.50 usec
 PL1 5.00 dB
 SFO1 150.9178988 MHz

===== CHANNEL f2 =====
 CPDPRG2 waitz16
 NUC2 1H
 PCPD2 70.00 usec
 PL12 16.87 dB
 PL13 19.97 dB
 PL2 4.00 dB
 SFO2 600.1324005 MHz

F2 - Processing parameters
 SI 65536
 SF 150.9028090 MHz
 MDW 0
 EM 0
 LB 1.00 Hz
 GB 0
 PC 1.40

