universität wien

DIPLOMARBEIT

Titel der Diplomarbeit

SYNTHESE HETEROCYCLISCHER ANALOGA VON XANTHIONEN

Verfasserin

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angestrebter akademischer Grad

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Meinem Betreuer Herrn Ao. Univ.-Prof. Dipl.-Ing. Dr. techn. Wolfgang Holzer möchte ich sehr herzlich für die kompetente fachliche Unterstützung während der praktischen Arbeit und beim Verfassen der Diplomarbeit sowie für die Aufnahme einer Vielzahl von NMR-Spektren danken.

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Weiters gilt mein Dank:

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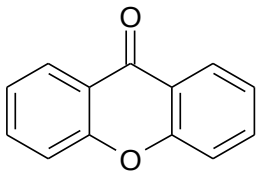
I N H A L T S V E R Z E I C H N I S :

1. EINLEITUNG UND PROBLEMSTELLUNG

1.1 Bedeutung von Xanthon-Derivaten in der pharmazeutischen Chemie

Chemische Xanthone sind heterocyclische Verbindungen mit einem Dibenzo-γ-pyron-Grundgerüst[1] **(I)** (Schema 1). In der Natur findet man Xanthon-Derivate besonders in 2 Pflanzenfamilien, den Gentianaceae und Guttiferae, aber sie kommen auch in einigen Pilzen und Flechtenarten vor.[2] Das Xanthon-Ringsystem ist in vielen Bereichen der medizinischen Chemie von großem Interesse, da dieses planare, tricyclische System als Grundgerüst in einer Vielzahl natürlicher und synthetischer biologisch aktiver Moleküle vorkommt. [3,4]

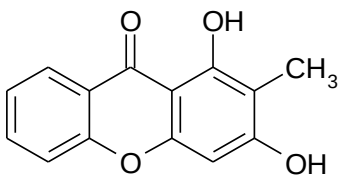
Schema 1.



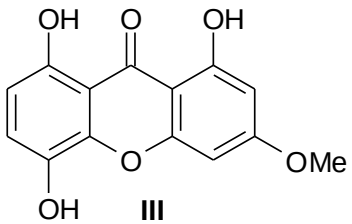
I

So gibt es zum Beispiel Xanthon-Derivate, die als selektive und reversible Monoaminooxidase-A-Hemmer[5,6] **(II**, Bellidifolin **III)** wirken (Schema 2). Das Enzym Monoaminooxidase (MAO) spielt eine Schlüsselrolle bei der Regulierung von Adrenalin und Noradrenalin und ist Angriffspunkt für einige Antidepressiva.[7]

Schema 2.



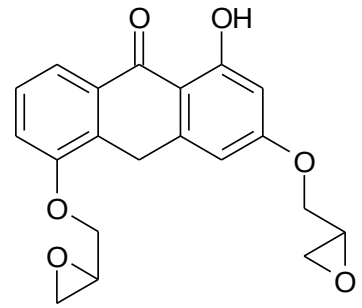
II



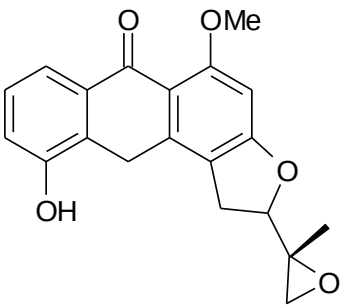
III

Andere Derivate mit substituierten 2,3-Epoxypropoxy-Gruppen in Position 3 und 5 (**IV**)[8] zeigen cytotoxische Effekte gegen verschiedene Krebszelllinien durch Hemmung der Topoisomerase II. Unter diesen Verbindungen findet sich das natürlich vorkommende Dihydrofuranoxanthon-Epoxid Psorospermin (**V**).[9] (Schema 3)

Schema 3.



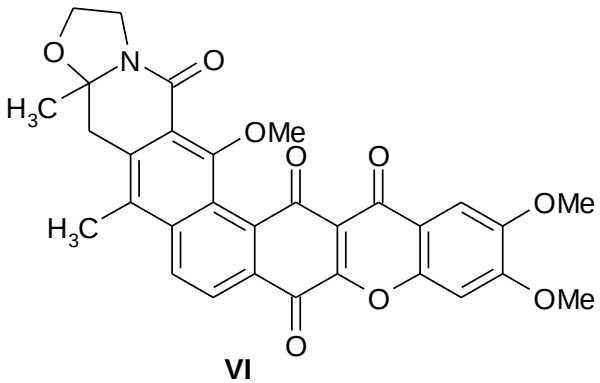
IV



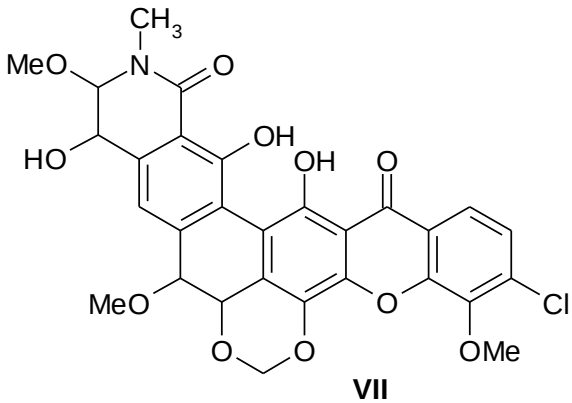
V

Weitere Vertreter mit Xanthon-Partialstruktur sind Cervinomycin (**VI**) und Lysolipin (**VII**) (Schema 4), die beide antibiotische Aktivität aufweisen. Cervinomycin A_1 und A_2 sind potenzielle Antibiotika gegen Anaerobier und Mycoplasmen.[10] Lysolipin, ein anelliertes, monochloriertes Xanthon, wirkt stark antibiotisch gegen grampositive Bakterien, indem es in die Zellwandbiosynthese der Bakterien eingreift und weist zudem Antitumorwirkung gegen verschiedene Krebszelllinien auf.[11, 12]

Schema 4.



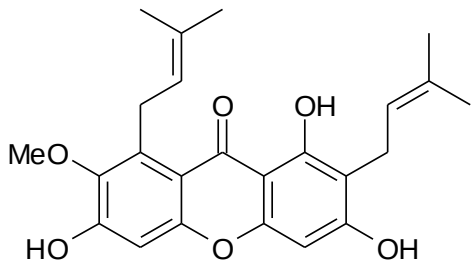
VI



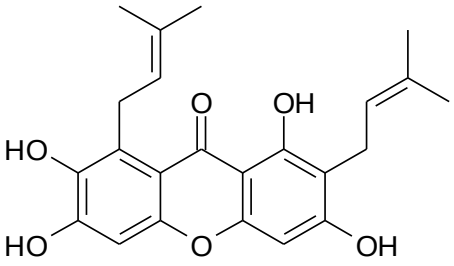
VII

Xanthon-Derivate aus der Pflanze Garcinia mangostana (Guttiferae) wie zum Beispiel α- und γ-Mangostin (**VIII** und **IX**) weisen antioxidative Eigenschaften auf.[13] Außerdem konnte antiinflammatorische Aktivität von γ-Mangostin, einem tetraoxigenierten, diprenylierten Xanthon-Derivat, durch direkte Hemmung der Cyclooxigenase nachgewiesen werden.[14] (Schema 5)

Schema 5.



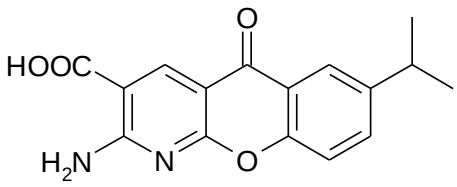
VIII



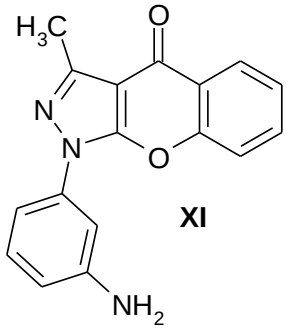
IX

Des Weiteren gibt es verschiedene ‚Xanthon-Derivate', bei denen ein oder beide Benzol-Ring(e) der Stammverbindung durch heteroaromatische Systeme ersetzt worden sind. Unter diesen finden sich einige bioaktive Verbindungen, z. B. der neue Wirkstoff Amlexanox[15] (Aphthasol ®) **(X)**, welcher antiinflammatorische und antiallergische Eigenschaften aufweist. Amlexanox wird zur Behandlung von Aphten und Mundschleimhautulzera, Asthma bronchiale sowie Rhinits allergica verwendet.[16] Ein weiteres Beispiel für eine bioaktive Verbindung ähnlichen Typs ist der A_2-Subtyp spezifische Adenosin-Rezeptor-Antagonist A [17] **(XI)**, bei dem ein Benzolring des Xanthons durch ein substituiertes Pyrazol-System ersetzt ist. (Schema 6)

Schema 6.



X

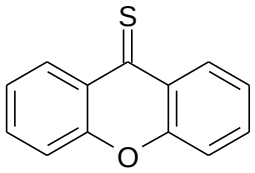


XI

1.2. Synthese von Thioanaloga

Die Synthese der Thioanaloga von Ketonen, Lactonen, Amiden, Estern sowie Flavonen, Isoflavonen und Xanthonen ist von nennenswertem Interesse aufgrund ihrer Bedeutung in Bereichen der Biologie und Phytochemie sowie ihrer Verwendung als Präcursoren zur Herstellung verschiedener synthetischer, organischen Verbindungen. [18,19] Das entsprechende Thioanalogon des Xanthons ist das in Schema 7 angeführte Xanthion **(XII)**.

Schema 7.



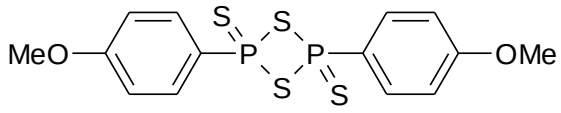
XII

Zur Überführung einer Carbonylfunktion in ihr entsprechendes Thioanalogon können verschiedene Reagenzien zur Anwendung kommen, unter ihnen Phosphorpentasulfid ($P_2S_5 = P_4S_{10}$)[20] sowie das Lawesson-Reagens **(XIII)** (Schema 8).[21]

Es gibt zudem eine Reihe anderer Thionierungsmöglichkeiten, z. B. mit Natriumhydrogensulfit, über Säure-katalysierte Reaktionen mit Hydrogensulfid, oder Herstellung von aromatischen Thioketonen über Friedel-Crafts-Reaktion mit Thiophosgen ($CSCl_2$).[22]

Lawesson-Reagens, LR, [2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiaphosphetan-2,4-disulfid], ist ein mildes und kommerziell erhältliches Agens zur Thionierung von Ketonen, Estern, Amiden und vielen weiteren funktionellen Gruppen.[23,24]

Schema 8.



XIII

Als sehr effizientes Thionierungsreagens erzielt man damit exzellente Ausbeuten und die einfache Handhabung, leichte Isolierung aus dem Reaktionsgemisch sowie die Eignung für milde Thionierungsreaktionen machen es zu einem beliebten Reagens in der organischen Synthese.[25, 26]

Die Reaktionen mit Phosphorpentasulfid (P_2S_5 = P_4S_{10}) werden normalerweise in kochendem Toluol, Xylol oder Pyridin durchgeführt[27] und benötigen große Mengen an Reagens. Außerdem sind die Reaktionszeiten länger, die Ausbeuten sind für gewöhnlich geringer und zudem schwankend.[28] Darum ist LR dem Phosphorpentasulfid überlegen.[29]

Lawesson-Reagens kann entweder aus der Reaktion von Anisol mit Phosphorpentasulfid (150°C, 6h) gewonnen werden oder aus Anisol mit rotem Phosphor und elementarem Schwefel beziehungsweise kann auch kommerziell erworben werden.[30]

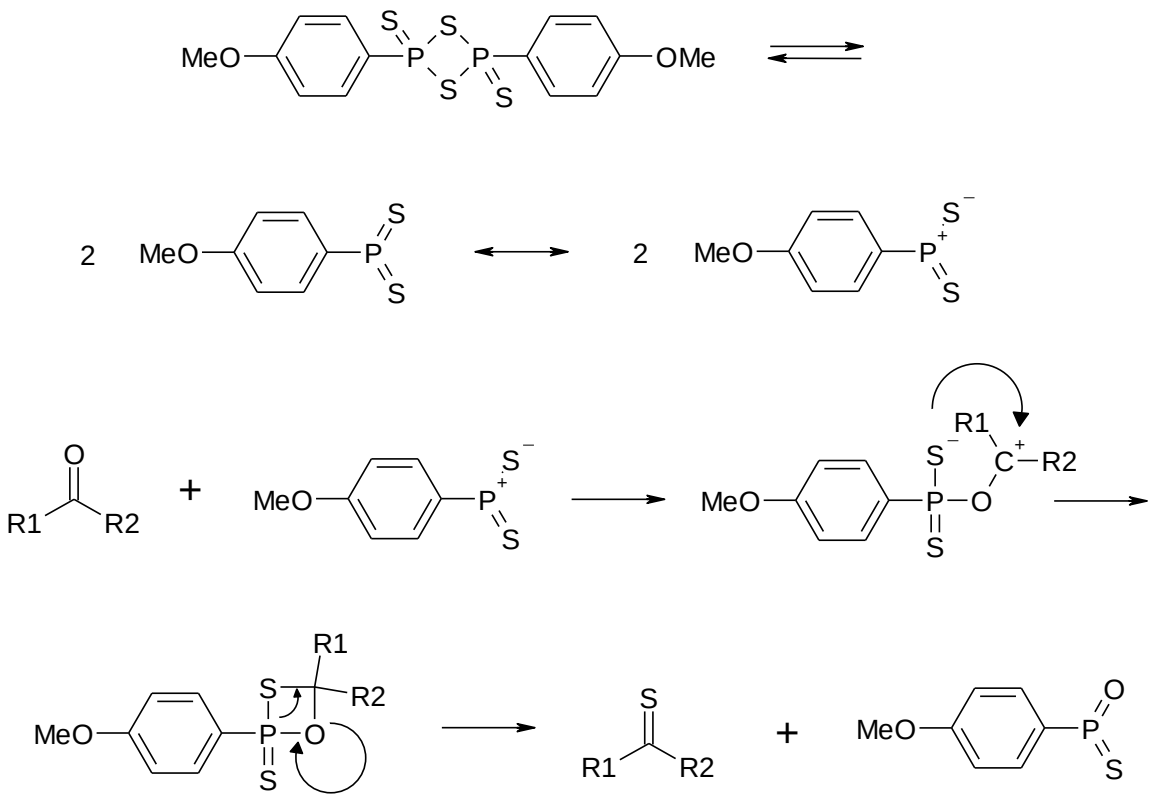
Es ist in Lösung bei Temperaturen über 110°C instabil und zersetzt sich langsam.[31]

Generell reagieren aromatische und aliphatische Ketone mit Lawesson-Reagens in kochendem Toluol oder Benzol bei durchschnittlich 110°C unter Rückfluss.[32] Eine weitere erfolgreich beschriebene Methode ist die schnelle und lösungsmittelfreie Mikrowellen-Reaktion, bei der die Substrate mit LR gemischt und dann in unter Einfluss von Mikrowellen-Strahlung miteinander reagieren.[33, 34]

Der Mechanismen für Thionierungsreaktionen mit Lawesson-Reagens wird im Folgenden behandelt. (Schema 9) Das LR steht in Lösung im Gleichgewicht mit dem

reaktiveren Dithiophosphin-Ylid. Die Reaktion mit einer Carbonyl-Gruppe führt zur Bildung eines Thiaoxaphosphetans, Triebkraft der Reaktion ist die Bildung einer stabilen P=O-Bindung in einer Ringöffnung, die dem Mechanismus der Wittig-Reaktion ähnelt.[35]

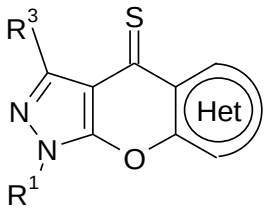
Schema 9.



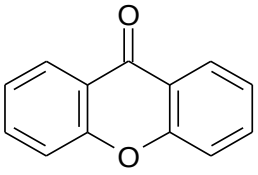
1.3. Problemstellung

Im Rahmen der vorliegenden Diplomarbeit sollten Untersuchungen zur Synthese kondensierter, polycyclischer Systeme mit [5,6]Pyrano[2,3-c]pyrazol-4(1*H*)thion-Partialstruktur angestellt werden. Diese tri- und tetracyclischen Verbindungen mit Pyrazol-Partialstruktur können als heterocyclische Thioanaloga des Xanthons[36] gesehen werden, bei denen einer der Benzolringe des Xanthon-Grundgerüsts durch ein Pyrazol-System und der andere durch verschiedene heteroaromatische Gruppen ersetzt wurde. (Schema 10)

Schema 10. Zielverbindungen und Vergleich mit Xanthon



Zielverbindungen



Xanthon

Als Ausgangsverbindungen für diese Thioanaloga wurden verschiedene [5,6]Pyrano[2,3-c]pyrazol-4(1*H*)-one verwendet, die im Zuge früherer Untersuchungen - ausgerichtet auf die Synthese neuer heterocyclischer Verbindungen als bioaktive Komponenten - hergestellt wurden. Unter ihnen befinden sich Systeme mit einem anellierten Pyridin (alle Isomere), einem Chinolin, einem Thiophen (alle Isomere), einem Benzo[*b*]thiophen und einem Thieno[2,3-*b*]thiophen als Heterocyclus am γ-Pyranon-Ring.[37,38,39]

Ziel der Diplomarbeit war nun die Synthese von Thioanaloga der oben genannten Verbindungen mittels Umwandlung des Pyran-4-ons in das entsprechende Pyran-4-thion. Konkret handelt es sich bei den Zielverbindungen um 3-Methyl-1-phenylpyrazolo[4´,3´:5,6]pyrano[3,2-*b*]pyridin-4(1*H*)thione **5a-d** (alle Isomere), 3-Methyl-1-phenylthieno[2´,3´:5,6]pyrano[2,3-*c*]pyrazol-4(1*H*)thione **5e-g** (alle Isomere),

3-Methyl-1-phenylpyrazolo[4´,3´:5,6]pyrazo[2,3-*b*]chinolin-4(1*H*)thion **5h**,

3-Methyl-1-phenyl[1]benzothieno[2´,3´:5,6]pyrano[2,3-*c*]pyrazol-4(*1H*)thion **5i** und

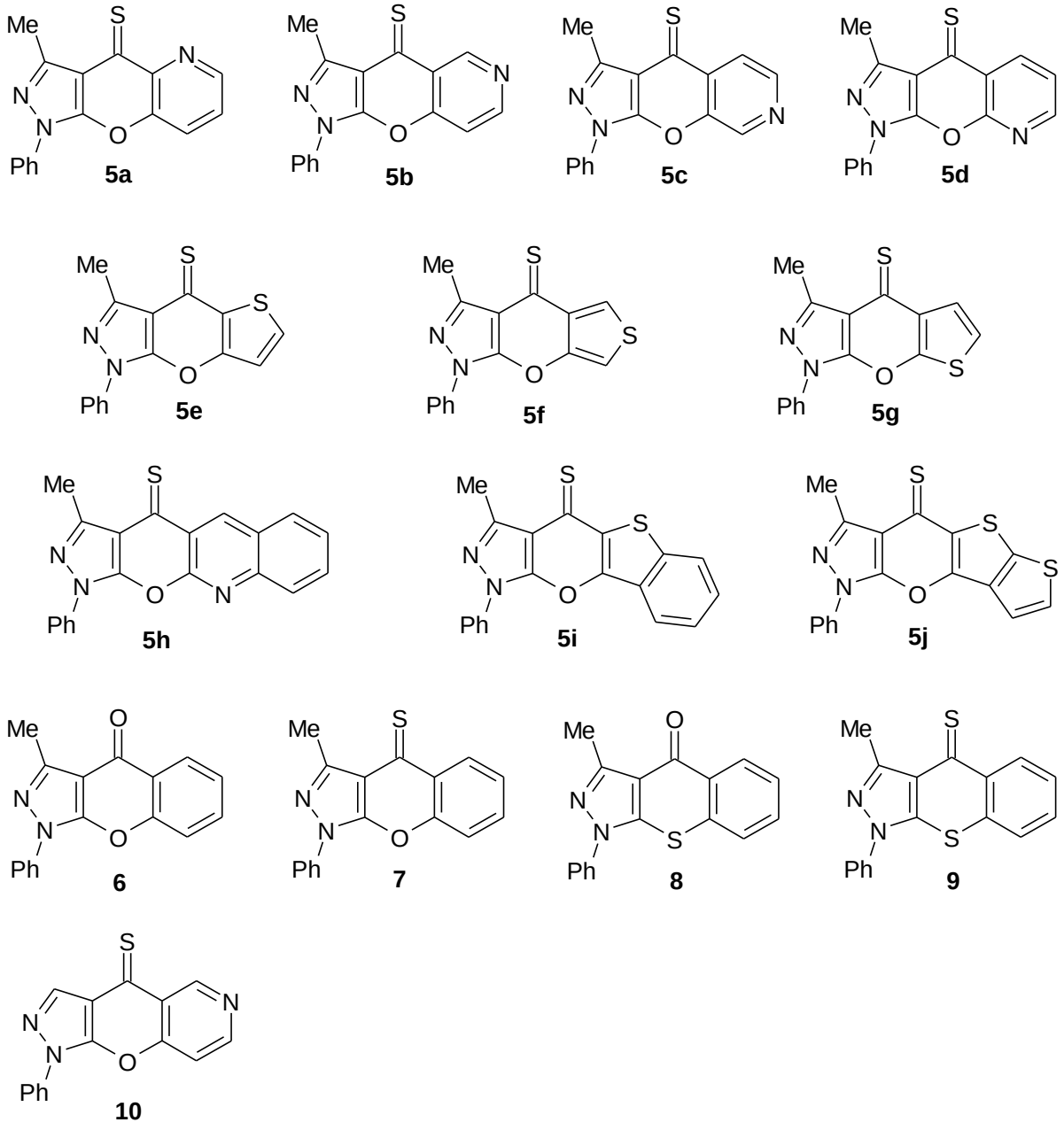
3-Methyl-1-phenylthieno[3´´,2´´:4´,5]´thieno[2´,3´:5,6]pyrano[2,3-*c*]pyrazol-4(1*H*)thion **5j**

sowie 1-Phenylpyrazolo[4´,3´:5,6]pyrano[3,2-*c*]pyridin-4(1*H*)thion **10**.

Weiters sollten zu Vergleichzwecken 3-Methyl-1-phenylchromeno[2,3-*c*]pyrazol-4(1*H*)thion **7** und 3-Methyl-1-phenylthiochromeno[2,3-*c*]pyrazol-4(1*H*)thion **9** aus

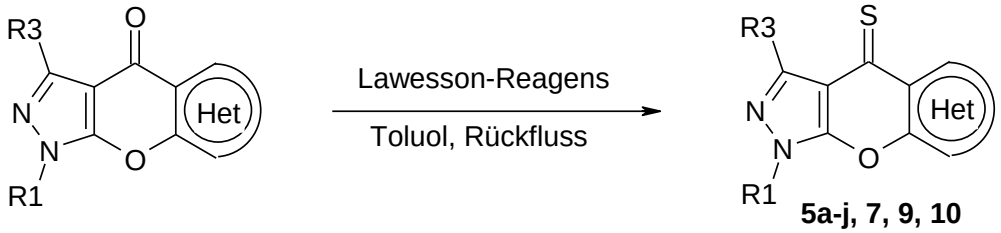
ihren entsprechenden Oxo-Systemen **6** und **8** hergestellt werden (Schema 11), wobei die Synthese von **6**[40,41] bzw. **8**[42] in Anlehnung an literaturbekannten Methoden erfolgen sollte.

Schema 11.



Die Umsetzung der Ketone in die entsprechenden Thioketone sollte jeweils durch Behandlung mit Lawesson-Reagens in siedendem Toluol erfolgen. (Schema 12)

Schema 12.


R3
O
N
N
Het
O
R1
Lawesson-Reagens
Toluol, Rückfluss
R3
S
N
N
Het
O
R1

5a-j, 7, 9, 10

2. EIGENE UNTERSUCHUNGEN ZUR SYNTHESE UND EXPERIMENTELLER TEIL

Die eigenen Untersuchungen zur Synthese und der dazugehörige experimentelle Teil der vorliegenden Diplomarbeit wurden bereits in Form zweier Manuskripte zusammengefasst, die mittlerweile in Fachzeitschriften publiziert wurden. Der Artikel über die Synthese heterocyclischer Analoga von Xanthionen ist in der Zeitschrift *Magnetic Resonance in Chemistry* erschienen: [43] V. Huemer, G. A. Eller and W. Holzer, Heterocyclic analogues of xanthiones: 5,6-fused 3-methyl-1-phenylpyrano[2,3-*c*]pyrazol-4(1*H*)thiones – synthesis and NMR (^{1}H, ^{13}C, ^{15}N) data, *Magn. Reson. Chem.*, **2010**, *48*, 476–482.

Das andere Manuskript, welches eine Einzelsubstanz beschreibt, die nicht in die vorher erwähnte Publikation passte, wurde in der Zeitschrift *Molbank* veröffentlicht:[44] V. Huemer and W. Holzer, 1-Phenylpyrazolo[4',3':5,6]pyrano[3,2-*c*]pyridine-4(1*H*)-thione, *Molbank*, **2010**, M678.

Die beiden Publikationen sind im Folgenden angeführt.

2.1.Heterocyclic analogs of xanthiones: 5,6-fused 3-methyl1phenylpyrano[2,3-c]pyrazol-4(1H)thiones - synthesisandNMR(^{1}H, ^{13}C,^{15}N) data

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Abstract

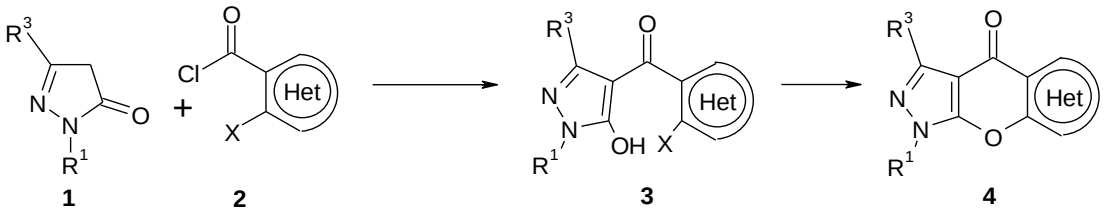
Various [5,6]pyrano[2,3-*c*]pyrazol-4(1*H*)-thiones are synthesized in high yields by treatment of the corresponding [5,6]pyrano[2,3-*c*]pyrazol-4(1*H*)-ones with Lawesson's reagent. Detailed NMR spectroscopic studies are undertaken with the title compounds. Complete and unambiguous assignment of chemical shifts (^{1}H, ^{13}C, ^{15}N) and coupling constants (^{1}H,^{1}H; ^{13}C,^{1}H) is achieved by combined application of various 1D and 2D NMR spectroscopic techniques. Unequivocal mapping of most ^{13}C,^{1}H spin coupling constants is accomplished by 2D (δ,*J*) long-range INEPT spectra with selective excitation.

Keywords: ^{1}H NMR; ^{13}C NMR; ^{15}N NMR; [5,6]pyrano[2,3-*c*]pyrazol-4(1*H*)-thiones, Lawesson's reagent

Introduction

In the course of a program devoted to the synthesis of new heterocyclic scaffolds for bioactive compounds[1–10] we recently presented the synthesis of various [5,6]pyrano[2,3-*c*]pyrazol-4(1*H*)-ones of type **4** via reaction of 2-pyrazolin-5-ones **1** with *o*-haloheteroarenecarbonyl chlorides **2** and subsequent ring closure of the resulting 4-heteroaroylpyrazol-5-ols **3** (Scheme 1). Following this approach, we have obtained type **4** compounds carrying – amongst others – a pyridine (all positional isomers),[1] quinoline,[1] thiophene (all positional isomers),[2,3] benzo[b]thiophene,[2]

and thieno[2,3-*b*]thiophene system[3] as the variable heteroaromatic moiety ('Het') condensed to the central γ-pyranone ring.



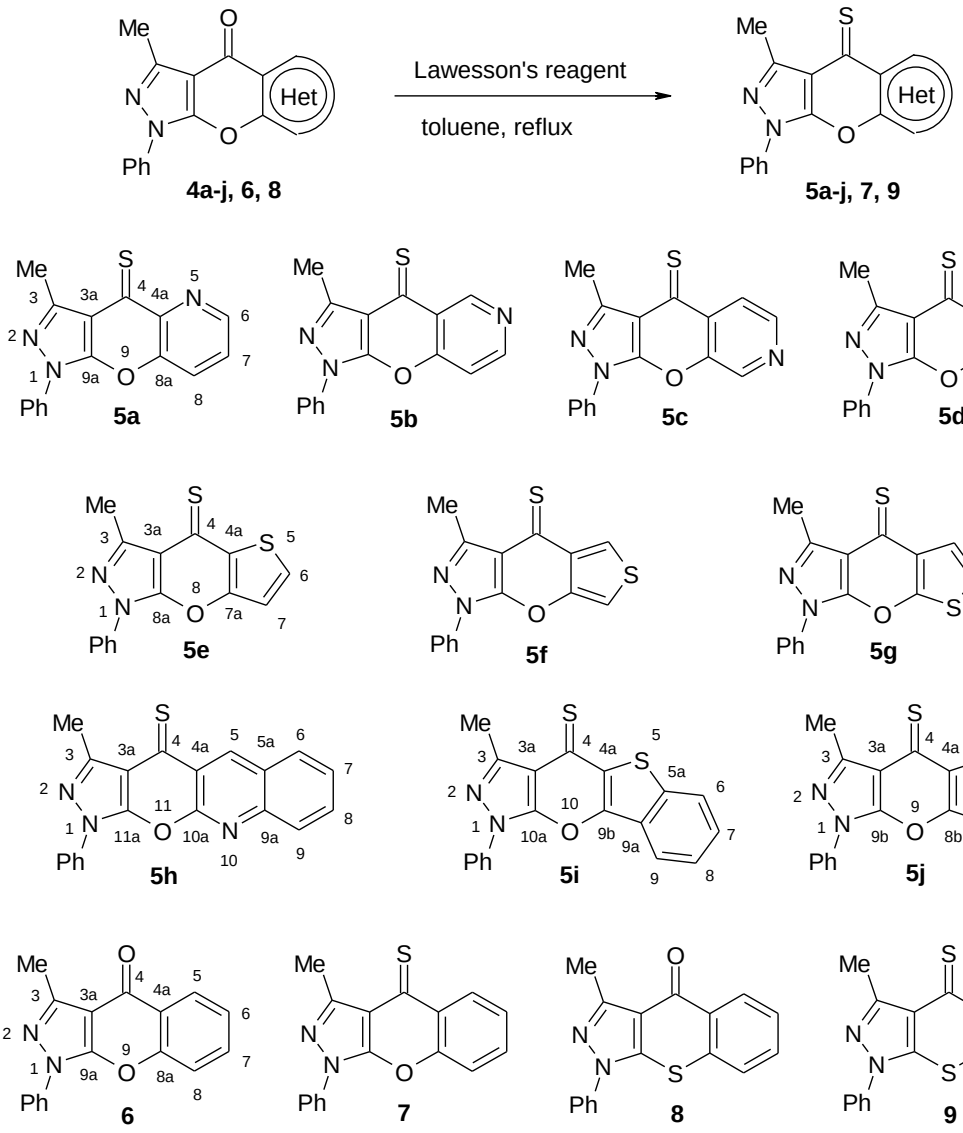
Scheme 1. Synthesis of [5,6]pyrano[2,3-*c*]pyrazol-4(1*H*)-ones **4**.

Thio analogues of flavones, isoflavones, xanthones and related systems have received considerable attention due to the importance of such molecules in biology and photochemistry as well as their usefulness as synthetic building blocks.[11] Considering these facts, in the present paper we report on the synthesis of thio analogues **5** of the above mentioned polycycles **4**, in which the pyran-4-one moiety is replaced by the corresponding pyran-4-thione. Moreover, we want to expose the results of extensive NMR (^{1}H, ^{13}C, ^{15}N) studies undertaken with the title compounds and some related systems, with full and unambiguous assignment of all chemical shifts and most spin coupling constants. The obtained data of our rare condensed heteroaromatic systems can be considered as valuable and reliable reference material for databases used in NMR prediction programs, such as CSEARCH[12]/NMRPREDICT[12,13] and ACD/C + H predictor.[14] Such programs have become very popular in the last few years, particularly for predicting ^{13}C-NMR chemical shifts.

Results and Discussion

Chemistry

The transformation of carbonyl compounds into their thio analogues can be achieved by the application of many different reagents.[11,15,16] The 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, known as Lawesson's reagent, has been commonly used for this purpose and usually permits efficient conversion of ketones into thioketones.[18-20] Employing this method, namely by treatment of compounds **4** with 0.5 equivalents of Lawesson's reagent in boiling toluene, we obtained the corresponding target compounds **5** in high yields (Scheme 2). In the same manner thiones **7** and **9**, required for comparison purposes, were synthesized from oxo compounds **6** and **8**, respectively (Scheme 2). The latter were prepared according to known procedures (**6**,[2,21] **8**[22]).



Scheme 2. Synthesis and atom numbering of investigated compounds.

NMR Spectroscopic Investigations

The ^{1}H NMR data of compounds **4a**–**j**, **6**–**9** are collected in Table 1. Assignment of signals due to *N*-phenyl system is facile considering the relative intensities and the coupling patterns (Ph-2,6 resembles a dublet, Ph-3,5 and Ph-4 a triplet). The mapping of signals of protons attached to the variable heterocyclic system ('Het') at the 'east end' of the condensed systems (according to Scheme 2) is mainly based on chemical shift considerations and on COSY, NOE-difference and 1D-TOCSY experiments.[23] Moreover, information from the ^{1}H-coupled ^{13}C NMR spectra can be employed to achieve unambiguous assignments. Thus, for instance, in thiophene containing systems **5e**, **5g** and **5j** carbons being in alpha position to the sulfur atom can be distinguished from those being in beta positions on basis of their $^{1}J(^{13}C,^{1}H)$ coupling constants (α-C: ^{1}J ~ 190 Hz, β-C: ^{1}J ~ 175 Hz)[24] (Table 3). Via correlations in the HSQC spectra then also the corresponding ^{1}H-signals can be easily assigned. Protons located in position 5 of the anellated ring system receive a downfield shift due to the magnetic anisotropy of the adjacent C=S bond. Thus, chemical shifts of H-5 in **5b** and **5h** (pyridine 2-H, quinoline 4-H) come close to 10 ppm.

The ^{13}C NMR chemical shifts of the investigated compounds are collected in Table 2. Assignments are based on HSCQ (HMQC), HMBC, and long-range INEPT experiments with selective excitation (INAPT).[23] In rare cases (for instance distinction of C-6 vs. C-8 in **9**) HMQC-COSY spectra were consulted. Within type **5** compounds the signals due to the *N*-phenyl ring show a high degree of consistency, this is also the case for δ (3-Me), δ(C-3) and δ(C-3a). The C=S (C-4) resonance is located between 190 and 198 ppm and is – of course – to some degree dependent on the nature of the variable heteroaromatic system. Comparison of the ^{13}C chemical shift data of compounds **5** with those of corresponding type **4** moieties[1-3] clearly shows the effects of replacing the central pyran-4-one by a pyran-4-thione system. Whereas this replacement has nearly no influence on the chemical shifts of the N-phenyl system or only small impact on those of 3-Me, C-3 and peripheral carbon

atoms of the heteroaromatic system, the chemical shifts of the carbon atoms belonging to the central pyrane ring change drastically. Thus, in compounds **4** there is a pronounced 'push-pull situation' leading to a strong polarization of the pyrane C=C bonds – reflected by large chemical shifts of carbons attached to the pyrane O-atom and small ones of those being in beta-position to the ring oxygen. In contrast, with compounds **5** this polarization effect is much less developed resulting in an upfield shift for carbons directly bonded to the pyrane O-atoms whereas those in beta-position receive a marked downfield shift compared to the corresponding signals in compounds **4**. Switching from compound **6** to **7** shows the same typical effects (C-3a: 104.9 → 116.3 ppm; C-4a: 123.3 → 127.9 ppm; C-8a: 154.4 → 149.7 ppm; C-9a: 152.9 → 146.5 ppm). The chemical shift of C-4 rises between 20 and 25 ppm in the transformation **4** → **5** or **6** → **7**. The order of magnitude regarding these changes is in good agreement with those found by Still and coworkers within the changeover from xanthone (9*H*-xanthen-9-one) to xanthione (9*H*-xanthene-9-thione), with C-8a/C-9a 121.5 → 128.7 ppm, C-4a/C-10a 155.7 → 150.1 ppm, and C-9 176.6 → 204.4 ppm (Figure 1).[25]

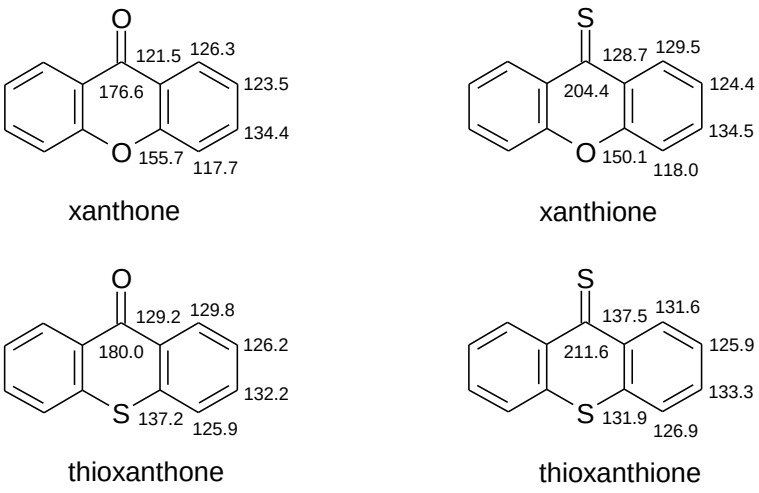


Figure 1. ^{13}C NMR chemical shifts of xanthone,[25] xanthione,[25] thioxanthone,[26] and thioxanthione[27] ($CDCl_3$)

Comparing the ^{13}C chemical shifts of compounds **6**, **7**, **8**, and **9** explicitly demonstrates the effect of replacing the ring oxygen by sulfur (**6** → **8**, **7** → **9**) and by

changing C=O to C=S (**6** → **7**, **8** → **9**) on the example of the benzene-fused tricycle (Figure 2, see also Table 2). In Figure 1, the corresponding changes can be recognized for the transitions xanthone → thioxanthone, xanthione → thioxanthione as well as for those of xanthone → xanthione and thioxathone → thioxanthione.[25-27]

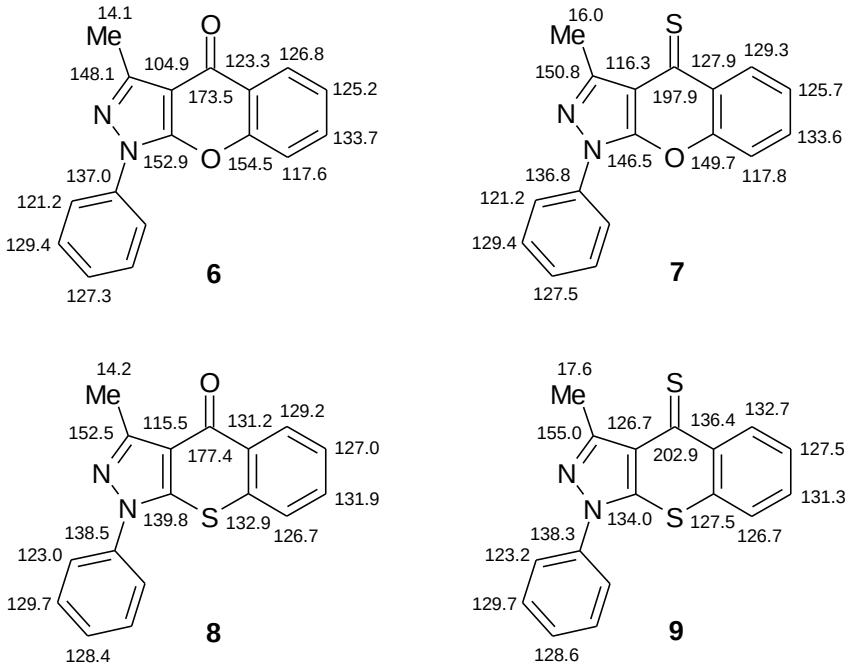


Figure 2. ^{13}C NMR chemical shifts of **6**–**9** ($CDCl_3$)

In Table 3 the ^{13}C,^{1}H coupling constants of the investigated compounds are summarized. The data are mainly extracted from the fully ^{1}H-coupled ^{13}C-NMR spectra (gated decoupling). In ambiguous cases 2D (δ,*J*) long-range INEPT spectra with selective excitation[28] are used for the definitive mapping of long-range ^{13}C,^{1}H coupling constants. Thus, for instance, in the ^{1}H-coupled ^{13}C NMR spectrum of **5b** the signal due to C-8a (155.1 ppm) is split by a 9.7, 7.6 and 3.8 Hz coupling. In a 2D (δ,*J*) long-range INEPT spectra with selective excitation of H-7 the signal of C-8a is split by 9.7 Hz − thus assigning ^{3}J(C8a,H7) to be 9.7 Hz − whereas in a similar experiment upon selective excitation of H-5 the C-8a signal is split-up by 7.6 Hz. Hence, the correct assignments ^{3}J(C8a,H7) = 9.7 Hz, ^{3}J(C8a,H5) = 7.6 Hz and ^{2}J(C8a,H8) = 3.8 Hz (following indirectly) can be unequivocally performed. Expectedly, ^{13}C,^{1}H coupling constants at the pyrazole moiety of compounds **5** are

scarcely different from the corresponding ones in **4**.[1-3] In this concern, also the changes of couplings within the variable heteroaromatic systems are not significant.

Finally, Table 4 comprises the ^{15}N NMR data of **5a**–**j** and **6**–**9**. Within the compound **5** series the ^{15}N chemical shifts of pyrazole nitrogen atoms N-1 (−196.5 to −194.3 ppm) and N-2 (−93.1 to −90.7 ppm) are very consistent, indicating the marginal influence of the variable heterocyclic system on these resonances. In contrast, the ^{15}N chemical shift of the pyridine N-atom in compounds **5a**−**d** are strongly influenced by the distinct electron donating resonance (+M) effect of the oxygen atom O-9: in **5d** O-9 and N-8 are located in 'ortho'-position leading to a considerable upfield shift of N-8 (−102.3 ppm). In **5b** ('para'-position of O-8 and N-6) this effect is less pronounced (δ N-6 77.4 ppm), whereas in **5a** (δ N-5 −65.7 ppm) and **5c** (δ N-7 −56.3 ppm) it has only little influence. Comparison of the ^{15}N chemical shifts of N-1 and N-2 in compounds **6**−**9** clearly indicates the effect of substituting C=O by C=S (**6**→**7**, **8**→**9**) as well as substitution of the ring oxygen atom by sulfur (**6**→**8**, **7**→**9**). Whereas the former transformation leads to only small effects (~ 3 ppm upfield shift for N-1, ~ 2.5 ppm downfield shift for N-2) the changeover from pyrane to thiopyrane affects δ(N-1) (~ 15 ppm downfield shift) and δ(N-2) (~ 20 ppm downfield shift) much more distinctively. Again, the latter effect can be casually explained by the less pronounced electron releasing mesomeric effect of sulfur compared to oxygen. Comparison of the ^{15}N chemical shift data of compounds **4**[1-3] with those of **5** in principle shows similar effects as found with the transformation **6**→**7**, namely 2–3 ppm upfield shift for pyrazole N-1 and 2–2.5 ppm downfield shift for pyrazole N-2. The pyridine ^{15}N atoms in **5a**–**d** suffer small downfield shifts in relation to the corresponding type **4** compounds.

In conclusion, we have presented an efficient synthesis of various novel [5,6]pyrano[2,3-*c*]pyrazol-4(1*H*)-thiones (**5a**–**j**) as well as full and unambiguous assignments of ^{1}H, ^{13}C and ^{15}N NMR chemical shifts. Moreover, an analysis of many spin coupling constants (^{1}H,^{1}H: ^{13}C,^{1}H) with the investigated systems was provided.

Table 1

Table 2

Table 3

Table 4

Experimental

All NMR experiments were performed using standard NMR spectroscopic techniques.[23] The ^{1}H NMR and ^{13}C NMR spectra were recorded from $CDCl_3$ solutions either on a Varian UnityPlus NMR spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C) or on a Bruker Avance 500 instrument (500 MHz for ^{1}H, 125 MHz for ^{13}C) at 25°C from using 5 mm direct detection broadband probes and deuterium lock. The center of the solvent signal was used as an internal standard which was related to tetramethylsilane with δ 7.26 ppm (^{1}H) and δ 77.0 ppm (^{13}C). The recording conditions were the following: ^{1}H NMR: pulse angle 30°, acquisition time 5 s, digital resolution 0.2 Hz/data point, spectral width 16 ppm, 16 transients, relaxation delay 5 s; broad-band decoupled ^{13}C-NMR spectra: pulse angle 30°, acquisition time 2 s, digital resolution 0.5 Hz/data point, spectral width 220 ppm, 128–1024 transients, relaxation delay 2 s, exponential multiplication with 1.0 Hz line broadening factor before FT; gated decoupled ^{13}C-NMR spectra: as above but acquisition time 2.5 s, digital resolution 0.4 Hz/data point, 512–8192 transients, relaxation delay 2.5 s, resolution enhancement by Gaussian weighting (Varian: lb = −0.15, gf = 0.7; Bruker: lb = −0.6, gb = 0.2) before FT. Full and unambiguous assignments were achieved by consequent application of fully ^{1}H-coupled ^{13}C-NMR spectra (gated decoupling), gs-HSQC[29] (1024 × 256 data matrix, 10 ppm for ^{1}H, 160 ppm for ^{13}C, 4 transients accumulated per t_1 increment; optimized for J = 160 Hz, qsine multiplication in both dimensions) and gs-HMBC[30] (1024 × 256 data matrix, 10 ppm for ^{1}H, 180 ppm for ^{13}C, 8 transients accumulated per t_1 increment; optimized for J = 8 Hz, sine multiplication in both dimensions) techniques to all compounds. The unequivocal mapping of ^{13}C,^{1}H coupling constants was performed via 2D long-range INEPT (δ,J) spectra with selective excitation (DANTE)[28] of unequivocally assigned proton

resonances (12–24 Hz excitation width, optimized for J = 8 Hz, 32 increments for 20 Hz width in F1, 128 transients accumulated per t_1 increment; zero-filling to 128 data points in the F1 dimension, shifted sine multiplication in F1). The ^{15}N-NMR spectra ($CDCl_3$) were obtained on a Bruker Avance 500 instrument (50.69 MHz) equipped with a 5 mm broadband observe probe (BBFO) at 25 °C and were referenced against external, neat nitromethane: ^{1}H,^{15}N gs-HMBC experiments (Bruker standard program 'inv4gplplrndqf',[30] 2048 × 256 data matrix, 10 ppm for ^{1}H, 200 ppm for ^{15}N, 32 transients accumulated per t_1 increment; 65 ms delay for the evolution of the ^{15}N,^{1}H long-range coupling, optimized for J = 8 Hz, zero-filling to 1K data points in the F1 dimension, sine multiplication in both dimensions) were undertaken.

Melting points were determined on a Reichert–Kofler hot-stage microscope and are uncorrected. The mass spectra were obtained on a Shimadzu QP 1000 instrument (EI, 70 eV). The elemental analyses (C, H, N) were performed at the Microanalytical Laboratory, University of Vienna.

General Procedure for the synthesis of 5a-j, 7, and 9

To a solution of the appropriate oxo compound (**4a-j**,[1-3] **6**,[2] **8**[22]) (1 mmol) in toluene (15 mL) was added Lawesson's reagent (202 mg, 0.5 mmol) and the mixture was heated to reflux overnight (~14 h). Then the solvent was removed under reduced pressure and the residue was subjected to column chromatography (silica gel, eluent: CH_2Cl_2 or CH_2Cl_2 – MeOH, 100:3) to afford the colored thiones **5a-j**, **7** and **9**. For analytical purposes the products were recrystallized from an appropriate solvent given below.

3-Methyl-1-phenylpyrazolo[4',3':5,6]pyrano[3,2-*b*]pyridine-4(1*H*)-thione (**5a**).

Yield: 88%; M.p.: 242–244°C (toluene); MS (70 eV): *m*/*z* (%) = 294 (M^++1, 20), 293 (M^+, 100), 292 (M^+−1, 41), 260 (22), 157 (34), 146 (22), 77 (42), 51 (27). Anal. Calcd. for $C_{16}H_{11}N_3OS$: C, 65.51; H, 3.78; N, 14.32. Found: C, 65.34; H, 3.58; N, 14.25.

3-Methyl-1-phenylpyrazolo[4',3':5,6]pyrano[3,2-*c*]pyridine-4(1*H*)-thione (**5b**).

Yield: 93%; M.p.: 205–207°C; MS (70 eV): *m*/*z* (%) = 294 (M^++1, 22), 293 (M^+, 100), 292 (M^+−1, 33), 77 (28), 51 (17). Anal. Calcd. for $C_{16}H_{11}N_3OS$: C, 65.51; H, 3.78; N, 14.32. Found: C, 65.49; H, 3.75; N, 13.94.

3-Methyl-1-phenylpyrazolo[4',3':5,6]pyrano[2,3-*c*]pyridine-4(1*H*)-thione (**5c**).

Yield: 94%; M.p.: 177–179°C (toluene); MS (70 eV): *m*/*z* (%) = 294 (M^++1, 20), 293 (M^+, 100), 292 (M^+−1, 31), 91 (19), 77 (33), 51 (20). Anal. Calcd. for $C_{16}H_{11}N_3OS$•0.1 H_2O: C, 65.11; H, 3.82; N, 14.24. Found: C, 65.38; H, 3.80; N, 13.83.

3-Methyl-1-phenylpyrazolo[4',3':5,6]pyrano[2,3-*b*]pyridine-4(1*H*)-thione (**5d**).

Yield: 90%; M.p.: 224–225°C (toluene); MS (70 eV): *m*/*z* (%) = 294 (M^++1, 19), 293 (M^+, 100), 292 (M^+−1, 27), 91 (21), 77 (36), 51 (22). Anal. Calcd. for $C_{16}H_{11}N_3OS$: C, 65.51; H, 3.78; N, 14.32. Found: C, 65.19; H, 3.61; N, 14.10.

3-Methyl-1-phenylthieno[2',3':5,6]pyrano[2,3-*c*]pyrazole-4(1*H*)-thione (**5e**).

Yield: 95%; M.p.: 177–178°C (toluene); MS (70 eV): *m*/*z* (%) = 299 (M^++1, 16), 298 (M^+, 100), 91 (11), 77 (19), 51 (13). Anal. Calcd. for $C_{15}H_{10}N_2OS_2$: C, 60.38; H, 3.38; N, 9.39. Found: C, 60.37; H, 3.24; N, 9.05.

3-Methyl-1-phenylthieno[3',4':5,6]pyrano[2,3-*c*]pyrazole-4(1*H*)-thione (**5f**).

Yield: 80%; M.p.: 208–210°C (toluene); MS (70 eV): *m*/*z* (%) = 299 (M^++1, 12), 298 (M^+, 100), 297 (M^+−1, 36), 225 (13), 97 (15), 91 (37), 83 (20), 77 (93), 71 (26), 69 (45), 57 (45), 51 (60). Anal. Calcd. for $C_{15}H_{10}N_2OS_2$: C, 60.38; H, 3.38; N, 9.39. Found: C, 60.38; H, 3.28; N, 9.11.

3-Methyl-1-phenylthieno[3',2':5,6]pyrano[2,3-*c*]pyrazole-4(1*H*)-thione (**5g**).

Yield: 99%; M.p.: 194–196°C; MS (70 eV): *m*/*z* (%) = 299 (M^++1, 17), 298 (M^+, 100), 121 (11), 105 (16), 91 (13), 77 (67), 51 (44). Anal. Calcd. for $C_{15}H_{10}N_2OS_2$: C, 60.38; H, 3.38; N, 9.39. Found: C, 60.58; H, 3.36; N, 9.08.

3-Methyl-1-phenylpyrazolo[4',3':5,6]pyrano[2,3-*b*]quinoline-4(1*H*)-thione (**5h**).

Yield: 71%; M.p.: 274–276°C (toluene); MS (70 eV): *m*/*z* (%) = 344 (M^++1, 20), 343 (M^+, 100), 172 (16), 91 (55), 77 (45), 69 (12), 57 (12), 51 (27). Anal. Calcd. for $C_{20}H_{13}N_3OS$•0.1 H_2O: C, 69.59; H, 3.85; N, 12.17. Found: C, 59.55; H, 3.69; N, 11.79.

3-Methyl-1-phenyl[1]benzothieno[2',3':5,6]pyrano[2,3-*c*]pyrazole-4(1*H*)-thione (**5i**).

Yield: 93%; M.p.: 236–237°C (toluene); MS (70 eV): *m*/*z* (%) = 349 (M^++1, 23), 348 (M^+, 100), 347 (M^+−1, 15), 174 (11), 104 (11), 77 (25), 76 (11), 51 (16). Anal. Calcd. for $C_{19}H_{12}N_2OS_2$: C, 60.38; H, 3.38; N, 9.39. Found: C, 65.40; H, 3.29; N, 7.98.

3-Methyl-1-phenylthieno[3'',2'':4',5']thieno[2',3':5,6]pyrano[2,3-*c*]pyrazole-4(1*H*)-thione (**5j**).

Yield: 83%; M.p.: 245–246°C (toluene); MS (70 eV): *m*/*z* (%) = 355 (M^++1, 20), 354 (M^+, 100), 177 (12), 77 (22), 51 (15). Anal. Calcd. for $C_{17}H_{10}N_2OS_3$: C, 67.60; H, 2.84; N, 7.90. Found: C, 57.47; H, 2.65; N, 7.80.

3-Methyl-1-phenylchromeno[2,3-*c*]pyrazole-4(1*H*)-thione (**7**).

Yield: 98%; M.p.: 185–187°C (lit.[21] m.p.: 189–190°C); MS (70 eV): *m*/*z* (%) = 293 (M^++1, 21), 292 (M^+, 100), 291 (M^+−1, 33), 146 (11), 91 (18), 77 (23), 51 (15).

3-Methyl-1-phenylthiochromeno[2,3-*c*]pyrazole-4(1*H*)-thione (**9**).

Yield: 86%; M.p.: 183–185°C (lit.[22] m.p.: 208–210°C); MS (70 eV): *m*/*z* (%) = 309 (M^++1, 23), 308 (M^+, 100), 307 (M+−1, 48), 263 (26), 172 (19), 146 (11), 138 (12), 120 (11), 83 (10), 77 (51), 69 (27), 57 (22), 55 (17), 51 (44).

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References

[1] G. A. Eller, V. Wimmer, A. W. Haring, W. Holzer, *Synthesis* **2006**, 4219–4229.

[2] G. A. Eller, A. W. Haring, B. Datterl, M. Zwettler, W. Holzer, *Heterocycles* **2007**, *71*, 87–104.

[3] G. A. Eller, W. Holzer, *Molecules* **2007**, *12*, 60–73.

[4] G. A. Eller, B. Datterl, W. Holzer, *J. Heterocycl. Chem*. **2007**, *44*, 1139–1143.

[5] G. A. Eller, V. Wimmer, W. Holzer, *Khim. Geterotsikl. Soedin*. **2007**, 1251–1255
(*Chem. Heterocycl. Comp*. **2007**, *43*, 1060–1064).

[6] G. A. Eller, D. Habicht, W. Holzer, *Khim. Geterotsikl. Soedin*. **2008**, 884–890 (*Chem. Heterocycl. Comp*. **2008**, *44*, 709–714).

[7] G. A. Eller, Q. Zhang, D. Habicht, B. Datterl, W. Holzer, *Acta Chim. Slov*. **2009**, *56*, 521–526.

[8] W. Holzer, K. Hahn, *J. Heterocycl. Chem*. **2003**, *40*, 303–308.

[9] W. Holzer, R. M. Claramunt, M. Perez-Torralba, D. Guggi, T. H. Brehmer, *J. Org. Chem*. **2003**, *68*, 7934–7950.

[10] F. C. Fuchs, G. A. Eller, W. Holzer, *Molecules* **2009**, *14*, 3814–3832.

[11] A. C. Williams, N. Camp, *Science of Synthesis* **2003**, *14*, 347–638; and references cited therein.

[12] H. Kalchhauser, W. Robien, *J. Chem. Inf. Comput. Sci.* **1985**, *25*, 103–108.

[13] NMR Predict, version 3.2.8, Modgraph Consultants, Ltd, Herts, UK, 2004; www.modgraph.co.uk/product_nmr.htm.

[14] ACD/C+H Predictors and DB, version 10.04, Advanced Chemistry Development, Inc., Toronto, ON, Canada, 2006; www.acdlabs.com.

[15] R. J. Cremlyn, *An Introduction to Organosulfur Chemistry*, John Wiley & Sons: New York, **1996**.

[16] F. Duus, In Comprehensive Organic Chemistry, D. H. R. Barton, W. D. Ollis, eds.; Vol. 3, 373–487, Pergamon Press: Oxford, **1979**.

[17] W. M. McGregor, D. C. Sherrington, *Chem. Soc. Rev*. **1993**, *22*, 199–204.

[18] R. A. Cherkasov, G. A. Kutyrev, A. N. Pudovik, *Tetrahedron* **1985**, *41*, 2567–2624.

[19] B. S. Pedersen, S. Scheibye, N. H. Nilsson, S.-O. Lawesson, *Bull. Soc. Chim. Belg*. **1978**, *87*, 223–228.

[20] M. Jesberger, T. P. Davis, L. Barner, *Synthesis* **2003**, 1929–1958.

[21] A. S. Sarenko, I. Ya. Kvitko, L. S. Efros, *Khim. Geterotsikl. Soedin*. **1972**, 799–804
(*Chem. Heterocyl. Comp.* **1972**, *8*, 722–727).

[22] A. S. Sarenko, L. N. Poznyakova, I. Ya. Kvitko, L. S. Efros, *Khim. Geterotsikl. Soedin*. **1972**, 805–808 (*Chem. Heterocyl. Comp.* **1972**, *8*, 728–730).

[23] S. Braun, H.-O. Kalinowski, S. Berger, *150 and More Basic NMR Experiments*, 2nd expanded ed., Wiley-VCH: Weinheim-New York, **1998**.

[24] H.-O. Kalinowski, S. Berger, S. Braun, *^{13}C-NMR-Spektroskopie*, Thieme: Stuttgart – New York, **1984**, p. 455.

[25] I. W. J. Still, G. W. Kutney, D. McLean, *J. Org. Chem*. **1982**, *47*, 555–560.

[26] A. L. Ternay Jr., J. A. Cushman, J. S. Harwood, C. P. Yu, *J. Heterocycl. Chem*. **1987**, *24*, 1067–1071.

[27] I. W. J. Still. N. Plavac, D. M. McKinnon, M. S. Chauhan, *Can. J. Chem*. **1976**, *54*, 280–289.

[28] T. Jippo, O. Kamo, N. Nagayama, *J. Magn. Reson.* **1986**, *66*, 344–348.

[29] L. E. Kay, P. Keifer, T. Saarinen, *J. Am. Chem. Soc*. **1992**, *114*, 10663–10665.

[30] W. Willker, D. Leibfritz, R. Kerssebaum, W. Bermel, *Magn. Reson. Chem*. **1993**, *31*, 287–292.

Table 1. ^{1}H NMR chemical shifts of **5a**–**j**, **6**–**9** (δ in ppm, $CDCl_3$)

comp.	Ph 2,6	Ph 3,5	Ph 4	3-Me	H-5	H-6	H-7	H-8	other H
5a	7.86	7.55	7.41	2.78	–	8.87[a]	7.64[a]	7-93[a]	–
5b	7.84	7.56	7.43	2.77	9.83[b]	–	8.80[b]	7.39[b]	–
5c	7.89	7.59	7.45	2.79	8.49[c]	8.66[c]	–	9.00[c]	–
5d	7.97	7.56	7.41	2.81	9.15[d]	7.51[d]	8.69[d]	–	–
5e	7.86	7.55	7.41	2.80	–	7.77[e]	7.22[e]	–	–
5f	7.85	7.55	7.41	2.77	8.36[f]	–	7.18[f]	–	–
5g	7.82	7.54	7.40	2.78	7.66[g]	6.95[g]	–	–	–
5h	8.00	7.58	7.43	2.83	9.64[h]	8.15	7.65	7.91	8.11 (H-9)
5i	7.94	7.61	7.45	2.77	–	7.81	7.55	7.48	8.02 (H-9)
5j	7.90	7.59	7.44	2.81	–	–	7.48[i]	7.44[i]	–
6	7.87	7.54	7.38	2.69	8.33	7.43	7.68	7.51	–
7	7.89	7.55	7.40	2.80	8.76	7.42	7.68	7.49	–
8	7.71	7.56	7.45	2.81	8.64	7.53	7.60	7.54	–
9	7.71	7.58	7.47	2.90	9.17	7.49	7.56	7.49	–

[a] $^{3}J(6,7)$ = 8.4 Hz, $^{4}J(6,8)$ = 1.4 Hz, $^{3}J(7,8)$ = 4.3 Hz. [b] $^{4}J(5,7) < 1$ Hz, $^{5}J(5,8) < 1$ Hz, $^{3}J(7,8)$ = 5.7 Hz.

[c] $^{3}J(5,6)$ = 5.3 Hz, $^{5}J(5,8) < 1$Hz, $^{4}J(6,8) < 1$ Hz. [d] $^{3}J(5,6)$ = 7.9 Hz, $^{4}J(5,7)$ = 2.0 Hz, $^{3}J(6,7)$ = 4.6 Hz.

[e] $^{3}J(6,7)$ = 5.6 Hz. [f] $^{4}J(5,7)$ = 3.8 Hz. [g] $^{3}J(5,6)$ = 6.0 Hz. [h] Singlet. [i] $^{3}J(7,8)$ = 5.4 Hz.

TABLE 2. ^{13}C NMR CHEMICAL SHIFTS OF **5A–J, 6–9** (Δ IN PPM, $CDCL_3$)

COMP.	PH 1	PH 2,6	PH 3,5	PH 4	3-ME	C-3	C-3A	C-4	C-4A	C-5	C-5A	C-6	C-7	C-8	OTHER C
5A	136.5	121.4	129.5	127.8	15.9	151.0	118.4	197.3	141.7	–	–	148.5	127.2	127.2	C-8A: 146.9 C-9A: 145.6
5B	136.4	121.6	129.6	128.0	15.8	150.9	117.2	196.6	123.0	152.3	–	–	153.0	112.2	C-8A: 155.1 C-9A: 145.7
5C	136.5	121.5	129.6	128.0	15.8	150.9	117.6	195.9	131.9	120.8	–	146.2	–	141.8	C-8A: 145.0 C-9A: 146.0
5D	136.6	121.4	129.6	127.8	15.7	150.8	116.5	197.3	122.8	139.8	–	122.7	152.2	–	C-8A: 154.4 C-9A: 147.1
5E	136.7	121.4	129.5	127.7	15.3	149.2	114.5	190.9	135.8	–	–	134.8	117.4	–	C-7A: 147.7; C-8A: 148.1
5F	136.7	121.6	129.4	127.7	15.9	150.9	114.8	195.1	135.3	127.4	–	–	105.6	–	C-7A: 146.5; C-8A: 148.3
5G	136.6	121.3	129.5	127.7	15.6	149.9	115.8	193.5	133.2	124.0	–	116.8	–	–	C-7A: 156.8, C-8A: 147.8
5H	136.6	121.8	129.6	127.9	15.9	151.2	115.8	197.9	121.7	141.9	127.3	129.9	127.1	133.2	C-9: 127.8; C-9A: 147.9; C-10A: 152.5; C-11A: 147.5
5I	136.9	121.1	129.6	127.7	15.3	149.0	115.6	191.1	135.0	–	140.8	123.7	128.8	125.5	C-9: 122.2; C-9A: 128.7; C-9B: 141.8; C-10B: 147.7
5J	136.8	121.4	129.6	127.8	15.4	149.0	114.3	190.4	138.8	–	145.0	–	130.1	118.5	C-8A: 134.9; C-8B: 140.3; C-9A: 147.5

6	137.0	121.2	129.4	127.3	14.1	148.1	104.9	173.5	123.3	126.8	–	125.2	133.7	117.6	C-8A: 154.5; C-9A: 152.9
7	136.8	121.2	129.4	127.5	16.0	150.8	116.3	197.9	127.9	129.3	–	125.7	133.6	117.8	C-8A: 149.7; C-9A: 146.5
8	138.5	123.0	129.7	128.4	14.2	152.5	115.5	177.4	131.2	129.2	–	127.0	131.9	126.7	C-8A: 132.9; C-9A: 139.8
9	138.3	123.2	129.7	128.6	17.6	155.0	126.7	202.9	136.4	132.7	–	127.5	131.3	126.7	C-8A: 127.5; C-9A: 134.0

Table 3. Selected $^{13}C,^{1}H$ spin coupling constants of **5a–j**, **6–9** (Hz, $CDCl_3$)

comp.	^{1}J(3-Me)	^{2}J(3,3-Me)	^{3}J(3a,3-Me)	^{3}J(4,5)	other couplings
5a	129.7	7.2	2.4	–	^{3}J(4a,6) = 12.3, ^{3}J(4a,8) = 3.8, ^{4}J(4a,7) = 1.2; ^{1}J(6) = 183.7, ^{2}J(6,7) = 3.0, ^{3}J(6,8) = 7.8; ^{1}J(7) = 166.8, ^{2}J(7,6) = 9.8; ^{1}J(8) = 166.9, ^{2}J(8,7) = 1.1, ^{3}J(8,6) = 6.5; ^{2}J(8a,8) = 3.7, ^{3}J(8a,7) = 9.7, ^{4}J(8a,6) = 1.7
5b	129.7	7.2	2.4		^{2}J(4a,5) = 6.4, ^{3}J(4a,8) = 3.8, ^{4}J(4a,7) = 1.4; ^{1}J(5) = 187.0, ^{3}J(5,7) = 12.0; ^{1}J(7) = 182.8, ^{2}J(7,8) = 1.4, ^{3}J(7,5) = 13.8; ^{1}J(8) = 168.2, ^{2}J(8,7) = 8.9, ^{4}J(8,5) = 1.6; ^{2}J(8a,8) = 3.8, ^{3}J(8a,5) = 7.6, ^{3}J(8a,7) = 9.7
5c	129.7	7.3	2.6	5.0	^{2}J(4a,5) = 1.1, ^{3}J(4a,6) = 7.4, ^{3}J(4a,8) = 4.0; ^{1}J(5) = 169.0, ^{2}J(5,6) = 9.5, ^{4}J(5,8) = 1.6; ^{1}J(6) = 183.1, ^{2}J(6,5) = 2.4, ^{3}J(6,8) = 11.9; ^{1}J(8) = 185.0, ^{2}J(8,6) = 11.5, ^{4}J(8,5) = 1.0; ^{2}J(8a,8) = 3.3, ^{3}J(8a,5) = 7.6, ^{4}J(8a,6) = 1.8

5d	129.6	7.2	2.7	4.9	^{2}J(4a,5) = 0, ^{3}J(4a,6) = 7.4, ^{4}J(4a,7) = 1.5; ^{1}J(5) = 168.2, ^{2}J(5,6) = 1.9, ^{3}J(5,7) = 6.5; ^{1}J(6) = 167.7, ^{2}J(6,5) = 0.9, ^{2}J(6,7) = 8.1; ^{1}J(7) = 182.8, ^{2}J(7,6) = 4.3, ^{3}J(7,5) = 8.9; ^{3}J(8a,5) = 8.5, ^{3}J(8a,7) = 13.5, ^{4}J(8a,6) = 1.4
5e	129.5	7.2	2.6	–	^{3}J(4a,6) = 5.2, ^{3}J(4a,7) = 5.8; ^{1}J(6) = 188.0, ^{2}J(6,7) = 4.5; ^{1}J(7) = 175.2, ^{2}J(7,6) = 4.1; ^{2}J(7a,7) 0.9, ^{3}J(7a,6) = 12.8
5f	129.5	7.2	2.4	2.8	^{2}J(4a,5) = 2.4, ^{3}J(4a,7) = 6.3; ^{1}J(5) = 193.2, ^{3}J(5,7) = 5.2; ^{1}J(7) = 190.2, ^{3}J(7,5) = 4.5; ^{2}J(7a,7) = 0, ^{3}J(7a,5) = 10.8
5g	129.6	7.2	2.5	0	^{2}J(4a,5) = 3.7, ^{3}J(4a,6) = 8.5; ^{1}J(5) = 176.1, ^{2}J(5,6) = 3.5; ^{1}J(6) = 191.7, ^{2}J(6,5) = 6.8; ^{3}J(7a,5) = 11.0, ^{3}J(7a,6) = 8.6
5h	129.5	7.1	2.6	5.5	^{1}J(5) = 166.4, ^{3}J(5,6) = 4.7; ^{3}J(10a,5) = 9.8
5i	129.5	7.2	2.7	–	^{3}J(9b,9) = 3.4
5j	129.5	7.2	2.8	–	^{3}J(5a,7) = 7.8, ^{3}J(5a,8) = 9.5; ^{1}J(7) = 188.5, ^{2}J(7,8) = 6.8; ^{1}J(8) = 174.2, ^{2}J(8,7) = 4.1; ^{2}J(8a,8) = 5.7, ^{3}J(8a,7) = 10.5
6	129.2	7.2	2.7	4.1	
7	129.6	7.2	2.5	5.2	^{2}J(4a,5) = 0, ^{3}J(4a,6) = 8.2, ^{3}J(4a,8) = 4.4, ^{4}J(4a,7) = 1.4; ^{1}J(5) = 165.4, ^{3}J(5,7) = 8.1; ^{1}J(6) = 163.3, ^{3}J(6,8) = 8.2; ^{1}J(7) = 161.7, ^{3}J(7,5) = 9.5; ^{1}J(8) = 163.6, ^{3}J(8,6) = 7.9; ^{2}J(8a,8) = 3.7, ^{3}J(8a,5) = 8.8, ^{3}J(8a,7) = 11.1, ^{4}J(8a,6) = 1.6
8	129.4	7.1	2.5	4.0	
9	129.7	7.1	2.2	5.4	^{3}J(4a,6) = 6.9, ^{3}J(4a,8) = 6.9

Table 4. ^{15}N NMR chemical shifts of **5a–j**, **6–9** (δ in ppm, $CDCl_3$)

comp.	N-1	N-2	other N	comp.	N-1	N-2	other N
5a	–196.1	–91.1	N-5: –65.7	**5h**	–194.3	–92.3	N-10: –116.4
5b	–194.6	–91.8	N-6: –77.4	**5i**	–195.2	–91.6	–
5c	–195.3	–90.7	N-7: –56.3	**5j**	–195.3	–91.4	–
5d	–194.7	–91.8	N-8: –102.3	**6**	–193.2	–96.2	–
5e	–195.7	–91.8	–	**7**	–196.2	–93.5	–
5f	–196.5	–93.1	–	**8**	–178.3	–75.8	–
5g	–196.0	–92.9	–	**9**	–181.6	–73.5	–

2.2. 1-Phenylpyrazolo[4',3':5,6]pyrano[3,2-*c*]pyridine-4(1*H*)-thione

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Short Note

1-Phenylpyrazolo[4',3':5,6]pyrano[3,2-*c*]pyridine-4(1*H*)-thione

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Abstract: The title compound is prepared by treatment of 1-phenylpyrazolo[4',3':5,6]pyrano[3,2-*c*]pyridin-4(1*H*)-one with Lawesson's reagent in refluxing toluene. Detailed spectroscopic data (^{1}H NMR, ^{13}C NMR, ^{15}N NMR, MS) are presented.

Keywords: phenylpyrazolo[4',3':5,6]pyrano[3,2-*c*]pyridine-4(1*H*)-thiones; Lawesson's reagent; thionation; NMR

Recently, we presented a short and generally applicable synthesis of various fused pyrano [2,3-*c*]pyrazol-4(1*H*)-ones of type **D** [1-7] *via* reaction of 1-substituted or 1,3-disubstituted

2-pyrazolin-5-ones (**A**) with *o*-halo(hetero)arenecarbonyl chlorides **B** under the conditions described by *Jensen* for the C-4 acylation of pyrazolones (calcium hydroxide, dioxane, reflux) [8]. The formed 4-aroylpyrazol-5-ols **C** can be smoothly cyclized into the target systems **D** in alkaline or – occasionally – acidic [7] medium (Figure 1). Type **D** compounds can be recognized as heterocyclic analogues of xanthone in which one benzene ring of the parent xanthone molecule is replaced by a pyrazole system and the other one by a variable heteroaromatic moiety (Figure 1). In consideration of the fact that thio analogues of flavones, xanthones and related systems have received considerable attention due to the importance of such molecules in biology and photochemistry as well as their usefulness as synthetic building blocks [9], we here report on the synthesis of a thio analogue **2** of the 'azaxanthone' **1**, in which the pyran-4-one moiety is replaced by the corresponding pyran-4-thione (Scheme 1). Compound **2** is a supplement to similar thiones we recently presented in the course of an NMR study [10].

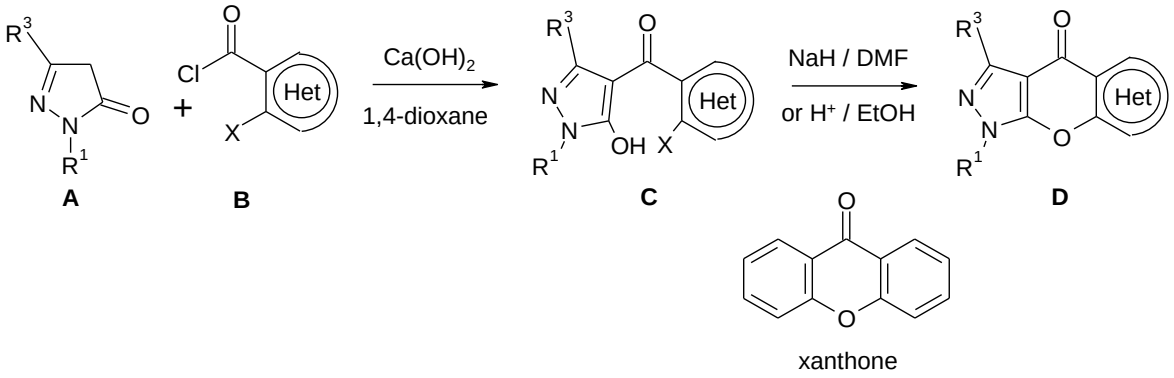
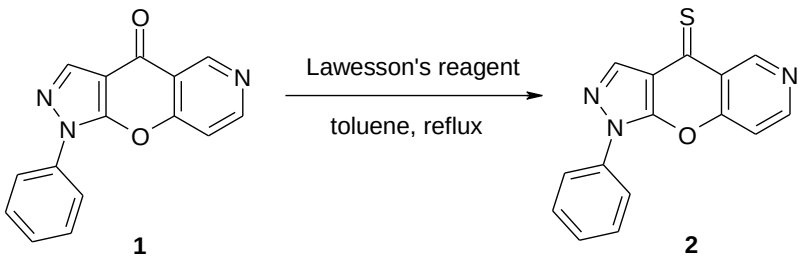


Figure 1

The conversion of ketones into the corresponding thiones can be achieved by the application of different reagents [9,11,12]. The 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, known as Lawesson's reagent, has been commonly used for this purpose and usually permits efficient conversion of ketones into thioketones [13-15]. Employing this method, namely by treatment of compound **1** with 0.5 equivalents of Lawesson's reagent in boiling toluene, we obtained the corresponding target compounds **2** in 97% yield (Scheme 1).



Scheme 1. Synthesis of the title compound **2.**

A detailed characterization of **2** including MS and NMR (^{1}H, ^{13}C, ^{15}N) spectral data as well as microanalytical data is given in the Experimental. Full and unambiguous assignment of all ^{1}H, ^{13}C and ^{15}N NMR resonances was achieved by combined application of standard NMR spectroscopic techniques such as ^{1}H-coupled ^{13}C-NMR (gated decoupling), APT, COSY, TOCSY, NOESY, gs-HSQC and gs-HMBC [16].

Experimental

The melting point was determined on a Kofler hot-stage microscope and is uncorrected. The mass spectrum was obtained on a Shimadzu QP 1000 instrument (EI, 70 eV). The elemental analysis was performed at the Microanalytical Laboratory, University of Vienna. The NMR spectra were recorded from $CDCl_3$ solutions at 298 K on a Varian UnityPlus instrument (300 MHz for ^{1}H, 75.4 MHz for ^{13}C) and on a Bruker Avance 500 instrument with a 'directly' detecting broadband observe probe (BBFO) (500.13 MHz for ^{1}H, 50.68 MHz for ^{15}N). The centre of the solvent signal was used as an internal standard which was related to TMS with δ = 7.26 ppm (^{1}H in $CDCl_3$) and δ = 77.0 ppm (^{13}C in $CDCl_3$). The digital resolutions were 0.2 Hz/data point in the ^{1}H and 0.4 Hz/data point in the ^{1}H-coupled ^{13}C-NMR spectra (gated decoupling). The ^{15}N NMR spectrum (gradient-selected ^{15}N,^{1}H-HMBC) was referenced against external nitromethane.

*1-Phenylpyrazolo[4',3':5,6]pyrano[3,2-*c*]pyridin-4(1*H*)-thione (**2**)*

To a solution of 1-phenylpyrazolo[4',3':5,6]pyrano[3,2-*c*]pyridin-4(1*H*)-one (**1**) [1] (263 mg,
1 mmol) in toluene (15 mL) was added Lawesson's reagent (202 mg, 0.5 mmol) and the mixture was heated to reflux overnight (~14 h). Then the solvent was removed under reduced pressure and the residue was subjected to column chromatography (silica gel, eluent: CH_2Cl_2 – MeOH, 100+2) to afford 271 mg (97%) of the title compound **2** as an orange-brown solid of mp 192–194 °C.

MS (EI, 70 eV): (*m/z*, %) 280 (M^++1, 21), 279 (M^+, 100), 278 (M^+-1, 74), 138 (35), 77 (85), 51 (54).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.45 (d, 1H, H-8, ^{3}J(H8,H7) = 5.8 Hz), 7.46 (m, 1H, Ph H-4), 7.58 (m, 2H, Ph H-3,5), 7.86 (m, 2H, Ph H-2,6), 8.40 (s, 1H, H-3), 8.85 (d, 1H, H-7, ^{3}J(H7,H8) = 5.8 Hz), 9.83 (s, 1H, H-5).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 112.4 (C-8, ^{1}J(C8,H8) = 168.2 Hz, ^{2}J(C8,H7) = 8.7 Hz, ^{4}J(C8,H5) = 1.5 Hz), 119.6 (C-3a, ^{2}J(C3a,H-3) = 9.5 Hz), 121.5 (Ph C-2,6), 122.6 (C-4a, ^{2}J(C4a,H5) = 6.8 Hz, ^{3}J(C4a,H8) = 3.9 Hz, ^{4}J(C4a,H7) = 1.3 Hz), 128.3 (Ph C-4), 129.6 (Ph C-3,5), 136.5 (Ph C-1), 138.8 (C-3, ^{1}J(C3,H3) = 196.3 Hz), 145.2 (C-9a, ^{3}J(C9a,H3) = 4.7 Hz), 152.3 (C-5, ^{1}J(C5,H5) = 187.1 Hz, ^{3}J(C5,H7) = 12.0 Hz), 153.4 (C-7, ^{1}J(C7,H7) = 183.0 Hz, ^{2}J(C7,H8) = 1.4 Hz, ^{3}J(C7,H5) = 13.7 Hz), 155.3 (C-8a, ^{2}J(C8a,H8) = 3.9 Hz, ^{3}J(C8a,H7) = 9.8 Hz, ^{3}J(C8a,H5) = 7.7 Hz), 195.7 (C-4).

^{15}N NMR (50 MHz, $CDCl_3$): δ (ppm) –186.8 (N-1), –83.5 (N-2), –75.8 (N-6).

Anal. Calcd for $C_{15}H_9N_3OS$: C, 64.50%; H, 3.25%; N, 15.04%. Found: C, 64.42%; H, 3.18%; N 14.70%.

References and Notes

1. Eller, G. A.; Wimmer, V.; Haring, A. W.; Holzer, W. An Efficient Approach to Heterocyclic Analogues of Xanthone: A Short Synthesis of all possible Pyrido[5,6]pyrano[2,3-*c*]pyrazol-4(1*H*)-ones. *Synthesis* **2006**, 4219–4229.
2. Eller, G. A.; Haring, A. W.; Datterl, B.; Zwettler, M.; Holzer W. Tri- and Tetracyclic Heteroaromatic Systems: Synthesis of Novel Benzo-, Benzothieno- and Thieno-Fused Pyrano[2,3-*c*]pyrazol-4(1*H*)-ones. *Heterocycles* **2007**, *71*, 87–104.
3. Eller, G. A.; Holzer, W. A Convenient Approach to Heterocyclic Building Blocks: Synthesis of Novel Ring Systems Containing a [5,6]Pyrano[2,3-*c*]pyrazol-4(1*H*)-one Moiety. *Molecules* **2007**, *12*, 60–73.
4. Eller, G. A.; Datterl, B.; Holzer, W. Pyrazolo[4',3':5,6]pyrano[2,3-*b*]quinoxalin-4(1*H*)-one: Synthesis and Characterization of a Novel Tetracyclic Ring System. *J. Heterocycl. Chem*. **2007**, *44*, 1139–1143.
5. Eller, G. A.; Wimmer, V.; Holzer, W. Synthesis of Novel Polycyclic Ring Systems Containing two Pyrano[2,3-*c*]pyrazol-4(1*H*)-one Moieties. *Khim. Geterotsikl. Soedin*. **2007**, 1251–1255(*Chem. Heterocycl. Comp*. **2007**, *43*, 1060–1064).
6. Eller, G. A.; Habicht, D.; Holzer, W. Synthesis of a Novel Pentacycle: 8-Methyl-10-phenylpyrazolo[4',3':5,6]pyrano[3,2-*c*][1,10]phenanthrolin-7(10*H*)-one. *Khim. Geterotsikl. Soedin*. **2008**, 884–890 (*Chem. Heterocycl. Comp*. **2008**, *44*, 709–714.
7. Eller, G. A.; Zhang, Q.; Habicht, D.; Datterl, B.; Holzer, W. Synthesis and NMR Data of Pyrazolo[4',3':5,6]pyrano[2,3-*b*]pyrazin-4(1*H*)-ones: Derivatives of a Novel Tricyclic Ring System. *Acta Chim. Slov*. **2009**, *56*, 521–526.
8. Jensen, B. S. The Synthesis of 1-Phenyl-3-methyl-4-acyl-pyrazolones-5. *Acta Chem. Scand*. **1959**,*13*, 1668–1670, (*Chem. Abstr*. **1962**, *56*, 66890).
9. Williams, A. C.; Camp, N. Product class 4: benzopyranones and benzopyranthiones. *Science of Synthesis* **2003**, *14*, 347–638; and references cited therein.
10. Huemer, V.; Eller, G. A.; Holzer, W. Heterocyclic analogues of xanthiones: 5,6-fused 3-methyl-1-phenylpyrano[2,3-*c*]pyrazol-4(1*H*)thiones – synthesis and NMR (^{1}H, ^{13}C, ^{15}N) data. *Magn. Reson. Chem*. **2010**, in press.
11. Cremlyn, R. J. *An Introduction to Organosulfur Chemistry*, John Wiley & Sons: New York, **1996**.
12. Duus, F. Thiocarbonyl compounds. In *Comprehensive Organic Chemistry*, D. H. R. Barton, W. D. Ollis, eds.; Vol. 3, 373–487, Pergamon Press: Oxford, **1979**.

13. Cherkasov, R. A.; Kutyrev, G. A.; Pudovik, A. N. Tetrahedron report number 186: Organothiophosphorus reagents in organic synthesis. *Tetrahedron* **1985**, *41*, 2567–2624.
14. Pedersen, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S.-O. Studies on organophosphorus compounds. XX. Syntheses of thioketones. *Bull. Soc. Chim. Belg*. **1978**, *87*, 223–228.
15. Jesberger, M.; Davis, T. P.; Barner, L. Application of Lawesson's Reagent in Organic and Organometallic Synthesis. *Synthesis* **2003**, 1929–1958.
16. Braun, S.; Kalinowski, H.-O.; Berger, S. 150 and More Basic NMR Experiments: A Practical Course – Second Expanded Edition, Wiley–VCH, Weinheim, **1998**, (*Chem. Abstr*. **1999**, *131*, 184497).

3. LITERATURVERZEICHNIS

[1] M. Pedro, F. Cerqueira, M.E. Sousa, M.S.J. Nascimento, M. Pinto, Xanthones as Inhibitors of Growth of Human Cancer Cell Lines and Their Effects on the Proliferation of Human Lymphocytes In Vitro. *Bioorg. Med. Chem*., **2002**, 10, 3725–3730.

[2] J.C. Roberts, Naturally Occurring Xanthones, *Chem. Rev.*, **1961**, 61, 591-605.

[3] M.M.M. Pinto, M.E. Sousa, M.S.J. Nascimento, Xanthone Derivatives: New insights in biological activities. *Curr. Med. Chem*., **2005**, 12, 2517–2538.

[4] A.C. Williams, N. Camp, Product Class 4: Benzopyranones and Benzopyranthiones. *Sci. Synth.*, **2003**, 14, 347-638; und darin enthaltene Zitate.

[5] U. Thull, S. Kneubühler, B. Testa, M.F.M. Borges, M.M.M. Pinto, Substituted Xanthones as Selective and Reversible Monoamine Oxidase A (MAO-A) Inhibitors, *Pharm. Research*, **1993**, 10, 1187-1190.

[6] K.R. Markham, Gentian pigments. I. Xanthones from Gentiana bellidiflora, *Tetrahedron*, **1964**, 20, 991-997.

[7] W. Forth, D. Henschler, W. Rummel; K. Aktories, U. Förstermann, F.B. Hofmann, K. Starke (Hrsg.): *Allgemeine und Spezielle Pharmakologie und Toxikologie*, 10 Auflage, Urban & Fischer in Elsevier: München, **2009**, 174-178.

[8] S. Woo, J. Jung, C. Lee, Y. Kwon, Y. Na, Synthesis of new xanthone analogues and their biological activity test – Cytotoxicity, topoisomerase II inhibition, and DNA cross-linking study, *Bioorg. Med. Chem. Lett*., **2007**, *17*, 1163–1166.

[9] I.M. Fellows, M. Schwaebe, T.S.Dexheimer, H. Vankayalapati, M. Gleason-Guzman, J.P. Whitten, L.H. Hurley, Determination of the importance of the stereochemistry of psorospermin in topoisomerase II–induced alkylation of DNA and in vitro and in vivo biological activity, *Mol. Cancer Ther.*, **2005**, 4, 1729-1739.

[10] A. Nagakawa, S. Omura: Structure of Cervinomycine, a novel Xantone Antibiotic against Anaerobe and Mycoplasma, *Journal of Antibiotics*, **1986**, Vol. XL, 3, 301-308.

[11] H. Bockholt, G. Udvarnoki, J. Rohr, Biosynthetic Studies on the Xanthone Antibiotics Lysolipins X and I, *J. Org. Chem.,* **1994**, 59, 2064-2069.

[12] H. Drautz, W. Keller-Schierlein, H. Zahner, Stoffwechselprodukte von Mikroorganismen. Lysolipin I, ein neues Antibiotikum aus Streptomyces violaceoniger, *Arch. Microbiol.,* **1975**,106, 175-190.

[13] H-A. Jung, B-N. Su, W.J. Keller, R.G. Mehta, A. D. Kinghorn, Antioxidant Xanthones from the Pericarp of Garcinia mangostana (Mangosteen), *J. Agric. Food Chem.*, **2006,** 54, 2077-2082.

[14] K. Nakatani, N. Nakahata, T. Arakawa, H.Yasuda,Y. Ohizumi, Inhibition of cyclooxygenase and prostaglandin E2 synthesis by ɣ-mangostin, a xanthone derivative in mangosteen, in C6 rat glioma cells, *Biochemical Pharmacology,* **2002**, 63, 73-79.

[15] A. Kleemann, J. Engel, *Pharmaceutical Substances*: 3rd edition, Thieme Verlag, Stuttgard-New York, **1999**, 91-92.

[16] J. Bell, Amlexanox for the Treatment of Recurrent Aphthous Ulcers, *Clin. Drug Invest.*, **2005**, 25(9), 555-566.

[17] V. Colotta, L. Cecchi, D. Catarzi, F. Melani, G. Filacchioni, C. Martini, P. Tacchi, A. Lucacchini, 1-(3-Aminophenyl)-3-methyl[1]benzopyrano[2,3-c]pyrazol-4-one: a new selective A2 adenosine receptor antagonist. *Pharm. Pharmacol. Lett.*, **1992**, *2*, 74–76; [*Chem. Abstr*. **1993**, 118, 32807].

[18] R.S. Varma, D. Kumar, Micowave-Accelerated Solvent-Free Synthesis of Thioketones, Thiolactones, Thioamides, Thionoesters, and Thioflavonoids, *Org. Letters* **1999**, 1, 697-700.

[19] Lit. [4], 347-638.

[20] R.J. Cremlyn, *An Introduction to Organosulfur Chemistry*, John Wiley&Sons: New York, **1996**, 21-22.

[21] B.S. Pedersen, S. Scheibye, N.H. Nikson, S.-O. Lawesson, Studies on organophosphorus compounds. XX. Syntheses of thioketones, *Bull. Soc. Chim. Belg.*, **1978**, 87, 223-228.

[22] Lit. [20], 17-27.

[23] M. Jesberger, T.O. Davis, L. Barner, Application of Lawesson's Reagent in Organic and Organometallic Syntheses, *Synthesis*, **2003**, No.13, 1929-1958.

[24] Lit. [20], 123.

[25] Lit. [23], 1929.

[26] R.A. Cherkasov, G.A. Kutyrev, A.N. Pudovik, Tetrahedron report number 186: Organothiophosphorus Reagents In Organic Synthesis, *Tetrahedron*, **1979**, 41, 2588-2589.

[27] Lit. [20], 21.

[28] Lit. [23], 1929.

[29] T. Ozturk, E. Ertas, O. Mert, A Berzelius Reagent, Phosphorus Decasulfide (P_4S_{10}) in Organic Syntheses, *Chem.Reviews*, **2010**, 110, 3473.

[30] Lit. [26] , 2588-2591.

[31] Lit. [23], 1929-1930.

[32] Lit. [20], 123, 131.

[33] J.A. Van Allen, G.A. Reynolds, J.F. Steinberg, Synthesis of pyranthiones,

J. Heterocycl. Chem., 1979, 16, 1661.

[34] S. Scheibye, R. Shabana, S.-O. Lawesson, C. Romming, Studies on organophosphorus compounds. XL. Reactions of ketones with 2,4-bis (4methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, *Tetrahedron*, **1982**, 38, 993-1001.

[35] Lit. [23], 1930-1931.

[36] G.A. Eller, A.W. Haring, B. Datterl, M. Zwettler, W. Holzer, Tri- and Tetracyclic Heteroaromatic Systems: Synthesis of Novel Benzo-, Benzothieno- and Thieno-Fused Pyrano[2,3-*c*]pyrazol-4(1*H*)-ones., *Heterocycles*, **2007,** 71, 87-104.

[37] G. A. Eller, V. Wimmer, A. W. Haring, W. Holzer, An Efficient Approach to Heterocyclic Analogues of Xanthone: A Short Synthesis of all possible Pyrido[5,6]pyrano[2,3-c]pyrazol-4(1H)-ones., *Synthesis*, **2006**, 4219–4229.

[38] Lit.[36] 87-104.

[39] G. A. Eller, W. Holzer, Convenient Approach to Heterocyclic Building Blocks: Synthesis of Novel Ring Systems Containing a [5,6]Pyrano[2,3-c]pyrazol-4(1H)-one Moiety. *Molecules*, **2007**, 12, 60–73.

[40] Lit.[36] 87-104.

[41] A.S. Sarenko, I. Ya. Kvitko, L.S. Efros, Khim. Geterotsikl. Soedin., Heterocyclic analogs of xanthones. II. C-Acylation of 5-pyrazolinones and synthesis of chromono[3,2-d]pyrazoles, **1972**, 799–804 (Chem. Heterocyl. Comp. **1972**, 8, 722–727).

[42] A.S. Sarenko, L.N. Poznyakova, I. Ya. Kvitko, L.S. Efros, Heterocyclic Analogs of Xanthones. III. Thiochromono[3,2-*d*]Pyrazoles, *Khim. Geterotsikl. Soedin*., **1972**, 805–808 (*Chem. Heterocyl. Comp.*, **1972**, 8, 728–730).

[43] V. Huemer, G.A. Eller, W. Holzer, Heterocyclic analogues of xanthiones: 5,6-Fused 3methyl-1-phenylpyrano[2,3-*c*]pyrazol-4(1*H*)thiones – synthesis and NMR (^{1}H, ^{13}C, ^{15}N) data. *Magn. Reson. Chem*., **2010**, 48, 476–482.

[44] V. Huemer, W. Holzer, 1-Phenylpyrazolo[4',3':5,6]pyrano[3,2-*c*]pyridine-4(1*H*) thione, *Molbank,* **2010**, M678; doi:10.3390/M678

4. ANHANG

4.1. Spektren

Abb.5a.1

VH20/CDCl3

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sw	7000.4	dres	undefined
fb	3800	homo	n
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tpwr	57	lb	not used
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dl	6.000	proc	ft
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ct	16		
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gain	52	wexp	
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il	n	wnt	
in	n		
dp	y		
hs	nn		
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vs	38		
sc	0		
wc	180		
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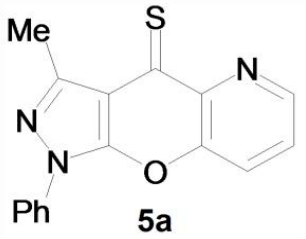
ai	ph		



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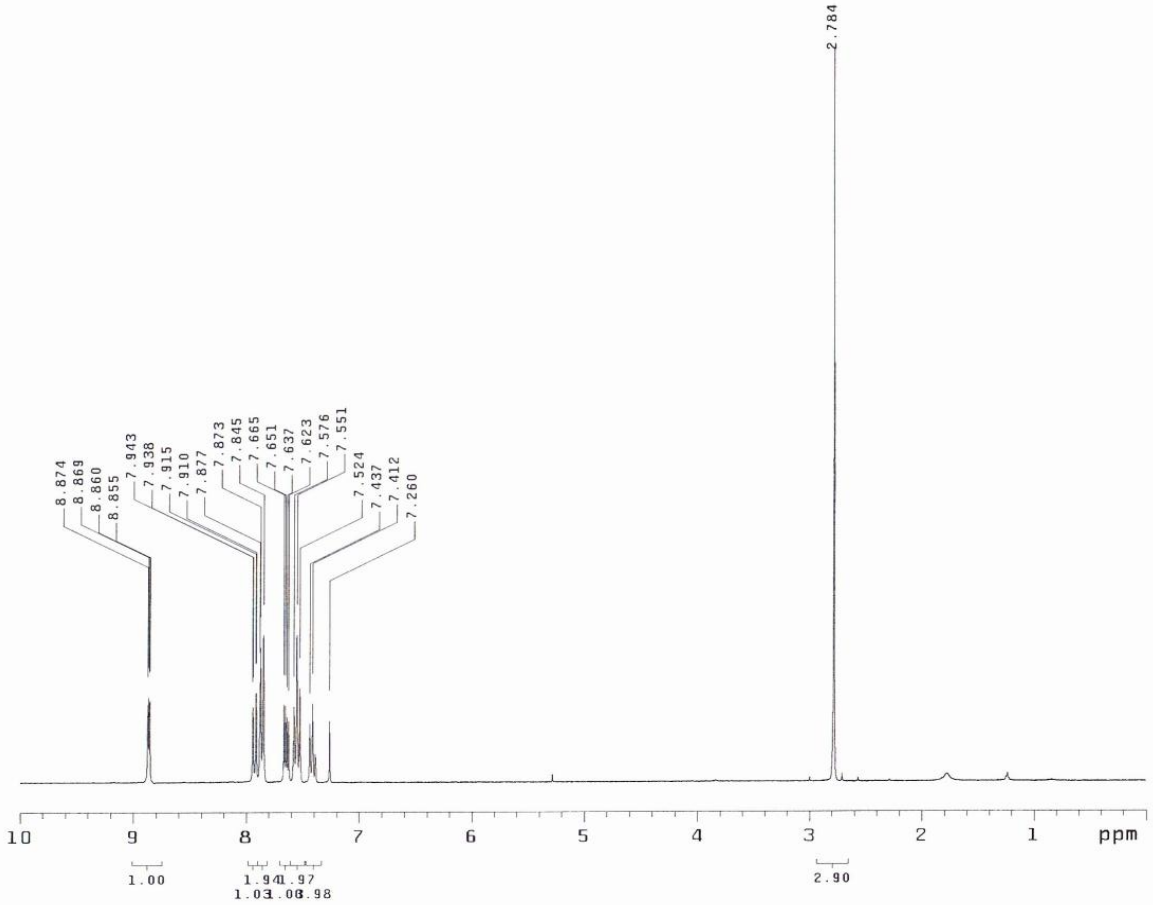

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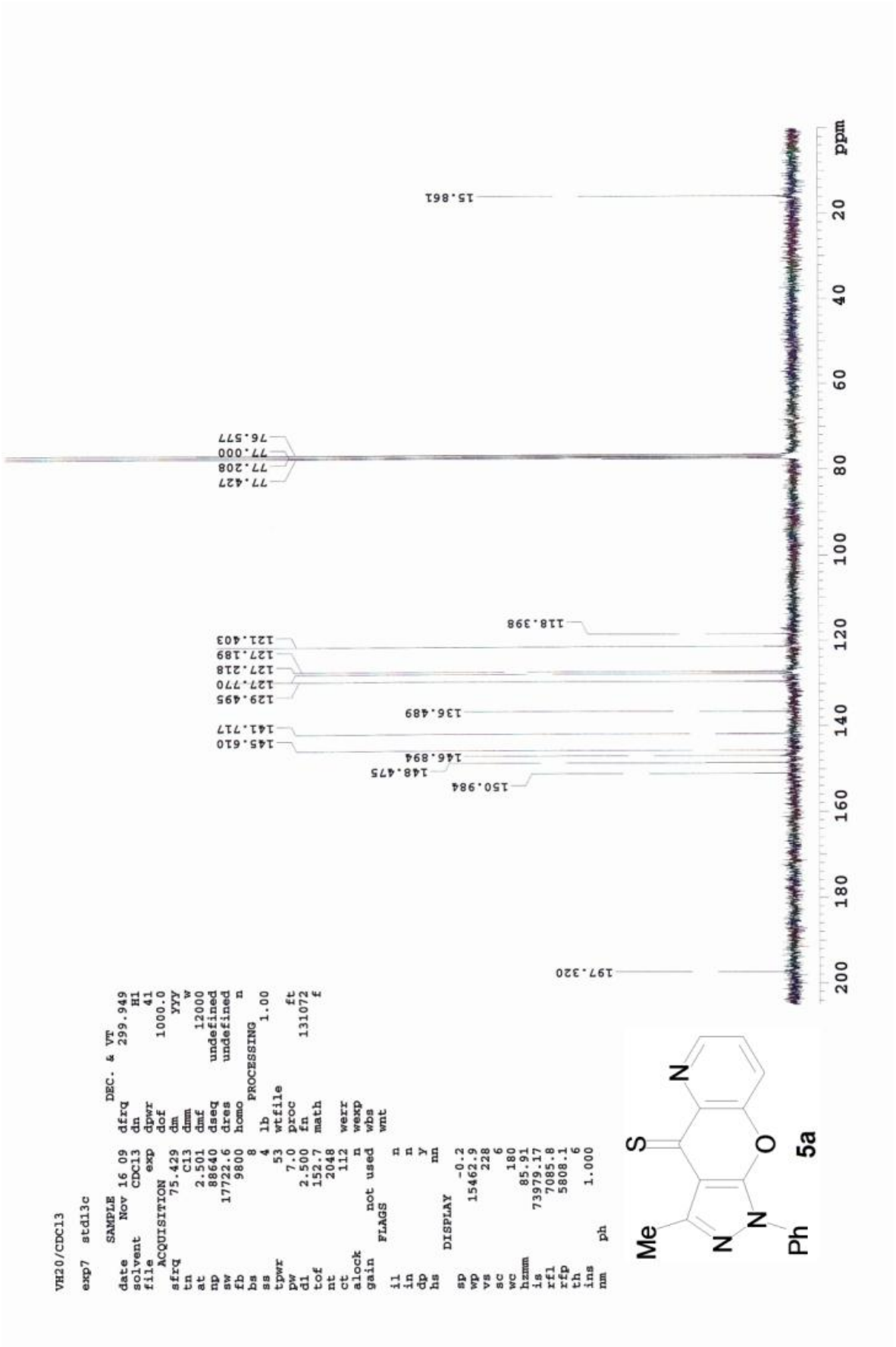
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ss 4
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d1 2.500
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nt 2048
ct 112
alock n
gain not used
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in n
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hs nn
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rfp 5808.1
th 6
ins 1.000
nm ph
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S
O
N
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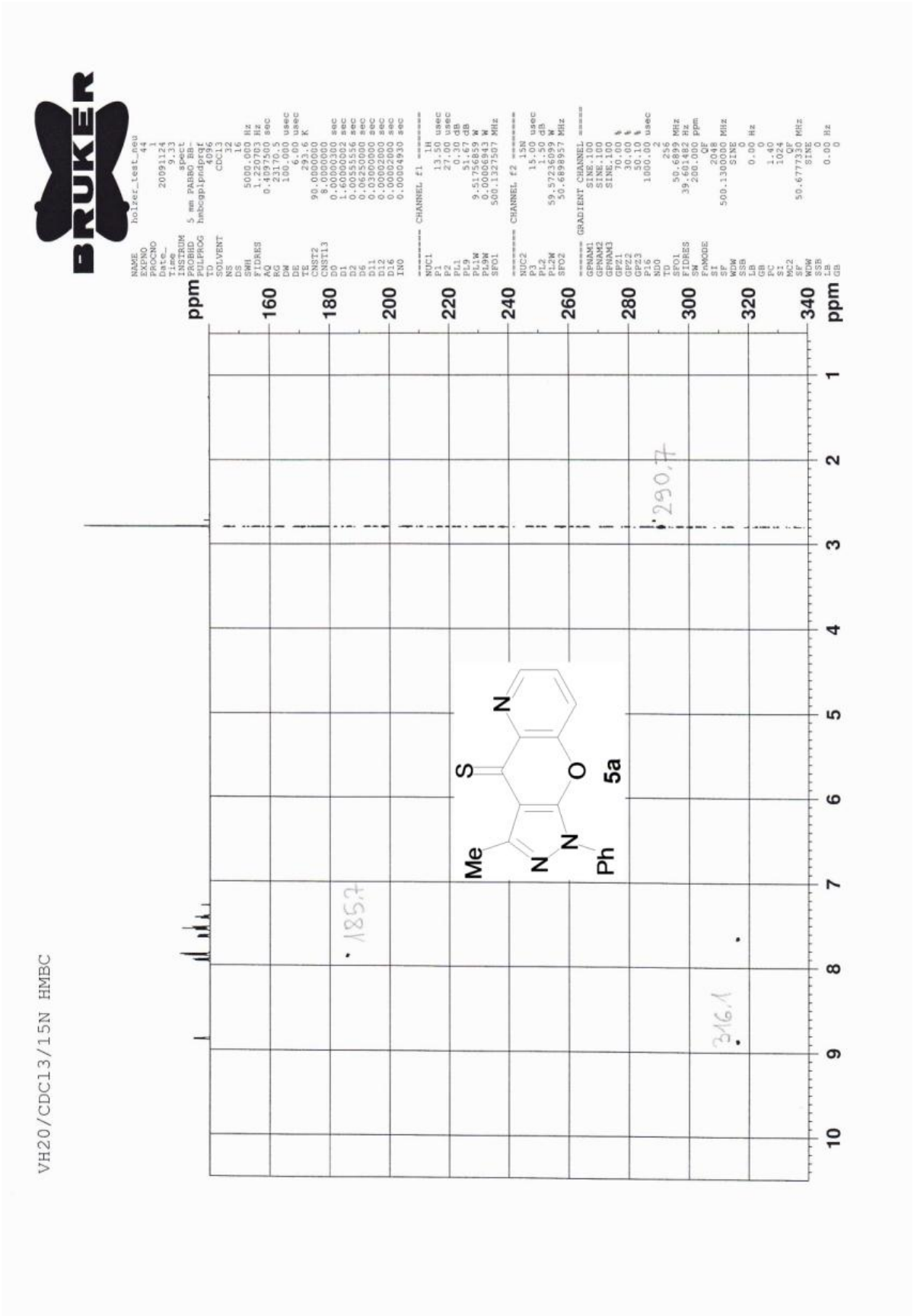
Ph
5a

Abb.5a.3



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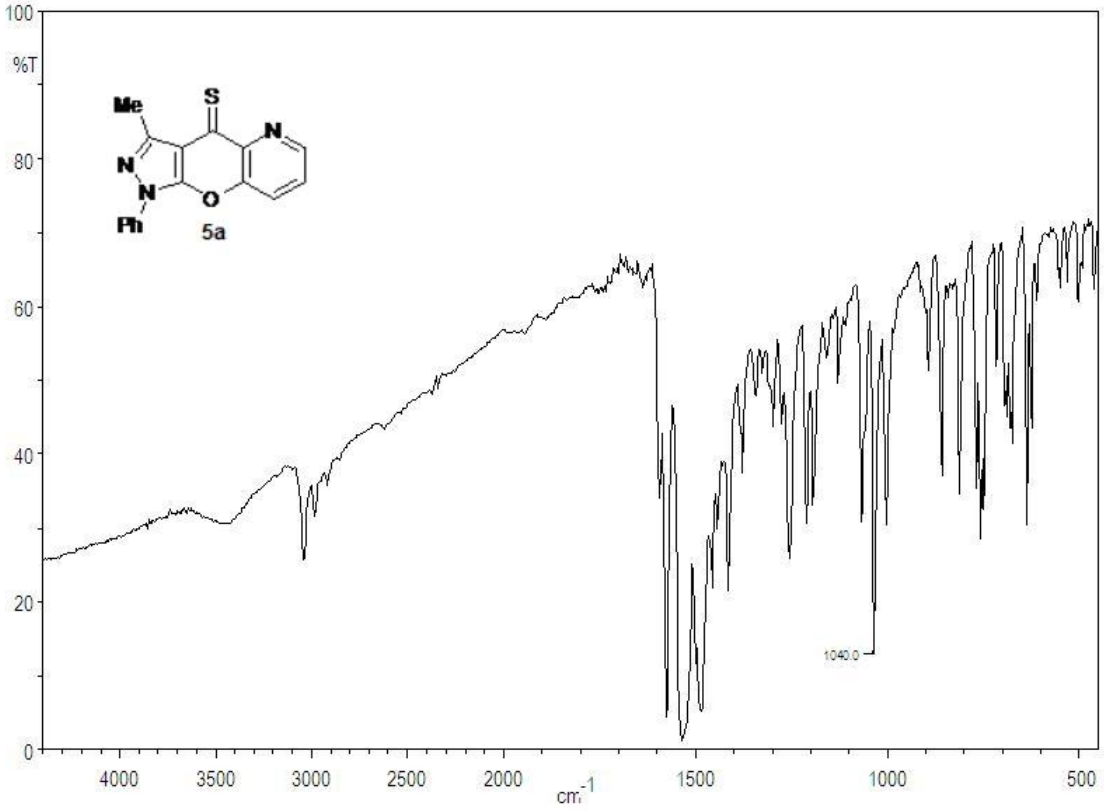

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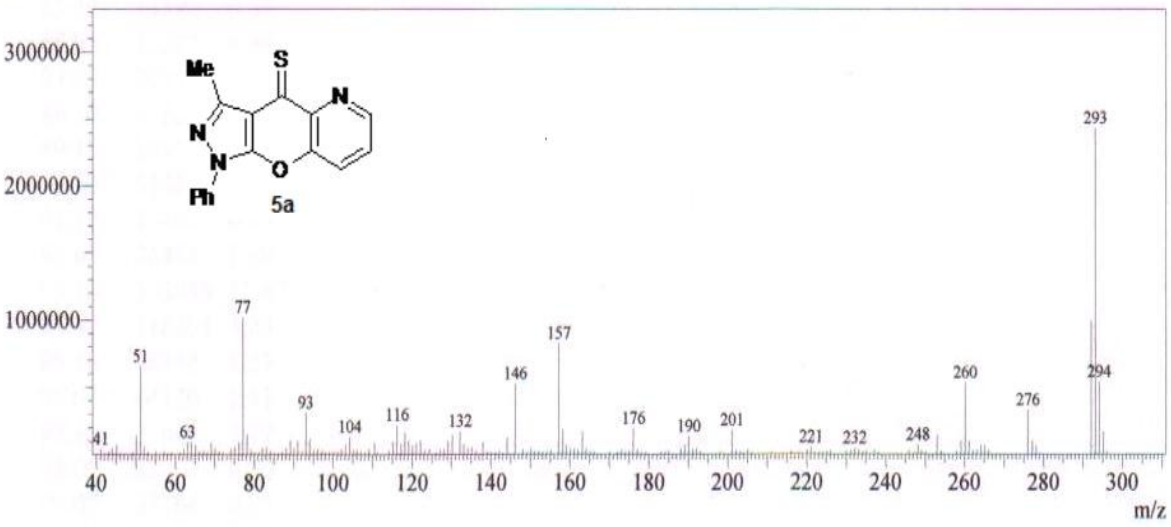

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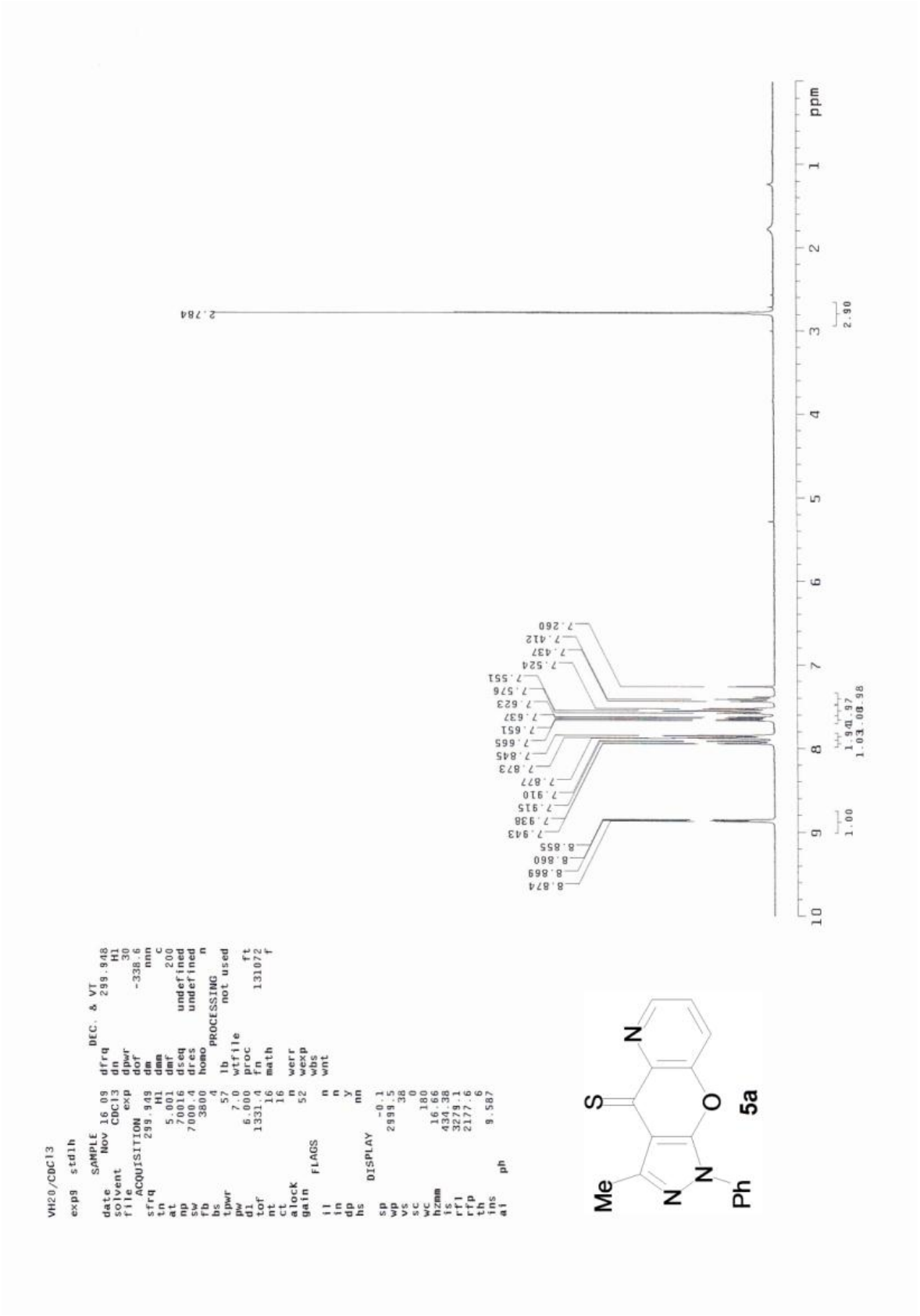
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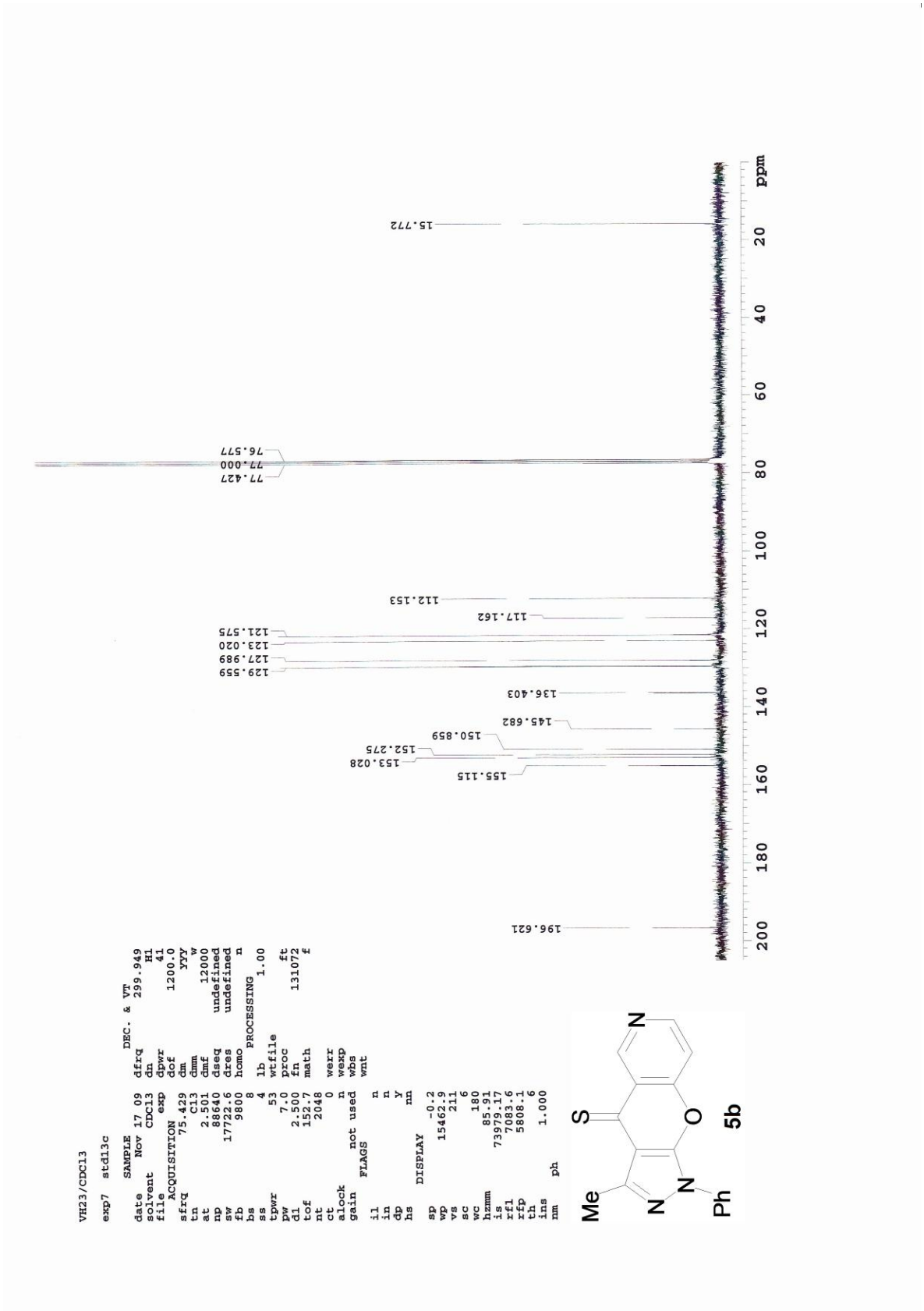
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180
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date Nov 17 09
solvent CDCl3
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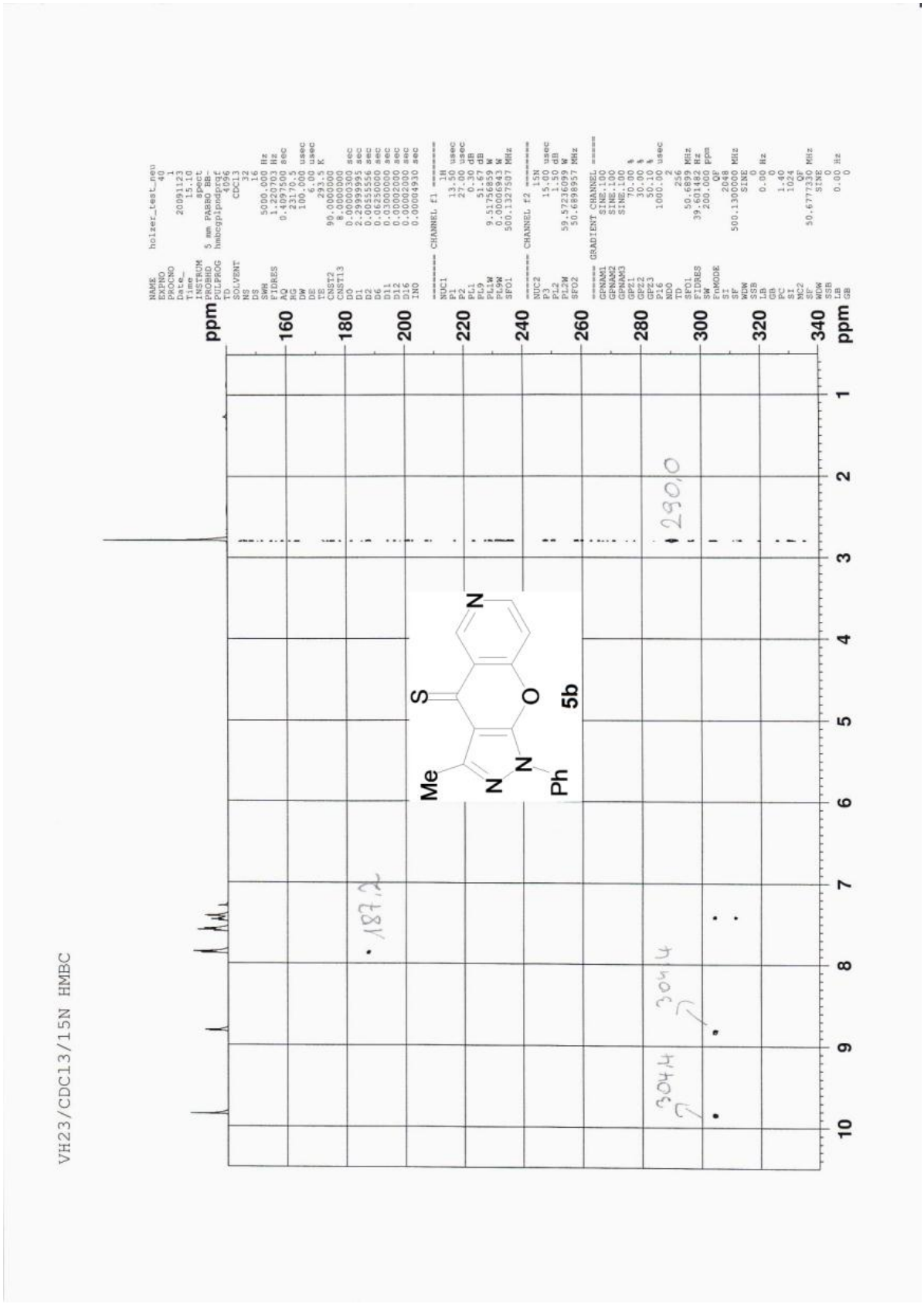
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Ph
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DE 6.00 usec
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CNST13 8.0000000
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D1 2.29999995 sec
D2 0.00555556 sec
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D11 0.03000000 sec
D12 0.00002000 sec
D16 0.00002000 sec
IN0 0.00004930 sec
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NUC1 1H
P1 13.50 usec
P2 27.00 usec
PL1 0.30 dB
PL9 51.67 dB
PL1W 9.51756859 W
PL9W 0.00006943 W
SFO1 500.1327507 MHz
CHANNEL f2
NUC2 15N
P3 15.00 usec
PL2 1.50 dB
PL2W 59.57236099 W
SFO2 50.6898957 MHz
GRADIENT CHANNEL
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GPNAM2 SINE.100
GPNAM3 SINE.100
GPZ1 70.00 %
GPZ2 30.00 %
GPZ3 50.10 %
P16 1000.00 usec
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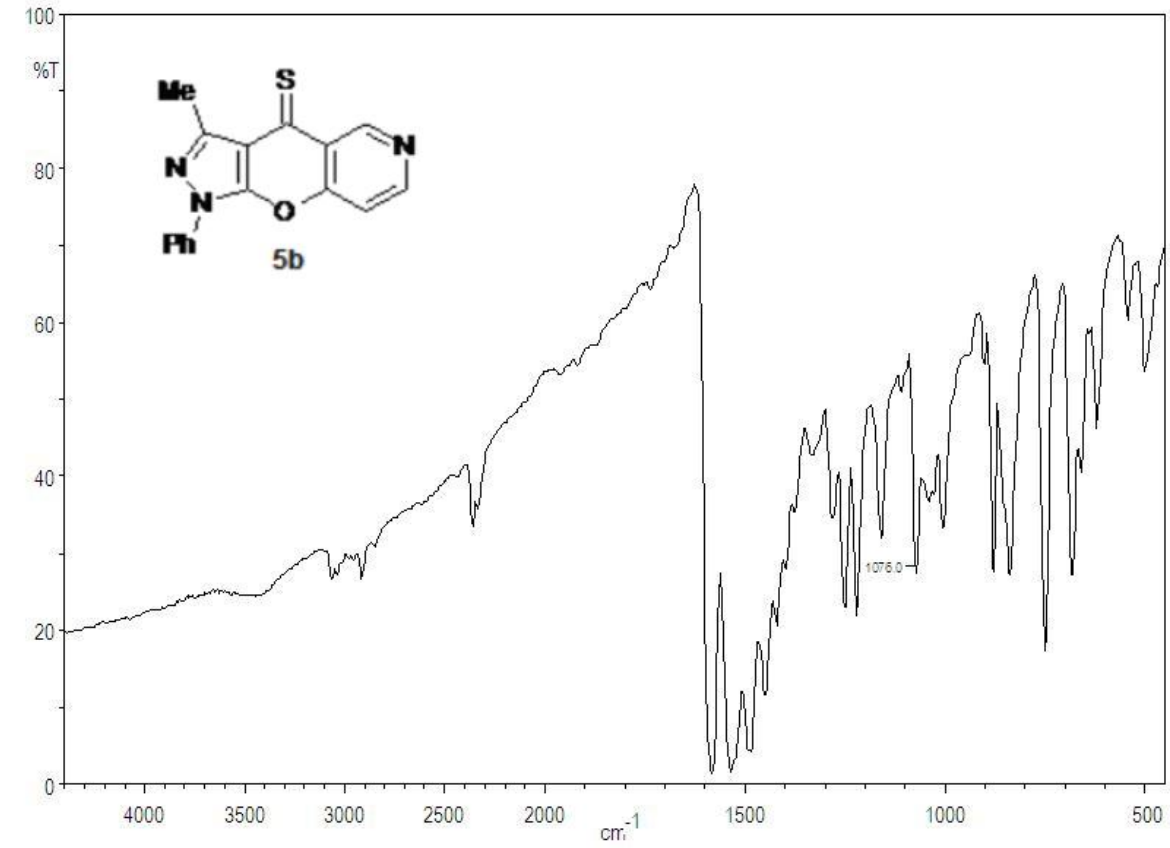
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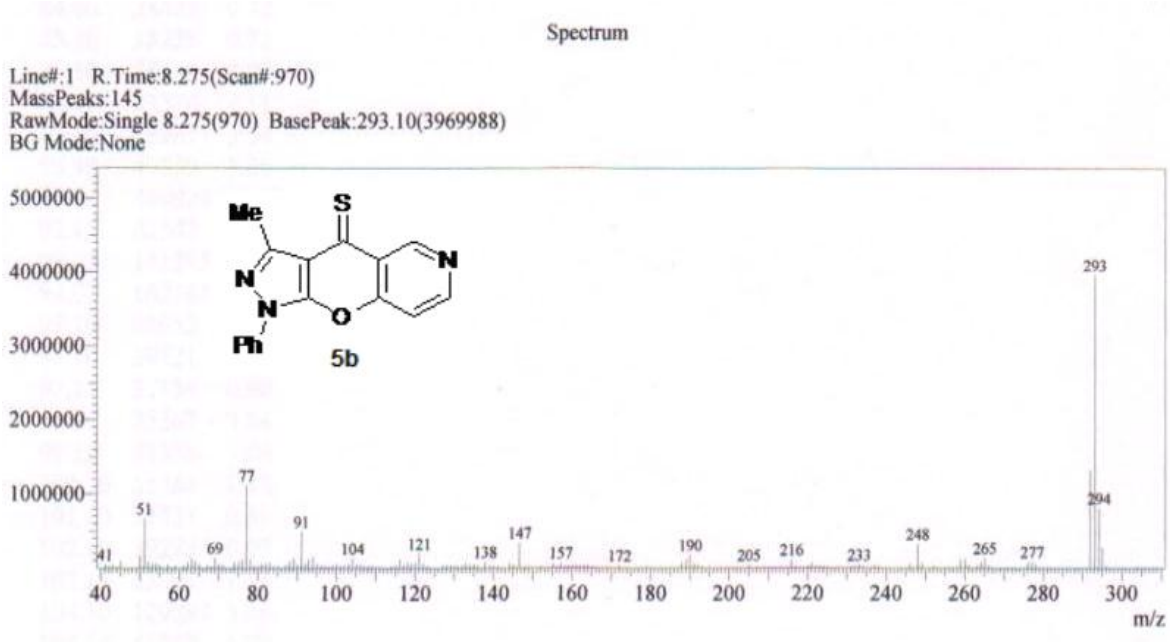
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Ph
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91
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121
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147
157
172
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205
216
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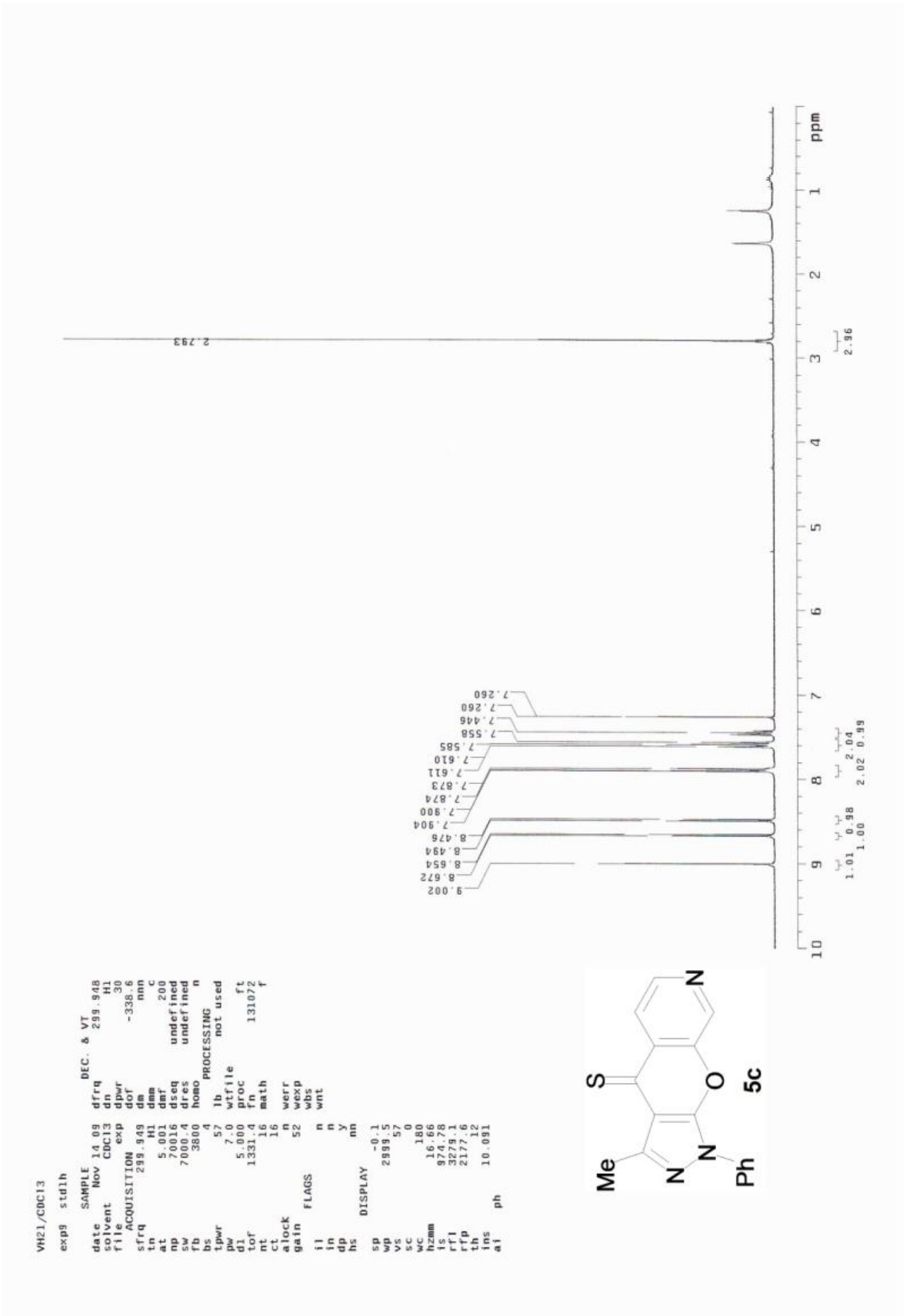
m/z

Abb.5c.1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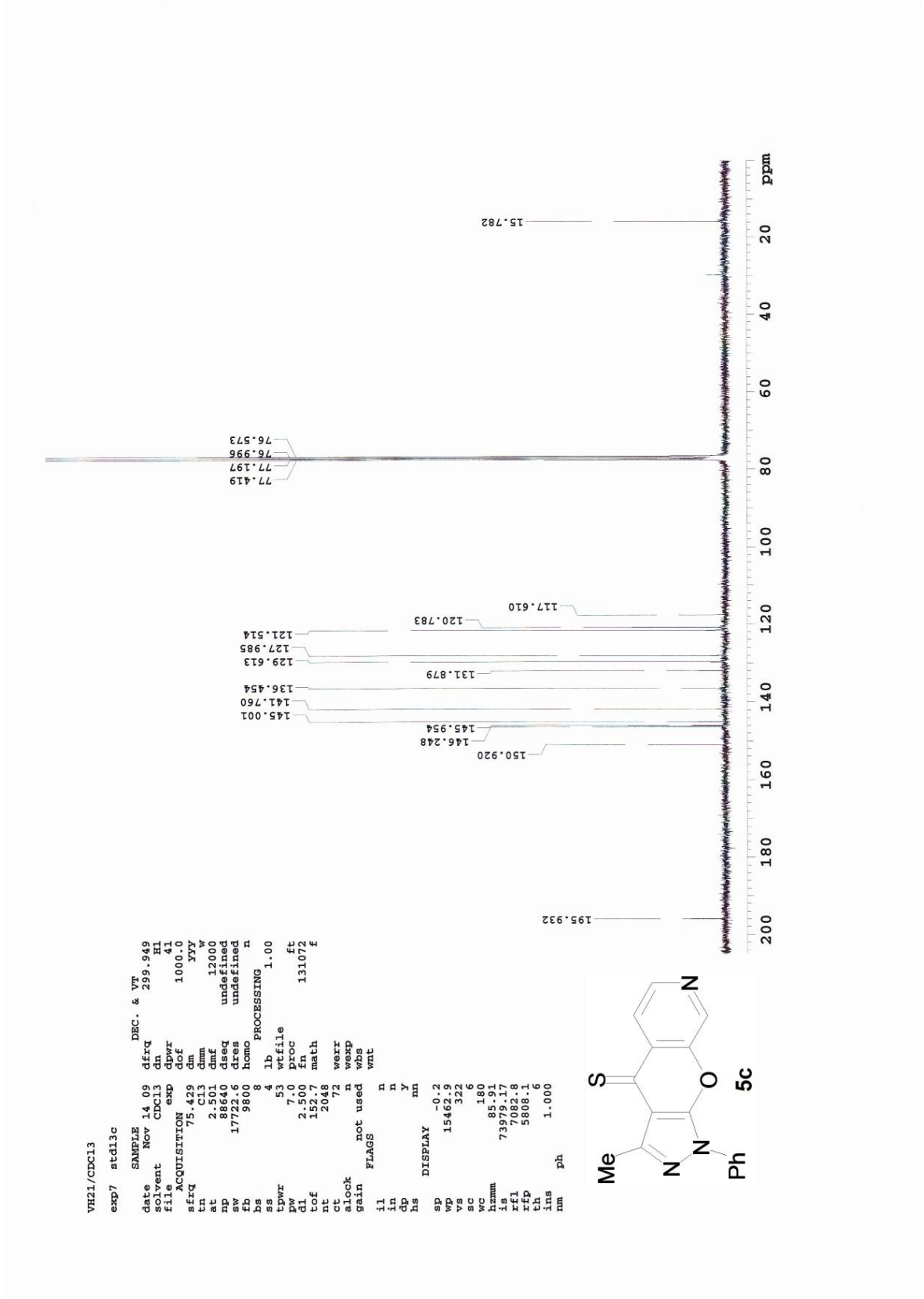
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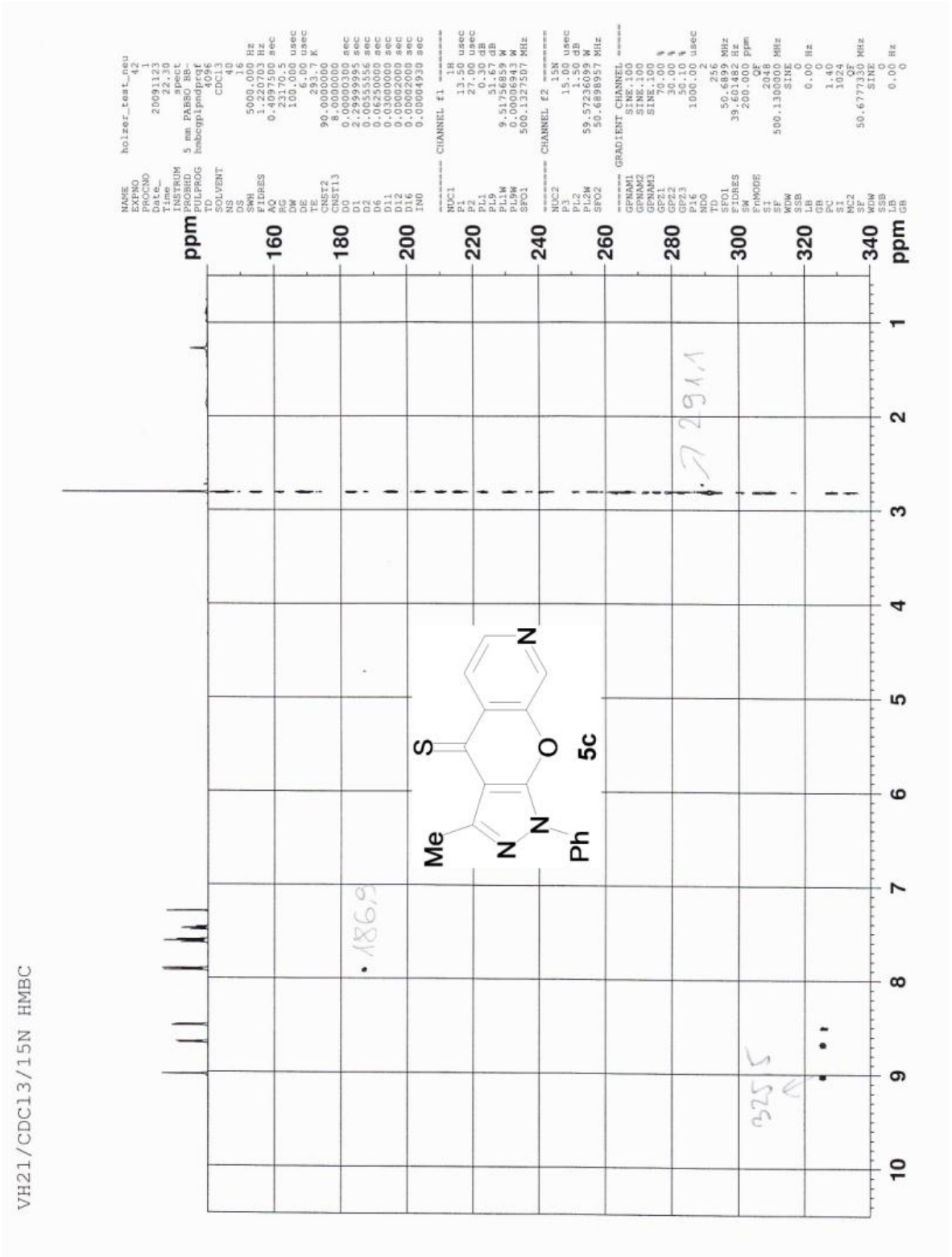

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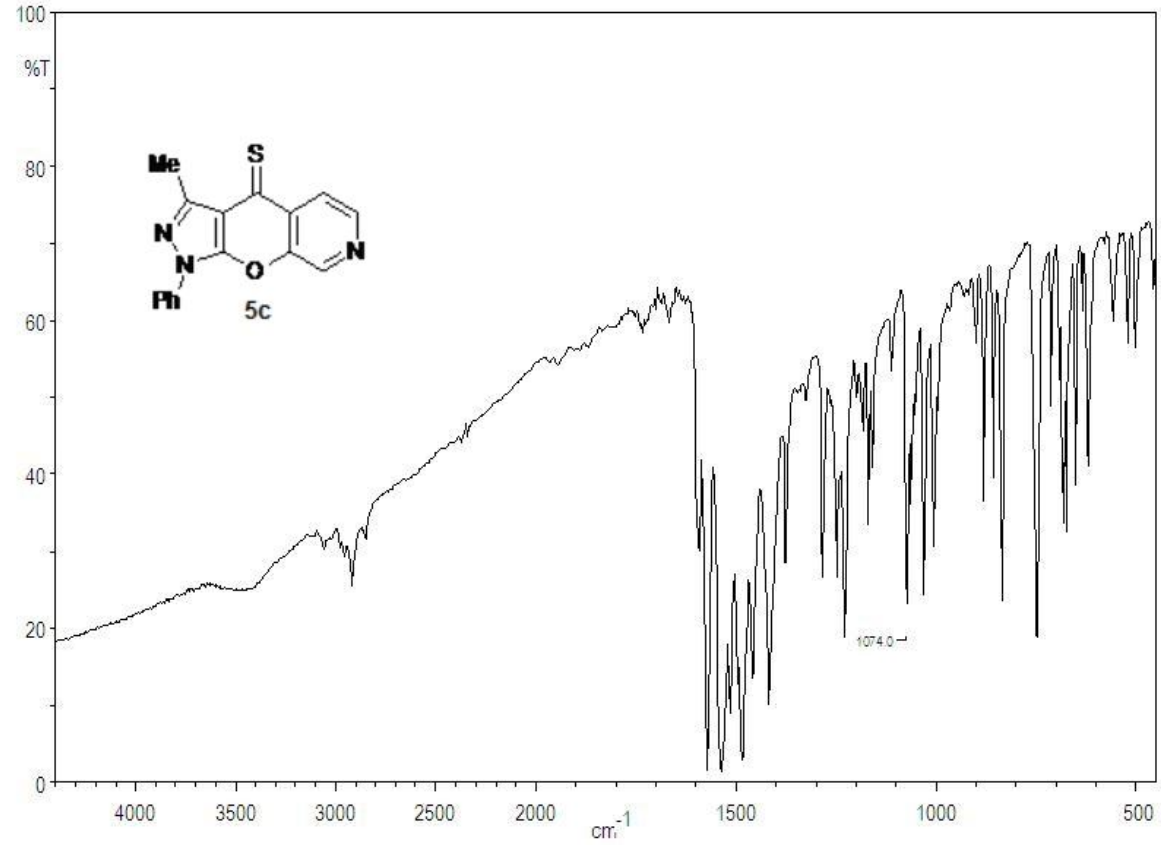

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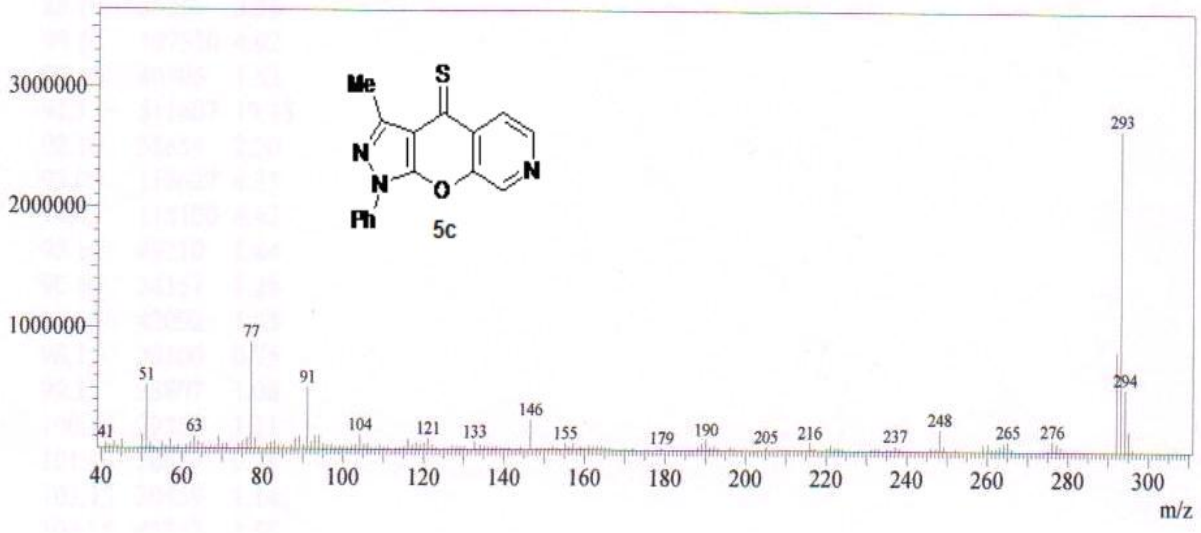

Abb.5d.1

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ct	16		
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hs	nn		
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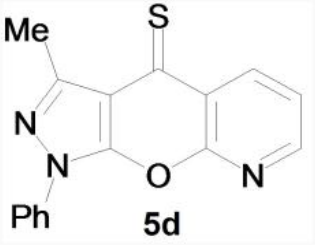
wp	2999.5		
vs	61		
sc	0		
wc	180		
hzmm	16.66		
is	1508.67		
rfl	3279.1		
rfp	2177.6		
th	6		
ins	9.375		
ai	ph		



5d

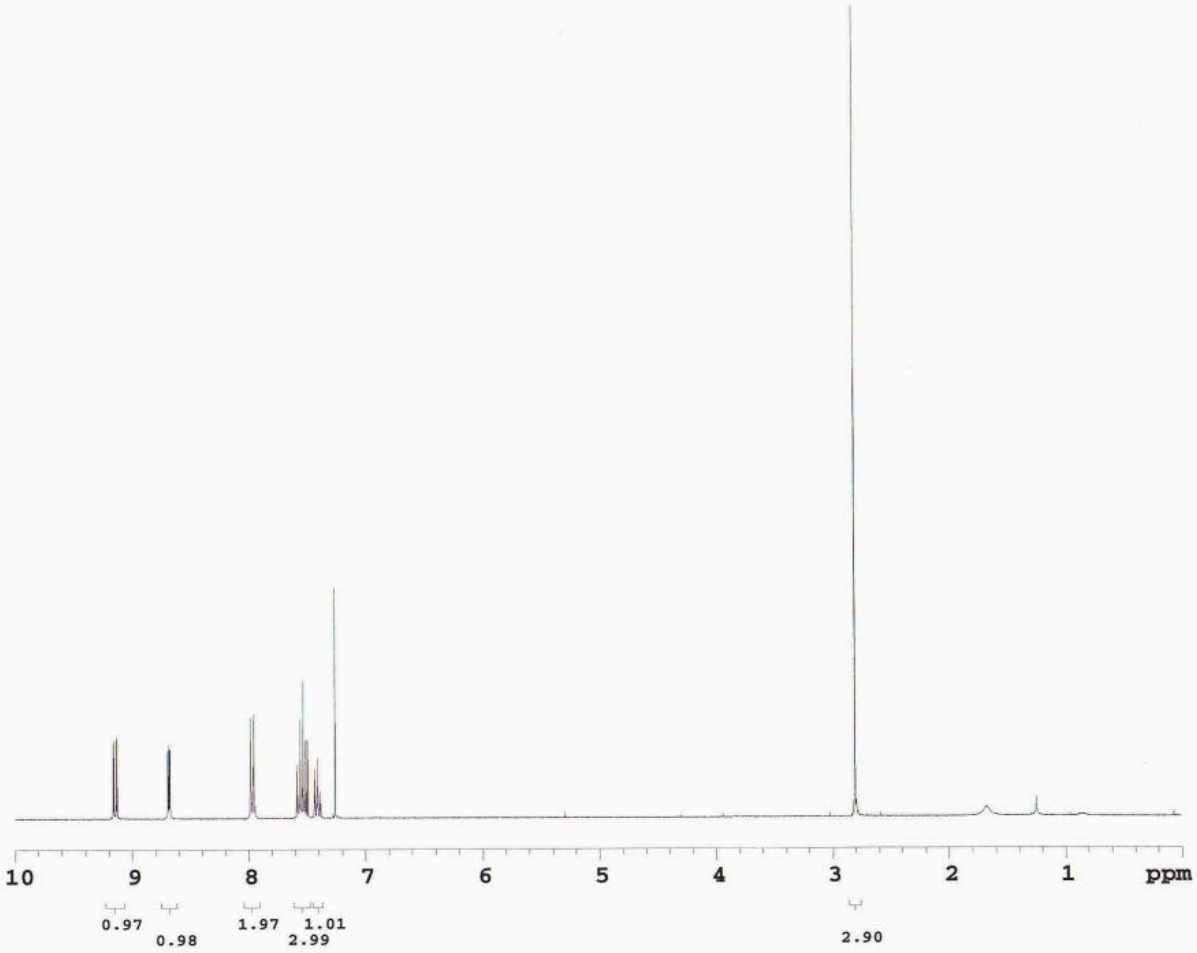


Abb.5d.2

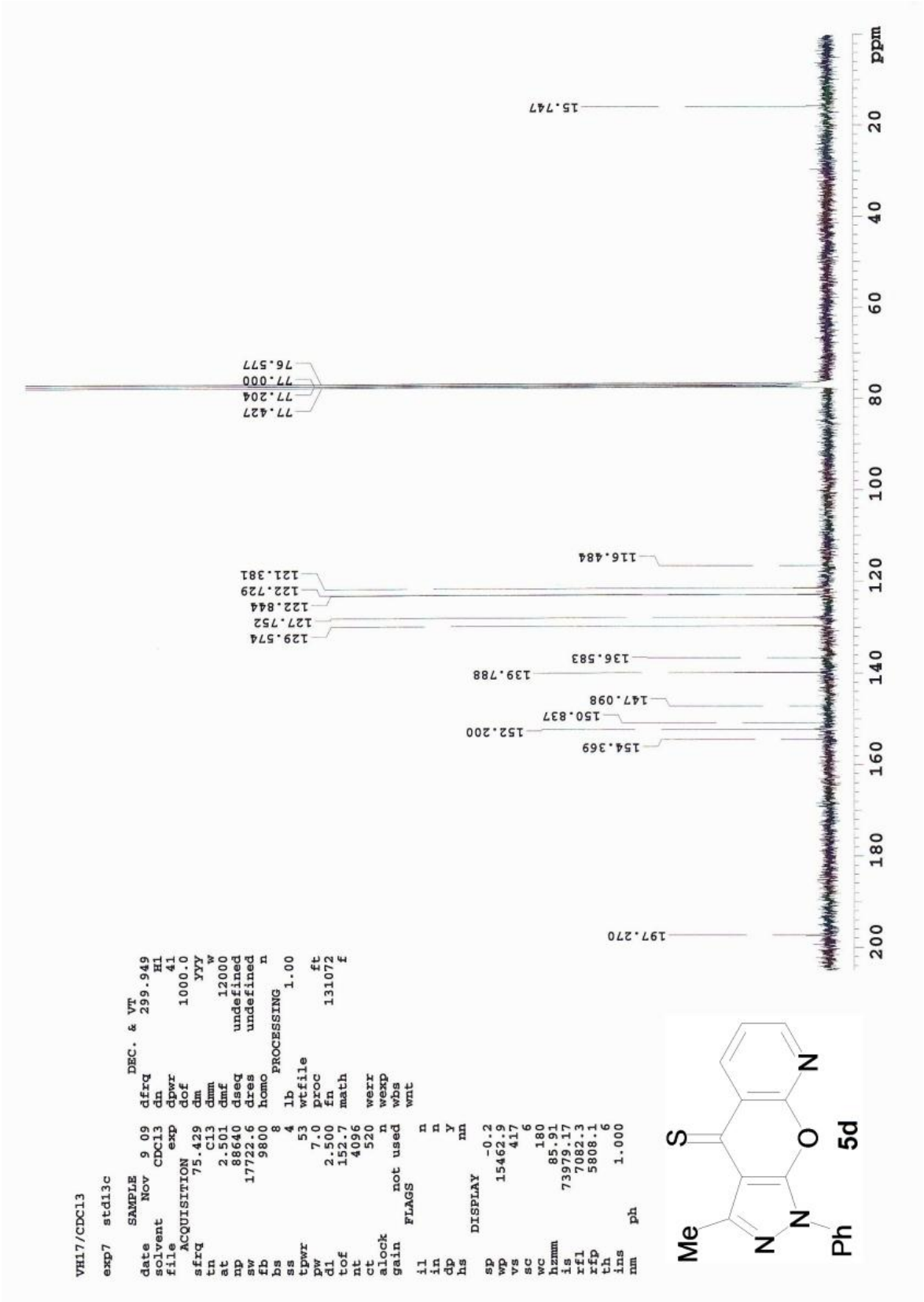

VH17/CDC13
exp7 std13c
SAMPLE
date Nov 9 09
solvent CDC13
file exp
ACQUISITION
sfrq 75.429
tn C13
at 2.501
np 88640
sw 17722.6
fb 9800
bs 8
ss 4
tpwr 53
pw 7.0
d1 2.500
tof 152.7
nt 4096
ct 520
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -0.2
wp 15462.9
vs 417
sc 6
wc 180
hzmm 85.91
is 73979.17
rfl 7082.3
rfp 5808.1
th 6
ins 1.000
nm ph
DEC. & VT
dfrq 299.949
dn H1
dpwr 41
dof 1000.0
dm yyy
dmm w
dmf 12000
dseq undefined
dres undefined
homo n
PROCESSING
lb 1.00
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
197.270
154.369
152.200
150.837
147.098
139.788
136.583
129.574
127.752
122.844
122.729
121.381
116.484
77.427
77.204
77.000
76.577
15.747
ppm
Me
N
N
S
O
N
Ph
5d

Abb.5d.3

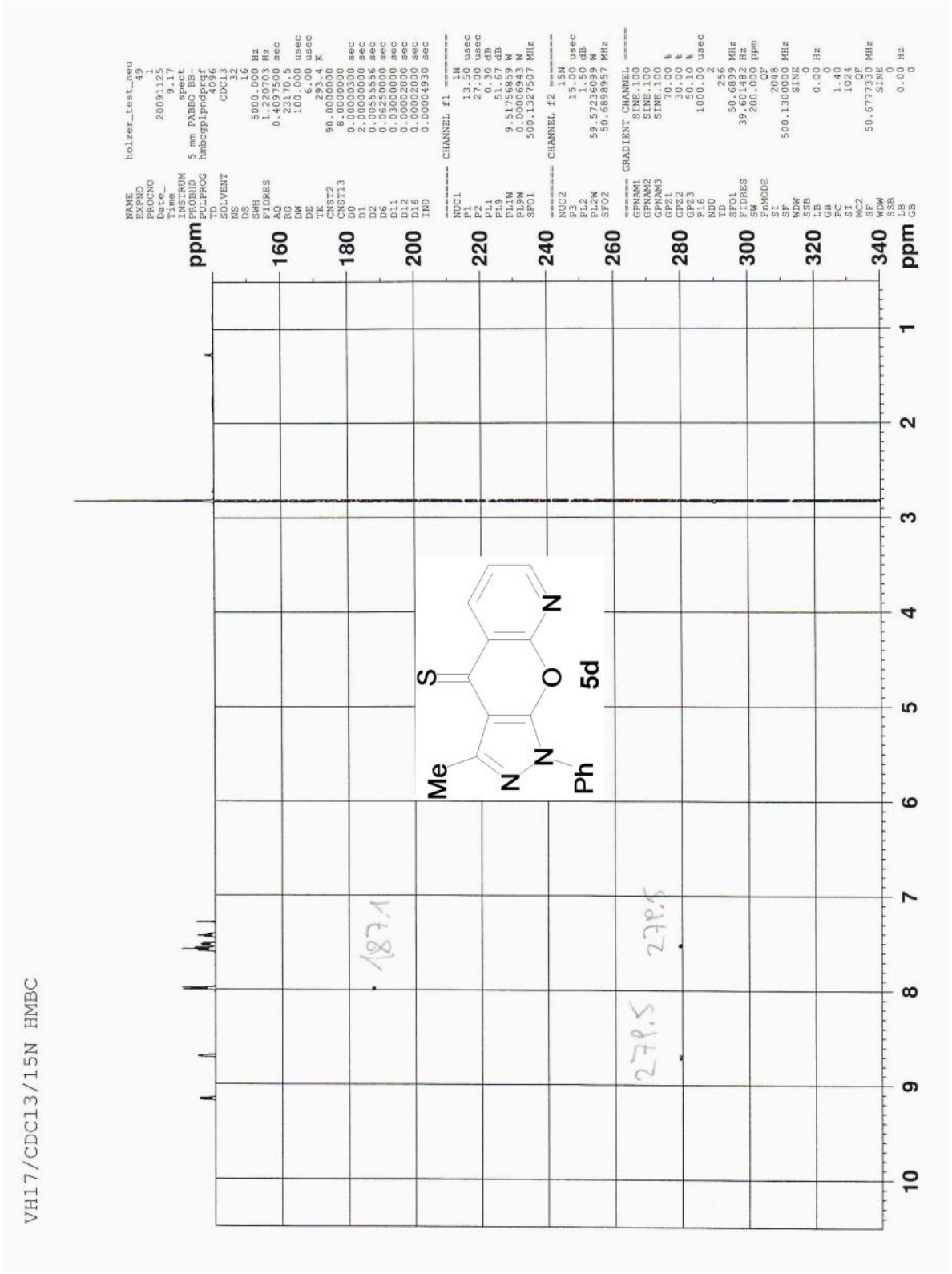
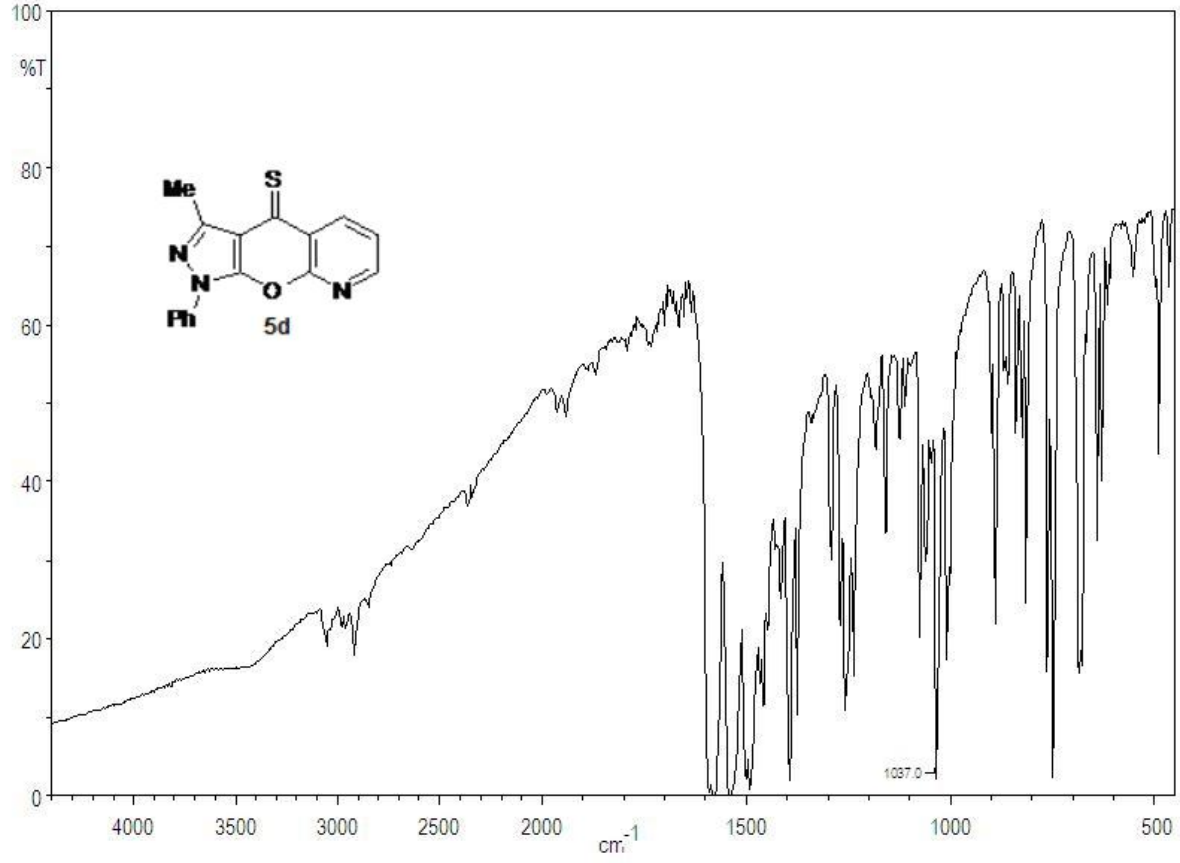


Abb.5d.4


100
%T
80
60
40
20
0
4000
3500
3000
2500
2000
cm-1
1500
1000
500
1037.0
Me
S
N
N
O
N
Ph
5d

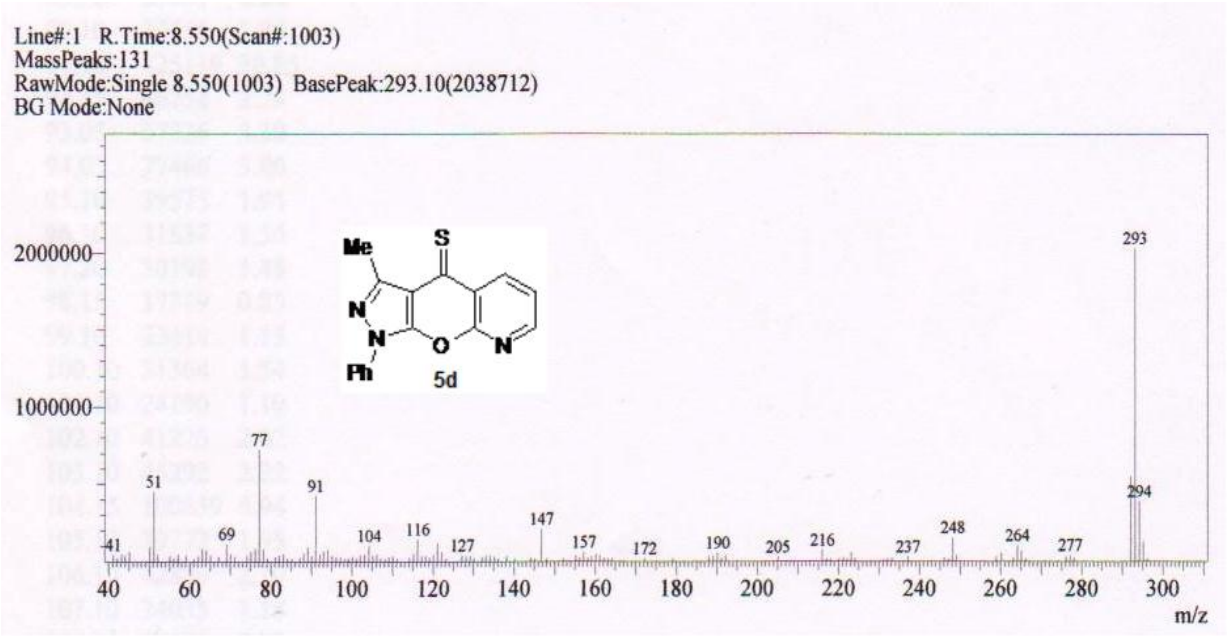
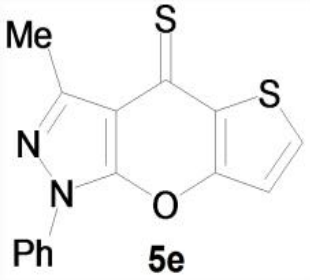

Line#:1 R.Time:8.550(Scan#:1003)
MassPeaks:131
RawMode:Single 8.550(1003) BasePeak:293.10(2038712)
BG Mode:None
2000000
1000000
Me
S
N
N
O
N
Ph
5d
293
294
77
51
91
41
69
104
116
127
147
157
172
190
205
216
237
248
264
277
40
60
80
100
120
140
160
180
200
220
240
260
280
300
m/z

Abb.5e.1

VH27/CDCl3

exp9 std1h

SAMPLE		DEC. & VT	
date	Nov 24 09	dfrq	299.949
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	610.0
sfrq	299.949	dm	nnn
tn	H1	dmm	c
at	5.001	dmf	200
np	70016	dseq	undefined
sw	7000.4	dres	undefined
fb	3800	homo	n
bs	4	PROCESSING	
tpwr	57	lb	not used
pw	7.0	wtfile	
d1	6.000	proc	ft
tof	1331.4	fn	131072
nt	16	math	f
ct	16		
alock	n	werr	
gain	50	wexp	
FLAGS		wbs	
il	n	wnt	
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-0.1		
wp	2999.5		
vs	28		
sc	0		
wc	180		
hzmm	16.66		
is	674.37		
rfl	3279.1		
rfp	2177.6		
th	7		
ins	7.706		
ai	ph		



5e

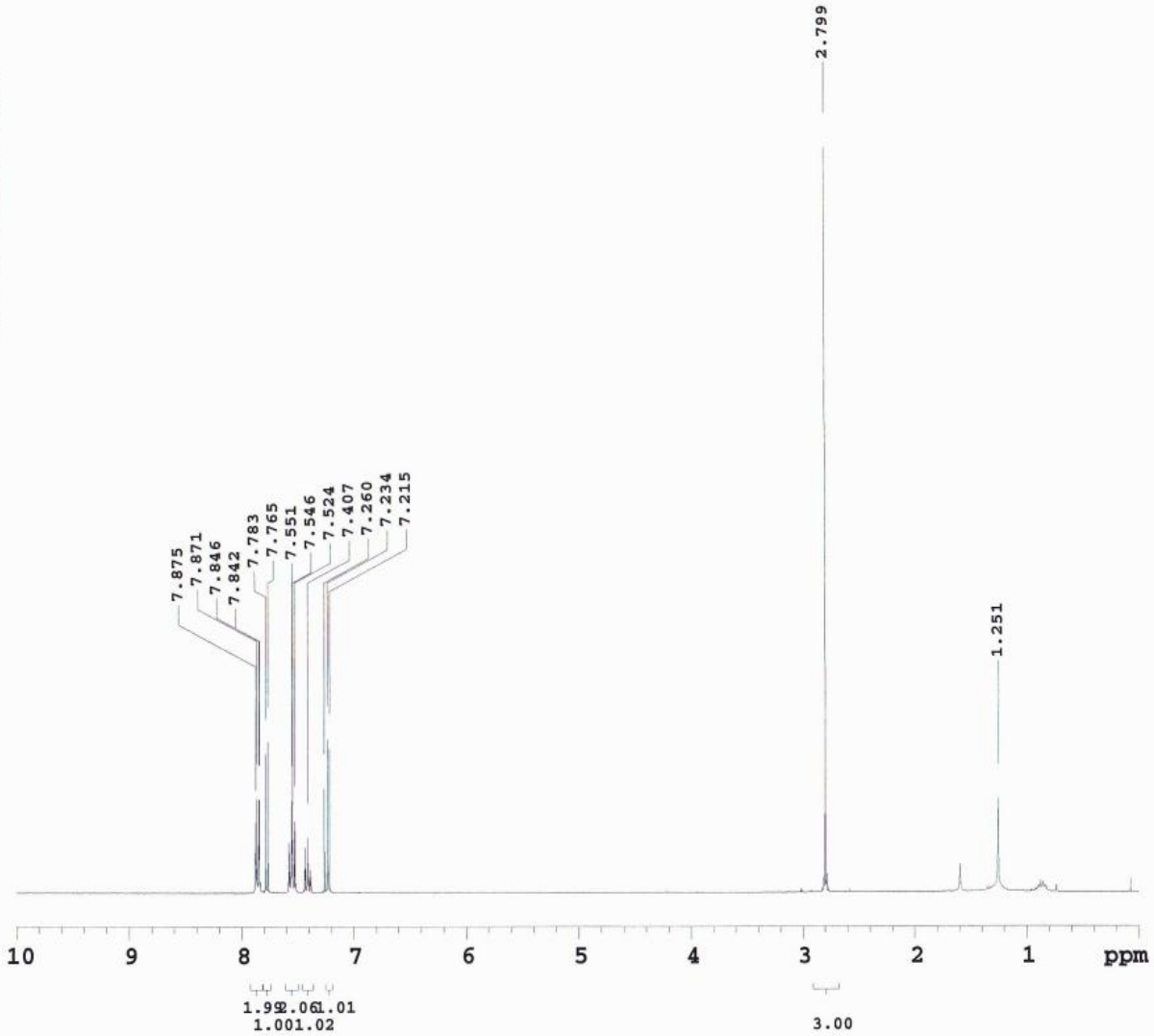


Abb.5e.2

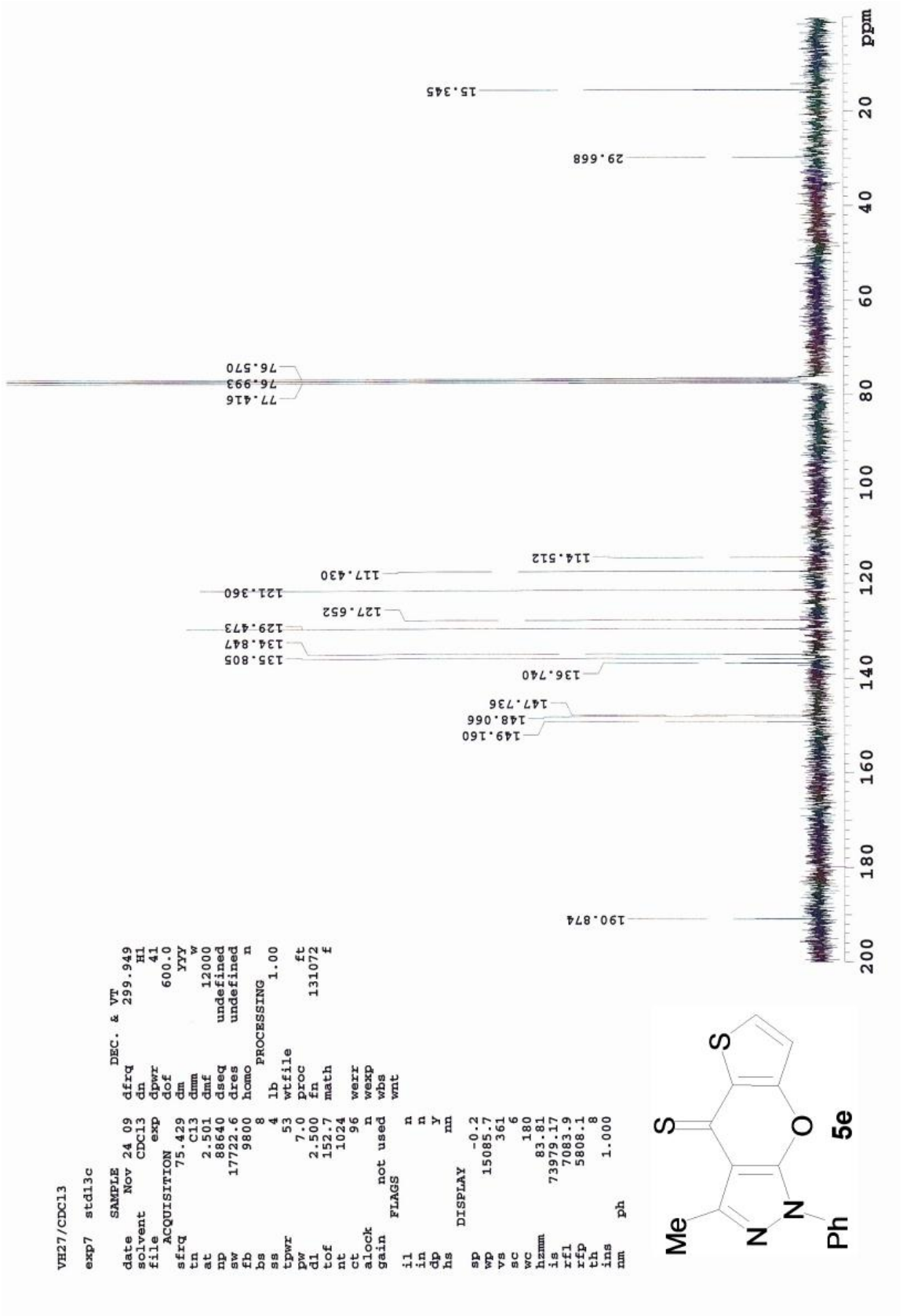

15.345
29.668
76.570
76.993
77.416
114.512
117.430
121.360
127.652
129.473
134.847
135.805
136.740
147.736
148.066
149.160
190.874
ppm
20
40
60
80
100
120
140
160
180
200
VH27/CDCl3
exp7 std13c
SAMPLE
date Nov 24 09
solvent CDCl3
file exp
ACQUISITION
sfrq 75.429
tn C13
at 2.501
np 88640
sw 17722.6
fb 9800
bs 8
ss 4
tpwr 53
pw 7.0
d1 2.500
tof 152.7
nt 1024
ct 96
alock n
gain not used
FLAGS
i1 n
in n
dp y
hs nn
DISPLAY
sp -0.2
wp 15085.7
vs 361
sc 6
wc 180
hzmm 83.81
is 73979.17
rfl 7083.9
rfp 5808.1
th 8
ins 1.000
nm ph
DEC. & VT
dfrq 299.949
dn H1
dpwr 41
dof 600.0
dm yyy
dmm w
dmf 12000
dseq undefined
dres undefined
homo n
PROCESSING
lb 1.00
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
Me
N
N
S
S
O
Ph
5e

Abb.5e.3

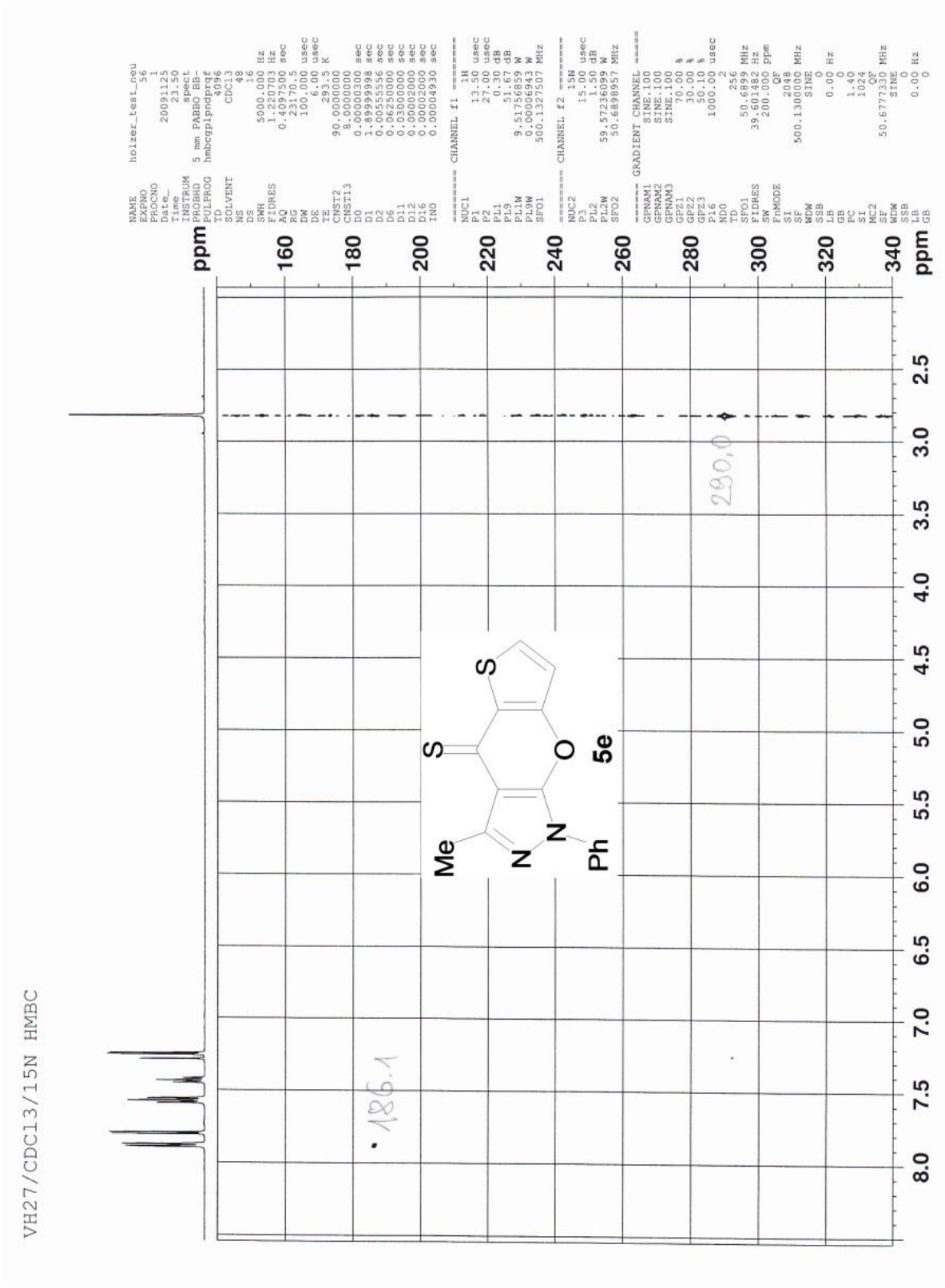
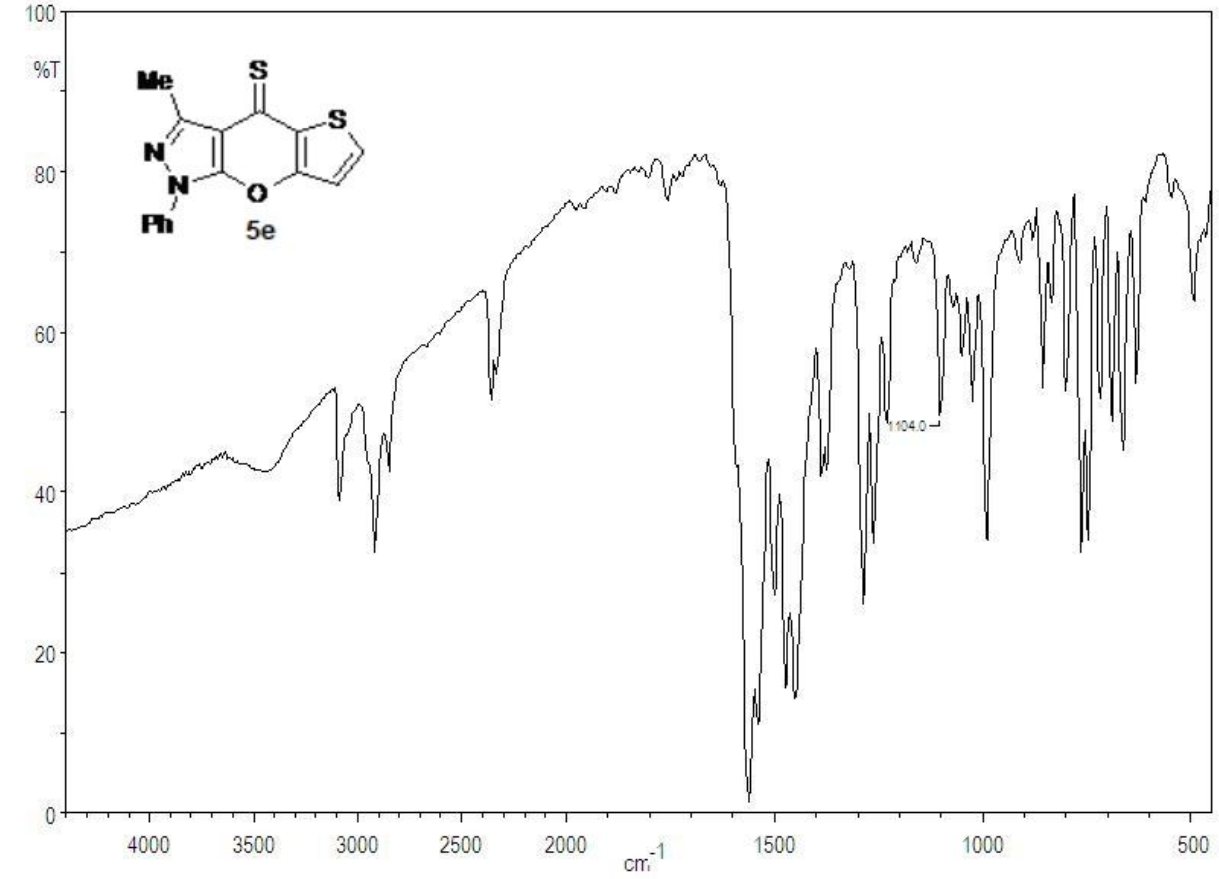


Abb.5e.4


100
%T
80
60
40
20
0
Me
S
N
N
O
S
Ph
5e
1104.0
4000
3500
3000
2500
2000
cm-1
1500
1000
500

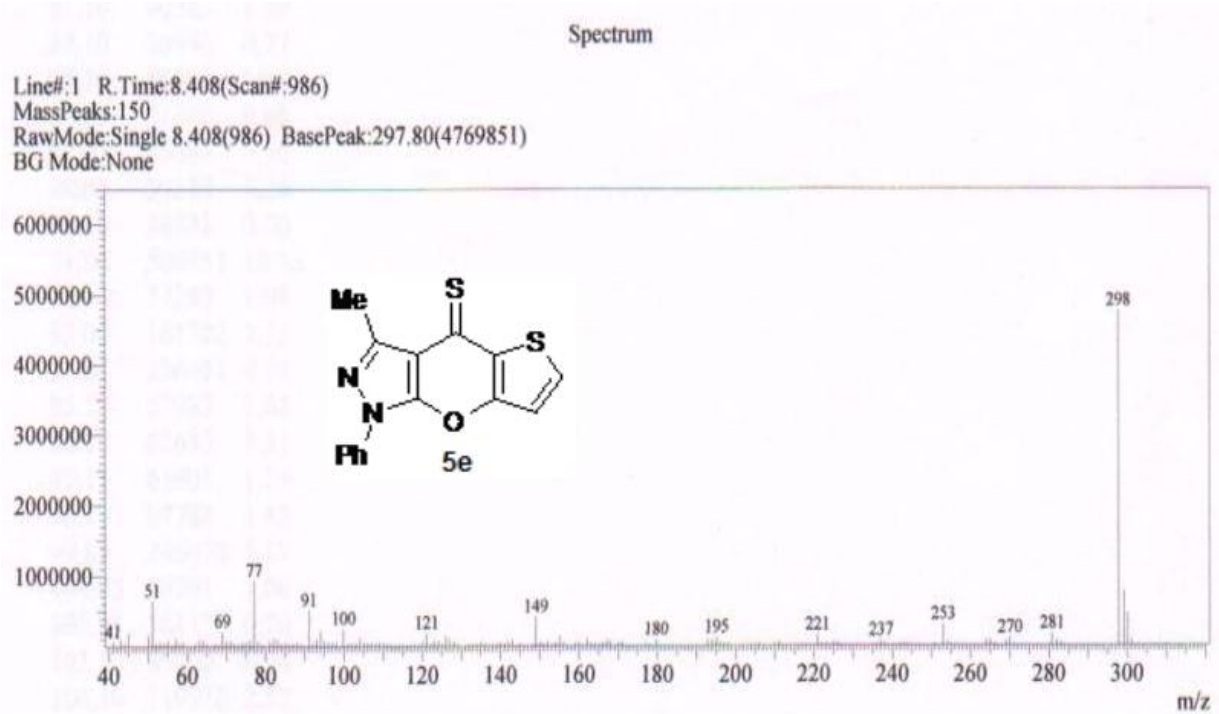

Spectrum
Line#:1 R.Time:8.408(Scan#:986)
MassPeaks:150
RawMode:Single 8.408(986) BasePeak:297.80(4769851)
BG Mode:None
6000000
5000000
4000000
3000000
2000000
1000000
Me
S
N
N
O
S
Ph
5e
298
77
51
91
69
100
121
149
41
180
195
221
237
253
270
281
40
60
80
100
120
140
160
180
200
220
240
260
280
300
m/z

Abb.5f.1

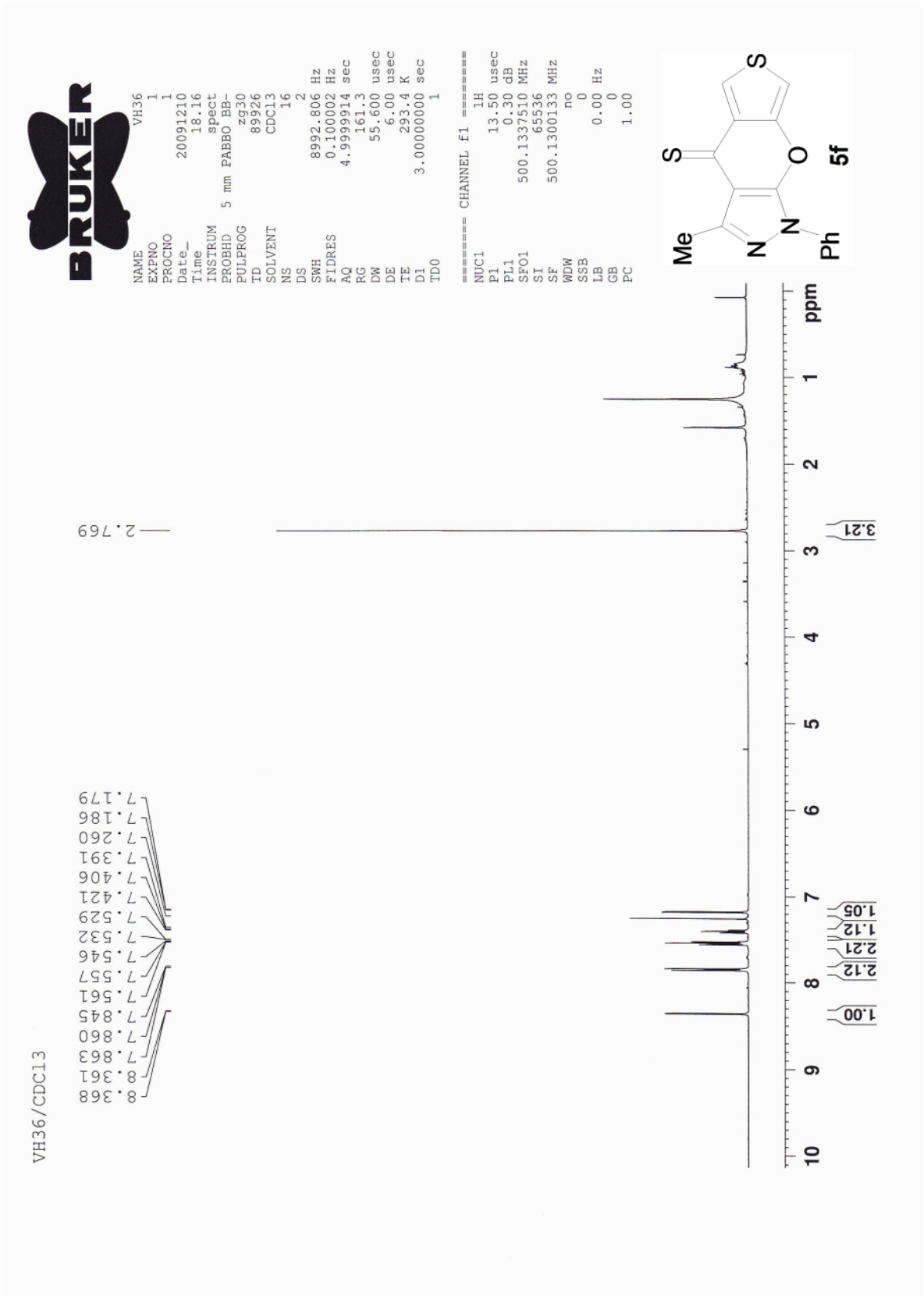

BRUKER
NAME VH36
EXPNO 1
PROCNO 1
Date_ 20091210
Time 18.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 89926
SOLVENT CDCl3
NS 16
DS 2
SWH 8992.806 Hz
FIDRES 0.100002 Hz
AQ 4.9999914 sec
RG 161.3
DW 55.600 usec
DE 6.00 usec
TE 293.4 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 0.30 dB
SFO1 500.1337510 MHz
SI 65536
SF 500.1300133 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
Me
N
N
S
O
S
Ph
5f
2.769
8.368
8.361
7.863
7.860
7.845
7.561
7.557
7.546
7.532
7.529
7.421
7.406
7.391
7.260
7.186
7.179
VH36/CDCl3
ppm
3.21
1.00
2.12
2.21
1.12
1.05

Abb.5f.2

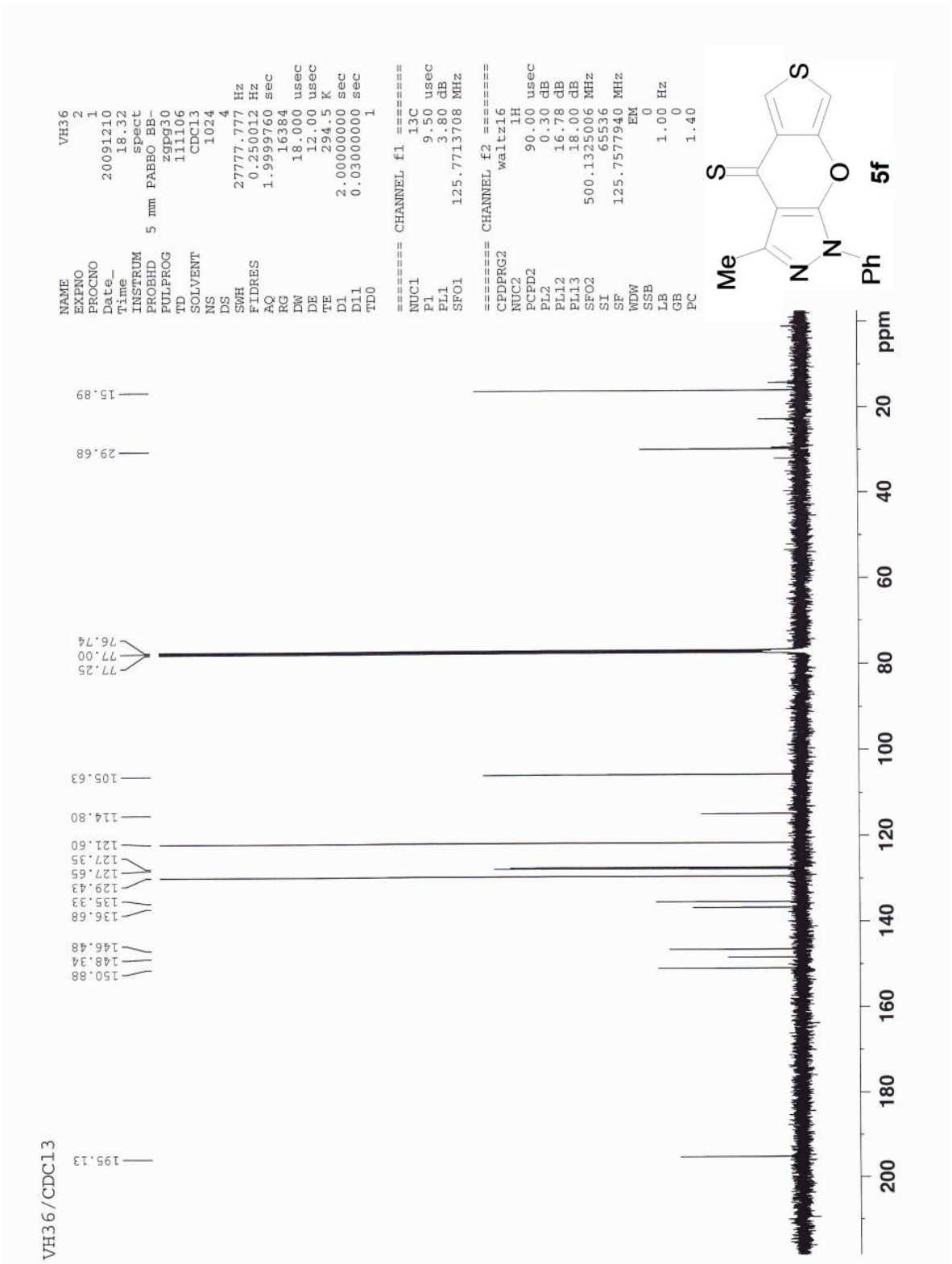

VH36/CDC13
195.13
150.88
148.34
146.48
136.68
135.33
129.43
127.65
127.35
121.60
114.80
105.63
77.25
77.00
76.74
29.68
15.89
NAME VH36
EXPNO 2
PROCNO 1
Date_ 20091210
Time 18.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 111106
SOLVENT CDCl3
NS 1024
DS 4
SWH 27777.777 Hz
FIDRES 0.250012 Hz
AQ 1.9999760 sec
RG 16384
DW 18.000 usec
DE 12.00 usec
TE 294.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 3.80 dB
SFO1 125.7713708 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.30 dB
PL12 16.78 dB
PL13 18.00 dB
SFO2 500.1325006 MHz
SI 65536
SF 125.7577940 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
S
S
O
Me
N
N
Ph
5f
200
180
160
140
120
100
80
60
40
20
ppm

Abb.5f.3

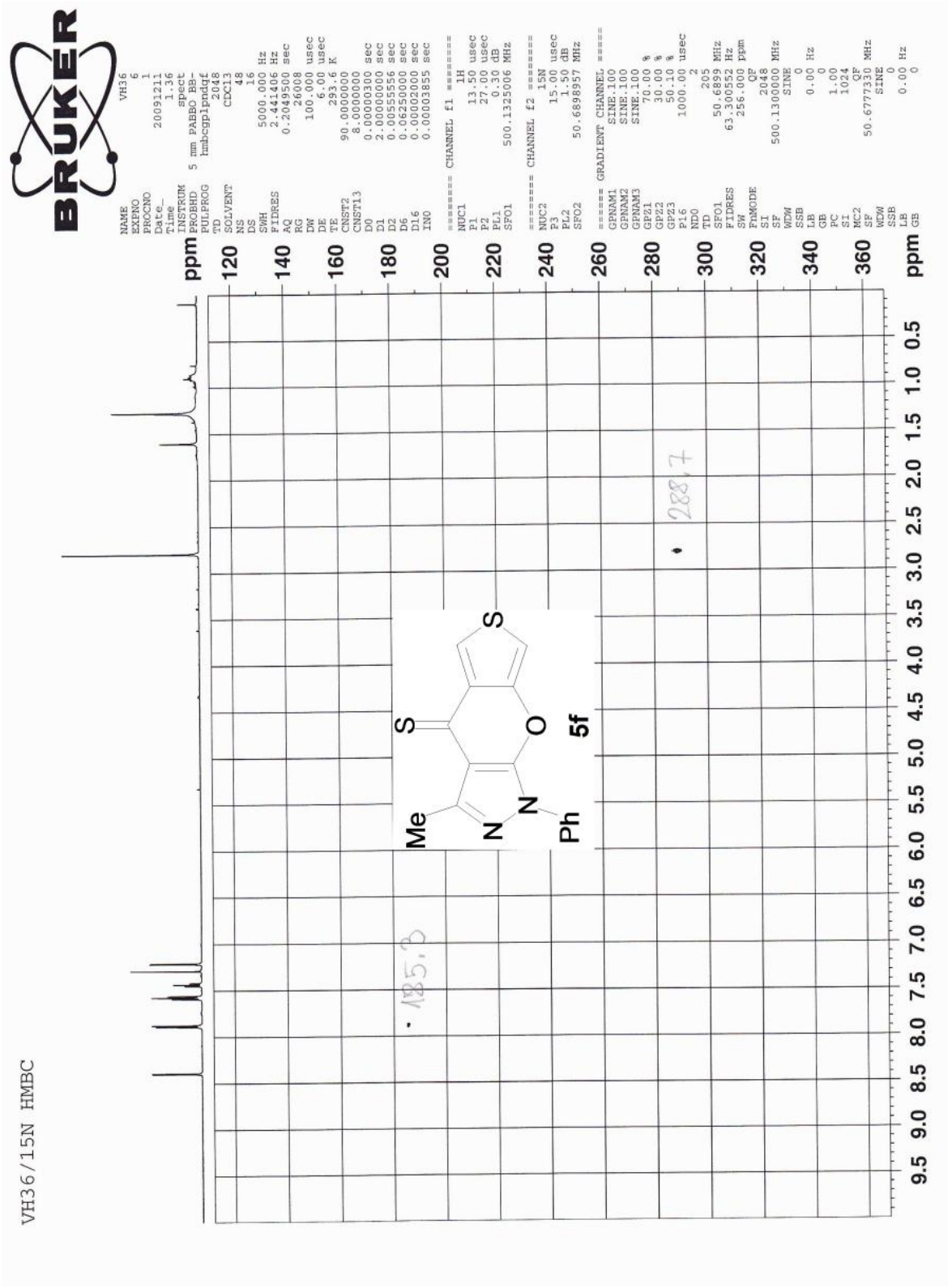
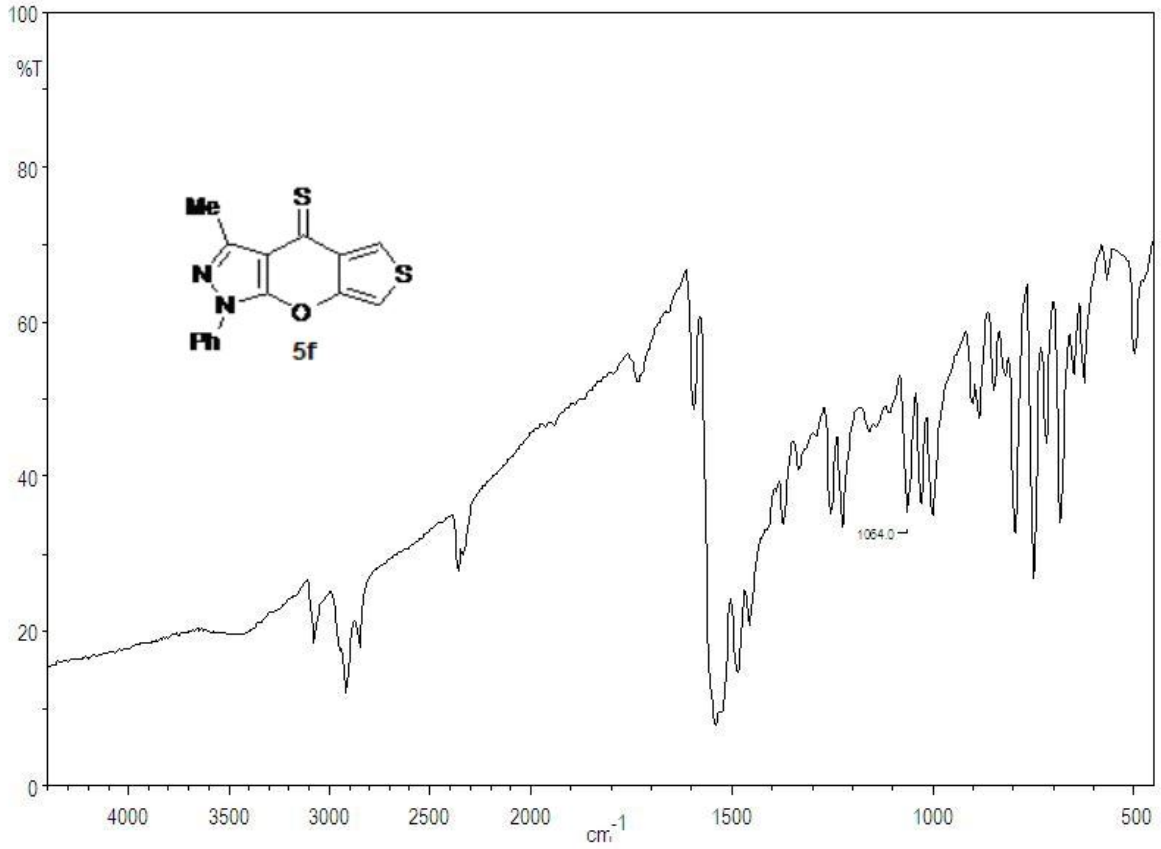


Abb.5f.4


100
%T
80
60
40
20
0
Me
S
N
N
O
S
Ph
5f
1064.0
4000
3500
3000
2500
2000
cm-1
1500
1000
500

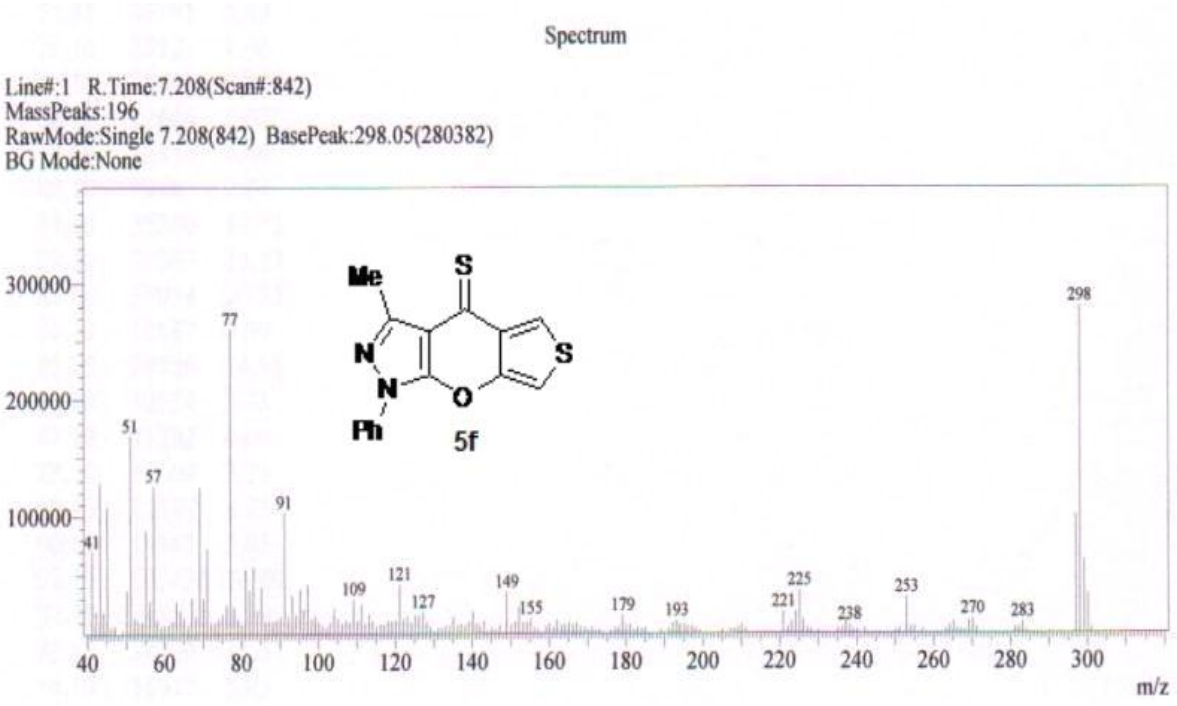

Spectrum
Line#:1 R.Time:7.208(Scan#:842)
MassPeaks:196
RawMode:Single 7.208(842) BasePeak:298.05(280382)
BG Mode:None
300000
200000
100000
Me
S
N
N
O
S
Ph
5f
298
77
51
57
91
41
109
121
127
149
155
179
193
221
225
238
253
270
283
40
60
80
100
120
140
160
180
200
220
240
260
280
300
m/z

Abb.5g.1

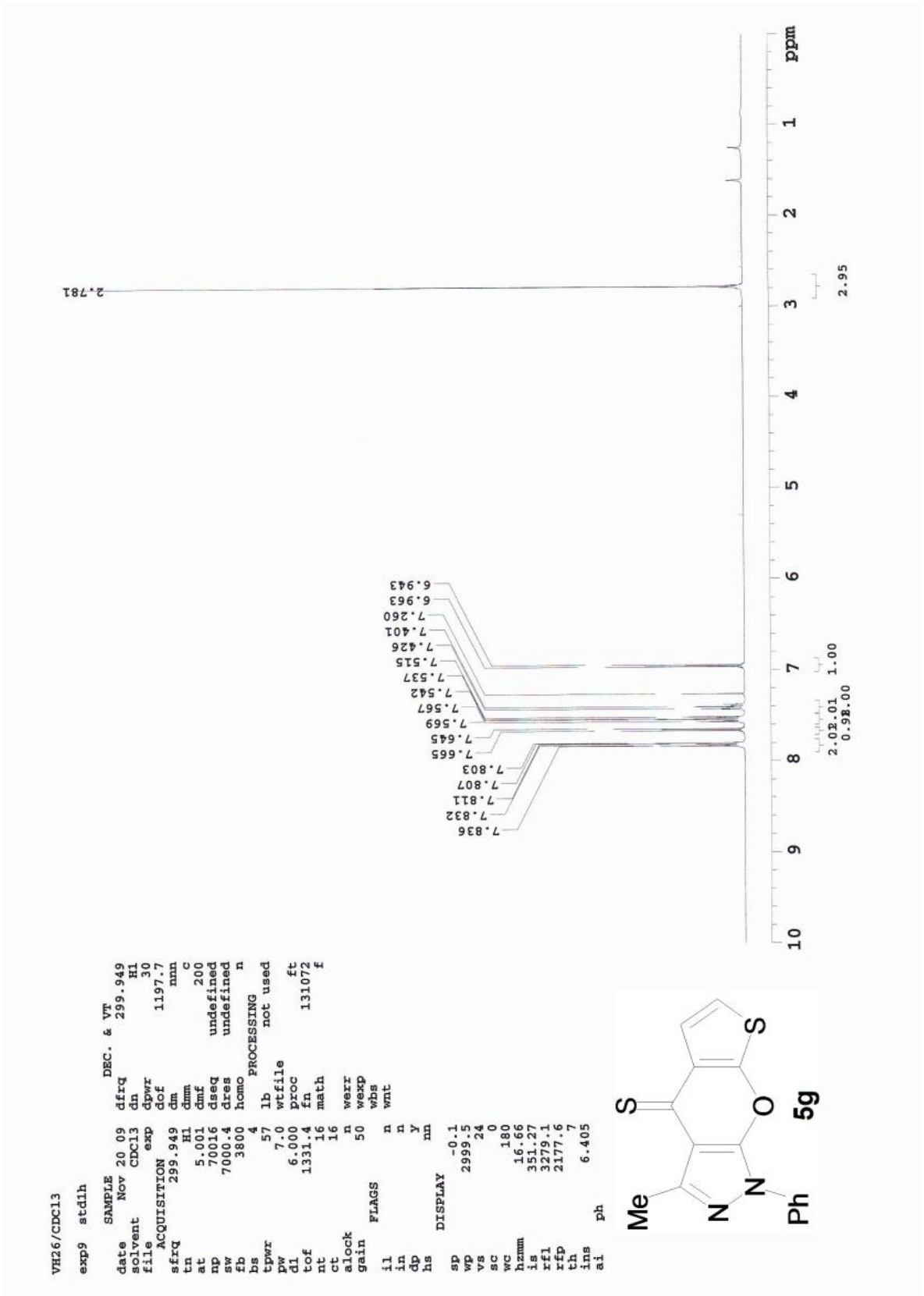

VH26/CDCl3
exp9 stdih
SAMPLE
date Nov 20 09
solvent CDCl3
file exp
ACQUISITION
sfrq 299.949
tn H1
at 5.001
np 70016
sw 7000.4
fb 3800
bs 4
tpwr 57
pw 7.0
d1 6.000
tof 1331.4
nt 16
ct 16
alock n
gain 50
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -0.1
wp 2999.5
vs 24
sc 0
wc 180
hzmm 16.66
is 351.27
rfl 3279.1
rfp 2177.6
th 7
ins 6.405
ai ph
DEC. & VT
dfrq 299.949
dn H1
dpwr 30
dof 1197.7
dm nnn
dmm c
dmf 200
dseq undefined
dres undefined
homo n
PROCESSING
lb not used
wtfile
proc ft
fn 131072
math f
wexr
wexp
wbs
wnt
2.781
7.836
7.832
7.811
7.807
7.803
7.665
7.645
7.569
7.567
7.542
7.537
7.515
7.426
7.401
7.260
6.963
6.943
2.02.01 1.00
0.98.00
2.95
ppm
Me
N
N
S
O
S
Ph
5g

Abb.5g.2

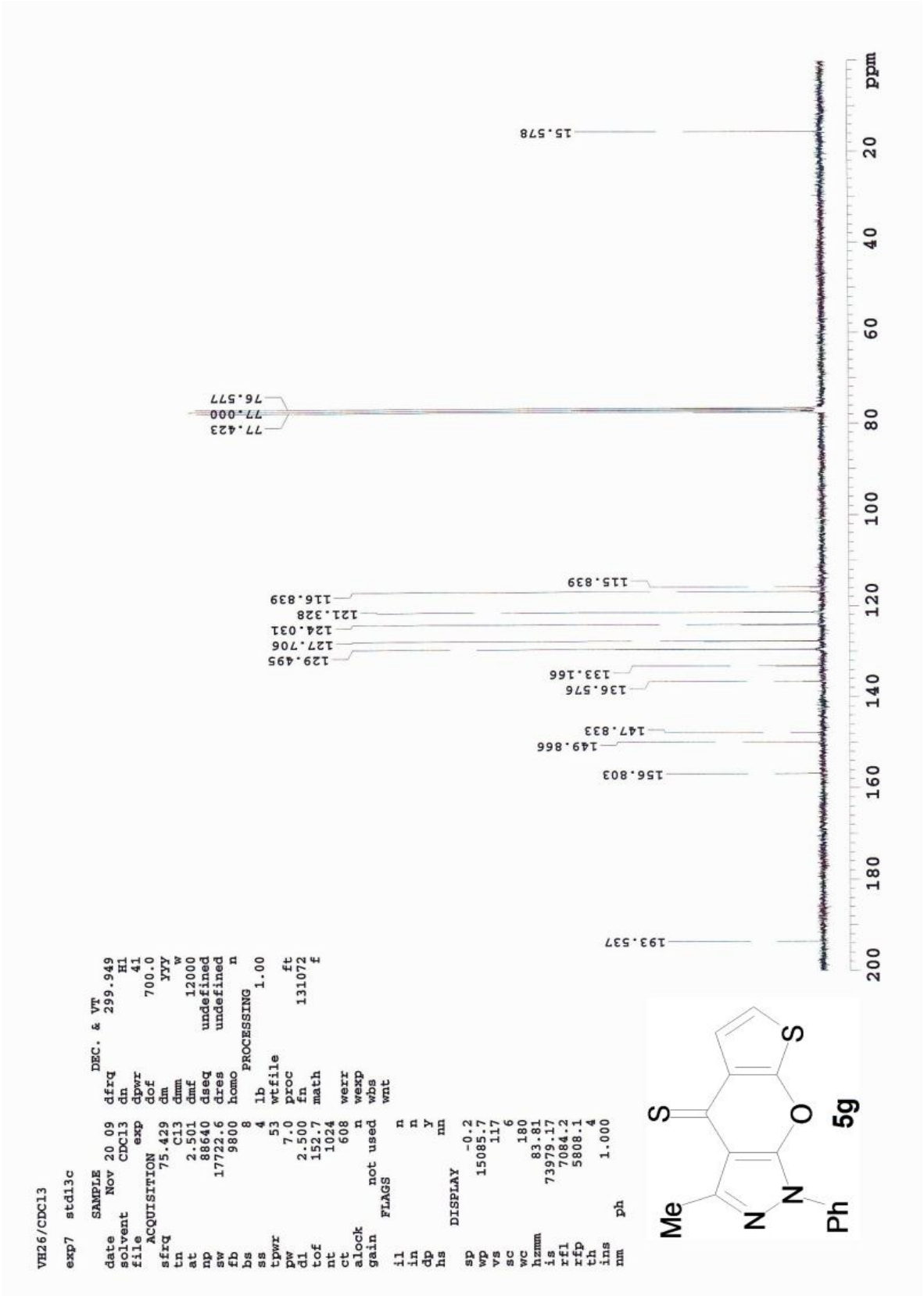

VH26/CDCl3
exp7 std13c
SAMPLE
date Nov 20 09
solvent CDCl3
file exp
ACQUISITION
sfrq 75.429
tn C13
at 2.501
np 88640
sw 17722.6
fb 9800
bs 8
ss 4
tpwr 53
pw 7.0
d1 2.500
tof 152.7
nt 1024
ct 608
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -0.2
wp 15085.7
vs 117
sc 6
wc 180
hzmm 83.81
is 73979.17
rfl 7084.2
rfp 5808.1
th 4
ins 1.000
nm ph
DEC. & VT
dfrq 299.949
dn H1
dpwr 41
dof 700.0
dm yyy
dmm w
dmf 12000
dseq undefined
dres undefined
homo n
PROCESSING
lb 1.00
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
15.578
76.577
77.000
77.423
115.839
116.839
121.328
124.031
127.706
129.495
133.166
136.576
147.833
149.866
156.803
193.537
ppm
Me
N
N
Ph
O
S
S
5g

Abb.5g.3

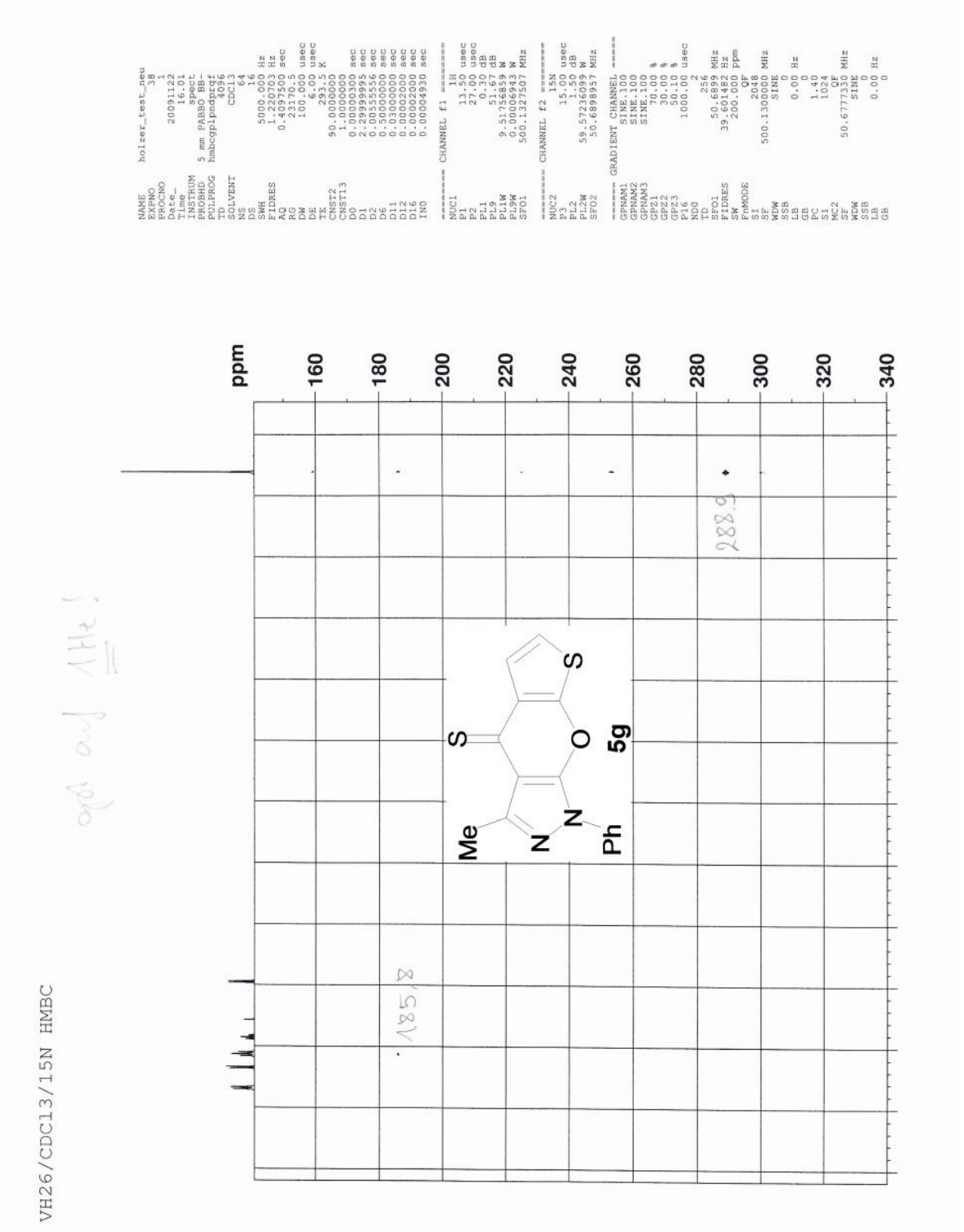
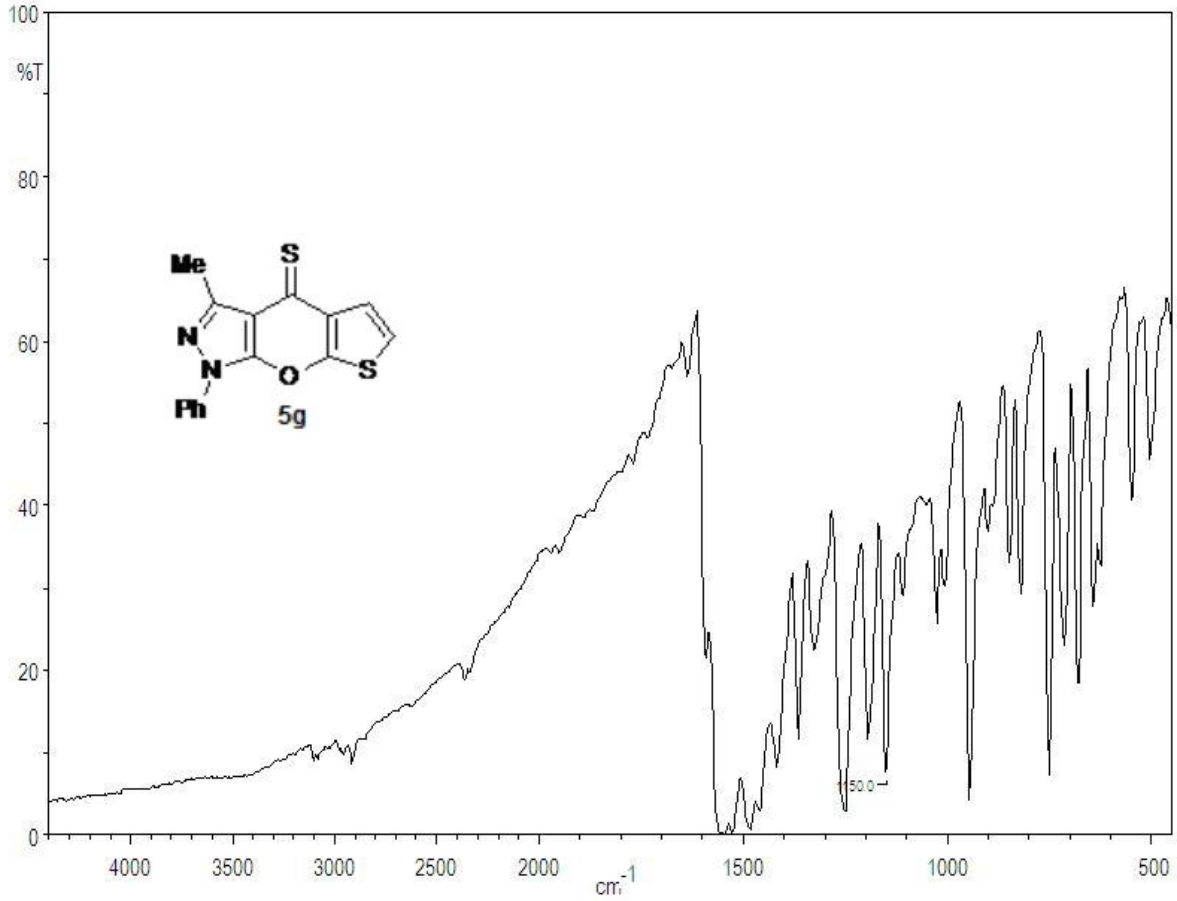

VH26/CDC13/15N HMBC
ppm
160
180
200
220
240
260
280
300
320
340
Me
N
N
Ph
S
O
S
5g

Abb.5g.4



Spectrum

Line#:1 R.Time:8.208(Scan#:962)
MassPeaks:194
RawMode:Single 8.208(962) BasePeak:297.90(871006)
BG Mode:None

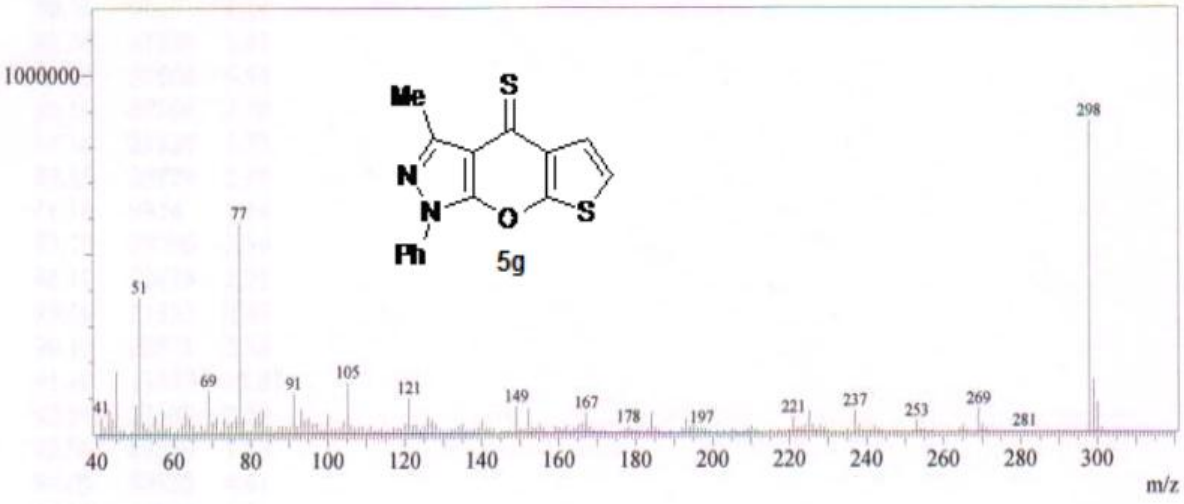


Abb.5h.1

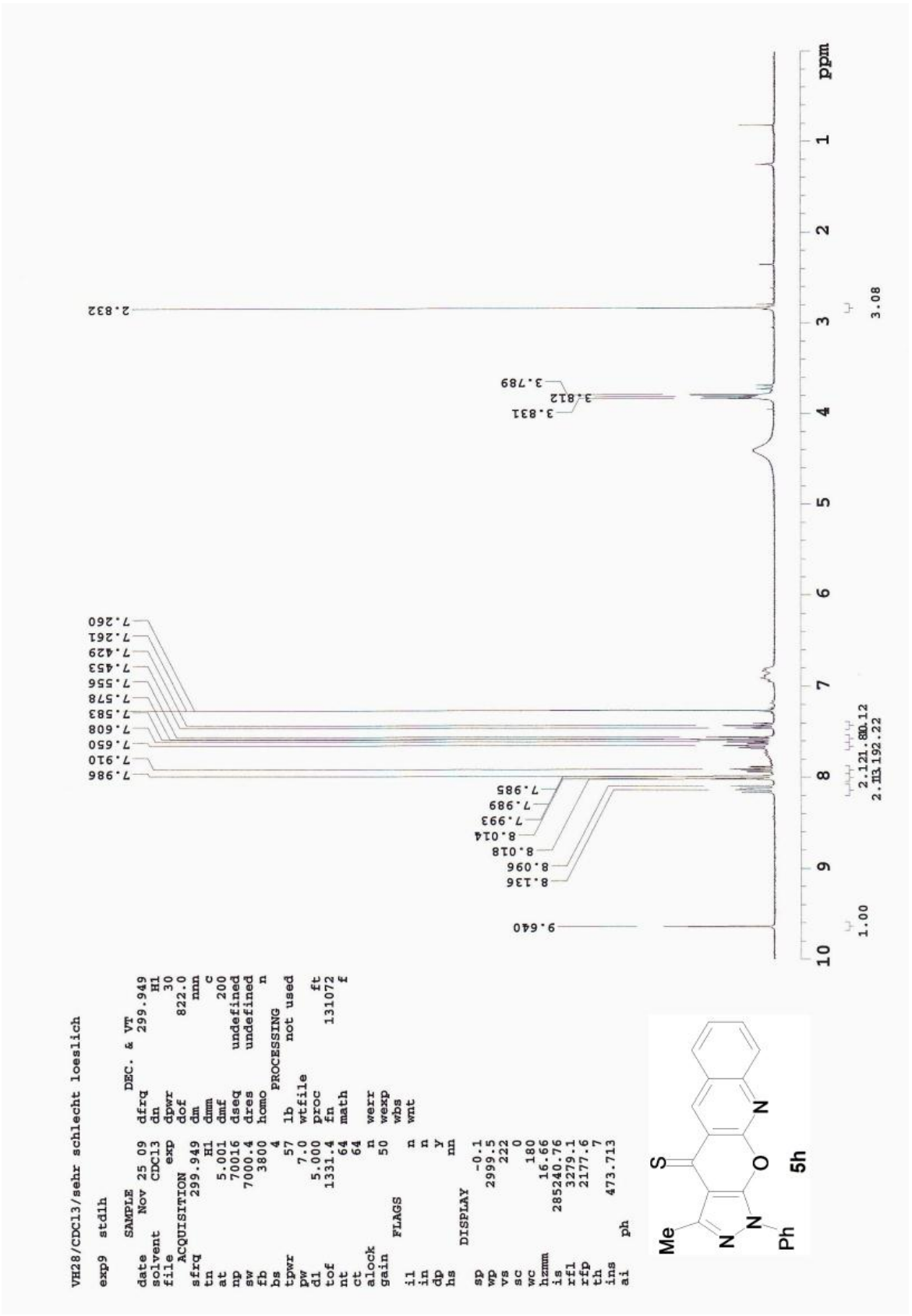

VH28/CDCl3/sehr schlecht loeslich
exp9 std1h
SAMPLE
date Nov 25 09
solvent CDCl3
file exp
ACQUISITION
sfrq 299.949
tn H1
at 5.001
np 70016
sw 7000.4
fb 3800
bs 4
tpwr 57
pw 7.0
d1 5.000
tof 1331.4
nt 64
ct 64
alock n
gain 50
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -0.1
wp 2999.5
vs 222
sc 0
wc 180
hzmm 16.66
is 285240.76
rfl 3279.1
rfp 2177.6
th 7
ins 473.713
ai ph
DEC. & VT
dfrq 299.949
dn H1
dpwr 30
dof 822.0
dm nnn
dmm c
dmf 200
dseq undefined
dres undefined
homo n
PROCESSING
lb not used
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
2.832
3.789
3.812
3.831
7.260
7.261
7.429
7.453
7.556
7.578
7.583
7.608
7.650
7.910
7.986
7.985
7.989
7.993
8.014
8.018
8.096
8.136
9.640
1.00
3.08
2.121.80.12
2.113.192.22
ppm
Me
S
O
N
N
N
Ph
5h

Abb.5h.2

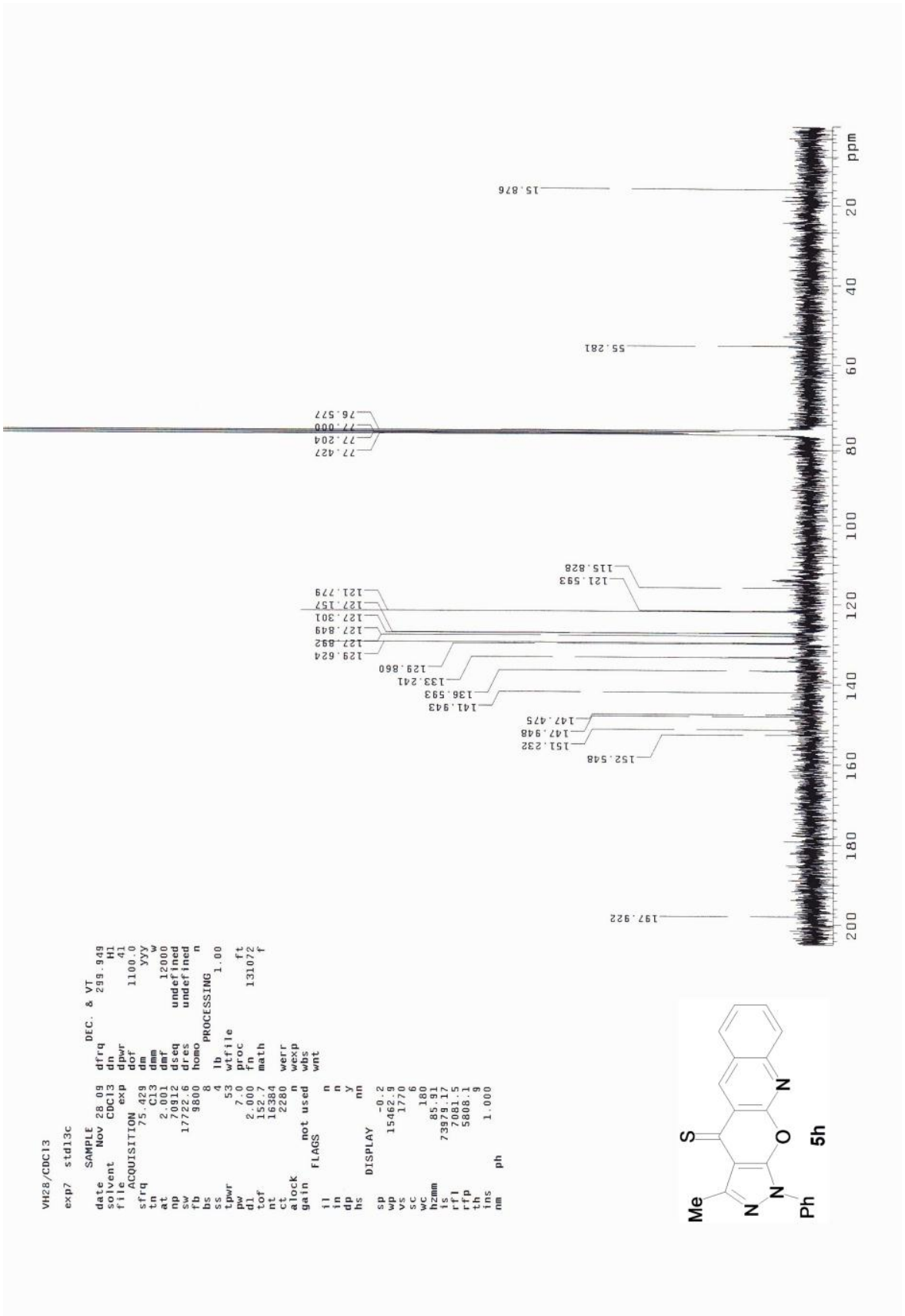

15.876
55.281
76.577
77.000
77.204
77.427
115.828
121.593
121.779
127.157
127.301
127.849
127.892
129.624
129.860
133.241
136.593
141.943
147.475
147.948
151.232
152.548
197.922
ppm
20
40
60
80
100
120
140
160
180
200
VH28/CDCl3
exp7 std13c
SAMPLE
date Nov 28 09
solvent CDCl3
file exp
ACQUISITION
sfrq 75.429
tn C13
at 2.001
np 70912
sw 17722.6
fb 9800
bs 8
ss 4
tpwr 53
pw 7.0
d1 2.000
tof 152.7
nt 16384
ct 2280
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -0.2
wp 15462.9
vs 1770
sc 6
wc 180
hzmm 85.91
is 73979.17
rfl 7081.5
rfp 5808.1
th 9
ins 1.000
nm ph
DEC. & VT
dfrq 299.949
dn H1
dpwr 41
dof 1100.0
dm yyy
dmm w
dmf 12000
dseq undefined
dres undefined
homo n
PROCESSING
lb 1.00
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
S
O
N
N
N
Me
Ph
5h

Abb.5h.3

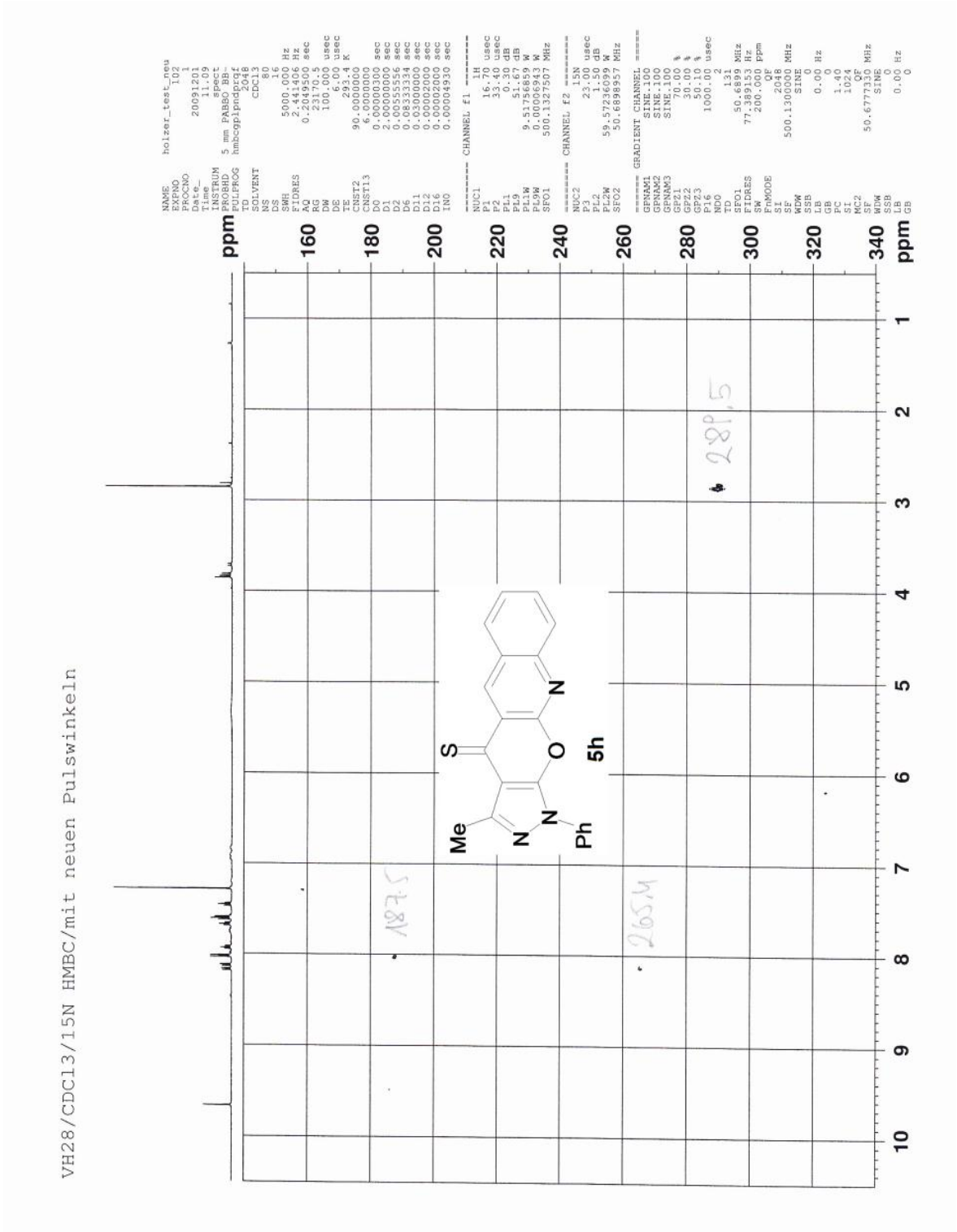
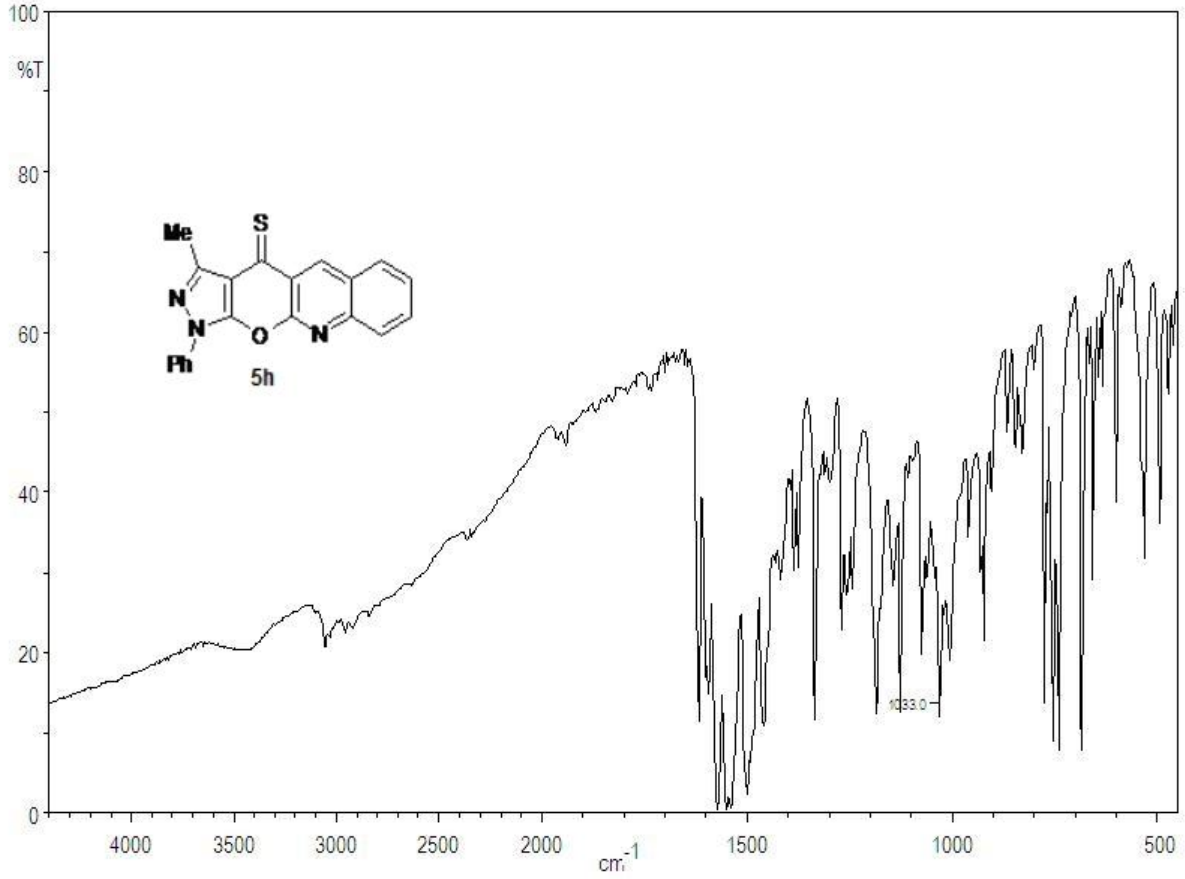

VH28/CDC13/15N HMBC/mit neuen Pulswinkeln
ppm
Me
N
S
O
N
N
Ph
5h
1875
2654
2815

Abb.5h.4


100
%T
80
60
40
20
0
4000
3500
3000
2500
2000
cm-1
1500
1000
500
1033.0
Me
S
N
N
O
N
Ph
5h

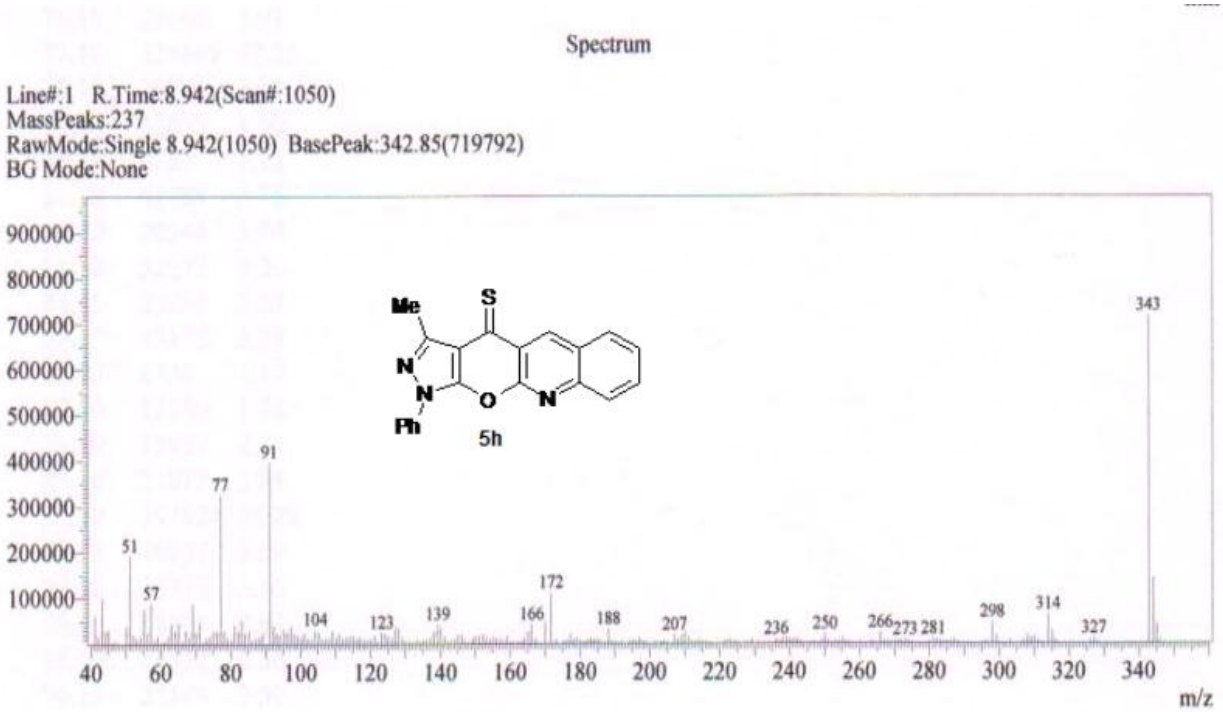

Spectrum
Line#:1 R.Time:8.942(Scan#:1050)
MassPeaks:237
RawMode:Single 8.942(1050) BasePeak:342.85(719792)
BG Mode:None
900000
800000
700000
600000
500000
400000
300000
200000
100000
Me
S
N
N
O
N
Ph
5h
343
91
77
51
57
172
104
123
139
166
188
207
236
250
266
273
281
298
314
327
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
m/z

Abb.5i.1

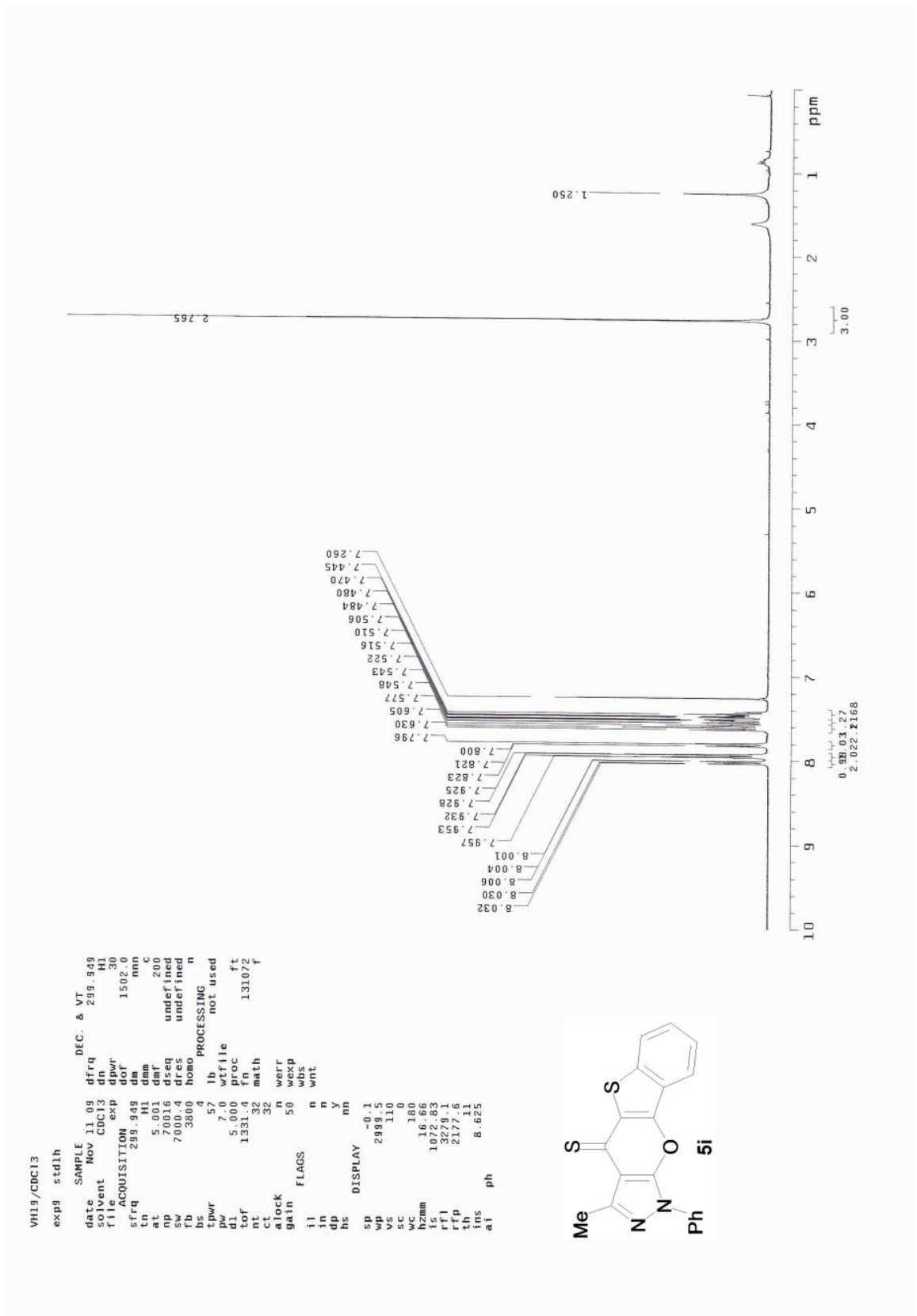

VH19/CDCl3
exp1 stdlh
SAMPLE
date Nov 11 09
solvent CDCl3
file exp
ACQUISITION
sfrq 299.949
tn H1
at 5.001
np 70016
sw 7000.4
fb 3800
bs 4
tpwr 57
pw 7.0
d1 5.000
tof 1331.4
nt 32
ct 32
alock n
gain 50
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -0.1
wp 2999.5
vs 110
sc 0
wc 180
hzmm 16.66
is 1072.83
rfl 3279.1
rfp 2177.6
th 11
ins 8.625
ai ph
DEC. & VT
dfrq 299.949
dn H1
dpwr 30
dof 1502.0
dm nnn
dmm c
dmf 200
dseq undefined
dres undefined
homo n
PROCESSING
lb not used
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
2.765
1.250
7.796
7.800
7.821
7.823
7.925
7.928
7.932
7.953
7.957
8.001
8.004
8.006
8.030
8.032
7.260
7.445
7.470
7.480
7.484
7.506
7.510
7.516
7.522
7.543
7.548
7.577
7.605
7.630
0.98 03.27
2.022.2168
3.00
ppm
Me
N
N
Ph
S
S
O
5i

Abb.5i.2

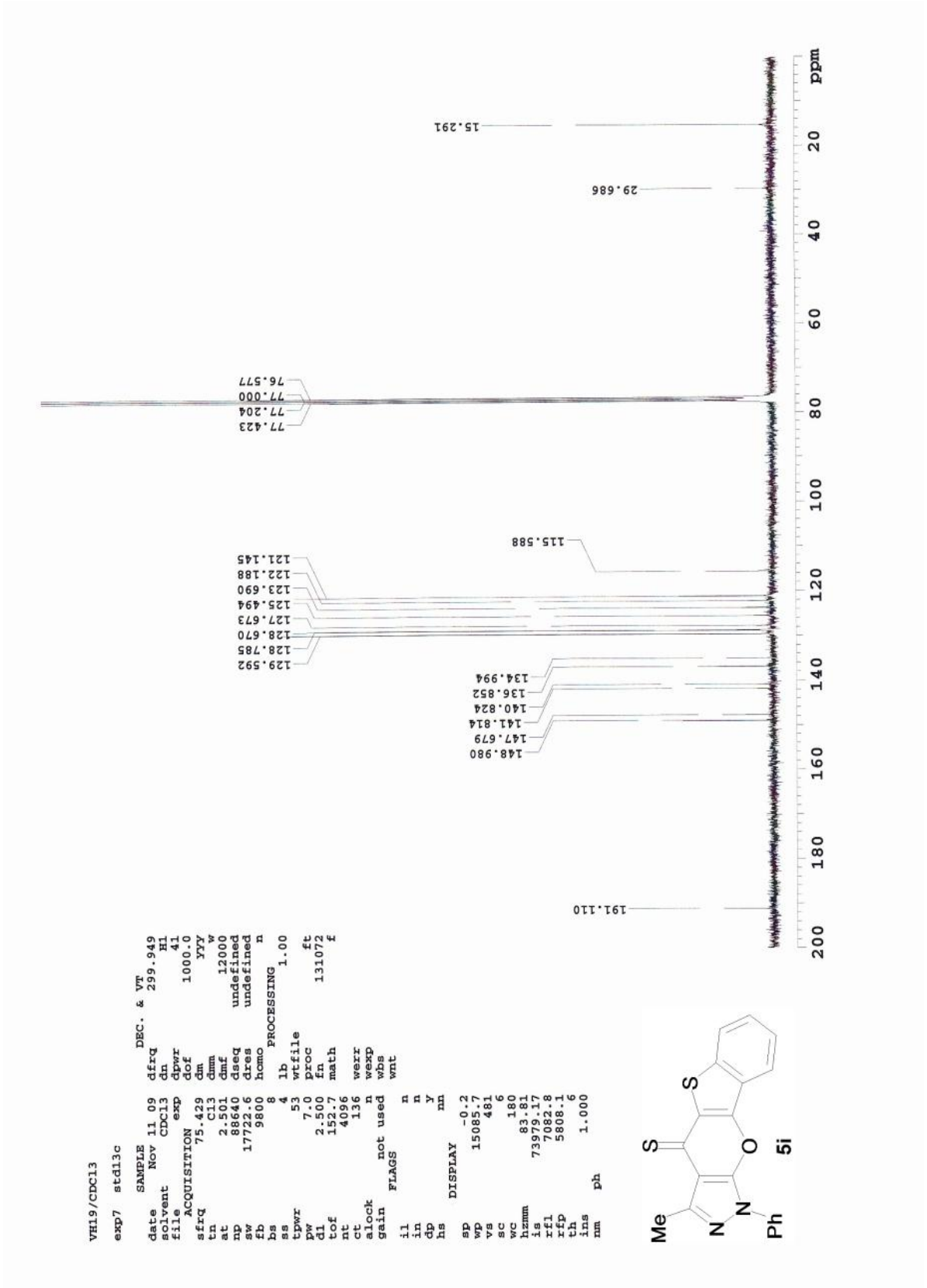

15.291
29.686
76.577
77.000
77.204
77.423
115.588
121.145
122.188
123.690
125.494
127.673
128.670
128.785
129.592
134.994
136.852
140.824
141.814
147.679
148.980
191.110
ppm
Me
Ph
5i

Abb.5i.3

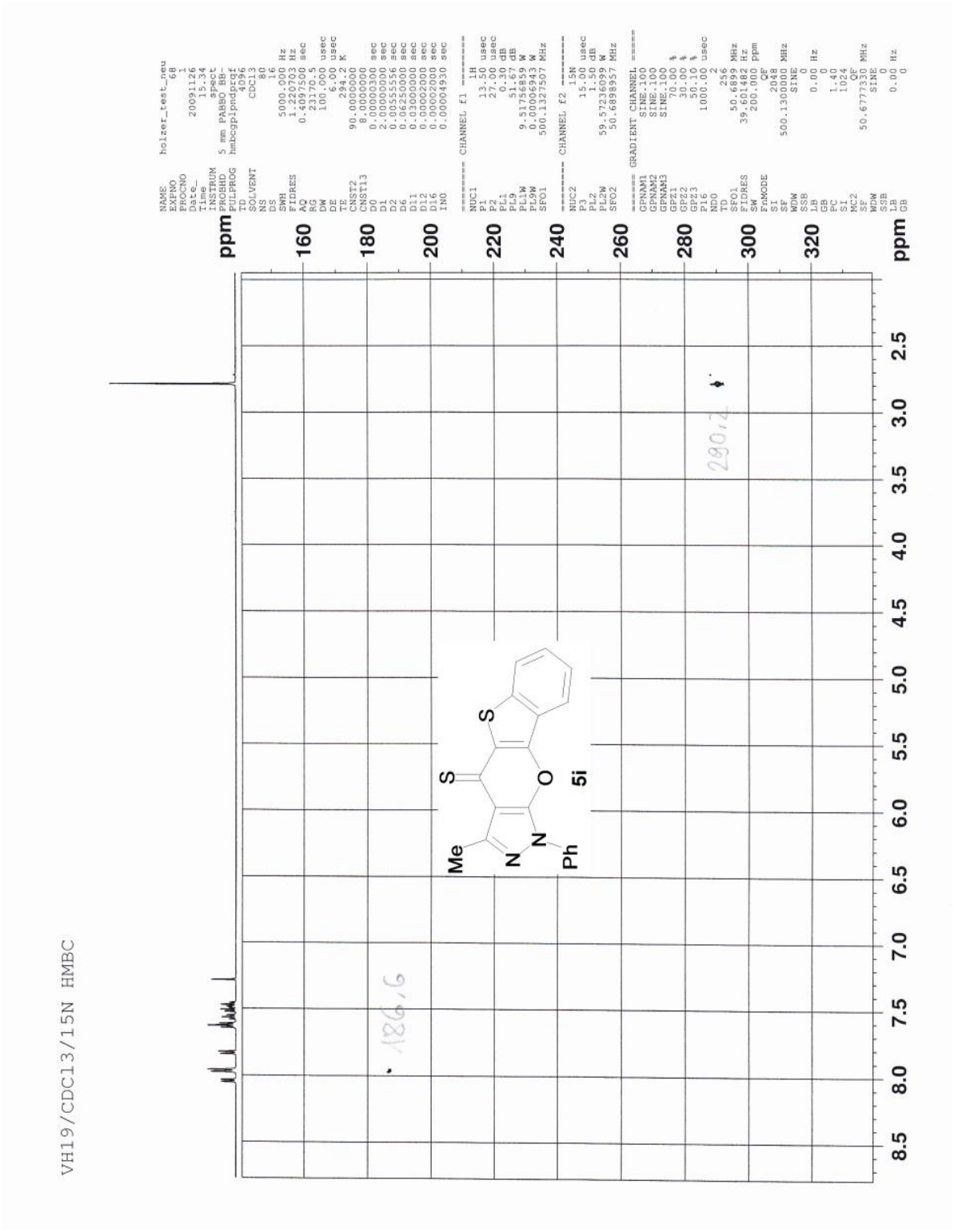
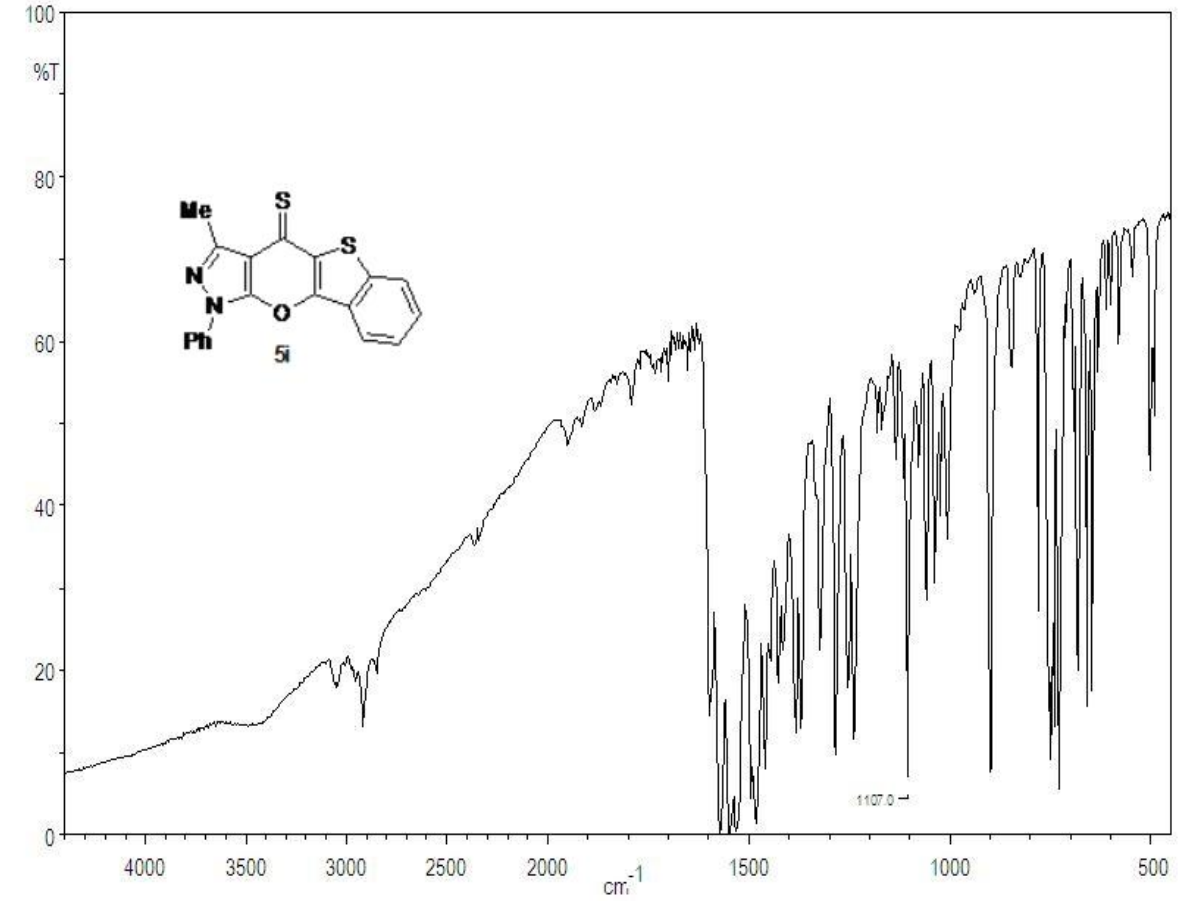

VH19/CDC13/15N HMBC
ppm
NAME holzer_test_neu
EXPNO 68
PROCNO 1
Date_ 20091126
Time 15.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG hmbcgplpndprgf
TD 4096
SOLVENT CDCl3
NS 80
DS 16
SWH 5000.000 Hz
FIDRES 1.220703 Hz
AQ 0.4097500 sec
RG 23170.5
DW 100.000 usec
DE 6.00 usec
TE 294.2 K
CNST2 90.0000000
CNST13 8.0000000
D0 0.00000300 sec
D1 2.00000000 sec
D2 0.00555556 sec
D6 0.06250000 sec
D11 0.03000000 sec
D12 0.00002000 sec
D16 0.00002000 sec
IN0 0.00004930 sec
CHANNEL f1
NUC1 1H
P1 13.50 usec
P2 27.00 usec
PL1 0.30 dB
PL9 51.67 dB
PL1W 9.51756859 W
PL9W 0.00104643 W
SFO1 500.1327507 MHz
CHANNEL f2
NUC2 15N
P3 15.00 usec
PL2 1.50 dB
PL2W 59.57236099 W
SFO2 50.6898957 MHz
GRADIENT CHANNEL
GPNAM1 SINE.100
GPNAM2 SINE.100
GPNAM3 SINE.100
GPZ1 70.00 %
GPZ2 30.00 %
GPZ3 50.10 %
P16 1000.00 usec
NDO 2
TD 256
SFO1 50.6898 MHz
FIDRES 39.601482 Hz
SW 200.000 ppm
FnMODE QF
SI 2048
SF 500.1300000 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
SI 1024
MC2 QF
SF 50.6777330 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
S
O
N
N
Me
Ph
5i
290,7
186,6

Abb.5i.4


100
%T
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
cm-1
1107.0
Me
S
N
N
O
S
Ph
5i

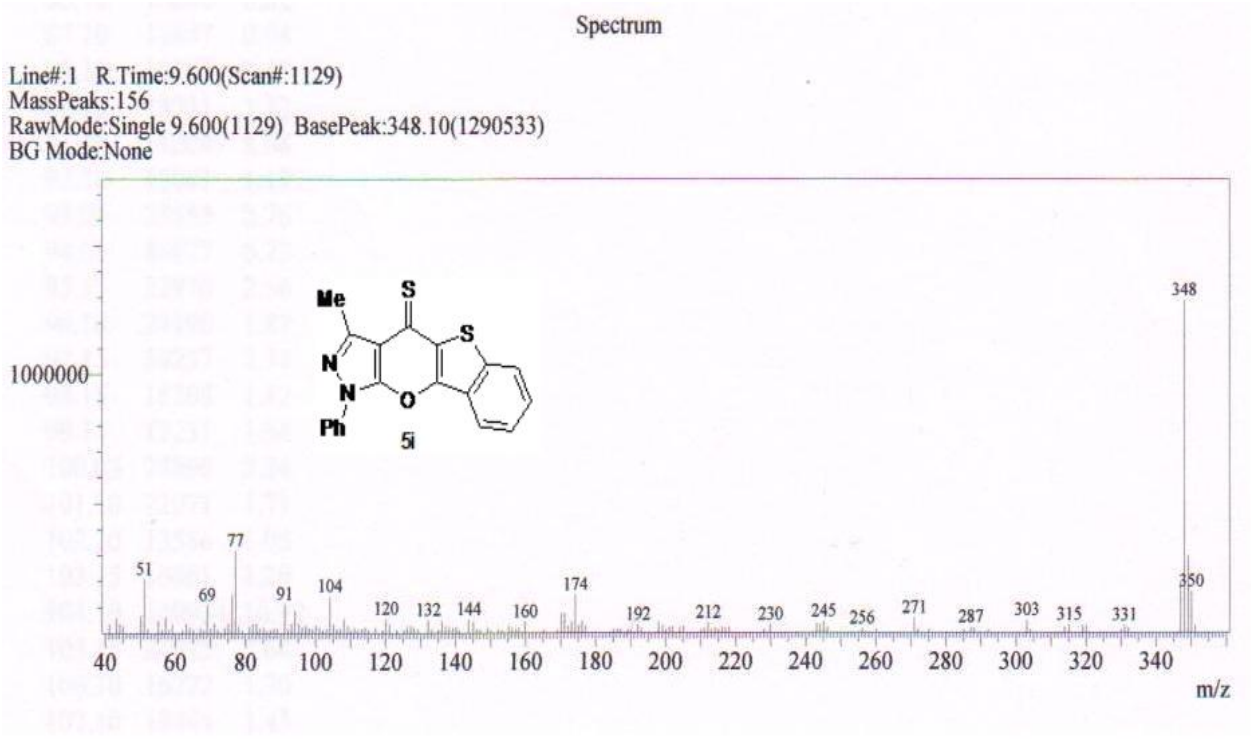

Spectrum
Line#:1 R.Time:9.600(Scan#:1129)
MassPeaks:156
RawMode:Single 9.600(1129) BasePeak:348.10(1290533)
BG Mode:None
1000000
Me
S
N
N
O
S
Ph
5i
348
350
77
51
69
91
104
120
132
144
160
174
192
212
230
245
256
271
287
303
315
331
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
m/z

Abb.5j.1

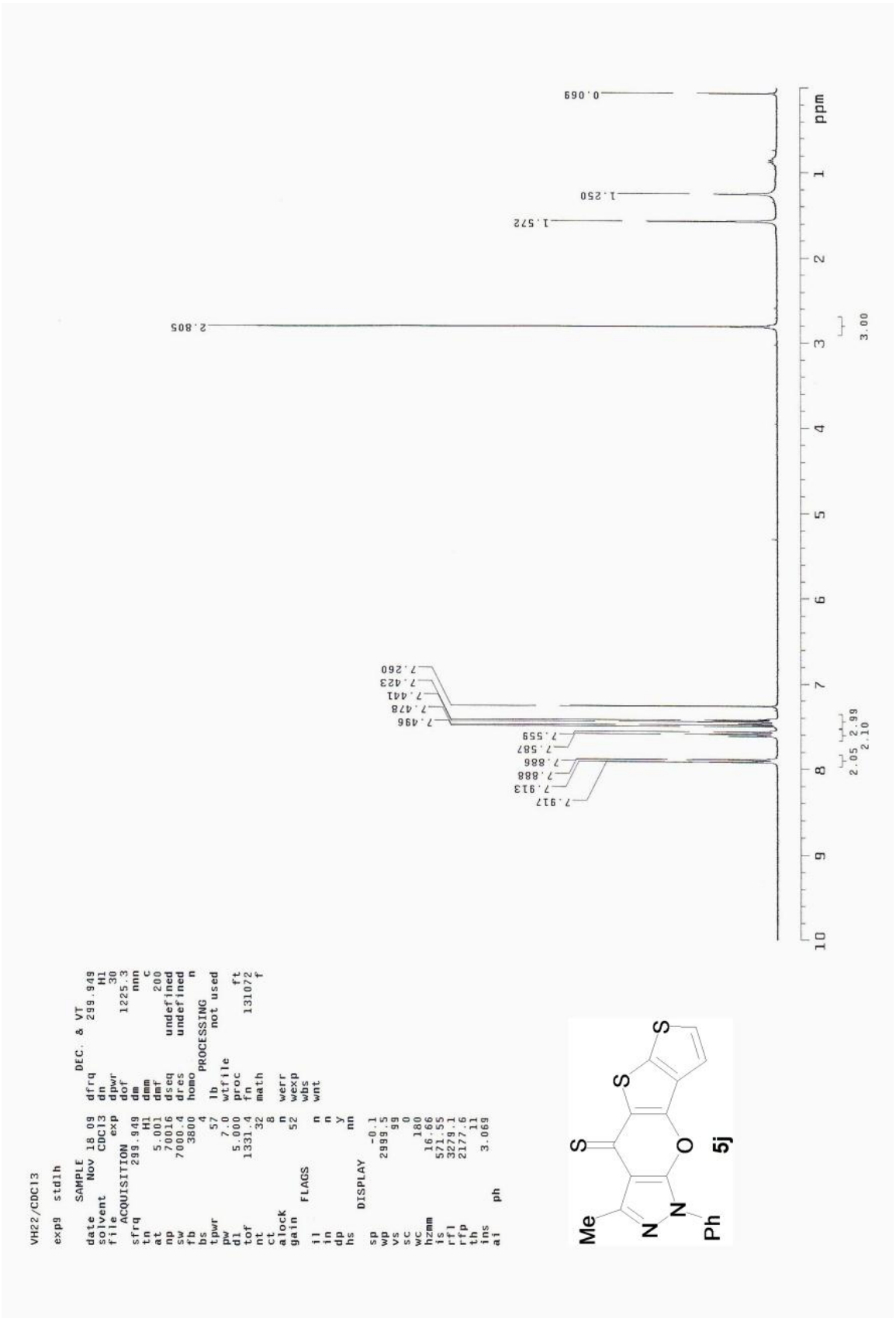

0.069
1.250
1.572
2.805
7.260
7.423
7.441
7.478
7.496
7.559
7.587
7.886
7.888
7.913
7.917
ppm
3.00
2.05 2.99
2.10
Me
N
N
Ph
S
S
S
O
5j

Abb.5j.2

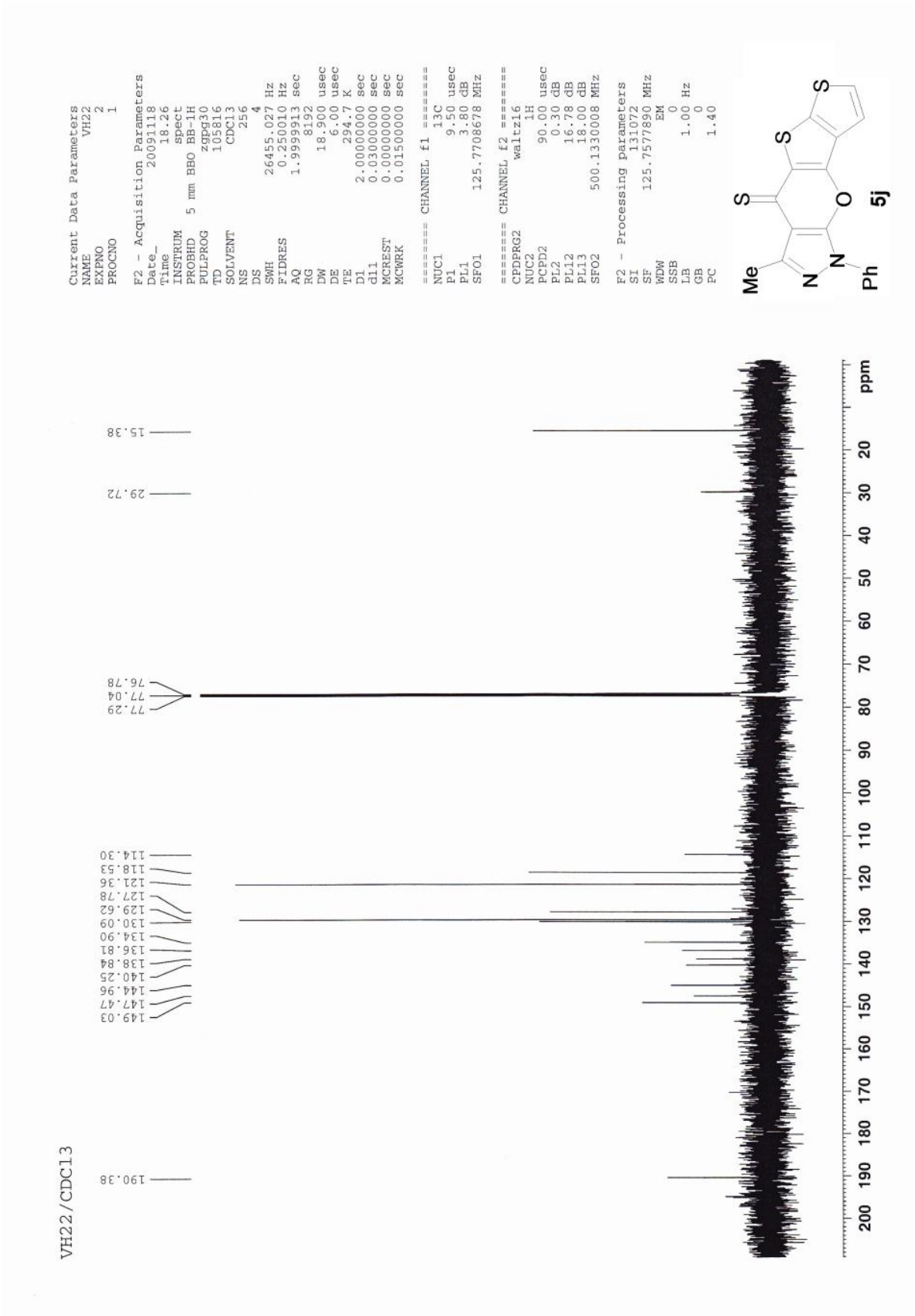

VH22/CDC13
Current Data Parameters
NAME VH22
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091118
Time 18.26
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 105816
SOLVENT CDCl3
NS 256
DS 4
SWH 26455.027 Hz
FIDRES 0.250010 Hz
AQ 1.9999913 sec
RG 8192
DW 18.900 usec
DE 6.00 usec
TE 294.7 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 3.80 dB
SFO1 125.7708678 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.30 dB
PL12 16.78 dB
PL13 18.00 dB
SFO2 500.1330008 MHz
F2 - Processing parameters
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Me
N
N
O
S
S
S
Ph
5j
190.38
149.03
147.47
144.96
140.25
138.84
136.81
134.90
130.09
129.62
127.78
121.36
118.53
114.30
77.29
77.04
76.78
29.72
15.38
ppm

Abb.5j.3

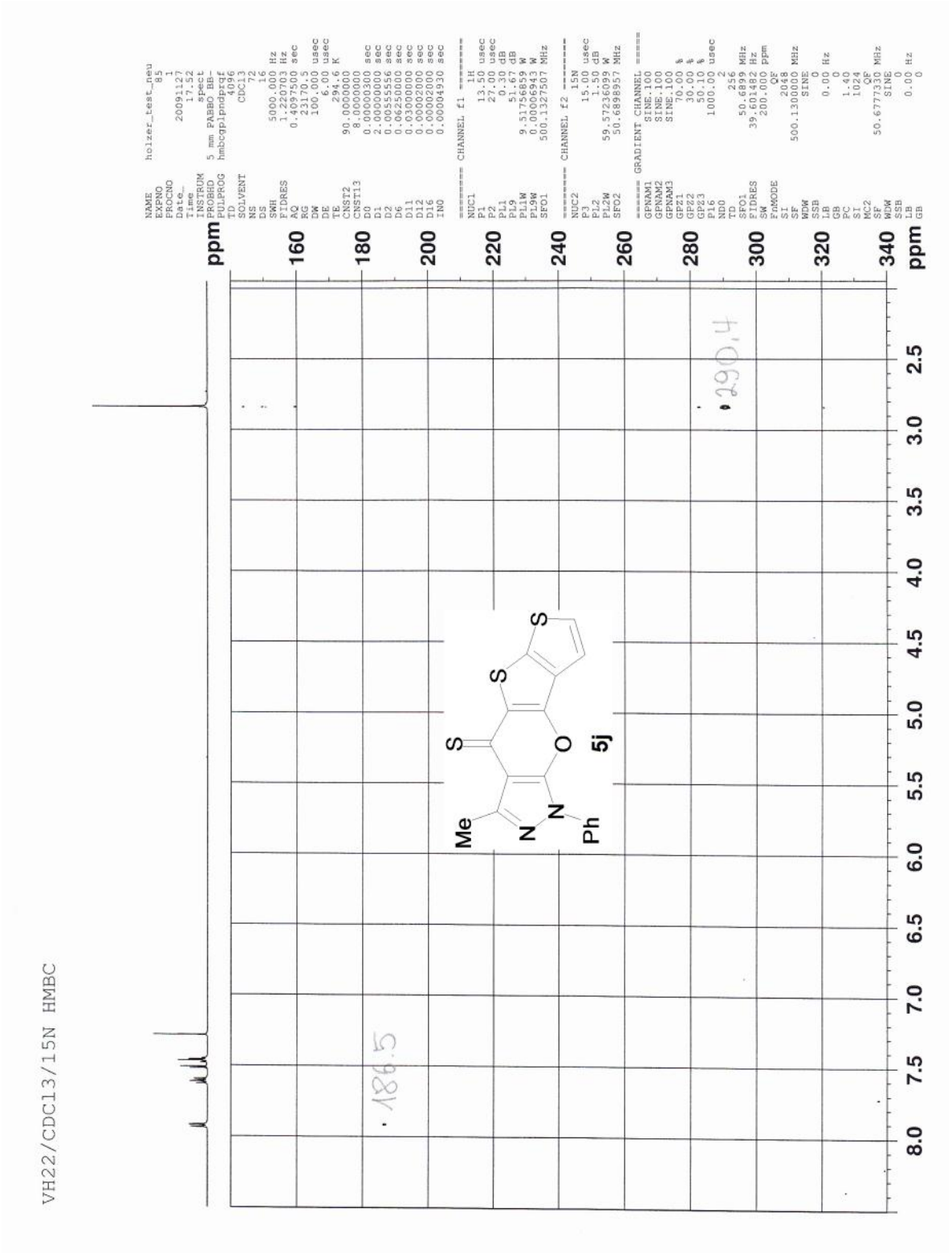
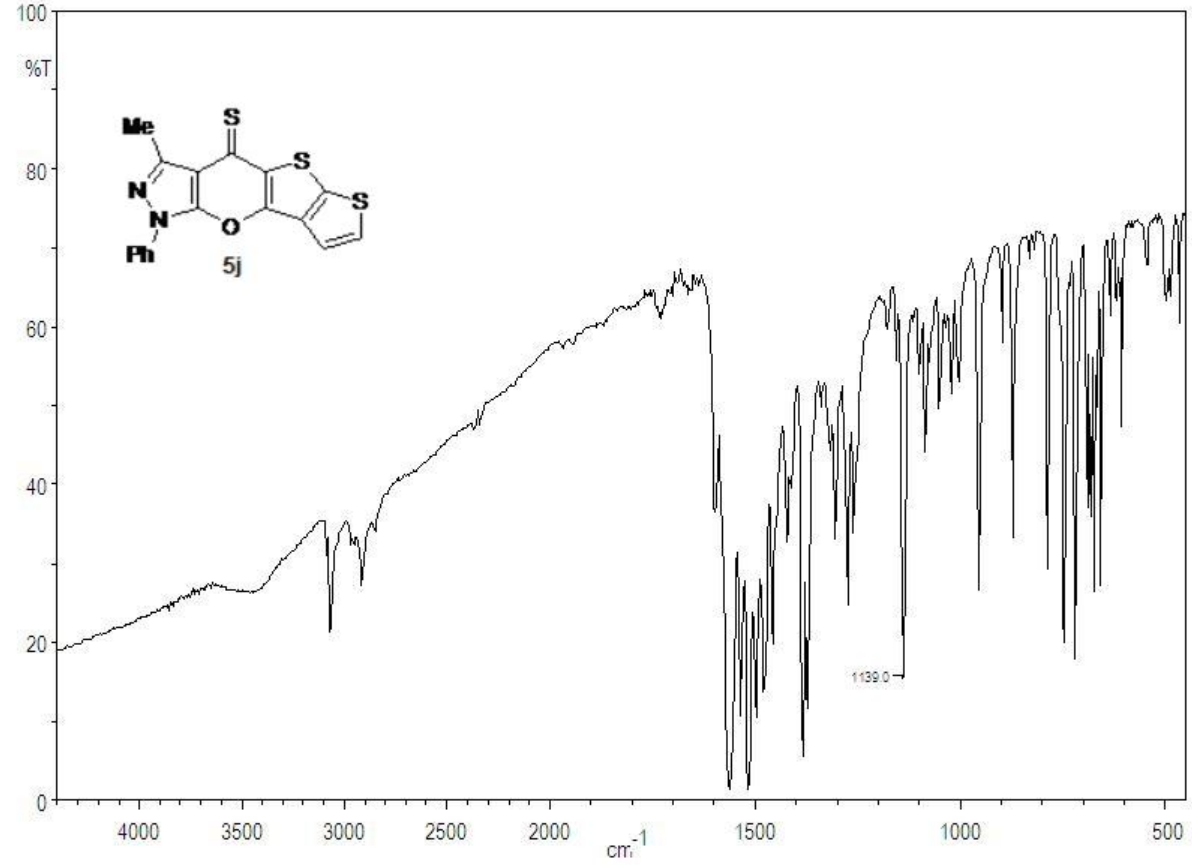

VH22/CDC13/15N HMBC
ppm
160
180
200
220
240
260
280
300
320
340
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
Me
N
N
Ph
S
S
S
O
5j
186.5
29.4

Abb.5j.4



Spectrum

Line#:1 R.Time:9.800(Scan#:1153)
MassPeaks:191
RawMode:Single 9.800(1153) BasePeak:353.90(2009563)
BG Mode:None

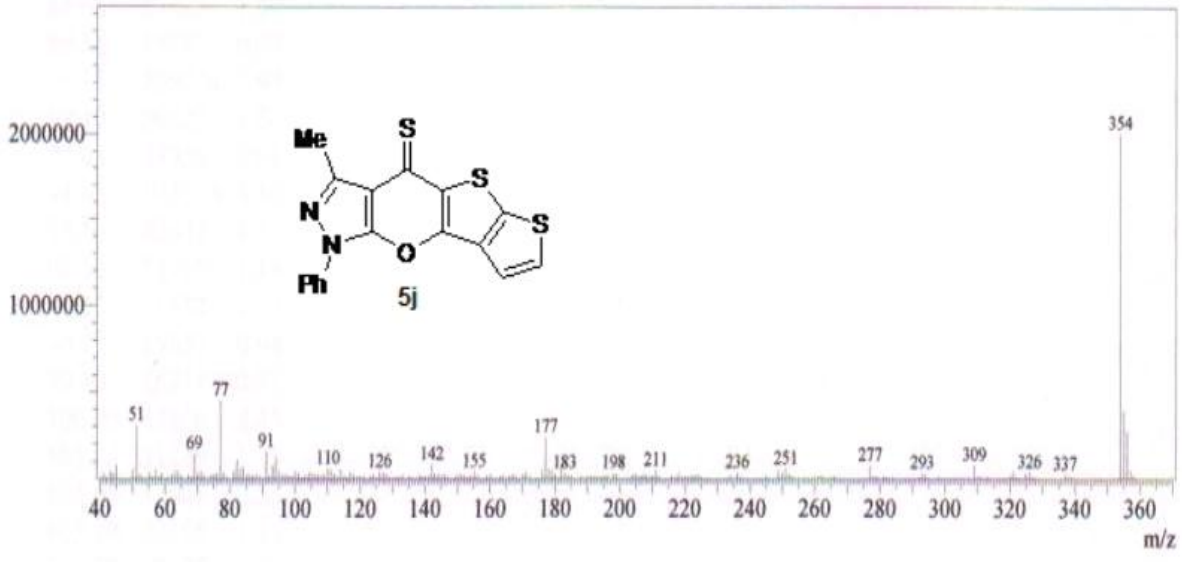


Abb.7.1

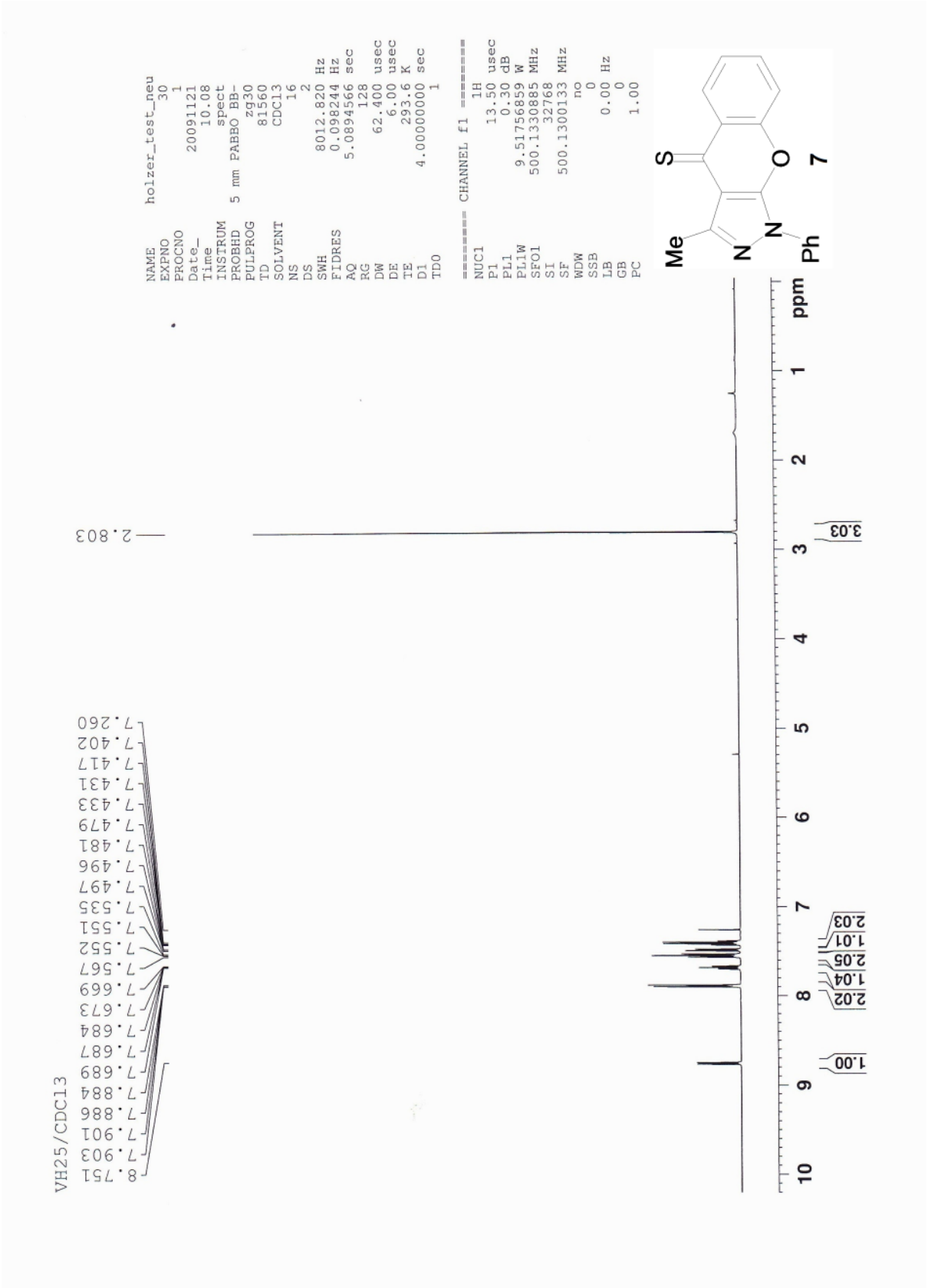

VH25/CDC13
8.751
7.903
7.901
7.886
7.884
7.689
7.687
7.684
7.673
7.669
7.567
7.552
7.551
7.535
7.497
7.496
7.481
7.479
7.433
7.431
7.417
7.402
7.260
2.803
NAME holzer_test_neu
EXPNO 30
PROCNO 1
Date_ 20091121
Time_ 10.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 81560
SOLVENT CDC13
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.098244 Hz
AQ 5.0894566 sec
RG 128
DW 62.400 usec
DE 6.00 usec
TE 293.6 K
D1 4.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 0.30 dB
PL1W 9.51756859 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300133 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
S
O
Me
N
N
Ph
7
ppm
10
9
8
7
6
5
4
3
2
1
1.00
2.02
1.04
2.05
1.01
2.03
3.03

Abb.7.2

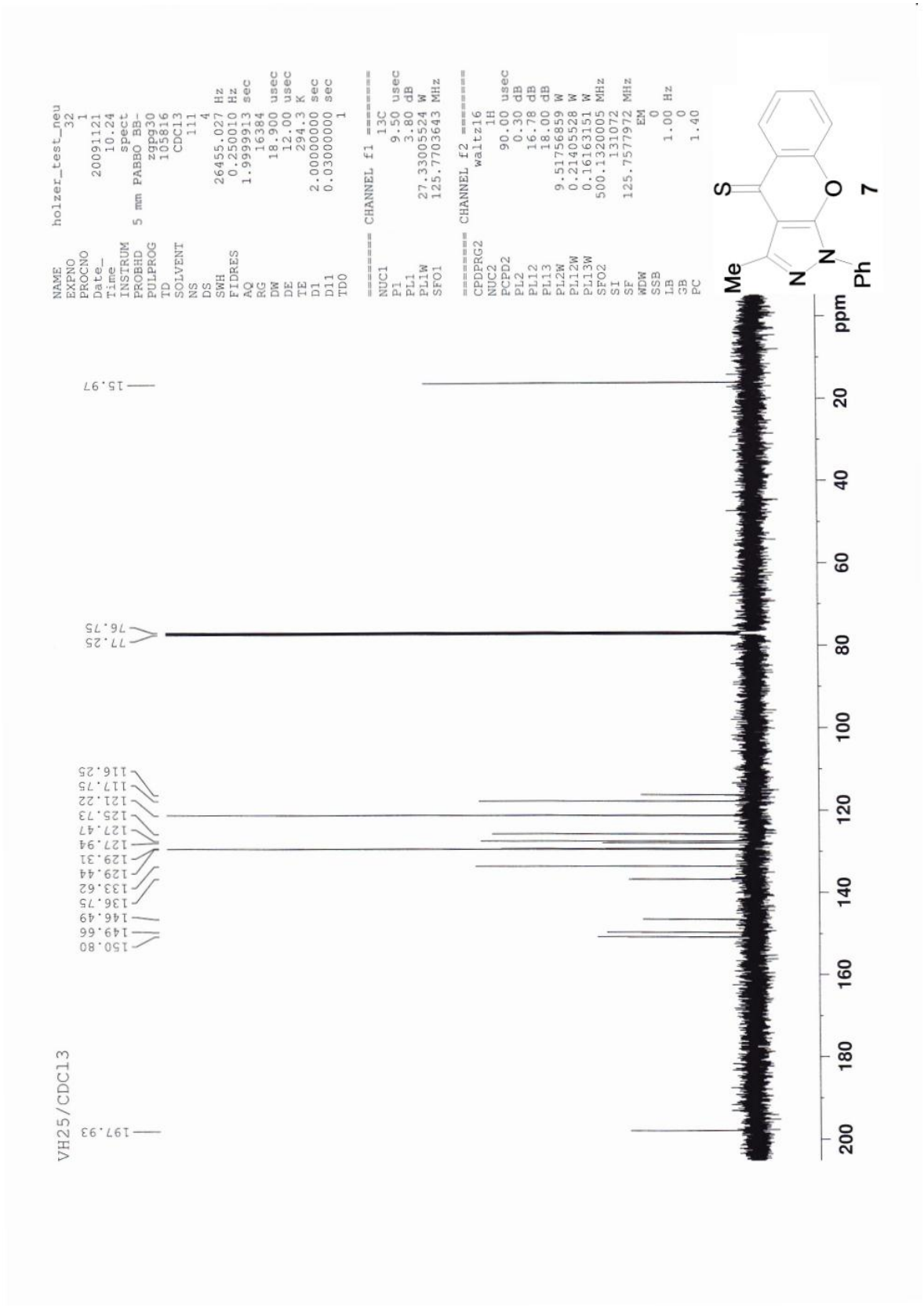

VH25/CDC13
197.93
150.80
149.66
146.49
136.75
133.62
129.44
129.31
127.94
127.47
125.73
121.22
117.75
116.25
77.25
76.75
15.97
S
O
N
N
Me
Ph
7
ppm
200
180
160
140
120
100
80
60
40
20

Abb.7.3

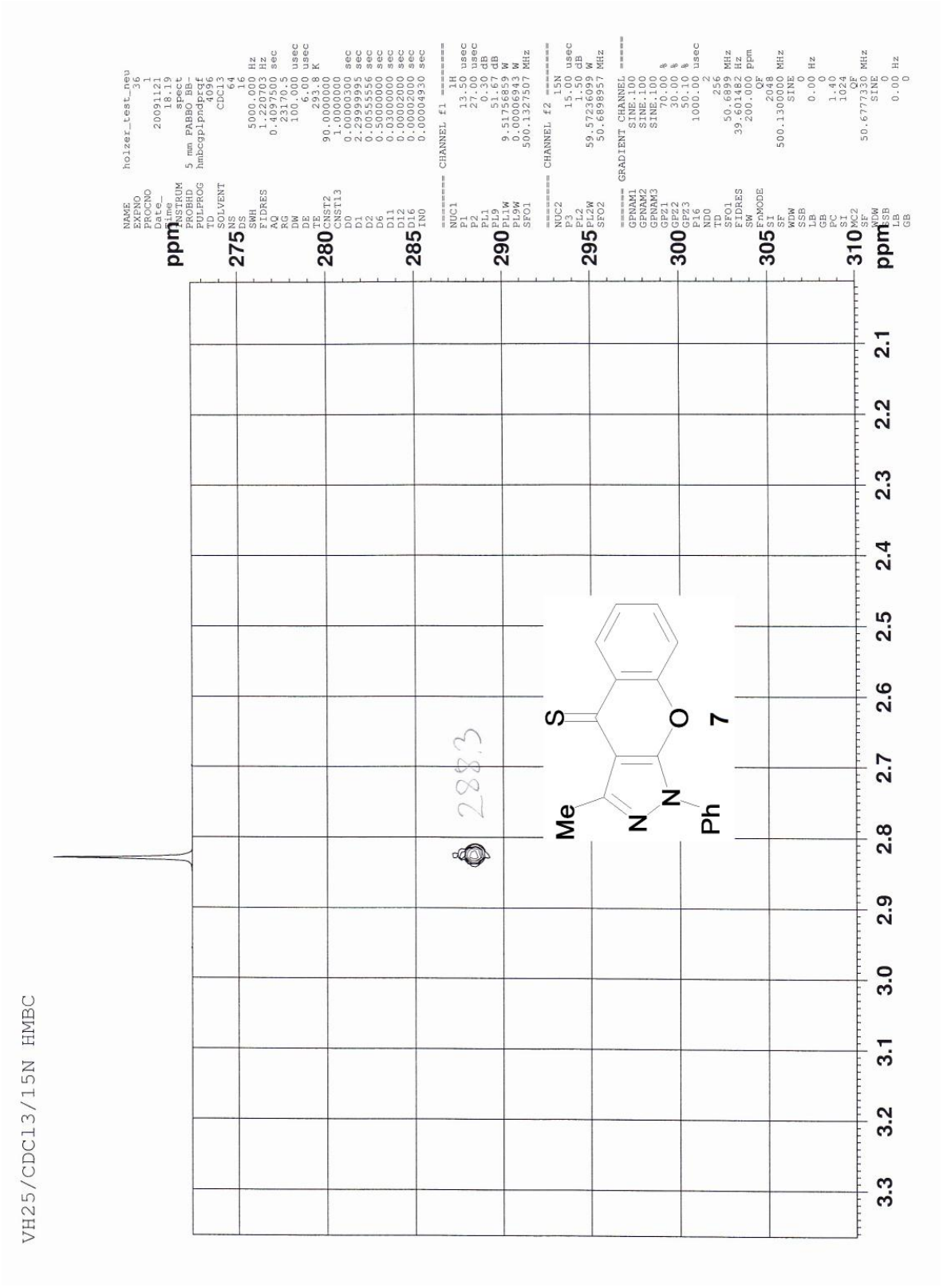
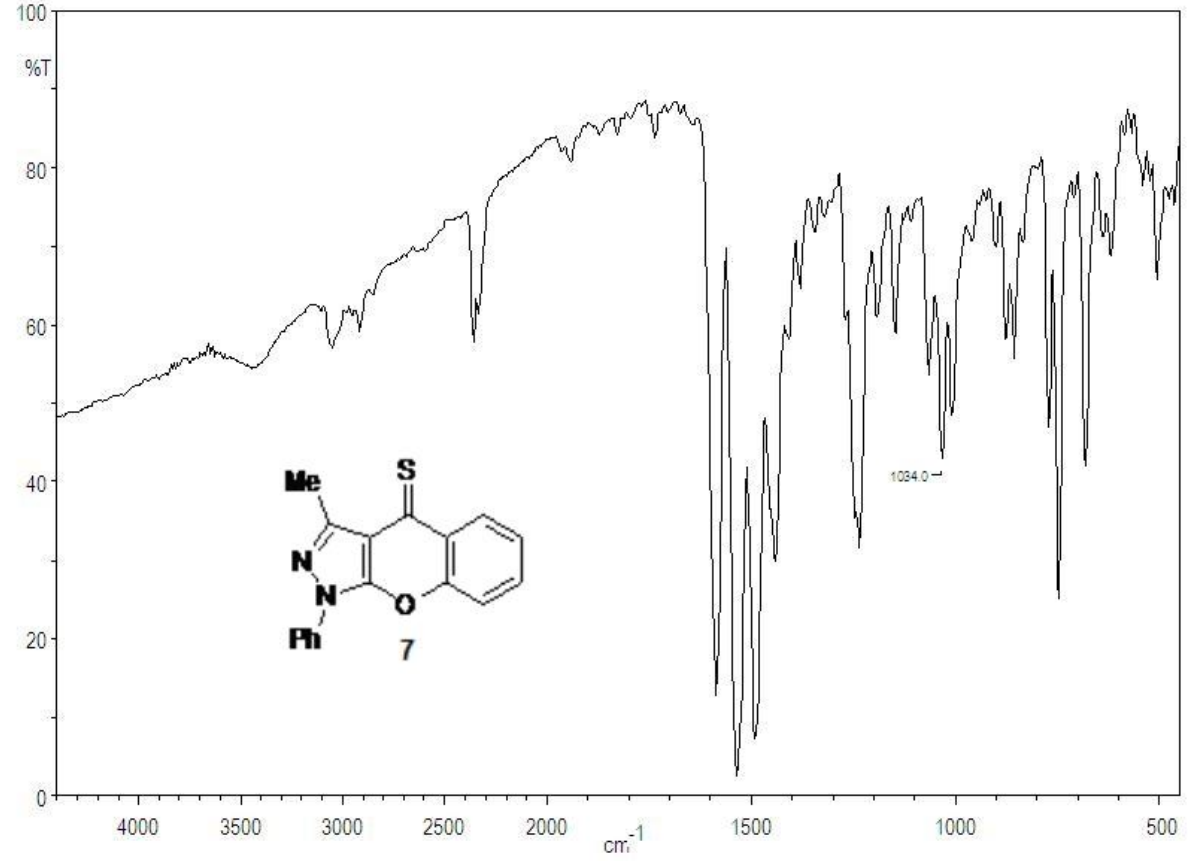


Abb.7.4


100
%T
80
60
40
20
0
4000
3500
3000
2500
2000
cm-1
1500
1000
500
1034.0
Me
S
N
N
O
Ph
7

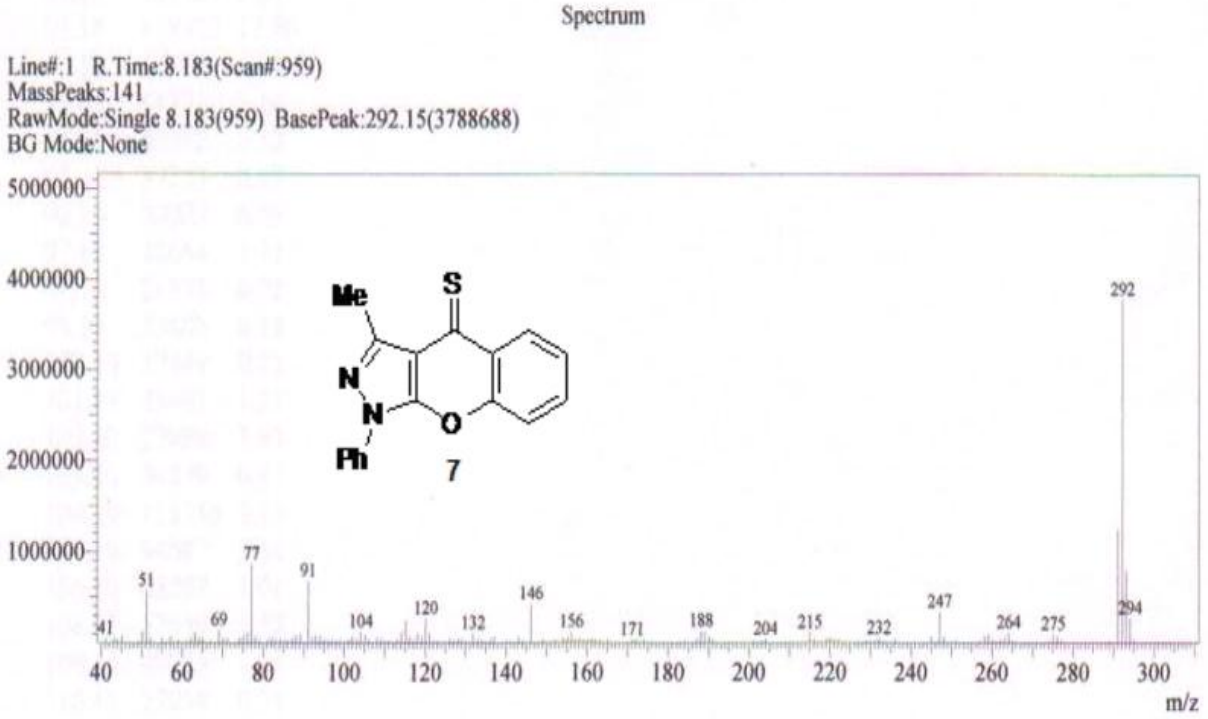
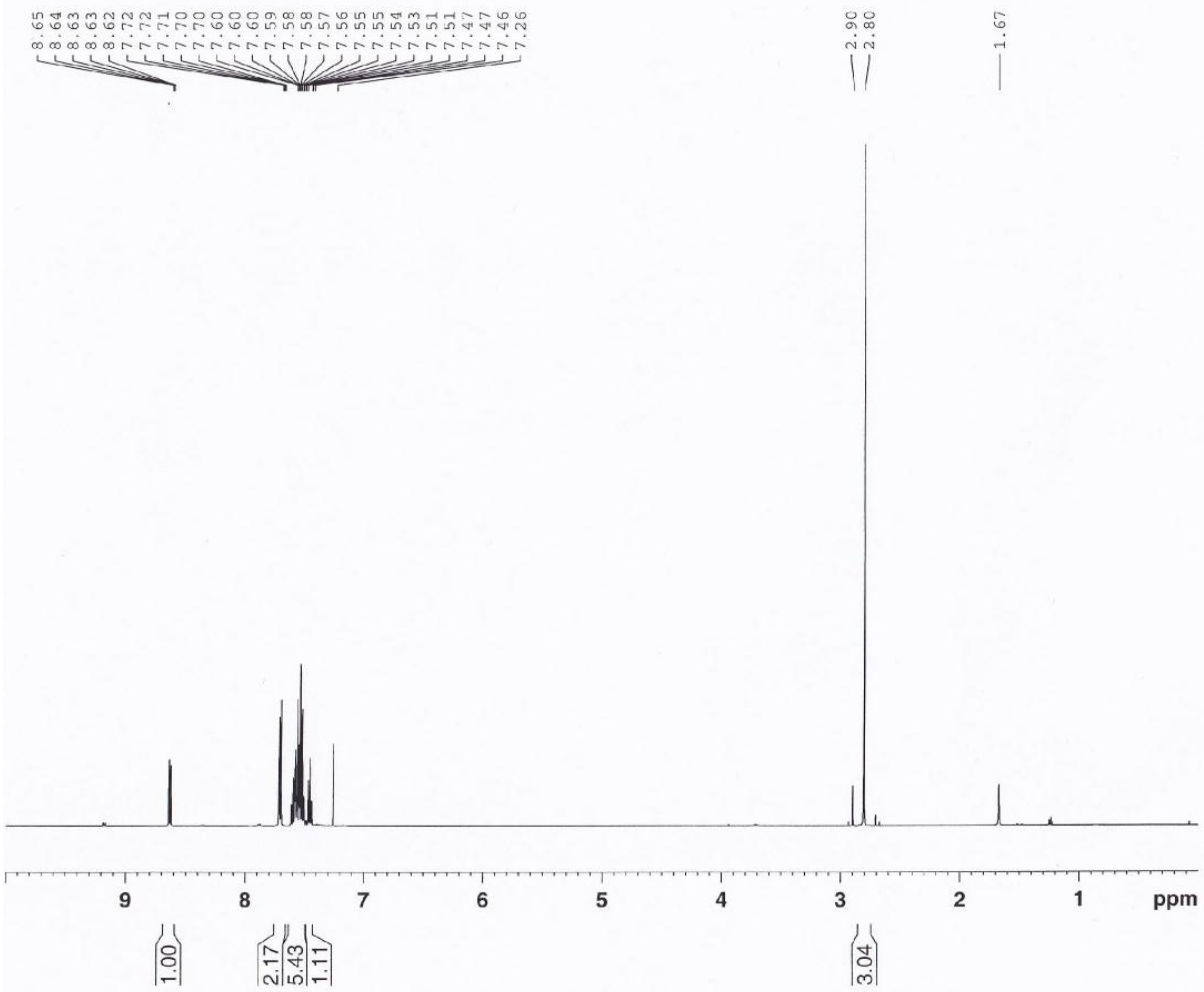

Spectrum
Line#:1 R.Time:8.183(Scan#:959)
MassPeaks:141
RawMode:Single 8.183(959) BasePeak:292.15(3788688)
BG Mode:None
5000000
4000000
3000000
2000000
1000000
Me
S
N
N
O
Ph
7
292
294
77
91
51
69
104
120
132
146
156
171
188
204
215
232
247
264
275
41
40
60
80
100
120
140
160
180
200
220
240
260
280
300
m/z

Abb.8.1

AH8/"Thioxanthon"/CDCl3

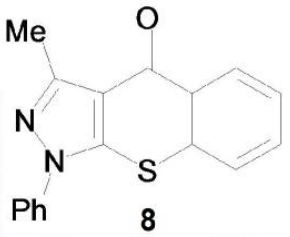



```
Current Data Parameters
NAME                  AH8
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20091029
Time                9.13
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 70026
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             7002.801 Hz
FIDRES             0.100003 Hz
AQ              4.9999776 sec
RG                 161.3
DW                 71.400 usec
DE                  6.00 usec
TE                 293.4 K
D1              3.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.50 usec
PL1                  0.30 dB
SFO1          500.1332508 MHz

F2 - Processing parameters
SI                  65536
SF            500.1300134 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```



8

Abb.8.2

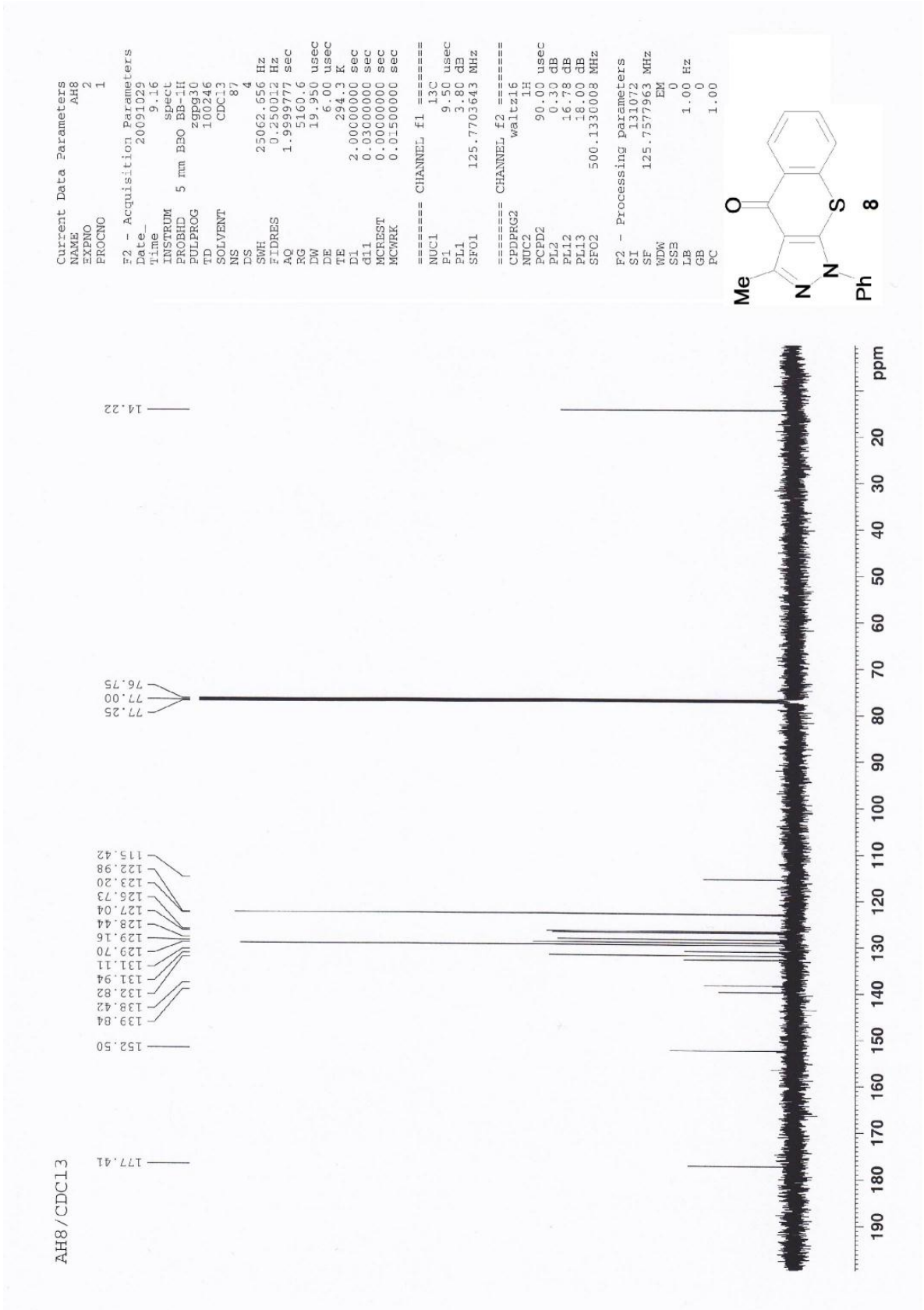

Current Data Parameters
NAME AH8
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091029
Time 9.16
INSTRUM spect
PROBHD 5 mm B3O BB-1H
PULPROG zgpg30
TD 100246
SOLVENT CDCl3
NS 4
DS 4
SWH 25062.656 Hz
FIDRES 0.250012 Hz
AQ 1.9999777 sec
RG 5160.6
DW 19.950 usec
DE 6.00 usec
TE 294.3 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 3.80 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.30 dB
PL12 16.78 dB
PL13 18.00 dB
SFO2 500.1330008 MHz
F2 - Processing parameters
SI 131072
SF 125.7577963 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
Me
N
N
Ph
O
S
8
AH8/CDCl3
177.41
152.50
139.84
138.42
132.82
131.94
131.11
129.70
129.16
128.44
127.04
126.73
123.20
122.98
115.42
77.25
77.00
76.75
14.22
ppm

Abb.8.3

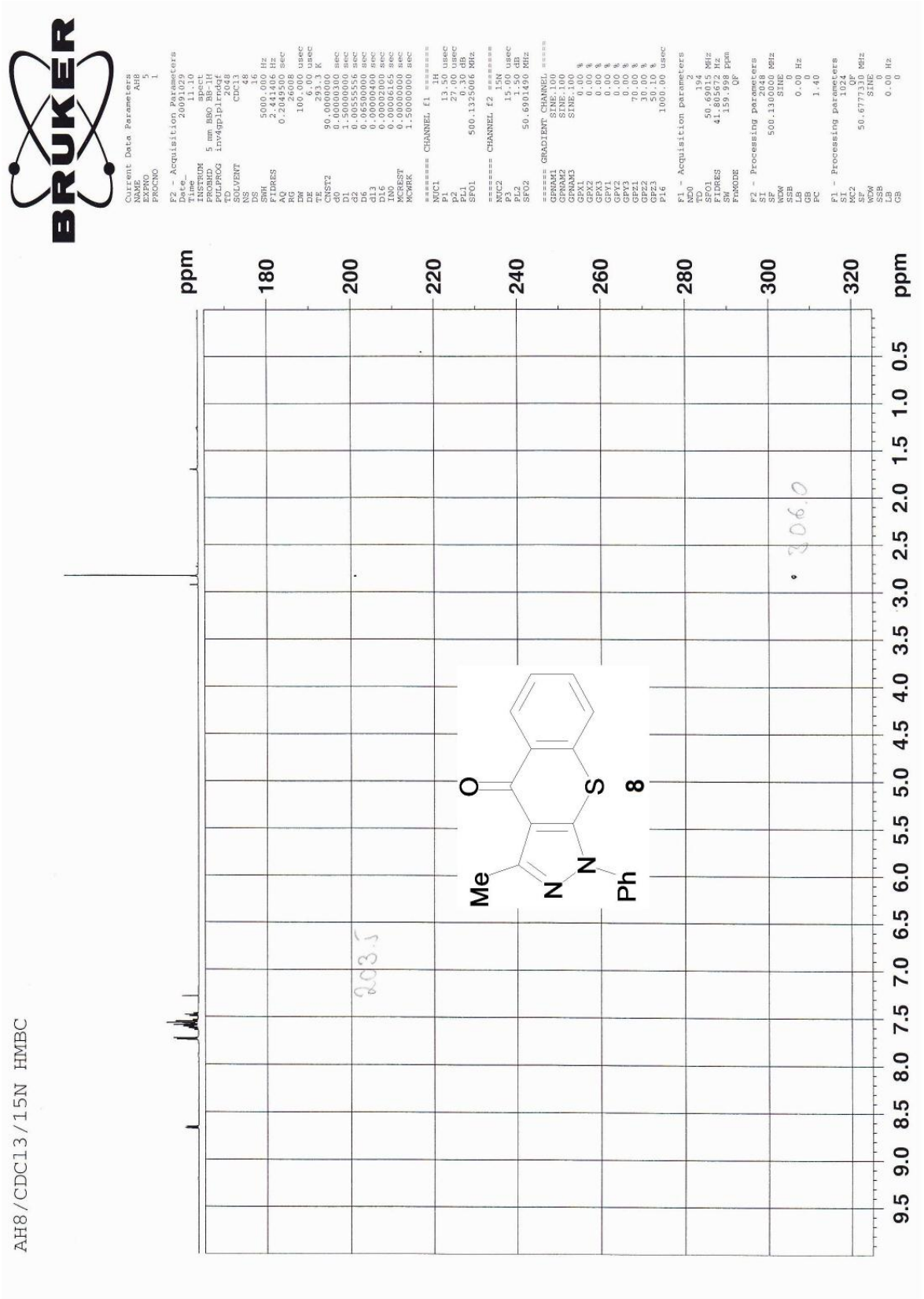

AH8/CDCl3/15N HMBC
BRUKER
Current Data Parameters
NAME AH8
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20011029
Time 11.10
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG inv4gp1lrndqf
TD 2048
SOLVENT CDCl3
NS 48
DS 16
SWH 5000.000 Hz
FIDRES 2.441406 Hz
AQ 0.2097608 sec
RG 203.6
DW 100.000 usec
DE 6.00 usec
TE 293.3 K
CNST2 90.0000000
D0 0.0000030 sec
D1 1.5000000 sec
d2 0.00555556 sec
D6 0.06500000 sec
d13 0.00004000 sec
D16 0.0002000 sec
D20 0.00006500 sec
MCREST 0.00000000 sec
MCWRK 1.50000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
p2 27.00 usec
PL1 0.30 dB
SFO1 500.1325006 MHz
======== CHANNEL f2 ========
NUC2 15N
P3 15.00 usec
PL2 1.50 dB
SFO2 50.6901490 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPNAM3 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPX3 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPY3 0.00 %
GPZ1 30.00 %
GPZ2 30.00 %
GPZ3 50.10 %
P16 1000.00 usec
F1 - Acquisition parameters
ND0 2
TD 194
SFO1 50.69015 MHz
FIDRES 41.805672 Hz
SW 159.998 ppm
FnMODE QF
F2 - Processing parameters
SI 2048
SF 500.1300000 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
F1 - Processing parameters
SI 1024
MC2 QF
SF 50.6777330 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
ppm
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
180 200 220 240 260 280 300 320
O
S
Me
N
N
Ph
8

Abb.8.4

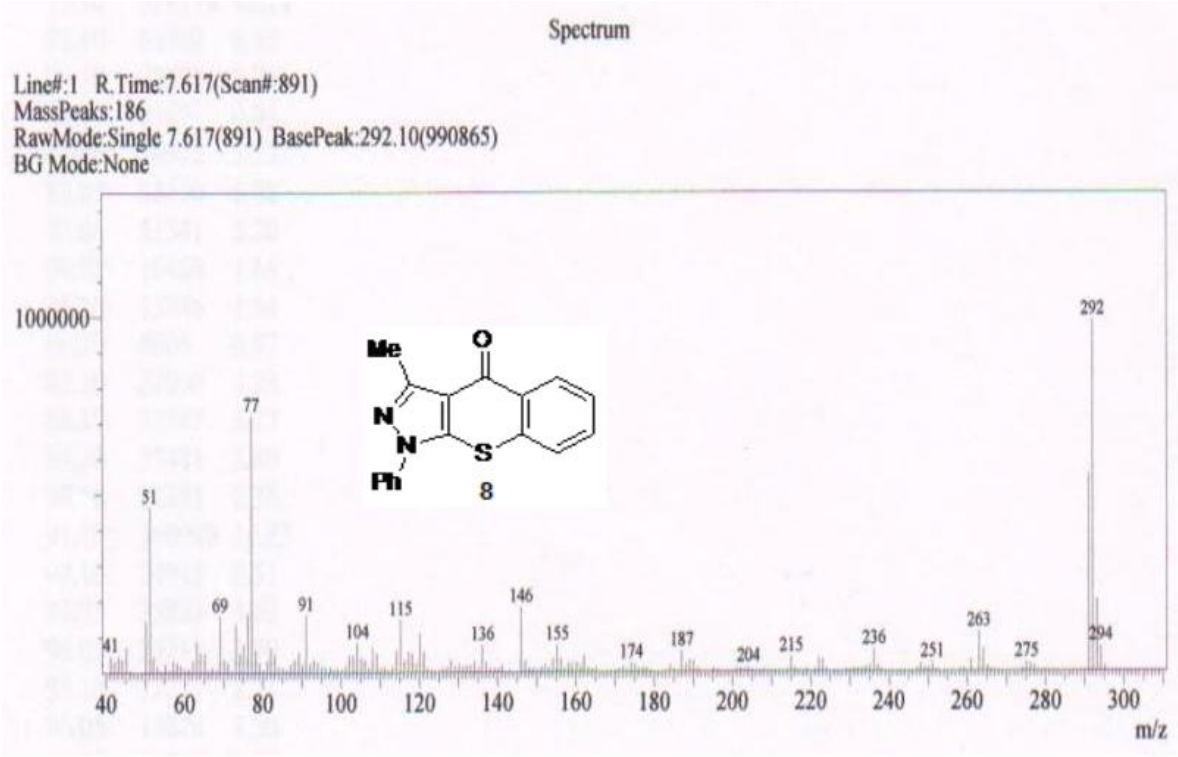

Spectrum
Line#:1 R.Time:7.617(Scan#:891)
MassPeaks:186
RawMode:Single 7.617(891) BasePeak:292.10(990865)
BG Mode:None
1000000
Me
O
N
N
S
Ph
8
292
77
51
69
91
115
146
104
136
155
174
187
204
215
236
251
263
275
294
41
40
60
80
100
120
140
160
180
200
220
240
260
280
300
m/z

Abb.9.1

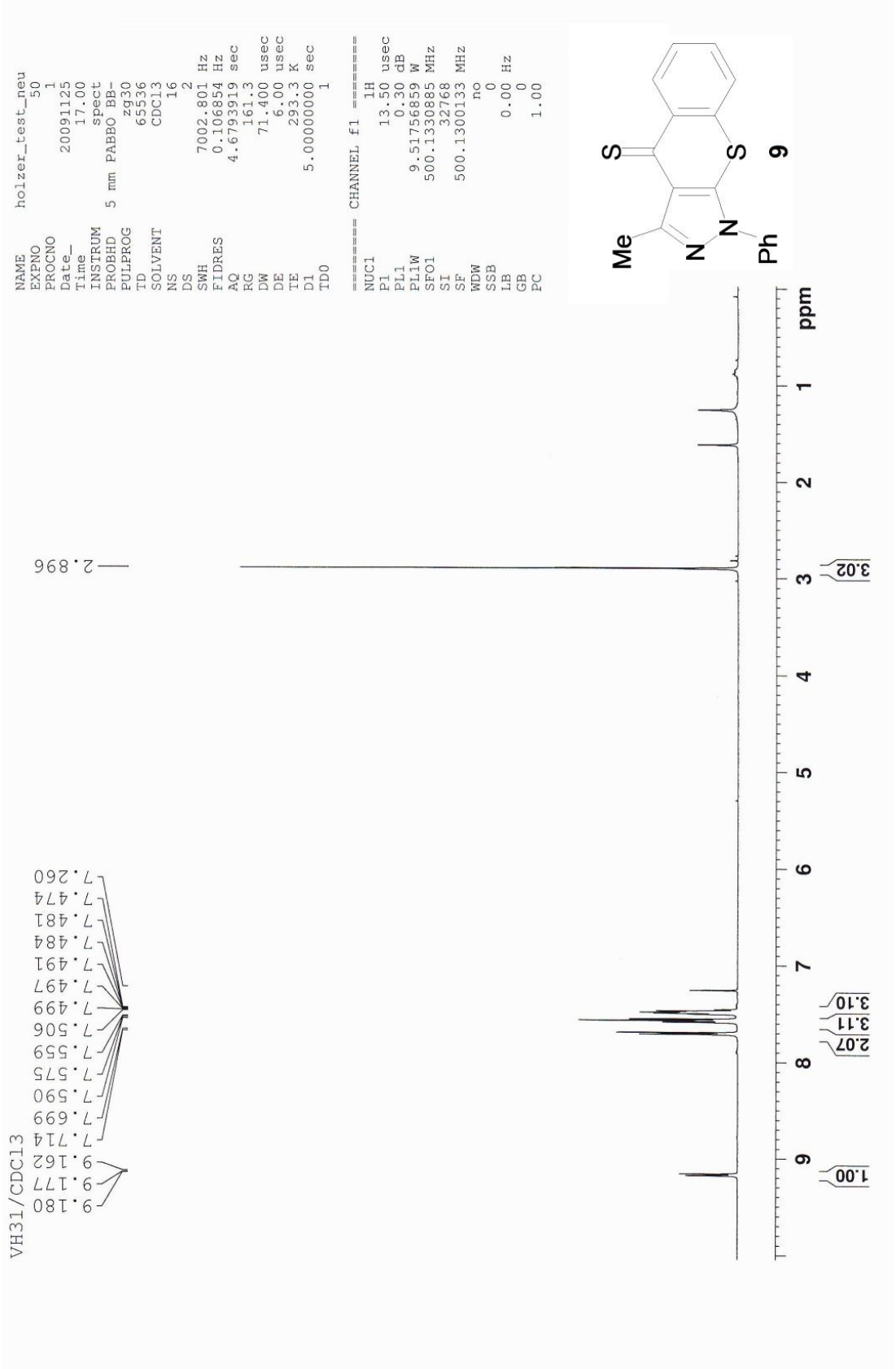

NAME holzer_test_neu
EXPNO 50
PROCNO 1
Date_ 20091125
Time 17.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 7002.801 Hz
FIDRES 0.106854 Hz
AQ 4.6793919 sec
RG 161.3
DW 71.400 usec
DE 6.00 usec
TE 293.3 K
D1 5.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 0.30 dB
PL1W 9.51756859 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300133 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
S
S
Me
N
N
Ph
9
VH31/CDC13
9.180
9.177
9.162
7.714
7.699
7.590
7.575
7.559
7.506
7.499
7.497
7.491
7.484
7.481
7.474
7.260
2.896
3.02
1.00
3.10
3.11
2.07
ppm

Abb.9.2

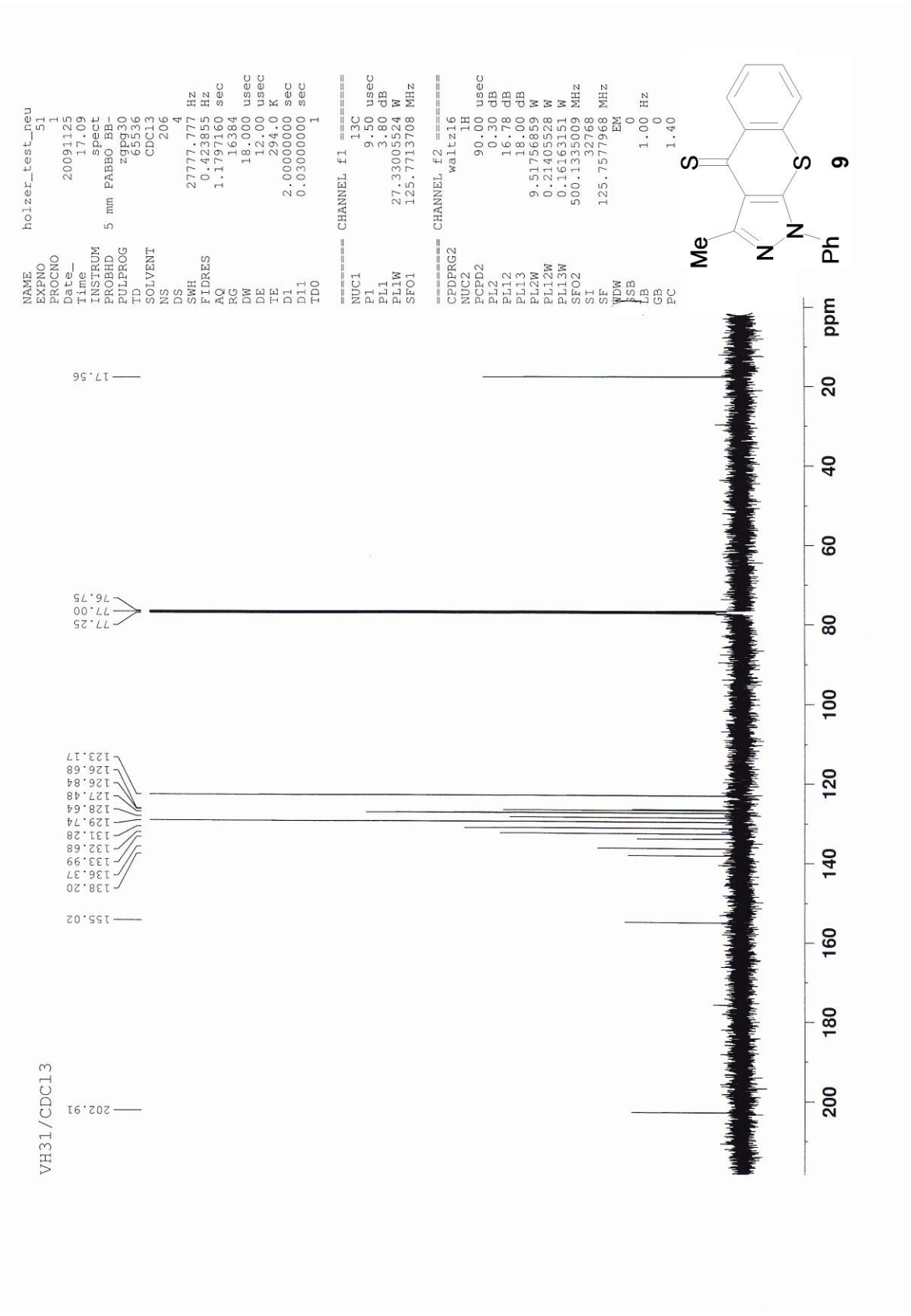
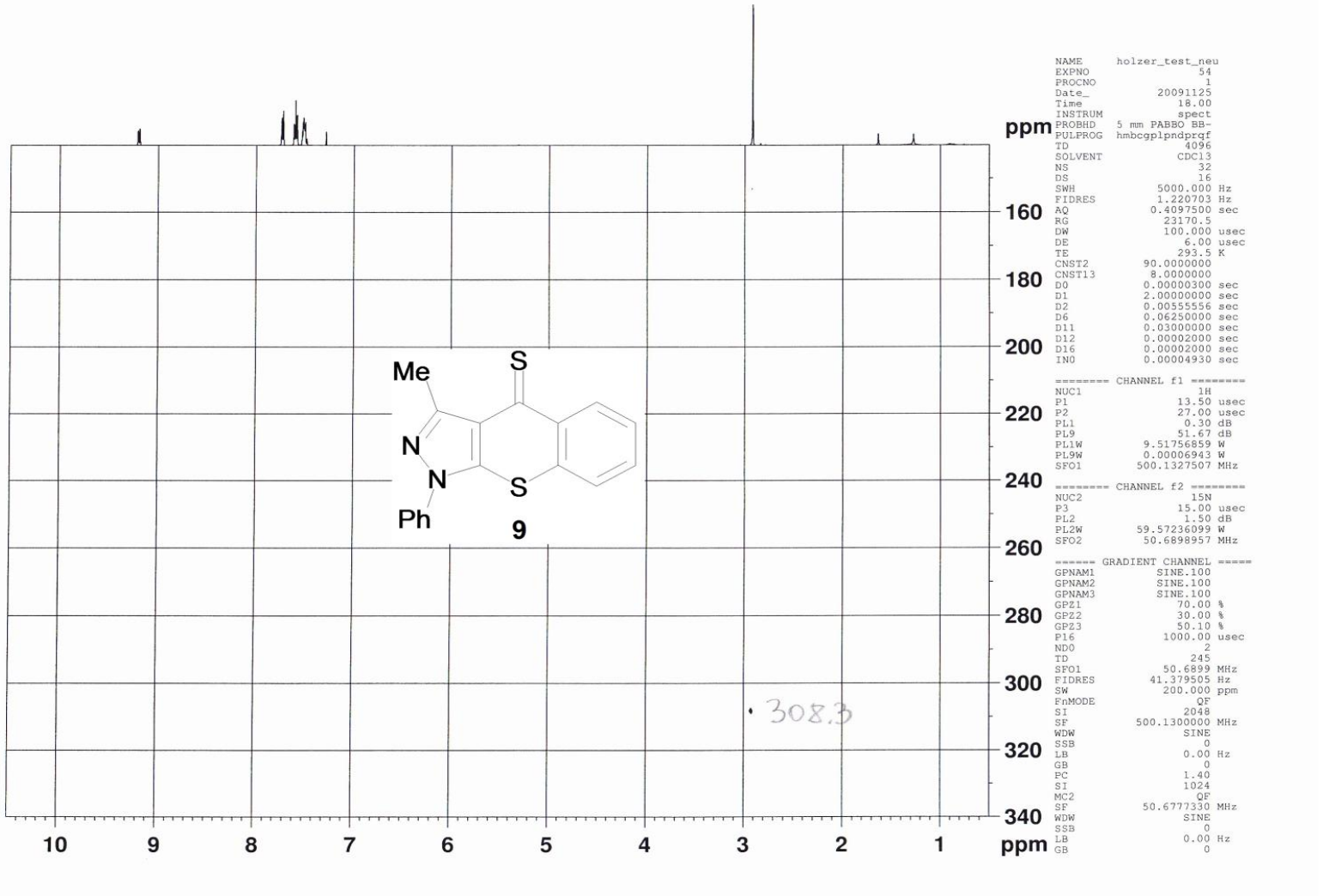

VH31/CDC13
202.91
155.02
138.20
136.37
133.99
132.68
131.28
129.74
128.64
127.48
126.84
126.68
123.17
77.25
77.00
76.75
17.56
S
S
N
N
Me
Ph
9
ppm
20
40
60
80
100
120
140
160
180
200

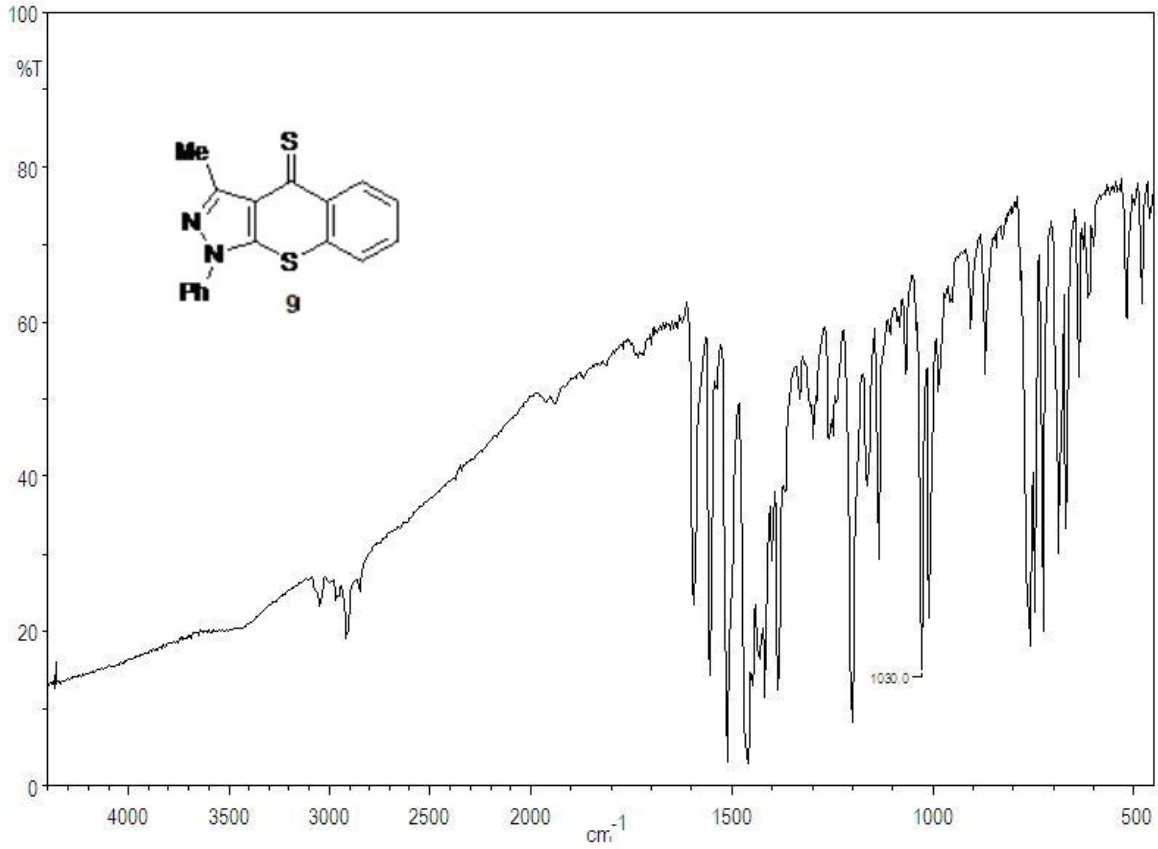
Abb.9.3

VH31/CDCl3/15N HMBC



NAME	holzer_test_neu
EXPNO	54
PROCNO	1
Date_	20091125
Time	18.00
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	hmbcgplpndprqf
TD	4096
SOLVENT	CDCl3
NS	32
DS	16
SWH	5000.000 Hz
FIDRES	1.220703 Hz
AQ	0.4097500 sec
RG	23170.5
DW	100.000 usec
DE	6.00 usec
TE	293.5 K
CNST2	90.0000000
CNST13	8.0000000
D0	0.00000300 sec
D1	2.00000000 sec
D2	0.00555556 sec
D6	0.06250000 sec
D11	0.03000000 sec
D12	0.00002000 sec
D16	0.00002000 sec
IN0	0.00004930 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	13.50 usec
P2	27.00 usec
PL1	0.30 dB
PL9	51.67 dB
PL1W	9.51756859 W
PL9W	0.00006943 W
SFO1	500.1327507 MHz
======== CHANNEL f2 ========	
NUC2	15N
P3	15.00 usec
PL2	1.50 dB
PL2W	59.57236099 W
SFO2	50.6898957 MHz
====== GRADIENT CHANNEL =====	
GPNAM1	SINE.100
GPNAM2	SINE.100
GPNAM3	SINE.100
GPZ1	70.00 %
GPZ2	30.00 %
GPZ3	50.10 %
P16	1000.00 usec
ND0	2
TD	245
SFO1	50.6899 MHz
FIDRES	41.379505 Hz
SW	200.000 ppm
FnMODE	QF
SI	2048
SF	500.1300000 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.40
SI	1024
MC2	QF
SF	50.6777330 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

Abb.9.4


100
%T
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
cm-1
1030.0
Me
S
N
N
S
Ph
9

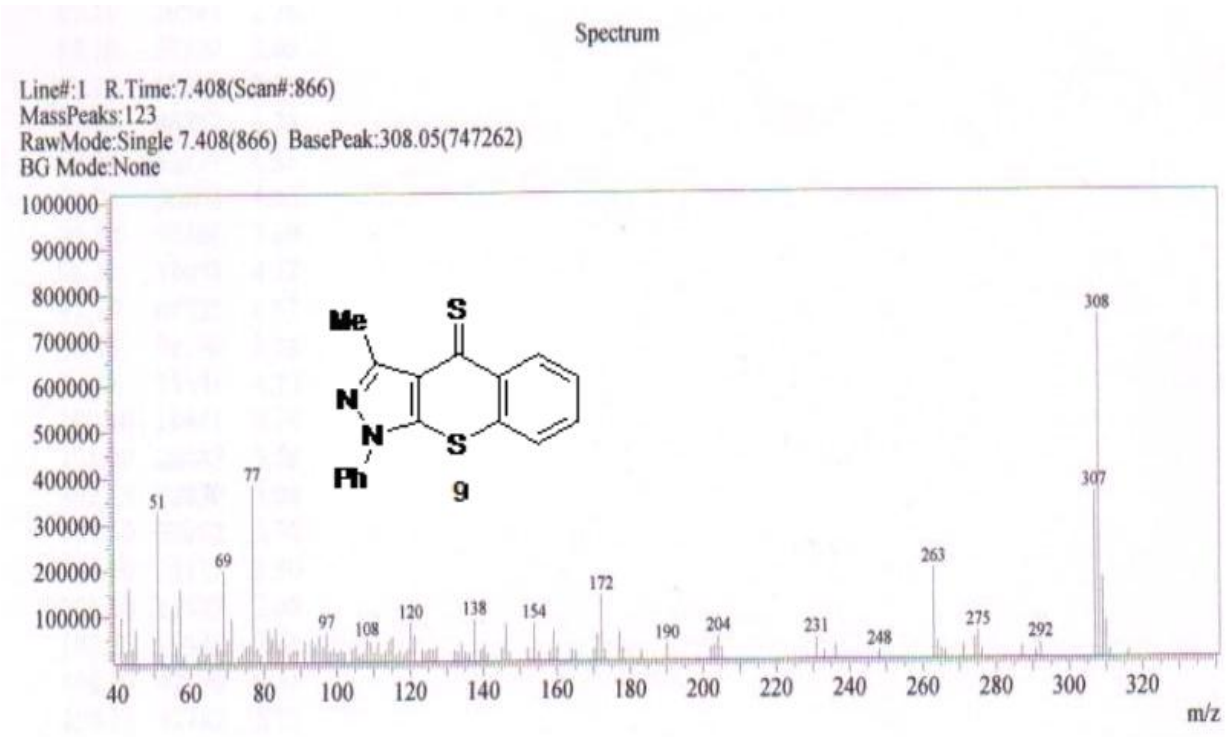

Spectrum
Line#:1 R.Time:7.408(Scan#:866)
MassPeaks:123
RawMode:Single 7.408(866) BasePeak:308.05(747262)
BG Mode:None
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
m/z
Me
S
N
N
S
Ph
9
308
307
263
275
292
248
231
204
190
172
154
138
120
108
97
77
69
51

Abb.10.1

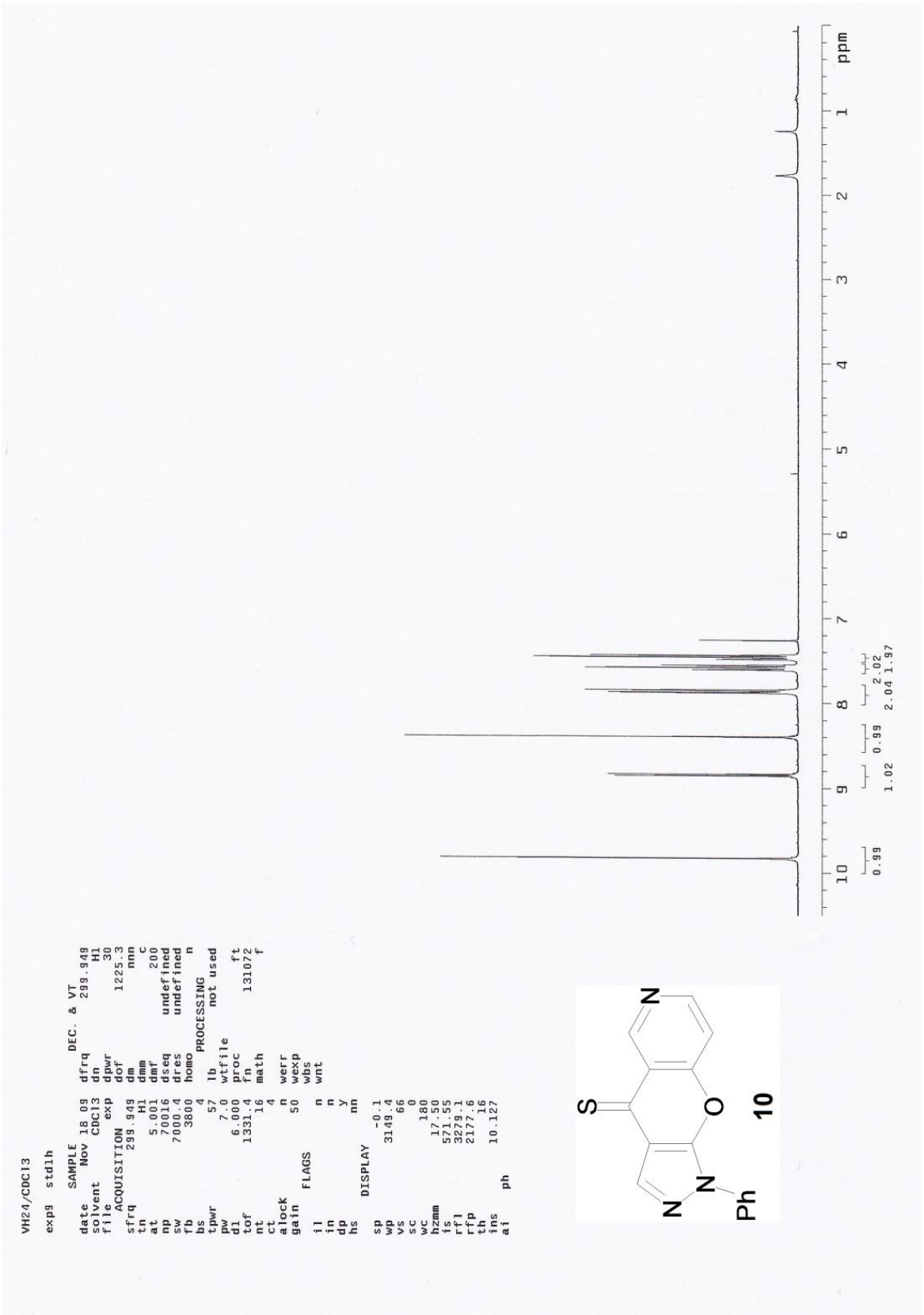

VH24/CDCl3
exp9 stdih
SAMPLE
date Nov 18 09
solvent CDCl3
file exp
ACQUISITION
sfrq 299.949
tn H1
at 5.001
np 70016
sw 7000.4
fb 3800
bs 4
tpwr 57
pw 7.0
d1 6.000
tof 1331.4
nt 16
ct 4
alock n
gain 50
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -0.1
wp 3149.4
vs 66
sc 0
wc 180
hzmm 17.50
is 571.55
rfl 3279.1
rfp 2177.6
th 16
ins 10.127
ai ph
DEC. & VT
dfrq 299.949
dn H1
dpwr 30
dof 1225.3
dm nnn
dmm c
dmf 200
dseq undefined
dres undefined
homo n
PROCESSING
lb not used
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
S
O
N
N
N
Ph
10
ppm
0.99
1.02
0.99
2.02
2.04
1.97

Abb.10.2

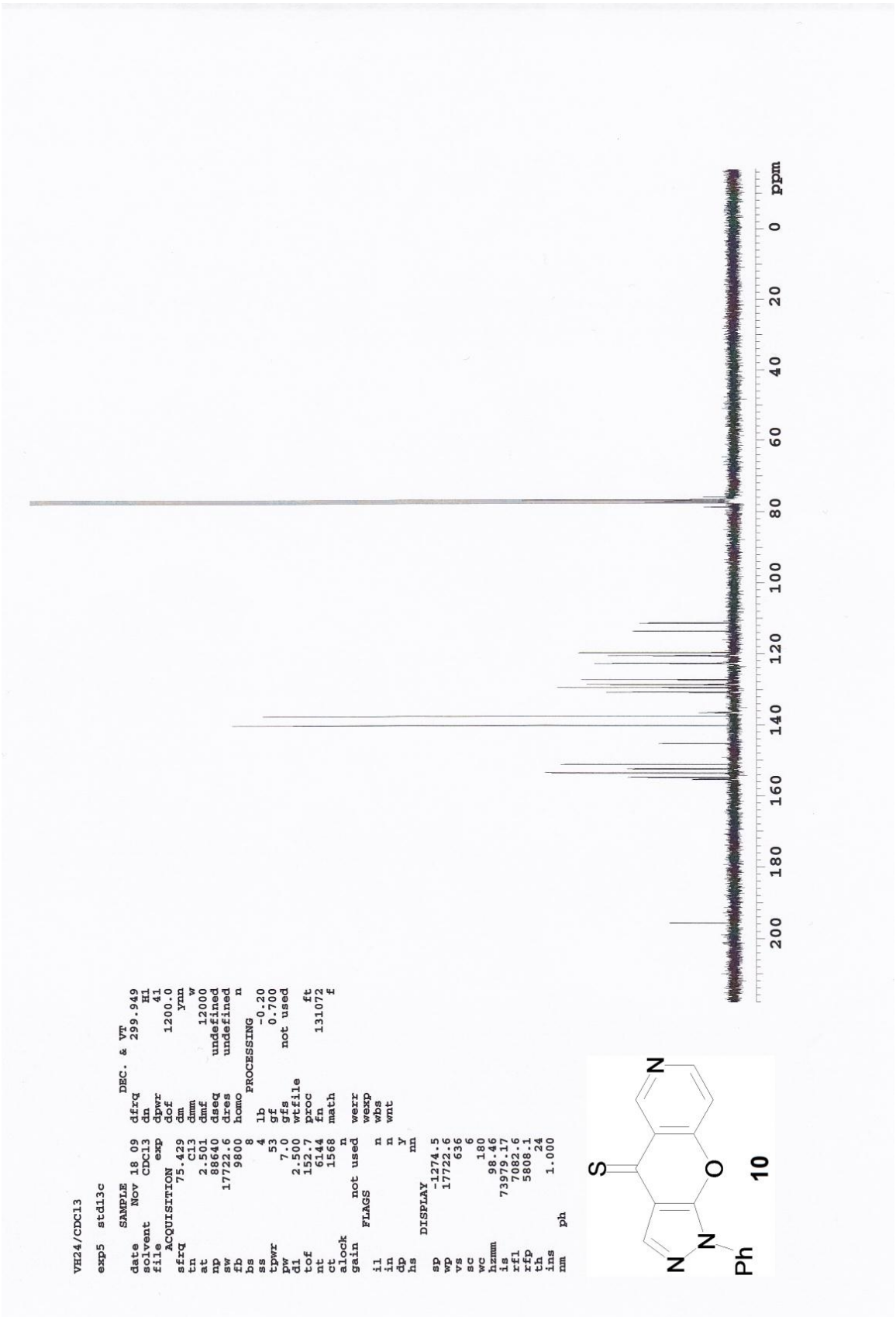

VH24/CDC13
exp5 std13c
SAMPLE
date Nov 18 09
solvent CDCl3
file exp
ACQUISITION
sfrq 75.429
tn C13
at 2.501
np 88640
sw 17722.6
fb 9800
bs 8
ss 4
tpwr 53
pw 7.0
d1 2.500
tof 152.7
nt 6144
ct 1568
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1274.5
wp 17722.6
vs 636
sc 6
wc 180
hzmm 98.46
is 73979.17
rfl 7082.6
rfp 5808.1
th 24
ins 1.000
nm ph
DEC. & VT
dfrq 299.949
dn H1
dpwr 41
dof 1200.0
dm y nn
dmm w
dmf 12000
dseq undefined
dres undefined
homo n
PROCESSING
lb -0.20
gf 0.700
gfs not used
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
200 180 160 140 120 100 80 60 40 20 0 ppm
S
O
N
N
N
Ph
10

Abb.10.3

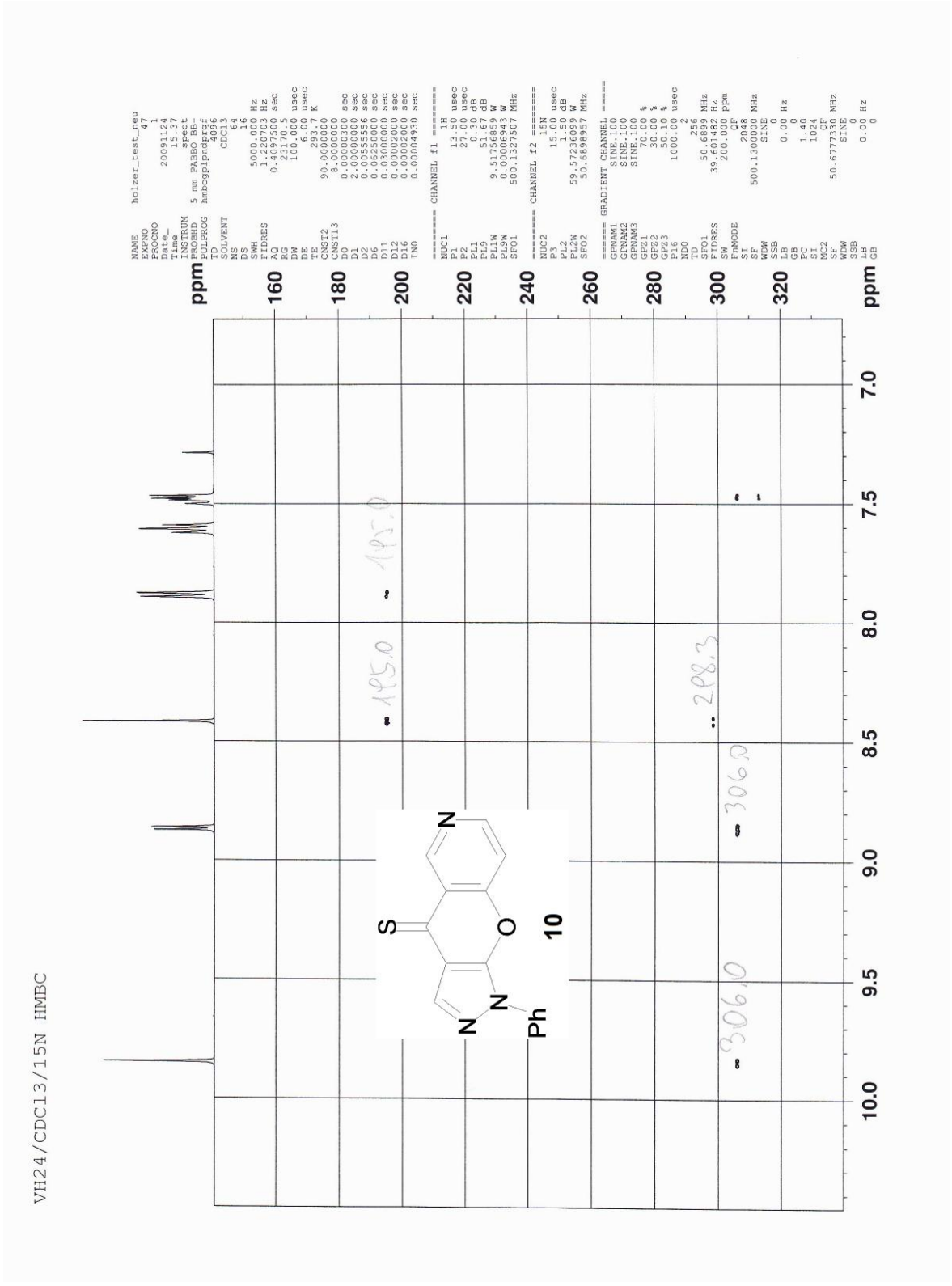
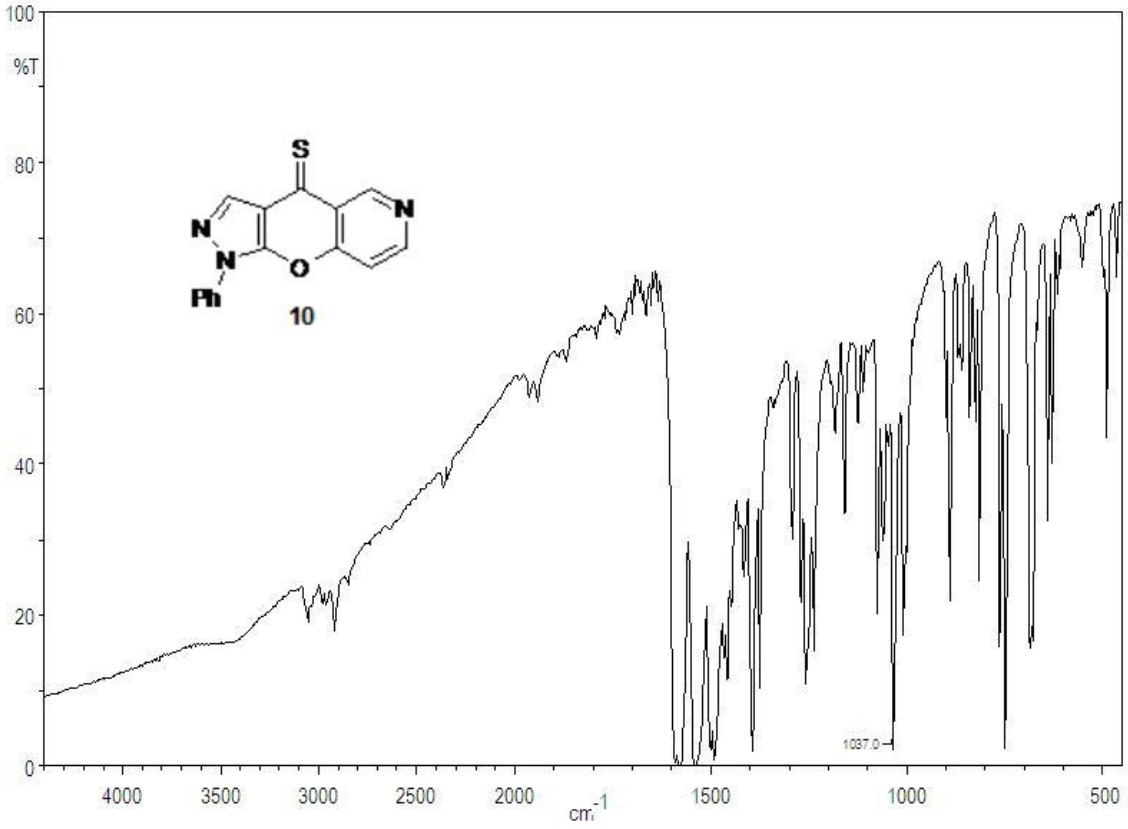
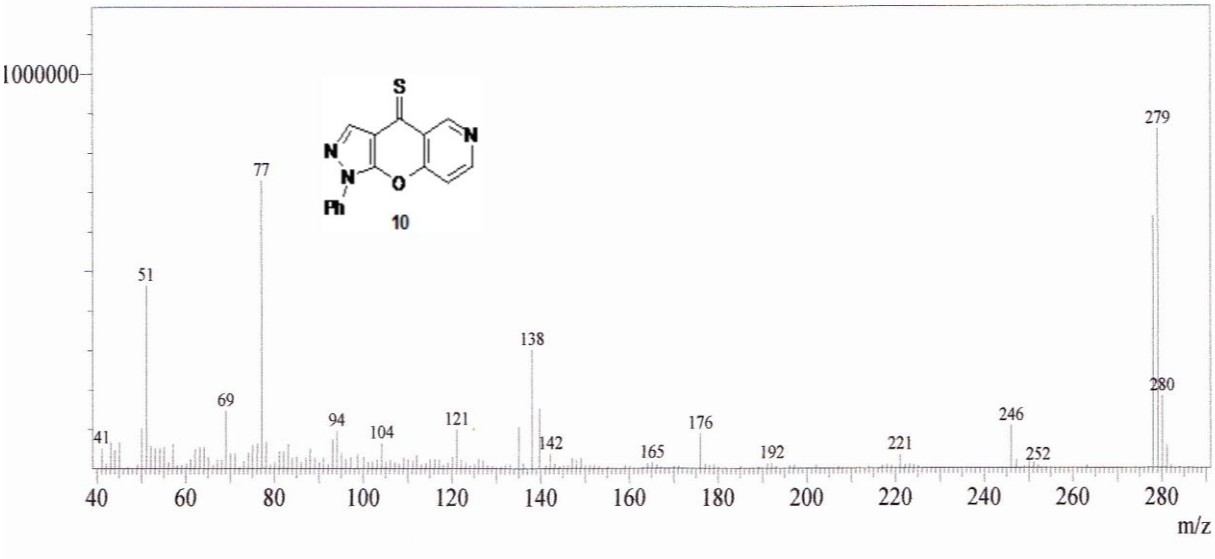

VH24/CDC13/15N HMBC
ppm
160
180
200
220
240
260
280
300
320
7.0
7.5
8.0
8.5
9.0
9.5
10.0
S
O
N
N
N
Ph
10
= 185.0
= 185.0
= 208.3
= 306.0
= 306.0

Abb.10.4



Spectrum

Line#:1 R.Time:7.858(Scan#:920)
MassPeaks:152
RawMode:Single 7.858(920) BasePeak:279.10(857004)
BG Mode:None



4.2. Zusammenfassung

Die vorliegende Diplomarbeit beschäftigt sich mit Untersuchungen zur Synthese kondensierter, polycyclischer Systeme mit [5,6]Pyrano[2,3-c]pyrazol-4(1*H*)thion-Partialstruktur.

Als Ausgangsverbindungen wurden verschiedene [5,6]Pyrano[2,3-c]pyrazol-4(1*H*)-one verwendet, die durch Behandlung mit Lawesson-Reagens in siedendem Toluol in ihre entsprechenden Thioanaloga übergeführt werden sollten.

Als Zielverbindungen wurden 3-Methyl-1-phenylpyrazolo[4´,3´:5,6]pyrano[3,2-*b*]pyridin-4(1*H*)thione **5a-d** (alle Isomere), 3-Methyl-1-phenylthieno[2´,3´:5,6]pyrano[2,3-*c*]pyrazol-4(1*H*)thione **5e-g** (alle Isomere), 3-Methyl-1-phenylpyrazolo[4´,3´:5,6]pyrazo[2,3-*b*]chinolin-4(1*H*)thion **5h**, 3-Methyl-1-phenyl[1]benzothieno[2´,3´:5,6]pyrano[2,3-*c*]pyrazol-4(*1H*)thion **5i** und 3-Methyl-1-phenylthieno[3´´,2´´:4´,5]´thieno[2´,3´:5,6]pyrano[2,3-*c*]pyrazol-4(1*H*)thion **5j** sowie 1-Phenylpyrazolo[4´,3´:5,6]pyrano[3,2-*c*]pyridin-4(1*H*)thion **10**. in hohen Ausbeuten synthetisiert und mittels spektroskopischer Methoden (^{1}H-NMR, ^{13}C-NMR, ^{15}N-NMR, MS, IR) sowie CHN-Analyse untersucht. Weiters sollten zu Vergleichszwecken 3-Methyl-1-phenylchromeno[2,3-*c*]pyrazol-4(1*H*)thion **7** und 3-Methyl-1-phenylthiochromeno[2,3-*c*]pyrazol-4(1*H*)thion **9** aus ihren entsprechenden Oxo-Systemen **6** und **8** hergestellt werden.

4.3. Lebenslauf

Persönliche Daten

Name:	Valerie Anita Huemer
Geburtsdatum und -ort:	19.05.1984 Kirchdorf an der Krems
Staatsbürgerschaft:	Österreich

Ausbildung

1990-1994: Volksschule Mühldorf

1994-2002: Stiftsgymnasium Schlierbach

Seit WS 2002: Universität Wien

- Studium der Pharmazie

- Studium Molekulare Biologie seit 10/2005

Berufliche Tätigkeiten

Juli 2004: Praktikum in der Anstaltsapotheke des Klinikum Kreuzschwestern Wels

Juli 2005: Praktikantin in der Sternapotheke Wels

April und August 2007: Sternapotheke Wels

April 2008 – Oktober 2008: Praktikantin Maria Schutz Apotheke, 1050 Wien

Seit Februar 2011: Europa-Apotheke, 1140 Wien