SUPRAMOLECULAR CHEMISTRY ON CARBON DIOXIDE

by

HEXIANG ZHANG

Presented to the Faculty of the Graduate School of

The University of Texas at Arlington in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE IN CHEMISTRY

THE UNIVERSITY OF TEXAS AT ARLINGTON

December 2007

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to Professor Dmitry M. Rudkevich for his guidance and dedication to my education as a chemist. Dear Dr. Rudkevich, thank you for bringing me into this wonderful field of organic chemistry. I will never forget your encouragement and support; I am always proud of being your student.

I would also like to thank the members of my committee, Professors Carl Lovely, Daniel Armstrong, Martin Pomeranz, who challenged me and provided insight during the progress of this work.

I would like to thank all my colleagues in Dr. Rudkevich's group: Dr. Heng Xu, Dr. Valcav Stastny, Dr. Alexandre Leontyev, Dr. Organo Volaire, Mr. Anas Saleh, Mr. Eranda Wanigasekara, Mr. Luis Reyes, Mr. Zak Nixon for their assistance and friendship.

This work was supported by the Petroleum Research Fund and by NSF.

Finally, I would like to thank my parents and my fiancée, Jingyi Wei, for their unending love and support during the last several years; none of this would have been possible without them.

November 21, 2007

ABSTRACT

SUPRAMOLECULAR CHEMISTRY ON CARBON DIOXIDE

Publication No. _____

Hexiang Zhang, MS

The University of Texas at Arlington, 2007

Supervising Professor: Dr. Dmitry M. Rudkevich*, Dr. Martin Pomerantz

This dissertation describes approaches towards designs, syntheses, characterizations, and applications of supramolecular chemistry on carbon dioxide. Chapter 1 briefly overviews the field of supramolecular chemistry and highlights its horizons, also introduces the progress of sensing devices on chemical warfare agents. Chapter 2 introduces a modular approach to detect chemical warfare agent: phosgene by Fluorescence Resonance Energy Transfer (FRET). It combines the chemical reactivity between amines and phosgene with fluorescence properties of coumarin fluorophores, forms a fast, selective and reliable sensing system. Chapter 3 overviews the chemistry between amines and carbon dioxide and introduces the applications of this reaction in the molecular recognition, organic gelations and cation separations. A novel strategy for

alkali metal cation separations is demonstrated by introducing dibenzo-18-crown-6 and lysine derivatives, which successfully extract metal ions from aqueous solution. CO_2 was used to build reversible, supramolecular polymeric materials. Formation of cross-linked, porous supramolecular polymers leads to instant entrapment of organic guest species. These can be stored and then released upon changing solvent polarity, temperature, pH, and concentration. Chapter 4 presents a calix[4]arene based novel strategy for sodium cation separation. Because of high affinity towards sodium cations, calix[4]arene tetraester is selected and functionlized by ethylenediamine on the lower rims. After entrapment of sodium cations, CO_2 gas constructs these calix[4]arene sodium complexes into cross-linked supramolecular polymers. These polymers employ dynamic, thermally reversible carbamate bonds. This approach shows high efficiency and accuracy.

* Deceased August 4, 2007. Supervisorship is substituted by Dr. Martin Pomerantz

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

CHAPTER 1

INTRODUCTION

1.1 Supramolecular Chemistry and Hydrogen Bonding

Supramolecular chemistry has developed in the past decades as a borderline scientific field between chemistry, physics, and biology. The concept and term of supramolecular chemistry were introduced by Lehn et al. in 1978.[1] This chemistry was defined as "chemistry beyond the molecule", based on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces.[2]

As molecular chemistry deals with molecules, supramolecular chemistry deals with supramolecular species, which are usually called "molecular receptor" and "substrate" (Figure 1.1). Binding of a substrate by a receptor yields supramolecules, and the binding process reflects molecular recognition. Numerous papers have appeared in this field. The substrates are usually cations, anions, neutral organic molecules, and even gases, while receptor molecules have complimentary molecular size, shape and architecture with the substrates, establishing non-covalent binding interactions.[3] Macrocyclic compounds possess numerous branches, bridges and connections, and thus become the favorite receptors, which in most cases contain intramolecular cavities for a variety of substrates. Among these macrocyclic compounds, crown ethers, cyclodexdrins, and calixarenes are most intensively investigated.

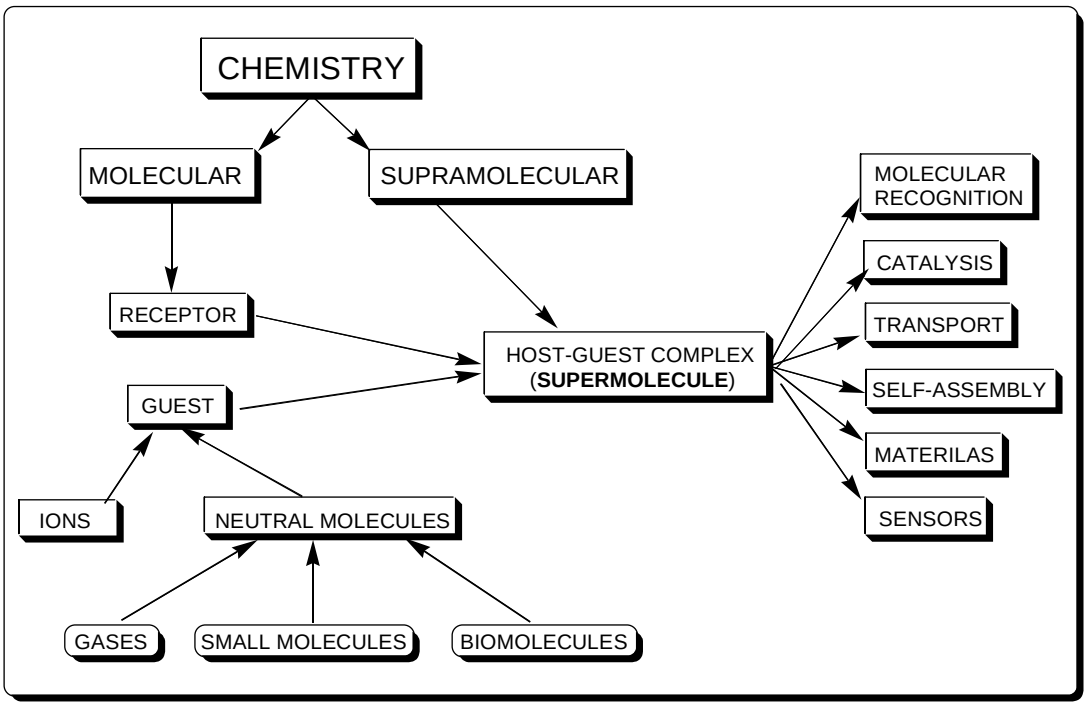


Figure 1.1 From molecular to supramolecular chemistry.

Crown ethers are macrocyclic compounds. They were discovered in the middle of 1960s by Charles Pedersen and are based on repeating -OCH_2CH_2- units, derived from ethylene glycol.[4] Varying the number of these units results in different size of the crown ether (Figure 1.2A). These compounds showed strong affinities for metal cations, such as Li^+, Na^+, K^+. The applications of crown ethers led to phase-transfer catalysis, biological ion transfer, membrane transport, extractions, etc .[5]

Cryptands are another important class of macrocyclic compounds which contain three-dimensional, spherical cavities (Figure 1.2B). This work started in 1967 by Lehn[6] shortly after discovery of crown ethers. Cryptands entirely surround the bound ions and form stronger complexes than the flat shaped macrocycles, thus displaying *spherical*

recognition of appropriate cations and anions. Numerous effects from these strong complexes have been brought about and studied in detail, such as: stabilization of alkalides and electrides, dissociation of ion pairs, anion activation, isotope separation, toxic metal binding, etc.[7]

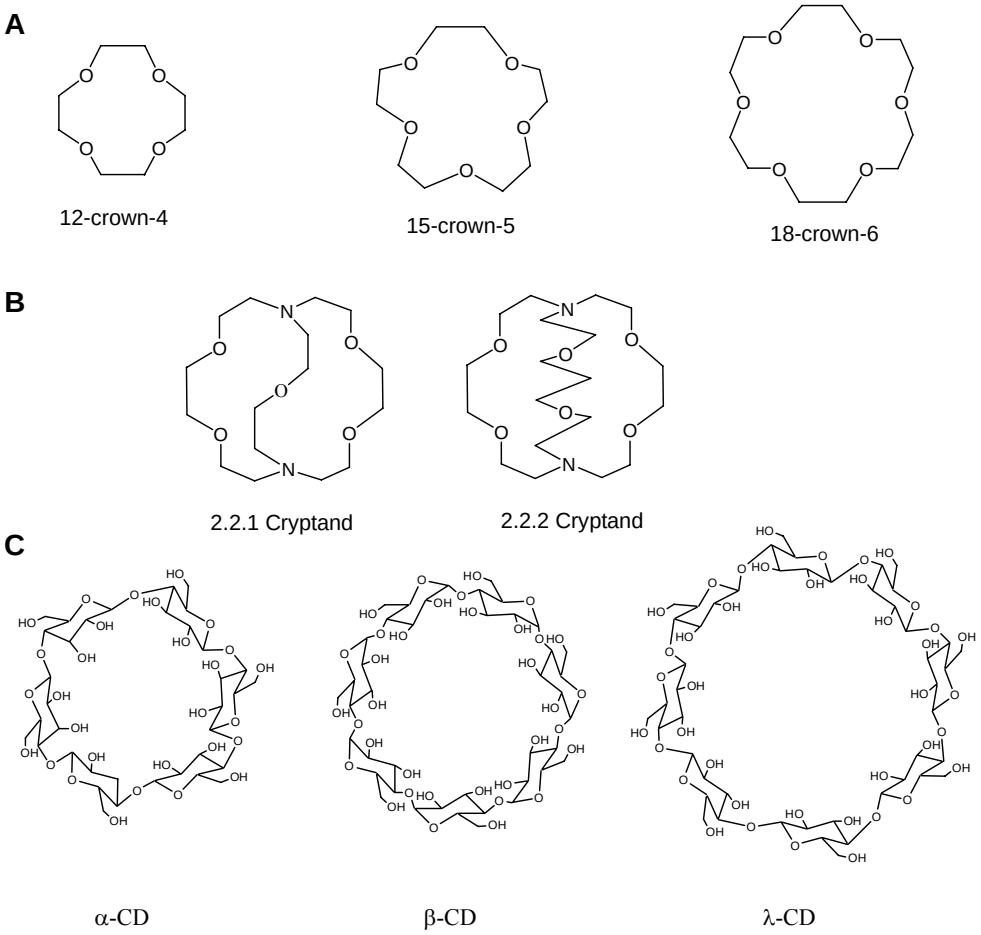


Figure 1.2 Structures of crown ethers (A), cryptands (B), and cyclodextrins (C)

Naturally occurring cyclodextrins are bucket-shaped oligosaccharides produced from starch (Figure 1.2C). Due to their molecular structure and shape, they possess a unique ability to act as molecular containers by entrapping guest molecules in

their internal cavities. The resulting inclusion complexes are one of most popular classes of host-guest supramolecules in academic research and they also offer a number of potential advantages in pharmaceutical formulations.[8]

Calixarenes were introduced in 1978 by C. D. Gutsche[9] as cup-like shapes, capable of complexing guest molecules. Since then, calixarenes have attracted a lot of research attention in this field. Earlier work focused on functionalizing calixarenes on both its upper and lower rims to afford a variety of cavities of different shapes and sizes. Those calixarenes were mostly studied as receptors for metal cations. More recently, calixarenes have been utilized to construct cavitands, (hemi)carcerands and self-assembling capsules, in which larger neutral organic molecules, cations, anions, were bound.[10]

Besides binding of one molecule by another, supramolecular chemistry studies the self-assembly of multiple molecules into supramolecular structures. Self-assembly is the autonomous organization of components into patterns or structures without human intervention.[11] Since self-assembling processes are common throughout nature and technology, it was first studied in biology and physics.[12,13] Supramolecular chemistry provides ways and means for chemical science to explore this area and apply its power of design and control. By self–assembly processes, receptors, transport agents, enzyme models, and extended arrays are constructed. These artificial assemblies are being utilized to mimic biological systems and applied to emerging scientific fields, especially nanotechnology. Self-assembly has become a rapidly growing field for two reasons. First, it is a crucial concept to understand many biologically important structures.

Second, it provides a solution to the problem of synthesizing larger structures. Although total synthesis of complex molecules can be achieved nowadays, synthesis of molecular structures with molecular weights >1000 Da through the stepwise formation of covalent bonds is still a formidable challenge.

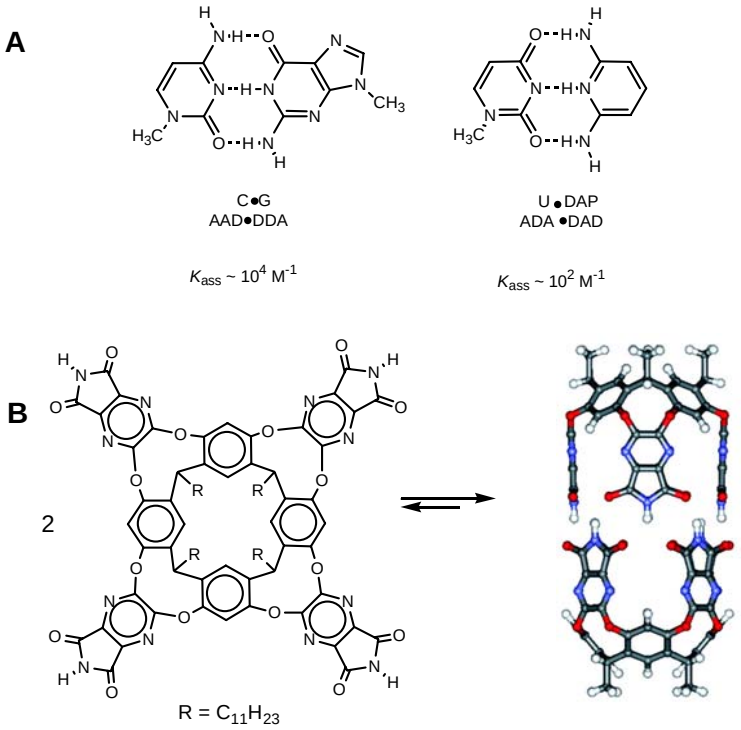


Figure 1.3 Hydrogen-bonded self-assemblies.

Hydrogen bonding is most frequently utilized in self-assembling systems, because it is directional, specific, and biologically relevant. Numerous self-assembly models on organic supramolecular structures have been reported in the literature, which can be categorized as dimers, multimers, capsules, polymers and nano-scale architectures, etc .[14]

Stable H-bond directed assemblies in most cases require multiple hydrogen bonds, while a variety of small organic functionalities, such as phenols, amines, and amides can dimerize through single H-bond. For stable assemblies, the number of hydrogen bonds is certainly not the only important parameter. "Cooperativity" is usually considered a key factor in increasing the stability of assemblies. The Jorgensen model was used as a basic rule to qualitatively predict the association constant between the individual units. These differences in stability can be largely attributed to attractive and repulsive secondary interactions. Stabilization arises from electrostatic attraction between positively and negatively polarized atoms in adjacent H-bonds, whereas destabilization is likewise the result of electrostatic repulsion between two positively or negatively polarized atoms (Figure 1.3 A).[15] According to this model, AA•DD (A refers to Acceptor, D refers to Donor) in 2-H-bond modules and AAA•DDD in 3-H-bond modules were predicted to have highest association constant values. These predictions have been proven by experimental data.[16] In 4-H-bond modules, AADD•DDAA arrays have been designed and demonstrated high stability with the association constant over 1×10^{6} M^{-1}.[17] Apart from the expected increase in stability, the even number of H-bond donors and acceptors in 4-H-bond modules allows self-complementarity to be introduced in these motifs. Self-complementarity provides an attractive property for applications in polymeric materials or molecular capsules.

The development, characterization, and exploitation of novel materials based on the assembly of molecular components is an exceptionally active and rapidly expanding materials field. Electronic, magnetic, optical, structural, mechanical, and chemical

characteristics were considered. The formation of supramolecular entities from photoactive components may be expected to show the ground-state and excited-state properties of the individual species, giving rise to novel properties. Assembling individual components into supramolecular systems may initialize a number of processes: excitation energy migration, photo-induced charge separation by electron and proton transfer, perturbation of optical transitions and polarizabilities, modification of redox potentials, selective photochemical reactions, etc. For example, efficient energy transfer devices have been designed and synthesized based on a rigid linear array of porphyrin units.[19] Self-assembled heterocyclic ribbons were shown to allow the directed long-range transfer of protons, thus functioning as proton-conducting channels.[20]

Beyond the molecule, supramolecular chemistry aims at developing highly complex chemical systems from components interacting by noncovalent intermolecular forces. It has been growing into a major field over a quarter of the last century and fueled numerous developments at the interface with physics and biology. New horizons are still emerging to bring this field into a more complex, informational, selective, and practical world.[21] Through appropriate manipulations of intermolecular noncovalent interactions, storage of information at the molecular level has become feasible and retrieval, transfer, and processing of the information can then be accomplished. This venture involves design and investigation of well pre-organized receptors, capable of binding to substrate with high efficiency and selectivity. Supramolecular chemistry opens new perspectives in materials science toward an area of supramolecular materials, ‘‘smart’’ materials whose features depend on molecular information. It allows the

design of materials and the control of their build-up from suitable units by self-organization. Supramolecular chemistry is gaining a lot of attention in the field of nanoscience. Indeed, the spontaneous but controlled generation of well-defined, functional supramolecular nanostructures through self-organization offers a very powerful alternative to nanofabrication and nanomanipulation, bypassing the implementation of tedious procedures and providing a chemical approach to nanoscience and technology.[22]

1.2 Fluorescent Sensors for the Detection of Chemical Warfare Agents

Since early utilization in World War I, many different types of chemical warfare agents (CWAs) have been developed in laboratories around the world. Along with biochemical and nuclear threats, these weapons have become some of the most feared and least predictable mass destruction agents on the battlefield and in the hands of terrorists. CWAs were defined by one United Nations report at 1969 as "…chemical substances, whether gaseous, liquid, or solid, which might be employed because of their direct toxic effects on man, animals, and plants…". Some common representatives of the major classes of CWAs are shown in Figure 1.4. These include vesicants (blister or mustard agents), nerve agents (such as Sarin and Soman), blood agents (e.g. hydrogen cyanide), and pulmonary agents (choking agents such as phosgene). Another class of important chemical warfare agents includes natural toxins, such as the protein Ricin and the alkaloid Saxitoxin. The nerve agents represent one of the most important and lethal classes of chemical warfare agents. Their rapid and severe effects on human and animal health stem from their ability to block the action of acetylcholinesterase (AChE), a

critical central nervous system enzyme that is responsible for the breakdown of the neurotransmitter acetylcholine.

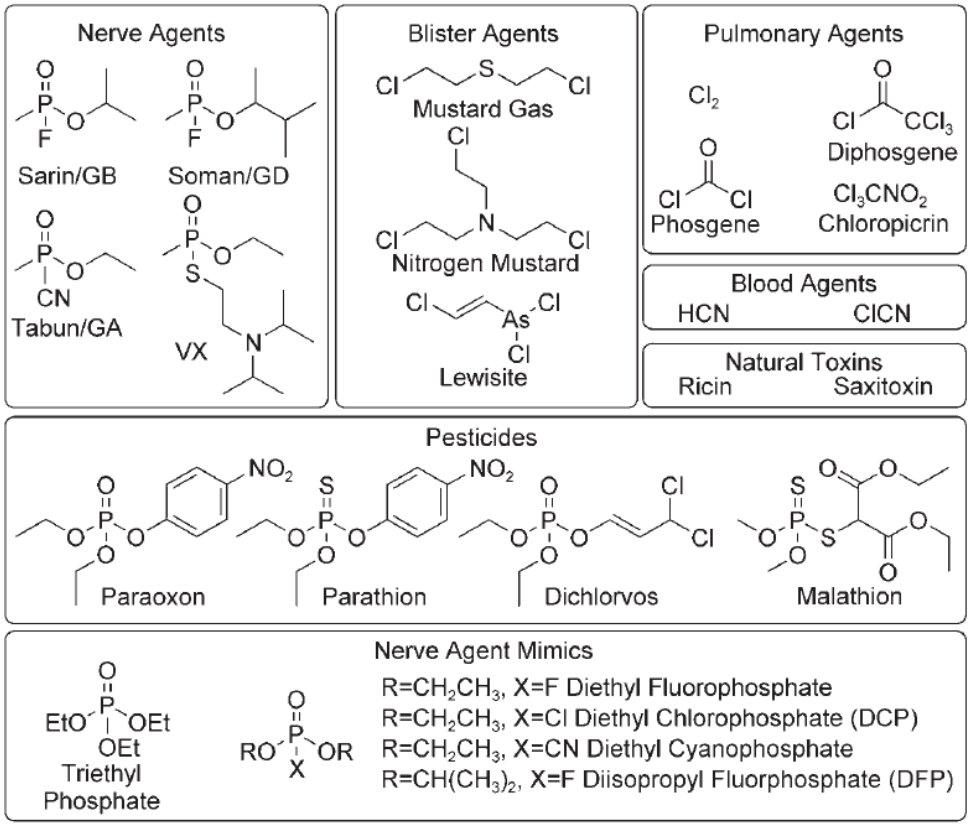


Figure 1.4 Major classes of chemical warfare agents, pesticides, and nerve agent mimics and chemical structures of common representatives.

Most of nerve agents are organophosphates (OPs) and capable of reacting with the esteratic site of the enzyme leading to a loss of enzyme function. Compared to the normal acylated intermediate complex, the phosphorylated enzyme is very stable and very slowly breaks down, leading to a loss of enzyme function.[23] This results in a build up of acetylcholine in the body, which can lead to organ failure and eventual death. The enzyme function can be restored with compounds that can dephosphorylate the enzyme

and as a consequence such compounds can be used as antidotes. Examples of such reactivating agents include oximes, such as Pralidoxime chloride.[23] OP nerve agents are generally stable, easy to disperse, and highly toxic. They can be absorbed through the skin, by ingestion, or by respiration and are generally classified into two groups, G-agents and V-agents. The G-series is older (developed in the World War II era) and encompasses compounds that are generally volatile, for example Tabun, Sarin, and Soman. The more modern V-series (developed in the 1950s) consists of nerve agents that are typically less volatile oils, such as VX. The V-agents generally degrade slower than G-agents, which along with their reduced volatility makes them more persistent. Furthermore, V-agents tend to be more toxic than representatives of the G-series (e.g. VX is about ten times more toxic than Sarin) and, as a consequence of their physicochemical properties, are primarily, although not exclusively, absorbed through the skin. Organophosphorus nerve agents were used in the Iraq–Iran war in the 1980s and as recently as 1995, in the Aum Shinrikyo terrorist attacks on the Tokyo subway system. In addition to CWAs, several organophosphorus derivatives, for example, paraoxon, parathion, dichlorvos, and malathion, have found commercial use as pesticides (Figure 1.4).[24] Their chemical structures closely resemble those of the above-discussed nerve agents, and hence, the development of detection systems for these compounds follows similar design principles.

In response to the serious threats to national and global security that result from the comparatively easy access to nerve agents, intense research efforts have been directed over the years to develop sensitive and selective schemes for the detection of

such organophosphorus derivatives.[25] Several different approaches have been used to detect organophosphorus compounds, including but not limited to: potentiometric methods,[26] colorimetric methods,[27] surface acoustic wave spectroscopy,[28] gas chromatography/mass spectrometry,[29] and interferometry.[30] One of the most convenient and simplest means of chemical detection is generating an optical event, such as a change in absorption or fluorescence intensity/color.[31]

1.2.1 Chemically Reactive Sensors

Chemically reactive sensors are compounds which alter specific properties (e.g., optical) upon reaction with an analyte of interest. The general reaction mechanism exploited by chemically reactive sensors for the detection of OP CWAs mimics the chemical framework of the AChE inhibition by CWAs, namely nucleophilic attack of the sensor molecule on the electrophilic OP analyte. Upon reaction with the OP, the reactive sensor molecules are converted into phosphate esters. This process can lead, either directly or through subsequent reactions that are enabled by the activating nature of the phosphate ester formation, to a change of the sensor molecule's fluorescence characteristics. The first fluorescent reactive chemosensors for the detection of organophosphates were reported by Pilato et al.[32] A non-emissive platinum 1,2-enedithiolate complex with an appended primary alcohol was used as the chemosensor (Figure 1.5 top). Upon exposure to an electrophilic OP analyte and an activating agent (triazole) in dichloromethane, the alcohol is converted into the phosphate ester. This intermediate then undergoes a rapid intramolecular ring-closing reaction that is accompanied by the loss of a phosphate monoanion and affords a fluorescent cyclic

product. The rate-determining step of this reaction is the nucleophilic attack of the sensor on the OP analyte. When immobilized in plasticized cellulose acetate/triethylcitrate films, chemosensors based on platinum 1,2-enedithiolate complexes were able to detect $PO(OEt)_2X$, (X = Cl, F, and CN) vapor in a nitrogen atmosphere. The fastest response time reported for such sensors was 15 s. The main limitation of this particular series of sensor molecules appears to be the fact that the fluorescence of the cyclic platinum complexes is quenched by oxygen, which, of course, stifles the use of these sensors in ambient conditions.

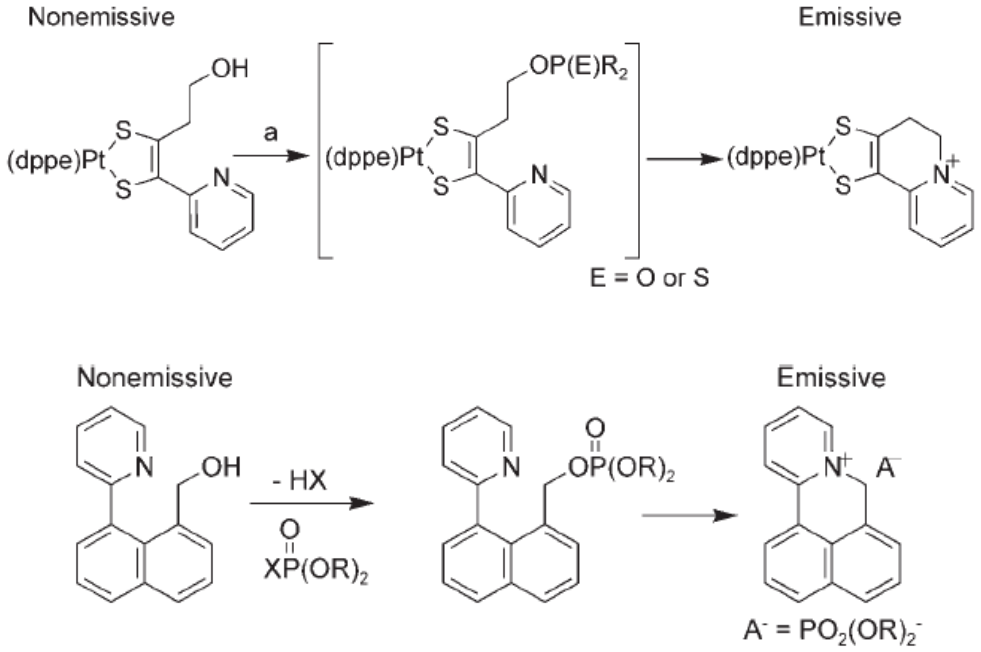


Figure 1.5 Mechanism of the chemically reactive sensor developed by Pilato and co-workers (top), and by Swager and coworkers (bottom).

Utilizing a similar concept, Swager and co-workers[33] developed an organophosphate sensor that can be used in an ambient atmosphere. In this case a

naphthalene scaffold (Figure 1.5 bottom) effectively replaces the platinum complex utilized by Pilato and co-workers. As in Pilato's system, the mechanism involves the reaction of the alcohol group of the sensor molecule with the analyte to yield a phosphate ester intermediate that is converted into a fluorescent cyclic product. The naphthylpyridyl sensor molecule studied by Swager was found to react with the analyte under pseudo-first-order kinetics in CH_2Cl_2 with an observed rate constant (k_{obs}) > 0.024 s^{-1}. Chemosensors produced by impregnating a cellulose acetate film with this sensor molecule showed a complete response to 10 ppm diisopropylfluorophosphate (DFP) vapor within five minutes.

Recently, Rebek and co-workers[34] reported a reactive chemical sensor that utilizes a similar reaction mechanism as the sensor molecules designed by Pilato and Swager. Rebek's sensor relies on the suppression of a photo-induced electron transfer (PET) process to trigger a fluorescent signal (Figure 1.6).[35] In this case, as in the previous examples, a hydroxyl group reacts with the analyte to yield a reactive intermediate which undergoes an intramolecular reaction with a tertiary amine that is part of the sensor molecule. The system is designed so that the electron pair of the unreacted tertiary amine quenches the emission of a fluorescent moiety attached to the sensor compound by way of PET. As the chemosensor is exposed to the OP analyte (diethylchlorophosphate, DCP), an intramolecular cyclization reaction occurs. In the case of the sensor molecules designed by Rebek et al., a quaternary azaadamantane ammonium salt is formed. Upon loss of the lone electron pair on the nitrogen atom, the PET is suppressed and the fluorophore (pyrene) is rendered fluorescent. A maximum

increase of the fluorescence intensity of up to 22 times of the original signal was observed upon exposure of the sensor molecules to DCP. Interestingly, minor structural variations proved to have rather significant effects; maximum "contrast" was achieved if one methylene unit was used as the spacer between the nitrogen and the fluorophore, while a butylene spacer only displayed a 1.1-fold increase in fluorescence upon exposure to DCP. The sensor complexes investigated by Rebek and co-workers were deposited on a piece of filter paper. The simple solid-state sensors thus produced displayed a practical instantaneous (5 s) fluorescence upon exposure to vapor comprising 10 ppm of DCP. This sensor system offers the distinct advantage of being useful in conjunction with many existing fluorophores.

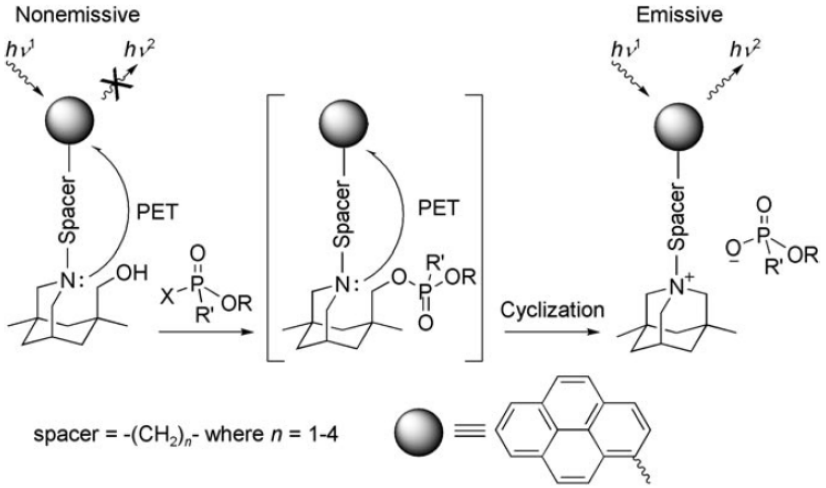


Figure 1.6 The chemically reactive sensor developed by Rebek and coworkers.

The severe threat of exposure to chemical warfare agents on both the battlefield and through terrorist attacks has lead to a recent surge in the research aimed at the detection of these highly toxic compounds. Focusing on fluorescent sensors developed

to counter the threat of nerve agents, a wide variety of approaches are being studied, many of which are also applicable to transduction schemes involving effects other than fluorescence changes, for example, changes of optical absorption, electrical conductivity, and so on. Fluorescence sensing offers a number of benefits from the perspective of detecting chemical warfare agents, such as high sensitivity, large signal changes, and even on-off responses. This is a field that is going to continue to grow over the next decade as more and more researchers commit resources to this issue.

CHAPTER 2

SUPRAMOLECULAR SENSING DEVICES FOR PHOSGENE BY FRET

2.1 Design

2.1.1. Fluorescence Resonance Energy Transfer

Förster Resonance Energy Transfer (FRET), named after the German scientist Theodor Förster, describes an energy transfer mechanism between two chromophores. A donor chromophore in its excited state can transfer energy by a nonradiative, long-range dipole-dipole coupling mechanism to an acceptor chromophore in close proximity (typically <10 nm). This energy transfer mechanism is termed "Förster resonance energy transfer" (FRET), When both molecules are fluorescent, the term "fluorescence resonance energy transfer" is often used, although the energy is not actually transferred by fluorescence.[36] Here we design phosgene sensors based on FRET.[37] It includes a selective chemical reaction between phosgene and donor and acceptor fluorophores, which bring them together, within the appropriate Förster distance (Figure 2.1). Phosgene serves here as a cross-linking agent. When the emission spectrum of the donor overlaps with the absorption spectrum of the acceptor, FRET occurs upon irradiation of the donor and strong emission of the acceptor can be detected.

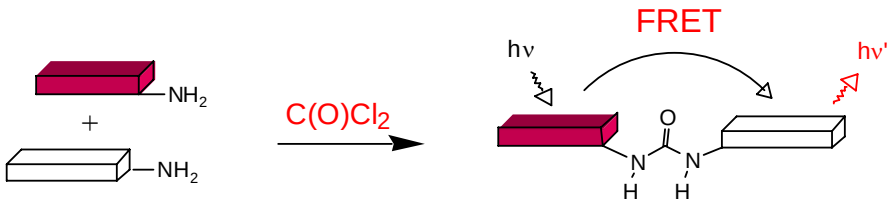
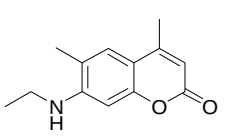


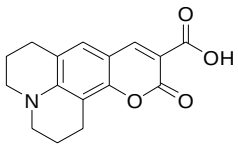
Figure 2.1 A FRET based approach to the detection of phosgene.

To realize this concept we review carefully the properties of the chromophores currently available from commercial sources. We eventually choose the laser dye coumarin 2 as the donor terminal chromophore, and coumarin 343 as the acceptor chromophore (Figure 2.2). A favorable intramolecular charge transfer takes place in the excited state of these molecules, and accounts for their high extinction coefficients and high dipole moments, which are necessary for a strong dipole − dipole interaction. This pair of chromophores meets the basic requirement for energy transfer: the donor emission band strongly overlaps the acceptor absorption band (resonance condition). In addition, the emission of coumarin 2 displays a large Stokes shift, which lowers the probability of self-quenching between the numerous peripheral chromophores. Furthermore, because of their high fluorescence quantum yields and their solubility-a decisive advantage for building multichromophoric macromolecules-these coumarins are used extensively in dye lasers and are therefore commercially available in high purity (>99%).



Coumarin 2

λ_{max} = 365 nm, λ_{em} = 435 nm



Coumarin 343

λ_{max} = 446 nm, λ_{em} = 490 nm

Figure 2.2 Structures and spectral characteristics of the donor and acceptor dyes.

2.1.2. Phosgene Sensor

Phosgene ($C(O)Cl_2$) is a highly toxic and chemically reactive gas that has been used as a chemical warfare agent.[38] It is a lung irritant and a very insidious poison, which does not irritate immediately, even when fatal concentrations are inhaled. Inhalation of phosgene causes severe lung injury, the full effects appearing several hours after exposure. Phosgene first came into battlefield during World War I, when it was used, either alone or mixed with chlorine, against troops. A renewed interest occurs in the development of phosgene sensors due to the increased threat of weapons deployment by terrorists. Sensing methods for phosgene are typically electrochemical or based on remote spectroscopic detection techniques.[39] At the same time, optical sensors for this gas are very rare.[40] This is interesting since reactive chromophores and fluorophores are now actively used for sensing other chemical agents.[33-35] Such sensors utilize a change of absorption or fluorescence upon detection and better address the needs of military and homeland security in that they are simple, fast and reliable.

2.2 Synthesis

To take advantage of this chemical property, commercially available laser

dyes[41] coumarin 2 and coumarin 343 were functionalized with primary amino groups (Figure 2.3). Coumarin 2 refluxed with methyl 4-(bromomethyl)benzoate, potassium carbonate in CH_3CN, to obtain compound **1**. **1** was hydrolyzed by tetrabutylammonium hydroxide (TBA^+OH^-) in H_2O/THF to get free carboxylic acid **2**. Coupling reaction between **2** and Boc-ethylenediamine was carried on in CH_2Cl_2 in presence of *N*-ethyl-*N*'-(3-dimethylaminopropyl)carbodiimide (EDC), 1-hydroxybenzotriazole (HOBt) and *N*-methylmorpholine (NMM), to give compound **3**. Donor amine **4** was obtained by deprotection of **3** in trifluoroacetic acid (TFA) and $CHCl_3$. Analogously, acceptor amine **6** was also obtained. Fluorescence studies showed donor amine **4** excitation wavelength λ_{ex} = 343 nm, emission wavelength λ_{em} = 425 nm. As for **6**, λ_{ex} = 435 nm, λ_{em} = 468 nm. Moreover, no strong emission was detected for acceptor amine **6** when the excitation wavelength was 343 nm (Figure 2.4). Measurements were taken in $CHCl_3$ at rt, [c] = 1×10^{-6} M.

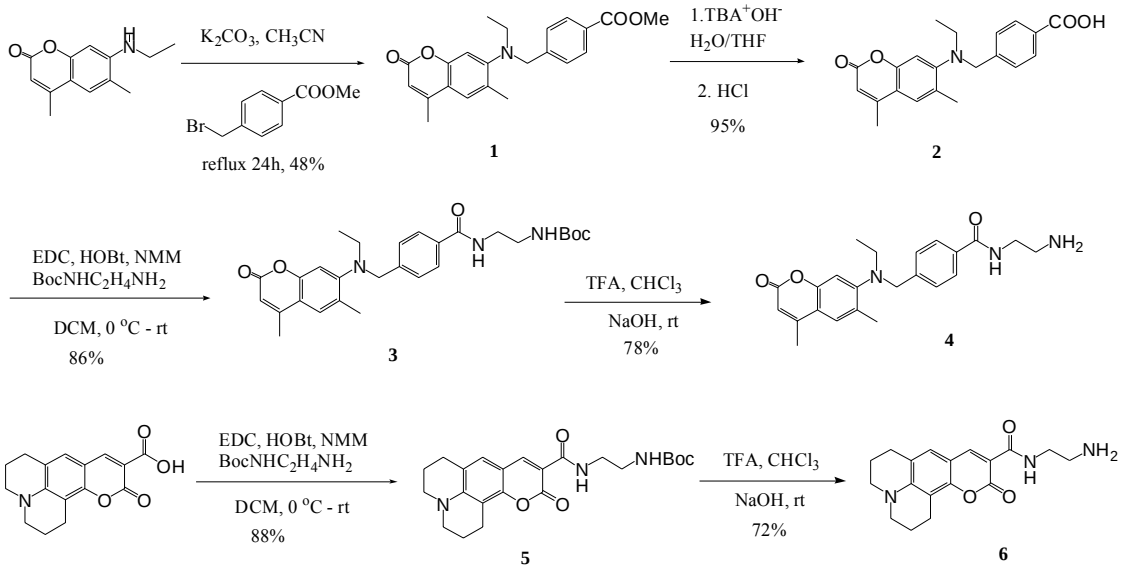


Figure 2.3 Synthesis of donor amine **4** and acceptor amine **6**.

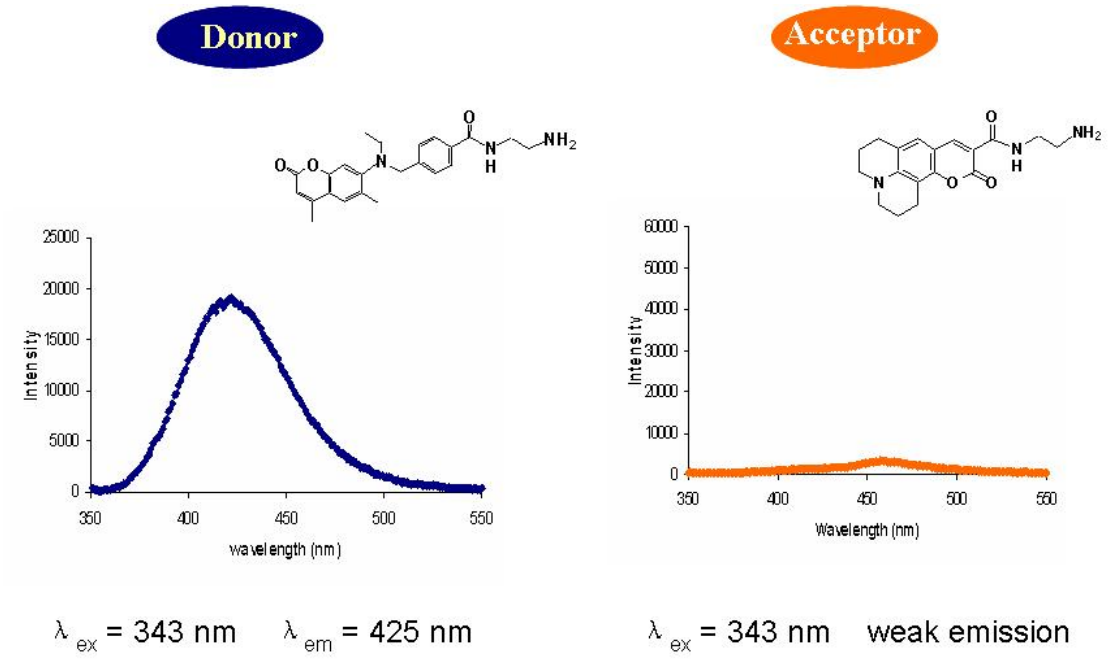


Figure 2.4 Fluorescence spectra of compound **4** and **6**.

For the laboratory synthesis of ureas, triphosgene ($CCl_3OC(O)OCCl_3$) was used as a phosgene simulant. It is less toxic and easier to handle. In organic chemistry, triphosgene has been utilized as a safe reagent for making ureas.[42] Taken separately, thus prepared coumarin derivatives **4** and **6** smoothly reacted with triphosgene at room temperature in $CHCl_3$ in the presence of triethylamine (TEA) with the formation of the corresponding ureas (Figure 2.5). In molecule **9**, Macromodel calculation shows the donor and acceptor units are covalently linked and positioned within ~20 Å of one another. Similarly to urea **9**, donor-donor urea **7** and acceptor-acceptor urea **8** were synthesized and fully characterized.

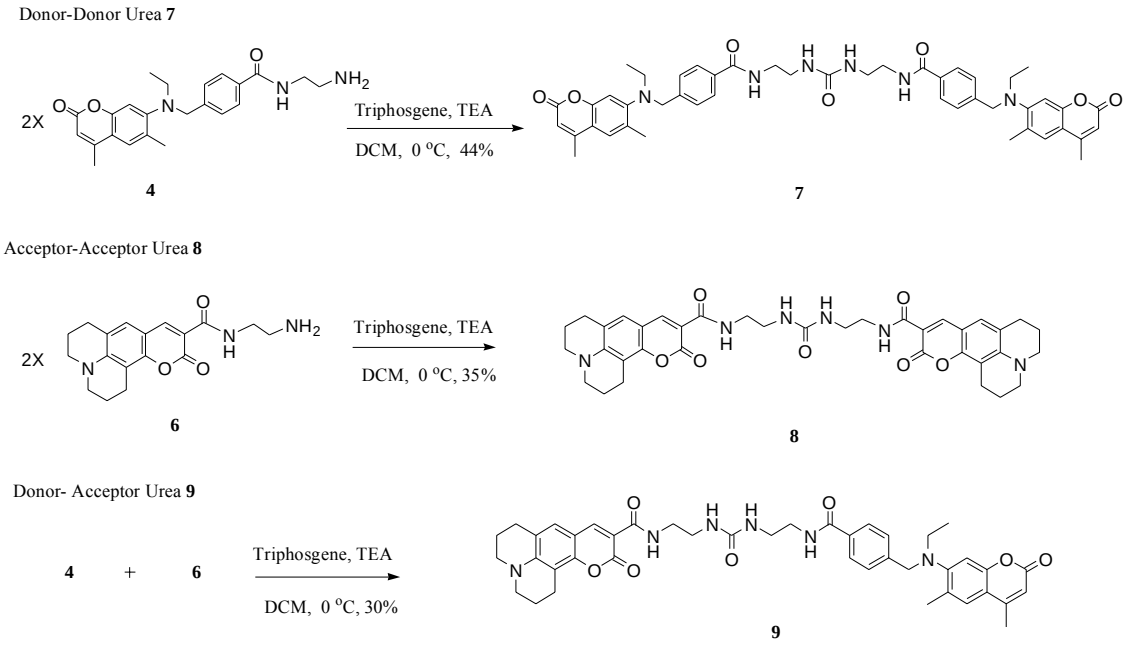


Figure 2.5 Synthesis of ureas **7**, **8**, **9**.

In the fluorescence studies of **7**-**9**, all measurements were taken in dried $CHCl_3$ at rt, [c] = 1×10^{-6} M. **7** showed a similar result as donor amine **4**, λ_{ex} = 344 nm, λ_{em} = 424 nm, as for acceptor-acceptor urea **8**, wavelengths are 435 nm and 462 nm, respectively. The absorption spectrum of **9** showed two strong bands at 343 and 438 nm which belong to the coumarin 2 and coumarin 343 units, respectively.

2.3 Titrations and Discussions

The phosgene sensing titration experiment involves the formation of urea **9** and its fluorescence. Coumarins **4** and **6** were mixed in a 1:1 ratio at the concentration range between 5 x 10^{-4} and 10^{-2} M in $CHCl_3$, TEA (~10 eq) was added and then triphosgene was introduced. Addition of TEA prevented protonation of the amino groups. Control

experiments confirmed that TEA did not affect the fluorescence. Aliquots were taken and diluted to 10^{-6} M, and the emission was recorded upon excitation at λ_{ex} = 343 nm.

For compound **9**, more important is that at low concentrations of $\leq 5\times10^{-5}$ M, the donor excitation at λ_{em} = 343 nm leads to the acceptor emission at λ_{em} = 464 nm (Figure 2.6). The shoulder around 424 nm still represents the emission of donor chromophore, but it is obviously less strong than emission at 464 nm. In a control experiment only utilizing donor amine **4** and acceptor amine **6**, no emission was detected around 460 nm upon the same conditions. This implied a FRET phenomenon in urea **9**.

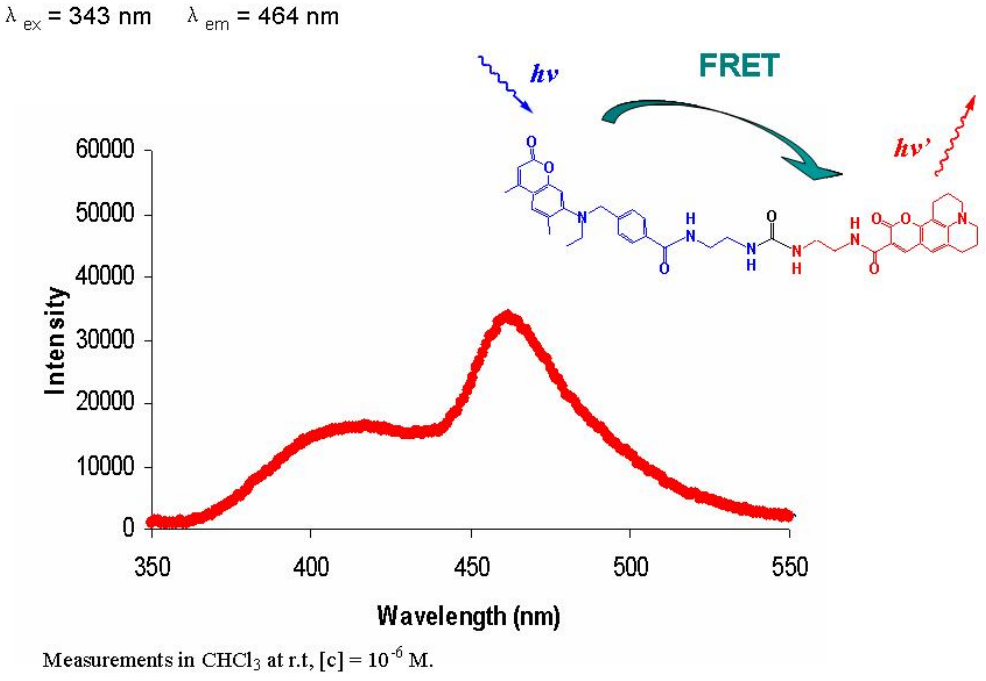


Figure 2.6 Fluorescence spectrum of compound **9**.

In the phosgene sensing titration experiment, significant fluorescence enhancement at λ_{em2} = 464 nm was detected (Figure 2.7). Coumarins **4** and **6** were

mixed in a 1:1 ratio at 10^{-3} M in $CHCl_3$, TEA (10 eq) was added and then triphosgene (0.03 to 5 eq) was introduced. Aliquots were taken and diluted to 10^{-6} M, and the emission was recorded upon excitation at 343 nm. The arrows indicate the fluorescence changes upon increasing the triphosgene concentration.

This is particularly important since the acceptor unit alone does not emit under those conditions. The fluorescence increase is obviously due to the formation of urea **9**.[43] Simultaneously, the fluorescence from the donor unit at λ_{em1} = 424 nm decreased. This is due to the quenching, indicating that efficient energy transfer took place from the donor to the acceptor. The fluorescence changes were clearly seen already upon addition of as little as ~0.1 eq of phosgene (recalculated from 0.03 eq triphosgene), which places the detection limit for this particular FRET system at ~5 x 10^{-5} M.

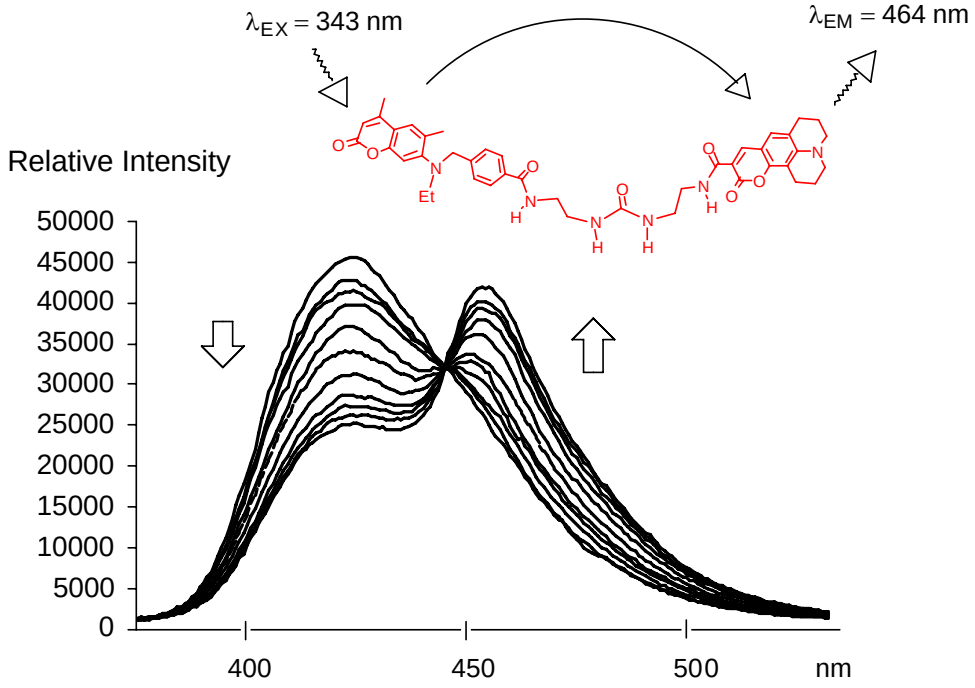


Figure 2.7 Typical changes in fluorescence emission spectra upon titrations with triphosgene.

In addition to fluorescence spectroscopy, the response of compounds **4** and **6** to triphosgene can be conveniently followed even with the naked eye (Figure 2.8). Left: coumarins **4** and **6** in $CHCl_3$ before addition of triphosgene. Right: after addition of ~5 eq of triphosgene. The experiments were performed at 10^{-3} M, and the solutions were then diluted to 10^{-6} M. Both vials are irradiated at λ = 365 nm with a laboratory UV lamp. The increased fluorescence intensity was clearly observed within seconds after the addition of triphosgene.

Figure 2.8 The "naked eye" detection of triphosgene.

It is now possible to detect phosgene utilizing a designed FRET system. This systems is selective, since no other gas can serve as a cross-linking agent.[44] This sensor design is clearly not limited to coumarins: the dyes do not react with phosgene but rather report on its presence. In principle, any other FRET acceptors and donors can be used. Further synthetic modification is also possible, to achieve more colorful responses. It would also be important to modify the system for phosgene detection at the gas-solid interface.

CHAPTER 3

CARBON DIOXIDE AND SUPRAMOLECULAR MATERIALS

3.1 Introduction to Supramolecular Chemistry of CO_2

Carbon dioxide is one of the major greenhouse gases.[45] It circulates in the environment through a variety of processes known as the *carbon cycle* (Figure 3.1). Large-scale industrial processes, volcanoes and living systems release huge quantities of CO_2 into the atmosphere. On the other hand, plants and also oceans, lakes, and rivers collect it. Although the concentration of CO_2 in the earth's atmosphere is low (~0.04% by volume), CO_2 is a very important component, because it absorbs infrared radiation and enhances the greenhouse effect. CO_2 in the atmosphere is accumulating much faster than the Earth's natural processes can absorb it. The CO_2 levels in the atmosphere have risen by more than 30% over the last 250 years and these concentrations may well double or even triple in the next century. Such extensive CO_2 circulation in the atmosphere, industry and agriculture requires not only its systematic monitoring under a variety of conditions, but more importantly, necessitates the development of improved methods of the CO_2 chemical utilization.

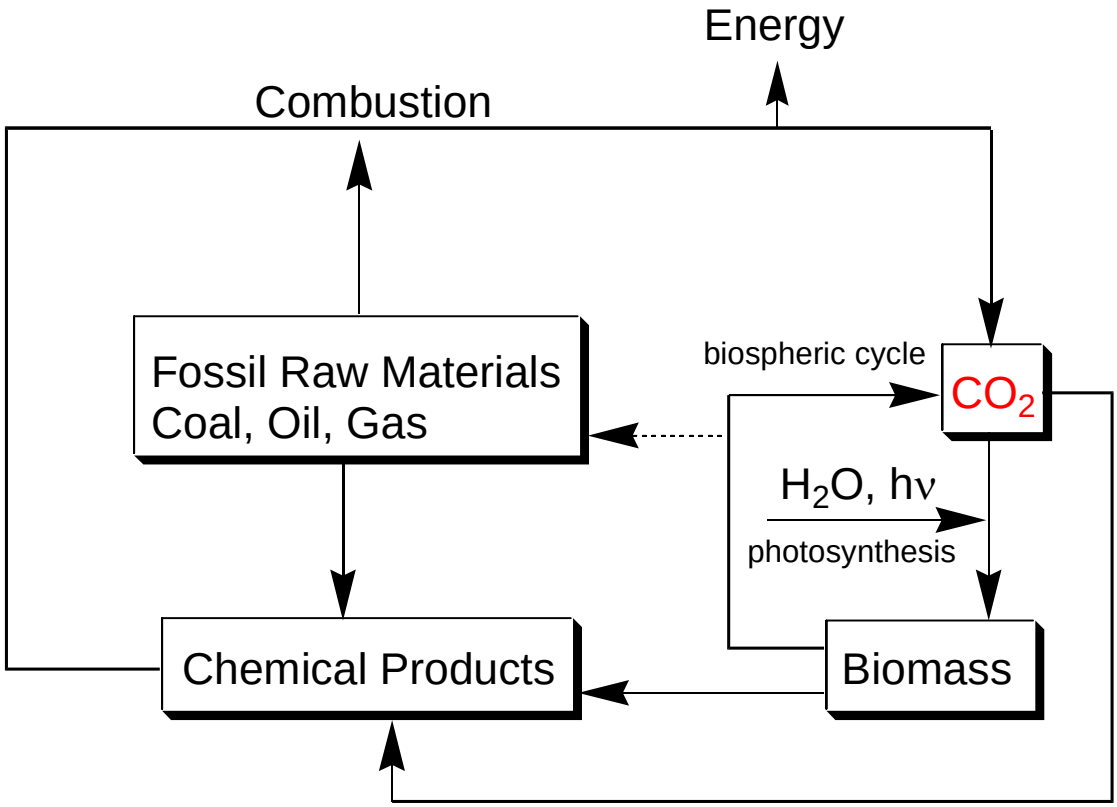


Figure 3.1 Circulation of carbon dioxide: *Carbon Cycle*.

The reactions between CO_2 and amines readily occur at ordinary temperatures and pressures to yield carbamates, presumably by way of the corresponding carbamic acids. Notably, carbamates are thermally unstable and release CO_2 upon heating (Figure 3.2).[46]

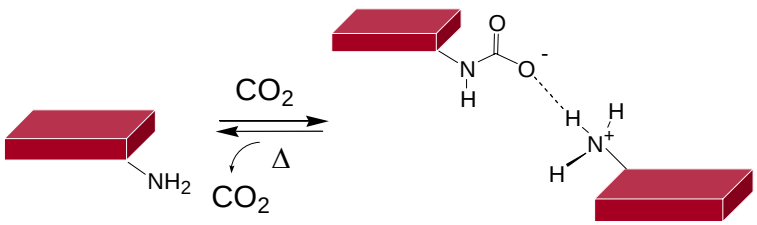


Figure 3.2 Reversible covalent chemistry between CO_2 and amines: self-assembly of molecular blocks.

Accordingly, polymer-bound amines have been employed in industry as reusable CO_2 scrubbers, removing CO_2 from industrial exhaust streams.[47] It has been demonstrated that amines containing ionic liquid also trap CO_2 (Figure 3.3).[48] Imprinted polymers have been introduced, in which a template can be attached and then removed through a carbamate linker.[49]

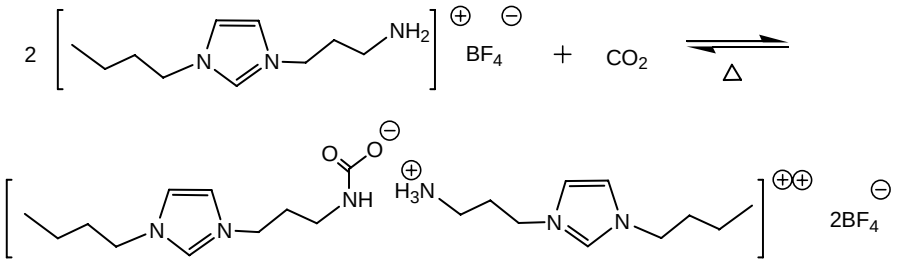


Figure 3.3 Structure of a CO_2-trapping ionic liquid.

Finally, reactions between CO_2 and immobilized amines have been employed by our laboratory for the gas sensing (Figure 3.4).[50] Specifically, 1-aminomethylpyrene readily reacts with CO_2 in polar aprotic solvent to form the corresponding carbamic acid, which exhibits at least 10 times more fluorescence emission than the amine. Here, the disruption of proton induced electron transfer quenching by resonance between the lone pair on nitrogen atom and carbonyl oxygen is responsible for the increased fluorescence.

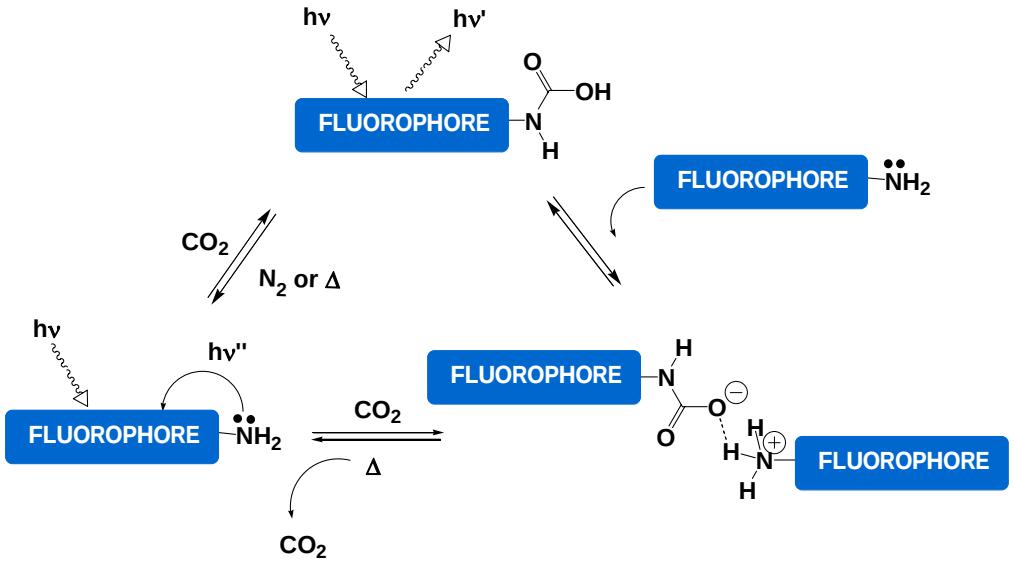


Figure 3.4 Model for fluorimetric sensing of CO_2.

Dynamic covalent chemistry (DCC) is now quickly emerging as a promising alternative to noncovalent self-assembly.[51] It simply offers an elegant opportunity to perform supramolecular chemistry with covalent bonds. One of the most important advantages here is the robustness of covalently organized structures, which on the other hand can be reversibly broken, at will. Our research has proposed, that carbamate bonds could be employed for wider variety of DCC experiments.[50]

Non-covalent self-assembly has been very well explored in the past two decades and leads to well defined nano-scale structures, such as capsules, supramolecular polymers, etc. Covalent, still reversible, assembly is only at the beginning in supramolecular chemistry. This carbamate chemistry, simply introduced from CO_2 and alkyl amines, could offer us a good opportunity to quickly assemble a variety of robust

nanostructures and "smart" materials. Furthermore, the reversible nature of carbamate bonds may lead to possibilities of switching structures and properties.

Simultaneously with us, Weiss and co-workers demonstrated that chemically reversible organogels could be prepared with CO_2 and aliphatic amines as latent gelators.[52] The organogelation process was simple and reliable. Rapid uptake of CO_2 by aliphatic amines produced the ammonium carbamate-based gel, while thermal release of CO_2 transformed the gel into the amine solutions. The gel-solution cycles can be repeated for at least 10 times without losing efficiency. Gels are viscoelastic liquid-like or viscoelastic solid-like materials. Due to their thermo-reversibility and great diversity of structures on the microscale and mesoscale, gels will attract more attention in the field of supramolecular chemistry.[53]

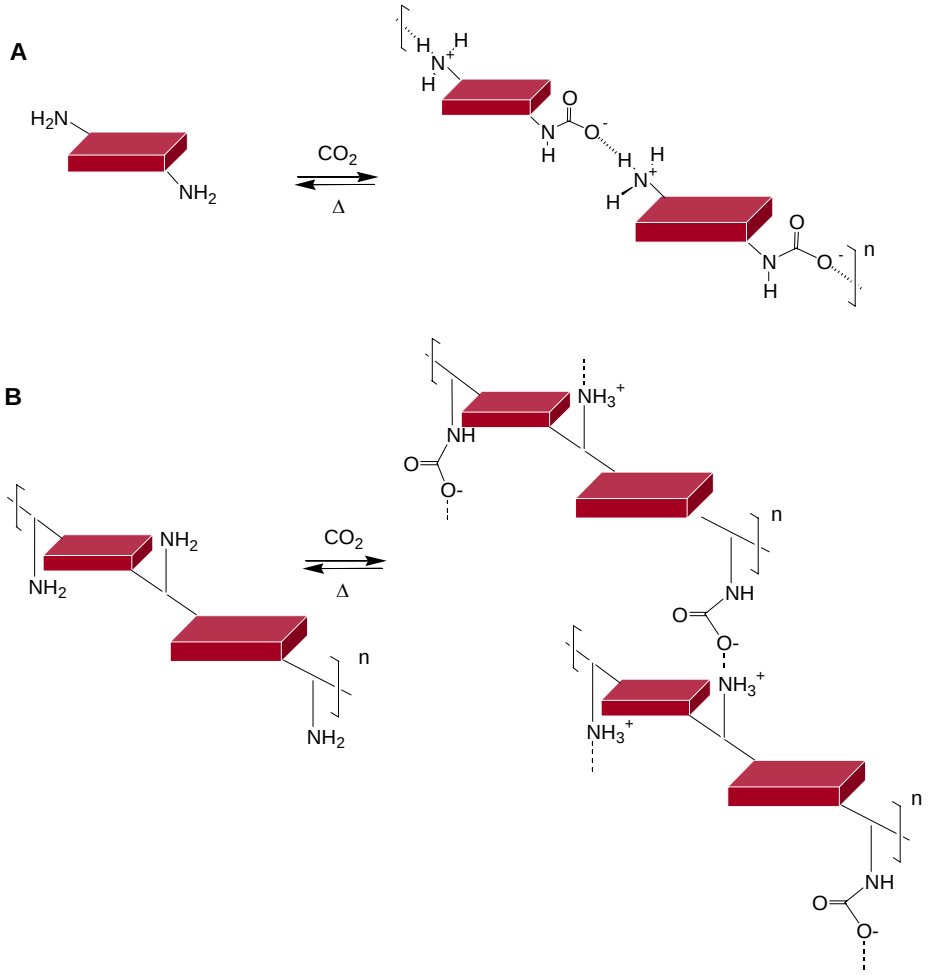


Figure 3.5 Reversible covalent chemistry between CO_2 and amines. Self-assembly of molecular blocks leads to linear (case A) and cross-linked polymers (case B).

The reactions between CO_2 and di- or even polyamines are very interesting, since they can lead to reversibly formed polymeric chains or even cross-linked 3D networks (Figure 3.5A and 3.5B). In one case, such structures have been proposed for polycarbamate $[---H_3N^+(CH_2)_{12}NHC(O)O^-{---}H_3N^+(CH_2)_{12}NHC(O)O^-{---}]_n$, which forms thermally reversible organogels. [52]

With this in mind, we employed CO_2 as a cross-linking agent to build supramolecular polymeric materials.[54-56] Supramolecular polymers represent a novel class of macromolecules, in which monomeric units are held together by reversible forces. Supramolecular polymers combine features of conventional polymers with properties resulting from the bonding reversibility. Structural parameters of supramolecular polymeric materials, in particular their two- and three-dimensional architectures, can be switched "on-off" through the main chain assembly dissociation processes. On the other hand, their strength and degree of polymerization relies on how tight the monomeric units are aggregated. In this chapter, we introduce a strategy to build supramolecular polymers for cation separation, which utilizes hydrogen bonding and takes advantage of dynamic, reversible chemistry between CO_2 and amines. These polymers are also functional. We demonstrate that macrocyclic receptor and CO_2-amine chemistry leads to switchable materials, which selectively trap, store and then release alkali metal cations. And finally using CO_2, we convert linear supramolecular polymeric chains into supramolecular, three-dimensional polymeric networks.

3.2 Separation Strategy by Using CO_2

Separation processes are central to the chemical, materials, energy, and pharmaceutical industries. Generally speaking, distillation, filtration, extraction, membrane transport process, crystallization and various chromatography are the most traditional separation techniques. Nowadays molecular recognition is becoming a new area which gets more attention. The impact of molecular receptors and molecular containers in chemistry and chemical technology has been very impressive.[57,58] A great

number of chemically, industrially and biologically significant molecules and ions have been complexed. However, most of these "host-guest" complexes exist in solution and often break or dissociate upon separation. Another severe problem is the usage of large quantities of solvents, which may very often be toxic and generate environmental problems. Polymers and materials, functionalized with molecular recognition sites, have also been prepared. In these cases, recognition/complexation events take place not in homogenic solution but at the solid-liquid or gas-solid interface, which means not effective.

Recently we described a novel separation strategy,[59] which combined selective complexation by macrocyclic receptors and CO_2-induced molecular switching,[56] leading to effective precipitation. Earlier, we established that unique materials could be prepared from CO_2 and primary amines, especially derived from amino acids.[55,56] CO_2 reacts rapidly with amine building blocks, at normal temperatures and pressures, with the formation of alkylammonium - N^+H_3 ••• $O^-C(O)NH$ - carbamate salts.[46,50,52] The carbamate formation is rapid at room temperature, and loss of CO_2 from the formed ammonium salt can be readily achieved upon gentle heating (~60 ºC) or by simply adding HCl or TFA.[60] These carbamate materials can be called supramolecular. Supramolecular polymers represent a novel class of macromolecules, in which monomeric units are held together by reversible forces.[61]

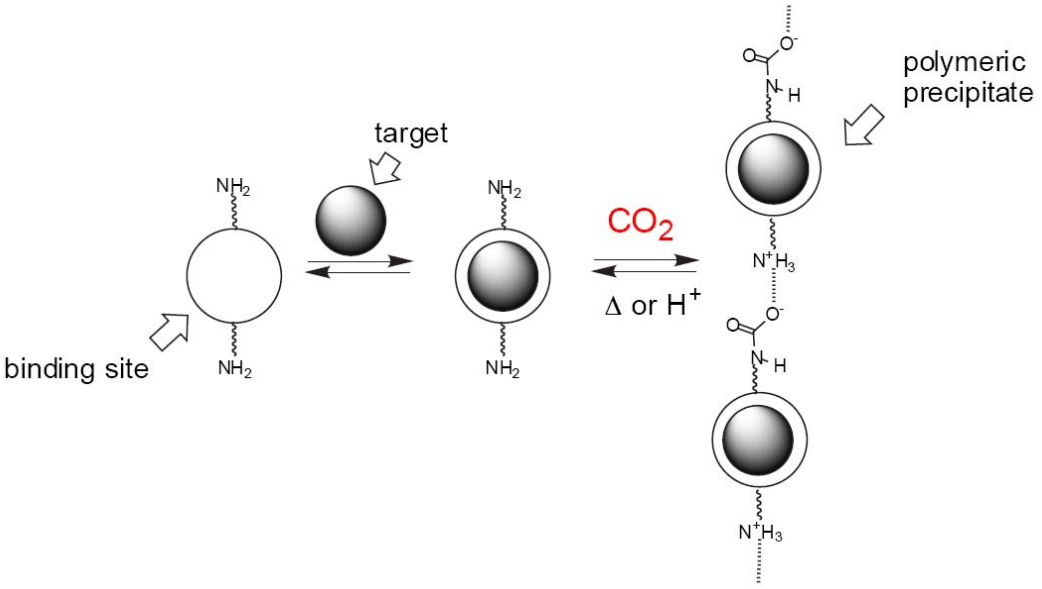


Figure 3.6 Separation strategy uses CO_2 as a cross-linking agent in the formation of supramolecular carbamate polymers.

Our separation strategy involves supramolecular polymers and is presented on Figure 3.6. Receptors can be prepared, which also possess multiple primary amino groups capable of reacting with CO_2. After complexation of target species by these receptors, CO_2 is introduced (rt, 1 atm), which reacts with the terminal amino groups of the receptors. As the result, cross-linked carbamate polymers will form and precipitate. These polymers incorporate the target complexes within their structures. The process will separate the complexed species from the bulk solution and uncomplexed species. The precipitated materials can be collected and stored. On the other hand, they can release CO_2 and dissociate back to monomers upon heating or addition of acid, and subsequently release the complexed species in their pure form.

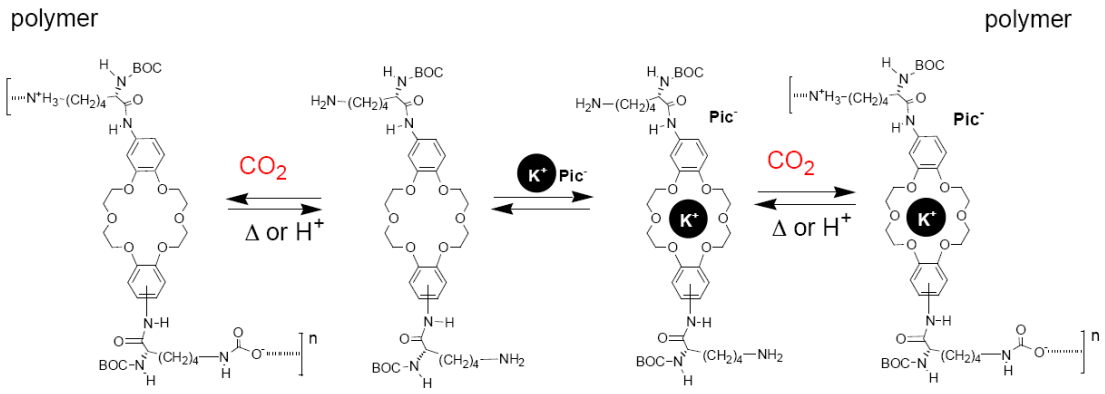


Figure 3.7 Potassium separation by dibenzo-18-crown-6 Lysine derivatives. Reaction with CO_2 leads to the formation of insoluble in $CHCl_3$ supramolecular polymeric materials **b** and **d**, which could be separated by simple filtration. Polymer **d** also separates K^+Pic^- by complexation. Polymers **b** and **d** can dissociate back to the corresponding monomers upon heating or addition of acid.

It was established already by C. J. Pedersen that potassium (K^+) cations could be selectively extracted by dibenzo-18-crown-6 ether in the presence of other cations.[62] Our research group combined the dibenzo-18-crown-6 with two *l*-lysine fragments on the periphery (Figure 3.7), since preliminary results showed recently that the free lysine ε-amino groups readily react with CO_2 in apolar solution.[54-56] Receptor **a** was then used for the extraction of potassium picrate (K^+Pic^-) from water to $CHCl_3$. Then CO_2 was introduced, which quickly reacted with the lysine ε-amino groups and cross-linked complex **c** into insoluble polymeric carbamate **d**.

This strategy is unique in all respects. It involves structural switching, which works together with complexation. The architecture and recognition properties of the separating materials can be programmed through synthesis at the stage of their monomers. In contrast to known separating polymers and materials, which impose

significant phase-transfer restrictions on complexation, the proposed receptors complex guests in solution, as monomers, and only polymerize upon reaction with CO_2. Due to effective precipitation, large quantities of solvent can be recovered and reused. The storage is accomplished without the use of solvent, which is economically preferred. For the first time CO_2 gas can be used as a building block for separating materials. Considering the huge significance of CO_2 in industry and environment, the strategy offers means for creating environmentally responsive processes for separation.

CHAPTER 4

SEPARATION OF SODIUM BY CALIXARENE AND CARBON DIOXIDE

4.1 Design

Preliminary results from our lab showed switchable, supramolecular polymers could be prepared by CO_2.[56] More recently, we found that such polymers can be employed for metal ion separation.[59] Separation of ions through molecular recognition typically involves extraction. Macrocyclic receptors have been synthesized that selectively complex metal salts and solubilize them in organic solvents. Polymer-supported macrocyclic receptors have also been introduced. One significant problem here is the handling and storage of large quantities of organic solvents that are often expensive and/or environmentally toxic. This is particularly important for storage of toxic metal wastes in solution after the extraction. On the other hand, when polymers with appended receptors are used, the complexation takes place not in homogeneous solution but at the solid-liquid interface, which is often not effective. We are developing an approach, which eliminates these problems. It combines solution complexation/extraction by macrocyclic receptors and subsequent CO_2-induced precipitation of the complexes (Figure 4.1).[59]

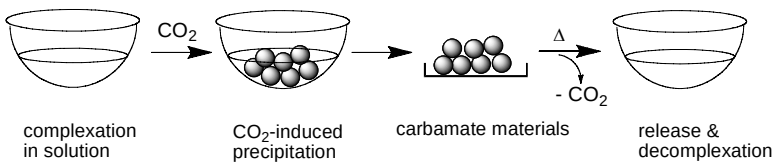


Figure 4.1 Separation strategy using CO_2.

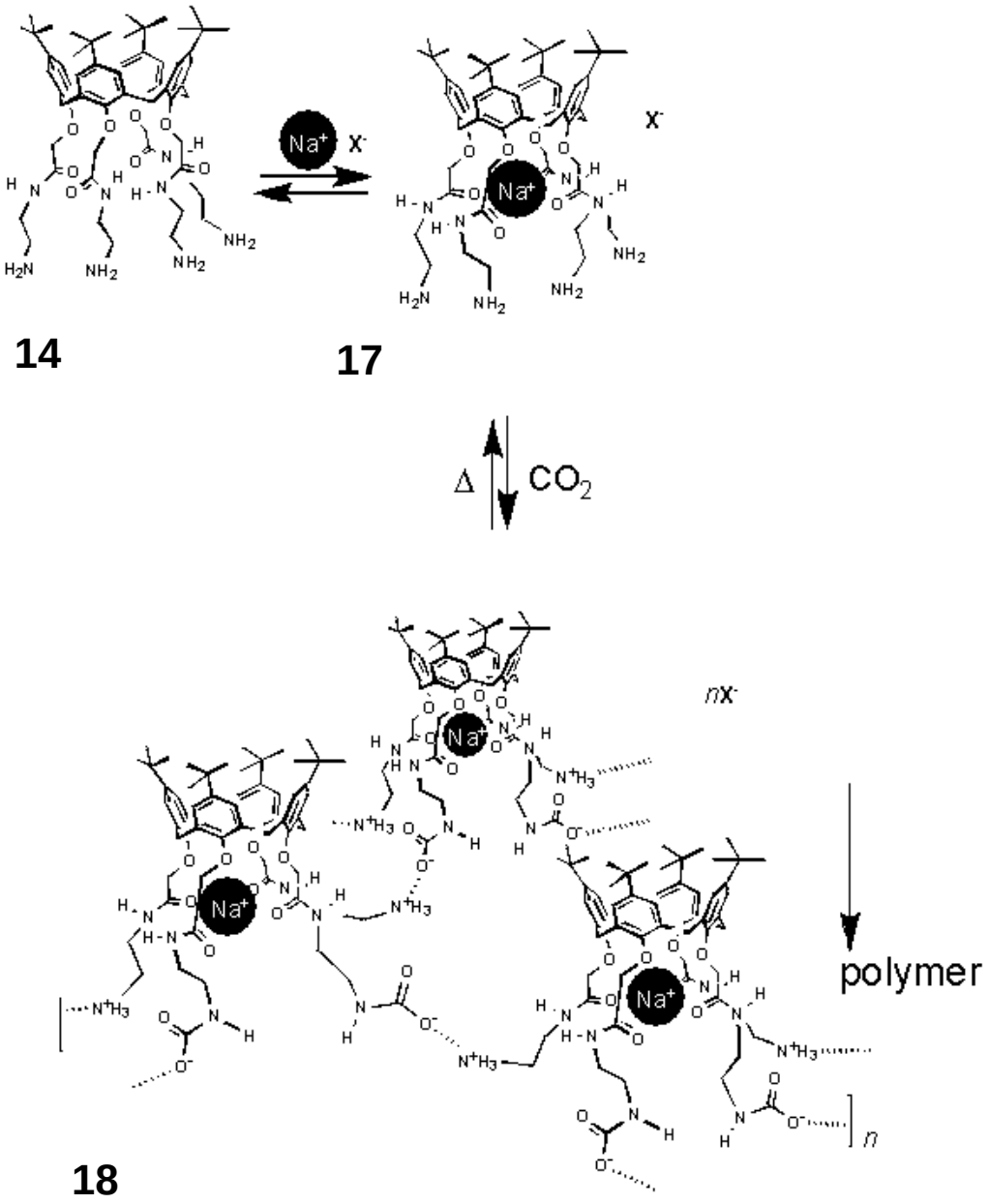


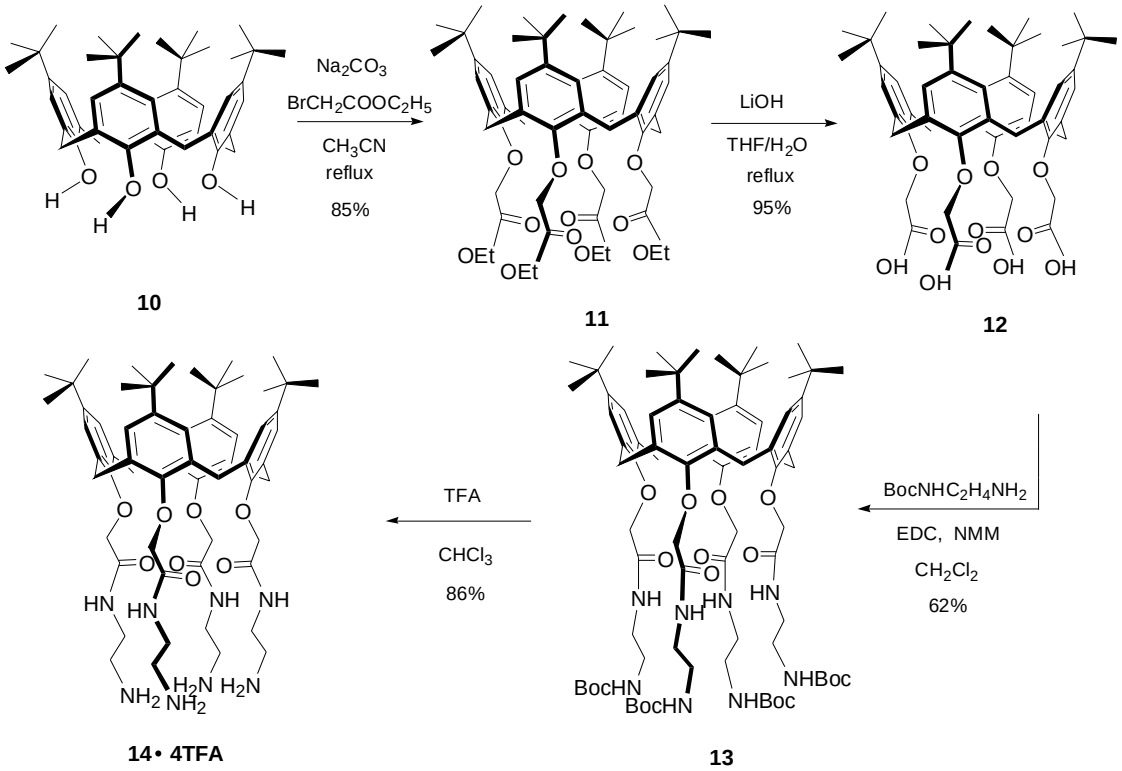
Figure 4.2 Separation of Na^+ involves calix[4]arene receptor **14** and CO_2.

There is a significant interest in Na^+ separation in industry, including nuclear waste treatments and desalination of seawater, and therefore we demonstrate selective separation of Na^+ salts using CO_2 and calix[4]arene based receptors.

Calix[4]arene **14** has four $CH_2C(O)NH$ amide groups at the lower rim (Figure 4.2). The carbonyl oxygen atoms and four ether oxygens provide eight preorganized coordination sites for binding Na^+. According to the literature, such structural arrangement offers a very high affinity towards sodium cation; the binding constants over 10^5 M^{-1} and selectivities levels of $Na^+/K^+ > 10^4$ have been documented.[63] Receptor **14** also possesses four primary amino groups on the periphery that are capable of reacting with CO_2 to form cross-linked ammonium carbamates.[46a]

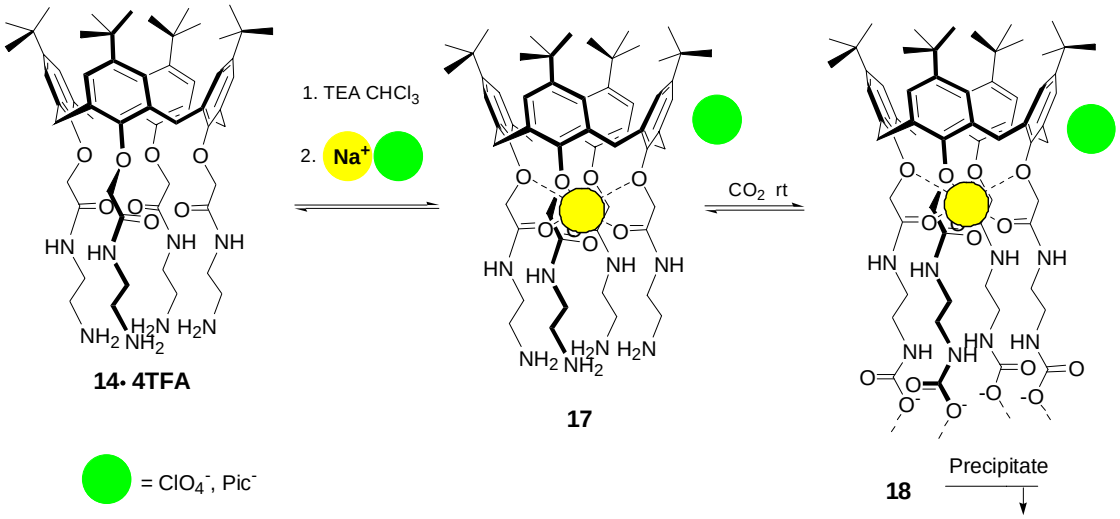
4.2 Synthesis and Extractions

Parent tetrahydroxycalix[4]arene **10** was prepared according to the published procedures.[64] Then it was functionalized to introduce the four ester group as Na^+ binding sites and primary amino groups as sites to be linked with CO_2 (Figure 4.3). Compound **11** was prepared by refluxing tetrahydroxycalix[4]arene with ethyl bromoacetate and sodium carbonate in dried CH_3CN. Calix[4]arene tetraacid **12** was obtained by LiOH hydrolysis in H_2O/THF. Boc protected tetraamide **13** was prepared by coupling reaction with *N*-ethyl-*N*'-(3-dimethylaminopropyl)carbodiimide (EDC), boc-ethylenediamine, and *N*-methylmorpholine (NMM). After deprotection by trifluoroacetic acid (TFA), calix[4]arene tetraamine module **14** was ready for extraction and separation. CO_2 was introducted to DMSO-d_6 and $CDCl_3$ solutions in the presence of triethylamine (TEA), carlix[4]arene tetramine carbamic acid **15** and carbamate **16** were obtained respectively.



Figiure 4.3 Synthesis of calix[4]arene derivatives for sodium separation.

The general procedure for extraction of alkali-metal perchlorates ($M^+ClO_4^-$) and picrates (M^+Pic^-) by calixarene **14** (Figure 4.4)was as follows, Compound **14** was stirred with alkali-metal perchlorate in $CHCl_3$ in the presence of TEA overnight and the solution was separated. CO_2 (or $^{13}CO_2$) was then introduced and the precipitate was collected and dried. The ^{13}C NMR spectrum of calixarene-Na^+ carbamate polymer **18** was measured with $^{13}CO_2$ gas.



Figiure 4.4 Extraction, entrapment and separation of sodium ions.

4.3 Results and Discussions

We found that receptor **14** selectively extracts Na^+ salts *vs* K^+ and Cs^+ and complex **17** can subsequently be precipitated upon reacting with CO_2 (Figure 4.2). In detail, the TFA salt of calixarene **14** was dissolved in $CHCl_3$ in the presence of triethylamine (TEA) (~15 eq) and, as expected, quantitatively extracted $Na^+ClO_4^-$ from the solid phase. Complex **17** was characterized by ^1H NMR spectroscopy in DMSO-d_6, showing significant changes compared to free receptor **14** (Figure 4.5). For example, the aromatic protons shifted from 6.83 in free **14** to 7.12 ppm in **17**, which is attributed to the electron-withdrawing nature of Na^+. The CH_2 protons of the methylene bridges between the aromatic rings shifted from 4.52 and 3.22 in **14** to 4.34 and 3.34 ppm in **17**, respectively. This phenomenon is known and caused by fixation of Na^+ cation at the lower rim.[65] Under the same conditions, no extraction of $K^+ClO_4^-$ and $Cs^+ClO_4^-$ was observed; no

changes in the ^{1}H NMR spectra were detected. Similar selectivity was also observed for $Na^{+}Pic^{-}$ over $K^{+}Pic^{-}$ and $Cs^{+}Pic^{-}$.

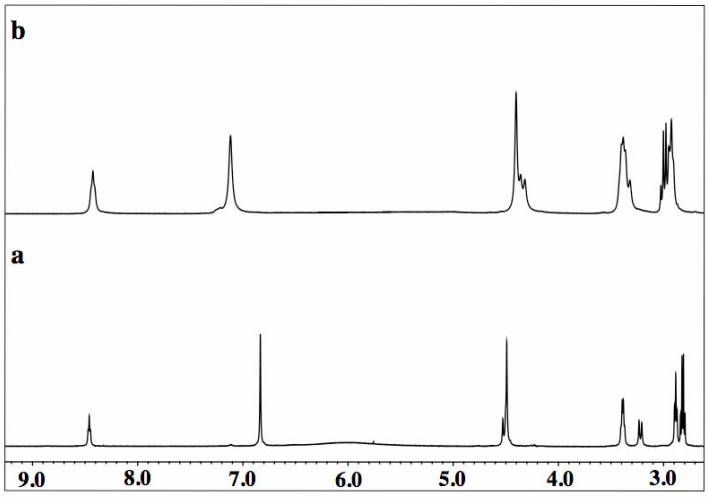


Figure 4.5 Portions of the ^{1}H NMR spectra (500 MHz, rt, DMSO-d_6) of: a) receptor **14**; b) Na^{+}-complex **17**. The residual Et_3N quartet is at ~2.8 ppm.

After the extraction, the solution was separated and CO_2 gas was introduced (rt, 1 atm). A fine white precipitate quickly formed (Figure 4.6), which was identified as cross-linked carbamate polymer **18**. The right tube: Na^{+}-complex **17** in $CHCl_3$ after the extraction. The left tube: same solution after bubbling CO_2. While the ^{1}H NMR spectrum was broad, ^{13}C NMR spectroscopy provided an unambiguous proof of the carbamate formation. Specifically, when ^{13}C-labeled CO_2 was used, a strong carbamate *C*=O signal at ~160 ppm was clearly seen (in DMSO-d_6). In additional experiments, metal-free receptor **14** also reacted with CO_2 both in $CHCl_3$ and DMSO, forming the corresponding carbamate precipitate and carbamic acid, respectively. For example, when CO_2 was bubbled through the DMSO-d_6 solution of **14**, the carbamic CH_2NHC(O) methylene and

NH signals were detected at 3.03 and 6.68 ppm in the ^{1}H NMR spectrum, respectively. In the COSY spectrum, a cross-peak between these two signals was observed. These data agree well with the published spectra for alkylammonium carbamates.[50, 52a]

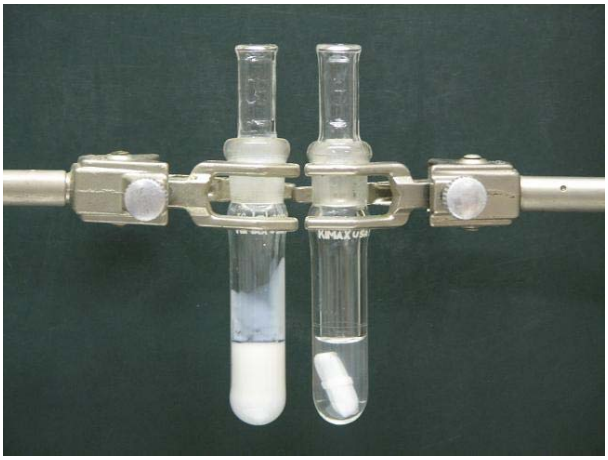


Figure 4.6 The formation of polymeric carbamate using CO_2.

More inportant, polymer **18** incorporates the Na^+ cations. Control experiments, involving the use of $KClO_4$ and $CsClO_4$, revealed no entrapment of these cations. The process thus separates the complexed species from the bulk solution. Considering that neither K^+ nor Cs^+ were complexed under the described conditions, this approach offers a selective Na^+ separation. Precipitate **18** was collected and stored for several weeks. On the other hand, it released CO_2 and dissociated back to the monomers simply upon heating and flushing with nitrogen (40-50 ºC). The Na^+ can subsequently be released in the pure form simply upon washing with water.

It is possible to selectively separate Na^+-salts through binding in solution and subsequent precipitation with CO_2. The Na^+-storage can now be accomplished without solvent, which is economically preferred and prevents environmentally dangerous

leaching. Combined with the increasing role of CO_2 in separations[66] and green chemistry,[67] our approach offers means for creating environmentally responsive processes.

CHAPTER 5

EXPERIMENTAL SECTION

5.1 General Information

Melting points were determined on a Mel-Temp apparatus (Laboratory Devices, Inc.) and are uncorrected. ^{1}H, ^{13}C NMR, COSY and HMBC NMR spectra were recorded at 295 ± 1 ^{o}C on JEOL 300 and 500 MHz spectrometers. Chemical shifts were measured relative to residual non-deuterated solvent resonances. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer. UV-vis spectra were measured on a Varian Cary-50 spectrophotometer. Fluorescence spectra were recorded on a JOBIN YVON FluoroMax-3 spectrofluorometer. Mass spectra were recorded at the Scripps Center for Mass Spectrometry (La Jolla, CA). High Resolution MALDI FT mass spectra were obtained on an IonSpec Ultima FTMS. MALDI TOF mass spectra were obtained on an Applied Biosytems Voyager STR (2). Elemental analysis was performed on a Perkin-Elmer 2400 CHN analyzer.

All experiments with moisture- and/or air-sensitive compounds were run under a dried nitrogen atmosphere. For column chromatography, Silica Gel 60 Å (Sorbent Technologies, Inc.; 200–425 mesh) was used. Parent tetrahydroxycalix[4]arene **10**[64] was prepared according to the published procedures. Calixarenes **11**[68] and **12**[69] were

prepared by known protocols, and their data matched literatures. Molecular modeling was performed using commercial MacroModel 7.1.

5.2 Synthesis and Characterizations

Methyl 4-[[(4,6-dimethyl-2-oxo-2H-1-benzopyran-7-yl)ethylamino]methyl] benzoate (1)

This compound was prepared according to a modification of the literature procedure.[41c] Coumarin 2 (217 mg, 1.0 mmol), methyl 4-(bromomethyl)benzoate (275 mg, 1.2 mmol) and potassium carbonate (690 mg, 5.0 mmol) were mixed in distilled acetonitrile (30 mL) and refluxed under nitrogen for 72 hours. The solvent was evaporated and the residue was subject to column chromatography (CH_2Cl_2/CH_3OH 50:1) to give **1** as slightly yellow power (175 mg, 48%), mp 92-93 ^oC. ^1H NMR (DMSO-d_6, 500 MHz): δ 7.87 (d, J = 8 Hz, 2H), 7.54 (s, 1H), 7.46 (d, J = 8 Hz, 2H), 7.01 (s, 1H), 6.18 (s, 1H), 4.36 (s, 2H), 3.81 (s, 3H), 3.07 (q, J = 7 Hz, 2H), 2.37 (s, 3H), 2.36 (s, 3H), 1.05 (t, J = 7 Hz, 3H). ^{13}C NMR (DMSO-d_6, 500 MHz): δ 170.0, 161.6, 153.4, 152.7, 152.4, 143.7, 129.9, 129.8, 129.6, 128.1, 126.7, 126.5, 115.1, 112.8, 109.4, 64.6, 56.4, 52.1, 47.0, 18.7, 18.6, 11.9. Elemental analysis: $C_{22}H_{25}NO_4$, calcd. C, 71.91; H, 6.86; N, 3.81; O, 17.42; found C, 71.81; H, 6.90; N, 3.78; O, 17.51.

4-[[(4,6-Dimethyl-2-oxo-2H-1-benzopyran-7-yl)ethylamino]methyl]benzoic acid (2). Compound **1** (175 mg, 0.48 mmol), and tetrabutylammonium hydroxide (40% w/w 0.78 mL, 1.2 mmol) were added to a solution of THF (5 mL) and water (5 mL), stirred 2 hours and treated with hydrochloric acid (1 M) until weakly acidic. The precipitate was

filtrated and washed with water (3 × 20 mL). White powder (160 mg, >95%) was obtained after drying, mp 203-204 ^{o}C. UV-vis spectrum showed the maximum absorption is 342 nm, which matched the literature.[41c] ^{1}H NMR (DMSO-d_6, 500 MHz): δ 7.85 (d, J = 8 Hz, 2H), 7.54 (s, 1H), 7.43 (d, J = 7 Hz, 2H), 7.01 (s, 1H), 6.18 (s, 1H), 4.35 (s, 2H), 3.08 (q, J = 7 Hz, 2H), 2.38 (s, 3H), 2.37 (s, 3H), 1.05 (t, J = 7 Hz, 3H). ^{13}C NMR (DMSO-d_6, 500 MHz): δ 167.7, 160.8, 153.6, 152.6, 144.4, 130.1, 129.9, 129.6, 128.6, 127.6, 114.8, 112.4, 109.1, 55.3, 47.6, 18.8, 18.5, 12.4.

_N_-[2-[(1,1-dimethylethoxy)-formylamido]ethyl]-4-[[(4,6-dimethyl-2-oxo-2H-1-benzopyran-7-yl)ethylamino]methyl]benzamide (3)

N-Boc ethylenediamine (0.126 mL, 0.8 mmol), compound **2** 140 mg, 0.4 mmol) were mixed with EDC•HCl (153 mg, 0.8 mmol), HOBt (108 mg, 0.8 mmol) and NMM (0.1 mL) in dry CH_2Cl_2 (25 mL) and stirred at 0 ºC overnight. The solution was evaporated to dryness. The solid was dissolved in CH_2Cl_2 (50 mL) and washed with 5% aqueous HCl (50 mL). The organic layer was separated, washed with water (3×50 mL), and evaporated. Column chromatography (CH_2Cl_2/CH_3OH, 50:1) afforded the product as yellow powder. Yield 169 mg (86%), mp 86–87 ^{o}C. ^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.40-8.30 (br. s, 1H), 7.73 (d, J = 7 Hz, 2H), 7.52 (s, 1H), 7.38 (d, J = 7 Hz, 2H), 6.98 (s, 1H), 6.90-6.82 (br. s, 1H), 6.17 (s, 1H), 4.32 (s, 2H), 3.25 (q, J = 6 Hz, 2H), 3.15-3.00 (m, 4H), 2.37 (s, 3H), 2.36 (s, 3H), 1.05 (m, 3H). ^{13}C NMR (DMSO-d_6, 500 MHz) δ 166.7, 160.8, 156.3, 153.7, 153.6, 152.6, 142.4, 133.8, 129.6, 128.3, 127.8, 127.6, 114.7,

112.3, 109.2, 78.2, 55.5, 55.1, 47.7, 28.8, 18.8, 18.6, 12.4. ESI-TOF high-res. MS: calcd. for [MH^+] $C_{28}H_{38}N_3O_5$ 496.2810, found 496.2816.

_N_-(2-aminoethyl)-4-[[(4,6-dimethyl-2-oxo-2H-1-benzopyran-7-yl)ethylamino]methyl]benzamide (4)

Compound **3** (148 mg, 0.3 mmol) and trifluoroacetic acid (5 mL, 0.067 mol) were dissolved in dry CH_2Cl_2 (10 mL) and stirred overnight. The solvent was evaporated and the residue was washed with 5% aqueous NaOH (25 mL) and water (3 × 25 mL). The organic layer was dried by Na_2SO_4 and evaporated to obtain yellowish powder (92 mg, 78%), mp 97-98 ^oC. ^1H NMR (DMSO-d_6, 300 MHz): δ 8.27 (t, J = 6 Hz, 1H), 7.71 (d, J = 8 Hz, 2H), 7.50 (s, 1H), 7.35 (d, J = 8 Hz, 2H), 6.96 (s, 1H), 6.14 (s, 1H), 4.30 (s, 2H), 3.31-3.15 (m, 2H), 3.04 (q, J = 7 Hz, 2H), 2.60 (t, J = 6 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 1.02 (t, J = 7 Hz, 3H). ^{13}C NMR (DMSO-d_6, 500 MHz): δ 166.8, 160.8, 153.7, 152.6, 142.3, 134.0, 129.6, 128.3, 127.8, 127.6, 114.7, 112.3, 109.1, 55.5, 55.1, 47.6, 43.5, 41.8, 18.8, 18.6, 12.4. IR (KBr, cm^{-1}): ν 3361, 2928, 2869, 1718, 1612, 1540, 1502, 1390, 1350, 1268, 1158, 1060. ESI-TOF high-res. MS, [MH^+] calcd for $C_{23}H_{28}N_3O_3$ 394.2125, found 394.2130. Fluorescence: λ_{ex} = 343 nm, λ_{em} = 422 nm in $CHCl_3$, [c] = 1 × 10^{-6} M.

{2-[4-[[(4,6-dimethyl-2-oxo-2H-1-benzopyran-7-yl)ethylamino]methyl]benzoylamido]ethyl}carbamic acid (4a)

CO_2 was introduced to the NMR sample of compound **4** for 5 mins. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.39 (t, J = 5 Hz, 1H), 7.73 (d, J = 8 Hz, 2H), 7.52 (s, 1H), 7.38 (d, J = 8 Hz, 2H), 6.98 (s, 1H), 6.79 (t, J = 6 Hz, 1H), 6.16 (s, 1H), 4.32 (s, 2H), 3.29-3.25 (q, J = 6 Hz, 2H), 3.10-3.04 (m, 4H), 2.37 (s, 3H), 2.35 (s, 3H), 1.05 (t, J = 7 Hz, 3H). ^{13}C NMR (DMSO-d_6, 500 MHz): δ 166.7, 160.8, 157.8, 153.8, 153.7, 153.6, 152.5, 142.4, 133.7, 129.5, 128.3, 127.7, 127.6, 124.7 (CO$_2$), 114.7, 112.3, 109.0, 55.0, 47.6, 18.8, 18.5, 12.4.

***N*-[2-(1,1-dimethylethoxy-formylamido)ethyl]-2,3,6,7-tetrahydro-11-oxo-1H,5H,11H-[]benzopyrano[6,7,8-ij]quinolizine-10-carboxamide (5)**

Similarly to compound **3**, bright yellow *N*-boc acceptor amine **5** was also synthesized. Compound **5**: mp 220 ^{o}C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.72 (t, J = 6 Hz, 1H), 8.47 (s, 1H), 7.20 (s, 1H), 6.91 (t, J = 5 Hz, 1H), 3.36-3.30 (m, 6H), 3.08 (q, J = 6 Hz, 2H), 2.72-2.68 (m, 4H), 1.89-1.84 (m, 4H), 1.37 (s, 9H). ^{13}C NMR (DMSO-d_6, 500 MHz): δ 163.3, 162.2, 156.3, 152.6, 148.5, 148.0, 127.6, 119.9, 108.4, 107.8, 105.1, 78.2, 50.1, 49.5, 28.7, 27.3, 21.0, 20.1.

***N*-(2-aminoethyl)-2,3,6,7-tetrahydro-11-oxo-1H,5H,11H-[1]benzopyrano[6,7,8-ij]quinolizine-10-carboxamide (6)**

Similarly to compound **4**, brown acceptor amine **5** was also synthesized. mp > 300 ^{o}C (dec.). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.05 (t, J = 6 Hz, 1H), 8.52 (s, 1H), 6.96 (s, 1H), 3.59-3.52 (m, 2H), 3.34-3.27 (m, 4H), 3.02 (t, J = 5 Hz, 2H), 2.89-2.79 (m, 2H), 2.78-

2.71 (m, 2H), 2.02-1.88 (m, 4H). ^{13}C NMR ($CDCl_3$, 500 MHz: δ 164.5, 163.1, 152.8, 148.3, 148.2, 127.2, 119.7, 108.8, 108.3, 105.7, 50.3, 49.9, 41.8, 41.7, 27.5, 21.2, 20.3, 20.2. IR (KBr, cm^{-1}) ν 3320, 2938, 2854, 1692, 1616, 1517, 1367, 1309, 1212, 1174. ESI-TOF high-res. MS, [MH^+] calcd. for $C_{18}H_{22}N_3O_3$: 328.1656, found 328.1653. Fluorescence: λ_{ex} = 435 nm, λ_{em} = 462 nm in $CHCl_3$, [c] = 1×10^{-6} M.

{2-[2,3,6,7-Tetrahydro-11-oxo-1H,5H,11H-[1]benzopyrano[6,7,8-ij]quinolizine-10-formylamido]ethyl}carbamic acid (6a)

CO_2 was introduced to the NMR sample of compound **6** for 5 mins. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.73 (t, J = 6 Hz, 1H), 8.52 (s, 1H), 7.26 (s, 1H), 6.80 (t, J = 5 Hz, 1H), 3.11-3.07 (q, J = 6 Hz, 2H), 2.76-2.70 (m, 4H), 1.92-1.85 (m, 4H). ^{13}C NMR (DMSO-d_6, 500 MHz): δ 163.3, 162.3, 157.8, 152.6, 148.5, 148.0, 127.6, 127.4 (CO_2), 119.9, 108.3, 107.8, 105.1, 50.1, 49.5, 27.3, 21.0, 20.1.

1,3-Bis{2-[4-[[(4,6-dimethyl-2-oxo-2H-1-benzopyran-7-yl)ethylamino]methyl]benzoylamido]-ethyl}urea (7).

To a dried CH_2Cl_2 (10 mL) solution of coumarin **4** (40 mg, 0.1 mmol) and dried TEA (0.1 mL), triphosgene (9.89 mg, 0.033 mmol) were added. The mixture was stirred at 0 ^{o}C for 30 min after another equivalent of coumarin **4** was added in CH_2Cl_2 (5 mL). The reaction mixture was stirred for an hour, the solvent was removed in vacuo, and the residue was applied to column chromatography, (CH_2Cl_2/MeOH, 20:1) to give product **7** as a pale yellow powder. Yield 35mg (44%), mp >300 ^{o}C (decomp). IR (KBr, cm^{-1}): ν

3382, 2926, 2855, 1717, 1613, 1547, 1502, 1391, 1267, 1158, 1060. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71 (d, J = 8 Hz, 4H), 7.67 (br. s, 2H), 7.33 (s, 2H), 7.25 (m, 4H), 6.79 (s, 2H), 6.08 (s, 2H), 5.79 (br. s, 2H), 4.20 (s, 4H), 3.48-3.36 (m, 4H), 3.36-3.26 (m, 4H), 3.02 (q, J = 7 Hz, 4H), 2.38 (s, 6H), 2.35 (s, 6H), 1.05 (t, J = 7 Hz, 6H). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 167.9, 161.7, 160.5, 153.4, 152.7, 152.6, 141.8, 133.1, 129.6, 128.3, 127.3, 126.7, 114.9, 112.6, 109.3, 56.1, 53.5, 47.1, 41.9, 40.1, 39.9, 29.8, 18.7, 18.6, 12.0. ESI-TOF high-res. MS: calcd. for [MH^+] $C_{47}H_{53}N_6O_7$ 813.3970, found 813.3966.

1,3-Bis{2-[2,3,6,7-tetrahydro-11-oxo-1H,5H,11H-[1]benzopyrano[6,7,8-ij] quinolizine-10-formylamido]ethyl}urea (8)

To a dried CH_2Cl_2 (10 mL) solution of coumarin **6** (33 mg, 0.1 mmol) and dried TEA (0.1 mL), triphosgene (9.89 mg, 0.033 mmol) was added. The mixture was stirred at 0 ^{o}C for 30 mins after which another equivalent of coumarin **6** was added in CH_2Cl_2 (5 mL). The reaction mixture was stirred for an hour, the solvent was removed in vacuo, and the residue was applied to column chromatography, (CH_2Cl_2/MeOH, 15:1) to give compound **8** as a bright yellow powder. Yield 26mg (35%), mp >300 ^{o}C (decomp). IR (KBr, cm^{-1}): ν 3337, 2941, 2845, 1687, 1616, 1519, 1457, 1367, 1309, 1211, 1176. ^{1}H NMR ($CDCl_3$ + 10 % CD_3OD, 500 MHz): δ 8.40 (s, 2H), 6.91 (s, 2H), 3.50-3.43 (m, 8H), 3.32-3.26 (m, 8H), 2.83-2.62 (m, 8H), 2.01-1.82 (m, 8H). ^{13}C NMR ($CDCl_3$ + 10 % CD_3OD, 500 MHz): δ 164.9, 163.1, 159.3, 152.7, 148.5, 148.1, 127.2, 119.9, 108.2,

107.7, 105.5, 50.7, 50.2, 49.8 (*C*D_3OD), 40.0, 39.8, 29.6, 27.4, 21.0, 20.0, 19.9. ESI-TOF high-res. MS: calcd for [MH^+] $C_{37}H_{41}N_6O_7$ 681.3031, found 681.3032.

_N_-{2-[4-[[(4,6-dimethyl-2-oxo-2H-1-benzopyran-7-yl)ethylamino]methyl]benzoylamido]ethyl}-_N'_-{2-[2,3,6,7-tetrahydro-11-oxo-1H,5H,11H-[1]benzopyrano[6,7,8-ij]quinolizine-10-formylamido]ethyl}urea (9)

To a dried CH_2Cl_2 (10 mL) solution of coumarin **4** (40 mg, 0.1 mmol) and TEA (0.1 mL), triphosgene (9.89 mg, 0.033 mmol) were added. The mixture was stirred at 0 ^oC for 15 min after which coumarin **6** (33 mg, 0.1 mmol) was added in CH_2Cl_2 (5 mL). The reaction mixture was stirred for an hour, the solvent was removed in vacuo, and the residue was applied to column chromatography, (CH_2Cl_2/ MeOH, 15:1) to give product **9** as a yellow powder. Yield 23 mg (30%), mp >300 ^oC (decomp.); IR (KBr, cm^{-1}): ν 3295, 2928, 2490, 1689, 1616, 1531, 1309, 1175, 1062. ^1H NMR ($CDCl_3$, 500 MHz): δ 9.06 (t, J = 6 Hz, 1H), 8.38 (s, 1H), 8.18 (t, J = 4 Hz, 1H), 7.77 (d, J = 8 Hz, 2H), 7.68 (s, 2H), 7.33 (s, 1H), 7.27 (d, J = 8 Hz, 2H), 7.09 (br., 6H), 6.86 (s, 1H), 6.82 (s, 1H), 6.10 (s, 1H), 6.02 (br., 1H), 5.81 (br., 1H), 4.15 (s, 2H), 3.54-3.45 (m, 4H), 3.45-3.40 (m, 2H), 3.39-3.34 (m, 2H), 3.34-3.24 (m, 4H), 3.00 (q, J = 7 Hz, 2H), 2.76 (t, J = 6 Hz, 2H), 2.71 (t, J = 6.0 Hz, 2H), 2.36 (s, 3H), 2.35 (s, 3H), 2.01-1.87 (m, 4H). 1.01 (t, J = 7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 500 MHz): δ 167.8, 164.8, 163.1, 161.8, 160.0, 153.7, 152.7, 152.6, 148.5, 148.0, 141.8, 135.4, 133.3, 129.7, 128.2, 127.4, 127.2, 126.7, 122.1, 121.9, 119.9, 114.9, 112.6, 109.2, 108.2, 105.6, 56.3 50.3, 49.9, 46.7, 42.5, 40.8, 39.9,

39.8, 31.0, 29.8, 27.5, 21.1, 20.2, 20.1, 18.7, 18.8, 11.9. ESI-TOF high-res. MS: calcd. for [MH^+] $C_{42}H_{47}N_6O_7$ 747.3501, found 747.3492.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetra-{[[*N*-[2-(1,1-dimethylethoxy)formylamido)]ethyl]carbonylimino]methyl}calix[4]arene (13)

N-boc-ethylenediamine (0.24 mL, 1.5 mmol) and *t*-Bu-calixarene tetraacid **12** (220 mg, 0.25 mmol) were mixed with EDC•HCl (191 mg, 1.0 mmol), HOBt (135 mg, 1.0 mmol) and NMM (0.1 mL) in dry CH_2Cl_2 (25 mL) and stirred at 0 ºC overnight. The solution was evaporated to dryness. The solid was dissolved in CH_2Cl_2 (50 mL) and washed with 5% aq HCl (50 mL) and water (3 x 50 mL) and evaporated. The residue was recrystallized form MeOH to give tetraamide **13** as a white solid (259 mg, 62 %); m.p. > 240 ^oC (decomp); IR (KBr, cm^{-1}): ν 2964, 2880, 1692, 1534, 1480, 1392, 1365, 1251, 1174, 1126, 1043, 871; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.98 (br., 4H), 6.78 (s, 8H), 5.48 (br., 4H), 4.53 (m, 4H), 4.50 (s, 8H), 3.50 (m, 8H), 3.29 (m, 8H), 3.24 (d, J = 13 Hz, 4H), 1.41 (s, 36H), 1.07 (s, 36H); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 170.4, 156.6, 152.8, 146.0, 132.7, 126.0, 79.2, 74.3, 45.0, 40.8, 39.5, 34.0, 31.4, 28.5; ESI-TOF m/z 1449.8880, ([M + H^+], calcd for $C_{80}H_{120}N_8O_{16}$ 1449.8895); Calcd for $C_{80}H_{120}N_8O_{16}$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.36; H, 8.17; N, 7.96.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetra-[[*N*-(2-aminoethyl)carbonylimino]methyl]calix[4]arene TFA salt (14·4TFA)

Tetraamide **13** (145 mg, 0.1 mmol) and TFA (0.5 mL, 6.5 mmol) were dissolved in dry CH_2Cl_2 (10 mL) and stirred overnight. The solvent was removed, and Et_2O (20 mL) was added to precipitate tetraamine **14** as a TFA salt (129 mg, 86 %); m.p. 182-185 ^oC (decomp); IR (KBr, cm^{-1}): ν 2964, 2083, 1659, 1535, 1461, 1392, 1363, 1300, 1178, 1135, 1052, 872 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ 8.43 (br t, 4H), 7.90 (br, 12H), 6.81 (s, 8H), 4.49 (m, 4H), 4.47 (s, 8H), 3.40-3.38 (m, 8H), 3.20 (d, J = 13 Hz, 4H), 2.90 (br, 8H), 1.02 (s, 36H); ^{13}C NMR (DMSO-d_6, 300 MHz): δ 170.6, 159.4 (q, J = 125 Hz, CF_3C=O), 151.8, 146.8, 134.3, 126.3, 117.6 (q, J = 1185 Hz, CF_3C=O), 74.8, 42.8, 41.8, 34.1, 31.6; ESI-TOF m/z 1049.6782, ([Free amine + H^+], calcd. for $C_{60}H_{89}N_8O_8$ 1449.6803); Calcd for $C_{68}H_{92}F_{12}N_8O_{16}$: C, 54.25; H, 6.16; N, 7.44. Found: C, 54.36; H, 6.17; N, 7.36.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetra-[[*N*-(2-aminoethyl)carbonylimino]methyl]calix[4]arenecarbamic acid (15)

Compound **14•4TFA** (15 mg, 0.01 mmol) was dissolved in DMSO-d_6 (0.5 mL), TEA (0.02 mL) was added. Then CO_2 was introduced for 5 mins to form carbamic acid **15**: ^1H NMR (DMSO-d_6, 300 MHz): δ 8.34 (br, 4H), 6.81 (s, 8H), 6.70 (br, 4H), 4.53 (d, J = 13.0 Hz, 4H), 4.46 (s, 8H), 3.20 (d, J = 13.0 Hz, 4H), 3.03 (br., 8H), 1.04 (s, 36H).

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra-[[*N*-(2-aminoethyl)carbonylimino]methyl]calix[4]arene carbamate (16)

Compound **14•4TFA** (15 mg, 0.01 mmol) was suspended in 1 mL $CHCl_3$. TEA (0.02 mL) was added to dissolve **14**. Then CO_2 was introduced for 10 mins to form white precipitate **16**, which was isolated and dried in vacuo. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.50 (br t, 4H), 6.83 (s + br. s, 12H), 6.80-6.00 (br), 4.46-4.53 (m, 12H), 3.42 (br., 8H), 3.21 (d, J = 12 Hz, 4H), 2.90-2.85 (m, 24H), 1.02 (m, 60H). ^{13}C NMR (DMSO-d_6, 300 MHz): δ 170.5, 159.1 (q, J = 121 Hz, CF_3C=O), 153.3, 145.1, 133.4, 125.9, 117.7 (q, J = 1187 Hz, CF_3C=O), 74.4, 46.2, 37.6, 34.1, 31.6, 10.1. Due to the low concentration, the carbamate *C*=O singlet could not be detected.[52b,e]

Extraction of alkali-metal perchlorates ($MClO_4$) by calixarene (14); a general procedure

Compound **14** (15.0 mg, 0.01 mmol) was dissolved in 1 mL of $CHCl_3$ in the presence of TEA (0.02 mL). Alkali-metal perchlorate (0.01 mmol) was added and the suspension was stirred overnight. The solution was separated. CO_2 (or $^{13}CO_2$) was then introduced and the precipitate was collected and dried. The ^{13}C NMR spectrum of calixarene-Na^+ carbamate polymer **18** was measured with $^{13}CO_2$ gas.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetra-[[*N*-(2-aminoethyl)carbonylimino]methyl]calix[4]arene $NaClO_4$ complex (17):

^{1}H NMR (DMSO-d_6, 300 MHz): δ 8.43 (br, 4H), 7.12 (s, 8H), 4.40 (s, 8H), 4.34 (d, J = 12.0 Hz, 4H),3.40-3.32 (m, 12H), 3.03-2.88 (m, 14H), 1.12 (m, 45H); ^{13}C NMR

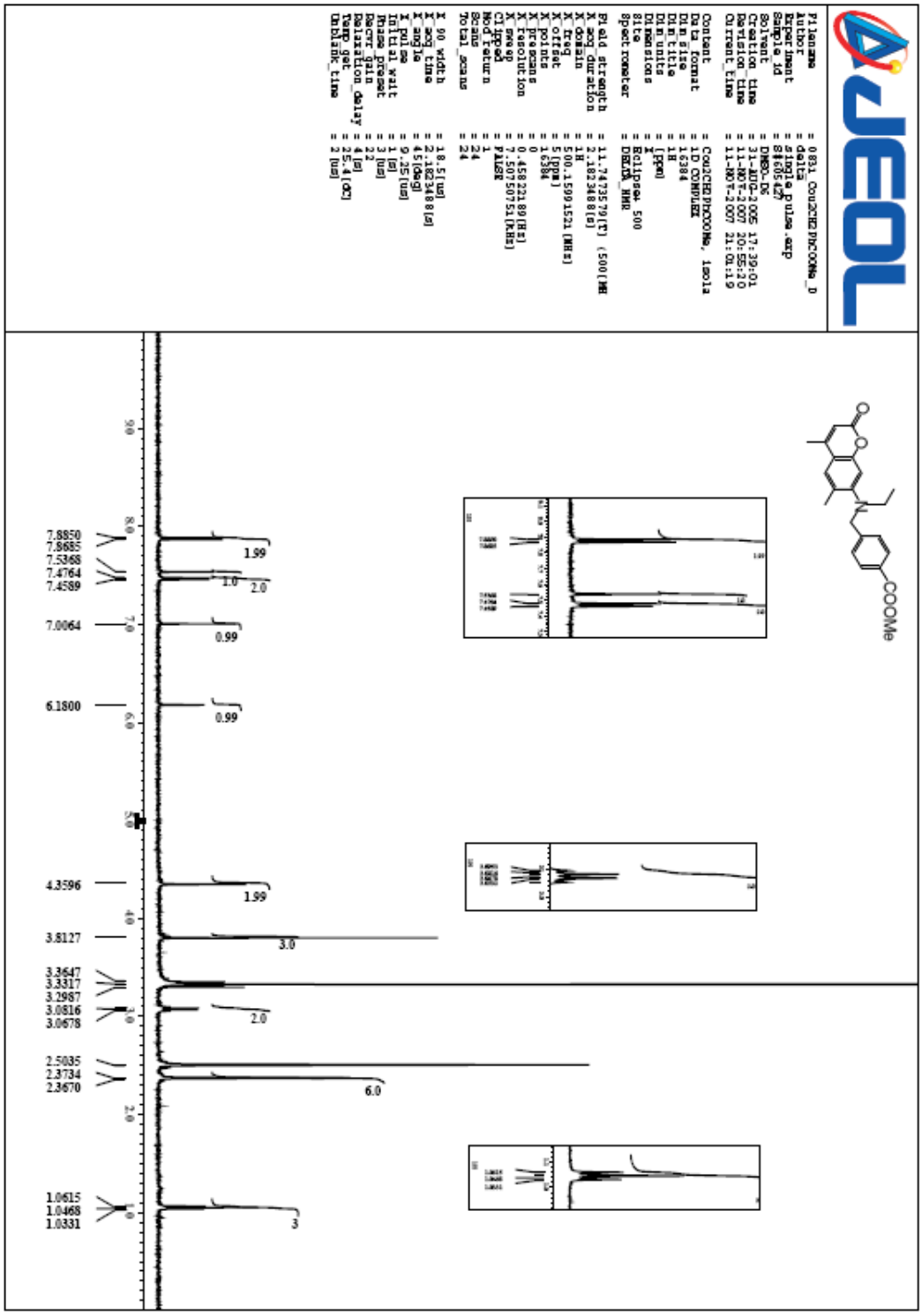
(DMSO-d_6, 300 MHz): δ 170.6, 160.0 (q, CF_3C=O), 151.8, 147.0, 134.3, 126.3, 117.6 (q, CF_3C=O),74.8, 46.2, 34.4, 31.5, 30.6, 9.4.

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra-[[*N*-(2-aminoethyl)carbonylimino]methyl]calix[4]arene $NaClO_4$ complex carbamate (18): Carbamate **18** was obtained from **17** using ^{13}C-labeled CO_2. ^{13}C NMR (DMSO-d_6, 300 MHz): δ 160.4 (^{13}C=O), 159.7 (m, CF_3C=O), 151.6, 147.0, 134.5, 126.3, 117.7 (m, CF_3C=O), 74.9, 46.2, 37.8, 34.5, 31.5, 30.6, 10.1

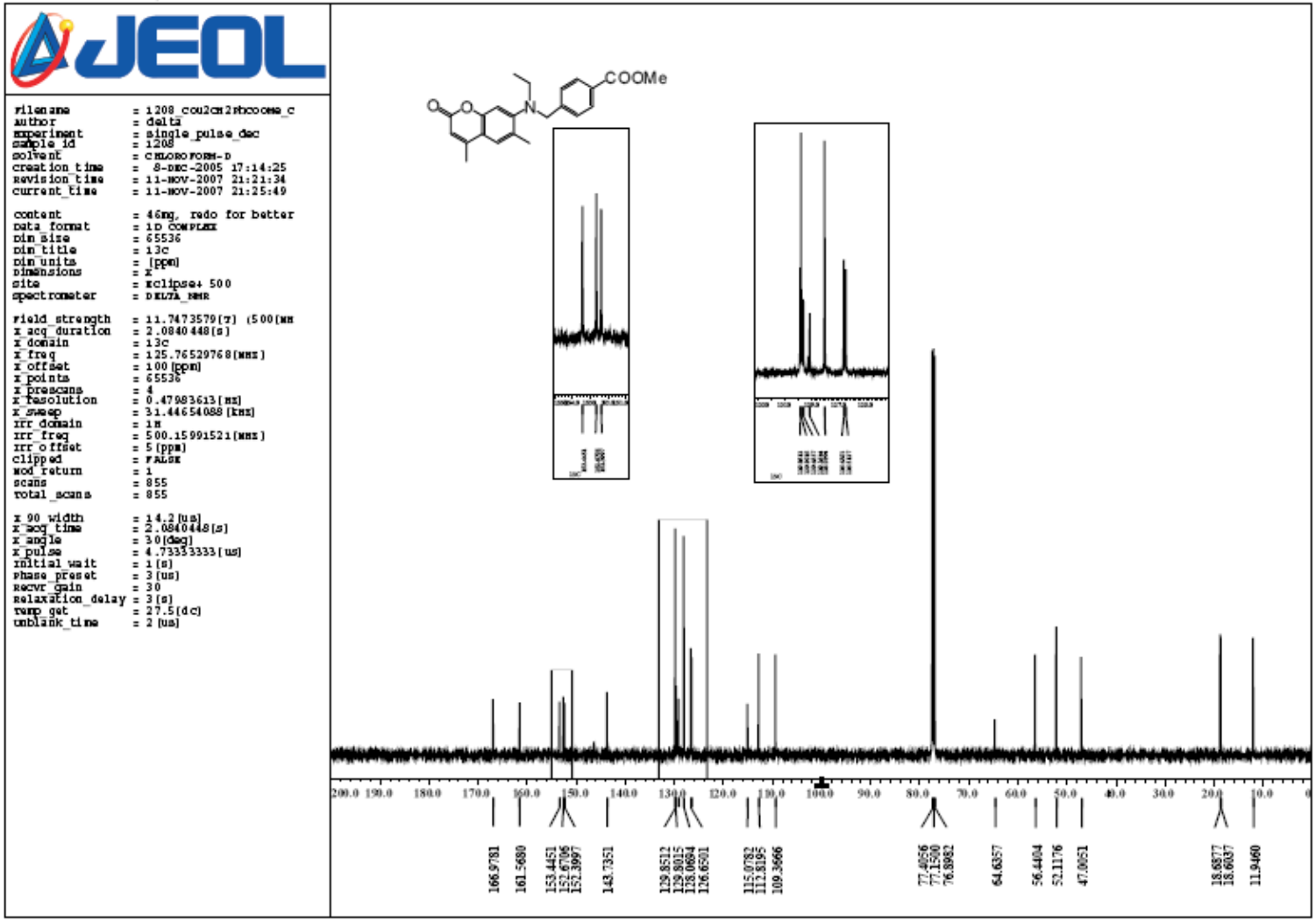
APPENDIX A

NMR SPECTRA OF COMPOUNDS **1-9**,**12-18**

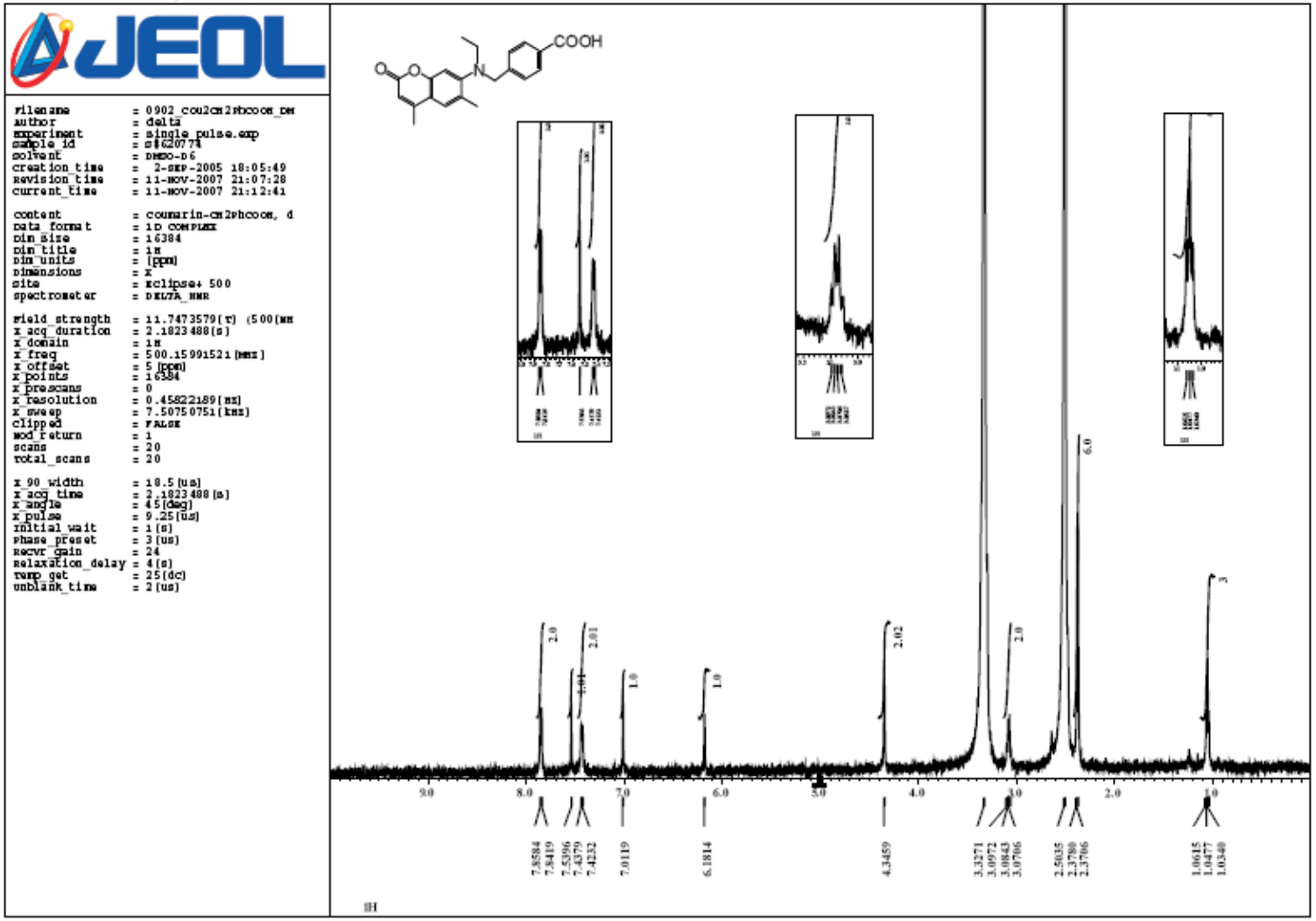
^{1}H NMR in $CDCl_3$ for compound **I**



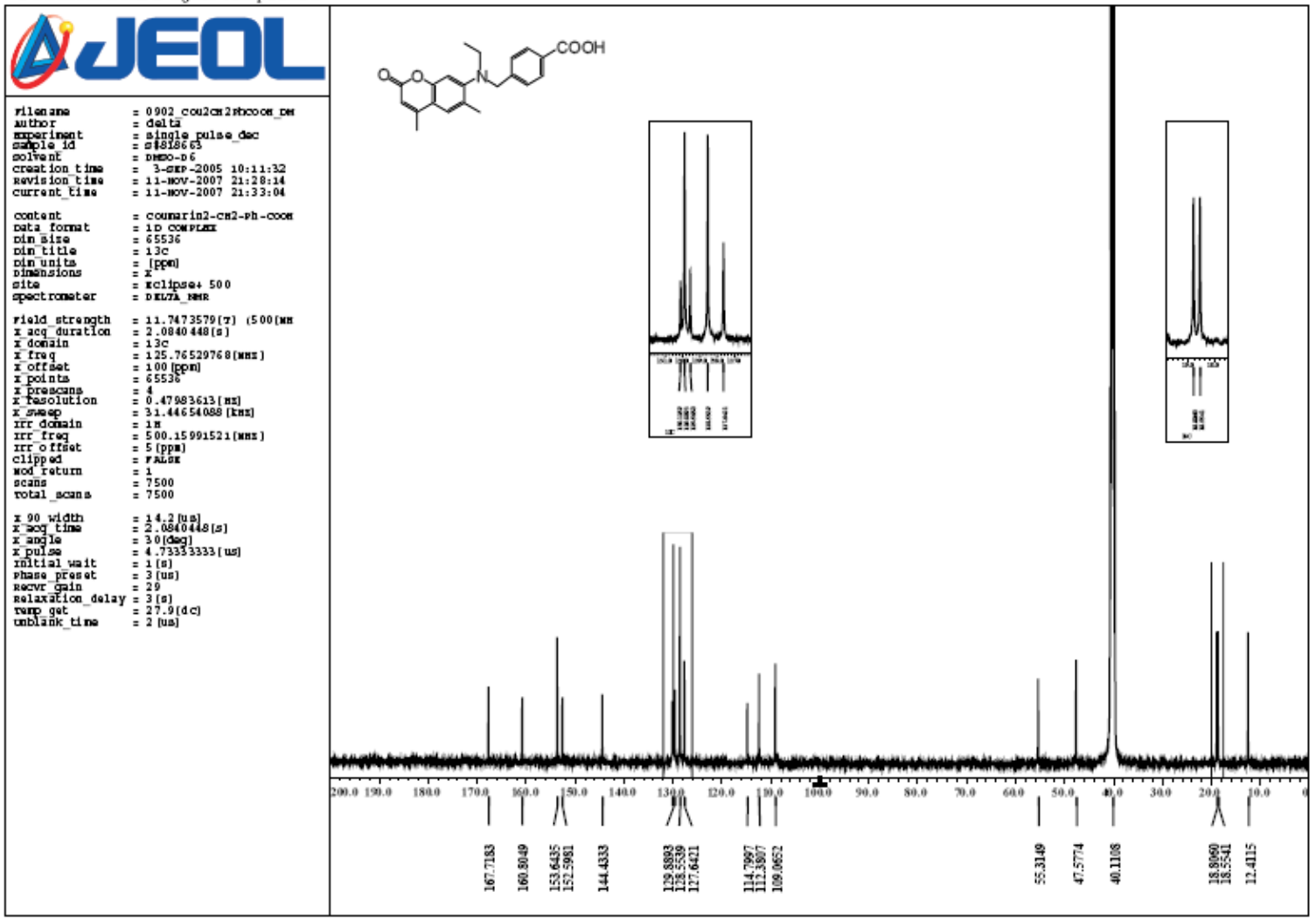
^{13}C NMR in $CDCl_3$ for compound **1**



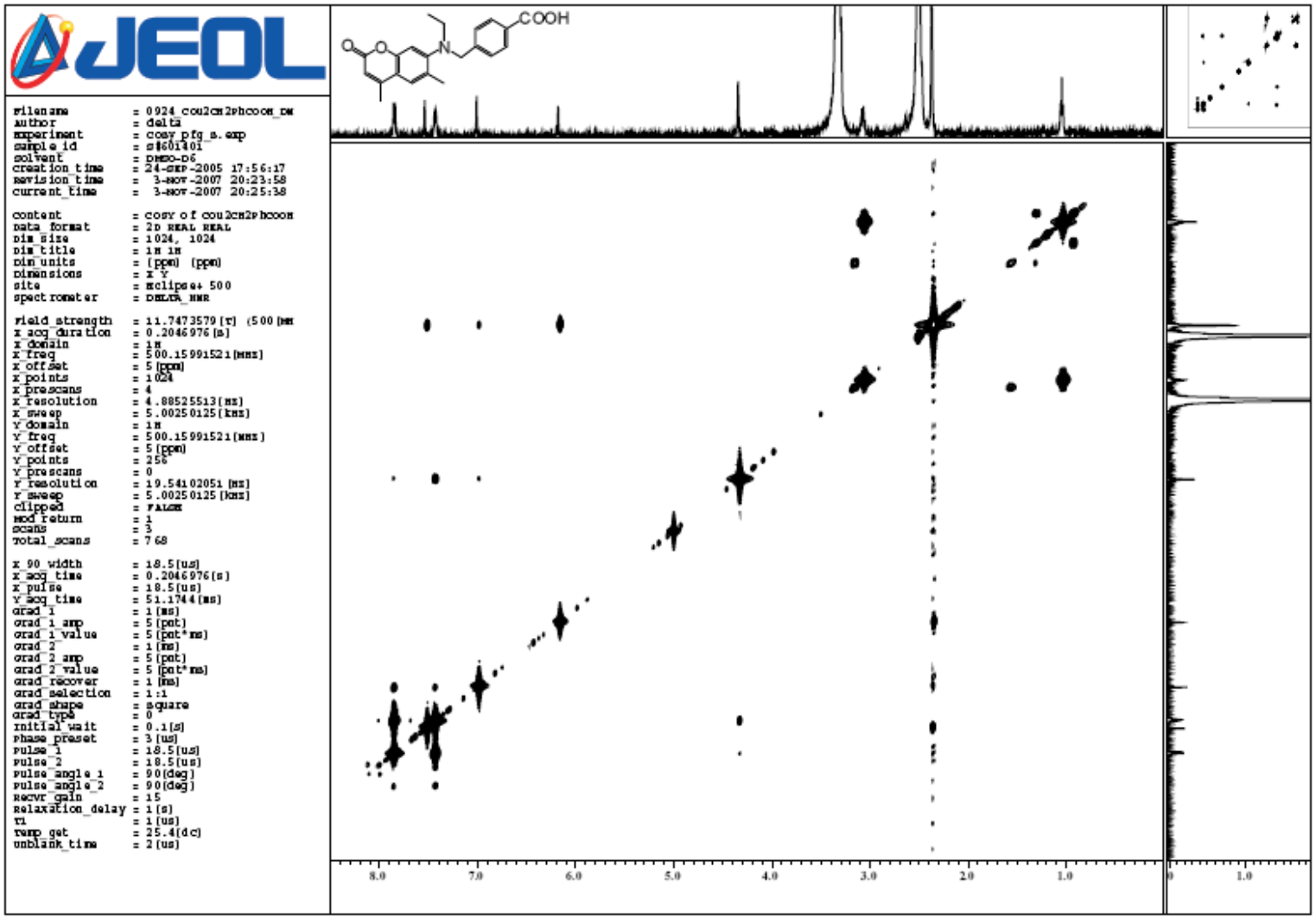
^{1}H NMR in DMSO-d_6 for compound **2**



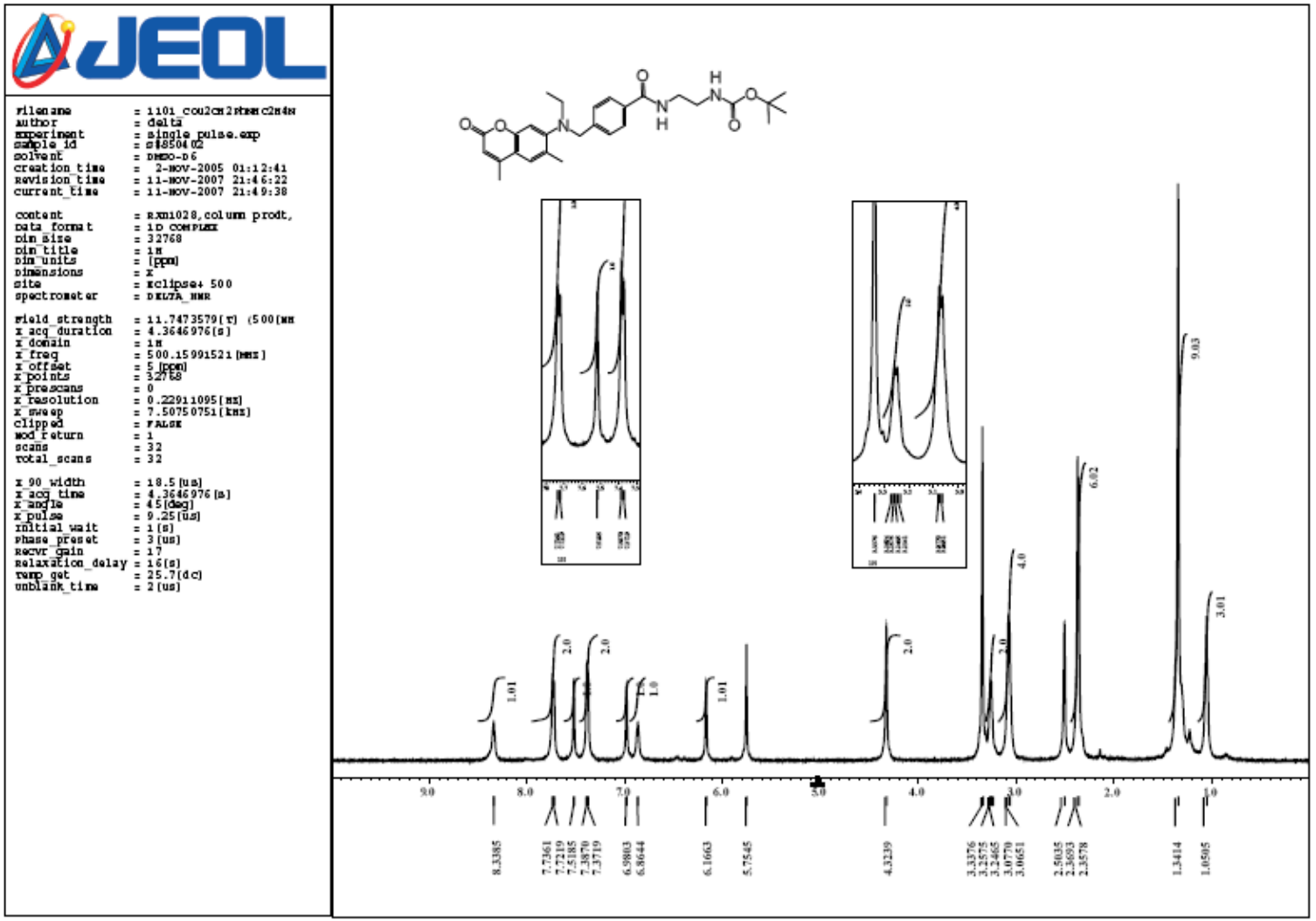
^{13}C NMR in DMSO-d_6 for compound **2**



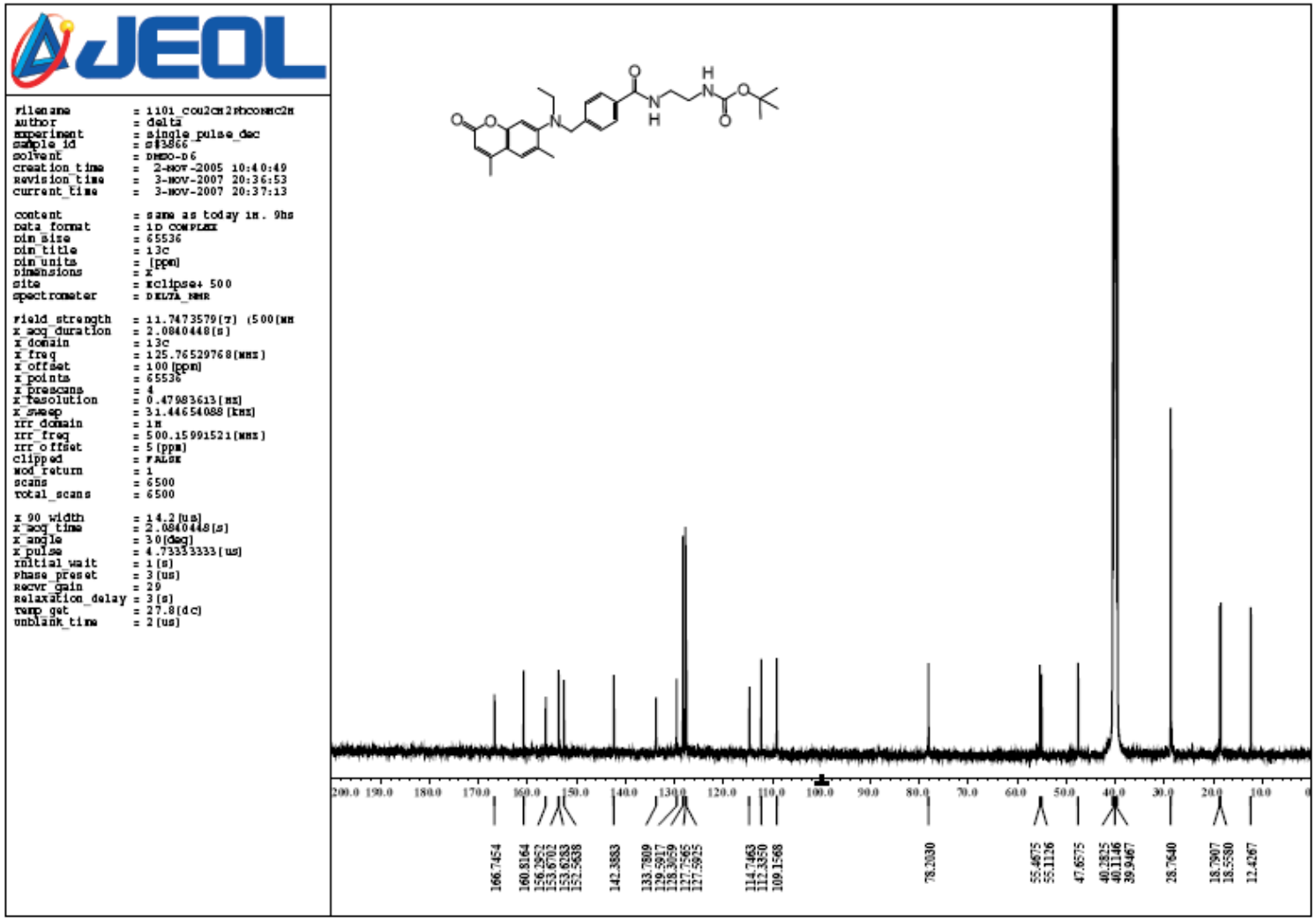
^{1}H-^{1}H COSY NMR in DMSO-d_6 for compound **2**



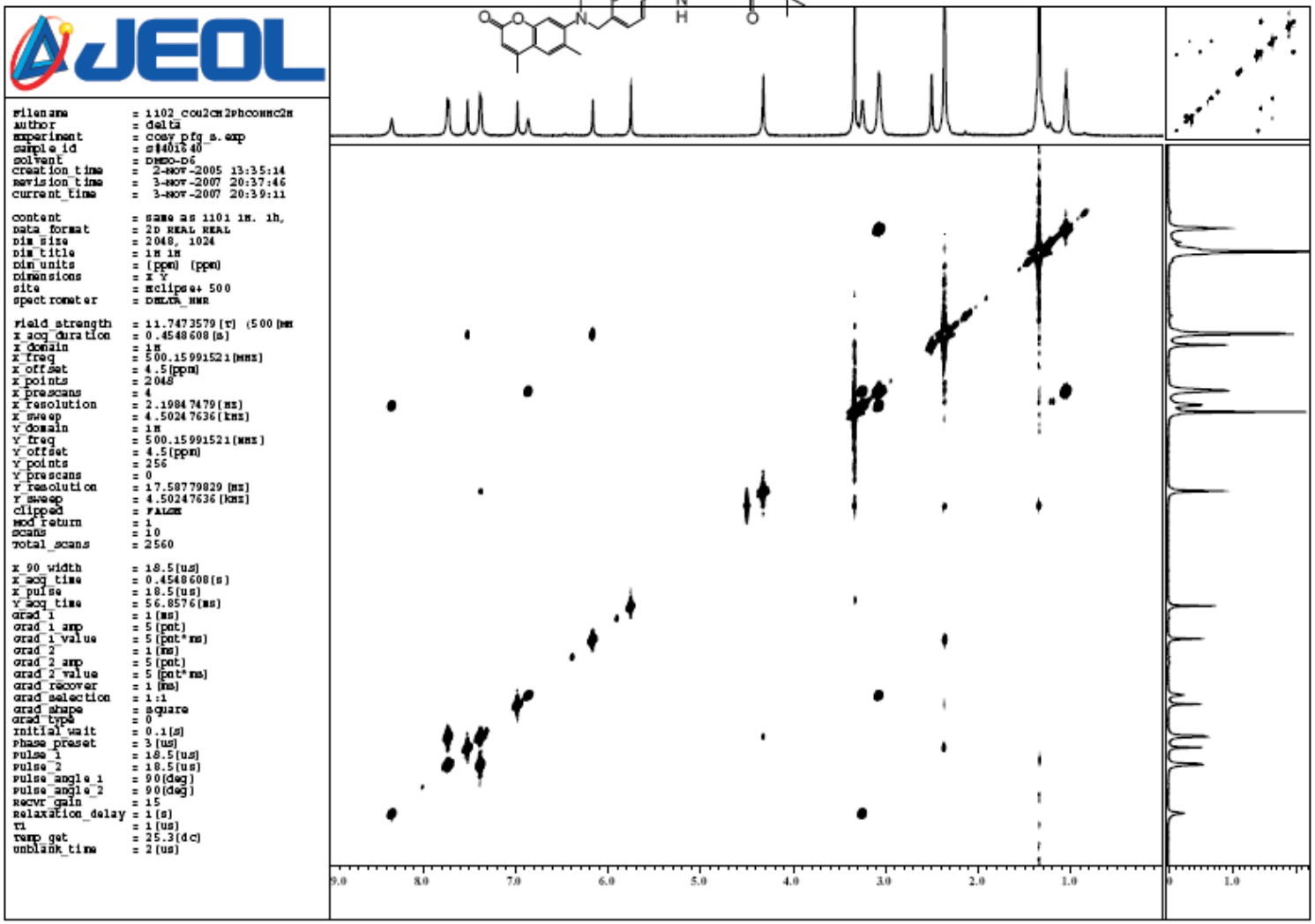
^{1}H NMR in DMSO-d_6 for compound **3**



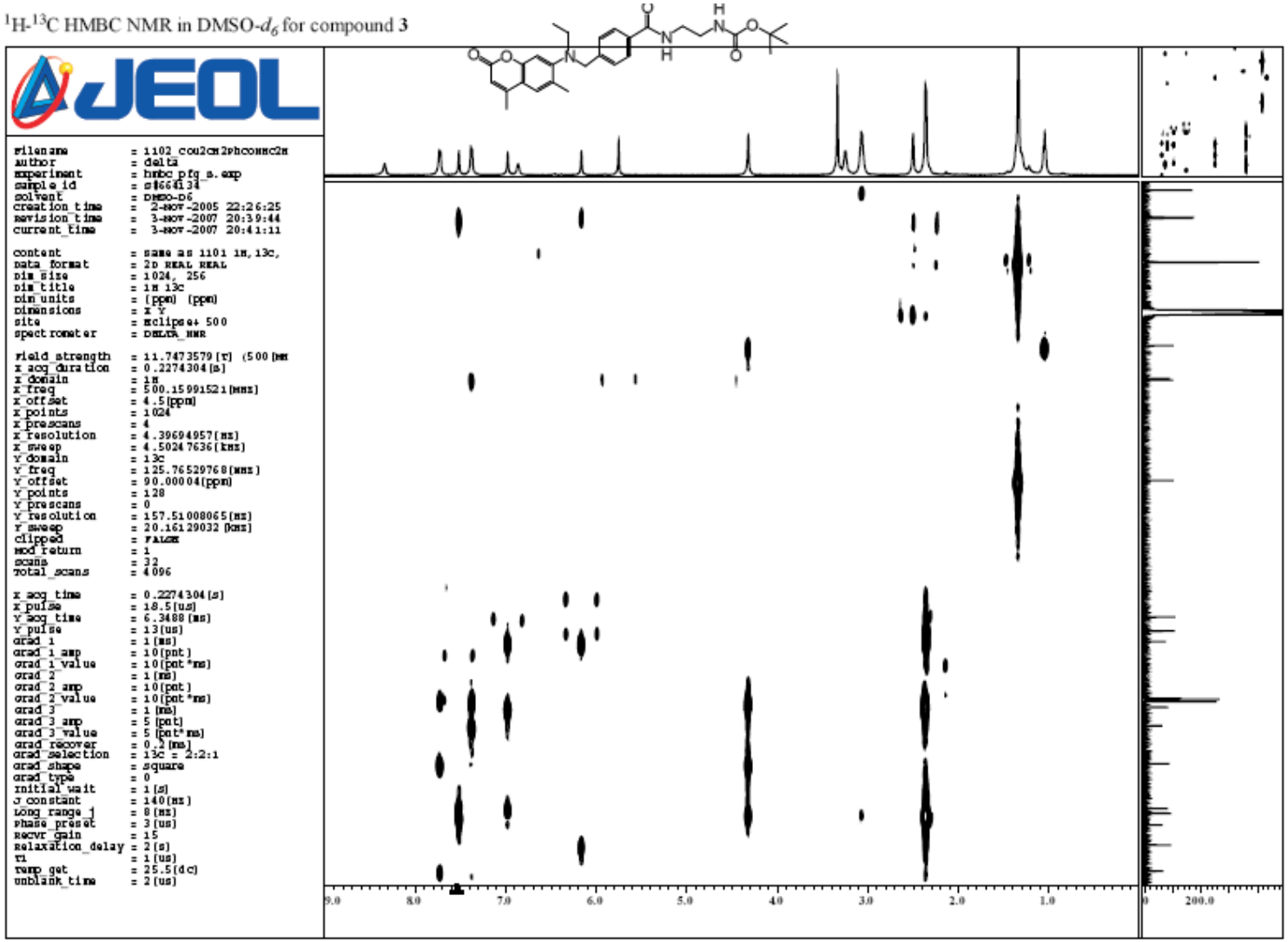
^{13}C NMR in DMSO-d_6 for compound **3**



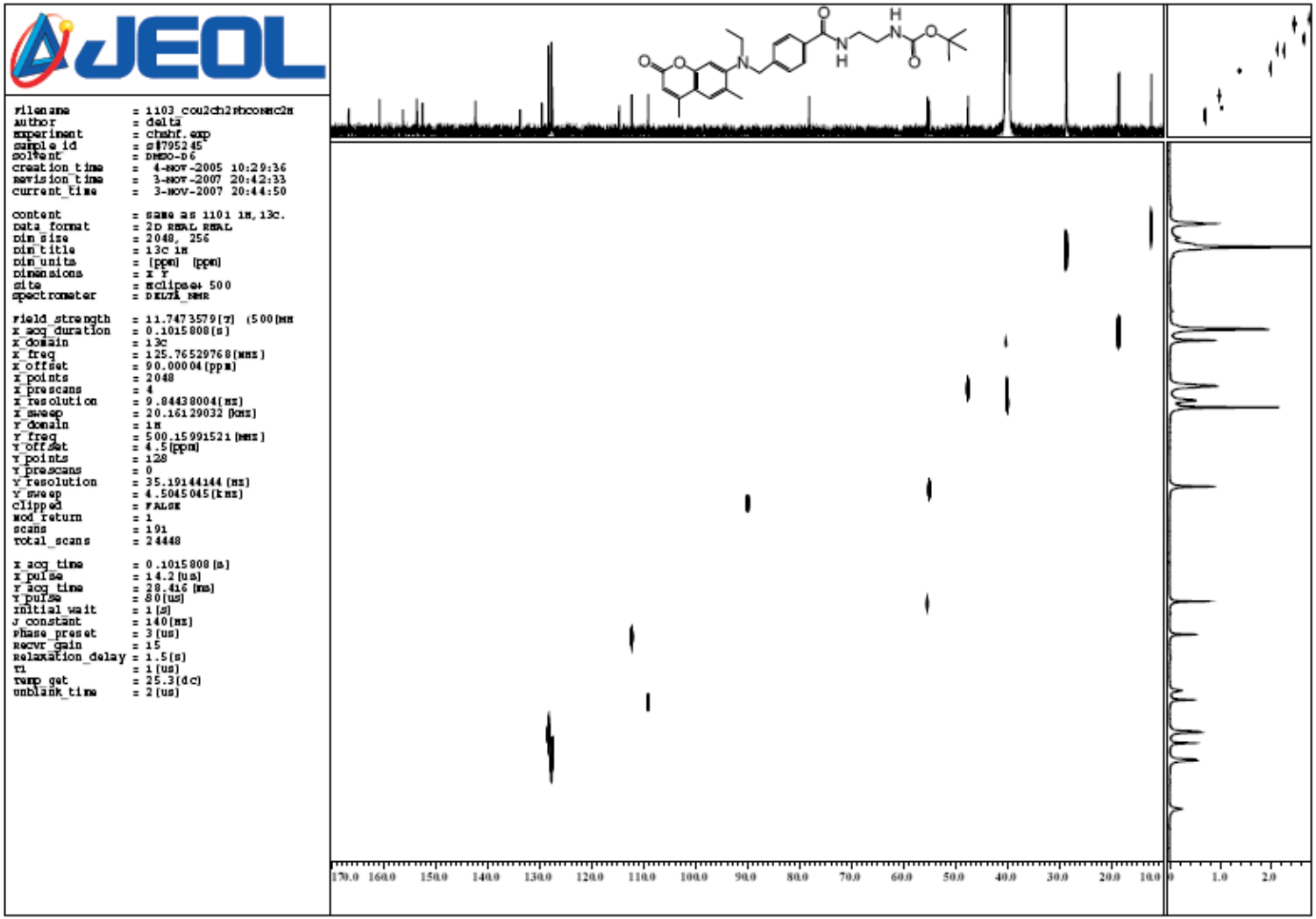
^{1}H-^{1}H COSY NMR in DMSO-d_6 for compound **3**



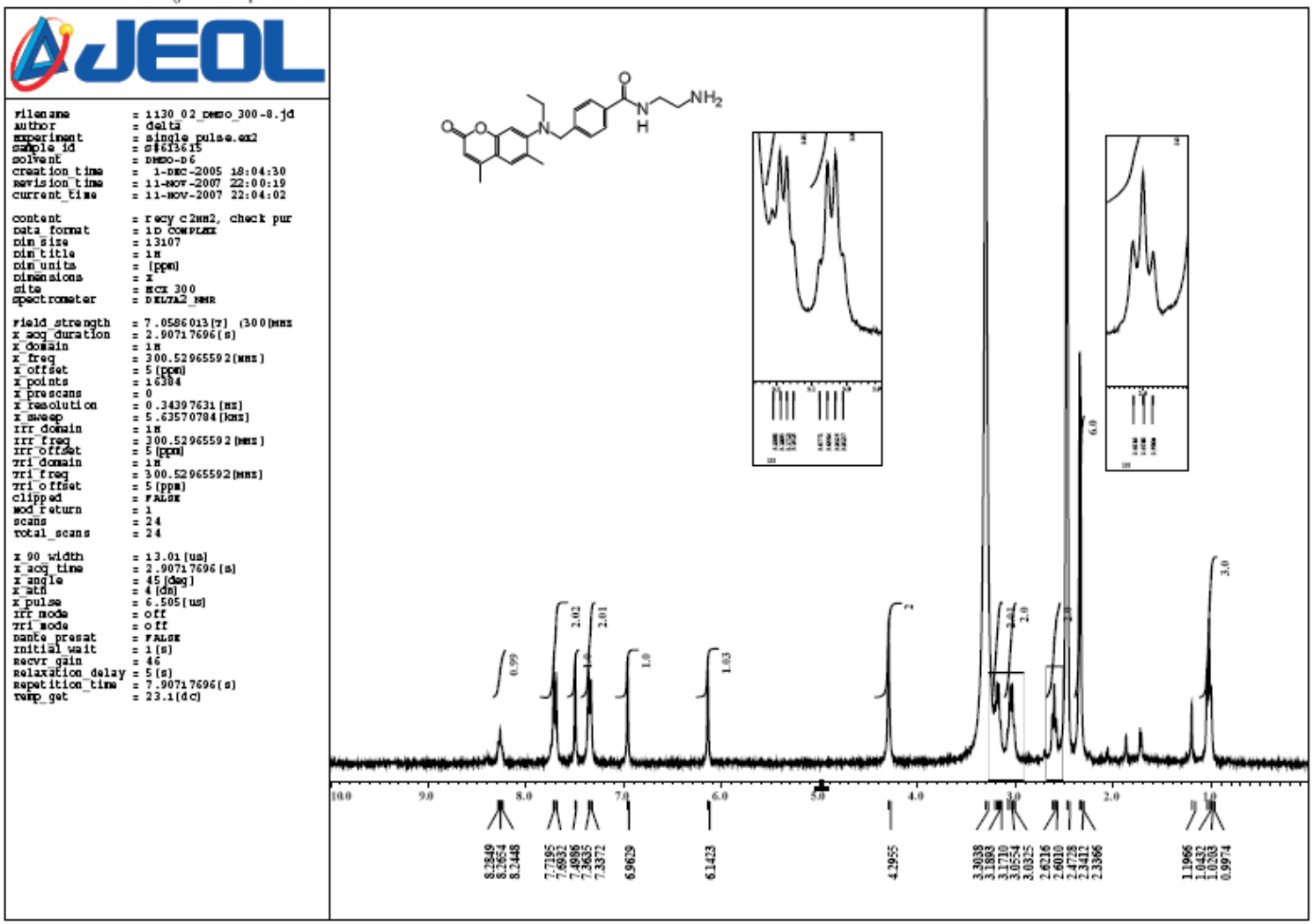
^{1}H-^{13}C HMBC NMR in DMSO-d_6 for compound **3**



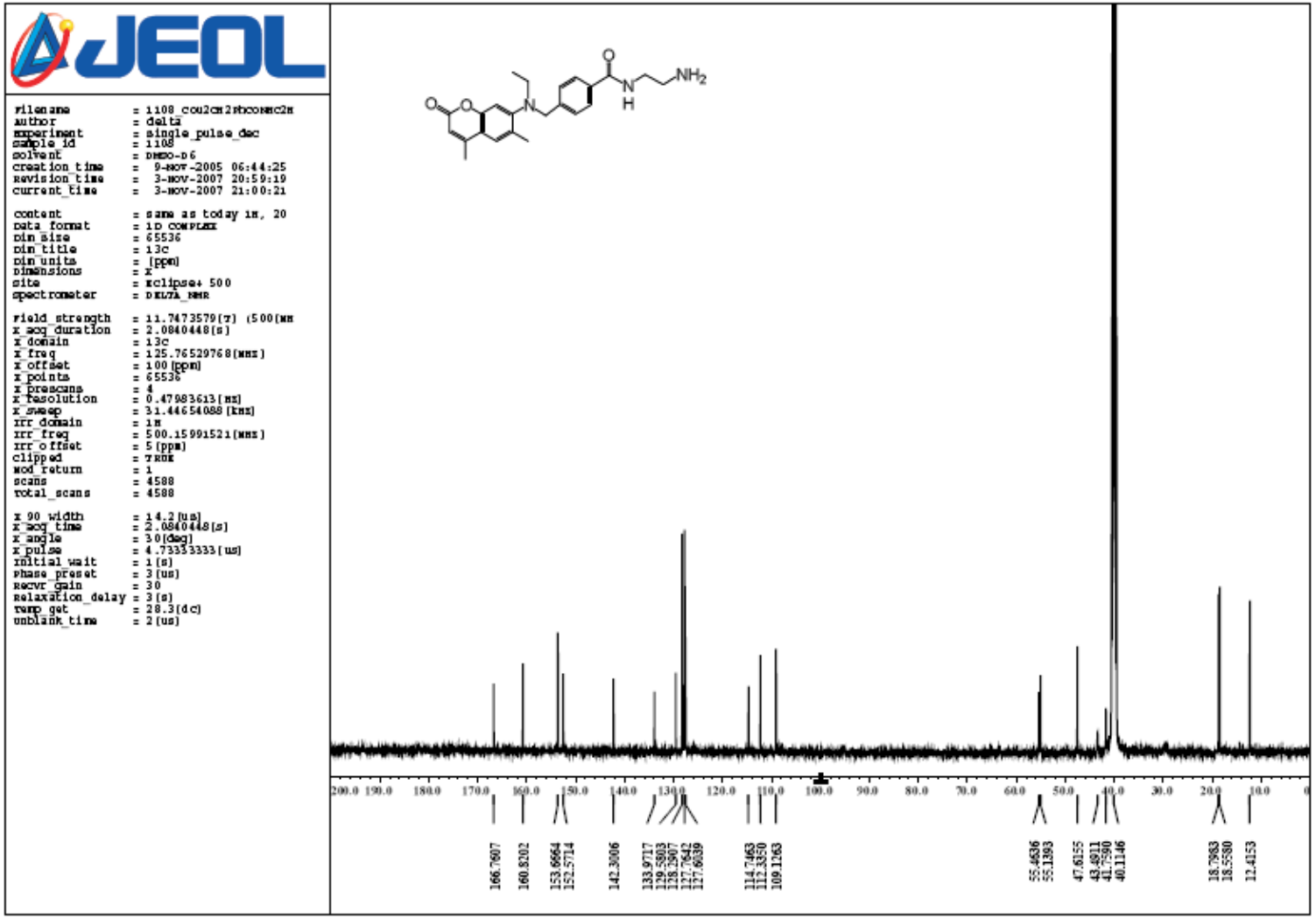
^{13}C-^{1}H HETCOR NMR in DMSO-d_6 for compound **3**



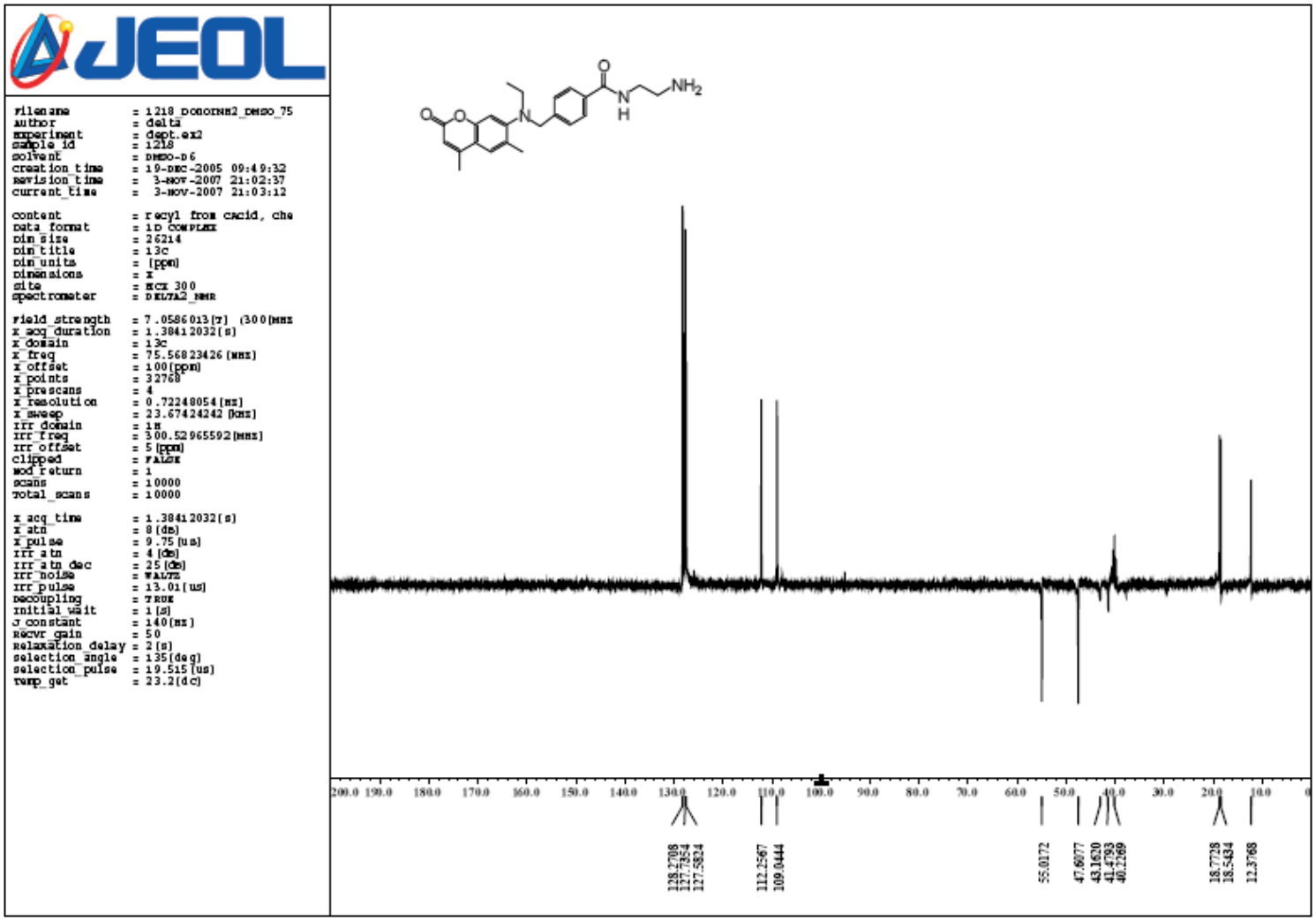
^{1}H NMR in DMSO-d_6 for compound **4**



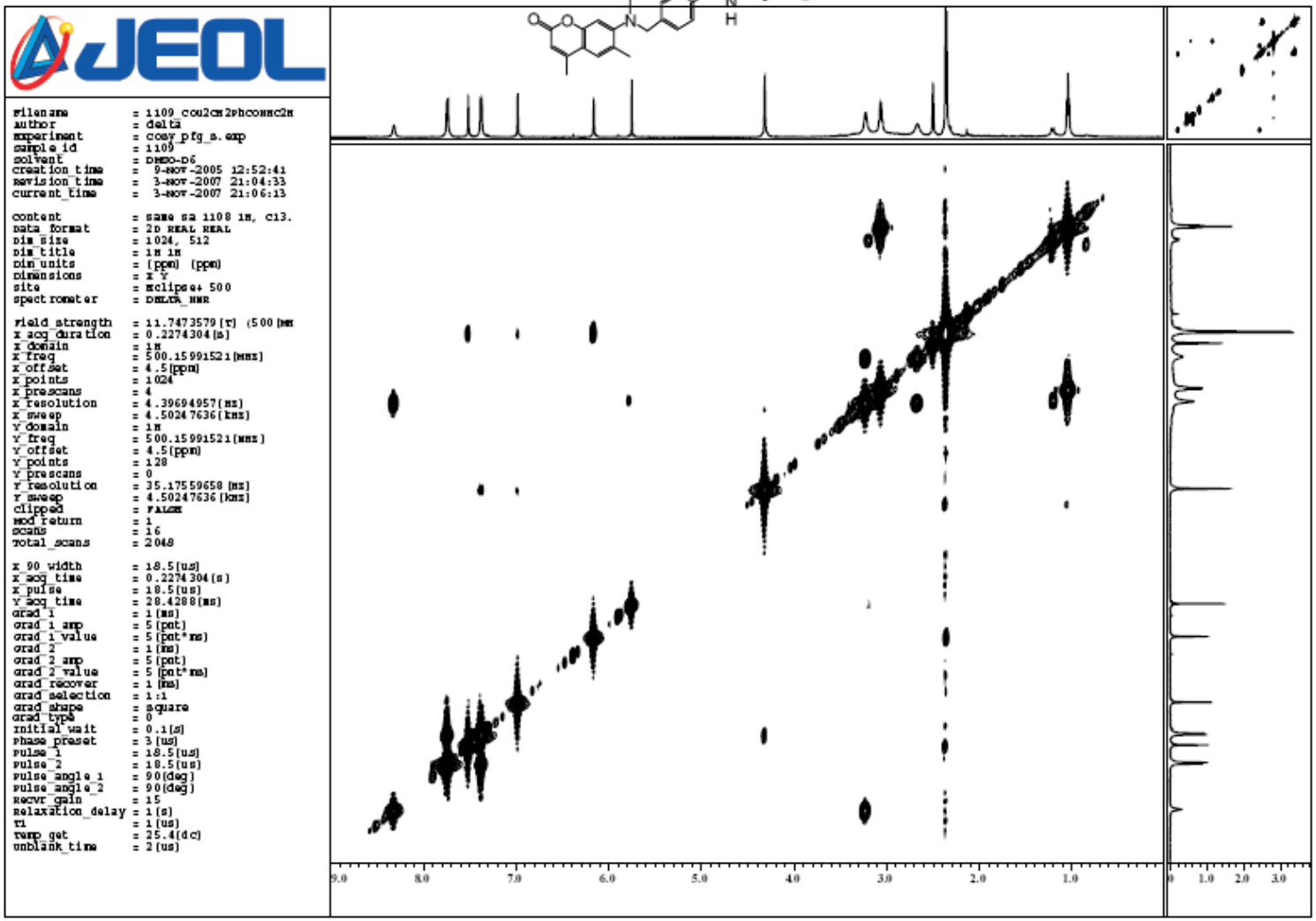
^{13}C NMR in DMSO-d_6 for compound **4**



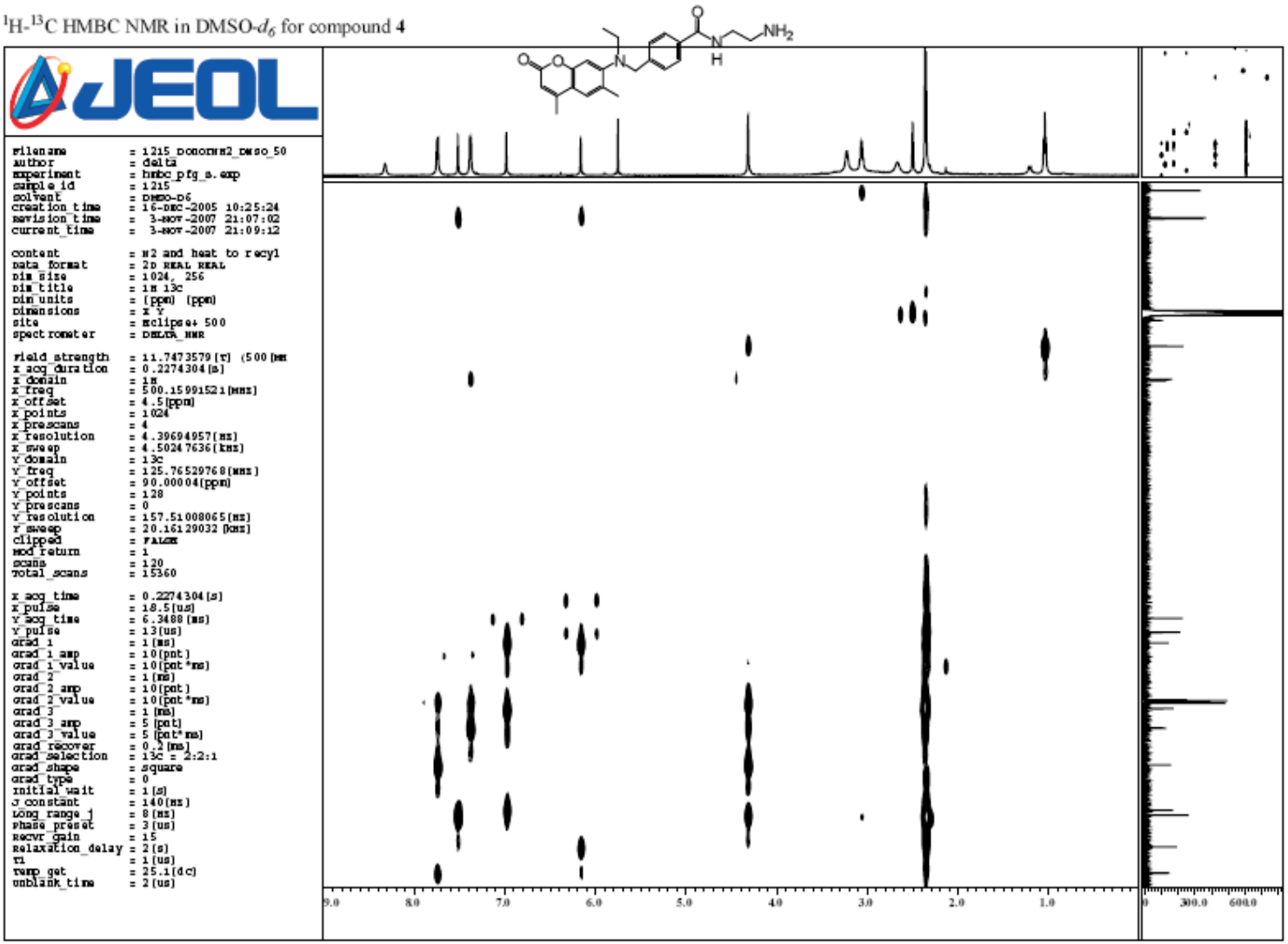
^{13}C DEPT NMR in DMSO-d_6 for compound **4**



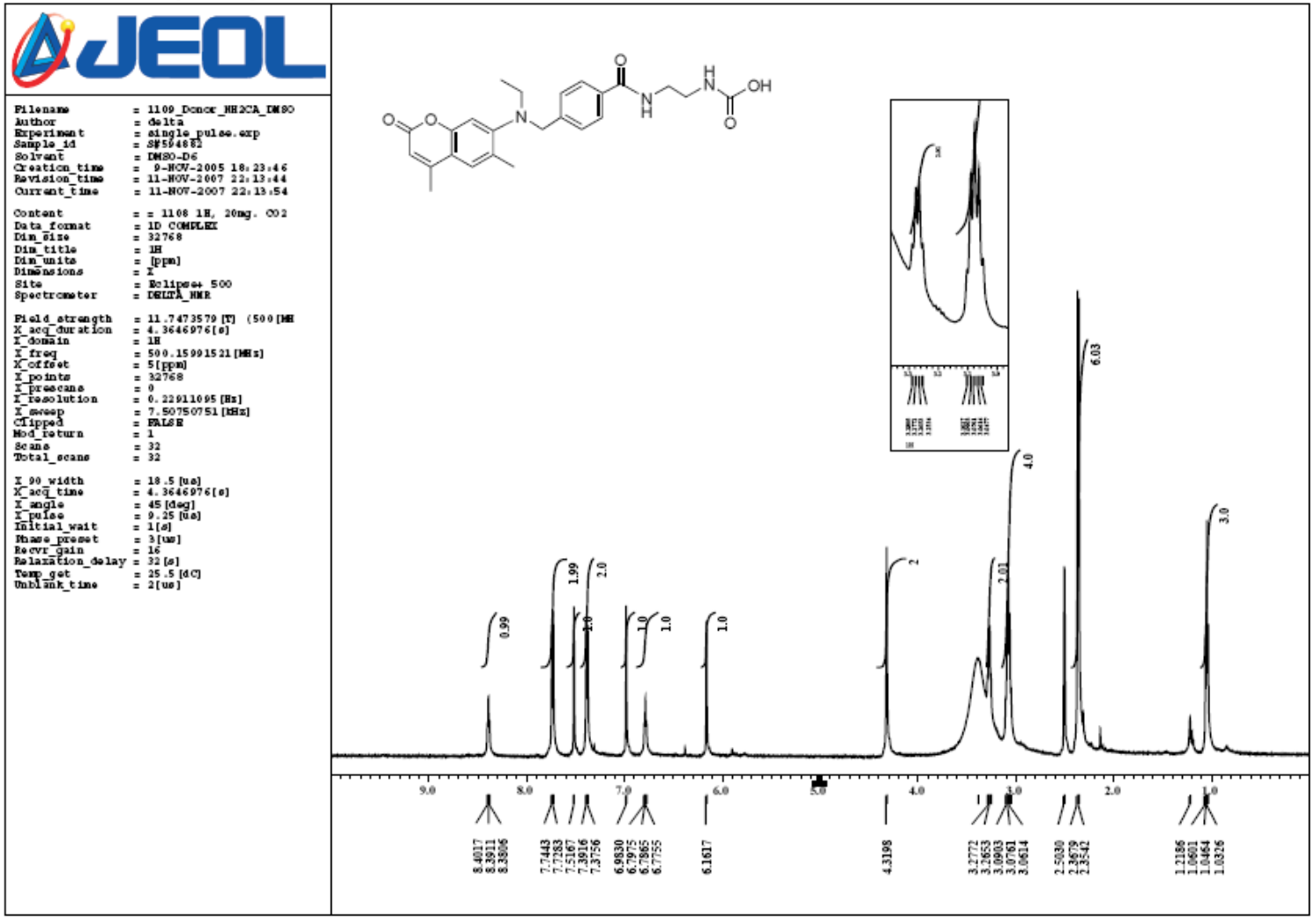
^{1}H-^{1}H COSY NMR in DMSO-d_6 for compound **4**



^{1}H-^{13}C HMBC NMR in DMSO-d_6 for compound **4**

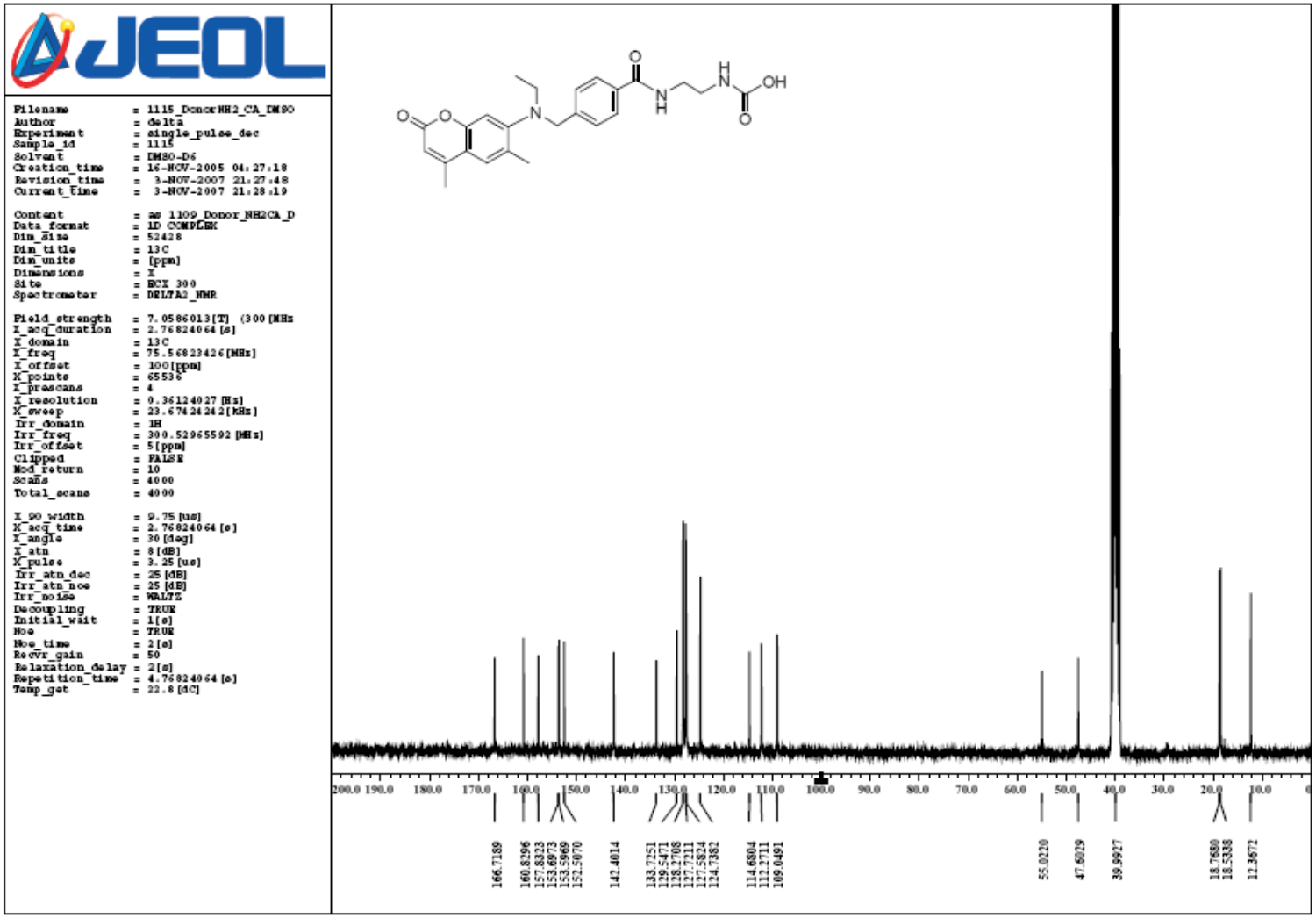


^{1}H NMR in DMSO-d_6 for compound **4a**



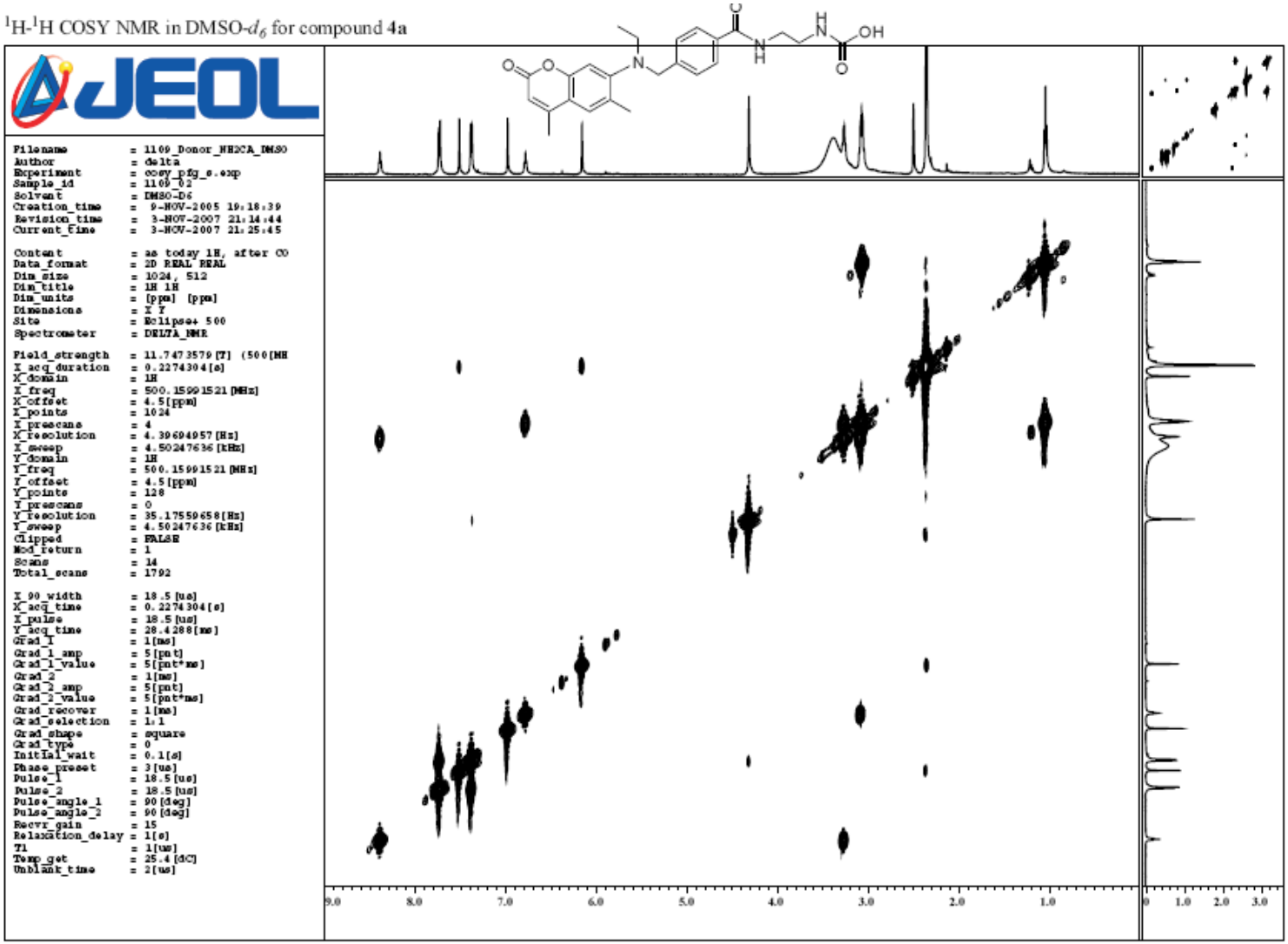
```
Filename          = 1109_Donor_NH2CA_DMSO
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#594882
Solvent           = DMSO-D6
Creation_time     =  9-NOV-2005 18:23:46
Revision_time     = 11-NOV-2007 22:13:44
Current_time      = 11-NOV-2007 22:13:54

Content           = = 1108 1H, 20mg. C02
Data_format       = 1D COMPLEX
Dim_size          = 32768
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 4.3646976[s]
X_domain          = 1H
X_freq            = 500.1599152l[MHz]
X_offset          = 5[ppm]
X_points          = 32768
X_prescans        = 0
X_resolution      = 0.22911095[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 32
Total_scans       = 32

X_90_width        = 18.5[us]
X_acq_time        = 4.3646976[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 16
Relaxation_delay  = 32[s]
Temp_get          = 25.5[dC]
Unblank_time      = 2[us]
```

^{13}C NMR in DMSO-d_6 for compound **4a**

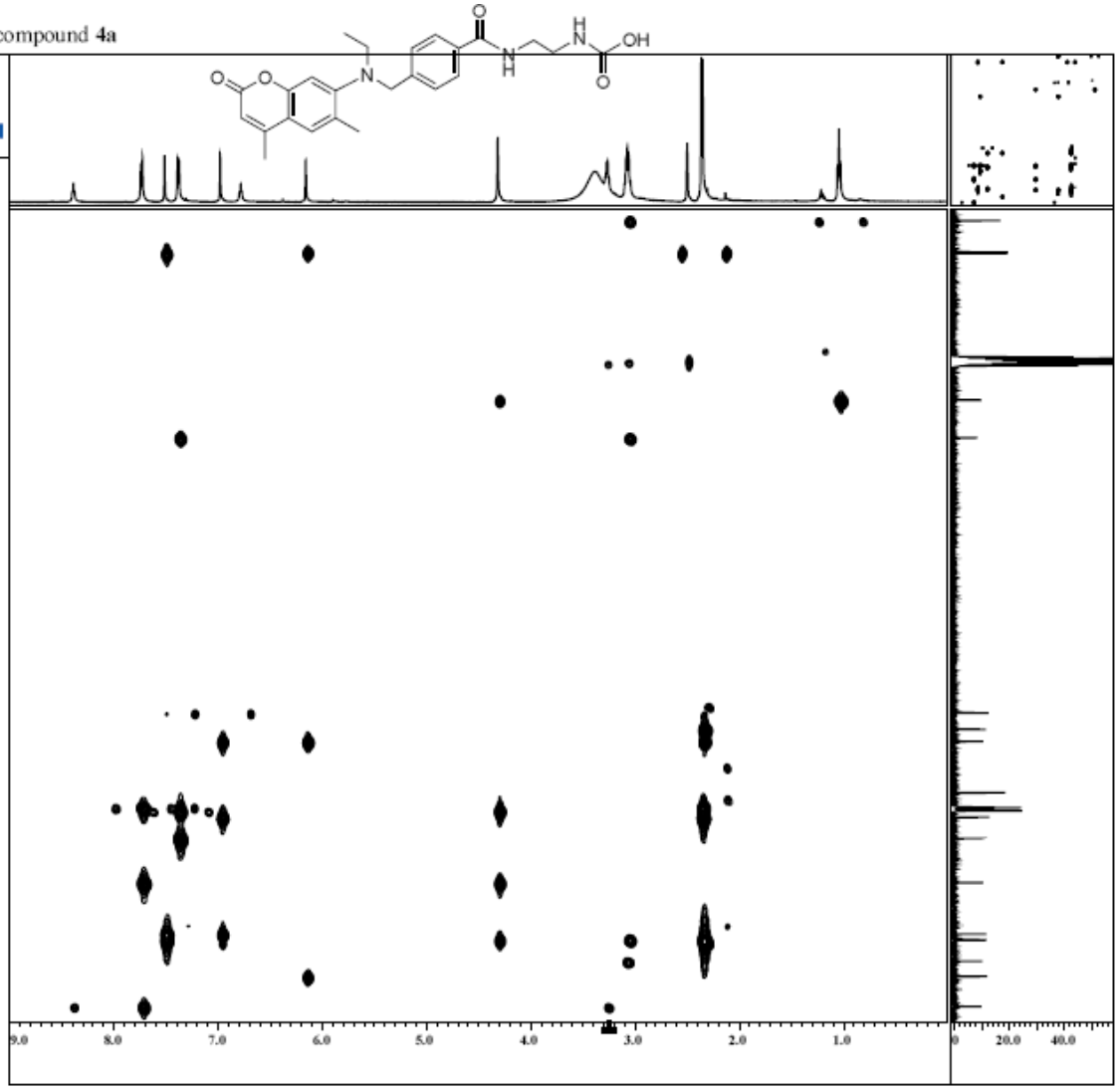


```
Filename          = 1115_DonorNH2_CA_DMSO
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1115
Solvent           = DMSO-D6
Creation_time     = 16-NOV-2005 04:27:18
Revision_time     =  3-NOV-2007 21:27:48
Current_time      =  3-NOV-2007 21:28:19

Content           = as 1109_Donor_NH2CA_D
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = BCX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T]  (300[MHz
X_acq_duration    = 2.76824064[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.36124027[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 10
Scans             = 4000
Total_scans       = 4000

X_90_width        = 9.75[us]
X_acq_time        = 2.76824064[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 50
Relaxation_delay  = 2[s]
Repetition_time   = 4.76824064[s]
Temp_get          = 22.8[dC]
```

^{1}H-^{1}H COSY NMR in DMSO-d_6 for compound **4a**

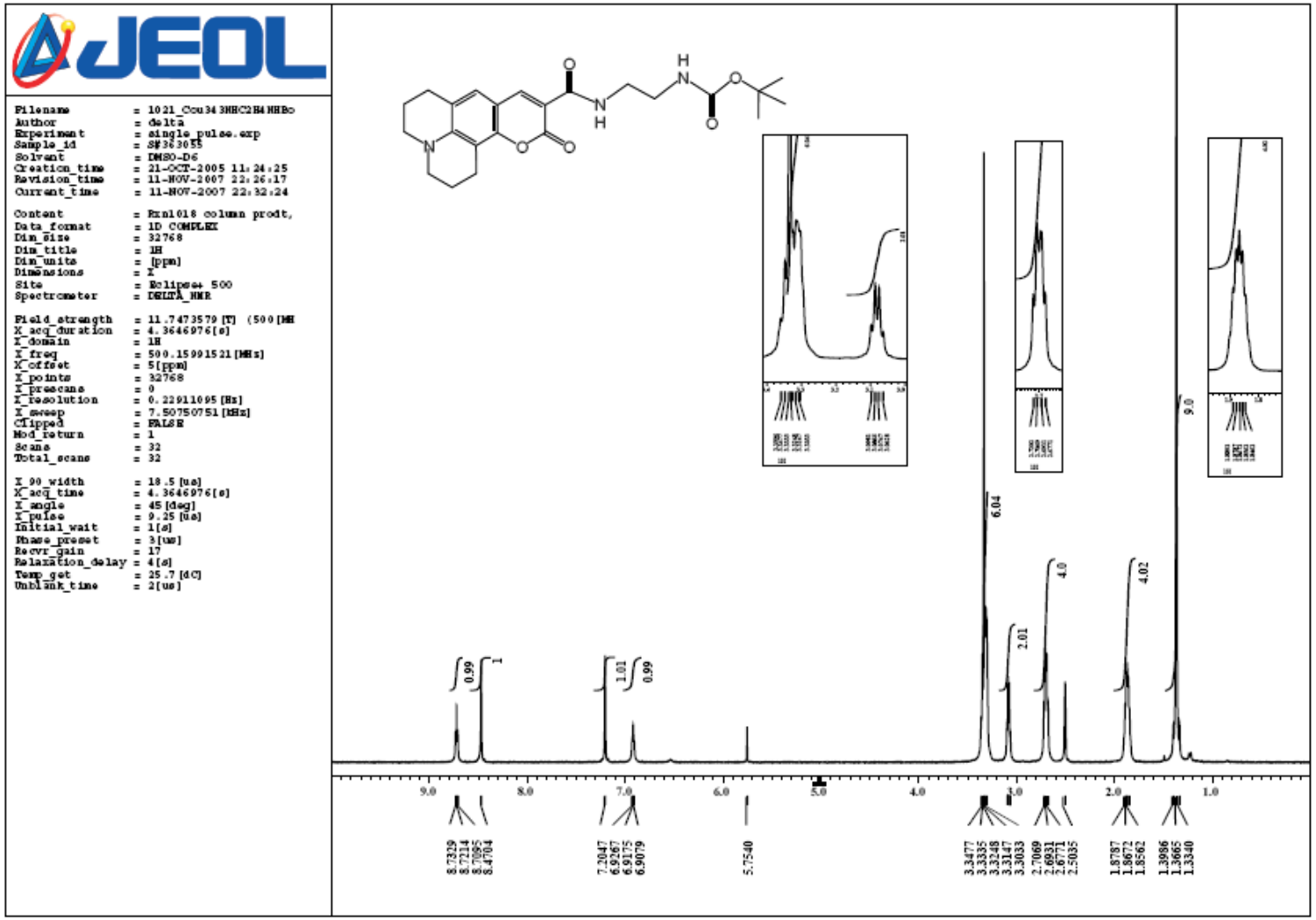


^{1}H-^{13}C HMBC NMR in DMSO-d_6 for compound **4a**

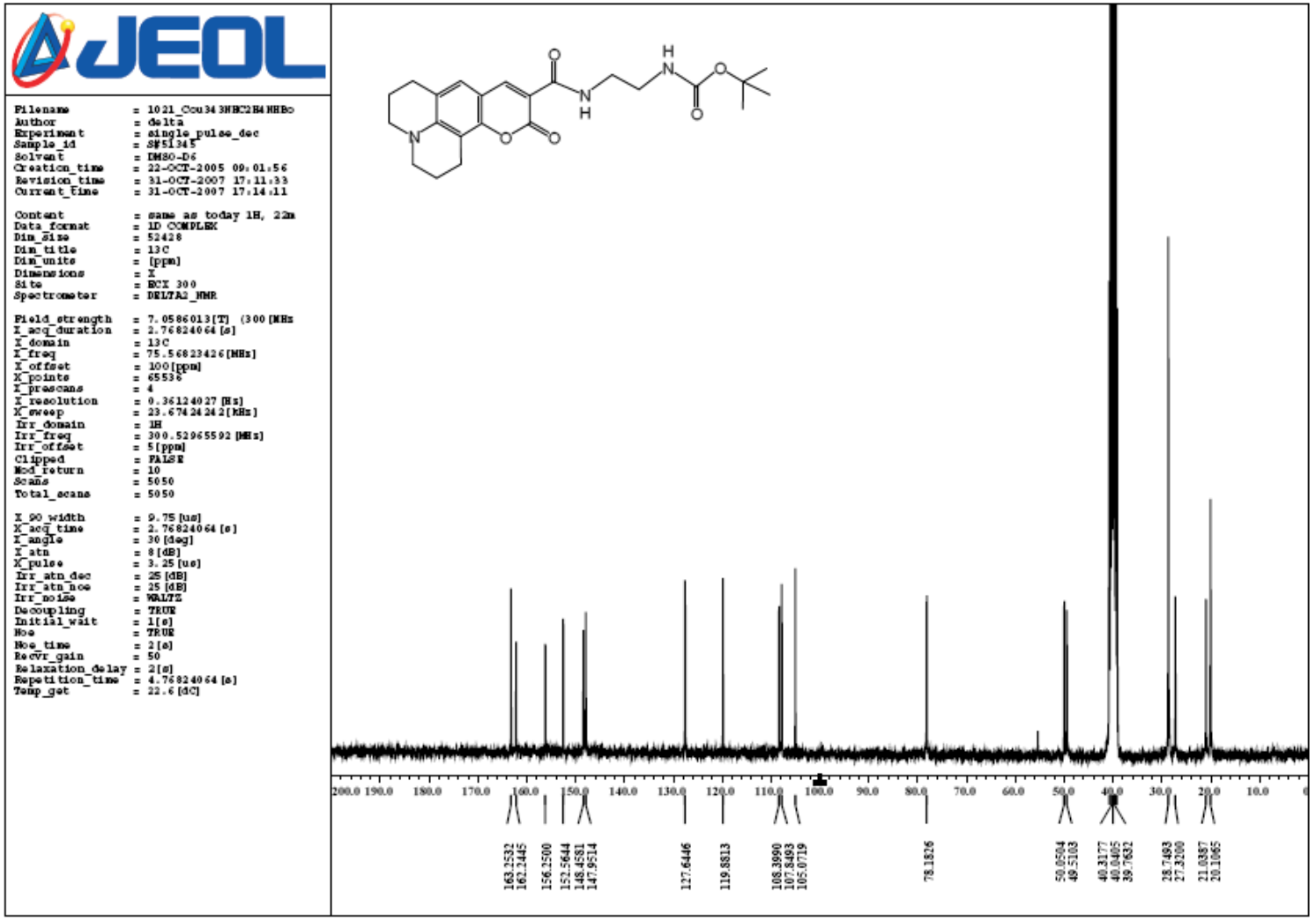



```
Filename              = 1204_DonorNH2_CA_DMSO
Author                = delta
Experiment            = hmbc_pfg.exp
Sample_id             = 1204
Solvent               = DMSO-D6
Creation_time         =  5-DEC-2005 09:20:13
Revision_time         =  3-NOV-2007 21:36:36
Current_time          =  3-NOV-2007 21:39:41

Content               = Donor CAcid, as 1115
Data_format           = 2D REAL REAL
Dim_size              = 1638, 512
Dim_title             = 1H 13C
Dim_units             = [ppm]  [ppm]
Dimensions            = X Y
Site                  = RCI 300
Spectrometer          = DELTA2_NMR

Field_strength        = 7.0586013[T]  (300[MHz
X_acq_duration        = 0.6053888[s]
X_domain              = 1H
X_freq                = 300.52965592[MHz]
X_offset              = 4.50075[ppm]
X_points              = 2048
X_prescans            = 4
X_resolution          = 1.65183102[Hz]
X_sweep               = 3.38294993[kHz]
Y_domain              = 13C
Y_freq                = 75.56823426[MHz]
Y_offset              = 90.00128[ppm]
Y_points              = 256
Y_prescans            = 0
Y_resolution          = 47.24540397[Hz]
Y_sweep               = 12.09482342[kHz]
Tri_domain            = 1H
Tri_freq              = 300.52965592[MHz]
Tri_offset            = 5[ppm]
Clipped               = FALSE
Mod_return            = 1
Scans                 = 68
Total_scans           = 17408

X_acq_time            = 0.6053888[s]
X_atn                 = 4[dB]
X_pulse               = 13.01[us]
Y_acq_time            = 21.16608[ms]
Y_atn                 = 8[dB]
Y_pulse               = 9.75[us]
Tri_mode              = Off
Dante_preset          = FALSE
Delta                 = 62.5[ms]
Grad_1                = 1[ms]
Grad_1_amp            = 60[%]
Grad_2                = 1[ms]
Grad_2_amp            = 60[%]
Grad_3                = 1[ms]
Grad_3_amp            = 30.18108652[%]
Grad_recover          = 0.1[ms]
Grad_selection        = 13C = 1.988:1.98
Grad_shape            = SINE
Initial_wait          = 1[s]
J_constant            = 140[Hz]
Long_range_J          = 8[Hz]
Recvr_gain            = 50
Refocus_comp          = 2.57142857[ms]
Relaxation_delay      = 1.5[s]
Repetition_time       = 2.1053888[s]
T1                    = 1[us]
```

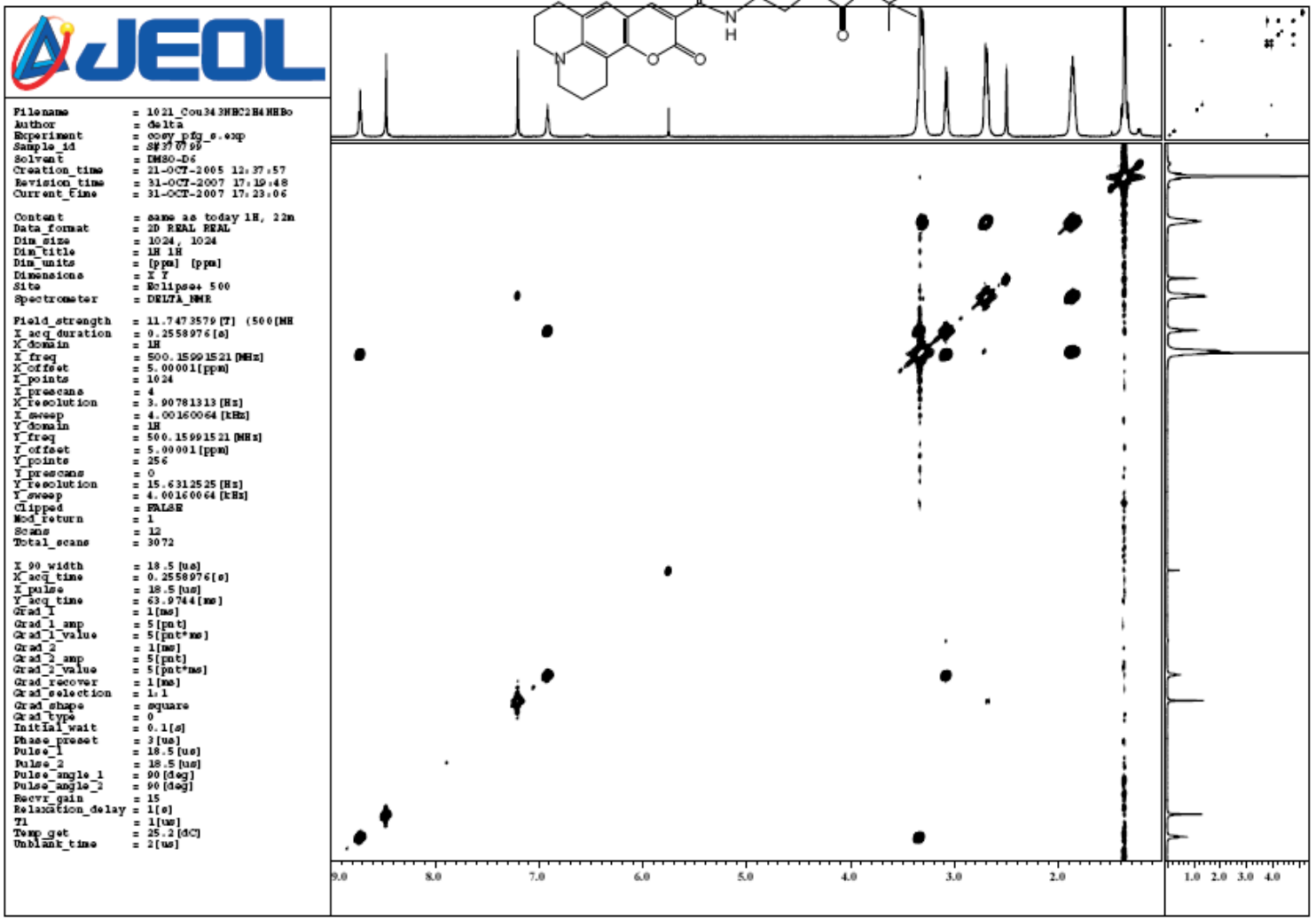
^{1}H NMR in DMSO-d_6 for compound **5**



^{13}C NMR in DMSO-d_6 for compound **5**

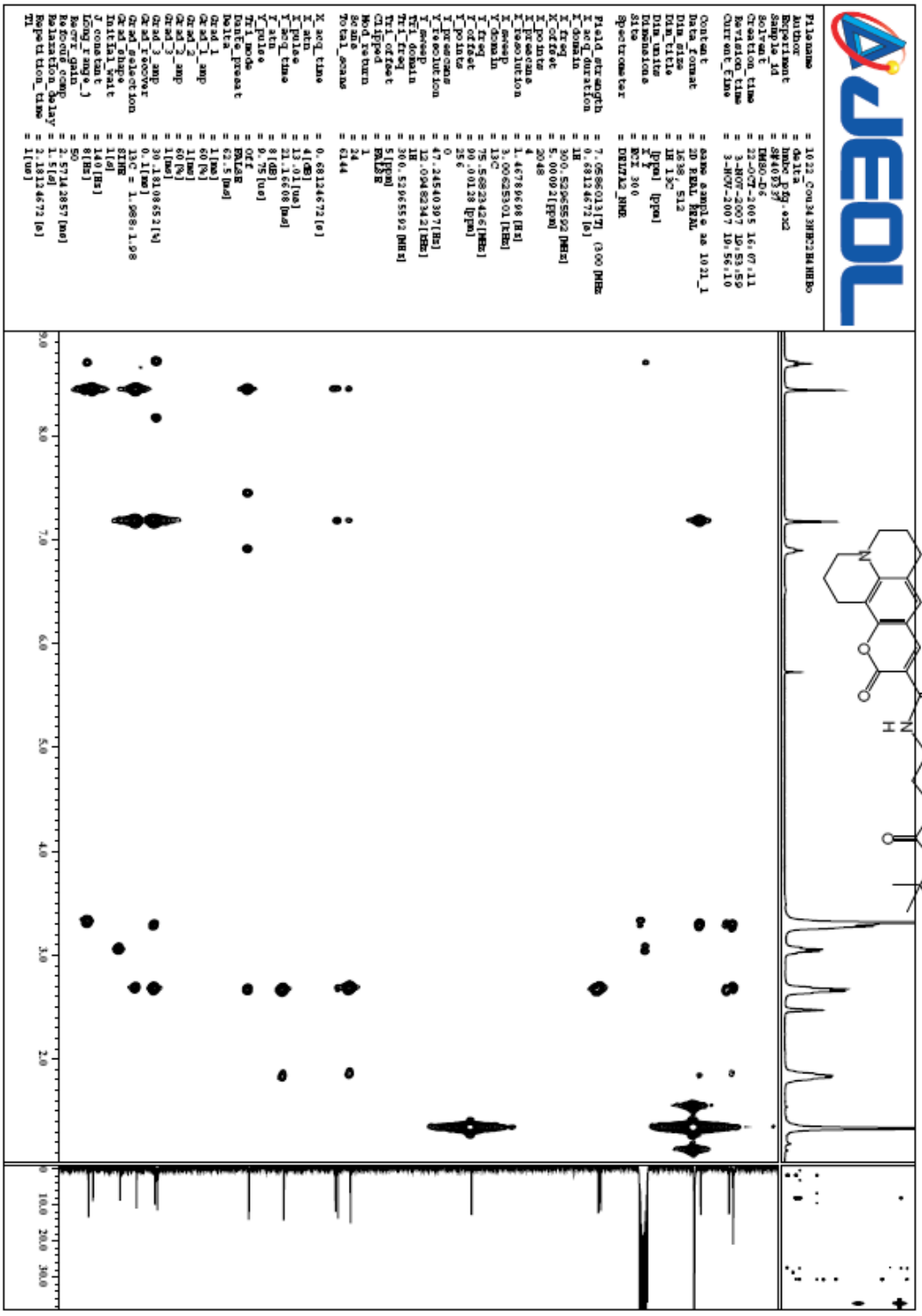


^{1}H-^{1}H COSY NMR in DMSO-d_6 for compound 5

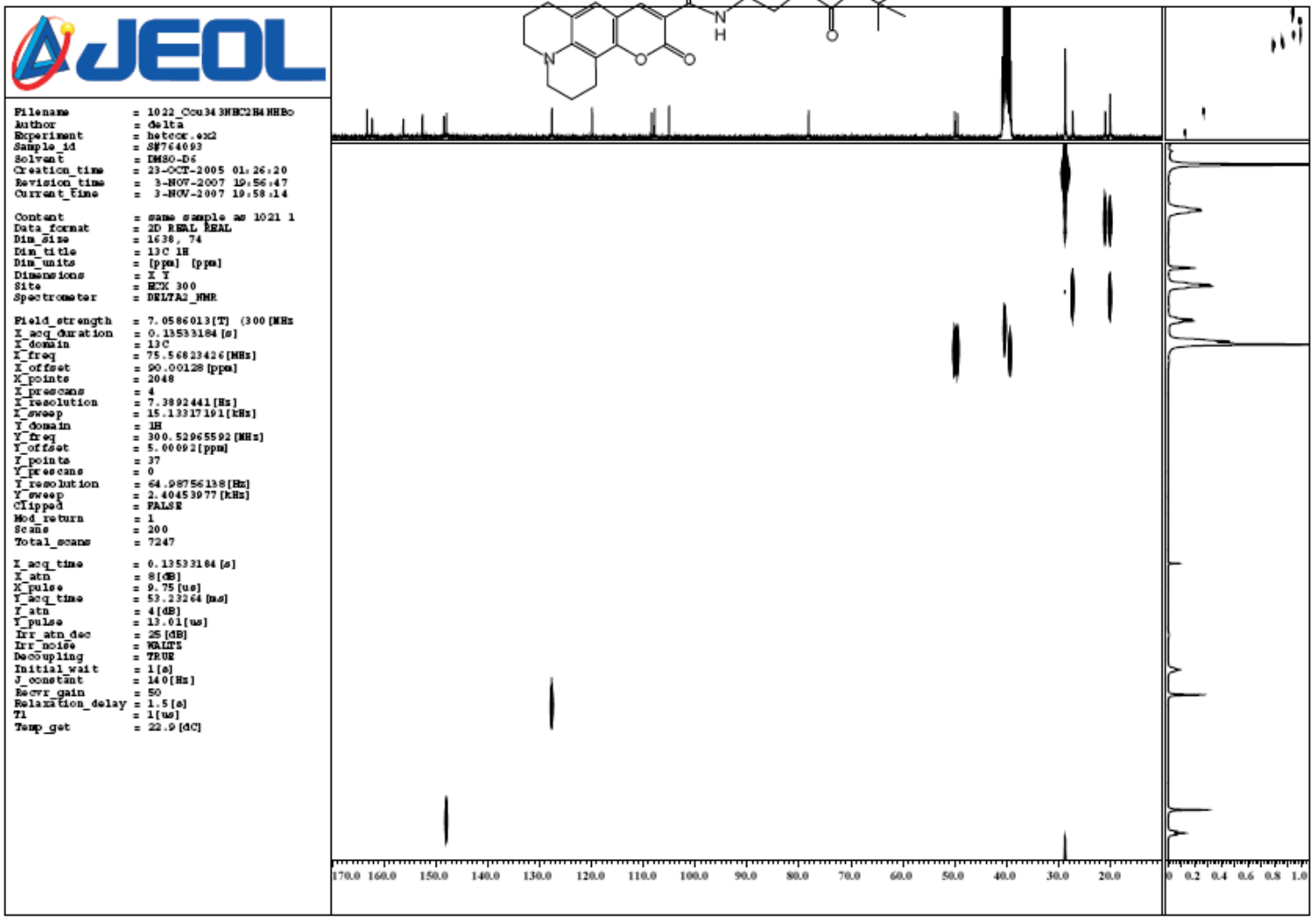


```
Filename          = 1021_Cou34JHBC2H4NHBo
Author            = delta
Experiment        = cosy.ptg_s.exp
Sample_id         = SH270799
Solvent           = DMSO-D6
Creation_time     = 21-OCT-2005 12:37:57
Revision_time     = 31-OCT-2007 17:19:48
Current_time      = 31-OCT-2007 17:23:06

Content           = same as today 1H, 22m
Data_format       = 2D REAL REAL
Dim_size          = 1024, 1024
Dim_title         = 1H 1H
Dim_units         = [ppm] [ppm]
Dimensions        = X Y
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.2558976[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.00001[ppm]
X_points          = 1024
X_prescans        = 4
X_resolution      = 3.90781313[Hz]
X_sweep           = 4.00160064[kHz]
Y_domain          = 1H
Y_freq            = 500.15991521[MHz]
Y_offset          = 5.00001[ppm]
Y_points          = 256
Y_prescans        = 0
Y_resolution      = 15.6312525[Hz]
Y_sweep           = 4.00160064[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 12
Total_scans       = 3072

X_90_width        = 18.5[us]
X_acq_time        = 0.2558976[s]
X_pulse           = 18.5[us]
Y_acq_time        = 63.9744[ms]
Grad_1            = 1[ms]
Grad_1_amp        = 5[pnt]
Grad_1_value      = 5[pnt*ms]
Grad_2            = 1[ms]
Grad_2_amp        = 5[pnt]
Grad_2_value      = 5[pnt*ms]
Grad_recover      = 1[ms]
Grad_selection    = 1:1
Grad_shape        = square
Grad_type         = 0
Initial_wait      = 0.1[s]
Phase_preset      = 3[us]
Pulse_1           = 18.5[us]
Pulse_2           = 18.5[us]
Pulse_angle_1     = 90[deg]
Pulse_angle_2     = 90[deg]
Recvr_gain        = 15
Relaxation_delay  = 1[s]
T1                = 1[us]
Temp_get          = 25.2[dC]
Unblank_time      = 2[us]
```

^{1}H-^{13}C HMBC NMR in DMSO-d_6 for compound 5

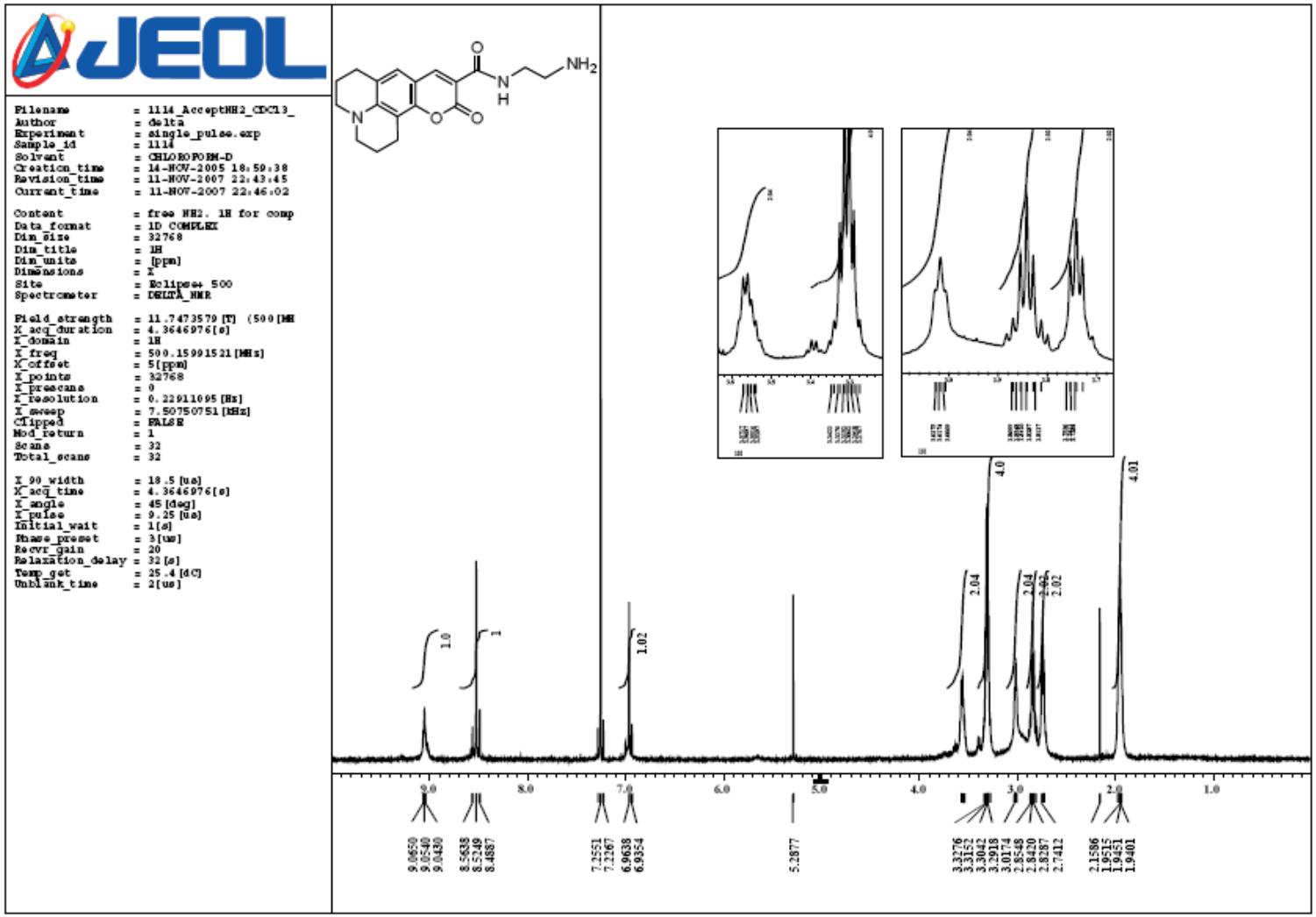


^{13}C-^{1}H Hetcor NMR in DMSO-d_6 for compound 5

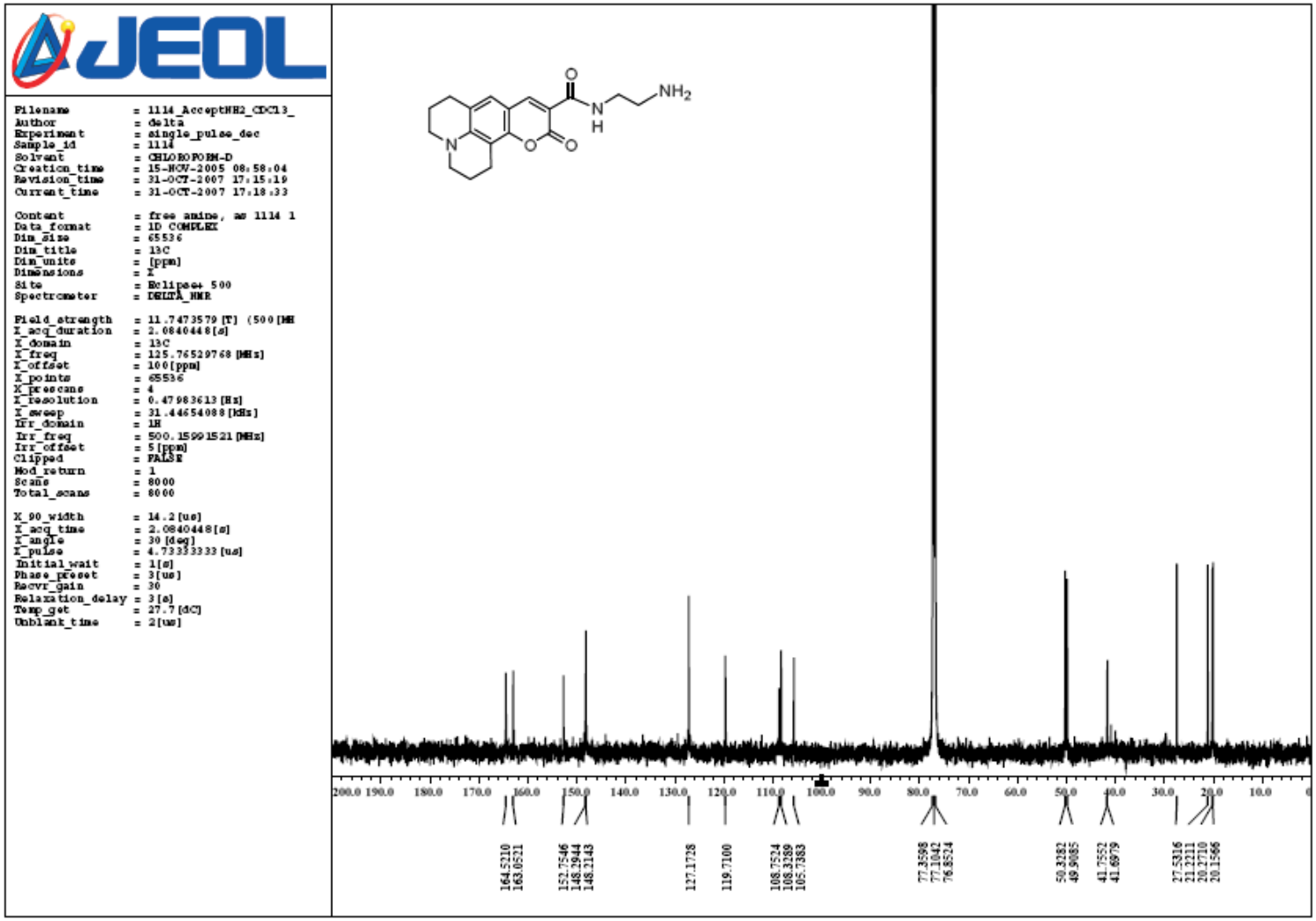


```
Filename          = 1022_Cou34NHC2H4NHBo
Author            = delta
Experiment        = hetcor.ex2
Sample_id         = SM764093
Solvent           = DMSO-D6
Creation_time     = 29-OCT-2005 01:26:20
Revision_time     =  3-NOV-2007 19:56:47
Current_time      =  3-NOV-2007 19:58:14

Content           = same sample as 1021 1
Data_format       = 2D REAL REAL
Dim_size          = 1638, 74
Dim_title         = 13C 1H
Dim_units         = [ppm]  [ppm]
Dimensions        = X Y
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T]  (300[MHz
X_acq_duration    = 0.13533184[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 90.00128[ppm]
X_points          = 2048
X_prescans        = 4
X_resolution      = 7.3892441[Hz]
X_sweep           = 15.13317191[kHz]
Y_domain          = 1H
Y_freq            = 300.52965592[MHz]
Y_offset          = 5.00092[ppm]
Y_points          = 37
Y_prescans        = 0
Y_resolution      = 64.98756138[Hz]
Y_sweep           = 2.40453977[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 200
Total_scans       = 7247

X_acq_time        = 0.13533184[s]
X_atn             = 8[dB]
X_pulse           = 9.75[us]
Y_acq_time        = 53.23264[ms]
Y_atn             = 4[dB]
Y_pulse           = 13.01[us]
Irr_atn_dec       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
J_constant        = 140[Hz]
Recvr_gain        = 50
Relaxation_delay  = 1.5[s]
T1                = 1[us]
Temp_get          = 22.9[dC]
```

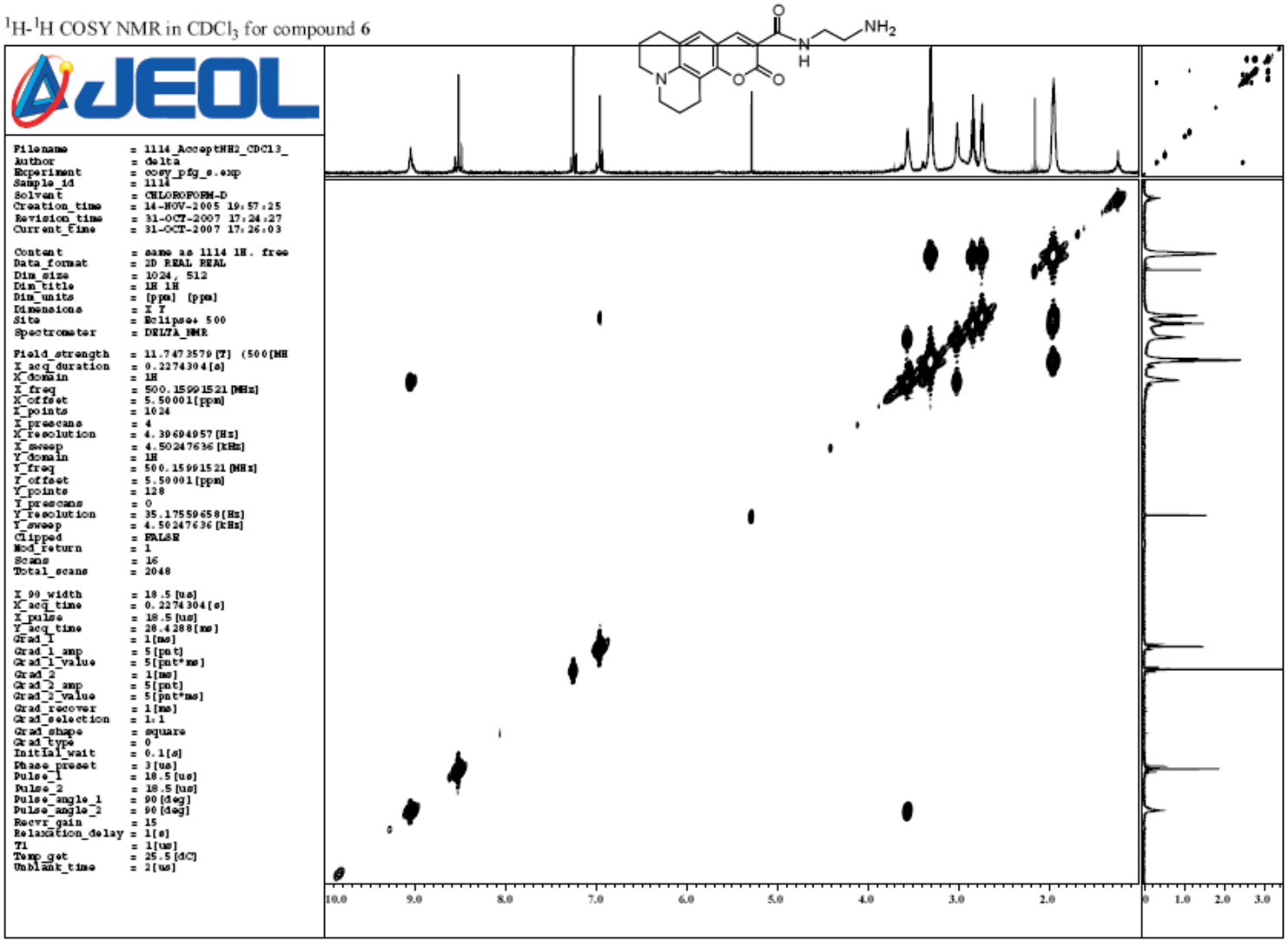
^{1}H NMR in $CDCl_3$ for compound **6**



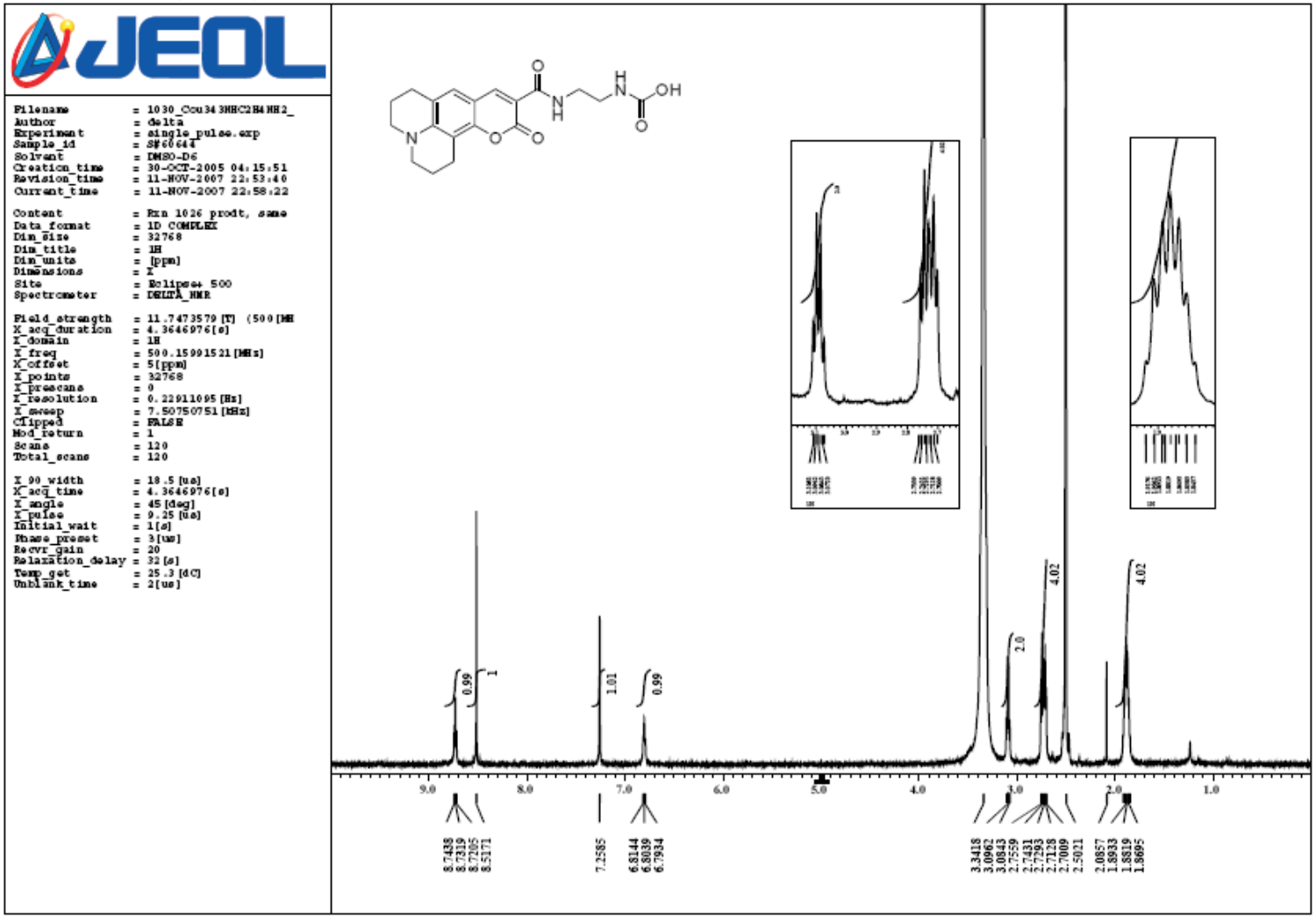
^{13}C COSY NMR in $CDCl_3$ for compound **6**



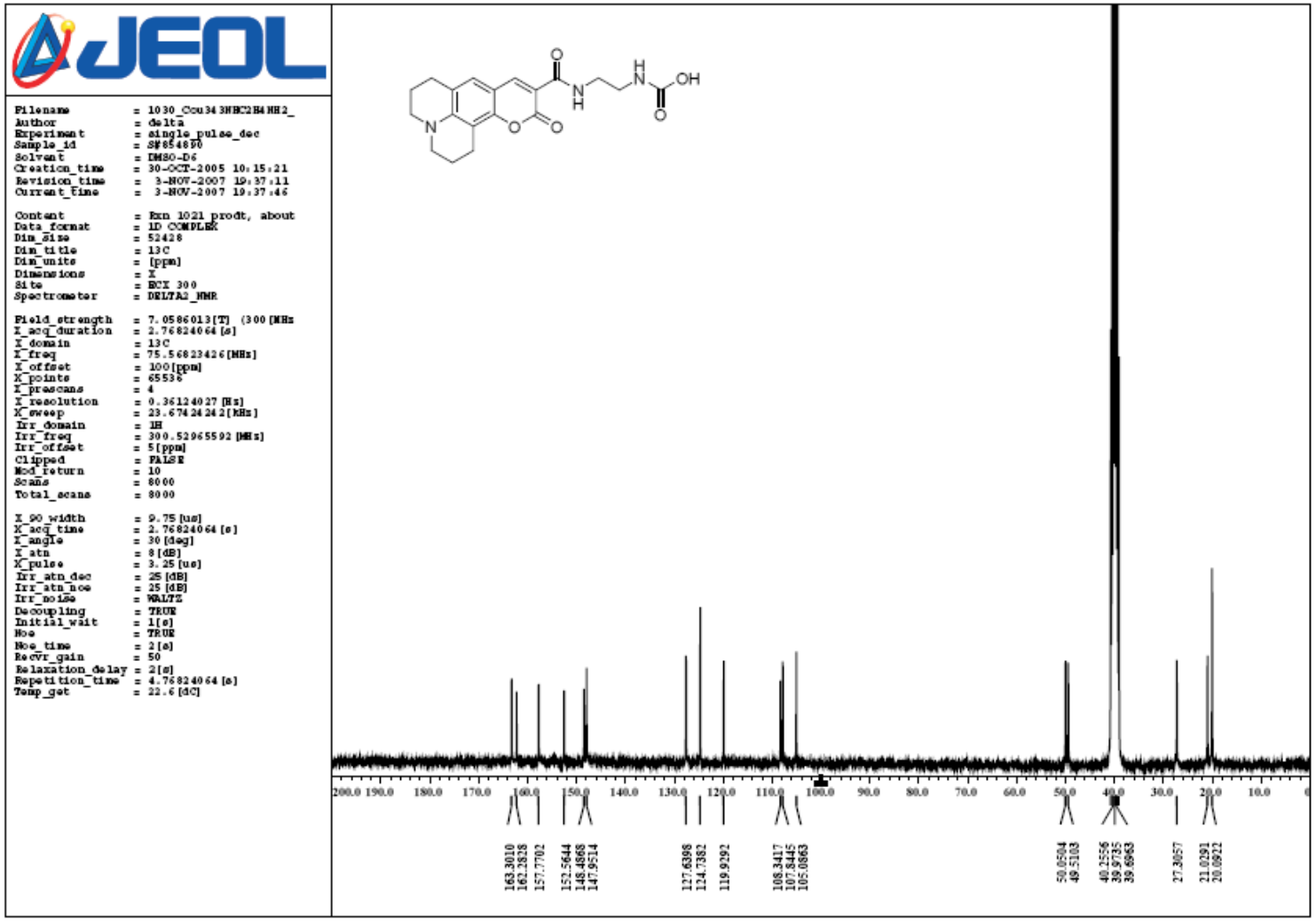
^{1}H-^{1}H COSY NMR in $CDCl_3$ for compound 6



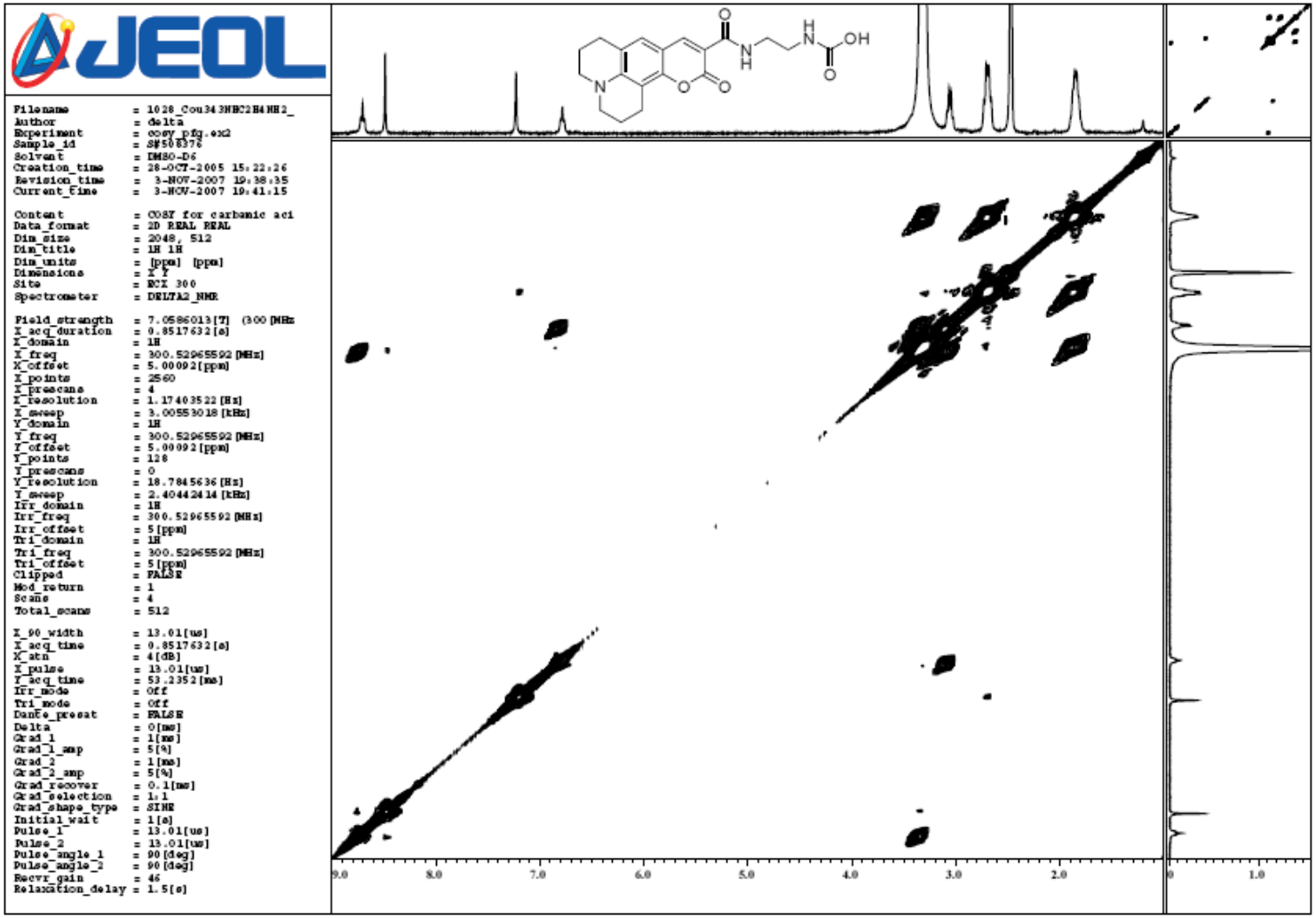
^{1}H NMR in DMSO-d_6 for compound **6a**



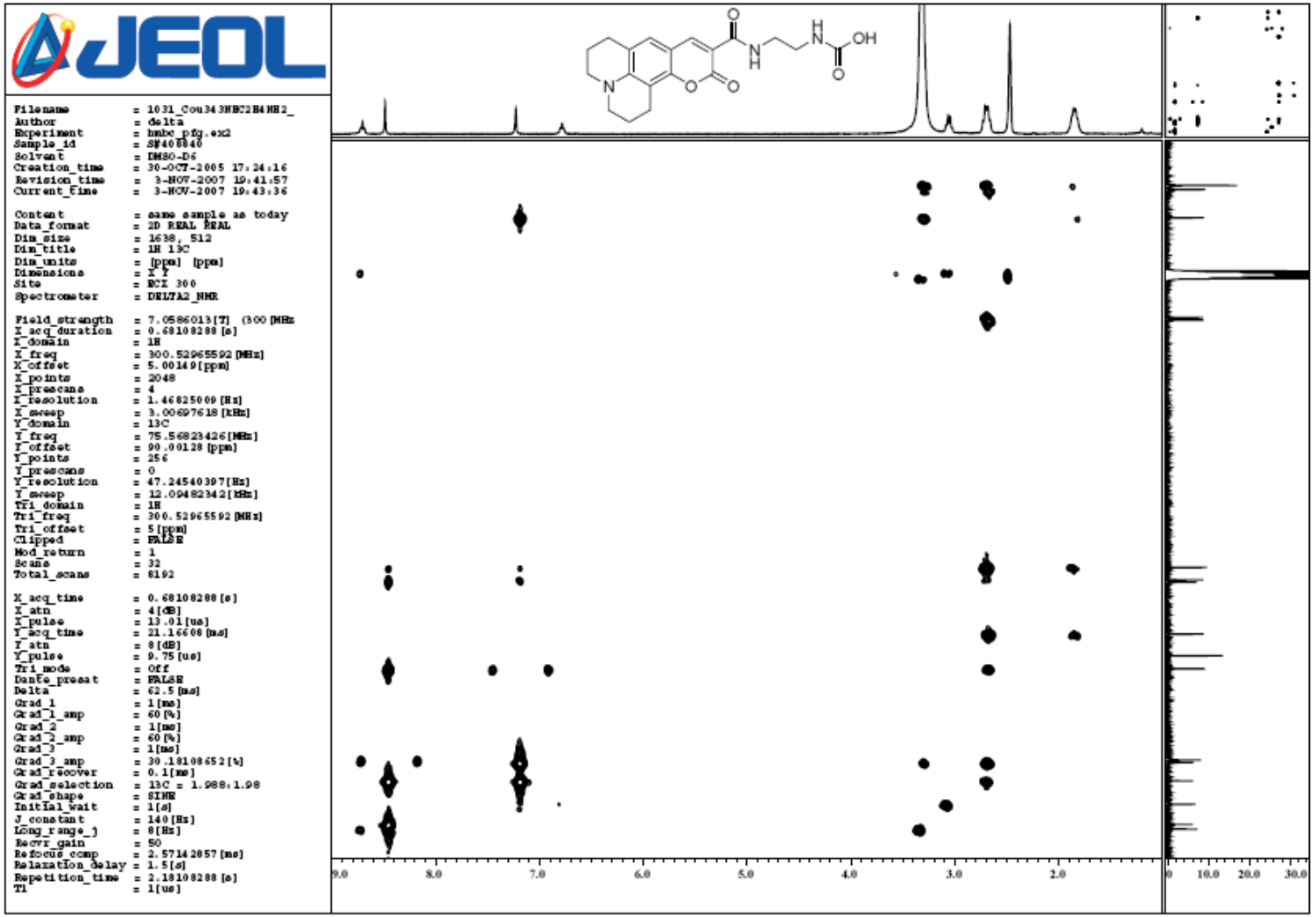
^{13}C NMR in DMSO-d_6 for compound **6a**



^{1}H-^{1}H COSY NMR in DMSO-d_6 for compound **6a**

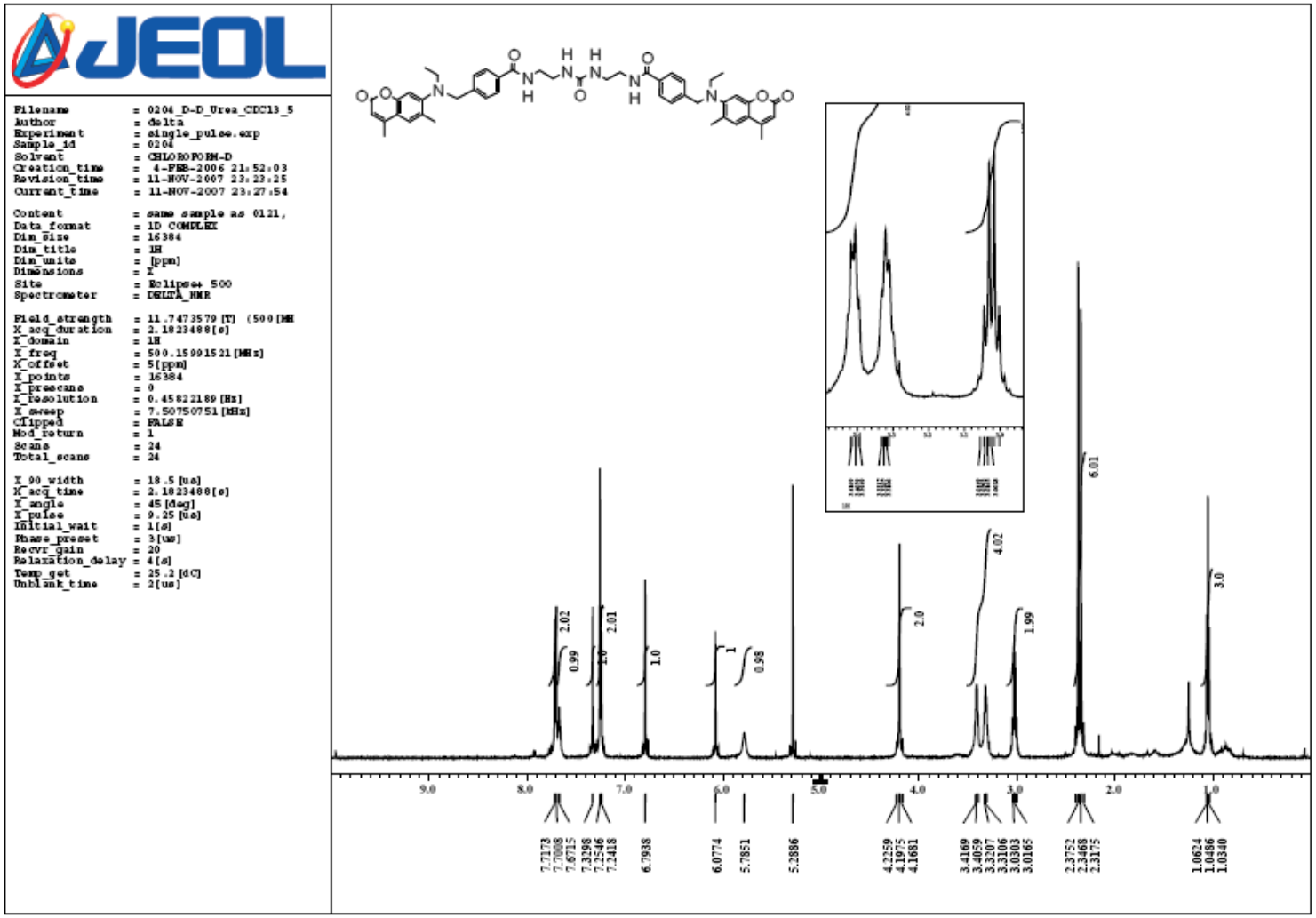


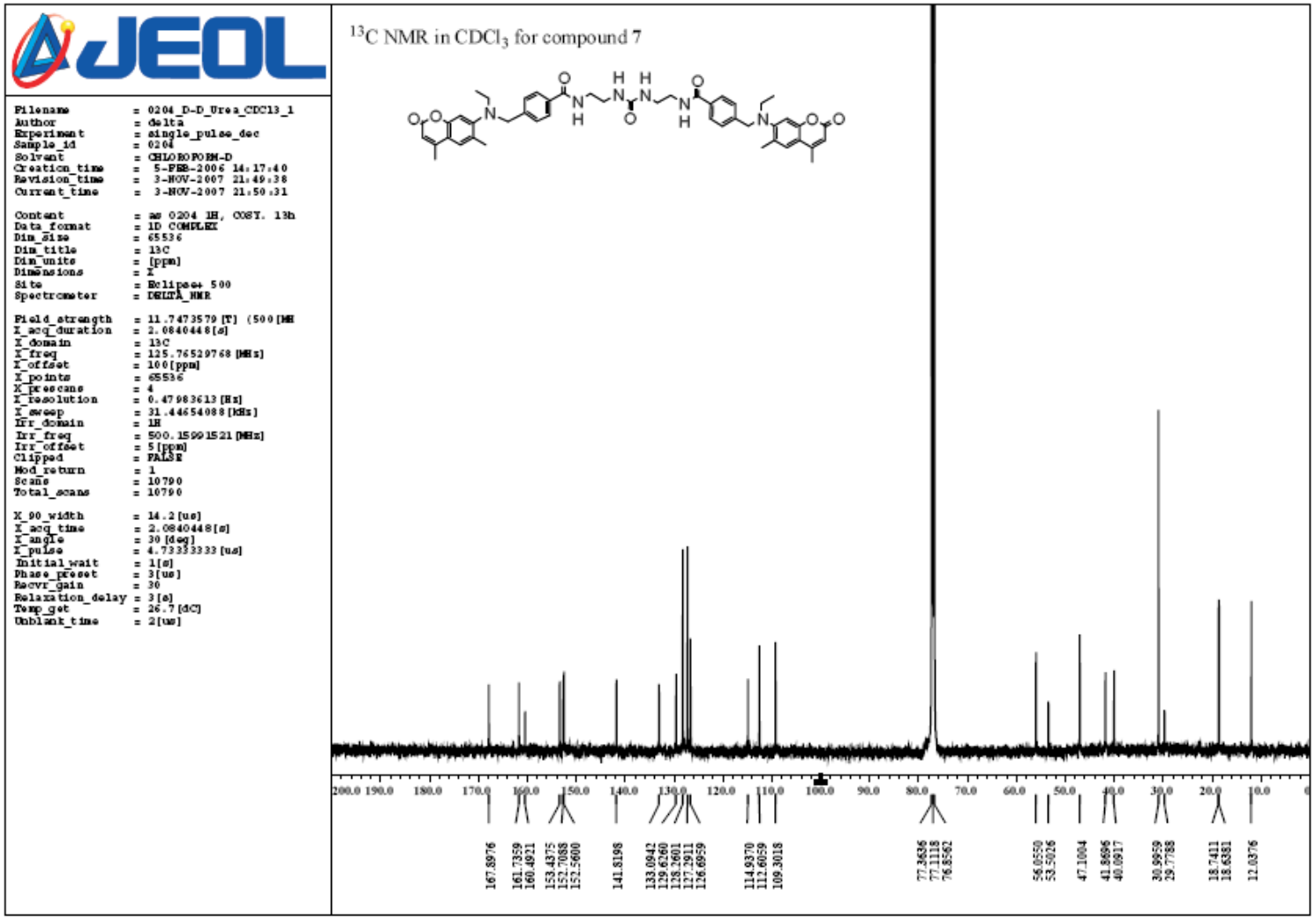
^{1}H-^{13}C HMBC NMR in DMSO-d_6 for compound **6a**



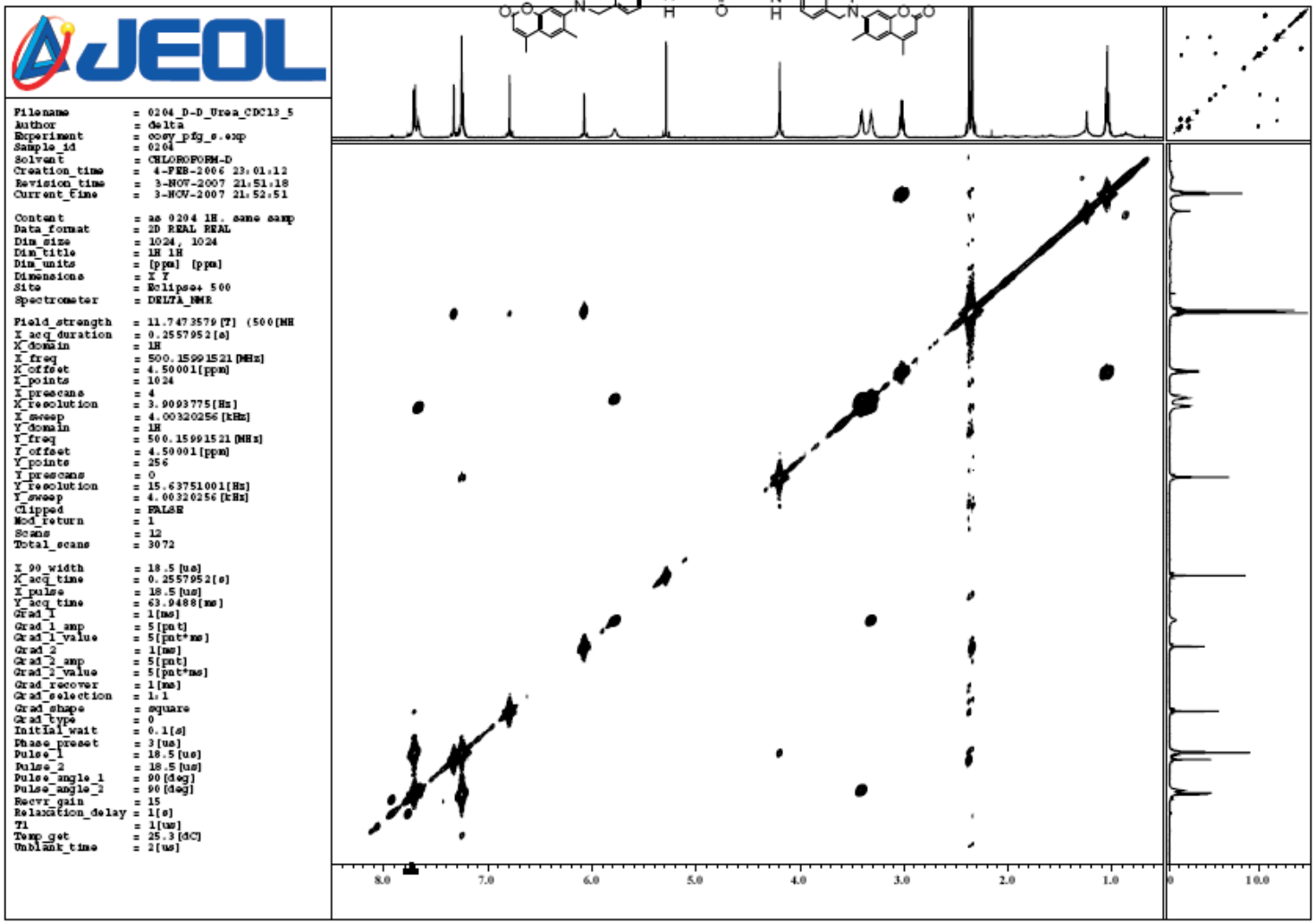
```
Filename          = 1031_Cou343HBC2H4NH2_
Author            = delta
Experiment        = hmbc_pfg.ex2
Sample_id         = S#408840
Solvent           = DMSO-D6
Creation_time     = 30-OCT-2005 17:24:16
Revision_time     =  3-NOV-2007 19:41:57
Current_time      =  3-NOV-2007 19:43:36

Content           = same sample as today
Data_format       = 2D REAL REAL
Dim_size          = 1638, 512
Dim_title         = 1H 13C
Dim_units         = [ppm] [ppm]
Dimensions        = X Y
Site              = RCI 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T]  (300[MHz
X_acq_duration    = 0.68108288[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5.00149[ppm]
X_points          = 2048
X_prescans        = 4
X_resolution      = 1.46825009[Hz]
X_sweep           = 3.00697618[kHz]
Y_domain          = 13C
Y_freq            = 75.56823426[MHz]
Y_offset          = 90.00128[ppm]
Y_points          = 256
Y_prescans        = 0
Y_resolution      = 47.24540307[Hz]
Y_sweep           = 12.09482342[kHz]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 32
Total_scans       = 8192

X_acq_time        = 0.68108288[s]
X_atn             = 4[dB]
X_pulse           = 13.01[us]
Y_acq_time        = 21.16608[ms]
Y_atn             = 8[dB]
Y_pulse           = 9.75[us]
Tri_mode          = Off
Dante_presat      = FALSE
Delta             = 62.5[ms]
Grad_1            = 1[ms]
Grad_1_amp        = 60[%]
Grad_2            = 1[ms]
Grad_2_amp        = 60[%]
Grad_3            = 1[ms]
Grad_3_amp        = 30.18108652[%]
Grad_recover      = 0.1[ms]
Grad_selection    = 13C = 1.988:1.98
Grad_shape        = SINE
Initial_wait      = 1[s]
J_constant        = 140[Hz]
LSng_range_J      = 8[Hz]
Recvr_gain        = 50
Refocus_comp      = 2.57142857[ms]
Relaxation_delay  = 1.5[s]
Repetition_time   = 2.18108288[s]
T1                = 1[us]
```

^{1}H NMR in $CDCl_3$ for compound 7



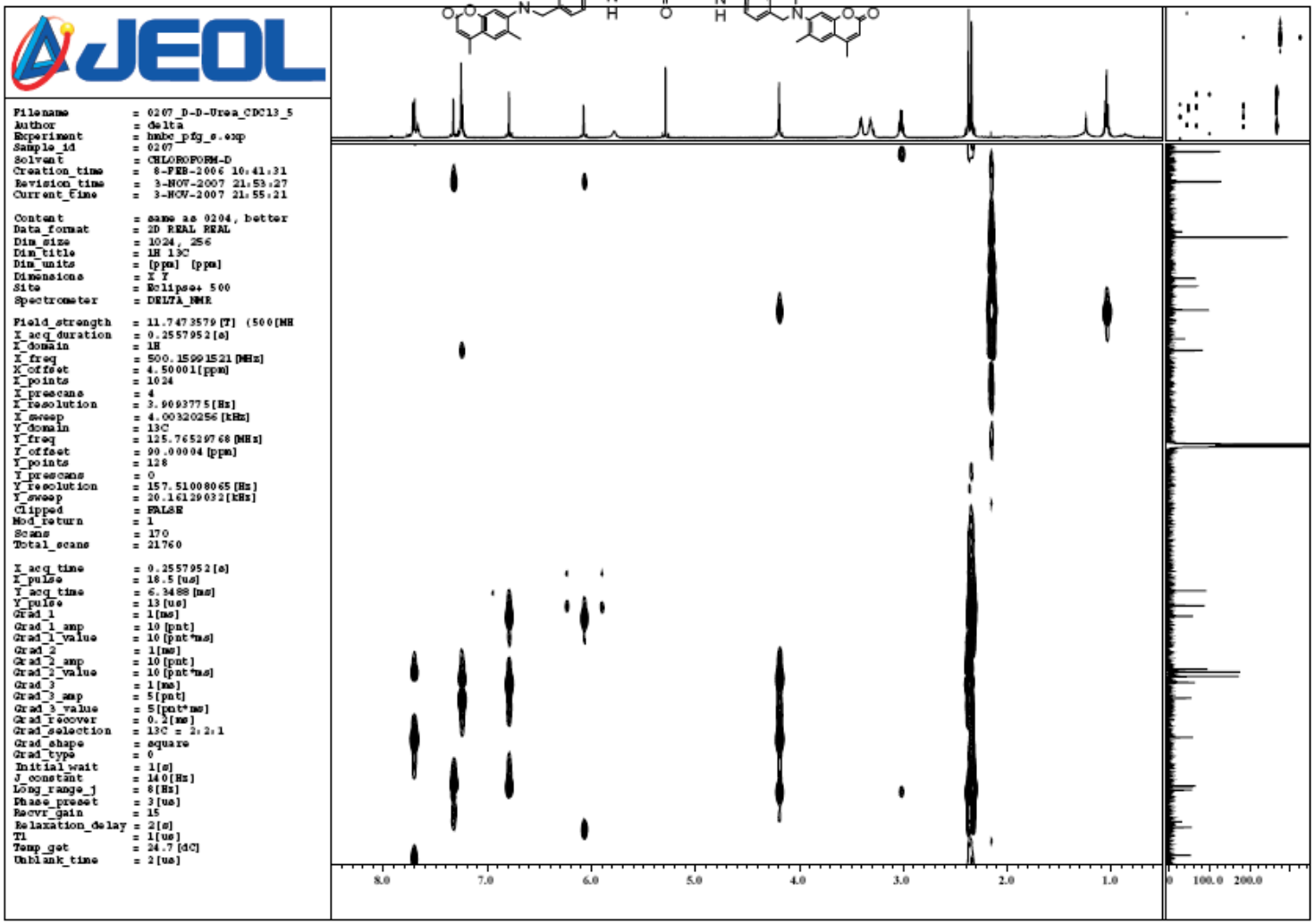

^{13}C NMR in $CDCl_3$ for compound 7
Filename = 0204_D-D_Urea_CDCl3_1
Author = delta
Experiment = single_pulse_dec
Sample_id = 0204
Solvent = CHLOROFORM-D
Creation_time = 5-FEB-2006 14:17:40
Revision_time = 3-NOV-2007 21:49:38
Current_time = 3-NOV-2007 21:50:31
Content = as 0204 1H, COST. 13h
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579 [T] (500 [MH
X_acq_duration = 2.0840448 [s]
X_domain = 13C
X_freq = 125.76529768 [MHz]
X_offset = 100 [ppm]
X_points = 65536
X_prescans = 4
X_resolution = 0.47983613 [Hz]
X_sweep = 31.44654088 [kHz]
Irr_domain = 1H
Irr_freq = 500.15991521 [MHz]
Irr_offset = 5 [ppm]
Clipped = FALSE
Mod_return = 1
Scans = 10790
Total_scans = 10790
X_90_width = 14.2 [us]
X_acq_time = 2.0840448 [s]
X_angle = 30 [deg]
X_pulse = 4.73333333 [us]
Initial_wait = 1 [s]
Phase_preset = 3 [us]
Recvr_gain = 30
Relaxation_delay = 3 [s]
Temp_get = 26.7 [dC]
Unblank_time = 2 [us]
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
167.8976
161.7359
160.4921
153.4375
152.7088
152.5600
141.8198
133.0942
129.6260
128.1601
127.2911
126.6959
114.9370
112.6059
109.3018
77.3636
77.1118
76.8562
56.0550
53.5026
47.1004
41.8696
40.0917
30.9959
29.7788
18.7411
18.6381
12.0376

H-H COSY NMR in $CDCl_3$ for compound 7



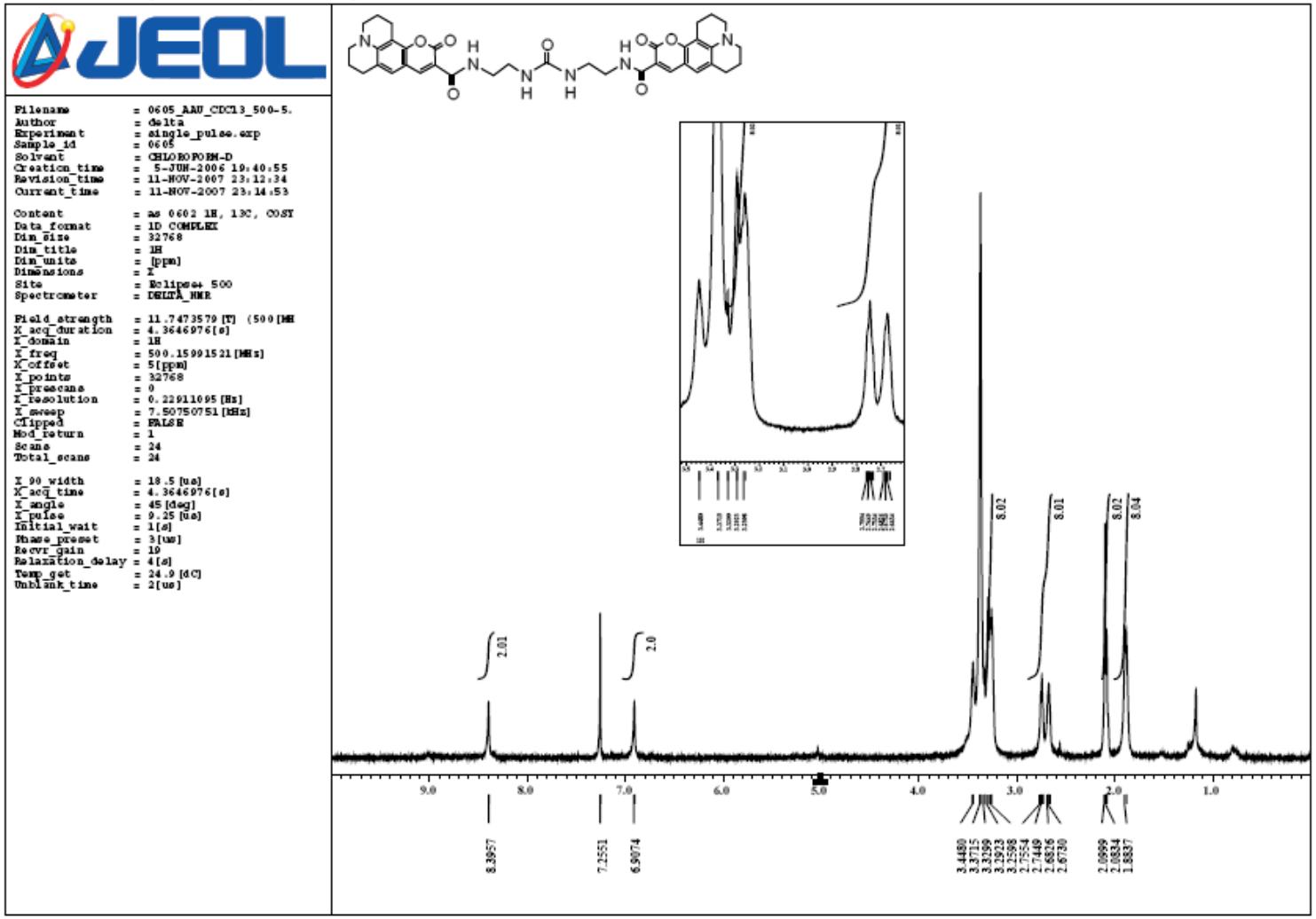
```
Filename          = 0204_D-D_Urea_CDCl3_5
Author            = delta
Experiment        = cosy_pfg_s.exp
Sample_id         = 0204
Solvent           = CHLOROFORM-D
Creation_time     =  4-FEB-2006 23:01:12
Revision_time     =  3-NOV-2007 21:51:18
Current_time      =  3-NOV-2007 21:52:51

Content           = as 0204 1H. same samp
Data_format       = 2D REAL REAL
Dim_size          = 1024, 1024
Dim_title         = 1H 1H
Dim_units         = [ppm]  [ppm]
Dimensions        = X Y
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.2557952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 4.50001[ppm]
X_points          = 1024
X_prescans        = 4
X_resolution      = 3.9093775[Hz]
X_sweep           = 4.00320256[kHz]
Y_domain          = 1H
Y_freq            = 500.15991521[MHz]
Y_offset          = 4.50001[ppm]
Y_points          = 256
Y_prescans        = 0
Y_resolution      = 15.63751001[Hz]
Y_sweep           = 4.00320256[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 12
Total_scans       = 3072

X_90_width        = 18.5[us]
X_acq_time        = 0.2557952[s]
X_pulse           = 18.5[us]
Y_acq_time        = 63.9488[ms]
Grad_1            = 1[ms]
Grad_1_amp        = 5[pnt]
Grad_1_value      = 5[pnt*ms]
Grad_2            = 1[ms]
Grad_2_amp        = 5[pnt]
Grad_2_value      = 5[pnt*ms]
Grad_recover      = 1[ms]
Grad_selection    = 1:1
Grad_shape        = square
Grad_type         = 0
Initial_wait      = 0.1[s]
Phase_preset      = 3[us]
Pulse_1           = 18.5[us]
Pulse_2           = 18.5[us]
Pulse_angle_1     = 90[deg]
Pulse_angle_2     = 90[deg]
Recvr_gain        = 15
Relaxation_delay  = 1[s]
T1                = 1[us]
Temp_get          = 25.3[dC]
Unblank_time      = 2[us]
```

HMBC NMR in $CDCl_3$ for compound 7

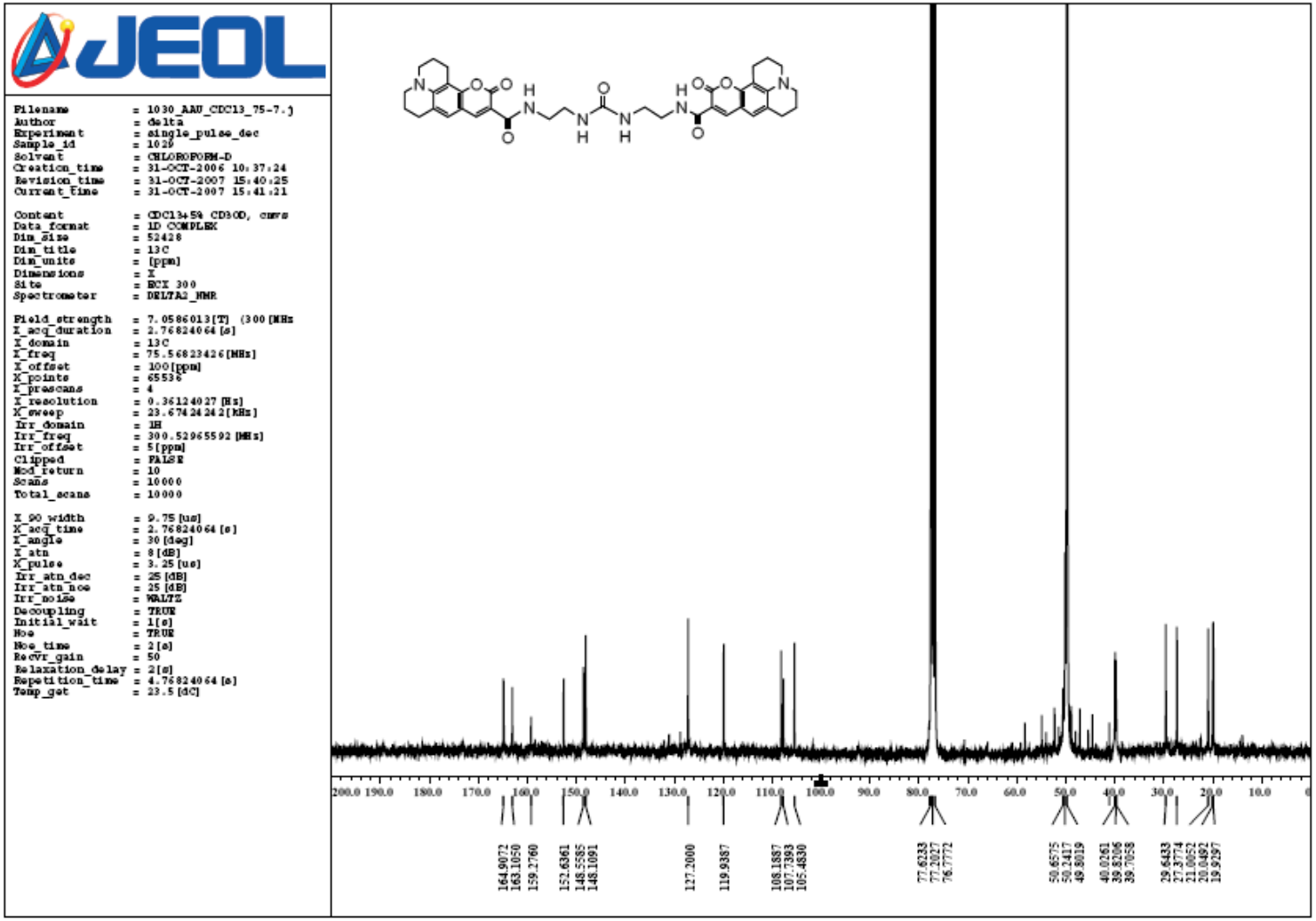


```
Filename          = 0207_D-D-Urea_CDCl3_5
Author            = delta
Experiment        = hmbc_pfg_e.exp
Sample_id         = 0207
Solvent           = CHLOROFORM-D
Creation_time     =  8-FEB-2006 10:41:31
Revision_time     =  3-NOV-2007 21:53:27
Current_time      =  3-NOV-2007 21:55:21

Content           = same as 0204, better
Data_format       = 2D REAL REAL
Dim_size          = 1024, 256
Dim_title         = 1H 13C
Dim_units         = [ppm] [ppm]
Dimensions        = X Y
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.2557952[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 4.50001[ppm]
X_points          = 1024
X_prescans        = 4
X_resolution      = 3.9093775[Hz]
X_sweep           = 4.00320256[kHz]
Y_domain          = 13C
Y_freq            = 125.76529768[MHz]
Y_offset          = 90.00004[ppm]
Y_points          = 128
Y_prescans        = 0
Y_resolution      = 157.51008065[Hz]
Y_sweep           = 20.16129032[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 170
Total_scans       = 21760

X_acq_time        = 0.2557952[s]
X_pulse           = 18.5[us]
Y_acq_time        = 6.3488[ms]
Y_pulse           = 13[us]
GRad_1            = 1[ms]
Grad_1_amp        = 10[pnt]
Grad_1_value      = 10[pnt*ms]
Grad_2            = 1[ms]
Grad_2_amp        = 10[pnt]
Grad_2_value      = 10[pnt*ms]
Grad_3            = 1[ms]
Grad_3_amp        = 5[pnt]
Grad_3_value      = 5[pnt*ms]
Grad_recover      = 0.2[ms]
Grad_selection    = 13C = 2:2:1
Grad_shape        = square
Grad_type         = 0
Initial_wait      = 1[s]
J_constant        = 140[Hz]
Long_range_J      = 8[Hz]
Phase_preset      = 3[us]
Recvr_gain        = 15
Relaxation_delay  = 2[s]
T1                = 1[us]
Temp_get          = 24.7[dC]
Unblank_time      = 2[us]
```

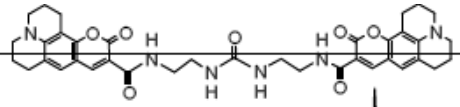
^{1}H NMR in $CDCl_3$ + 10% CD_3OD for compound **8**



^{13}C NMR in $CDCl_3$ + 10% CD_3OD for compound **8**

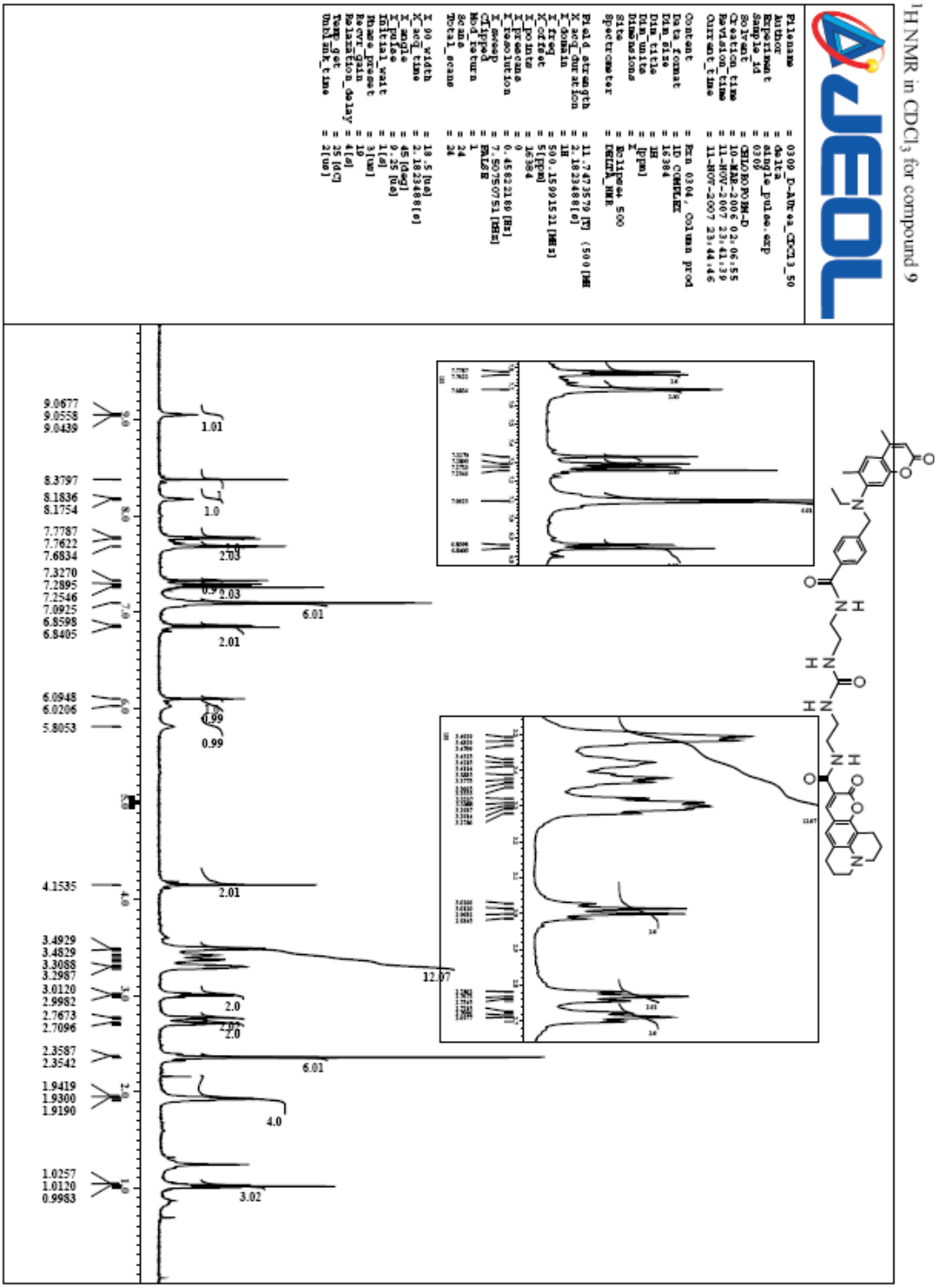


^{1}H-^{1}H COSY NMR in $CDCl_3$ + 10% CD_3OD for compound **8**

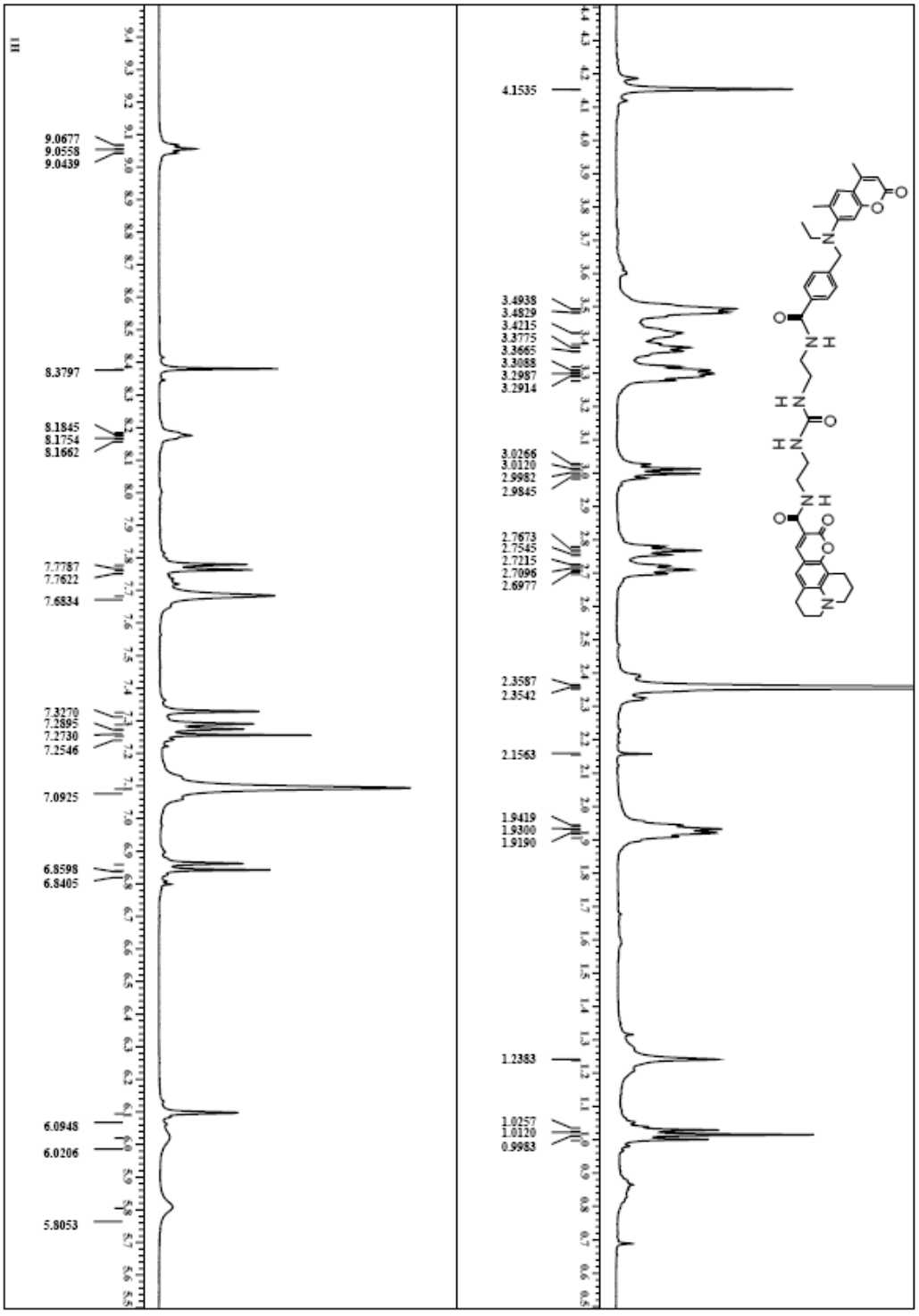



```
Filename          = 0602_AAU_CDCl3_500-2.
Author            = delta
Experiment        = cosy_pfg_s.exp
Sample_id         = 0602
Solvent           = CHLOROFORM-D
Creation_time     =  2-JUN-2006 23:25:37
Revision_time     =  3-NOV-2007 19:09:14
Current_time      =  3-NOV-2007 19:11:31

Content           = as 0602 1H, + little
Data_format       = 2D REAL REAL
Dim_size          = 1024, 512
Dim_title         = 1H 1H
Dim_units         = [ppm]  [ppm]
Dimensions        = X Y
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.2046976[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 1024
X_prescans        = 4
X_resolution      = 4.88525513[Hz]
X_sweep           = 5.00250125[kHz]
Y_domain          = 1H
Y_freq            = 500.15991521[MHz]
Y_offset          = 5[ppm]
Y_points          = 128
Y_prescans        = 0
Y_resolution      = 39.08204102[Hz]
Y_sweep           = 5.00250125[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 48
Total_scans       = 6144

X_90_width        = 18.5[us]
X_acq_time        = 0.2046976[s]
X_pulse           = 18.5[us]
Y_acq_time        = 25.5872[ms]
Grad_1            = 1[ms]
Grad_1_amp        = 5[pnt]
Grad_1_value      = 5[pnt*ms]
Grad_2            = 1[ms]
Grad_2_amp        = 5[pnt]
Grad_2_value      = 5[pnt*ms]
Grad_recover      = 1[ms]
Grad_selection    = 1:1
Grad_shape        = square
Grad_type         = 0
Initial_wait      = 0.1[s]
Phase_preset      = 3[us]
Pulse_1           = 18.5[us]
Pulse_2           = 18.5[us]
Pulse_angle_1     = 90[deg]
Pulse_angle_2     = 90[deg]
Recvr_gain        = 15
Relaxation_delay  = 1[s]
T1                = 1[us]
Temp_get          = 24.7[dC]
Unblank_time      = 2[us]
```

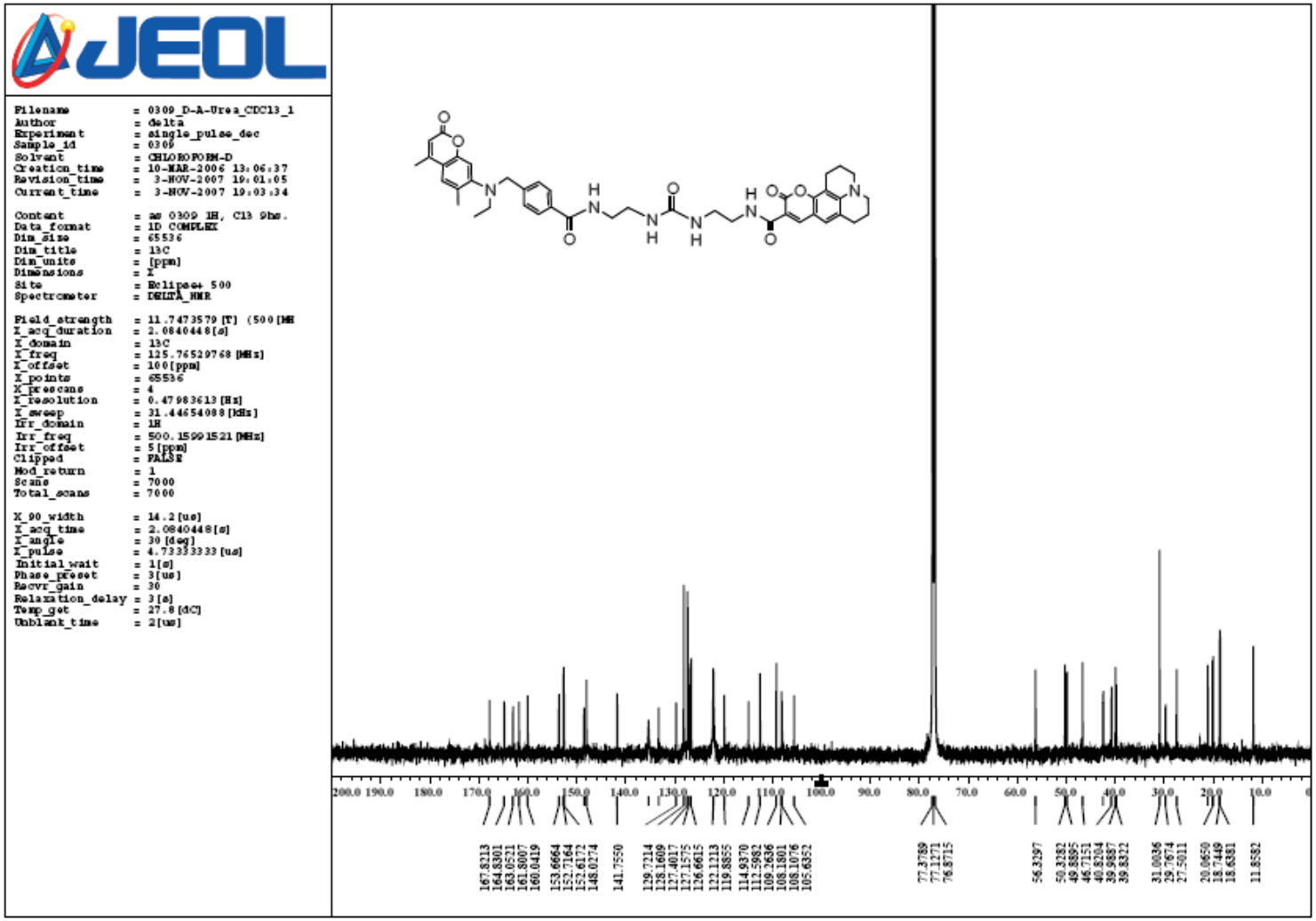
^{1}H NMR in $CDCl_3$ for compound 9



^{1}H NMR in $CDCl_3$ for compound 9

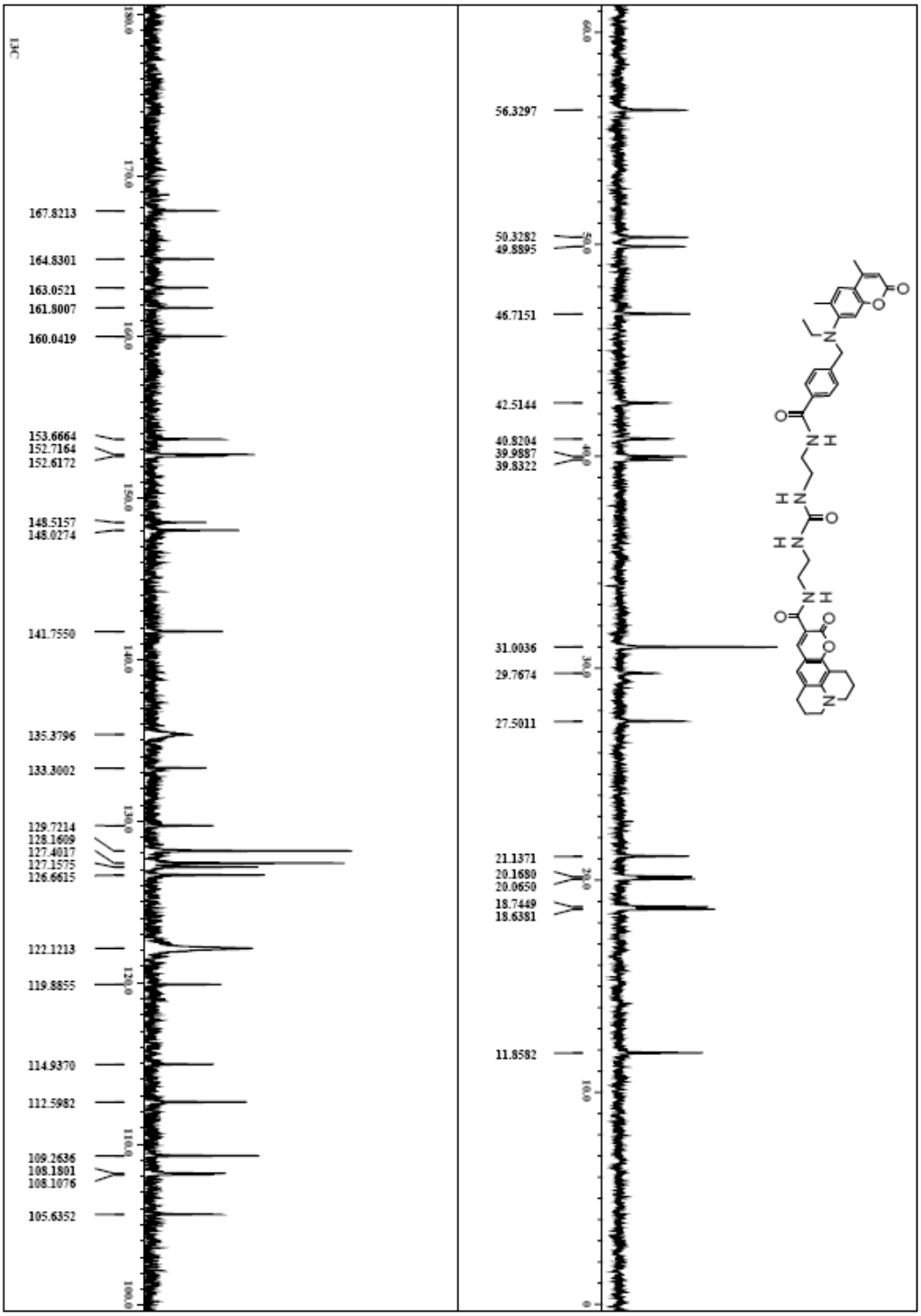


^{13}C NMR in $CDCl_3$ for compound 9

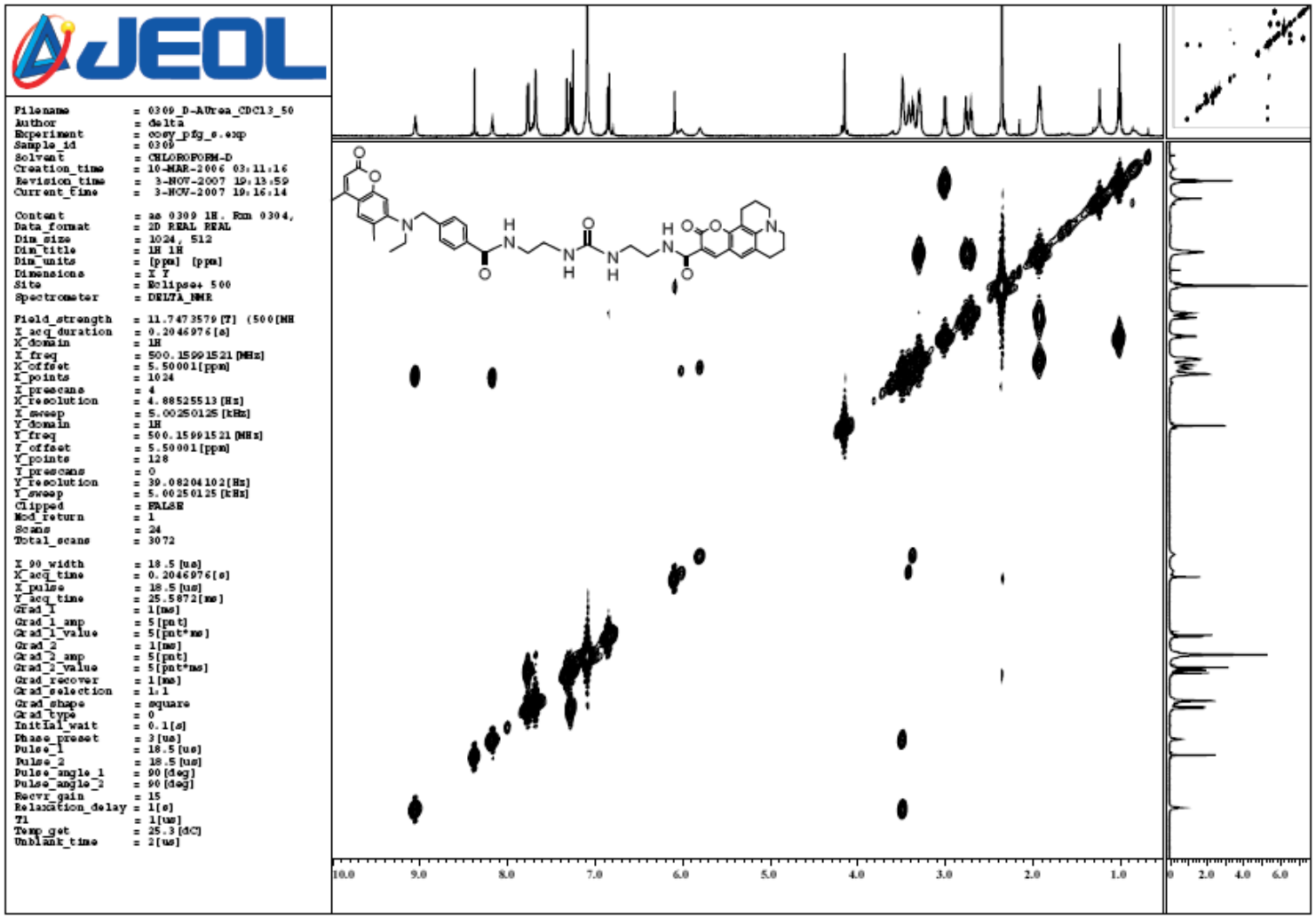


```
Filename          = 0309_D-A-Urea_CDCl3_1
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 0309
Solvent           = CHLOROFORM-D
Creation_time     = 10-MAR-2006 13:06:37
Revision_time     =  3-NOV-2007 19:01:05
Current_time      =  3-NOV-2007 19:03:34

Content           = as 0309 1H, C13 9hs.
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579 [T]  (500 [MH
X_acq_duration    = 2.0840448 [s]
X_domain          = 13C
X_freq            = 125.76529768 [MHz]
X_offset          = 100 [ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613 [Hz]
X_sweep           = 31.44654088 [kHz]
Ifr_domain        = 1H
Irr_freq          = 500.15991521 [MHz]
Irr_offset        = 5 [ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 7000
Total_scans       = 7000

X_90_width        = 14.2 [us]
X_acq_time        = 2.0840448 [s]
X_angle           = 30 [deg]
X_pulse           = 4.73333333 [us]
Initial_wait      = 1 [s]
Phase_preset      = 3 [us]
Recvr_gain        = 30
Relaxation_delay  = 3 [s]
Temp_get          = 27.8 [dC]
Unblank_time      = 2 [us]
```

^{13}C NMR in $CDCl_3$ for compound 9

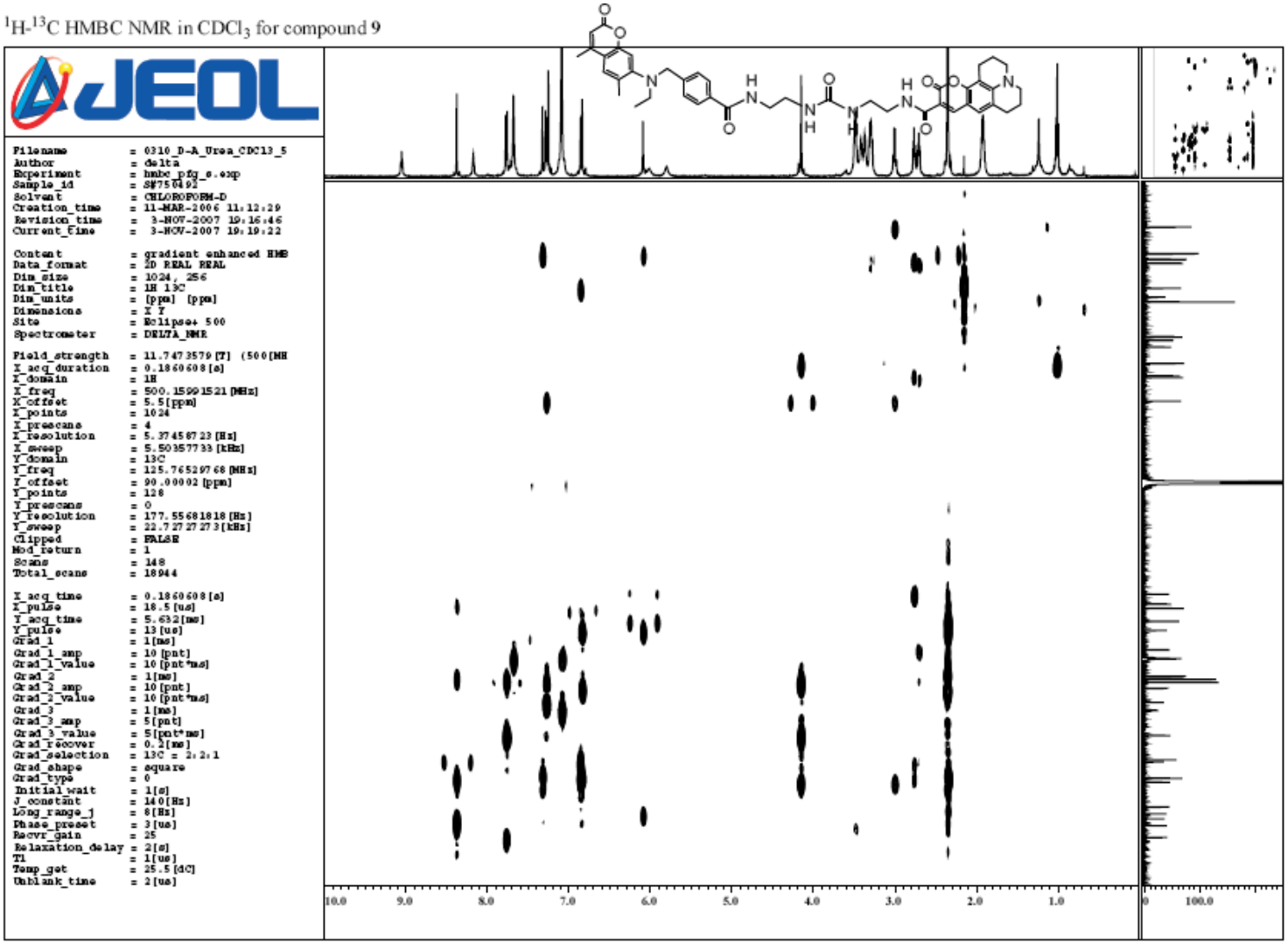


^{1}H-^{1}H COSY NMR in $CDCl_3$ for compound 9



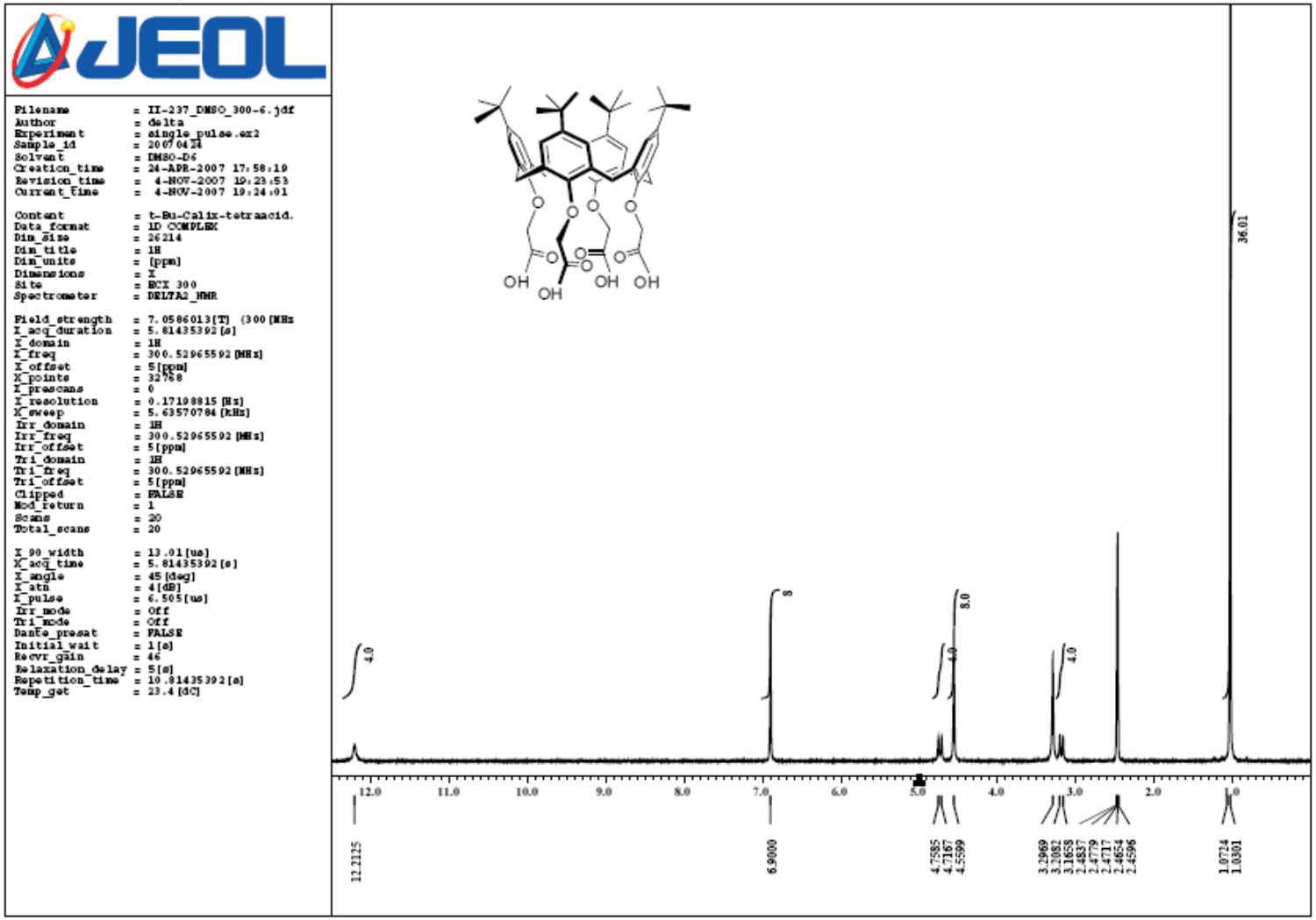
```
Filename          = 0309_D-AUrea_CDCl3_50
Author            = delta
Experiment        = cosy_pfg_s.exp
Sample_id         = 0309
Solvent           = CHLOROFORM-D
Creation_time     = 10-MAR-2006 03:11:16
Revision_time     =  3-NOV-2007 19:13:59
Current_time      =  3-NOV-2007 19:16:14

Content           = as 0309 1H. Exn 0304,
Data_format       = 2D REAL REAL
Dim_size          = 1024, 512
Dim_title         = 1H 1H
Dim_units         = [ppm]  [ppm]
Dimensions        = X Y
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.747357 9[T]  (500[MH
X_acq_duration    = 0.2046976[s]
X_domain          = 1H
X_freq            = 500.1599152 1[MHz]
X_offset          = 5.50001[ppm]
X_points          = 1024
X_prescans        = 4
X_resolution      = 4.88525513[Hz]
X_sweep           = 5.00250125[kHz]
Y_domain          = 1H
Y_freq            = 500.1599152 1[MHz]
Y_offset          = 5.50001[ppm]
Y_points          = 128
Y_prescans        = 0
Y_resolution      = 39.08204102[Hz]
Y_sweep           = 5.00250125[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 24
Total_scans       = 3072

X_90_width        = 18.5[us]
X_acq_time        = 0.2046976[s]
X_pulse           = 18.5[us]
Y_acq_time        = 25.5872[ms]
Grad_1            = 1[ms]
Grad_1_amp        = 5[pnt]
Grad_1_value      = 5[pnt*ms]
Grad_2            = 1[ms]
Grad_2_amp        = 5[pnt]
Grad_2_value      = 5[pnt*ms]
Grad_recover      = 1[ms]
Grad_selection    = 1:1
Grad_shape        = square
Grad_type         = 0
Initial_wait      = 0.1[s]
Phase_preset      = 3[us]
Pulse_1           = 18.5[us]
Pulse_2           = 18.5[us]
Pulse_angle_1     = 90[deg]
Pulse_angle_2     = 90[deg]
Recvr_gain        = 15
Relaxation_delay  = 1[s]
T1                = 1[us]
Temp_get          = 25.3[dC]
Unblank_time      = 2[us]
```

^{1}H-^{13}C HMBC NMR in $CDCl_3$ for compound 9

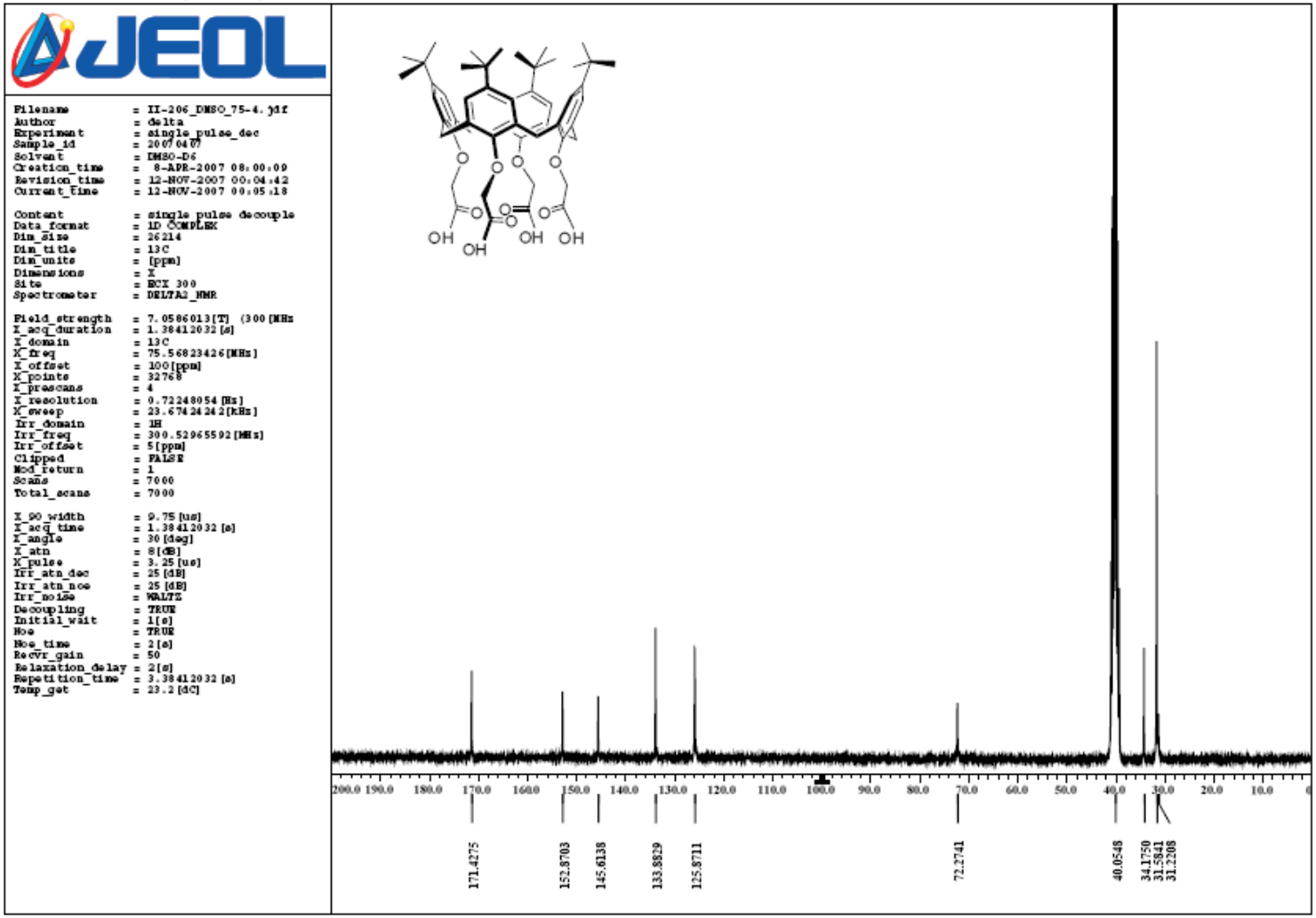


```
Filename          = 0310_D-A_Urea_CDCl3_5
Author            = delta
Experiment        = hmbc_pfg_s.exp
Sample_id         = SM750493
Solvent           = CHLOROFORM-D
Creation_time     = 11-MAR-2006 11:12:29
Revision_time     =  3-NOV-2007 19:16:46
Current_time      =  3-NOV-2007 19:19:22

Content           = gradient enhanced HMB
Data_format       = 2D REAL REAL
Dim_size          = 1024, 256
Dim_title         = 1H 13C
Dim_units         = [ppm] [ppm]
Dimensions        = X Y
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.1860608[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5.5[ppm]
X_points          = 1024
X_prescans        = 4
X_resolution      = 5.37458723[Hz]
X_sweep           = 5.50357733[kHz]
Y_domain          = 13C
Y_freq            = 125.76529768[MHz]
Y_offset          = 90.00002[ppm]
Y_points          = 128
Y_prescans        = 0
Y_resolution      = 177.55681818[Hz]
Y_sweep           = 22.72727273[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 148
Total_scans       = 18944

X_acq_time        = 0.1860608[s]
X_pulse           = 18.5[us]
Y_acq_time        = 5.632[ms]
Y_pulse           = 13[us]
Grad_1            = 1[ms]
Grad_1_amp        = 10[pnt]
Grad_1_value      = 10[pnt*ms]
Grad_2            = 1[ms]
Grad_2_amp        = 10[pnt]
Grad_2_value      = 10[pnt*ms]
Grad_3            = 1[ms]
Grad_3_amp        = 5[pnt]
Grad_3_value      = 5[pnt*ms]
Grad_recover      = 0.2[ms]
Grad_selection    = 13C = 2:2:1
Grad_shape        = square
Grad_type         = 0
Initial_wait      = 1[s]
J_constant        = 140[Hz]
Long_range_J      = 8[Hz]
Phase_preset      = 3[us]
Recvr_gain        = 25
Relaxation_delay  = 2[s]
T1                = 1[us]
Temp_get          = 25.5[dC]
Unblank_time      = 2[us]
```

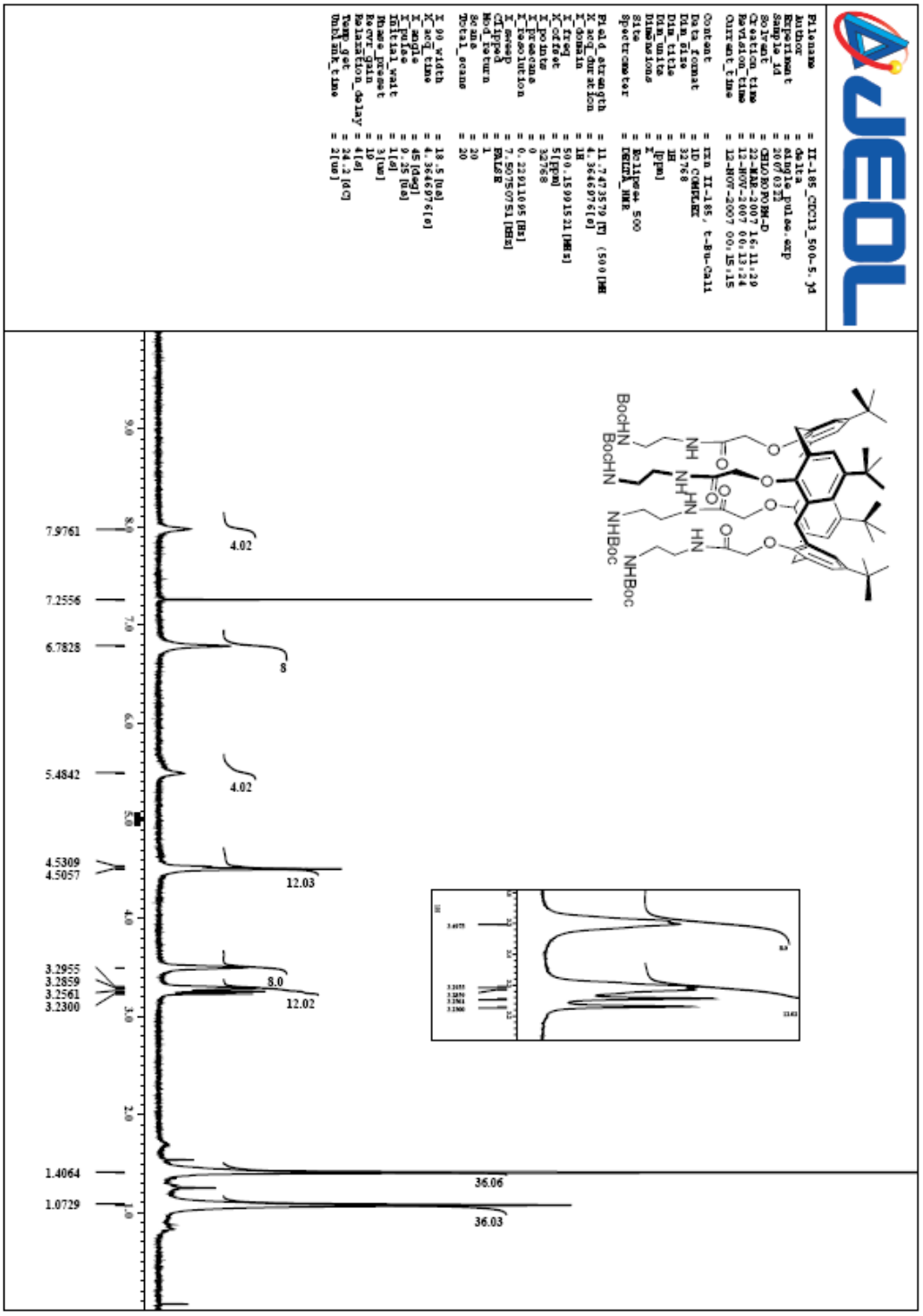
^{1}H NMR in DMSO-d_6 for compound **12**



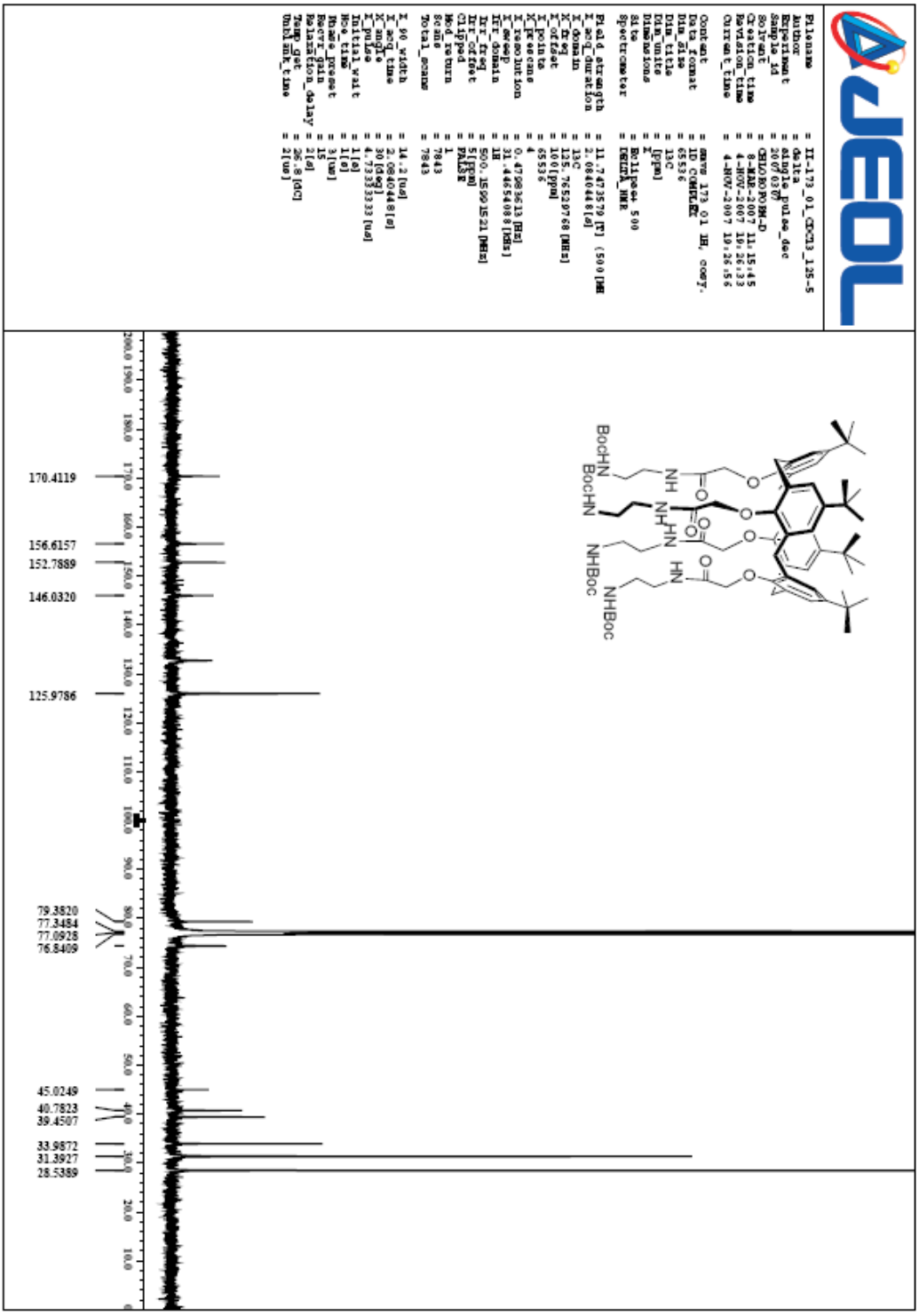
^{13}C NMR in DMSO-d_6 for compound **12**



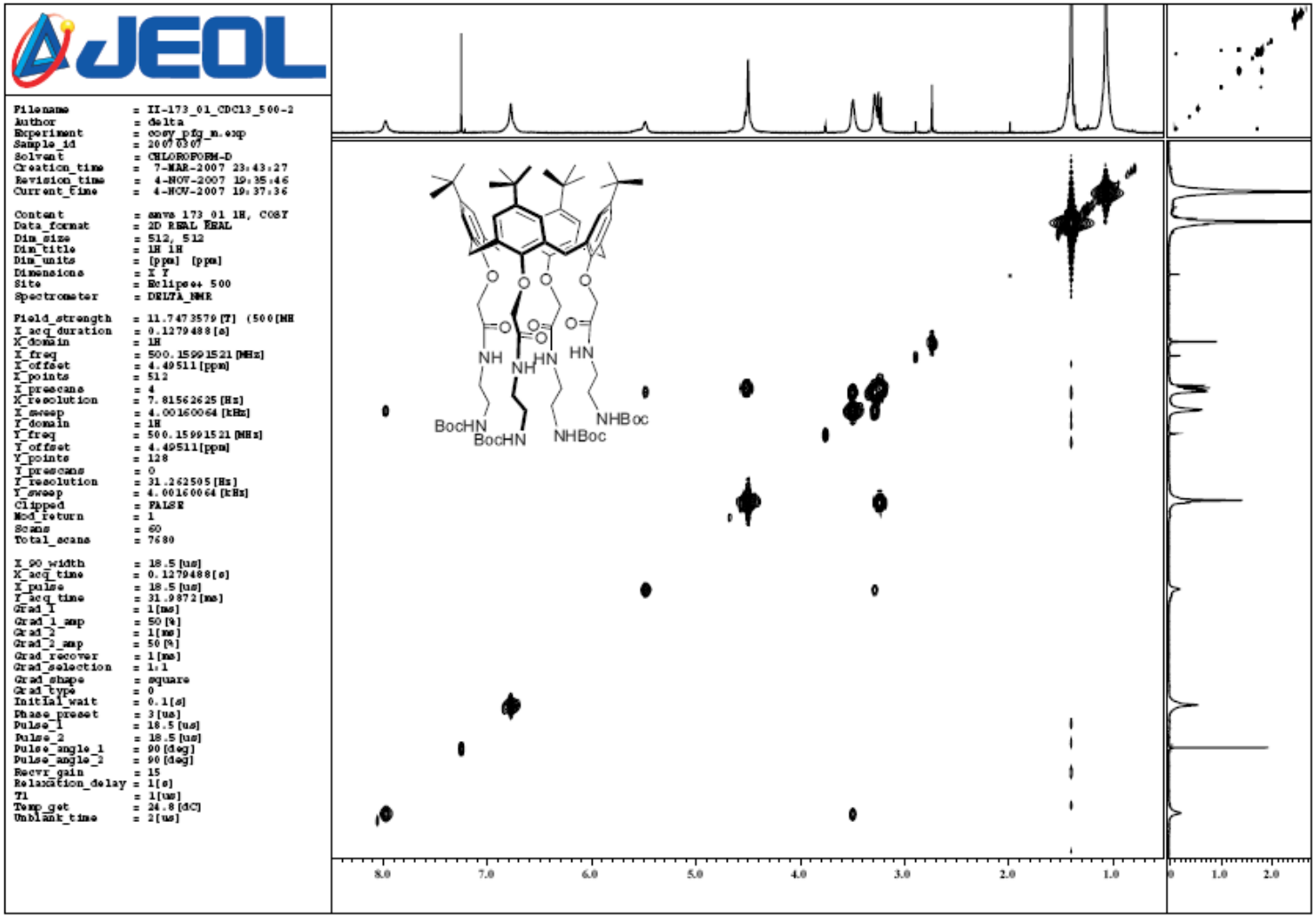
^{1}H NMR in $CDCl_3$ for compound 13



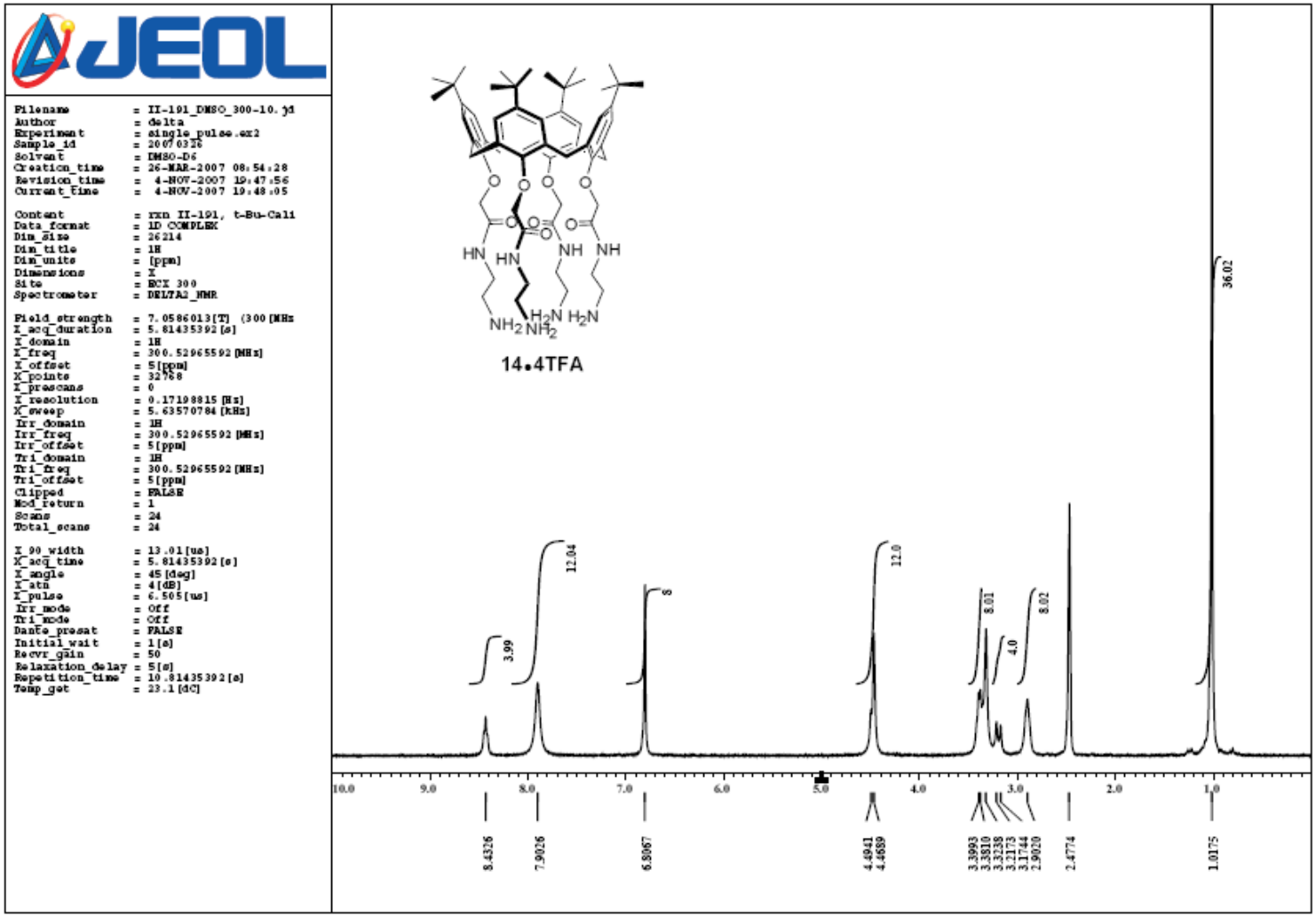
^{13}C NMR in $CDCl_3$ for compound **13**



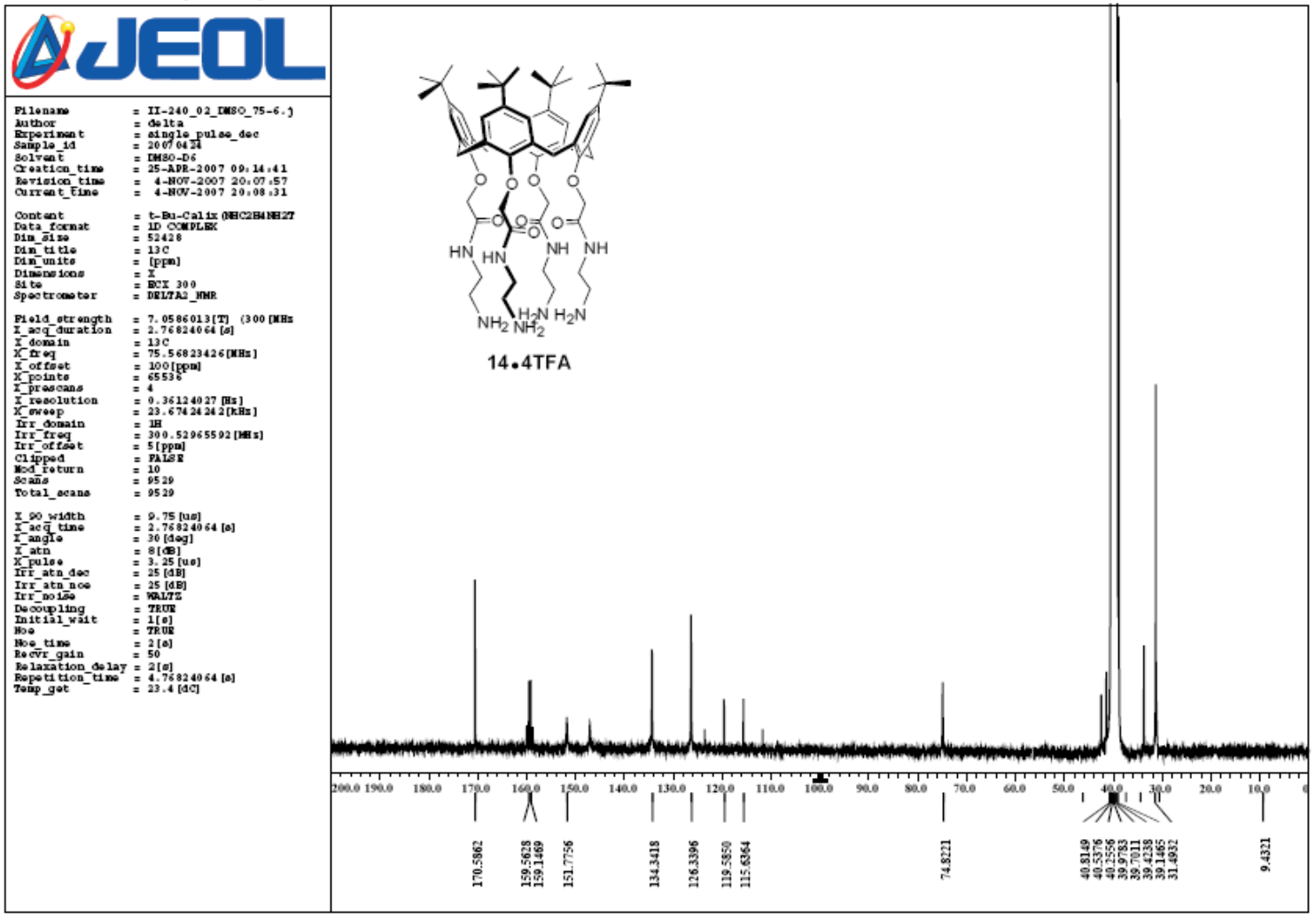
^{1}H-^{1}H COSY NMR in $CDCl_3$ for compound **13**



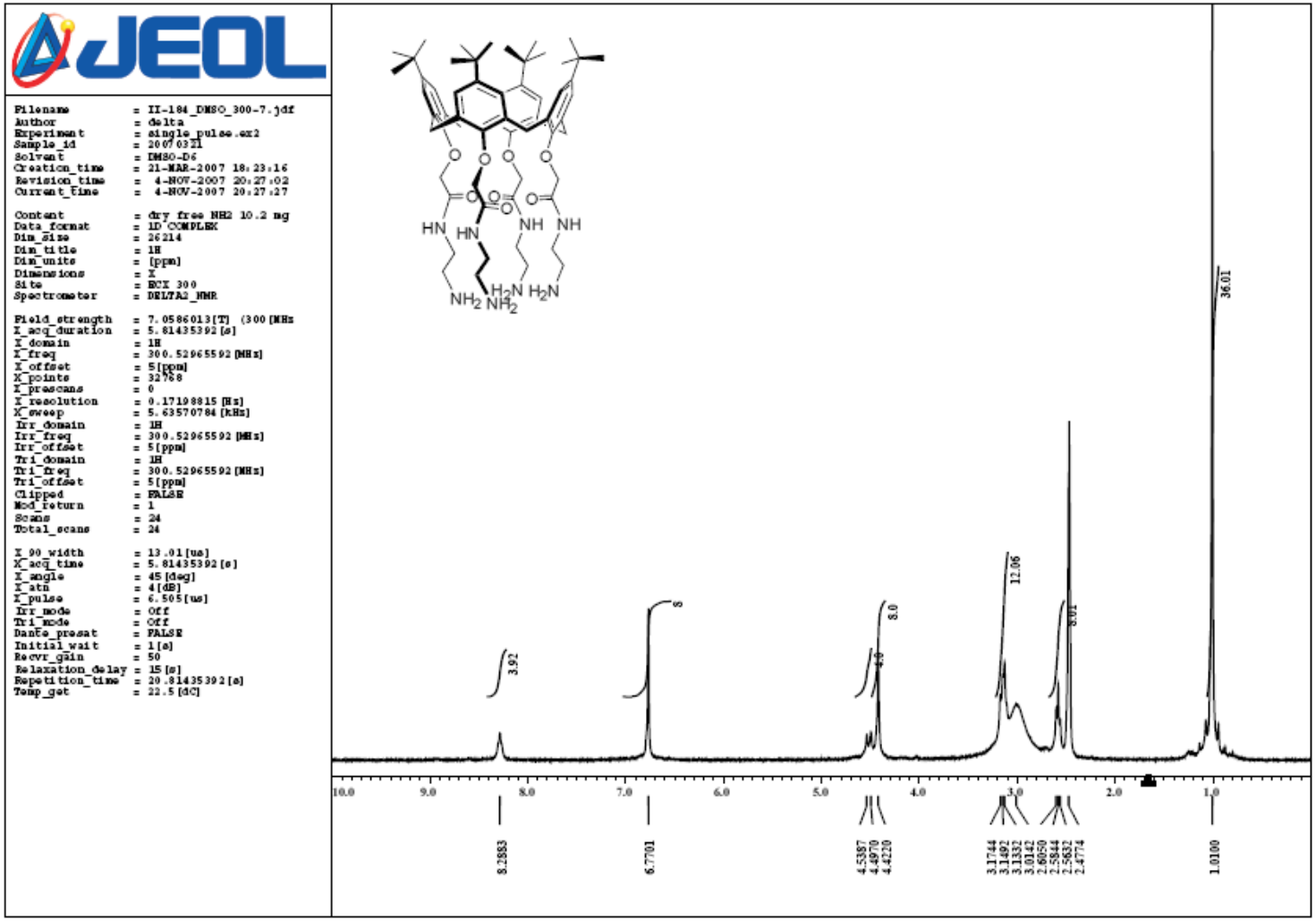
^{1}H NMR in DMSO-d_6 for compound **14•4TFA**



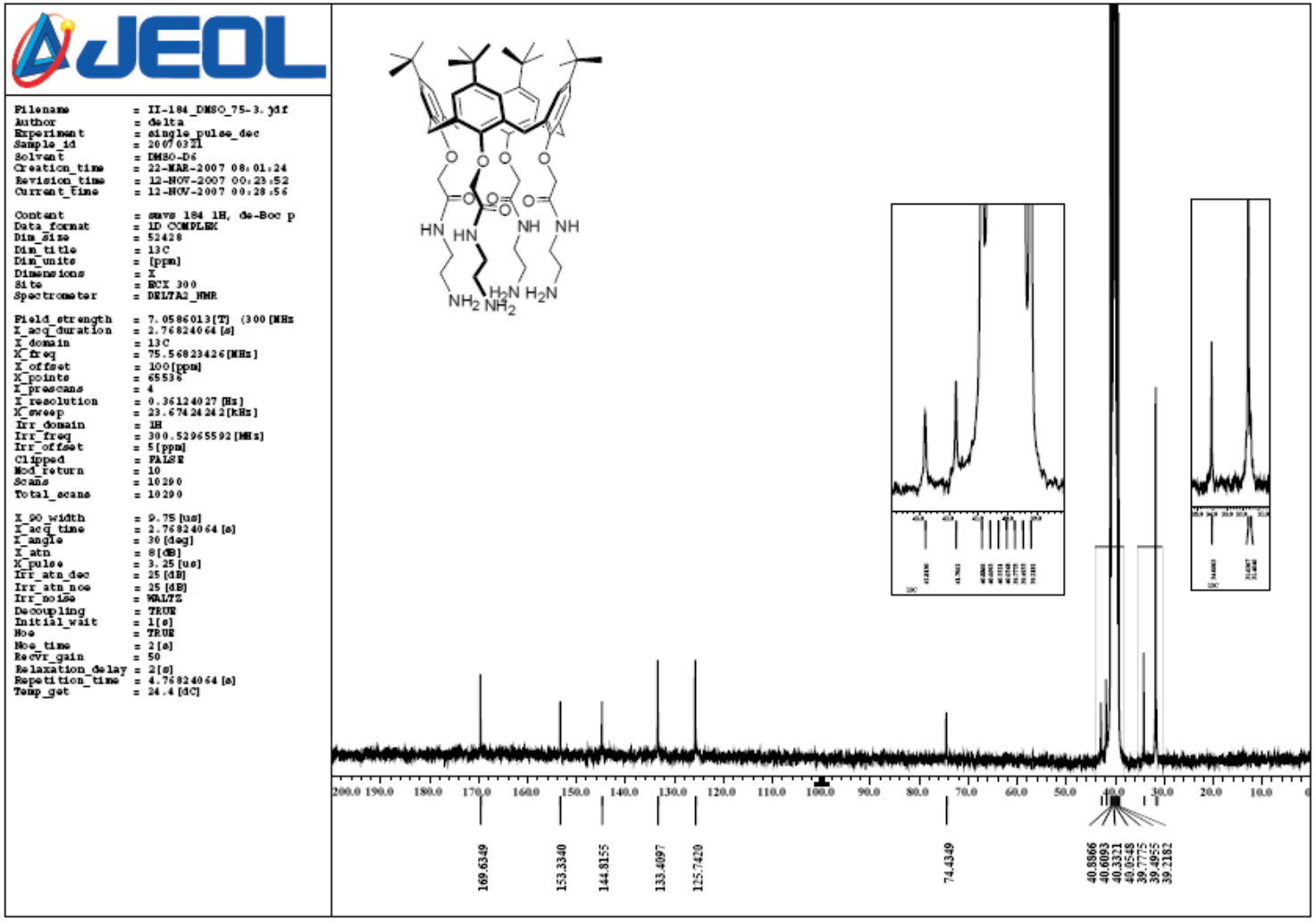
^{13}C NMR in DMSO-d_6 for compound **14•4TFA**



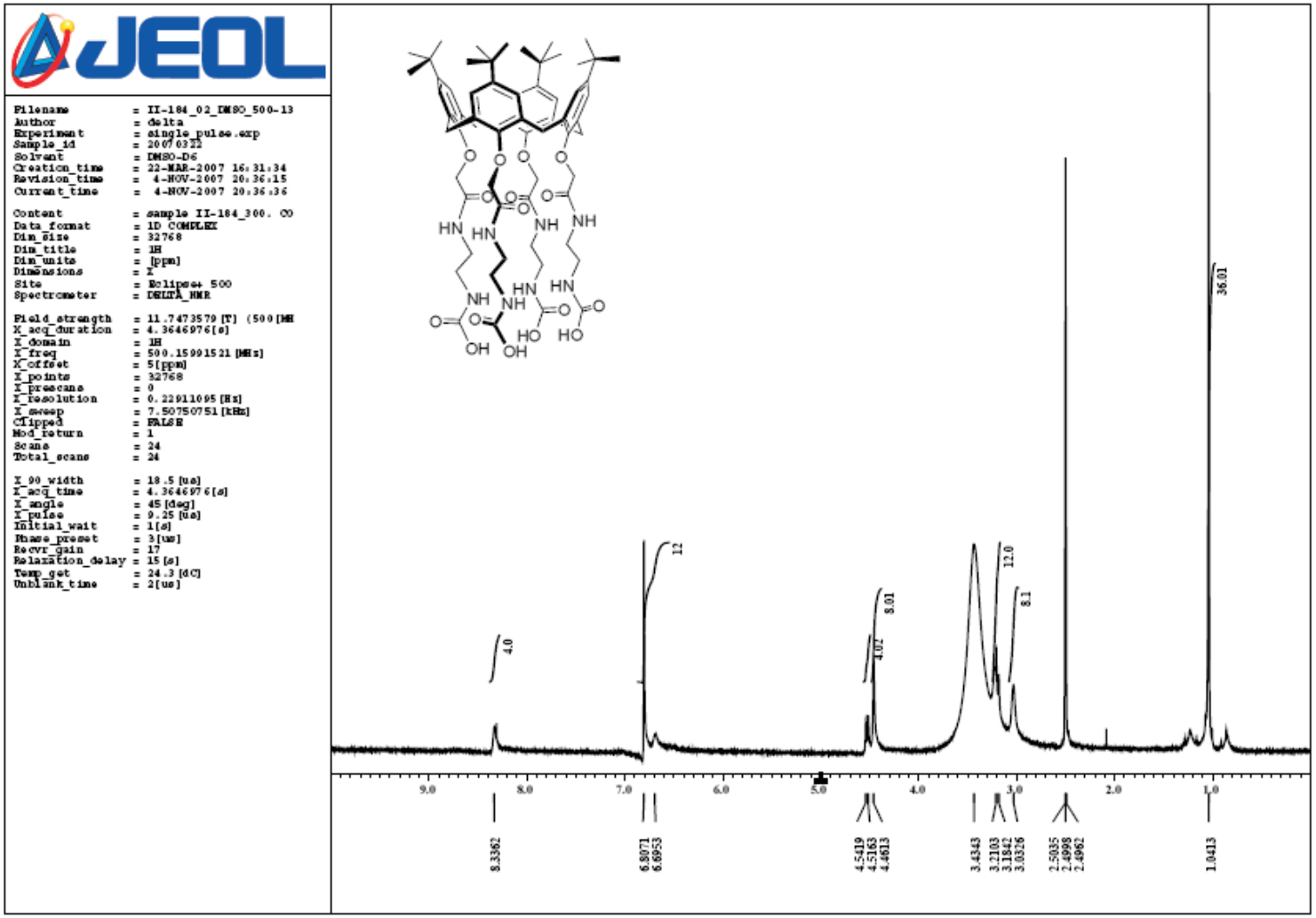
^{1}H NMR in DMSO-d_6 for compound **14**



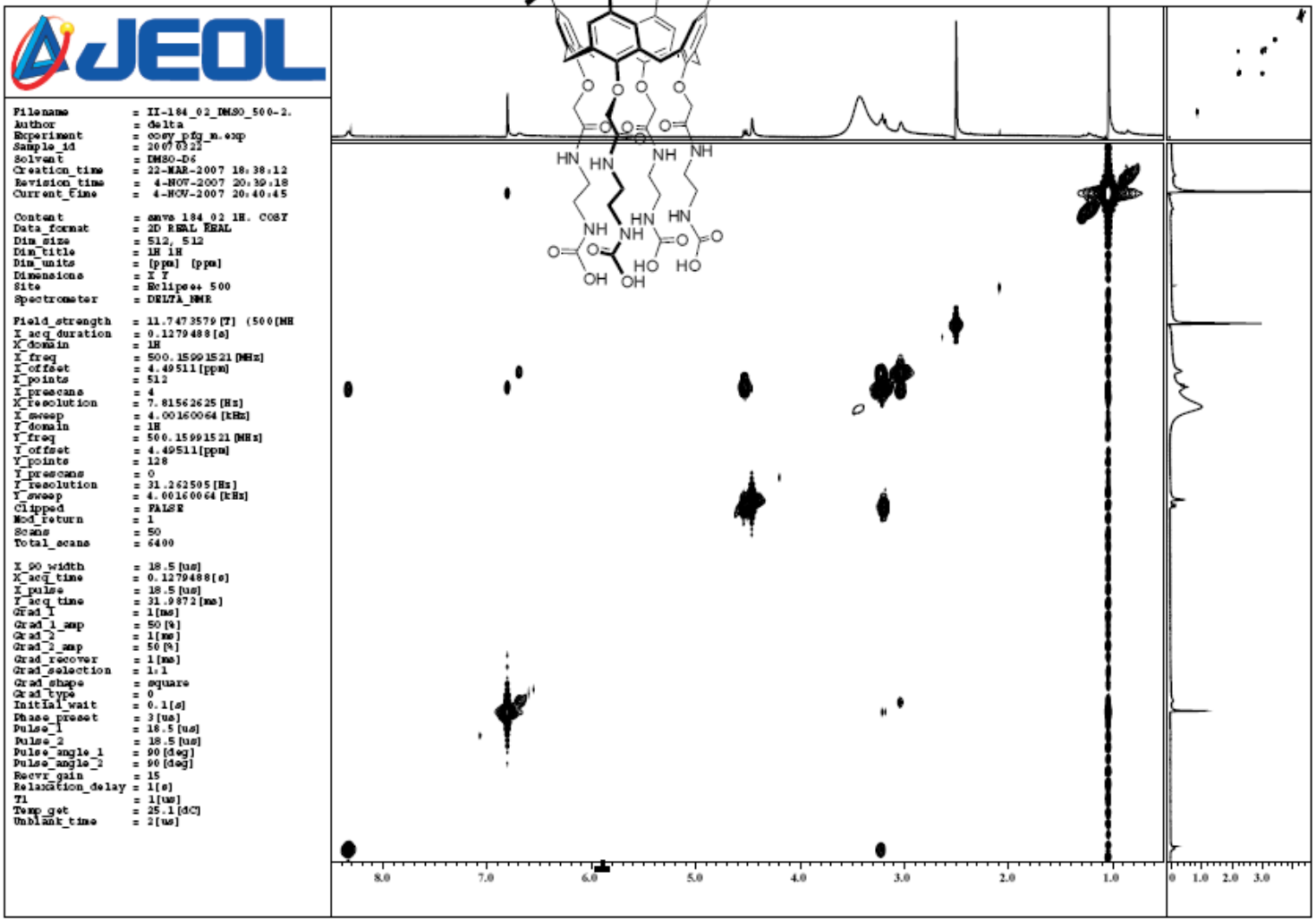
^{13}C NMR in DMSO-d_6 for compound **14**



^{1}H NMR in DMSO-d_6 for compound **15**

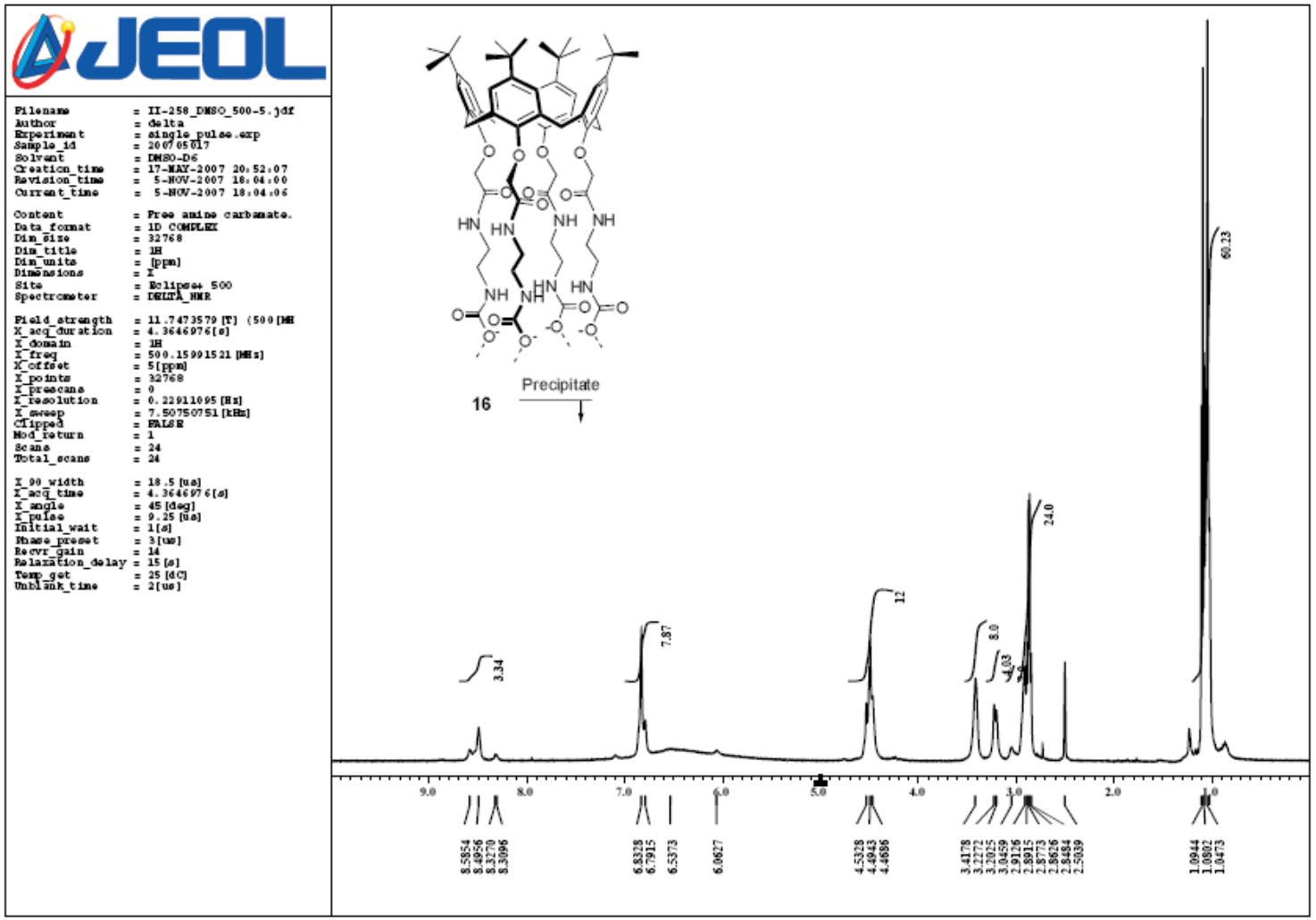


^{1}H-^{1}H COSY NMR in DMSO-d_6 for compound **15**

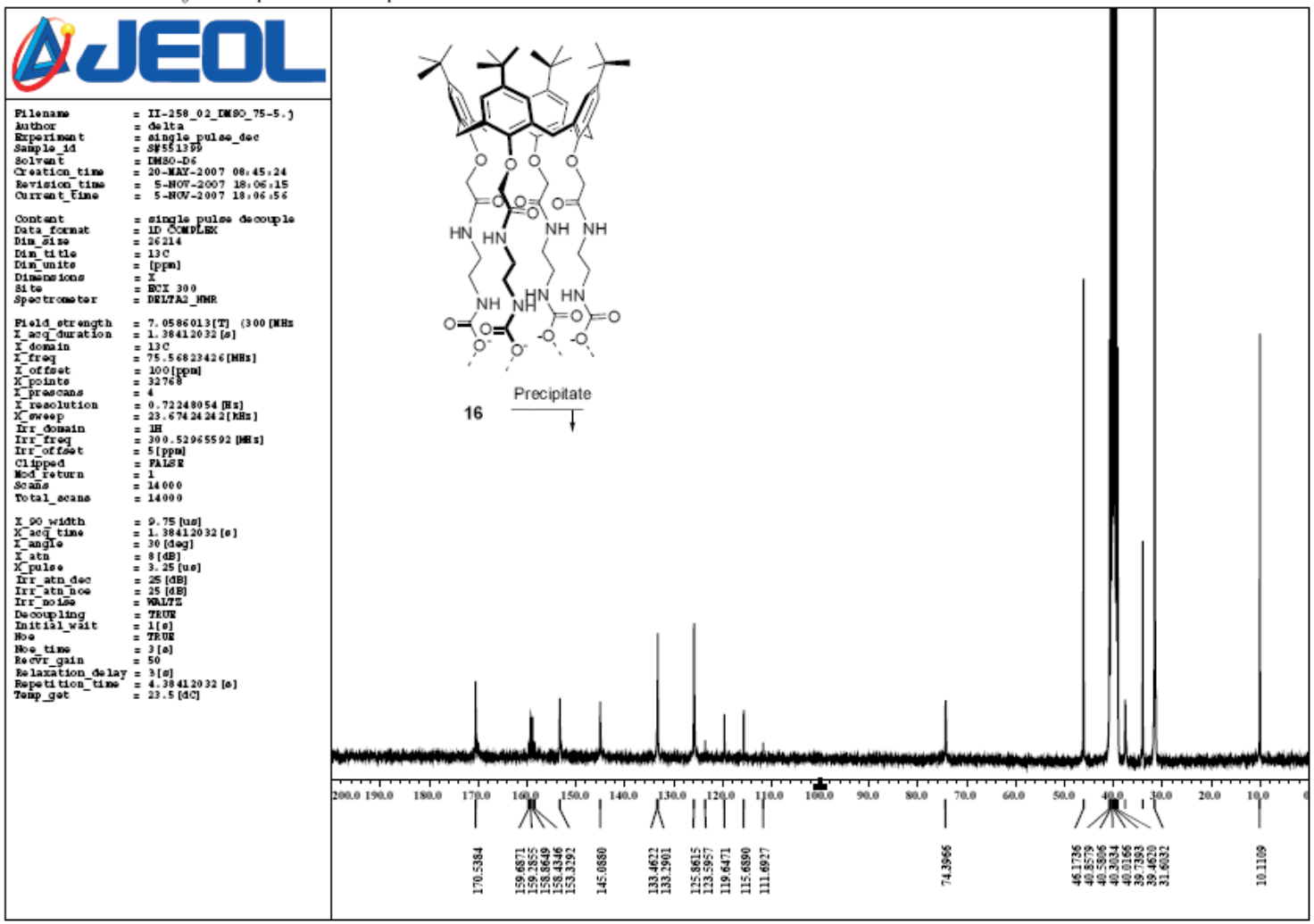


```
Filename          = II-184_02_DMSO_500-2.
Author            = delta
Experiment        = cosy.pfg.m.exp
Sample_id         = 20070322-
Solvent           = DMSO-D6
Creation_time     = 22-MAR-2007 18:38:12
Revision_time     =  4-NOV-2007 20:39:18
Current_time      =  4-NOV-2007 20:40:45

Content           = anva 184_02 1H. COSY
Data_format       = 2D REAL REAL
Dim_size          = 512, 512
Dim_title         = 1H 1H
Dim_units         = [ppm]  [ppm]
Dimensions        = X Y
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 0.1279488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 4.49511[ppm]
X_points          = 512
X_prescans        = 4
X_resolution      = 7.81562625[Hz]
X_sweep           = 4.00160064[kHz]
Y_domain          = 1H
Y_freq            = 500.15991521[MHz]
Y_offset          = 4.49511[ppm]
Y_points          = 128
Y_prescans        = 0
Y_resolution      = 31.262505[Hz]
Y_sweep           = 4.00160064[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 50
Total_scans       = 6400

X_90_width        = 18.5[us]
X_acq_time        = 0.1279488[s]
X_pulse           = 18.5[us]
Y_acq_time        = 31.9872[ms]
Grad_1            = 1[ms]
Grad_1_amp        = 50[%]
Grad_2            = 1[ms]
Grad_2_amp        = 50[%]
Grad_recover      = 1[ms]
Grad_selection    = 1:1
Grad_shape        = square
Grad_type         = 0
Initial_wait      = 0.1[s]
Phase_preset      = 3[us]
Pulse_1           = 18.5[us]
Pulse_2           = 18.5[us]
Pulse_angle_1     = 90[deg]
Pulse_angle_2     = 90[deg]
Recvr_gain        = 15
Relaxation_delay  = 1[s]
T1                = 1[us]
Temp_get          = 25.1[dC]
Unblank_time      = 2[us]
```

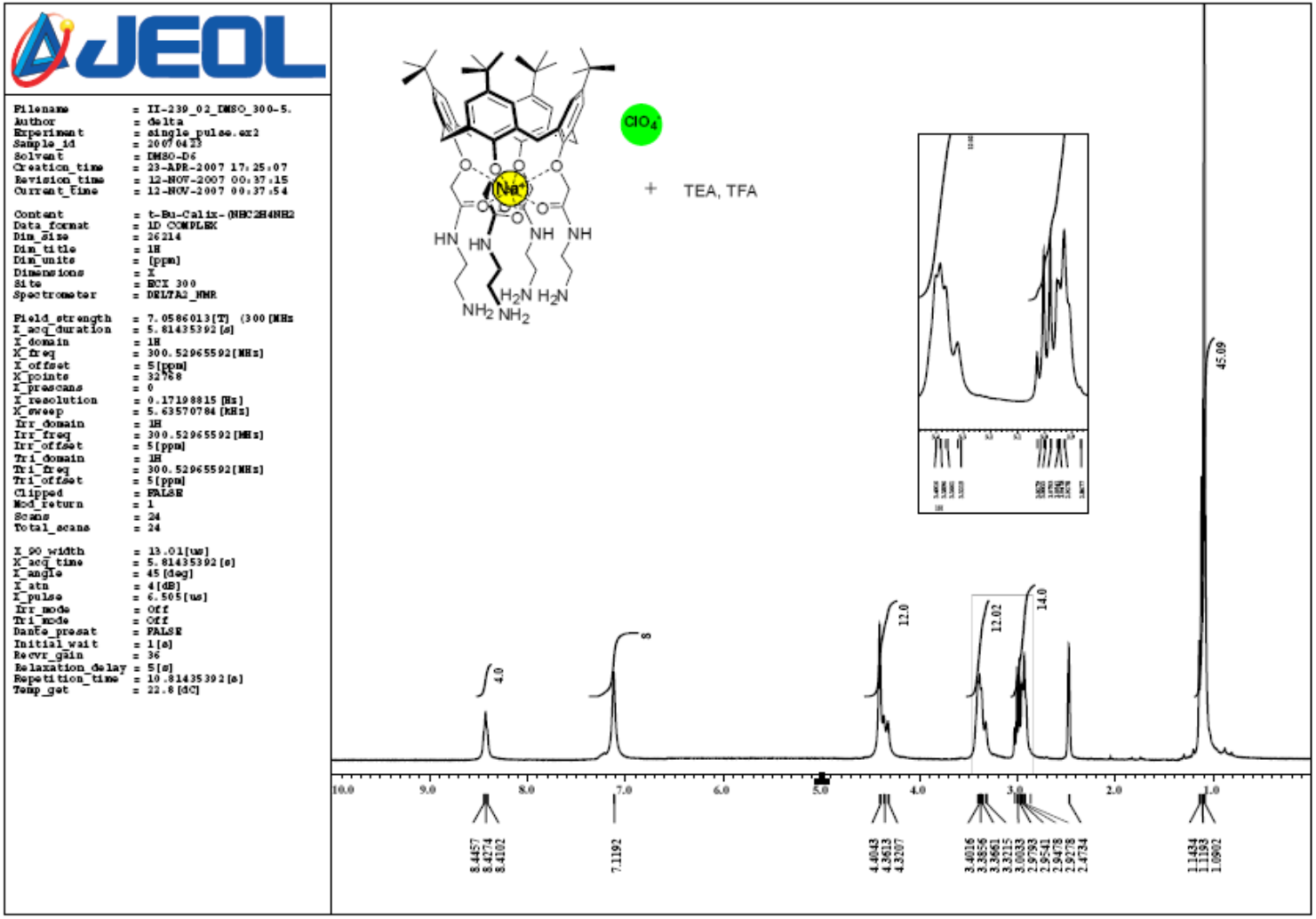
^{1}H NMR in DMSO-d_6 for compound **16** in the presence of TEA



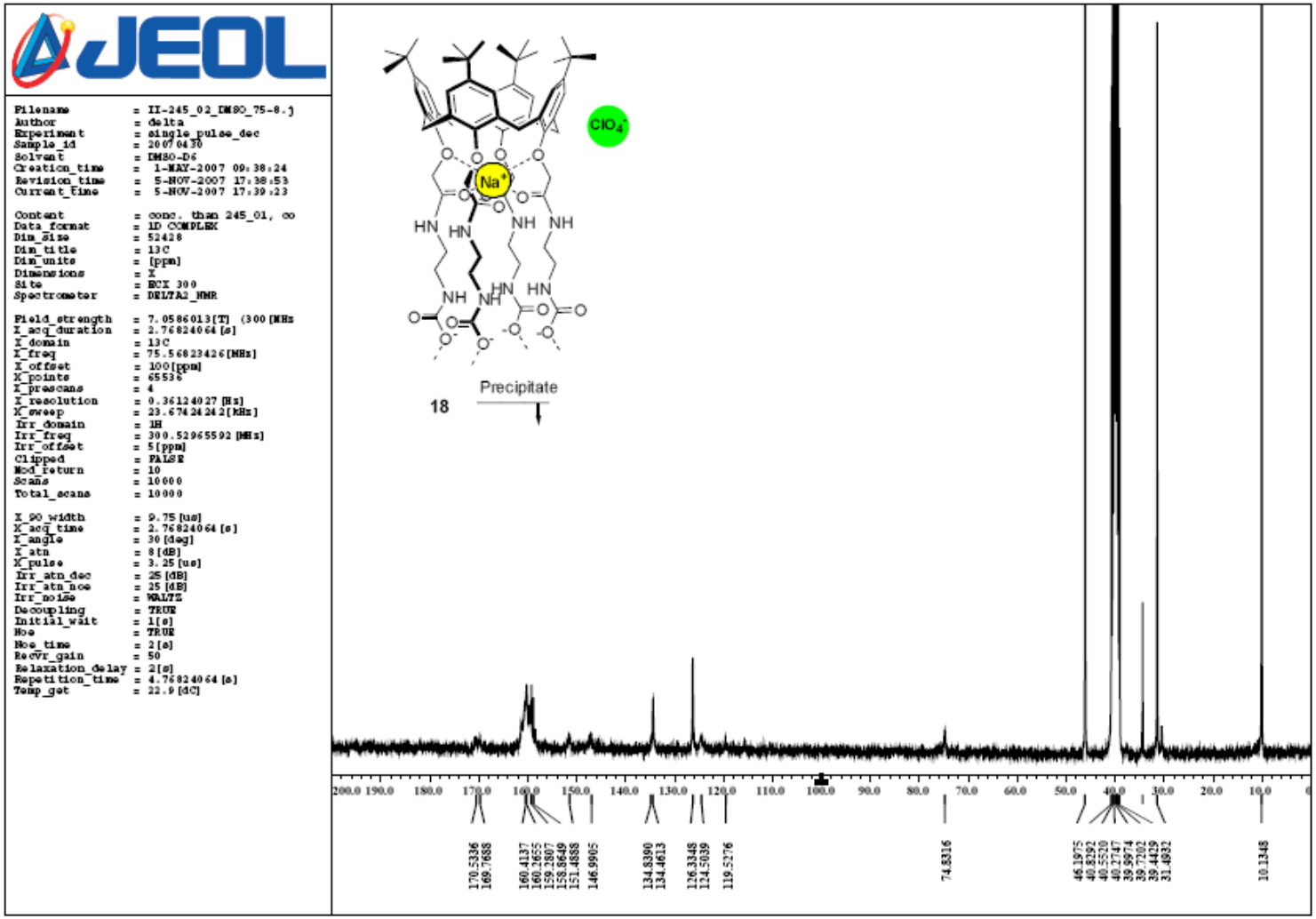
^{13}C NMR in DMSO-d_6 for compound **16** in the presence of TEA



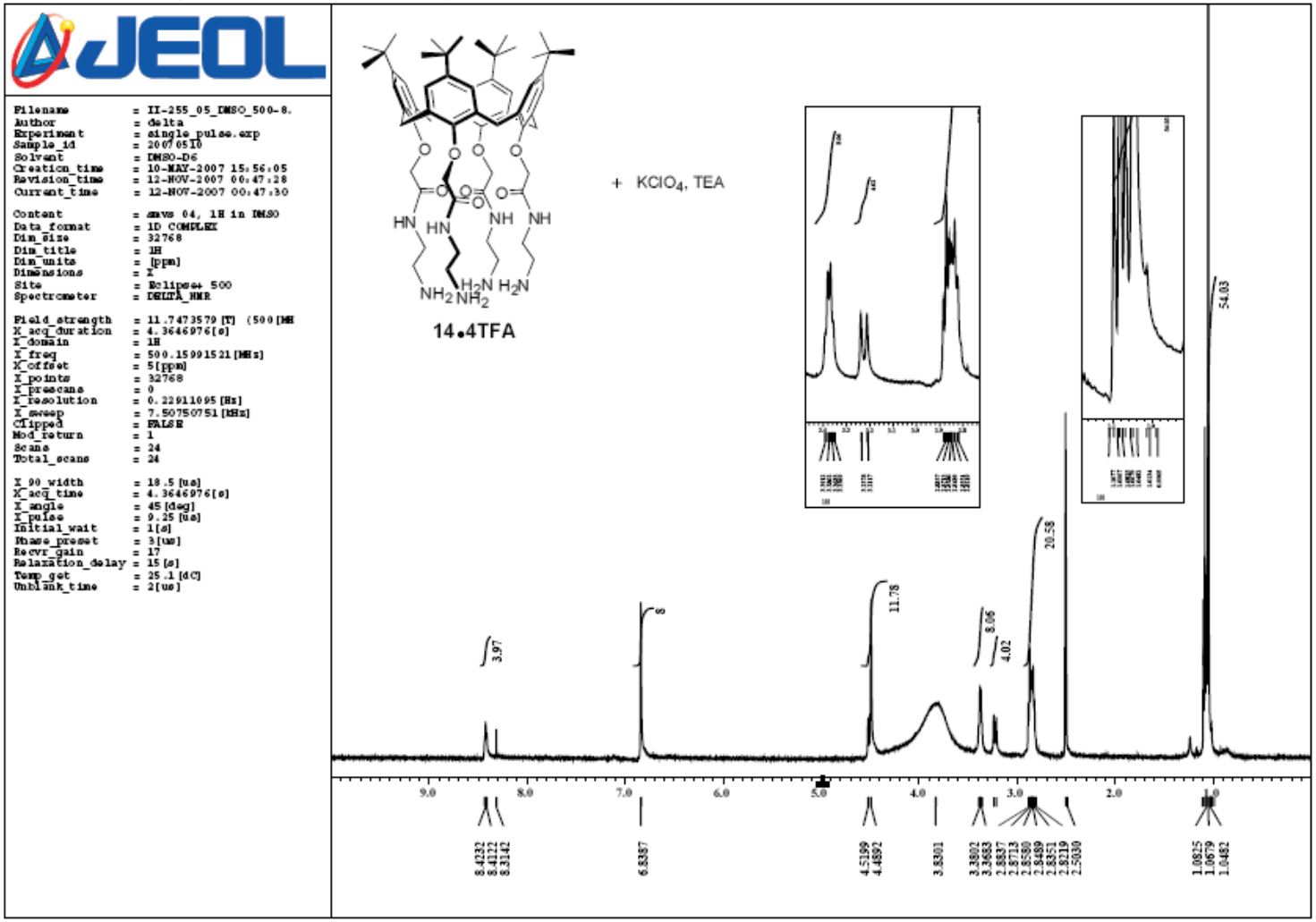
^{1}H NMR in DMSO-d_6 for complex **17** in the presence of TEA



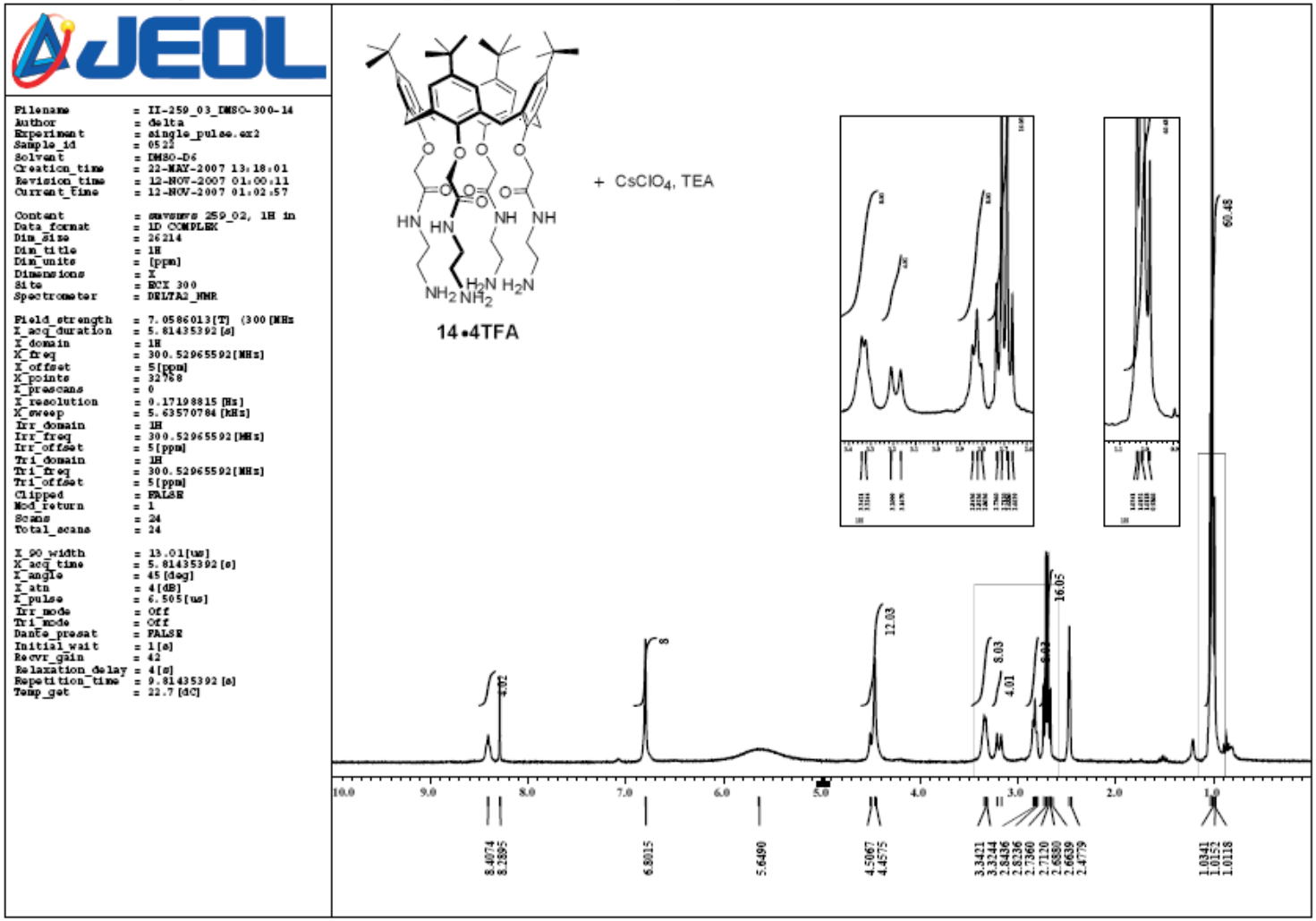
^{13}C NMR in DMSO-d_6 for complex **18** in the presence of TEA and $NaClO_4$, prepared by $^{13}CO_2$



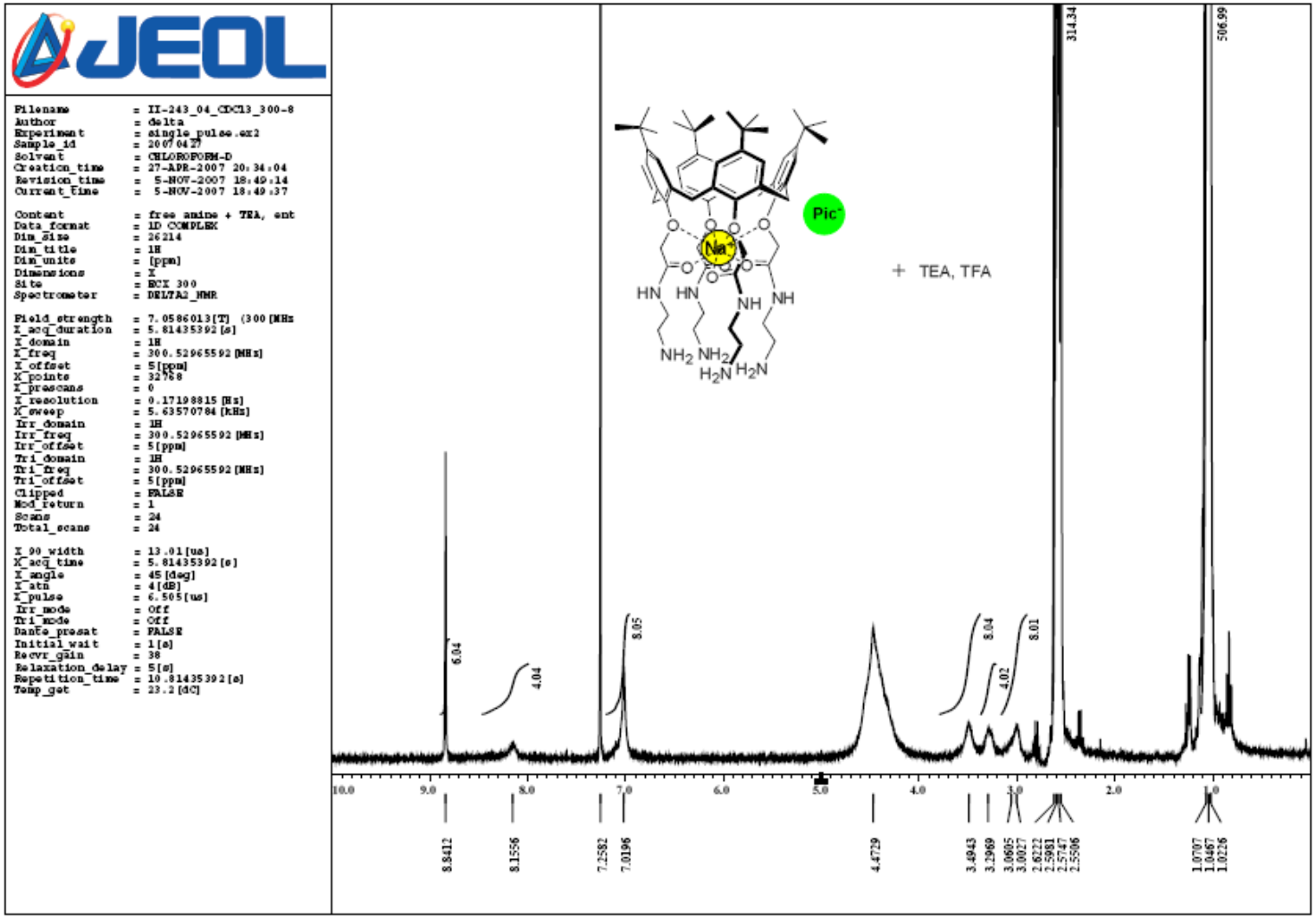
^{1}H NMR in DMSO-d_6 for compound **14•4TFA** in the presence of TEA and $KClO_4$



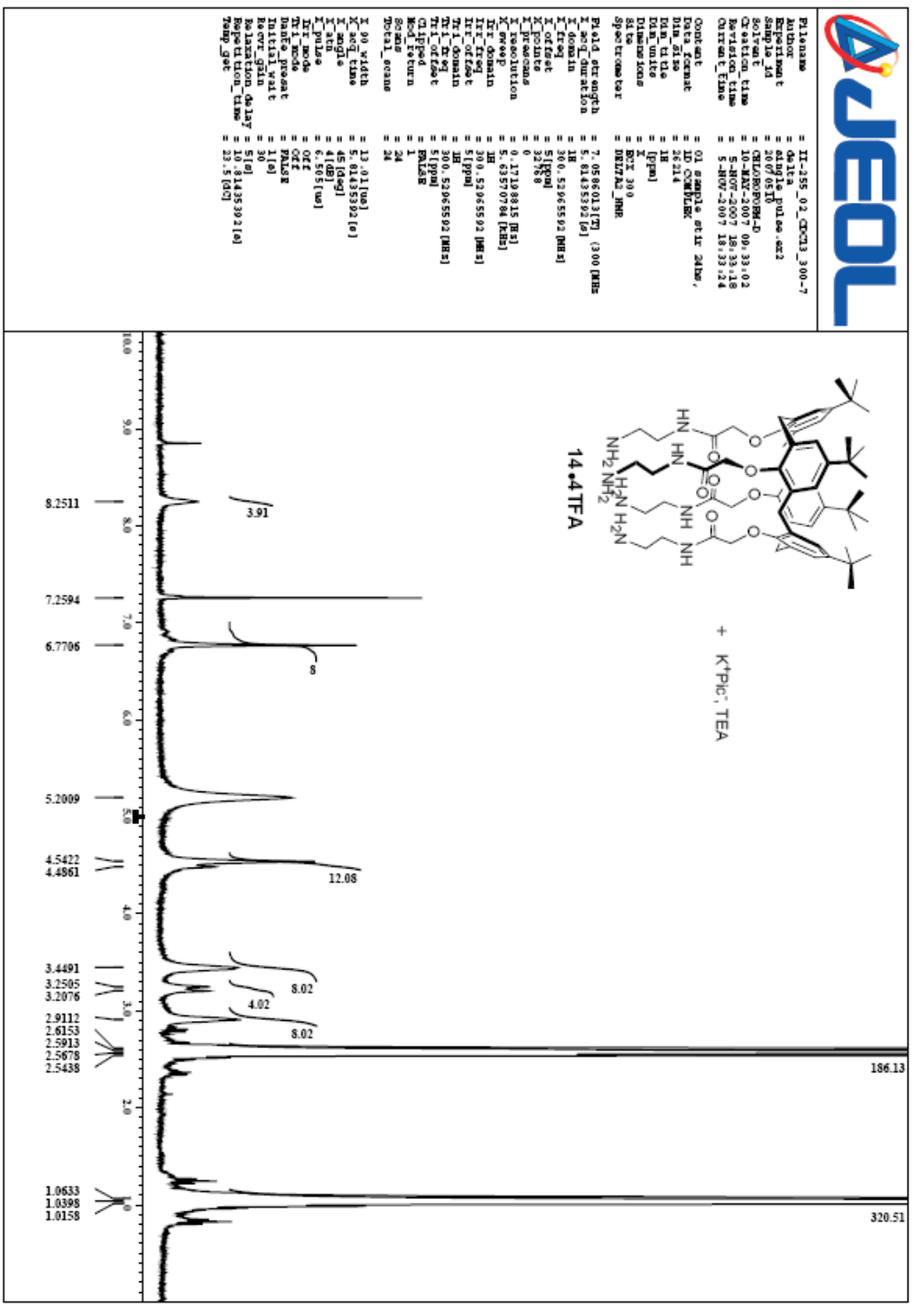
^{1}H NMR in DMSO-d_6 for compound **14•4TFA** in the presence of TEA and $CsClO_4$



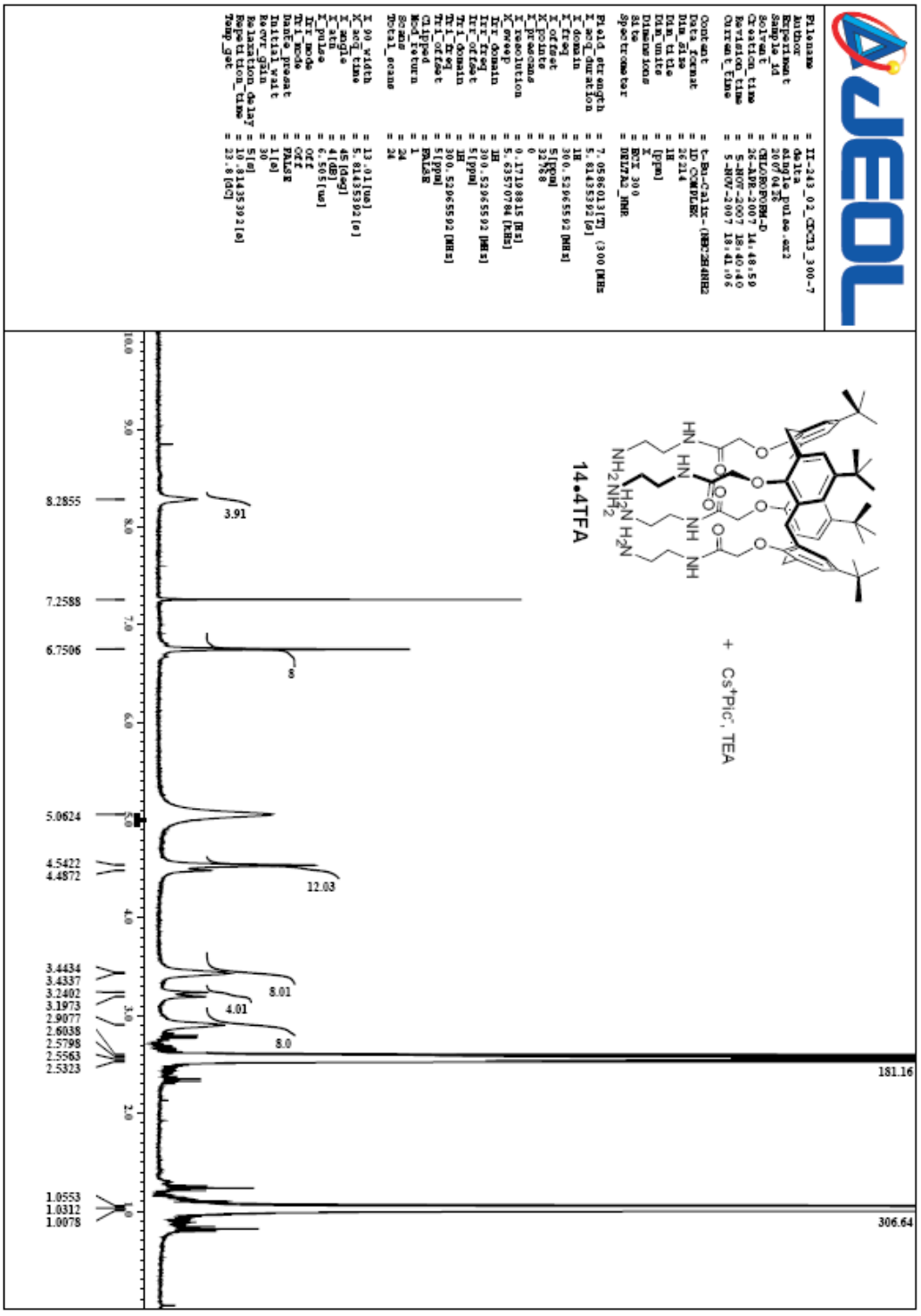
^{1}H NMR in $CDCl_3$ for compound **14•4TFA** in the presence of TEA and Na^+Pic^-



^{1}H NMR in $CDCl_3$ for compound **14•4TFA** in the presence of TEA and K^+Pic^-



^{1}H NMR in $CDCl_3$ for compound **14**•4TFA in the presence of TEA and Cs^+Pic^-

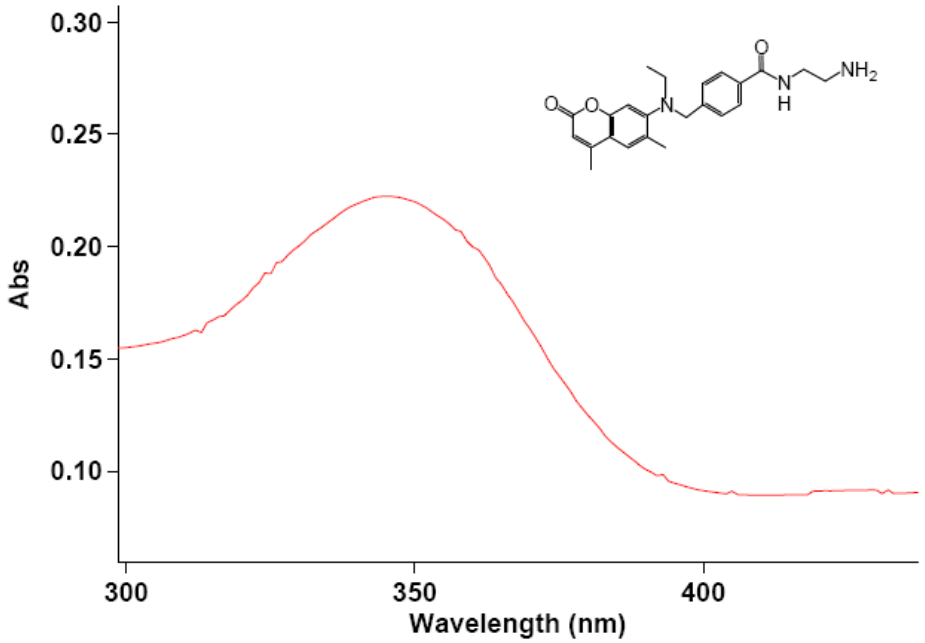


APPENDIX B

UV-VIS AND FLUORESCENCE SPECTRA

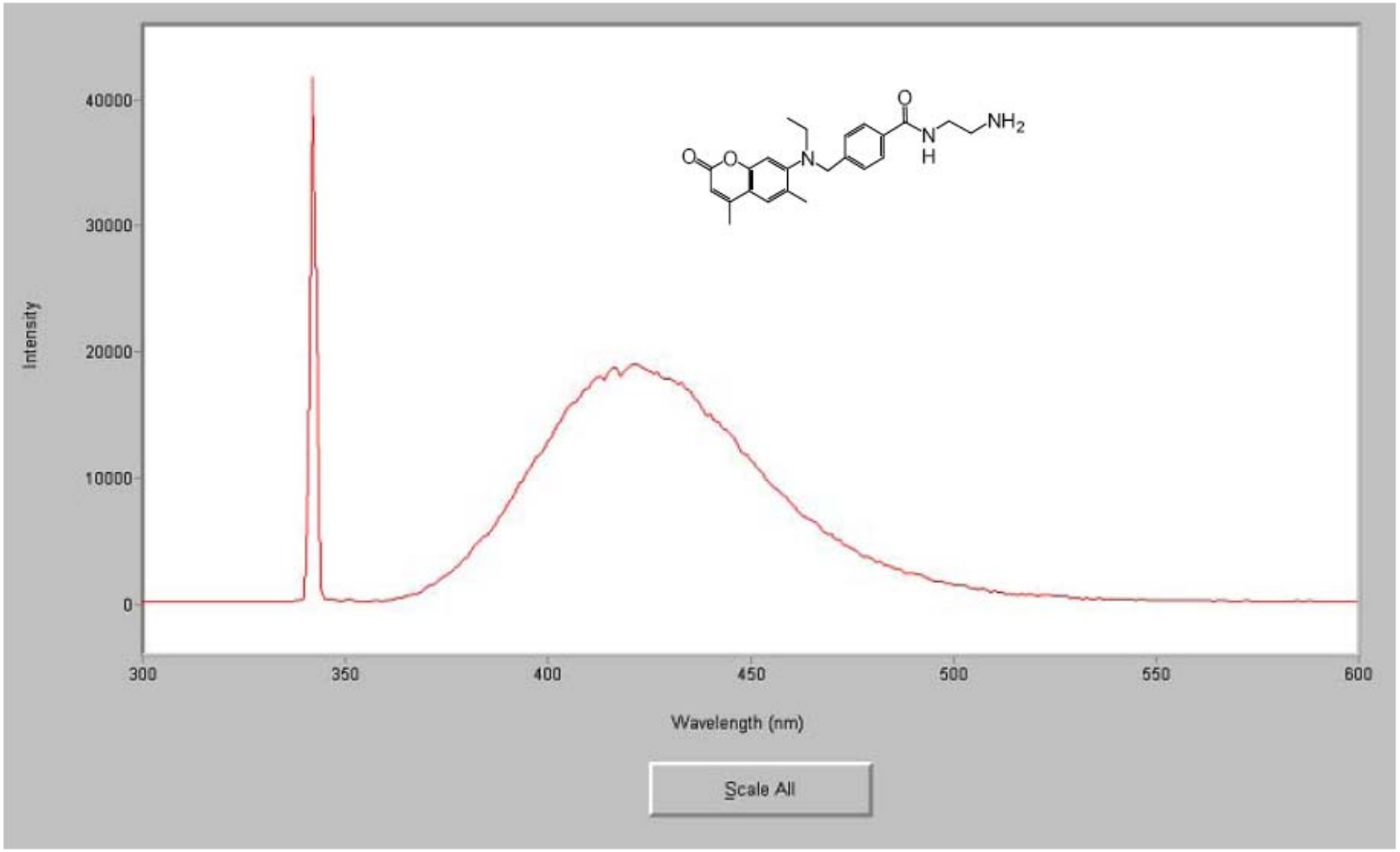
UV-vis Spectrum

Compound **4**: [c] = 1 x 10^{-6} M, λ_{max} = 343 nm



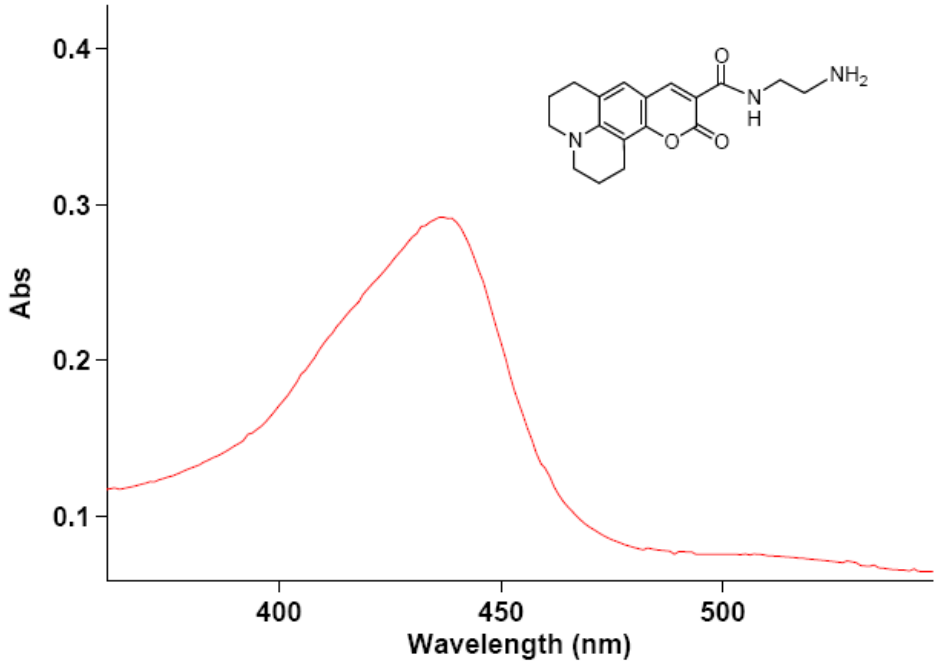
Fluorescence Spectrum:

Compound **4**: [c] = 1 x 10^{-6} M. λ_{ex} = 343 nm, λ_{em} = 425 nm



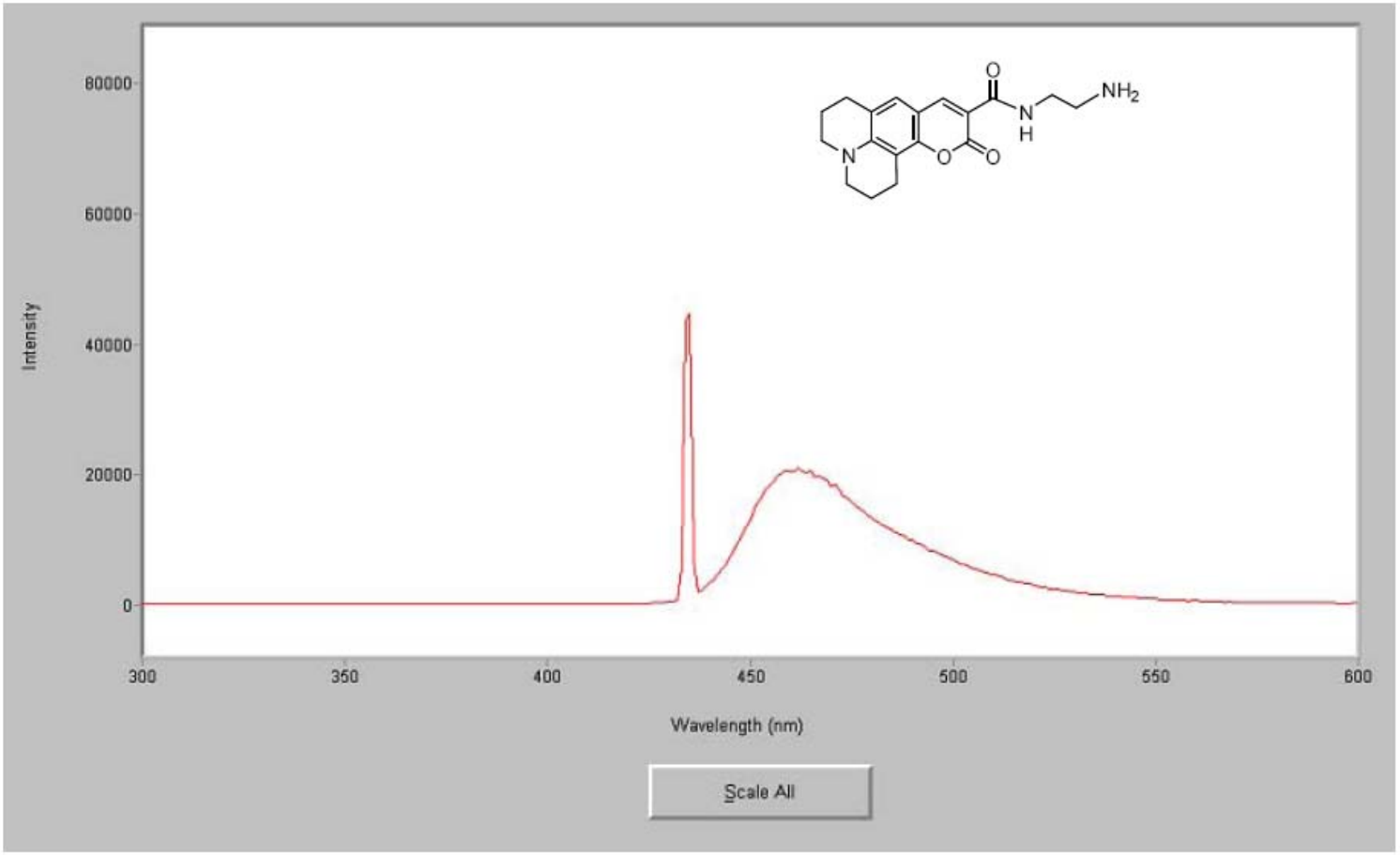
UV-vis Spectrum

Compound **6**: [c] = 1 x 10^{-6} M, λ_{max} = 435 nm



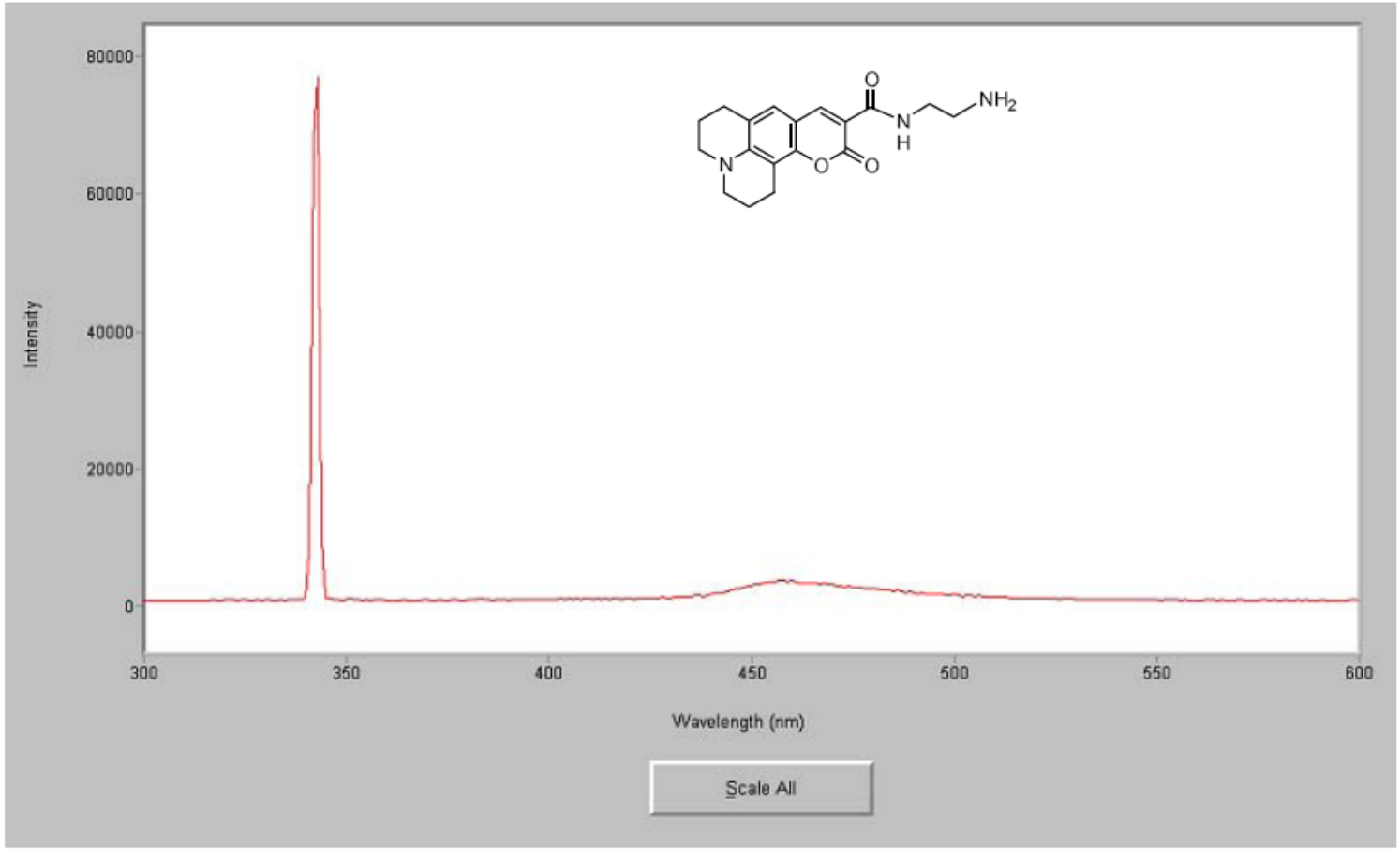
Fluorescence Spectrum:

Compound **6**: [c] = 1 x 10^{-6} M. λ_{ex} = 435 nm, λ_{em} = 468 nm



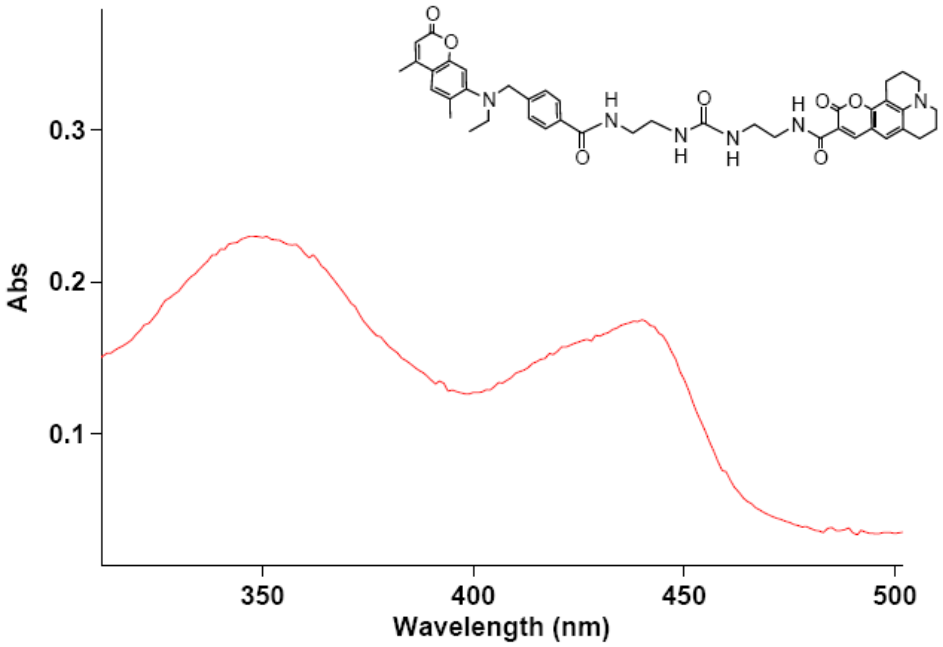
Fluorescence Spectrum:

Compound **6**: [c] = 1 x 10^{-6} M. λ_{ex} = 343 nm, Emission is weak.



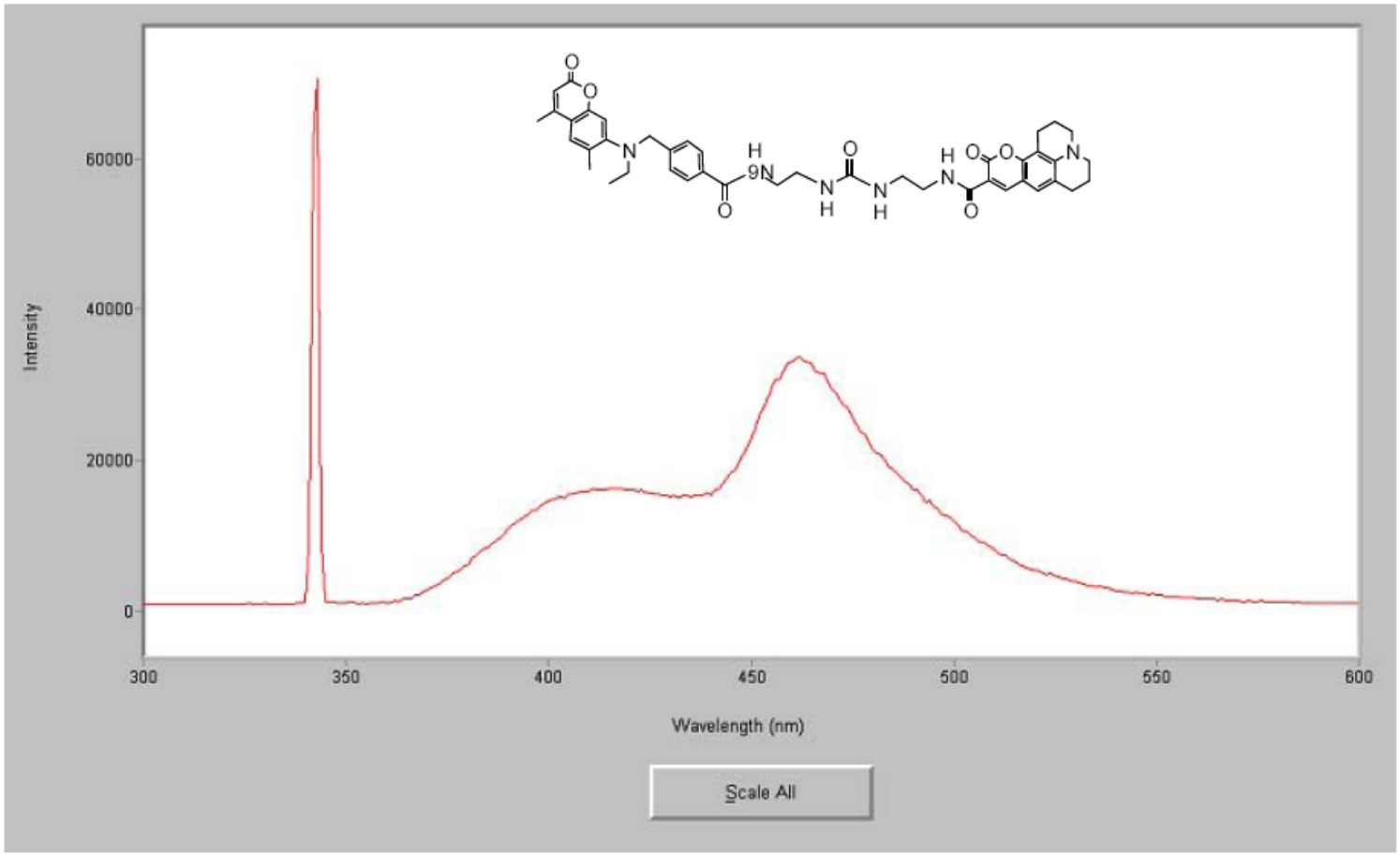
UV-vis Spectrum

Compound **9**: [c] = 1 x 10^{-6} M, λ_{max1} = 343 nm, λ_{max2} = 438 nm



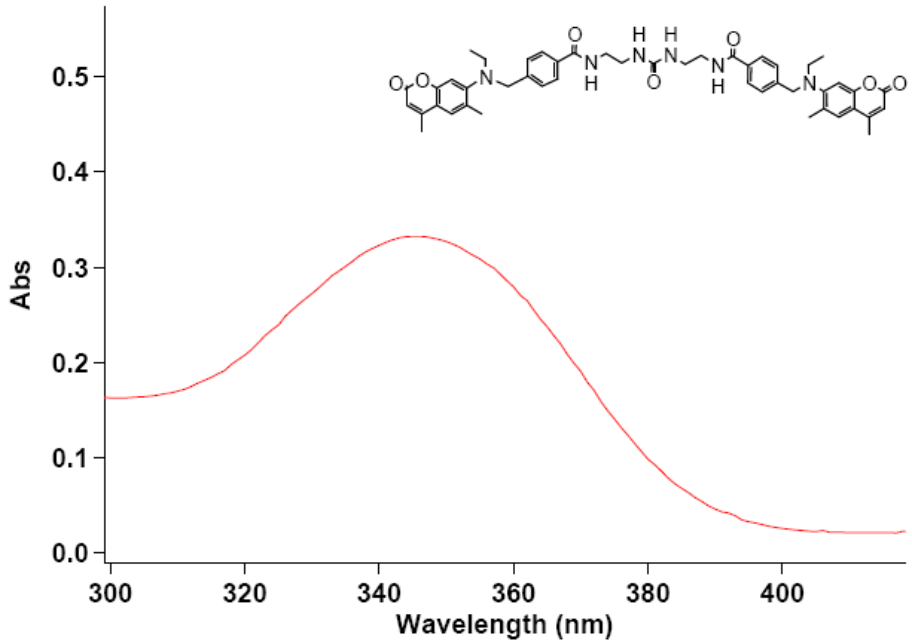
Fluorescence Spectrum:

Compound 9: [c] = 1 x 10^{-6} M. λ_{ex} = 343 nm, λ_{em1} = 422 nm, λ_{em2} = 464 nm.



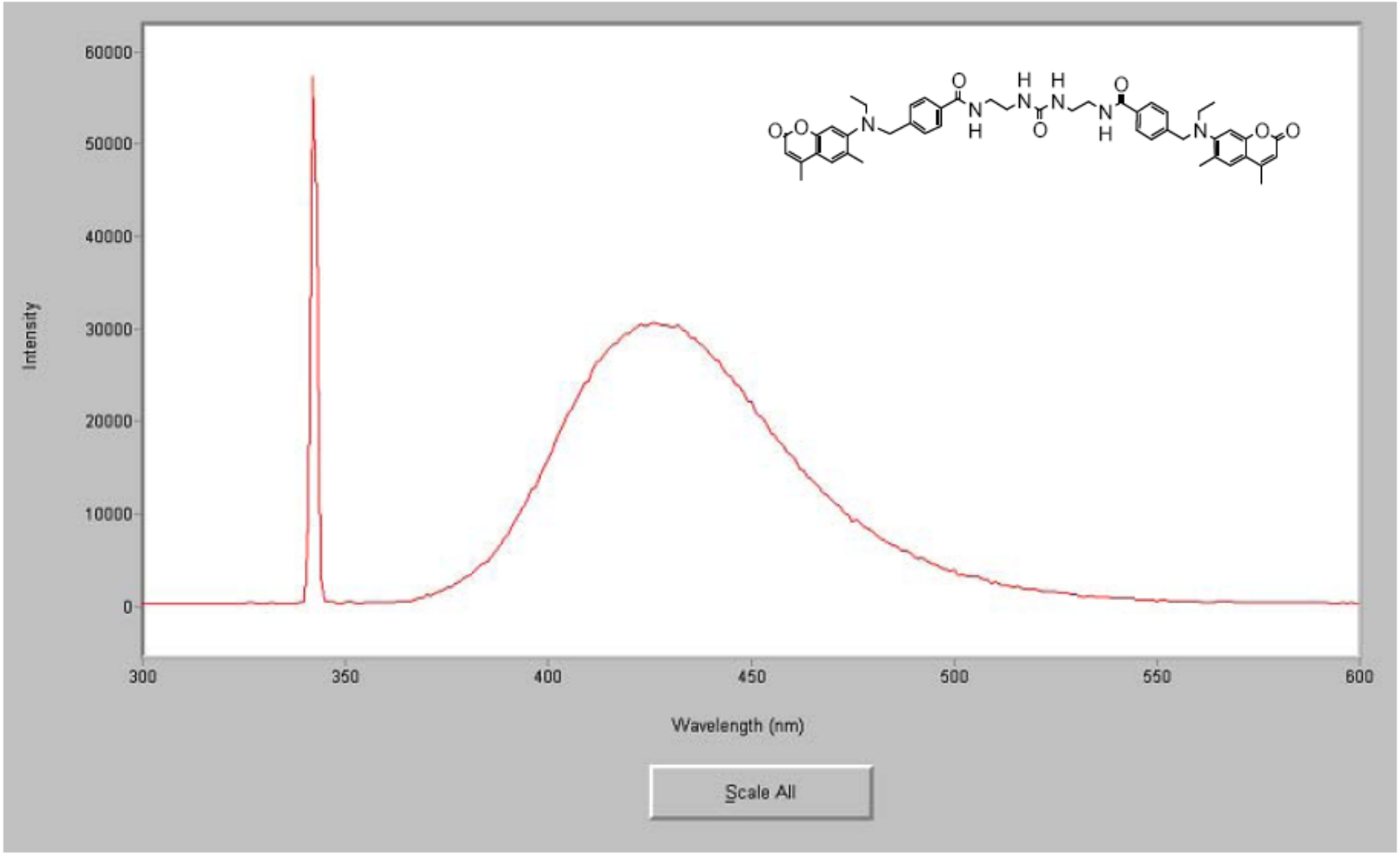
UV-vis Spectrum

Compound **7**: [c] = 1 x 10^{-6} M, λ_{max} = 344 nm



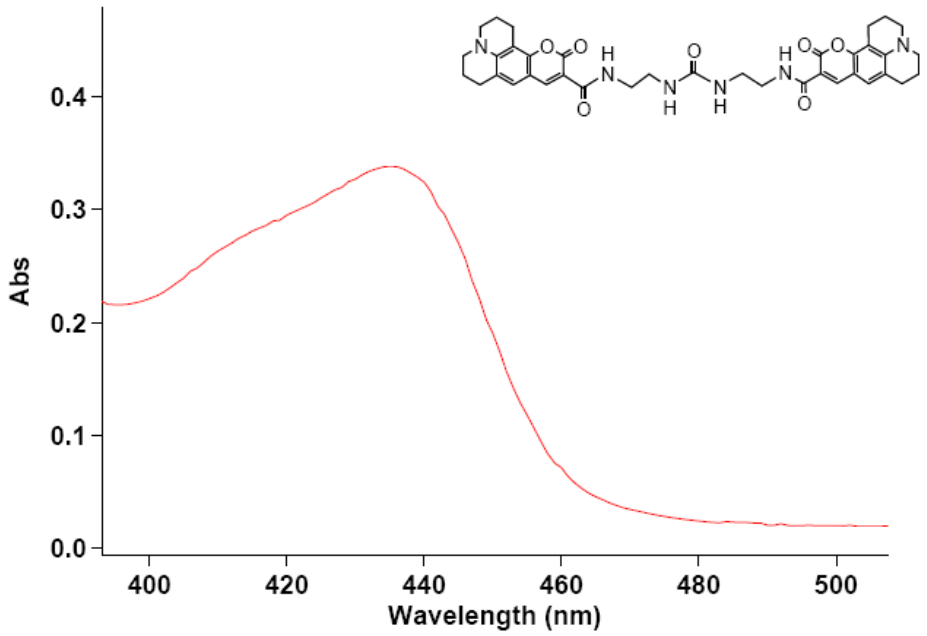
Fluorescence Spectrum:

Compound 7: [c] = 1 x 10^{-6} M. λ_{ex} = 344 nm, λ_{em} = 424 nm



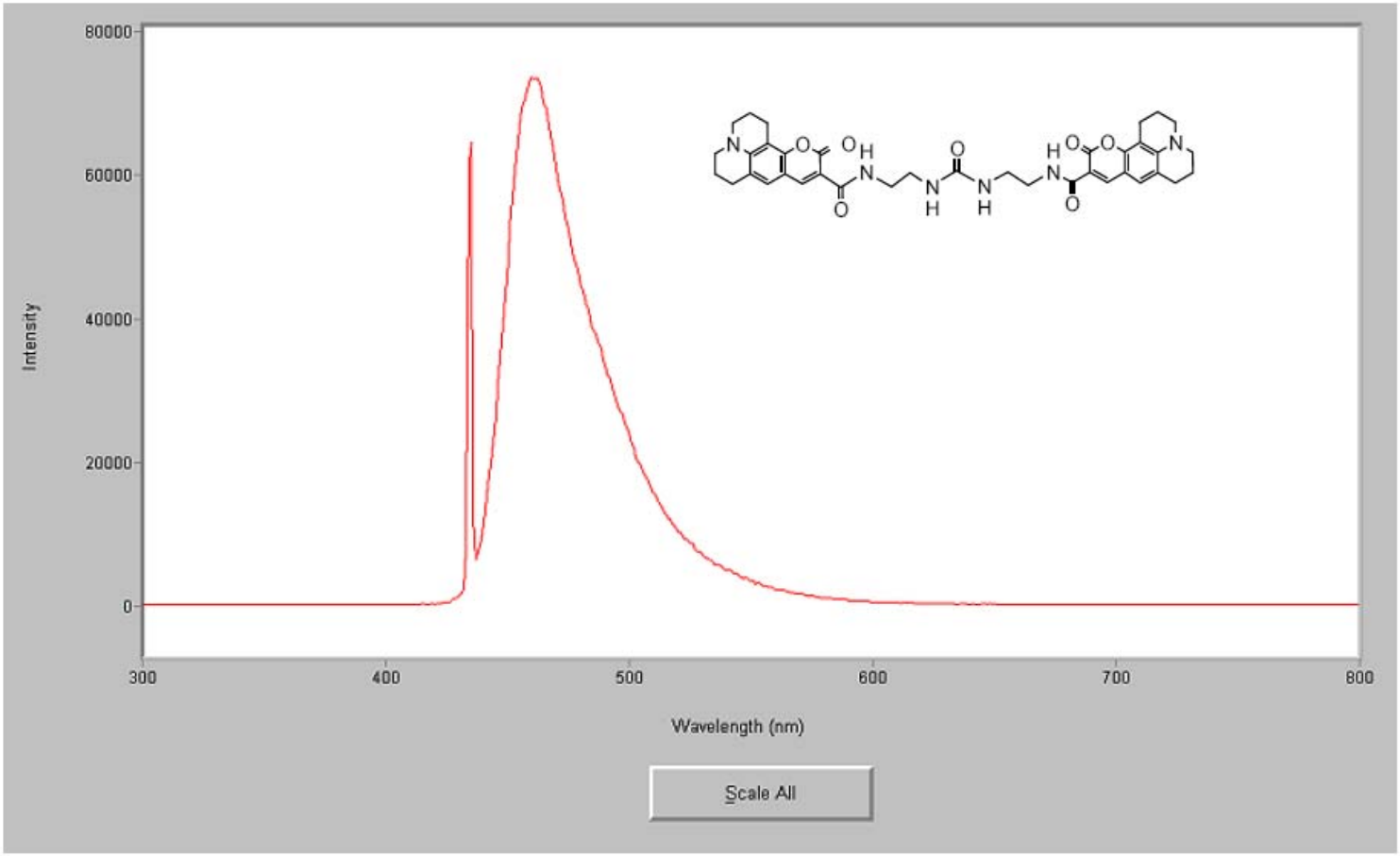
UV-vis Spectrum

Compound **8**: [c] = 1 x 10^{-6} M, λ_{max} = 435 nm



Fluorescence Spectrum:

Compound **8**: [c] = 1 x 10^{-6} M. λ_{ex} = 435 nm, λ_{em} = 462 nm



APPENDIX C

TITRATION RESULTS

Titration Results:

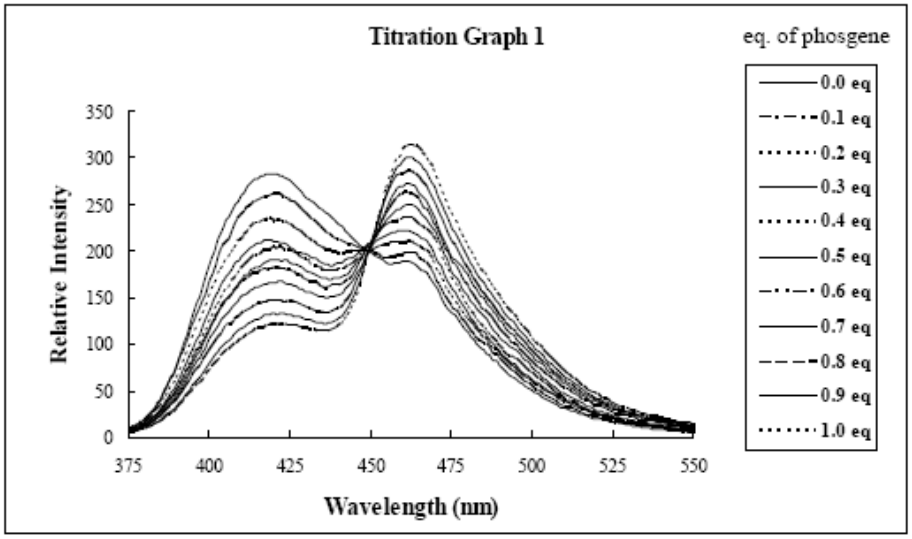


Fig. 1. Fluorescence emission spectra on titration with triphosgene. Coumarins **4** and **6** were mixed in 1:1 ratio at 1 x 10^{-2} M in $CHCl_3$, TEA (10 eq) was added. 1/3 equivalent triphosgene (equal to 1 equivalent phosgene) was added step by step. Aliquots were taken and diluted to 10^{-5} M then emission spectra were recorded. The similar result was shown in 10^{-6} M dilutions.

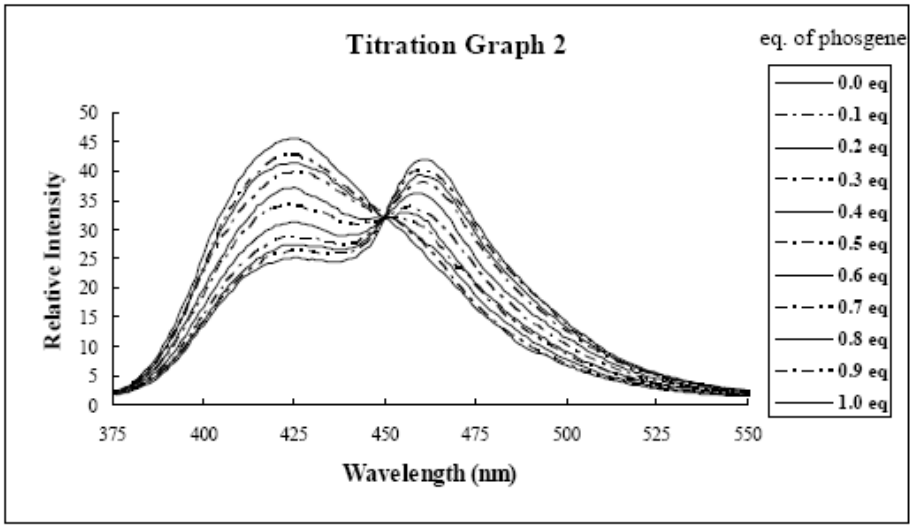


Fig. 2. Fluorescence emission spectra on titration with triphosgene. Coumarins **4** and **6** were mixed in 1:1 ratio at 1x 10^{-3} M in $CHCl_3$, TEA (10 eq) was added. 1/3 equivalent triphosgene (equal to 1 equivalent phosgene) was added step by step. Aliquots were taken and diluted 10^{-6} M then emission spectra were recorded

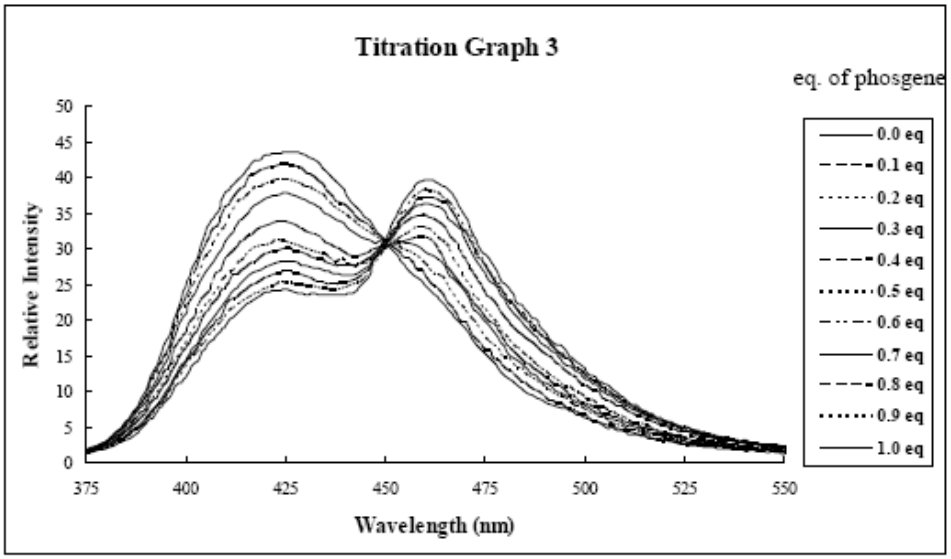


Fig. 3. Fluorescence emission spectra on titration with triphosgene. Coumarins **4** and **6** were mixed in 1:1 ratio at 5 x 10^{-4} M in $CHCl_3$, TEA (10 eq) was added. 1/3 equivalent triphosgene (equal to 1 equivalent phosgene) was added step by step. Aliquots were taken and diluted to 10^{-6} M then emission spectra were recorded

REFERENCES

(1) Lehn, J.-M. *Pure Appl. Chem.* **1978**, *50*, 871-892.

(2) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89-112.

(3) Lehn, J.-M. *Supramolecular Chemistry. Concepts and Perspectives*; VCH: Weinhein, Germany, 1995.

(4) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017-7036.

(5) Pedersen, C. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1021-1027.

(6) Dietrich, B.; Lehn, J.-M.; Sauvage, J.-P. *Tetrahedron Lett.* **1969**, *34*, 2885-2888.

(7) Lehn, J.-M. *Acc. Chem. Res.* **1978**, *11,* 49-57.

(8) Uekama, K; Hirayama, F.; Irie, T. *Chem. Rev.* **1998,** *98,* 2045-2076.

(9) Gutsche, C. D.; Muthukrishnan, R. *J. Org. Chem.* **1978**, *43*, 4905-4906.

(10) (a) Gutsche, C. D. *Calixarenes Revisited*; The Royal Society of Chemistry: Cambridge, UK, 1998. (b) Asfari, Z.; Böhmer, V.; Harrowfield, J.; Vicens, J. *Calixarene 2001*; Kluwer Academic Publishers: Dordrecht, Netherlands, **2001**.

(11) Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418-2421.

(12) Lehninger, A. L. *Biochemistry*, 2nd ed., Worth Publishers Inc.: New York, 1975.

(13) Cramer, F. *Chaos and Order. The Complex Structure of Living Systems*; VCH: Weinheim, Germany, 1993.

(14) Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2382-2426.

(15) (a) Jorgenson, W. L.; Pranata, J. *J. Am. Chem. Soc.* **1990**, *112*, 2008-2010. (b) Pranata, J.; Wierschke, S. G.; Jorgenson, W. L. *J. Am. Chem. Soc.* **1991**, *113*, 2810-2819.

(16) (a) Murray, T. J.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1992**, *114*, 4010-4011. (b) Fenlon, E. E.; Murray, T. J.; Baloga, M. H.; Zimmerman, S. C. *J. Org. Chem.* **1993**, *58*, 6625-6628.

(17) (a) Beijer, F. H.; Kooijman, H.; Spek, A. L.; Sijbesma, R. P.; Meijer, E. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 75-78. (b) Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 6761-6769.

(18) Heinz, T.; Rudkevich, D. M.; Rebek, Jr., J. *Nature* **1998**, *394*, 764-766.

(19) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759-9760.

(20) Lehn, J.-M.; Mascal, M.; DeCian, A.; Fischer, J. *J. Chem. Soc., Perkin Trans. 2,* **1992**, 461-467.

(21) Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F.; Lehn, J.-M. *Comprehensive Supramolecular Chemistry*; Elsevier Science: Oxford, UK, 1996.

(22) Lehn, J.-M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4763–4768.

(23) (a) Silver, A. *The Biology of Cholinesterases*; American Elsevier: New York, 1974, pp. 449-488. (b) Hardman, J. G.; Limbird, L. E.; Gilman, A. G. *The*

Pharmacological Basis of Therapeutics; 10th. ed., McGraw-Hill: New York, 2001, pp. 175-191.

(24) Matsumura, F. *Toxicology of Insecticides*, Plenum: New York, 1975, pp. 67-78.

(25) (a) Ashley, J. A.; Lin, C. -H.; Wirsching, P.; Janda, K. D. *Angew. Chem., Int. Ed.* **1999**, *38*, 1793-1795. (b) Richardson, S. D. *Chem. Rev.* **2001**, *101*, 211-254. (c) Prosnitz, D. *Science* **2005**, *310*, 978.

(26) (a) Stein, K.; Schwedt, G. *Anal. Chim. Acta* **1993**, *272*, 73-81; (b) Ristori, C.; Del Carlo, C.; Martini, M., Barbaro, A.; Ancarni, A. *Anal. Chim. Acta* **1996**, *325*, 151-160.

(27) Novak, T. J.; Daasch, L. W.; Epstein, J. *Anal. Chem.* **1979**, *51*, 1271-1275.

(28) Niewenhuizen, M. S.; Harteveld, J. L. N. *Sens. Actuators B* **1997**, *40*, 167-173.

(29) Steiner, W. E.; Klopsch, S. J.; English, W. A.; Clowers, B. H.; Hill, H. H. *Anal. Chem.* **2005**, *77*, 4792-4799.

(30) Sohn, H.; Letant, S.; Sailor, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **2000**, *122*, 5399-5400.

(31) De Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxyley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Ric, T. E. *Chem. Rev.* **1997**, *97*, 1515-1566.

(32) Van Houten, K. A.; Heath, D. C.; Pilato, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 12359-12360.

(33) Zhang, S. -W.; Swager, T. *J. Am. Chem. Soc.* **2003**, *125*, 3420-3421.

(34) Dale, T. J.; Rebek, J. Jr. *J. Am. Chem. Soc.* **2006**, *128*, 4500-4501.

(35) For some recent reactive sensors which utilize PET or fluorescence resonance

energy transfer (FRET) see: (a) Zhang, H.; Rudkevich, D. M. *Chem. Commun.* **2007**, 1238-1239. (b) Tal, S.; Salman, H.; Abraham, Y.; Botoshansky, M.; Eichen, Y. *Chem.-Eur. J.* **2006**, *12*, 4858-4864. (c) Albers, A. E.; Okreglak, V. S.; Chang, C. J. *J. Am. Chem. Soc.* **2006**, *128*, 9640-9641. (d) Knapton, D.; Burnworth, M.; Rowan, S. J.; Weder, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 5825-5829.

(36) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; 2nd ed., Plenum Publishing Corp.: New York, 1999.

(37) (a) Sapsford, K. E.; Berti, L.; Medintz, I. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 4562-4588. (b) Juskowiak, B. *Anal. Chim. Acta* **2006**, *568*, 171-180. (c) Valeur, B. *Molecular Fluorescence. Principles and Applications*; Wiley-VCH: Weinheim, Germany, 2002.

(38) The US Department of Health and Human Services link: http://www.bt.cdc.gov/agent/phosgene/basics/facts.asp.

(39) (a) Yun, K.-Y.; Baek, W.-W.; Choi, N.-J.; Lee, D.-D.; Kim, J.-C.; Huh, J.-S. *Chem. Sens.* **2004**, *20*, 668-669. (b) Harig, R.; Rusch, P.; Dyer, C.; Jones, A.; Moseley, R.; Truscott, B. *Proc. SPIE-The International Society for Optical Engineering* **2005**, *5995*, 599510/1-599510/12. (c) Toon, G. C.; Blavier, J. -F.; Sen, B.; Drouin, B. J. *Geophys. Res. Lett.* **2001**, *28*, 2835-2838. (d) Hill, H. H.; Martin, S. J. *Pure Appl. Chem.* **2002**, *74*, 2281-2291.

(40) Frye-Mason, G.; Leuschen, M.; Wald, L.; Paul, K.; Hancock, L. F. *Proc. SPIE-The International Society for Optical Engineering* **2005**, *5778*, Pt. 1, 337-346.

(41) (a) Gilat, S. L.; Adronov, A.; Frechet, J. M. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1422-1427. (b) Castellano, R. K.; Craig, S. L.; Nuckolls, C.; Rebek, Jr., J. *J. Am. Chem. Soc.* **2000**, *122*, 7876-7882. (c) Kishimoto, A.; Mutai, T.; Araki, K. *Chem. Commun.* **2003**, 742-743.

(42) (a) Bigi, F.; Maggi, R.; Sartori, G. *Green Chem.* **2000**, *2*, 140-148. (b) Cotarca, L.; Delogu, P.; Nardelli, A.; Sunjic, V. *Synthesis* **1996**, *5*, 553-576.

(43) The formation of urea **9** under these conditions was confirmed by ^{1}H NMR spectroscopy. In addition to **9**, two other, symmetrical ureas **7**, **8** are also formed with two donor or two acceptor fragments. However, they do not emit fluorescence around 464 nm upon excitation at λ = 343 nm at these concentrations.

(44) Some possible exceptions could be thionyl chloride ($S(O)Cl_2$), oxalyl chloride ($(COCl)_2$), or dimethyl carbonate ($(CH_3CO)_2O$). However, as liquid at rt, none of them has vapor pressure over 10% of phosgene.

(45) (a) Stigliani, W. M.; Spiro, T. G.; *Chemistry of the Environment;* 2nd ed., Prentice Hall: Upper Saddle River, USA, 2003, pp. 3-178; (b) Schimel, D. S.; House, J. I.; Hibbard, K. A.; Bousquet, P.; Ciais, P.; Peylin, P.; Braswell, B. H.; Apps, M. J.; Baker, D.; Bondeau, A.; and et al. *Nature* **2001**, *414*, 169-172;

(46) (a) Dell' Amico, D. B.; Calderazzo, F.; Labella, L.; Marchetti, F.; Pampaloni, G. *Chem. Rev.* **2003**, *103*, 3857-3898. (b) McGhee, W. D.; Riley, D.; Christ, K.; Pan, Y.; Parnas, B. *J. Org. Chem*. **1995**, *60*, 2820-2830. (c) Waldman, T. E.; McGhee, W. D. *J. Chem. Soc., Chem. Comm.* **1994**, 957-958. (d) Salvatore, R. N.; Shin, S. I.; Nagle, A. S.; Jung, K. W. *J. Org. Chem.* **2001**, *66*, 1035-1037. (e) Aresta, M.; Quaranta, E. *Tetrahedron* **1992**, *48*, 1515-1530.

(47) (a) Yamaguchi, T.; Boetje, L. M.; Koval, C. A.; Noble, R. D.; Bowman, C. N. *Ind. Eng. Chem. Res.* **1995**, *34*, 4071-4077. (b) Yamaguchi, T.; Koval, C. A.; Nobel, R. D.; Bowman, C. N. *Chem. Eng. Sci.* **1996**, *51*, 4781-4789. (c) Sada, E.; Kumazawa, H.; Han, Z. *Chem. Eng. J.* **1985**, *31*,109-115. (d) Kovvali, A. S.; Sirkar, K. K. *Ind. Eng. Chem. Res.* **2001**, *40*, 2502-2511.

(48) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, Jr., J. H. *J. Am. Chem. Soc.* **2002**, *124*, 926-927.

(49) Ki, C. D.; Oh, C.; Oh, S.-G.; Chang, J. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14838-14839.

(50) Hampe, E. M.; Rudkevich, D. M. *Tetrahedron* **2003**, *59*, 9619-9625.

(51) (a) Lehn, J.-M. *Chem.-Eur. J.* **1999**, *5*, 2455-2463. (b) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 898-952.

(52) (a) George, M.; Weiss, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 10393-10394. (b) George, M.; Weiss, R. G. *Langmuir* **2002**, *18*, 7124-7135. (c) Carretti, E.; Dei, L.; Baglioni, P.; Weiss, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 5121-5129. (d)

George, M.; Weiss, R. G. *Langmuir* **2003**, *19*, 1017-1025. (e) George, M.; Weiss, R. G. *Langmuir* **2003**, *19*, 8168-8176.

(53) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133–3159.

(54) Xu, H.; Hampe, E. M.; Rudkevich, D. M. *Chem. Commun.* **2003**, 2828-2829.

(55) Xu, H.; Rudkevich, D. M. *Chem.-Eur. J.* **2004**, *10*, 5432-5442.

(56) Rudkevich, D. M.; Xu, H. *Chem. Commun.* **2005**, 2651-2659.

(57) (a) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; John Wiley & Sons Ltd.: Chichester, UK, 2000. (b) Beer, P. D.; Gale, P. A.; Smith, D. K. *Supramolecular Chemistry*; Oxford University Press: Oxford, UK 1999. (c) Dodziuk, H. *Introduction to Supramolecular Chemistry*; Kluwer Academic Publishers: Dordrecht, Netherlands, 2002.

(58) *Comprehensive Supramolecular Chemistry*; *Vol 1. Molecular Recognition: Receptors for Cationic Guests;* Gokel, G. W.; *Vol. 2. Molecular Recognition: Receptors for Molecular Guests;* Vögtle, F.; Elsevier Science: Oxford, UK, 1996.

(59) Stastny, V.; Rudkevich, D. M. *J. Am. Chem. Soc.* **2007**, *129*, 1018-1019.

(60) Xu, H.; Rudkevich, D. M. *Org. Lett.* **2005**, *7*, 3223-3226.

(61) Ciferri, A. *Supramolecular Polymers*; 2nd ed., CRC Press: Boca Raton, USA, 2005.

(62) Pedersen, C. J.; Frensdorff, H. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 16-25.

(63) (a) Arnaud-Neu, F.; Collins, E. M.; Deasy, M.; Ferguson, G.; Harris, S. J.; Kaitner, B.; Lough, A. J.; McKervey, M. A.; Marques, E.; Ruhl, B. L.; and et al. *J. Am. Chem. Soc.* **1989**, *111*, 8681-8691.

(64) a) Gutsche, C. D.; Iqbal, M. *Org. Synth.* **1990**, *68*, 234-237; (b) Gutsche, C. D.; Levine, J. A.; Sujeeth, P. K. *J. Org. Chem.* **1985**, *50*, 5802-5806.

(65) Yamada, A.; Murase, T.; Kikukawa, K.; Matsuda, T.; Shinkai, S. *Chem. Lett.* **1990**, 455-458.

(66) (a) Liu, Y.; Jessop, P. G.; Cunningham, M.; Eckert, C. A.; Liotta, C. L. *Science* **2006**, *313*, 958-960. (b) Jessop, P. G.; Heldebrant, D. J.; Li, X.; Eckert, C. A.; Liotta, C. L. *Nature* **2005**, *436*, 1102.

(67) (a) Ballivet-Tkatchenko, D.; Camy, S.; Condoret, J. S. *Environ. Chem.* **2005**, 541-552. (b) Beckman, E. J. *Chem. Commun.* **2004**, 1885-1886.

(68) McKervey, M. A.; Seward, E. M.; Ferguson, G.; Ruhl, B.; Harris, S. J. *J. Chem. Soc., Chem. Commun.* **1985**, *7*, 386-388.

(69) Arduini, A.; Pochini, A.; Reverberi, S.; Ungaro, R. *J. Chem. Soc., Chem. Commun.* **1984**, 981.

BIOGRAPHICAL INFORMATION

Hexiang Zhang, born in 1979 in Tangshan, Hebei Province, P.R.China, obtained his B.S. in 2001 from Dalian University of Technology, Dalian, China. He came to The United States in 2004 and began his M.S. study at the University of Texas at Arlington under the supervision of Professor Dmitry. M. Rudkevich. He received his M.S. degree in Chemistry in 2007. His research interests are in supramolecular chemistry on carbon dioxide.