SYNTHESIS AND CHARACTERIZATION OF POLYTHIOPHENE DERIVATIVES

by

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ABSTRACT

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POLYTHIOPHENE DERIVATIVES

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In Chapter 1, the history of conducting polymers, especially polythiophene and its derivatives, was briefly reviewed. Different approaches of structural modifications to afford small bandgap polythiophene derivatives were discussed. The emergence of metal-containing polymers (metallopolymers) as functional materials has attracted tremendous attention around the world. Introduction of metals into thiophene-based oligomers and polymers, whether the backbone or the side chain of the π-conjugated framework, the electronic, optical, or magnetic properties of the material are expected

to be significantly affected by metals through various mechanisms. Synthesis methods to prepare poly(thienylene vinylene) were also briefly reviewed in this chapter.

In Chapter 2, the motivations and objectives were briefly discussed. Two structurally similar compounds, thieno[3,4-*d*]-1,3-dithiole-2-thione and thieno[3,4-*d*]-1,3-dithiol-2-one are the starting point of this project due to their unique carbondithiolate structures, which may lead to metal-dithiolate coordinated oligomers or/and polymers, or polymers crosslinked by DTTTF units. For the preparation of monomers, six types of reactions were systematically studied with focus on thieno[3,4-*d*]-1,3-dithiol-2-one to prepare different direvatives. Different halogenated compounds, Mannich bases, chloromethylated compounds, a number of nucleophilic substituted derivatives and a DTTTF analogue from chloromethylated compounds were successful synthesized. All products were fully characterized through ^{1}H and ^{13}C-NMR, FT-IR, ESI-TOF high resolution mass spectroscopy. The halogenated products were prepared through halogensuccinimides or other halogenation reagents such as Br_2, I_2. These halogenated compounds may be candidates to prepare homopolymer and/or copolymers bearing carbondithiolate structures by cross-coupling reactions. 4,6-Bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one and its nucleophilic derivatives may be good monomers for the two-step precursor polymerization to achieve fully conjugated poly(thienylene vinylene) derivatives and even metallopolymers with metal-dithiolate coordinations.

Attempted polymerization reactions to homopolymers and copolymers through directly C-C coupling, such as transitional metal catalyzed cross-coupling, Stille reaction, and Ullman reaction, et. al. were discussed in the beginning of Chapter 3.

Base-promoted and acid-promoted polymerizations were attempted to afford soluble precursor polymers with carbondithiolate structures. However, all the symmetrical thiophene derivatives did not successfully yield processable precursor polymers; asymmetrical monomers generated some possibilities for future study. Synthesis of thiophene-based oligomers, such as dimmers (dithienyl compounds), trimers (trithienyl compounds), and heptamers were also explored in chapter 3, followed by preparation of thiophene-based copolymers through Wittig-Horner reactions. Properties of oligomers, especially trimers were well characterized by NMR, FT-IR, and ESI-TOF. Several conjugated DTTTF derivatives from trimers were prepared by the triethyl phosphite cross-coupling method. These conjugated DTTTF compounds posses some unique properties. They are stable in solid forms, but may be doped in solution forms. The copolymers were characterized by elemental analysis, and FT-IR. UV-Vis spectra of copolymers show their bandgap values are aroud 1.87eV (UV edge calculation).

In the Experimental chapter, all reaction conditions of preparation of new annulated thiophene derivatives and oligomers were documented in details. Physical and spectroscopic properties of these new compounds were also presented in this chapter.

KEY WORDS: polythiophene, oligomer, conjugation, synthesis, characterization, DTTTF, metallopolymer

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Ac: acetyl

Bu: butyl

CTC: charge-transfer complex

DMF: *N, N*-dimethylformamide

DMSO: dimethylsulfoxide

DTTTF: $\Delta^{2,2'}$-bithieno[3,4-*d*]-1,3-dithiole; or 2-thieno[3,4-*d*]-1,3-dithiol-2-ylidene-thieno[3,4-*d*]-1,3-dithiole

EDOT: 2,3-dihydrothieno[3,4-*b*]-1,4-dioxin

ESI: electrospray ionization

GRIM: Grignard metathesis

HOMO: the highest occupied molecular orbital

IBX: *o*-iodoxybenzoic acid

LUMO: the lowest unoccupied molecular orbital

NBS: *N*-bromosuccinimide

NCS: *N*-chlorosuccinimide

NIS: *N*-iodosuccinimide

PCC: pyridinium chlorochromate

PEDOT: poly(3,4-ethylene dioxythiophenes)

PI: polydispersity index

PITN: poly(isothianapthene)

TCNQ: tetracyanoquinodimethane

THF: tetrahydrofuran

TLC: thin layer chromatography

TMS: trimethylsilyl

TOF: time-of-flight

TTF: tetrathiafulvalene

CHAPTER 1

BACKGROUND

1.1 Overview

1.1.1 Conducting polymers

The discovery of semiconducting and metallic properties of polyacetylene by A. G. MacDiarmid, A. J. Heeger, H. Shirakawa and coworkers in 1977[1-5] triggered a tremendous research activity including the participation and coordination of synthetic chemists, physicists, materials scientists, and electrical engineers. The concept of conducting polymer was quickly broadened from polyacetylene to all other conjugated hydrocarbon and aromatic heterocyclic polymers such as polythiophene (PT), poly(*p*-phenylene) (PPP), poly(phenylene sulfide) (PPS), polypyrrole (PPy), and polyaniline (PAni). The most widely studied conductive polymers are list in Table 1.1. 2000 Nobel Prize for Chemistry was awarded to A. G. MacDiarmid, A. J. Heeger, H. Shirakawa for their pioneering work in conducting polymers, which was the fourth time for research on polymer chemistry and physics.

From molecular structure point of view, the conducting polymers posses a highly delocalized π-conjugation system. Fig. 1.1 shows the evolution of band structure of polythiophene upon oxidative doping. Upon oxidative doping (oxidation reactions) with oxidants, an electron is removed from the π-system of polythiophene backbone

producing a free radical and a spinless positive charge. The radical and cation are coupled to each other via local resonance of the charge and the radical. The structural distortion site has higher energy level than the rest of polymer chain. This combination of the charged site and paramagnetic defect site is viewed as a polaron, and it creats a new localized energy state in the gap with a single electron occupies the lower energy state (Fig 1.1 b). Upon further doping (oxidation), the bipolaron (two separated charged defects) can be produced through either removing free radicals from polarons or recombination of polarons. Thus at higher doping level, polarons are replaced with bipolarons. The bipolaron states are located in a band gap of 0.71eV from the edge of conduction band and 0.61eV from the edge of valence band for polythiophene respectively (Fig.1.1 c). Upon continuous doping, bipolaron states will gradually form a

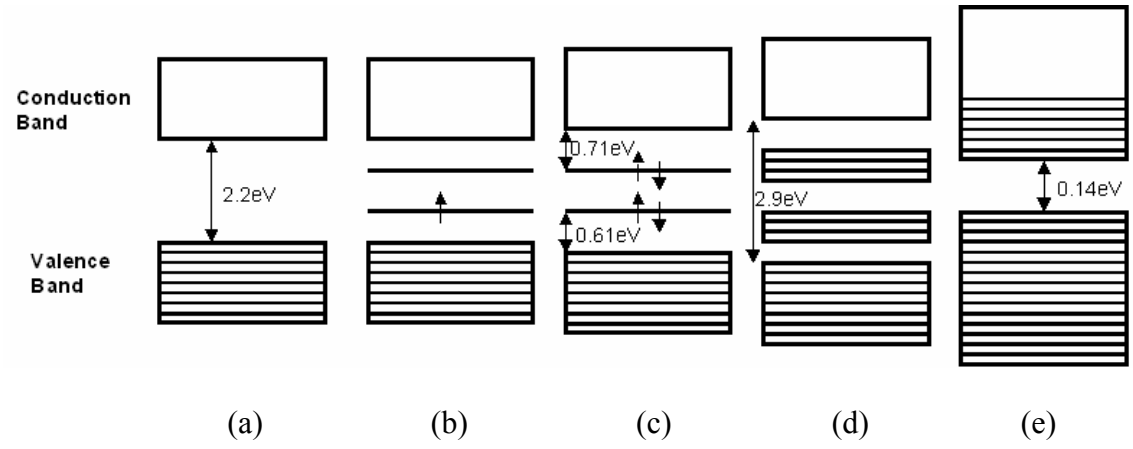
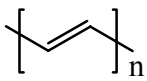
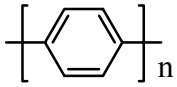
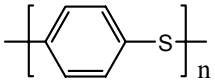
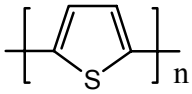
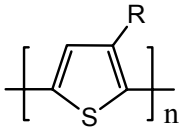
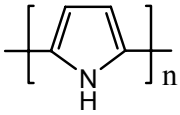
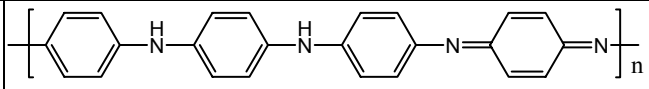
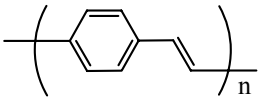
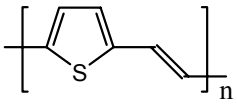
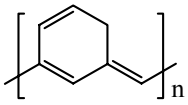


Fig. 1.1 Evolution of band structure of polythiophene on doping.

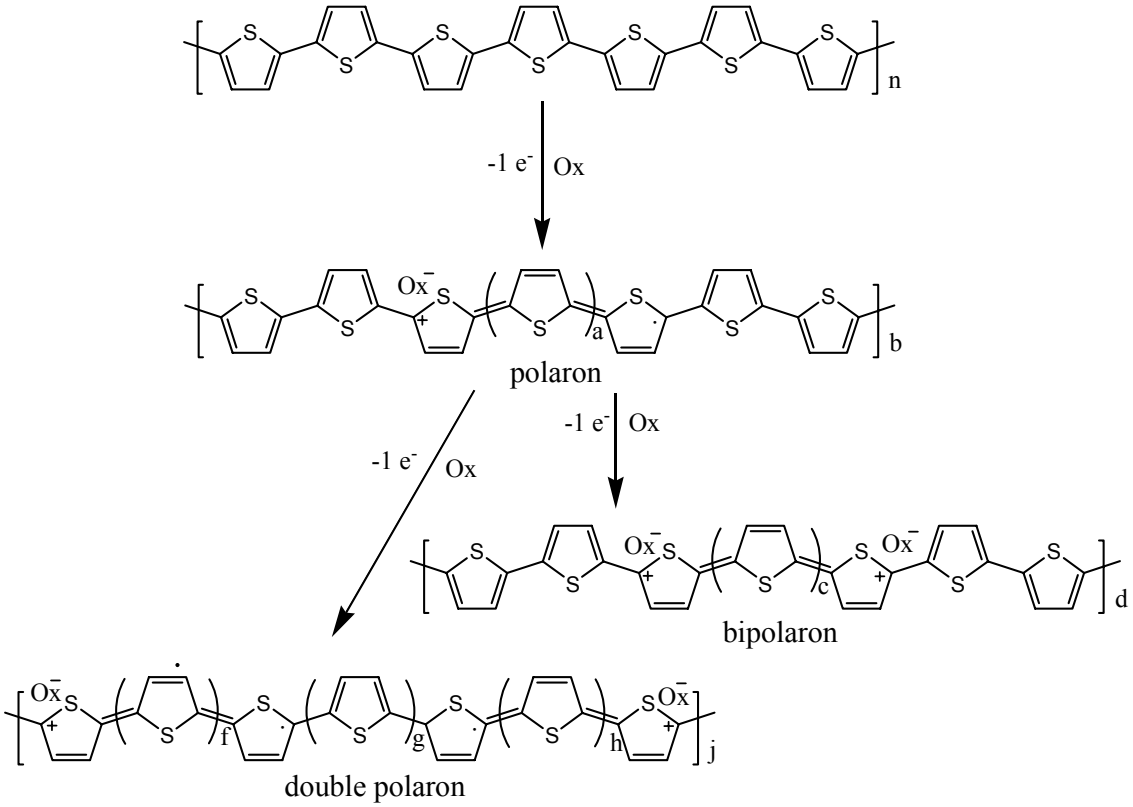
(a) neutral polythiophene, (b) 0.1% doping level with formation of polaron states, (c) few percent doping with formation of bipolaron states, (d) 30% doping level with formation of bipolaron bands, (e) hypothetical 100% doping level with appearance of quasi-metallic band structure.[15]

Table 1.1 List of the most widely investigated conjugated polymer systems

Conjugated Polymer	Structure	Ref.
Polyacetylene (PA)		(4)
Poly(*p*-phenylene) (PPP)		(6)
Poly(*p*-phenylene sulfide) (PPS)		(7)
Polythiophene (PT)		(8)
Poly(3-alkylthiophene) (P3AT)		(9)
Polypyrrole (PPy)		(10)
Polyaniline (PAni) (Emeraldine base)		(11)
Poly(phenylene vinylene) (PPV)		(12)
Poly(thienylene vinylene) (PTV)		(13)
Poly(1,6-heptadiyne)		(14)

continuous bipolaron bands (Fig.1.1 d). Theoretically, at 100% doping level, the upper and the lower bipolaron bands will merge with the conduction and the valence bands respectively to produce partially filled bands and metallic conductivity (Fi.g.1.1 e).[15] The structural change of polythiophene upon p-doping was illustrated in Scheme 1.1.[16]

Scheme 1.1 Structural change of polythiophene upon p-doping



For conjugated polymers with nondegenerate states such as polythiophene, bipolaron-transport model well fit the conduction mechanism with experimental data. Conjugated polymer (such as *trans*-polyacetylene) with a degenerate ground state have a slightly different mechanism that involved with the formation of solitons.[17-18]

Conduction by polarons or bipolarons is now generally accepted as the dominant mechanism of interchain transport. Charges on the polymer backbone must hop from chain to chain, as well as move along the chain, for bulk conductivity to be possible.[19]

Applications of conducting polymers can be classified as two main categories: (1) utilizing of electrical conductivity. In this category, applications of conducting polymers include: anti-electrostatic coating, conducting adhesive, electro-magnetic interference shielding, anti-corrosion coating, electrode, organic field effect transistor (FET) and nanoelectronic device. (2) utilizing of electroactivity. Applications in this category include: polymer light emitting diode (or flexible flat panel display), electrochromic devices (or smart window), chemical or moisture sensor, rechargeable battery, solar cell (or other solid electrolyte), electromechanical actuator, molecular electronic device, optical switch, nonlinear optical device, radar/microwave absorbing coating and biomedical applications, such as artificial nerve, drug release system.[20-21] Some applications have been commercialized during the past decade; some are still under comprehensive laboratory investigations.

1.1.2 Thiophene-based conjugated polymers

Thiophene-based conjugated polymers have attracted considerable attention during the past two decades due to a wide range of unique electrochemical, electronic, and optical applications. Especially low bandgap thiophene-based polymers are very promising materials with high conductivities, high degrees of optical transparency, and

enhanced nonlinear responsed.[22] Other important factors that determine polythiophene (PT) and its derivatives could be one of the most likely candidates for commercial applications are because of the high stability of both its doped and undoped states, ease of structural modification of polymer backbone, and very good solubility of 3-substituted polythiophene derivatives.

1.2 Structure modification of polythiophene

Because polythiophene posses so manyunique properties for possible wide range of applications, structural modifications of polythiphene are of great importance. Two main objectives of functionalizing polythiophene are, (1) improving electrical property: to obtain low bandgap polythiophene derivatives with good conductivity; (2) improving physical property: to obtain processable polythiophene derivatives with long term stability.

During the past two decades, tremendous efforts were put into searching for low bandgap polythiophene derivatives due to their possessed some practical advantages over other higher band-gap materials. The reasons for low band-gap conducting polymers include: (1) easy doping with possible intrinsic metallic conductivity, (2) improved photoconductivities for solar cell application, (3) large nonlinear optical coefficients, and (4) possible transparent materials in doped states.[23]

There are some other special features which polythiophene usually does not afford, such as: good solubility, fast nonlinear optical (NLO) response, excellent crystallinity, and better mechanical properties, could possibly achieved by structural

modification approaches. In this section, several approaches proved for effectively lowering the bandgap, or enhancing other electrical and/or mechanical properties of polythiophene derivatives are briefly reviewed.

1.2.1 Functionalization of polythiophenes

Initial purpose of functionalization of polythiophene is to synthesize processable polythiophene. A milestone in the development of polythiophene derivatives is the successful synthesis of poly(3-alkylthiophene) by introducing an alkyl group into the β-position of thiophene ring by R. L. Elsenbaumer's group.[24-25] Poly(3-alkylthiophene) not only can readily be melt- or solution processed into film that after p-doping shows reasonable conductivity,[20] but also allowed the polymer to be fully characterized by chemical and physical methods. Since then, comprehensive reseach efforts targeting functionalization of polythiophene were extended to several categories: (1) attachment of pendant side chains to polythiophene backbone; (2) annulation of thiophene ring; (3) introduction of conjugated spacers; (4) synthesis of regioregular polythiophene derivatives; (5) synthesis of thiophene-based copolymers; and (6) synthesis of thiophene-based metallopolymers.

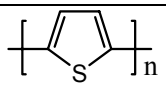
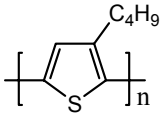
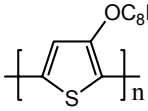
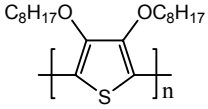
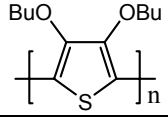
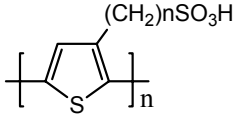
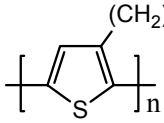
Other physical methods or techniques such as: polymer blend (composite)[26] are also extensively explored approaches for functionalization of thiophene-based polymers, since they are beyond the scope of our research activities, those physical methods are not covered in this brief review.

1.2.2 Attachment of pendant side chains

From the electronic effect point of view, the presence of electron donating substituent group such as alkyl or alkoxy group can raise the energy level of the highest occupied molecular orbital (HOMO), which result in narrowing the band gap of the polythiophene derivative;[27] but from the steric effect point of view, introduction of substituent groups will reduce the coplanarity of polythiophene backbone, which consequently will increase the band gap of polythiophene derivatives.[28] This effect is clearly prominent in 3,4-disubstituted polythiophenes. Finding a balance point of both electronic and steric effects is a very pivotal step in choosing appropriate substituent function groups, which will benefit lowering the band gap of polythiophene derivatives.

Another advantage of attaching side chain(s) to the thiophene ring is that steric factor can prevent α-α and α-β coupling of thiophene moieties during polymerization which can result in undesired properties of polymers.[29] Table 1.2 demonstrates how mesomeric and steric effects affect the bandgaps of 3-substituted and 3,4-disubstituted polythiophene derivatives. From item 1 to item 4, the bandgap data clearly show that attaching electron donating groups, such as alkyl group, oxyalkyl group, can lower the bandgap of polythiophene derivatives. Study on poly(3-butoxythiophene) and poly(3,4-dibutoxythiophene) shows steric effect is the predominant factor over electronic effect in determining bandgaps of polythiophene derivatives.[41]

Table 1.2 Structures and properties of substituted polythiophene derivatives

No.	Structures	λ_{max}/nm (bandgap eV)	*M*n (PI)(*)	σ S/cm (dopant)	Ref.
1		418-480 (2-2.5)	--	100 (ClO_4^-)	30-32
2		Regiorandom 432 (2.1) Regioregular 610 (1.7)	- -	5 (I_2) 1350 (I_2)	33
3		570 (1.6)*	-	-	34-35
4		548 (1.9)*	-	-	34-35
5		460 (1.75)	-	10^{-5} ($FeCl_3$)	36
6		n =2 431(2.6) n =6 402	$5.1x10^5$ (1.02) $5.1x10^5$ (1.02)	10^{-2} (no dopant) 10^{-4} (no dopant)	37-39
7		558	$1.1x10^4$ (1.6)	-	40

Notes: * bandgap values were estimated from published spectra.

Polymers with –alkyl-SO_3H function groups are not only soluble in water, but also can be naturally doped (self-doping) under ambient conditions.[37-39] The UV-Vis spectra of poly[2-(3'-thienyl)ethanesulfonic acid] (P3TESH) and poly[6-(3'-thienyl) hexanesulfonic acid] (P3THSH) (Fig 1.2) exhibits a π-π^* transition peaks around 450nm as usual polythiophene derivatives, and they also gives peaks around 800nm, which is accounted for formation of polaron and/or bipolaron states in the polythiophene main chain.[37] Hydroxy-functionalized polythiophenes provide the opportunities of forming

hydrogen bonds between the side chains reduces the rotational mobility of the polythiophene backbone while favouring states which are conformationally better ordered.[42-43]

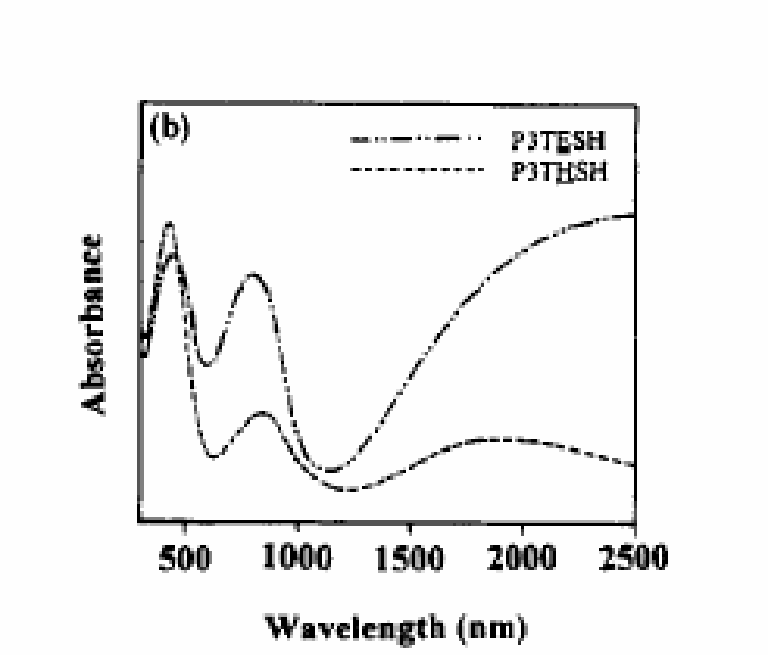
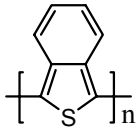
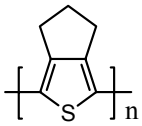
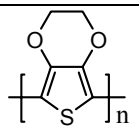
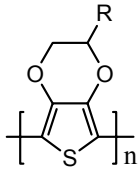
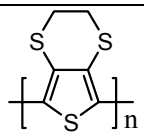
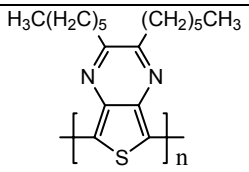
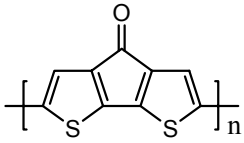
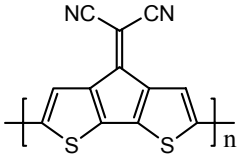
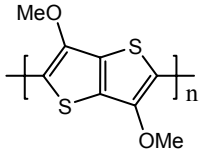


Fig. 1.2 UV-Vis-near-IR spectra of poly[2-(3'-thienyl)ethanesulfonic acid] (P3TESH) and poly[6-(3'-thienyl)hexanesulfonic acid] (P3THSH)[37]

1.2.3 Annulation of thiophene ring

Poly(isothianapthene) (PITN) was the pioneering work of introducing fused ring to attach the thiophene ring which was reported by Wudl in 1984.[44] The annulation of the thiophene ring with a cyclohexadiene system afford a highly planarized polymer structure which shows a very low band gap of around 1ev. Saturated alkyl ring did not show favorable effects on narrowing bandgap or enhancing conductivities. Steric

Table1.3 Polymer structures and properties of annulated polythiophenes

No.	Structures	λ_{max}/nm (bandgap eV)	*M*n (PI)	Conductivity (S cm^{-1})	Ref.
1		885 (~1)	-	50 (I_2)	44-46
2		510 (~1.8)	-	5 ($FeCl_3$)	47
3		630 (1.6)	-	5-10($FeCl_3$) 200 (anodic)	48-49
4		R=$C_{14}H_{29}$ 577 (1.78) R=C_6H_{13} 546 (~1.75*)	$5.65x10^3$ (1.93) $5.4x10^3$ (1.57)	- -	50 51
5		413 (2.19) 419 (2.14)	$3.03x10^3$ (1.9) $4.75x10^3$ (1.7)	0.1($FeCl_3$) 0.4 (ClO_4^-)♦	52
6		915 (0.95)	-	$3.6x10^{-2}$ ($NOBF_4$)	53-54
7		740 (~1.2)	-	-	55-57
8		950 (~0.8)	-	-	55-57
9		592 (1.65)	-	10^{-2} (PF_4^-) ♦	58

Notes: * Calculated according to published spectra. ♦electrochemically doped.

torsion especially for those fused with a big cycloalkyl rings, will increase bandgaps by decreasing the coplanarity of adjacent thiophene rings. Study on poly(cycloalkyl[c] thiophene) yield similar result as that on poly(3-alkylthiophene), ring size and interchain interaction (steric factor) play a dominant role in determining the bandgap and conductivities.[47] Table 1.3 shows some fused ring systems and their properties of annulated thiophene-based polymer systems.

Polythiophene derivatives fused with unsaturated structure usually afford a rigid polymer backbone with well-maintained coplanarity of neighboring thiophenes, but result in an insoluble and infusible material (Table 1.3, entry 1). The table clearly demonstrated that the bandgap can be tuned in the range of 1.0 - 2.2eV. Extremely low bandgap values of poly(cyclopenta[2,1-*b*;3,4-*b*']dithiophene-4-one) (Table 1.3 Entry 7) and poly(4-dicyanomethylene-4H-cyclopenta[2,1-*b*;3,4-*b*']dithiophene) (Table 1.3 Entry 8) can be explained by the alternating electron donating and accepting units in polymer backbones,[55-57] this donor-acceptor theory will be discussed in more detail in section 1.2.6.

Among all polythiophene derivatives in this class, poly(3,4-ethylene dioxythiophenes) (PEDOT) is the most comprehensively studied material due to its interesting properties since it was first synthesized by researchers in Bayer AG in late 1980s.[59] Oxidatively doped PEDOT possessed high conductivity (up to 300 S/cm), high transparency, and high thermal stability in atmospheric environment.[60] The insolubility problem soon was overcome by (1) using water soluble poly(styrene sulfonic acid) (PSS)[61] as the charge-balancing dopant during polymerization to yield

PEDOT/PSS; or (2) attaching an alkyl group on the dioxane ring to afford a soluble PEDOT derivatives.[62] Both monomer 2,3-dihydrothieno[3,4-*b*]-1,4-dioxine (or 3,4-ethylenedioxythiophene, EDOT) and polymer PEDOT/PSS were made commercially available by Bayer AG under trade name BAYTRON M® and BAYTRON P®, respectively. Driven by the properties, utilities of PEDOT and commercial availability of monomers, thousands of journal papers and patents were published focusing on synthesis and application in the past 15 years.

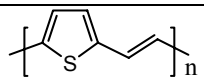
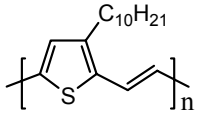
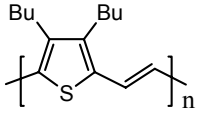
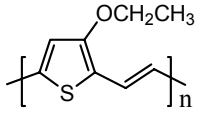
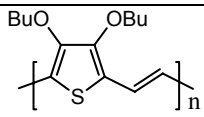
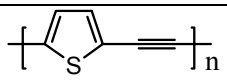
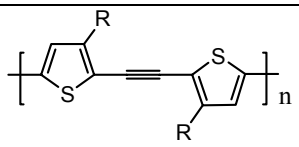
1.2.4 Introducing conjugated ring spacers

As it was pointed out in the early sections, effective conjugation length and coplanarity of thiophene backbone are two dominant factors which determine the bandgap and conductivity of conducting polythiophene derivatives. Introducing a conjugated spacer, such as C=C double bond or C≡C triple bond not only extend the conjugation system of polymer backbone, but also reduce the steric torsion caused by interaction between adjacent thiophene rings or its β position substituent groups, thus result in narrowing down the bandgap and increasing intrinsic conductivity of the polymers. Here we only include vinylene and acetylene groups as conjugated spacers, other more complicated structures such as aromatic group will be discussed in the latter section as copolymers.

Table 1.4 shows some polythiophene derivatives and their properties tuned by conjugated spacers. It clearly indicates that vinylene and acetylene groups can reduce

bandgaps about 0.5 and 1.0eV than the parent polythiophene (*E*g = 2.1eV), respectively (Entry 1 and 6).

Table 1.4 Examples of polythiophene derivatives with conjugated spacers

No.	Structures	λ_{max}/nm (E_g eV)	*M*n (PI)	Conductivity (S cm^{-1})	Ref.
1		540 (1.64)	-	40 (I_2)	63
2		605 (1.8)	$5.4x10^3$ (1.6)	10^{-2}(I_2)	64
3		550 (1.7)	$2.8x10^3$ (1.5)	10^{-2}(I_2)	64
4		600 (1.5)	-	1.8 ($FeCl_3$)	65-66
5		702 (1.2) 609 (1.62)	$8.7x10^4$ (2.2) $5.7x10^4$ (-)	1.0 ($FeCl_3$) 1.0 ($FeCl_3$)	67 68-69
6		496 (1.0)	-	-	70
7		R=H 519 (1.8) R=C_4H_9 535 (1.7)	$1.5x10^3$ (1.5) $5.5x10^3$ (1.8)	1.5 (I_2) $3x10^{-2}$ (I_2)	71

Generally, conjugated spacers can be introduced into polymer backbone by two approaches, (1) metal-catalysized Grignard coupling of thiophene moieties with dihaloethylene or dihaloacetylene;[65-66] and (2) two-step precursor polymerization consists preparation of a precursor polymer, which is then thermally treated to yield

conjugated polymer chains.[63, 72-73] This convenient technique has been developed into a widely-accepted method for synthesis of poly(aromatic vinylene)s, which will be discussed in Section 1.4 in greater details.

1.2.5 Regioregular polythiophenes

Since most thiophene derivative monomers are not symmetrical molecules, especially well studied 3-alkylthiophene monomers. Because of the lack of symmetry, 3-alkylthiophenes can be incorporated into a polymer chain with three different regioregularities: head-to-tail (HT), head-to-head (HH), tail-to-tail (TT). This gives rise to four triad regioisomers in polymer chain: HT-HT, HT-HH, TT-HH, and TT-HT[74-75] (Fig 1.3)

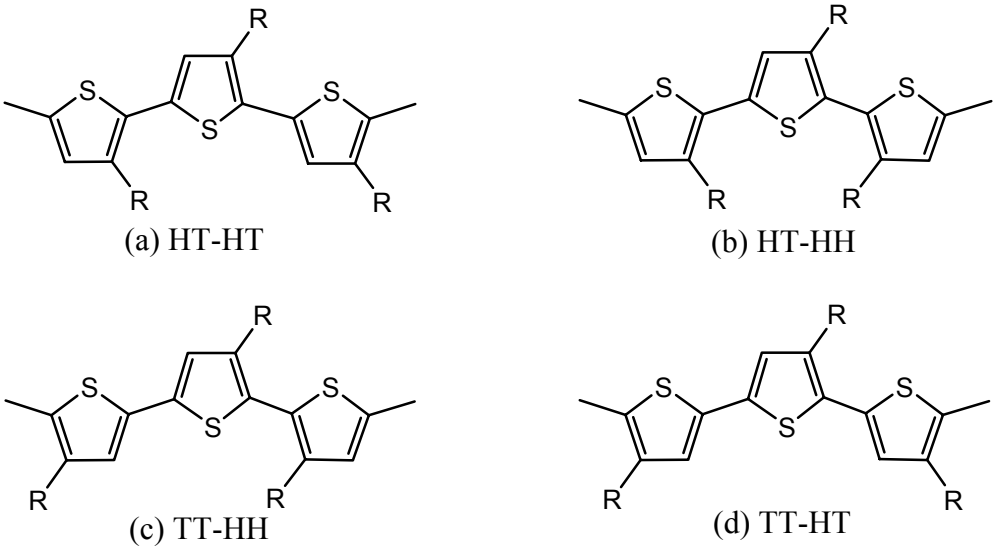


Fig 1.3 Possible triad regioisomers of poly(3-alkylthiophene)

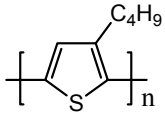
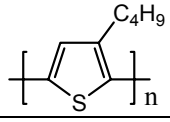
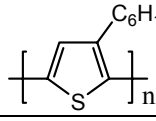
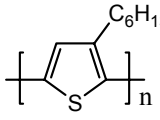
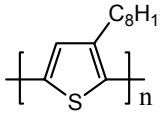
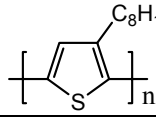
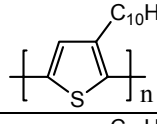
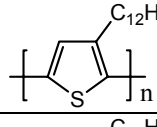
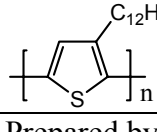
It has been shown that HT regiospecific poly(3-alkylthiophene) surpass their HH regiospecific or regiorandom counterparts in electrical, optical, magnetic and mechanical properties. More sterically hindered HH linkages can cause defects in the conjugated polymer chains and reduce the desired physical properties of the materials. The higher regularity and longer conjugation length of the polymer chain results in a lower bandgap and higher intrinsic conductivity.[76-77] Table 1.5 lists the comparative study of some poly(3-alkylthiophene)s.

Compared with regiorandom counterparts, UV-Vis absorption wavelength (λ_{max}) of regioregular poly(3-alkylthiophene)s have red-shifts of 40 to 90 nm, which indicates the reducing of the bandgap values of respective regioregular polymers. McCullough group's study[78-79, 83-84] also shows the electrical conductivities (doped with I_2) and λ_{max} have similar trend, and the longer pendant alkyl groups show better conductivities: poly(3-dodecylthiophene)>poly(3-octylthiophene)>poly(3-hexyl thiophene). These data might be interpreted by considering that the longer alkyl side chain, the more flexible substituted group, the easier the polymer chain can align itself, which result in more extensive π-π conjugation and a larger number of conjugated domains.

Highly regioregular poly(3-alkylthiophene)s (HT >90%) can be achieved by (1) LDA lithiation of 2-bromo-3-alkylthiophene followed by metal catalyzed Kumada[85] cross-coupling of thiophene Grignard reagents (McCullough's method);[78-79] (2) Selective oxidative addition of Reike zinc (Zn^*) followed by a Negishi[86] cross-

coupling reaction (Reike's method).[80-82] Both methods can afford highly regioselective products, and they are illustrated in Scheme 1.2 and Scheme1.3.

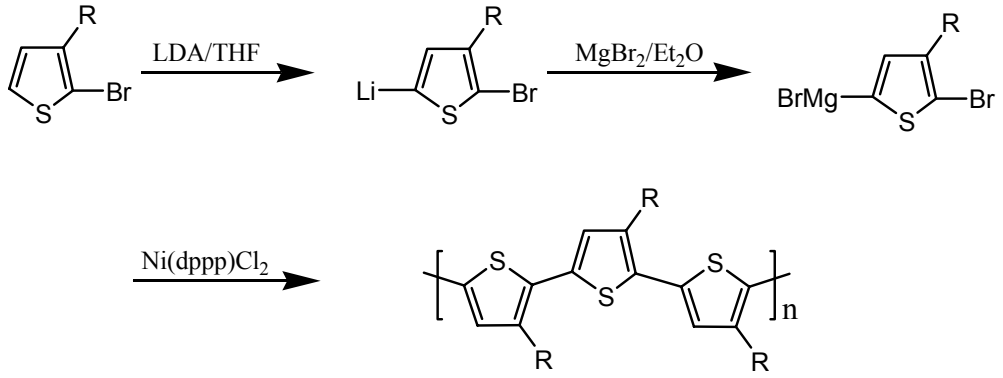
Table 1.5 Structures and properties of some regioregular poly(3-alkylthiophenes)

No.	Structures	HT /HH Ratio	λ_{max}/nm# (Eg eV)	*M*n (PI)	σ S/cm (dopant)	Ref.
1		50/50	433	-	-	80-82
2		97/3	605	-	-	80-82
3		50/50 Regiorandom*	438 (2.1) 480	$5.65x10^3$ (4.32) -	10 (I_2) 1	80-82 78-79
4		HT>98.5% HT≥99%	610 (1.7) 613	$2.55x10^4$ (1.48) -	~10^3 (I_2) 100 (I_2)	83 78-79
5		Regiorandom*	480	-	1	78-79
6		HT>98.5% HT≥99%	608 620	$3.46x10^4$ (1.13) -	 200	80-82 83,
7		HT>98.5%	606	$3.05x10^4$ (1.39)	-	80-82
8		HT≅54	436	-	10	84
9		HT≥99	630	$1.16x10^4$	10^3	84

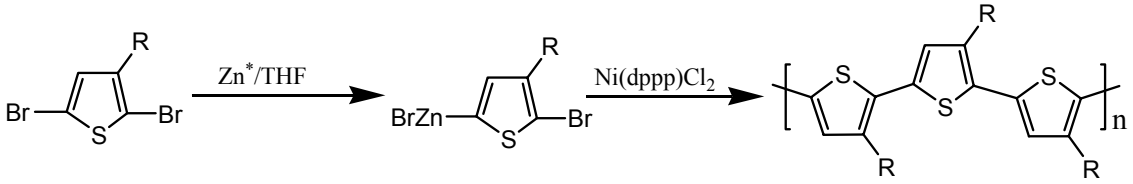
Notes: * Prepared by $FeCl_3$, HT-HH ratio unavailable.

UV-Vis absorption data were solid-state film.

Scheme 1.2 McCullough's approach to regioregular poly(3-alkylthiophene)s



Scheme 1.3 Rieke's approach to regioregular poly(3-alkylthiophene)s

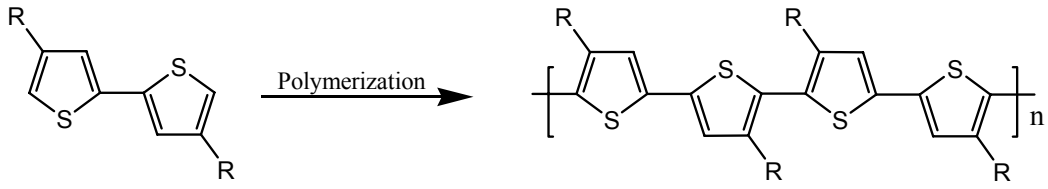


Other metal catalyzed cross-coupling reactions such as Stille[87-88] and Suzuki[89-90] methods were also applied to the reggioselective systhesis of poly(3-alkylthiophene)s. Both approaches use LDA for cryogenic lithiation of 2-halo-3-alkylthiophenes and subsequent treatment by organostannanes or organoboron electrophiles to yield suitable monomers. These monomers undergo regiospecific polymerization to afford regioregular polythiophenes. McCullough and coworkers[91] reported using magnesium-halogen exchange reaction followed by a Ni(II) metallated cross-coupling polymerization to synthesis of regioregular polythiophenes, which is

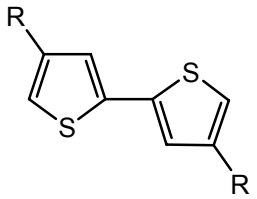
called Grignard metathesis (**GRIM**), and this method can give a poly(3-alkylthiophene)s with >95% HT-HT coupling.

Application of symmetrically β-substituted 2,2'-bithiophenes to prepared polythiophenes with only one backbone structure was also explored (Scheme 1.4),[92-93] which usually gives HH-TT style regiospecific polymers. Some bithiophenes were list in Figure 1.2. This type regioregularity neither reduces badgap of polymer, nor enhance

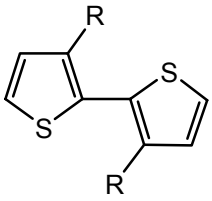
Scheme 1.4 Synthesis of regiospecific polythiophene through bithiophene



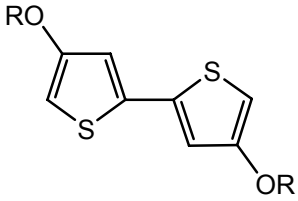
conductivity. The reason is evident that there is significant nonplanarity exists in these polymers due to strong steric interactions between alkyl substitutents in the head-to-head coupled rings.[94]



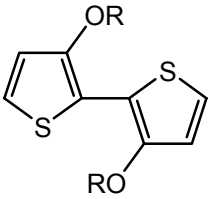
(a) 4,4'-dialkyl-2,2'-bithiophene



(b) 3,3'-dialkyl-2,2'-bithiophene



(c) 4,4'-dialkoxy-2,2'-bithiophene



(d) 3,3'-dialkoxy-2,2'-bithiophene

Fig.1.4 Structural illustrations of some bithiophene monomers[92-93]

1.2.6 Thiophene-based copolymers

Copolymerization of thiophene derivatives for molecular designing of novel polymers possessing desired electrical or physical properties started almost simultaneously with the successful synthesis of polyheterocycles.[20] Among all copolymers of polythiophene derivatives, two major categories of research efforts were conducted world widely (1) synthesis of doner-acceptor alternating copolymers to tailer electronic property tuning electronic property such as lowering bandgap, increasing intrinsic conductivities, and help better understand the charge-transfer (CT) mechanism in these polymer backbones; (2) copolymerization of thiophene derivatives with special function groups to afford some specific physical or chemical properties such as better solubility; regioregularity; liquid crystallinity; self-assembling structure; etc.

1.2.6.1 Donor-acceptor alternating copolymers

Effectively lowing bandgap with alternating electron donating and electron withdrawing units in the polymer backbone structure was proposed by Havinga and coworkers[95-96] in 1992. The principal idea is that regular alternation of strong electron donating units (donor) which have higher HOMO and electron-accepting units (acceptor) which have lower LUMO, intrachain charge transfer will effectively lower the bandgap. Visualize a conjugated polymer formed by a regular alternation of donor and acceptor-like moieties, which is similar to inorganic doped n-i-p-i superlattice structure[97] (Fig.1.4). It's known that in such a structure both the valence and conduction bands are curved by space charge effects. The bandgap Eg has not changed at each place at itself, but a small bandgap Eg_x is formed when the spatial alternation of the level of the bands is taken in account.[95-96] However, calculations have shown that the hybridization of the energy levels of the donor and the acceptor, particularly the high-lying HOMO of the donor fragment and the low-lying LUMO of the acceptor fragment, yield a D-A monomer with an unusually small HOMO-LUMO separation (Fig.1.5, Eg is the bandgap and Eg_x is the smaller bandgap when the spatial alternation of the level of the band is taken into account.[97]). Further hybridization upon chain extension then converges to the small band gaps.[98-100] Moreover, the steric repulsions between adjacent units relating coplanarity should be taken into account too,[101] especially when dealing with copolymers with a bulky side chains.

Most donor-acceptor alternating copolymers were conveniently prepared by one of the two approaches: (1) electrochemical or cross-coupling polymerization of D-A-D

(donor-acceptor-donor) or A-D-A (acceptor-donor-acceptor) type terthieyl monomers; (2) polymerization of A-D (or D-A) type monomers.

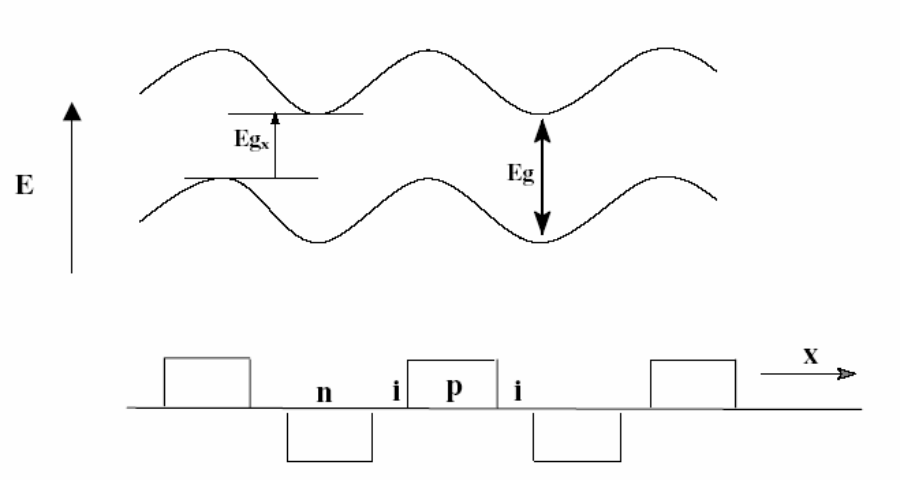


Fig. 1.5 Schematic band structure of a n-i-p-i superlattice structure.

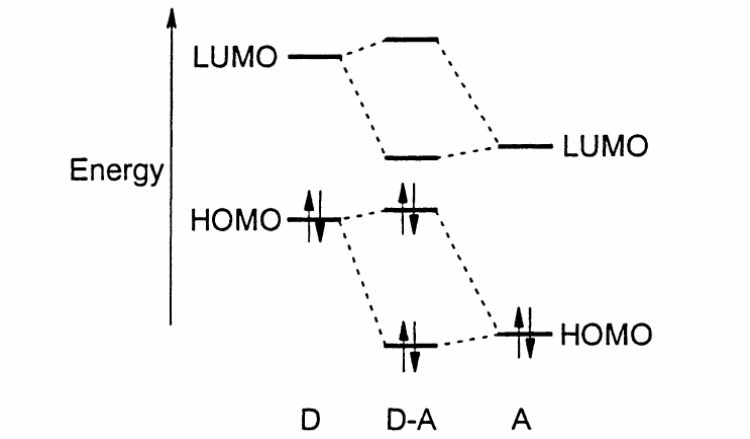


Fig. 1.6 Hybridization of the energy levels of a donor (D) and acceptor (A) fragment leads to a D-A monomer with an unusually narrow HOMO-LUMO energy separation.[98]

It's well known in chemistry that five-member ring heterocycles such as thiophene, furan have a π-electron excessive nature due to the mesomeric effect of conjugation with electron lone pair of S or N atoms, which generally are considered as electron donors, six-member ring compounds have a π-deficiency nature, thus are electron acceptors.[102]

❶ *Copolymers from A-D-A(orD-A-D) terthieyl type monomers*

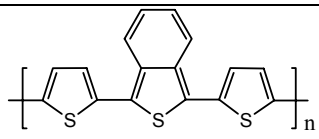
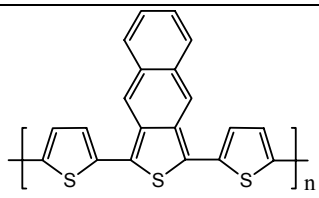
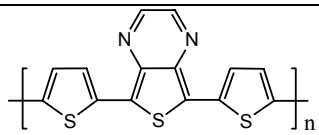
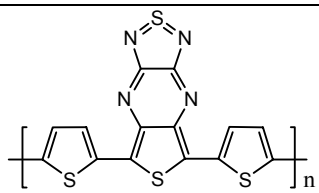
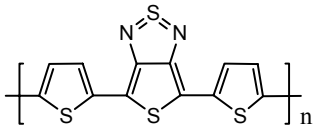
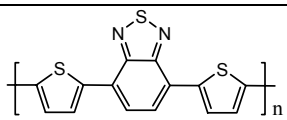
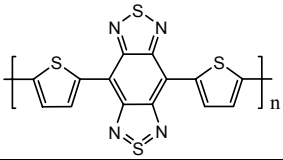
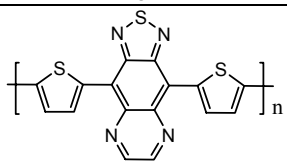
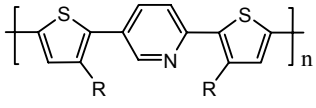
Terthienyl type monomers are conveniently available, and easily undergo electrochemical polymerization to afford polythiophene derivatives. They are readily converted into corresponding bishaloterthienyl monomer, followed by polycondensation reactions to yield alternating copolymers. Table 1.6 lists some copolymers electrochemically synthesized from terthienyl monomers with their corresponding bandgap data. Table 1.6 shows badgaps can be reduced down to 0.5ev by alternating donor-acceptor strategy (Entry 1-8). Even though some monomers are not true terthienyl monomers (Entry 6-9), they share similar structural pattern with terthienyl monomers. Exceptional high bandgap of copolymer with pyridine units (Entry 9) might be explained by very weak donor of pyridine, steric repulsion of HH-TT alkyl side chain configurations, and low molecular weights.[111]

❷ *Copolymers from D-A type monomer*

Copolymerization of D-A type monomers were generally achieved by metal-catalyzed cross-coupling reactions. These CT-type copolymers synthesized by chemical methods have well-determined donor-acceptor alternating structures. Electrochemical approaches were also used to polymerize D-A type monomers. Table 1.7 listed some CT-type copolymers. Copolymer of 4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene and 3,4-ethylenedioxythiophene was estimated have a bandgap value of 0.19eV, which is the lowest ever reported.[114]

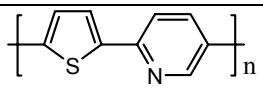
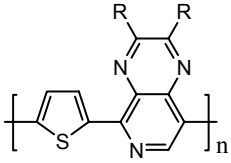
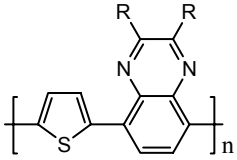
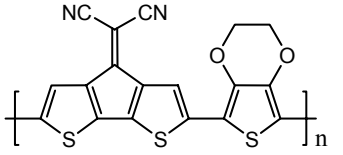
Although donor-acceptor theory is very populous among synthetic chemist for providing guidelines for molecular designing of low bandgap conducting copolymer, some research point out that concept cannot be used to design organic conductors with small bandgap and wide bands.[115] Systematic studies on donor-acceptor polymers have not done much yet, especially research efforts dealing with oligomers and low molecular model compounds are inadequate . Additionally, most of this charge transfer polymer systems were synthesized by electrochemical method. The structural defects and residual doping might cause some deviations from accurate interpretation of spectrum and conductivity data.[115-116] Another inherent problem of the D-A copolymers are most copolymers bear rigid backbone structures which generally result in impossible full characterization of products.

Table1.6 Structures and properties of copolymers from terthienyl monomers

No.	Structures	λ_{max}/nm (bandgap eV)	*M*n (PI)$^{(*)}$	σ S/cm (dopant)	Ref.
1		584 (1.58)	-	0.014 (I_2)	103
2		1240 (0.65)	-	0.02(PF_6^-)*	104
3		- (1.0)	-	-	105
4		- (0.5)	-	-	106
5		934 (0.95)	-	-	107
6		- (1.1)	-	-	108
7		-(0.50)	-	$5.6x10^{-3}$ (I_2)	108
8		- (0.7)	-	-	109
9		R=C_8H_{17} 458 (2.34)	$6.7x10^3$ (1.8)	$8.26x10^{-5}$ ($FeCl_3$)	110

Notes: * Electrochemically doped.

Table1.7 Alternating CT-type copolymers from D-A monomers

No.	Structures	λ_{max}/nm (bandgap eV)	M_w (PI)$^{(*)}$	σ S/cm (dopant)	Ref.
1		477 (-)	$5.4x10^3$	-	112
2		R=Ph 633(1.61)*	-	10^{-6} (I_2)	113
3		603 (-)	-	$<10^{-8}$ (Intrinsic)	113
4		-(0.19)#	-	$6.9x10^{-4}$ (Intrinsic)	114

Notes: * Band gap value is calculated from spectra.

Band gap value is electrochemically calculated

❸ *D-A copolymers from dihydroxycopounds*

Dihydroxycompounds are another type of monomers which can provide a unique approach to D-A copolymers by acid-induced polycondensation (Scheme 1.5). The band gap values of these polymers are listed in Table 1.8.

Scheme 1.5 Elimination reaction of dihydroxycompounds

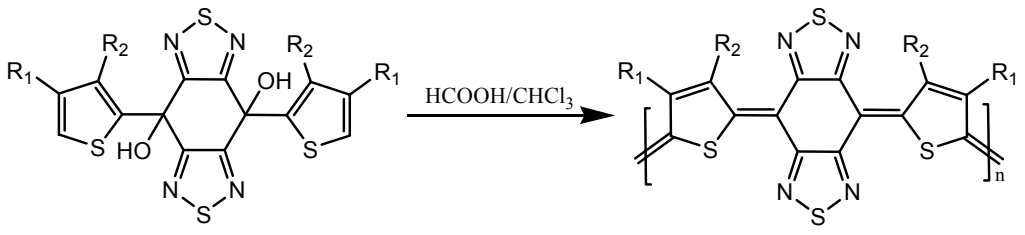
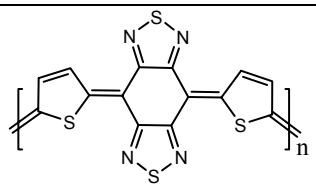
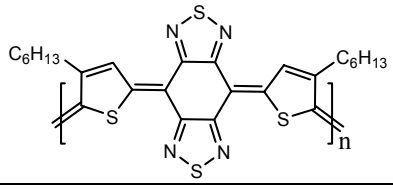
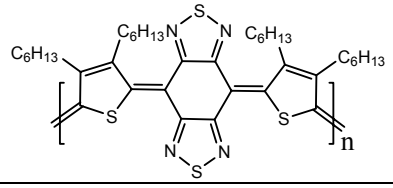
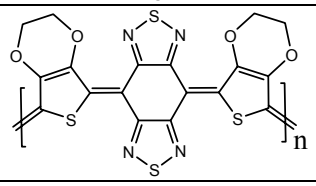


Table 1.8 Band gap values of D-A copolymers from dihydroxycompounds

No.	Structure	λ_{max} (nm)	Band gap (eV)	σ S/cm (dopant)	Ref.
1		751	-		117-118
2		939	0.9		117-118
3		961	0.9		119
4		1069	0.3	1 (salicylic acid)	120-121

1.2.6.2 Special thiophene-based copolymers

Minimization of band gap is just one of many directions of manipulation of structure-property relationship through copolymerization, Others include synthesis of "double-cable" copolymers of enhancing photoinduced charge transfer process for photovoltaic devices,[122] high band gap (2.7-2.9eV) copolymers for blue light LEDs,[123] etc. J. W. Brown et al.[124] reported that copolymerization of 3-alkylthiophene with certain thiophene moieties contained special side chains can help alignment of polymer backbone, thus increase conductivity of bulk material (Fig. 1.6).

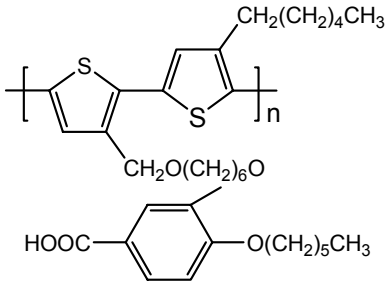


Fig 1.7 Special polythiophene copolymer

1.2.7 Summary

Self-assembly is emerging as an elegant, `bottom-up' method for fabricating nano-structured materials.[125] Self-assembly in conjugated polymers is highly desirable in order to generate conducting polymers with high electrical conductivities and large nonlinear optical responses.[126] The specific physical and chemical interactions of the molecules and components with the surfaces are the driving forces for the formation of stable organized films at solid substrates.[127]

Polythiophene derivatives with strong polar side groups can be self-assembled into a stable mono-molecular (or mutli-) layer of π-stacked conjugated polymers which are processable on the nanometer scale.[128] Until now, most studies of self-assembling of polythiophene derivatives focus on regioregular poly(3-alkylthiophene), and mono-layer, multi-layer self-assembled structures have been synthesized through polythiophene derivatives with certain pendant function groups, such as carboxylic acid,[129-130] ether,[131-132] and urea.[133] The conformational order and solid state organization are remarkably sensitive to the placement and nature of the substituent chains,[134] intermolecular hydrogen bonding and environments are also key factors in

determining successful formation of self-assembly structure. From structure point of view, self-assembly of polythiophene derivatives belongs to approach 1 (section 1.2.2), attaching pendant side chains to functionalize polythiophene. More recently, crystal-like ordered films of PEDOT were prepared via an aqueous low-temperature technique using liquid crystals as templates to direct the orientation of the growing molecules. The highly ordered film looks just like a liquid crystal in terms of its domain structure and birefringence, an optical property characteristic of liquid-crystalline materials.[135] Self-assembly of oligothiophenes was featured in several recent reviews.[136]

Other physical methods such as: polymer composite (or polymer blend),[137] polymer laminates[138] are also extensively explored approaches for functionalization of thiophene-based polymers. Some polythiophenes or its derivatives composites with selective nano-dimensional inorganic oxides or sulfides such as TiO_2,[139-140] SiO_2,[141] CdS, ZnS,[142] and polymers such as PVC, PS, PBT, etc. were reported.[143] Poly(3-octylthiophene) blends with PS, PE, PP showed better environmental stability while conductivities with 10^{-2} S/cm.[144] Generally, physical blend can afford better mechanical, thermal properties, and improved stability at the expense of conductivity of bulk materials. Conducting polymer nanocomposites are intimate combinations (up to almost molecular level) of one or more inorganic nanoparticles with conducting polythiophene (or derivatives) that unique electronic properties of the latter can be taken together with the existing qualities of the former.[145]

Structural design and synthesis, combined with self-assembly and Langmuir-Blodgett (LB) techniques, to obtain well-defined π-conjugated nanoscale materials, such as nanofibers (nanowires), nanotubes, and/or nanotube dendrites, will remain a challenging object in the field of studies on functionalization of polythiophene derivatives in the near future. Better understanding of the structure-property relationship of polythiophenes derivatives can provide guidelines for choosing specific functioning groups to achieve well-controlled structures with high performance electrical and mechanical properties.

1.3 Metal containing thiophene-based oligomers and polymers

Many of the fascinating properties and spectacular functions of biological and synthetic materials can be attributed to the presence of metallic elements.

The introduction of metals into polymers to form metal-polymer complexes (metallopolymers) poly(vinylferrocene) was first reported in 1955.[146] Since then, a great deal of research efforts was put into preparation of similar, transition metal based molecular complexes to mimic these conducting properties. At the same time, progress in conducting polymers also accelerated research activities in synthesis and study of conjugated polymer systems containing transition metals.[147]

1.3.1 Metal-containing π- conjugated polymers

Conjugated metallopolymers can be classified by the kind of interactions metals have with polymer backbones (Fig 1.6). In Type I metallopolymer, a metal or metal ion

is tethered to a side chain (generally, an alkyl chain) of linear or cross-linked macromolecule, polymer acts primarily as a conductive support. For Type II metallopolymer, the ligand of a metal complex is a part of polymer backbone, the metal and the macromolecular backbone are electronically coupled. The communication between them can affect each others' properties. In Type III metallopolymer, the metal

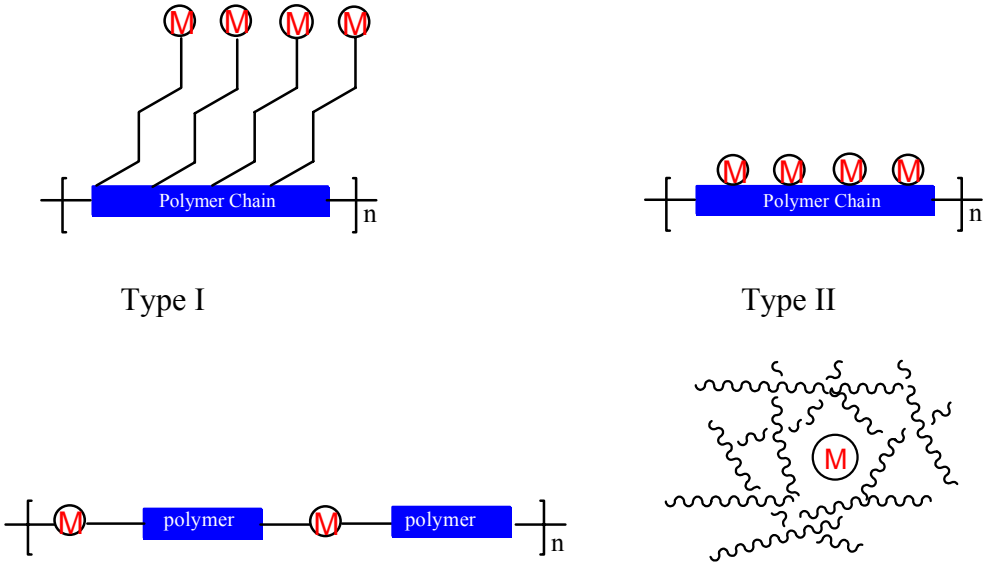


Fig 1.8 Schematic representations of metallopolymer classification

or metal group is directly a polymer chain. For this type of arrangement, strong electronic interaction and tuned optical and electronic properties are expected. Physical incorporation of metal or metal ions in macromolecules results in formation of Type IV metallopolymer.[148] Type IV metallopolymer is a class of polymer composite (blend), which is not included in this brief review.

Metals of metallopolymers function in several distinctive ways (1) electronically coupling with π-conjugation system of polymer to modify electrical properties of polymers; (2) modifying properties of polymers in a detectable way (3) providing structural or mechanical support for polymers, and/or stabilizing polymers; (4) was used as scaffold in molecular imprinted polymers (MIPs).[149-151] During the past decade, there is steady and growing effort to integrating redox-active metal centers into conducting polymer framework to create highly efficient redox conductivity in such hybrid metallopolymer materials. Based on interactions between metal centers and conducting polymers, electron transfer leads to two distinctively different conductivity mechanisms: inner sphere and outer sphere electron transfer. Inner sphere electron transfer involves the communication of two metal centers via a mutually bridging ligand (conducting polymer backbone).[152]

The incorporation of metals into conductive polymers has the potential to find applications in four key areas such as new catalysts, sensors, electroluminescent materials, and biomedical implants.[153]

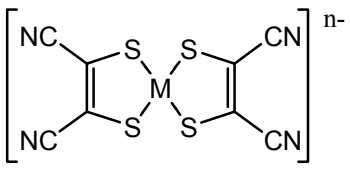
1.3.2 Metal-containing oligothiophenes and polythiophenes

Using oligothiophenes or polythiophenes as ligands was mainly motivated by the synthetic accessaibility of a large number of functionalized thiophenes which may be used as monomers, as well as the chemical stability of many of these monomers.[154]

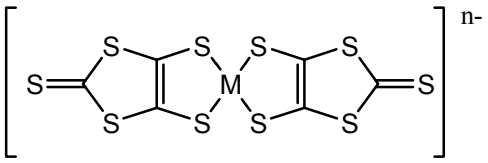
Metal-containing oligothiophenes or polythiophenes can be synthesized by polymerization of thiophene-derivatized metal complexes, or incorporation metals into polythiophenes with suitable ligands.[155-156]

1.3.3 Metal-thiolate coordination complexes

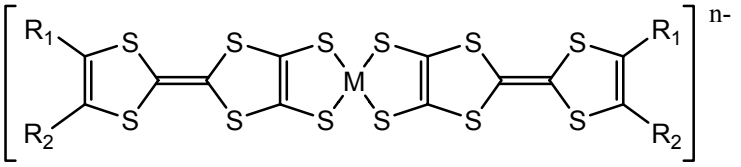
Thiolate is one of the soft ligands in the field of transition metal complexes, the relatively large sulfur $p\pi$ orbital lobe of thiolate can readily interact with metal *d* orbitals to form metal-thiolate coordinative bonds (dative covalent bond). Research on metal-thiolate coordination focus on two distinctive directions (1) metal-thiolate structure present in active sites of metalloenzymes (metalloprotein),[157-158] (2) organic metal complexes bearing extended TTF-like dithiolate ligand. This class of metal complexes is the most extensively studied synthetic metal-thiolate materials due to their possible applications as organic conductor or superconductor. Fig. 1.7 illustrated some complex examples of TTF-like dithiolate lagands binding to metals.



$[M(mnt)_2]^{n-}$
M=Ni, Pd, Pt



$[M(dmit)_2]^{n-}$
M=Ni, Pd, Pt



M=Ni, Pd, Pt, Co, Au

Figure 1.9 Some examples of metal-thiolate coordination in TTF-like complexes

1.4 Synthesis of poly(thienylene vinylene) derivatives

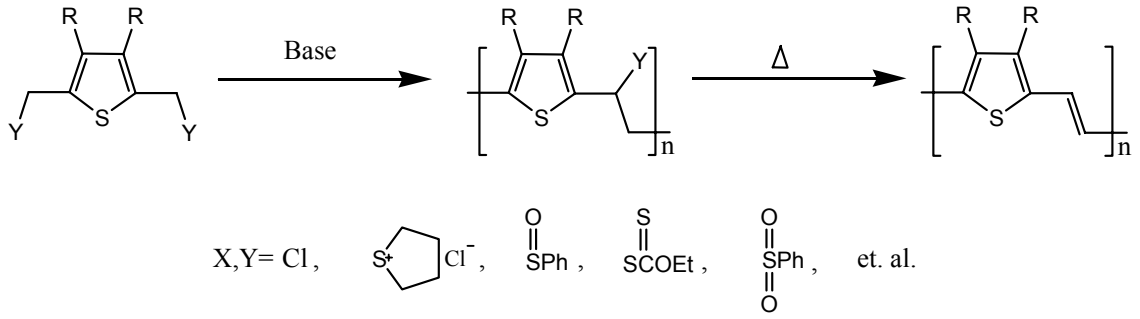
It's well known that the structure plays a dominant role in determining the physical and electrical properties of conducting polymers, more and more research has focused on manipulating synthesis techniques or methods to achieve desired structures which give better physical stability and electronic performance.

1.4.1 Two-step precursor polymerization

Two-step precursor polymerization involves the first stage of preparing soluable and high molecular weight nonconjugated precursor polymer under basic (or acidic) condition, followed by the removal of leaving groups under thermal treatment to form C=C double bonds between aromatic rings, the process was illustrated in Scheme 1.8.

Due to its advantages over other direct methods, i.e. processability and high molecular weight of products, two-step precursor approach remains as one of major routes to introducing conjugated spacers between thienyl rings. A series of different leaving groups were attempted in the past 20 years.[63, 65-66, 159-160]

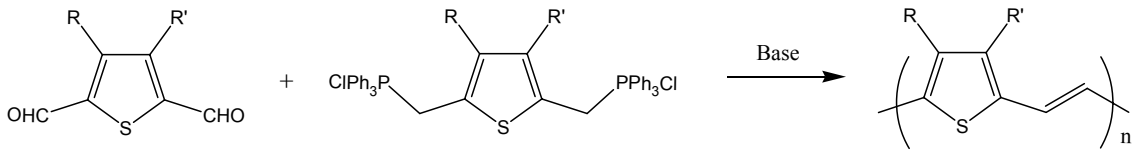
Scheme 1.6 General process of two-step precursor polymerization



1.4.2 Wittig-Horner reaction

Wittig-Horner olefination was also used to build ethylene linkages in the polymer, which was illustrated in Scheme 1.9. Although Wittig condensation usually affords oligomers or low molecular weight products, it is a versatile and straightforward method, allows the ready introduction of a wide variety of aromatic rings and manipulation of polymer (or copolymer) structure in a controllable manner.[161-163]

Scheme 1.7 Wittig-Horner condensation

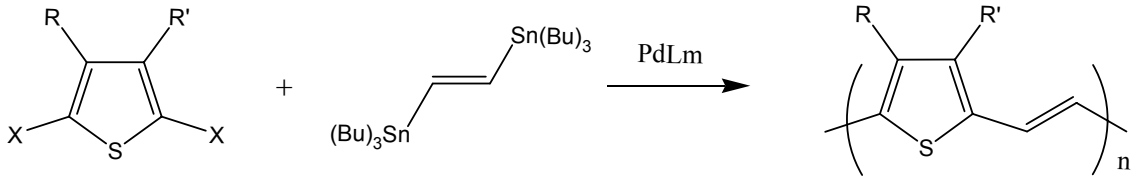


R=H, alkyl, alkyloxy; R'=H, alkyl, alkyloxy

1.4.3 Stille coupling reaction

Pd-catalyzed Stille coupling of vinyl organostannanes with thienyl halides represent a very straight approach to build C=C bond between thienyl rings.[164-166]

Scheme 1.8 Stille coupling reaction

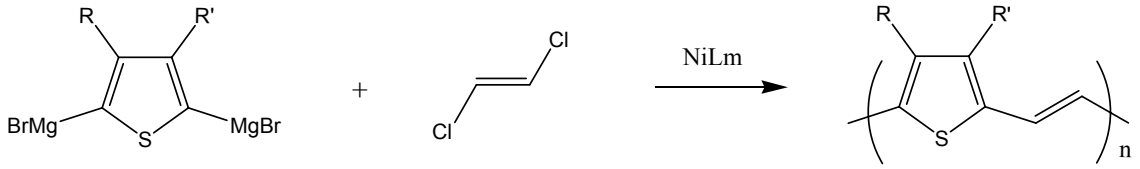


R=H, alkyl, alkyloxy; R'=H, alkyl, alkyloxy

*1.4.4 Grignard metathesis (**GRIM**)*

Grignard metathesis is another straightforward cross-coupling reaction catalyzed by Ni complex to form vinyl link between aromatic rings.[167-168]

Scheme 1.9 Grignard metathesis

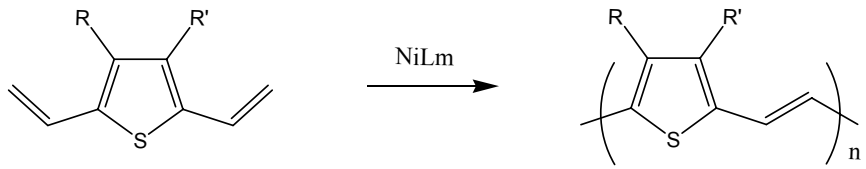


R=H, alkyl, alkyloxy; R'=H, alkyl, alkyloxy

1.4.5 Acyclic diene metathesis

Reaction of 3-alkyl-2,5-divinylthiophene with the Schrock catalyst (Mo based catalysit) yields poly(3-alkyl-thienylene vinylene) of highly pure repeat units with defined end groups.[169]

Scheme 1.10 Acyclic diene metathesis[169]

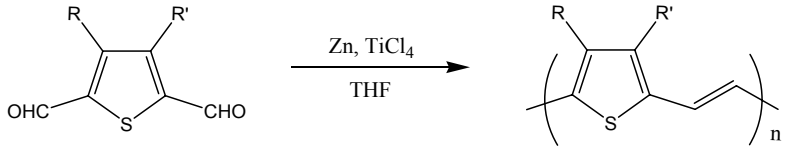


R=H, alkyl; R'=H, alkyl

1.4.6 McMurry reaction

MaMurry reaction is a titanium-induced coupling of carbaldehydes. Self-coupling reaction of alkylthiophene-2,5-dicarbaldehydes directly afford poly(thienylenevinylene)s.[170-171] which was illustrated in Scheme 1.12. McMurry reaction was also used to prepare thienylenevinylene oligomers with well-defined structures.[172-173]

Scheme 1.11 McMurry reaction

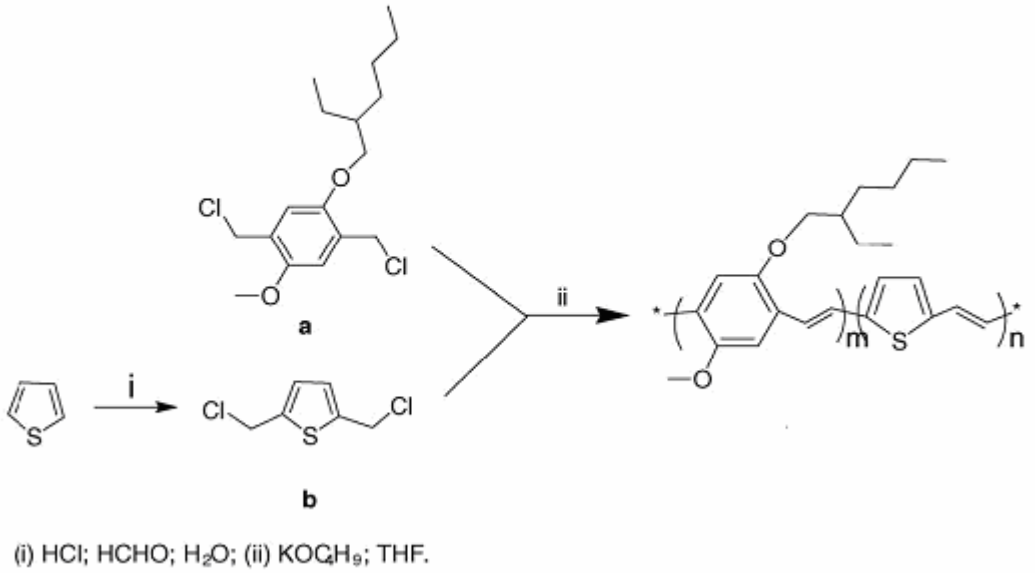


R=H, alkyl, alkyloxy; R'=H, alkyl, alkyloxy

1.4.7 Miscellaneous methods

Li [174] reported a random polythienylenevinylene compolymer prepared in strong base, which is identical to Gilch route for PPV.[175]

Scheme 1.12 Synthesis of random copolymers



(i) HCl; HCHO; H_2O; (ii) KOC_4H_9; THF.

1.5 Summary

Since polythiophene systems are one class of the most promising commercial conducting polymers. It is well understood that manipulating the structure of monomers

is of great importance to achieve high performance conducting materials and to fully comprehend the structure-property relationship of conjugated polymers.

As far as synthesis chemists are concerned, it is predictable that several research trends will stay on the focus of studies of polythiophene derivatives.

(1) Molecular design and synthesis of new thiophene derivative monomers for high performance (which include high conductivity, good mechanical strength and stability, and ease processibility) polythiophene derivatives

(2) Synthesizing and/or assembling of highly regioregular and high molecular weight linear polythiophene derivatives.

(3) Synthesizing metal-incorporated polythiophenes or thiophene-based metallated oligomers. The interactions of metal-metal and metal-π conjugation are believed to be able enhance either conductivity of material or catalytical capability of metal centers.

The synthetic chemistry of thiophene derivatives provides a high level of structural flexibility, which allows the electronic and physical properties of the resultant polymers to be well tunable. Many new applications involved polythiophene derivatives might be commercialized in the foreseeable future.

CHAPTER 2

SYNTHESIS OF THIOPHENE DERIVATIVES

2.1 Introduction

1 **2**

Fig 2.1 Thieno[3,4-*d*]-1,3-dithiole-2-thione (**1**) and thieno[3,4-*d*]-1,3-dithiol-2-one (**2**)

Thieno[3,4-*d*]-1,3-dithiole-2-thione (**1**) and thieno[3,4-*d*]-1,3-dithiol-2-one (**2**) (Fig. 2.1) are structurally similar heterocyclic compounds. Both have five-membered rings fused with a thiophene ring at the 3 and 4 positions. Compounds **1** and **2** were chosen for this study for the following reasons:

(1) Compared with 3,4-disubstituted thiophene, fused five-membered rings with thiophene might help minimize steric effects, therefore improve coplanarity, extend conjugation length along polymer chains, and reduce the band gap of the material.

(2) By having sulfur directly attached to the 3 and 4 positions of thiophene ring, the intrinsic conductivity might be improved and the bandgap lowered due to the electron-donating ability of sulfur.

(3) A reversible carbondithioate (thieno[3,4-*d*]-1,3-dithiol-2-one) structure could possibly undergo metal-thiolate coordination to form metal-polymer complex.

(4) Preparing $\Delta^{2,2'}$-bithieno[3,4-*d*]-1,3-dithiole (DTTTF) analogues by coupling reaction (trialkyl phosphite method[176]) might be possible. The links through DTTTF between neighboring oligomer or polymer chains may significantly improve 2-dimensional charge mobility, even afford "superconductive" oligomers or polymers. Although tetrathiafulvalene (TTF) derivatives and conducting polymers represented two distinctive approaches in pursuing organic conducting materials at the early days, during the past several years, synthetic chemistry of TTF derivatives has moved to some new directions, i.e. intergrating TTF unit with conjugated polymer backbone to afford quasi-two-dimensional dendrimers, oligomers, and even polymers is now being investigated.[177-179]

(5) The increase of sulfur content in the structure might improve dimensionality of TTF derivatives, thereby stabilizing the compound.[180]

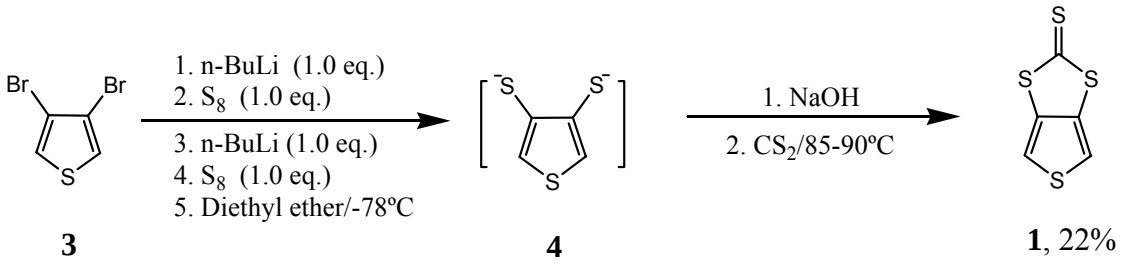
2.2 Annulations of thiophene ring

*2.2.1 Synthesis of thieno[3,4-d]-1,3-dithiole-2-thione (**1**)*

Thieno[3,4-*d*]-1,3-dithiole-2-thione (**1**) was prepared according to the reference literature.[176] 3,4-Dibromothiophene (**3**) was consecutively treated twice with *n*-butyllithium (1.0 equiv.) followed by the addition of elemental sulfur to afford lithium 3,4-dimercaptothiophene (**4**) as an intermediate. Without further purification, the

reaction mixture was allowed to react with carbon disulfide in aqueous alkaline solution to produce compound **1**, which illustrated in Scheme 2.1. The yield of **1** is about 22%.

Scheme 2.1 Synthesis of thieno[3,4-*d*]-1,3-dithiole-2-thione

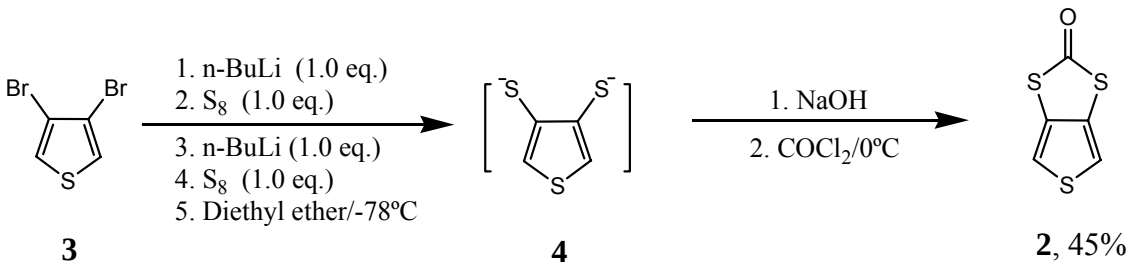


3 **4** **1**, 22%

*2.2.2 Synthesis of thieno[3,4-d]-1,3-dithiol-2-one**(2)***

Thieno[3,4-*d*]-1,3-dithiol-2-one (**2**) was also synthesized by a modification method (Scheme 2.2). The synthesis begins with the preparation of the same intermediate **4**, followed by treating **4** with excess $COCl_2$ solution to afford **2**. This one pot $COCl_2$ method provide better yield in comparison with the oxidation of thieno[3,4-*d*]-1,3-dithiole-2-thione (**1**) by $Hg(OAc)_2$. This one pot method is more convenient and efficient giving 40-45% yield of the product. The overall yield of the oxidation with $Hg(OAc)_2$ is about 20%[176], Overall, the phosgene method shows a significant improvement in terms of simplicity and yield.

Scheme 2.2 Synthesis of thieno[3,4-*d*]-1,3-dithiol-2-one



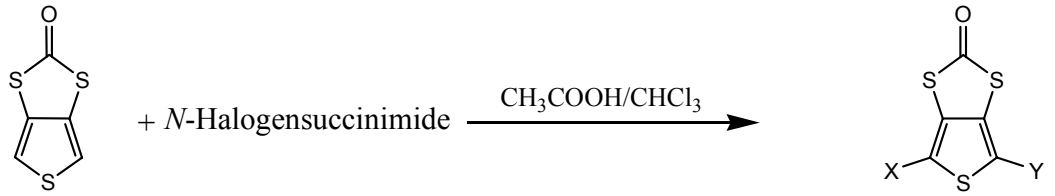
3 **4** **2**, 45%

2.3 Halogenation reactions

Transitional metal catalyzed polycondensation reactions are commonly used methods for direct formation of π-conjugated polymer systems. Synthesis of halogenated monomers (halide derivatives) becomes a crucial step for the success of organometallic polycondensation.

Halogenation reaction of compound **2** with mild halogenated reagents such as *N*-halogensuccinimides, such as *N*-chlorosuccinimide (NCS), *N*-bromosuccinimide (NBS), and *N*-iodosuccinimide (NIS), can selectively substitute the 4 and/or 6 positions and give a variety of halogenated products with fairly good yields and stability (Scheme 2.3). Results of these reactions are listed in Table 2.1.

Scheme 2.3 Substitution reactions with *N*-halogensuccinimide



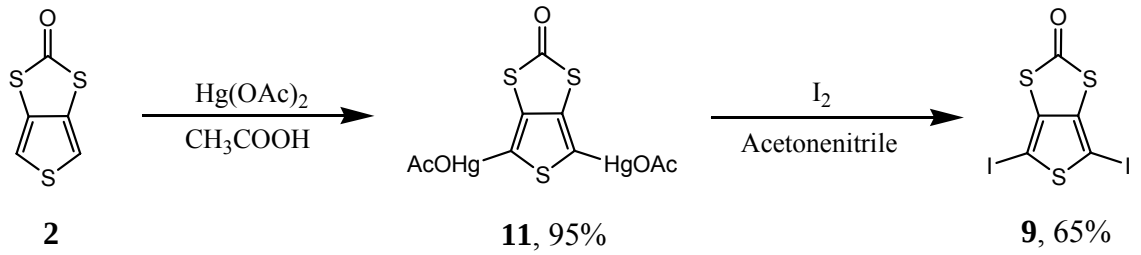
2 **5-10**

5 X=Y=Cl, **6** X=H Y=Cl
7 X=Y=Br, **8** X=H Y=Br
9 X=Y=I, **10** X=H Y=I

Dibrominated compound **7** can also be prepared with direct bromination using Br_2 in carbon tetrachloride in 95% yield before purification. Diiodinated compound **9** was successfully synthesized either by iodination with *N*-iodosuccinimide (NIS) or by a two-step procedure shown in Scheme 2.4. The two-step procedure involves treating

compound **2** with mercury acetate at room temperature to give 4,6-diacetoxymercuri-thieno[3,4-*d*]-1,3-dithiol-2-one (compound **11**), followed by iodination in dry acetonenitrile to afford **9** with an overall yield of 60% after column purification. Compound **9** shows limited solubility in regular organic solvents, such as dichloromethane, chloroform, and ethyl acetate.

Scheme 2.4 Two-step preparation of 4,6-diiodothieno[3,4-*d*]-1,3-dithiol-2-one

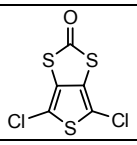
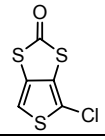
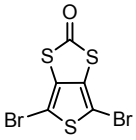
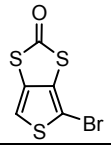
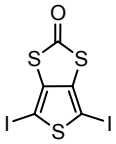
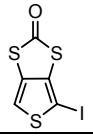


2 **11**, 95% **9**, 65%

Bromination and iodination reactions of thieno[3,4-*d*]-1,3-dithiole-2-thione (compound **1**)were also attempted without success. Charge-transfer complexes, such as those reported from the reactions of 4,5-bismethylthio-1,3-dithiole-2-thione with dihalogens (I_2, Br_2), might be forming during the halogenation process.[181-182]

To summarize, several halogenated derivatives of thieno[3,4-*d*]-1,3-dithiol-2-one were successfully synthesized with fairly good yield. In addition, all bis-substituted halides show very good stability at room temperature. With proper catalysts, those compounds might be polymerized through cross-coupling reactions to afford homopolymers or copolymers. Possible transitional metals catalyzed cross-coupling polymerization reactions are still under further investigations in our laboratory.

Table 2.1 Halogenated products of thieno[3,4-*d*]-1,3-dithiol-2-one

Number	Structure	Reagent	Yield (%)
5		NCS	84
6		NCS	72
7		NBS Br_2	87 95
8		NBS	81
9		NIS I_2	82 60
10		NIS	68

2.4 Aminoalkylation reactions

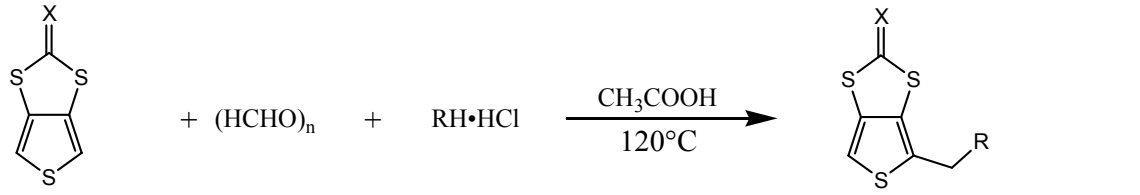
Mannich bases of thiophenes are very convenient intermediates for the transformation and elaboration into other functional groups. This in turn, might lead to the successful preparation of precursor polymers. The first genuine Mannch reactions of the thiophene ring were reported by Baker et. al.[183] A number of 3,4-dialkoxythiophene prepared using Mannich reactions were reported in 2001,[184]

however, no five-membered annulated thiophene moieties have been studied so far, especially sulfur rich derivatives.

2.4.1 Synthesis of mono-substituted Mannich bases

For both starting materials **1** and **2**, using paraformaldehyde and three different secondary amines at elevated temperature can afford mono-substituted Mannich bases in fairly good yields, the experiment are shown in Scheme 2.5.

Scheme 2.5 Preparation of mono-substituted Mannich bases



1, **2**

1 X=S
2 X=O

12-17

12 X=O R=  72%

15 X=S R=  75%

13 X=O R=  43%

16 X=S R=  48%

14 X=O R=  12%

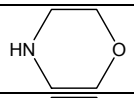
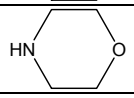
17 X=S R=  15%

In order to compare the reactivities of three amines, all reactions were performed under identical conditions. The results show that the morpholine gives the highest yields, followed by piperidine, diethylamine

2.4.2 Initial study of mono-substitution Mannich reactions

In order to achieve optimum yield of products, effect of solvent and temperature were evaluated. The preliminary results are listed in Table 2.2.

Table 2.2 Factors affect the yield of compound **10**

Amine	Solvent	Temperature (ºC)	Yield
	CH_3COOH	115	72
	$CH_3COOH/CHCl_3$ 1/1	115 (pressure tube)	32
	CH_3COOH	80	52
	CH_3COOH	150 (pressure tube)	32
	$CHCl_3$	80 (pressure tube)	No product

Notes: All reactions were run for 24 hours

Results show that less polar solvents such as chloroform afford lower yield. In contrast, extra high temperatures do not necessarily show an improvement in the yield, it can be explained that extremely high temperature result in the evaporization of formaldehyde, and less formaldehyde getting involved in the reaction.

2.4.3 Synthesis of bis-substituted Mannich bases

Our successful synthesis of mono-substituted Mannich bases leads us to embark upon a study of the preparation of the bis-substituted analogues. Unfortunately, further aminomethylation on the 6-position has proven to be very difficult, even in the presence of the most active morpholine hydrochloride, mainly starting materials were recovered (TLC observation) with only low yield of products (Scheme 2.6), results are summarized in Table 2.3. Bis-substituted Mannich bases **18** and **20** were isolated with

extremely low yields (12-16%). In addition, small amounts of acetate derivatives (**19** and **21**) were also isolated and characterized. Equilibrium reactions plus strong polar solvent might be blamed for low yields of these reactions.

Scheme 2.6 Preparation of bis-substituted Mannich bases

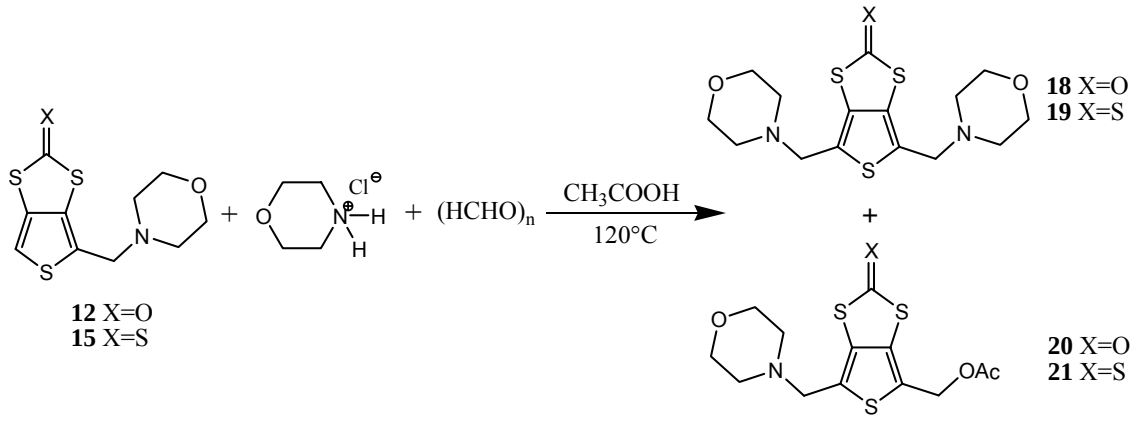


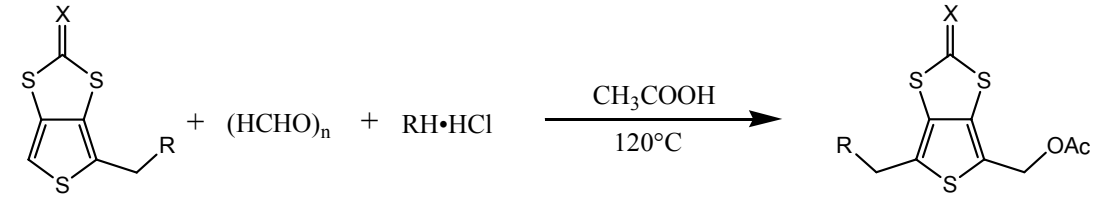
Table 2.3 Bis-substituted Mannich bases

Compound No.	X	Yield (%)
18	O	12
19	S	14
20	O	9
21	S	8

2.4.4 Synthesis of asymmetrical Mannich bases

Aminoalkylation reactions of mono-substituted Mannich bases with less active piperidine or diethylamine do not proceed to yield symmetrical bis-substituted compounds. Instead reactions give asymmetrical acetate derivatives with very low yields. The reactions and yields are illustrated in Scheme 2.7. The formation of these acetate derivatives might due to the same reason as that observed in the reactions of morpholine analogues in section 2.3.4.

Scheme 2.7 Preparation of asymmetrical Mannich bases



13, 14, 16, 17

13 X=O R= 

14 X=O R= 

16 X=S R= 

17 X=S R= 

22-25

22 X=O R=  , 9%

23 X=O R=  , 6%

24 X=S R=  , 12%

25 X=S R=  , 8%

2.4.5 Summary

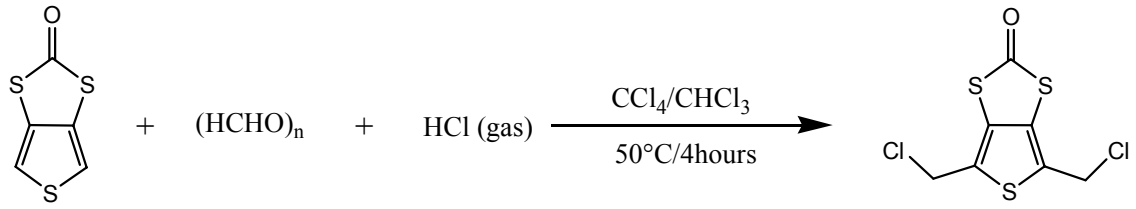
1. A series of mono-substituted Mannich bases of annulated thiophene derivatives have been successfully synthesized with good yields.
2. Bis-substituted Mannich bases were prepared in low yields due to the possible competitive alkylation reactions with the solvent.

3. Through the study of aminoalkylation reactions of our two annulated thiophene derivatives, the reactivities of different amines were comparatively assessed as morpholine > piperidine > diethylamine.
4. Reactivities of thieno[3,4-*d*]-1,3-dithiole-2-thione (**1**) and thieno[3,4-*d*]-1,3-dithiol-2-one (**2**) undergoing Mannich reactions under identical condition gave similar results.
5. In very polar solvents, the reactions with less reactive amines such as piperidine or diethylamine result in the formation of asymmetrical acetate products, rather than the formation of the symmetrical bis-substituted Mannich bases

2.5 Chloromethylation reactions

Among all bifunctional thiophene derivatives, 2,5-bis(chloromethyl)thiophene is regarded as a useful key compound toward the formation of various 2,5-bis-substituted thiophenes.[185] The chloromethylation reaction of thieno[3,4-*d*]-1,3-dithiol-2-one (**2**) proceeded similarly as the chloromethylation of thiophene,[186] and afforded 4,6-bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (**26**) with good yields (40 to 58%). Similar reaction conditions were attempted for the chloromethylation of thieno[3,4-*d*]-1,3-dithiole-2-thione (**1**) without success. This may be due to possible decomposing of the product at room temperature.

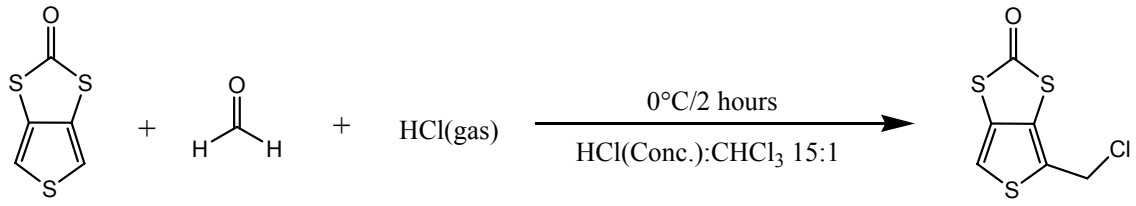
Scheme 2.8 Synthesis of 4,6-bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (**26**)



2 **26**, 58%

Mono-chloromethylation was performed using concentrated hydrochloric acid in the presence of formaldehyde at low temperature. Column purification afford 4-(chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**27**) in 60% yield (Scheme 2.9)

Scheme 2.9 Preparation of 4-(chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**27**)



2 **27**, 60%

2.6 Functionalization reactions

4.6-Bis(chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**26**) is regarded as a very useful intermediate in the preparation of monomers for polythienylene vinylene (PTV). It can be readily converted into other functionalized thiophene derivatives which can be good candidates for two-step precursor polymerization. As the brief review of synthesis

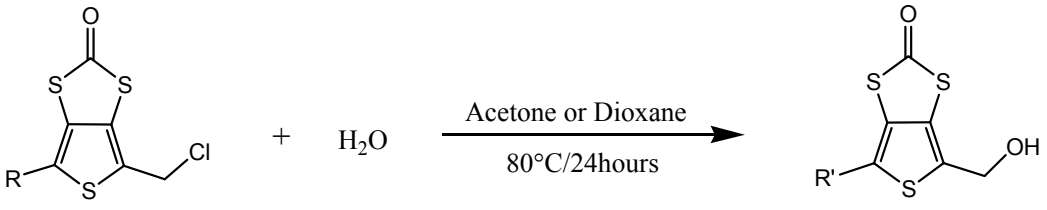
of poly(thienylene vinylene) mentioned in the previous chapter, monomers with certain functional groups are possible candidates for the synthesis of polythienylene vinylenes through a precursor route.

Nucleophilic substitution reactions were explored in transformation of **26** and **27** into various derivatives having different leaving groups.

2.6.1 Synthesis of alcohol

4,6-Bis(hydroxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**28**) can be easily prepared from **26** under mild condition in a fairly good yield (91%). The diol shows limited solubility in dichloromethane, chloroform, ethyl acetate; but good solubility was observed in strong polar solvents such as DMSO, and DMF. 4-(hydroxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**29**) was prepared by hydrolysis of **27** using water**.** The reactions are shown in Scheme 2.10 below.

Scheme 2.10 Preparation of alcohols



26, **27**

26 R=CH_2Cl
27 R=H

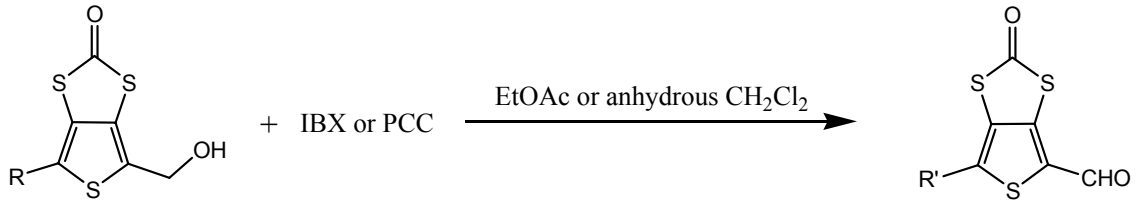
28, **29**

28 R=CH_2OH
29 R=H

2.6.2 Synthesis of aldehydes

Both IBX and PCC are effective oxidation reagents for synthesis of aldehydes from alcohols.[187-188] Both **28** and **29** were conveniently oxidized into their aldehyde derivatives, respectively, using these oxidizing reagents (Scheme 2.11)

Scheme 2.11 Preparation of aldehydes through oxidation



28, **29**

28 R=CH_2OH
29 R=H

30, **31**

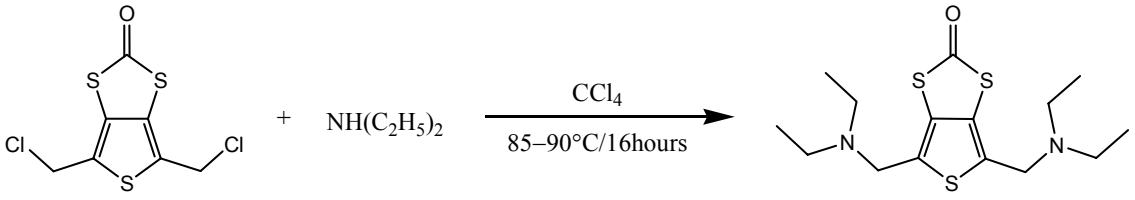
30 R'=CHO
31 R'=H

2.6.3 Synthesis of Mannich base

Mannich bases can be synthesized by the nucleophilic substitution reactions of less active secondary amines such as diethylamine with 4,6-bis(chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**26**) under mild conditions with better yields in comparison with the aminoalkylation reactions which were performed in harsh conditions (Section 2.3.3 and Section 2.3.4). As we discussed in Section 2.3, the less reactive amines were very difficult to afford symmetrical bis-substituted Mannich bases. However, nucleophilic substitution reactions of 4,6-bis(chloromethyl([3,4-*d*]-1,3-dithiol-2-one (**26**) is a better alternative, as will be discussed below.

Synthesis of 4,6-bis((diethylamino)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**32**) is illustrated in Scheme 2.12.

Scheme 2.12 Preparation of Mannich base

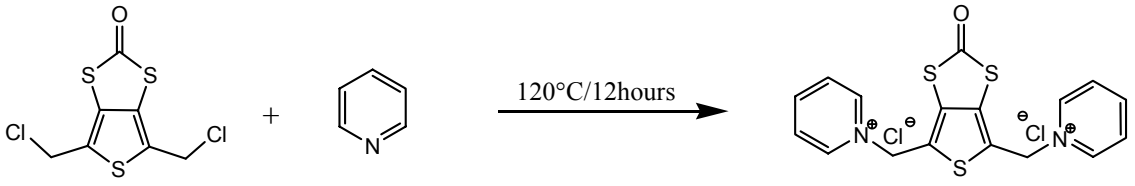


26 **32**, 36%

2.6.4 Synthesis of bis-pyridinium salt

1,1'-[(4,6-thieno[3,4-*d*]-1,3-dithiol-2-one-diyl)bismethylene] bis[pyridinium chloride] (**33**) was prepared by refluxing **26** with excess pyridine.

Scheme 2.13 Preparation of bis-pyridinium chloride salt

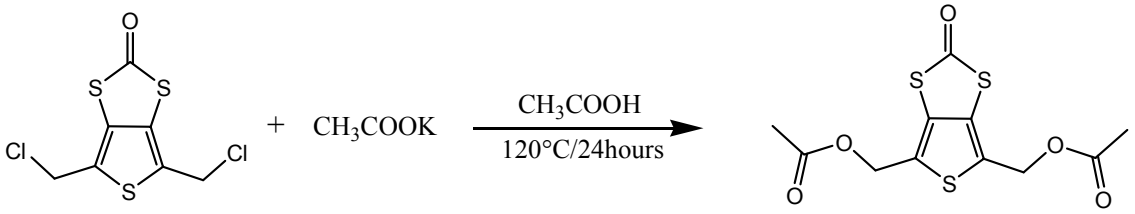


26 **33**, 95%

2.6.5 Synthesis of ester (acetate)

4,6-bis(acetoxymethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (**34**) was synthesized with potassium acetate in glacial acetic acid (Scheme 2.14).

Scheme 2.14 Preparation of 4,6-bis(acetoxymethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (**34**)

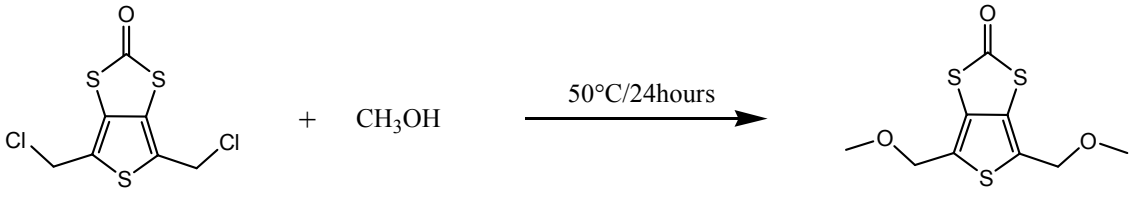


26 **34**, 68%

2.6.6 Synthesis of ether

Attempts to synthesize bis-sulfonium salts in methanol did not afford the target salts. Instead 4,6-bis(methoxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**35**) was isolated with good yield (60%), the reaction are shown in Scheme 2.15.

Scheme 2.15 Preparation of 4,6-bis(methoxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**35**)

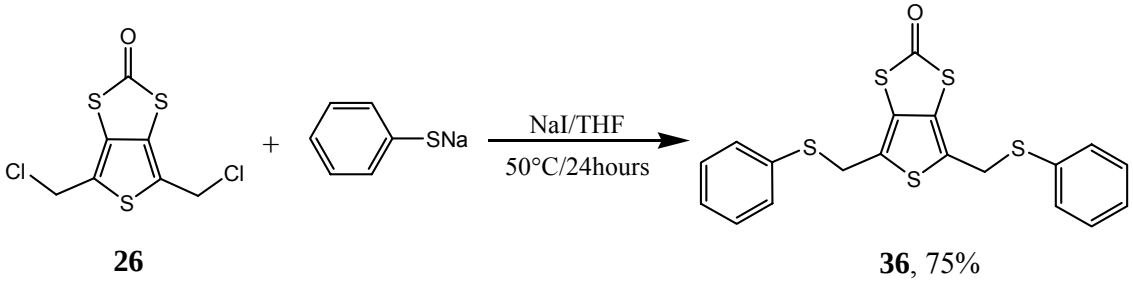


26 **35**, 60%

2.6.7 Synthesis of bis-substituted sulfide

Preparation of 4,6-bis((phenylthio)methyl)thieno[3,4-*d*]-1,3- dithiol-2-one (**36**) is presented in Scheme 2.16. The exact mechanism is unkown. The formation of iodomethyl derivative as intermediate followed by nucleophilic displacement of the iodine group by thiol might be possible pathway for this reaction.

Scheme 2.16 Synthesis of bis-subsituted sulfide



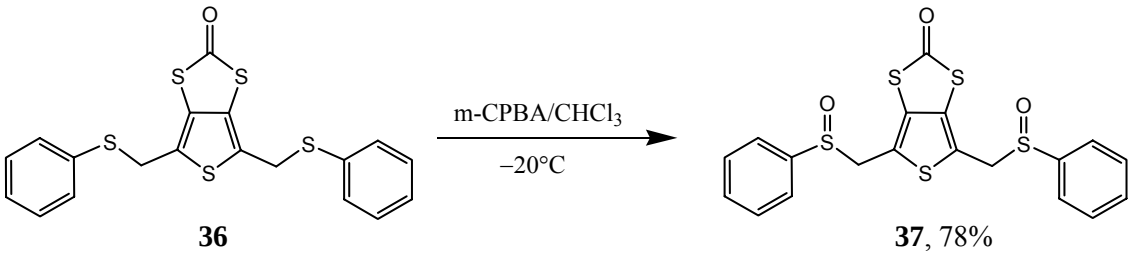
26 **36**, 75%

2.6.8 Synthesis of bis-substituted sulfoxide

Compound **36** was oxidized with 2 equvalents of *m*-chloroperoxybenzoic acid (*m*-CPBA) in low temperature to yield 4,6-bis((phenylsulfinyl)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**37**). A distinctive doublet of doublet signal was observed in ^{1}H-NMR, as a result of the presence of α-methylene protons. These protons cause H-H coupling caused by the two chiral sulfur atoms of the sulfoxide moiety (Scheme 2.17).

Compound **37** shows limited solubility in chloroform, dichloromethane, DMF, and DMSO.

Scheme 2.17 Synthesis of bis-subsituted sulfoxide



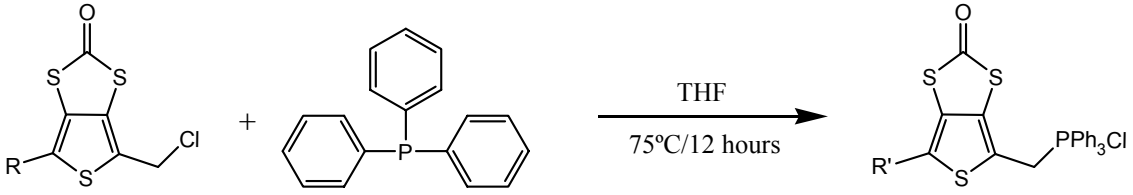
36 **37**, 78%

2.6.9 Synthesis of triphenylphosphonium salts

Triphenylphosphonium salt derivatives were key ingredients for the Wittig olefination reactions. Both chloro derivatives **26** and **27** readily formed triphenylphosphonium salts in THF at elevated temperatures to give **38** (95% yield) and **39** (92% yield), respectively (Scheme 2.18). Triphenylphosphonium salts **38** and **39** are soluble in both $CHCl_3$ and DMSO.

UV-Vis spectra of both triphenylphosphonium salts in $CHCl_3$ solution were illustrated in Fig. 2.2. The λ_{max} of both **38** and **39** are observed in the UV region. This is artributed to π-π^* absorption of the aromatic rings.

Scheme 2.18 Preparation of triphenylphosphonium salts



26, 27

26 R=CH_2Cl
27 R=H

38, 39

38 R'=CH_2PPh_3Cl
39 R'=H

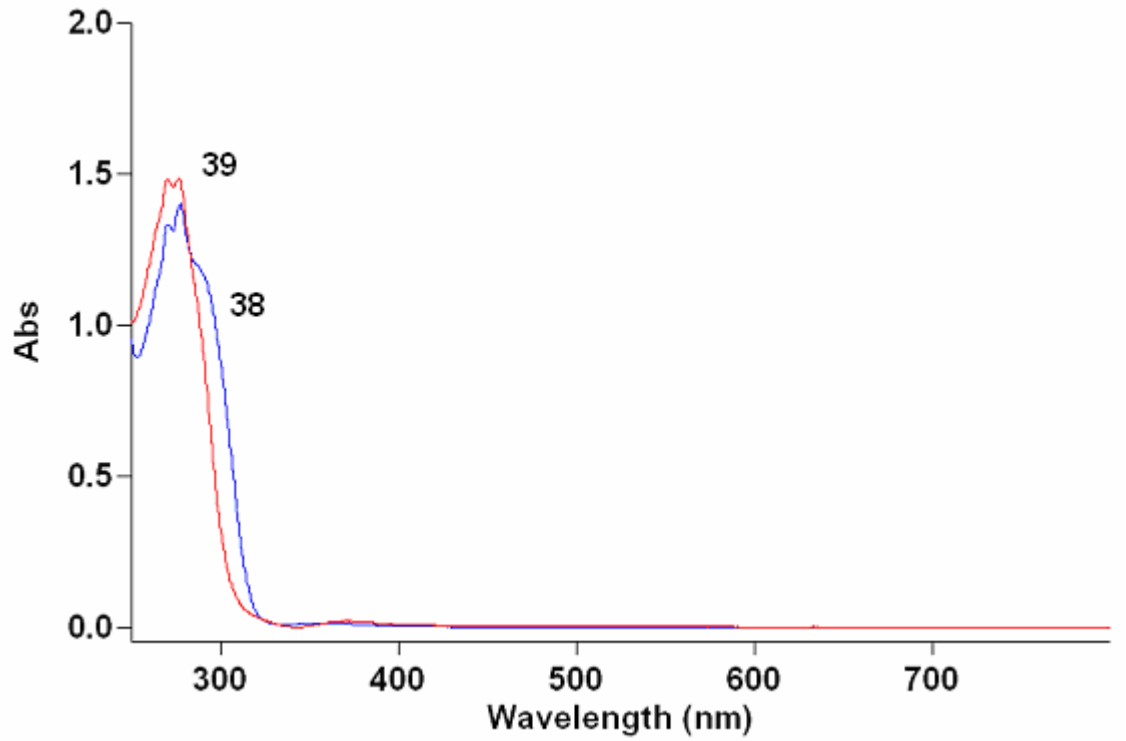
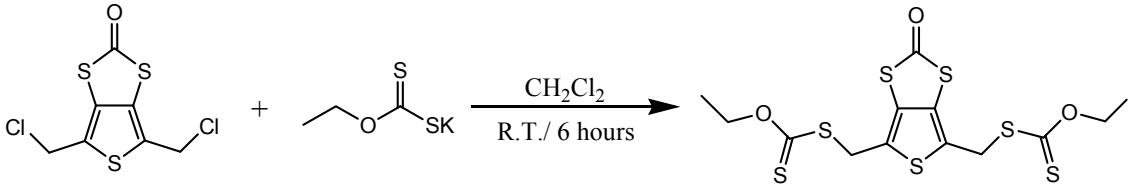


Fig. 2.2 UV-Vis spectra of Compound **38 and 39**

2.6.10 Synthesis of xanthate

It was reported[189-190] that xanthate-leaving groups do not react with indium-tin oxide, a commonly used electrode materials for LED fabrications. Hence, xanthate derivatives are perfect candidates for the precursor polymerization method. 4,6-bis[ethoxy(thiocarbonyl)thiomethyl]thieno[3,4-*d*]-1,3-dithiol-2-one (**40**) was prepared by a nucleophilic substitution reaction with potassium *O*-ethyl axanthate on **26** as shown in Scheme 2.19.

Scheme 2.19 Preparation of xanthate

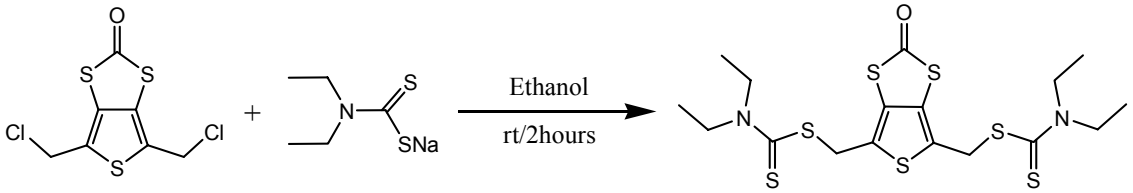


26 **40**, 97%

2.6.11 Synthesis of thiocarbomate

Thiocarbomate derivative is one of the newest discovered compounds which can undergo precursor polymerization to give polythienylenevinylene.[191] 4,6-Bis(*N,N*-diethyldithiocarbomate-methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**41**) was successfully synthesized under mild conditions.

Scheme 2.20 Preparation of thiocarbomate



26 **41**, 52%

2.6.12 Synthesis of asymmetric derivatives

Asymmetrical derivatives are of great interests for precursor polymerization synthesis. Asymmetrical monomers usually bearing a polarizable group in the α position, i.e. S(O)R, that can help stabilize the anion (quinodimethane) intermediate

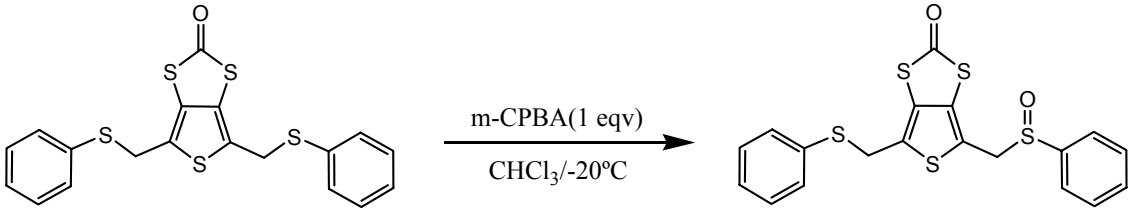
formed by deprotonation. A good leaving group in the α' position, such as Cl, can benefit the formation of a precursor polymer.[192]

These polarizable groups are also good leaving groups at elevated temperatures and commonly yield conjugated polymers upon heating (elimination).

(1) Asymmetrical sulfoxide

One equivalent of m-CPBA can oxidize the bis-substituted sulfide to asymmetric 4-((phenylsulfinyl)methyl)-6-((phenylthio)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**42**) as major product as shown in Scheme 2.21.

Scheme 2.21 Preparation of asymmetrical sulfoxide

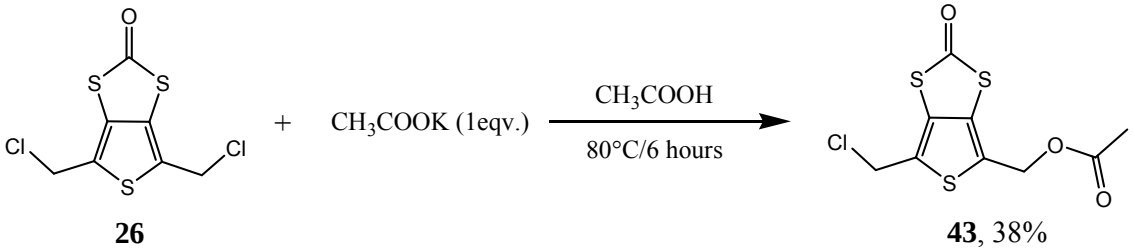


36 **42**, 83%

(2) Asymmetrical acetate

4-(Chloromethyl)-6-(acetoxylmethyl)-thieno[3,4-*d*]-1,3-dithiol-2-one (**43**) (Scheme 2.22) was synthesized under similar conditions for preparation of bis-acetate derivative **34** shown in Scheme 2.14.

Scheme 2.22 Synthesis of asymmetrical acetate

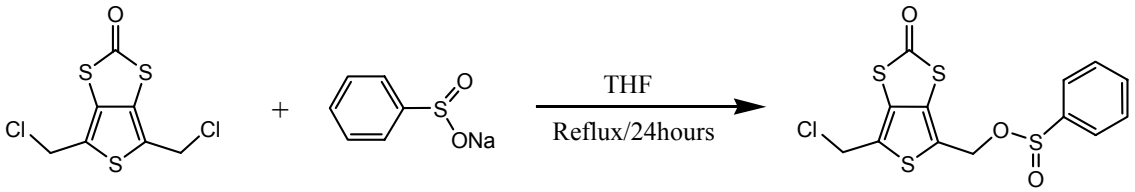


26 **43**, 38%

(3) Asymmetrical benzenesulfinate

4-(Chloromethyl)-6-(phenylsulfinyloxylmethyl)-thieno[3,4-*d*]-1,3-dithiol-2-one (**44**) was prepared by a refluxing reaction of **26** with sodium benzenesulfinate in THF as shown in Scheme 2.23.

Scheme 2.23 Synthesis of asymmetrical benzenesulfinate

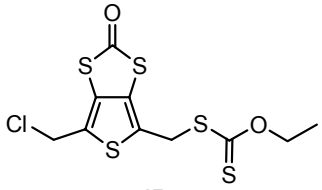


26 **44**, 68%

(4) Asymmetrical xanthate

One equivalent of potassium xanthogenate gave a mixture of asymmetrical xanthate 4-chloromethyl-6-ethyoxy(thiocarbonyl)thiomethyl-thieno[3,4-*d*]-1,3-dithiol-2-one (**45**), that structure is illustrated in Fig. 2.3, and bis-substituted 4,6-bis[ethoxy(thiocarbonyl)thiomethyl]thieno[3,4-*d*]-1,3-dithiol-2-one (**40**). Column

separation with silical gel did not afford pure asymmetrical xanthate compound due to similar polarity of two products.



45

Fig. 2.3 Asymmetric xanthate

2.6.13 Summary

1. 4,6-Bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (**26**) was successfully functionalized into a number of symmetrical derivatives possesing various leaving groups.

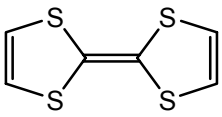
2. 4-(Chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (**27**) was also subject to nucleophilic reactions to afford some mono-substituted derivatives.

3. Some of those thiophene derivatives may be good candidates for precursor polymerization, which are still under further investigation in our laboratory to achieve polythienylene vinylene polymers. Some of intial work will be discussed in Chapter 3.

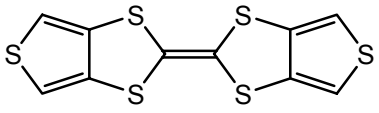
2.7 Synthesis of DTTTF derivative

Tetrathiafulvalene (TTF) (Fig. 2.4) is one of the simplest symmetrical tetrachalogenafulvalenes. Many charge-transfer salts incorporating TTF units exhibit

metallic conductivity and even superconductivity.[193] The attempted coupling reactions of thieno[3,4-*d*]-1,3-dithiole-2-thione (**1**) or thieno[3,4-*d*]-1,3-dithiol-2-one (**2**) with triethyl phosphite were not successful. Chiang et. al reported several multi-step approaches to prepare 2-thieno[3,4-*d*]-1,3-dithiol-2-ylidene-thieno[3,4-*d*]-1,3-dithiole (DTTTF).[176] These synthetic methods lead to tedious work and low overall yield.



46



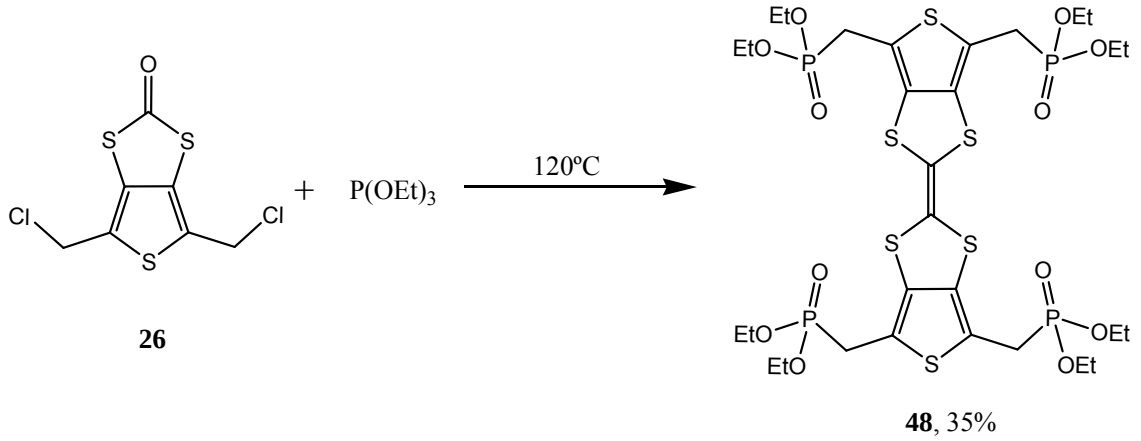
47

Fig 2.4 TTF (**46**) and DTTTF(**47**)

Insertion of a π-conjugating spacer between two 1,4-dithiafulvenyl groups has been attracted tremendous interests because of the increased dimensionality and hence improved charge transport properties expected for the corresponding cation radical salts in the general frame of the chemistry of extended TTF analogues.[194] More recent work also shown that these hybrid π-conjugated systems are potentially low bandgap organic semiconductors and may be used as building blocks with chromophores for second or third-order nonlinear optics.[195-197]

The coupling reaction of **24** with triethyl phosphite gave an unique compound 4,4',6,6'-tetra(diethoxyphosphorylmethyl)-(-2-(thieno[3,4-*d*]-1,3-dithiol-2-ylidene) thieno[3,4-*d*]-1,3-dithiole (**48**) with 35% yield (Scheme 2.24).

Scheme 2.24 Synthesis of DTTTF-methylphosphonate



26

48, 35%

This phosphonate derivative might undergo Wittig-Horner reaction with aldehydes to form hybrid π-conjugated systems incorporating DTTTF units in their backbones. Polymerization of this DTTTF analogue is still under investigation is our lab. Such a polymer might afford a very unique cross-linking polymeric structure and fascinating electronic properties.

2.8 Conclusion

1. Successful synthesis of thieno[3,4-*d*]-1,3-dithiole-2-thione (**1**) and thieno[3,4-*d*]-1,3-dithiol-2-one (**2**) with one-pot reactions. The phosgene solution method to prepare compound **2** provides better yield than oxidation of compound **1**.

2. Successful halogenation reactions of thieno[3,4-*d*]-1,3-dithiol-2-one (**2**) afford different bis- and mono-substituted halogenated compounds with very good yields, and these halogenated derivatives were fully characterized.

3. Aminoalkylatioin reactions of thieno[3,4-*d*]-1,3-dithiole-2-thione (**1**) and thieno[3,4-*d*]-1,3-dithiol-2-one (**2**) gave mono-substituted Mannich bases with fairly good yields. Preparation of symmetrical Mannich bases was very difficult.

4. 4,6-bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (**26**) and 4-chloromethylthieno[3,4-*d*]-1,3-dithiol-2-one (**27**) were successfully synthesized. A number of symmetrical and asymmetrical thiophene derivatives were prepared from both chloromethylated compounds via the nucleophilic reactions.

5. A phosphoonate derivative bearing a DTTTF structure was also prepared from 4,6-bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (**26**).

CHAPTER 3

SYNTHESIS OF THIOPHENE OLIGOMERS AND POLYMERS

3.1 Introduction

As we demonstrated on Chapter 2, thieno[3,4-*d*]-1,3-dithiol-2-one (**2**) was successfully converted into the halogenated compounds (**5-10**), two chloromethylated compounds and other derivatives. Since the main objective of this project is the preparation of oligomers and/or polymers bearing carbondithiolate structures in their oligomer and/or polymer backbones for possible metal-dithiolate coordination study in the future. Our efforts of this chapter will focus on preparation of oligomers and polymers with carbondithiolate structures through different approaches.

Metal-catalyzed reactions are applied to those halogenated derivatives (**5-10**) to afford oligomers and polymers are the first reasonable approach. Other functionalized derivatives from chloromethylated compounds can undergo base-promoted polymerization reactions to achieve soluble precursor polymers, which may be converted directly into conjugated polymers or metal-coordinated polymers followed by thermal elimination reaction to yield conjugated metallopolymers. Other reactions which were reviewed in Section 1.4 can also be considered as possible routes to realize conjugated oligomers and/or polymers with carbondithiolate structures, especially Wittg reactions.

3.2 Attempted synthesis of homopolymers

Homopolymer (**P1**) bearing a carbondithiolate structure in its repeating units may be a fascinating polymer (Fig. 3.1), which may be converted a DTTTF-like crosslinked polymer or metal-dithiolate coordinated metallopolymer. Several unsuccessful approaches were attempted in preparation of this unique homopolymer.

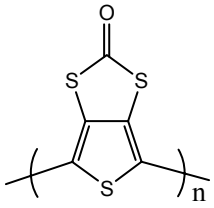
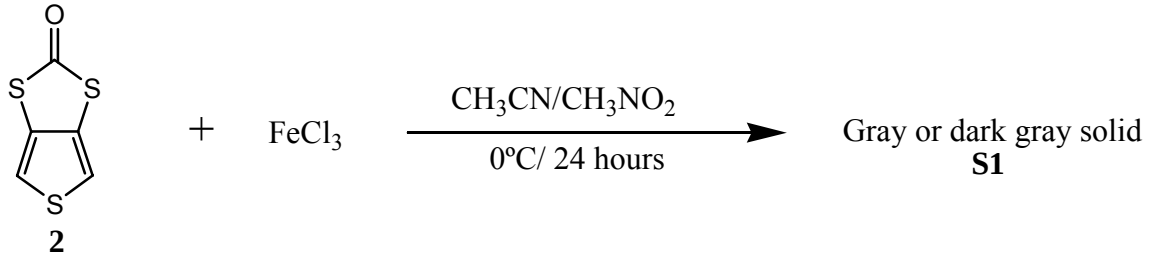


Fig. 3.1 Homopolymer **P1**

3.2.1 Chemical polymerization with $FeCl_3$

When compound **1** was treated with $FeCl_3$ in the presence of either CH_3CN or CH_3NO_2, the formation of solid precipitates was not observed as expected. TLC analysis showed that the starting materials had disappeared but, the appearance of a streak down the TLC was observed. Attempts to isolate any products or byproducts were unsuccessful.

Scheme 3.1 Attempted oxidation reactions of compound **2**

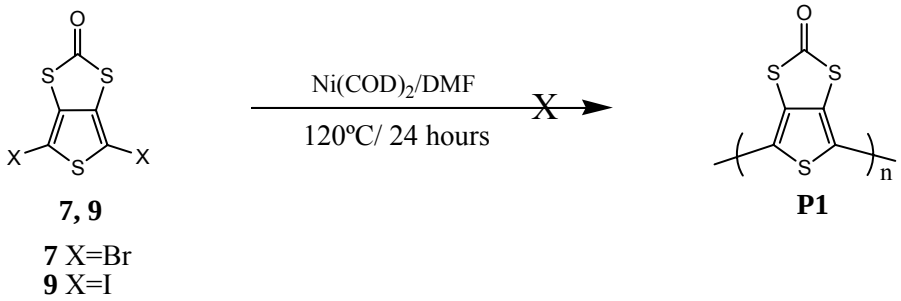


The $FeCl_3$ chemical polymerization of compound **2** was then investigated (Scheme 3.1). Thieno[3,4-*d*]-1,3-dithiol-2-one (**2**) was treated with $FeCl_3$ in presence of either CH_3CN or CH_3NO_2. From this reaction, a gray (or dark gray) color solid (**S1**), which was not soluable in most common organic solvents, such as chloroform, dichloromethane, DMF, and DMSO was isolated. In the FT-IR spectra of the gray solid **S1**, a strong absorption peak at 1716 cm^{-1} was observed, which was assigned as carbonyl C=O stretching. The "dedoping" of **S1** was performed with either hydrazine hydrate-water (1:1 *v/v*) or ammonium hydroxide-water (1:1 *v/v*) solutions.[71] Treatment with hydrazine resulted in a deep blue solution, and no solid residue was recovered. The gray solid **S1** was also stirred with ammonium hydroxide solution for 24 hours yielded an unidentifiable deep dark solid (**S2**). FT-IR analysis of **S2** showed the disappearance of the carbonyl C=O stretching absorption. This led us to believe that the carbondithiolate structure has been destroyed during the "dedoping" process.

3.2.2 Cross-coupling polymerization of halide derivatives

Bis(1,5-cyclooctadiene) nickel(0) ($Ni(COD)_2$) is a very efficient transition-metal complex catalyst for cross-coupling polymerization of halogenated aromatic compounds.[198]

Scheme 3.2 Cross-coupling polymerization reactions



7, 9

7 X=Br
9 X=I

P1

The cross-coupling reactions of both monomers **7** and **9** catalyzed by $Ni(COD)_2$ (Scheme 3.2) did not give the desired homopolymer **P1**. Monomers **7** and **9**, instead gave a black unidenfiable solids (**S3** and **S4**), respectively. Starting materials had disappeared on TLC plates, however. In addition, the carbonyl C=O stretching absorptions were not observed on FR-IR spectra of both solid residues.

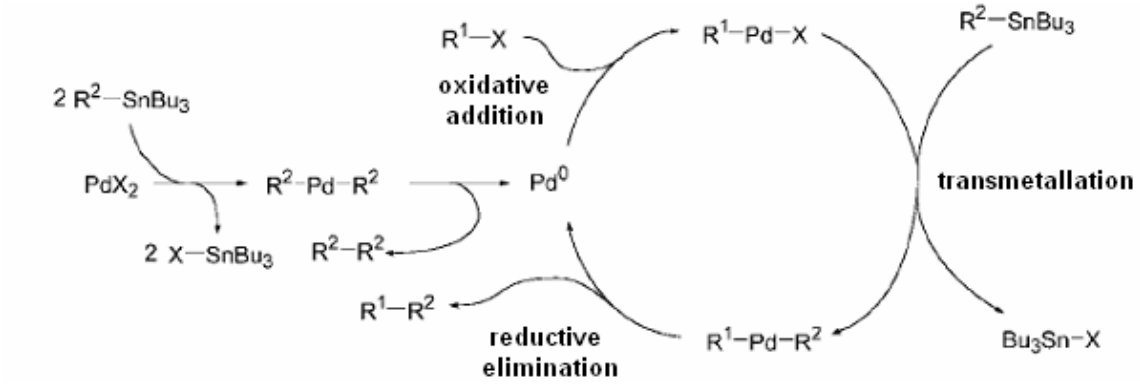
3.2.3 Ullman reaction

Ullman reaction has been successfully exercised for the preparation of polythiophene derivatives bearing a carboxylate side chain.[199] Similar reaction conditions were applied to compound **7** for polymerization. The copper catalyzed Ullman reaction gave a gray-brown solid (**S5**) as the product. Characterization by FT-IR showed similar absorption feartures as that of solid obtained by cross-coupling polymerization, In addition, no carbonyl C=O stretching absorption around 1710cm^{-1} was observed.

3.3 Attempted synthesis of copolymers

The Stille reaction is also a popular method to build a C-C bond between aromatic halides with organotin compounds.[200-201] Palladium(II) complexes PdL_n, such as [1,1'-bis(diphenylphosphine) ferrocene] dichloropalladium(II) ($Pd(dppf)Cl_2$), and bis(triphenylphosphine)palladium(II) dichloride ($Pd(pph_3)_2Cl_2$) are the most widely used catalysts. The mechanism of the polymerization involves a reduction process of Pd(II) to give the anionic Pd(0) complex species, which then undergos the formation C-C coupling.[202-203] The C-C coupling process involves three steps: oxidative addition of Pd(0), transmetallation, followed by a reductive elimination.[204] The simplified scheme of the mechanism of Stille reaction is illustrated in Scheme 3.3.

Scheme 3.3 Schematic mechanism of Stille reaction



The aromatic organotin compounds **49-56** (shown in Fig. 3.2) were prepared in our lab according to reference literature procedures.[200] Synthesis include the treatments of thiophene with NBS to give 2- and/or 5-bromothiophene, followed by lithium-

bromine exchange reaction with *n*-butyllithium. The reaction is then quenched with tributyltin chloride to afford the organotin compounds. All of the tributyltin compounds are sensitive to regular silica gel column or distillation, flushing through basified silica gel columns can only remove baseline impurities. Therefore, the thiophenetin analogues were used without further purification.

E-1,2-bis(tri-n-butylstannyl)ethylene **(57)** was purchased from TCI America. Attempted Stille reactions to afford the oligomers are illustrated in Scheme 3.4 and the results are summarized in Table 3.1.

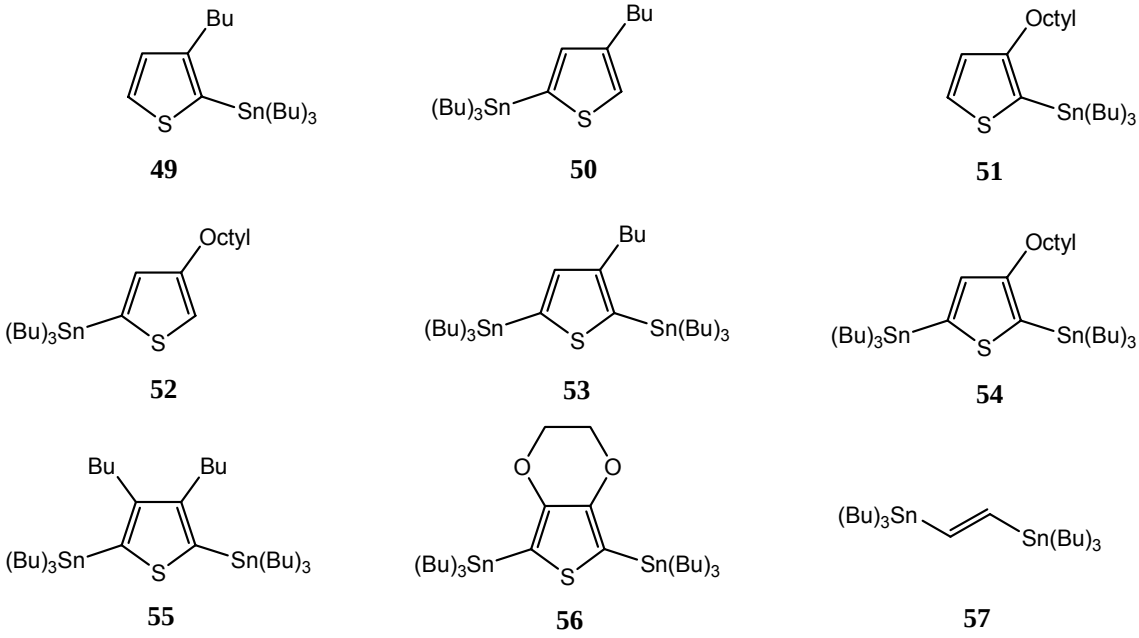
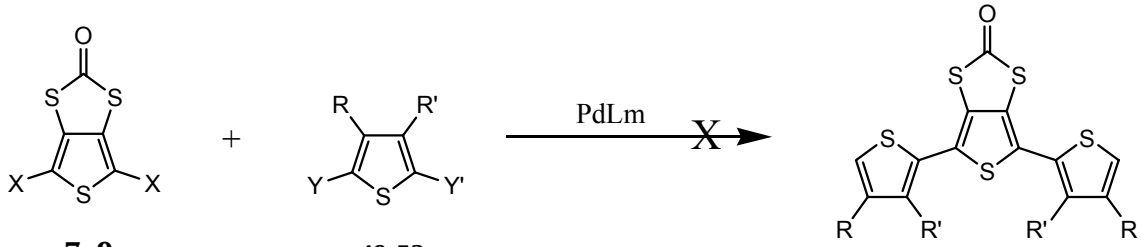


Fig. 3.2 Schematic presentation of organotin compounds

Scheme 3.4 Attempted Stille reactions to oligothiophenes



7, 9

7 X=Br
9 X=I

49-52

Y=H, $Sn(Bu)_3$
Y'=H, $Sn(Bu)_3$

R=H, butyl, octyl
R'=H, butyl, octyl

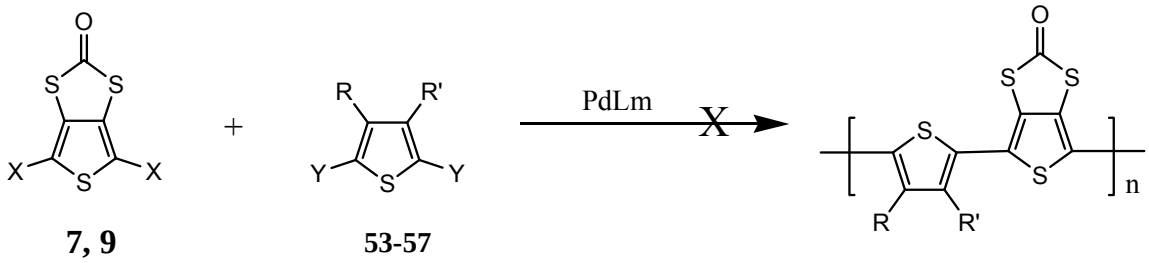
Table 3.1 Stille reactions to oligothiophenes

Starting material	Organotin	Temp. (ºC)	Catalyst	Solvent	Notes
7	**49**	75	$Pd(pph_3)_2Cl_2$	THF	Recovered strating material **7**
7	**49**	120	$Pd(pph_3)_2Cl_2$	DMF	Complex mixture of products
7	**50**	75	$Pd(pph_3)_2Cl_2$	THF	Recovered starting material **7**
7	**50**	120	$Pd(pph_3)_2Cl_2$	DMF	Complex mixture of products
9	**50**	100	$Pd(pph_3)_2Cl_2$	DMF	Complex mixture of products
7	**51**	120	$Pd(pph_3)_2Cl_2$	DMF	Complex mixture of products
7	**52**	120	$Pd(pph_3)_2Cl_2$	DMF	Complex mixture of products
7	**51**	80	$Pd(pddf)Cl_2$	THF	Recovered strating material **7**

The recovery of starting materials in all of the above described reactions led us to assume that the presence of Pd(II) may not necessarily decompose the carbondithiolate structure present in the starting materials. Due to the difficulty of the purification process of these mono-organotin compounds, it is reasonable to assume that

the impurities may be responsible for the failure of obtaining the target oligothiophenes. Therefore, we decided to proceed the polymerization reactions with disubstituted organotin compounds (**53-57**). The polymerization reactions are illustrated in Scheme 3.5, and the results are summarized in Table 3.2.

Scheme 3.5 Attempted Stille reactions to copolymers



7, 9

7 X=Br
9 X=I

53-57

Y=Sn(Bu)$_3$

R=H, butyl, octyl
R'=H, butyl, octyl
R=R'=OCH_2CH_2O

Table 3.2 Stille reactions to copolymers

Halide	Organotin compounds	Catalyst	Solvent	Temp. (ºC)	Product
7	**53**	Pd(dppf)Cl_2	DMF	100	**S6** (redish brown solid)
7	**54**	Pd(dppf)Cl_2	DMF	100	**S7** (redish black solid)
7	**55**	Pd(dppf)Cl_2	DMF	150	**S8** (black solid)
7	**56**	Pd(dppf)Cl_2	DMF	150	**S9** (black solid)
7	**57**	Pd(dppf)Cl_2	DMF	150	**S10** (black solid)
9	**57**	Pd(dppf)Cl_2	DMF	150	**S11** (black solid)

The Stille reactions of **7** or **9** with the different disubstituted organotin compounds (**53-57**) generally afforded deep color solid (**S6-S11**) as the products. The

FT-IR sepectra of all unidentifiable solids show the disappearance of carbonyl C=O strectching (1710 cm^{-1}). That led us to assume that the disruption of carbondithiolate structure of starting material **7** and **9** under the harsh conditions occurred during the Stille reactions.

Both back solids **S10** and **S11** showed that neither the characteristic absorption peak of vinylene C-H out-of-plane bending (~930 cm^{-1}) was observed, nor was vinylene C-H strectching absorption (~3010 cm^{-1}) detected. These results confirmed there was no C=C bond successfully formed during these reactions, resulting in the black solids **S10** and **S11**.

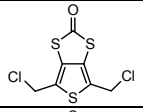
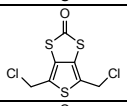
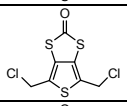
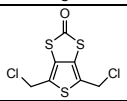
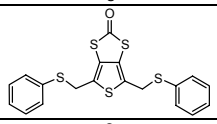
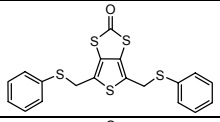
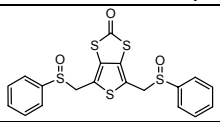
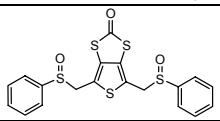
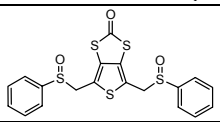
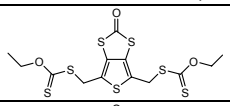
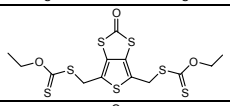
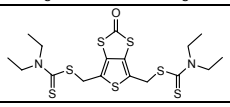
3.4 Attempted synthesis of precursor polymers

After all the attempts through metal-catalyzed coupling reactions to make homopolymers or copolymers bearing a carbondithiolate structure were exhausted, preparing precursor polymers became a rational choice to retain the carbondithiolate structure in the repeating unit of polymer.

The synthesis of precursor polymers was generally performed in dry THF at low temperatures. One equivalent of sodium ethoxide (NaOEt), potassium *t*-butoxide (*t*-BuOK), sodium methoxide (MeONa), or lithium diisopropylamide (LDA) was used as the base for the deprotonation of acidic α-protons on the pendant groups. The reaction mixtures were quenched by pouring into methanol after reactions were complete. These target polymers precipitated in methanol and were collected by filtration. The

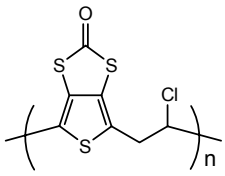
preliminary results of some attempted precursor polymerization reactions are summarized in Table 3.3.

Table 3.3 Attempted precursor polymerization reactions

Starting Material	Structure	Base	Solvent	Temp. (ºC)	Time (hours)	Product
26		*t*-BuOK	THF	0 r.t.	20 48	**S12** (orange solid)
26		*t*-BuOK	THF	-78 r.t.	12 24	**S13** (orange black solid)
26		NaOEt	THF	0 r.t.	1 24	**S14** (yellowish gray solid)
26		NaOEt	THF	-78 r.t.	1 24	**S15** (yellow solid)
36		*t*-BuOK	THF	-78 r.t.	8 24	No precipitates in CH_3OH
36		*t*-BuOK	THF	0 r.t.	8 24	No precipitates in CH_3OH
37		*t*-BuOK	THF	-78 r.t.	12 24	No precipitates in CH_3OH
37		*t*-BuOK	CH_2Cl_2/ THF (1:1 *v*/*v*)	-78 r.t.	12 24	No precipitates in CH_3OH
37		*t*-BuOK	DMSO	r.t.	48	No precipitates in CH_3OH
40		*t*-BuOK	THF	-78	24	No precipitates in CH_3OH
40		NaOEt	THF	0 r.t.	12 24	No precipitates in CH_3OH
41		*t*-BuOK	THF	r.t.	24	No precipitates in CH_3OH

All unidifiable solids **S12**, **S13**, **S14** and **S15** were not soluble in the regular organic solvents such as CH_2Cl_2, $CHCl_3$, THF, DMF, DMSO, and NMP. The projected structure of this polymer is shown in Fig. 3.3. As shown in Fig 3.4, All FT-IR spectra of these solids show a distinctive carbonyl C=O stretching at 1720cm^{-1}.

Compound **36** did not give any precursor polymers at the room temperature or the low temperature. Due to the limited solubility of compound **37** in THF, DMSO, the low concentration of reaction mixtures may be blamed for the failure of polymerization reactions. Neither compound **40** nor **41** yield precursor polymers.



P2

Fig. 3.3 The projected structure of **S12-S15**

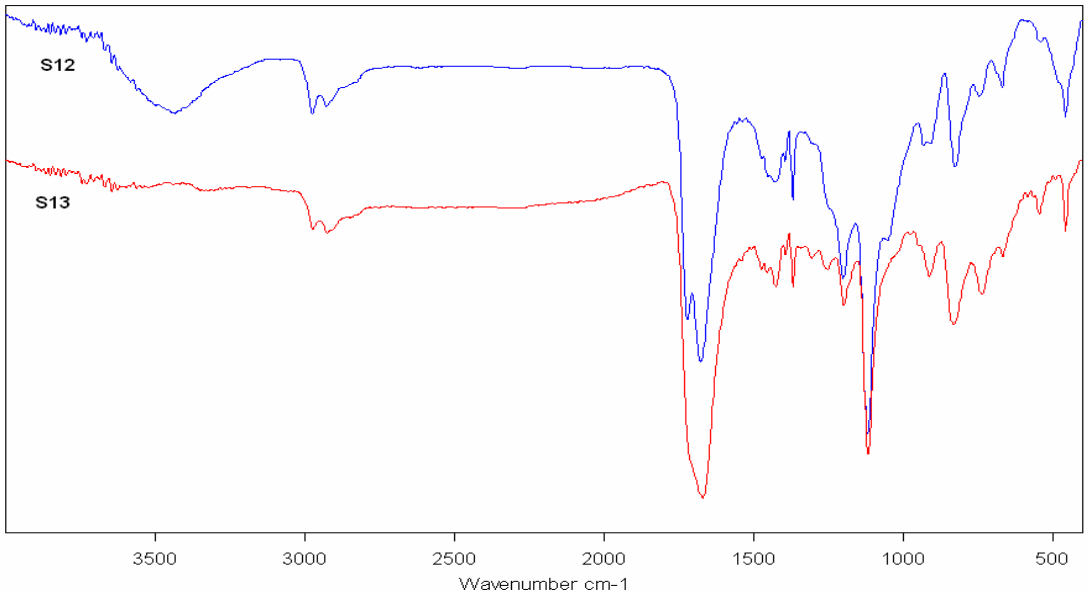
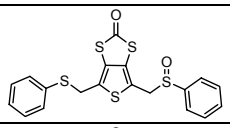
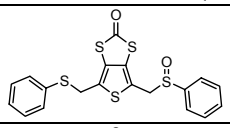
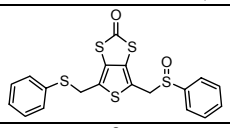
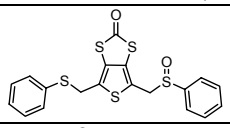
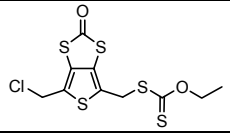


Fig 3.4 FT-IR spectra of **S12** and **S13**

Based on the results observed for the polymerization of compound **26**, we can reasonably assume that the Cl is a very good leaving group for the formation of precursor polymers, but the poor processability of the formed precursor polymer bearing a Cl group results in the loss of the true meaning of a good "precursor". Therefore, these asymmetrical monomers (**42-45)**, especially those with chloromethylene groups, become very promising for the successful precursor polymers with carbondithiolate structures. The Cl group benefits the formation of the precursor polymer, the other remaining group help improve the solubility of it. The results of polymerization reactions of some asymmetrical monomers are listed in Table 3.4.

Table 3.4 The precursor polymerization reactions of some asymmetrical monomers

Starting material	Structure	Base	Solvent	Temp. (ºC)	Time (hours)	Product
42		NaOEt	THF	-78	24	No precipitates in MeOH
42		MeONa	THF	r.t.	24	No precipitates and starting material recovered
42		*t*-BuOK	THF	r.t.	24	**S16** (Gray balck solid)
42		NaOEt	THF	r.t.	24	**P3** (yellow solid)
45*		*t*-BuOK	THF	r.t.	24	**S17** (light yellow solid)

***** Compound **45** is used as a mixture with 20~25% compound **40** as impurity.

Table 3.4 shows that the reaction of compound **42** with sodium methoxide did not proced to form a polymer, and recovery of starting material **42** was observed. **S16** was droped as a precursor polymer because of poor solubility in common organic solvents. ^{1}H-NMR and FT-IR spectrum of **P3** are inconclusive (Fig. 3.5 and Fig. 3.6).

P3 was subjected to a thermal elimination reaction in a vaccum oven at 200ºC for 8 hours yield a deep brown colored film. The characteristic odor of benzenethiol was detected upon heating. This led us to reasonably assume that the sulfide might be the pendant group of **P3**, and the projected structure is shown in Fig. 3.7.

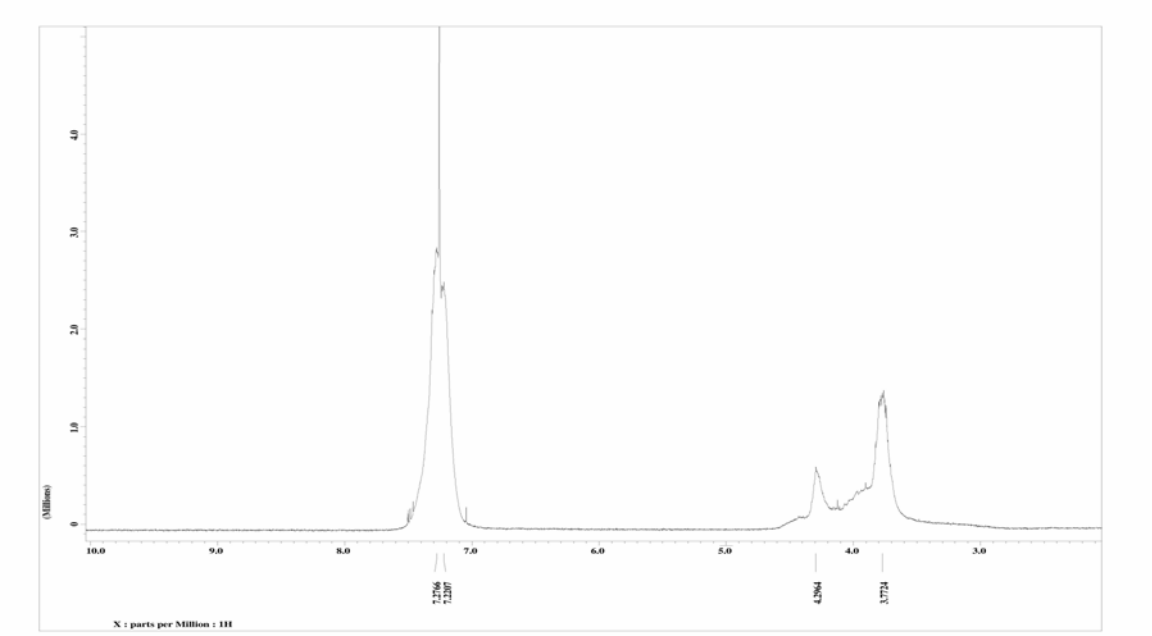


Fig. 3.5 ^{1}H-NMR spectrum of **P3**

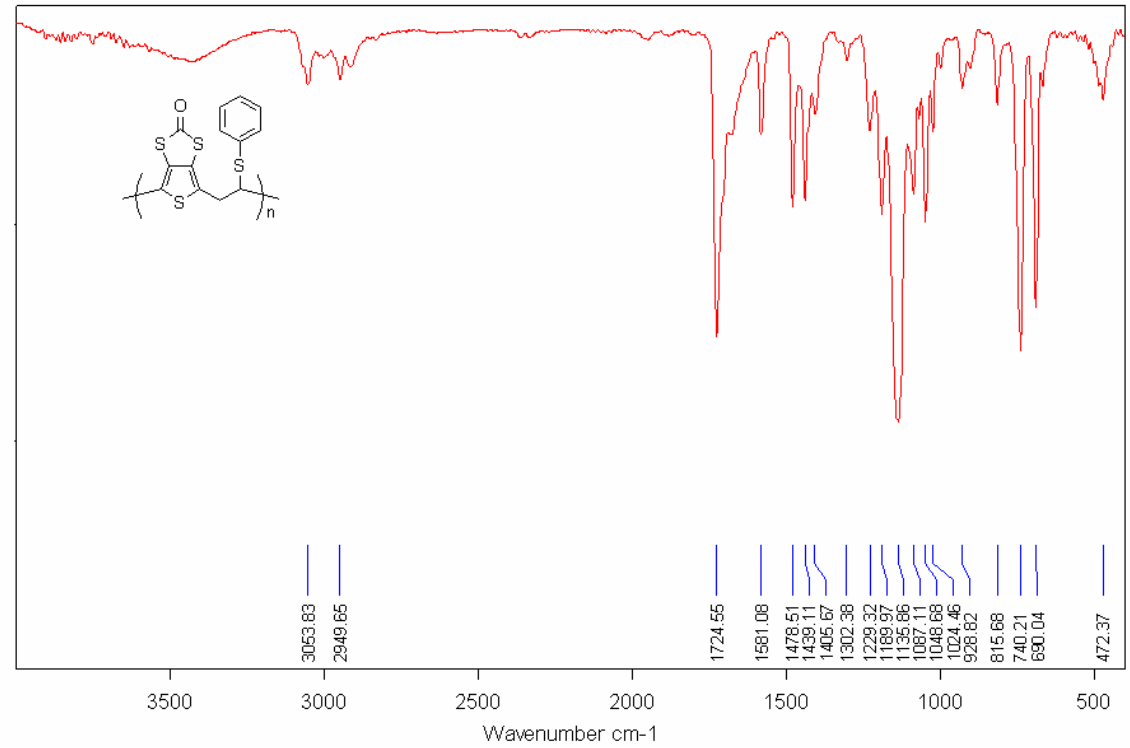
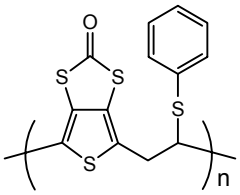


Fig. 3.6 FT-IR spectrum of **P3**

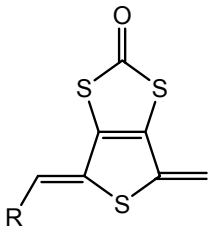


P3

Fig. 3.7 Schematic presentation of **P3**

NMR and FT-IR analysis of **S17** is inconclusive. The thermal elimination reaction (220ºC) yields a black solid. FT-IR spectrum of the resulted black solid does not show the characteristic vinylene C-H strectching at 3010 cm^{-1}, nor the vinylene C-H out-of-plane bending at 930cm^{-1}.

An acid-promoted polymerization method was also applied to several monomers without success. The mechanism of the trifluoroacetic acid (TFA) promoted polymerization is similar to the base-promoted process. The polymerization proceeds through a quinodimethane intermediate (**58**) generated by protonation, rather than by deprotonation which happens in the base-promoted polymerization.



58

Fig. 3.8 The projected quinodimethane intermediate

The reactions of TFA with compound **37** and **42** were complicated. The reactions were monitered by TLC. The disappearance of the starting materials was observed. The byproduct was isolated by column chromatography. The NMR analysis of the byproducts shows that the isolated compounds may be benzenesulfenic acid.[205] That indicates the protonation process occurred.

3.5 Synthesis of thiophene-based oligomers

Conjugated monodisperse oligomers play a significant role in the study of the properties of organic semiconductors. Detailed knowledge of their molecular structure is more easily obtained than their polymeric counterparts. Moreover, conjugated oligomers may present the same electrical and optical features of the related high molecular weight

polymers.[206] Therefore, synthesis of oligomers is of great importance not only as model compounds for the study of polymer synthesis but also as very useful organic materials.

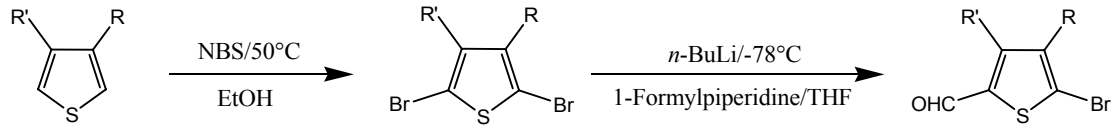
3.5.1 Preparation of alkylthiophene carboxaldehydes

Alkylthiophene carboxaldehydes were synthesized from bromo-alkylthiophenes by treatment with organolithium, followed by a quenching reaction with 1-formylpiperidine to generate the desired carboxaldehydes. In general, *n*-butyllithium is considered as the most efficient reagent in lithium-bromine exchange reactions. However in our case, *tert*-butyllithium generated less isomeric impurities and other byproducts than *n*-butyllithium, which lead to easier isolation, especially in the preparation of dicarboxaldehyde derivatives.

3.5.1.1 Synthesis of 5-bromo-alkylthiophene-2-carboxaldehydes

The preparation of 5-bromo-alkylthiophene-2-carboxaldehydes is shown in Scheme 3.6. 2,5-Dibromoalkythiophenes (**60a-c**) were first treated with one equivalent *n*-butyllithium, followed by a quenching reaction with 1-formylpiperidine to afford 5-bromo-alkythiophene-2-carboxaldehydes (**61a-c**)

Scheme 3.6 Synthesis of 5-bromo-alkythiophene-2-carboxaldehydes



59a-c **60a-c** **61a-c**

59a R=butyl, R' =H
59b R=octyl, R' =H
59c R=R' =butyl

60a R=butyl, R' =H
60b R=octyl, R' =H
60c R=R' =butyl

61a R=butyl, R' =H
61b R=octyl, R' =H
61c R=R' =butyl

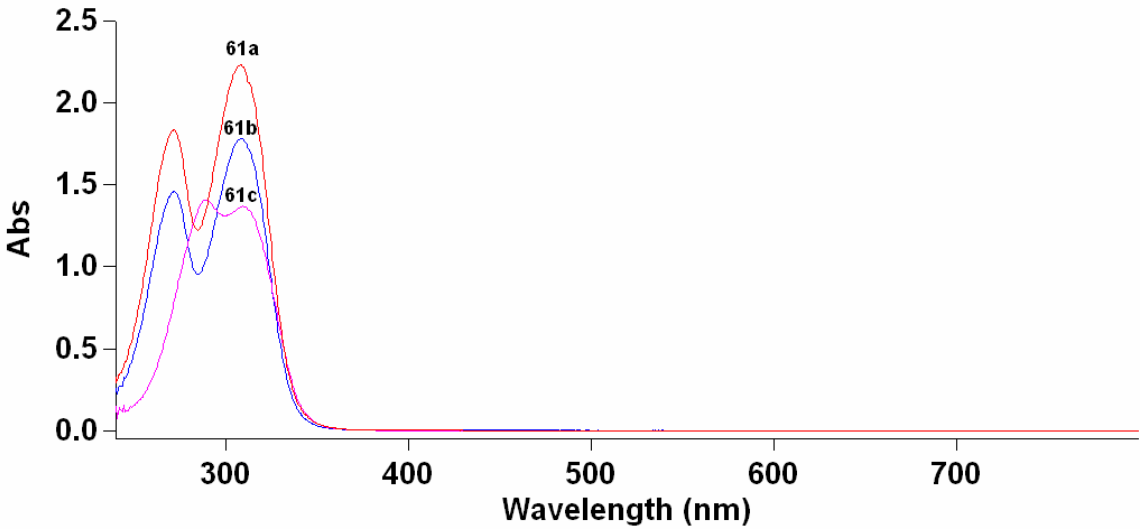


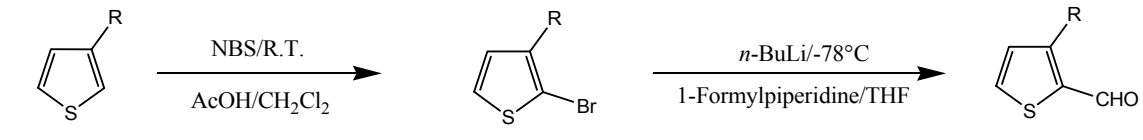
Fig. 3.9 UV-Vis spectra of 5-bromo-alkylthiophene-2-carboxaldehydes ($CHCl_3$)

UV-Vis spectra of 5-bromo-alkylthiophene-2-carboxaldehydes were illustrated in Fig. 3.9. All 5-bromo-alkylthiophene-2-carboxaldehydes show λ_{max} around 315 nm, which corresponding to the aromatic π-π^* transition.

3.5.1.2 Synthesis of 3-alkylthiophene-2-carboxaldehydes

3-Alkylthiophene-2-carboxaldehydes (**63a** and **b**) were prepared by lithiation of 2-bromo-3-alkylthiophene (**62a** and **b**) followed by a quenching reaction with 1-formylpiperidine as shown in Scheme 3.7.

Scheme 3.7 Synthesis of 3-alkylthiophene-2-carboxaldehydes



59a,b **62a,b** **63a,b**

59a R=butyl
59b R=octyl

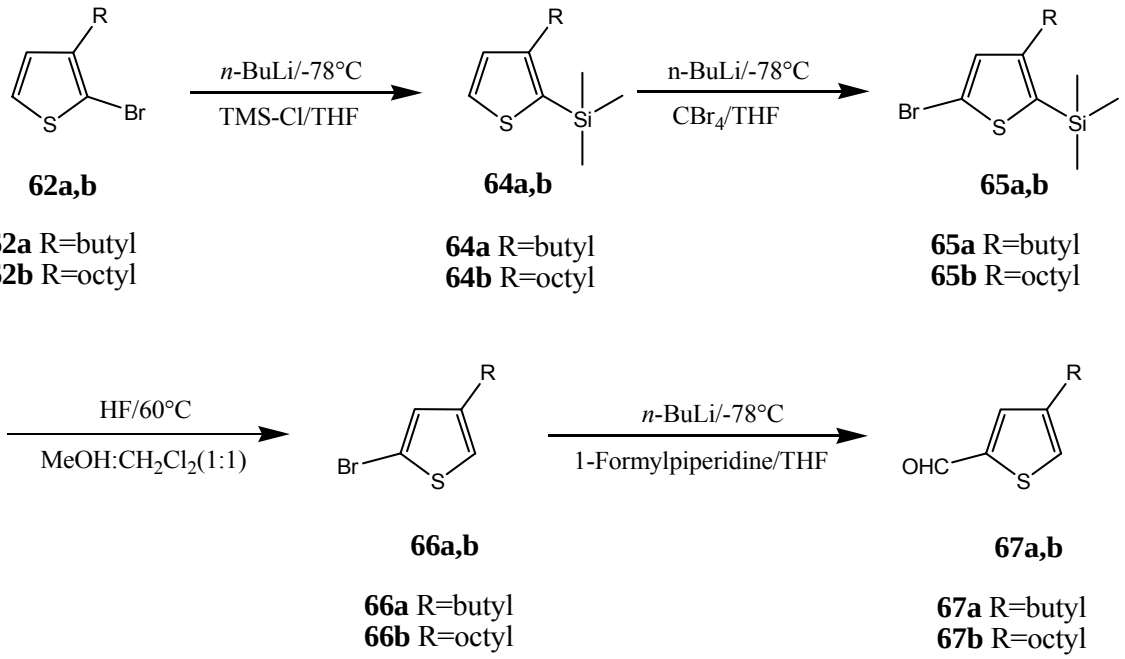
62a R=butyl
62b R=octyl

63a R=butyl
63b R=octyl

3.5.1.3 Synthesis of 4-alkylthiophene-2-carboxaldehydes

2-Bromo-4-alkylthiophenes (**66a** and **b**) were prepared accordinging to a reported literature procesure,[207] which gave highly pure compounds. Lithium-bromine exchang reactions followed by a quenching reaction with 1-formylpiperidine successfully generated 4-alkylthiophene-2-carboxaldehydes (**67a-b**) with fairly good yields (Scheme.3.8)

Scheme 3.8 Synthesis of 4-alkylthiophene-2-carboxaldehydes



62a,b

62a R=butyl
62b R=octyl

64a,b

64a R=butyl
64b R=octyl

65a,b

65a R=butyl
65b R=octyl

66a,b

66a R=butyl
66b R=octyl

67a,b

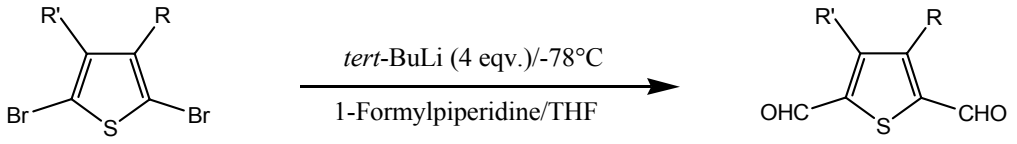
67a R=butyl
67b R=octyl

3.5.1.4 Synthesis of alkylthiophene-2,5-dicarboxaldehydes

A direct lithiation reaction of alkylthiophenes followed by quenching with DMF does not give alkylthiophene-2,5-dicarboxaldehydes as expected. Instead, if the 2,5-dibromoalkylthiophenes are treated with *tert*-BuLi instead of *n*-BuLi followed by a quenching reaction with 1-formylpiperidine, the desired alkylthiophene-2,5-

dicarboxaldehyde (**68a-c**) are isolated with satisfactory yields (Scheme 3.9). UV-Vis spectra of alkylthiophene-2,5-dicarboxaldehydes (**68a-c**) are shown in Fig.3.10, the λ_{max} of these alkylthiophene-2,5-dicarboxaldehydes (**68a-c**) are 290-310nm, which represent the aromatic π-π^* transitions.

Scheme 3.9 Preparation of alkylthiophene-2,5-dicarboxaldehydes



60a-c **68a-c**

60a R=butyl, R' =H
60b R=octyl, R' =H
60c R=R' =butyl

68a R=butyl, R' =H
68b R=octyl, R' =H
68c R=R' =butyl

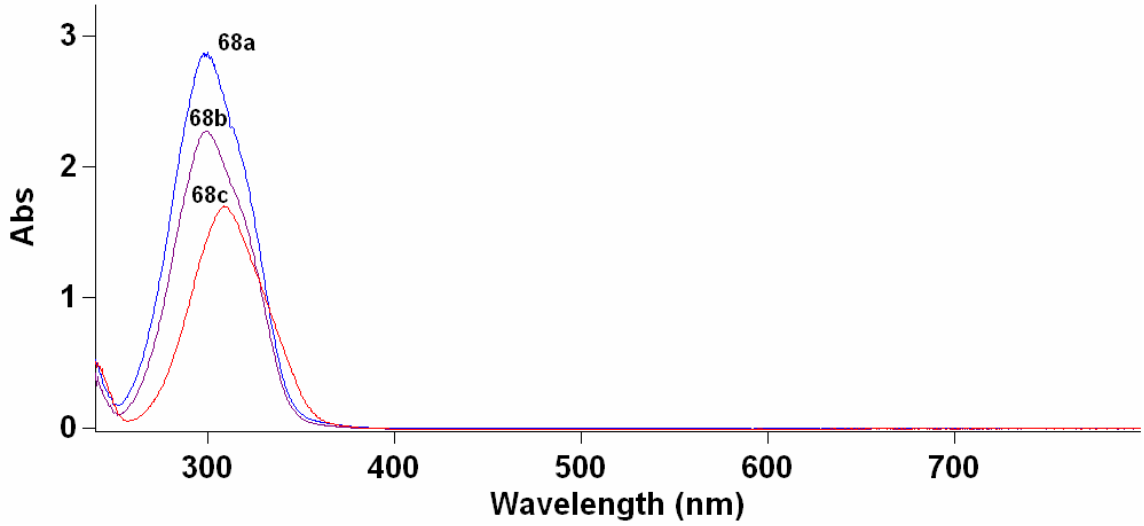


Fig. 3.10 UV-Vis spectra of alkylthiophene-2,5-dicarboxaldehydes ($CHCl_3$)

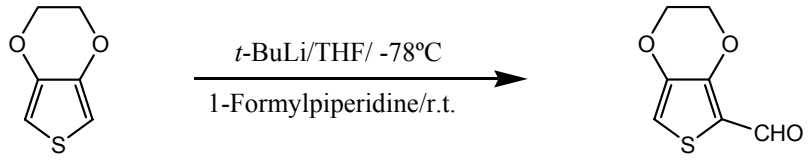
3.5.1.5 Synthesis of aldehydes of EDOT

Aldehyde derivatives, 2,3-dihydrothieno[3,4-*b*]-1,4-dioxin-5-carboxaldehyde (**70**) and 2,3-dihydrothieno[3,4-*b*]-1,4-dioxin-5,7-dicarboxaldehyde (**72**) were prepared

according to reported literature procedures.[208] The preparation scheme is shown below (Scheme 3.10 and Scheme 3.11).

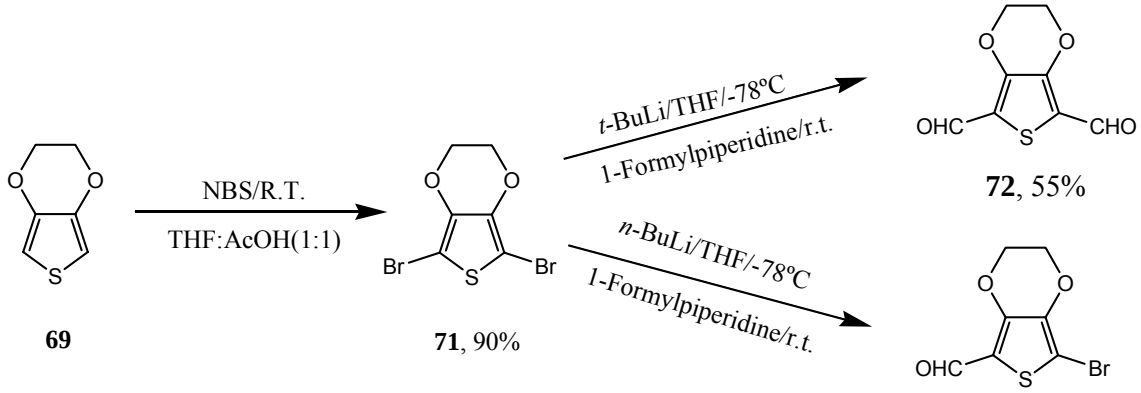
In both cases, the desired products were prepared in good yields. However, in the case of compound **72**, it was necessary to brominated first followed by the lithiation and quenching reactions.

Scheme 3.10 Preparation of aldehyde of EDOT



69 **70a**, 87%

Scheme 3.11 Preparation of bis-aldehyde of EDOT



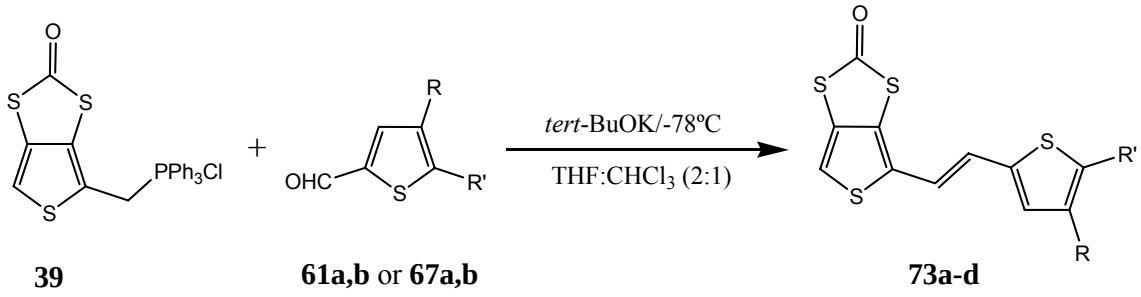
69 **71**, 90% **72**, 55% **70b**, 80%

3.5.2 Preparation of dimmers

Wittig's reactions of compound **39** with different thienyl aldehydes (shown on Scheme 3.12 and 3.13) were attempted in an effort to prepare dithienyl compounds **73a-d**, and **74**. The isolation and purification by column chromatography and precipitation

did not successfully yield pure compounds. This may be partially the result of the target compounds decomposing at room temperature and under the purification conditions.

Scheme 3.12 Preparation of dithienyl compounds

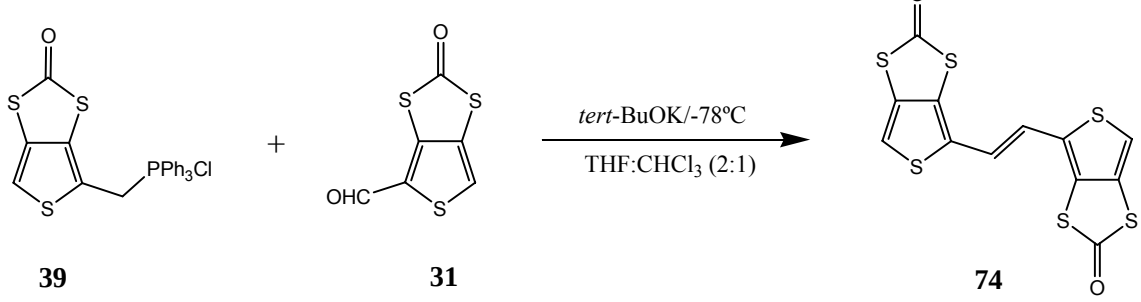


39 **61a,b** or **67a,b** **73a-d**

61a R=butyl, R' =Br
61b R=octyl, R' =Br
67a R=butyl, R' =H
67b R=octyl, R' =H

73a R=butyl, R' =Br
73b R=octyl, R' =Br
73c R=butyl, R' =H
73d R=octyl, R' =H

Scheme 3.13 Preparation of dimer



39 **31** **74**

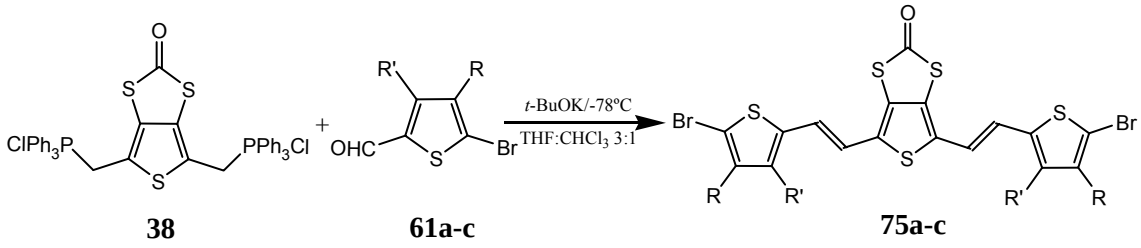
3.5.3 Preparation of trimers

Trimers (trithienyl compounds) were also prepared using Wittig's reactions. Three similar types of trimers were obtained using similar reaction conditions. To assess the steric effects of coupling reactions, the following oligothiophenes were examined as model compounds for the preparation of the copolymers. The results of these investigations will be discussed next.

*3.5.3.1 Type 1 trimers (**75a-c**)*

Type 1 trimers (**75a-c**) were prepared using *t*-BuOK as the base and the aldehydes **61a-c** (Scheme 3.14). Yields from these reactions vary from 28-48%. Relatively low yields are partially the result of the work-up and purification procdures. Purification usually included two consecutive column purifications followed by precipitation in methanol to afford pure target compounds **75a-c**.

Scheme 3.14 Preparation of type 1 trimers



38 **61a-c** **75a-c**

61a R=butyl, R' =H
61b R=octyl, R' =H
61c R=R' =butyl

75a R=butyl, R' =H
75b R=octyl, R' =H
75c R=R' =butyl

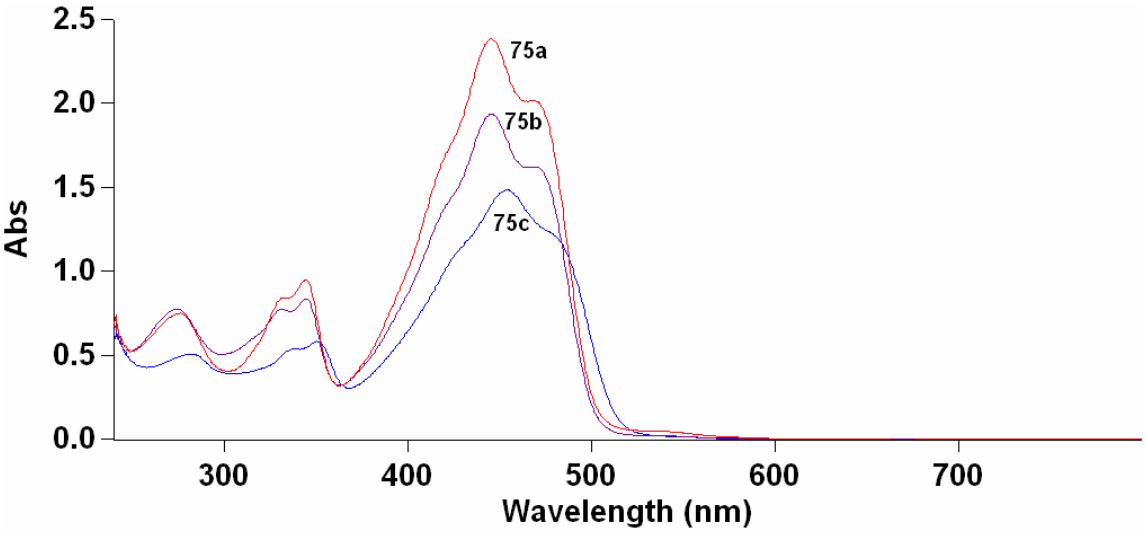


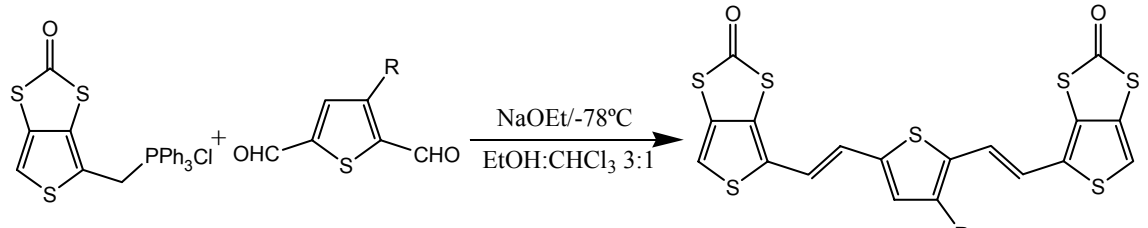
Fig. 3.11 UV-Vis Spectra of type 1 trimers ($CHCl_3$)

We found that bromine substitution appears to favor the stability of the trimers and improves the yields of the products. Steric effect can be considered a major factor that leads to significant drops in the yield of 3,4-dibutyl moieties. UV-Vis spectra of all three trimers bear similar pattern (λ_{max}) and are shown in Fig. 3.11.

*3.5.3.2 Type 2 trimers (**76a,b**)*

The preparation of type 2 trimers is presented in Scheme 3.15. Sodium ethoxide was used as the base instead of potassium *t*-butoxide. After the addition of the dialdehydes **68a** and **b**, the trimers **76a** and **76b** were obtained in 35% and 32%, respectively.

Scheme 3.15 Preparation of type 2 trimers



39 **68a,b** **76a,b**

68a R=butyl
68b R=octyl

76a R=butyl
76b R=octyl

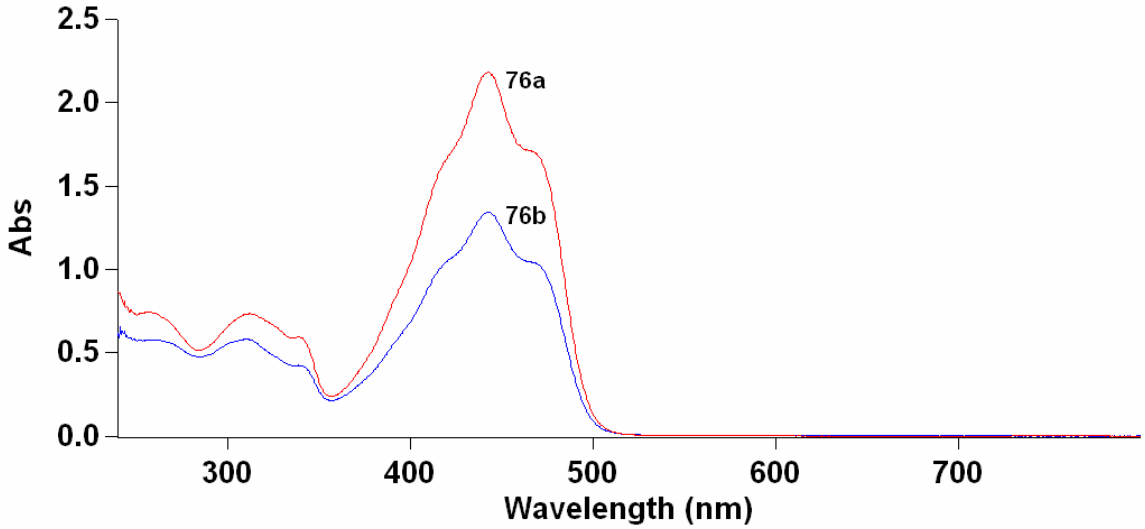


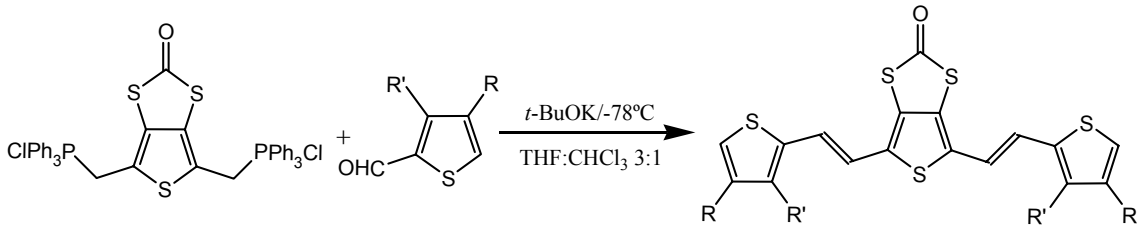
Fig. 3.12 UV-Vis Spectra of type 2 trimers (in $CHCl_3$)

The UV-Vis study (Fig. 3.12) shows the absorption of the π-π* transition with maximum at 443 nm for **76a** and 445 nm for **76b**. The characteristic IR absorptions and their assignments of type 1 and type 2 trimers are summarized in Table 3.6.

*3.5.3.3 Type 3 trimers (**77a-c**)*

Scheme 3.16 shows the preparation of type 3 trimers. Compared with the trimer **77a** (28% yield) and **77c** (32% yield)**,** relatively lower yield of the compound **77b** (18% yield) clearly demonstrated that alkyl substitution at the 3 position produces more steric resistance. Therefore, the formation of vinylene spacers at the 2 position of thienyl ring is not favored and leads to lower yield as observed.

Scheme 3.16 Preparation of type 3 trimers



38 **63a, 67a,b** **77a,b,c**

67a R=butyl, R' =H
63a R=H, R' =butyl
67b R=octyl, R' =H

77a R=butyl, R' =H
77b R=H, R' =butyl
77c R=octyl, R' =H

UV-Vis spectra of type 3 trimers are shown in Fig. 3.13. All type 3 trimers **77a, 77b** and **77c** have similar absorption patterns as that of type 1 trimers. Compared with their starting materials thienyl aldehydes, the λ_{max} is significantly red-shifted from 300nm to 435nm. FT-IR spectra of **77a** and **77b** were illustrated in Fig. 3.14. *trans* vinyl structures of all three types of trimers were confirmed by presence of strong absorptions at 913 – 921cm^{-1}.[202] Other characteristic absorptions and their assignments are similar to those of other types of trimers which are summarized in Table 3.6.

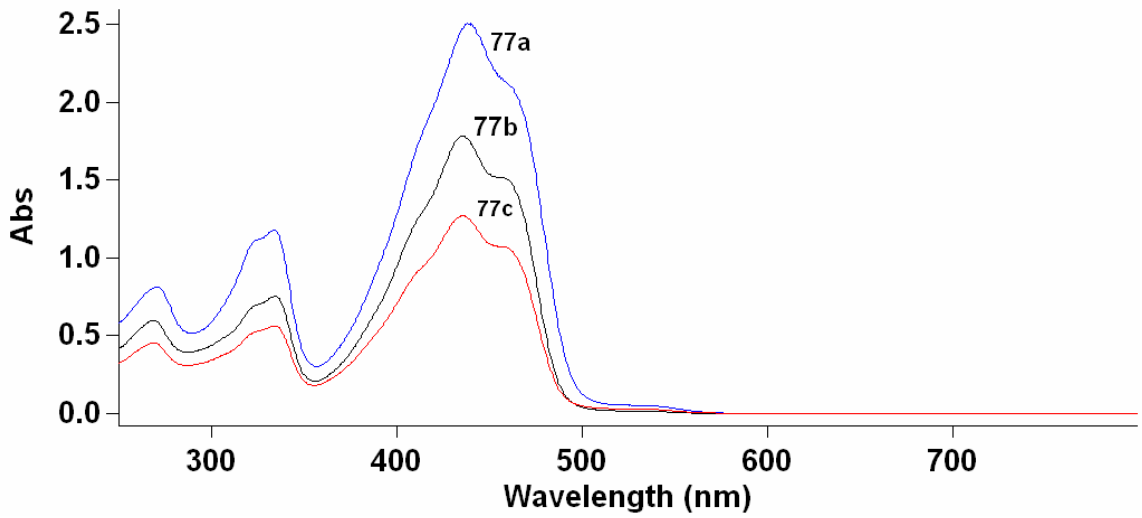


Fig. 3.13 UV-Vis spectra of type 3 trimers ($CHCl_3$)

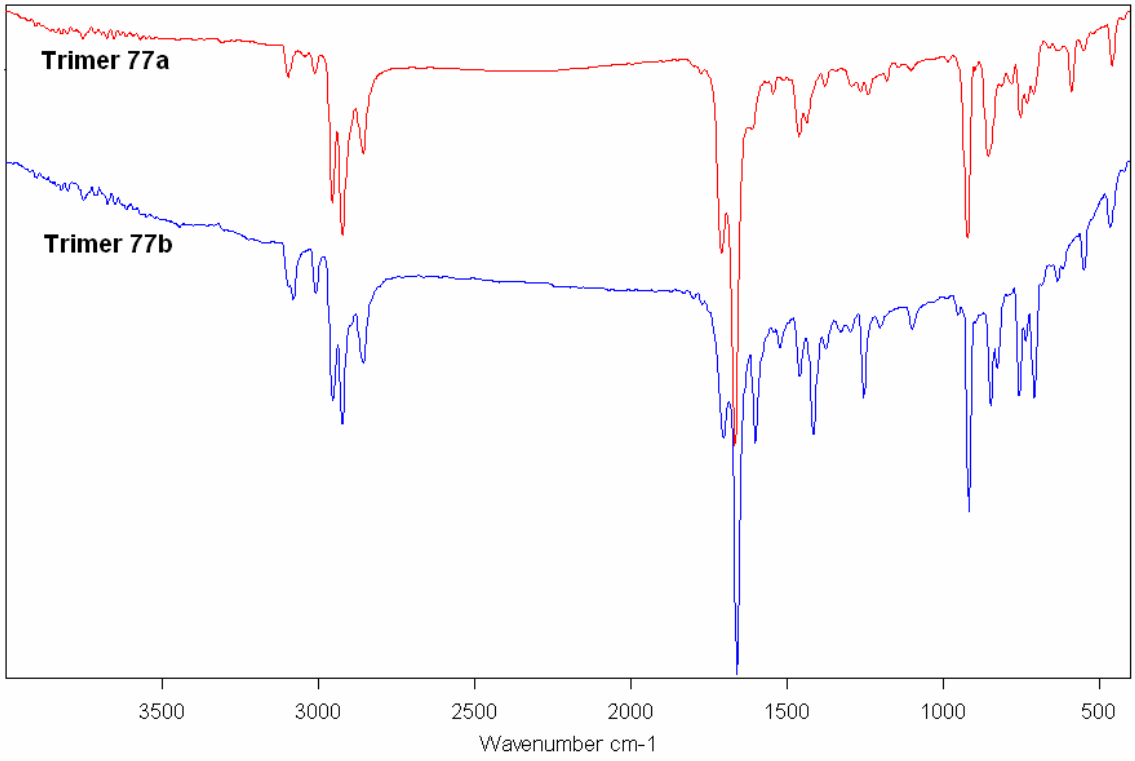


Fig. 3.14 FT-IR spectra of type 3 trimers

Table 3.5 Wittig reactions to trithienyl compounds

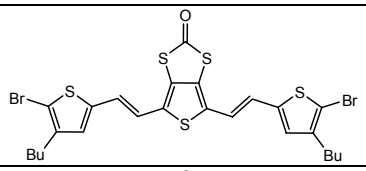
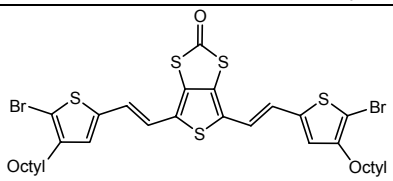
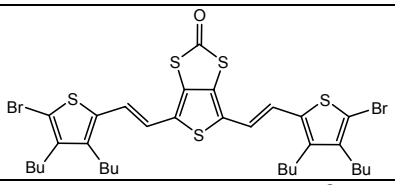
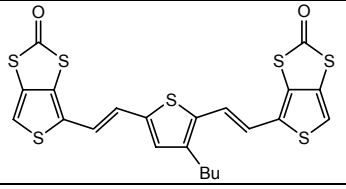
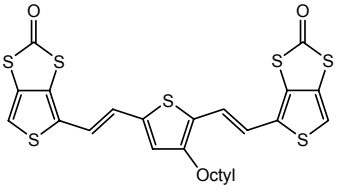
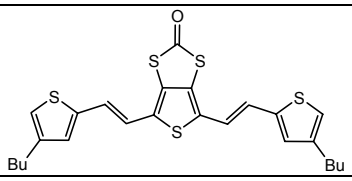
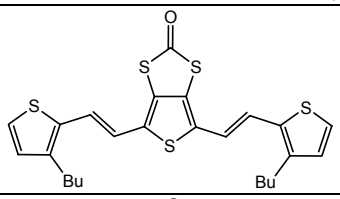
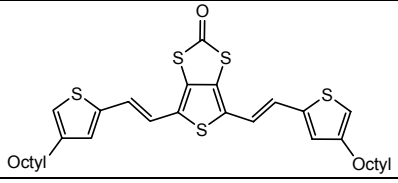
No.	Structure	Solvent	Yield (%)	UV λ_{max} (nm)
75a		THF/ $CHCl_3$	43	445
75b		THF/ $CHCl_3$	48	446
75c		THF/ $CHCl_3$	28	455
76a		EtOH/$CHCl_3$	35	443
76b		EtOH/$CHCl_3$	32	443
77a		THF/$CHCl_3$	25	434
77b		THF/$CHCl_3$	18	438
77c		THF/$CHCl_3$	32	435

Table 3.6 Characteristic IR absorptions and their assignments of trimers

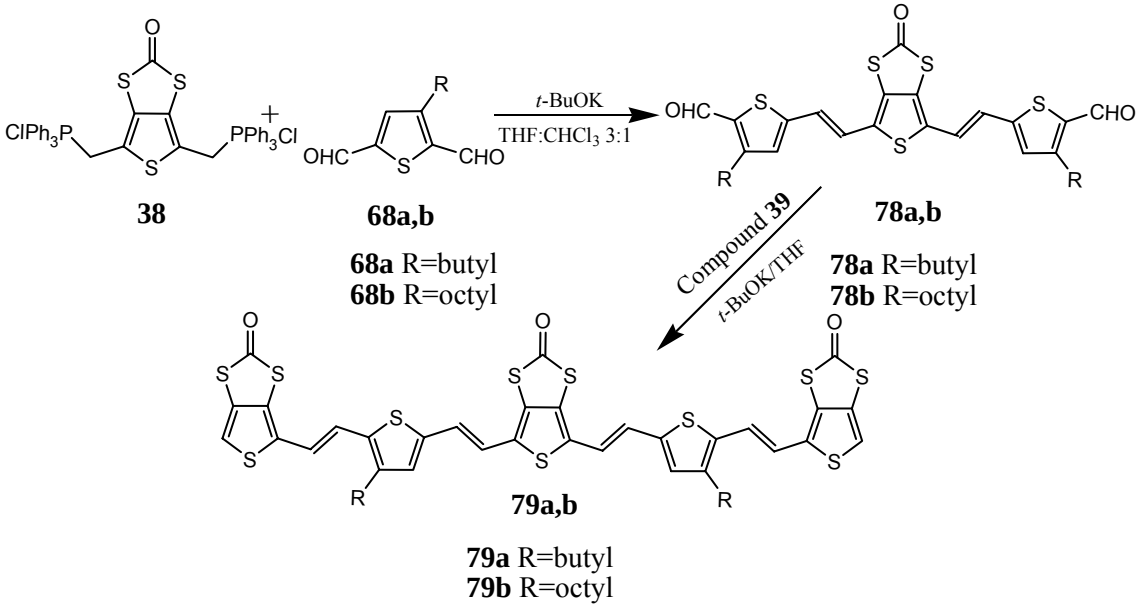
Assignments	**75a**	**75b**	**75c**	**76a**	**76b**
Aromatic C-H stretching (2,5 position of thienyl ring)	weak	Weak	weak	3104	3113
Vinylene C-H stretching	3007	3009	3015	3009	3015
Aliphatic (alkyl) C-H stretching	2954 2923 2855	2955 2922 2851	2956 2928 2858	2954 2923 2853	Overlap 2924 2853
Carbonyl C=O stretching	1712	1709	1709	1701	1704
Conjugated C=C-C=C stretching[209]	1672	1668	1665	1643	1647
Thienyl ring C-C stretching[210]	1608 1457 1431	1605 1463 1426	1600 1461 1431	overlap 1458 1435	Overlap 1460 1429
trans vinyl C-H out-of-plane bending	921	917	913	919	921
Thienyl C-H out-of-plane bending[210]	841	839	845	835	840

3.5.4 Synthesis of heptamers

Heptamers was prepared using two consective Wittig reactions. The first Wittig reaction affords aldehyde derivatives which were found to precipitate in methanol. Without further purification, the aldehyde derivatives **78a-b** and the monosubstituted triphenylphosphonium salts **39** were treated with *t*-BuOK in THF to give heptathienyl compounds (heptamers) **79a** and **79b** (Scheme 3.17). Characterization of the intermediate compounds **78a** and **78b** is still under inversitigation in our lab, ss a result

of the difficulty of the isolation and purification process. The characterization of the desired heptamers **79a** and **79b** has also not been diffcult. Work is still in progress in our lab to fully assign and characterize the target heptamers.

Scheme 3.17 Synthesis of heptamers (heptathienyl compounds)

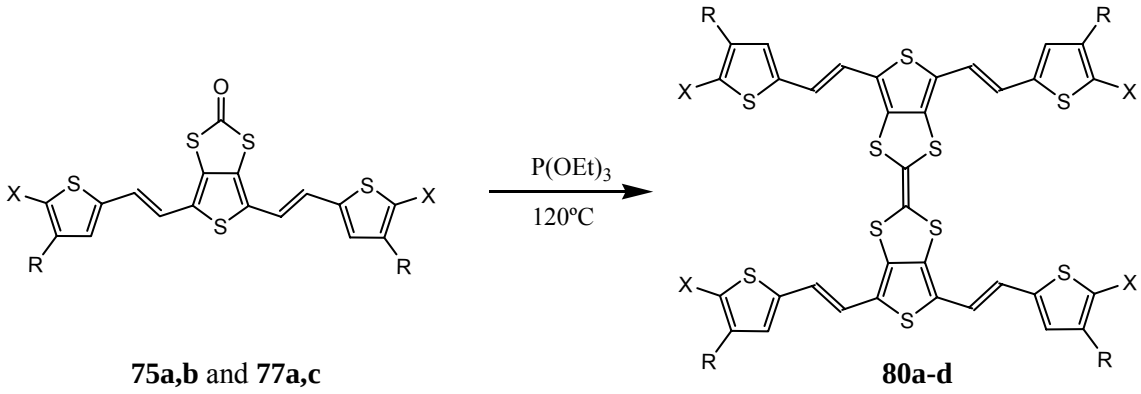


3.5.5 Synthesis of conjugated DTTTF derivatives

Conjugated DTTTF derivatives were prepared by triethylphosphite coupling reactions at an elevated temperature (120ºC). The results of these reactions are illustrated in Scheme 3.18.

We observed these conjugated DTTTF derivatives do not dissolve in regular organic solvents, such as dichloromethane, benzene, THF, DMF, and DMSO. They are only slightly soluble in chloroform.

Scheme 3.18 Preparation of DTTTF derivatives



75a,b and **77a,c**

75a R=butyl, X=Br
75b R=octyl, X=Br
77a R=butyl, X=H
77c R=octyl, X=H

80a-d

80a R=butyl, X=Br, 71%
80b R=octyl, X=Br, 73%
80c R=butyl, X=H, 48%
80d R=octyl, X=H, 32%

FT-IR spectrum of the compound **80a** shows a strong absorption band at 921 and 3007 cm^{-1}, which are characteristic of *trans* vinyl C-H out-of-plane bending and vinyl C-H stretching absorption. DTTTF derivatives **80b**, **80c** and **80d** bear similar FT-IR patterns as that of **80a**, The *trans* vinyl C-H out-of-plane bending was presented at 918 cm^{-1} for **80b**, 922 cm^{-1} for **80c**, and 921 cm^{-1} for **80d.** Also, vinyl C-H stretching at 3008 cm^{-1}, 3009 cm^{-1}, and 3011cm^{-1} were observed.

UV-Vis spectra of **80a** and **80b** show the absorption of the π-π* transition with a maximum at 441nm and 442nm, respectively. Compound **80c** shows a λ_{max} at 434nm, and compound **80d** at 433nm. As illustrated in Fig. 3.15, the UV-Vis spectra of DTTTF derivatives do not show significant changes from that of their trimer analogues (Fig. 3.11 and Fig. 3.13). This may be due to no direct conjugation across the TTF links.

Since compound **48** does not posses a conjugated structure as compounds **80a-d** do, the λ_{max} of **48** is shown in UV region at 265nm.

All four DTTTF derivatives (**80a-d**) show very good stability in the solid form. However, in solution form (such as in chloroform), doping by residual H^+ of solvent was observed by NMR. This results in the formation charge-transfer complexes, and subsequently, the loss of the disctictive doublet of doublet of vinylene protons.

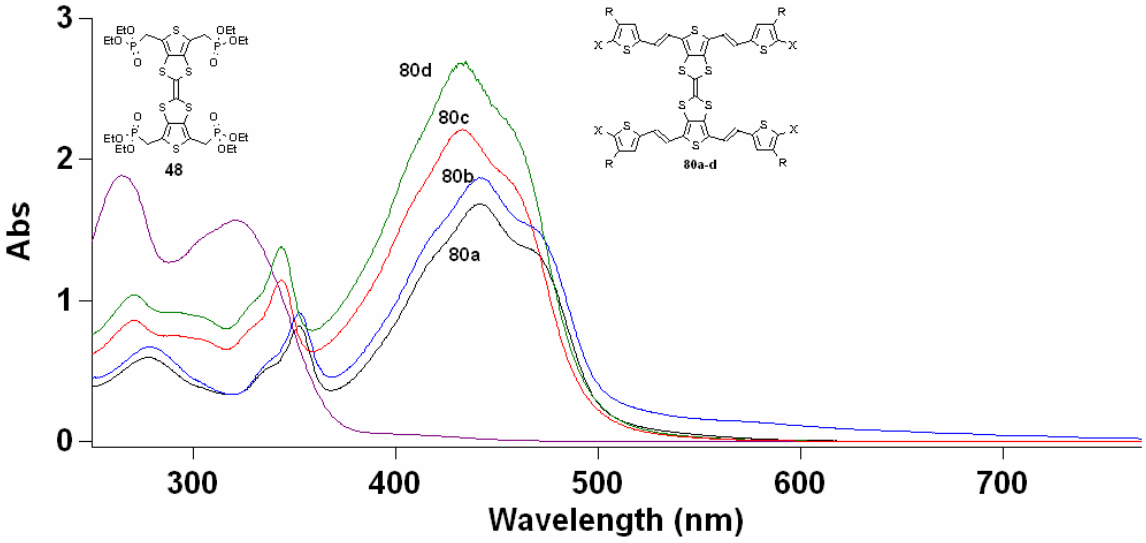


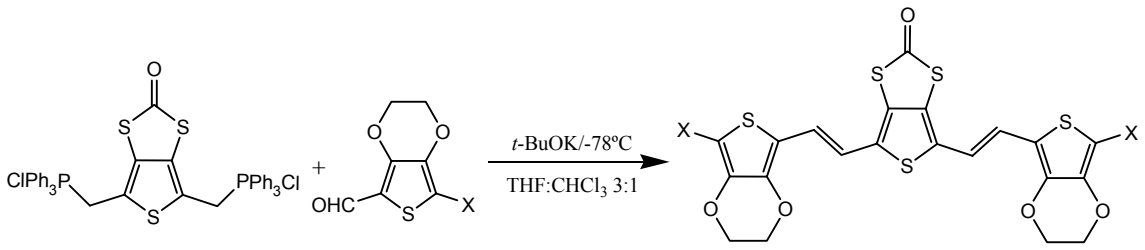
Fig. 3.15 UV-Vis Spectra of DTTTF derivatives ($CHCl_3$)

It was observed that the red color compounds **80a** and **80b** immediately turned into shinning metallic black color upon being heated to their respective melting points. This may be due to the thermal elimination of Br result in the formation of polymers and followed by an oxidation (doping) of polymers with the thermal elimination product Br_2. This subsequently, yields doped conjugated polymers. Their electrical properties are still under further inversitigation in our laboratory. DTTTF derivatives **80a** and **80b** can also

be good candidates for transitional metal catalyzed polymerizations too. **80c** and **80d** can be ideal monomers for an electrochemical polymerization study. Further studies still need to be evaluated of these DTTTF derivatives.

Scheme 3.19 shows the preparation of trimers bearing EDOT units. The synthesis of DTTTF derivatives with EDOT units are still under investigation in our labotory.

Scheme 3.19 Synthesis of trimers with EDOT units



38 **70a,b** **81a,b**

70a X=H
70b X=Br

81a X=H, 18%
81b X=Br, 32%

3.6 Synthesis of thiophene-based copolymers

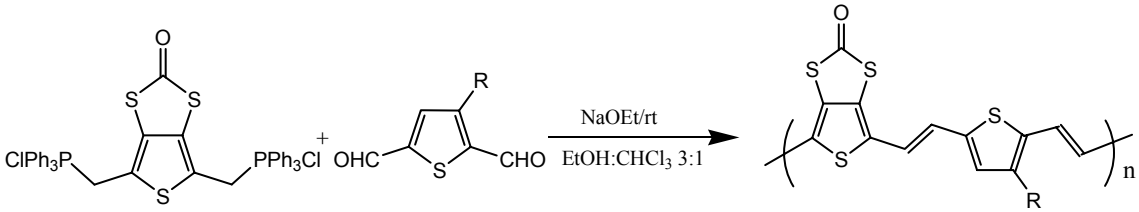
3.6.1 Preparation of copolymers

Wittig reactions to prepare copolymers were carried out in ethanol at room temperature with NaOEt as basefor 72hours (Scheme 3.20). Reactions typically take 72 hours for completion.

The two copolymer samples were subject to soxhelet extraction with methanol 48 hours to remove low molecule compounds (such as monomers, by-product triphenylphosphine oxide, impurities, etc.), followed by acetone to remove oligomers.

NMR analysis of oligomers extracted by acetone show that the repeating units of these oligomers are about 4, corresponding to about 8 thienyl rings. The final products were dried in vacuum oven at 60°C for 24hours. The copolymer **P4** was isolated in 48% yield while **P5** was isolated in 45% yield.

Scheme 3.20 Synthesis of polyalkylthiophene copolymers



38 **68a,b** **P4, P5**

68a R=butyl
68b R=octyl

P4 R=butyl
P5 R=octyl

3.6.2 Elemental analysis of copolymers

Elemental analysis results are illustrated in Table 3.7. The empirical formula of **P4** and **P5** based on elemental analysis are $C_{16.09}H_{15.66}O_{1.46}S_4$ and $C_{22.53}H_{25.15}O_{2.26}S_4$, respectively. These results are consistent with the theoretical formula of **P4** and **P5**, which are $(C_{17}H_{16}OS_4)_n$ and $(C_{21}H_{24}OS_4)_n$.

Table3.7 Elemental analysis results of copolymers

Sample No.		C (%)	H (%)	S (%)	P (%)
P4	Calculated	56.01	4.42	35.18	0
	Found	53.585	4.375	35.555	802 ppm
P5	Calculated	59.96	5.75	30.49	0
	Found	58.775	5.595	27.85	0.295

Copolymer **P5** might have tripheneylphosphine salt as end groups which might explain the high content of phosphorus residue (0.3%), and copolymer **P4** might be bearing aldehyde end groups, therefore, showing a very low phosphorus content residue.

3.6.3 FT-IR analysis of copolymers

The copolymer **P4** shows distinct peaks at 927 cm^{-1} for the vinylene out-of-plane C-H bending vibrations and 3011 cm^{-1} for the vinylene C-H strectching vibrations. The copolymer **P5** shows similar peaks at 925 cm^{-1} and 3009 cm^{-1} as a result of the same vibrations.

Table 3.8 further summarizes and characterizes the IR absorptions and their assignments for these two copolymers.

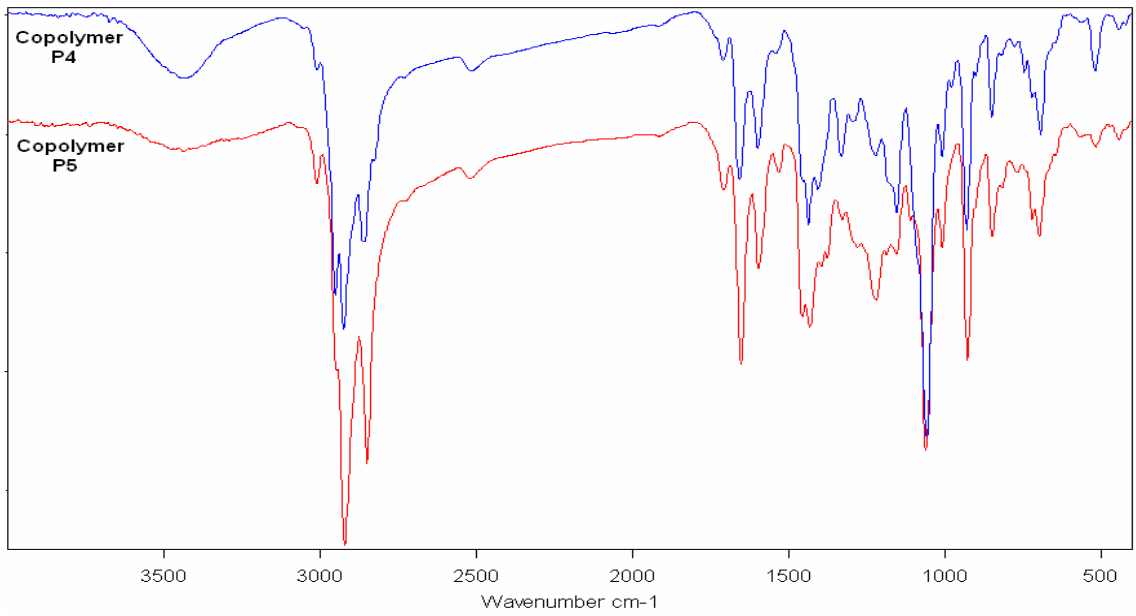


Fig. 3.16 FT-IR spectra of copolymers

Table 3.8 IR absorptions and their assigmments of copolymers

Copolymer **P4**	Copolymer **P5**	Assignments
3011	3009	Vinylene C-H stretching
2952, 2926, 2864	2950, 2922, 2851	Aliphatic C-H stretching
1703	1707	Carbonyl C=O stretching
1655	1650	Conjugated C=C-C=C stretching[203]
1598, 1454,1437	1590, 1455, 1433	Thiophene ring C-C stretching
1058	1063	Thiophene ring C-H in-plane bending
927	925	*Trans* vinylene out-of-plane bending
851	850	Thiophene C-H out-of-plane bending
747	721	Methylene rocking
694	698	Aromatic C-C out-of-plane bending

3.6.4 UV-Visible properties of copolymers

The UV-Vis spectrum of the copolymer **P4** shows the absorption of π-π^* transition with a maximum at 549nm, and the copolymer **P5** shows a maximum absorption at 551nm for the same π-π^* transition (Fig. 17)

Bandgap calculated from UV edge absorption was 1.87eV (λ_{edge}=660 nm) for **P4**, and 1.86eV (λ_{edge}=662 nm) for **P5**, respectively.

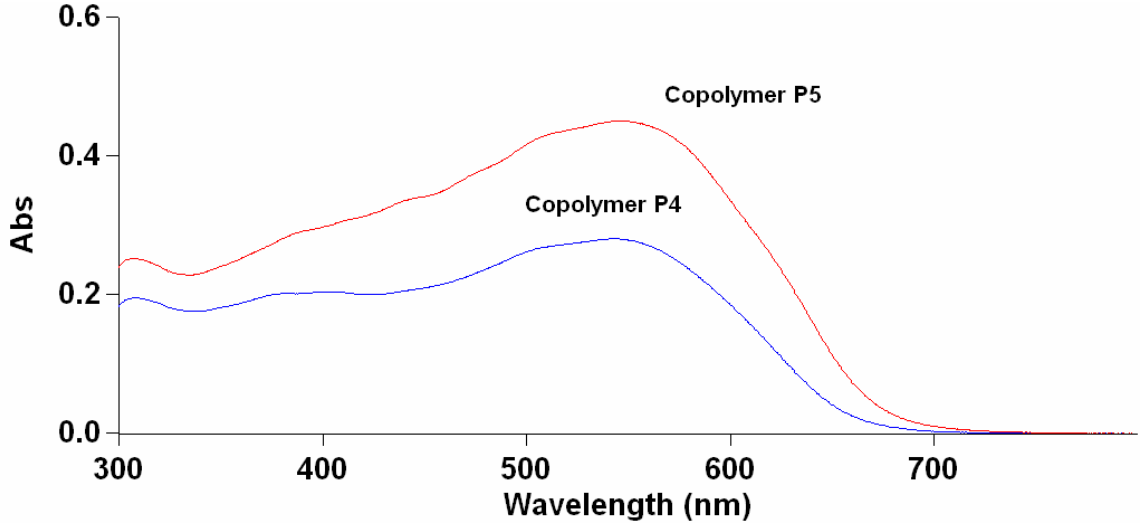


Fig. 3.17 UV-Vis spectra of copolymers (THF)

3.7 Conclusion

1. Attempted synthesis of homopolymer **P1** through different methods, such as $FeCl_3$ chemical polymerization reactions, transitional metal catalyzed cross-coupling reactions, and Ullman reaction, resulted in no success. All reactions gave solids that could not be identified by traditional methods such as NMR. FT-IR analysis shows the disappearance of the distinctive C=O stretching absorption for most compounds, which indicates that the carbondithiolate structure may be disrupted during polymerization reactions.

2. Stille reactions of the halogenated derivatives of thieno[3,4-*d*]-1,3-dithiol-2-one (**26**) with organotin compounds were also attempted to synthesize the conjugated oligomers and copolymers. The initial results show that the Stille reactions under harsh conditions (DMF/100-150ºC) generally yield deep colored solids that, once again, could

not be identified. FT-IR analysis of these solids shows that the disruption of the carbondithiolate structure of monomers might be accuring. Disappointantly, Stille reactions under mild conditions (THF/75ºC) did not accur at all either..

3. Base-promoted and acid-promoted polymerization reactions did not yield the desired precursor polymers. We did oberve the consumption of the starting materials by TLC analysis of these reactions, however. We also found that the selection of leaving groups is a crucial step to the successful preparation of soluable precursor polymers. Initial data suggests that the asymmetrical monomers might be the promissing direction for these kinds of reactions, especially those having a chloromethylene pendant group.

4. The preparation of dithienyl compounds (dimers) through Wittig reactions were attempted but were not successful characterized due to the instability of the compounds at room temperature and under the reaction conditions.

5. Three types of trithienyl compounds (trimers) were successfully synthesized and fully characterized by NMR, FT-IR, and ESI-TOF. As thiophene-based oligomers, their properties were examined. The UV spectroscopy shows λ_{max} of those trimers red-shift to the visible region (around 450 nm), which corresponds to the delocalization of π electrons in the extended of conjugated structure..

6. Four conjugated DTTTF derivatives were also synthesized by coupling reaction with triethyl phosphite. These DTTTF derivatives were characterized by ^{1}H-NMR, elemental analysis, and FT-IR. UV-Vis spectra of these conjugated DTTTF derivatives show similar λ_{max} values as their trimer analogues.

7. All four DTTTF derivatives were not soluable in common organic solvents, such as dichloromethane, THF, CH_3CN, DMF, and DMSO. However, these DTTTF derivatives are stable in solid forms, but the solvation process of the derivatives in chloroform leads to the formation of "doped" charge-tranfer complexes. This accurance was observed by NMR and UV-Vis analysis.

8. Two copolymers were successfully synthesized by Witting-Horner olefination reactions. Elemental analysis results show that the empirical formulas were consistant with the theoretical calculations.

9. UV-Vis analysis of copolymer **P4** and **P5** show λ_{max} at 549 and 551nm, respectively. Compared with model trithienyl compounds, which have λ_{max} around 440 ~455nm, the λ_{max} of copolymers show a significant red shift. This further demonstrates that the delocalization of π electrons due to extension of conjugation of thienyl backbones is accuring. Bandgap of **P4** and **P5** were 1.87eV and 1.86eV which were calculated from UV absorption edges.

3.8 Futurework

1. Electrochemistry study of compound **1**, **2**, trimers, DTTTF derivatives.

2. Selection of catalysts of cross-coupling reactions might be possible to afford polymers with carbondithiolate structures. In our work presented in this dissertation, only three catalysts were examined for cross-coupling reactions. Tests with other transitional metal complexes may yield homopolymers and/or copolymers bearing carbondithiolate structures.

3. Further investigation of synthesis of precursor polymers, especially synthesis of asymmetrical monomers, may lead to discovery of conjugated poly(thienylene vinylene) with carbondithiolate structures. Our initial study shows both chlorine and sulfoxide groups are good leaving groups for the preparation of non-conjugated precursor polymers, unfortunately chlorine is not good leaving group to yield conjugated polymers during thermal elimination reaction.

4. Polymerization reactions of DTTTF derivatives, such as compound **48** and **80a-d**. Conjugated polymers cross-linked by DTTTF units might posses some unique properties as conductive materials.

5. Study of metal-dithiolate coordination. Metal-coordinated trimers, polymers are still in progress in our lab. These oligomers and polymers with carbondithiolate structures presented in this dissertation are possible candidates for the introduction of metal ions to form metal-dithiolate coordination complexes.

6. Applications of copolymers and DTTTF derivatives.

CHAPTER 4

EXPERIMENTAL

4.1 General

Dry diethyl ether and tetrahydrofuran (THF) were freshly distilled from sodium benzophenone ketyl. Dry *N,N'*-dimethylformamide (DMF) was vacuum distilled with calcium hydride (CaH_2). Dry acetonitrile and dichloromethane was freshly distilled with calcium hydride. Dry chloroform was freshly distilled with calcium chloride. Methylsulfoxide (DMSO) was dried with 4Å molecular sieve. Other chemicals and solvents were used as received. *n*-Butyllithium in hexanes solution was purchased from Aldrich-Sigma Chemicals, and was titrated by diphenylacetic acid method.[211] 3,4-Dibromothiophene was either purchased from Oakwood Chemical or prepared in the lab from thiophene according to literature[212]. Other chemicals were purchased from Aldrich-Sigma Chemicals, and used without further purification.

^{1}H- and ^{13}C-NMR spectra were obtained on a JOEL Eclipse Plus 500 NMR spectrometer or JEOL ECX 300 NMR spectrometer. ^{1}H-NMR spectra were recorded at 500.16MHz (or 300.53MHz at ECX 300) in $CDCl_3$ (unless otherwise noted) and chemical shift were reported as δ (ppm) relative to internal standard tetramethylsilane (TMS) as 0.00 ppm. ^{13}C-NMR spectra were taken at 125.77MHz (or 75.57MHz at ECX 300) in $CDCl_3$ (unless otherwise specified) and reported in ppm relative to either TMS

at 0.00 or residual $CHCl_3$ at 77.05 ppm. For samples dissolved in DMSO-d_6, either TMS at 0.00 or residual DMSO were used as internal reference (δ=2.5 for ^{1}H-NMR and δ=39.5 for ^{13}C-NMR sepectra).

FT-IR spectra were obtained on Bruker Vector 22 FT-IR spectrometer. Powder samples were prepared as pellets with KBr; liquid samples were recorded on KBr plates in transmittance. The plots were reported in ν as cm^{-1}.

Melting points were obtained in capillary tubes on a Mel-Temp II apparatus, and the thermometer was uncorrected.

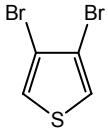
High resolution electrospray ionization time-of-flight (ESI-TOF) experiments were performed on an Agilent ESI-TOF mass spectrometer at Scripps Center for Mass Spectrometry (La Jolla, CA 92037). Sample was electrosprayed into the TOF reflectron analyzer at an ESI voltage of 4000V and a flow rate of 200 microliters/minutes. GC-MS experiments are performed on the Agilent 5973 Gas Chromatograph Mass Spectrometer at Scripps Center for Mass Spectrometry. The sample is first resolved into its components in the GC using a DB5 column and the effluent detected by generating positive ions in the electron ionization source and performing quadrupole mass analysis on these ions. Typically, 1μl of a 1mg/ml solution is injected into the GC mass spectrometer. Mass spectra were obtained on a Finnigan Mat TSQ70 mass spectrometer (EI mode) using a solid sampling probe at Department of Chemistry and Biochemistry.

UV-Visble spectra were obtained on Cary 50 UV-Visble spectrometer. Scan control parameters were set up as: average time 0.125second; data interval 0.5nm; scan rate 240nm/min; scan range 800-200nm.

C, H, N, and S elemental analysis were performed by Quantitative Technologies Inc. (Whitehouse, NJ 08888), or obtained on a Perkin-Elmer 2400 CHN analyzer.

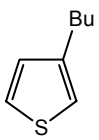
4.2 Synthesis

3,4-Dibromothiophene (**3**)



To a three-neck flask with reflux condenser 200g tetrabromothiophene (0.5mol), 500ml dry THF, and 48g magnesium turnings (2mol) were added and stirred vigorously, solution of 1,2-dibromoethane (189g, 1mol) in 1000ml THF was added dropwise into the flask cautiously (strong exothermic reaction) and the mixture was stirred at room temperature for 24 hours then poured into 2000ml cold water, the magnesium residues were removed by filtration. The organic layer was separated and aqueous layer was extracted with $CHCl_3$ (3 x 400ml). The combined organic phases were washes with brine (300ml), water (3 x 400ml), dried with magnesium sulfate, and evaporated. The dark oil-like residue was distilled *in vacuo*, yield 88g (73%, lit.[150] 75% yield) colorless liquid. ^{1}H-NMR ($CDCl_3$): 7.30 (s, 2H), ^{13}C-NMR ($CDCl_3$): 124.0, 114.1

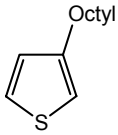
3-Butylthiophene (59a)



3-Butylthiophene was obtained by the similar method as that for 3,4-dibutylthiophene, using 3-bromothiophene instead as starting material. Vacuum distillation afforded 3-butylthiophene as colorless oil with 90% yield. ^{1}H-NMR ($CDCl_3$): 7.26-7.27(m, 1H), 6.97-6.98(m, 1H), 6.95-6.96(m, 1H), 2.68(t,

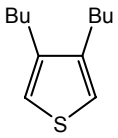
J=7.8Hz, 2H), 1.66(m, 2H), 1.42(m, 2H), 0.98(t, *J*=7.8Hz, 3H). ^{13}C-NMR ($CDCl_3$): 143.4, 128.5, 125.2, 120.0, 32.9, 30.2, 22.6, 14.1.

3-Octylthiophene (59b)



3-Octylthiophene was prepared by the same method as that for 3-butylthiophene, 1-bromooctane was used instead of 1-bromobutane as starting material. Vacuum distillation usually affords 3-octylthiophene as colorless oil with 92% yield. ^{1}H-NMR ($CDCl_3$): 7.23-7.22(m, 1H), 6.94-6.91(m, 2H), 2.62(t, *J*=7.3Hz, 2H), 1.66-1.57(m, 2H), 1.30-1.27(m, 10H), 0.90-0.86(t, *J*=7.3Hz, 3H). ^{13}C-NMR ($CDCl_3$): 143.4, 128.4, 125.1, 119.8, 32.0, 30.7, 30.4, 29.5, 29.4, 29.3, 22.8, 14.2.

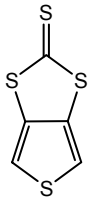
3,4-Dibutylthiophene (59c)



To magnesium turnings (2.4g, 100mmol) in 50ml dry diethyl ether was added dropwise 1-bromobutane ether solution (14.4g, 105mmol in 30mL diethyl ether) at room temperature. The reaction mixture was maintained to mild reflux until the disappearance of all magnesium and transferred via a cannula to a solution of 3,4-dibromothiophene (10g, 41mmol) and [1,3-bis(diphenylphosphino)propane]-nickel(II)chloride (55mg, 0.1mmol) in ether (75mL) at 0°C. The mixture was stirred at room temperature for overnight before being poured into cold water. The aqueous layer was extracted with diethyl ether (75ml x 3). The combined organic layers were washed with brine, water, and dried over $MgSO_4$. After solvent was removed under vacuum, the residue was purified by column chromatography (silica gel, hexanes) to afford 6.6g 3,4-

dibutylthiophene as colorless oil, which corresponding to a yield of 82%. ^{1}H-NMR ($CDCl_3$): 6.91 (s, 2H), 2.53(t, *J*=7.8Hz, 4H), 1.63(m, 4H), 1.42(m, 4H), 0.98(t, *J*=7.8Hz, 6H). ^{13}C-NMR ($CDCl_3$): 142.3, 120.1, 32.1, 28.7, 22.9, 14.2.

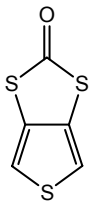
Thieno[3,4-*d*]-1,3-dithiole-2-thione (1)



A solution of 3,4-dibromothiophene (2.84g, 12mmol) in anhydrous diethyl ether (25ml) was stirred and cooled to -78ºC (dry ice and acetone bath) under argon for 30 minutes. 5.4ml *n*-butyllithium (2.2M in hexanes, calibrated by diphenylacetic acid method) was added via syringe pump at speed of 10ml/hour. The solution was stirred for 30 minutes, then 381mg sulfur (12mmol) was added. After being stirred for 45 minutes, *n*-butyllithium (5.4ml, 12mmol) was added and the reaction mixture was stirred at -78ºC for another 30 minutes, sulfur (380mg. 12mmol) was added and the mixture was stirred for additional 45 minutes to give a yellow solution. 0.5ml H_2O was dropped into the reaction mixture by syringe, then the mixture was kept at -78ºC for overnight (about 8-10 hours). The solution was allowed to come to ambient temperature while diethyl ether was removed by vacuum. 25ml 2M NaOH was added to the pale-yellow solid. After the solid fully dissolved into an amber color solution, 8ml CS_2 was added by syringe under argon protection. The mixture was refluxed under argon for 4 hours at heated oil bath (85-90ºC) and then allowed to stand at room temperature for additional 8-10 hours. After removed the excess carbon disulfide under vacuum, the dark reaction mixture was filtered and washed with D.I. water to give a yellow solid. Recrystallization of the solid from dichloromethane-

hexanes (1:5 *v/v*) gave 524mg (22% yield, usually yield varies from 10% ~ 22%) of thieno[3,4-*d*]-1,3-dithiol-2-thione as amber needles. Melting point: 142-143°C (lit.[126b] 142-143°C). ^{1}H-NMR ($CDCl_3$): 7.24 (s, 2H). ^{13}C-NMR ($CDCl_3$): 218.8, 138.0, 113.4 FT-IR: 3083, 1448, 1414, 1319, 1113, 1066, 868, 836, 7760, 498, 448 cm^{-1}. MS: m/e188.9. Elemental Analysis: Anal. Calcd. for $C_5H_2S_4$: C 31.55, H 1.06, S 67.39. Found C 31.90, H 0.91, S 67.00

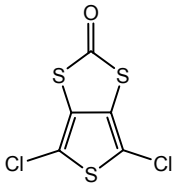
Thieno[3,4-*d*]-1,3-dithiol-2-one (2)



A solution of 3,4-dibromothiophene (3.20g, 13mmol) in anhydrous diethyl ether (25ml) was stirred and cooled to -78ºC (dry ice and acetone bath) under argon for 30 minutes. 5.5ml (14mmol) *n*-butyllithium (2.5M in hexanes, calibrated by diphenylacetic acid method) was added via syringe at a speed of 10ml/hour. The solution was stirred for 30 minutes, then 423mg sulfur (13mmol) was added. After being stirred for 60 minutes, n-butyllithium (5.5ml, 14mmol) was added by syringe and the reaction mixture was stirred at -78ºC for 0.5h. Sulfur (423mg. 13mmol) was added and the mixture was stirred for additional 1 hour to give a yellow solution. 1ml H_2O was dropped into the reaction mixture by syringe, then the mixture was kept at -78ºC for overnight (about 8-10 hours), the solution was allowed to come to ambient temperature while diethyl ether was removed by vacuum. 25ml 2M NaOH was added to the pale-yellow solid after ether was removed. After the solid fully dissolved into an amber color solution, 15g $COCl_2$ solution (~20% phosgene in tolune, excess) was added by syringe at 0 ºC under argon protection. The mixture was kept in ice bath (0ºC) under

argon for 4 hours and then allowed to stand at room temperature for additional 8 hours to give a yellow mixture. The yellow mixture was extracted with benzene (3 x 40ml). The organic phase was washed with brine (120ml), D.I. water (3 x 120ml), and dried with $MgSO_4$, the solvent was removed *in vacuo*. Column chromatography (silica gel, dichloromethane-hexanes 1:2.5 *v/v*) gave 1.07g thieno[3,4-*d*]-1,3-dithiol-2-one (48% yield, general yield varies from 40~48 %) as white powder. Melting point: 106-107°C (lit.[126b] 107-108°C). ^{1}H-NMR ($CDCl_3$): 7.31 (s, 2H). ^{13}C-NMR ($CDCl_3$): 193.9, 128.5, 115.3 FT-IR: 3098, 1686, 1635, 1473, 1398, 1316, 1162, 1118, 974, 875, 855, 844, 824, 780, 692, 541, 495, 461, 441 cm^{-1}. MS: 173.1. Elemental Analysis: Anal. Calcd. for $C_5H_2OS_3$: C 34.46, H 1.16, S 55.20, Found C 34.50, H 0.98, S 54.40

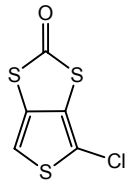
4,6-Dichlorothieno[3,4-*d*]-1,3-dithiol-2-one (5)



To a stirred solution of thieno[3,4-*d*]-1,3-dithiol-2-one 510mg, 3mmol) dissolved in a 1:1 solvent mixture of chloroform (25 mL) and acetic acid (25 mL) was added slowly *N*-chlorosuccinimide (NCS 1.20g, 9mmol) at room temperature under argon protection. The mixture was allowed to stir at room temperature for overnight, then poured into water. The organic layer was separated, and water layer was extracted with chloroform (50 mL x 3). The combined organic layers were washed with saturated Na_2CO_3 solution, D.I. water, brine, dried over magnesium sulfate, and concentrated under vacuum. Column purification (silica gel, CH_2Cl_2-hexanes 1:5 *v/v*) gives 610mg 4,6-dichlorothieno[3,4-*d*]-1,3-dithiol-2-one as white needles corresponding to a yield of 84%. Melting point: 112-113°C. ^{13}C-NMR

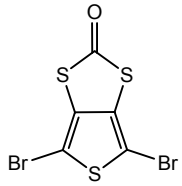
($CDCl_3$): 189.6, 126.3, 117.0 FT-IR (KBr): 1698, 1653, 1530, 1293, 1077, 905, 839, 812, 665, 537, 462 cm^{-1}. GC-MS(M^+.): 242

4-Chlorothieno[3,4-*d*]-1,3-dithiol-2-one (6)



4-chlorothieno[3,4-*d*]-1,3-dithiol-2-one was obtained by the same method as that for 4,6-dichlorothieno[3,4-*d*]-1,3-dithiol-2-one, using 1.0eqv. NCS instead. White solid, yield 72%, melting point: 95-96°C. ^{1}H-NMR ($CDCl_3$): 7.11 (s, 1H). ^{13}C-NMR ($CDCl_3$): 191.8, 127.5, 127.1, 120.2, 113.6 FT-IR (KBr): 3118, 1701, 1673, 1641, 1518, 1432, 1307, 1138, 1060, 939, 868, 851, 837, 776, 727, 541, 463 cm^{-1}. GC-MS (M^+.): 208

4,6-Dibromothieno[3,4-*d*]-1,3-dithiol-2-one (7)

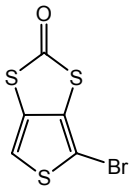


Method 1. 4,6-dibromothieno[3,4-*d*]-1,3-dithiol-2-one was synthesized by a method similar to that for 4,6-dichlorothieno[3,4-*d*]-1,3-dithiol-2-one, using *N*-bromosuccinimide (NBS) instead. Column purification afforded 87% yield of 4,6-dibromothieno[3,4-*d*]-1,3-dithiol-2-one as white needles.

Method 2. To a solution of thieno[3,4-*d*]-1,3-dithiol-2-one (1.74 g, 10 mmol) in CCl_4 at 0°C was added dropwise of Br_2 (1.5 mL, 29 mmol). After addition of bromine, the reaction mixture was allowed to warm up to room temperature, and to stir for another 4 hours. 75 mL chloroform was added into reaction mixture and washed with 0.1M NaOH, saturated Na_2CO_3, D.I. water, brine, and dried over $MgSO_4$. Removing

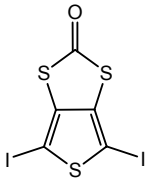
solvent *in vacuo* gives 3.15 g of dibromothieno[3,4-*d*]-1,3-dithiol-2-one with 95% yield. Melting point: 130-131°C. ^{13}C-NMR ($CDCl_3$): 189.1, 130.0, 101.0 FT-IR (KBr): 1734, 1700, 1648, 1519, 1278, 1046, 899, 837, 792, 612, 542, 471, 459cm^{-1}. GC-MS (M^+.): 330

4-Bromothieno[3,4-*d*]-1,3-dithiol-2-one (8)



4-Bromothieno[3,4-*d*]-1,3-dithiol-2-one was obtained by the same method as that for 4-chlorothieno[3,4-*d*]-1,3-dithiol-2-one, using 1 equivalent *N*-bromosuccinimide (NBS) instead. White solid, yield 81%, melting point: 100-101°C. ^{1}H-NMR ($CDCl_3$): 7.24 (s, 1H). ^{13}C-NMR ($CDCl_3$): 191.6, 130.8, 127.5, 116.5, 102.1 FT-IR (KBr): 3116, 1698, 1664, 1638, 1509, 1422, 1301, 929, 866, 833, 758, 726, 534 cm^{-1}. GC-MS (M^+.): 252

4,6-Diiodothieno[3,4-*d*]-1,3-dithiol-2-one (9)

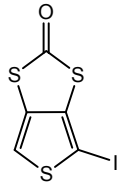


Method 1: To a stirred suspension of 4,6-diacetoxymercuri-thieno[3,4-*d*]-1,3-dithiol-2-one (558 mg, 0.8 mmol) in 50mL dry CH_3CN was added dropwise of a solution of iodine (447 mg, 1.8mmol) in acetonitrile (25mL) . The reaction mixture was allowed to stir for overnight to give a pale-green suspension. After solvent was removed under vacuum, the white solid residue was dissolved in a KI aqueous solution. The product was extracted with chloroform (100mL x 3), washed with D.I. water, brine, dried over $MgSO_4$, and concentrated *in vacuo*.

Column purification (silica gel, CH_2Cl_2-hexanes 1:5 *v*/*v*) afford 218mg pale-yellow needle of 4,6-diiodothieno[3,4-*d*]-1,3-dithiol-2-one in a yield of 65%. The corresponding overall yield of two steps is 60%.

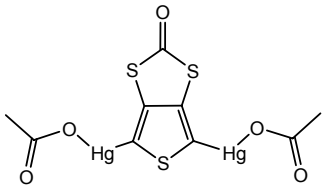
Method 2 (NIS): A suspension of 175mg thieno[3,4-*d*]-1,3-dithiol-2-one and 565mg *N*-iodosuccinimide (NIS) in 7.5ml glacial acetic acid and 7.5ml chloroform was heated to 55°C and stirred for 8 hours. After cooled to room temperature, the reaction mixture was poured into water, extracted with $CHCl_3$ (75mlx3), washed with water, dried over $MgSO_4$, and concentrated in *in vacuo*. Column purification afford 350mg 4,6-diiodothieno[3,4-*d*]-1,3-dithiol-2-one corresponding to a yield of 82%. Melting point: 185-186°C. ^{13}C-NMR ($CDCl_3$): 188.1, 136.1, 64.8 FT-IR (KBr): 1727, 1689, 1644, 1272, 892, 842, 775, 583, 459 cm^{-1}. GC-MS (M^+.): 426

4-Iodothieno[3,4-*d*]-1,3-dithiol-2-one (10)



4-Iodothieno[3,4-*d*][1,3]dithiol-2-one was obtained by similar method of preparation of 4,6-diiodothieno[3,4-*d*]-1,3-dithiol-2-one (Method 2). 1eqv. *N*-iodosuccinimide (NIS) was used instead of 2.5eqv. Pale-yellow solid, yield: 68%. Melting point: 114-115°C. ^{1}H-NMR ($CDCl_3$): 7.36 (s, 1H). ^{13}C-NMR ($CDCl_3$): 190.9, 136.8, 127.4, 120.9, 62.4 FT-IR (KBr): 3104, 1696, 1633, 1294, 908, 864, 842, 828, 732, 548, 524, 459 cm^{-1}. GC-MS (M^+.): 300

4,6-Diacetoxymercuri-thieno[3,4-*d*]-1,3-dithiol-2-one (11)

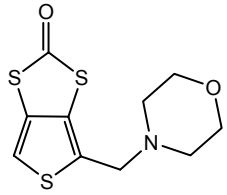


To a solution of thieno[3,4-*d*]-1,3-dithiol-2-one (174 mg, 1 mmol) in glacial acetic acid (10 mL) was added dropwise of a solution of mercury (II) acetate (675 mg, 2.1 mmol) in acetic acid (10 mL) over 30 minutes. A white precipitate formed during addition process, and the reaction mixture was allowed to stir for another 8 hours. The white precipitate was collected by gritted glass filter, washed with methanol, diethyl ether, and dried in vacuum oven at 50°C for overnight to give a white solid of 4,6-diacetoxymercuri- thieno[3,4-*d*]-1,3-dithiol-2-one (660 mg, yield 95%). The compound is insoluble in common organic solvents, m.p.>250°C, ^{1}H-NMR (DMSO-d_6): 1.94 (s, 6H), ^{13}C-NMR (DMSO-d_6): 195.0, 174.9, 138.3, 133.8. 23.3

General procedure for synthesis of mono-substituted Mannich bases

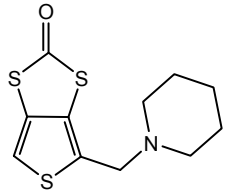
A mixture of thieno[3,4-*d*]-1,3-dithiol-2-one (or thieno[3,4-*d*]-1,3-dithiole-2-thione, 5 mmol), paraformaldhyde (6mmol), amines (6mmol), and 20 ml glacial acetic acid was heated to 120°C in sealed tube. The solution was kept at 120°C for 24 hours. After it cooled to room temperature, 20ml H_2O was added, the reaction mixture was extracted with $CHCl_3$, and washed with saturated $NaHCO_3$, brine, D.I. water. Drying over $MgSO_4$ and column chromatography purification on silica gel (eluent EtOAc-hexanes) afforded mono-substituted Mannich bases.

4-(Morpholinomethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (12)



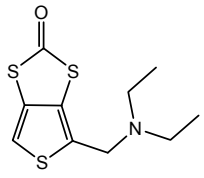
Purification by column chromatography (silica gel, EtOAc:Hexanes 1:4 *v/v*) affords 4-(Morpholinomethyl)thieno[3,4-*d*]-1,3-dithiol-2-one as pale-yellow solid with a yield of 72%. Melting point: 61-62°C. ^{1}H-NMR ($CDCl_3$): 7.15(s, 1H), 3.75(t, *J*=4.6Hz, 4H), 3.65(s, 2H), 2.52 (t, *J*=4.6Hz, 4H). ^{13}C-NMR ($CDCl_3$): 195.1, 130.7, 125.6, 113.4, 66.7, 56.4, 53.4. FT-IR (KBr): 31296, 2964, 2852, 2812, 1632, 1452, 1351, 1294, 1111, 1029, 995, 949, 924, 857, 824, 761, 616, 462 cm^{-1}. MS: m/e 273.0. ESI-TOF(High Accuracy): MH^+ 274.0031, expected 274.0025

4-((Piperidin-1-yl)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (13)



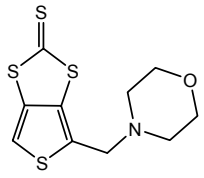
Purification by column chromatography (silica gel, EtOAc:hexanes 1:10 *v/v*) affords 4-((piperidin-1-yl)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one as colorless oil with a yield of 43%. ^{1}H-NMR ($CDCl_3$): 7.10(s, 1H), 3.57(s, 2H), 2.44(brs, 4H), 1.58-1.63(m, 4H), 1.45(brs, 2H). ^{13}C-NMR ($CDCl_3$): 195.7, 132.0, 127.7, 125.5, 112.9, 56.7, 54.4, 25.7, 24.1. FT-IR (KBr): 3109, 2935, 2852, 2800, 2758, 1700, 1647, 1442, 1346, 1300, 1157, 1111, 1038, 994, 947, 821, 776, 460 cm^{-1}. MS: m/e 271.0. ESI-TOF(High Accuracy): MH^+ 272.0244, expected 272.0232.

4-((Diethylamino)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (14)



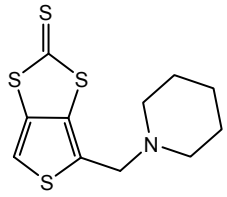
Purification by column chromatography (silica gel, EtOAc:Hexanes 1:15 *v*/*v*) affords 4-((diethylamino)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one as colorless oil with a corresponding yield of 12%. ^{1}H-NMR ($CDCl_3$): 7.11(s, 1H), 3.70(s, 2H), 2.58 (t, *J*=7.3Hz, 4H), 1.06 (t, *J*=7.3Hz, 6H). ^{13}C-NMR ($CDCl_3$): 195.8, 133.4, 127.8, 125.0, 112.8, 51.5, 46.9, 11.6. FT-IR (KBr): 3108, 2969, 2933, 2814, 1699, 1641, 1456, 1373, 1309, 1202, 1167, 1060, 947, 839, 715, 632, 473, 457 cm^{-1}. ESI-TOF(High Accuracy): MH^+ 260.0226, expected 260.0232

4-(Morpholinomethyl)thieno[3,4-*d*]-1,3-dithiole-1-thione (15)



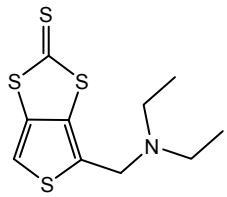
Purification by column chromatography (silica gel, EtOAc:Hexanes 1:10 *v*/*v*) affords 4-(morpholinomethyl)thieno[3,4-*d*]-1,3-dithiole-1-thione as yellow needles with a yield of 75%. Melting point: 94-95°C. ^{1}H-NMR ($CDCl_3$): 7.08(s, 1H), 3.77(t, *J*=4.6Hz, 4H), 3.62(s, 2H), 2.53(t, *J*=4.6Hz, 4H), ^{13}C-NMR ($CDCl_3$): 221.1, 137.1, 135.0, 128.5, 111.0, 66.6, 56.0, 53.4 FT-IR (KBr): 3098, 2971, 2858, 2804, 1454, 1346, 1330, 1288, 1173, 1112, 1056, 997, 910, 862, 765, 734, 619, 543, 543, 500 cm^{-1}. MS: m/e 289.0. ESI-TOF(High Accuracy): MH^+ 289.9810, expected 289.9796

4-((Piperidin-1-yl)methyl)thieno[3,4-*d*]-1,3-dithiole-2-thione (16)



Purification by column chromatography (silica gel, EtOAc:hexanes 1:10 *v/v*) affords 4-((piperidin-1-yl)methyl)thieno[3,4-*d*]-1,3-dithiole-2-thione as amber solid of a 48% yield. Melting point: 89-91°C. ^{1}H-NMR ($CDCl_3$): 7.04(s, 1H), 3.54(s, 2H), 2.45(m, 4H), 1.64(m, 4H), 1.46(m, 2H) ^{13}C-NMR ($CDCl_3$): 222.1, 137.0, 135.0, 130.0, 110.6, 56.6, 54.6, 25.7, 24.2 FT-IR (KBr): 3100, 2935, 2851, 2800, 2758, 1441, 1367, 1346, 1299, 1157, 1109, 1060, 994, 858, 824, 775, 713, 496, 469, 439 cm^{-1} MS: m/e 286.9 ESI-TOF(High Accuracy): MH^+ 288.0016, expected 288.0004

4-((Diethylamino)methyl)thieno[3,4-*d*]-1,3-dithiole-2-thione (17)



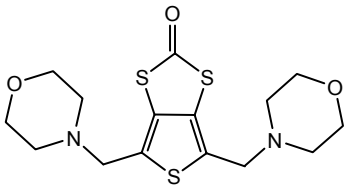
Purification by column chromatography (Silica gel, EtOAc:Hexanes 1:10 *v/v*) affords 4-((diethylamino)methyl)thieno[3,4-*d*]-1,3-dithiole-2-thione as an amber oil with a 12% yield. ^{1}H-NMR ($CDCl_3$): 7.04(s, 1H) 3.66(s, 2H), 2.60(q, *J*=7.3Hz, 4H), 1.07(t, *J*=7.3Hz, 6H) ^{13}C-NMR ($CDCl_3$): 222.3, 136.9, 134.7, 131.3, 110.4, 51.0, 47.0, 11.5 FT-IR (KBr): 3103, 2969, 2932, 2817, 1454, 1373, 1309, 1201, 1166, 1060, 994, 857, 827, 712, 496, 465 cm^{-1} ESI-TOF(High Accuracy): MH^+ 276.0007, expected 276.0004

General procedure for synthesis of bis-substituted Mannich bases

A mixture of thieno[3,4-*d*]-1,3-dithiol-2-one (or thieno[3,4-*d*]-1,3-dithiole-2-thione, 5 mmol), paraformaldhyde (12.5mmol), amines (12.5mmol), and 20 ml glacial

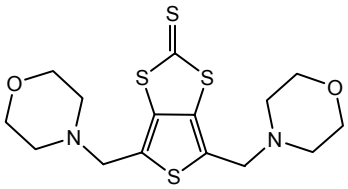
acetic acid was heated to 120°C. The solution was kept at 120°C for 24 hours. After cooled down to room temperature, 20ml H_2O was added, the reaction mixture was extracted with $CHCl_3$, and washed with saturated $NaHCO_3$, brine, D.I. water. Drying over $MgSO_4$ and column chromatography purification (silica gel, eluent EtOAc-hexanes) afforded bis-substituted Mannich bases.

4,6-Bis(morpholinomethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (18)



Purification by column chromatography (silica gel, EtOAc: hexanes 1:10 *v*/*v*) affords 4,6-bis(morpholinomethyl) thieno[3,4-*d*]-1,3-dithiol-2-one as pale-orange needles with a yield of 12%. Melting point: 128-134°C (decomposed). ^{1}H-NMR ($CDCl_3$): 3.74 (t, *J*=4.6Hz, 8H), 3.60 (s, 4H), 2.52 (t, *J*=4.6Hz, 8H) ^{13}C-NMR ($CDCl_3$): 195.9, 128.6, 125.3, 66.8, 56.5, 53.4 FT-IR (KBr): 2972, 2915, 2865, 2803, 1645, 1451, 1349, 1332, 1302, 1113, 1065, 1032, 1008, 919, 859, 802, 625 cm^{-1} MS: m/e 372.0 ESI-TOF(High Accuracy): MH^+ 373.0718, expected 373.0709

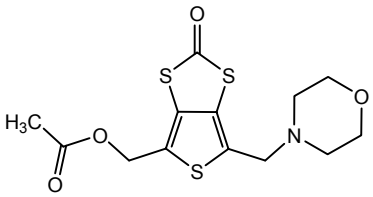
4,6-Bis(morpholinomethyl)thieno[3,4-*d*]-1,3-dithiole-2-thione (19)



Purification by column chromatography (silica gel, EtOAc: hexanes 1:12.5 *v*/*v*) affords 4,6-bis(morpholinomethyl) thieno[3,4-*d*]-1,3-dithiole-2-thione as yellow needles with a yield of 14%. Melting point: 150-154°C (Decomposed) ^{1}H-NMR ($CDCl_3$): 3.77(t, *J*=4.6Hz, 8H), 3.57(s, 4H), 2.53(t, *J*=4.6Hz, 8H) ^{13}C-NMR ($CDCl_3$): 223.0, 134.5,

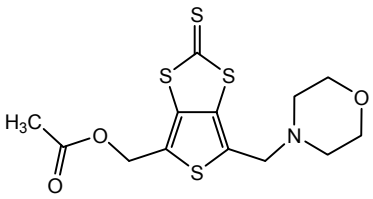
126.0, 66.8, 56.2, 53.5 FT-IR (KBr): 2956, 2851, 2817, 1451, 1348, 1276, 1114, 1063, 1006, 927, 861, 789 cm^{-1} MS: m/e 388.0 ESI-TOF(High Accuracy): MH^+ 389.0493, expected 389.0486

(4-(Morpholinomethyl)-2-oxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate (20)



Purification by column chromatography (silica gel, EtOAc: hexanes 1:10) affords (4-(morpholinomethyl)-2-oxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate as pale-white solid with a yield of 8%. Melting point: 57-58°C ^{1}H-NMR ($CDCl_3$): 5.17(s, 2H), 3.75(t, *J*=4.6Hz, 4H), 3.62(s, 2H), 2.53(m, 4H), 2.11(s, 3H) ^{13}C-NMR ($CDCl_3$): 194.1, 170.5, 131.6, 128.6, 125.2, 125.1, 66.7, 59.3, 56.3, 53.4, 33.4, 20.7 FT-IR(KBr): 2964, 2942, 2856, 2810, 1738, 1661, 1450, 1374, 1353, 1291, 1230, 1144, 1107, 1065, 1022, 1005, 957, 924, 905, 855, 820, 789, 753, 620, 597, 555,458, 428 cm^{-1} MS: m/e 343.0 ESI-TOF(High Accuracy): MH^+ 346.0231, expected 346.0236

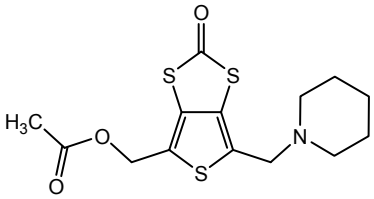
(4-Morpholinomethyl)-2-thioxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate (21)



Purification process was performed on column chromatography (silica gel, EtOAc: hexanes 1:10) to provide (4-morpholinomethyl)-2-thioxothieno[3,4-*d*]-1,3-dithiol-6-yl) methyl acetate as amber oil with a yield of 12%. ^{1}H-NMR ($CDCl_3$): 5.14(s, 2H), 3.77(t, *J*=4.6Hz, 4H), 3.58(s, 2H), 2.54(t, *J*=4.1Hz, 4H), 2.12(s, 3H) ^{13}C-NMR ($CDCl_3$): 220.3, 170.4, 137.4, 134.6, 128.9, 122.6, 66.7, 59.0, 56.1, 53.5, 20.7 FT-

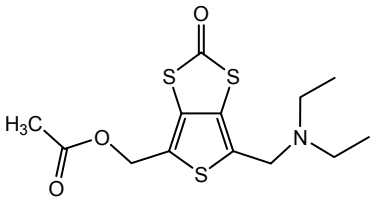
IR (KBr): 2957, 2857, 2820, 1740, 1453, 1223, 1108, 1067, 1008, 953, 923, 859, 826, 788, 750, 625, 531 cm^{-1} MS: m/e 361.0 ESI-TOF(High Accuracy): MH^+ 362.0019, expected 362.0008

(4-(Piperidin-1-yl)methyl)-2-oxothieno[3,4-*d*]-1,3-dithiol-6-yl)methylacetate (22)



Column purification (silica gel, EtOAc: hexanes 1:10 *v*/*v*) affords (4-(piperidin-1-yl) methyl)-2-oxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate as colorless oil with a yield of 9%. ^{1}H-NMR ($CDCl_3$): 5.16(s, 2H), 3.55(s, 2H), 2.45(brs, 4H), 2.15(s, 3H), 1.60-1.64(m, 4H), 1.45(brs, 2H) ^{13}C-NMR ($CDCl_3$): 194.7, 170.4, 133.0, 128.4, 124.8, 124.5, 59.3, 56.7, 54.5, 25.6, 24.1, 20.6 FT-IR (KBr): 2936, 2854, 2801, 1744, 1668, 1442, 1374, 1222, 1110, 1038, 962, 918, 813, 460, 435, 419, 406 cm^{-1} MS: m/e 343.0 ESI-TOF(High Accuracy): MH^+ 344.0452, expected 344.0443

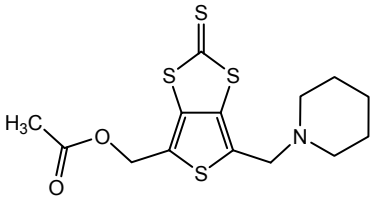
(4-(Diethylamino)methyl)-2-oxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate (23)



Column purification (silica gel, EtOAc: hexanes 1:10 *v*/*v*) affords (4-(diethylamino)methyl)-2-oxothieno[3,4-*d*]-1,3 -dithiol-6-yl)methyl acetate as colorless oil with a yield of 6%. ^{1}H-NMR ($CDCl_3$): 5.17(s, 2H), 3.66(s, 2H), 2.58(q, *J*=7.3Hz, 4H), 2.11(s, 3H), 1.06(t, *J*=7.3Hz, 6H) ^{13}C-NMR ($CDCl_3$): 194.8, 170.6, 134.5, 128.6, 124.5, 124.5, 59.5, 51.5, 47.0, 20.8, 11.6 FT-IR (KBr):2970, 2816, 1744, 1669, 1454, 1376, 1116, 1021,

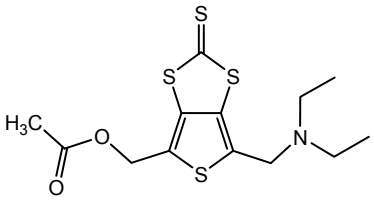
963, 913, 809, 773, 543, 460 cm^{-1} ESI-TOF(High Accuracy): MH^+ 332.0447, expected 332.0443

(4-(Piperidin-1-yl)methyl)-2-thioxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate (24)



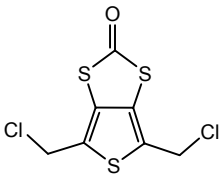
Column purification (silica gel, EtOAc: hexanes 1:10 *v*/*v*) yields (4-(piperidin-1-yl)methyl)-2-thioxothieno [3,4-*d*]-1,3-dithiol-6-yl) methyl acetate as amber oil of 8% yield. ^{1}H-NMR ($CDCl_3$): 5.13(s, 2H), 3.51(s, 2H), 2.46(brs, 4H), 2.11(s, 3H), 1.62-1.67(m, 4H), 1.46(brs, 2H) ^{13}C-NMR ($CDCl_3$): 221.2, 170.4, 134.4, 130.4, 122.0, 59.1, 56.4,54.7, 25.7, 24.1, 20.7 FT-IR (KBr): 2935, 2853, 2802, 1743, 1661, 1441, 1374, 1221, 1109, 1067, 962, 857, 776, 407 cm^{-1} MS: m/e 358.9 ESI-TOF(High Accuracy): MH^+ 360.0224, expected 360.0215

(4-(Diethylamino)methyl)-2-thioxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate (25)



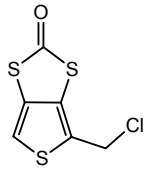
Column purification (silica gel, EtOAc: hexanes 1:10 *v*/*v*) yields (4-(diethylamino)methyl)-2-thioxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate as amber oil with a yield of 8 %. ^{1}H-NMR ($CDCl_3$): 5.14(s, 2H), 3.62(s, 2H), 2.60(q, *J*=7.3Hz, 4H), 2.12(s, 3H), 1.07(t, *J*=7.3Hz, 6H) ^{13}C-NMR ($CDCl_3$): 221.1, 170.5, 137.3, 134.3, 131.7, 122.0, 59.2, 51.0, 47.1, 20.7, 11.5 FT-IR (KBr): 2969, 2817, 1743, 1659, 1452, 1376, 1221, 1115, 963, 826, 758, 617, 496 cm^{-1} ESI-TOF(High Accuracy): MH^+ 348.0216, expected 348.0215

4,6-Bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (26)



Through a stirred mixture of thieno[3,4-*d*]-1,3-dithiol-2-one (1.05g, 6mmol), paraformaldehyde (405mg, 12.6mmol), and anhydrous zinc chloride (571mg, 4.2mmol) in CCl_4 (60ml) was passed dry HCl gas at 50-55°C for 2.5 hours. 30ml $CHCl_3$ was added into the mixture and then dry HCl gas passed through the solution for an additional 1 hour. After the whole mixture was cooled to room temperature, it was filtered through gritted glass filter.The clear solution was washed with saturated $NaHCO_3$, D.I. water, dried over $MgSO_4$. The solvent was removed *in vacuo*. The pale-yellow solid residue was gone through column chromatography (silica gel, CH_2Cl_2:hexanes 1:2 *v/v*) to give 914 mg 4,6-bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one as white needles with a yield of 56.5% Melting point: 108-113°C (decomposed or polymerized) ^{1}H-NMR ($CDCl_3$): 4.72 (s, 4H) ^{13}C-NMR ($CDCl_3$): 191.1, 128.8, 128.5, 38.9 FT-IR(KBr): 3025, 1736, 1683, 1638, 1469, 1433, 1314, 1262, 1217, 1199, 1152, 1121, 952, 912, 824, 742, 684, 640, 537, 461cm^{-1} GC-MS M^+. 270 Elemental Analysis: Anal. Calcd. for $C_7H_4Cl_2OS_3$: C 31.00, H 1.49, Cl 26.14, S 35.47, Found: C 31.15, H 1.47, Cl 25.96, S 35.29

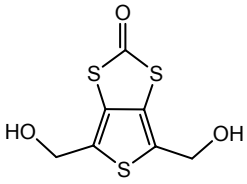
4-(Chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (27)



A mixture of 200mg thieno[3,4-*d*]-1,3-dithiol-2-one dissolved in 2ml chloroform and 20ml concentrated hydrochloric acid was stirred vigorously, maintained at a temperature of 0-5°C by ice bath, and bubbled with hydrogen chloride gas. 1.0ml of 37% formaldehyde water solution (diluted 10

times) was slowly added. After addition of formaldehyde, the reaction mixture was stirred for 45 minutes at 0-5°C, and extracted with $CHCl_3$. The extract was washed with water and then with saturated sodium bicarbonate solution, dried over $MgSO_4$ and solvent was removed by rotary evaporator. The residue was purified by column chromatography (silica gel, eluent: EtOAc/hexanes 1:15 *v*/*v*) and gave 156mg (yield 61%) 4-(chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one as white solid. Melting point: 93-94°C ^{1}H-NMR ($CDCl_3$): 7.27(s, 1H), 4.75(s, 2H) ^{13}C-NMR ($CDCl_3$): 192.6, 128.7, 128.6, 128.3, 115.5, 39.1 FT-IR (KBr): 3111, 3003, 2956, 1686, 1644, 1434, 1309, 1265, 1210, 1130, 960, 877, 839, 741, 679, 638, 548, 514, 463 cm^{-1} ESI-TOF(High Accuracy): MH^+ 222.9107, expected 222.9107

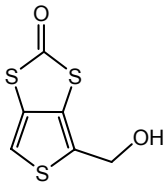
4,6-Bis(hydroxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (28)



4,6-Bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (445mg, 1.64 mmol) was dissolved in 10ml acetone and 4 ml H_2O, the solution then was heated to 80°C (reflux) under N_2 protection for 24 hours. After the solution cooled down to room temperature, acetone was removed under vacuumn to afford 348 mg pale-white solid of 4,6-bis(hydroxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one corresponding to a yield of 91%. Further purification was performed with column chromatography (silica gel, EtOAc/hexanes 1:2 *v*/*v*) to afford 4,6-bis(hydroxymethyl)thieno [3,4-*d*]-1,3-dithiol-2-one as white neddles. Melting point: 104.5 -106.0°C ^{1}H-NMR (DMSO-d_6): 5.89 (t, *J*=5.2Hz, 2H), 4.64 (d, *J*=4.6Hz, 4H) ^{13}C-NMR (DMSO): 194.9, 133.6, 122.0, 57.7 FT-IR (KBr): 3217, 2864, 1709, 1656, 1507,

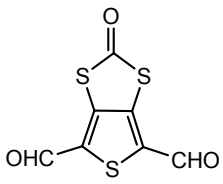
1463, 1398, 1327, 1219, 1161, 1029, 916, 791, 683, 460 cm^{-1}. MS: m/e 234.1 ESI-TOF(High Accuracy): MH^+ 234.9552, expected 234.9552 Elemental Analysis: Anal. Calcd. for $C_7H_6O_3S_3$: C 35.88, H 2.59, S 41.05. Found: C 36.15, H 2.34, S 41.19

4-(Hydroxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (29)



550mg 4-(Chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one dissolved in 25mL acetone and 5mL water. The reaction mixture was stirred at 70ºC for 24 hours (mild reflux). After cooling to room temperature, acetone was removed under vacuum, and the residue was dissolved in 100mL $CHCl_3$. After washed with D.I. water, dried under $MgSO_4$, $CHCl_3$ removed by rotary evaporator, the residue was purified with silica gel column chromatography (EtOAc/Hexanes 1:3 *v/vv*), and afforded 425mg (84% yield) 4-(hydroxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one as white solid. Melting point: 62-63°C ^{1}H-NMR ($CDCl_3$): 7.22(s, 1H), 4.83(s, 2H), 2.39(s, 1H) ^{13}C-NMR ($CDCl_3$): 194.0, 132.8, 128.1, 125.8, 114.4, 59.6 FT-IR (KBr): 3218, 3100, 2917, 2853, 1688, 1647, 1449, 1376, 1314, 1168, 1121, 1030, 1005, 947, 878, 827, 725, 619, 547, 463 cm^{-1}. ESI-TOF(High Accuracy): MH^+ 204.9446, expected 204.9446

2-Oxothieno[3,4-*d*]-1,3-dithiole-4,6-dicarbaldehyde (30)

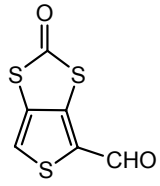


Method 1 (PCC oxidation). To a stirred suspension of pyridinium chlorochromate (PCC) (480mg, 2.2mmole) and sodium acetate

(180mg, 2.2mmole) in 20 ml dry dichloromethane with 30mg pre-treated 4Å molecular sieve was added a suspension of diol 4,6-bis(hydroxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (235mg, 1mmole) in 35ml dry dichloromethane at room temperature. After 4 hours, the gray suspension was filtered through grit-glass filter filled with Celite® 521, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (eluent: dichloromethane/hexanes 5:1 *v/v*) to give 172mg (75% yield) 2-oxothieno[3,4-*d*]-1,3-dithiole-4,6-dicarbaldehyde as pale-yellow needles.

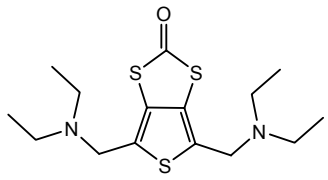
Methpd 2 (IBX oxidation). A mixture of 4,6-bis(hydroxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (235mg, 1mmole) and 2-iodoxybenzoic acid (IBX, 860 mg, 3 mmole) in 30 ml ethyl acetate was heated to 80°C for 4 hours. After cooling, the reaction mixture was filtered through glass filter, and solid residue was washed with additional 40 ml ethyl acetate. Combined organic phase was washed with water and brine, and dried over magnesium sulfate. After solvent removed under vacuum, the residue was purified with silica gel column chromatography, and afforded 189mg (82% yield) of 2-oxothieno[3,4-*d*]-1,3-dithiole-4,6-dicarbaldehyde as pale- yellow needles. Melting point: 215-216°C ^{1}H-NMR (DMSO): 10.07(s, 2H) ^{13}C-NMR (DMSO): 195.1, 184.0, 135.3, 132.7 FT-IR (KBr): 2886, 1717, 1667, 1489, 1429, 1396, 1326, 1304, 1169, 1147, 944, 917, 857, 804, 612, 557, 514, 468 cm^{-1} ESI-TOF(High Accuracy): MH^{+} 230.9239, expected 230.9250

2-Oxothieno[3,4-*d*]-1,3-dithiole-4-carbaldehyde (31)



Experiment procedures of synthesis of 2-oxothieno[3,4-*d*]-1,3-dithiole-4-carbaldehyde is similar to preparation of 2-oxothieno[3,4-*d*]-1,3-dithiole-4,6-dicarbaldehyde, 1 equivalent IBX was used as oxidant. Purification by silica gel column chromatography (EtOAC/hexanes 1:3 *v/v*) afforded 2-oxothieno[3,4-*d*]-1,3-dithiole-4-carbaldehyde as white needles with 82% yield. Melting point: 165-166°C ^{1}H-NMR: 9.88(s, 1H), 7.71(s, 1H) ^{13}C-NMR: 193.6, 179.8, 135.5, 130.7, 130.6, 123.5 FT-IR (KBr): 3110, 2892, 1688, 1646, 1498, 1403, 1328, 1174, 965, 937, 848, 824, 769, 651, 543 cm^{-1} ESI-TOF(High Accuracy): MH^{+} 202.9290, expected 202.9298

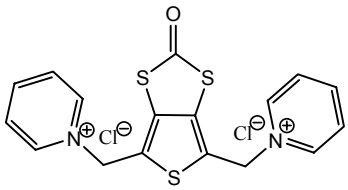
4,6-Bis((diethylamino)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (32)



A solution of 135mg 4,6-bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (0.5 mmol) and 0.5ml diethylamine (excess) in 10ml CCl_4 was heated to 50°C for 12 hours to give an amber-yellow solution. The reaction solution was then added 10ml $CHCl_3$, washed with saturated $NaHCO_3$ solution, water, dried over $MgSO_4$, and concentrated under vacuum. Column purification gave 64mg 4,6-bis((diethylamino)methyl)thieno[3,4-*d*] -1,3-dithiol-2-one as an amber oil corresponding to a yield of 37%. ^{1}H-NMR ($CDCl_3$): 3.65(s, 4H), 2.57(q, *J*=6.87, 8H), 1.06 (t, *J*=6.87Hz, 12H) ^{13}C-NMR ($CDCl_3$): 197.0, 130.8, 124.4, 51.5, 46.9, 11.6 FT-IR (KBr): 2969, 2934, 2813, 1667, 1455, 1385, 1357,

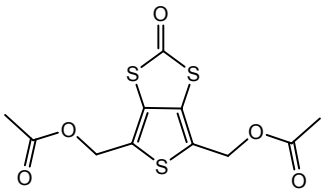
1295, 1202, 1167, 1117, 1060, 996, 920, 796, 735, 482, 469 cm^{-1} ESI-TOF(High Accuracy): MH^+ 345.1125, expected 345.1123

1, 1'-[(4,6-Thieno[3,4-d]-1,3-dithiol-2-one-diyl)bismethylene]bis[pyridinium chloride] (33)



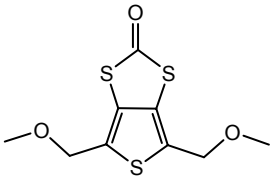
271 mg 4,6-Bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (1 mmol) was dissolved in 5 ml pyridine. The solution heated to 90°C as white precipitates started forming from the clear solution, and stood at 90°C for 12 hours till all starting material disappeared on TLC plate. After the reaction mixture cooled to room temperature, pale-white solid was filtered and washed with diethyl ether and hexanes. The solid was dissolved in CH_2Cl_2, and precipitated in diethyl ether, then filtered. The final product was dried in vacuum oven at 60°C for 24 hours, and gave 407 mg pale-white solid 1, 1'-[(4,6-thieno[3,4-*d*]-1,3-dithiol-2-one-diyl)bismethylene]bis[pyridinium chloride] which is corresponding to a yield of 95%. Melting point: > 400°C (decomposed after 250°C, color turns into black) ^{1}H-NMR (D_2O): 8.78-8.79 (m, 4H), 8.48-8.51 (m, 2H), 7.98-8.01 (m, 4H), 6.03 (s, 4H) ^{13}C-NMR (D_2O): 193.0, 147.1, 144.2, 132.3, 128.9, 125.6, 57.6 FT-IR (KBr): 3016, 2941, 2854, 1682, 1628, 1500, 1485, 1449, 1219, 1162, 1138, 831, 758, 686 cm^{-1} ESI-TOF(High Accuracy): MNa^+ 450.9517, expected 450.9537 Elemental Analysis: Anal. Calcd. for $C_{17}H_{14}Cl_2N_2OS_3$: C 47.55, H 3.29, Cl 16.51, N 6.52, S 22.40. Found: C 45.22, H 3.22, Cl 14.47, N 5.93, S 20.68.

4,6-Bis(acetoxymethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (34)



A mixture of 4,6-bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (271mg, 1mmol) and potassium acetate (245mg, 2.5mmol) in 10ml glacial acetic acid was heated to 120°C under N_2 protection for 8 hours. The reaction mixture was extracted with $CHCl_3$, column purification (silica gel, EtOAc/hexanes 1:2 *v*/*v*), the pale-yellow residue gave 216mg white solid of 4,6-bis(acetoxymethyl) thieno[3,4-*d*]-1,3-dithiol-2-one corresponding to a yield of 68%. Melting point: 118.5 -119.5°C ^{1}H-NMR ($CDCl_3$): 5.18(s, 4H), 2.11 (s, 6H) ^{13}C-NMR ($CDCl_3$): 192.1, 170.4, 128.3, 127.9, 59.3, 20.6 FT-IR (KBr): 2954, 1734, 1681, 1438, 1383, 1270, 1214, 1020, 961, 842, 817, 770, 753, 614, 581, 549, 445 cm^{-1} MS: m/e 318.0 ESI-TOF(High Accuracy): MNa^+ 340.9571, expected 340.9583 Elemental Analysis: Anal. Calcd. for $C_{11}H_{10}O_5S_3$: C 41.49, H 3.17, S 30.21. Found: C 41.44, H 3.11, S 29.79

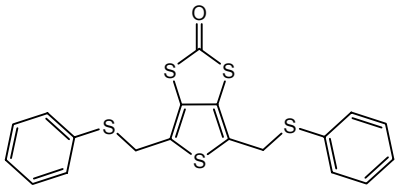
4,6-Bis(methoxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (35)



135mg 4,6-Bis(chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (0.5 mmol) was dissolved in 10ml methanol, the solution then was heated to 50-55°C (reflux) under N_2 protection for 48 hours until all starting material was disappeared in TLC plate. Regular workup procedures were applied. Column chromatographic purification (silica gel, EtOAc/hexanes 1:5 *v*/*v*) gave 78mg white solid of 4,6-bis(methoxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one corresponding to a yield of 60%. Melting point: 54-55°C ^{1}H-NMR ($CDCl_3$): 4.58 (m,

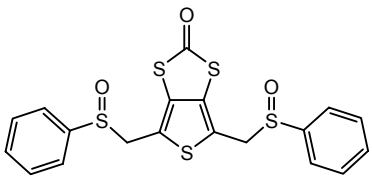
4H), 3.41 (m, 6H) ^{13}C-NMR ($CDCl_3$): 193.7, 129.4, 126.3, 68.3, 58.4 FT-IR (KBr): 2937, 2828, 1699, 1655, 1466, 1372, 1191, 1090, 967, 948, 928, 842, 787, 744, 543, 461 cm^{-1}. MS: m/e 261.9 ESI-TOF(High Accuracy): MH^+ 262.9857, expected 262.9865

4,6-Bis((phenylthio)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (36)



A mixture of 4,6-bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (2.834g, 10.4mmol), sodium thiophenolate (4.60g, 30.0mmol), and sodium iodide (4.71g, 30.0mmol) in 150ml dry THF was heated to 50-55°C under N_2 protection for 4 hours, then cool to room temperature. After removal of THF under vacuum, the solid residue was subject to column purification (silica gel, THF/hexanes 1:10), 3.133g white solid of 4,6-bis((phenylthio)methyl)thieno[3,4-*d*]-1,3- dithiol-2-one was collected, which corresponding to a yield of 75%. Melting point: 94-96°C ^{1}H-NMR ($CDCl_3$): 7.23-7.29 (m, 10H), 4.13 (s, 4H) ^{13}C-NMR ($CDCl_3$): 192.8, 133.9, 131.2, 129.1, 127.6, 126.0, 33.8 FT-IR (KBr): 3076, 3058, 2911, 1730, 1671, 1631, 1470, 1438, 1408, 1298, 1230, 1142, 1102, 1065, 1022, 927, 912, 843, 822, 731, 692, 545, 515, 491, 455 cm^{-1} ESI-TOF(High Accuracy): MH^+ 418.9732, expected 418.9721

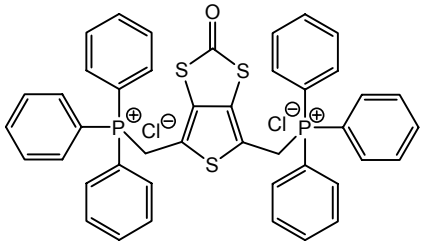
4,6-Bis((phenylsulfinyl)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (37)



A solution of 465mg 4,6-bis((phenylthio)methyl) thieno[3,4-*d*]-1,3-dithiol-2-one (1.1mmol) in 10ml

$CHCl_3$ was cooled to -15~-18°C by NaCl/ice bath for 30 minutes. 22 ml 0.1M m-CPBA solution was slowly added into the flask by syringe, the reaction mixture was stirred for another two hours, and monitored by TLC. Then the reaction mixture was put into freezer (-20°C) for overnight, and regular work up procedures were applied. Column chromatographic purification (silica gel, CH_3OH/CH_2Cl_2 1:25 *v/v*) gave 395mg 4,6-bis((phenylsulfinyl)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one as white solid corresponding to a yield of 78%. Melting point: 183-184 °C (decomposed) ^{1}H-NMR (DMSO-d_6): 7.45-7.56 (m, 10H), 4.66(d, *J*=14.10, 2H), 4.45(d, *J*=14.10, 2H) ^{13}C-NMR (DMSO-d_6): 192.6, 142.0, 131.3, 129.1, 127.6, 124.4, 122.3, 54.8 FT-IR (KBr): 3054, 2965, 2916, 1722, 1667, 1635, 1582, 1475, 1444, 1388, 1305, 1110, 1087, 1048, 913, 824, 747, 691, 548, 527, 502cm^{-1} ESI-TOF(High Accuracy): MNa^+ 472.9455, expected 472.9439

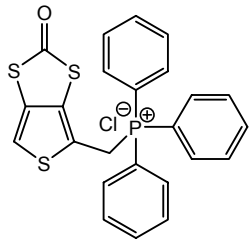
1,1'-[(4,6-Thieno[3,4-*d*]-1,3-dithiol-2-one-diyl)bismethylene] bis[triphenyl phosphonium chloride] (38)



274mg 4,6-Bis(chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (1 mmol) and 655mg triphenyl phosphine (2.5 mmols) was dissolved in 10ml dry THF in an one-neck flask with condenser, the clear solution then was heated to 80-85°C (mild reflux) under N_2 protection for 24 hours until all starting material was disappeared on TLC plate. White precipitates were collected by gritted glass filter, washed with diethyl ether several times, and dried over vacuum oven for overnight at 60°C gave 758g 1,1'-[(4,6-thieno[3,4-*d*]-1,3-dithiol-2-one-diyl)bismethylene] bis[triphenyl

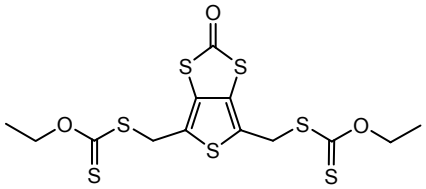
phosphonium chloride] as a white solid corresponding yield of 95%. Melting point: >250°C (decomposed after 200°C, white solid turns into black) ^{1}H-NMR (300MHz, DMSO-d_6): 7.91-7.96(m, 6H), 7.70-7.73(m, 24H), 5.87(d, J_{P-H}=13.07Hz, 4H) ^{13}C-NMR (300MHz, DMSO-d_6): 191.6, 135.4, 133.6-133.8(m), 130.0-130.2(m), 130.0, 120.8-120.9(m), 117.0(d, J_{c-p}=86.7Hz), 24.6((d, J_{c-p}=52.0Hz) FT-IR (KBr): 3053, 2987, 2826, 2744, 1642, 1586, 1485, 1437, 1320, 1111, 996, 936, 882, 753, 741, 731, 712, 689, 549, 514, 483, 459 cm^{-1} ESI-TOF(High Accuracy): MNa^{+} 817.0520, expected 817.0516

[(4-Thieno[3,4-*d*]-1,3-dithiol-2-one-yl)methylene] [triphenylphosphonium chloride] (39)



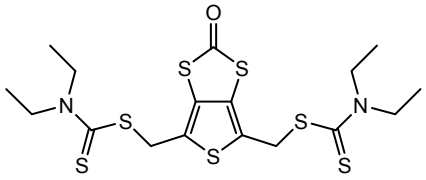
Preparation procedures were similar to that of **38** yield [(4-thieno[3,4-*d*]-1,3-dithiol-2-one-yl)methylene] [triphenyl phosphonium chloride] as a white solid with 92% yield. Melting point: >250°C. ^{1}H-NMR (300MHz, DMSO-d_6): 7.90-7.96(m, 4H), 7.71-7.82(m, 12H), 5.67(d, J_{P-H}=14.2Hz, 2H) ^{13}C-NMR (300MHz, DMSO-d_6): 193.5, 135.4(d, J_{c-p}=2.2Hz), 134.0(d, J_{c-p}=10.1Hz), 130.4(d, J_{c-p}=8.7Hz), 130.2(d, J_{c-p}=13.0Hz), 126.5(d, J_{c-p}=3.6Hz), 120.0(d, J_{c-p}=4.3Hz), 119.2(d, J_{c-p}=10.1Hz), 117.2(d, J_{c-p}=86.0Hz), 24.8(d, J_{c-p}=50.0Hz)[213] FT-IR (KBr): 2993, 2834, 2757, 1689, 1640, 1484, 1435, 1328, 1109, 995, 948, 901, 843, 735, 689, 537, 502 cm^{-1} ESI-TOF(High Accuracy): $[M-H]^{-}$ 482.9872, expected 482.9873

4,6-Bis[ethoxy(thiocarbonyl)thiomethyl]thieno[3,4-*d*]-1,3-dithiol-2-one (40)



A solution of 4,6-bis(chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (820mg, 3.05mmol), *O*-ethoxyanthic acid potassium salt (1.250g, 7.5mmol), and tetra-*n*-butylammonium bromide (320mg, 1mmol) in dry dichloromethane (60ml) was stirred at room temperature for 8 hours. The concentrated residue was purified by column chromatography (silica gel, CH_2Cl_2/hexanes 1:1 *v*/*v*) to give 1.307g (yield 97%) 4,6-bis[ethoxy(thiocarbonyl)thiomethyl]thieno[3,4-*d*]-1,3-dithiol-2-one as a white solid. Melting point: 98-100°C ^{1}H-NMR ($CDCl_3$): 4.67(q, *J*=7.22Hz, 4H), 4.48(s, 4H), 1.43(t, *J*=7.22Hz, 6H) ^{13}C-NMR ($CDCl_3$): 212.0, 191.9, 127.8, 126.7, 70.9, 34.5, 13.8 FT-IR (KBr): 2981, 2941, 2900, 1713, 1677, 1455, 1387, 1361, 1259, 1232, 1151, 1110, 1042, 930, 903, 816, 741, 695, 544, 461 cm^{-1} ESI-TOF(High Accuracy): MH^+ 442.9065, expected 442.9061

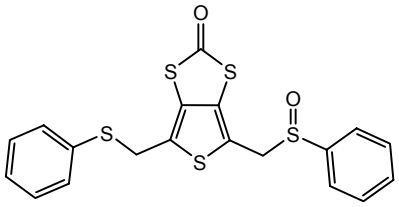
4,6-Bis(*N*,*N*-diethyldithiocarbomate-methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (41)



To a 50 mL ethanol solution of 4,6-bis (chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (272mg, 1mmol), sodium diethyldithiocarbamate trihydrate (580mg. 2.5mmol) was added as a solid. The reaction mixture was stirred at room temperature for 2 hours. After ethanol was removed under vacuum, the solid residue was dissolved in 80mL chloroform, then washed with water and brine, and dried

over $MgSO_4$. Concentration under vacuum followed by column chromatography (silica gel, EtOAC/hexanes 1:2.5 *v/v*) afforded 418mg 4,6-bis(*N,N*-diethyldithiocarbomate-methyl)thieno[3,4-*d*]-1,3-dithiol-2-one as yellowish amber color gel which corresponding to a yield of 85%. ^{1}H-NMR ($CDCl_3$): 4.72(s, 4H), 4.02(q, *J*=6.88Hz, 4H), 3.73(q, *J*=6.88Hz, 4H), 1.30(t, *J*=6.88Hz, 6H), 1.29(t, *J*=6.88Hz, 6H) ^{13}C-NMR ($CDCl_3$): 193.0, 192.8, 128.3, 126.3, 50.0, 47.0, 35.7, 12.6, 11.6 FT-IR (KBr): 2976, 2932, 2871, 1671, 1489, 1458, 1419, 1379, 1354, 1300, 1271, 1204, 1144, 1069, 1008, 982, 916, 830, 562, 458, 429 cm^{-1} ESI-TOF(High Accuracy): MNa^+ 518.9826, expected 518.9834

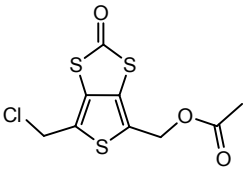
4-((Phenylsulfinyl)methyl)-6-((phenylthio)methyl)methyl)thieno[3,4-*d*]-1,3- dithiol-2-one (42)



A solution of 419mg 4,6-bis((phenylthio)methyl) thieno[3,4-*d*]-1,3-dithiol-2-one (1mmol) in 10ml $CHCl_3$ was cooled to -15~-18°C by NaCl/ice bath for 30 minutes. 10ml 0.1M m-CPBA solution (1 eqv.) was slowly added into the flask by syringe, the reaction mixture was stirred for another two hours after the addition of m-CPBA. Then the reaction mixture was washed with water, and concentrated *in vacuo*. Column chromatography purification (silica gel, EtOAc/CH_2Cl_2 1:10 *v/v*) gave 360mg compound **42** as white solid corresponding to a yield of 83%. Melting point: 152-154°C. ^{1}H-NMR ($CDCl_3$): 7.25-7.50(m, 10H), 4.18(s, 2H), 4.14(d, *J*=14.10Hz, 1H), 4.06(d, *J*=14.1Hz, 1H) ^{13}C-NMR ($CDCl_3$): 191.9, 141.9, 133.9, 132.0, 131.9, 131.0, 129.8, 129.3, 129.2, 127.7,

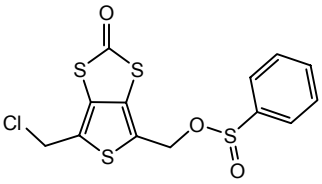
126.1, 124.3, 118.4, 57.3, 33.61 FT-IR (KBr): 3057, 2964, 1727, 1669, 1634, 1473, 1439, 1401, 1302, 1231, 1107, 1087, 1068, 1048, 998, 913, 824, 741, 693, 533, 492, 470, 456 cm^{-1} ESI-TOF(High Accuracy): MNa^+ 456.9478, expected 456.9495

4-(Chloromethyl)-6-(acetoxylmethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (43)



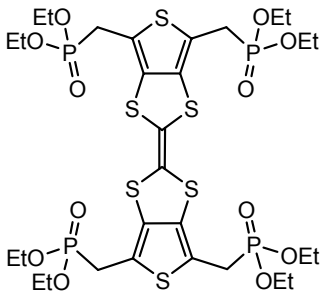
Synthesis of 4-(chloromethyl)-6-(acetoxylmethyl)thieno[3,4-*d*]-1,3-dithiol-2-one was similar to the preparation of 4,6-bis(acetoxymethyl) thieno[3,4-*d*]-1,3-dithiol-2-one. One equivalent of potassium acetate was used in stead. Column purification (silica gel, EtOAc/hexanes 1:5 *v/v*) affords compound as white solid with 38% yield. Melting point: 88-89°C. ^{1}H-NMR ($CDCl_3$): 5.19(s, 2H), 4.71(s, 2H), 2.12(s, 2H) ^{13}C-NMR ($CDCl_3$): 191.6, 170.4, 129.1, 128.6, 128.3, 127.7, 59.2, 39.0, 20.6 FT-IR (KBr): 3026, 2949, 1736, 1677, 1649, 1440, 1379, 1270, 1222, 1171, 1015, 959, 824, 746, 688, 641, 546, 464 cm^{-1} ESI-TOF(High Accuracy): MH^+ 294.9305, expected 294.9319

4-(Chloromethyl)-6-(phenylsulfinyloxylmethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (44)



Yield 68%, Melting point: 136-137°C. ^{1}H-NMR ($CDCl_3$): 7.75-7.77(m, 2H), 7.67-7.70(m, 1H), 7.52-7.56(m, 2H), 4.68(s, 2H), 4.45(s, 2H) ^{13}C-NMR ($CDCl_3$): 190.8, 137.1, 134.7, 131.2, 130.7, 129.6, 128.6, 128.2, 119.0, 57.1, 38.8 FT-IR (KBr):3061, 2968, 2916, 1686, 1476, 1446, 1396, 1322, 1265, 1210, 1138, 1082, 931, 824, 740, 688, 644, 622, 547, 529, 458 cm^{-1} ESI-TOF(High Accuracy): MH^+ 376.9195, expected 376.9196

4,4',6,6'-Tetra(diethoxyphosphorylmethyl)-(-2-(thieno[3,4-*d*]-1,3-dithiol-2-ylidene) thieno[3,4-*d*]-1,3-dithiole (48)

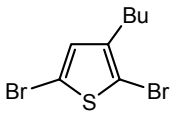


Preparation of DTTTF-type derivative was performed as following: 274mg 4,6-bis(chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (1 mmol) and 1.0g triethyl phosphite (excess) was put in an one-neck flask with condenser, the mixture then was heated to 150-160°C under N_2 protection for 4 hours until all starting material was disappeared on TLC plate. After the mixture cooled down to room temperature, the yellow precipitates were collected by filter, and washed with diethyl ether and hexanes several times. Dry under vacuum at 65°C for overnight affords 146mg product as yellow needles corresponding to a yield of 32%. Melting point: 167-168°C ^{1}H-NMR ($CDCl_3$): 4.12(m, 8H), 3.13(t, J_{P-H} =18.8Hz , 8H), 1.32(t, J=7.3Hz, 24H) ^{13}C-NMR ($CDCl_3$): 134.0(m), 119.6, 118.4, 29.2, 27.2, 16.5 FT-IR (KBr): 2981, 2940, 2904, 1477, 1443, 1392, 1368, 1315, 1252, 1163, 1098, 1028, 970, 887, 783, 639, 539cm^{-1} ESI-TOF(High Accuracy): MH^+ 917.0496, expected 917.0493 Elemental Analysis: Anal. Calcd. for $C_{30}H_{48}O_{12}P_4S_6$: C 39.29, H 5.28 Found: C: 39.30, H 5.02

General procedures for bromination of alkylthiophenes

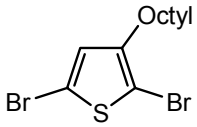
A mixture of 10 mmol alkylthiophene and 1.78 g (10 mmol) NBS in 30 ml ethanol was stirred at 50ºC for 4 hours. The reaction mixture was extracted with chloroform. The organic layer was washed with water, brine, and concentrated under vacuum. The liquid residue was purified by column chromatography (silica gel, hexanes).

2,5-Dibromo-3-butylthiophene (60a)



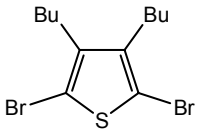
Colorless oil, ^{1}H-NMR ($CDCl_3$): 6.77(s, 1H), 2.51(t, *J*=7.3Hz, 2H), 1.50-1.56(m, 2H), 1.31-1.38(m, 2H), 0.93(t, *J*=7.3Hz, 3H) ^{13}C-NMR ($CDCl_3$): 143.0, 131.0, 110.3, 107.9, 31.7, 29.2, 22.2, 13.8 FT-IR (KBr): 2956, 2928, 2858, 1542, 1464, 1417, 1378, 1179, 1087, 1010, 997, 911, 826, 746, 650, 476 cm^{-1}

2,5-Dibromo-3-octylthiophene (60b)



Colorless oil, ^{1}H-NMR ($CDCl_3$): 6.77(s, 1H), 2.50(t, *J*=7.57Hz, 2H), 1.48-1.58(m, 2H), 1.26-1.31(m, 10H), 0.88(t, *J*=6.9Hz, 3H) ^{13}C-NMR ($CDCl_3$): 143.0, 131.0, 110.3, 108.0, 31.9, 29.6, 29.5, 29.4, 29.2, 29.1, 22.7, 14.1 FT-IR (KBr): 2925, 2853, 1539, 1460, 1409, 1376, 1225, 991, 829, 713, 684, 635, 580 cm^{-1}

2,5-Dibromo-3,4-dibutylthiophene (60c)



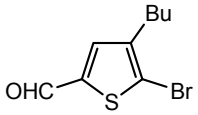
Colorless oil, ^{1}H-NMR ($CDCl_3$): 2.54(m, 4H), 1.36-1.48(m, 8H), 0.95(t, *J*=7.3Hz, 6H) ^{13}C-NMR ($CDCl_3$): 141.4, 107.9, 31.7, 28.7, 22.7, 13.9 FT-IR (KBr): 2957, 2929, 2860, 1544, 1464, 1378, 1299, 1252, 1193, 1143, 1104, 1086, 968, 927, 746, 728 cm^{-1}

General procedure for synthesis of 5-bromo-alkyl-2-thiophenecarboxaldehydes

A solution of 2,5-dibromo-alkylthiophene (5mmol) in anhydrous THF (30ml) was stirred and cooled to -78ºC under argon for 30 minutes. 5.5mmol *n*-butyllithium was added slowly via a syringe pump. The solution was stirred for another 30 minutes, 1-

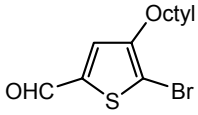
formylpiperidine (6mmol in 10ml THF) was added dropwise. The reaction mixture was allowed to warm up to room temperature for overnight, poured in water, and extracted with chloroform. Column purification (silica gel, EtOAc/hexanes) affords 5-bromo-4-alkyl-2-thiophenecarboxaldehydes.

5-Bromo-4-butyl-2-thiophenecarboxaldehyde (61a)



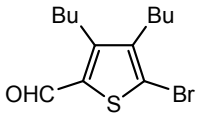
Pale-yellow oil, yield 85%. ^{1}H-NMR ($CDCl_3$): 9.75(s, 1H), 7.46(s, 1H), 2.61(t, *J*=7.8Hz, 2H), 1.57-1.63(m, 2H), 1.34-1.42(m, 2H), 0.95(t, *J*=7.3Hz, 3H) ^{13}C-NMR ($CDCl_3$): 181.9, 143.9, 142.9, 136.8, 122.1, 31.6, 29.2, 22.2, 13.8 FT-IR (KBr): 2957, 2929, 2860, 1670, 1544, 1429, 1376, 1236, 1155, 1086, 1004, 852, 731, 668, 489 cm^{-1}

5-Bromo-4-octyl-2-thiophenecarboxaldehyde (61b)



Yellow oil, yield 78%. ^{1}H-NMR ($CDCl_3$): 9.76(s, 1H), 7.46(s, 1H), 2.59(t, *J*=7.6Hz, 2H), 1.56-1.65(m, 2H), 1.27-1.33(m, 10H), 0.88(t, *J*=6.5Hz, 3H) ^{13}C-NMR ($CDCl_3$): 181.9, 144.0, 142.9, 136.8, 122.1, 31.9, 29.5, 29.3, 29.2, 29.1, 22.7, 14.1 (carbon peaks of octyl groups overlapped, only seven alkyl carbon peaks were counted) FT-IR (KBr): 2926, 2855, 1674, 1544, 1429, 1376, 1236, 1153, 1100, 1004, 853, 728, 668 cm^{-1}

5-Bromo-3,4-dibutyl-2-thiophenecarboxaldehyde (61c)

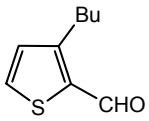


Pale-yellow oil, yield 68%. ^{1}H-NMR ($CDCl_3$): 9.92(s, 1H), 2.89(t, *J*=7.2Hz, 2H), 2.56(t, *J*=7.2Hz, 2H), 1.36-1.62(m, 8H), 0.93-0.99(m, 6H) ^{13}C-NMR ($CDCl_3$): 181.3, 151.4, 143.7, 138.3, 122.5, 34.4, 31.6, 27.7, 27.5, 22.7, 13.9, 13.8 FT-IR (KBr): 2957, 2930, 2861, 1660, 1535, 1437, 1387, 1365, 1282, 1232, 1127, 1081, 933, 676 cm^{-1}

General procedure for synthesis of 3- or 4-alkyl-2-thiophenecarboxaldehydes

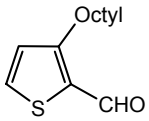
A solution of 2-bromo-3(or 4)-alkylthiophene (10mmol) in anhydrous THF (40ml) was stirred and cooled to -78ºC under argon for 30 minutes. 4.4ml *n*-butyllithium (2.5 M in hexanes, 1.1 equivalents) was slowly added via syringe pump. After addition of *n*-butyllithium, the solution was stirred for another 30 minutes, then 1.7g 1-formylpiperidine (15mmol in 10ml THF) was added dropwise. The reaction mixture was allowed to warm up to room temperature, and stirred for overnight to give a pale-yellow solution. The reaction mixture was quenched with water, and extracted with chloroform. The organic phase was washed with water and brine, dried over $MgSO_4$. After solvent removed under vacuum, the oil-like residue was purified by column chromatography (silica gel, EtOAc/hexanes 1:20 *v/v*) to afford 3- or 4-alkyl-2-thiophenecarboxaldehydes.

3-Butylthiophene-2-carboxaldehyde (63a)



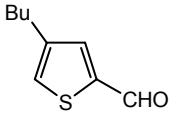
Colorless oil, 85% yield. ^{1}H-NMR ($CDCl_3$): 10.04(d, *J*=1.0Hz, 1H), 7.64(d, *J*=4.8Hz, 1H), 7.01(d, *J*=4.8Hz, 1H), 2.97(t, *J*=7.6Hz, 2H), 1.60-1.80(m, 2H), 1.32-1.45(m, 2H), 0.91-0.96(t, *J*=7.2Hz, 3H). ^{13}C-NMR ($CDCl_3$): 182.1, 152.8, 137.5, 134.3, 130.6, 33.4, 28.1, 22.3, 13.7 FT-IR (KBr): 3101, 2957, 2930, 2862, 1659, 1525, 1458, 1425, 1390, 1241, 1223, 1081, 840, 743, 666cm^{-1}

3-Octylthiophene-2-carboxaldehyde (63b)



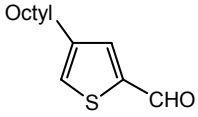
Pale-yellow oil, 82% yield. ^{1}H-NMR ($CDCl_3$): 10.04(d, *J*=1.0Hz, 1H), 7.62(d, *J*=4.8Hz, 1H), 7.00(d, *J*=5.2Hz, 1H), 2.96(t, *J*=7.6Hz, 2H), 1.62-1.70(m, 2H), 1.26-1.32(m, 2H), 0.88(t, *J*=7.2Hz, 1H) ^{13}C-NMR ($CDCl_3$): 182.2, 152.9, 137.6, 134.4, 130.7, 31.8, 31.4, 29.3, 29.2, 29.1, 28.4, 22.6, 14.0 FT-IR (KBr): 3102, 2926, 2855, 2725, 1662, 1526, 1464, 1391, 1378, 1242, 1212, 839, 746, 667cm^{-1}

4-Butylthiophene-2-carboxaldehyde (67a)



Pale-yellow oil, yield 87%. ^{1}H-NMR ($CDCl_3$): 9.87(d, *J*=1.4Hz, 1H), 7.61(d, *J*=1.4Hz, 1H), 7.37(bs, 1H), 2.65((t, *J*=7.6Hz, 2H), 1.57-1.67(m, 2H), 1.31-1.43(m, 2H), 0.94(t, *J*=7.2Hz, 3H) ^{13}C-NMR ($CDCl_3$): 183.0, 144.7, 143.6, 137.2, 130.4, 32.5, 29.8, 22.2, 13.8 FT-IR (KBr): 3006, 2957, 2930, 2860, 1672, 1543, 1435, 1389, 1238, 1186, 1134, 860, 773, 666cm^{-1}

4-Octylthiophene-2-carboxaldehyde (67b)

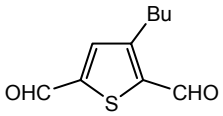


Pale-yellow oil, yield 85%. ^{1}H-NMR ($CDCl_3$): 9.88(d, *J*=1.4Hz, 1H), 7.61(d, *J*=1.4Hz, 1H), 7.37(bs, 1H), 2.64(t, *J*=7.6Hz, 2H), 1.58-1.68(m, 2H), 1.26-1.36(m, 10H), 0.88(t, *J*=6.9Hz, 3H) ^{13}C-NMR ($CDCl_3$): 183.0, 144.8, 143.6, 137.2, 130.4, 31.9, 30.4, 30.2, 29.4, 29.2, 29,1, 22.7, 14.1 FT-IR (KBr): 3087, 2926, 2854, 1672, 1544, 1435, 1388, 1237, 1189, 1133, 865, 774, 665cm^{-1}

General procedure for synthesis of alkyl-2,5-thiophenedicarboxaldehydes

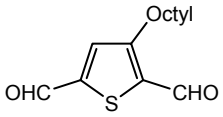
A solution of 2,5-dibromo-alkylthiophene (10mmol) in anhydrous THF (40ml) was stirred and cooled to -78ºC under argon. 24.7ml *tert*-butyllithium (1.7M in pentane, 4.2 equivalents) was added dropwise. After addition of *tert*-butyllithium, the solution was stirred for another 30 minutes, 2.9g 1-formylpiperidine in 10 ml THF was added. The reaction mixture was allowed to warm up to room temperature, and stirred for overnight to give a pale-yellow solution. The reaction mixture was quenched with water, and extracted with chloroform. The organic phase was washed with water, dried over $MgSO_4$. After solvent removed under vacuum, the oil-like residue was purified by column chromatography (silica gel, EtOAc/hexanes) to afford alkyl-2,5-thiophene dicarboxaldehydes.

3-Butyl-2,5-thiophenedicarboxaldehyde (68a)



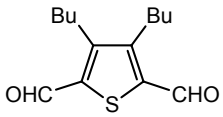
Colorless oil, yield 81%. ^{1}H-NMR ($CDCl_3$): 10.14(s, 1H), 9.97(s, 1H), 7.66(s, 1H), 3.01(t, *J*=7.8Hz, 2H), 1.65-1.71(m, 2H), 1.36-1.42(m, 2H), 0.96(t, *J*=7.3Hz, 3H) ^{13}C-NMR ($CDCl_3$): 183.4, 183.0, 152.0, 147.9, 143.4, 137.3, 33.3, 28.3, 22.4, 13.8 FT-IR (KBr): 2958, 2931, 2861, 1667, 1533, 1458, 1399, 1212, 1153, 860, 732, 683, 495 cm^{-1}

3-Octyl-2,5-thiophenedicarboxaldehyde (68b)



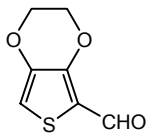
Pale-red oil, yield 62%. ^{1}H-NMR ($CDCl_3$): 10.14(s, 1H), 9.98(s, 1H), 7.65(s, 1H), 3.00(t, *J*=7.8Hz, 2H), 1.65-1.71(m, 2H), 1.23-1.38(m, 10H), 0.88(t, *J*=6.9Hz, 3H) ^{13}C-NMR ($CDCl_3$): 183.4, 183.0, 152.1, 147.9, 143.3, 137.2, 31.8, 31.1, 29.3, 29.2, 29.1, 28.5, 22.6, 14.1 FT-IR (KBr): 2926, 2855, 1669, 1533, 1458, 1399, 1377, 1223, 1150, 864, 742, 692 cm^{-1}

3,4-Dibutyl-2,5-thiophenedicarboxaldehyde (68c)



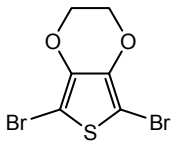
White solid, yield 67%. Melting point: 60-61°C. ^{1}H-NMR ($CDCl_3$): 10.12(s, 2H), 2.92(t, *J*=7.8Hz, 4H), 1.54-1.69(m, 4H), 1.41-1.48(m, 4H), 0.97(t, *J*=7.3Hz, 6H) ^{13}C-NMR ($CDCl_3$): 183.3, 151.7, 143.3, 34.3, 26.4, 22.7, 13.8 FT-IR (KBr): 2958, 2931, 2872, 1674, 1524, 1458, 1379, 1232, 1118, 1066, 702 cm^{-1}

2,3-Dihydrothieno[3,4-*b*]-1,4-dioxin-5-carboxaldehyde (70a)



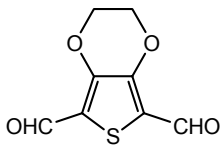
White solid, yield 82%, melting point: 137-138°C. ^{1}H-NMR ($CDCl_3$): 9.91(d, *J*=1.37Hz, 1H), 6.80(d, *J*=1.37Hz, 1H), 4.36-4.38(m, 2H), 4.27-4.29 (m, 2H) ^{13}C-NMR ($CDCl_3$): 180.2, 148.5, 141.8, 118.6, 110.8, 65.3, 64.4. FT-IR(KBr): 3107, 2958, 2843, 1649, 1493, 1441, 1374, 1264, 1177, 1061, 1012, 960, 909, 846, 761, 669, 570, 454 cm^{-1}

2,5-Dibromo-3,4-ethylenedioxythiophene (71)



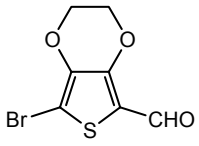
Silver gray solid, yield: 87%, melting point: 98-99ºC. ^{1}H-NMR ($CDCl_3$): 4.27(s, 4H) ^{13}C-NMR ($CDCl_3$): 139.7, 86.6, 65.0

2,3-Dihydrothieno[3,4-*b*]-1,4-dioxin-5,7-dicarboxaldehyde (72)



Yellow needle, Yield: 55%, melting point: 141-142ºC. ^{1}H-NMR ($CDCl_3$): 10.03(s, 2H), 4.47(s, 4H) ^{13}C-NMR ($CDCl_3$): 181.0, 147.3, 124.0, 65.1 FT-IR (KBr): 2958, 2837, 1665, 1647, 1503, 1465, 1394, 1369, 1271, 1232, 1200, 1104, 1080, 1008, 845, 801, 694 cm^{-1}

7-Bromo-2,3-dihydrothieno[3,4-*b*]-1,4-dioxine-5-carboxaldehyde (70b)

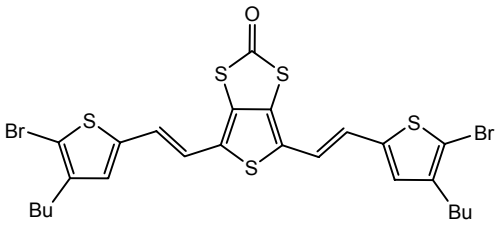


White solid, yield 80%. ^{1}H-NMR ($CDCl_3$): 9.82(s, 1H), 4.35-4.38(m, 4H) ^{13}C-NMR ($CDCl_3$): 178.9, 147.7, 140.2, 118.5, 101.7, 65.3, 64.8 FT-IR (KBr): 2956, 2874, 1642, 1498, 1435, 1380, 1360, 1251, 1231, 1131, 1088, 1023, 989, 956, 911, 843, 667, 517 cm^{-1}

General procedures for preparation of type 1 trimers

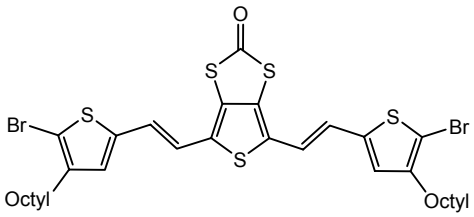
A solution of 0.5mmol 1,1'-[(4,6-thieno[3,4-*d*]-1,3-dithiol-2-one-diyl)bismethylene] bis[triphenylphosphonium chloride] and 1 mmol 5-bromo-2-carboxaldehyde alkylthiophene in anhydrous THF (10ml) and dry $CHCl_3$ 10ml was stirred and cooled to -78ºC under argon for 10 minutes. 10ml potassium *tert*-butoxide solution (0.5M in THF) was added slowly via syringe. After addition of the base, the reaction mixture was allowed to warm up to room temperature, and stirred for 24 hours. The reaction mixture was quenched with glacial acetic acid, and extracted with chloroform. Organic layer was collected, washed with water, dried over $MgSO_4$, and concentrated. Crude products were purified by silica gel columns (EtOAc:hexanes) to afford type 1 oligomers.

4,6-Bis((E)-2-(5-bromo-4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (75a)



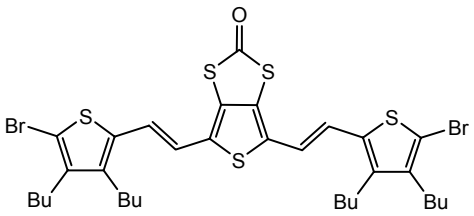
Orange red solid, yield 43%. Melting point: 148-149ºC. ^{1}H-NMR ($CDCl_3$): 6,76(d, *J*=15.8Hz, 2H), 6.75(s, 2H), 6.54(d, *J*=15.8Hz, 2H), 2.51(t, *J*=7.2Hz, 4H), 1.51-1.61(m, 4H), 1.30-1.42(m, 4H), 0.94(t, *J*=7.6Hz, 6H) ^{13}C-NMR ($CDCl_3$): 191.1, 143.2, 140.8, 130.3, 128.3, 126.0, 123.5, 118.0, 109.8, 31.7, 29.2, 22.3, 13.9 FT-IR (KBr): 3007, 2954, 2923, 2855, 1713, 1671, 1607, 1542, 1458, 1432, 1374, 1260, 1084, 1000, 919, 841, 808, 777, 749, 648, 567, 546,499, 458 cm^{-1} ESI-TOF(High Accuracy): MH^+ 658.8879, expected 658.8870

4,6-Bis((E)-2-(5-bromo-4-Octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (75b)



Orange red solid, yield 48%. Melting point: 109-110 ºC. ^{1}H-NMR ($CDCl_3$): 6.75(d, *J*=15.6Hz, 2H), 6.74(s, 2H), 6.53(d, *J*=15.6Hz, 2H), 2.49 (t, *J*=7.3Hz, 4H), 1.53-1.58(m, 4H), 1.25-1.31(m, 20H), 0.89(t, *J*=6.9Hz, 6H) ^{13}C-NMR ($CDCl_3$): 191.1, 143.2, 140.7, 130.1, 128.3, 126.0, 123.6, 117.9, 109.9, 31.9, 29.6, 29.5, 29.4, 29.3, 22.7, 14.2(carbon peaks of octyl groups overlapped) FT-IR (KBr):3009, 2922, 2851, 1709, 1667, 1606, 1544, 1463, 1426, 1369, 1264, 1165, 1003, 940, 917, 839, 802, 756, 701, 579, 453 cm^{-1} ESI-TOF(High Accuracy): MH^+ 771.0129, expected 771.0122

4,6-Bis((E)-2-(5-bromo-3,4-dibutylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3- dithiol-2-one (75c)

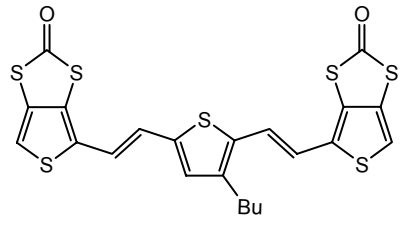


Red solid, yield 28%. Melting point: 105-106ºC. ^{1}H-NMR ($CDCl_3$): 6.92(d, *J*=15.6Hz, 2H), 6.60(d, *J*=15.6Hz, 2H), 2.62(t, *J*=7.3Hz, 4H), 2.51(t, *J*=7.3Hz, 4H), 1.39-1.51(m, 16H), 0.95-1.00(m, 12H) ^{13}C-NMR ($CDCl_3$): 191.5, 142.8, 141.8, 135.8, 130.4, 125.3, 122.3, 117.4, 109.9, 33.5, 31.7, 28.2, 27.6, 22.8, 22.7, 14.0, 13.9 1 (carbon peaks of butyl groups overlapped) FT-IR (KBr): 3015, 2928, 2860, 1709, 1666, 1600, 1461, 1431, 1382, 1255, 1083, 914, 847, 747, 707, 454 cm^{-1} ESI-TOF(High Accuracy): MH^+ 771.0102, expected 771.0122

General procedures for preparation of type-2 trimers

A solution of 1mmol [(4,6-thieno[3,4-*d*]-1,3-dithiol-2-one-yl)methylene] [triphenyl phosphonium chloride] and 0.5 mmol 2,5-dicarboxaldehyde of alkylthiophene in anhydrous EtOH (20ml) and dry $CHCl_3$ 10ml was stirred and cooled to -78ºC under argon. 10ml sodium ethoxide solution (0.8M in ethanol) was added slowly via syringe. After addition of the base, the reaction mixture was allowed to room temperature, and stirred for 24 hours. The reaction mixture was quenched with glacial acetic acid, and extracted with chloroform. Organic layer was collected, washed with water, dried over $MgSO_4$, and concentrated. Crude products were purified by columns (silica gel, EtOAc:hexanes), followed by precipitation in methanol to afford type 2 trimers.

4-((1E)-2-(4-Butyl-5-((E)-2-(2-oxothieno[3,4-*d*]-1,3-dithiol-4-yl)vinyl)thiophen-2-yl) vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (76a)

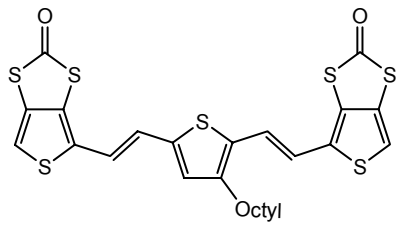


Deep red solid, yield 35%. Melting point: 138-139ºC. ^{1}H-NMR ($CDCl_3$): 7.16(s, 2H), 7.00(d, *J*=15.8Hz, 1H), 6.94(d, *J*=15.8Hz, 1H), 6.88(s, 1H), 6.78(d, *J*=15.8Hz, 1H), 6.77(d, *J*=15.8Hz, 1H), 2.64(t, *J*=7.6Hz, 2H), 1.51-1.65(m, 2H), 1.34-1.43(m, 2H), 0.97(t, *J*=7.2Hz, 3H) ^{13}C-NMR ($CDCl_3$): 192.8, 192.7, 143.7, 139.7, 135.5, 132.4, 132.0, 130.7, 128.7, 125.5, 124.9, 123.7, 122.1, 119.0, 118.3, 113.7, 113.5, 32.9, 28.2, 22.4, 14.0 (carbon peaks of aromatic regions overlapped, only 15 aromatic carbon peaks were counted) FT-IR (KBr): 3105, 3010, 2954, 2923, 2853,

1701, 1642, 1458, 1375, 1311, 1263, 1161, 949, 919, 835, 717, 581, 547, 519, 460 cm^{-1}

ESI-TOF(High Accuracy): MH^+ 536.9262, expected 536.9268

4-((1E)-2-(4-Octyl-5-((E)-2-(2-oxothieno[3,4-*d*]-1,3-dithiol-4-yl)vinyl) thiophen-2-yl) vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (76b)

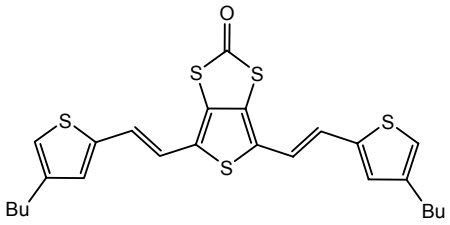


Deep red solid, yield 32%. Melting point: 145-146ºC. ^{1}H-NMR ($CDCl_3$): 7.16(s, 2H), 7.00(d, *J*=15.8Hz, 1H), 6.94(d, *J*=15.8Hz, 1H), 6.88(s, 1H), 6.78(d, *J*=15.8Hz, 1H), 6.76(d, *J*=15.8Hz, 1H), 2.62(t, *J*=7.2Hz, 2H), 1.59-1.64(m, 2H), 1.25-1.35(m, 10H), 0.88(t, *J*=6.5Hz, 3H) ^{13}C-NMR ($CDCl_3$): 192.8, 192.7, 143.9, 139.7, 135.5, 132.4, 132.1, 130.8, 128.9, 125.6, 125.0, 123.8, 122.1, 119.1, 118.3, 113.8, 113.6, 32.0, 30.9, 29.5, 29.3, 28.5, 22.8, 14.2 (carbon peaks of aromatic regions overlapped, only 15 aromatic carbon peaks were counted) FT-IR (KBr): 3110, 2924, 2853, 1704, 1647, 1540, 1521, 1458, 1432, 1315, 920, 838, 724, 656, 548, 521, 462 cm^{-1} ESI-TOF(High Accuracy): MH^+ 592.9888, expected 592.9894

General procedures for preparation of type 3 trimers

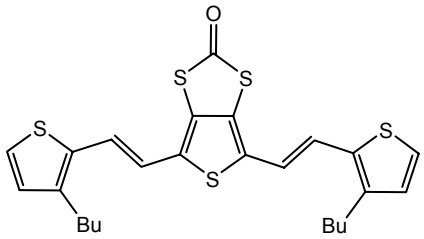
Synthesis of type 3 trimers was similar to the preparation of type 1 trimers. Further purification process was achieved by column (silica gel, hexanes/EtOAc), followed by dissolving in chloroform, and droping slowly into methanol. Precipitates were coloected by filtering, washed with methanol and a few milliliters hexanes, and dried over vacuum oven at 45ºC for overnight.

4,6-Bis((E)-2-(4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (77a)



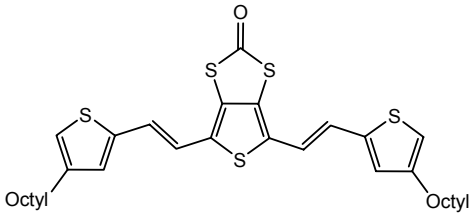
Yellow solid, yield 25%, melting point: 105-106 ºC. ^{1}H-NMR ($CDCl_3$): 6.95(s, 2H), 6.93(d, *J*=15.6Hz, 2H), 6.85(s, 2H), 6.73(d, *J*=15.6Hz, 2H), 2.57(t, *J*=7.2Hz, 4H), 1.57-1.63(m, 4H), 1.34-1.39(m, 4H), 0.94(t, *J*=7.2Hz, 6H) ^{13}C-NMR ($CDCl_3$): 191.6, 144.2, 141.0, 130.2, 128.7, 125.6, 124.3, 120.6, 117.8, 32.5, 30.1, 22.3, 13.9 FT-IR (KBr): 3097, 3013, 2956, 2924, 2857, 1709, 1666, 1544, 1461, 1436, 1378, 1240, 923, 857, 780, 754, 732, 590 cm^{-1} ESI-TOF (High Accuracy): MH^+ 503.0654, expected 503.0660

4,6-Bis((E)-2-(3-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (77b)



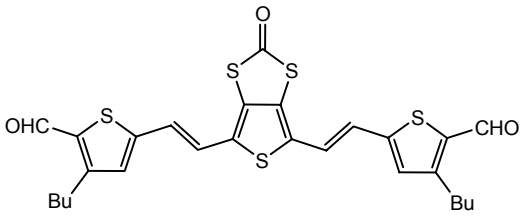
Red solid, yield 18%, melting point: 87-88 ºC. ^{1}H-NMR ($CDCl_3$): 7.15(d, *J*=5.2Hz, 2H), 7.00(d, *J*=15.6Hz, 2H), 6.87(d, *J*=5.2Hz, 2H), 6.71(d, *J*=15.6Hz, 2H), 2.68(t, *J*=7.3Hz, 4H), 1.57-1.63(m, 2H), 1.35-1.43(m, 4H), 0.96(t, *J*=7.3Hz, 6H) ^{13}C-NMR ($CDCl_3$): 191.8, 142.8, 135.2, 130.4, 130.1, 125.2, 124.4, 122.6, 117.5, 33.1, 28.3, 22.5, 14.0 FT-IR (KBr): 3082, 3009, 2955, 2924, 2857, 1702, 1660, 1600, 1459, 1415, 1254, 918, 848, 827, 757, 709, 634cm^{-1} ESI-TOF(High Accuracy): MH^+ 503.0648, expected 503.0660

4,6-Bis((E)-2-(4-octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (77c)



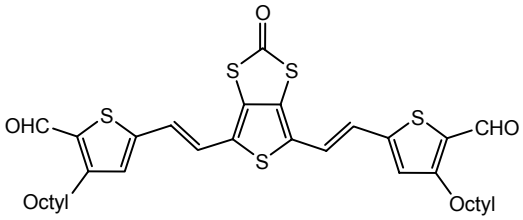
Red solid, yield 32%. Melting point: 102-103ºC. ^{1}H-NMR ($CDCl_3$): 6.94(s, 2H), 6.92(d, *J*=15.6Hz, 2H), 6.85(s, 2H), 6.72(d, *J*=15.6Hz, 2H), 2.56(t, *J*=7.8Hz, 4H), 1.58-1.62(m, 4H), 1.27-1.31(m, 20H), 0.89(t, *J*=6.9Hz, 6H) ^{13}C-NMR ($CDCl_3$): 191.6, 144.3, 141.0, 130.2, 128.7, 125.6, 124.3, 120.6, 117.8, 31.9, 30.4, 30.3, 29.4, 29.3, 29.2, 22.7, 14.1. FT-IR (KBr): 3089, 3006, 2955, 2919, 2849, 1711, 1667, 1606, 1467, 1241, 921, 845, 757, 724, 700, 651, 587 cm^{-1} ESI-TOF (High Accuracy): MH^+ 615.1918, expected 615.1912

4,6-Bis((E)-2-(5-formyl-4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (78a)



Red solid. ^{1}H-NMR ($CDCl_3$): 10.00(s, 2H), 7.03(s, 2H), 6.98(d, *J*=15.6Hz, 2H), 6.93(d, *J*=15.6Hz, 2H), 2.93(t, *J*=7.8Hz, 4H), 1.65-1.70(m, 4H), 1.37-1.45(m, 4H), 0.96(t, *J*=7.3Hz, 6H).

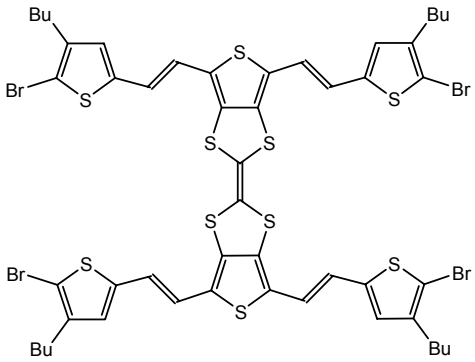
4,6-Bis((E)-2-(5-formyl-4-octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (78b)



Deep red solid. ^{1}H-NMR ($CDCl_3$): 10.00(s, 2H), 7.02(s, 2H), 6.98(d, *J*=15.6Hz, 2H),

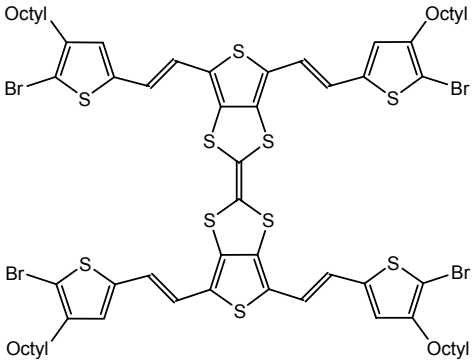
6.93(d, *J*=15.6Hz, 2H), 2.92(t, *J*=7.8Hz, 4H), 1.65-1.72(m, 4H), 1.25-1.37(m, 20H), 0.89(t, *J*=6.9Hz, 6H).

2-(4,6-Bis((E)-2-(5-bromo-4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-ylidene)-4,6-bis((E)-2-(5-bromo-4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiole (80a)



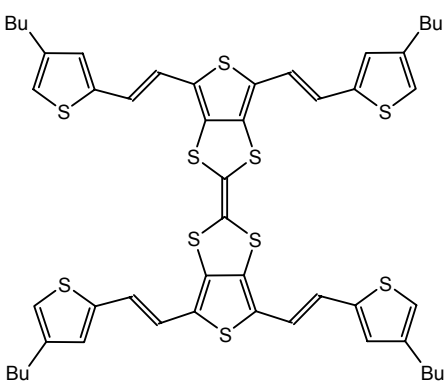
To a dry flask equipped with a condenser added 90mg (0.136mmol) (4,6-bis((E)-2-(5-bromo-4-butylthiophen-2-yl)vinyl)thieno [3,4-*d*]-1,3-dithiol-2-one (**75a**) and 1g triethyl phophite (excess), the mixture was stirred at 120ºC for 8hours under argon protection. After cooled down to room temperature, the reaction mixture was filtered, solid portion was collected, washed with small amount of diethyl ether, hexanes, and dried over vacuum oven at 60ºC for 24 hours afford 62mg 2-(4,6-Bis((E)-2-(5-bromo-4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-ylidene)-4,6-bis((E)-2-(5-bromo-4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiole as red solid corresponding to a yield of 71%. Melting point: 211-212ºC (decomposed, turned into black immediately) ^{1}H-NMR ($CDCl_3$): 6.51(s, 4H), 6.31(d, *J*=15.6Hz, 4H), 6.17(d, J=15.6Hz, 4H), 2.35(t, *J*=7.2Hz, 8H), 1.46-1.52(m, 8H), 1.32-1.39(m, 8H), 0.96(t, *J*=7.2Hz, 12H) FT-IR (KBr):3007, 2953, 2925, 2857, 1648, 1542, 1510, 1459, 1429, 1318, 1258, 1007, 920, 830, 766 cm^{-1} Elemental Analysis: Anal. Calcd. for $C_{50}H_{48}Br_4S_{10}$: C 46.58, H 3.75 Found: C 46.50, H 3.47. MADLI-TOF: [M] 1283.7, expected: 1283.8

2-(4,6-Bis((E)-2-(5-bromo-4-octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-ylidene)-4,6-bis((E)-2-(5-bromo-4-octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiole (80b)



Preparation of **80b** is similar to that of **80a**, which affords the product as a red solid with a yield of 73%. Melting point: 155-157ºC (decomposed, turned into black immediately). ^{1}H-NMR ($CDCl_3$): 6.69(s, 4H), 6.58(d, *J*=15.6Hz, 4H), 6.43(d, *J*=15.6Hz, 4H), 2.46(d, *J*=7.2Hz, 8H), 1.53-1.57(m, 8H), 1.29-1.34(m, 40H), 0.90(t, *J*=7.2Hz, 12H) FT-IR (KBr): 3007, 2924, 2853, 1648, 1545, 1513, 1462, 1433, 1315, 1261, 1016, 918, 834, 767 cm^{-1} Elemental Analysis: Anal. Calcd. for $C_{66}H_{80}Br_4S_{10}$: C 52.37, H 5.33 Found: C 52.21, H 5.10 MALDI-TOF: [M] 1508.01, expected: 1508.02

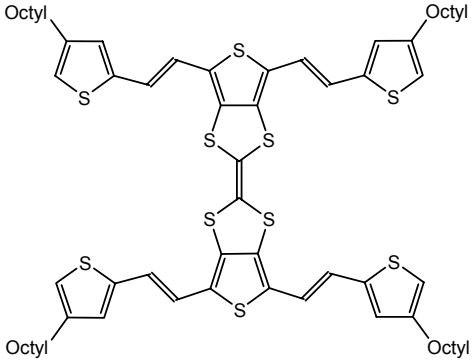
2-(4,6-Bis((E)-2-(4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-ylidene)-4,6-bis((E)-2-(4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiole (80c)



Preparation process is similar to synthesis of **80a.** Red solid, yield 48%. Melting point: 221-222ºC (turned into black from red). ^{1}H-NMR($CDCl_3$): 6.94(s, 4H), 6.82(s, 4H), 6.81(d, *J*=15.6Hz, 4H), 6.66(d, *J*=15.6Hz, 4H), 2.57(t, *J*=7.2Hz, 8H), 1.58-

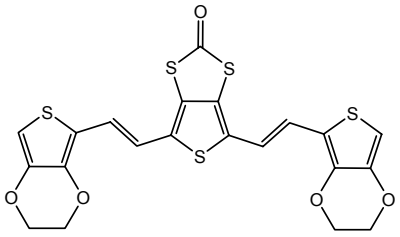
1.64(m, 8H), 1.35-1.40(m, 8H), 0.94(t, *J*=7.2Hz, 12H) ^{13}C-NMR($CDCl_3$): 144.0, 141.4, 132.7, 128.3, 126.4, 123.6, 120.1, 118.7, 118.1, 32.5, 30.1, 22.4, 13.9 FT-IR(KBr): 3092, 3009, 2953, 2923, 2856, 1645, 1541, 1460, 1322, 1262, 1237, 922, 842, 741 cm^{-1}. Elemental Analysis: Anal. Calcd. for $C_{50}H_{52}S_{10}$: C 61.68, H 5.38 Found: C 61.48, H 5.19 MALDI-TOF: [M] 972.16, expected: 972.13

2-(4,6-Bis((E)-2-(4-octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-ylidene)-4,6-bis((E)-2-(4-octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiole (80d)



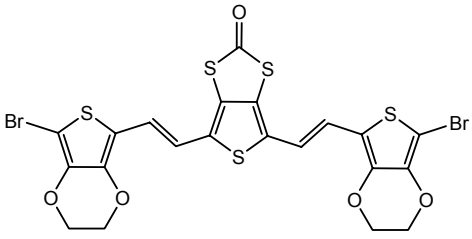
The preparation of compound **80d** is same as that of **80c**. Red solid, yield 32%. ^{1}H-NMR ($CDCl_3$): 6.85(s, 4H), 6.74(s, 4H), 6.70(d, *J*=15.6Hz, 4H), 6.56(d, *J*=15.6Hz, 4H), 2.51(t, *J*=7.8Hz, 8H), 1.56-1.62(m, 8H), 1.26-1.32(m, 40H), 0.90(t, *J*=6.9Hz, 12H) ^{13}C-NMR ($CDCl_3$): 144.0, 141.5, 132.9, 128.2, 126.3, 123.4, 120.0, 118.2, 118.1, 32.0, 30.5, 30.4, 29.5, 29.4, 29.3, 22.7, 14.2. FT-IR: 3012, 2921, 2851, 1602, 1543, 1462, 1375, 1298, 1266, 1180, 923, 860, 807, 767, 722, 585 cm^{-1} Elemental analysis: Anal. Calcd. for $C_{66}H_{84}S_{10}$: C 66.17, H 7.07 Found: C 65.98, H 6.82 MALDI-TOF: [M] 1196.4, expected 1196.4

4-((E)-2-(2,3-Dihydrothieno[3,4-*b*]-1,4-dioxin-5-yl)vinyl)-6-((E)-2-(2,3-dihydro thieno[3,4-*b*]-1,4-dioxin-7-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (81a)



Red solid, yield 18%. Melting point: 230-232ºC (decomposed). ^{1}H-NMR ($CDCl_3$): 6.86(d, *J*=15.5Hz, 2H), 6.73(d, *J*=15.5Hz, 2H), 6.29(s, 2H), 4.30-4.32(m, 4H), 4.22-4.25(m, 4H) ^{13}C-NMR ($CDCl_3$): 192.0, 142.1, 140.3, 130.6, 125.5, 120.5, 116.5, 116.0, 99.4, 65.0, 64.7 FT-IR (KBr): 3101, 2978, 2920, 2871, 1711, 1660, 1602, 1500, 1482, 1441, 1365, 1255, 1168, 1067, 961, 928, 904, 851, 712, 677cm^{-1} ESI-TOF (High Accuracy): MH^+ 506.9515, expected 506.9518.

4,6-Bis((E)-2-(5-bromo-2,3-dihydrothieno[3,4-*b*]-1,4-dioxin-7-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (81b)



Red solid, yield 32%. Melting point: >250ºC ^{1}H-NMR ($CDCl_3$): 6.62(d, *J*=11.5Hz, 2H), 6.34(d, *J*=11.5Hz, 2H), 4.24-4.26(m, 4H), 4.21-4.22(m, 4H) FT-IR (KBr):2979, 2927, 2872, 1718, 1666, 1608, 1578, 1487, 1435, 1362, 1267, 1089, 952, 915, 805, 762, 584 cm^{-1}. ESI-TOF (High Accuracy): MH^+ 662.7722, expected 662.7728.

APPENDIX 1

^{1}H and ^{13}C-NMR spectra of thieno[3,4-*d*]-1,3-dithiole-2-thione (1)

```
Filename          = xc-iii-17-5.jdf
Experiment        = single_pulse.exp
Sample_id         = S#706989
Solvent           = CHLOROFORM-D
Creation_time     = 31-JAN-2003 00:02:01
Revision_time     =  5-FEB-2007 12:35:48
Current_time      =  5-FEB-2007 12:36:29

Content           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
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X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Mod_return        = 1
Scans             = 16

X_90_width        = 15[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 7.5[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 25
Relaxation_delay  = 1[s]
Temp_get          = 21.1[dC]
Unblank_time      = 2[us]
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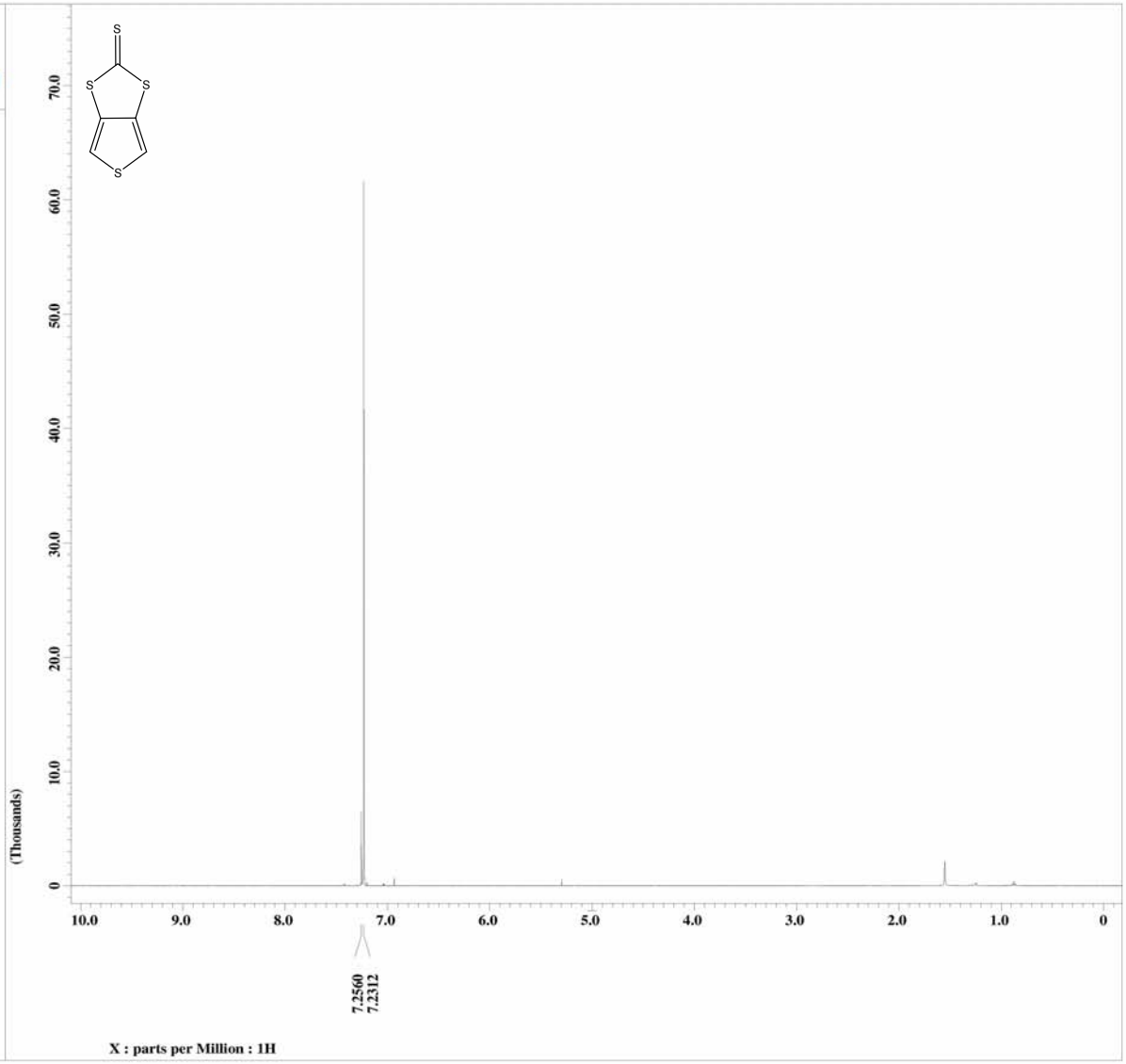

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Revision_time     =  5-FEB-2007 12:38:33
Current_time      =  5-FEB-2007 12:38:55

Content           = Single Pulse with Bro
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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]
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Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Mod_return        = 1
Scans             = 793

X_90_width        = 14[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.66666667[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 29
Relaxation_delay  = 2[s]
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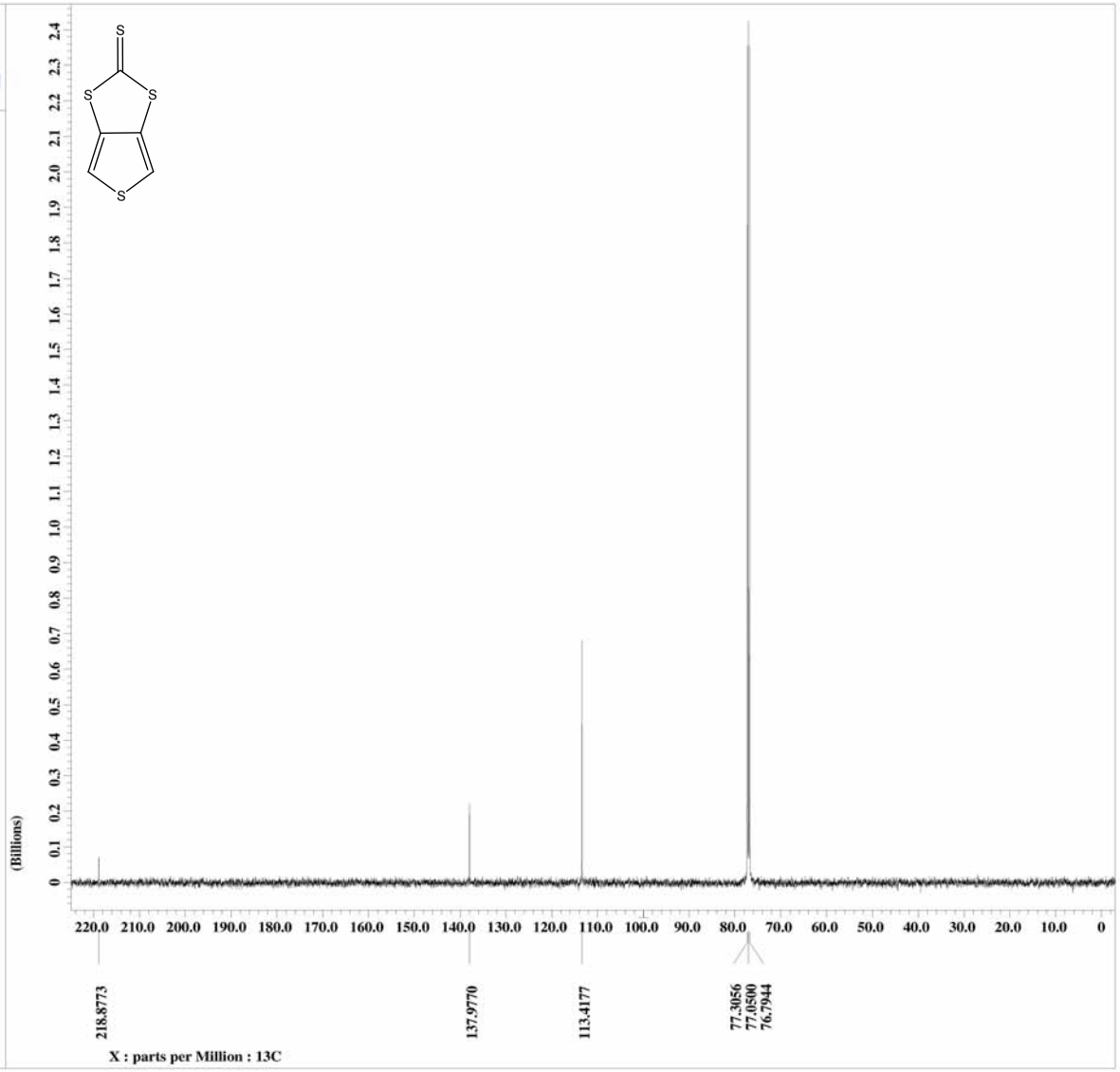
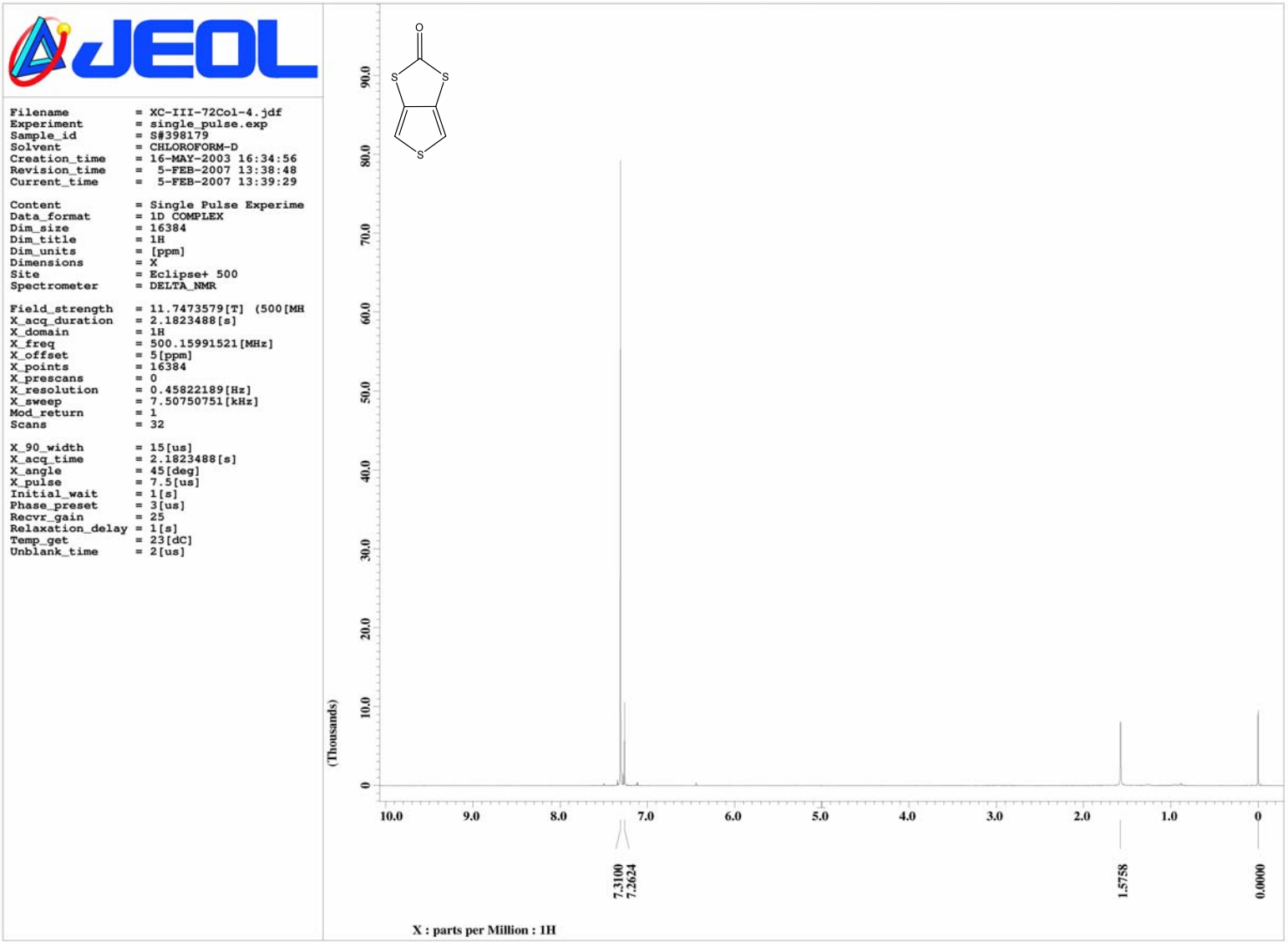


APPENDIX 2

^{1}H and ^{13}C-NMR spectra of thieno[3,4-*d*]-1,3-dithiol-2-one (2)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Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
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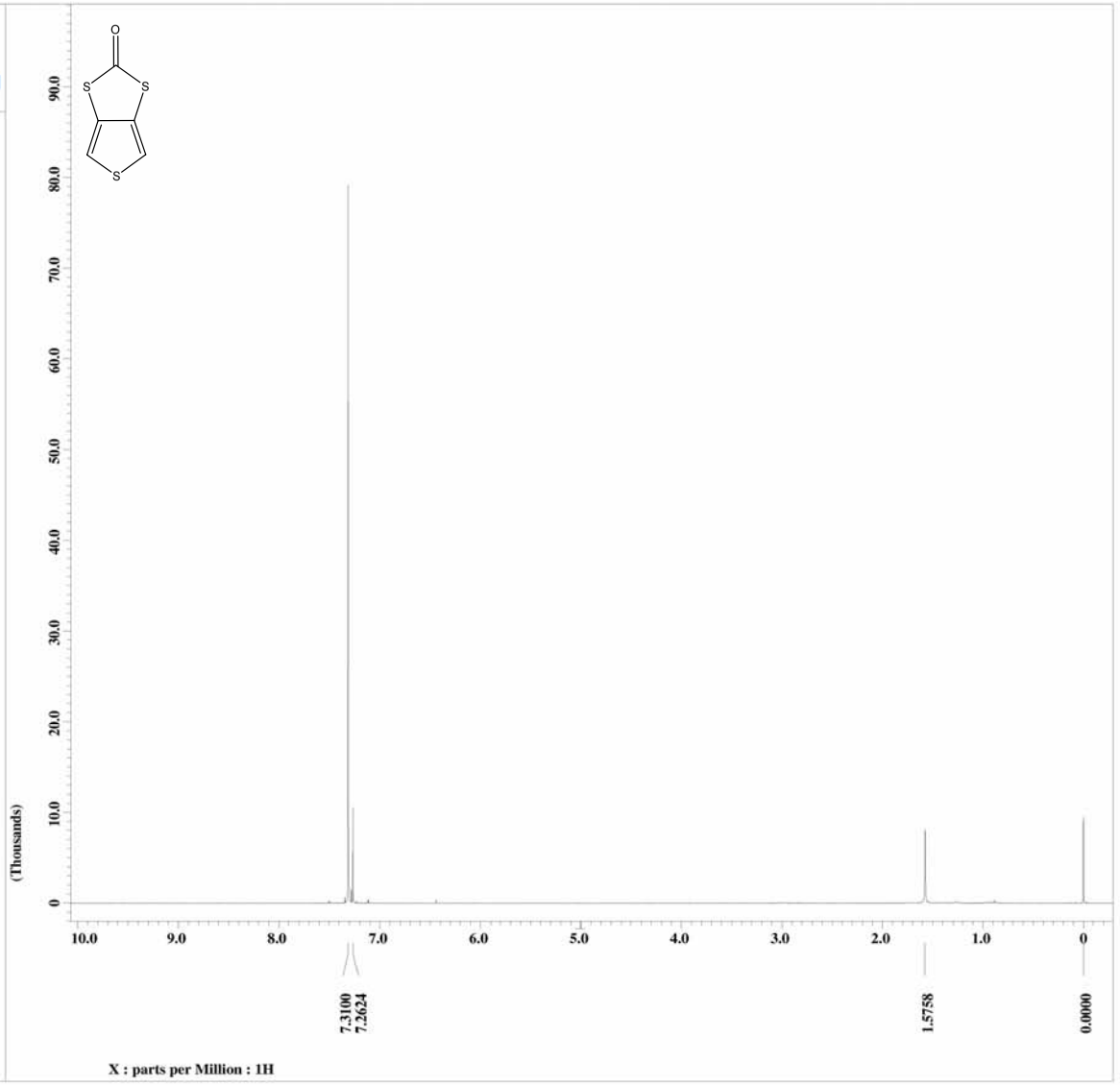
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 25
Relaxation_delay = 1[s]
Temp_get = 23[dC]
Unblank_time = 2[us]
O
S
S
S
(Thousands)
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3100
7.2624
1.5758
0.0000
X : parts per Million : 1H

```
Filename          = XC-III-72Col-4.jdf
Experiment        = single_pulse.exp
Sample_id         = S#398179
Solvent           = CHLOROFORM-D
Creation_time     = 16-MAY-2003 16:34:56
Revision_time     =  5-FEB-2007 13:38:48
Current_time      =  5-FEB-2007 13:39:29

Content           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

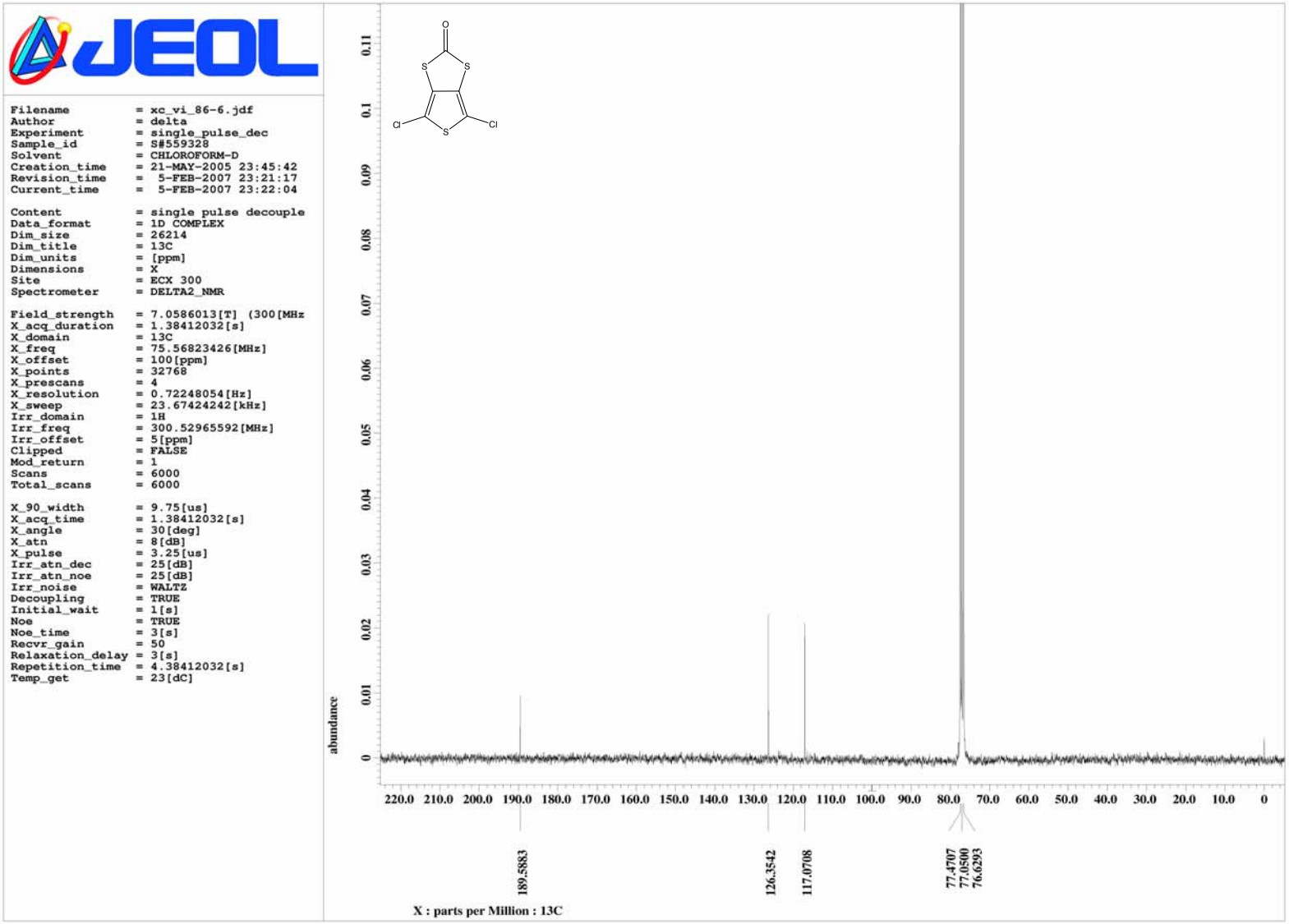
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Mod_return        = 1
Scans             = 32

X_90_width        = 15[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 7.5[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 25
Relaxation_delay  = 1[s]
Temp_get          = 23[dC]
Unblank_time      = 2[us]
```



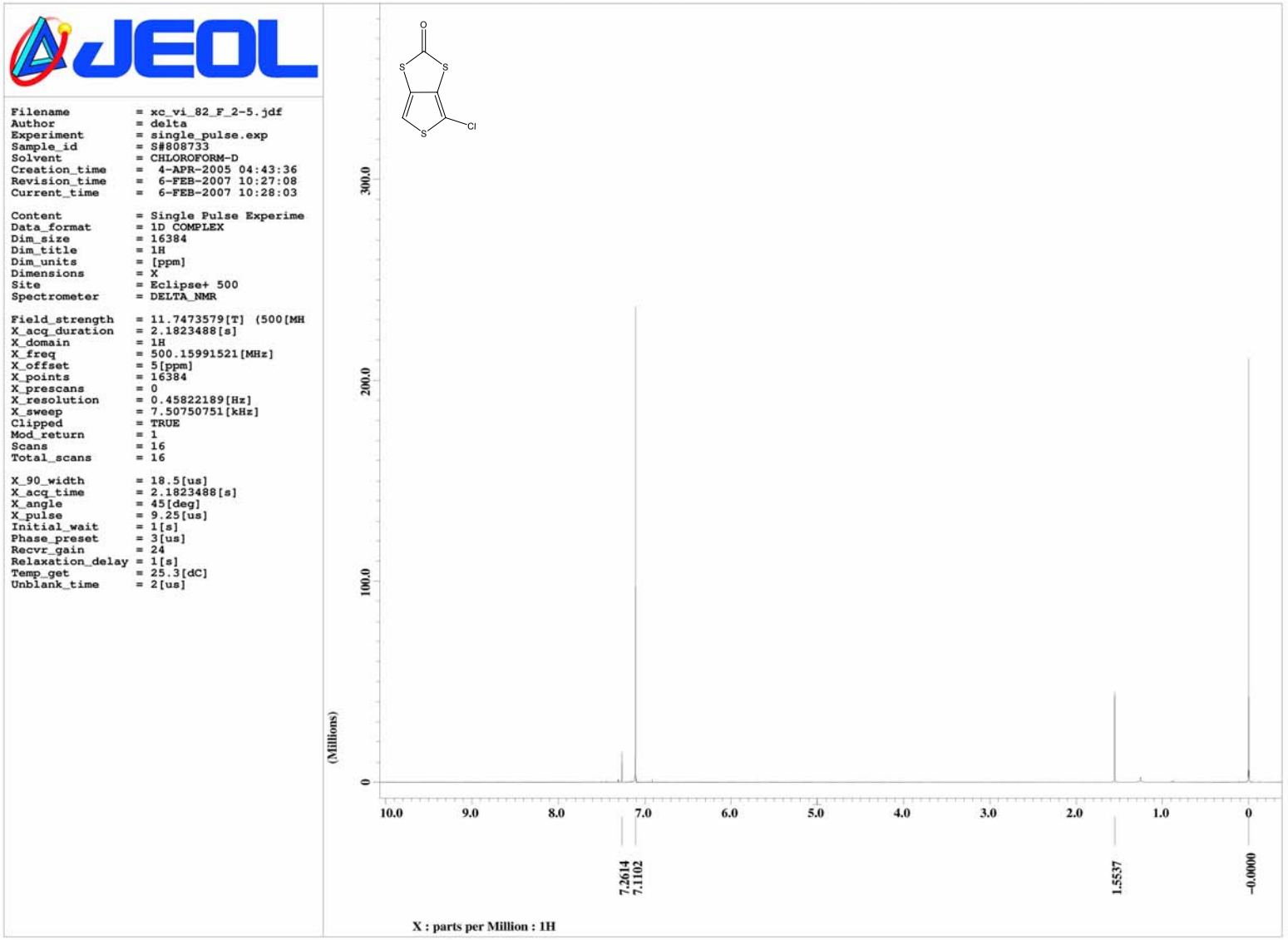
APPENDIX 3

^{13}C-NMR spectrum of 4,6-dichlorothieno[3,4-*d*]-1,3-dithiol-2-one (5)


Filename = xc_vi_86-6.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#559328
Solvent = CHLOROFORM-D
Creation_time = 21-MAY-2005 23:45:42
Revision_time = 5-FEB-2007 23:21:17
Current_time = 5-FEB-2007 23:22:04
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 1.38412032[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.72248054[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 6000
Total_scans = 6000
X_90_width = 9.75[us]
X_acq_time = 1.38412032[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 = 3[s]
Recvr_gain = 50
Relaxation_delay = 3[s]
Repetition_time = 4.38412032[s]
Temp_get = 23[dC]
O
S
S
Cl
S
Cl
abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
189.5883
126.3542
117.0708
77.4707
77.0500
76.6293
X : parts per Million : 13C

APPENDIX 4

^{1}H and ^{13}C-NMR spectrum of 4-chlorothieno[3,4-*d*]-1,3-dithiol-2-one (6)

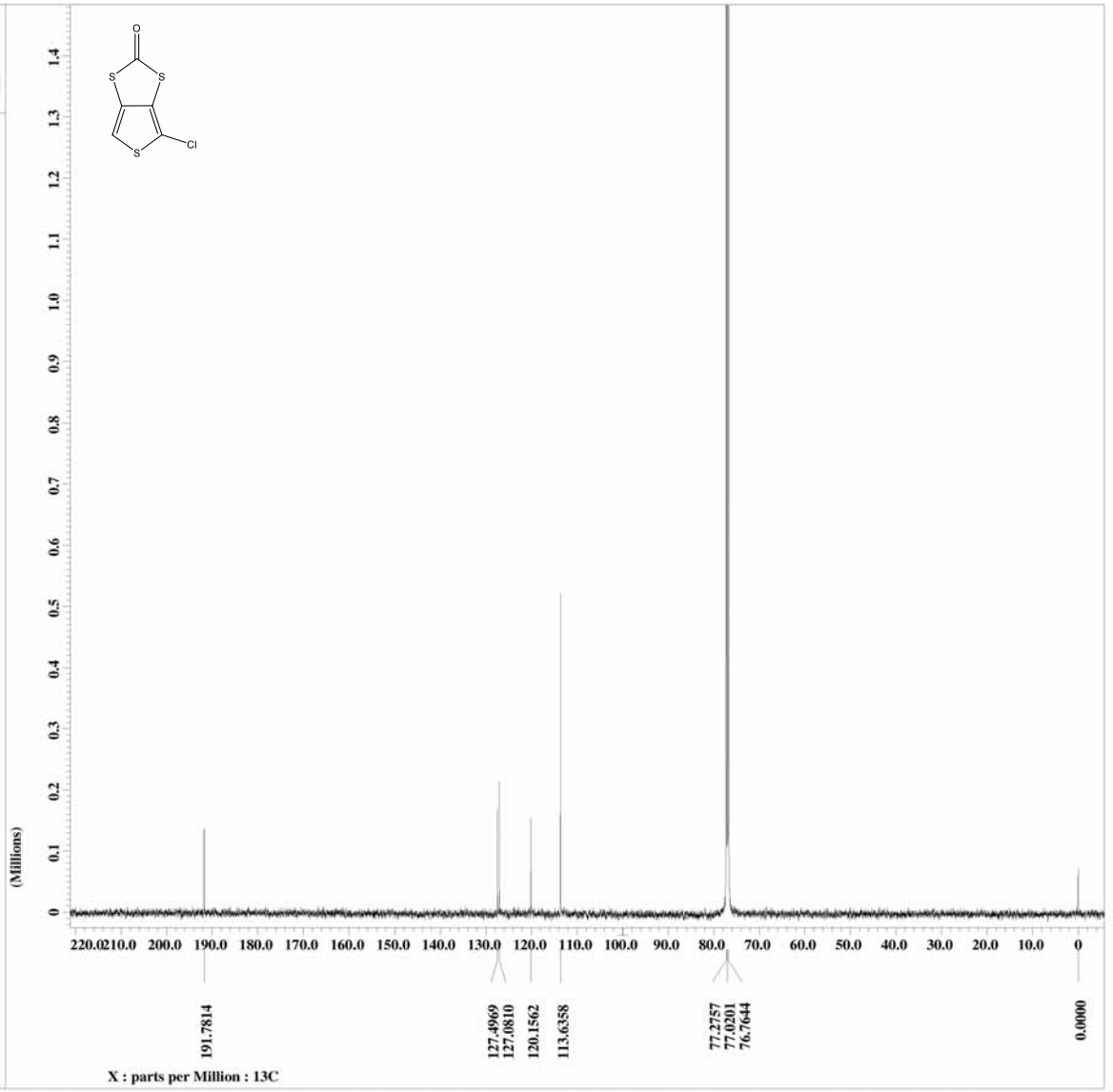

Filename = xc_vi_82_F_2-5.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#808733
Solvent = CHLOROFORM-D
Creation_time = 4-APR-2005 04:43:36
Revision_time = 6-FEB-2007 10:27:08
Current_time = 6-FEB-2007 10:28:03
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = TRUE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 24
Relaxation_delay = 1[s]
Temp_get = 25.3[dC]
Unblank_time = 2[us]
O
S
S
S
Cl
300.0
200.0
100.0
0
(Millions)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2614
7.1102
1.5537
-0.0000
X : parts per Million : 1H

```
Filename          = xc_vi_129-6.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#828219
Solvent           = CHLOROFORM-D
Creation_time     = 11-JUL-2005 11:05:06
Revision_time     =  6-FEB-2007 10:31:00
Current_time      =  6-FEB-2007 10:31:42

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

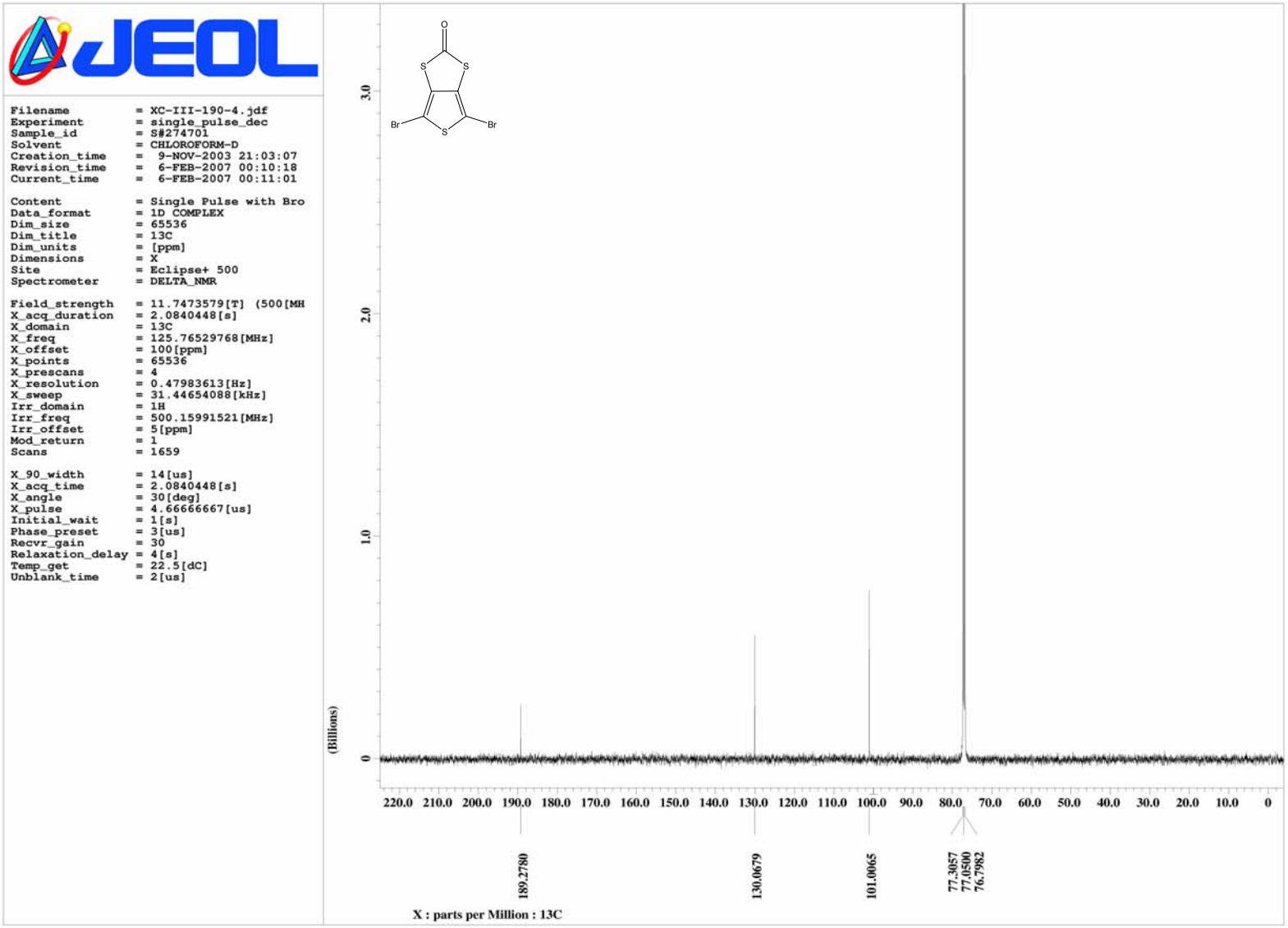
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 5996
Total_scans       = 5996

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]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 4[s]
Temp_get          = 27.3[dC]
Unblank_time      = 2[us]
```



APPENDIX 5

^{13}C-NMR spectrum of 4,6-dibromothieno[3,4-*d*]-1,3-dithiol-2-one (7)



```
Filename          = XC-III-190-4.jdf
Experiment        = single_pulse_dec
Sample_id         = S#274701
Solvent           = CHLOROFORM-D
Creation_time     =  9-NOV-2003 21:03:07
Revision_time     =  6-FEB-2007 00:10:18
Current_time      =  6-FEB-2007 00:11:01

Content           = Single Pulse with Bro
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]
Mod_return        = 1
Scans             = 1659

X_90_width        = 14[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.66666667[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 4[s]
Temp_get          = 22.5[dC]
Unblank_time      = 2[us]
```

APPENDIX 6

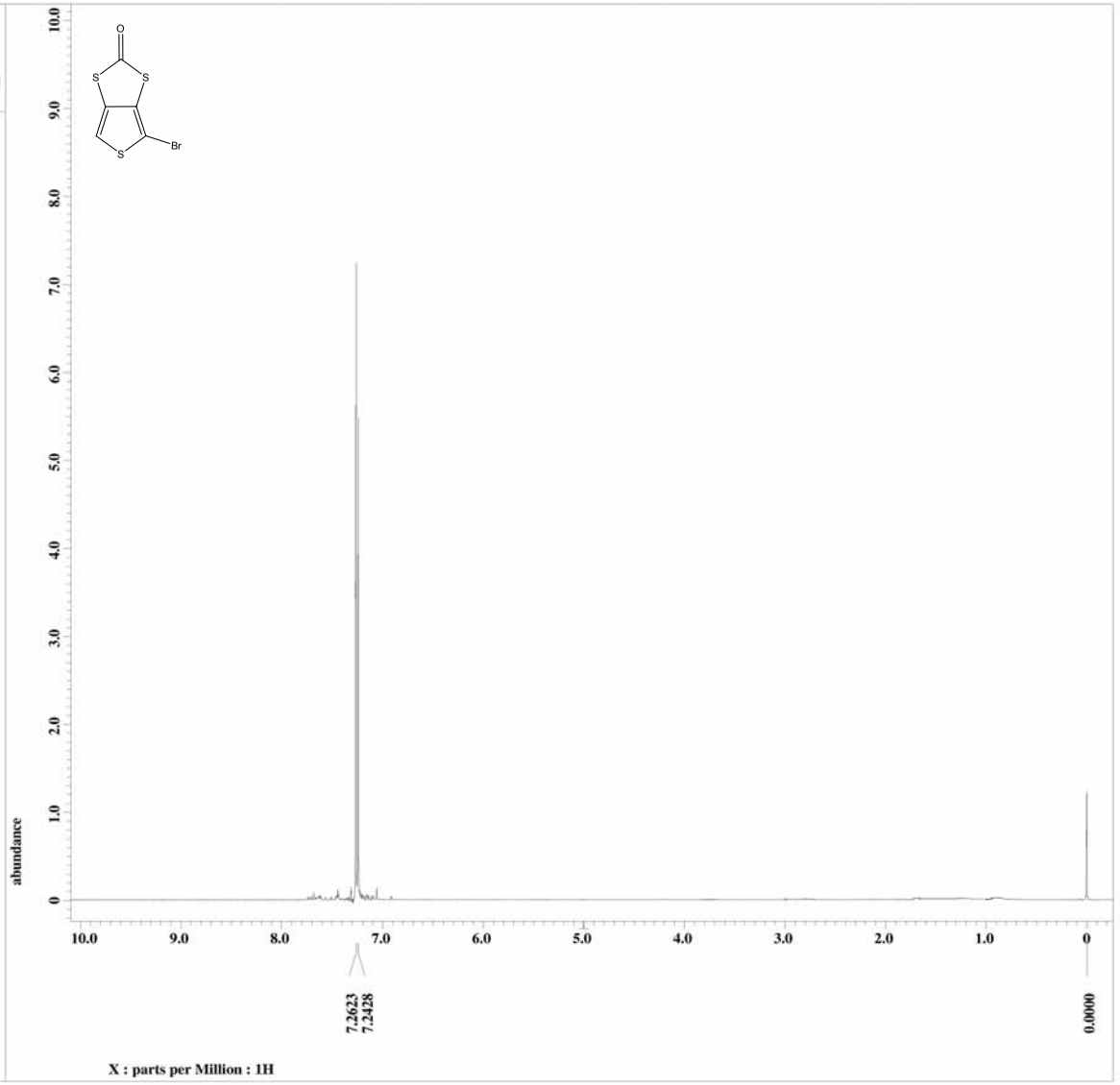
^{1}H and ^{13}C-NMR spectra of 4-bromothieno[3,4-*d*]-1,3-dithiol-2-one (8)

```
Filename          = xc_vi_93-10.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#621448
Solvent           = CHLOROFORM-D
Creation_time     =  2-JUN-2005 18:13:33
Revision_time     =  5-FEB-2007 23:47:46
Current_time      =  5-FEB-2007 23:48:16

Content           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 46
Relaxation_delay  = 2[s]
Repetition_time   = 4.90717696[s]
Temp_get          = 22.8[dC]
```

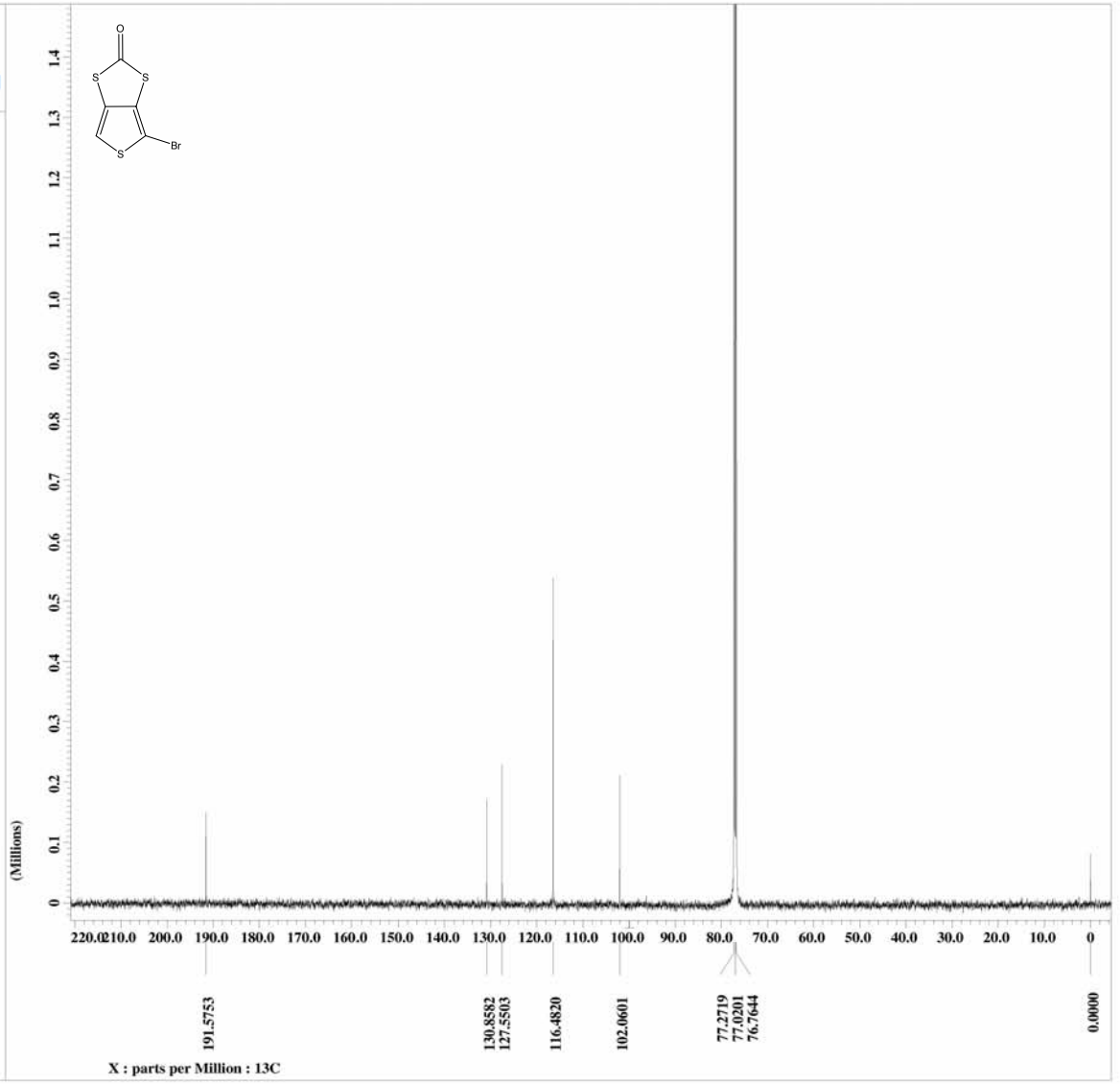


```
Filename          = xc_vi_130-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#16126
Solvent           = CHLOROFORM-D
Creation_time     = 10-JUL-2005 11:15:56
Revision_time     = 10-JUL-2005 13:19:12
Current_time      =  6-FEB-2007 10:39:37

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

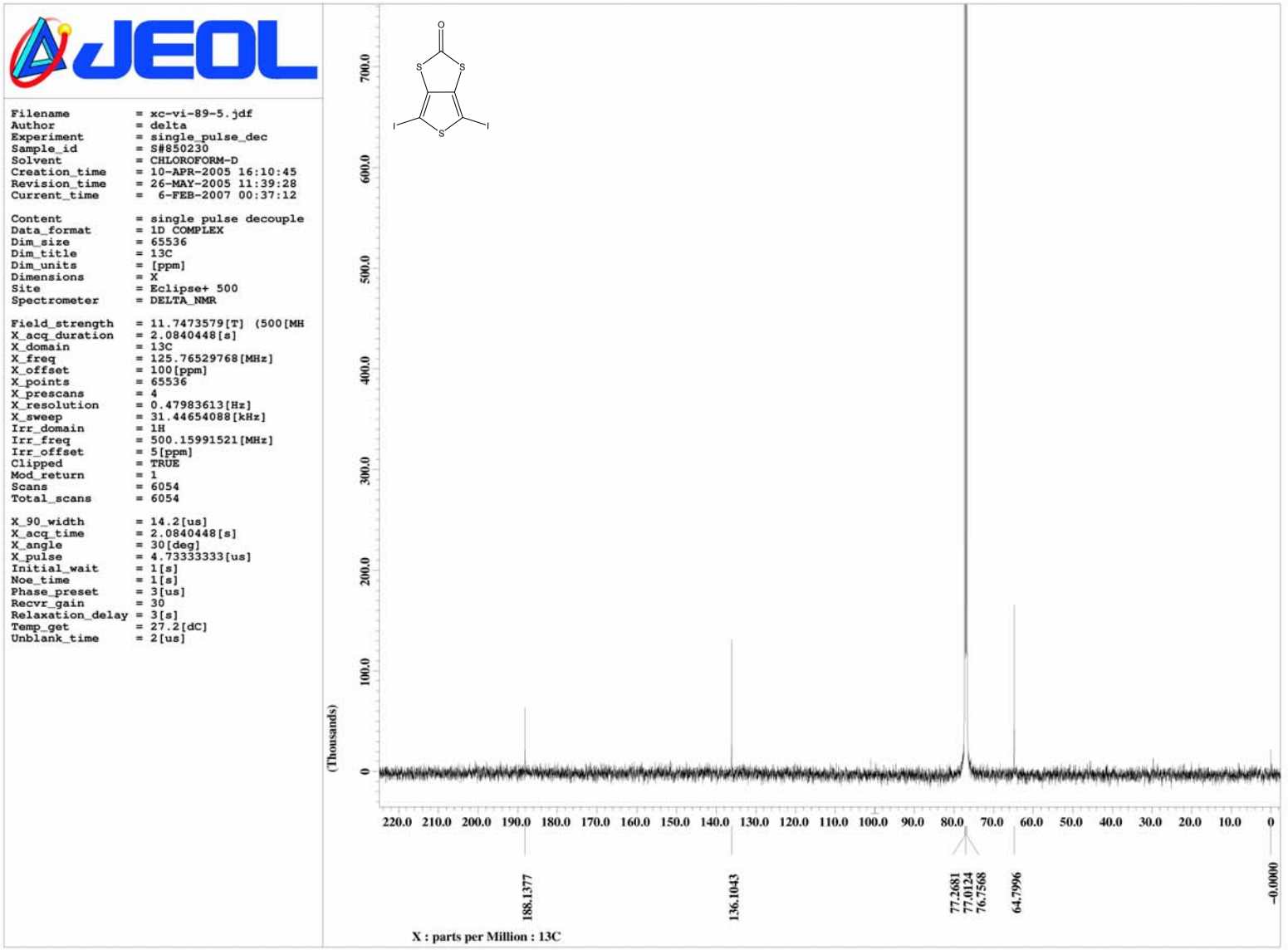
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 5360
Total_scans       = 5360

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]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 4[s]
Temp_get          = 27[dC]
Unblank_time      = 2[us]
```



APPENDIX 7

^{13}C-NMR spectrum of 4,6-diiodothieno[3,4-*d*]-1,3-dithiol-2-one (9)


Filename = xc-vi-89-5.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#850230
Solvent = CHLOROFORM-D
Creation_time = 10-APR-2005 16:10:45
Revision_time = 26-MAY-2005 11:39:28
Current_time = 6-FEB-2007 00:37:12
Content = single pulse decouple
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 = TRUE
Mod_return = 1
Scans = 6054
Total_scans = 6054
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 3[s]
Temp_get = 27.2[dC]
Unblank_time = 2[us]
O
S
S
I
S
I
(Thousands)
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
188.1377
136.1043
77.2681
77.0124
76.7568
64.7996
-0.0000
X : parts per Million : 13C

APPENDIX 8

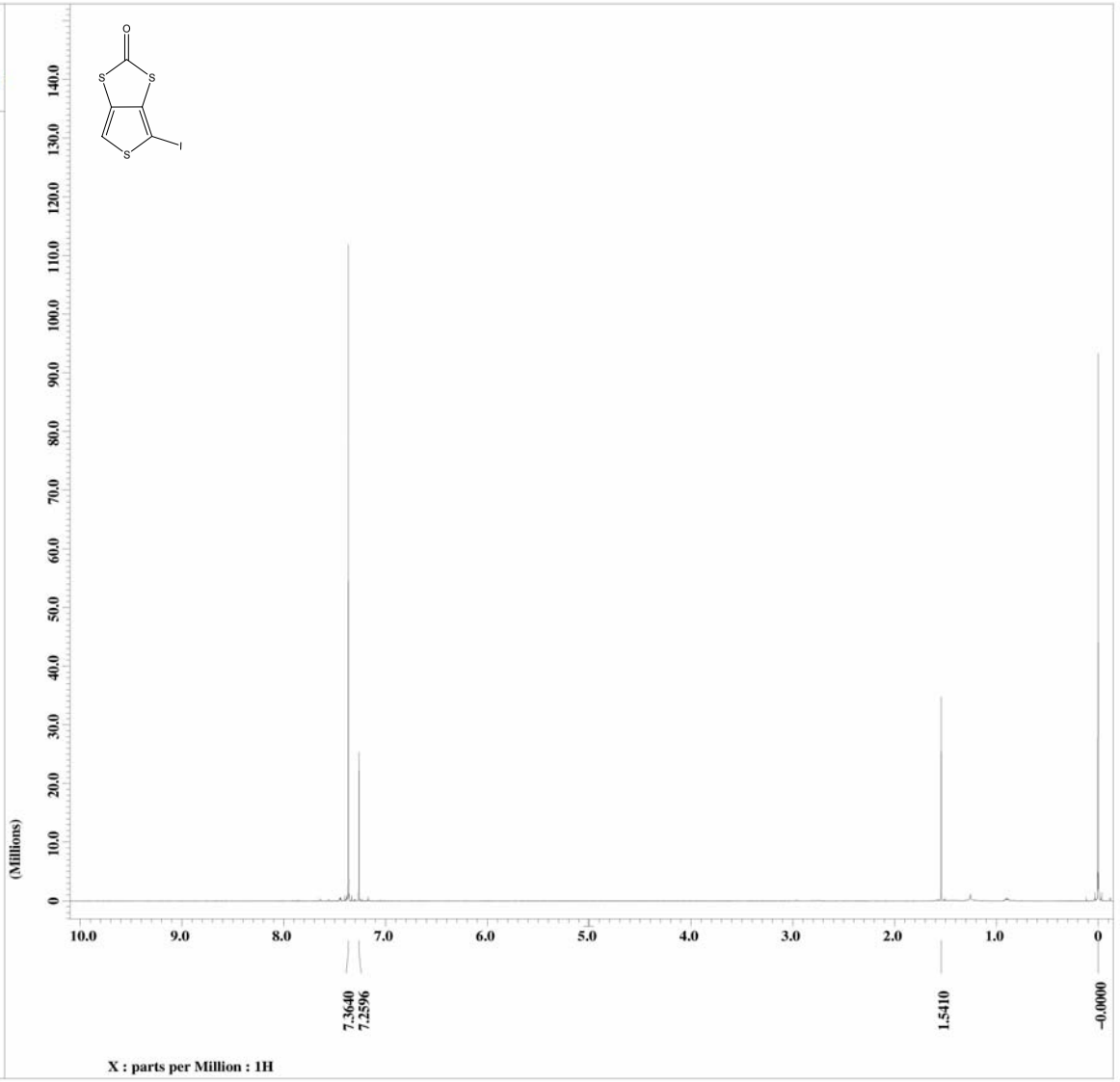
^{1}H and ^{13}C-NMR spectra of 4-iodothieno[3,4-*d*]-1,3-dithiol-2-one (10)

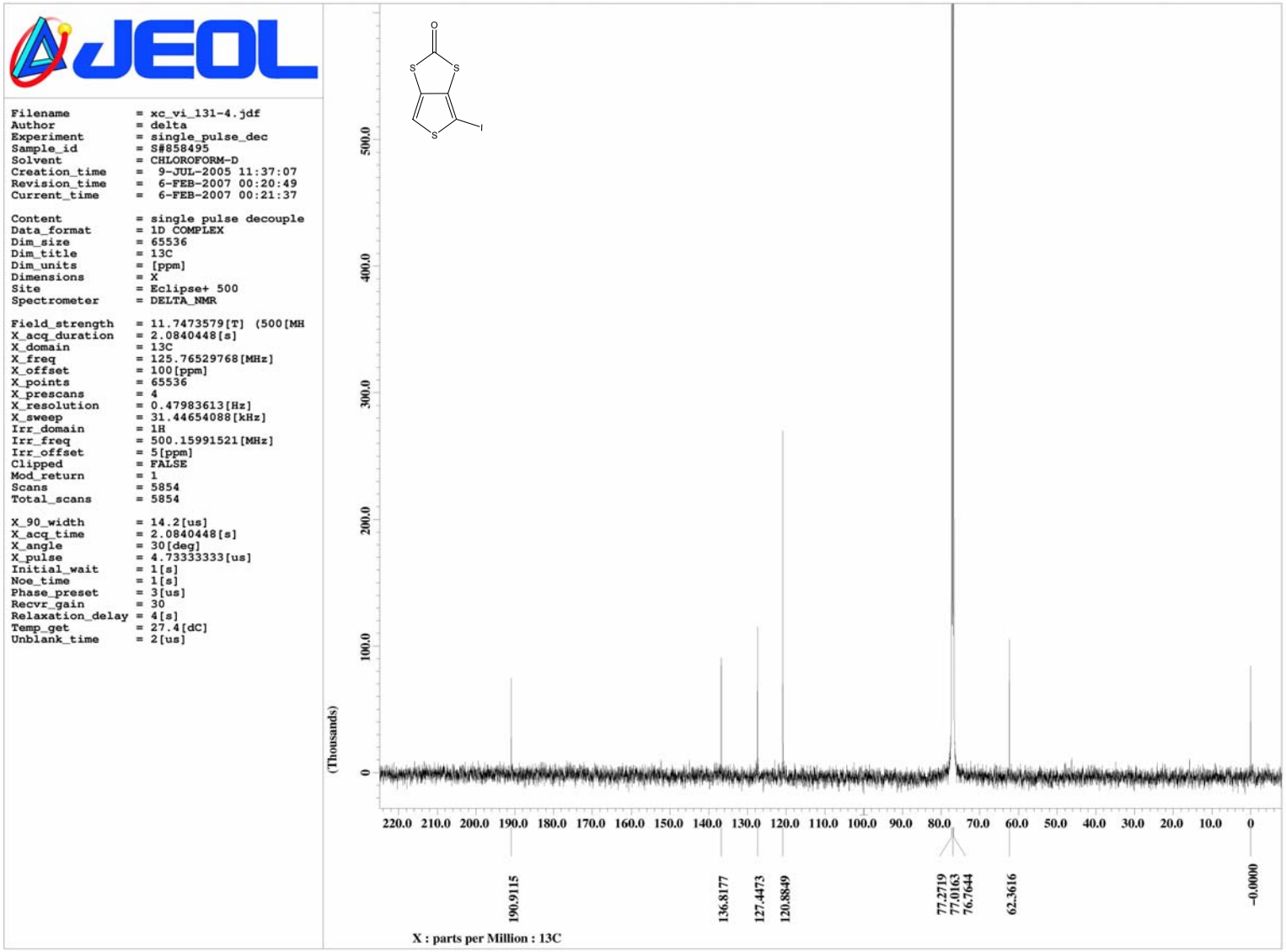
```
Filename          = xc_vi_131-5.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#856805
Solvent           = CHLOROFORM-D
Creation_time     =  9-JUL-2005 00:03:14
Revision_time     =  6-FEB-2007 00:26:43
Current_time      =  6-FEB-2007 00:27:29

Content           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 18.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 25
Relaxation_delay  = 4[s]
Temp_get          = 26[dC]
Unblank_time      = 2[us]
```





```
Filename          = xc_vi_131-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#858495
Solvent           = CHLOROFORM-D
Creation_time     =  9-JUL-2005 11:37:07
Revision_time     =  6-FEB-2007 00:20:49
Current_time      =  6-FEB-2007 00:21:37

Content           = single pulse decouple
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             = 5854
Total_scans       = 5854

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]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 4[s]
Temp_get          = 27.4[dC]
Unblank_time      = 2[us]
```

APPENDIX 9

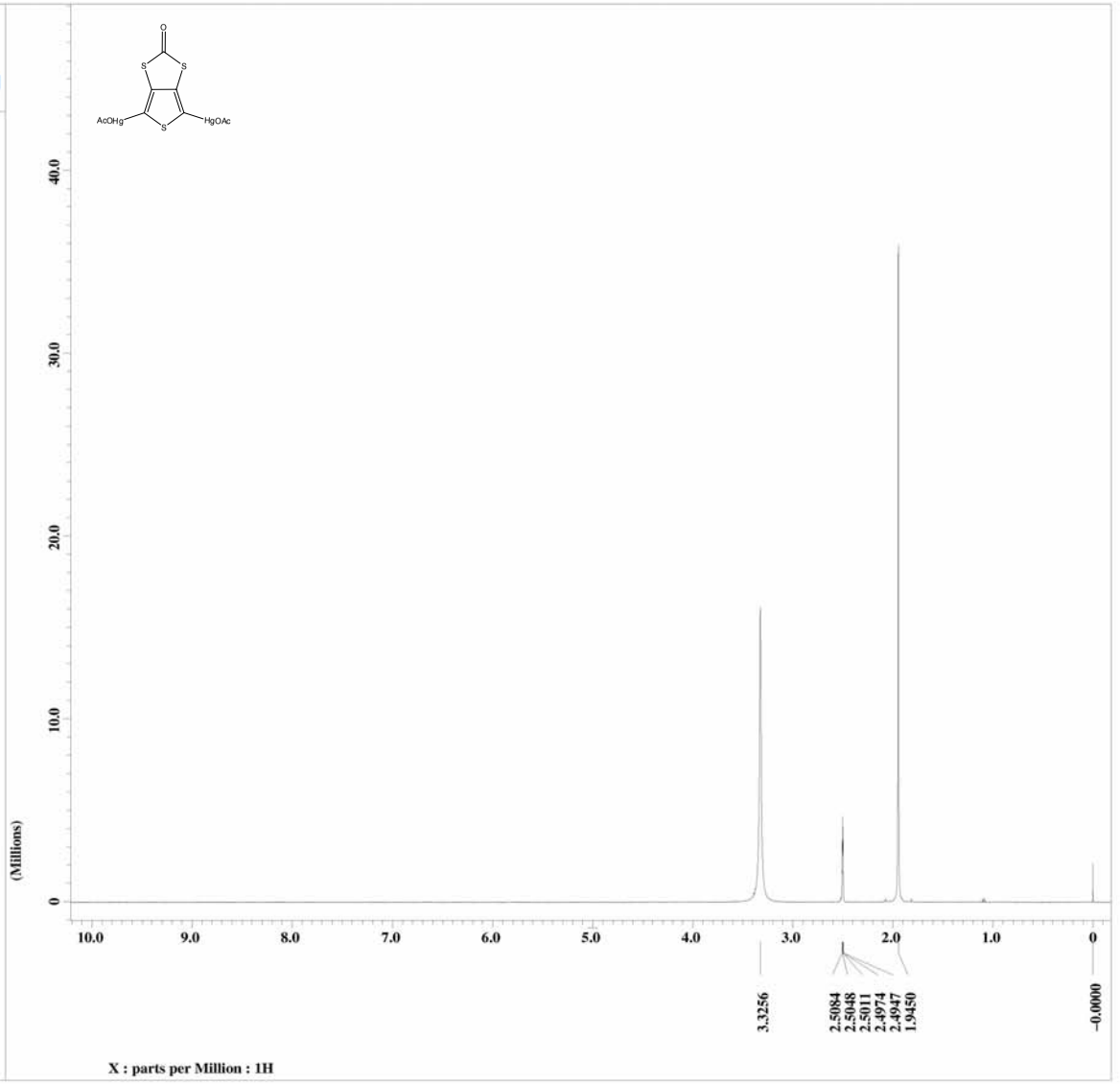
^{1}H and ^{13}C-NMR spectra of 4,6-diacetoxymercuri-thieno[3,4-*d*]-1,3-dithiol-2-one (11)

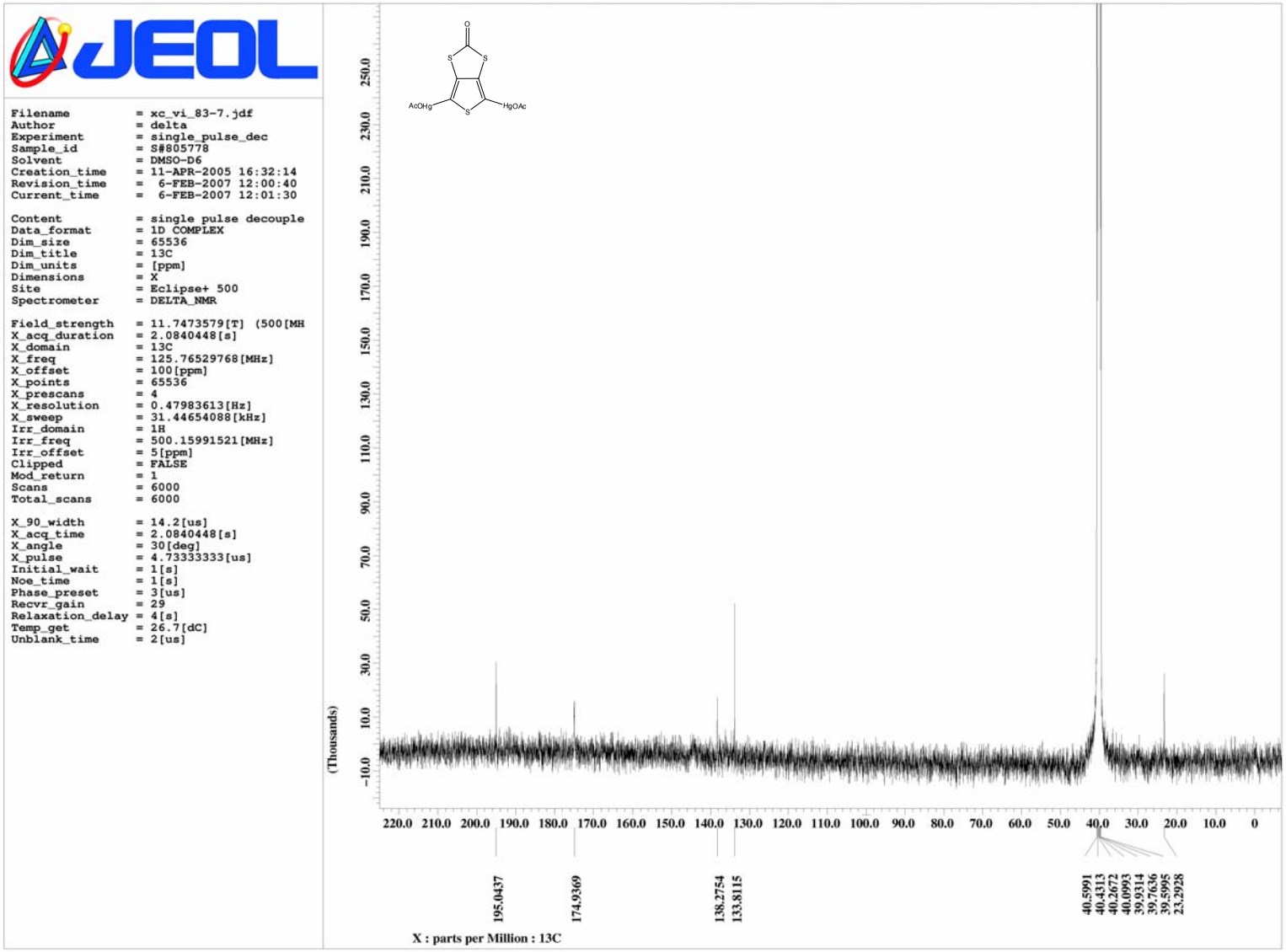
```
Filename          = xc_vi_83-4.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#804569
Solvent           = DMSO-D6
Creation_time     = 11-APR-2005 04:41:06
Revision_time     = 26-MAY-2005 22:24:01
Current_time      =  6-FEB-2007 00:51:37

Content           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

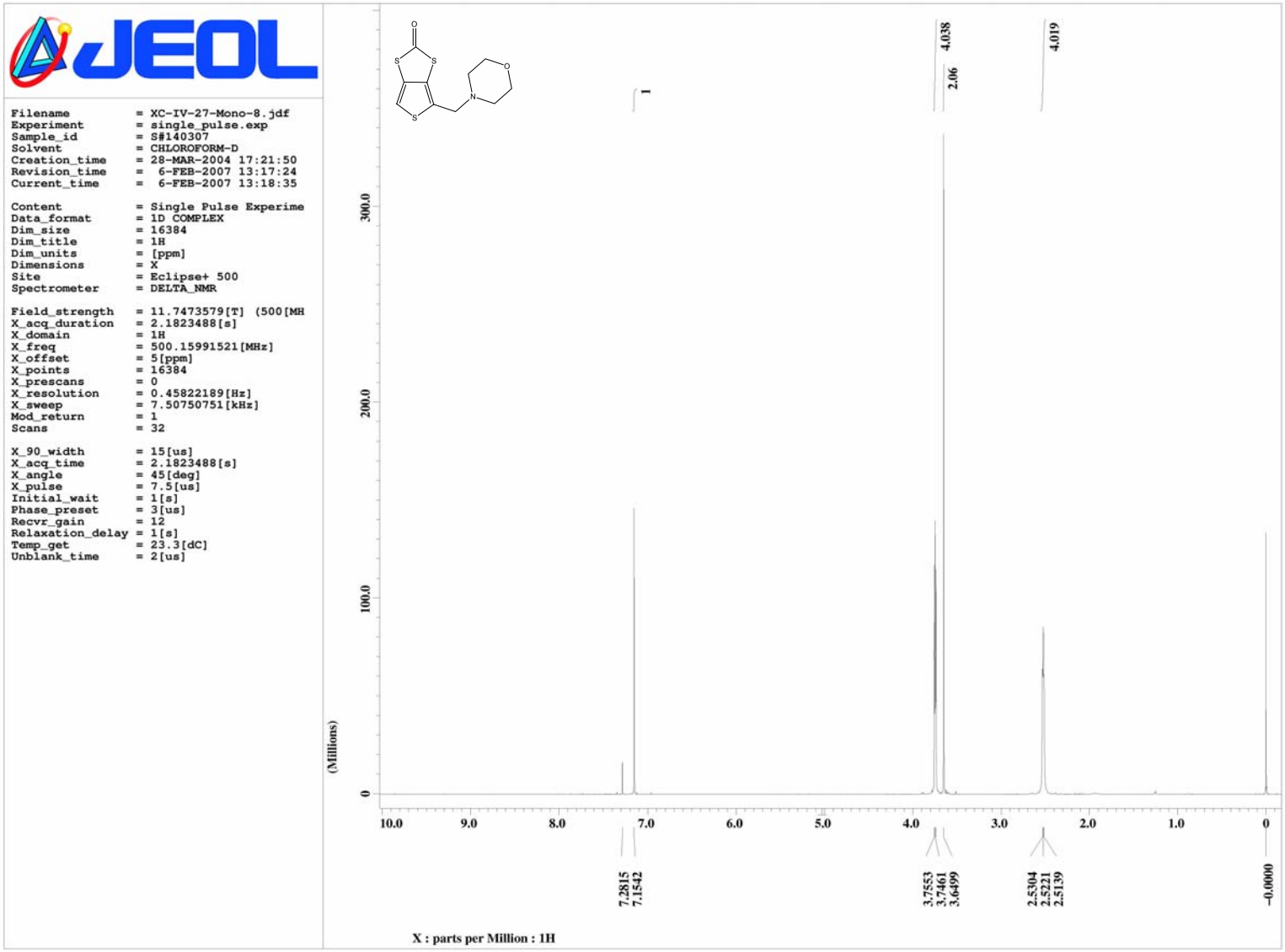
X_90_width        = 18.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 21
Relaxation_delay  = 1[s]
Temp_get          = 26.2[dC]
Unblank_time      = 2[us]
```

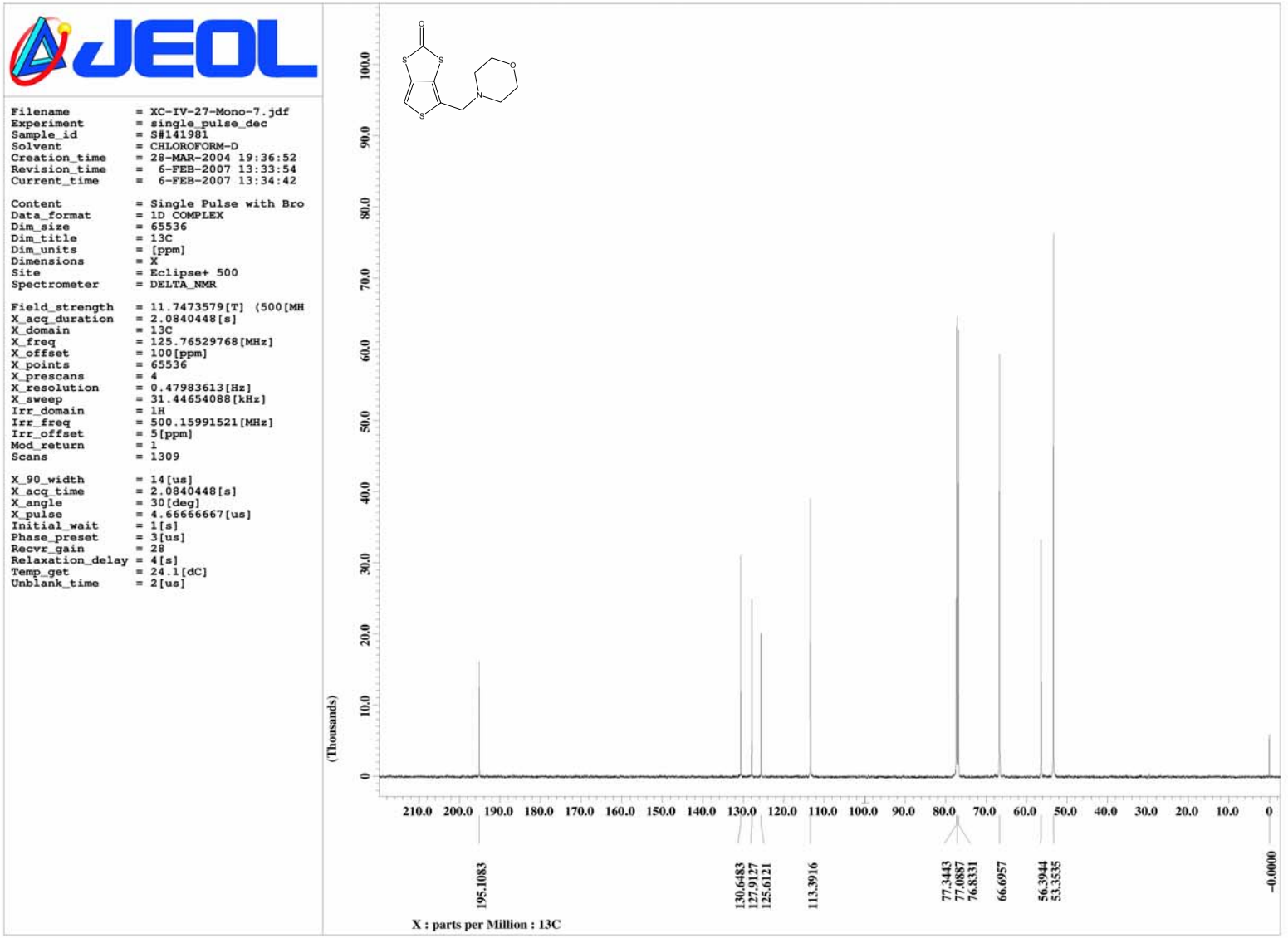



Filename = xc_vi_83-7.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#805778
Solvent = DMSO-D6
Creation_time = 11-APR-2005 16:32:14
Revision_time = 6-FEB-2007 12:00:40
Current_time = 6-FEB-2007 12:01:30
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 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 = 6000
Total_scans = 6000
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 4[s]
Temp_get = 26.7[dC]
Unblank_time = 2[us]
O
S
S
S
AcOHg
HgOAc
(Thousands)
250.0
230.0
210.0
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0
10.0
-10.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
195.0437
174.9369
138.2754
133.8115
40.5991
40.4313
40.2672
40.0993
39.9314
39.7636
39.5995
23.2928
X : parts per Million : 13C

APPENDIX 10

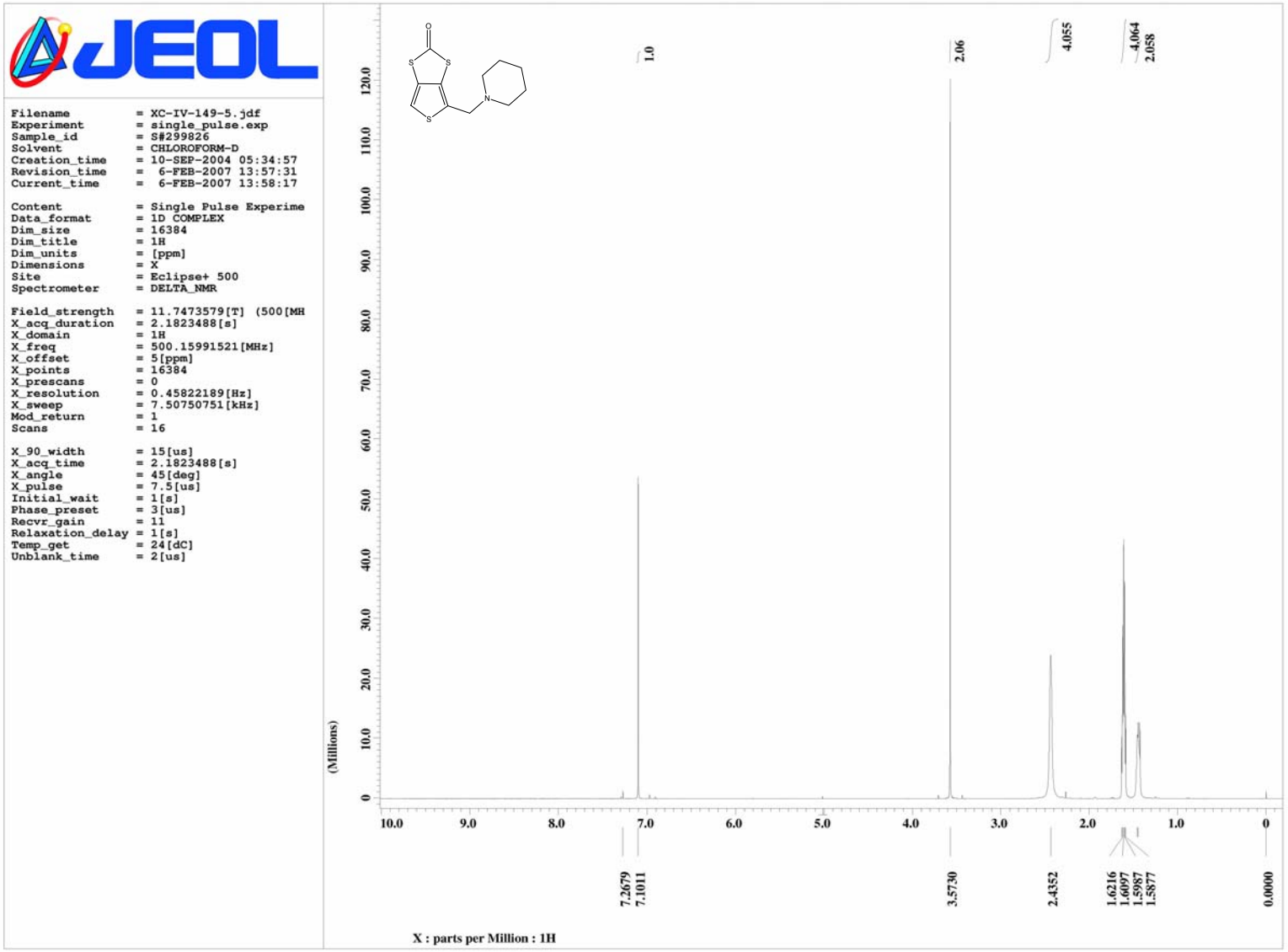
^{1}H and ^{13}C-NMR spectra of
4-(morpholinomethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (12)

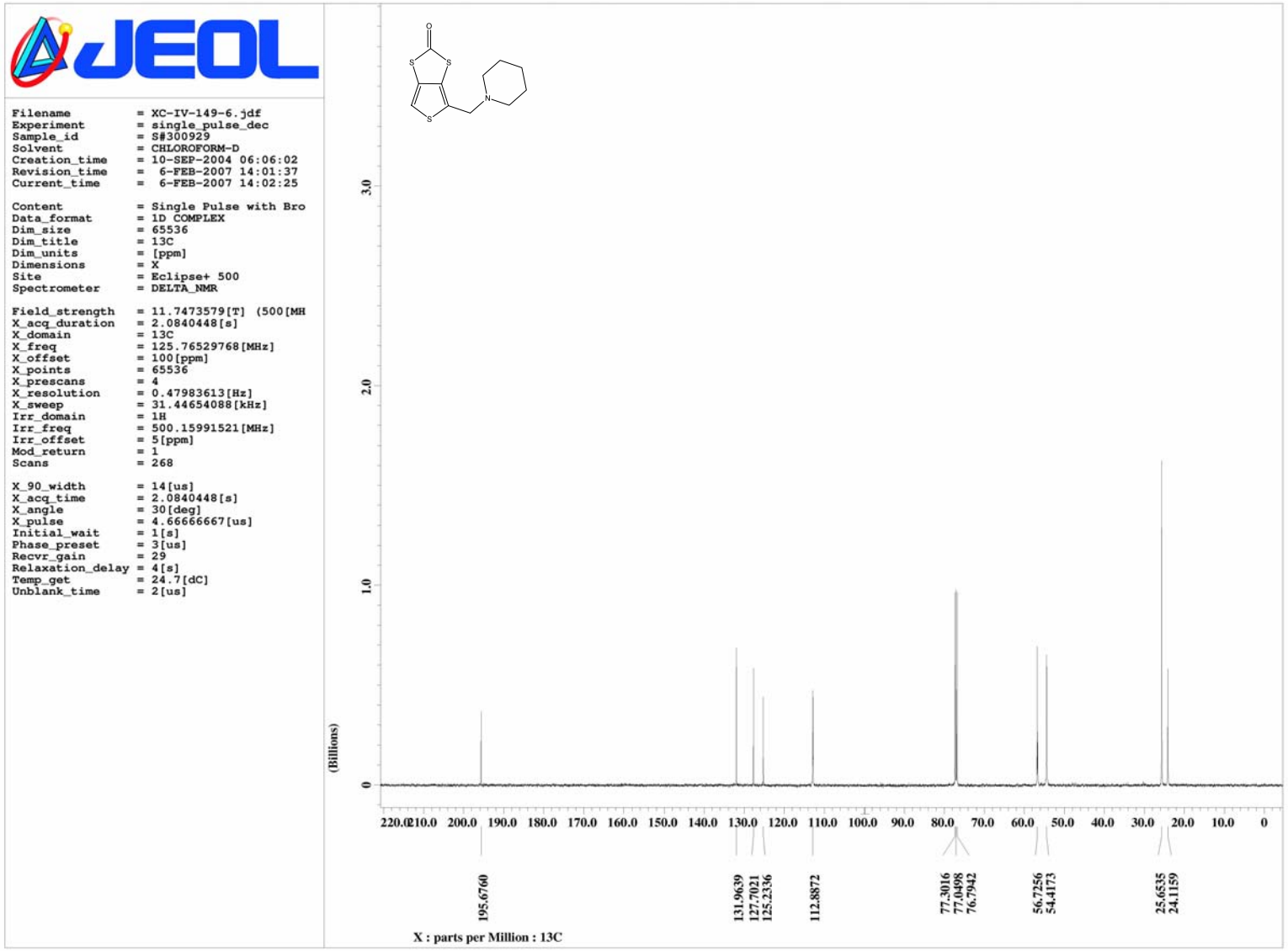

Filename = XC-IV-27-Mono-8.jdf
Experiment = single_pulse.exp
Sample_id = S#140307
Solvent = CHLOROFORM-D
Creation_time = 28-MAR-2004 17:21:50
Revision_time = 6-FEB-2007 13:17:24
Current_time = 6-FEB-2007 13:18:35
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 12
Relaxation_delay = 1[s]
Temp_get = 23.3[dC]
Unblank_time = 2[us]
1
4.038
2.06
4.019
(Millions)
300.0
200.0
100.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2815
7.1542
3.7553
3.7461
3.6499
2.5304
2.5221
2.5139
-0.0000
X : parts per Million : 1H


Filename = XC-IV-27-Mono-7.jdf
Experiment = single_pulse_dec
Sample_id = S#141981
Solvent = CHLOROFORM-D
Creation_time = 28-MAR-2004 19:36:52
Revision_time = 6-FEB-2007 13:33:54
Current_time = 6-FEB-2007 13:34:42
Content = Single Pulse with Bro
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]
Mod_return = 1
Scans = 1309
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 28
Relaxation_delay = 4[s]
Temp_get = 24.1[dC]
Unblank_time = 2[us]
(Thousands)
195.1083
130.6483
127.9127
125.6121
113.3916
77.3443
77.0887
76.8331
66.6957
56.3944
53.3535
-0.0000
X : parts per Million : 13C

APPENDIX 11

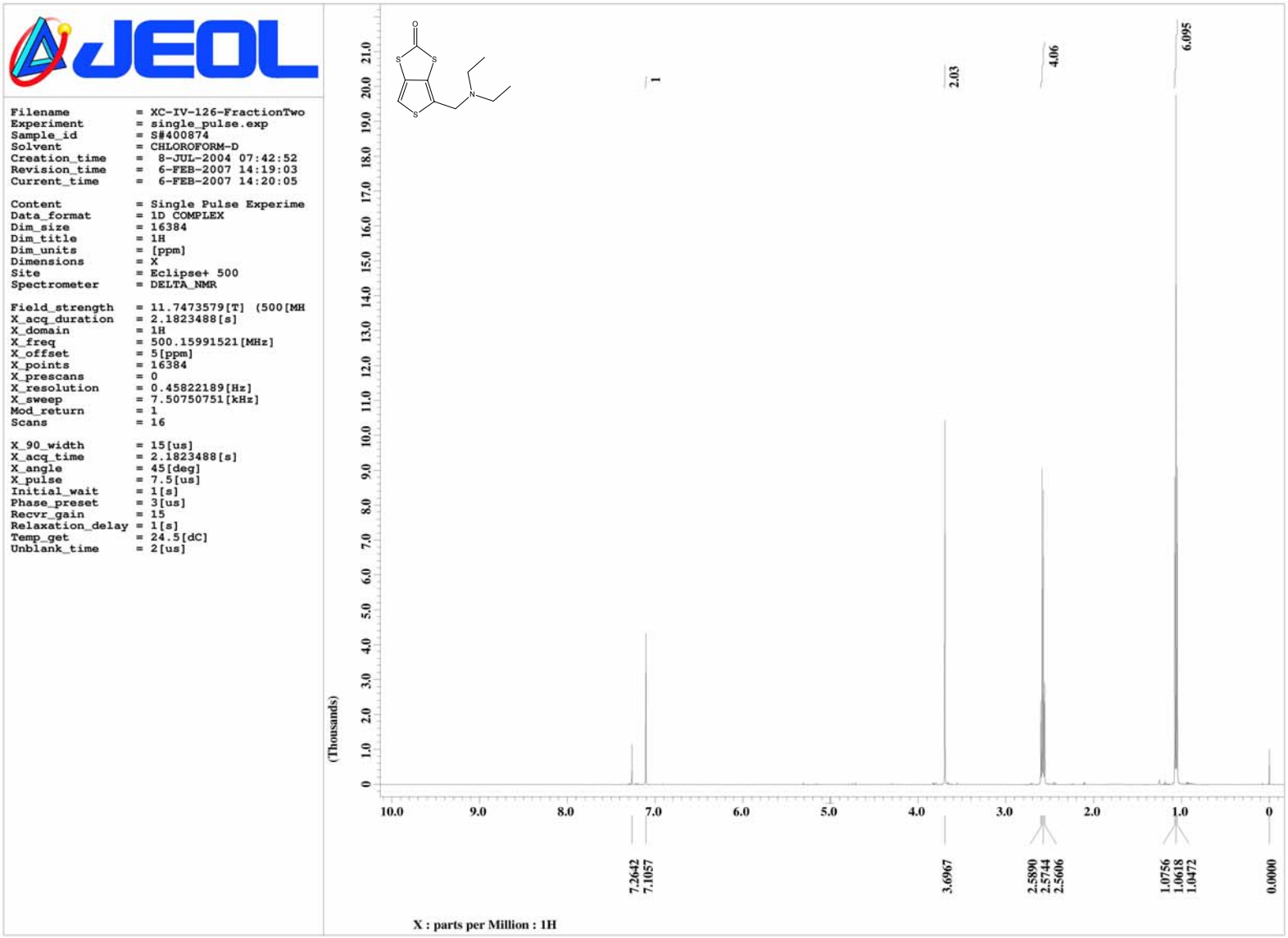
^{1}H and ^{13}C-NMR spectra of 4-((piperidin-1-yl)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (13)

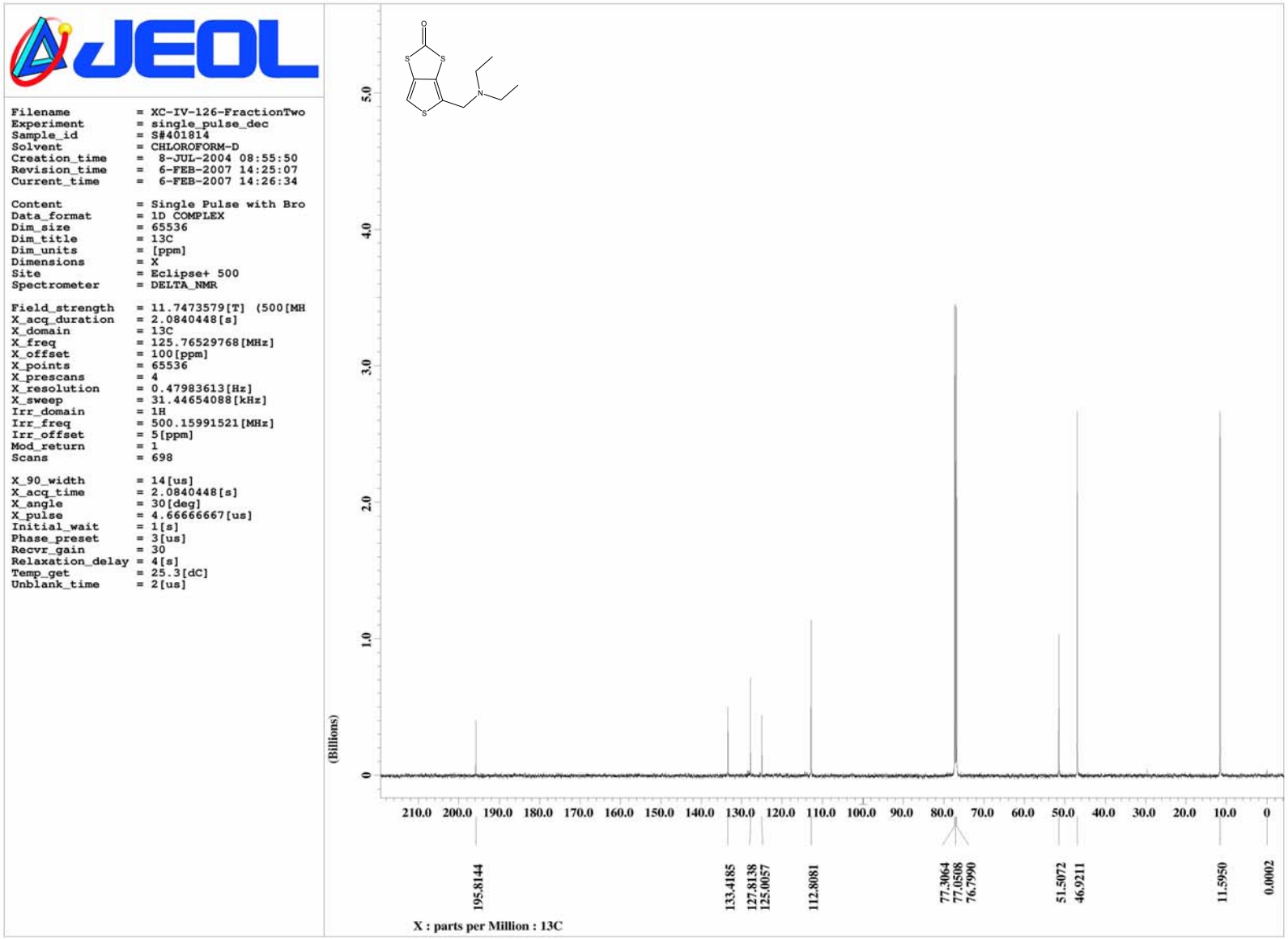

Filename = XC-IV-149-5.jdf
Experiment = single_pulse.exp
Sample_id = S#299826
Solvent = CHLOROFORM-D
Creation_time = 10-SEP-2004 05:34:57
Revision_time = 6-FEB-2007 13:57:31
Current_time = 6-FEB-2007 13:58:17
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 11
Relaxation_delay = 1[s]
Temp_get = 24[dC]
Unblank_time = 2[us]
1.0
2.06
4.055
4.064
2.058
(Millions)
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2679
7.1011
3.5730
2.4352
1.6216
1.6097
1.5987
1.5877
0.0000
X : parts per Million : 1H


Filename = XC-IV-149-6.jdf
Experiment = single_pulse_dec
Sample_id = S#300929
Solvent = CHLOROFORM-D
Creation_time = 10-SEP-2004 06:06:02
Revision_time = 6-FEB-2007 14:01:37
Current_time = 6-FEB-2007 14:02:25
Content = Single Pulse with Bro
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]
Mod_return = 1
Scans = 268
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 4[s]
Temp_get = 24.7[dC]
Unblank_time = 2[us]
O
S
S
S
N
(Billions)
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
195.6760
131.9639
127.7021
125.2336
112.8872
77.3016
77.0498
76.7942
56.7256
54.4173
25.6535
24.1159
X : parts per Million : 13C

APPENDIX 12

^{1}H and ^{13}C-NMR spectra of 4-((diethylamino)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (14)


Filename = XC-IV-126-FractionTwo
Experiment = single_pulse.exp
Sample_id = S#400874
Solvent = CHLOROFORM-D
Creation_time = 8-JUL-2004 07:42:52
Revision_time = 6-FEB-2007 14:19:03
Current_time = 6-FEB-2007 14:20:05
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 1[s]
Temp_get = 24.5[dC]
Unblank_time = 2[us]
(Thousands)
1
2.03
4.06
6.095
7.2642
7.1057
3.6967
2.5890
2.5744
2.5606
1.0756
1.0618
1.0472
0.0000
X : parts per Million : 1H


Filename = XC-IV-126-FractionTwo
Experiment = single_pulse_dec
Sample_id = S#401814
Solvent = CHLOROFORM-D
Creation_time = 8-JUL-2004 08:55:50
Revision_time = 6-FEB-2007 14:25:07
Current_time = 6-FEB-2007 14:26:34
Content = Single Pulse with Bro
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]
Mod_return = 1
Scans = 698
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 25.3[dC]
Unblank_time = 2[us]
(Billions)
5.0
4.0
3.0
2.0
1.0
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
195.8144
133.4185
127.8138
125.0057
112.8081
77.3064
77.0508
76.7990
51.5072
46.9211
11.5950
0.0002
X : parts per Million : 13C

APPENDIX 13

^{1}H and ^{13}C-NMR spectra of 4-(morpholinomethyl)thieno[3,4-*d*]-1,3-dithiole-2-thione (15)

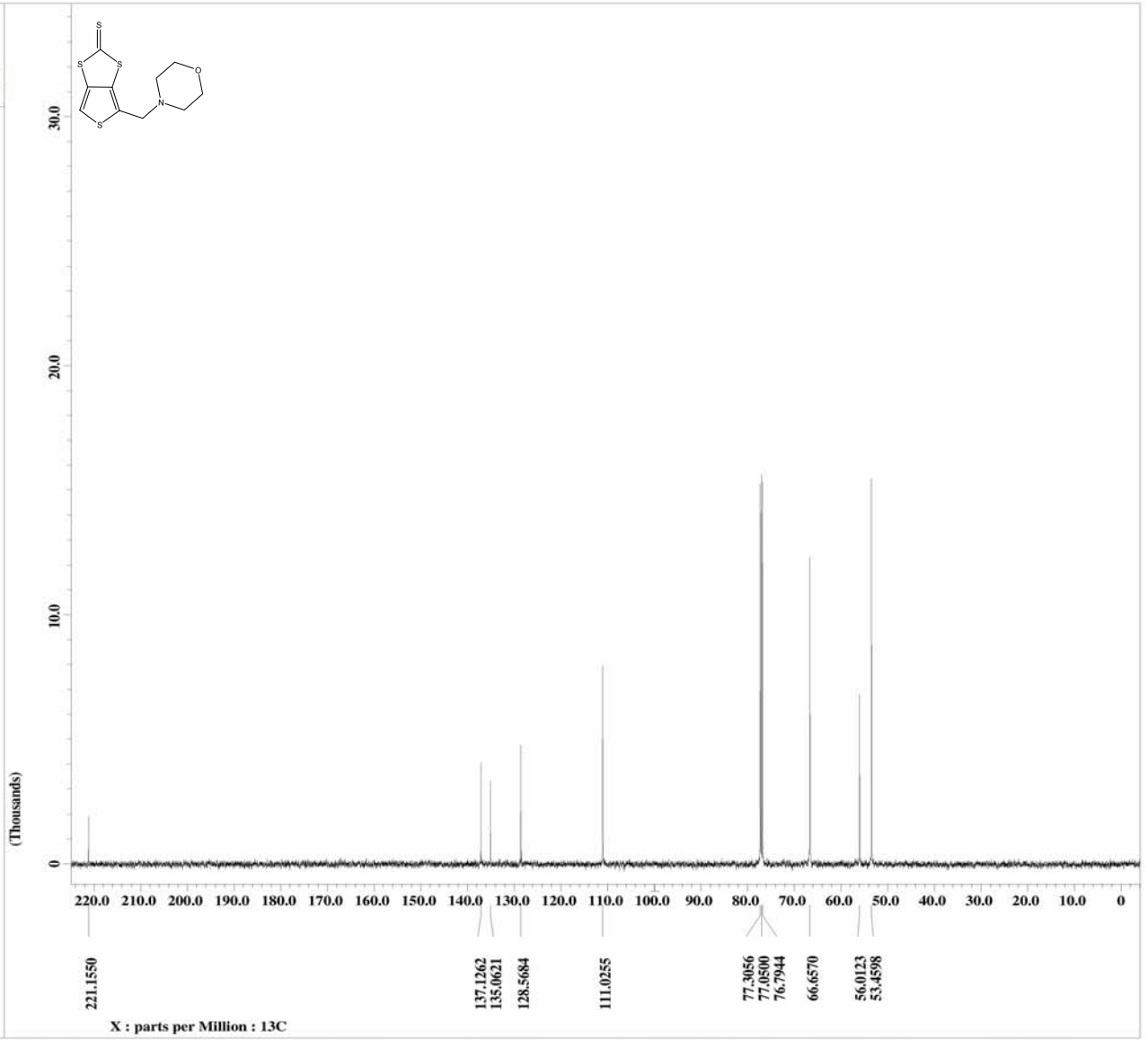
JEOL
Filename = XC-IV-154-7.jdf
Experiment = single_pulse.exp
Sample_id = SM7620?
Solvent = CHLOROFORM-D
Creation_time = 10-SEP-2004 23:22:35
Revision_time = 6-FEB-2007 14:41:44
Current_time = 6-FEB-2007 14:42:26
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 1[s]
Temp_get = 24.6[dC]
UnBlank_time = 2[us]
(Thousands)
4.0
3.0
2.0
1.0
0
I
4.094
2.098
4.097
7.2743
7.0782
3.7773
3.7691
3.7599
3.6161
2.5341
0.0000
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

```
Filename          = XC-IV-154-6.jdf
Experiment        = single_pulse_dec
Sample_id         = S#77117
Solvent           = CHLOROFORM-D
Creation_time     = 10-SEP-2004 23:42:56
Revision_time     =  6-FEB-2007 14:44:41
Current_time      =  6-FEB-2007 14:45:58

Content           = Single Pulse with Bro
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

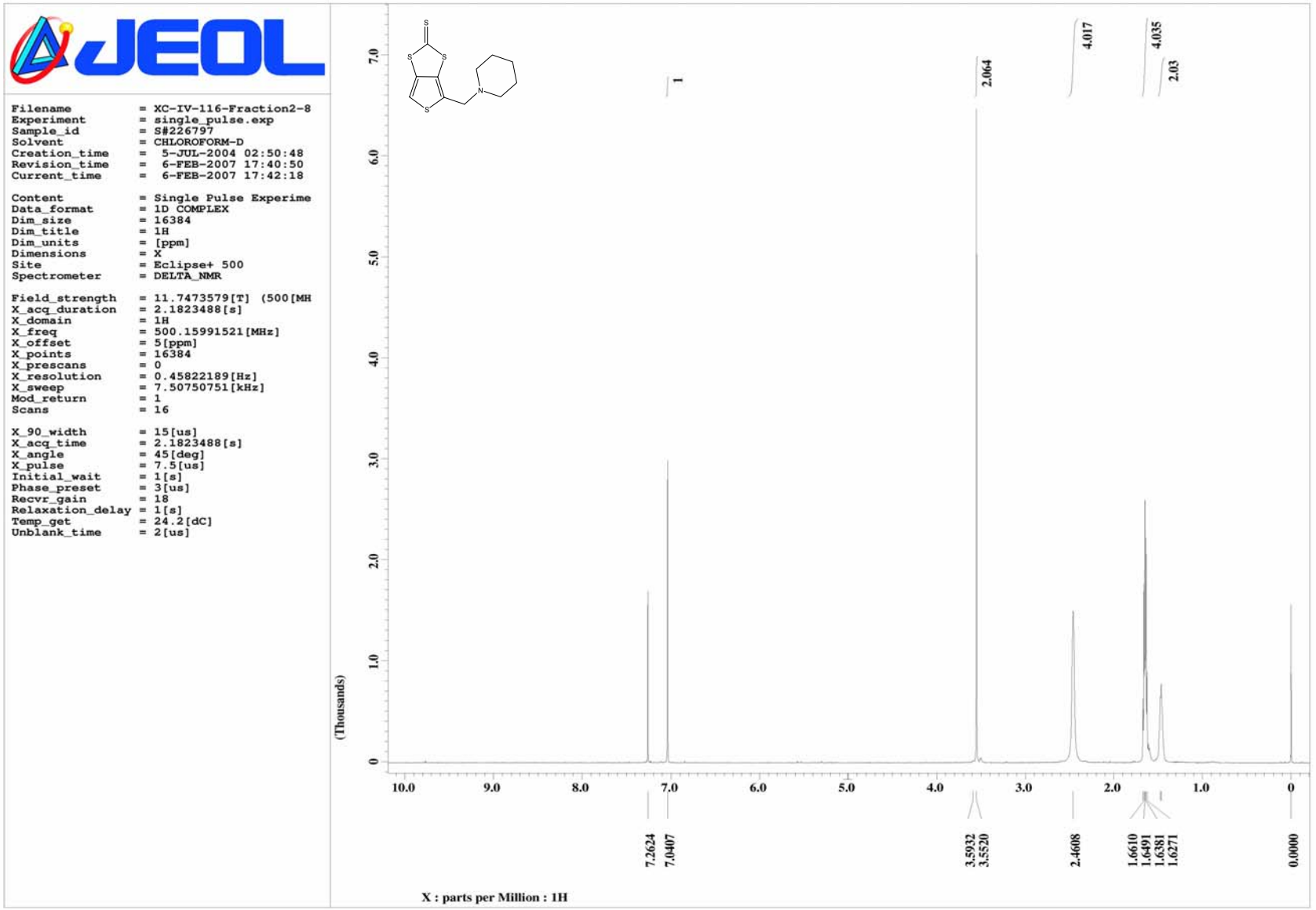
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Mod_return        = 1
Scans             = 276

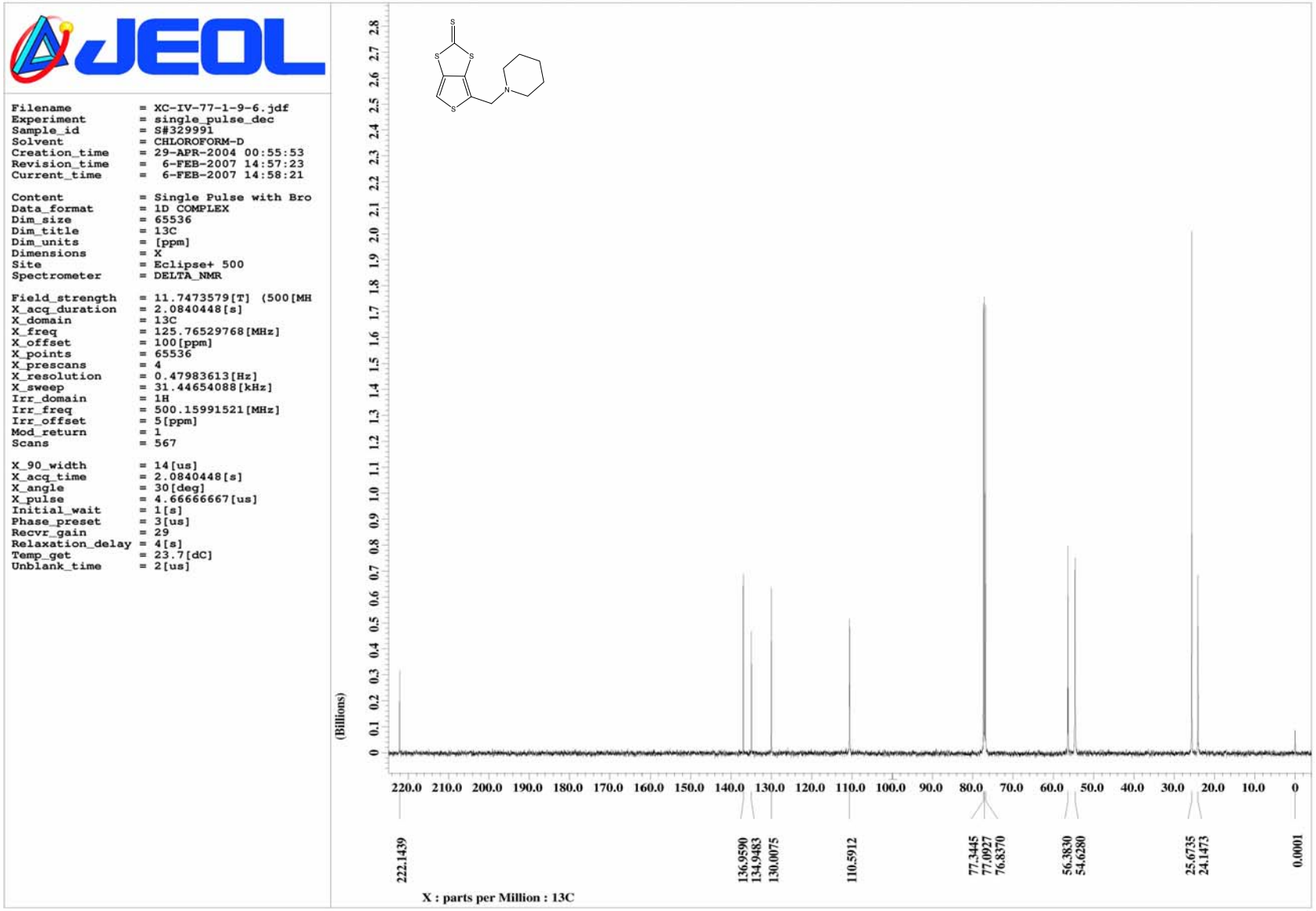
X_90_width        = 14[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.66666667[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Temp_get          = 25.3[dC]
Unblank_time      = 2[us]
```



APPENDIX 14

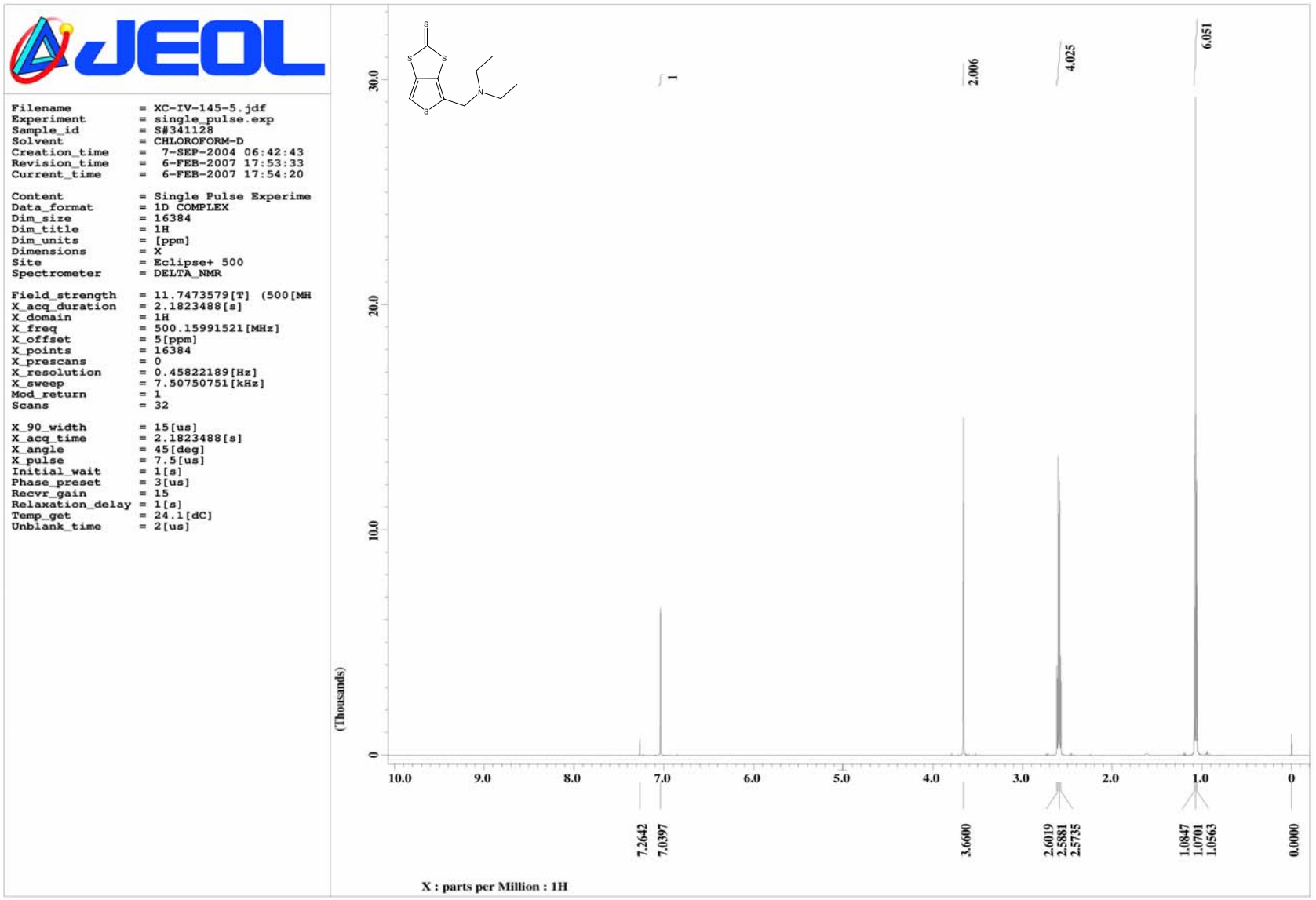
^{1}H and ^{13}C-NMR spectra of 4-((piperidin-1-yl)methyl)thieno[3,4-*d*]-1,3-dithiole-2-thione (16)

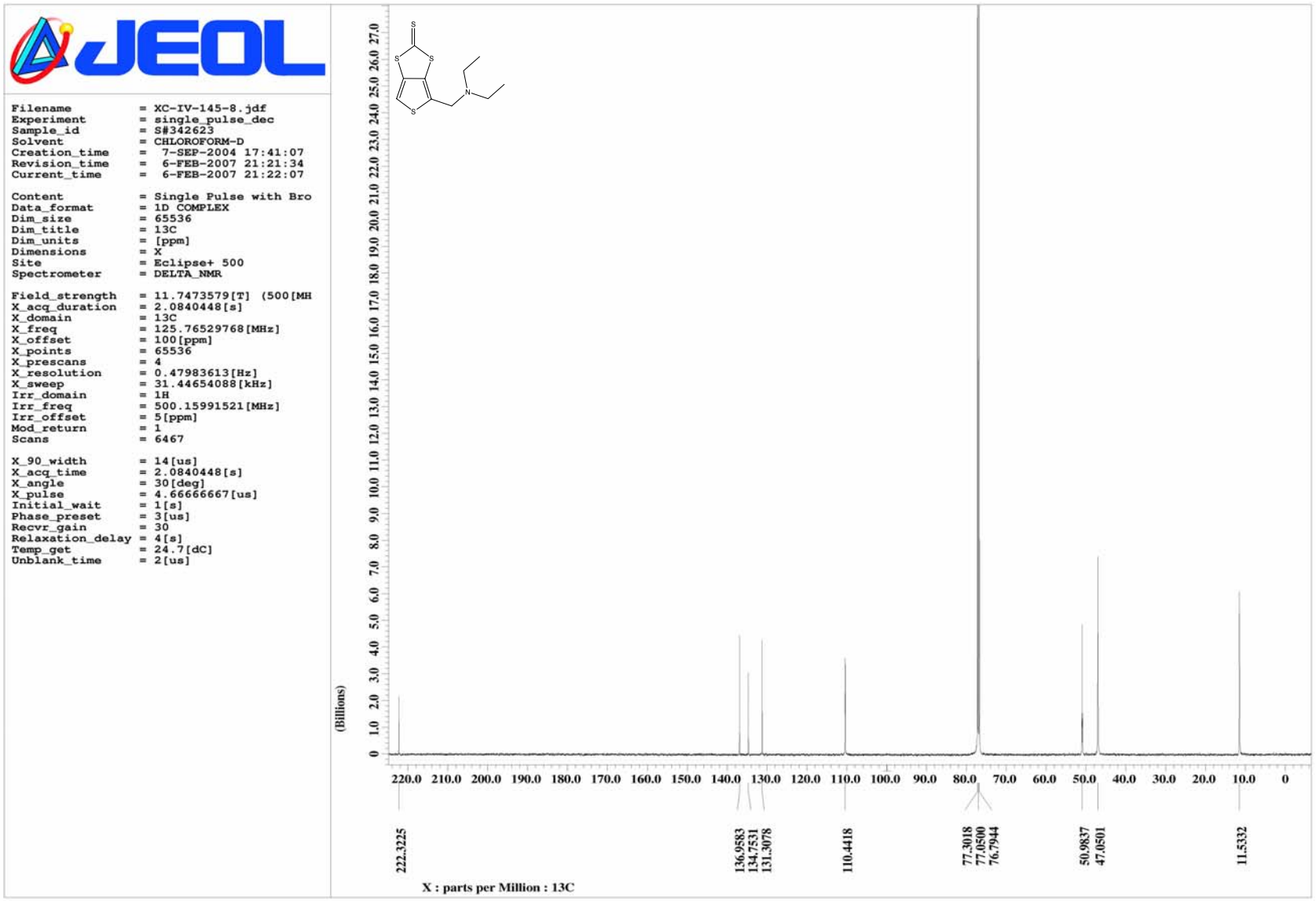

Filename = XC-IV-116-Fraction2-8
Experiment = single_pulse.exp
Sample_id = S#226797
Solvent = CHLOROFORM-D
Creation_time = 5-JUL-2004 02:50:48
Revision_time = 6-FEB-2007 17:40:50
Current_time = 6-FEB-2007 17:42:18
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 1[s]
Temp_get = 24.2[dC]
Unblank_time = 2[us]
1
2.064
4.017
4.035
2.03
(Thousands)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2624
7.0407
3.5932
3.5520
2.4608
1.6610
1.6491
1.6381
1.6271
0.0000
X : parts per Million : 1H


Filename = XC-IV-77-1-9-6.jdf
Experiment = single_pulse_dec
Sample_id = S#329991
Solvent = CHLOROFORM-D
Creation_time = 29-APR-2004 00:55:53
Revision_time = 6-FEB-2007 14:57:23
Current_time = 6-FEB-2007 14:58:21
Content = Single Pulse with Bro
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]
Mod_return = 1
Scans = 567
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 4[s]
Temp_get = 23.7[dC]
Unblank_time = 2[us]
(Billions)
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
222.1439
136.9590
134.9483
130.0075
110.5912
77.3445
77.0927
76.8370
56.3830
54.6280
25.6735
24.1473
0.0001
X : parts per Million : 13C

APPENDIX 15

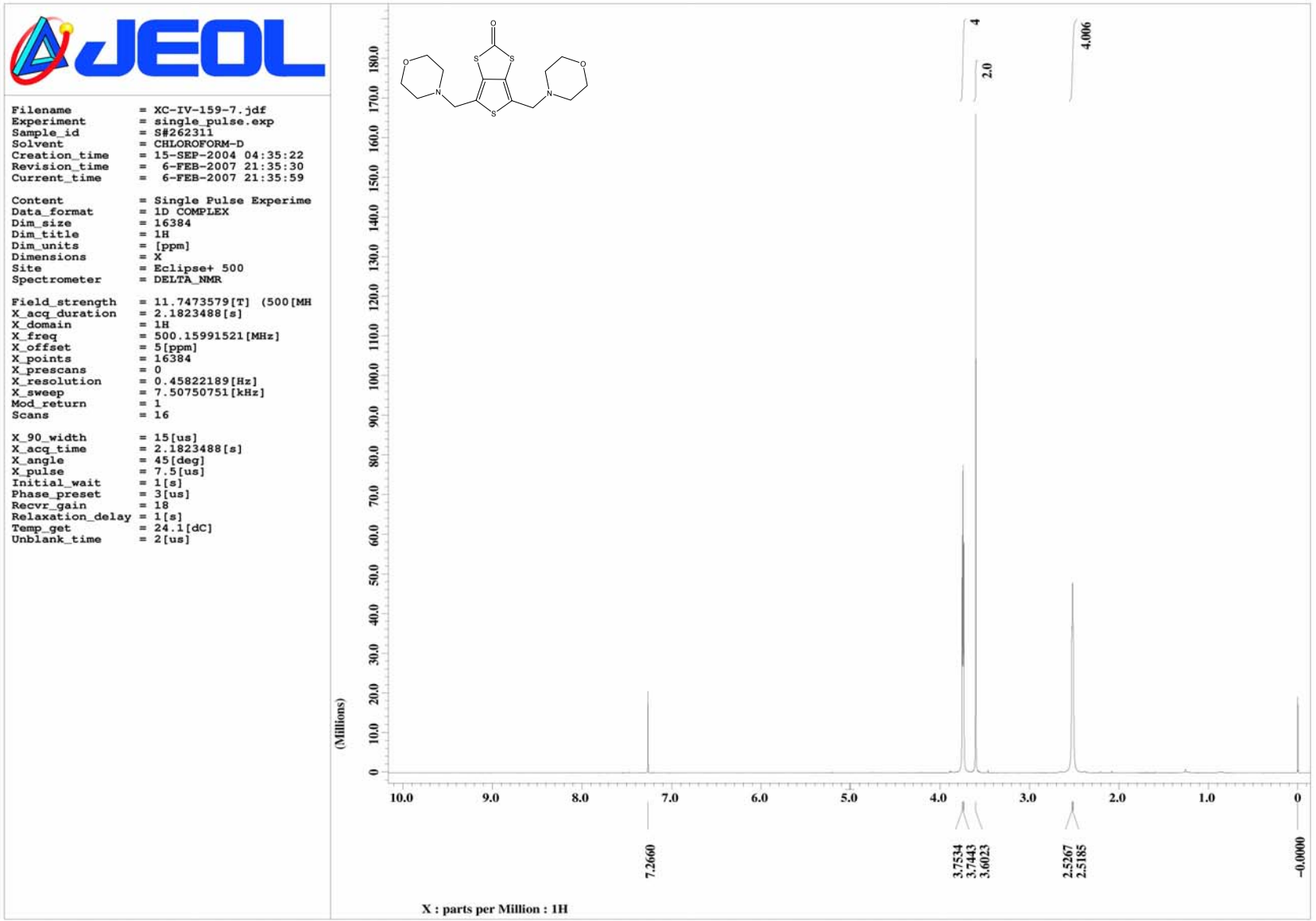
^{1}H and ^{13}C-NMR spectra of 4-((diethylamino)methyl)thieno[3,4-*d*]-1,3-dithiole-2-thione (17)


Filename = XC-IV-145-5.jdf
Experiment = single_pulse.exp
Sample_id = S#341128
Solvent = CHLOROFORM-D
Creation_time = 7-SEP-2004 06:42:43
Revision_time = 6-FEB-2007 17:53:33
Current_time = 6-FEB-2007 17:54:20
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 32
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 1[s]
Temp_get = 24.1[dC]
Unblank_time = 2[us]
1
2.006
4.025
6.051
(Thousands)
30.0
20.0
10.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2642
7.0397
3.6600
2.6019
2.5881
2.5735
1.0847
1.0701
1.0563
0.0000
X : parts per Million : 1H


Filename = XC-IV-145-8.jdf
Experiment = single_pulse_dec
Sample_id = S#342623
Solvent = CHLOROFORM-D
Creation_time = 7-SEP-2004 17:41:07
Revision_time = 6-FEB-2007 21:21:34
Current_time = 6-FEB-2007 21:22:07
Content = Single Pulse with Bro
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]
Mod_return = 1
Scans = 6467
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 24.7[dC]
Unblank_time = 2[us]
(Billions)
222.3225
136.9583
134.7531
131.3078
110.4418
77.3018
77.0500
76.7944
50.9837
47.0501
11.5332
X : parts per Million : 13C

APPENDIX 16

^{1}H and ^{13}C-NMR spectra of 4,6-bis(morpholinomethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (18)

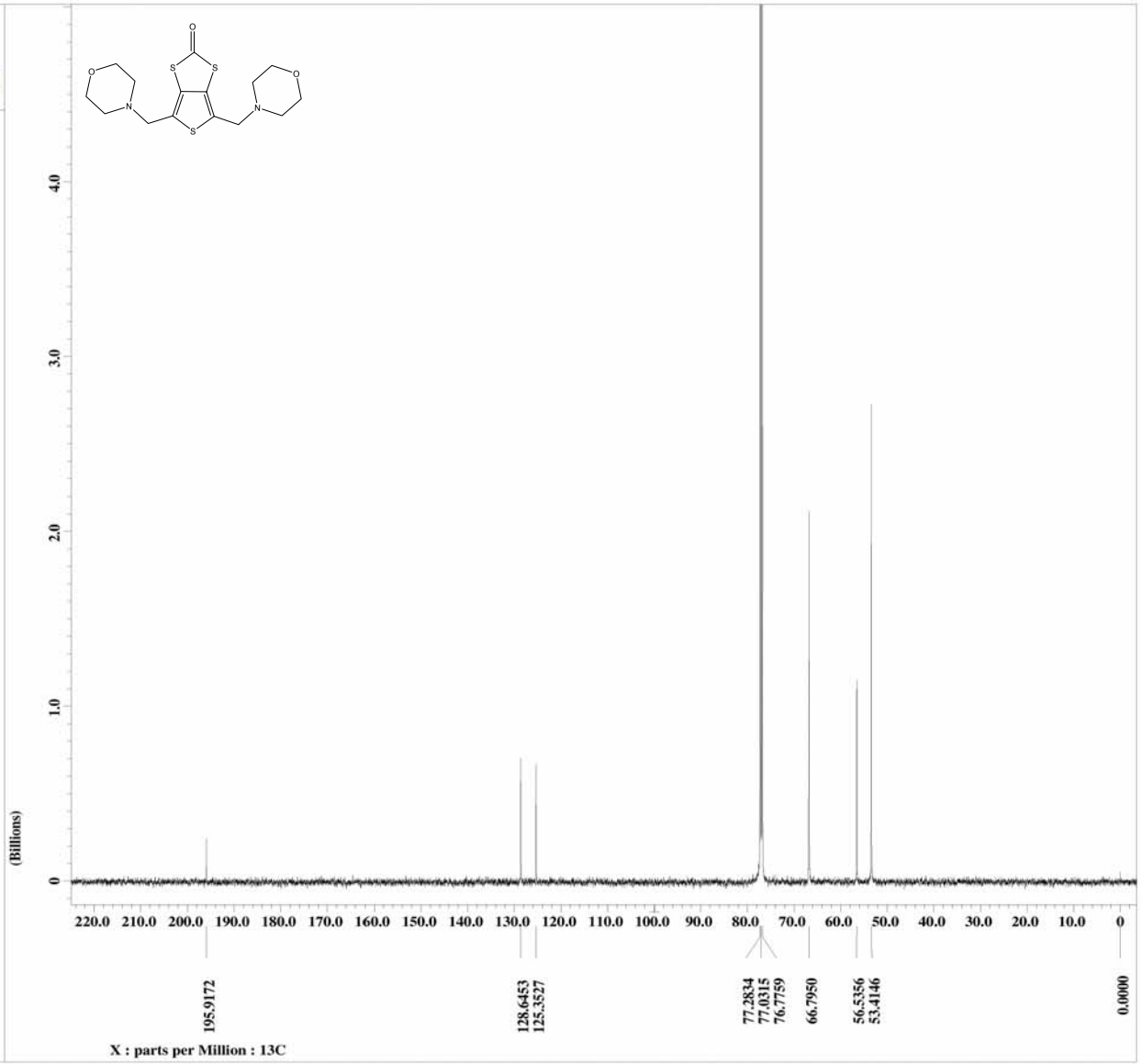

Filename = XC-IV-159-7.jdf
Experiment = single_pulse.exp
Sample_id = S#262311
Solvent = CHLOROFORM-D
Creation_time = 15-SEP-2004 04:35:22
Revision_time = 6-FEB-2007 21:35:30
Current_time = 6-FEB-2007 21:35:59
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 1[s]
Temp_get = 24.1[dC]
Unblank_time = 2[us]
(Millions)
4
2.0
4.006
7.2660
3.7534
3.7443
3.6023
2.5267
2.5185
0.0000
X : parts per Million : 1H

```
Filename          = XC-IV-159-7.jdf
Experiment        = single_pulse_dec
Sample_id         = S#201643
Solvent           = CHLOROFORM-D
Creation_time     = 20-SEP-2004 06:55:42
Revision_time     =  6-FEB-2007 21:38:41
Current_time      =  6-FEB-2007 21:39:36

Content           = Single Pulse with Bro
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

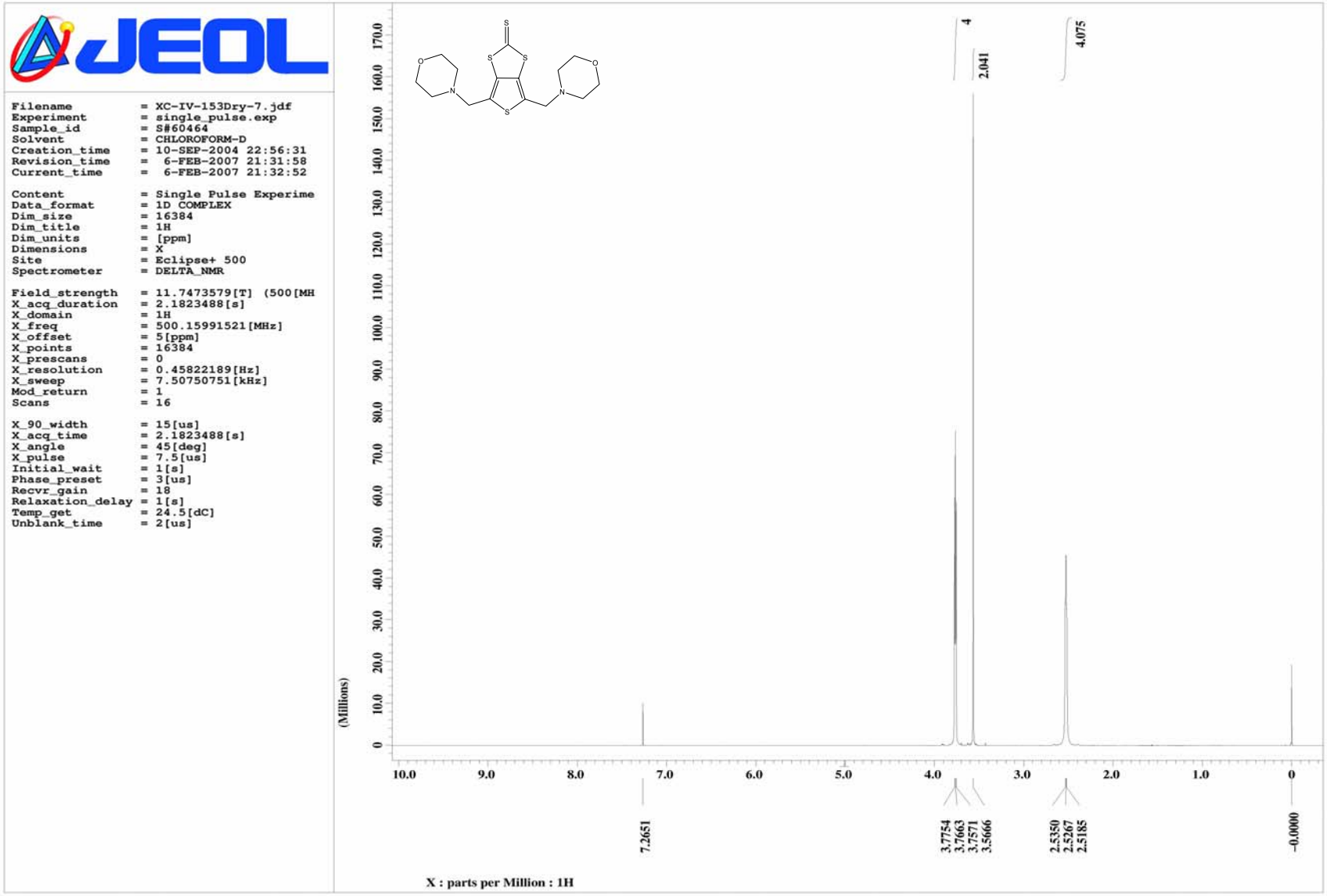
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Mod_return        = 1
Scans             = 2344

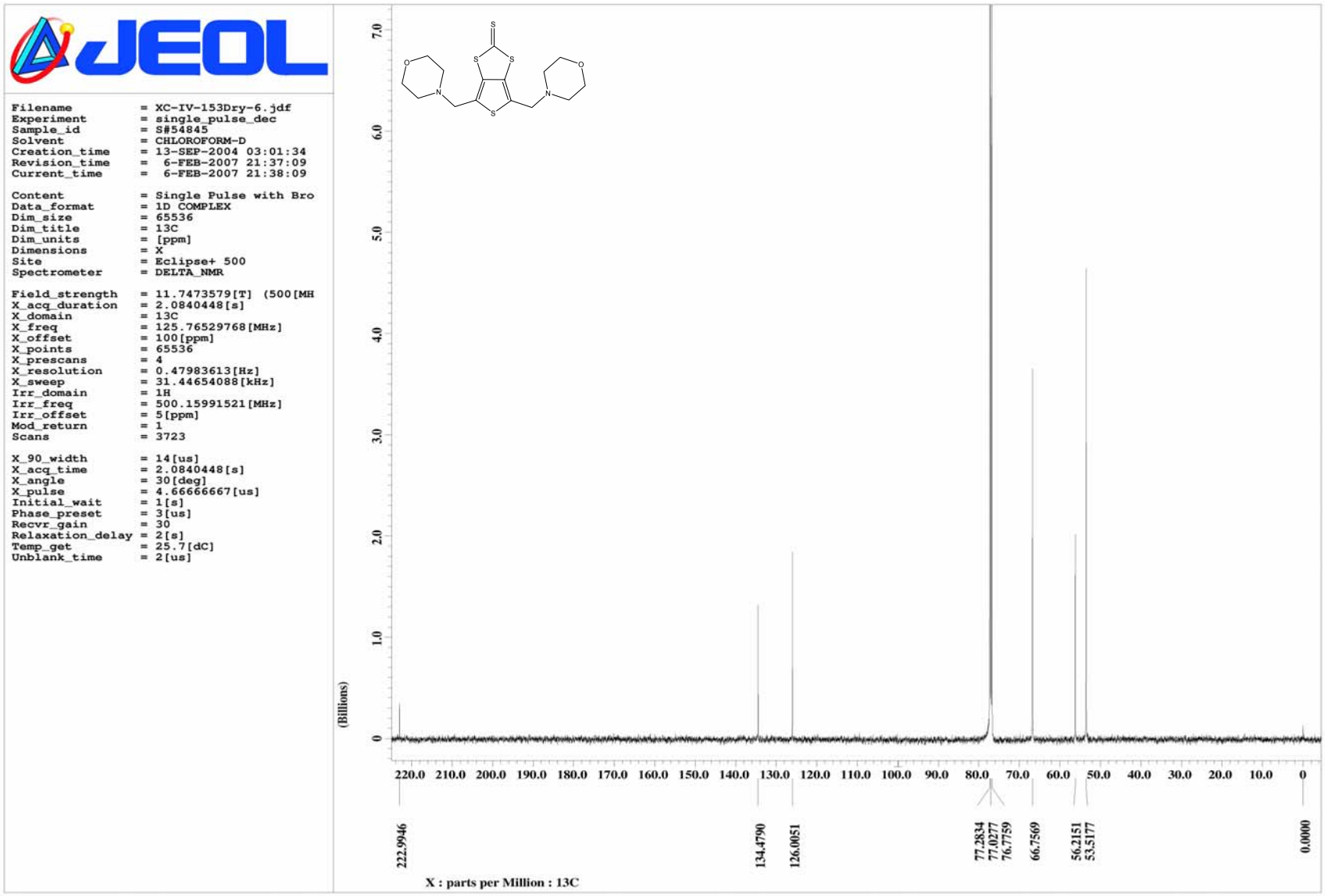
X_90_width        = 14[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.66666667[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 29
Relaxation_delay  = 4[s]
Temp_get          = 25[dC]
Unblank_time      = 2[us]
```



APPENDIX 17

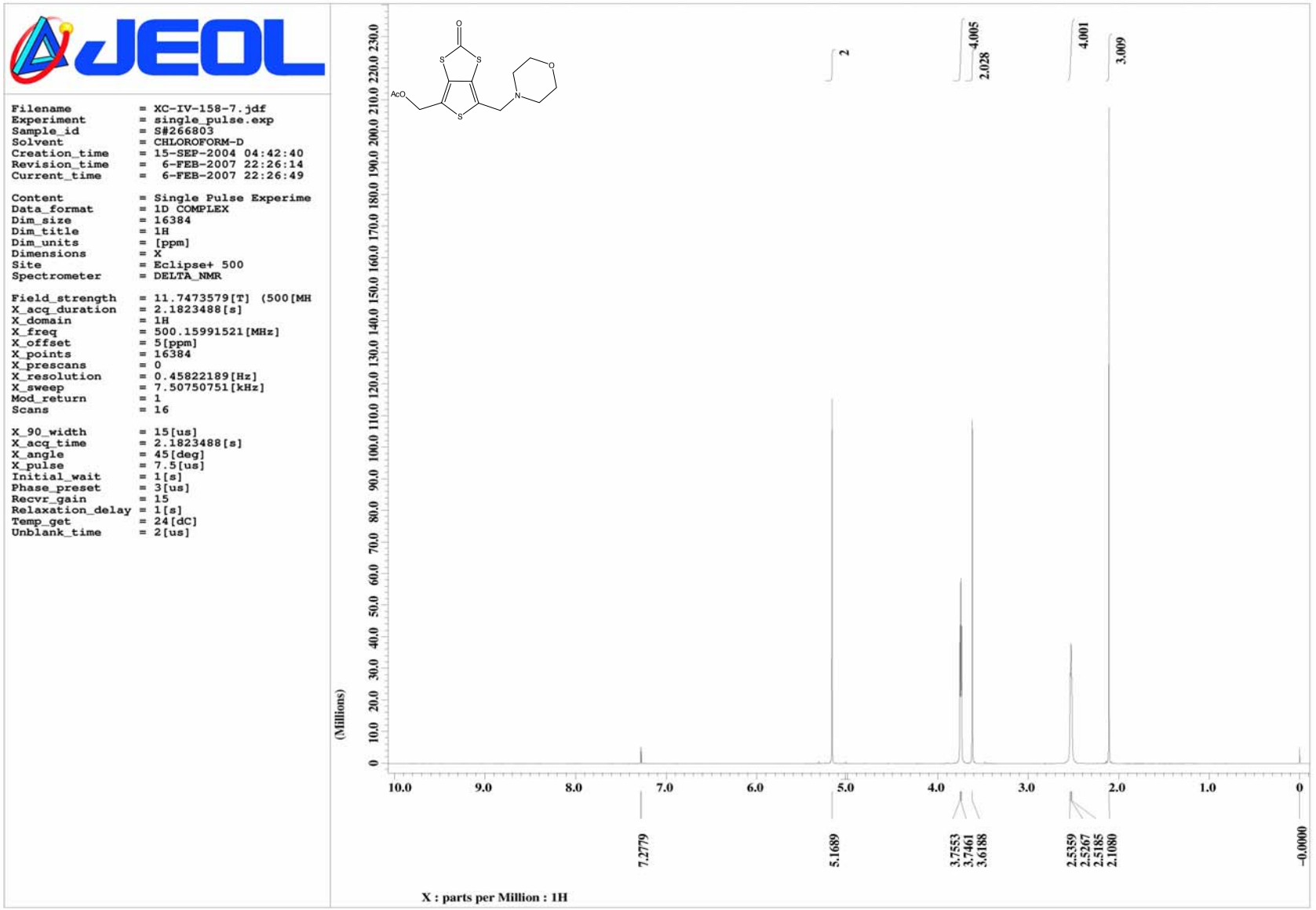
^{1}H and ^{13}C-NMR spectra of 4,6-bis(morpholinomethyl)thieno[3,4-*d*]-1,3-dithiole-2-thione (19)

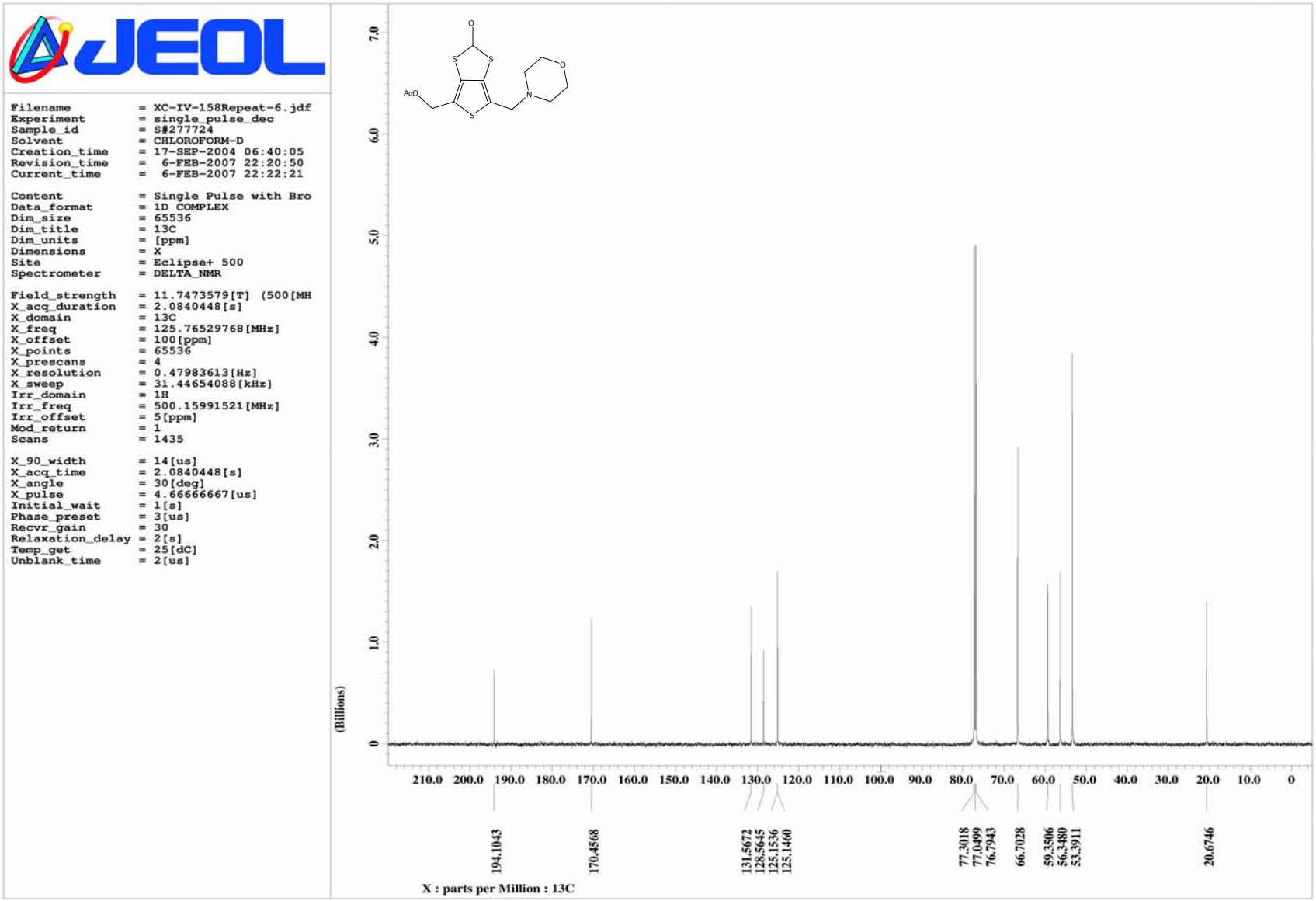

Filename = XC-IV-153Dry-7.jdf
Experiment = single_pulse.exp
Sample_id = S#60464
Solvent = CHLOROFORM-D
Creation_time = 10-SEP-2004 22:56:31
Revision_time = 6-FEB-2007 21:31:58
Current_time = 6-FEB-2007 21:32:52
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 1[s]
Temp_get = 24.5[dC]
Unblank_time = 2[us]
(Millions)
4
2.041
4.075
7.2651
3.7754
3.7663
3.7571
3.5666
2.5350
2.5267
2.5185
0.0000
X : parts per Million : 1H


Filename = XC-IV-153Dry-6.jdf
Experiment = single_pulse_dec
Sample_id = S#54845
Solvent = CHLOROFORM-D
Creation_time = 13-SEP-2004 03:01:34
Revision_time = 6-FEB-2007 21:37:09
Current_time = 6-FEB-2007 21:38:09
Content = Single Pulse with Bro
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]
Mod_return = 1
Scans = 3723
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 25.7[dC]
Unblank_time = 2[us]
(Billions)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
222.9946
134.4790
126.0051
77.2834
77.0277
76.7759
66.7569
56.2151
53.5177
0.0000
X : parts per Million : 13C

APPENDIX 18

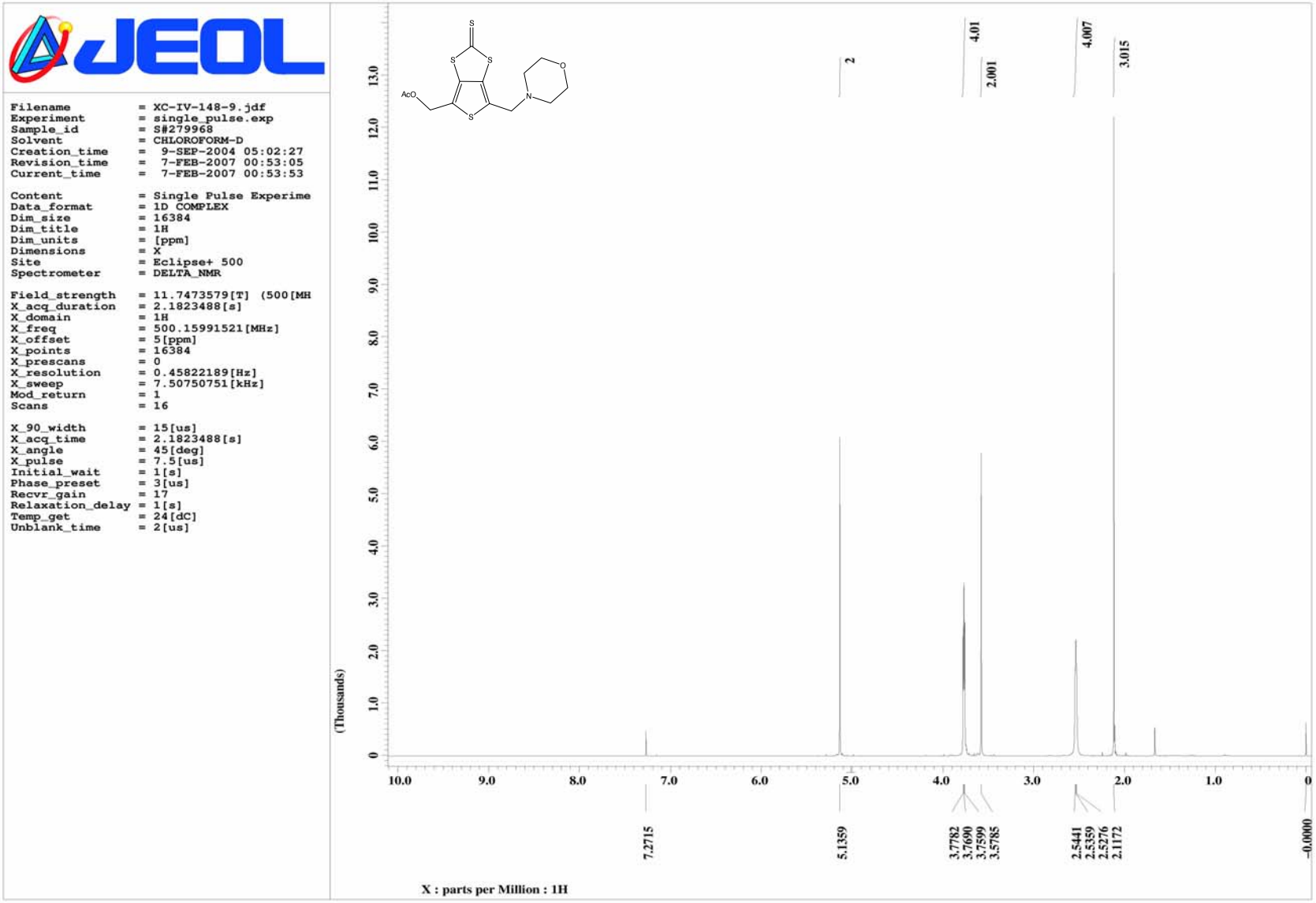
^{1}H and ^{13}C-NMR spectra of (4-(morpholinomethyl)-2-oxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate (20)


Filename = XC-IV-158-7.jdf
Experiment = single_pulse.exp
Sample_id = S#266803
Solvent = CHLOROFORM-D
Creation_time = 15-SEP-2004 04:42:40
Revision_time = 6-FEB-2007 22:26:14
Current_time = 6-FEB-2007 22:26:49
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 1[s]
Temp_get = 24[dC]
Unblank_time = 2[us]
AcO
O
S
S
S
N
O
2
4.005
2.028
4.001
3.009
(Millions)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
210.0
220.0
230.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2779
5.1689
3.7553
3.7461
3.6188
2.5359
2.5267
2.5185
2.1080
-0.0000
X : parts per Million : 1H


Filename = XC-IV-158Repeat-6.jdf
Experiment = single_pulse_dec
Sample_id = S#277724
Solvent = CHLOROFORM-D
Creation_time = 17-SEP-2004 06:40:05
Revision_time = 6-FEB-2007 22:20:50
Current_time = 6-FEB-2007 22:22:21
Content = Single Pulse with Bro
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]
Mod_return = 1
Scans = 1435
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2[s]
Temp_get = 25[dC]
Unblank_time = 2[us]
AcO
O
S
S
S
N
O
(Billions)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
194.1043
170.4568
131.5672
128.5645
125.1536
125.1460
77.3018
77.0499
76.7943
66.7028
59.3506
56.3480
53.3911
20.6746
X : parts per Million : 13C

APPENDIX 19

^{1}H and ^{13}C-NMR spectra of (4-morpholinomethyl)-2-thioxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate (21)

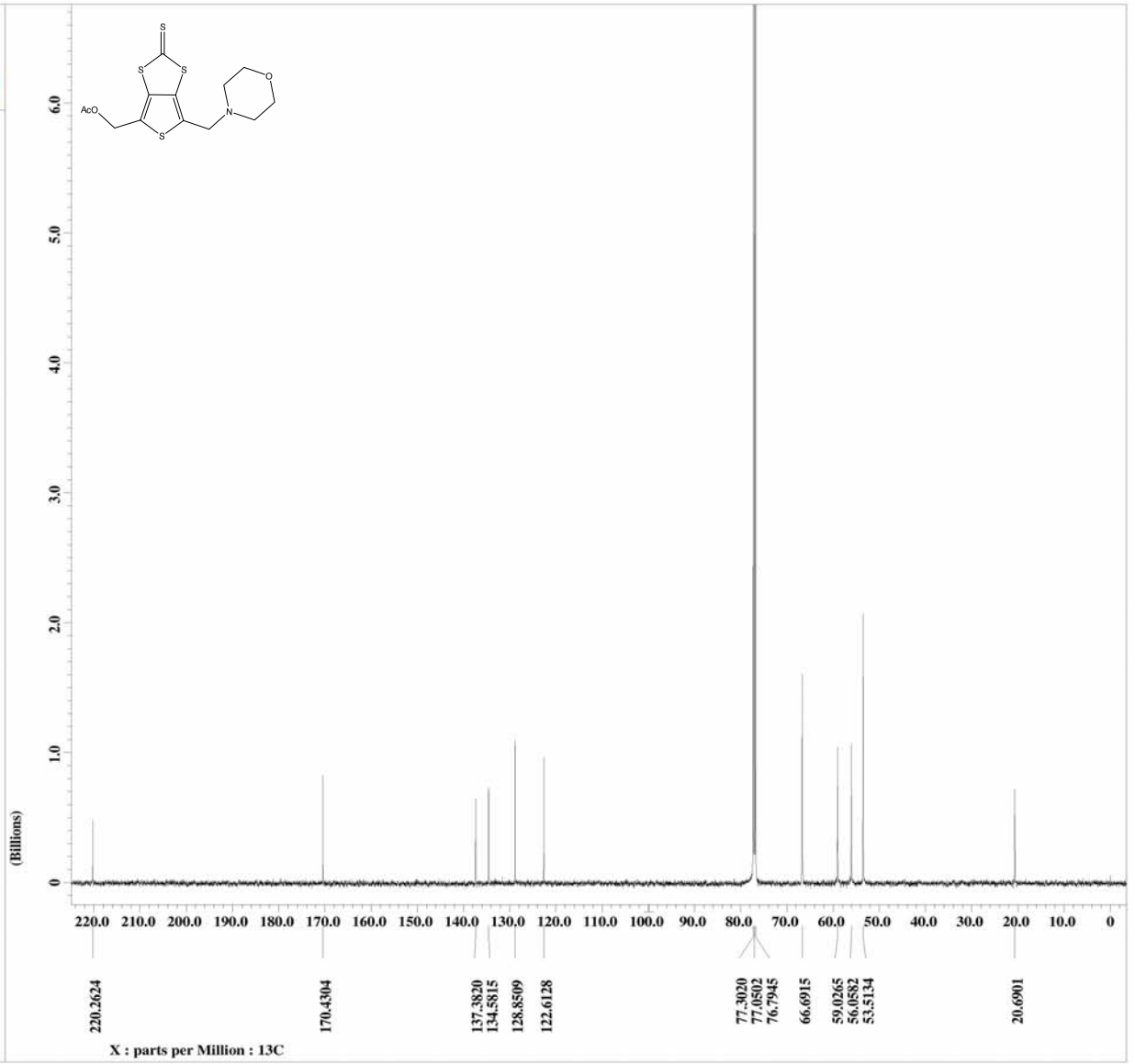

Filename = XC-IV-148-9.jdf
Experiment = single_pulse.exp
Sample_id = S#279968
Solvent = CHLOROFORM-D
Creation_time = 9-SEP-2004 05:02:27
Revision_time = 7-FEB-2007 00:53:05
Current_time = 7-FEB-2007 00:53:53
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 17
Relaxation_delay = 1[s]
Temp_get = 24[dC]
Unblank_time = 2[us]
AcO
S
S
S
S
O
N
2
4.01
2.001
4.007
3.015
(Thousands)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2715
5.1359
3.7782
3.7690
3.7599
3.5785
2.5441
2.5359
2.5276
2.1172
-0.0000
X : parts per Million : 1H

```
Filename          = XC-IV-148-8.jdf
Experiment        = single_pulse_dec
Sample_id         = S#281998
Solvent           = CHLOROFORM-D
Creation_time     =  9-SEP-2004 08:00:51
Revision_time     =  7-FEB-2007 00:55:37
Current_time      =  7-FEB-2007 00:56:18

Content           = Single Pulse with Bro
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

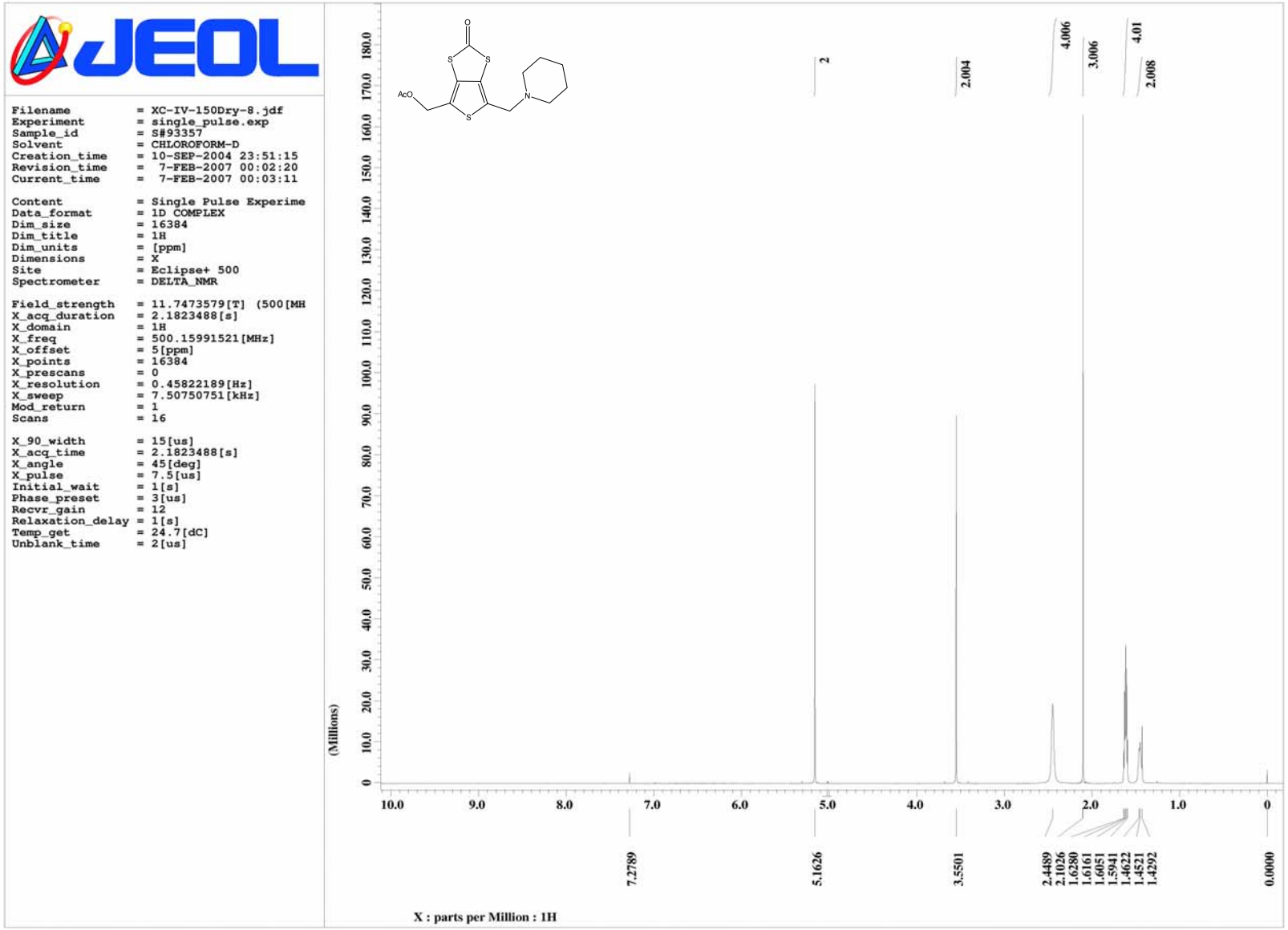
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Mod_return        = 1
Scans             = 2578

X_90_width        = 14[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.66666667[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 29
Relaxation_delay  = 2[s]
Temp_get          = 24.9[dC]
Unblank_time      = 2[us]
```



APPENDIX 20

^{1}H and ^{13}C-NMR spectra of (4-(piperidin-1-yl)methyl)-2-oxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate (22)

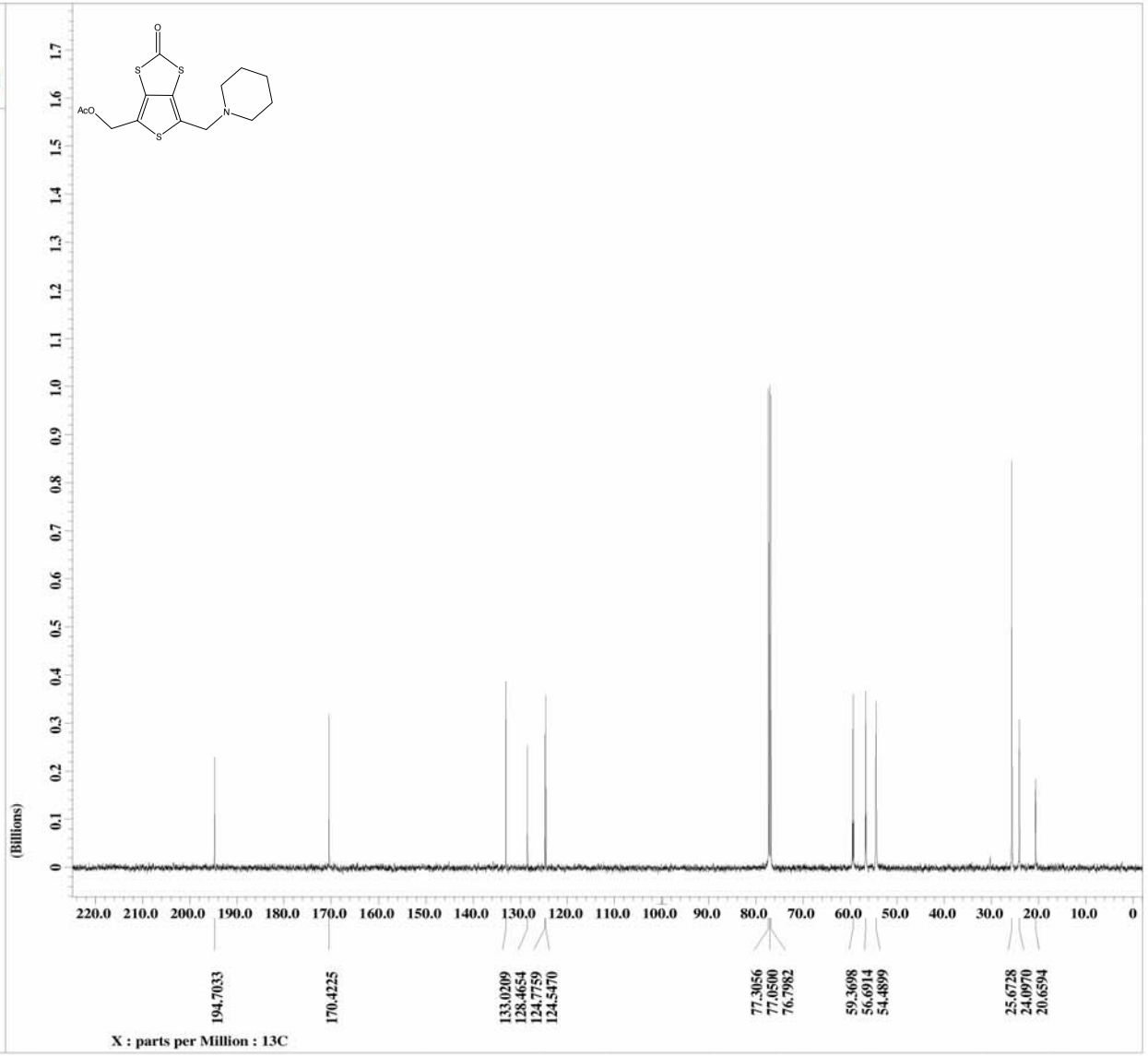

Filename = XC-IV-150Dry-8.jdf
Experiment = single_pulse.exp
Sample_id = S#93357
Solvent = CHLOROFORM-D
Creation_time = 10-SEP-2004 23:51:15
Revision_time = 7-FEB-2007 00:02:20
Current_time = 7-FEB-2007 00:03:11
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 12
Relaxation_delay = 1[s]
Temp_get = 24.7[dC]
Unblank_time = 2[us]
AcO
O
S
S
S
N
2
2.004
4.006
3.006
4.01
2.008
(Millions)
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
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2789
5.1626
3.5501
2.4489
2.1026
1.6280
1.6161
1.6051
1.5941
1.4622
1.4521
1.4292
0.0000
X : parts per Million : 1H

```
Filename          = XC-IV-150-7.jdf
Experiment        = single_pulse_dec
Sample_id         = S#325350
Solvent           = CHLOROFORM-D
Creation_time     = 10-SEP-2004 06:45:14
Revision_time     =  7-FEB-2007 00:07:47
Current_time      =  7-FEB-2007 00:08:24

Content           = Single Pulse with Bro
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

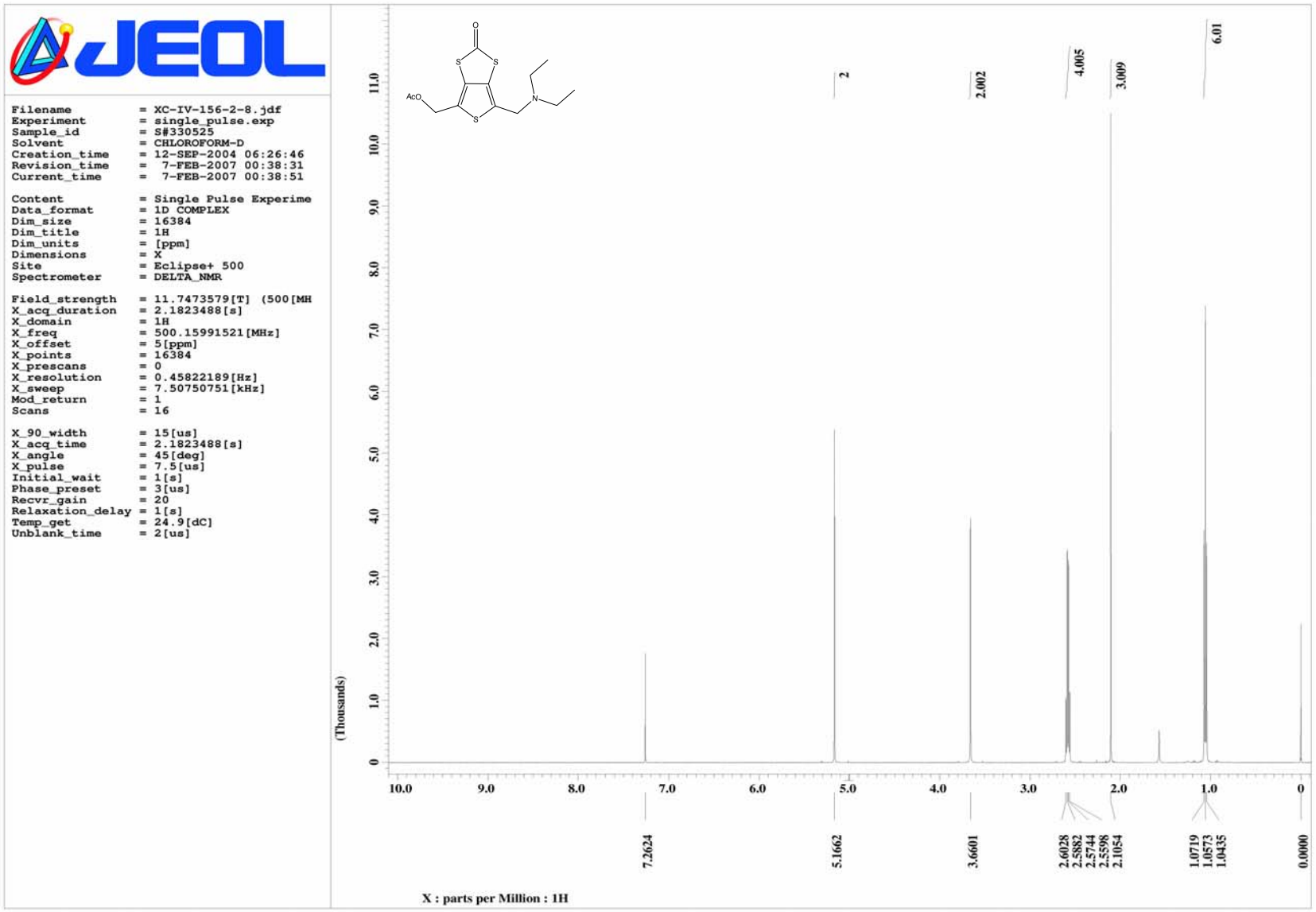
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Mod_return        = 1
Scans             = 269

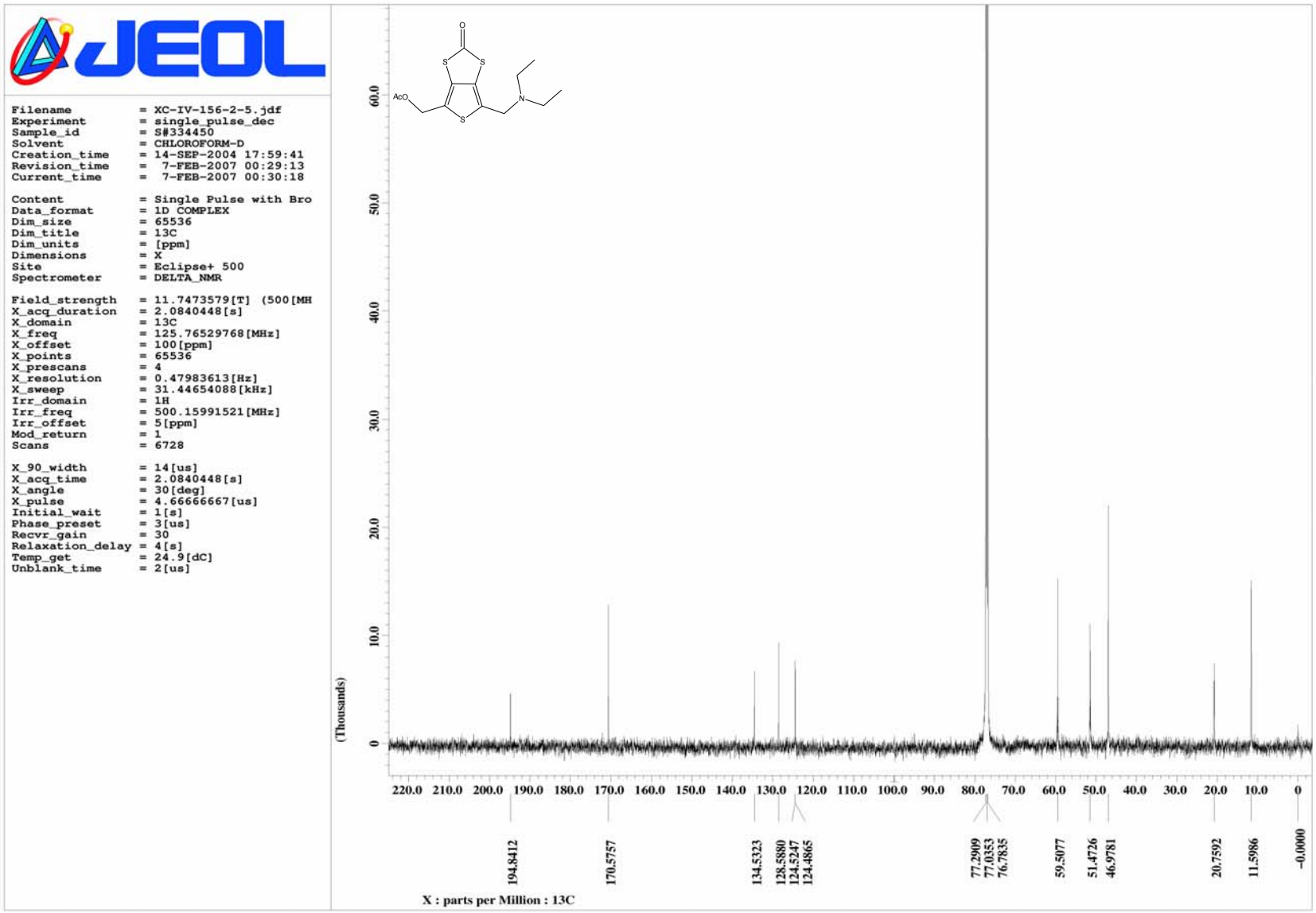
X_90_width        = 14[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.66666667[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 29
Relaxation_delay  = 4[s]
Temp_get          = 24.6[dC]
Unblank_time      = 2[us]
```



APPENDIX 21

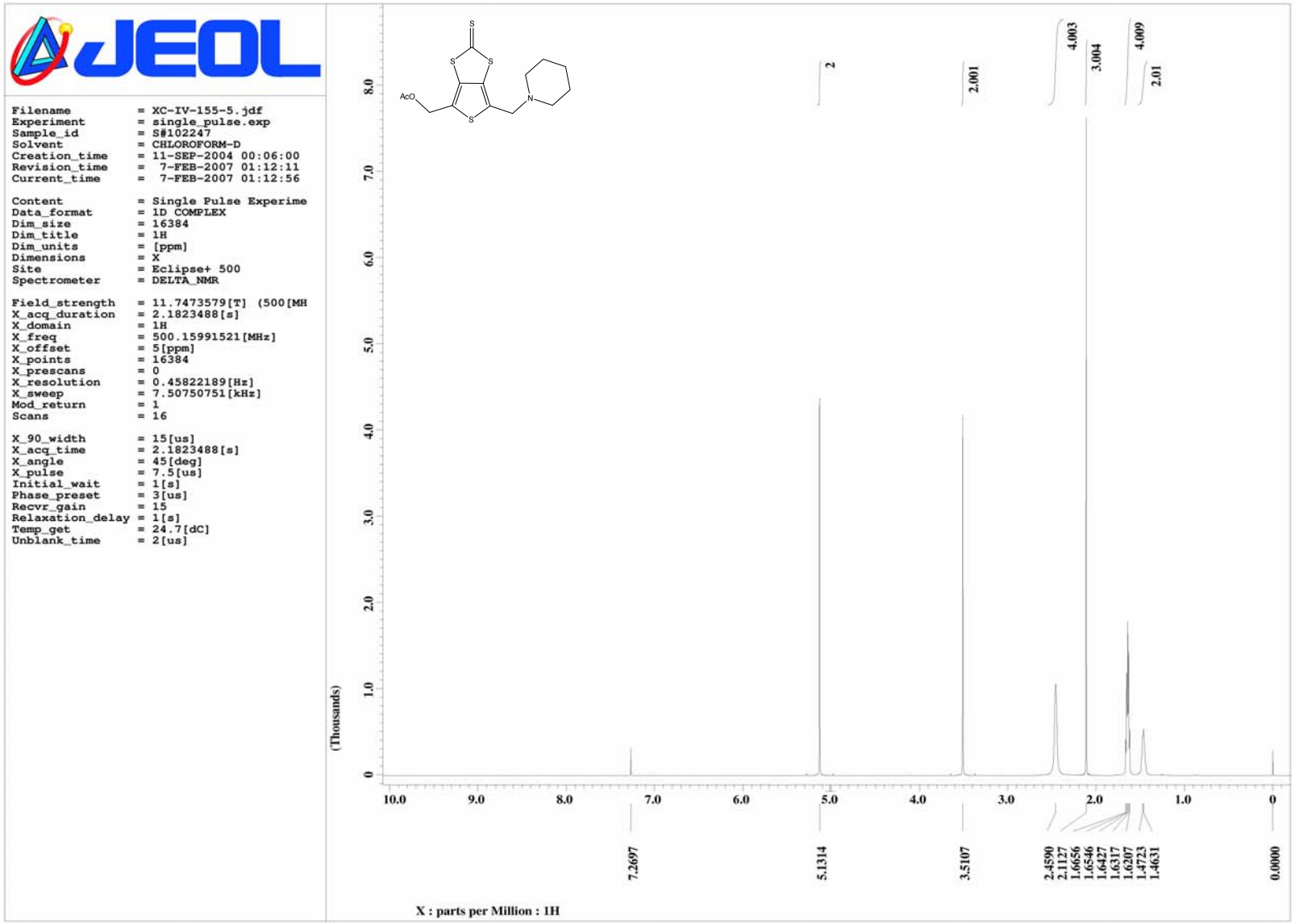
^{1}H and ^{13}C-NMR spectra of (4-(diethylamino)methyl)-2-oxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate (23)

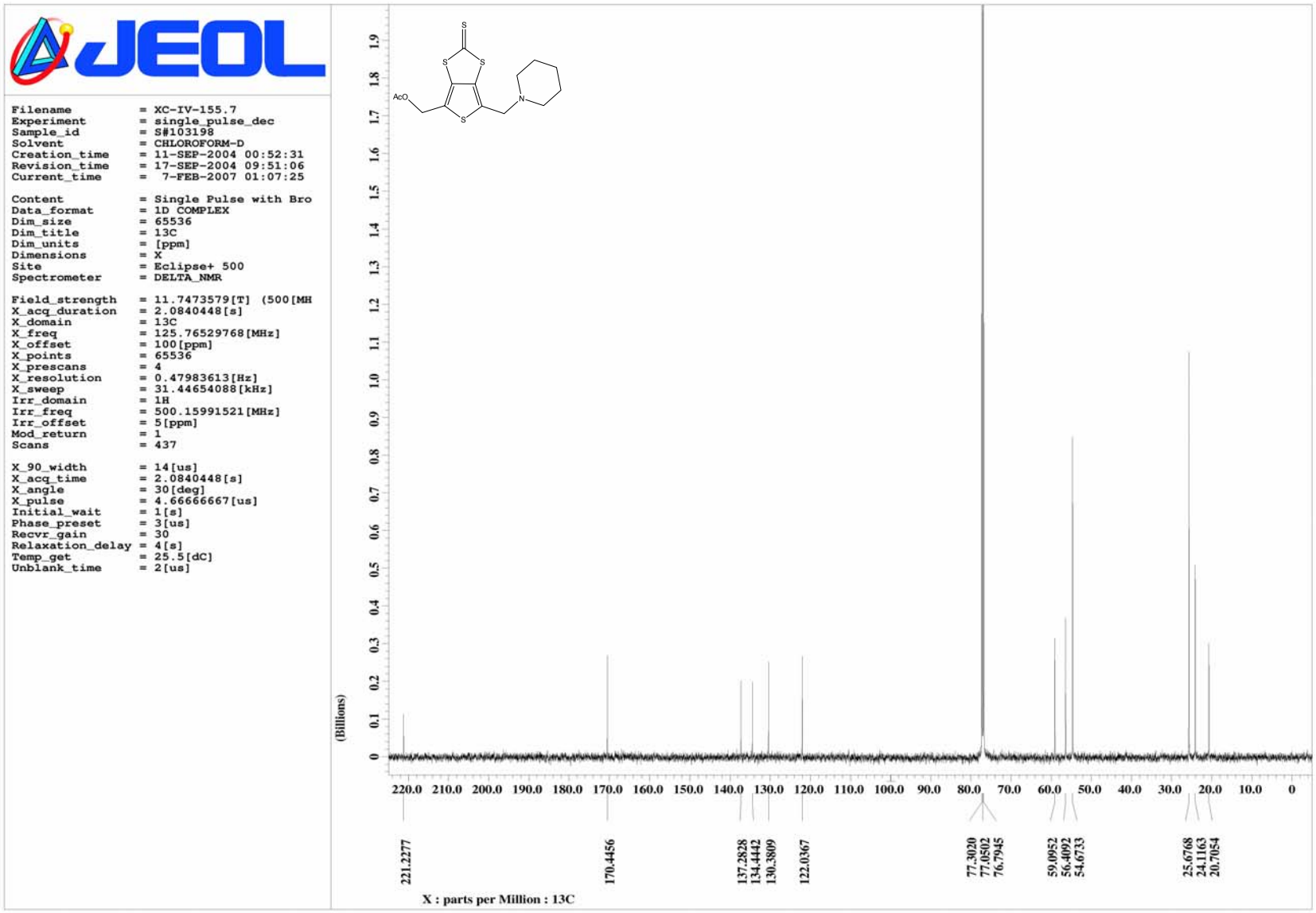

Filename = XC-IV-156-2-8.jdf
Experiment = single_pulse.exp
Sample_id = S#330525
Solvent = CHLOROFORM-D
Creation_time = 12-SEP-2004 06:26:46
Revision_time = 7-FEB-2007 00:38:31
Current_time = 7-FEB-2007 00:38:51
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 1[s]
Temp_get = 24.9[dC]
Unblank_time = 2[us]
AcO
N
S
O
(Thousands)
2
2.002
4.005
3.009
6.01
7.2624
5.1662
3.6601
2.6028
2.5882
2.5744
2.5598
2.1054
1.0719
1.0573
1.0435
0.0000
X : parts per Million : 1H


Filename = XC-IV-156-2-5.jdf
Experiment = single_pulse_dec
Sample_id = S#334450
Solvent = CHLOROFORM-D
Creation_time = 14-SEP-2004 17:59:41
Revision_time = 7-FEB-2007 00:29:13
Current_time = 7-FEB-2007 00:30:18
Content = Single Pulse with Bro
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]
Mod_return = 1
Scans = 6728
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 24.9[dC]
Unblank_time = 2[us]
AcO
O
S
S
S
N
(Thousands)
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
194.8412
170.5757
134.5323
128.5880
124.5247
124.4865
77.2909
77.0353
76.7835
59.5077
51.4726
46.9781
20.7592
11.5986
-0.0000
X : parts per Million : 13C

APPENDIX 22

^{1}H and ^{13}C-NMR spectra of (4-(piperidin-1-yl)methyl)-2-thioxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate (24)


Filename = XC-IV-155-5.jdf
Experiment = single_pulse.exp
Sample_id = S#102247
Solvent = CHLOROFORM-D
Creation_time = 11-SEP-2004 00:06:00
Revision_time = 7-FEB-2007 01:12:11
Current_time = 7-FEB-2007 01:12:56
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 1[s]
Temp_get = 24.7[dC]
Unblank_time = 2[us]
AcO
S
S
S
S
N
2
2.001
4.003
3.004
4.009
2.01
(Thousands)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2697
5.1314
3.5107
2.4590
2.1127
1.6656
1.6546
1.6427
1.6317
1.6207
1.4723
1.4631
0.0000
X : parts per Million : 1H


Filename = XC-IV-155.7
Experiment = single_pulse_dec
Sample_id = S#103198
Solvent = CHLOROFORM-D
Creation_time = 11-SEP-2004 00:52:31
Revision_time = 17-SEP-2004 09:51:06
Current_time = 7-FEB-2007 01:07:25
Content = Single Pulse with Bro
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]
Mod_return = 1
Scans = 437
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 25.5[dC]
Unblank_time = 2[us]
S
S
S
S
AcO
N
(Billions)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
221.2277
170.4456
137.2828
134.4442
130.3809
122.0367
77.3020
77.0502
76.7945
59.0952
56.4092
54.6733
25.6768
24.1163
20.7054
X : parts per Million : 13C

APPENDIX 23

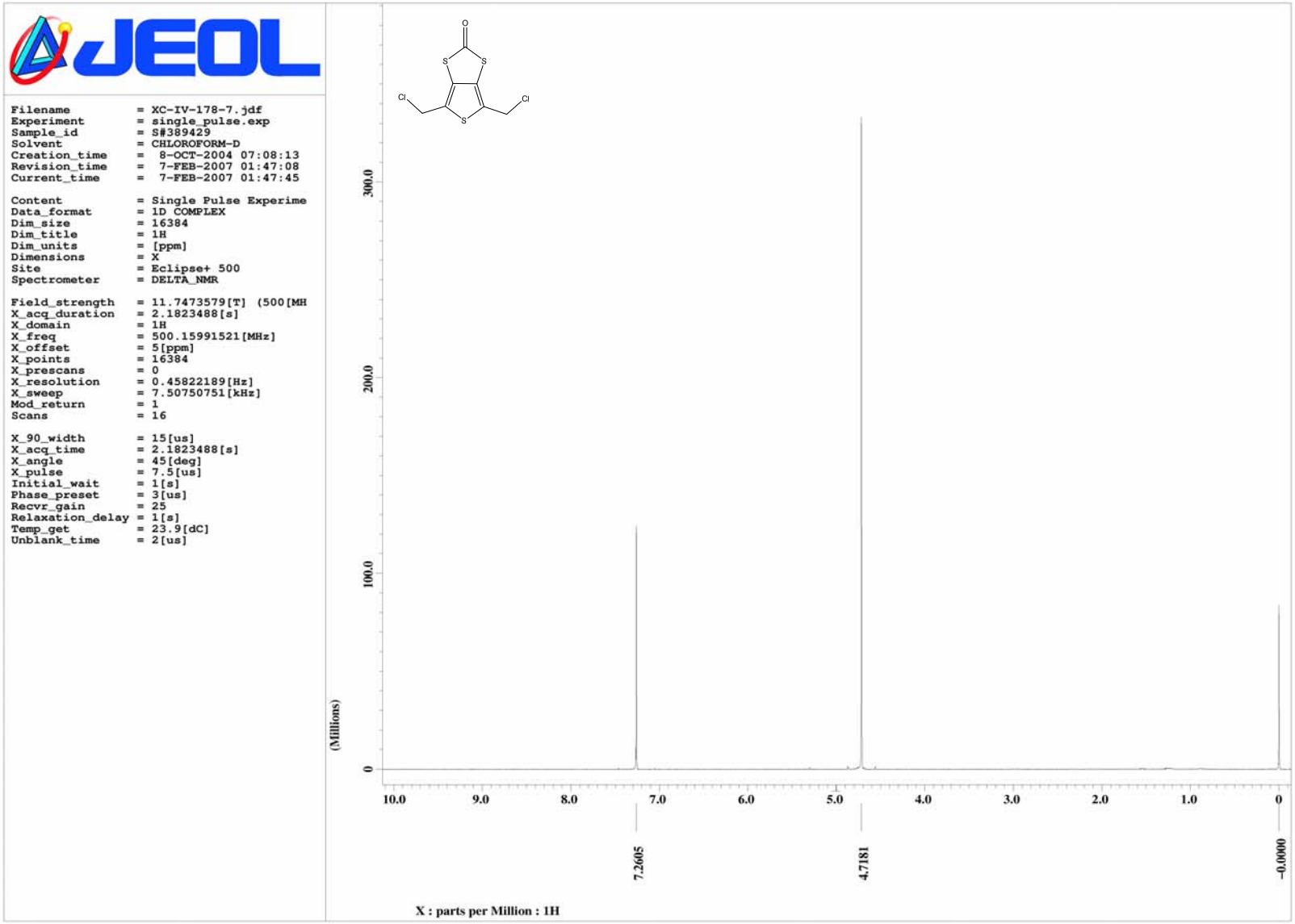
^{1}H and ^{13}C-NMR spectra of (4-(diethylamino)methyl)-2-thioxothieno[3,4-*d*]-1,3-dithiol-6-yl)methyl acetate (25)

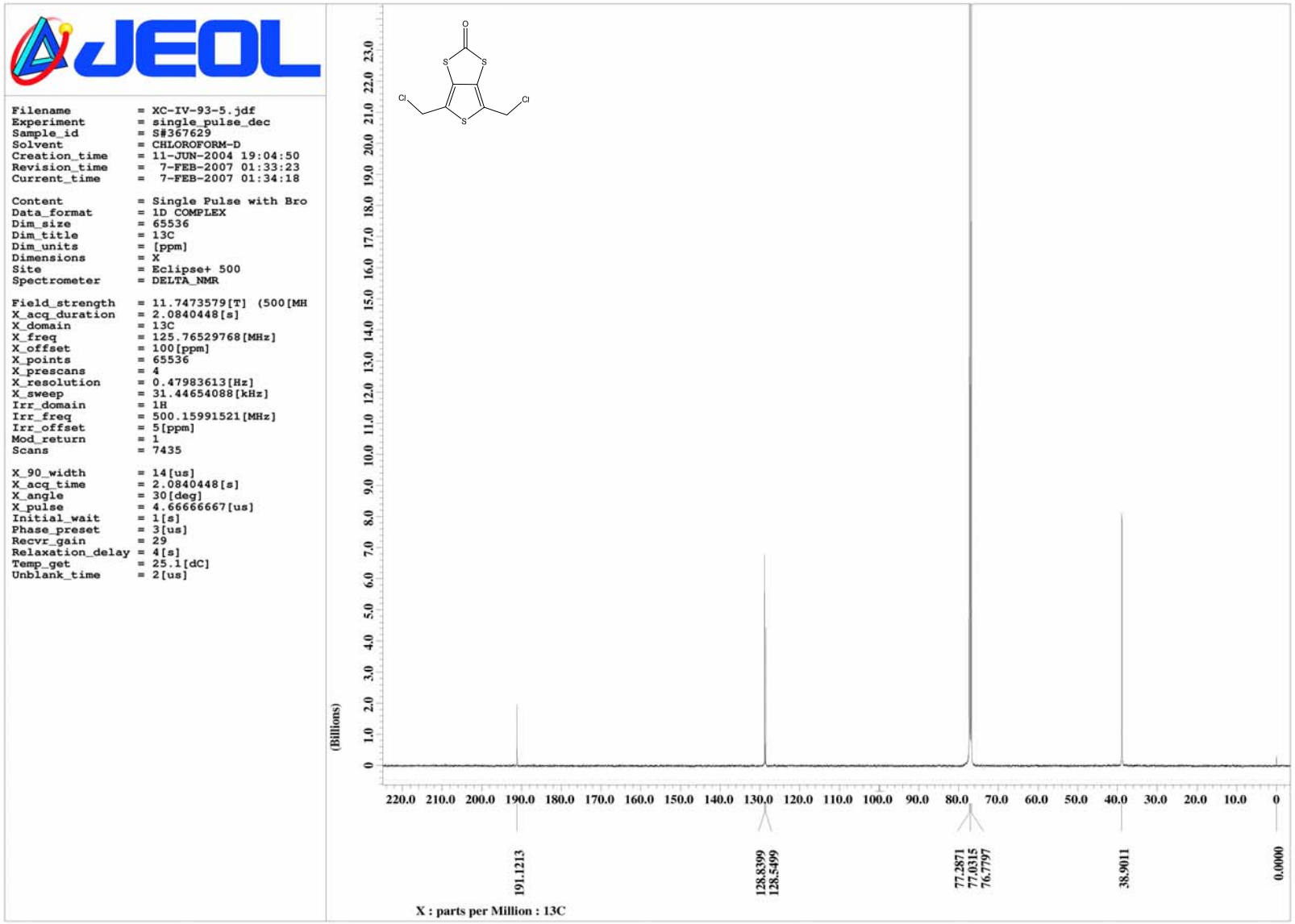
JEOL
Filename = XC-IV-157-2-8.jdf
Experiment = single_pulse.exp
Sample_id = S#363446
Solvent = CHLOROFORM-D
Creation_time = 11-SEP-2004 07:21:50
Revision_time = 7-FEB-2007 01:22:31
Current_time = 7-FEB-2007 01:24:04
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 3[s]
Phase_preset = 3[us]
Recvr_gain = 17
Relaxation_delay = 2[s]
Temp_get = 24.1[dC]
Unblank_time = 2[us]
(Thousands)
X : parts per Million : 1H
7.2651
5.1350
3.6225
2.6156
2.6019
2.5872
2.5735
2.1154
1.0811
1.0673
1.0527
0.0000
6.007
3.001
4.005
2.01
2
AcO

JEOL
Filename = XC-IV-157-2-5.jdf
Experiment = single pulse_dec
Sample_id = SH247026
Solvent = CHLOROFORM-D
Creation_time = 12-SEP-2004 06:19:42
Revision_time = 7-FEB-2007 01:25:05
Current_time = 7-FEB-2007 01:25:55
Content = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 2.08404481[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]
Mod_return = 1
Scans = 1936
X_90_width = 14[us]
X_acq_time = 2.08404481[s]
X_angle = 30.[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1.[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 2.[s]
Temp_get = 25.6[dC]
Unblank_time = 2[us]
AcO
(Billions)
3.0
2.0
1.0
0
X : parts per Million : 13C
221.3458
170.5065
137.2941
134.2876
131.6588
122.0061
77.3056
77.0500
76.7982
59.1561
51.0142
47.1111
20.7396
11.5370

APPENDIX 24

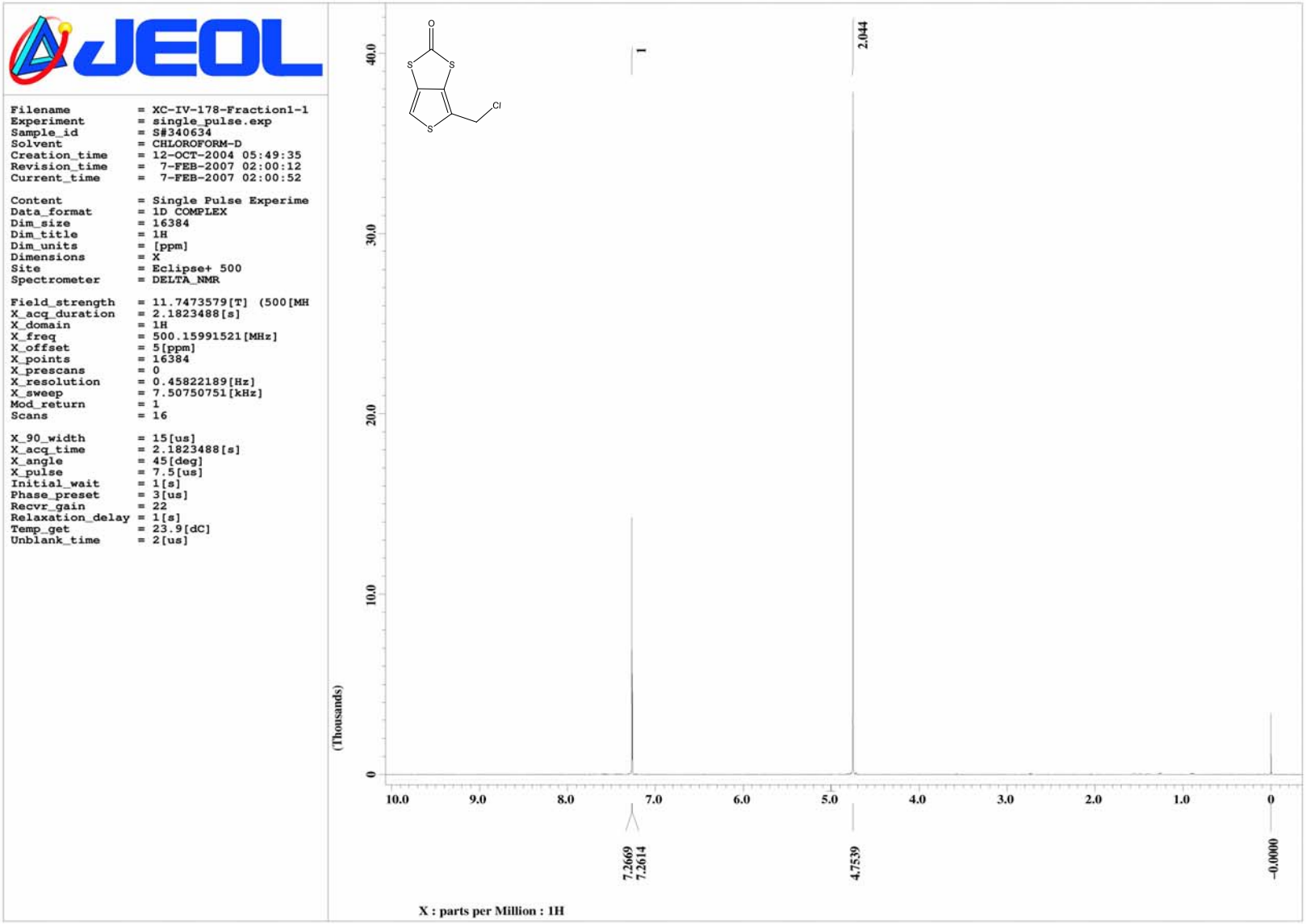
^{1}H and ^{13}C-NMR spectra of 4,6-bis(chloromethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (26)


Filename = XC-IV-178-7.jdf
Experiment = single_pulse.exp
Sample_id = S#389429
Solvent = CHLOROFORM-D
Creation_time = 8-OCT-2004 07:08:13
Revision_time = 7-FEB-2007 01:47:08
Current_time = 7-FEB-2007 01:47:45
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 25
Relaxation_delay = 1[s]
Temp_get = 23.9[dC]
Unblank_time = 2[us]
O
S
S
Cl
Cl
S
(Millions)
300.0
200.0
100.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2605
4.7181
-0.0000
X : parts per Million : 1H


Filename = XC-IV-93-5.jdf
Experiment = single_pulse_dec
Sample_id = S#367629
Solvent = CHLOROFORM-D
Creation_time = 11-JUN-2004 19:04:50
Revision_time = 7-FEB-2007 01:33:23
Current_time = 7-FEB-2007 01:34:18
Content = Single Pulse with Bro
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]
Mod_return = 1
Scans = 7435
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 4[s]
Temp_get = 25.1[dC]
Unblank_time = 2[us]
O
S
S
Cl
Cl
S
(Billions)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
191.1213
128.8399
128.5499
77.2871
77.0315
76.7797
38.9011
0.0000
X : parts per Million : 13C

APPENDIX 25

^{1}H and ^{13}C-NMR spectra of 4-(chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (27)

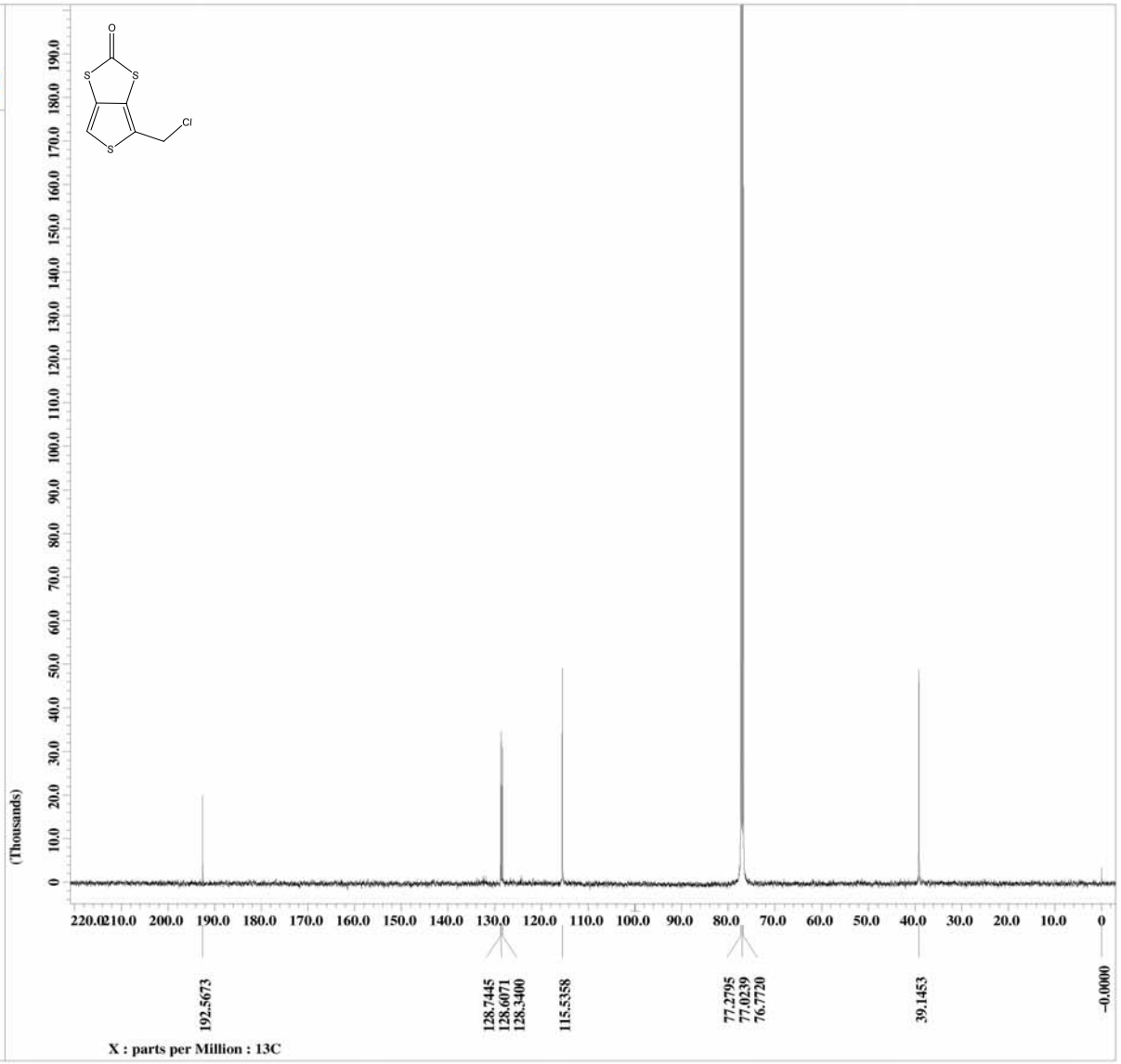

Filename = XC-IV-178-Fraction1-1
Experiment = single_pulse.exp
Sample_id = S#340634
Solvent = CHLOROFORM-D
Creation_time = 12-OCT-2004 05:49:35
Revision_time = 7-FEB-2007 02:00:12
Current_time = 7-FEB-2007 02:00:52
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 22
Relaxation_delay = 1[s]
Temp_get = 23.9[dC]
Unblank_time = 2[us]
O
S
S
S
Cl
1
2.044
40.0
30.0
20.0
10.0
0
(Thousands)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2669
7.2614
4.7539
0.0000
X : parts per Million : 1H

```
Filename          = XC-IV-178-Fraction1-5
Experiment        = single_pulse_dec
Sample_id         = S#341705
Solvent           = CHLOROFORM-D
Creation_time     = 12-OCT-2004 16:14:59
Revision_time     =  7-FEB-2007 02:02:14
Current_time      =  7-FEB-2007 02:03:23

Content           = Single Pulse with Bro
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

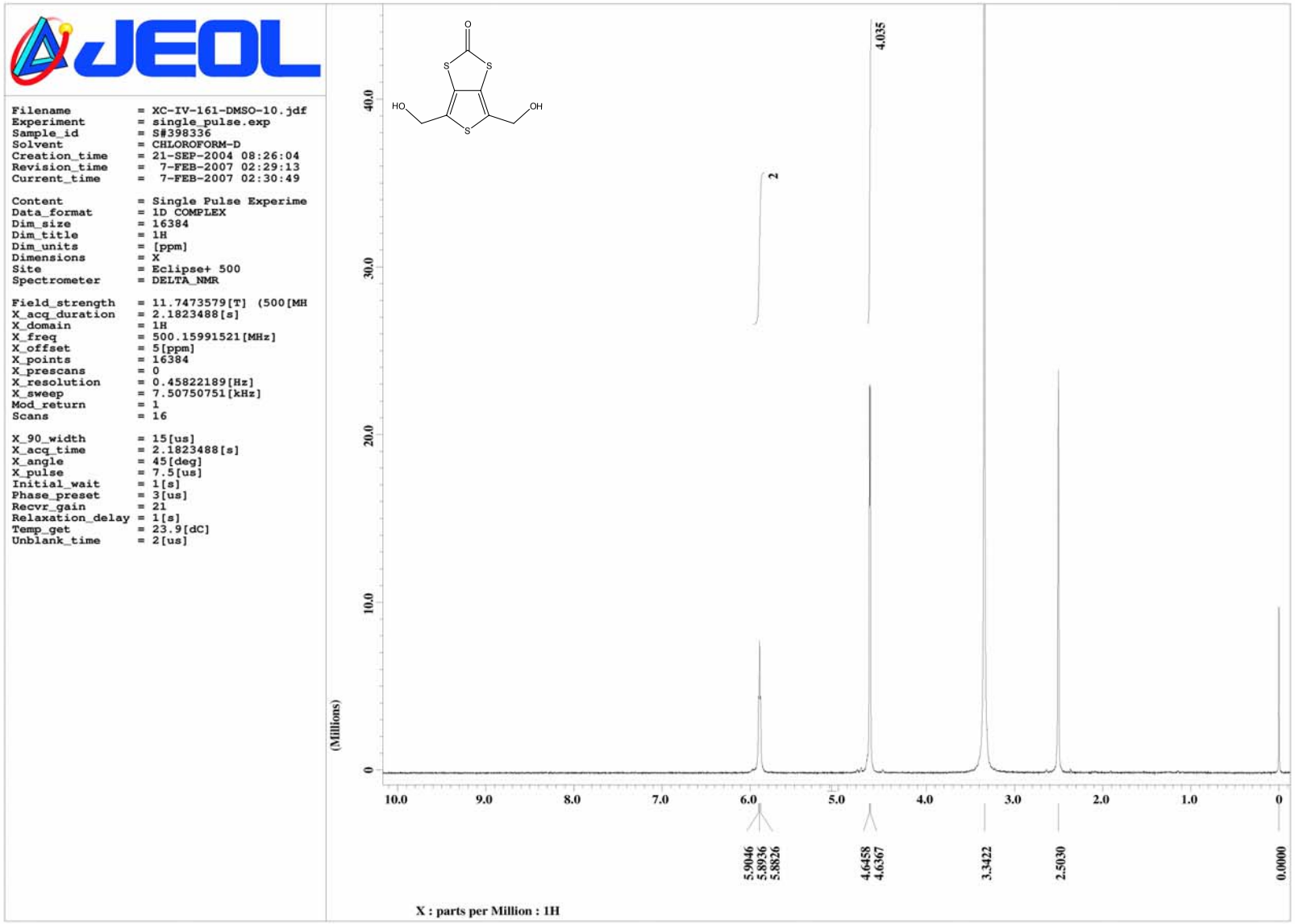
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Mod_return        = 1
Scans             = 6132

X_90_width        = 14[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.66666667[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 4[s]
Temp_get          = 24.9[dC]
Unblank_time      = 2[us]
```



APPENDIX 26

^{1}H and ^{13}C-NMR spectra of
4,6-bis(hydroxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (28)
(DMSO-d_6)

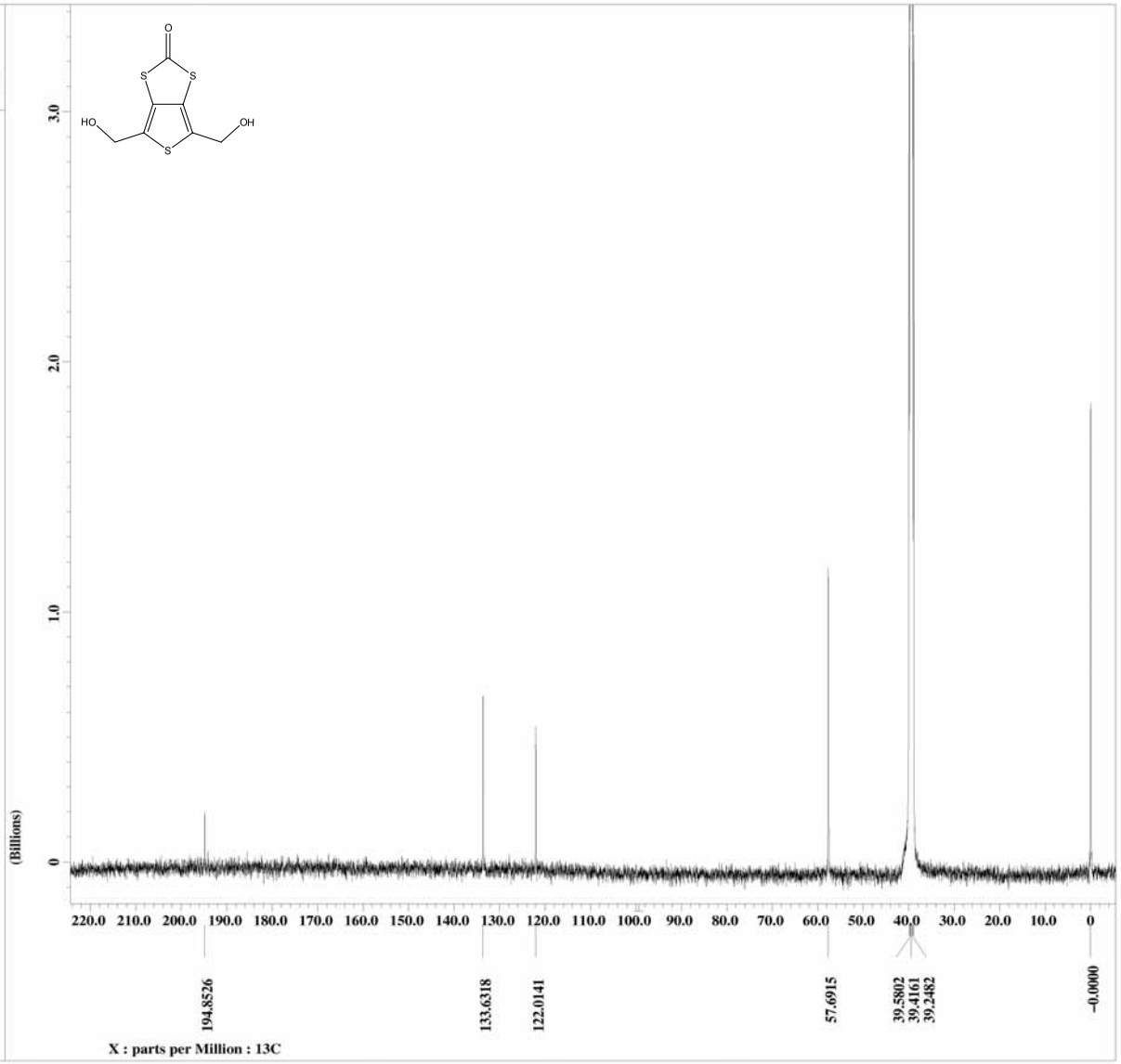

Filename = XC-IV-161-DMSO-10.jdf
Experiment = single_pulse.exp
Sample_id = S#398336
Solvent = CHLOROFORM-D
Creation_time = 21-SEP-2004 08:26:04
Revision_time = 7-FEB-2007 02:29:13
Current_time = 7-FEB-2007 02:30:49
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 21
Relaxation_delay = 1[s]
Temp_get = 23.9[dC]
Unblank_time = 2[us]
HO
OH
O
S
S
S
4.035
2
40.0
30.0
20.0
10.0
0
(Millions)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.9046
5.8936
5.8826
4.6458
4.6367
3.3422
2.5030
0.0000
X : parts per Million : 1H

```
Filename          = XC-IV-102DMSO-5.jdf
Experiment        = single_pulse_dec
Sample_id         = S#461638
Solvent           = CHLOROFORM-D
Creation_time     = 20-JUN-2004 22:11:21
Revision_time     =  7-FEB-2007 02:16:17
Current_time      =  7-FEB-2007 02:18:34

Content           = Single Pulse with Bro
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

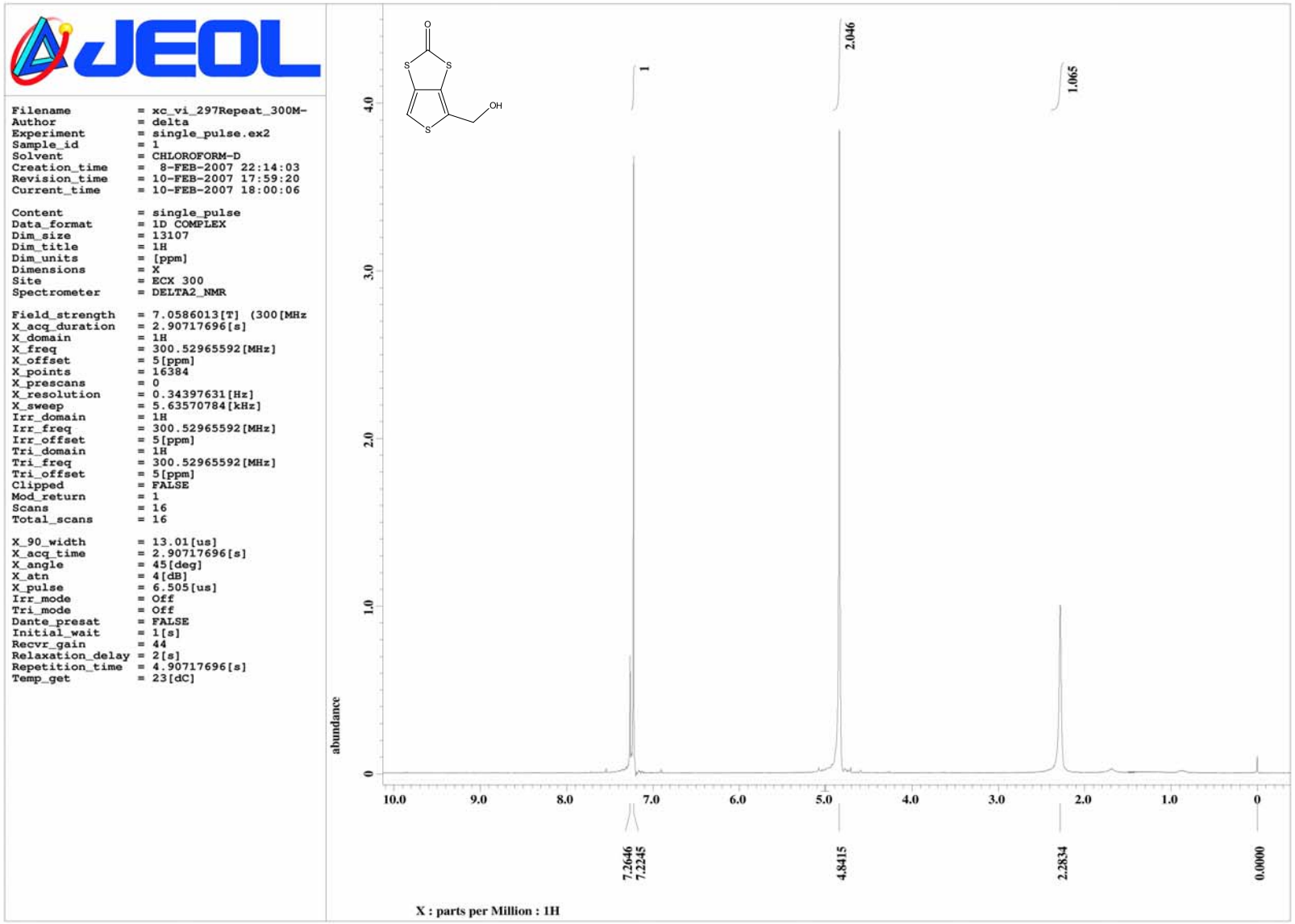
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Mod_return        = 1
Scans             = 7672

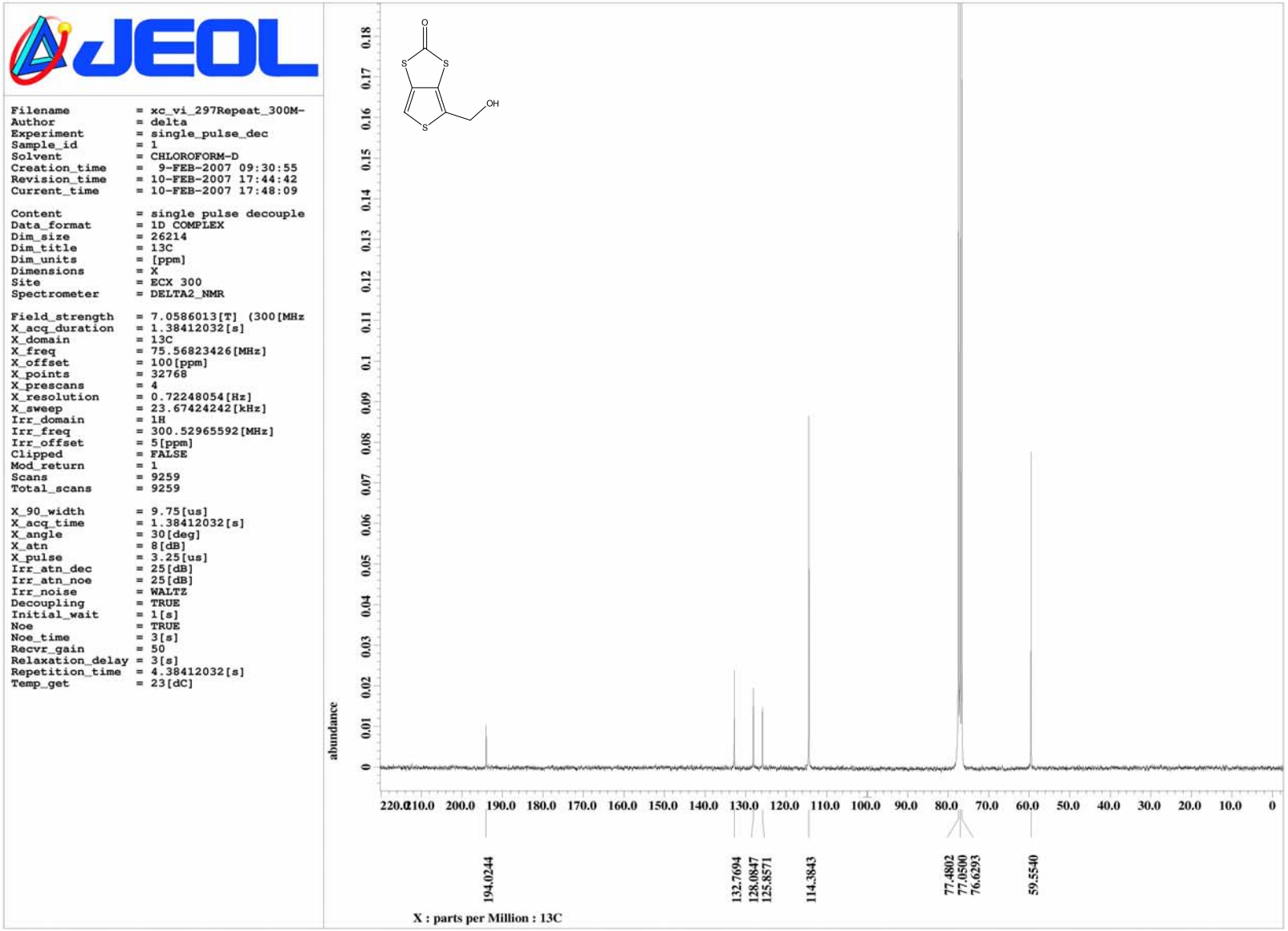
X_90_width        = 14[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.66666667[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 28
Relaxation_delay  = 4[s]
Temp_get          = 24.4[dC]
Unblank_time      = 2[us]
```



APPENDIX 27

^{1}H and ^{13}C-NMR spectra of 4-(hydroxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (29)


Filename = xc_vi_297Repeat_300M-
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 8-FEB-2007 22:14:03
Revision_time = 10-FEB-2007 17:59:20
Current_time = 10-FEB-2007 18:00:06
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 44
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 23[dC]
O
S
S
S
OH
1
2.046
1.065
abundance
4.0
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2646
7.2245
4.8415
2.2834
0.0000
X : parts per Million : 1H



```
Filename          = xc_vi_297Repeat_300M-
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     =  9-FEB-2007 09:30:55
Revision_time     = 10-FEB-2007 17:44:42
Current_time      = 10-FEB-2007 17:48:09

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 1.38412032[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.72248054[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 9259
Total_scans       = 9259

X_90_width        = 9.75[us]
X_acq_time        = 1.38412032[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          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 4.38412032[s]
Temp_get          = 23[dC]
```

APPENDIX 28

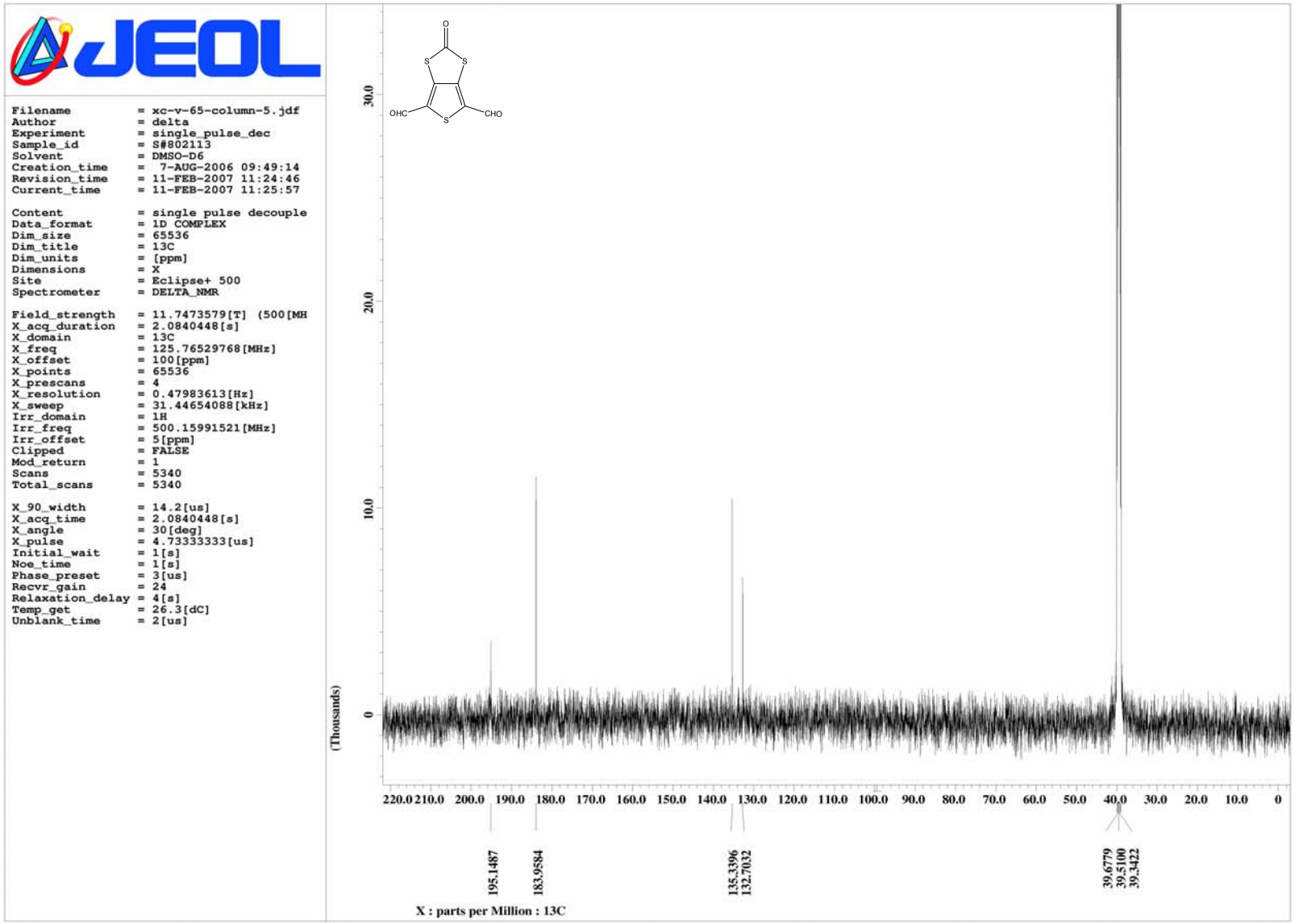
^{1}H and ^{13}C-NMR spectra of 2-oxothieno[3,4-*d*]-1,3-dithiole-4,6-dicarbaldehyde (30) (DMSO-d_6)

```
Filename          = xc-v-65-part-2-DMSO-5
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#362336
Solvent           = DMSO-D6
Creation_time     =  8-AUG-2006 11:05:19
Revision_time     = 11-FEB-2007 11:21:14
Current_time      = 11-FEB-2007 11:22:50

Content           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

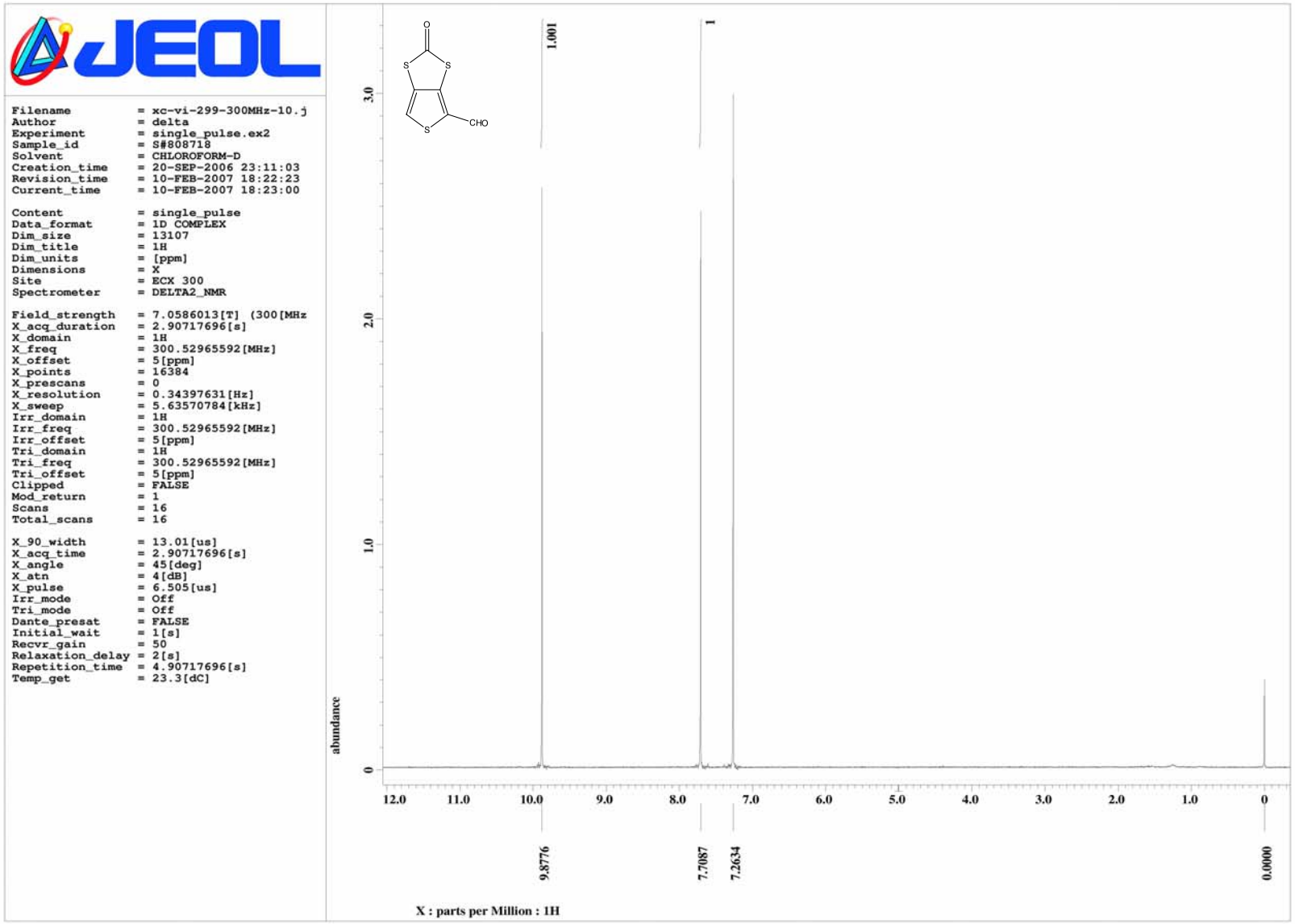
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

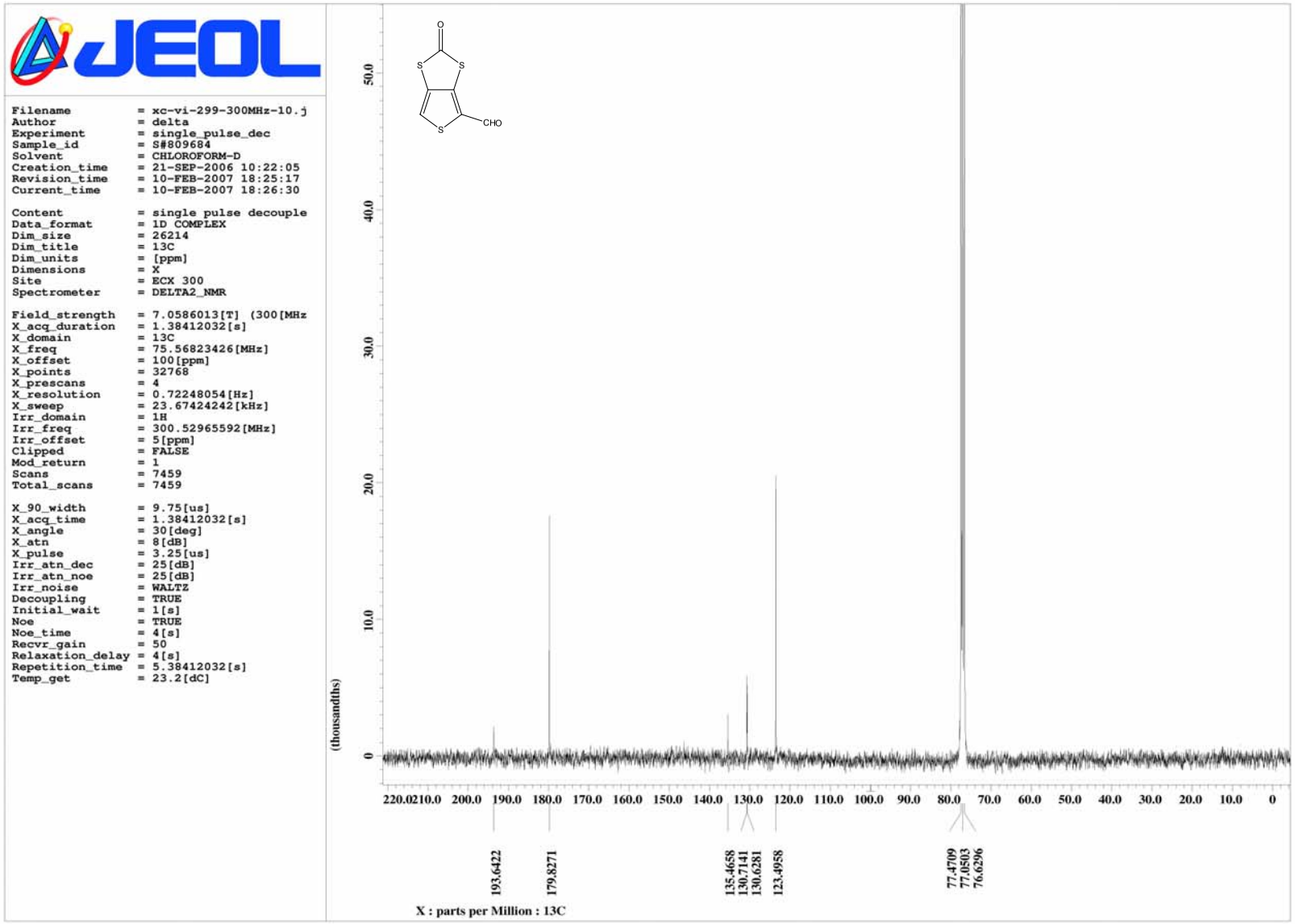
X_90_width        = 18.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 25
Relaxation_delay  = 1[s]
Temp_get          = 25[dC]
Unblank_time      = 2[us]
```


Filename = xc-v-65-column-5.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#802113
Solvent = DMSO-D6
Creation_time = 7-AUG-2006 09:49:14
Revision_time = 11-FEB-2007 11:24:46
Current_time = 11-FEB-2007 11:25:57
Content = single pulse decouple
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 = 5340
Total_scans = 5340
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 24
Relaxation_delay = 4[s]
Temp_get = 26.3[dC]
Unblank_time = 2[us]
O
S
S
OHC
CHO
S
30.0
20.0
10.0
0
(Thousands)
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
195.1487
183.9584
135.3396
132.7032
39.6779
39.5100
39.3422
X : parts per Million : 13C

APPENDIX 29

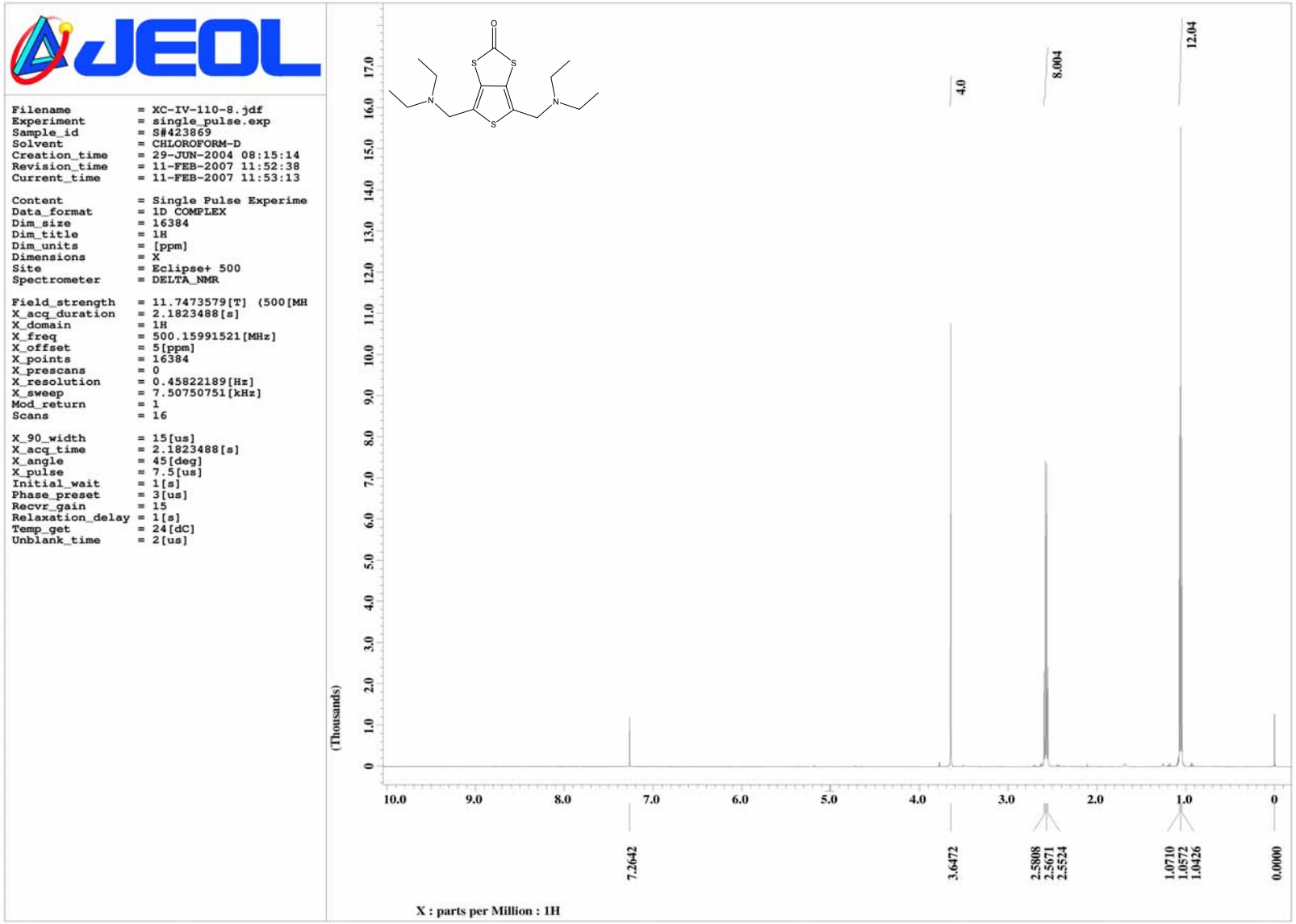
^{1}H and ^{13}C-NMR spectra of 2-oxothieno[3,4-*d*]-1,3-dithiole-4-carbaldehyde (31)

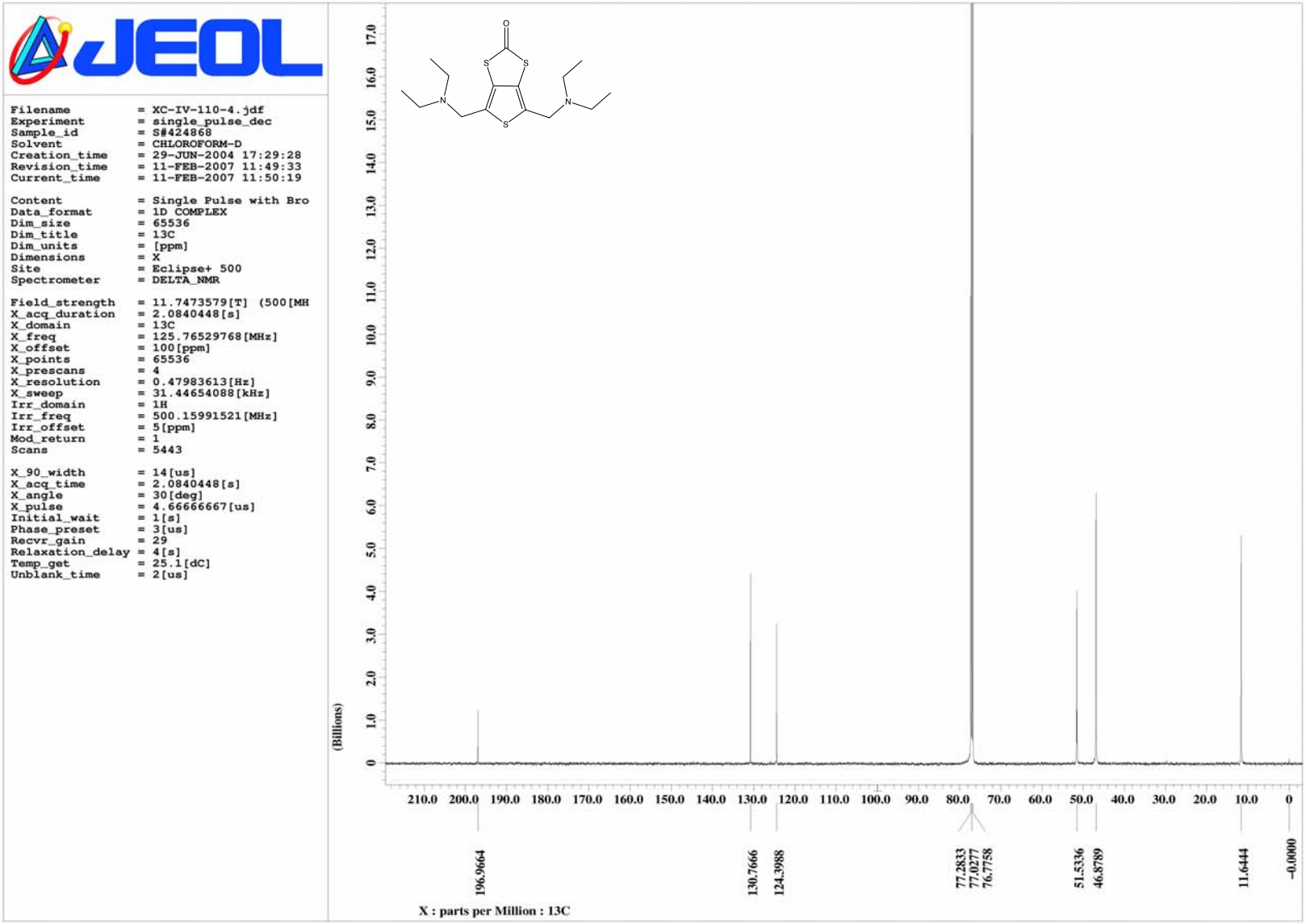

Filename = xc-vi-299-300MHz-10.j
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#808718
Solvent = CHLOROFORM-D
Creation_time = 20-SEP-2006 23:11:03
Revision_time = 10-FEB-2007 18:22:23
Current_time = 10-FEB-2007 18:23:00
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 23.3[dC]
O
S
S
S
CHO
1.001
1
abundance
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.8776
7.7087
7.2634
0.0000
X : parts per Million : 1H


Filename = xc-vi-299-300MHz-10.j
Author = delta
Experiment = single_pulse_dec
Sample_id = S#809684
Solvent = CHLOROFORM-D
Creation_time = 21-SEP-2006 10:22:05
Revision_time = 10-FEB-2007 18:25:17
Current_time = 10-FEB-2007 18:26:30
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 1.38412032[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.72248054[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 7459
Total_scans = 7459
X_90_width = 9.75[us]
X_acq_time = 1.38412032[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 = 4[s]
Recvr_gain = 50
Relaxation_delay = 4[s]
Repetition_time = 5.38412032[s]
Temp_get = 23.2[dC]
O
S
S
S
CHO
(thousandths)
50.0
40.0
30.0
20.0
10.0
0
220.0210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
193.6422
179.8271
135.4658
130.7141
130.6281
123.4958
77.4709
77.0503
76.6296
X : parts per Million : 13C

APPENDIX 30

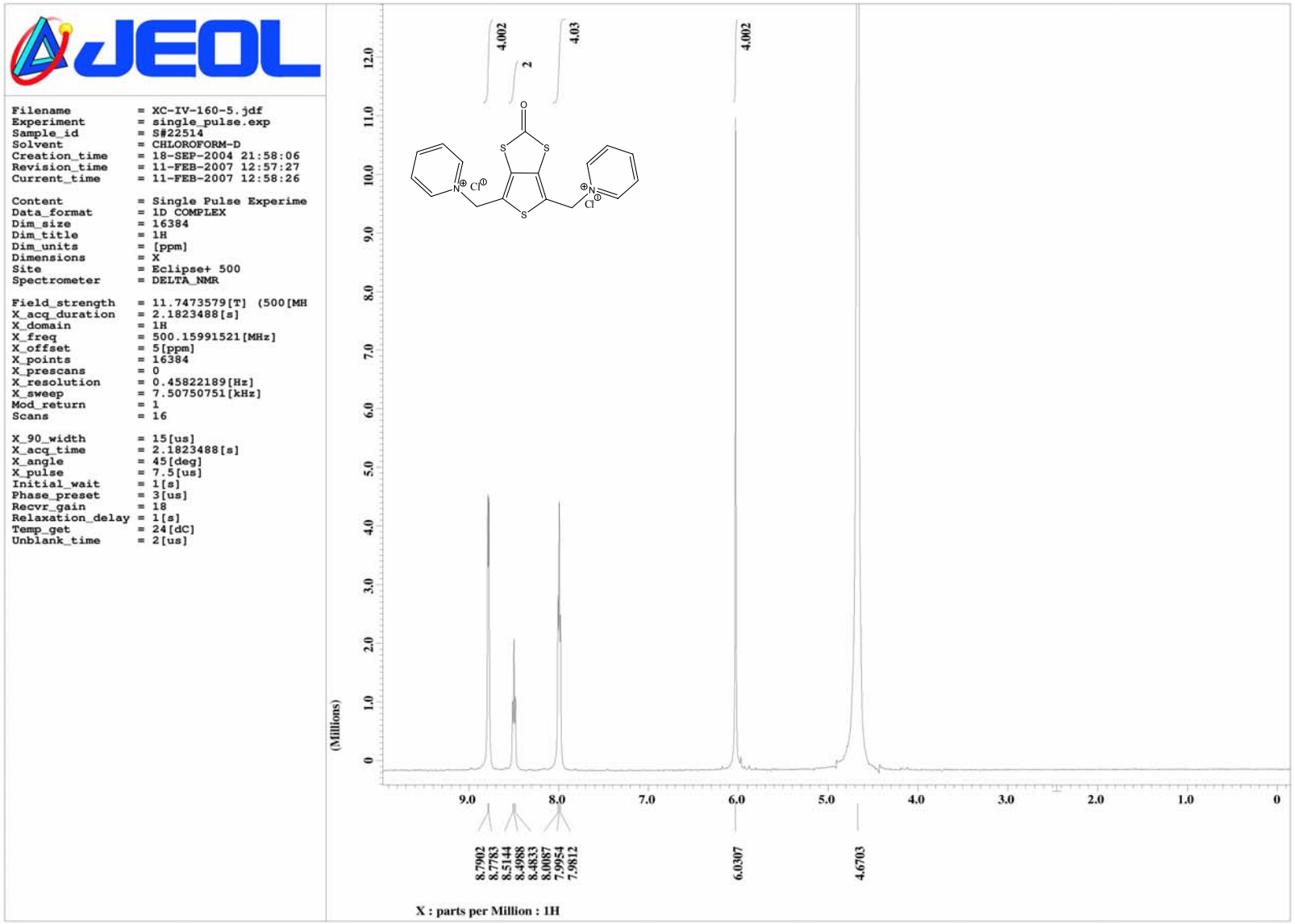
^{1}H and ^{13}C-NMR spectra of 4,6-bis((diethylamino)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (32)


Filename = XC-IV-110-8.jdf
Experiment = single_pulse.exp
Sample_id = S#423869
Solvent = CHLOROFORM-D
Creation_time = 29-JUN-2004 08:15:14
Revision_time = 11-FEB-2007 11:52:38
Current_time = 11-FEB-2007 11:53:13
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 1[s]
Temp_get = 24[dC]
Unblank_time = 2[us]
(Thousands)
4.0
8.004
12.04
7.2642
3.6472
2.5808
2.5671
2.5524
1.0710
1.0572
1.0426
0.0000
X : parts per Million : 1H


Filename = XC-IV-110-4.jdf
Experiment = single_pulse_dec
Sample_id = S#424868
Solvent = CHLOROFORM-D
Creation_time = 29-JUN-2004 17:29:28
Revision_time = 11-FEB-2007 11:49:33
Current_time = 11-FEB-2007 11:50:19
Content = Single Pulse with Bro
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]
Mod_return = 1
Scans = 5443
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 4[s]
Temp_get = 25.1[dC]
Unblank_time = 2[us]
O
S
S
N
N
S
(Billions)
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
210.0
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
0
196.9664
130.7666
124.3988
77.2833
77.0277
76.7758
51.5336
46.8789
11.6444
-0.0000
X : parts per Million : 13C

APPENDIX 31

^{1}H and ^{13}C-NMR spectra of
1, 1'-[(4,6-thieno[3,4-*d*]-1,3-dithiol-2-onediyl)bismethylene]bis[pyridinium chloride]
(33)
(D_2O)

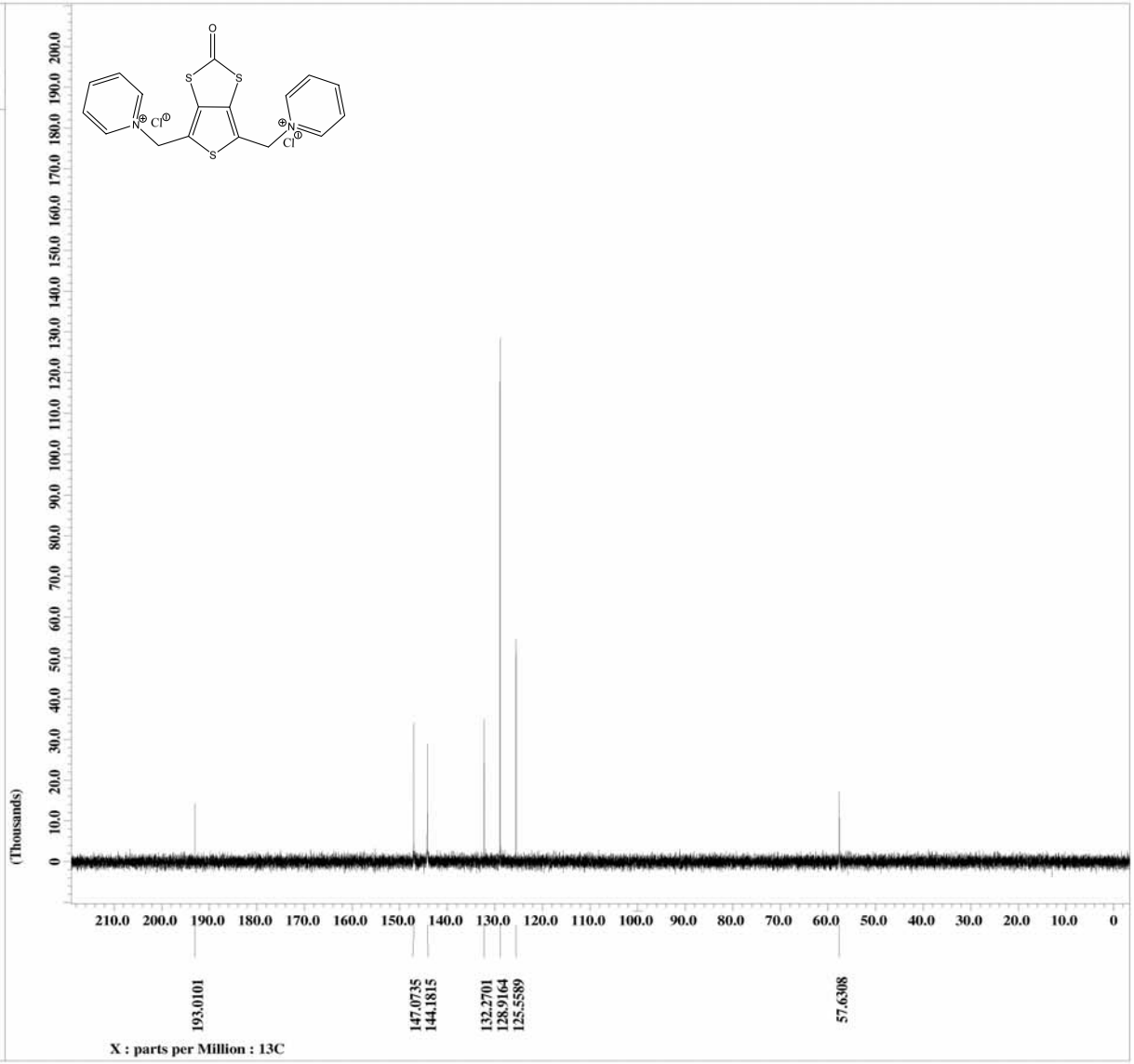

Filename = XC-IV-160-5.jdf
Experiment = single_pulse.exp
Sample_id = S#22514
Solvent = CHLOROFORM-D
Creation_time = 18-SEP-2004 21:58:06
Revision_time = 11-FEB-2007 12:57:27
Current_time = 11-FEB-2007 12:58:26
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 1[s]
Temp_get = 24[dC]
Unblank_time = 2[us]
4.002
2
4.03
4.002
(Millions)
8.7902
8.7783
8.5144
8.4988
8.4833
8.0087
7.9954
7.9812
6.0307
4.6703
X : parts per Million : 1H

```
Filename          = XC-IV-107D2O-2.jdf
Experiment        = single_pulse_dec
Sample_id         = S#383432
Solvent           = D2O
Creation_time     = 23-JUN-2004 18:05:44
Revision_time     = 11-FEB-2007 16:31:05
Current_time      = 11-FEB-2007 16:31:40

Content           = Single Pulse with Bro
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

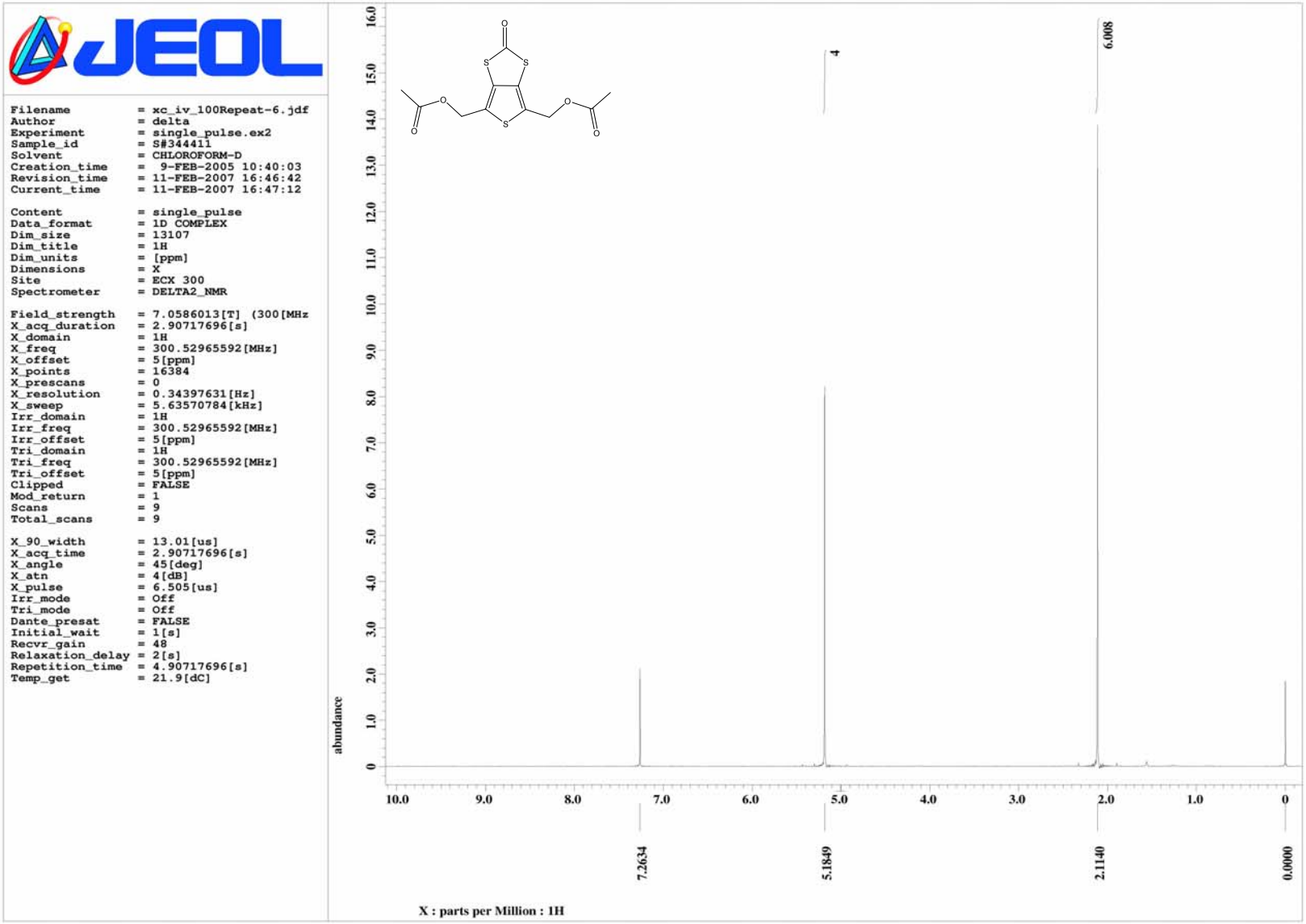
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Mod_return        = 1
Scans             = 6518

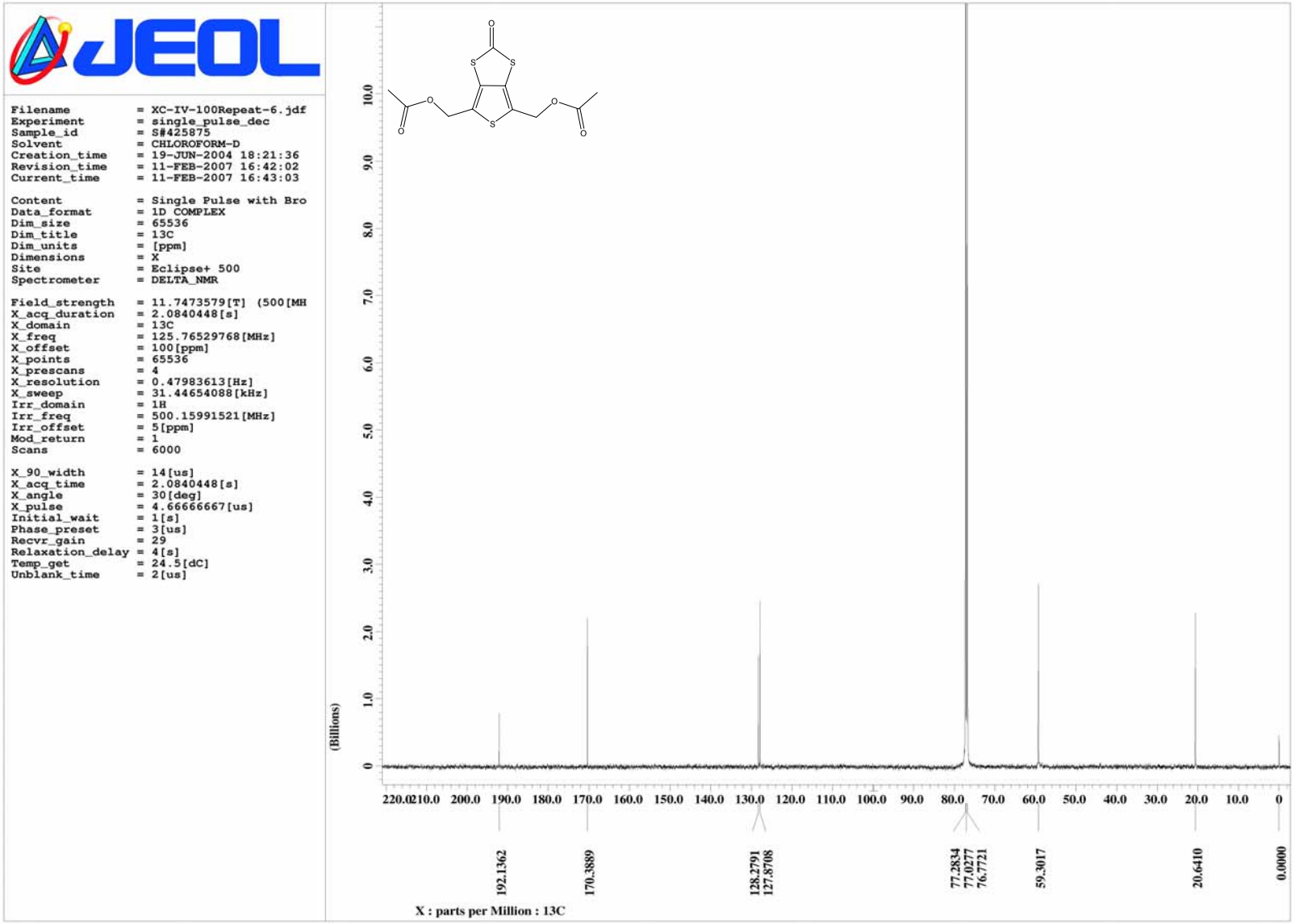
X_90_width        = 14[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.66666667[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 29
Relaxation_delay  = 4[s]
Temp_get          = 24.3[dC]
Unblank_time      = 2[us]
```



APPENDIX 32

^{1}H and ^{13}C-NMR spectra of 4,6-bis(acetoxymethyl) thieno[3,4-*d*]-1,3-dithiol-2-one (34)


Filename = xc_iv_100Repeat-6.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#344411
Solvent = CHLOROFORM-D
Creation_time = 9-FEB-2005 10:40:03
Revision_time = 11-FEB-2007 16:46:42
Current_time = 11-FEB-2007 16:47:12
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 9
Total_scans = 9
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 48
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 21.9[dC]
abundance
6.008
4
7.2634
5.1849
2.1140
0.0000
X : parts per Million : 1H



```
Filename          = XC-IV-100Repeat-6.jdf
Experiment        = single_pulse_dec
Sample_id         = S#425875
Solvent           = CHLOROFORM-D
Creation_time     = 19-JUN-2004 18:21:36
Revision_time     = 11-FEB-2007 16:42:02
Current_time      = 11-FEB-2007 16:43:03

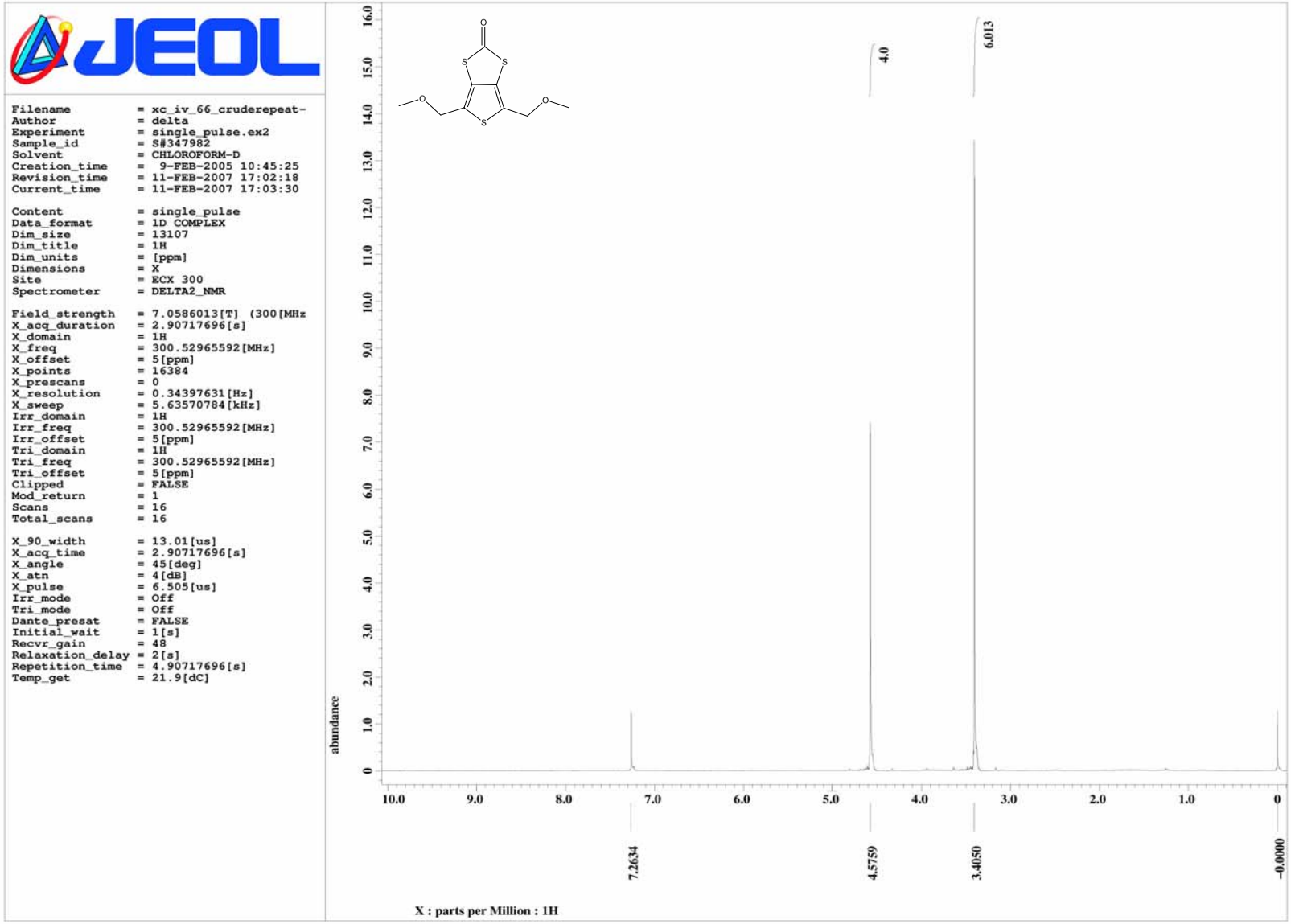
Content           = Single Pulse with Bro
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

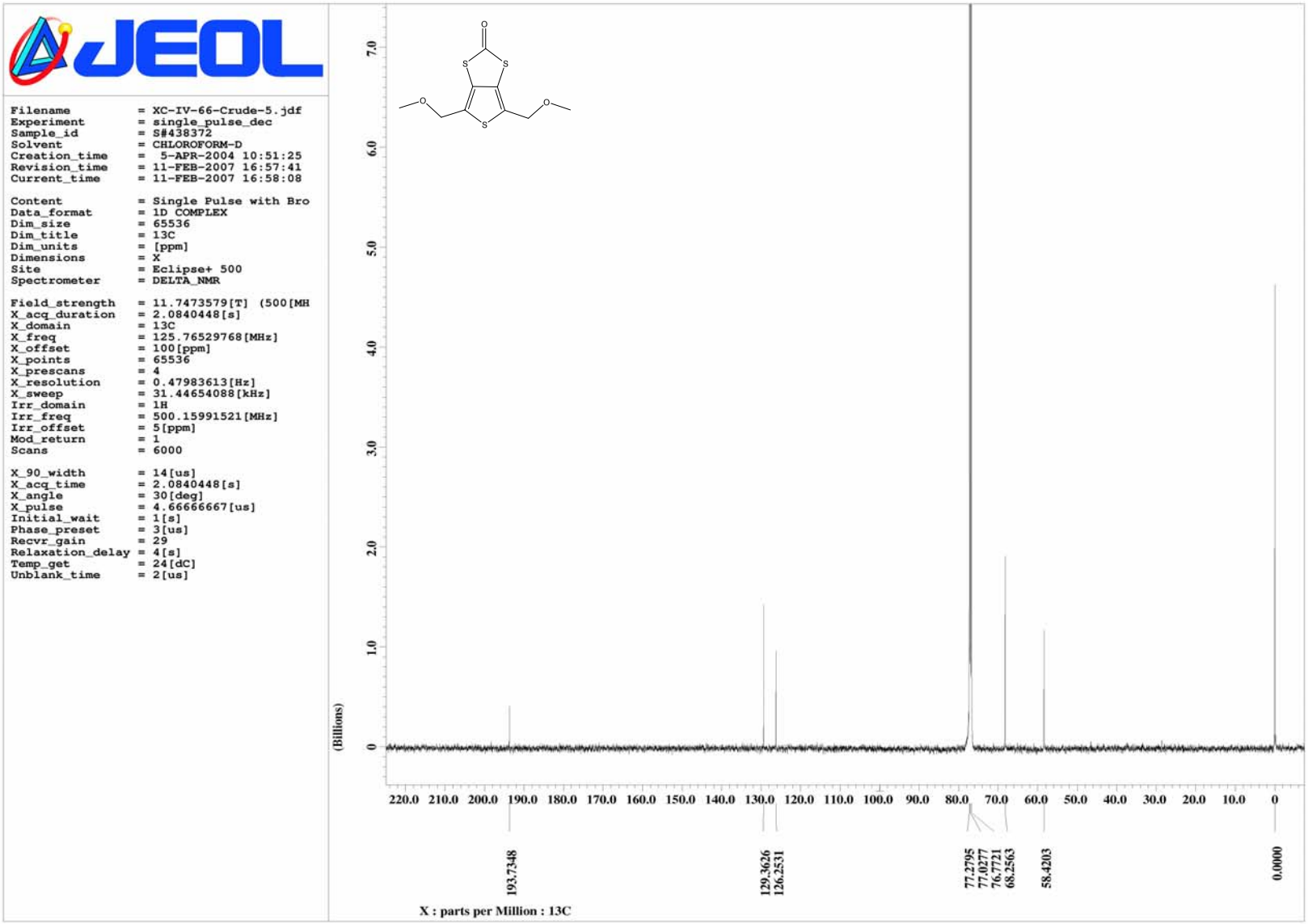
Field_strength    = 11.7473579[T]  (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Mod_return        = 1
Scans             = 6000

X_90_width        = 14[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.66666667[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 29
Relaxation_delay  = 4[s]
Temp_get          = 24.5[dC]
Unblank_time      = 2[us]
```

APPENDIX 33

^{1}H and ^{13}C-NMR spectra of 4,6-bis(methoxymethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (35)

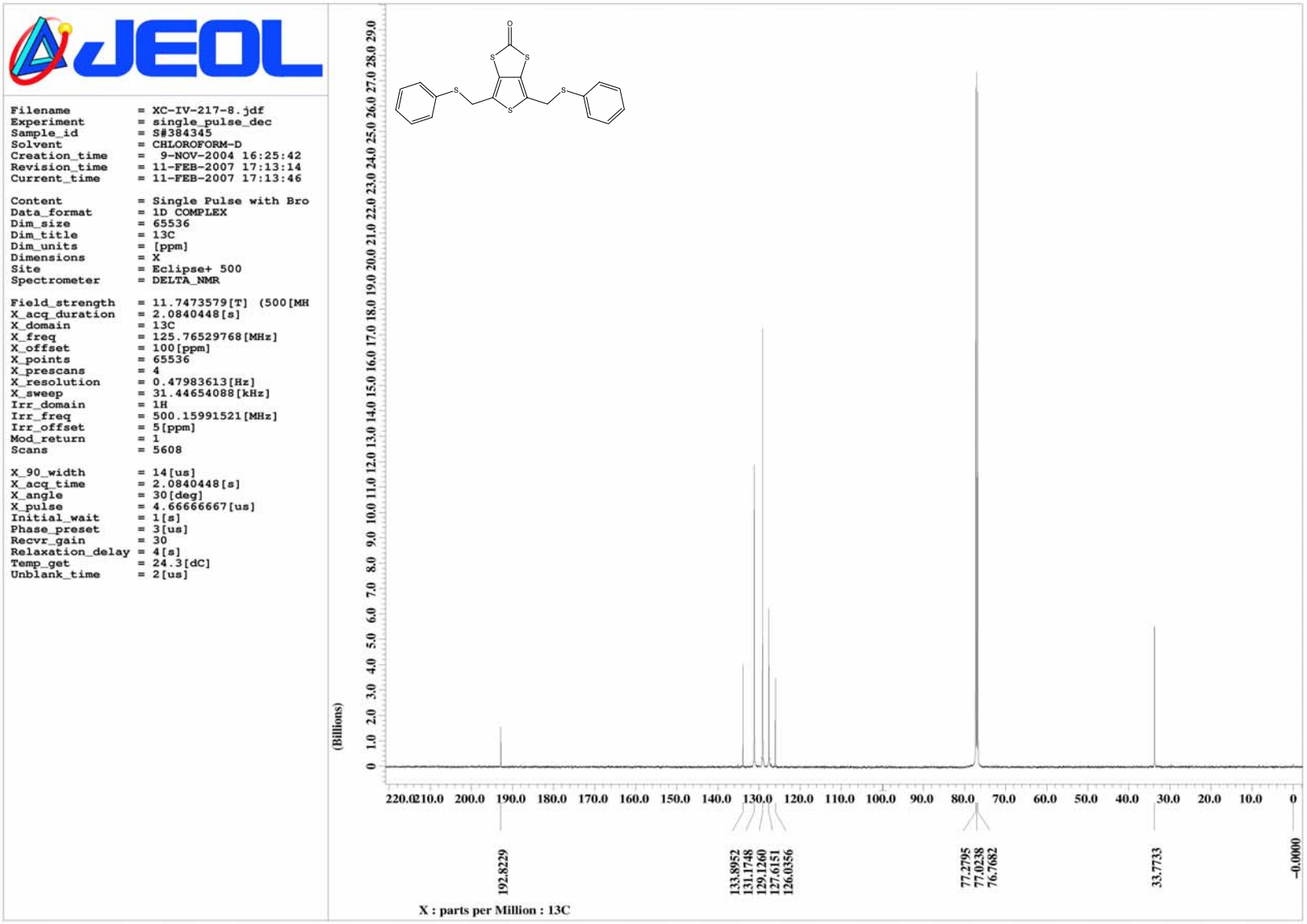

Filename = xc_iv_66_cruderepeat-
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#347982
Solvent = CHLOROFORM-D
Creation_time = 9-FEB-2005 10:45:25
Revision_time = 11-FEB-2007 17:02:18
Current_time = 11-FEB-2007 17:03:30
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 48
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 21.9[dC]
abundance
4.0
6.013
7.2634
4.5759
3.4050
-0.0000
X : parts per Million : 1H


Filename = XC-IV-66-Crude-5.jdf
Experiment = single_pulse_dec
Sample_id = S#438372
Solvent = CHLOROFORM-D
Creation_time = 5-APR-2004 10:51:25
Revision_time = 11-FEB-2007 16:57:41
Current_time = 11-FEB-2007 16:58:08
Content = Single Pulse with Bro
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]
Mod_return = 1
Scans = 6000
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 4[s]
Temp_get = 24[dC]
Unblank_time = 2[us]
O
S
S
O
O
S
(Billions)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
193.7348
129.3626
126.2531
77.2795
77.0277
76.7721
68.2563
58.4203
0.0000
X : parts per Million : 13C

APPENDIX 34

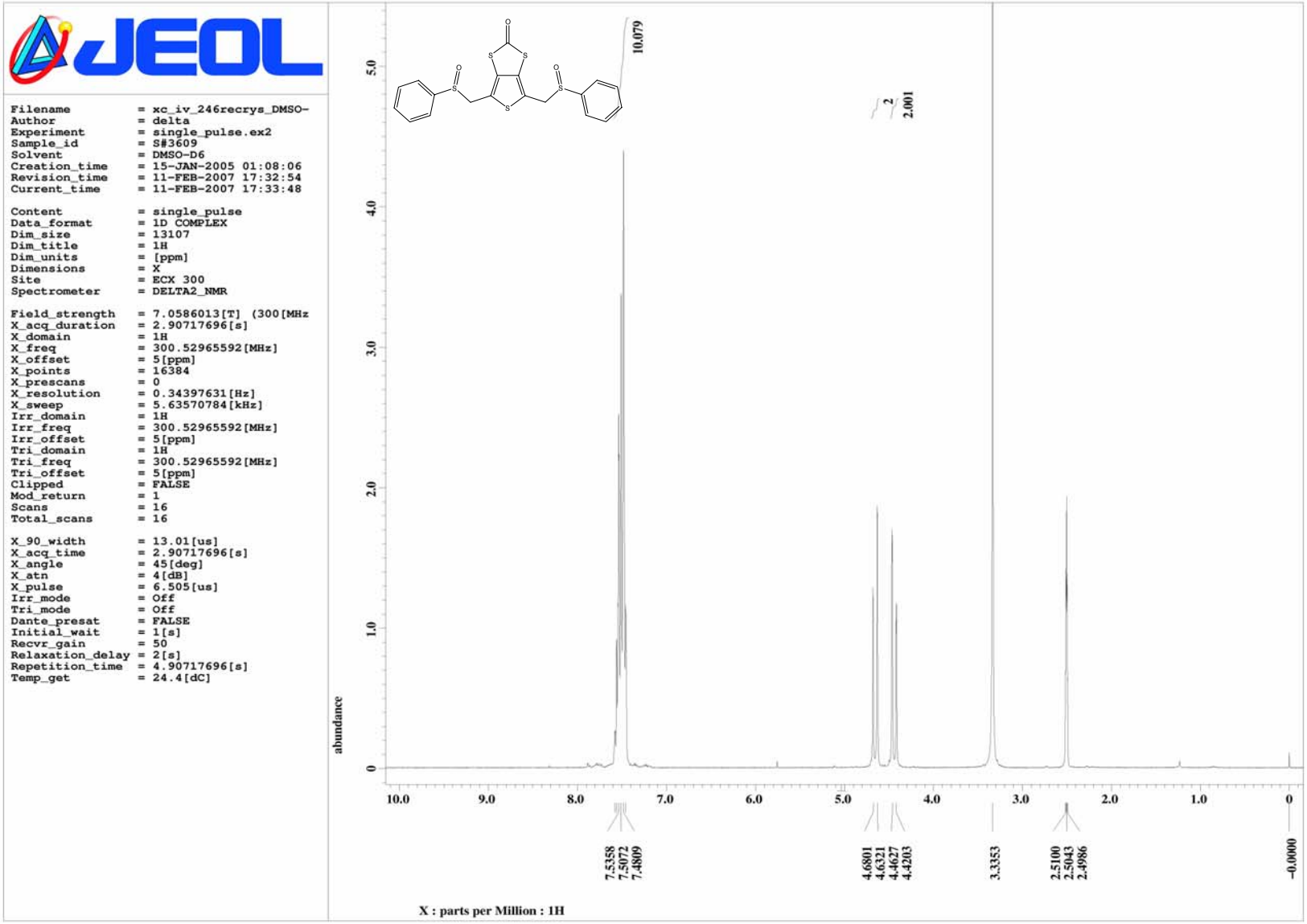
^{1}H and ^{13}C-NMR spectra of 4,6-bis((phenylthio)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (36)

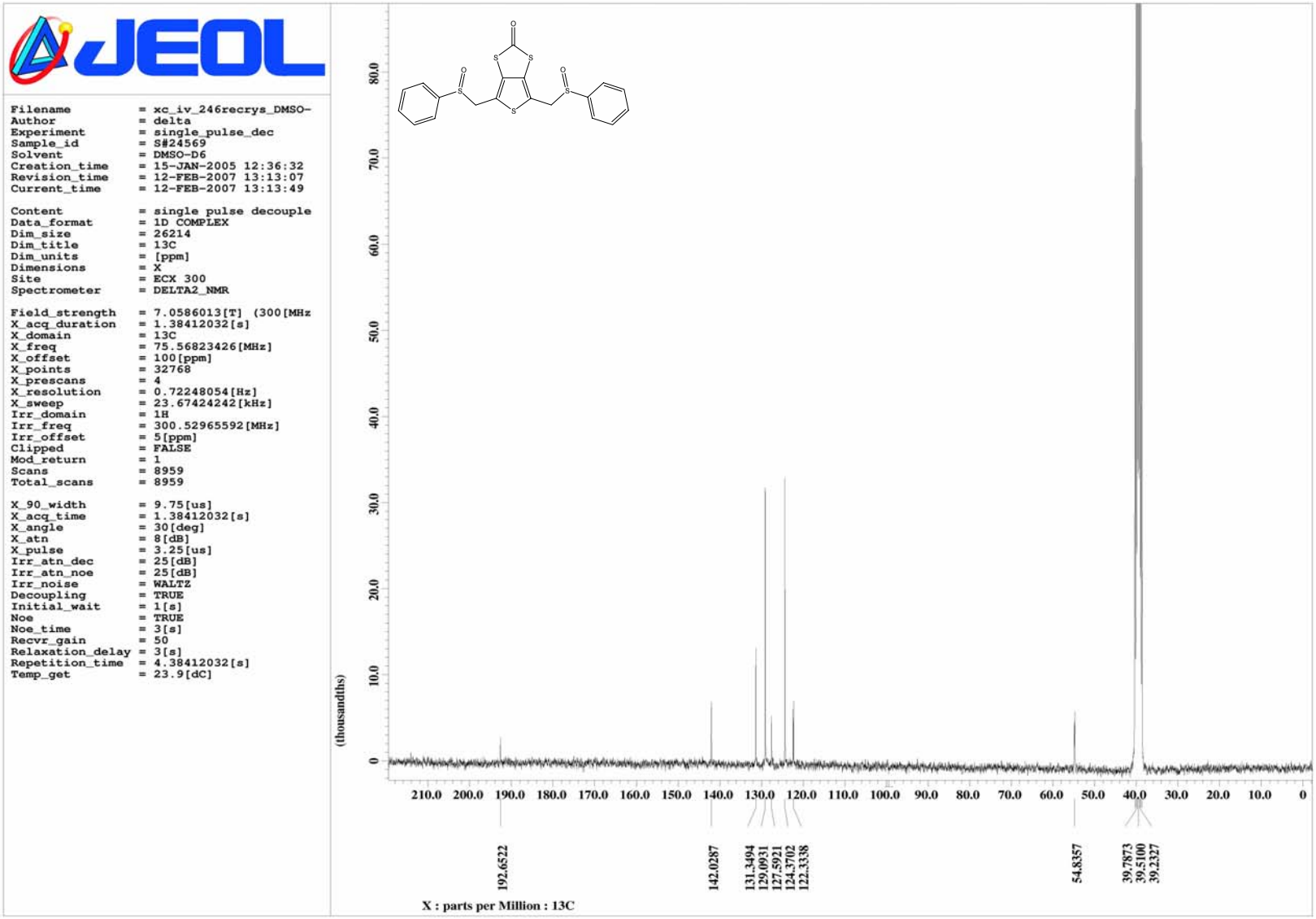
JEOL
Filename = XC-IV-217-8.jdf
Experiment = single_pulse.exp
Sample_id = SH83314
Solvent = CHLOROFORM-D
Creation_time = 9-NOV-2004 06:53:29
Revision_time = 11-FEB-2007 17:17:14
Current_time = 11-FEB-2007 17:17:29
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Mod_return = 1
Scans = 16
X_90_width = 15[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 7.5[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 17
Relaxation_delay = 1[s]
Temp_get = 23.2[dC]
Unblank_time = 2[us]
10.147
4
4.1209
7.2697
7.2477
7.2376
0.0000
(Millions)
X : parts per Million : 1H


Filename = XC-IV-217-8.jdf
Experiment = single_pulse_dec
Sample_id = S#384345
Solvent = CHLOROFORM-D
Creation_time = 9-NOV-2004 16:25:42
Revision_time = 11-FEB-2007 17:13:14
Current_time = 11-FEB-2007 17:13:46
Content = Single Pulse with Bro
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]
Mod_return = 1
Scans = 5608
X_90_width = 14[us]
X_acq_time = 2.0840448[s]
X_angle = 30[deg]
X_pulse = 4.66666667[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 24.3[dC]
Unblank_time = 2[us]
(Billions)
192.8229
133.8952
131.1748
129.1260
127.6151
126.0356
77.2795
77.0238
76.7682
33.7733
-0.0000
X : parts per Million : 13C

APPENDIX 35

^{1}H and ^{13}C-NMR spectra of 4,6-bis((phenylsulfinyl)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (37)


Filename = xc_iv_246recrys_DMSO-
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#3609
Solvent = DMSO-D6
Creation_time = 15-JAN-2005 01:08:06
Revision_time = 11-FEB-2007 17:32:54
Current_time = 11-FEB-2007 17:33:48
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 50
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 24.4[dC]
10.079
2
2.001
abundance
7.5358
7.5072
7.4809
4.6801
4.6321
4.4627
4.4203
3.3353
2.5100
2.5043
2.4986
-0.0000
X : parts per Million : 1H



```
Filename          = xc_iv_246recrys_DMSO-
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#24569
Solvent           = DMSO-D6
Creation_time     = 15-JAN-2005 12:36:32
Revision_time     = 12-FEB-2007 13:13:07
Current_time      = 12-FEB-2007 13:13:49

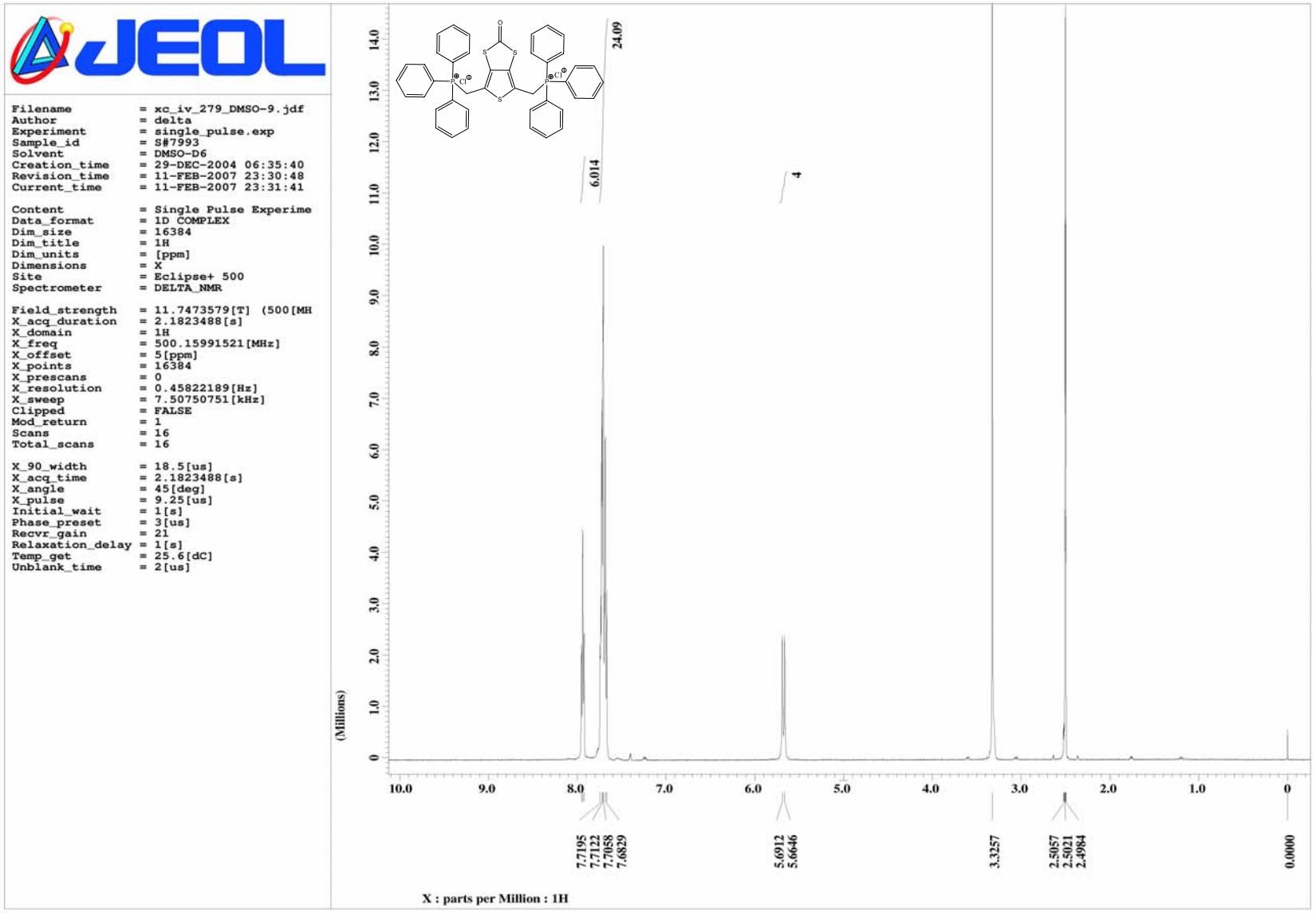
Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

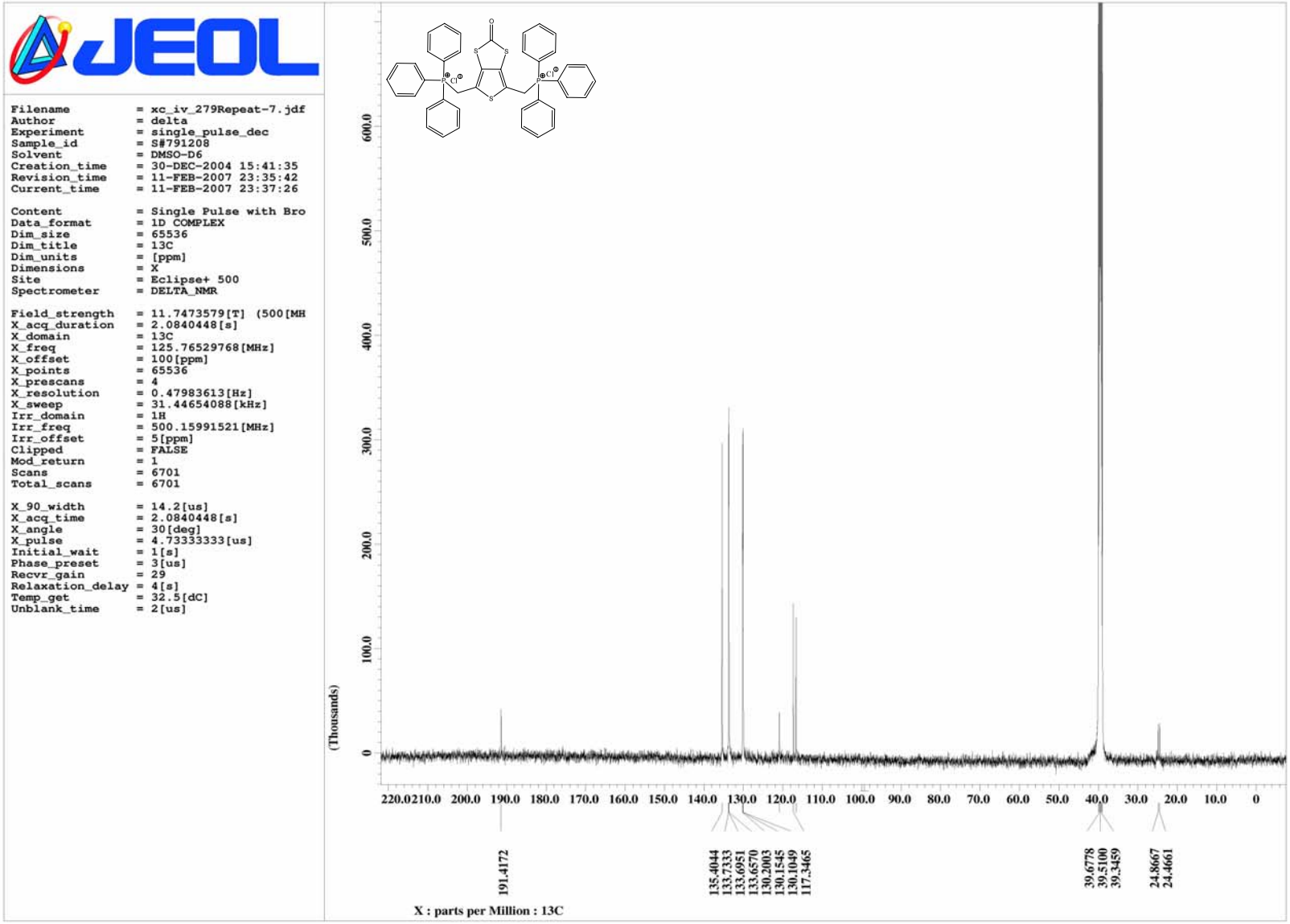
Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 1.38412032[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.72248054[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8959
Total_scans       = 8959

X_90_width        = 9.75[us]
X_acq_time        = 1.38412032[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          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 4.38412032[s]
Temp_get          = 23.9[dC]
```

APPENDIX 36

^{1}H and ^{13}C-NMR spectra of 1,1'-[(4,6-thieno[3,4-*d*]-1,3-dithiol-2-one-diyl) bismethylene] bis[triphenylphosphonium chloride] (38)


Filename = xc_iv_279_DMSO-9.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#7993
Solvent = DMSO-D6
Creation_time = 29-DEC-2004 06:35:40
Revision_time = 11-FEB-2007 23:30:48
Current_time = 11-FEB-2007 23:31:41
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 21
Relaxation_delay = 1[s]
Temp_get = 25.6[dC]
Unblank_time = 2[us]
24.09
6.014
4
(Millions)
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.7195
7.7122
7.7058
7.6829
5.6912
5.6646
3.3257
2.5057
2.5021
2.4984
0.0000
X : parts per Million : 1H



```
Filename          = xc_iv_279Repeat-7.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#791208
Solvent           = DMSO-D6
Creation_time     = 30-DEC-2004 15:41:35
Revision_time     = 11-FEB-2007 23:35:42
Current_time      = 11-FEB-2007 23:37:26

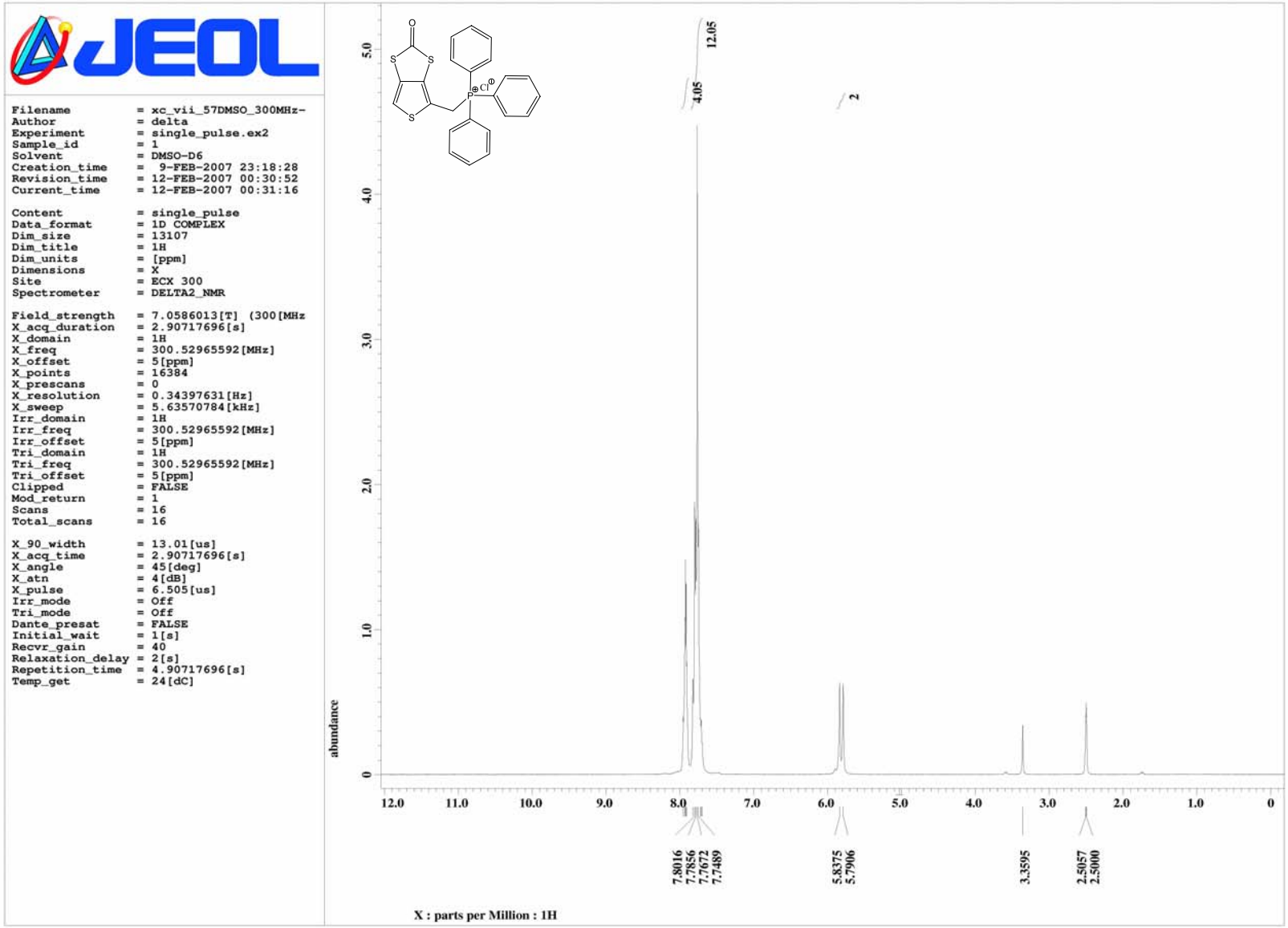
Content           = Single Pulse with Bro
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

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             = 6701
Total_scans       = 6701

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        = 29
Relaxation_delay  = 4[s]
Temp_get          = 32.5[dC]
Unblank_time      = 2[us]
```

APPENDIX 37

^{1}H and ^{13}C-NMR spectra of [(4-thieno[3,4-*d*]-1,3-dithiol-2-one-yl)methylene] [triphenylphosphonium chloride] (39)

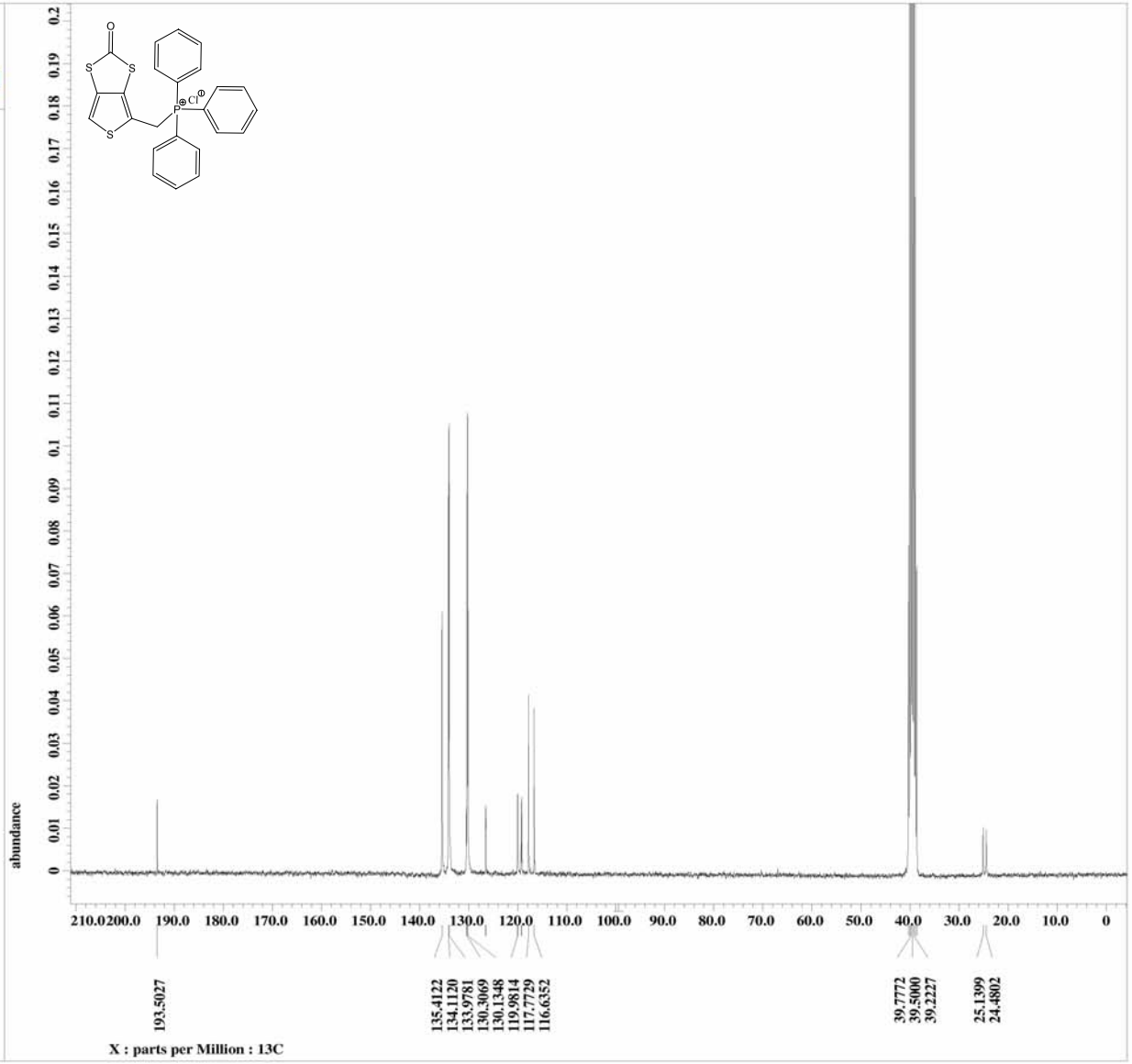

Filename = xc_vii_57DMSO_300MHz-
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = DMSO-D6
Creation_time = 9-FEB-2007 23:18:28
Revision_time = 12-FEB-2007 00:30:52
Current_time = 12-FEB-2007 00:31:16
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 40
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 24[dC]
12.05
4.05
2
abundance
5.0
4.0
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.8016
7.7856
7.7672
7.7489
5.8375
5.7906
3.3595
2.5057
2.5000
X : parts per Million : 1H

```
Filename          = xc_vii_57DMSO_300MHz-
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = DMSO-D6
Creation_time     = 10-FEB-2007 09:41:55
Revision_time     =  2-MAR-2007 20:03:39
Current_time      =  2-MAR-2007 20:04:15

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

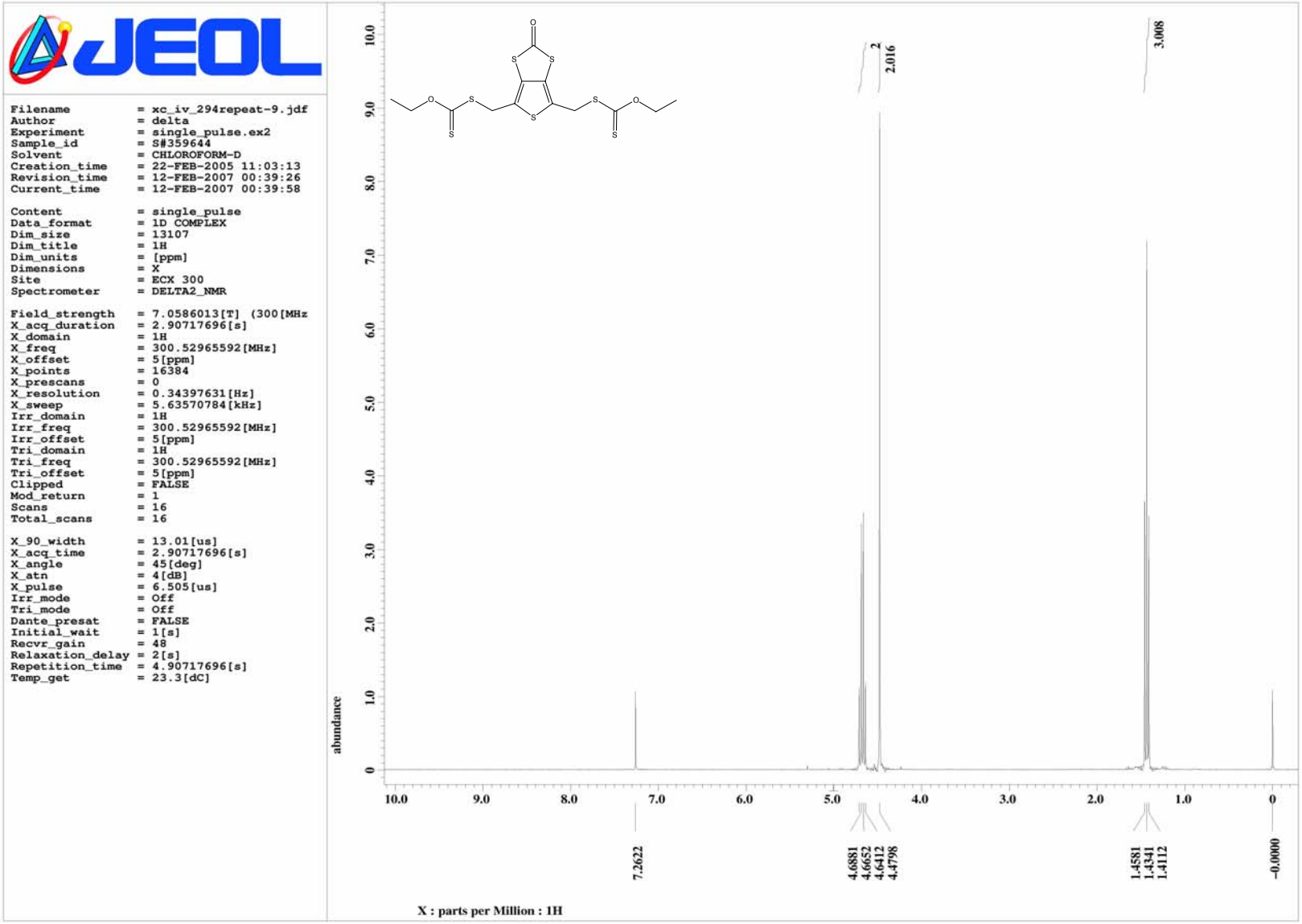
Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 1.38412032[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.72248054[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8512
Total_scans       = 8512

X_90_width        = 9.75[us]
X_acq_time        = 1.38412032[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          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 4.38412032[s]
Temp_get          = 23.5[dC]
```



APPENDIX 38

^{1}H and ^{13}C-NMR spectra of 4,6-bis[ethoxy(thiocarbonyl)thiomethyl]thieno[3,4-*d*]-1,3-dithiol-2-one (40)

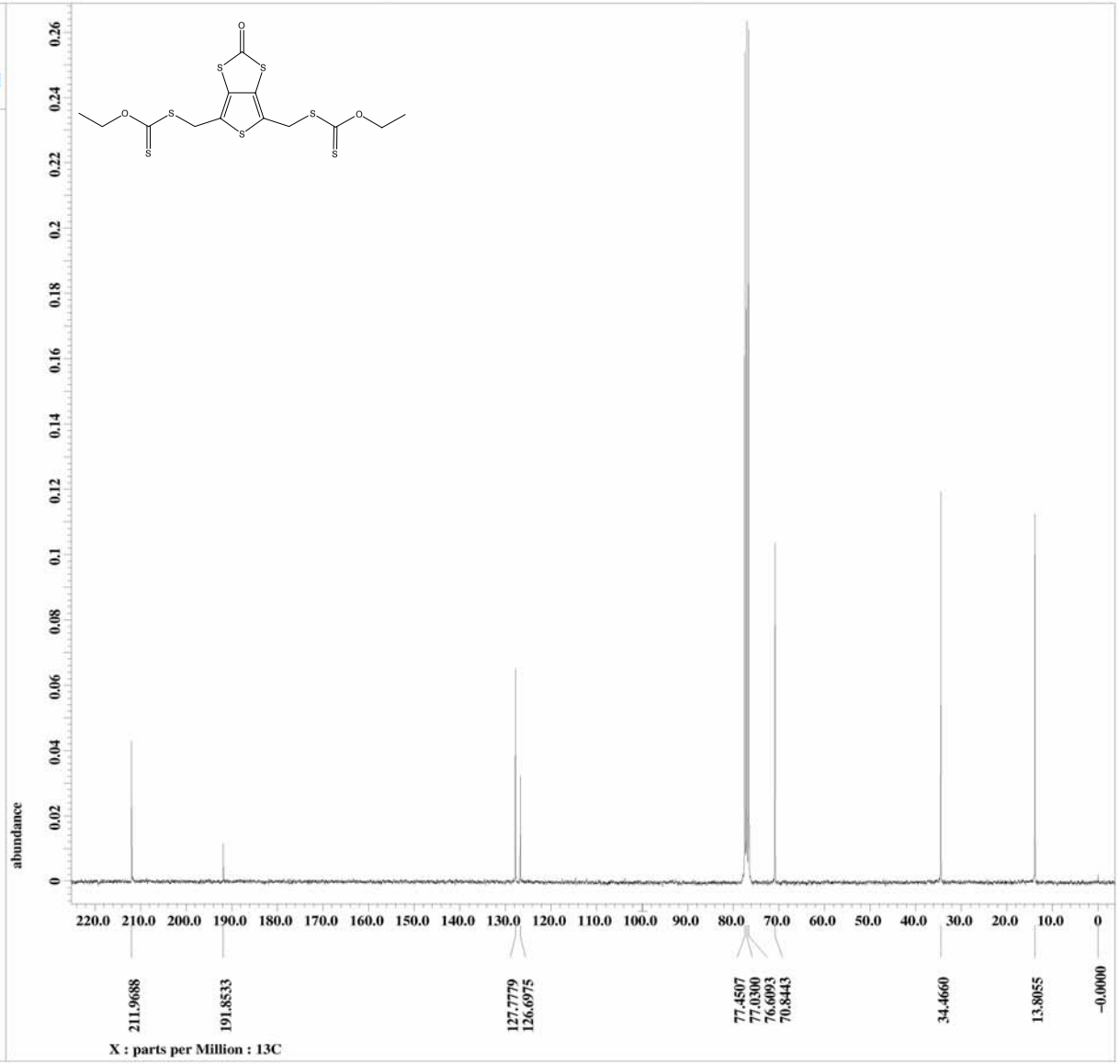

Filename = xc_iv_294repeat-9.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#359644
Solvent = CHLOROFORM-D
Creation_time = 22-FEB-2005 11:03:13
Revision_time = 12-FEB-2007 00:39:26
Current_time = 12-FEB-2007 00:39:58
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 48
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 23.3[dC]
abundance
2
2.016
3.008
7.2622
4.6881
4.6652
4.6412
4.4798
1.4581
1.4341
1.4112
-0.0000
X : parts per Million : 1H

```
Filename          = xc_iv_294-6.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#14534
Solvent           = CHLOROFORM-D
Creation_time     = 21-FEB-2005 10:12:28
Revision_time     = 12-FEB-2007 00:43:26
Current_time      = 12-FEB-2007 00:43:53

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

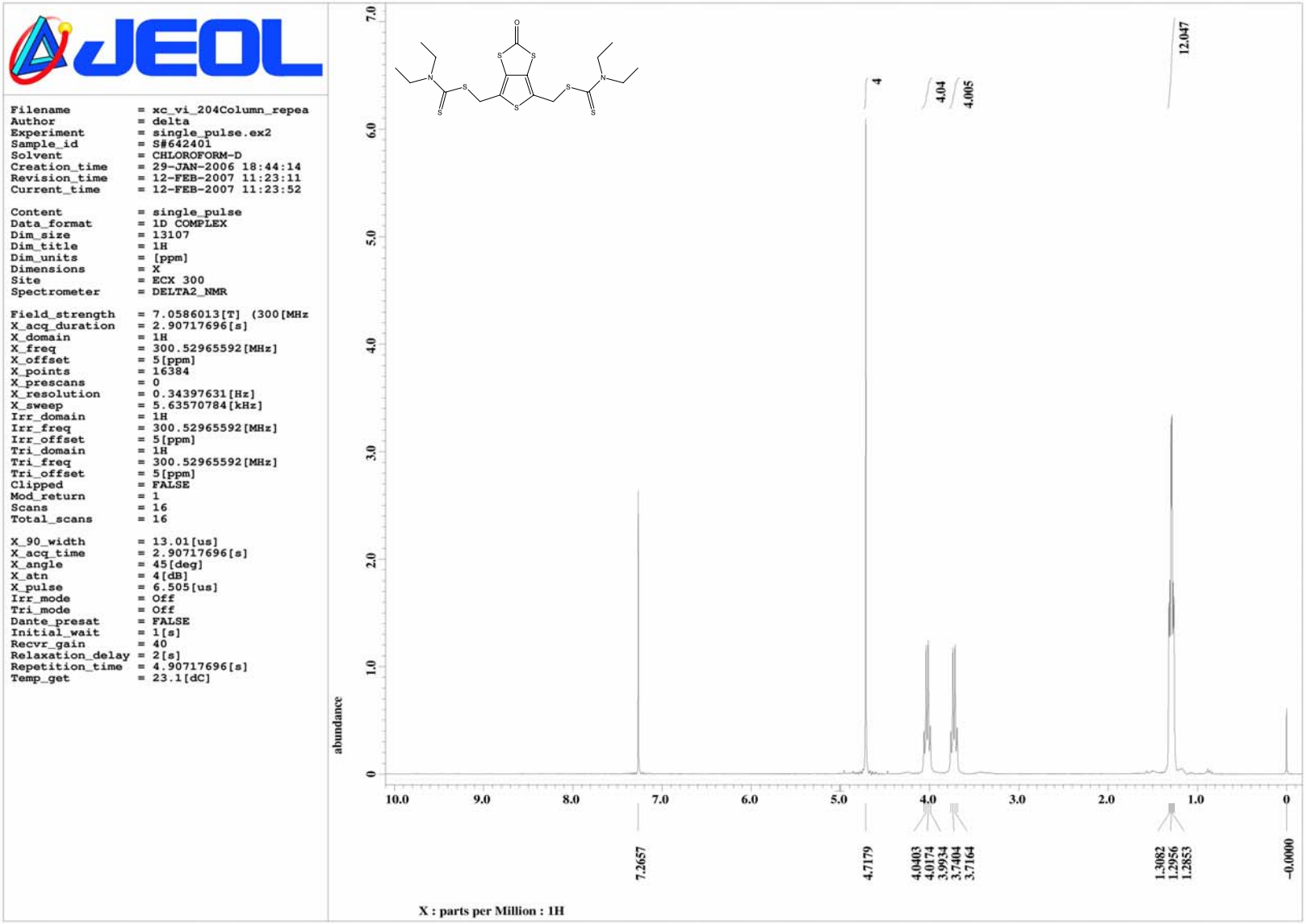
Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 1.38412032[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.72248054[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 7188
Total_scans       = 7188

X_90_width        = 9.75[us]
X_acq_time        = 1.38412032[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          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 4.38412032[s]
Temp_get          = 23.1[dC]
```



APPENDIX 39

^{1}H and ^{13}C-NMR spectra of 4,6-bis(*N*,*N*-diethyldithiocarbomate-methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (41)

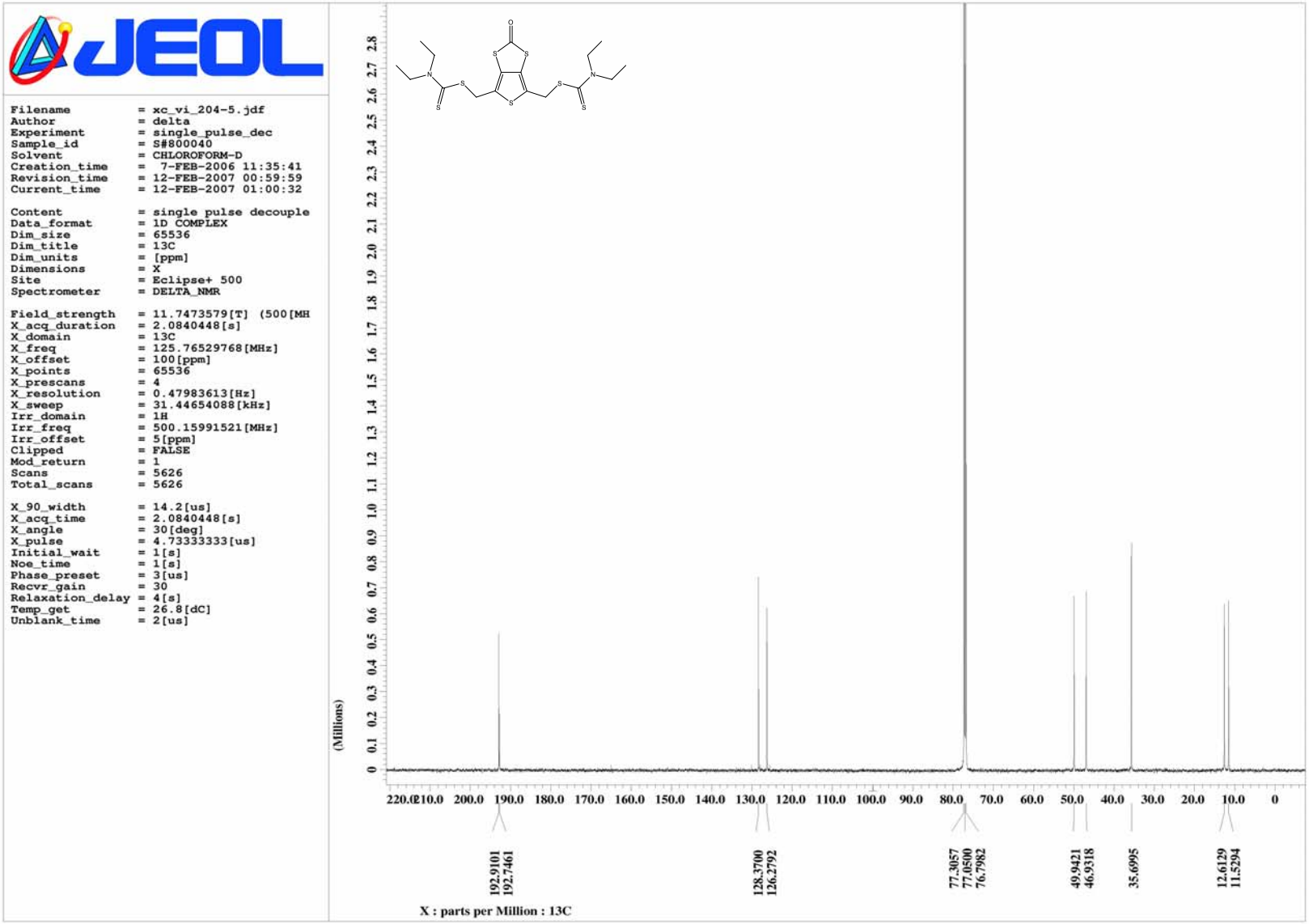


```
Filename          = xc_vi_204Column_repea
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#642401
Solvent           = CHLOROFORM-D
Creation_time     = 29-JAN-2006 18:44:14
Revision_time     = 12-FEB-2007 11:23:11
Current_time      = 12-FEB-2007 11:23:52

Content           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

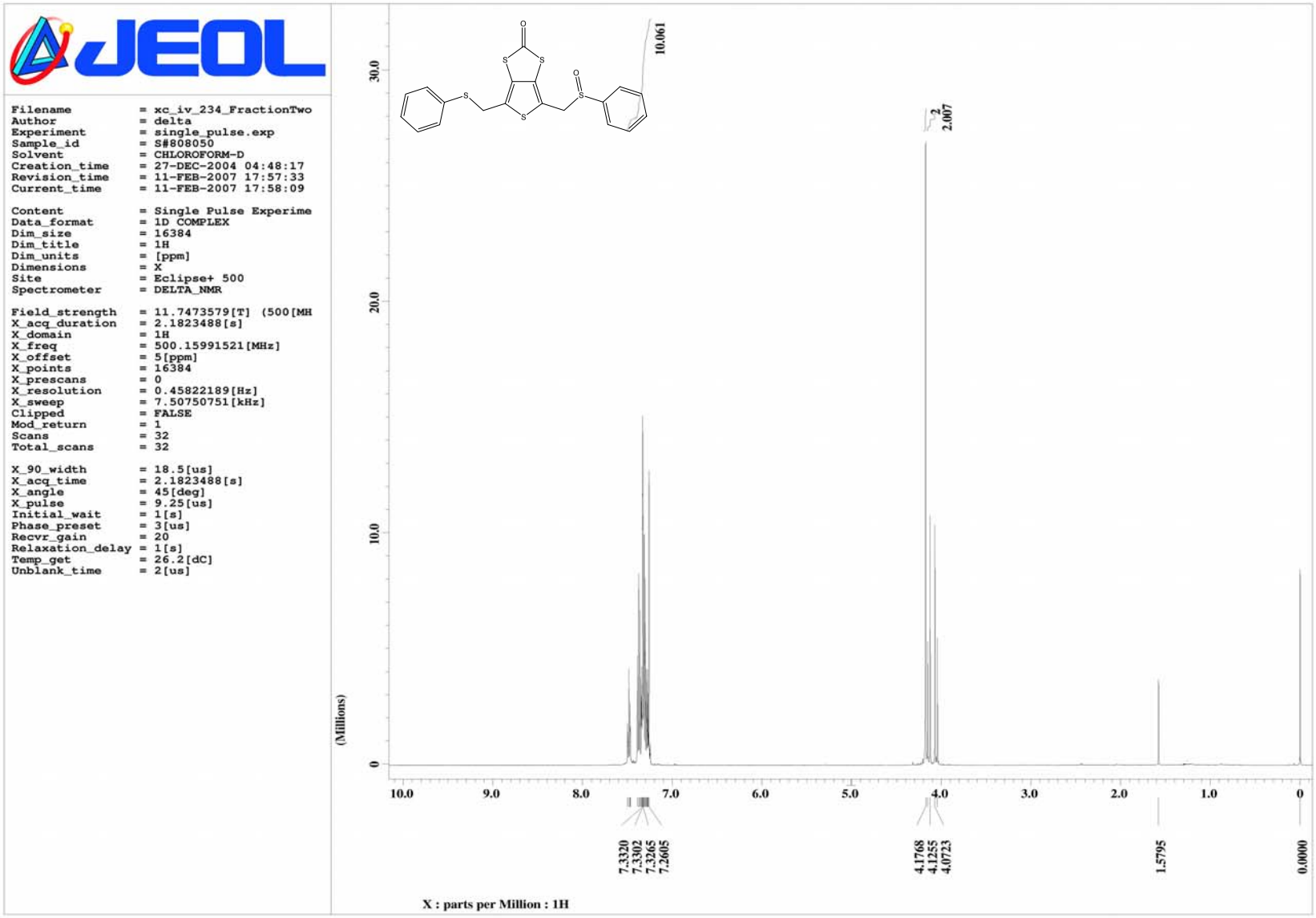
Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 40
Relaxation_delay  = 2[s]
Repetition_time   = 4.90717696[s]
Temp_get          = 23.1[dC]
```


Filename = xc_vi_204-5.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#800040
Solvent = CHLOROFORM-D
Creation_time = 7-FEB-2006 11:35:41
Revision_time = 12-FEB-2007 00:59:59
Current_time = 12-FEB-2007 01:00:32
Content = single pulse decouple
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 = 5626
Total_scans = 5626
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 26.8[dC]
Unblank_time = 2[us]
(Millions)
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
192.9101
192.7461
128.3700
126.2792
77.3057
77.0500
76.7982
49.9421
46.9318
35.6995
12.6129
11.5294
X : parts per Million : 13C

APPENDIX 40

^{1}H and ^{13}C-NMR spectra of 4-((phenylsulfinyl)methyl)-6-((phenylthio)methyl)methyl)thieno[3,4-*d*]-1,3-dithiol-2-one (42)

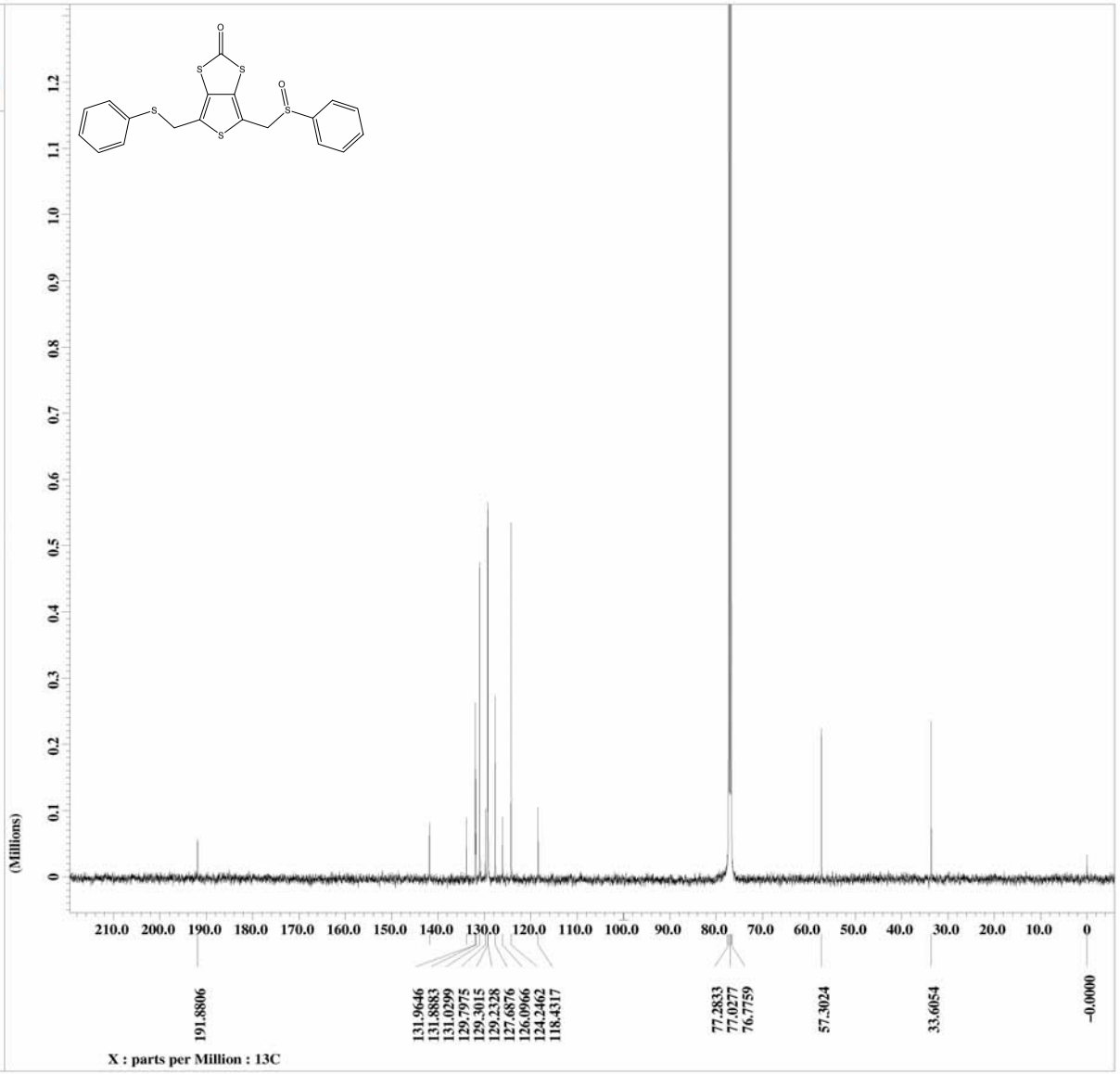

Filename = xc_iv_234_FractionTwo
Author = delta
Experiment = single_pulse.exp
Sample_id = S#808050
Solvent = CHLOROFORM-D
Creation_time = 27-DEC-2004 04:48:17
Revision_time = 11-FEB-2007 17:57:33
Current_time = 11-FEB-2007 17:58:09
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[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 = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 1[s]
Temp_get = 26.2[dC]
Unblank_time = 2[us]
10.061
2
2.007
(Millions)
30.0
20.0
10.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3320
7.3302
7.3265
7.2605
4.1768
4.1255
4.0723
1.5795
0.0000
X : parts per Million : 1H

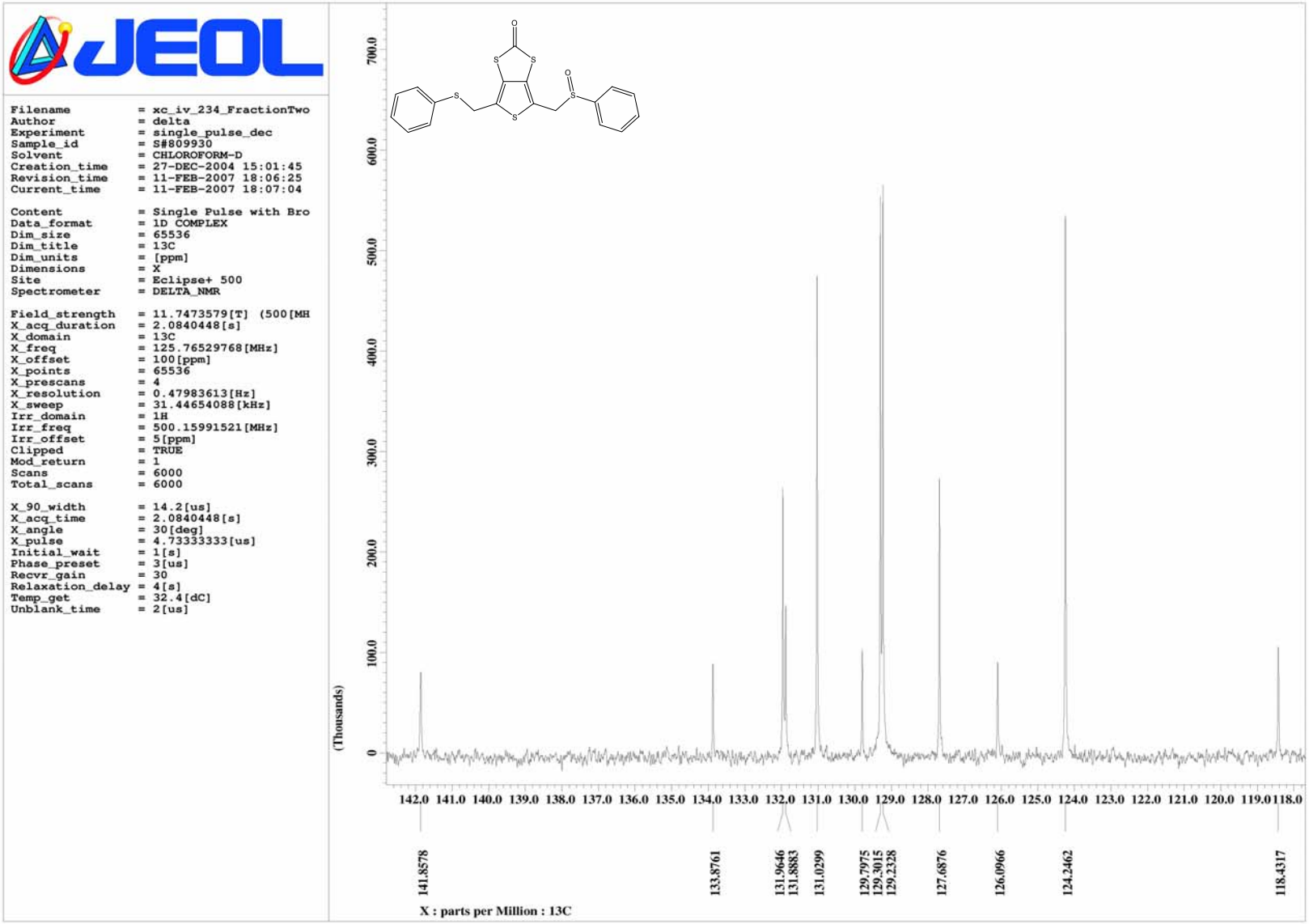
```
Filename          = xc_iv_234_FractionTwo
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#809930
Solvent           = CHLOROFORM-D
Creation_time     = 27-DEC-2004 15:01:45
Revision_time     = 11-FEB-2007 17:58:43
Current_time      = 11-FEB-2007 17:59:23

Content           = Single Pulse with Bro
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           = TRUE
Mod_return        = 1
Scans             = 6000
Total_scans       = 6000

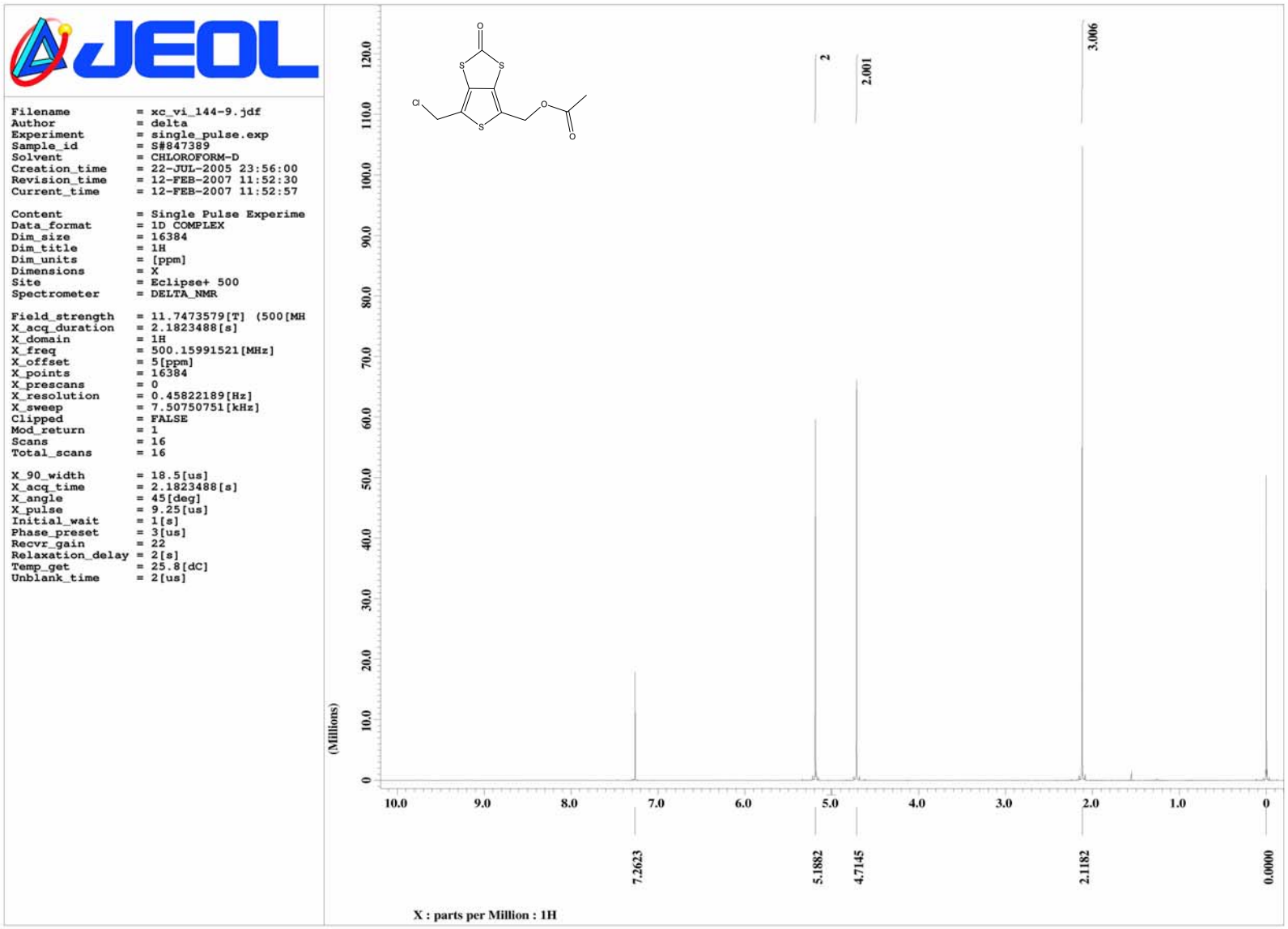
X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 4[s]
Temp_get          = 32.4[dC]
Unblank_time      = 2[us]
```




Filename = xc_iv_234_FractionTwo
Author = delta
Experiment = single_pulse_dec
Sample_id = S#809930
Solvent = CHLOROFORM-D
Creation_time = 27-DEC-2004 15:01:45
Revision_time = 11-FEB-2007 18:06:25
Current_time = 11-FEB-2007 18:07:04
Content = Single Pulse with Bro
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 = TRUE
Mod_return = 1
Scans = 6000
Total_scans = 6000
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 = 4[s]
Temp_get = 32.4[dC]
Unblank_time = 2[us]
(Thousands)
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
142.0 141.0 140.0 139.0 138.0 137.0 136.0 135.0 134.0 133.0 132.0 131.0 130.0 129.0 128.0 127.0 126.0 125.0 124.0 123.0 122.0 121.0 120.0 119.0 118.0
141.8578
133.8761
131.9646
131.8883
131.0299
129.7975
129.3015
129.2328
127.6876
126.0966
124.2462
118.4317
X : parts per Million : 13C

APPENDIX 41

^{1}H and ^{13}C-NMR spectra of 4-(chloromethyl)-6-(acetoxylmethyl)-thieno[3,4-*d*]-1,3-dithiol-2-one (43)

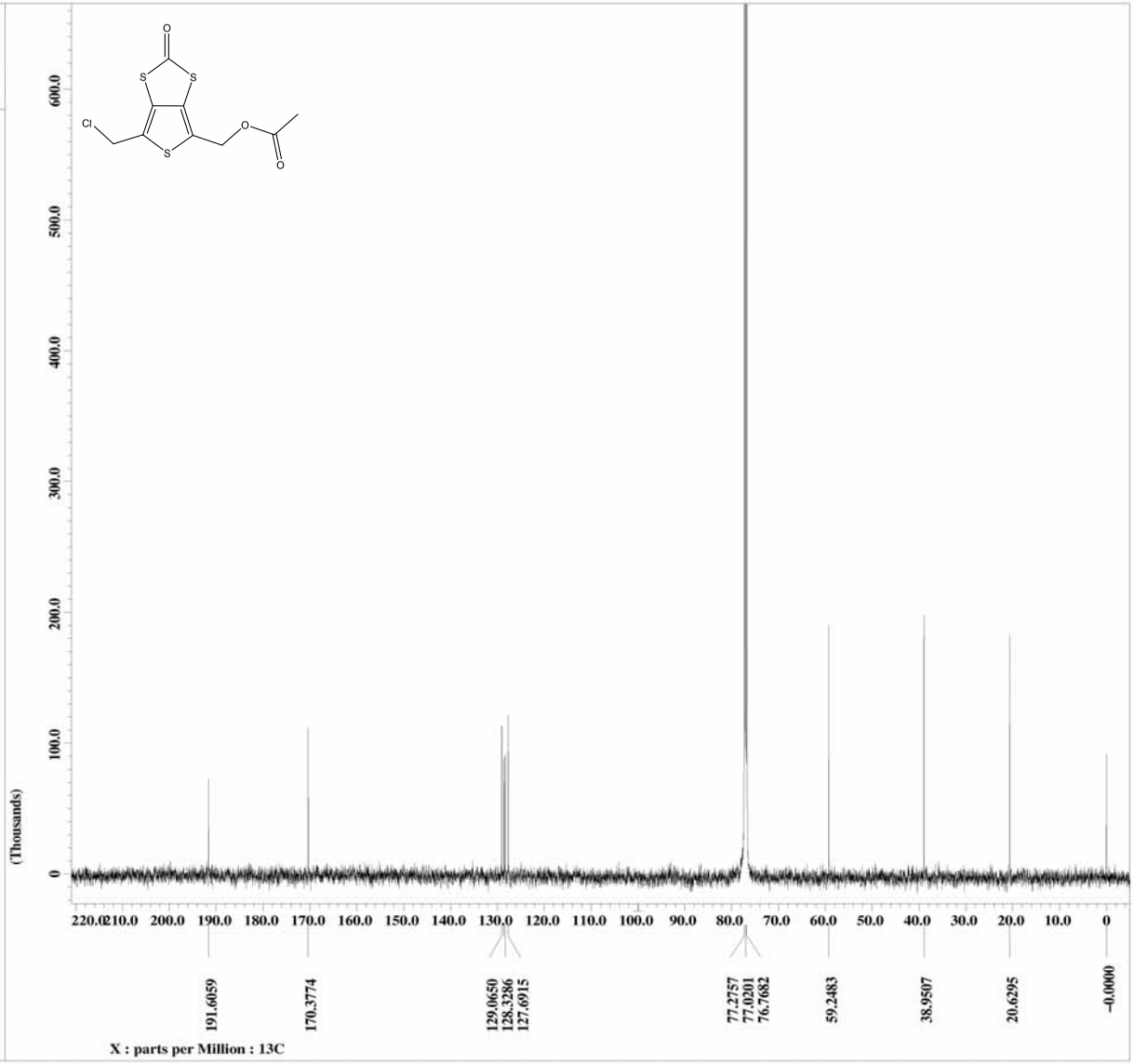

Filename = xc_vi_144-9.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#847389
Solvent = CHLOROFORM-D
Creation_time = 22-JUL-2005 23:56:00
Revision_time = 12-FEB-2007 11:52:30
Current_time = 12-FEB-2007 11:52:57
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 22
Relaxation_delay = 2[s]
Temp_get = 25.8[dC]
Unblank_time = 2[us]
(Millions)
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
2
2.001
3.006
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2623
5.1882
4.7145
2.1182
0.0000
X : parts per Million : 1H

```
Filename          = xc_vi_144-6.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#848657
Solvent           = CHLOROFORM-D
Creation_time     = 23-JUL-2005 11:47:12
Revision_time     = 12-FEB-2007 11:54:52
Current_time      = 12-FEB-2007 11:55:28

Content           = single pulse decouple
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             = 6000
Total_scans       = 6000

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]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 4[s]
Temp_get          = 26.9[dC]
Unblank_time      = 2[us]
```



APPENDIX 42

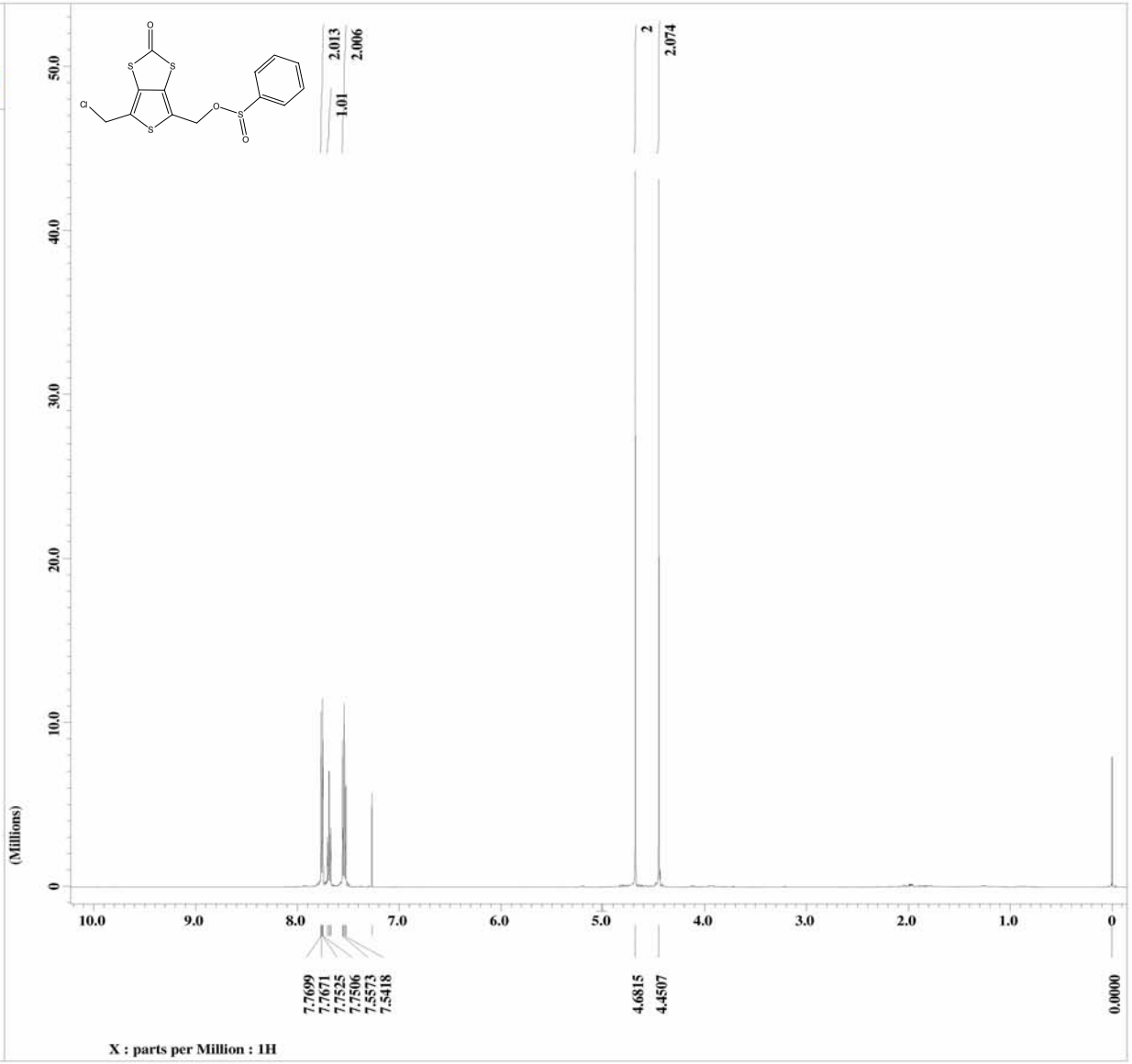
^{1}H and ^{13}C-NMR spectra of 4-(chloromethyl)-6-(phenylsulfinyloxylmethyl)-thieno[3,4-*d*]-1,3-dithiol-2-one (44)

```
Filename          = xc_vi_173_F_2repeat-5
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#770229
Solvent           = CHLOROFORM-D
Creation_time     =  6-OCT-2005 22:29:52
Revision_time     = 12-FEB-2007 13:47:24
Current_time      = 12-FEB-2007 13:48:08

Content           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 18.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 17
Relaxation_delay  = 2[s]
Temp_get          = 25.3[dC]
Unblank_time      = 2[us]
```

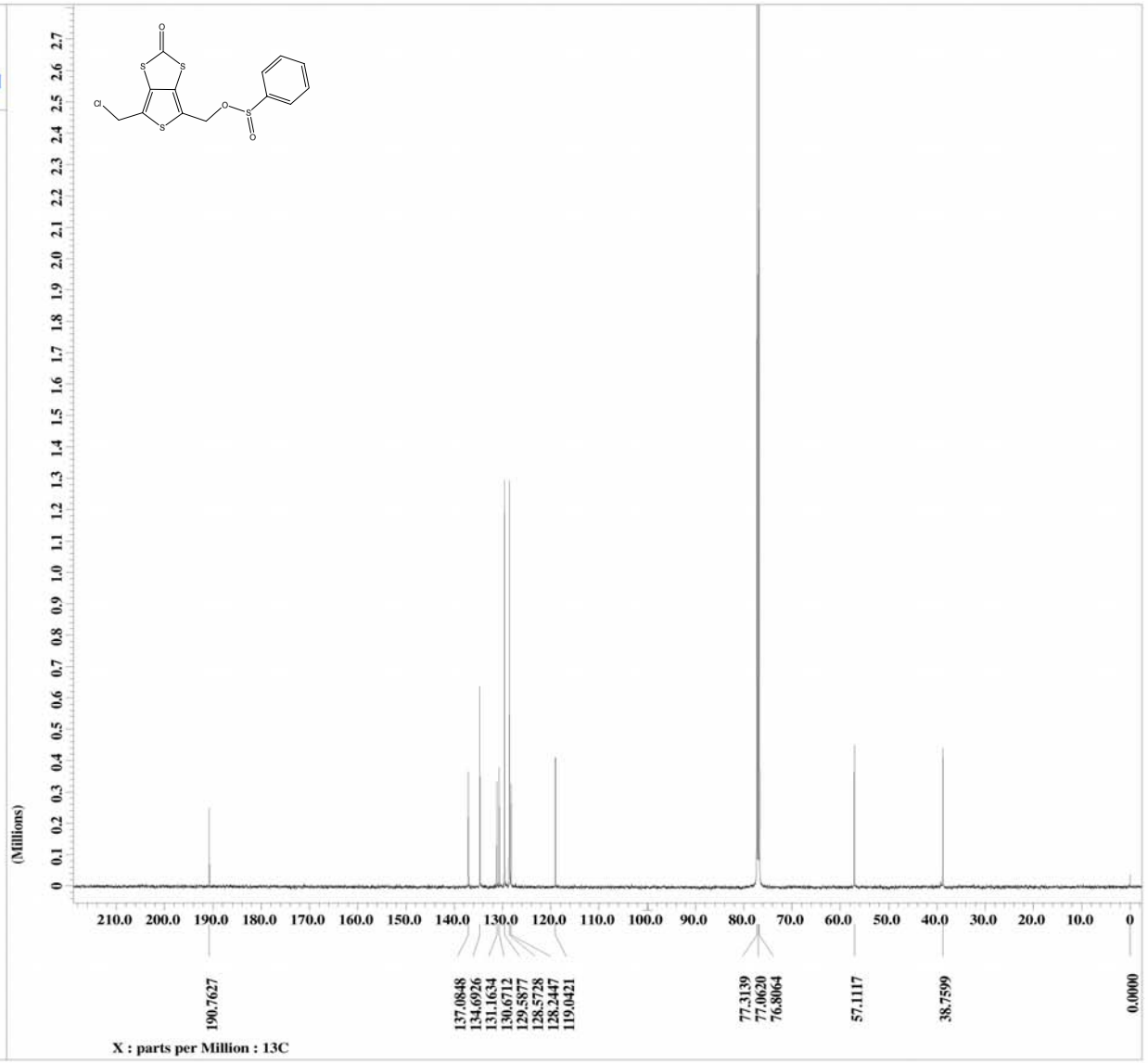


```
Filename          = xc_vi_173_F_2-5.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#772076
Solvent           = CHLOROFORM-D
Creation_time     =  7-OCT-2005 10:07:52
Revision_time     = 12-FEB-2007 13:49:47
Current_time      = 12-FEB-2007 13:50:18

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

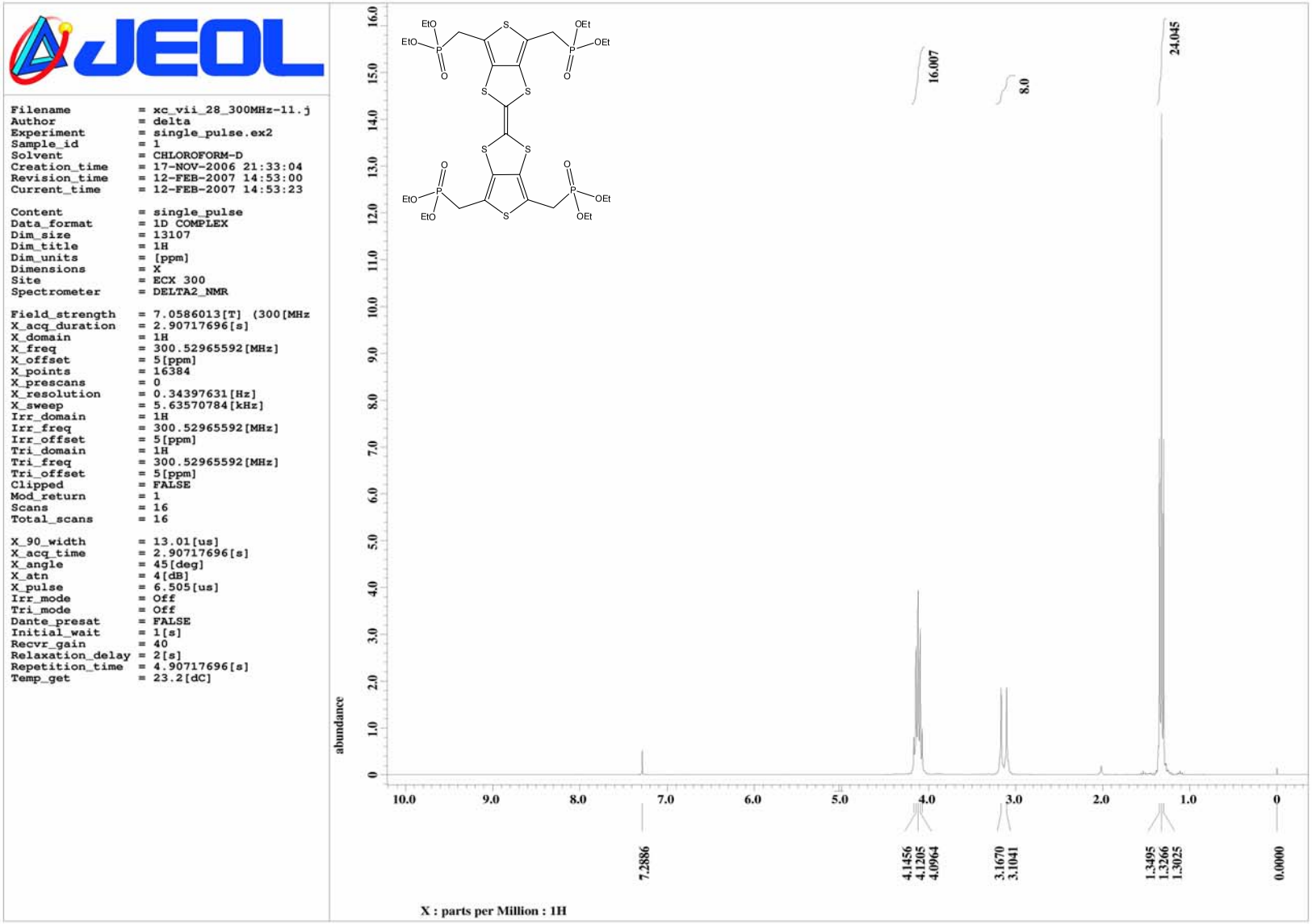
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 5882
Total_scans       = 5882

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]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 29
Relaxation_delay  = 4[s]
Temp_get          = 27.1[dC]
Unblank_time      = 2[us]
```



APPENDIX 43

^{1}H and ^{13}C-NMR spectra of 4,4',6,6'-tetra(diethoxyphosphorylmethyl)-(-2-(thieno[3,4-*d*]-1,3-dithiol-2-ylidene)thieno[3,4-*d*]-1,3-dithiole (48)

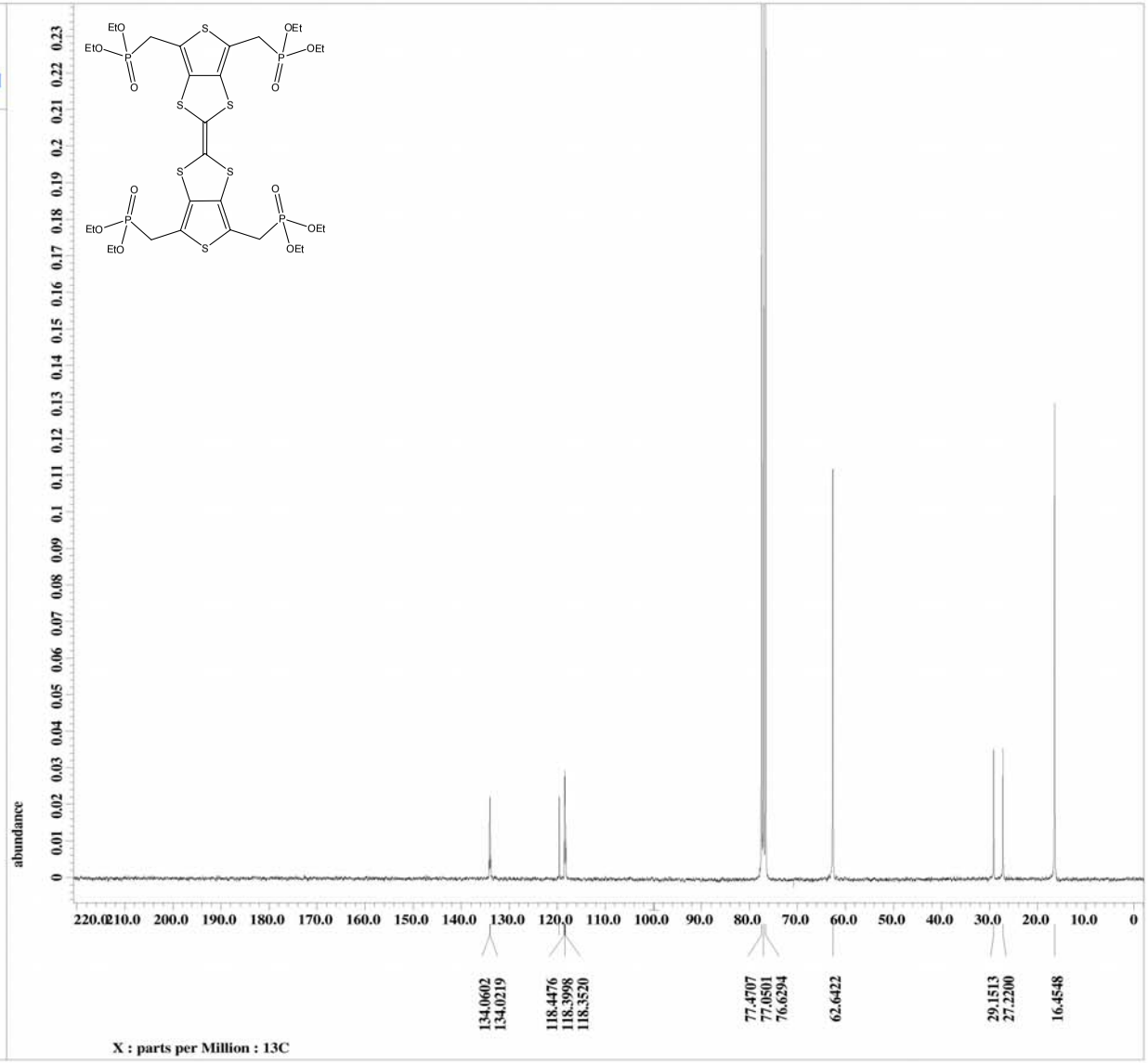

Filename = xc_vii_28_300MHz-11.j
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 17-NOV-2006 21:33:04
Revision_time = 12-FEB-2007 14:53:00
Current_time = 12-FEB-2007 14:53:23
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 40
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 23.2[dC]
16.007
8.0
24.045
abundance
7.2886
4.1456
4.1205
4.0964
3.1670
3.1041
1.3495
1.3266
1.3025
0.0000
X : parts per Million : 1H

```
Filename          = xc_vii_28_300MHz-6.jd
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 18-NOV-2006 09:44:06
Revision_time     = 12-FEB-2007 14:58:10
Current_time      = 12-FEB-2007 14:58:51

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

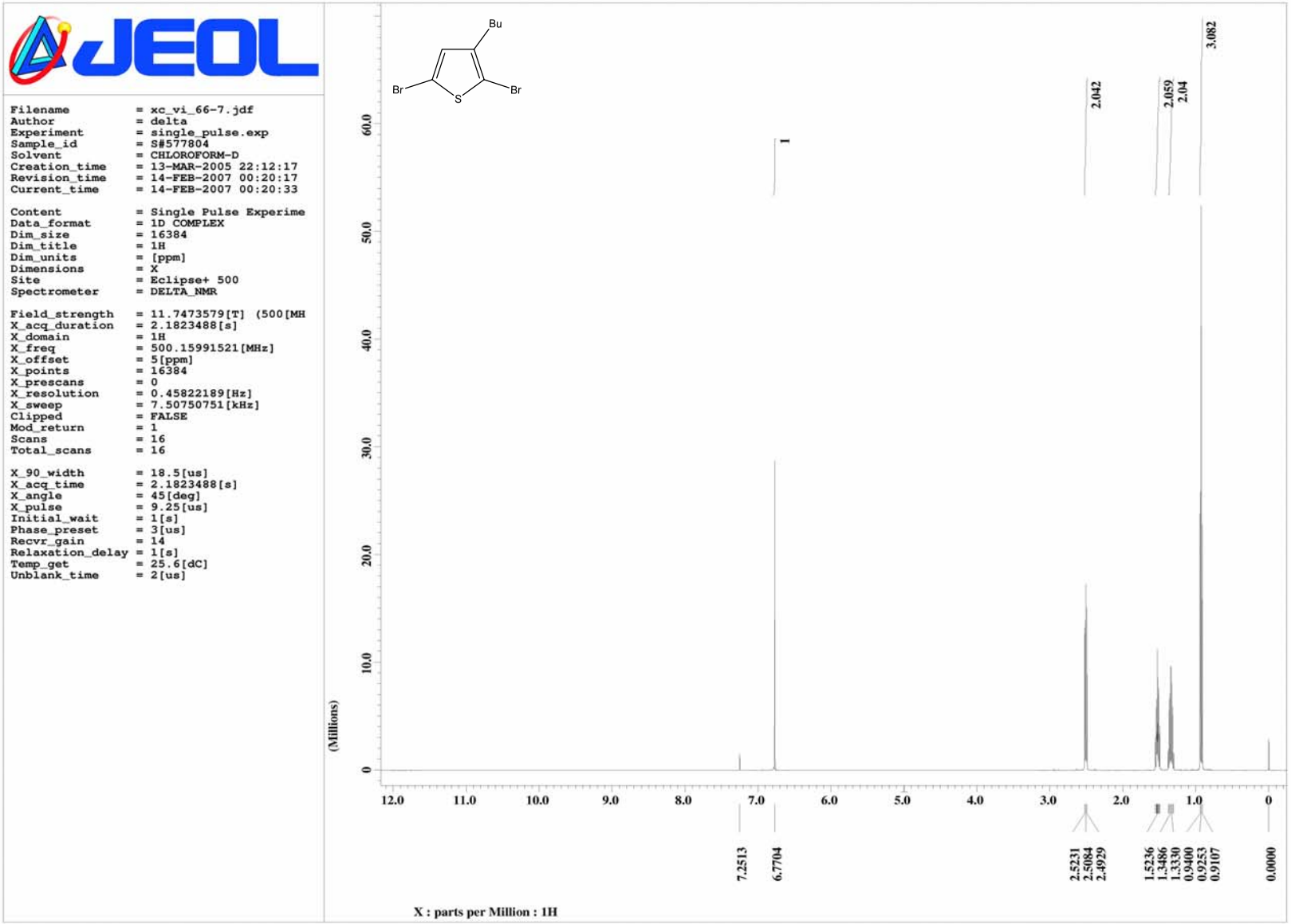
Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 1.38412032[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.72248054[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 10000
Total_scans       = 10000

X_90_width        = 9.75[us]
X_acq_time        = 1.38412032[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          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 4.38412032[s]
Temp_get          = 23.5[dC]
```



APPENDIX 44

^{1}H and ^{13}C-NMR spectra of 2,5-dibromo-3-butylthiophene (60a)

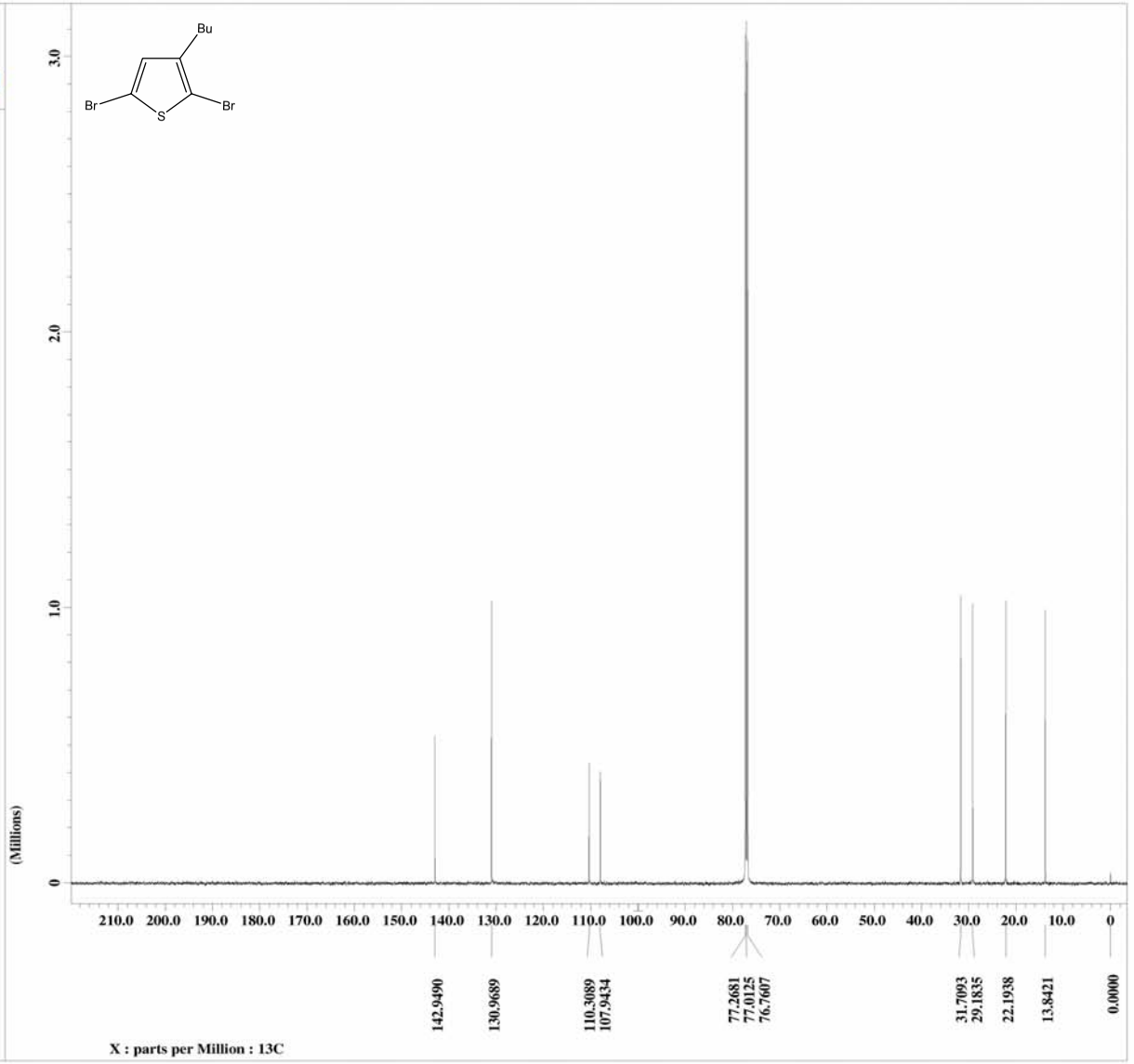

Filename = xc_vi_66-7.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#577804
Solvent = CHLOROFORM-D
Creation_time = 13-MAR-2005 22:12:17
Revision_time = 14-FEB-2007 00:20:17
Current_time = 14-FEB-2007 00:20:33
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 14
Relaxation_delay = 1[s]
Temp_get = 25.6[dC]
Unblank_time = 2[us]
Bu
Br
Br
S
(Millions)
60.0
50.0
40.0
30.0
20.0
10.0
0
1
2.042
2.059
2.04
3.082
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2513
6.7704
2.5231
2.5084
2.4929
1.5236
1.3486
1.3330
0.9400
0.9253
0.9107
0.0000
X : parts per Million : 1H

```
Filename          = xc_vi_66-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#666238
Solvent           = CHLOROFORM-D
Creation_time     = 11-MAR-2005 08:04:39
Revision_time     = 14-FEB-2007 00:20:39
Current_time      = 14-FEB-2007 00:21:06

Content           = single pulse decouple
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             = 5273
Total_scans       = 5273

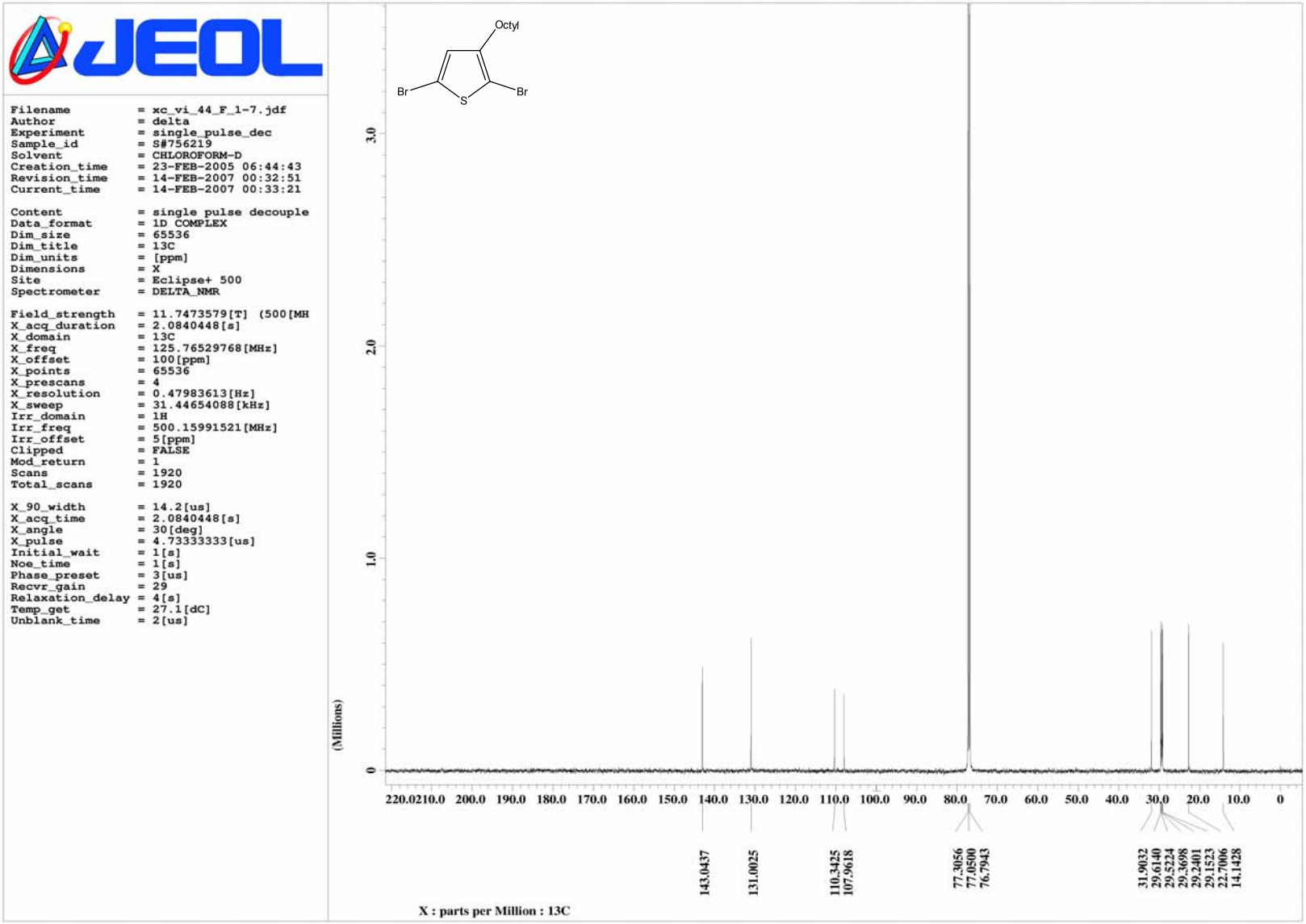
X_90_width        = 14.2[us]
X_acq_time        = 2.0840448[s]
X_angle           = 30[deg]
X_pulse           = 4.73333333[us]
Initial_wait      = 1[s]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 29
Relaxation_delay  = 2[s]
Temp_get          = 27.2[dC]
Unblank_time      = 2[us]
```



APPENDIX 45

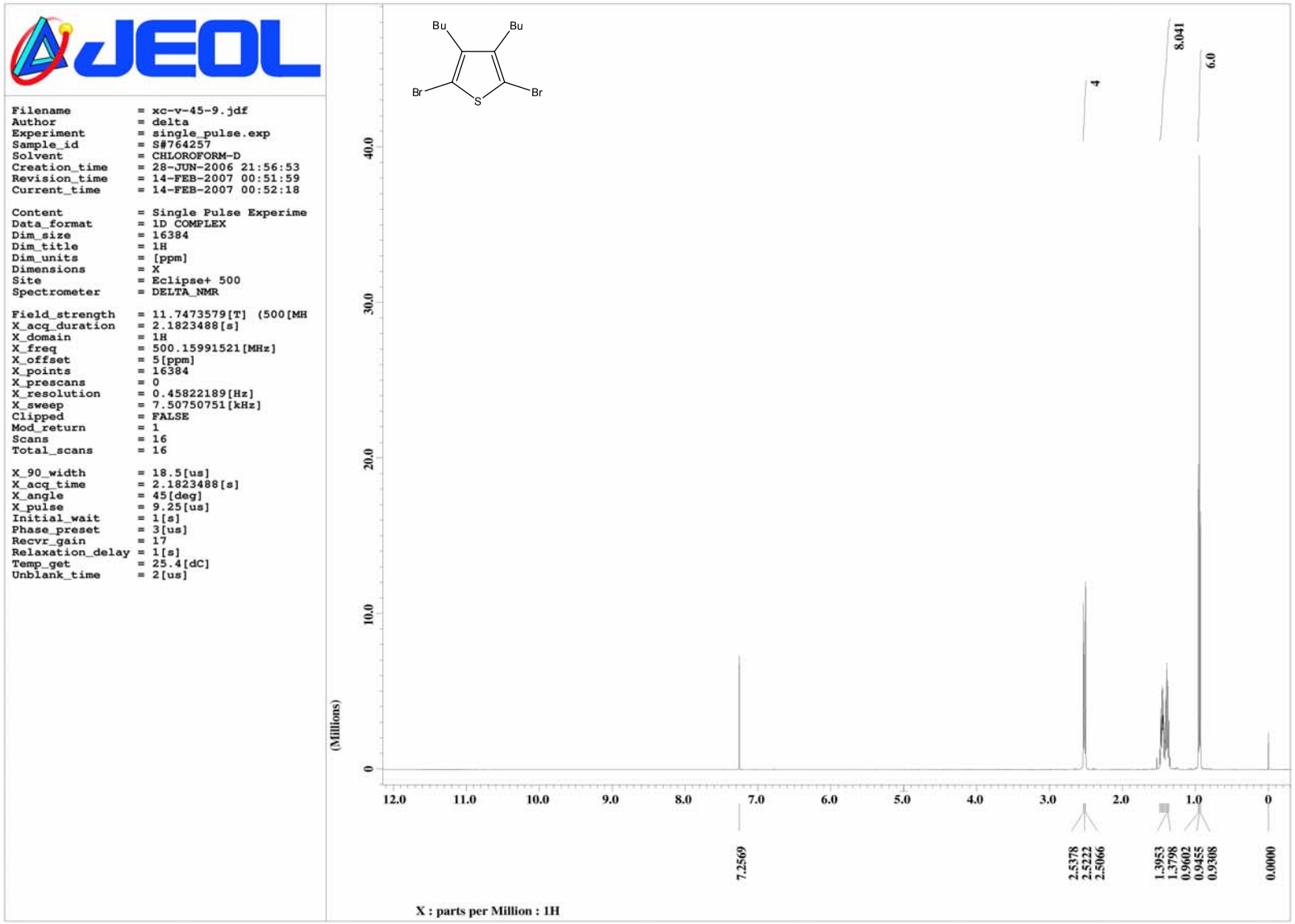
^{1}H and ^{13}C-NMR spectra of 2,5-dibromo-3-octylthiophene (60b)

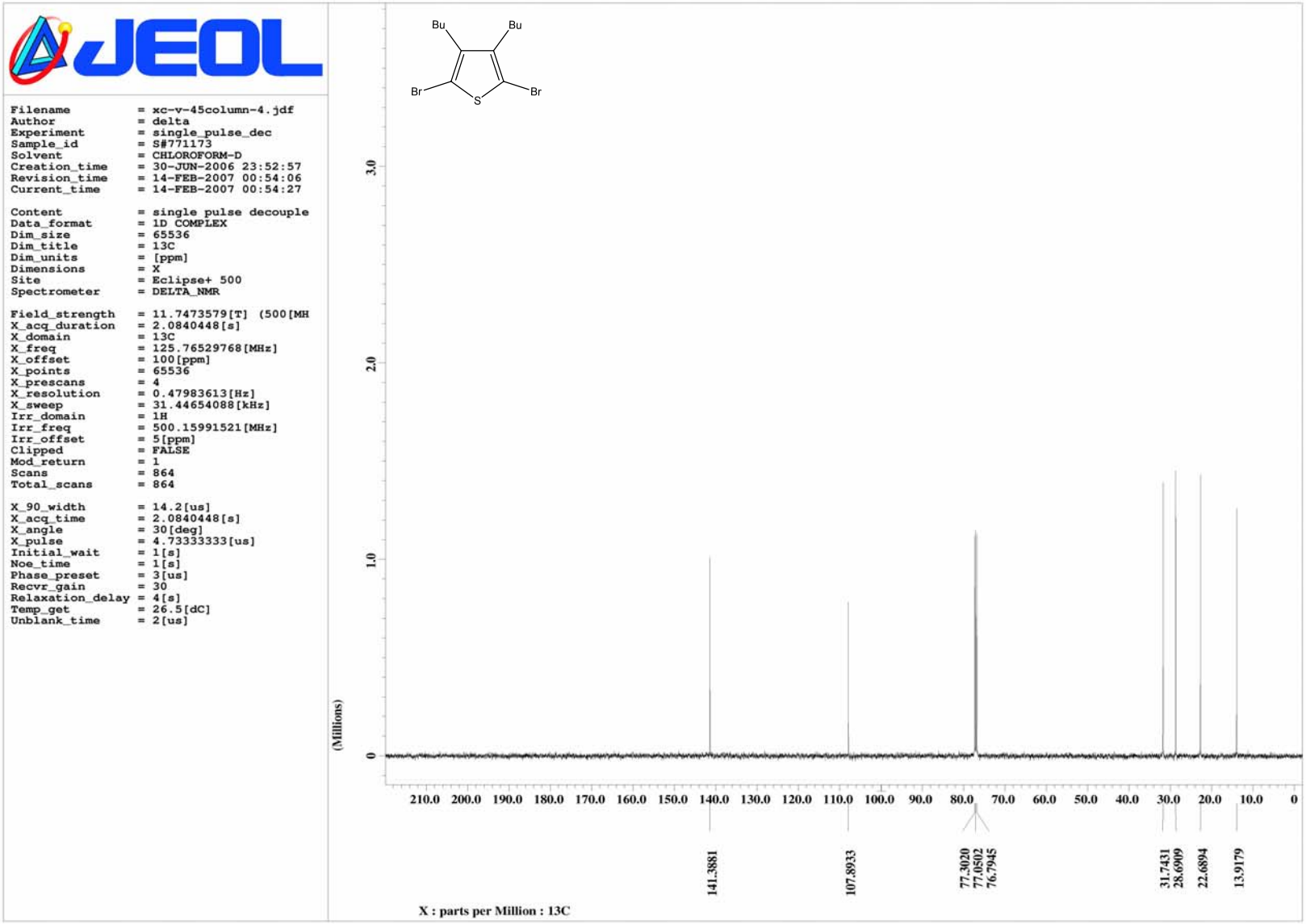
Octyl
Br
S
Br
(Millions)
X : parts per Million : 1H
7.2540
6.7703
2.5130
2.4974
2.4818
1.3009
1.2945
1.2734
1.2679
0.8822
0.8685
-0.0000
1
2.06
2.053
10.21
3.037


Filename = xc_vi_44_F_1-7.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#756219
Solvent = CHLOROFORM-D
Creation_time = 23-FEB-2005 06:44:43
Revision_time = 14-FEB-2007 00:32:51
Current_time = 14-FEB-2007 00:33:21
Content = single pulse decouple
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 = 1920
Total_scans = 1920
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 4[s]
Temp_get = 27.1[dC]
Unblank_time = 2[us]
Octyl
Br
Br
S
(Millions)
3.0
2.0
1.0
0
220.0210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
143.0437
131.0025
110.3425
107.9618
77.3056
77.0500
76.7943
31.9032
29.6140
29.5224
29.3698
29.2401
29.1523
22.7006
14.1428
X : parts per Million : 13C

APPENDIX 46

^{1}H and ^{13}C-NMR spectra of 2,5-dibromo-3,4-dibutylthiophene (60c)

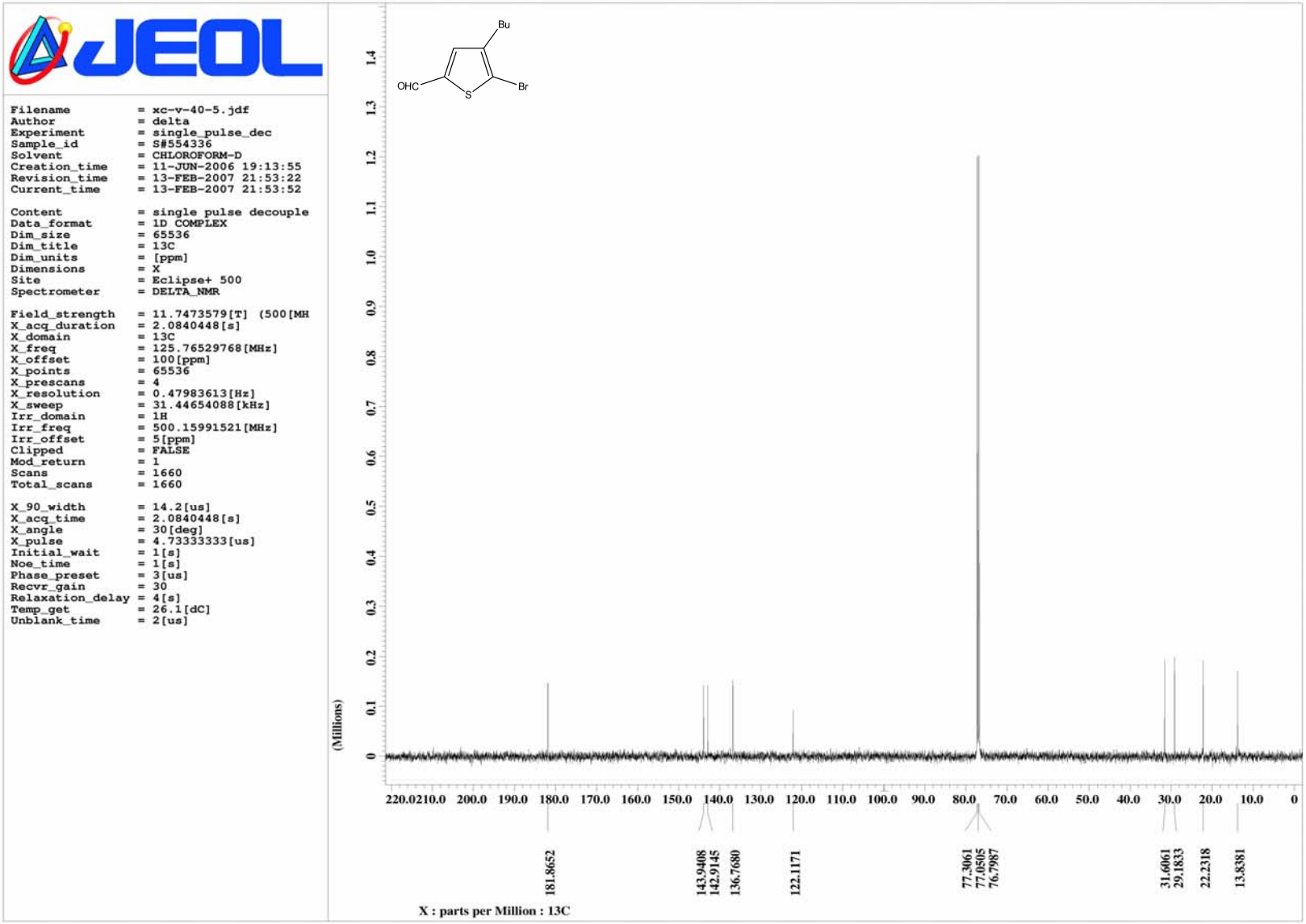

Filename = xc-v-45-9.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#764257
Solvent = CHLOROFORM-D
Creation_time = 28-JUN-2006 21:56:53
Revision_time = 14-FEB-2007 00:51:59
Current_time = 14-FEB-2007 00:52:18
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 17
Relaxation_delay = 1[s]
Temp_get = 25.4[dC]
Unblank_time = 2[us]
Bu
Bu
Br
Br
S
8.041
6.0
4
40.0
30.0
20.0
10.0
0
(Millions)
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2569
2.5378
2.5222
2.5066
1.3953
1.3798
0.9602
0.9455
0.9308
0.0000
X : parts per Million : 1H


Filename = xc-v-45column-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#771173
Solvent = CHLOROFORM-D
Creation_time = 30-JUN-2006 23:52:57
Revision_time = 14-FEB-2007 00:54:06
Current_time = 14-FEB-2007 00:54:27
Content = single pulse decouple
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 = 864
Total_scans = 864
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 26.5[dC]
Unblank_time = 2[us]
Bu
Bu
Br
Br
S
(Millions)
3.0
2.0
1.0
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
141.3881
107.8933
77.3020
77.0502
76.7945
31.7431
28.6909
22.6894
13.9179
X : parts per Million : 13C

APPENDIX 47

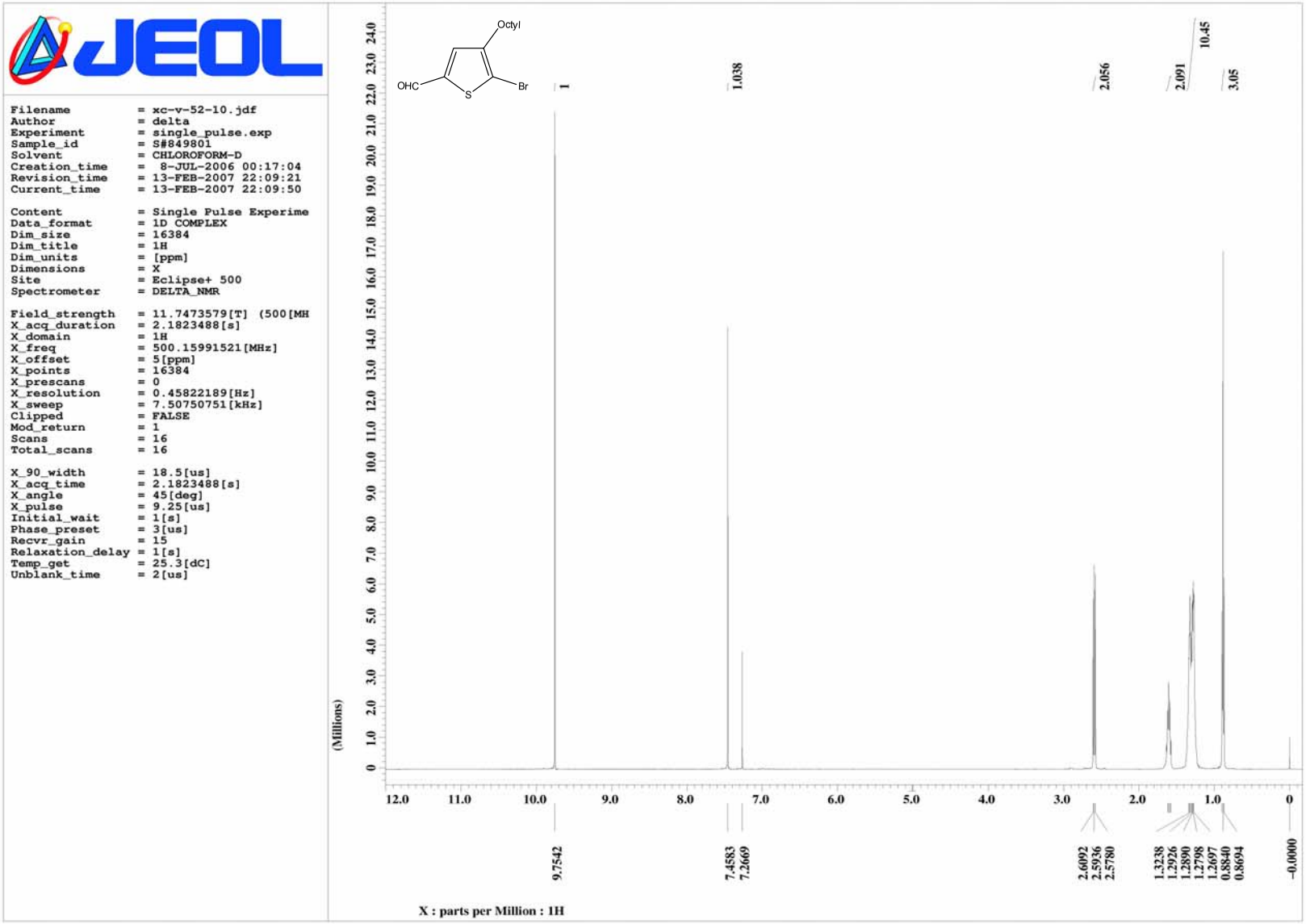
^{1}H and ^{13}C-NMR spectra of 5-bromo-4-butyl-2-thiophenecarboxaldehyde (61a)

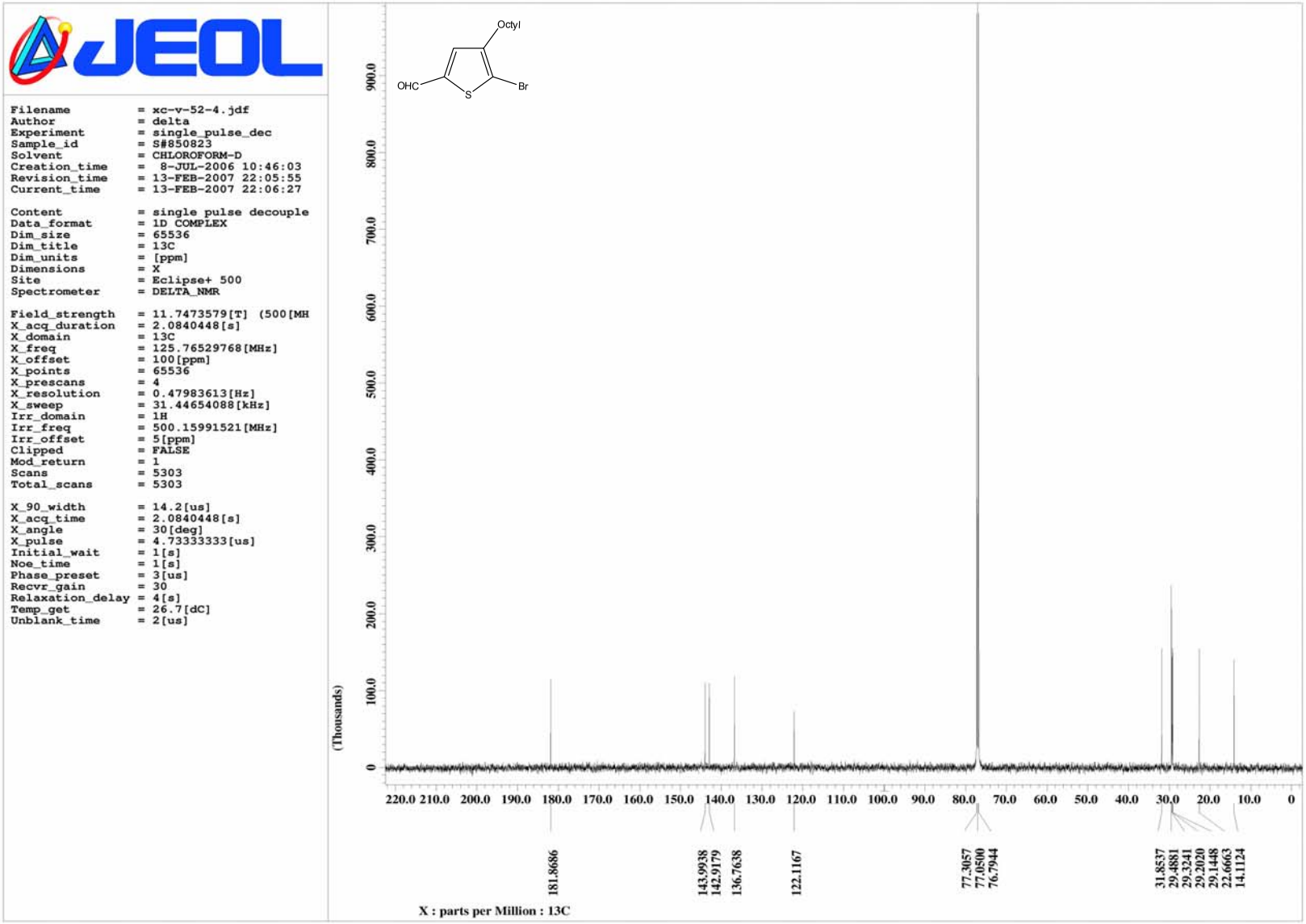
Filename = xc-y-40-13.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = SH55316
Solvent = CHLOROFORM-D
Creation_time = 11-JUN-2006 15:53:56
Revision_time = 13-FEB-2007 21:51:58
Current_time = 13-FEB-2007 21:52:36
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 17
Relaxation_delay = 1[s]
Temp_get = 25.2[dC]
Unblank_time = 2[us]
JEOL
Bu
Br
S
OHC
1
1.015
3.008
2.043
2.082
2.07
9.7543
7.4621
7.2697
2.6211
2.6055
2.5900
1.5969
1.3861
1.3706
0.9665
0.9519
0.9372
0.0000
(Millions)
X : parts per Million : 1H


Filename = xc-v-40-5.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#554336
Solvent = CHLOROFORM-D
Creation_time = 11-JUN-2006 19:13:55
Revision_time = 13-FEB-2007 21:53:22
Current_time = 13-FEB-2007 21:53:52
Content = single pulse decouple
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 = 1660
Total_scans = 1660
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 26.1[dC]
Unblank_time = 2[us]
Bu
OHC
S
Br
(Millions)
181.8652
143.9408
142.9145
136.7680
122.1171
77.3061
77.0505
76.7987
31.6061
29.1833
22.2318
13.8381
X : parts per Million : 13C

APPENDIX 48

^{1}H and ^{13}C-NMR spectra of 5-bromo-4-octyl-2-thiophenecarboxaldehyde (61b)


Filename = xc-v-52-10.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#849801
Solvent = CHLOROFORM-D
Creation_time = 8-JUL-2006 00:17:04
Revision_time = 13-FEB-2007 22:09:21
Current_time = 13-FEB-2007 22:09:50
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 1[s]
Temp_get = 25.3[dC]
Unblank_time = 2[us]
Octyl
OHC
S
Br
1
1.038
2.056
2.091
10.45
3.05
(Millions)
9.7542
7.4583
7.2669
2.6092
2.5936
2.5780
1.3238
1.2926
1.2890
1.2798
1.2697
0.8840
0.8694
-0.0000
X : parts per Million : 1H


Octyl
OHC
S
Br
Filename = xc-v-52-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#850823
Solvent = CHLOROFORM-D
Creation_time = 8-JUL-2006 10:46:03
Revision_time = 13-FEB-2007 22:05:55
Current_time = 13-FEB-2007 22:06:27
Content = single pulse decouple
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 = 5303
Total_scans = 5303
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 26.7[dC]
Unblank_time = 2[us]
(Thousands)
900.0
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
181.8686
143.9938
142.9179
136.7638
122.1167
77.3057
77.0500
76.7944
31.8537
29.4881
29.3241
29.2020
29.1448
22.6663
14.1124
X : parts per Million : 13C

APPENDIX 49

^{1}H and ^{13}C-NMR spectra of 5-bromo-3,4-dibutyl-2-thiophenecarboxaldehyde (61c)

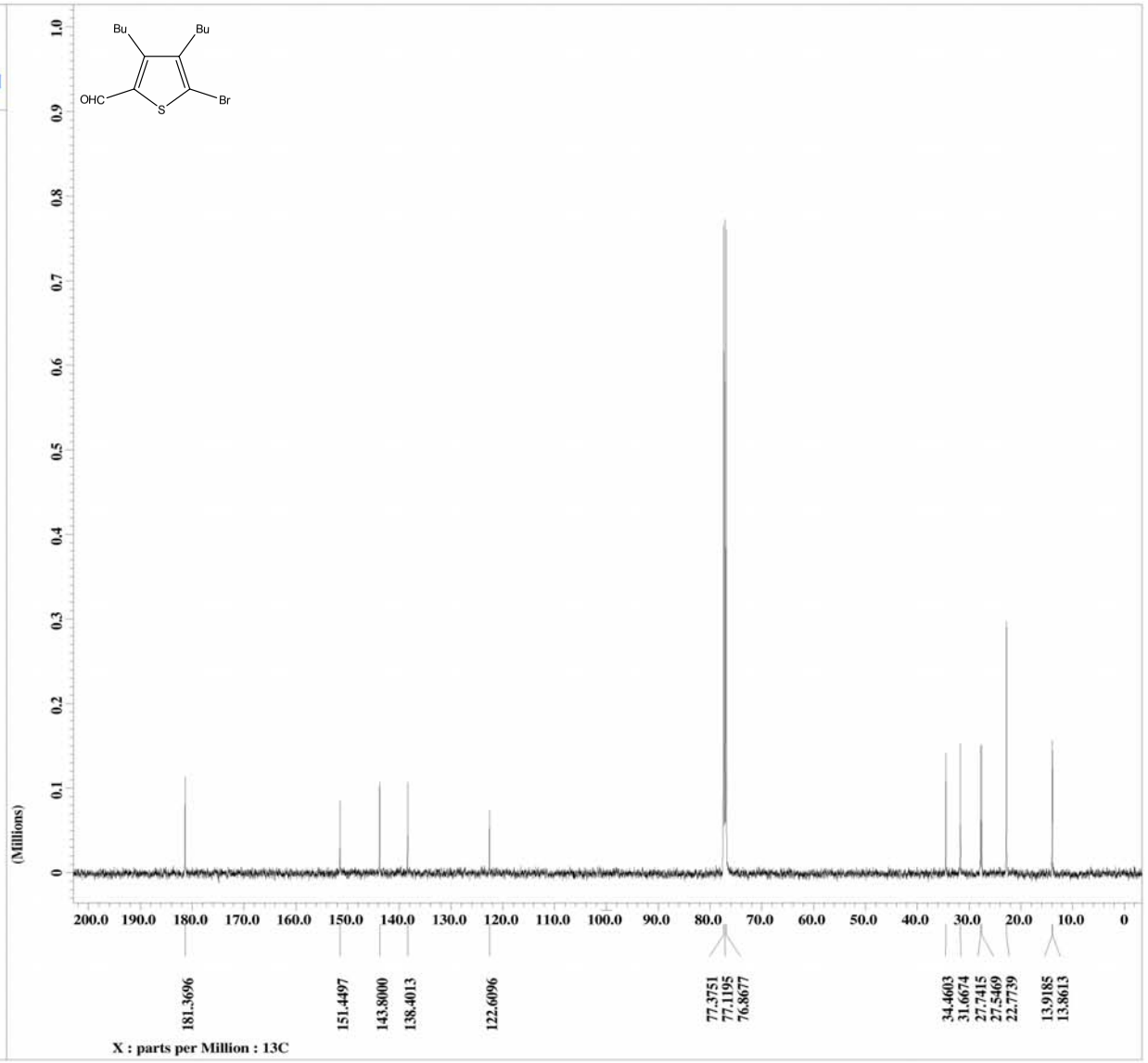
JEOL
Filename = XG-V-49-Final-13.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = SH784930
Solvent = CHLOROFORM-D
Creation_time = 5-JUL-2006 22:27:34
Revision_time = 13-FEB-2007 22:24:30
Current_time = 13-FEB-2007 22:25:03
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.74735791[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 15
Relaxation_delay = 1[s]
Temp_get = 24.9[dC]
Unblank_time = 2[us]
Bu
Br
Bu
S
OHC
I
6.079
8.06
2.053
2.066
9.9145
7.2714
2.9032
2.8867
2.8712
2.5395
1.5684
1.4328
1.4209
0.9637
0.9573
-0.0000
(Millions)
X : parts per Million : 1H

```
Filename          = xc-v-49-Final-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#786482
Solvent           = CHLOROFORM-D
Creation_time     =  6-JUL-2006 09:19:40
Revision_time     = 13-FEB-2007 22:26:18
Current_time      = 13-FEB-2007 22:27:07

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

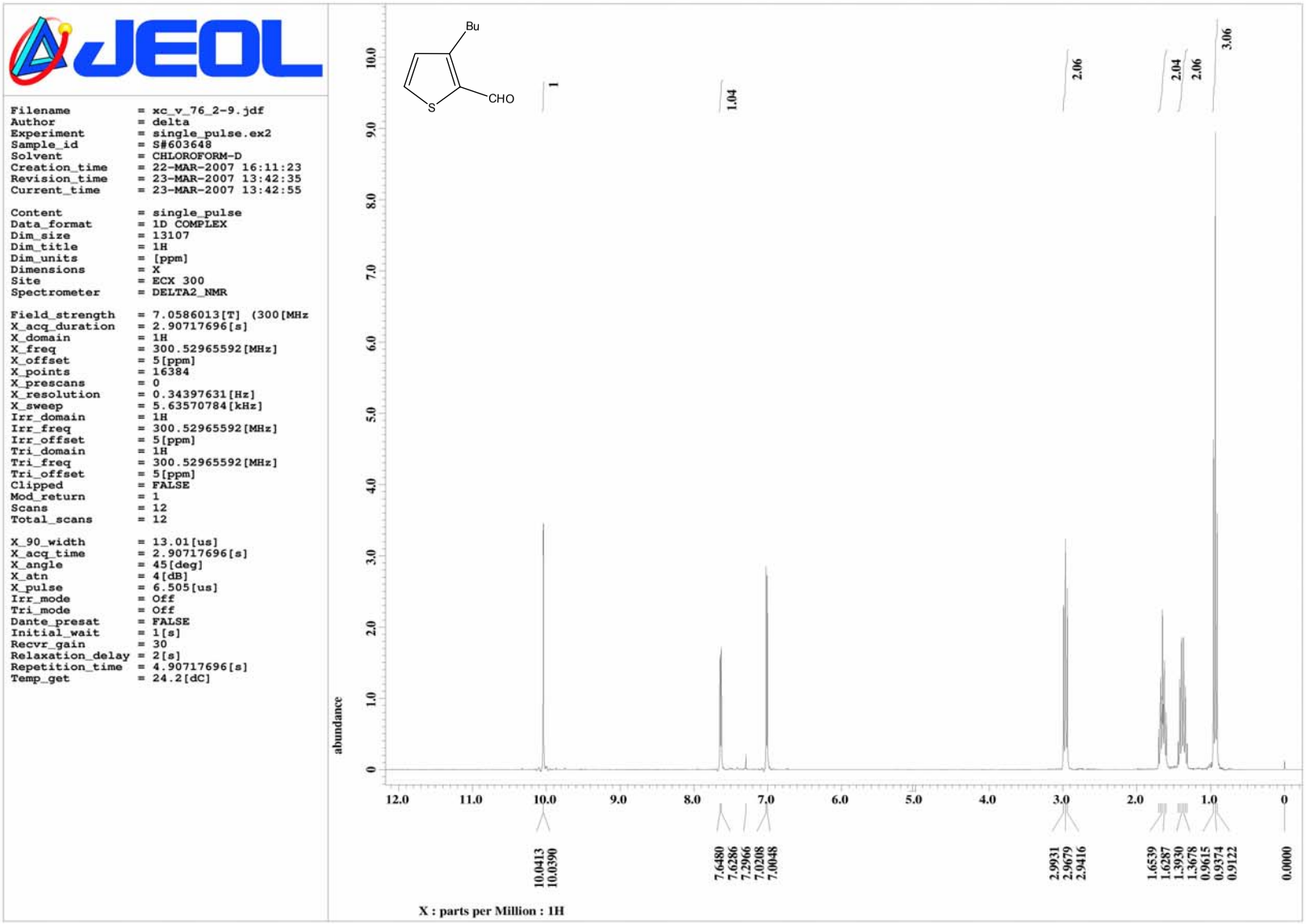
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 5477
Total_scans       = 5477

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]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 4[s]
Temp_get          = 26.6[dC]
Unblank_time      = 2[us]
```



APPENDIX 50

^{1}H and ^{13}C-NMR spectra of 3-butyl-2-thiophenecarboxaldehyde (63a)

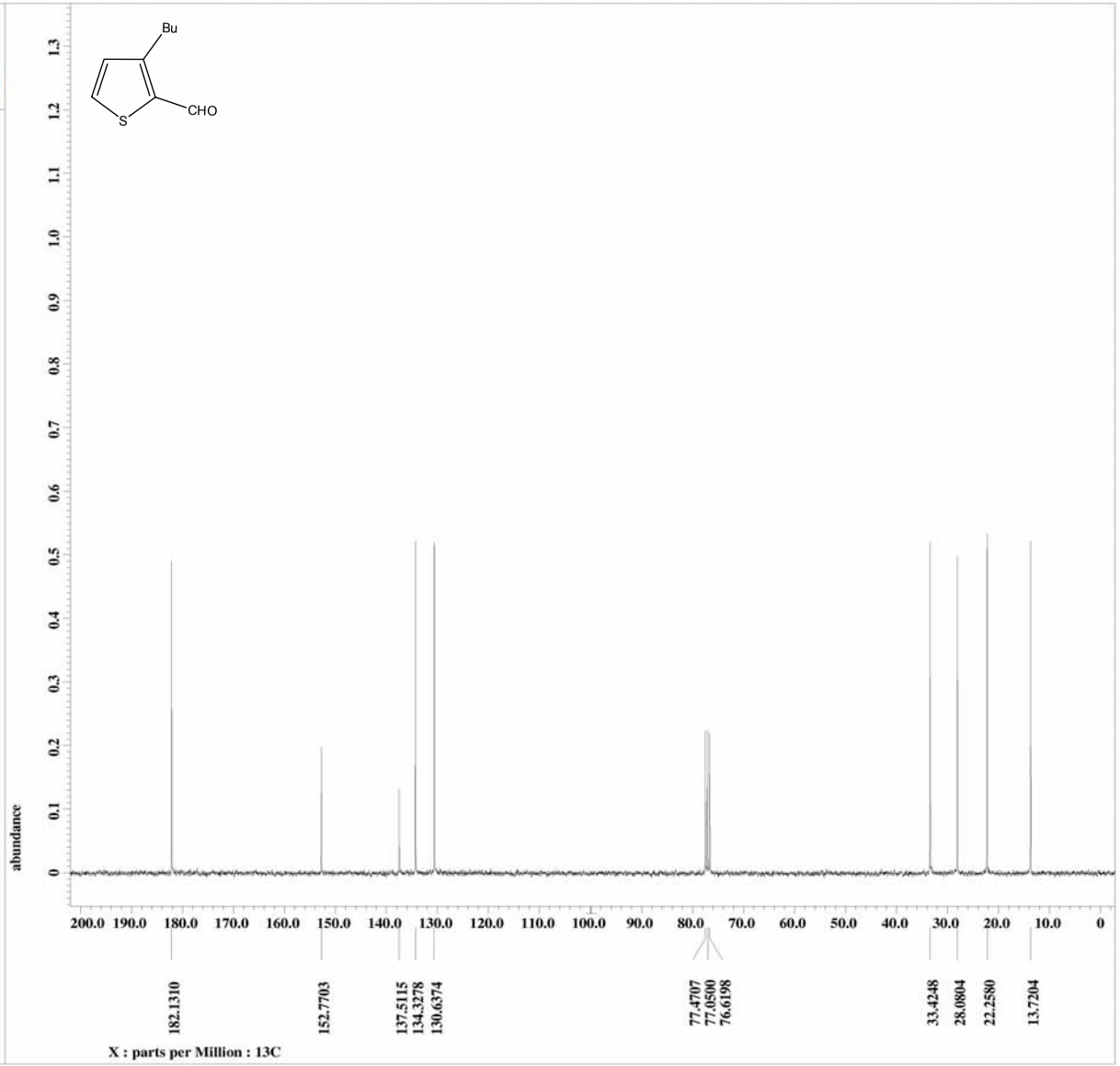

Filename = xc_v_76_2-9.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#603648
Solvent = CHLOROFORM-D
Creation_time = 22-MAR-2007 16:11:23
Revision_time = 23-MAR-2007 13:42:35
Current_time = 23-MAR-2007 13:42:55
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 12
Total_scans = 12
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 30
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 24.2[dC]
Bu
CHO
S
1
1.04
2.06
2.04
2.06
3.06
abundance
10.0413
10.0390
7.6480
7.6286
7.2966
7.0208
7.0048
2.9931
2.9679
2.9416
1.6539
1.6287
1.3930
1.3678
0.9615
0.9374
0.9122
0.0000
X : parts per Million : 1H

```
Filename          = xc_v_76-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#617824
Solvent           = CHLOROFORM-D
Creation_time     = 22-MAR-2007 16:43:11
Revision_time     = 23-MAR-2007 13:33:33
Current_time      = 23-MAR-2007 13:34:02

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

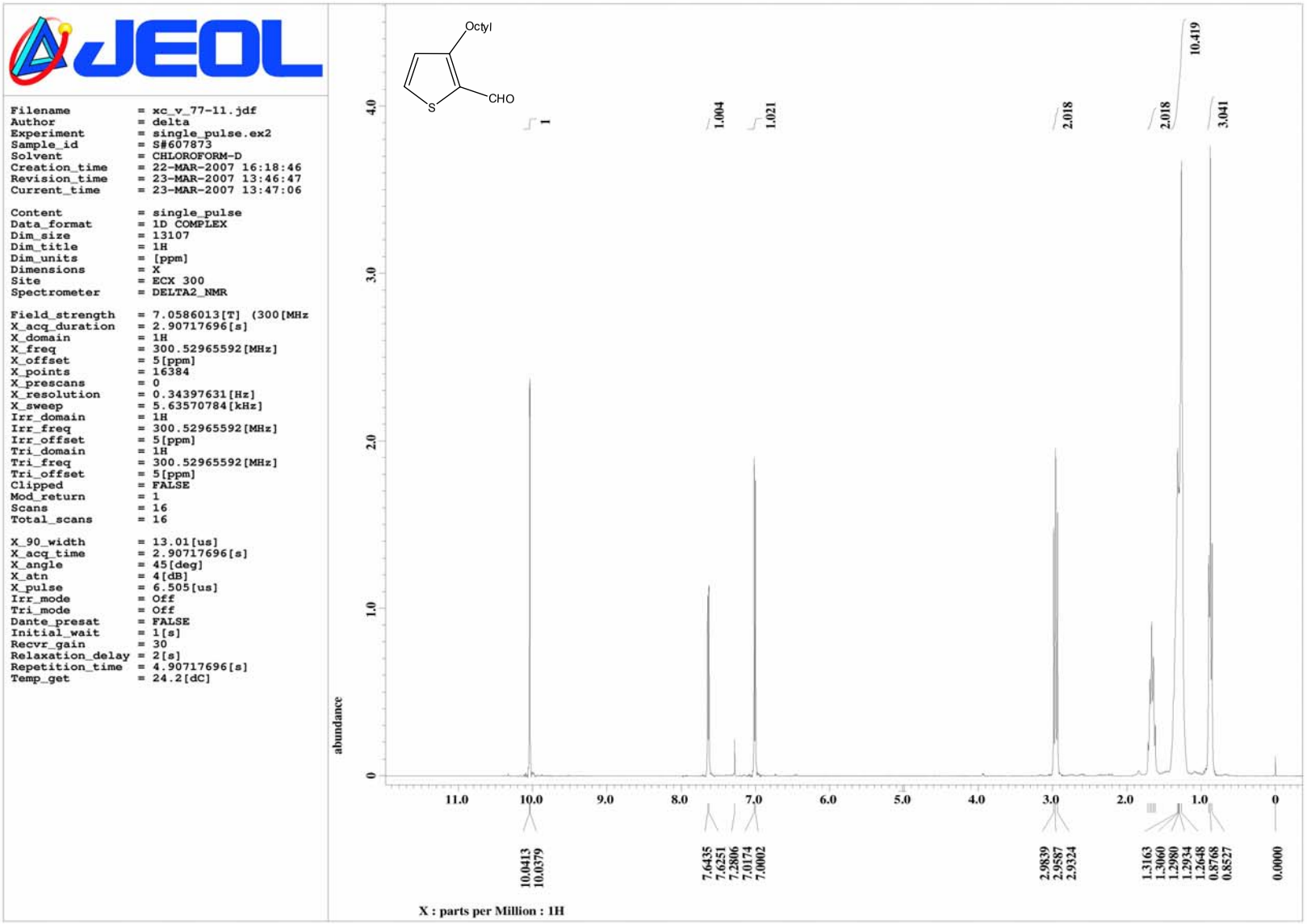
Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 1.38412032[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.72248054[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 163
Total_scans       = 163

X_90_width        = 9.75[us]
X_acq_time        = 1.38412032[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   = 3.38412032[s]
Temp_get          = 22.7[dC]
```



APPENDIX 51

^{1}H and ^{13}C-NMR spectra of 3-octyl-2-thiophenecarboxaldehyde (63b)

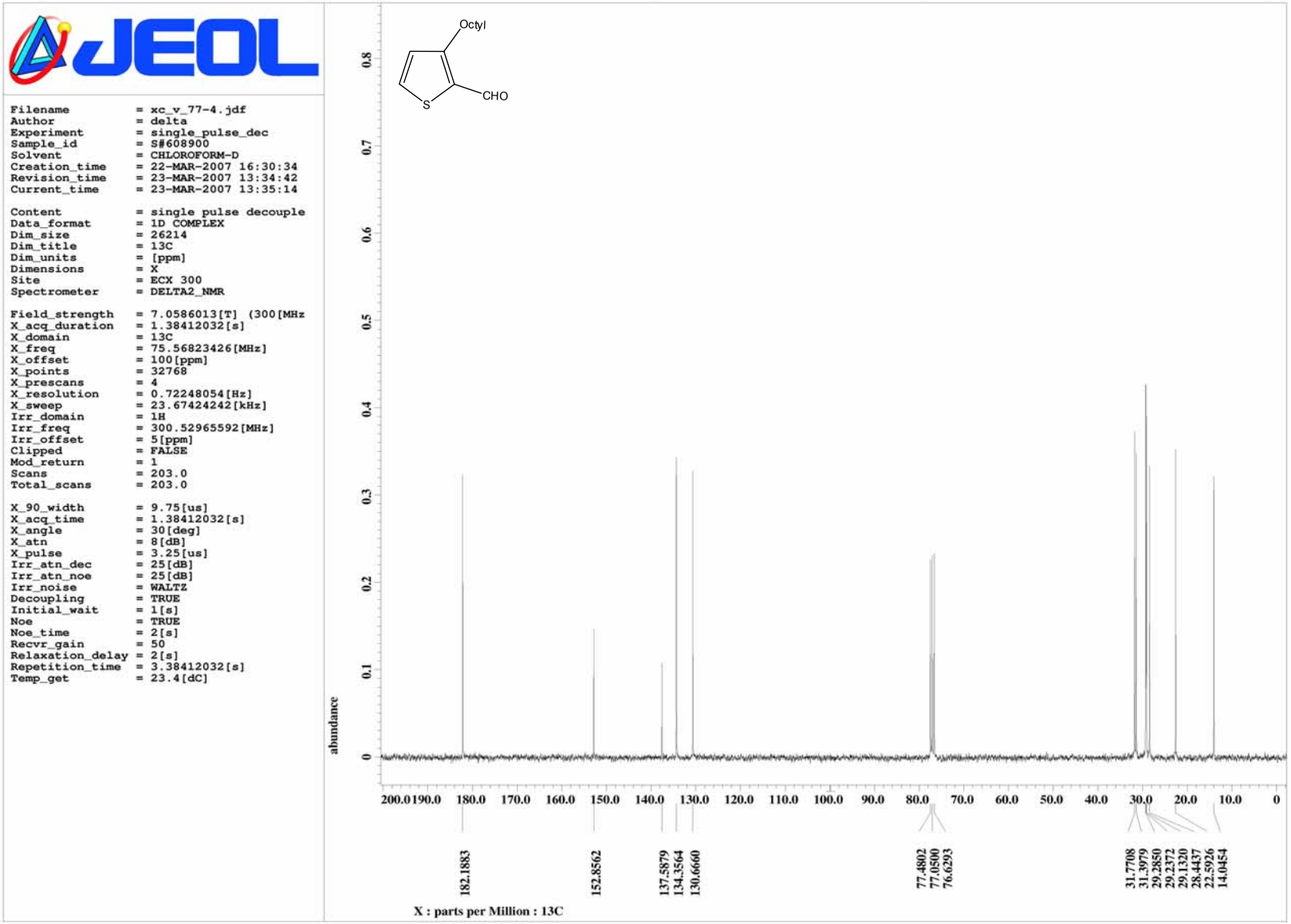



```
Filename          = xc_v_77-11.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#607873
Solvent           = CHLOROFORM-D
Creation_time     = 22-MAR-2007 16:18:46
Revision_time     = 23-MAR-2007 13:46:47
Current_time      = 23-MAR-2007 13:47:06

Content           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 30
Relaxation_delay  = 2[s]
Repetition_time   = 4.90717696[s]
Temp_get          = 24.2[dC]
```


Filename = xc_v_77-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#608900
Solvent = CHLOROFORM-D
Creation_time = 22-MAR-2007 16:30:34
Revision_time = 23-MAR-2007 13:34:42
Current_time = 23-MAR-2007 13:35:14
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 1.38412032[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.72248054[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 203.0
Total_scans = 203.0
X_90_width = 9.75[us]
X_acq_time = 1.38412032[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 = 3.38412032[s]
Temp_get = 23.4[dC]
Octyl
CHO
S
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
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 0
182.1883
152.8562
137.5879
134.3564
130.6660
77.4802
77.0500
76.6293
31.7708
31.3979
29.2850
29.2372
29.1320
28.4437
22.5926
14.0454
X : parts per Million : 13C

APPENDIX 52

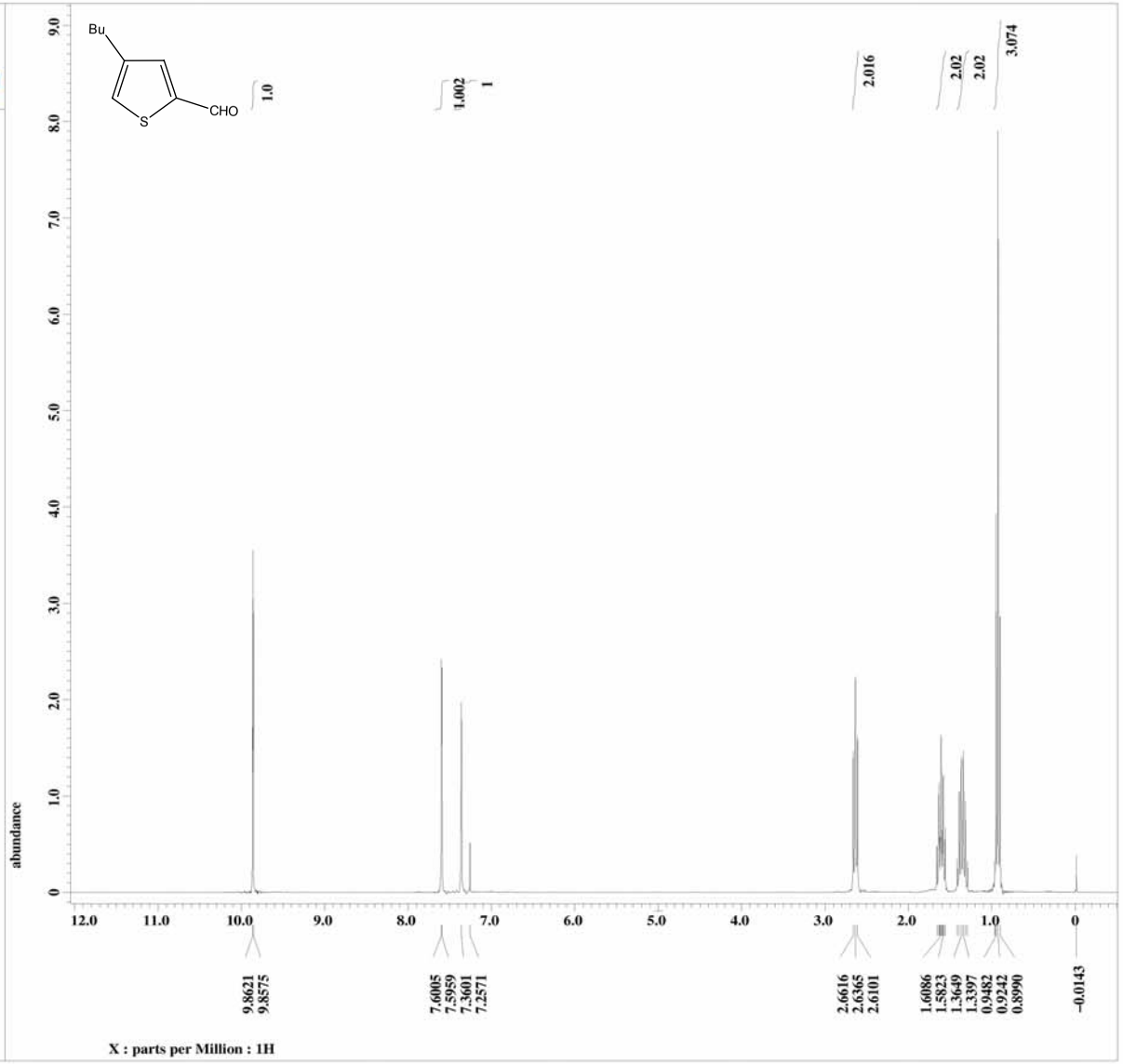
^{1}H and ^{13}C-NMR spectra of 4-butyl-2-thiophenecarboxaldehyde (67a)

```
Filename          = xc_v_81repeat-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 21-MAR-2007 16:55:16
Revision_time     = 23-MAR-2007 13:49:33
Current_time      = 23-MAR-2007 13:49:56

Content           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 36
Relaxation_delay  = 2[s]
Repetition_time   = 4.90717696[s]
Temp_get          = 23[dC]
```

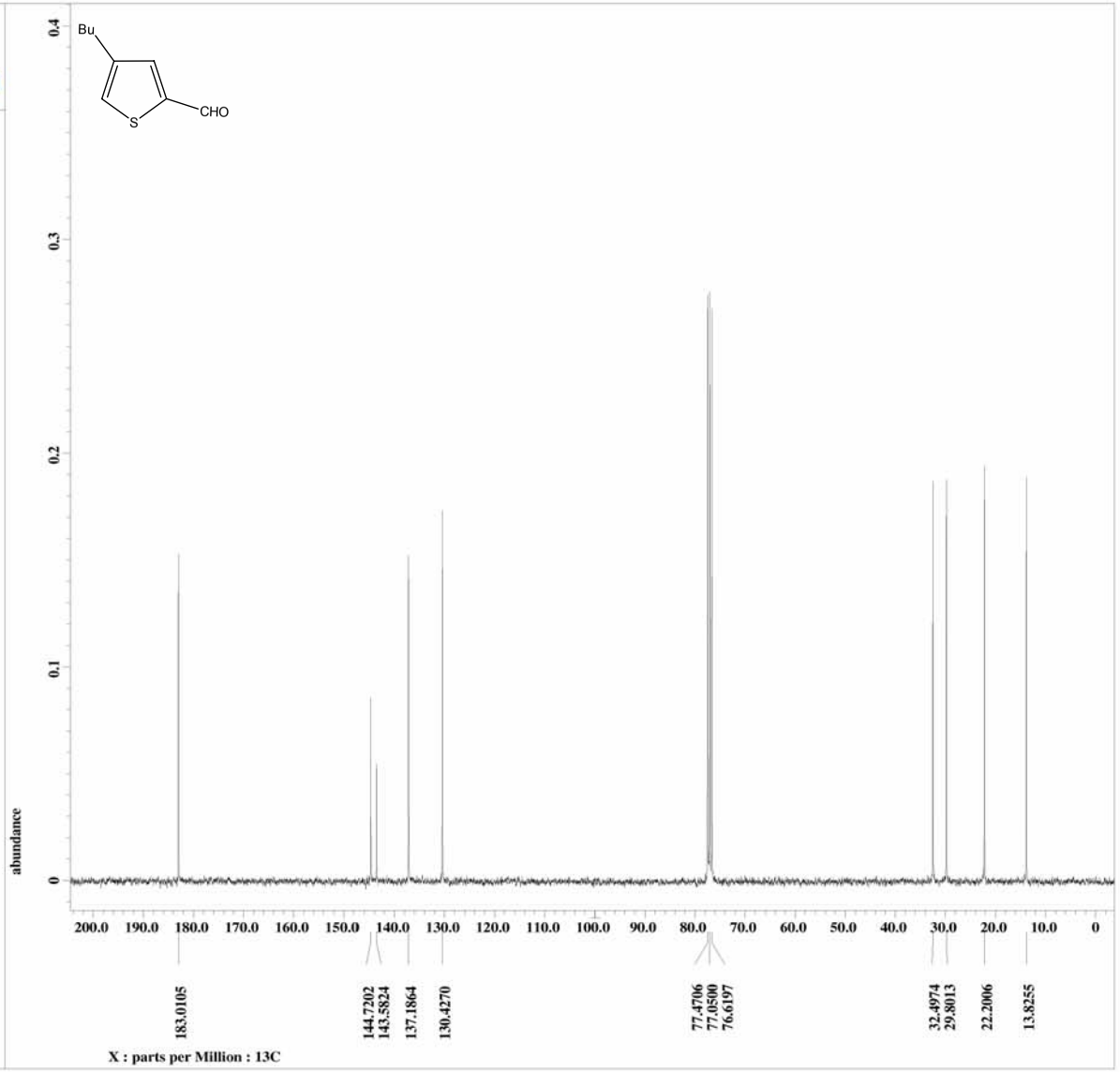


```
Filename          = xc_v_81repeat-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 21-MAR-2007 18:09:03
Revision_time     = 23-MAR-2007 13:35:54
Current_time      = 23-MAR-2007 13:36:22

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

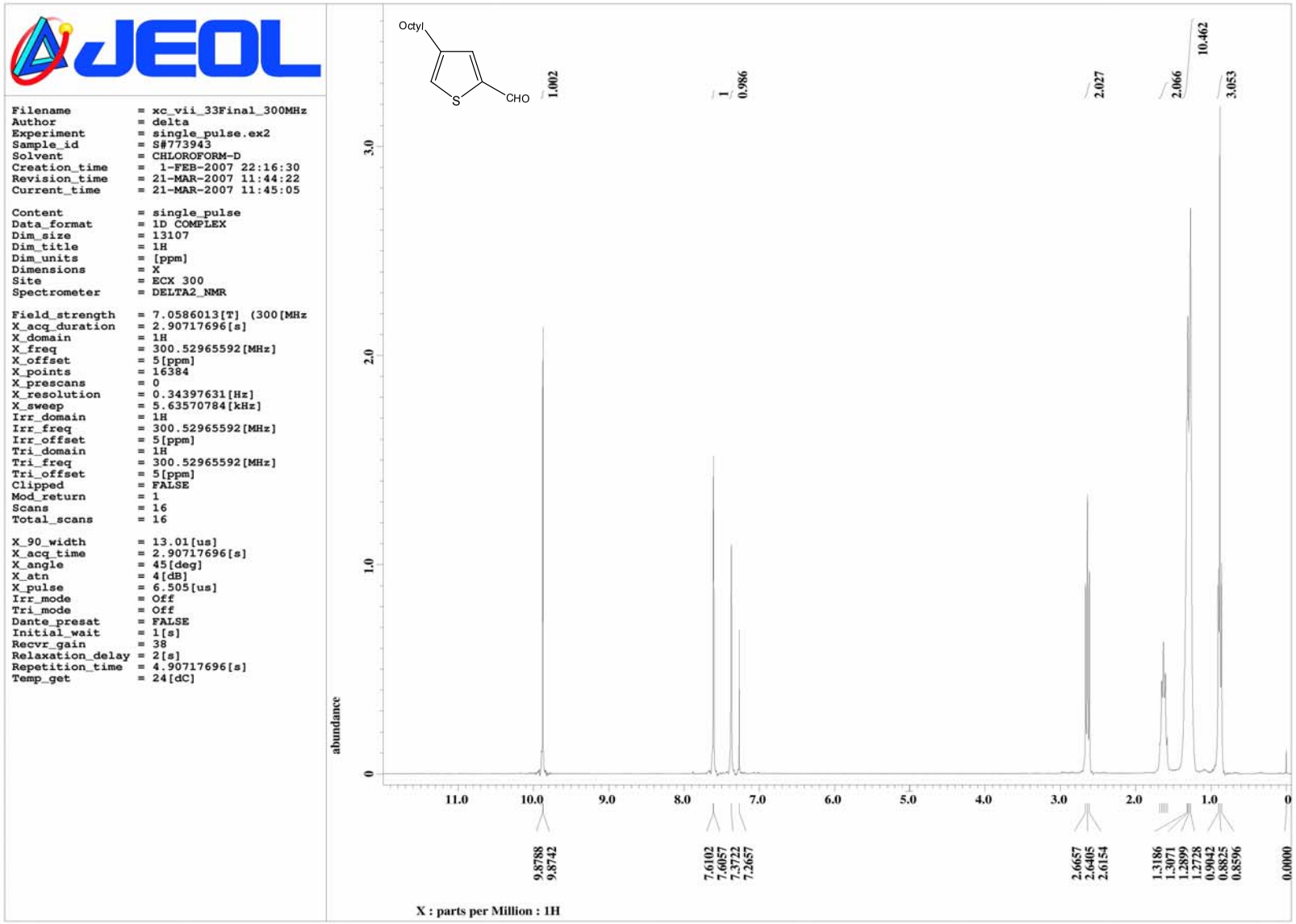
Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 1.38412032[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.72248054[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 990
Total_scans       = 990

X_90_width        = 9.75[us]
X_acq_time        = 1.38412032[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          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 4.38412032[s]
Temp_get          = 22.4[dC]
```



APPENDIX 53

^{1}H and ^{13}C-NMR spectra of 4-octyl-2-thiophenecarboxaldehyde (67b)

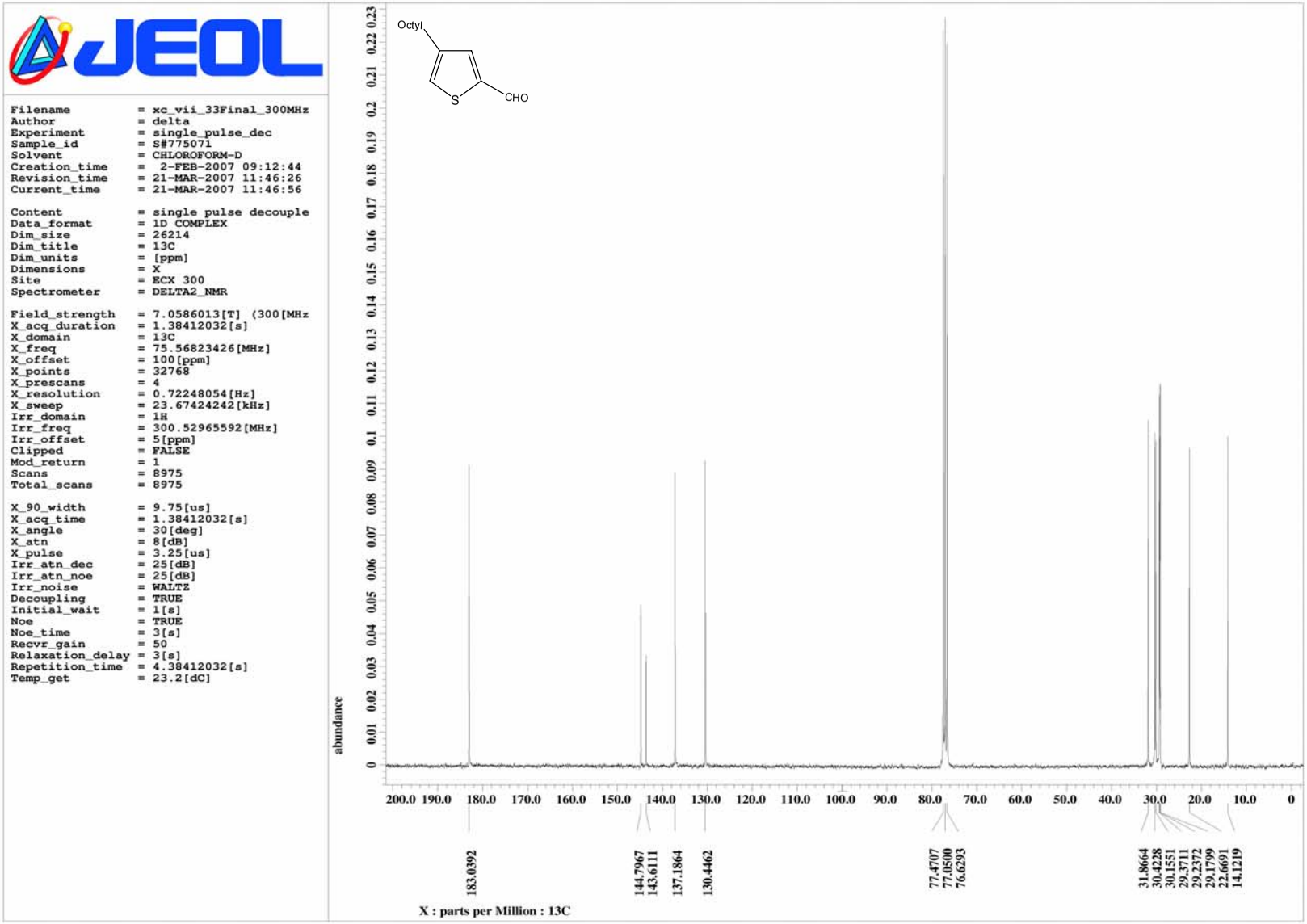



```
Filename          = xc_vii_33Final_300MHz
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#773943
Solvent           = CHLOROFORM-D
Creation_time     =  1-FEB-2007 22:16:30
Revision_time     = 21-MAR-2007 11:44:22
Current_time      = 21-MAR-2007 11:45:05

Content           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

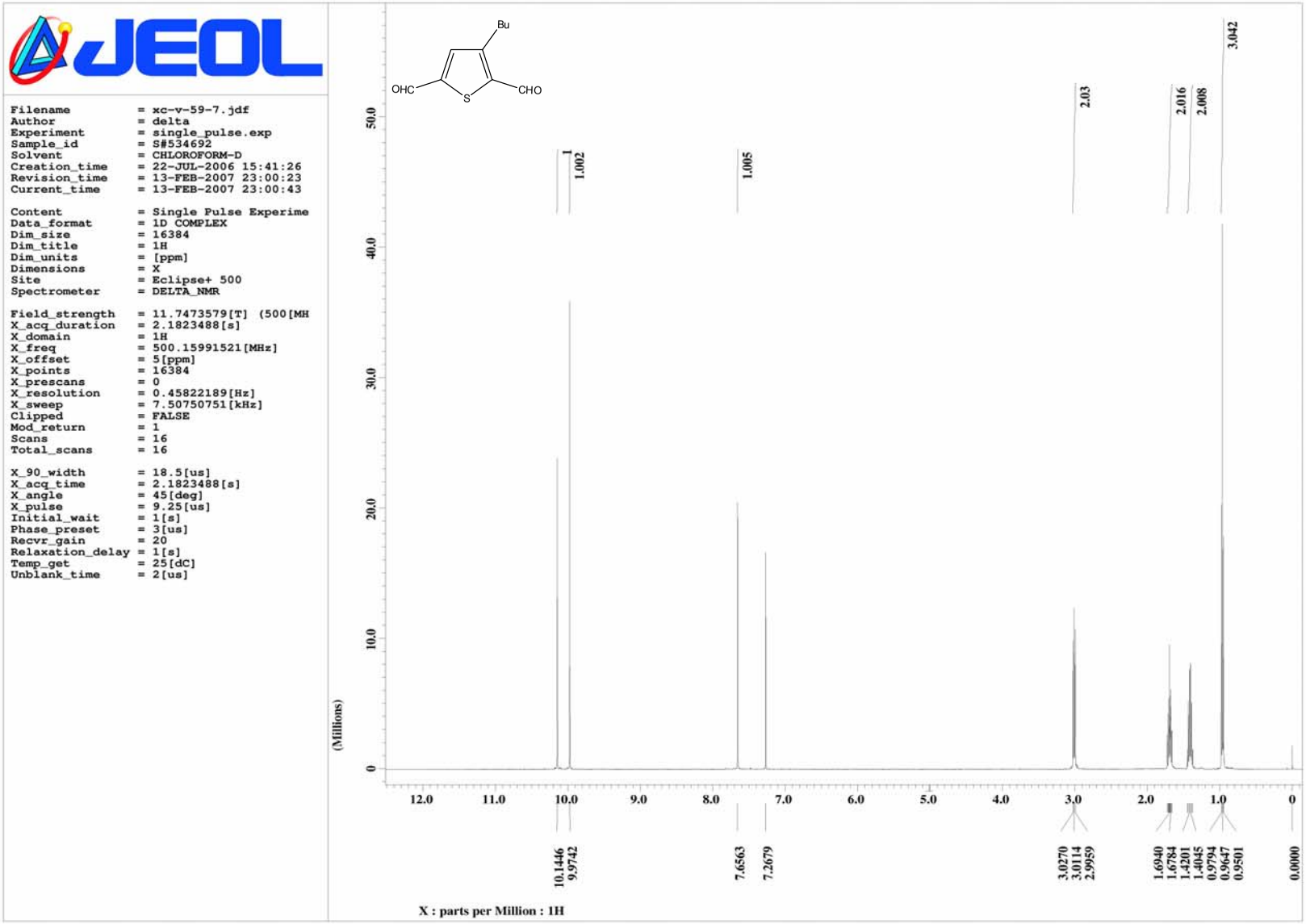
Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

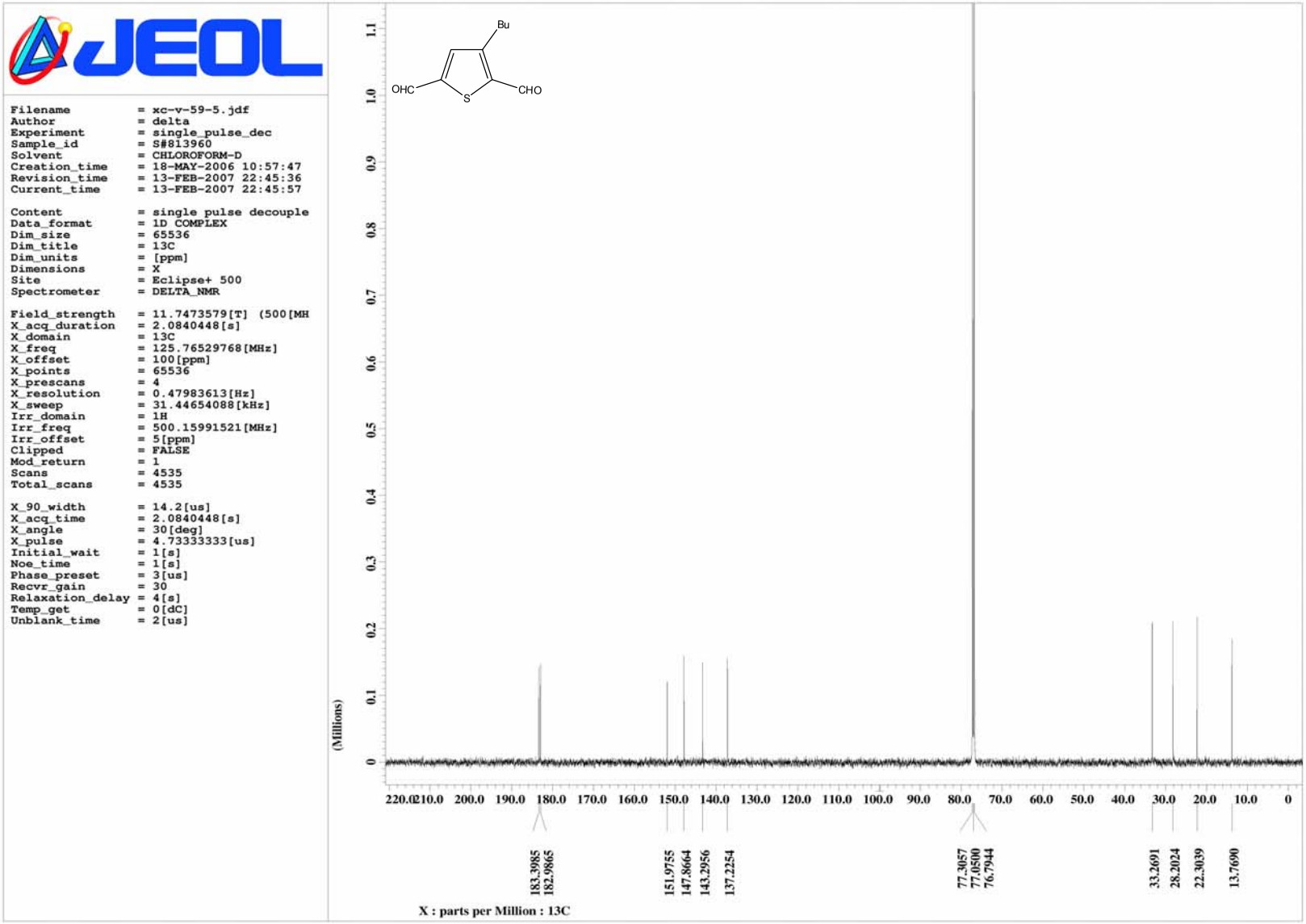
X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 38
Relaxation_delay  = 2[s]
Repetition_time   = 4.90717696[s]
Temp_get          = 24[dC]
```


Octyl
S
CHO
Filename = xc_vii_33Final_300MHz
Author = delta
Experiment = single_pulse_dec
Sample_id = S#775071
Solvent = CHLOROFORM-D
Creation_time = 2-FEB-2007 09:12:44
Revision_time = 21-MAR-2007 11:46:26
Current_time = 21-MAR-2007 11:46:56
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 1.38412032[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.72248054[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8975
Total_scans = 8975
X_90_width = 9.75[us]
X_acq_time = 1.38412032[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 = 3[s]
Recvr_gain = 50
Relaxation_delay = 3[s]
Repetition_time = 4.38412032[s]
Temp_get = 23.2[dC]
abundance
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15 0.16 0.17 0.18 0.19 0.2 0.21 0.22 0.23
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 0
183.0392
144.7967
143.6111
137.1864
130.4462
77.4707
77.0500
76.6293
31.8664
30.4228
30.1551
29.3711
29.2372
29.1799
22.6691
14.1219
X : parts per Million : 13C

APPENDIX 54

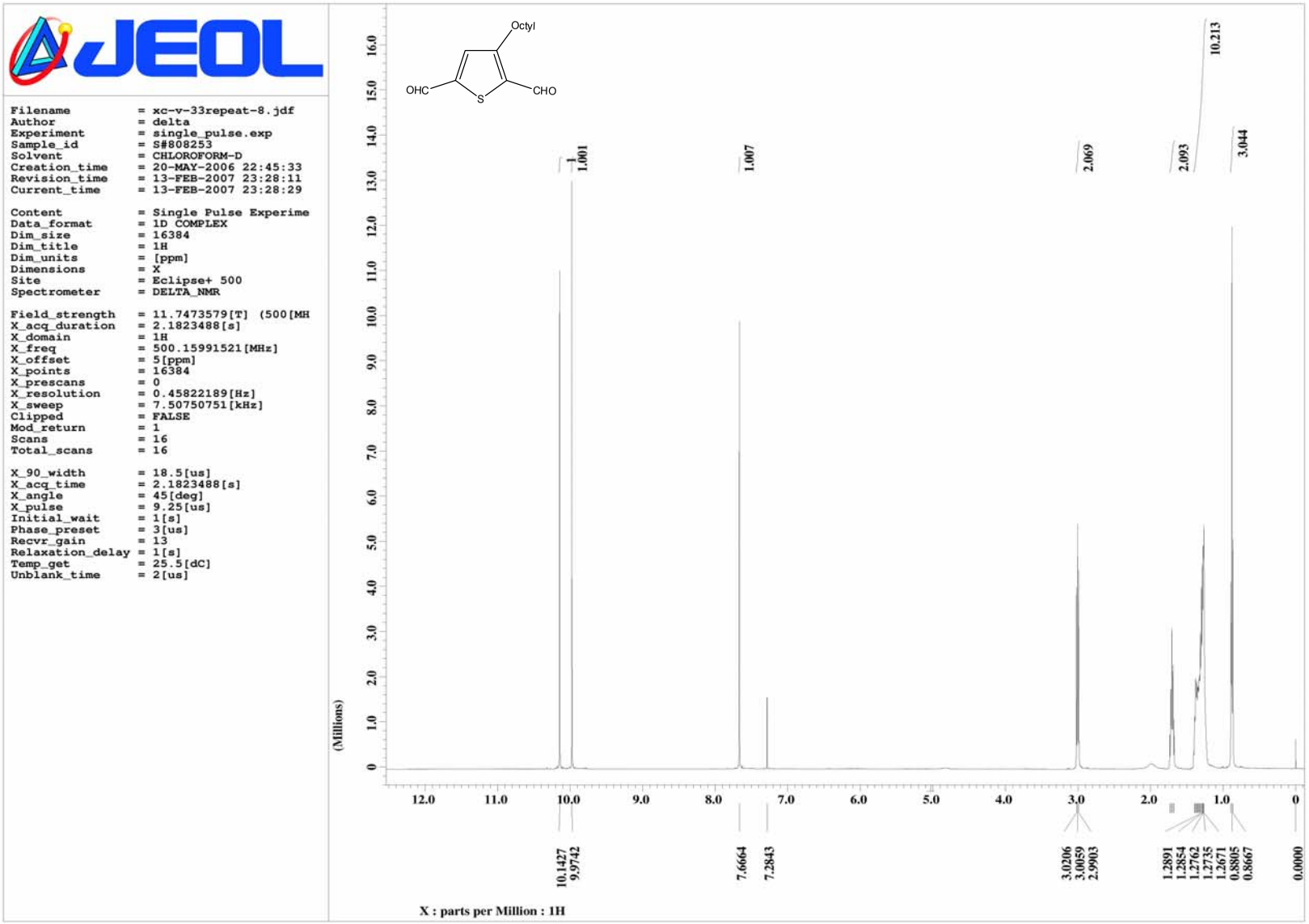
^{1}H and ^{13}C-NMR spectra of 3-butyl-2,5-thiophenedicarboxaldehyde (68a)


Filename = xc-v-59-7.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#534692
Solvent = CHLOROFORM-D
Creation_time = 22-JUL-2006 15:41:26
Revision_time = 13-FEB-2007 23:00:23
Current_time = 13-FEB-2007 23:00:43
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 1[s]
Temp_get = 25[dC]
Unblank_time = 2[us]
Bu
OHC
CHO
S
1
1.002
1.005
2.03
2.016
2.008
3.042
(Millions)
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.1446
9.9742
7.6563
7.2679
3.0270
3.0114
2.9959
1.6940
1.6784
1.4201
1.4045
0.9794
0.9647
0.9501
0.0000
X : parts per Million : 1H


Filename = xc-v-59-5.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#813960
Solvent = CHLOROFORM-D
Creation_time = 18-MAY-2006 10:57:47
Revision_time = 13-FEB-2007 22:45:36
Current_time = 13-FEB-2007 22:45:57
Content = single pulse decouple
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 = 4535
Total_scans = 4535
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 0[dC]
Unblank_time = 2[us]
Bu
OHC
CHO
S
(Millions)
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
183.3985
182.9865
151.9755
147.8664
143.2956
137.2254
77.3057
77.0500
76.7944
33.2691
28.2024
22.3039
13.7690
X : parts per Million : 13C

APPENDIX 55

^{1}H and ^{13}C-NMR spectra of 3-octyl-2,5-thiophenedicarboxaldehyde (68b)

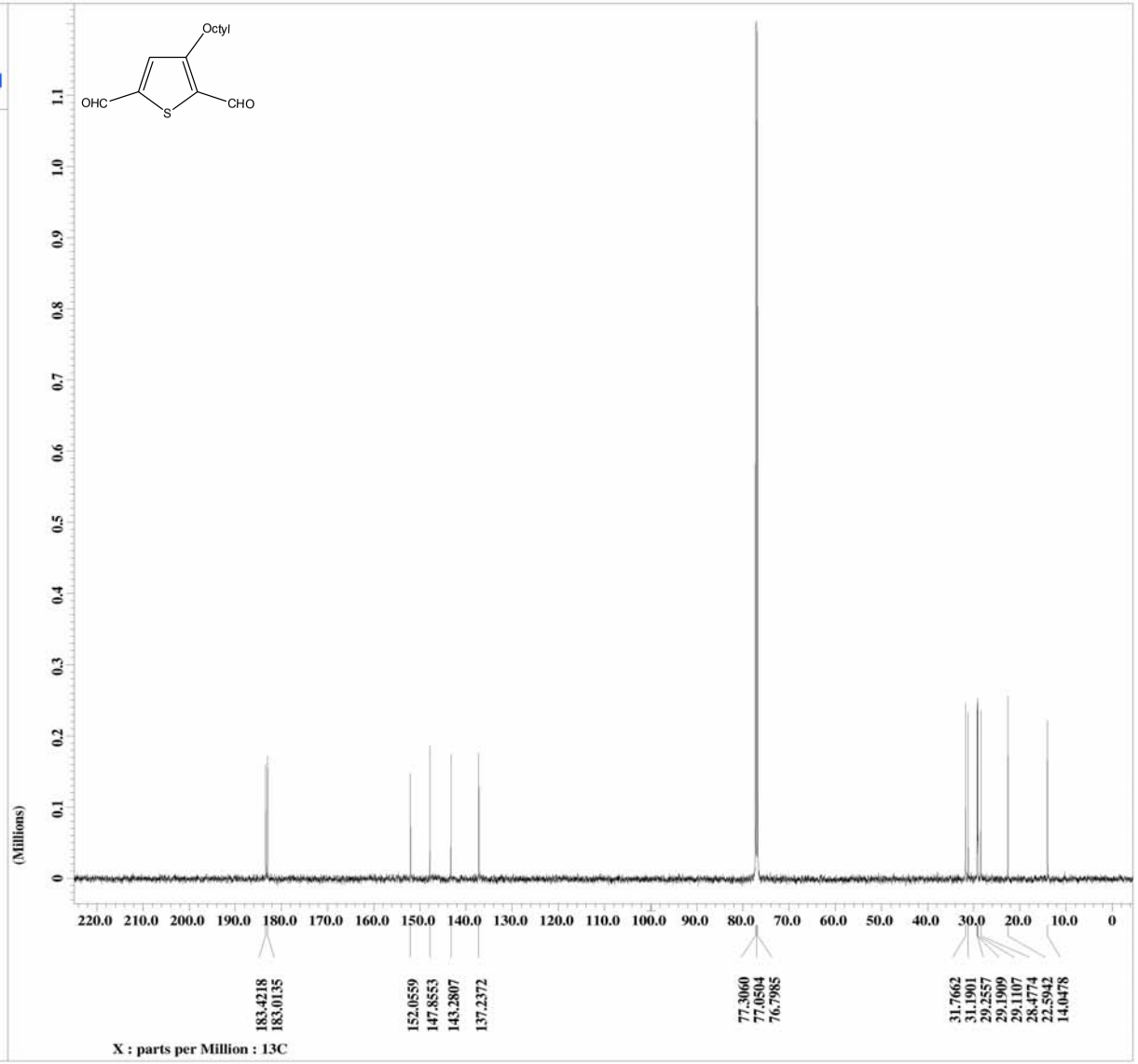

Filename = xc-v-33repeat-8.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#808253
Solvent = CHLOROFORM-D
Creation_time = 20-MAY-2006 22:45:33
Revision_time = 13-FEB-2007 23:28:11
Current_time = 13-FEB-2007 23:28:29
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 13
Relaxation_delay = 1[s]
Temp_get = 25.5[dC]
Unblank_time = 2[us]
Octyl
OHC
CHO
S
(Millions)
1.001
1.007
2.069
2.093
10.213
3.044
10.1427
9.9742
7.6664
7.2843
3.0206
3.0059
2.9903
1.2891
1.2854
1.2762
1.2735
1.2671
0.8805
0.8667
0.0000
X : parts per Million : 1H

```
Filename          = xc-v-33-4.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#809332
Solvent           = CHLOROFORM-D
Creation_time     = 21-MAY-2006 10:36:56
Revision_time     = 13-FEB-2007 23:28:41
Current_time      = 13-FEB-2007 23:29:00

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

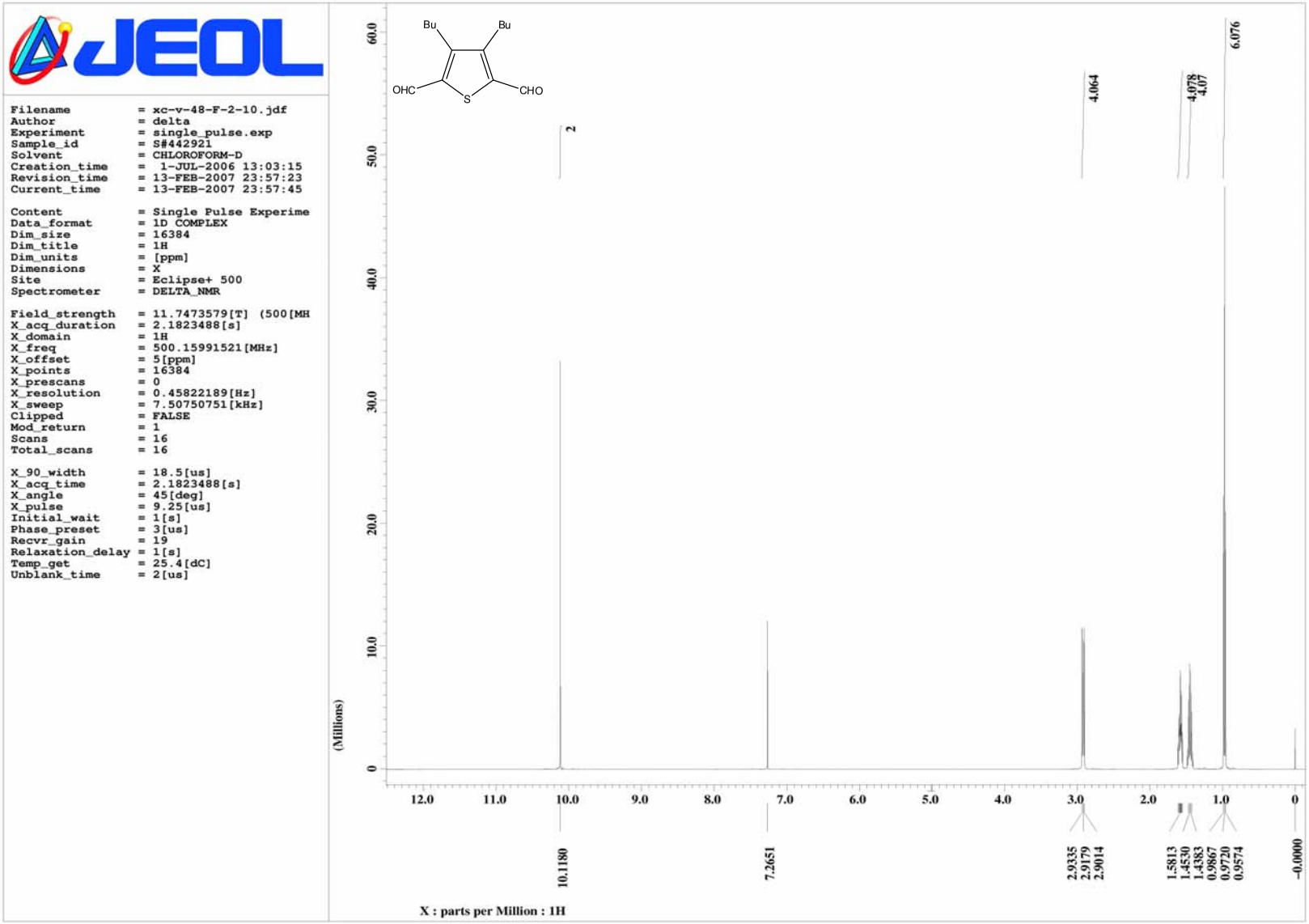
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 6000
Total_scans       = 6000

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]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 30
Relaxation_delay  = 4[s]
Temp_get          = 26.3[dC]
Unblank_time      = 2[us]
```



APPENDIX 56

^{1}H and ^{13}C-NMR spectra of 3,4-dibutyl-2,5-thiophenedicarboxaldehyde (68c)

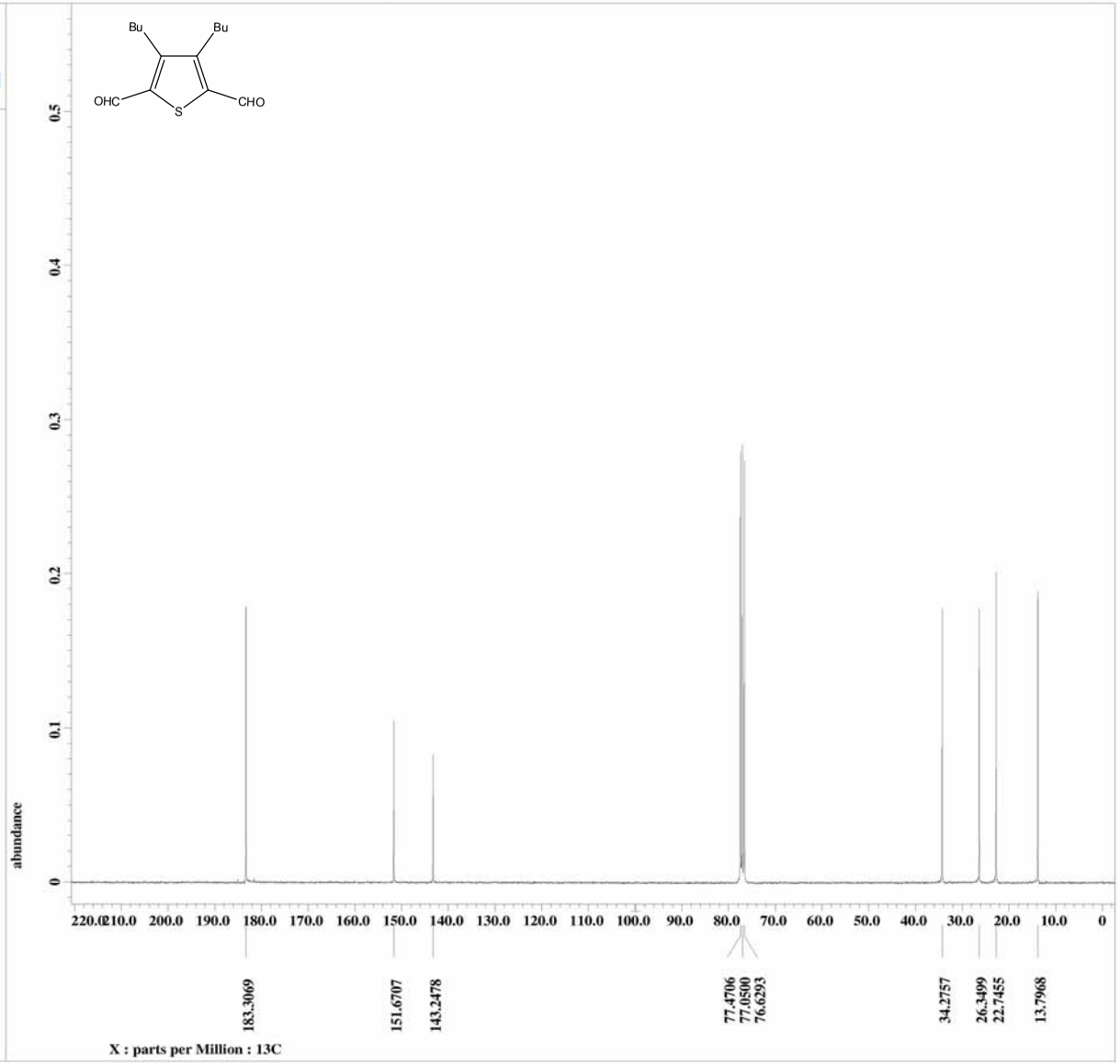

Filename = xc-v-48-F-2-10.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#442921
Solvent = CHLOROFORM-D
Creation_time = 1-JUL-2006 13:03:15
Revision_time = 13-FEB-2007 23:57:23
Current_time = 13-FEB-2007 23:57:45
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 19
Relaxation_delay = 1[s]
Temp_get = 25.4[dC]
Unblank_time = 2[us]
Bu
Bu
OHC
CHO
S
(Millions)
60.0
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2
4.064
4.078
4.07
6.076
10.1180
7.2651
2.9335
2.9179
2.9014
1.5813
1.4530
1.4383
0.9867
0.9720
0.9574
-0.0000
X : parts per Million : 1H

```
Filename          = xc-v-48-F-2-8.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#794301
Solvent           = CHLOROFORM-D
Creation_time     = 16-JUL-2006 10:51:22
Revision_time     = 13-FEB-2007 23:58:33
Current_time      = 13-FEB-2007 23:59:02

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

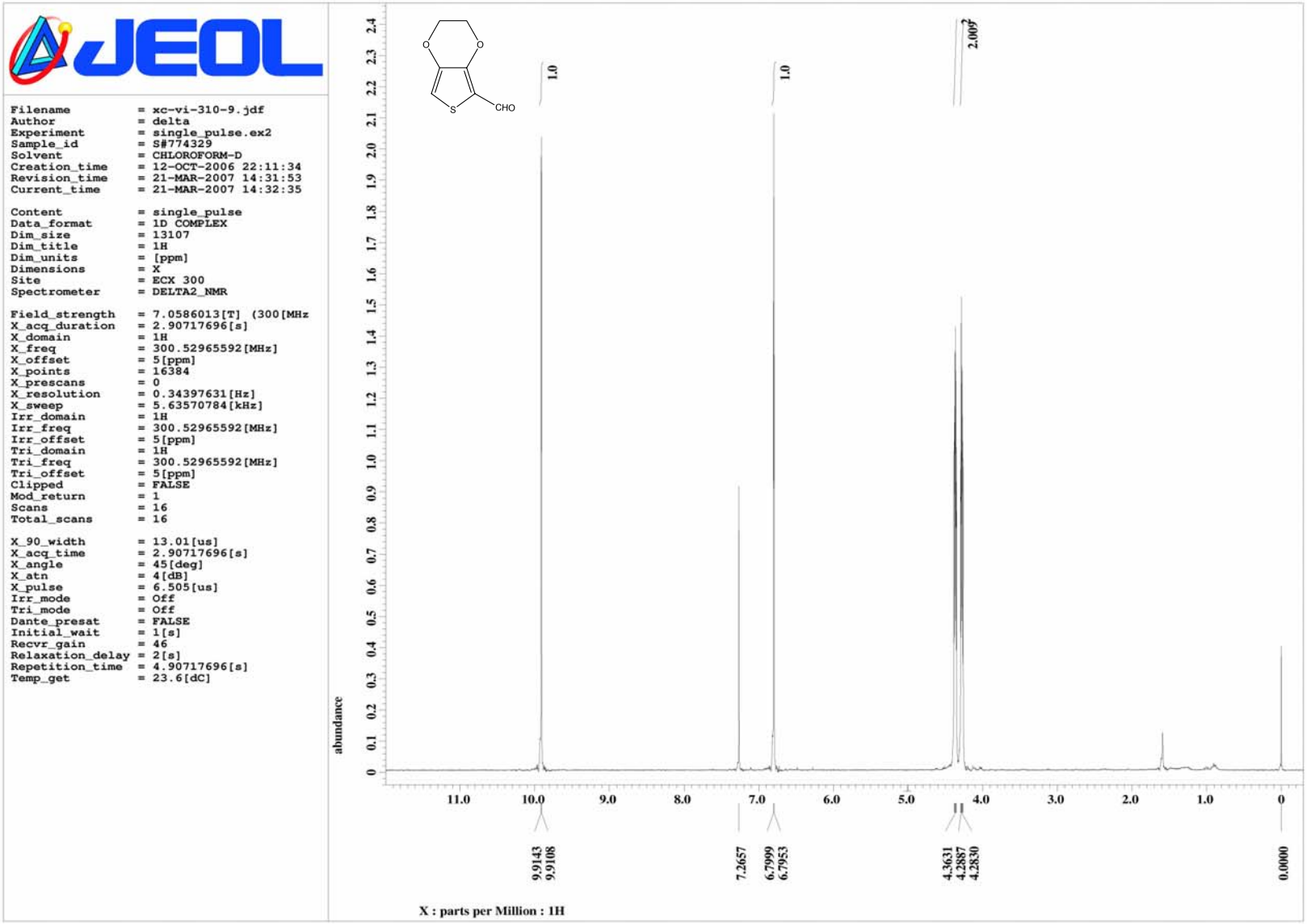
Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 1.38412032[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.72248054[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 10000
Total_scans       = 10000

X_90_width        = 9.75[us]
X_acq_time        = 1.38412032[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          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 4.38412032[s]
Temp_get          = 23.3[dC]
```



APPENDIX 57

^{1}H and ^{13}C-NMR spectra of 2,3-dihydrothieno[3,4-*b*]-1,4-dioxine-5-carboxaldehyde (70a)

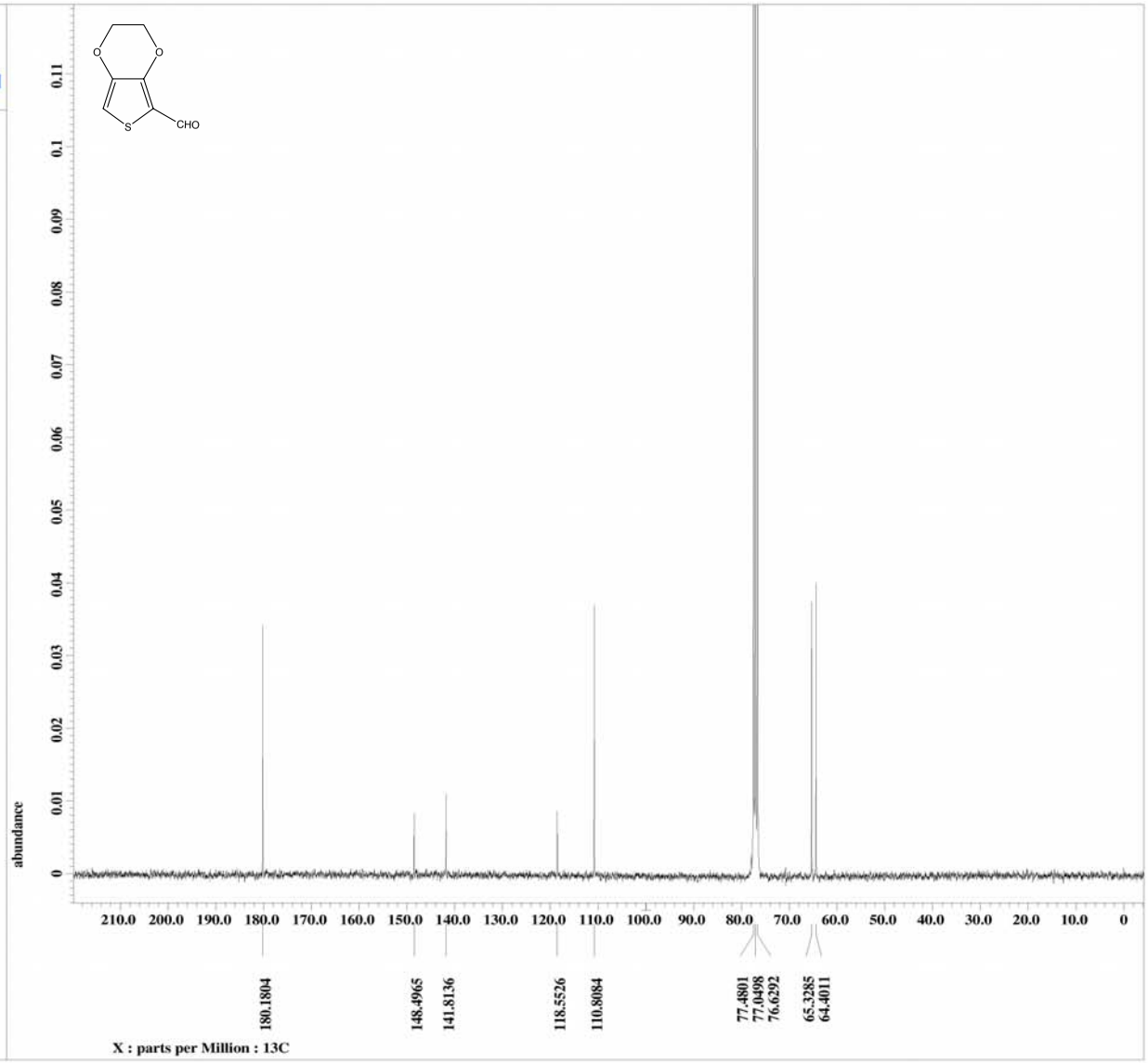

Filename = xc-vi-310-9.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#774329
Solvent = CHLOROFORM-D
Creation_time = 12-OCT-2006 22:11:34
Revision_time = 21-MAR-2007 14:31:53
Current_time = 21-MAR-2007 14:32:35
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 46
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 23.6[dC]
O
O
S
CHO
1.0
1.0
2.009
abundance
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.9143
9.9108
7.2657
6.7999
6.7953
4.3631
4.2887
4.2830
0.0000
X : parts per Million : 1H

```
Filename          = xc-vi-310-5.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#775340
Solvent           = CHLOROFORM-D
Creation_time     = 13-OCT-2006 09:51:40
Revision_time     = 21-MAR-2007 14:33:14
Current_time      = 21-MAR-2007 14:34:05

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

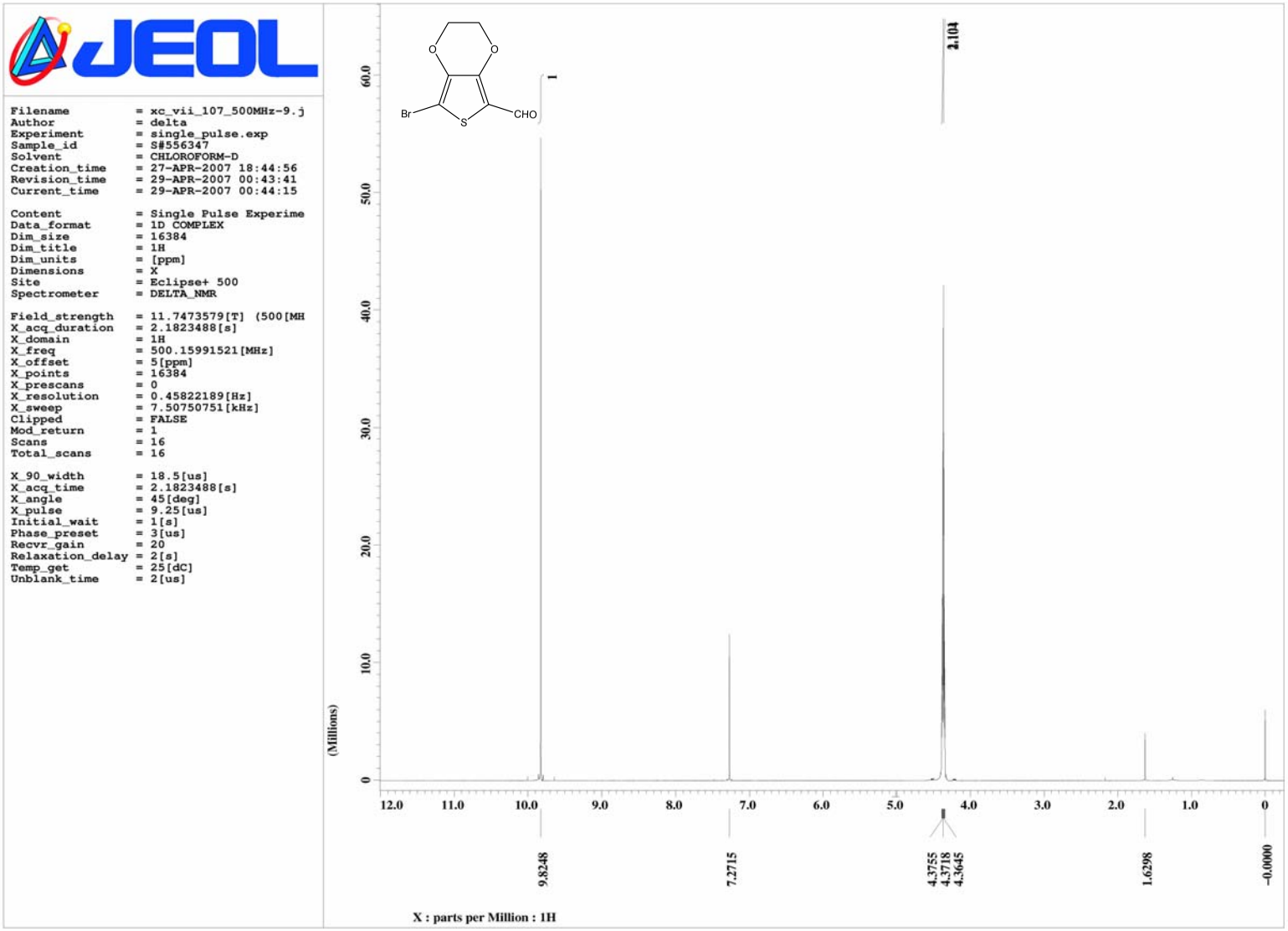
Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 1.38412032[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.72248054[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 9576
Total_scans       = 9576

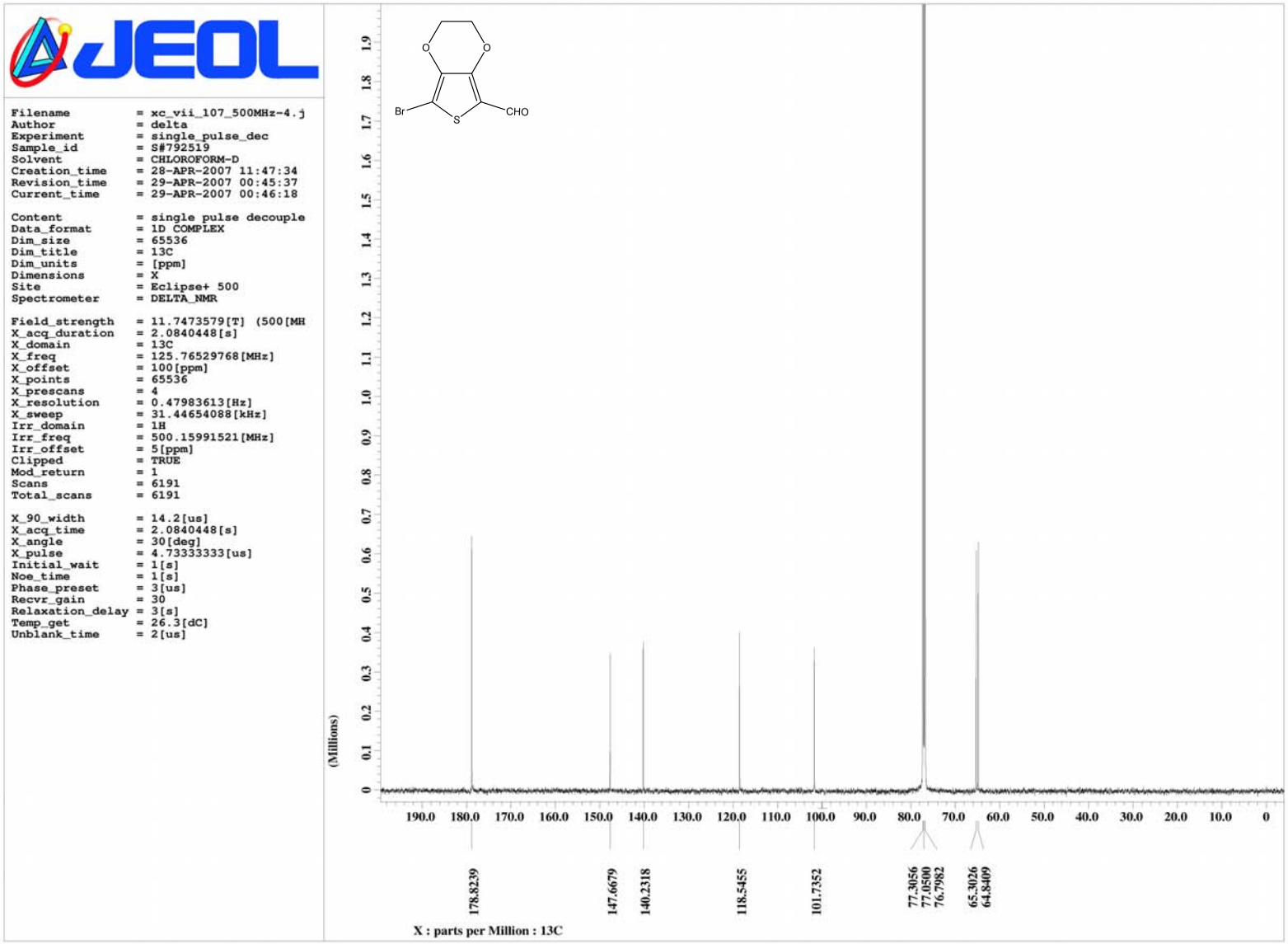
X_90_width        = 9.75[us]
X_acq_time        = 1.38412032[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 4.38412032[s]
Temp_get          = 23[dC]
```



APPENDIX 58

^{1}H and ^{13}C-NMR Spectra of 7-bromo-2,3-dihydrothieno[3,4-*b*]-1,4-dioxine-5-carboxaldehyde (70b)


Filename = xc_vii_107_500MHz-9.j
Author = delta
Experiment = single_pulse.exp
Sample_id = S#556347
Solvent = CHLOROFORM-D
Creation_time = 27-APR-2007 18:44:56
Revision_time = 29-APR-2007 00:43:41
Current_time = 29-APR-2007 00:44:15
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 20
Relaxation_delay = 2[s]
Temp_get = 25[dC]
Unblank_time = 2[us]
O
O
Br
S
CHO
1
2.104
(Millions)
60.0
50.0
40.0
30.0
20.0
10.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.8248
7.2715
4.3755
4.3718
4.3645
1.6298
-0.0000
X : parts per Million : 1H


Filename = xc_vii_107_500MHz-4.j
Author = delta
Experiment = single_pulse_dec
Sample_id = S#792519
Solvent = CHLOROFORM-D
Creation_time = 28-APR-2007 11:47:34
Revision_time = 29-APR-2007 00:45:37
Current_time = 29-APR-2007 00:46:18
Content = single pulse decouple
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 = TRUE
Mod_return = 1
Scans = 6191
Total_scans = 6191
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 3[s]
Temp_get = 26.3[dC]
Unblank_time = 2[us]
O
O
Br
S
CHO
(Millions)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
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
0
178.8239
147.6679
140.2318
118.5455
101.7352
77.3056
77.0500
76.7982
65.3026
64.8409
X : parts per Million : 13C

APPENDIX 59

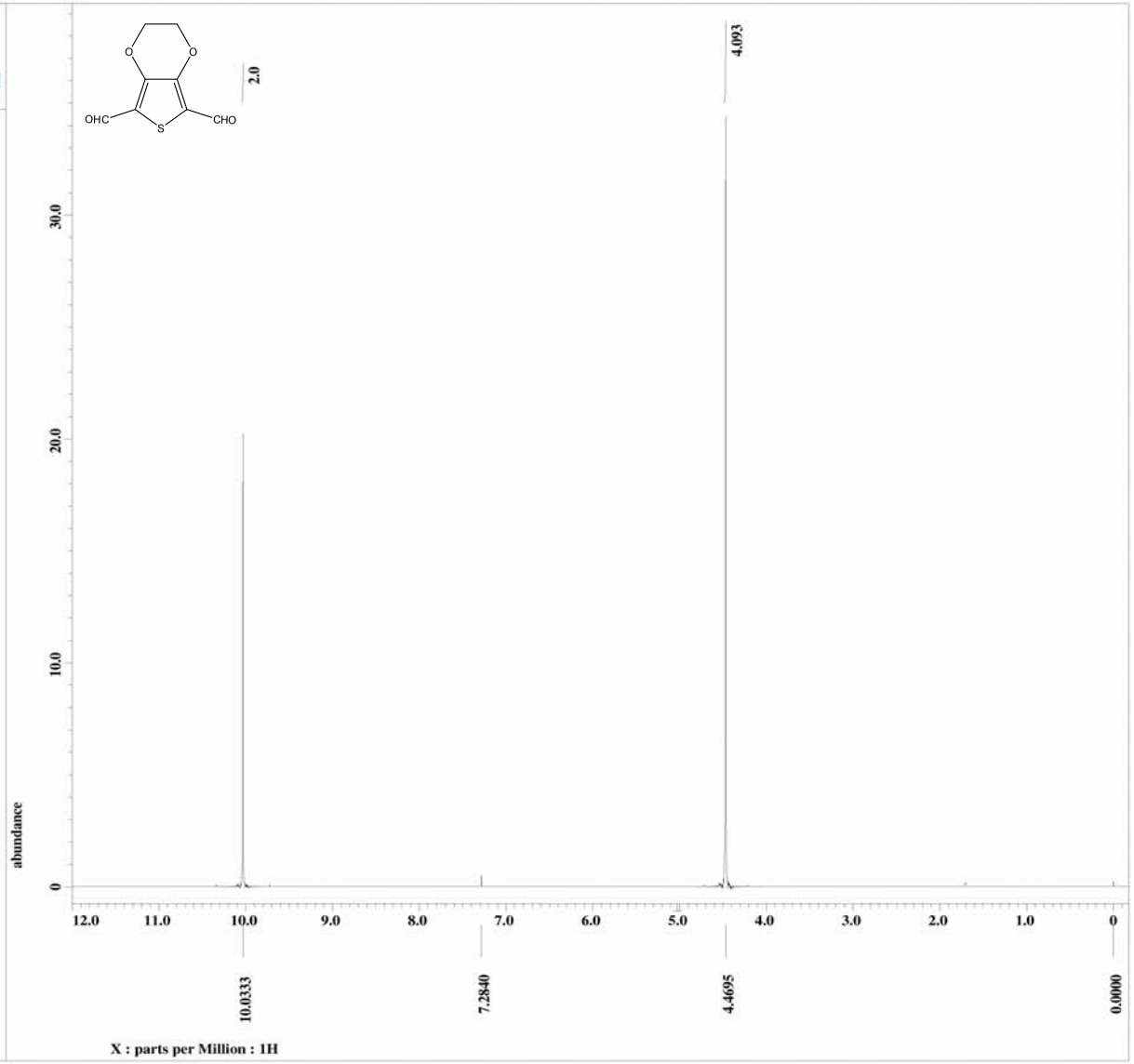
^{1}H and ^{13}C-NMR Spectra of 2,3-dihydrothieno[3,4-*b*]-1,4-dioxine-5,7-dicarboxaldehyde (72)

```
Filename          = xc_vii_3Final-10.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#343142
Solvent           = CHLOROFORM-D
Creation_time     = 18-OCT-2006 10:13:53
Revision_time     = 21-MAR-2007 14:49:36
Current_time      = 21-MAR-2007 14:49:58

Content           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 42
Relaxation_delay  = 2[s]
Repetition_time   = 4.90717696[s]
Temp_get          = 22.9[dC]
```

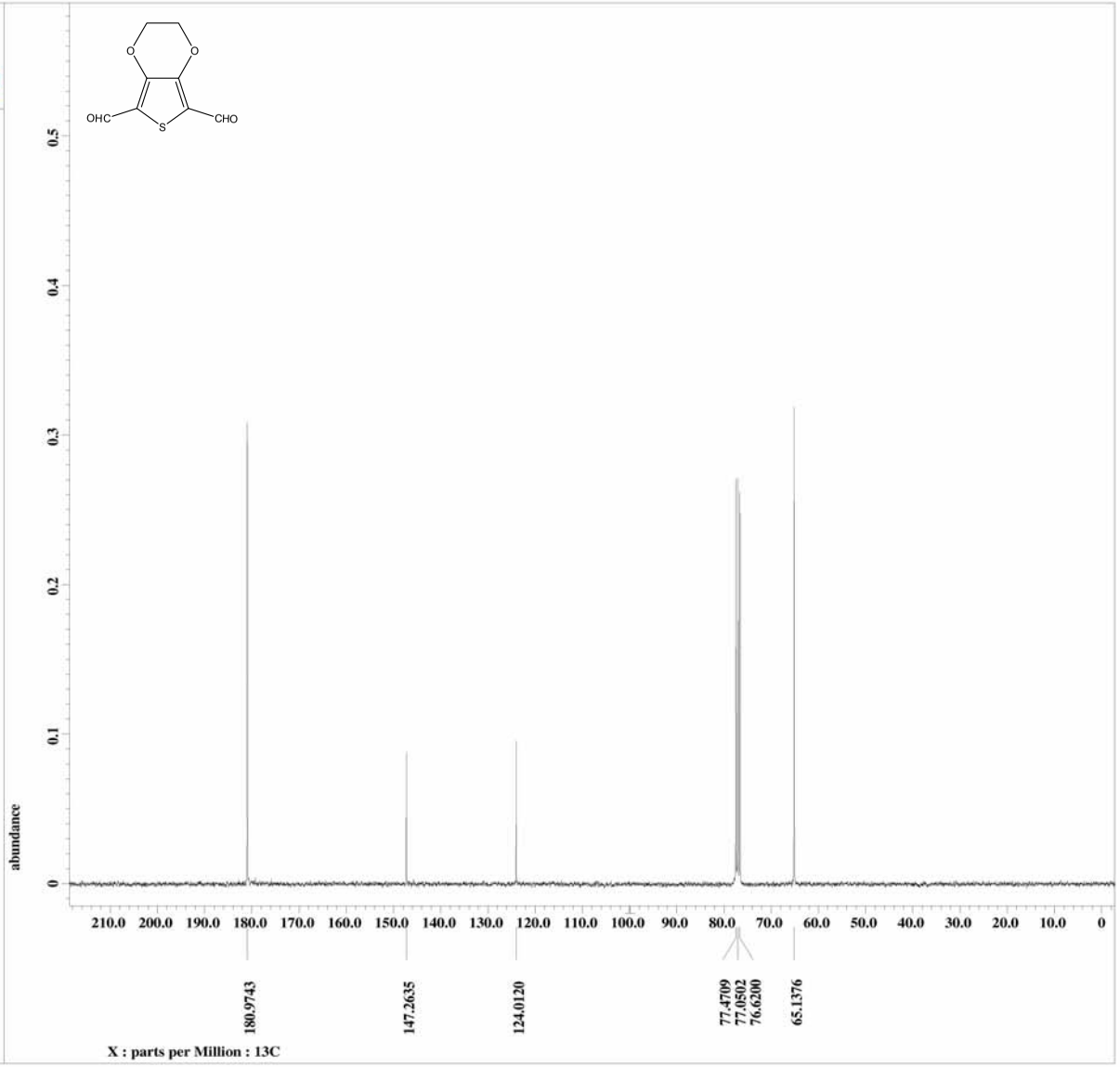


```
Filename          = xc_vii_3final-5.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#784882
Solvent           = CHLOROFORM-D
Creation_time     = 19-OCT-2006 23:56:36
Revision_time     = 21-MAR-2007 14:50:10
Current_time      = 21-MAR-2007 14:50:35

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

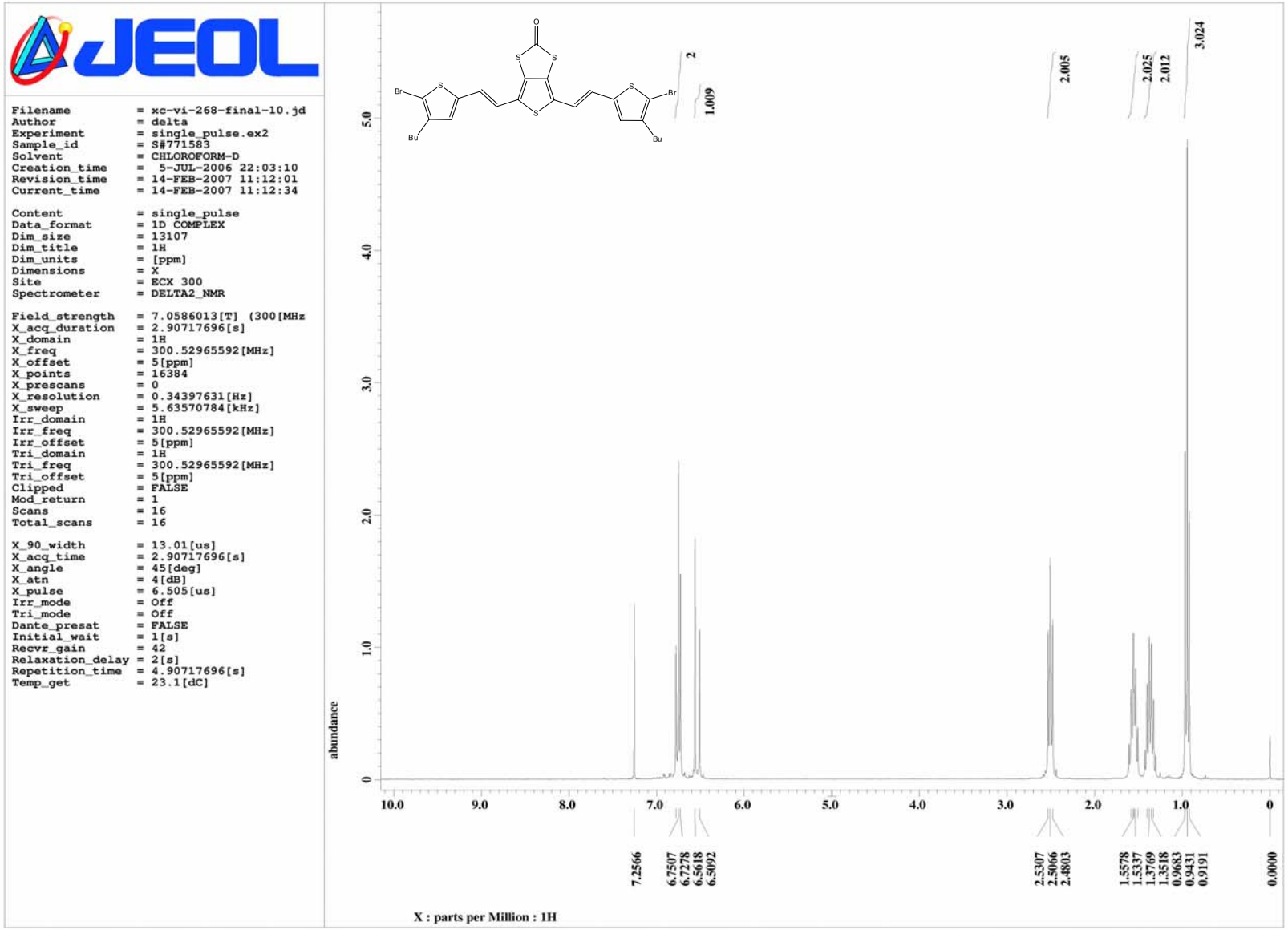
Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 1.38412032[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.72248054[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1186
Total_scans       = 1186

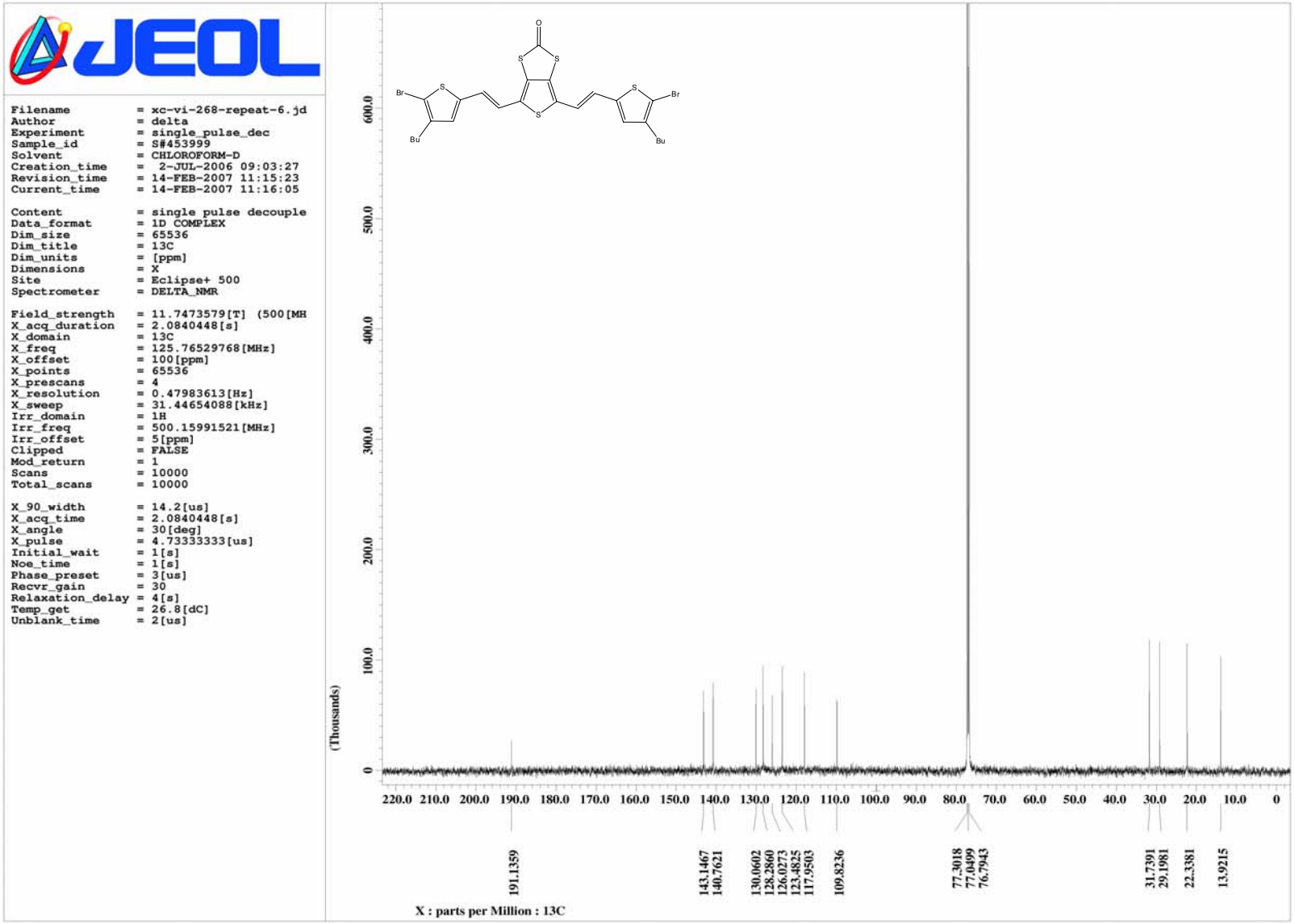
X_90_width        = 9.75[us]
X_acq_time        = 1.38412032[s]
X_angle           = 30[deg]
X_atn             = 8[dB]
X_pulse           = 3.25[us]
Irr_atn_dec       = 25[dB]
Irr_atn_noe       = 25[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 4.38412032[s]
Temp_get          = 23.1[dC]
```



APPENDIX 60

^{1}H and ^{13}C-NMR spectra of 4,6-bis((E)-2-(5-bromo-4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (75a)

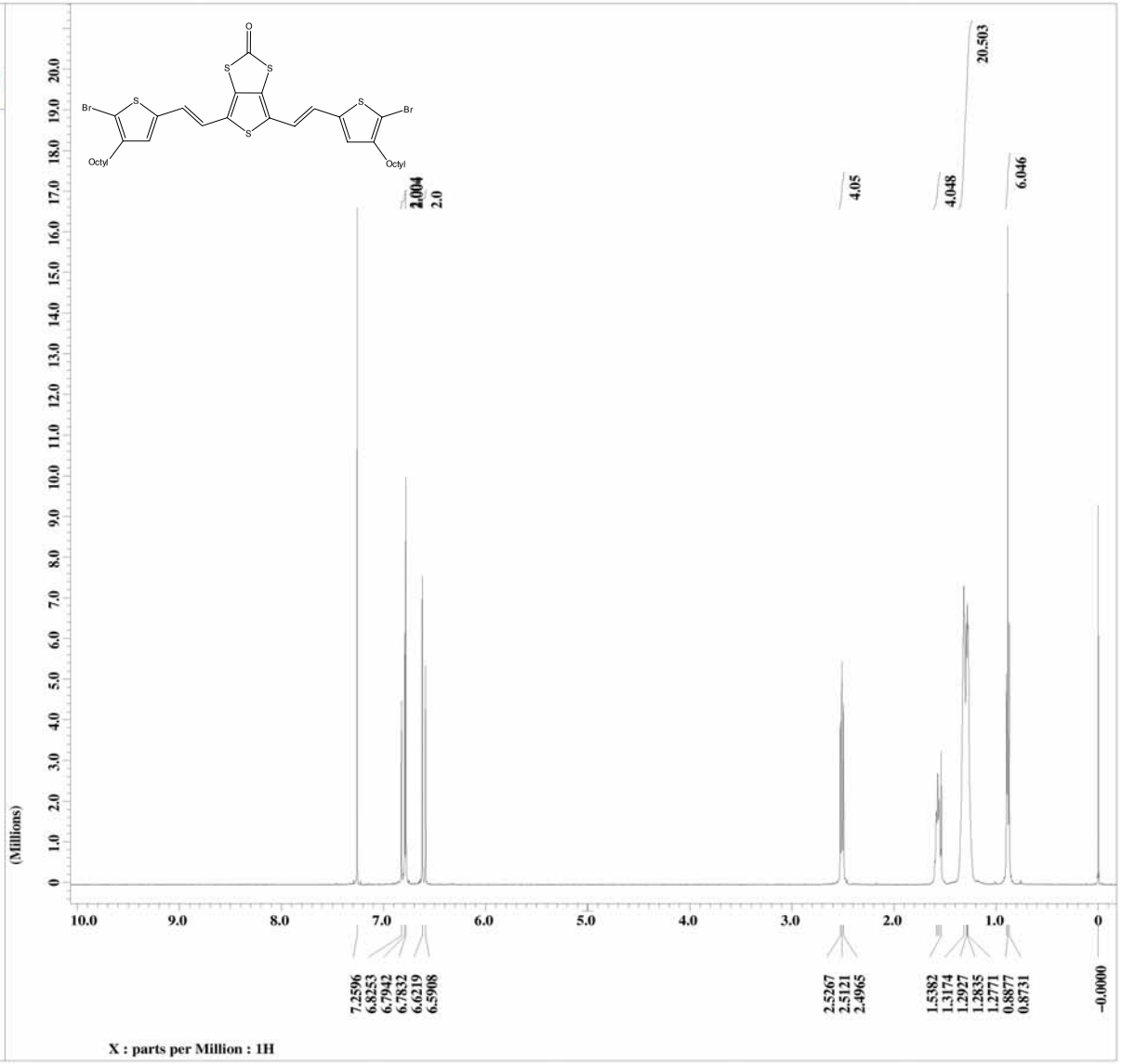

Filename = xc-vi-268-final-10.jd
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#771583
Solvent = CHLOROFORM-D
Creation_time = 5-JUL-2006 22:03:10
Revision_time = 14-FEB-2007 11:12:01
Current_time = 14-FEB-2007 11:12:34
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 42
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 23.1[dC]
Br
Bu
O
S
2
1.009
2.005
2.025
2.012
3.024
abundance
0
1.0
2.0
3.0
4.0
5.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2566
6.7507
6.7278
6.5618
6.5092
2.5307
2.5066
2.4803
1.5578
1.5337
1.3769
1.3518
0.9683
0.9431
0.9191
0.0000
X : parts per Million : 1H

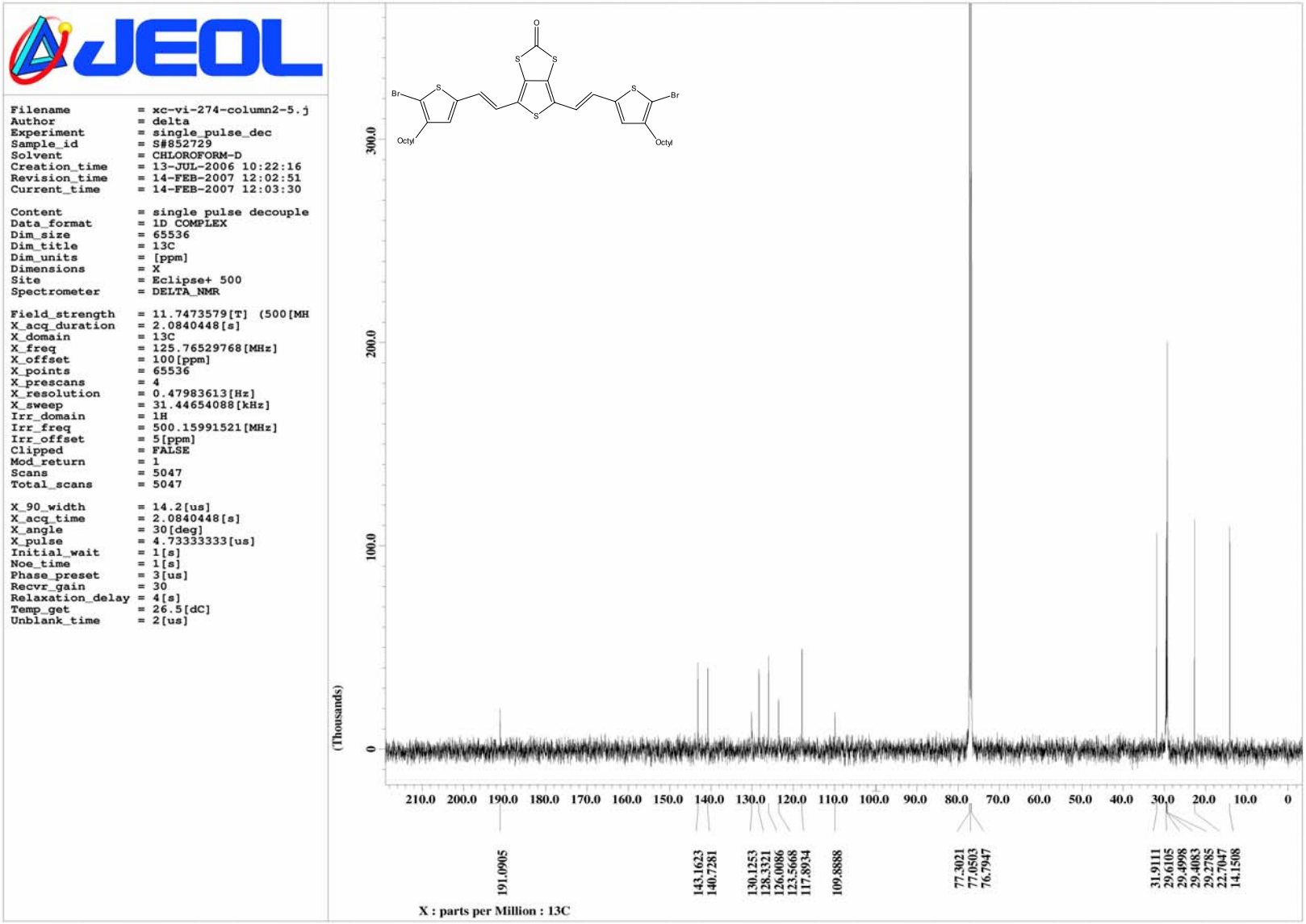

Filename = xc-vi-268-repeat-6.jd
Author = delta
Experiment = single_pulse_dec
Sample_id = S#453999
Solvent = CHLOROFORM-D
Creation_time = 2-JUL-2006 09:03:27
Revision_time = 14-FEB-2007 11:15:23
Current_time = 14-FEB-2007 11:16:05
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
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 = 10000
Total_scans = 10000
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 26.8[dC]
Unblank_time = 2[us]
(Thousands)
600.0
500.0
400.0
300.0
200.0
100.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
191.1359
143.1467
140.7621
130.0602
128.2860
126.0273
123.4825
117.9503
109.8236
77.3018
77.0499
76.7943
31.7391
29.1981
22.3381
13.9215
X : parts per Million : 13C

APPENDIX 61

^{1}H and ^{13}C-NMR spectra of 4,6-bis((E)-2-(5-bromo-4-octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (75b)

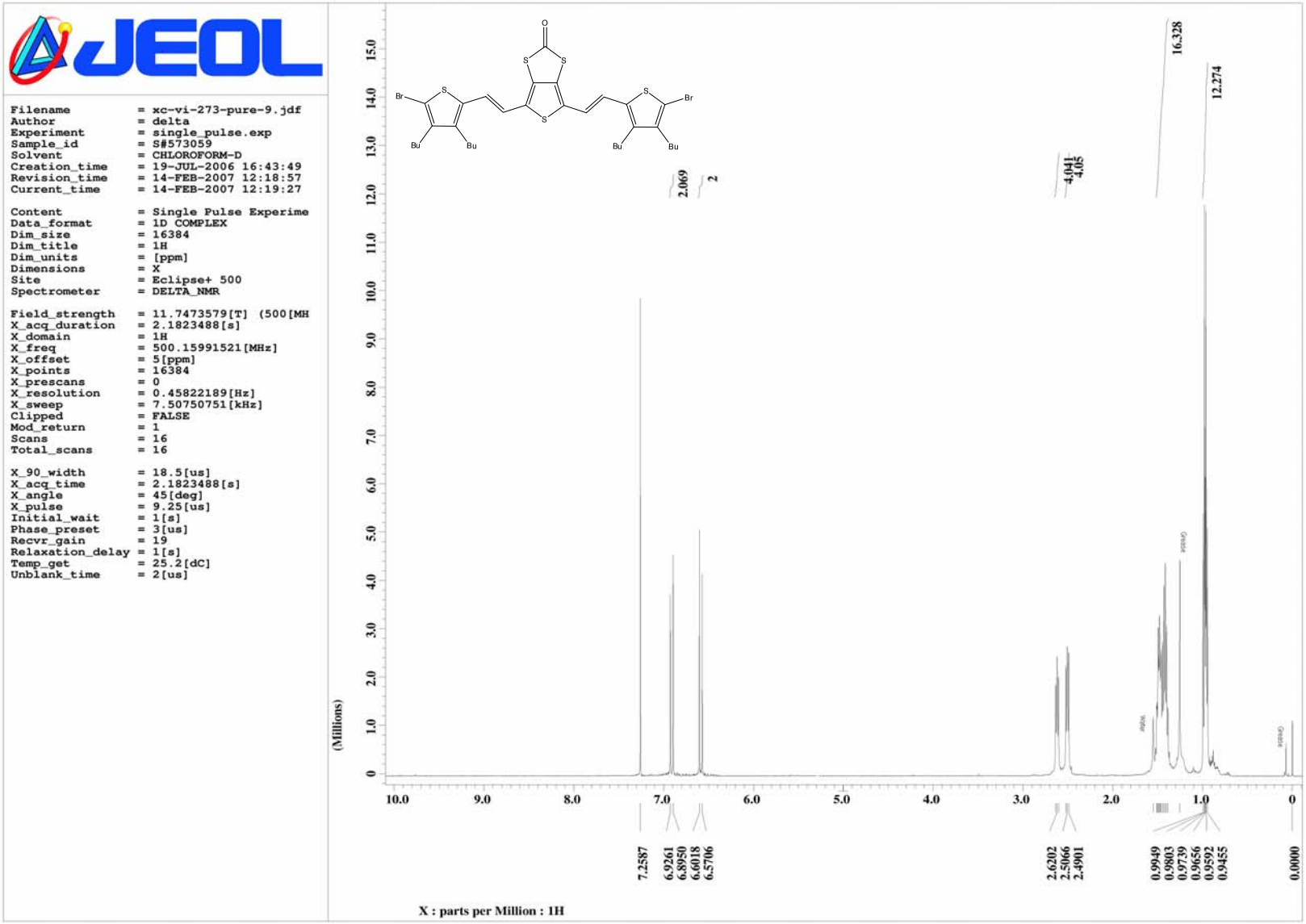
Filename	= xc_vii_83_P1-5.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_id	= S#550343
Solvent	= CHLOROFORM-D
Creation_time	= 27-MAR-2007 17:16:25
Revision_time	= 27-MAR-2007 16:03:31
Current_time	= 27-MAR-2007 16:04:09
Content	= Single Pulse Experime
Data_format	= 1D COMPLEX
Dim_size	= 16384
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= Eclipse+ 500
Spectrometer	= DELTA_NMR
Field_strength	= 11.7473579[T] (500[MH
X_acq_duration	= 2.1823488[s]
X_domain	= 1H
X_freq	= 500.15991521[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 0
X_resolution	= 0.45822189[Hz]
X_sweep	= 7.50750751[kHz]
Clipped	= FALSE
Mod_return	= 1
Scans	= 16
Total_scans	= 16
X_90_width	= 18.5[us]
X_acq_time	= 2.1823488[s]
X_angle	= 45[deg]
X_pulse	= 9.25[us]
Initial_wait	= 1[s]
Phase_preset	= 3[us]
Recvr_gain	= 20
Relaxation_delay	= 2[s]
Temp_get	= 24.6[dC]
Unblank_time	= 2[us]




Filename = xc-vi-274-column2-5.j
Author = delta
Experiment = single_pulse_dec
Sample_id = S#852729
Solvent = CHLOROFORM-D
Creation_time = 13-JUL-2006 10:22:16
Revision_time = 14-FEB-2007 12:02:51
Current_time = 14-FEB-2007 12:03:30
Content = single pulse decouple
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 = 5047
Total_scans = 5047
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 4[s]
Temp_get = 26.5[dC]
Unblank_time = 2[us]
O
S
S
S
S
Br
Octyl
Br
Octyl
(Thousands)
300.0
200.0
100.0
0
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
191.0905
143.1623
140.7281
130.1253
128.3321
126.0086
123.5668
117.8934
109.8888
77.3021
77.0503
76.7947
31.9111
29.6105
29.4998
29.4083
29.2785
22.7047
14.1508
X : parts per Million : 13C

APPENDIX 62

^{1}H and ^{13}C-NMR spectra of 4,6-bis((E)-2-(5-bromo-3,4-dibutylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3- dithiol-2-one (75c)

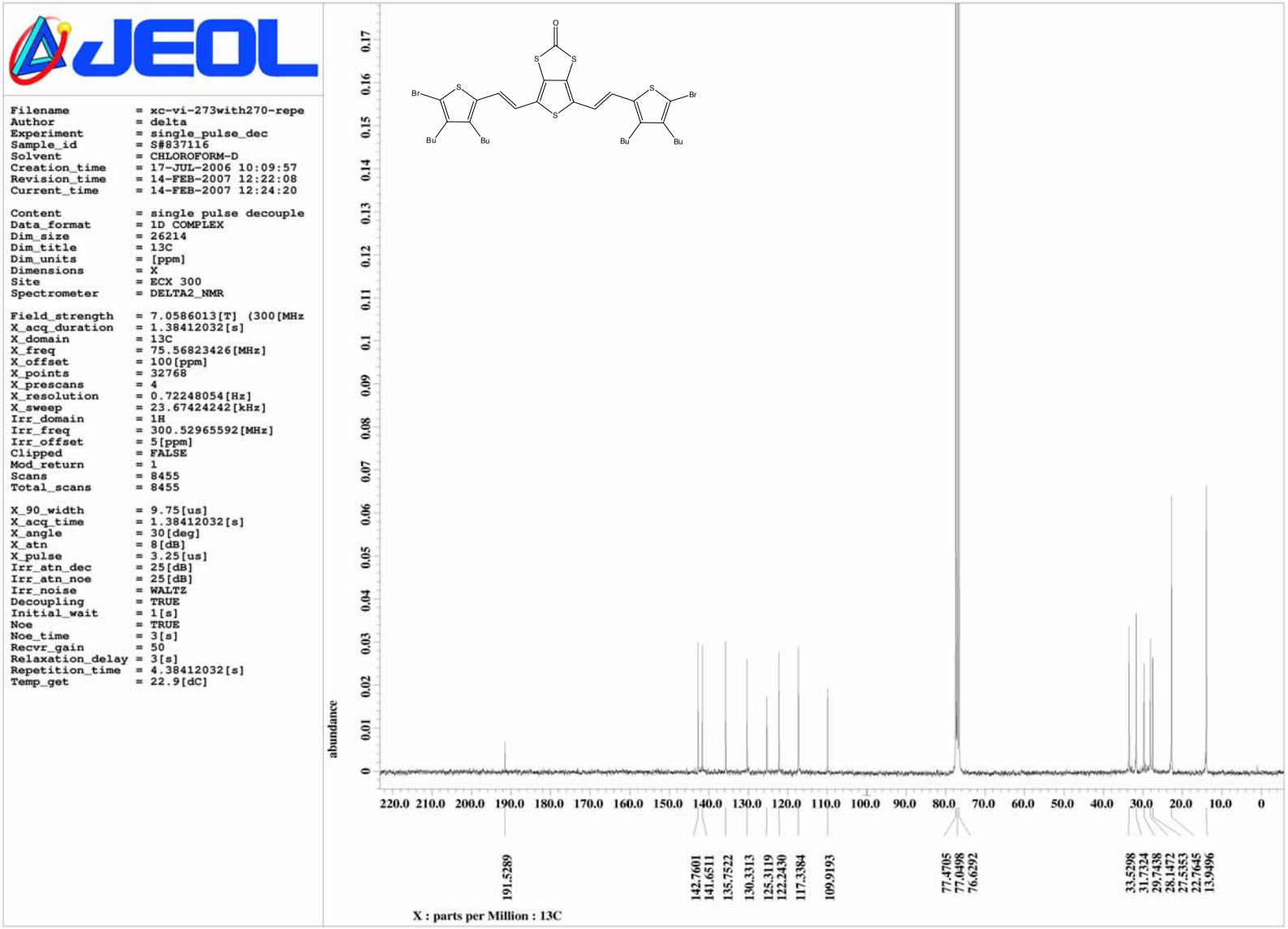


```
Filename          = xc-vi-273-pure-9.jdf
Author            = delta
Experiment        = single_pulse.exp
Sample_id         = S#573059
Solvent           = CHLOROFORM-D
Creation_time     = 19-JUL-2006 16:43:49
Revision_time     = 14-FEB-2007 12:18:57
Current_time      = 14-FEB-2007 12:19:27

Content           = Single Pulse Experime
Data_format       = 1D COMPLEX
Dim_size          = 16384
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.1823488[s]
X_domain          = 1H
X_freq            = 500.15991521[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.45822189[Hz]
X_sweep           = 7.50750751[kHz]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

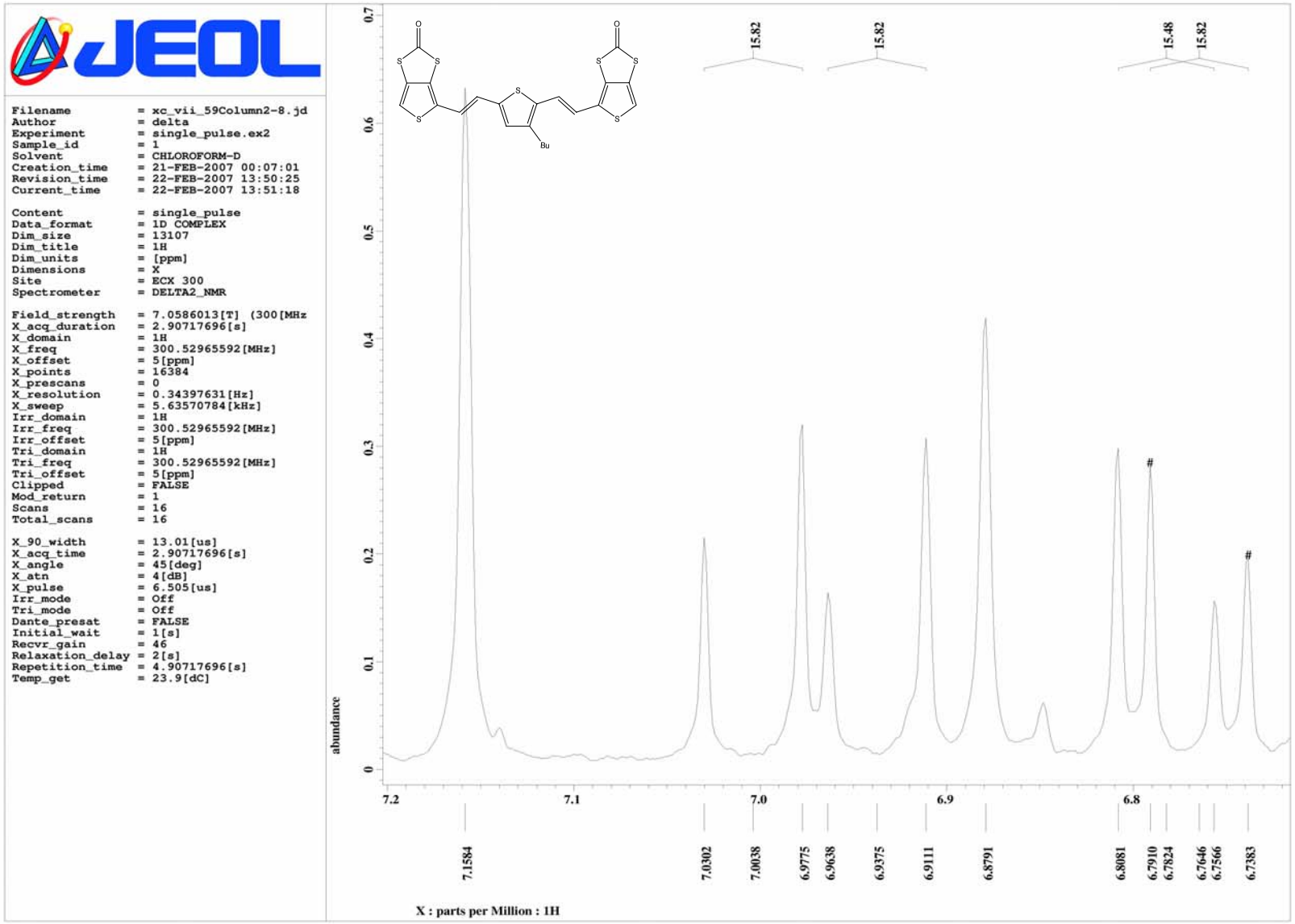
X_90_width        = 18.5[us]
X_acq_time        = 2.1823488[s]
X_angle           = 45[deg]
X_pulse           = 9.25[us]
Initial_wait      = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 19
Relaxation_delay  = 1[s]
Temp_get          = 25.2[dC]
Unblank_time      = 2[us]
```

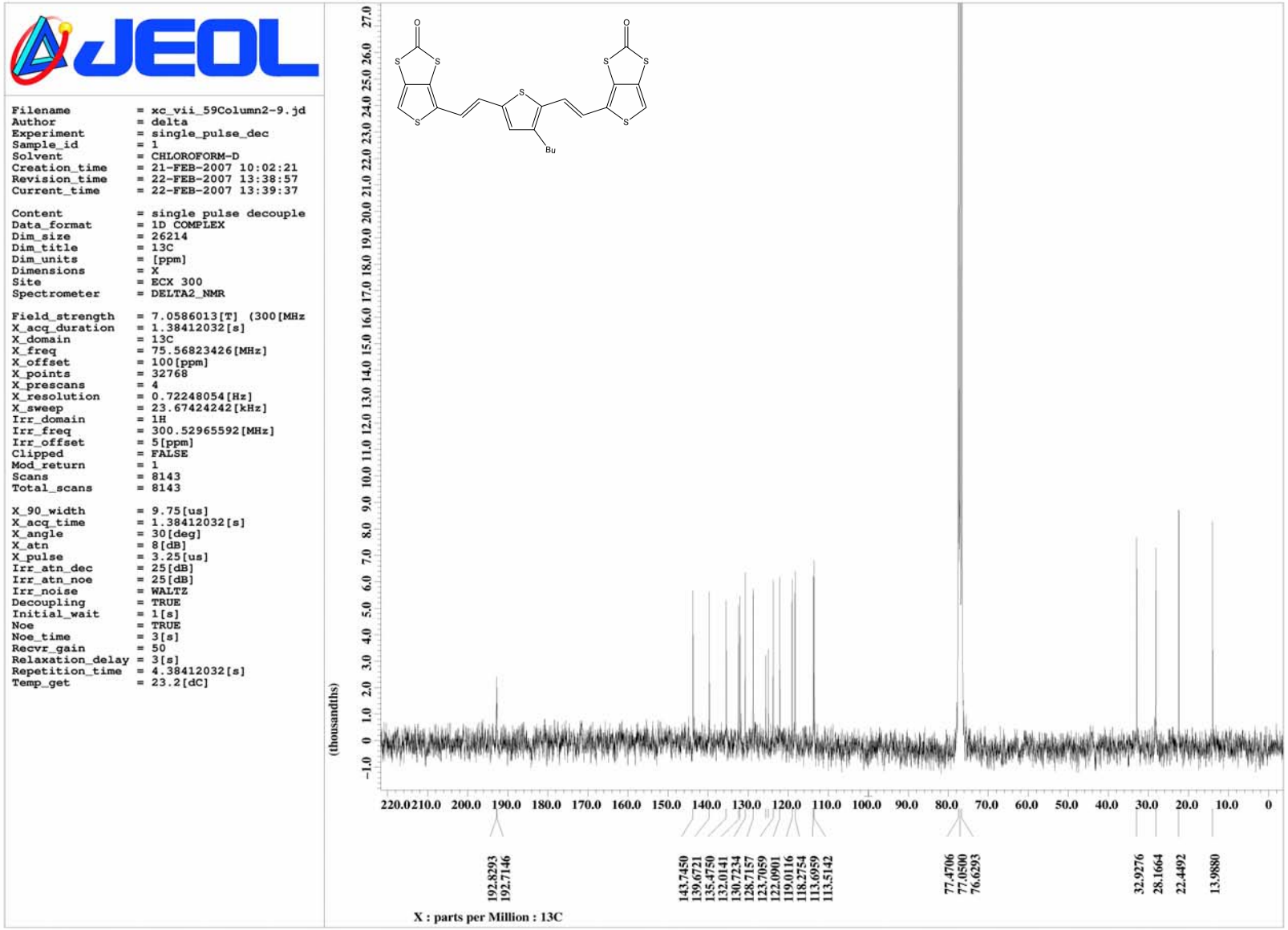

Filename = xc-vi-273with270-repe
Author = delta
Experiment = single_pulse_dec
Sample_id = S#837116
Solvent = CHLOROFORM-D
Creation_time = 17-JUL-2006 10:09:57
Revision_time = 14-FEB-2007 12:22:08
Current_time = 14-FEB-2007 12:24:20
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 1.38412032[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.72248054[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8455
Total_scans = 8455
X_90_width = 9.75[us]
X_acq_time = 1.38412032[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 = 3[s]
Recvr_gain = 50
Relaxation_delay = 3[s]
Repetition_time = 4.38412032[s]
Temp_get = 22.9[dC]
abundance
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15 0.16 0.17
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
191.5289
142.7601
141.6511
135.7522
130.3313
125.3119
122.2430
117.3384
109.9193
77.4705
77.0498
76.6292
33.5298
31.7324
29.7438
28.1472
27.5353
22.7645
13.9496
X : parts per Million : 13C

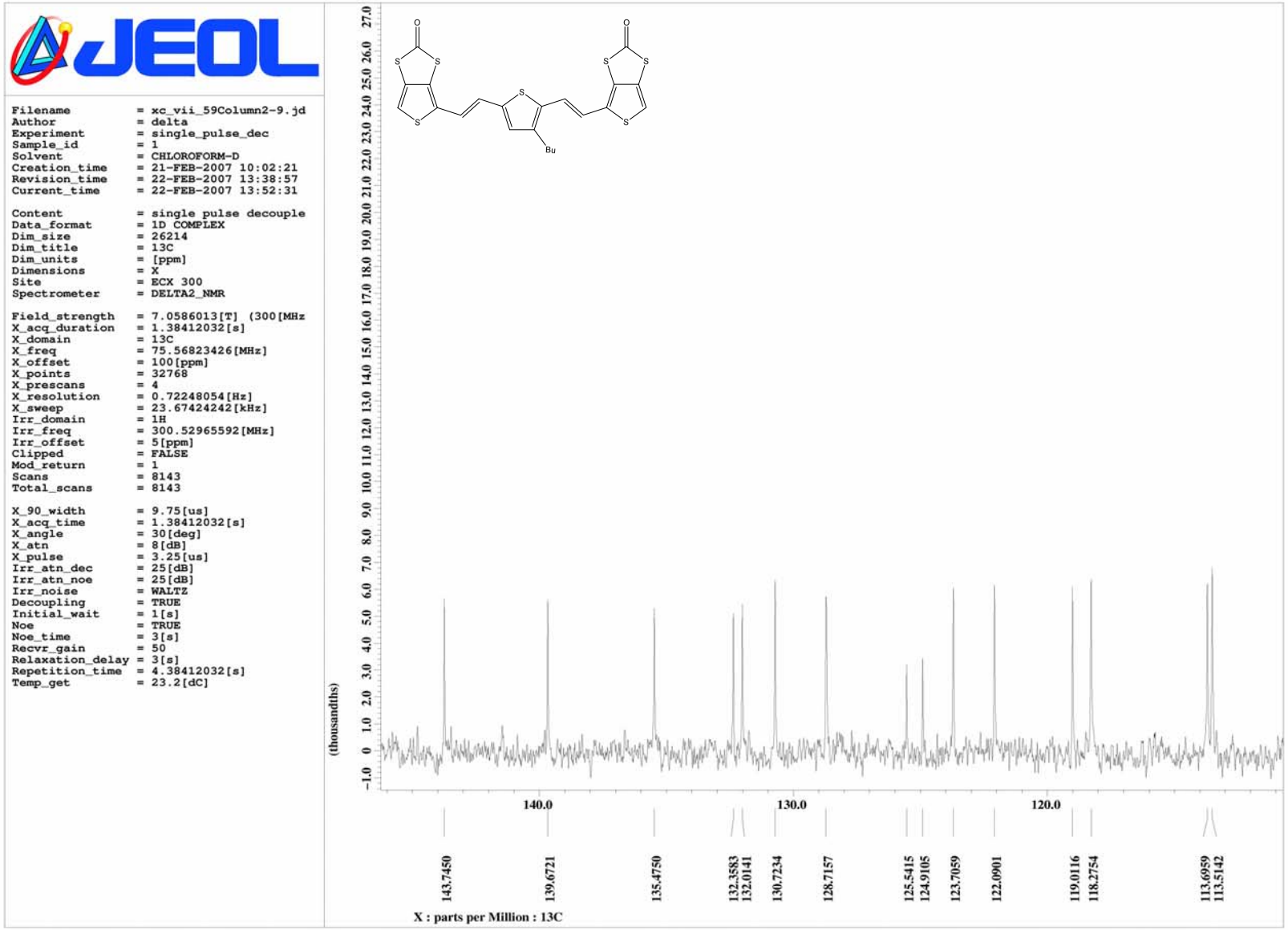
APPENDIX 63

^{1}H and ^{13}C-NMR spectra of 4-((1E)-2-(4-butyl-5-((E)-2-(2-oxothieno[3,4-*d*]-1,3-dithiol-4-yl)vinyl) thiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (76a)

JEOL
Filename = xc_vii_59Column2-8.jd
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 21-FEB-2007 00:07:01
Revision_time = 22-FEB-2007 13:36:24
Current_time = 22-FEB-2007 13:36:51
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX_300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 46
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 23.9[dC]
Bu
Water
Grease
abundance
X : parts per Million : 1H
7.2600
7.1582
6.9773
6.9109
6.8789
6.8079
2.6612
2.6360
2.6108
1.6047
1.5441
1.3792
1.2533
0.9855
0.9615
0.9374
0.0000
3.088
2.076
2.066
2.086
2.044

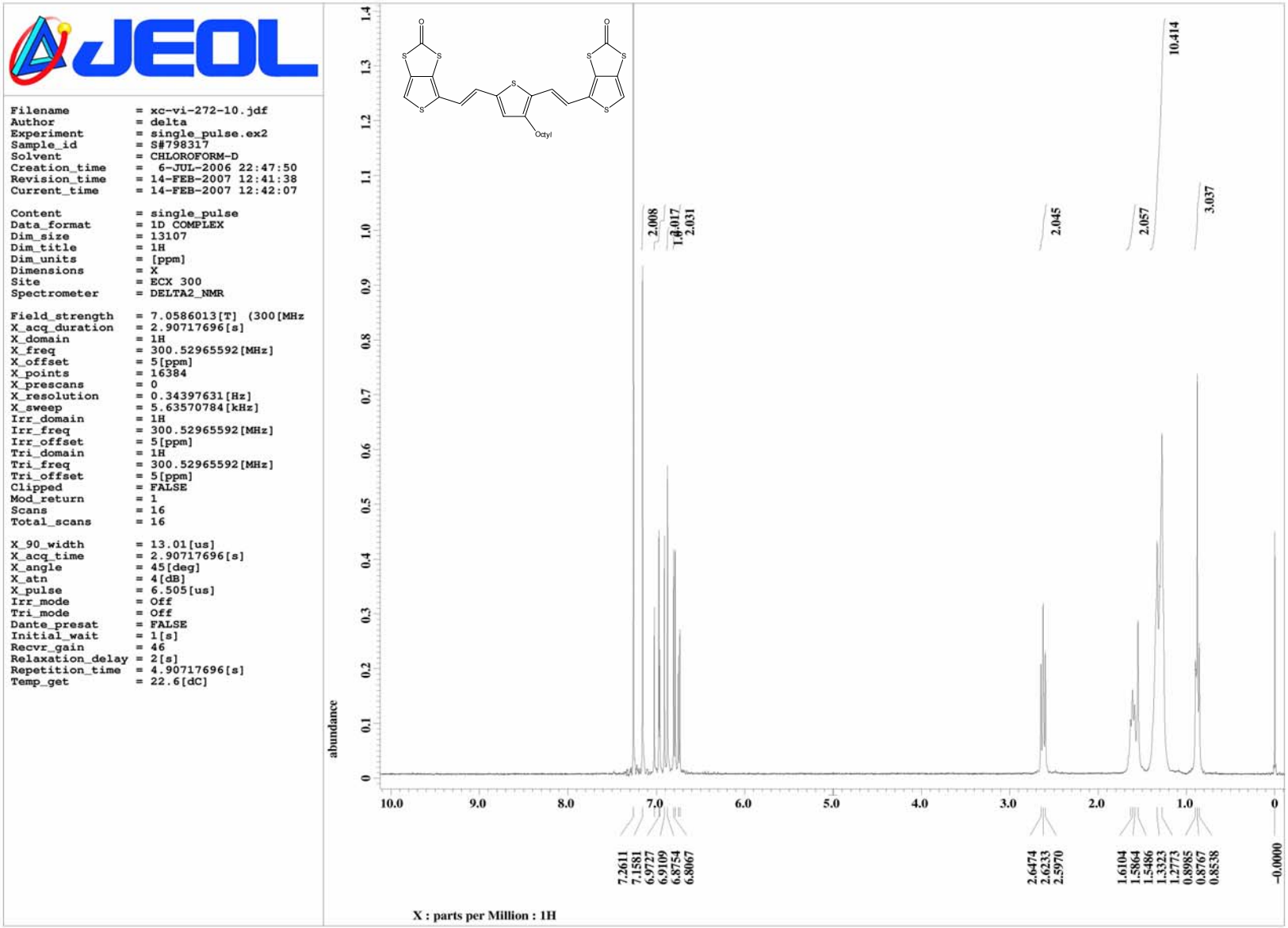

Filename = xc_vii_59Column2-8.jd
Author = delta
Experiment = single_pulse.ex2
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 21-FEB-2007 00:07:01
Revision_time = 22-FEB-2007 13:50:25
Current_time = 22-FEB-2007 13:51:18
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 46
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 23.9[dC]
Bu
15.82
15.82
15.48
15.82
#
#
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
7.2
7.1
7.0
6.9
6.8
7.1584
7.0302
7.0038
6.9775
6.9638
6.9375
6.9111
6.8791
6.8081
6.7910
6.7824
6.7646
6.7566
6.7383
X : parts per Million : 1H

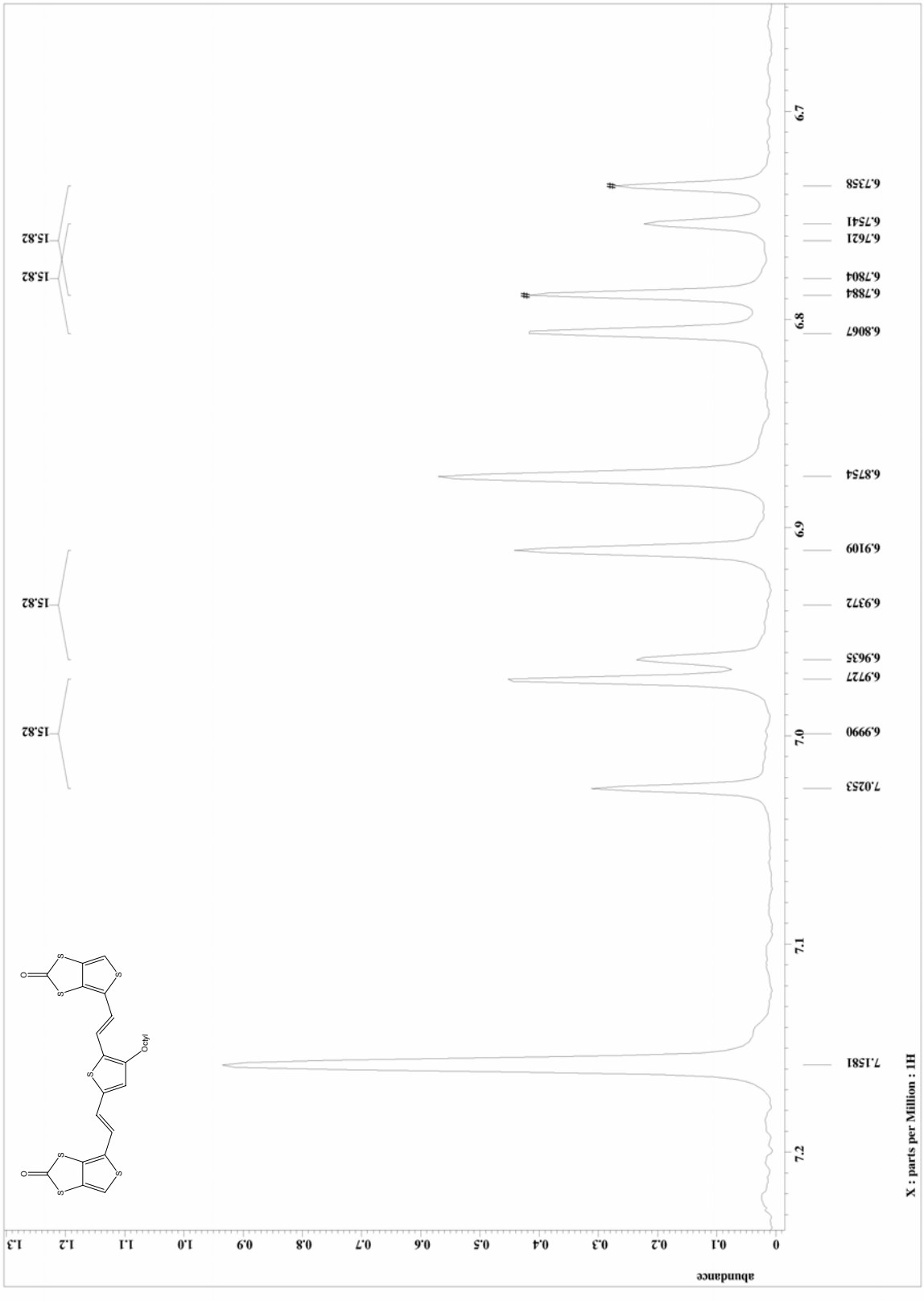

Filename = xc_vii_59Column2-9.jd
Author = delta
Experiment = single_pulse_dec
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 21-FEB-2007 10:02:21
Revision_time = 22-FEB-2007 13:38:57
Current_time = 22-FEB-2007 13:39:37
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 1.38412032[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.72248054[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8143
Total_scans = 8143
X_90_width = 9.75[us]
X_acq_time = 1.38412032[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 = 3[s]
Recvr_gain = 50
Relaxation_delay = 3[s]
Repetition_time = 4.38412032[s]
Temp_get = 23.2[dC]
O
S
Bu
(thousandths)
27.0 26.0 25.0 24.0 23.0 22.0 21.0 20.0 19.0 18.0 17.0 16.0 15.0 14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
192.8293
192.7146
143.7450
139.6721
135.4750
132.0141
130.7234
128.7157
123.7059
122.0901
119.0116
118.2754
113.6959
113.5142
77.4706
77.0500
76.6293
32.9276
28.1664
22.4492
13.9880
X : parts per Million : 13C

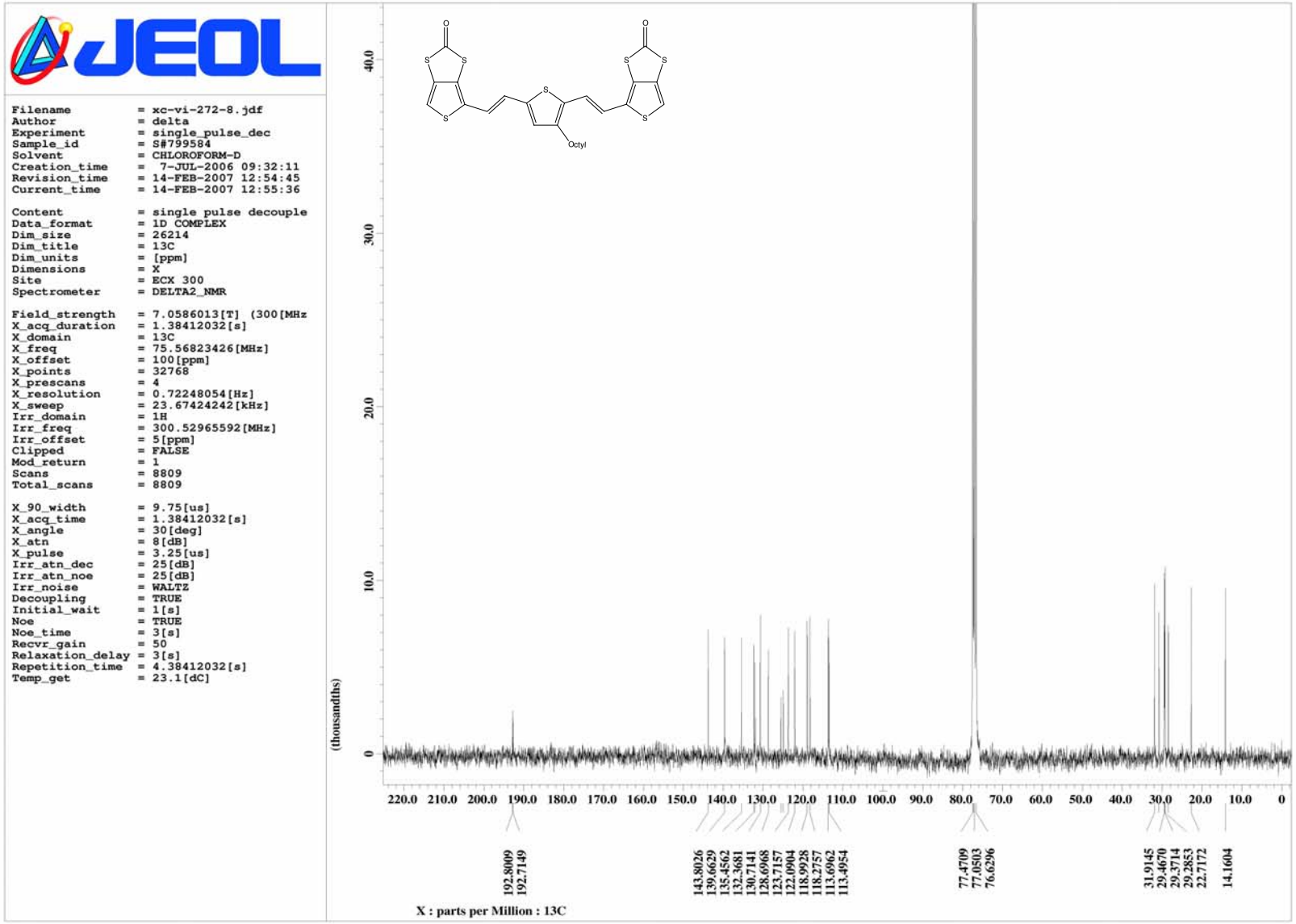

Filename = xc_vii_59Column2-9.jd
Author = delta
Experiment = single_pulse_dec
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 21-FEB-2007 10:02:21
Revision_time = 22-FEB-2007 13:38:57
Current_time = 22-FEB-2007 13:52:31
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 1.38412032[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.72248054[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8143
Total_scans = 8143
X_90_width = 9.75[us]
X_acq_time = 1.38412032[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 = 3[s]
Recvr_gain = 50
Relaxation_delay = 3[s]
Repetition_time = 4.38412032[s]
Temp_get = 23.2[dC]
O
S
Bu
(thousandths)
27.0
26.0
25.0
24.0
23.0
22.0
21.0
20.0
19.0
18.0
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
140.0
130.0
120.0
143.7450
139.6721
135.4750
132.3583
132.0141
130.7234
128.7157
125.5415
124.9105
123.7059
122.0901
119.0116
118.2754
113.6959
113.5142
X : parts per Million : 13C

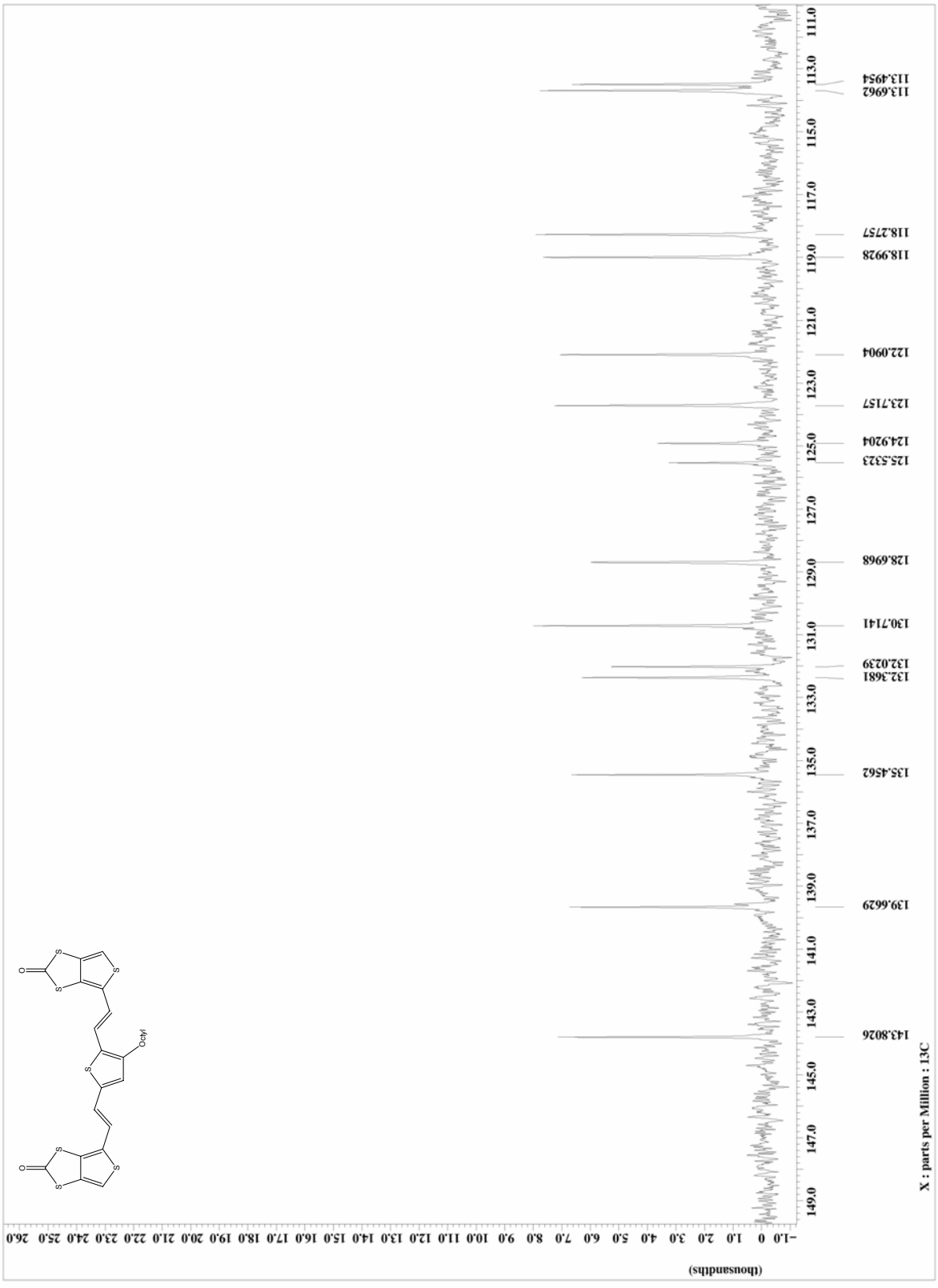
APPENDIX 64

^{1}H and ^{13}C-NMR Spectra of 4-((1E)-2-(4-octyl-5-((E)-2-(2-oxothieno[3,4-*d*]-1,3-dithiol-4-yl)vinyl) thiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (76b)


Filename = xc-vi-272-10.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#798317
Solvent = CHLOROFORM-D
Creation_time = 6-JUL-2006 22:47:50
Revision_time = 14-FEB-2007 12:41:38
Current_time = 14-FEB-2007 12:42:07
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 2.90717696[s]
X_domain = 1H
X_freq = 300.52965592[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.34397631[Hz]
X_sweep = 5.63570784[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 300.52965592[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 13.01[us]
X_acq_time = 2.90717696[s]
X_angle = 45[deg]
X_atn = 4[dB]
X_pulse = 6.505[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 46
Relaxation_delay = 2[s]
Repetition_time = 4.90717696[s]
Temp_get = 22.6[dC]
Octyl
abundance
2.008
2.017
2.031
2.045
2.057
10.414
3.037
7.2611
7.1581
6.9727
6.9109
6.8754
6.8067
2.6474
2.6233
2.5970
1.6104
1.5864
1.5486
1.3323
1.2773
0.8985
0.8767
0.8538
-0.0000
X : parts per Million : 1H

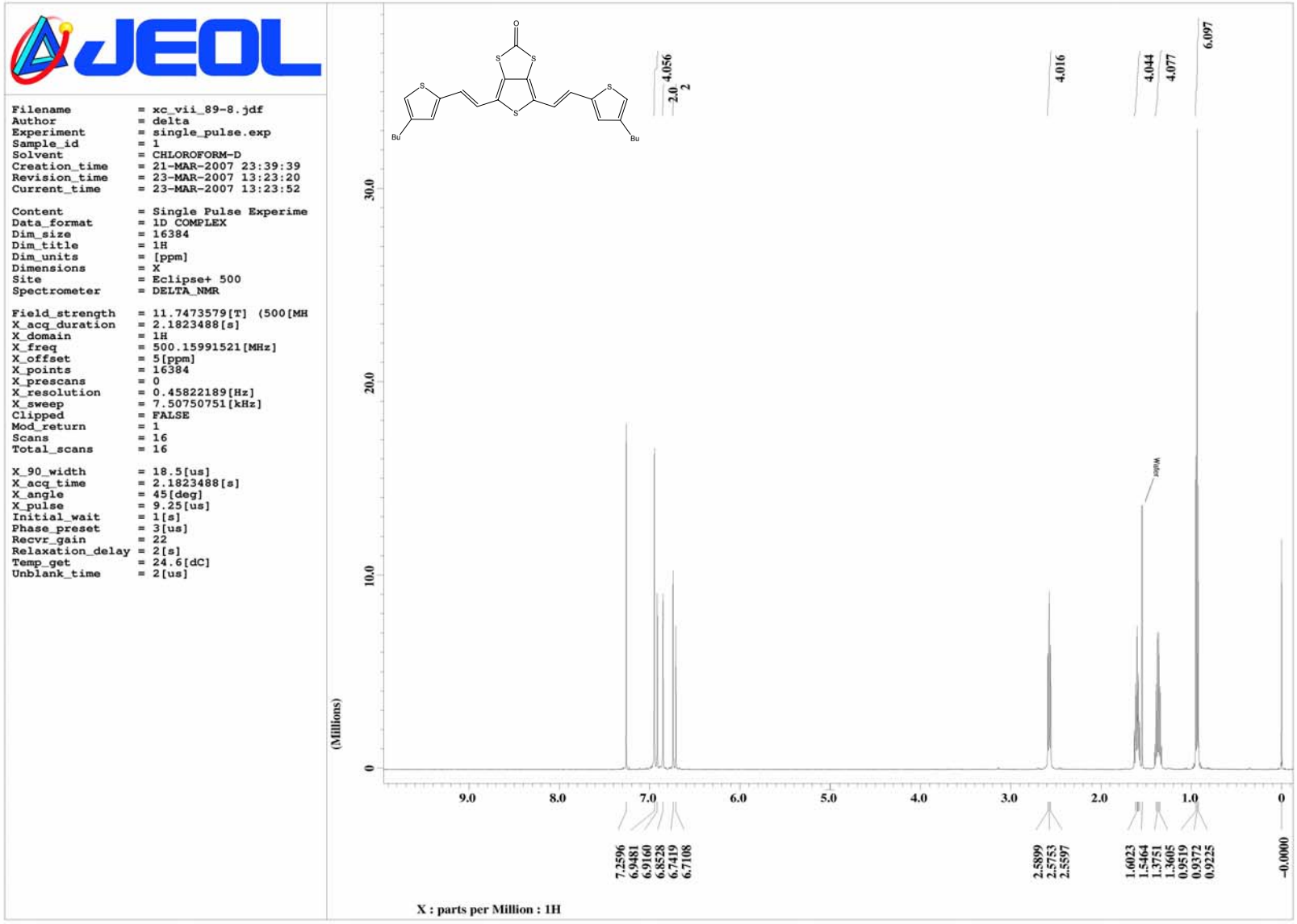

abundance
X : parts per Million : 1H
7.1581
7.0253
6.9990
6.9727
6.9635
6.9372
6.9109
6.8754
6.8067
6.7884
6.7804
6.7621
6.7541
6.7358
15.82
15.82
15.82
Octyl

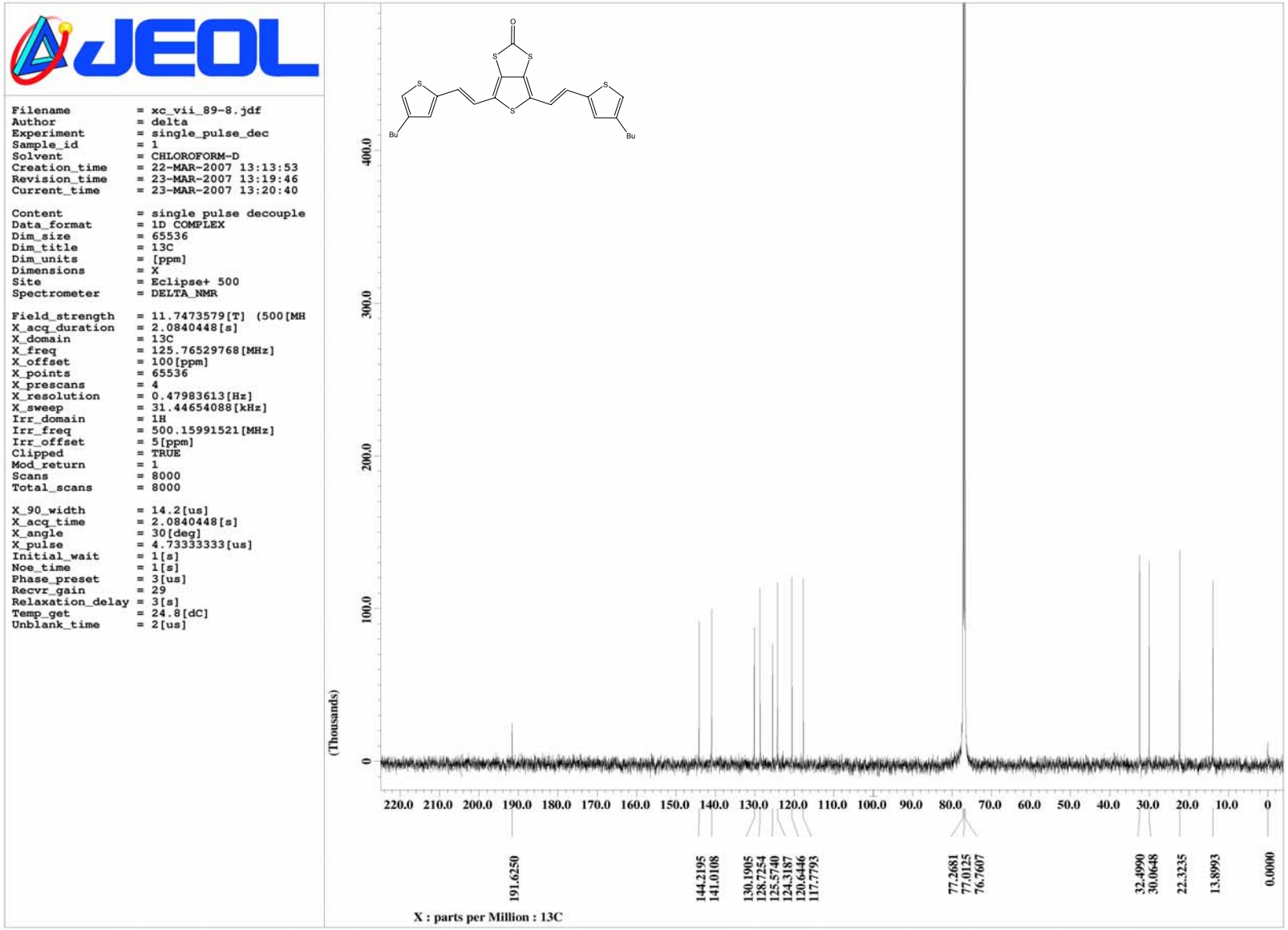

Filename = xc-vi-272-8.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#799584
Solvent = CHLOROFORM-D
Creation_time = 7-JUL-2006 09:32:11
Revision_time = 14-FEB-2007 12:54:45
Current_time = 14-FEB-2007 12:55:36
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 1.38412032[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.72248054[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8809
Total_scans = 8809
X_90_width = 9.75[us]
X_acq_time = 1.38412032[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 = 3[s]
Recvr_gain = 50
Relaxation_delay = 3[s]
Repetition_time = 4.38412032[s]
Temp_get = 23.1[dC]
Octyl
(thousandths)
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
192.8009
192.7149
143.8026
139.6629
135.4562
132.3681
130.7141
128.6968
123.7157
122.0904
118.9928
118.2757
113.6962
113.4954
77.4709
77.0503
76.6296
31.9145
29.4670
29.3714
29.2853
22.7172
14.1604
X : parts per Million : 13C


(thousandths)
X : parts per Million : 13C
143.8026
139.6629
135.4562
132.3681
132.0239
130.7141
128.6968
125.5323
124.9204
123.7157
122.0904
118.9928
118.2757
113.6962
113.4954
Octyl

APPENDIX 65

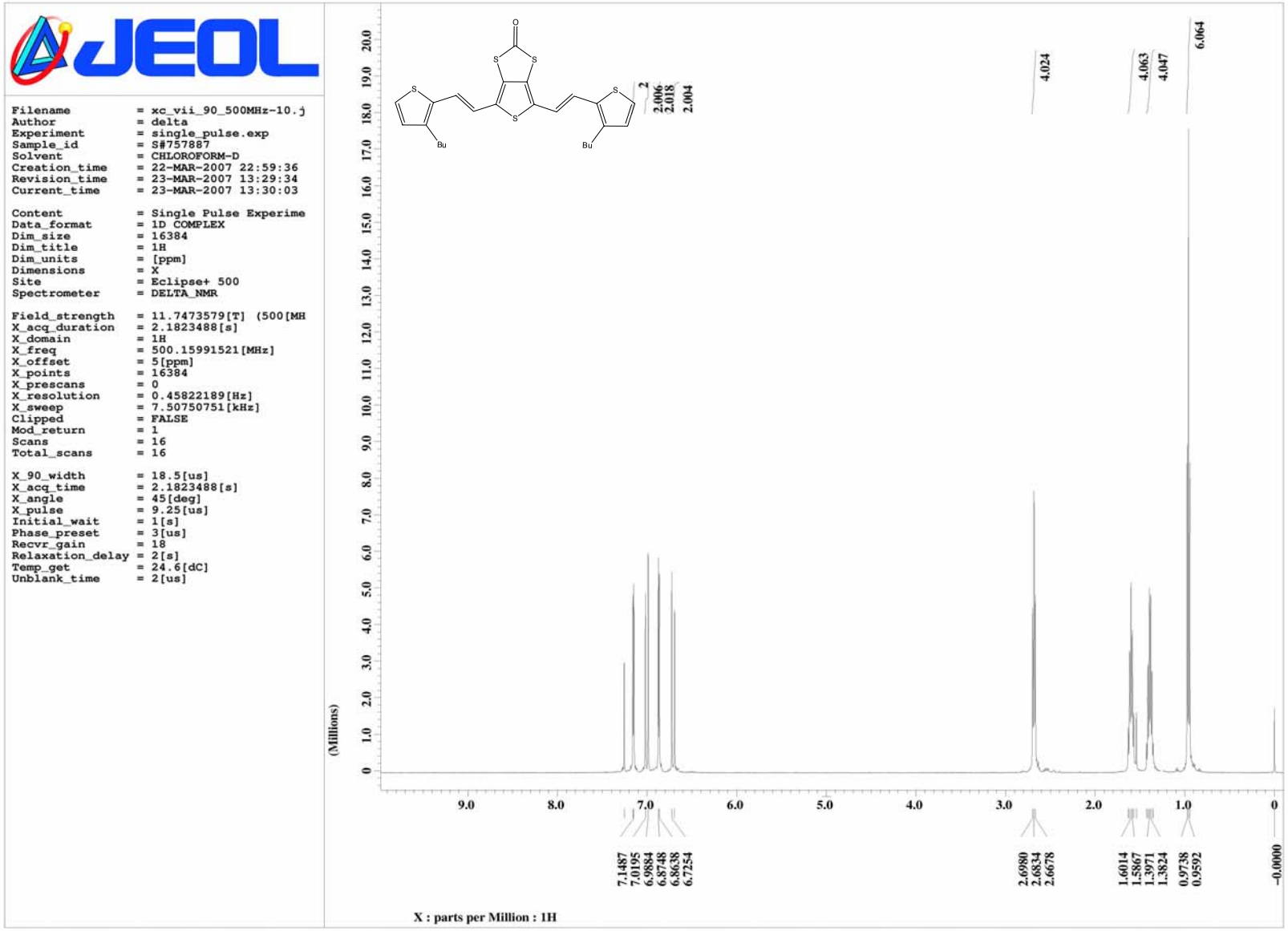
^{1}H and ^{13}C-NMR spectra of 4,6-bis((E)-2-(4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (77a)


Filename = xc_vii_89-8.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 21-MAR-2007 23:39:39
Revision_time = 23-MAR-2007 13:23:20
Current_time = 23-MAR-2007 13:23:52
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 22
Relaxation_delay = 2[s]
Temp_get = 24.6[dC]
Unblank_time = 2[us]
4.056
2.0
2
4.016
4.044
4.077
6.097
(Millions)
30.0
20.0
10.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2596
6.9481
6.9160
6.8528
6.7419
6.7108
2.5899
2.5753
2.5597
1.6023
1.5464
1.3751
1.3605
0.9519
0.9372
0.9225
-0.0000
X : parts per Million : 1H

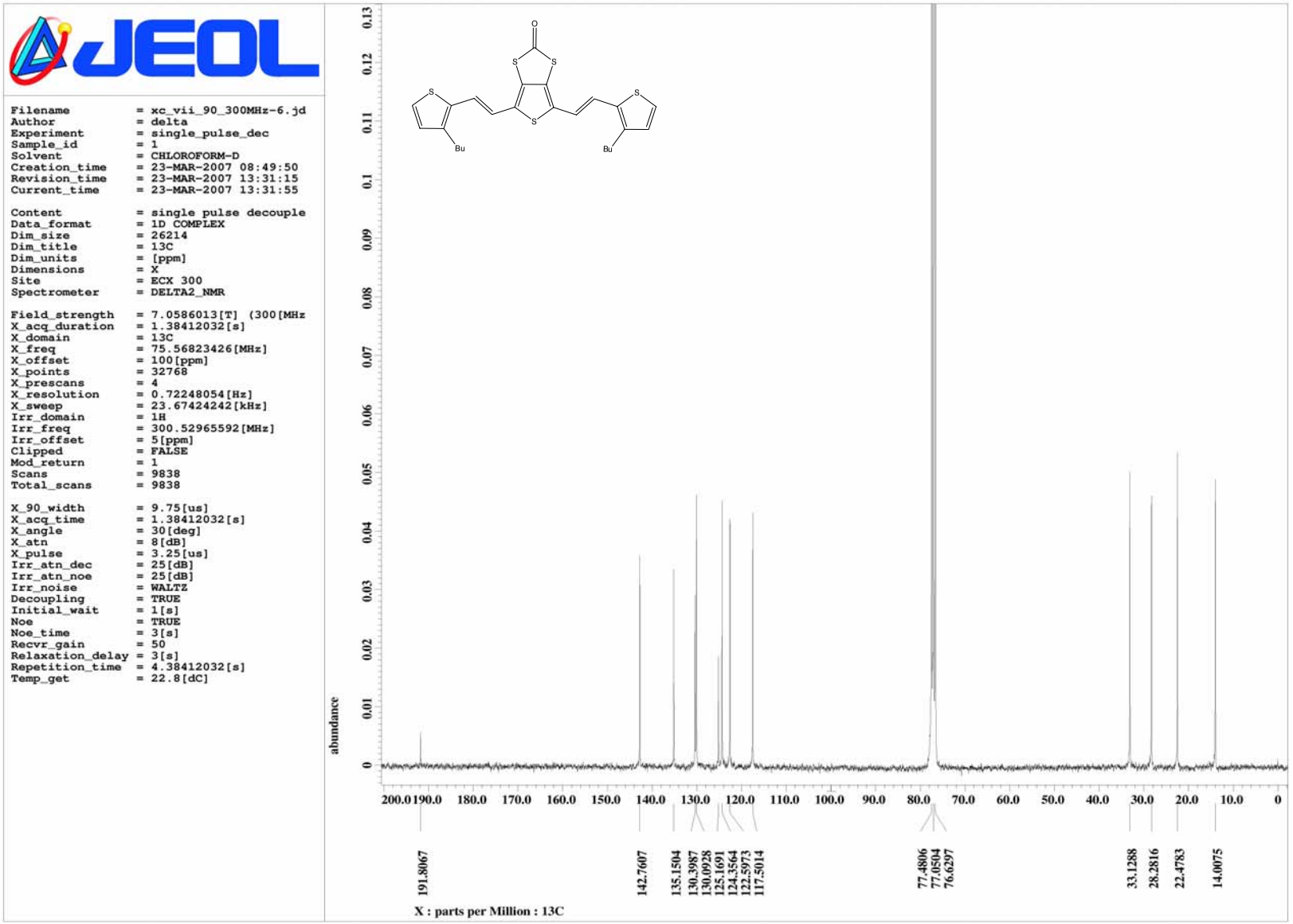

Filename = xc_vii_89-8.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 22-MAR-2007 13:13:53
Revision_time = 23-MAR-2007 13:19:46
Current_time = 23-MAR-2007 13:20:40
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 65536
Dim_title = 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 = TRUE
Mod_return = 1
Scans = 8000
Total_scans = 8000
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 29
Relaxation_delay = 3[s]
Temp_get = 24.8[dC]
Unblank_time = 2[us]
O
S
S
S
S
Bu
Bu
(Thousands)
400.0
300.0
200.0
100.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
191.6250
144.2195
141.0108
130.1905
128.7254
125.5740
124.3187
120.6446
117.7793
77.2681
77.0125
76.7607
32.4990
30.0648
22.3235
13.8993
0.0000
X : parts per Million : 13C

APPENDIX 66

^{1}H and ^{13}C-NMR spectra of 4,6-bis((E)-2-(3-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (77b)


Filename = xc_vii_90_500MHz-10.j
Author = delta
Experiment = single_pulse.exp
Sample_id = S#757887
Solvent = CHLOROFORM-D
Creation_time = 22-MAR-2007 22:59:36
Revision_time = 23-MAR-2007 13:29:34
Current_time = 23-MAR-2007 13:30:03
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 2[s]
Temp_get = 24.6[dC]
Unblank_time = 2[us]
(Millions)
4.024
4.063
4.047
6.064
2
2.006
2.018
2.004
7.1487
7.0195
6.9884
6.8748
6.8638
6.7254
2.6980
2.6834
2.6678
1.6014
1.5867
1.3971
1.3824
0.9738
0.9592
-0.0000
X : parts per Million : 1H

X : parts per Million : 1H
7.1627
7.1541
7.1456
7.0311
7.0053
6.9796
6.8777
6.8691
6.8606
6.7335
6.7078
6.6820
5.16
15.48
5.16
15.48
Bu
Bu
O
S
abundance



```
Filename          = xc_vii_90_300MHz-6.jd
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = 1
Solvent           = CHLOROFORM-D
Creation_time     = 23-MAR-2007 08:49:50
Revision_time     = 23-MAR-2007 13:31:15
Current_time      = 23-MAR-2007 13:31:55

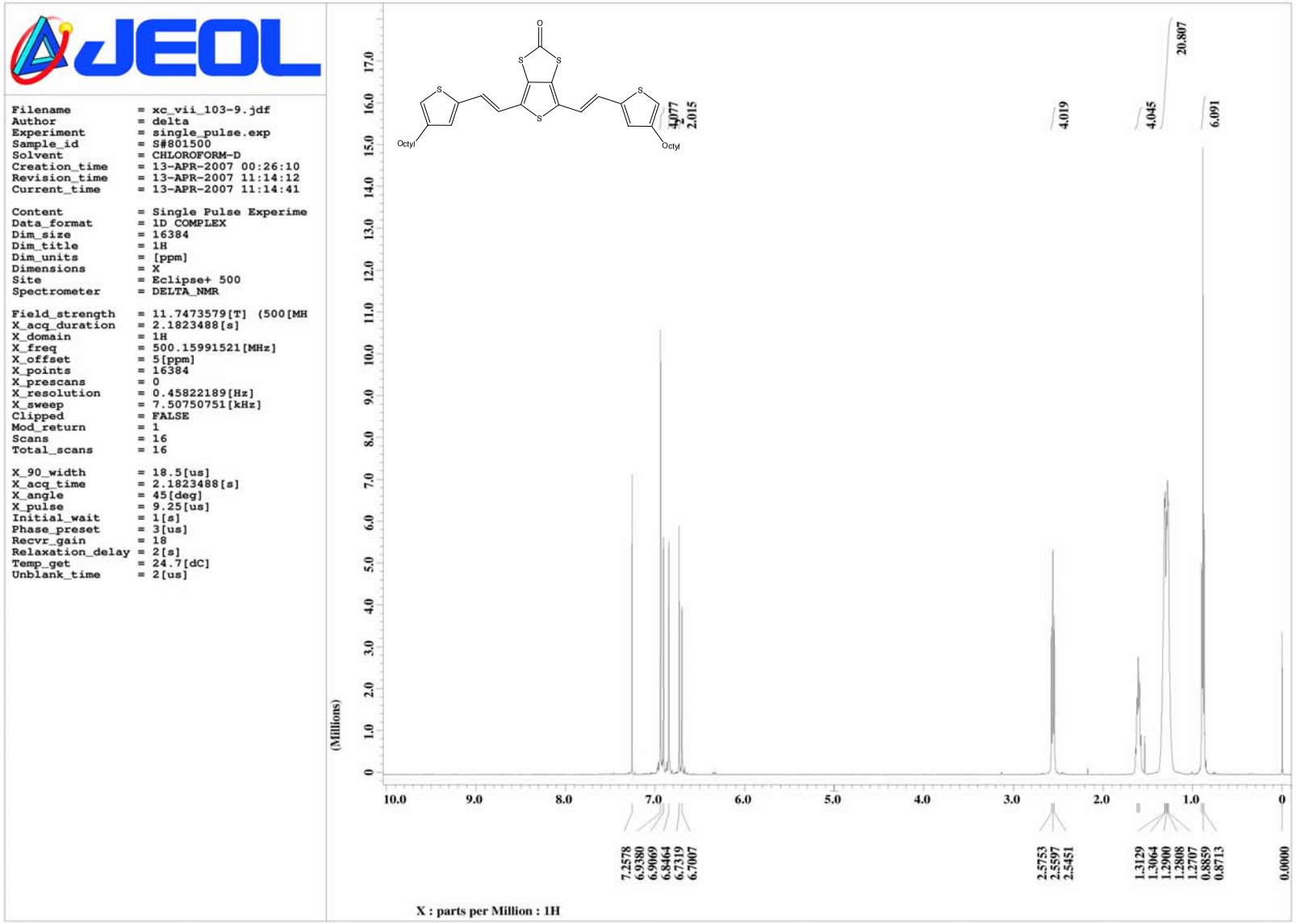
Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 1.38412032[s]
X_domain          = 13C
X_freq            = 75.56823426[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.72248054[Hz]
X_sweep           = 23.67424242[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 9838
Total_scans       = 9838

X_90_width        = 9.75[us]
X_acq_time        = 1.38412032[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          = 3[s]
Recvr_gain        = 50
Relaxation_delay  = 3[s]
Repetition_time   = 4.38412032[s]
Temp_get          = 22.8[dC]
```

APPENDIX 67

^{1}H and ^{13}C-NMR spectra of 4,6-bis((E)-2-(4-octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (77c)


Filename = xc_vii_103-9.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#801500
Solvent = CHLOROFORM-D
Creation_time = 13-APR-2007 00:26:10
Revision_time = 13-APR-2007 11:14:12
Current_time = 13-APR-2007 11:14:41
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 2[s]
Temp_get = 24.7[dC]
Unblank_time = 2[us]
Octyl
Octyl
4.077
2.015
4.019
4.045
20.807
6.091
(Millions)
X : parts per Million : 1H
7.2578
6.9380
6.9069
6.8464
6.7319
6.7007
2.5753
2.5597
2.5451
1.3129
1.3064
1.2900
1.2808
1.2707
0.8859
0.8713
0.0000

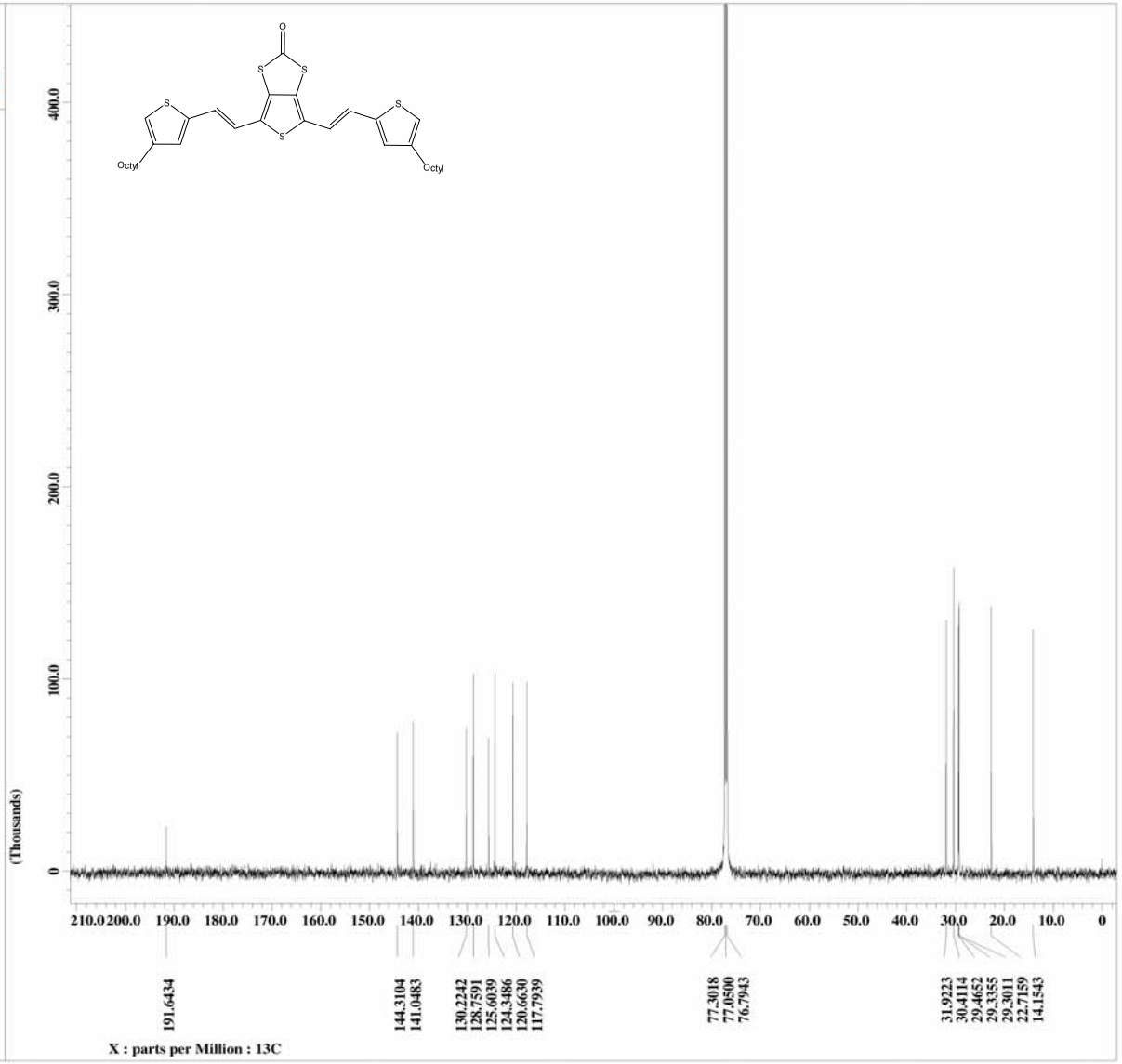
(Millions)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
7.05
7.04
7.03
7.02
7.01
7.0
6.99
6.98
6.97
6.96
6.95
6.94
6.93
6.92
6.91
6.9
6.89
6.88
6.87
6.86
6.85
6.84
6.83
6.82
6.81
6.8
6.79
6.78
6.77
6.76
6.75
6.74
6.73
6.72
6.71
6.7
6.69
6.68
6.67
6.66
6.65
6.64
6.9380
6.9225
6.9069
6.8464
6.7319
6.7163
6.7007
15.58
15.58
X : parts per Million : 1H
Octyl
Octyl
O
S
S
S
S
S

```
Filename          = xc_vii_103-3.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#802846
Solvent           = CHLOROFORM-D
Creation_time     = 13-APR-2007 12:16:52
Revision_time     = 13-APR-2007 11:17:23
Current_time      = 13-APR-2007 11:18:17

Content           = single pulse decouple
Data_format       = 1D COMPLEX
Dim_size          = 65536
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = Eclipse+ 500
Spectrometer      = DELTA_NMR

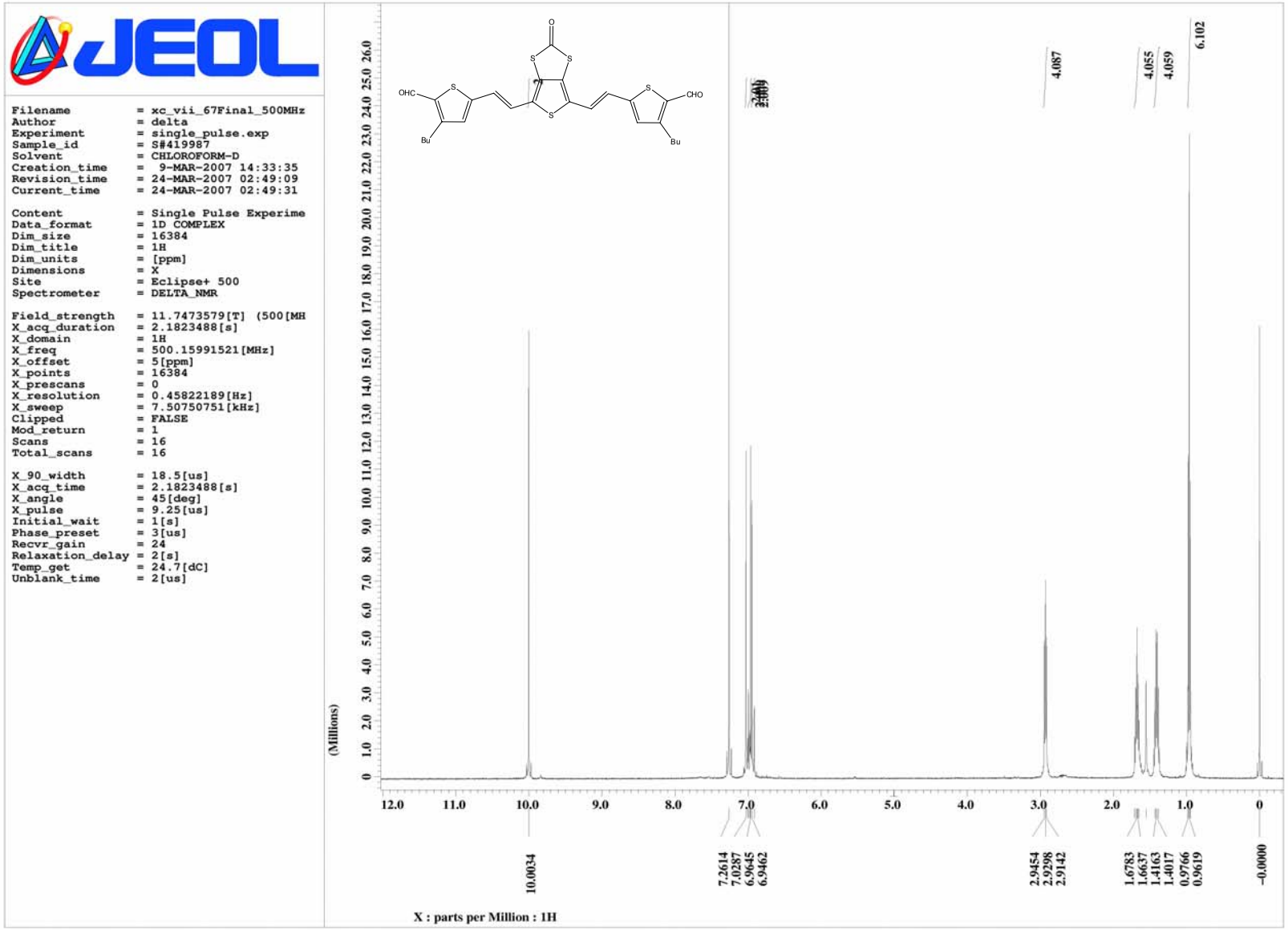
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 2.0840448[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 65536
X_prescans        = 4
X_resolution      = 0.47983613[Hz]
X_sweep           = 31.44654088[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 6000
Total_scans       = 6000

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]
Noe_time          = 1[s]
Phase_preset      = 3[us]
Recvr_gain        = 27
Relaxation_delay  = 4[s]
Temp_get          = 25.9[dC]
Unblank_time      = 2[us]
```



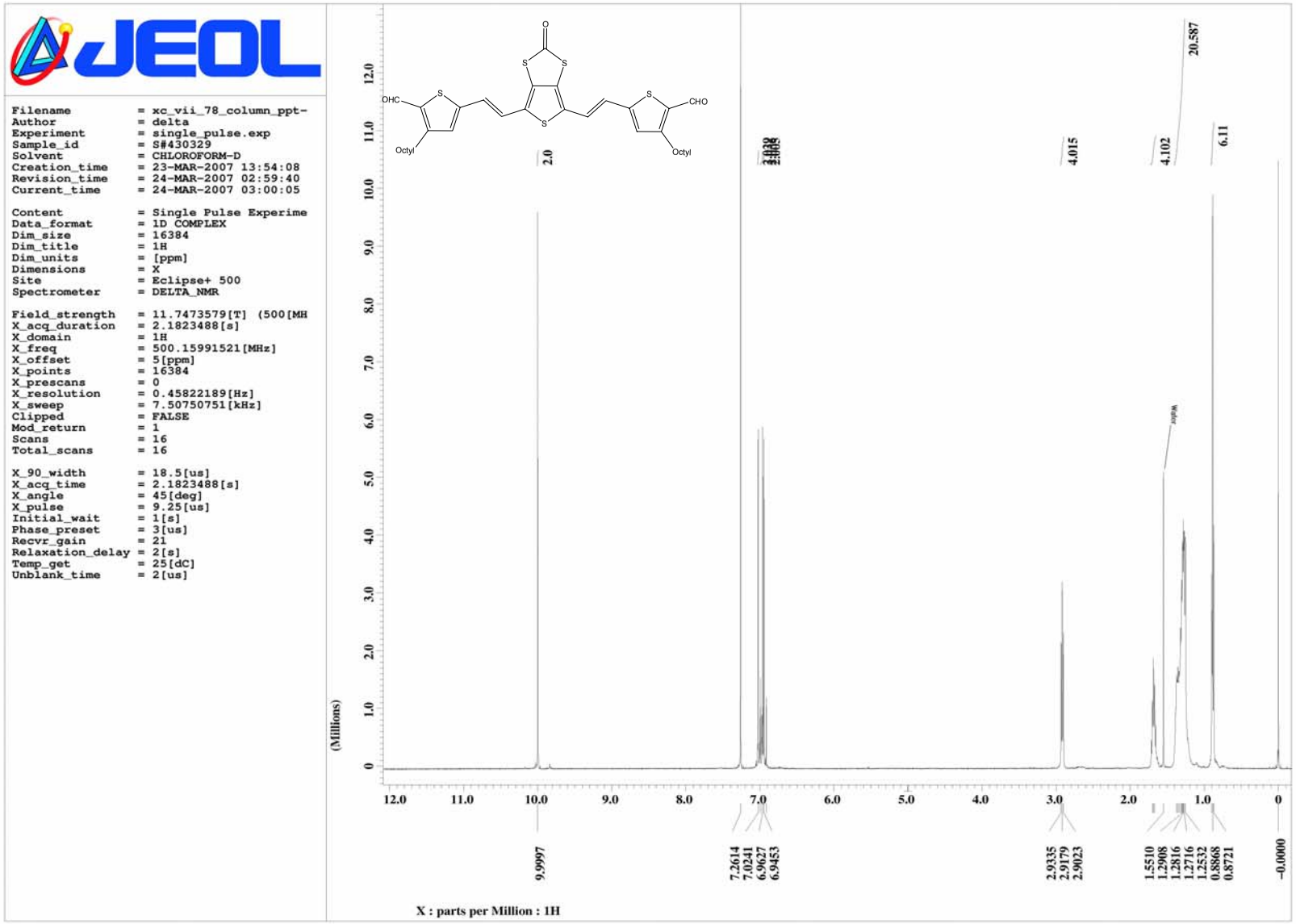
APPENDIX 68

^{1}H-NMR spectrum of
4,6-bis((E)-2-(5-formyl-4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one
(78a)


Filename = xc_vii_67Final_500MHz
Author = delta
Experiment = single_pulse.exp
Sample_id = S#419987
Solvent = CHLOROFORM-D
Creation_time = 9-MAR-2007 14:33:35
Revision_time = 24-MAR-2007 02:49:09
Current_time = 24-MAR-2007 02:49:31
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 24
Relaxation_delay = 2[s]
Temp_get = 24.7[dC]
Unblank_time = 2[us]
OHC
CHO
Bu
Bu
(Millions)
4.087
4.055
4.059
6.102
10.0034
7.2614
7.0287
6.9645
6.9462
2.9454
2.9298
2.9142
1.6783
1.6637
1.4163
1.4017
0.9766
0.9619
-0.0000
X : parts per Million : 1H

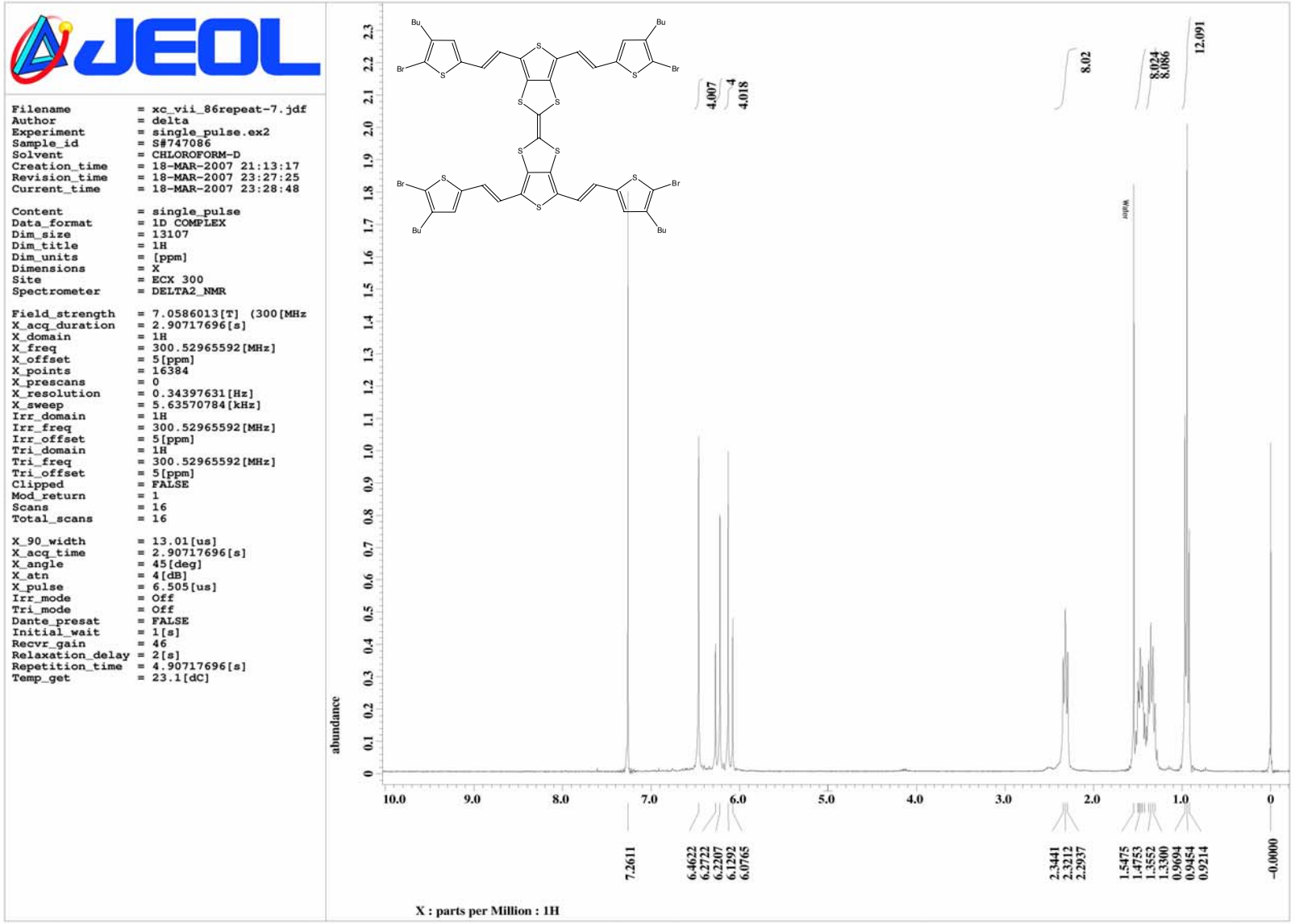
APPENDIX 69

^{1}H-NMR spectrum of
4,6-bis((E)-2-(5-formyl-4-octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one
(78b)


JEOL
Filename = xc_vii_78_column_ppt-
Author = delta
Experiment = single_pulse.exp
Sample_id = S#430329
Solvent = CHLOROFORM-D
Creation_time = 23-MAR-2007 13:54:08
Revision_time = 24-MAR-2007 02:59:40
Current_time = 24-MAR-2007 03:00:05
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 21
Relaxation_delay = 2[s]
Temp_get = 25[dC]
Unblank_time = 2[us]
OHC
CHO
Octyl
Octyl
2.0
4.015
4.102
20.587
6.11
(Millions)
9.9997
7.2614
7.0241
6.9627
6.9453
2.9335
2.9179
2.9023
1.5510
1.2908
1.2816
1.2716
1.2532
0.8868
0.8721
-0.0000
X : parts per Million : 1H

APPENDIX 70

^{1}H-NMR spectrum of 2-(4,6-bis((E)-2-(5-bromo-4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-ylidene)-4,6-bis((E)-2-(5-bromo-4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiole (80a)



```
Filename          = xc_vii_86repeat-7.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = S#747086
Solvent           = CHLOROFORM-D
Creation_time     = 18-MAR-2007 21:13:17
Revision_time     = 18-MAR-2007 23:27:25
Current_time      = 18-MAR-2007 23:28:48

Content           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECX 300
Spectrometer      = DELTA2_NMR

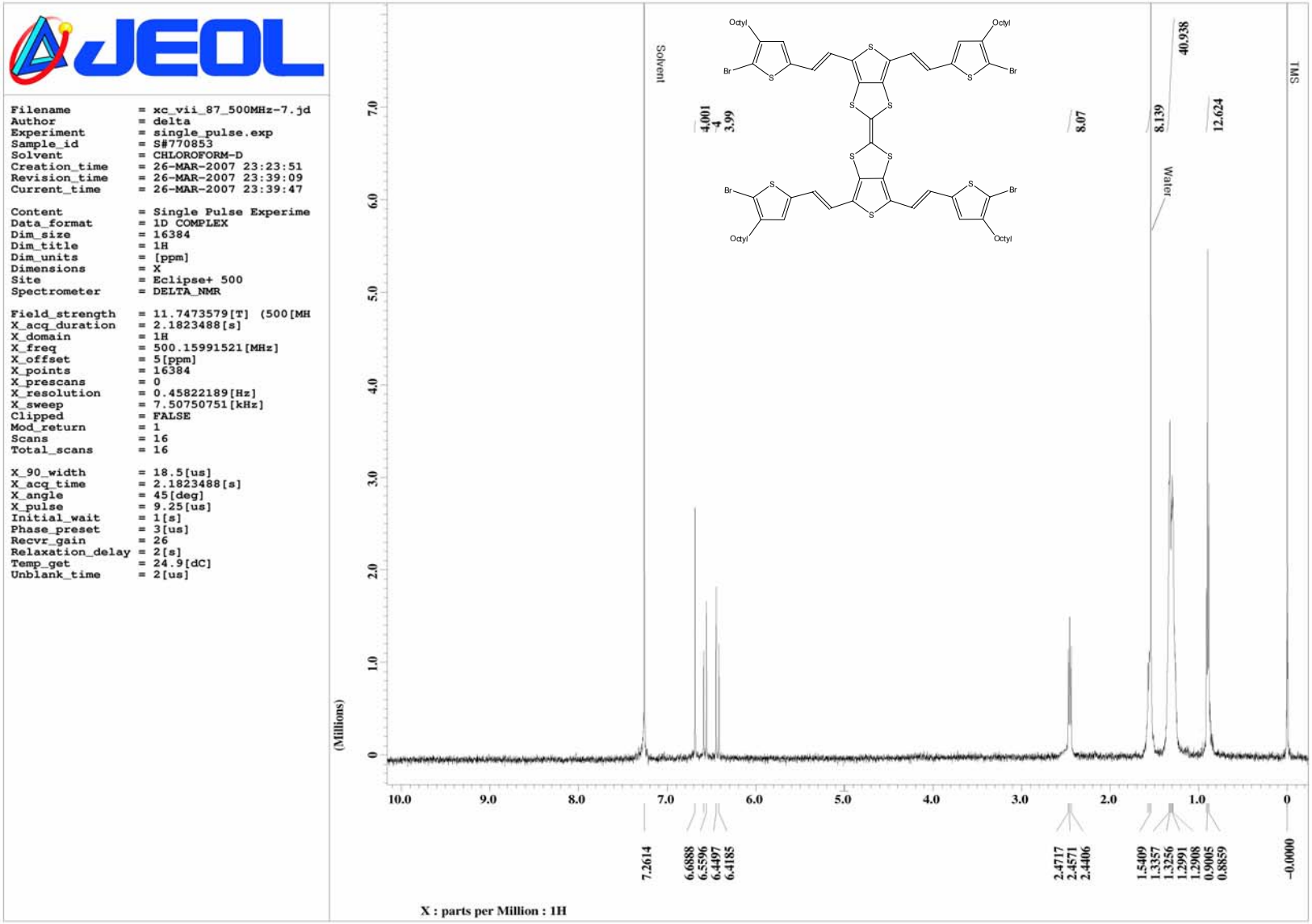
Field_strength    = 7.0586013[T] (300[MHz
X_acq_duration    = 2.90717696[s]
X_domain          = 1H
X_freq            = 300.52965592[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 0
X_resolution      = 0.34397631[Hz]
X_sweep           = 5.63570784[kHz]
Irr_domain        = 1H
Irr_freq          = 300.52965592[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 300.52965592[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 13.01[us]
X_acq_time        = 2.90717696[s]
X_angle           = 45[deg]
X_atn             = 4[dB]
X_pulse           = 6.505[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 46
Relaxation_delay  = 2[s]
Repetition_time   = 4.90717696[s]
Temp_get          = 23.1[dC]
```

abundance
X : parts per Million : 1H
6.4622
6.2722
6.2207
6.1292
6.0765
4.007
4.018
4

APPENDIX 71

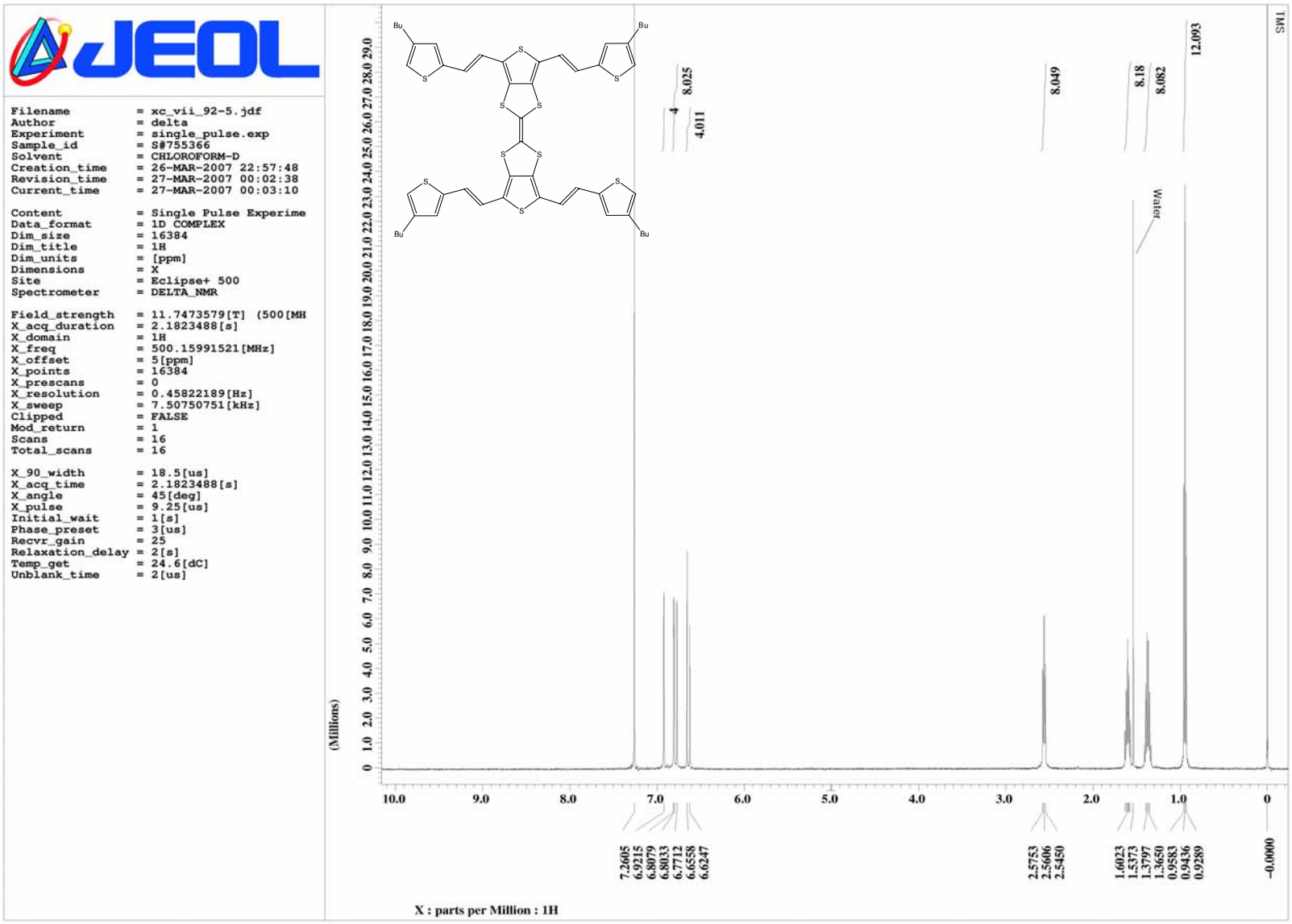
^{1}H-NMR spectrum of 2-(4,6-bis((E)-2-(5-bromo-4-octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-ylidene)-4,6-bis((E)-2-(5-bromo-4-octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiole (80b)


Filename = xc_vii_87_500MHz-7.jd
Author = delta
Experiment = single_pulse.exp
Sample_id = S#770853
Solvent = CHLOROFORM-D
Creation_time = 26-MAR-2007 23:23:51
Revision_time = 26-MAR-2007 23:39:09
Current_time = 26-MAR-2007 23:39:47
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 26
Relaxation_delay = 2[s]
Temp_get = 24.9[dC]
Unblank_time = 2[us]
Octyl
Br
S
Solvent
4.001
4
3.99
8.07
8.139
40.938
12.624
Water
TMS
(Millions)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2614
6.6888
6.5596
6.4497
6.4185
2.4717
2.4571
2.4406
1.5409
1.3357
1.3256
1.2991
1.2908
0.9005
0.8859
−0.0000
X : parts per Million : 1H

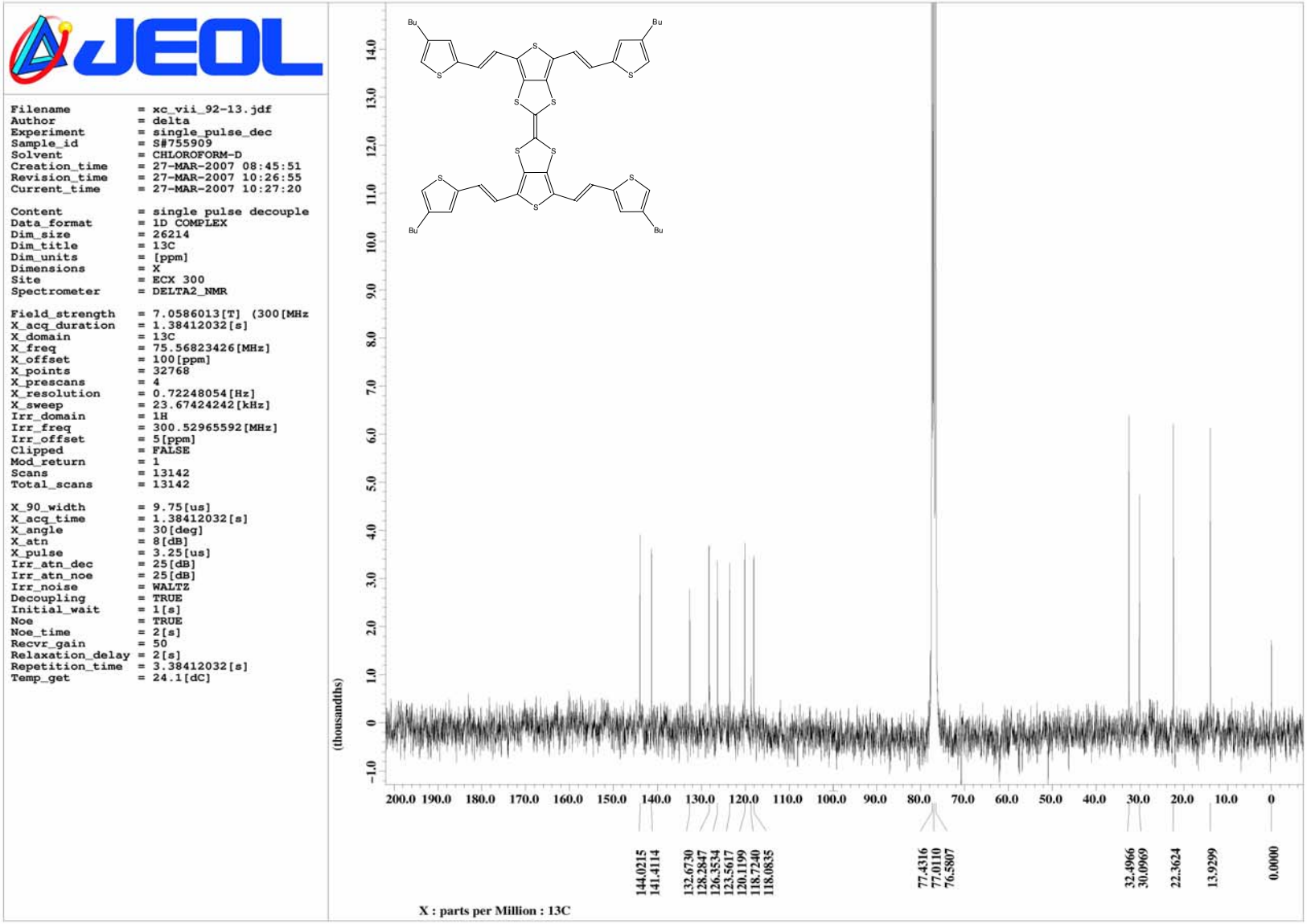
(Millions)
0
1.0
2.0
3.0
X : parts per Million : 1H
6.8
6.7
6.6
6.5
6.4
6.6888
6.5907
6.5752
6.5596
6.4497
6.4341
6.4185
15.58
15.58
Octyl
Br
Br
Octyl
Octyl
Br
Br
Octyl
S

APPENDIX 72

^{1}H and ^{13}C-NMR spectra of 2-(4,6-bis((E)-2-(4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-ylidene)-4,6-bis((E)-2-(4-butylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiole (80c)

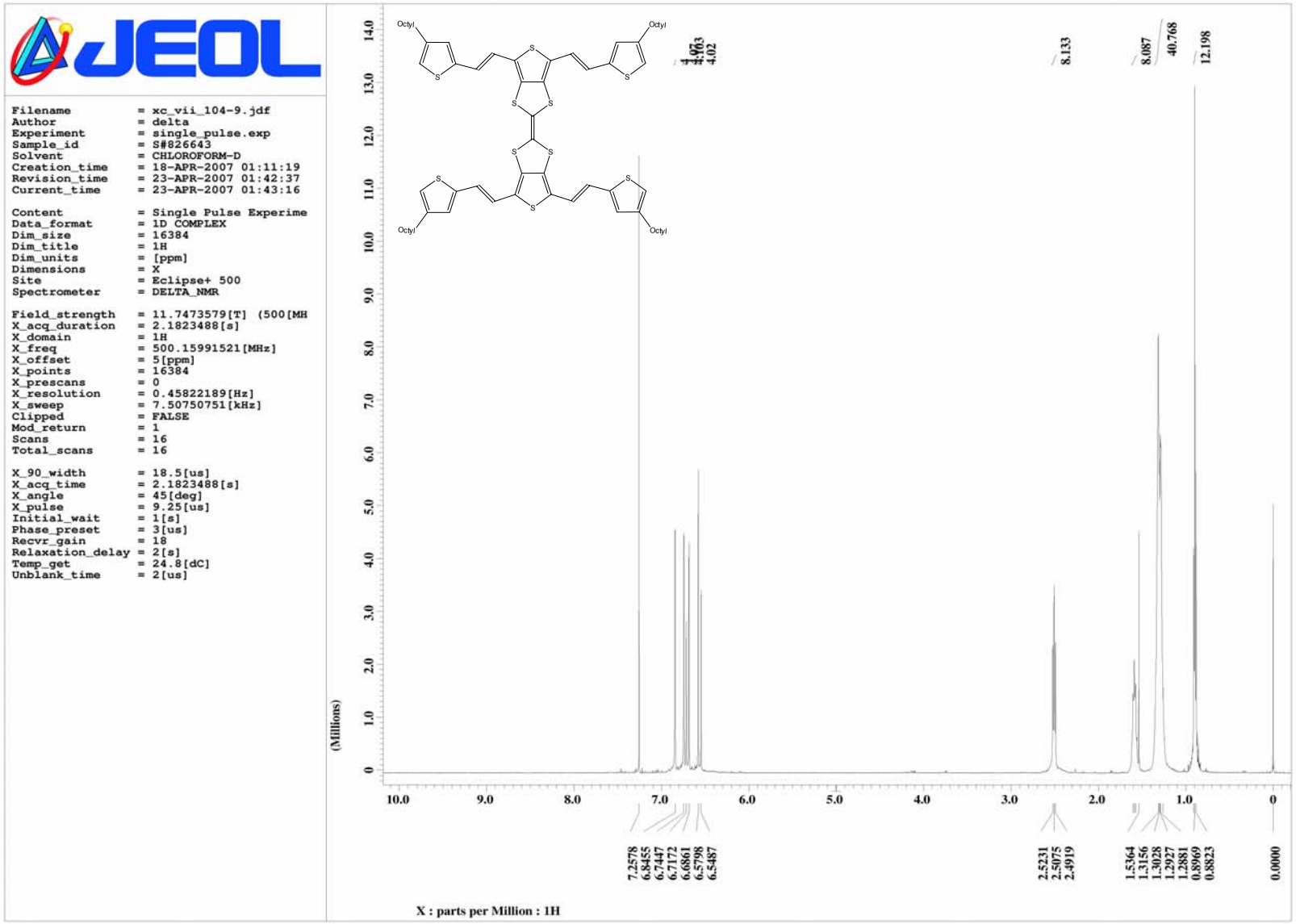

Filename = xc_vii_92-5.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#755366
Solvent = CHLOROFORM-D
Creation_time = 26-MAR-2007 22:57:48
Revision_time = 27-MAR-2007 00:02:38
Current_time = 27-MAR-2007 00:03:10
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 25
Relaxation_delay = 2[s]
Temp_get = 24.6[dC]
Unblank_time = 2[us]
Bu
S
8.025
4
4.011
8.049
8.18
8.082
12.093
Water
SW1
(Millions)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2605
6.9215
6.8079
6.8033
6.7712
6.6558
6.6247
2.5753
2.5606
2.5450
1.6023
1.5373
1.3797
1.3650
0.9583
0.9436
0.9289
-0.0000
X : parts per Million : 1H

(Millions)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
X : parts per Million : 1H
6.96 6.95 6.94 6.93 6.92 6.91 6.9 6.89 6.88 6.87 6.86 6.85 6.84 6.83 6.82 6.81 6.8 6.79 6.78 6.77 6.76 6.75 6.74 6.73 6.72 6.71 6.7 6.69 6.68 6.67 6.66 6.65 6.64 6.63 6.62 6.61 6.6 6.59
6.9215
6.8079
6.8033
6.7712
6.6558
6.6247
8.025
4.011
4
Bu
S

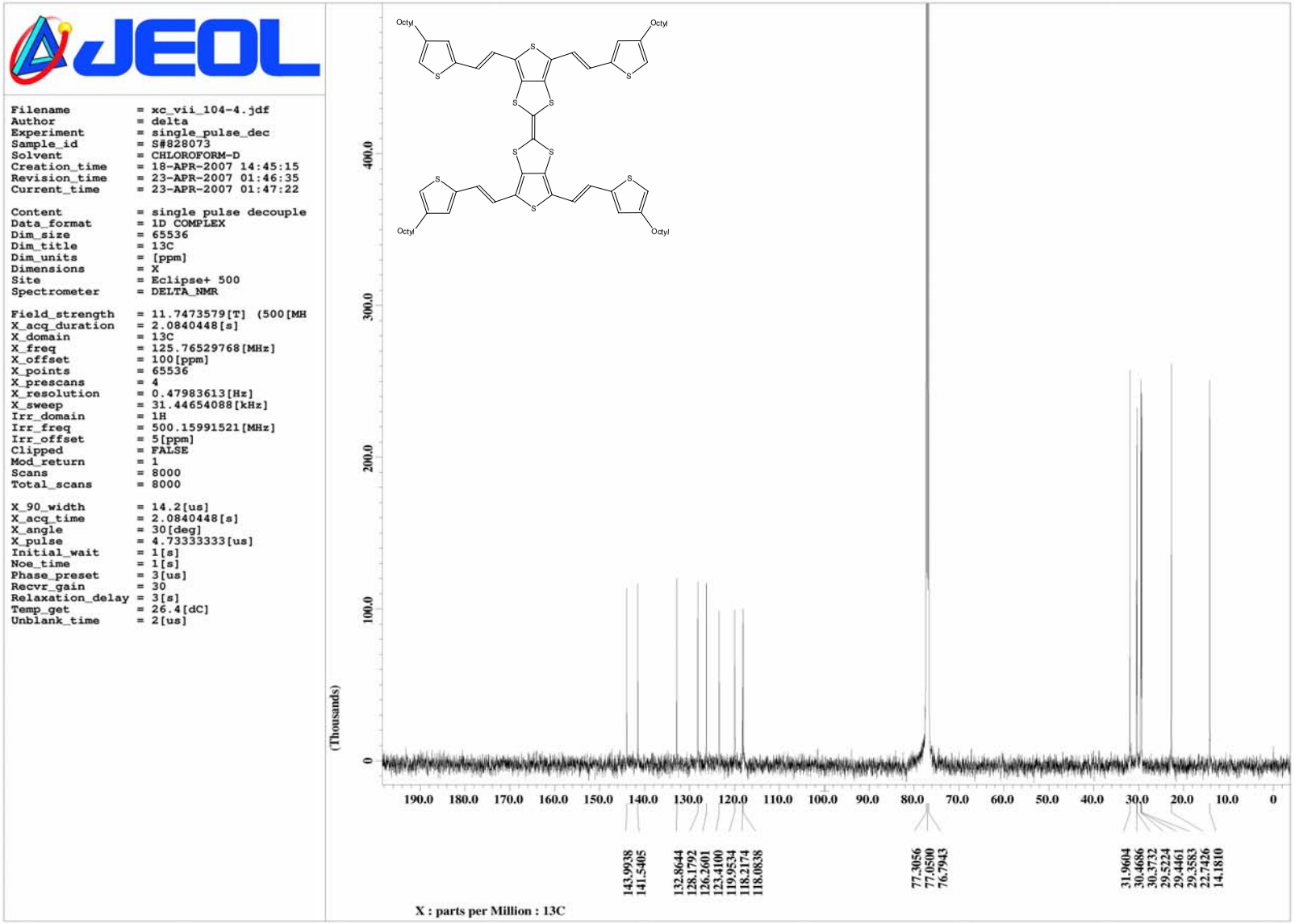

Filename = xc_vii_92-13.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#755909
Solvent = CHLOROFORM-D
Creation_time = 27-MAR-2007 08:45:51
Revision_time = 27-MAR-2007 10:26:55
Current_time = 27-MAR-2007 10:27:20
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.0586013[T] (300[MHz
X_acq_duration = 1.38412032[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.72248054[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 13142
Total_scans = 13142
X_90_width = 9.75[us]
X_acq_time = 1.38412032[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 = 3.38412032[s]
Temp_get = 24.1[dC]
Bu
S
(thousandths)
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
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 0
144.0215
141.4114
132.6730
128.2847
126.3534
123.5617
120.1199
118.7240
118.0835
77.4316
77.0110
76.5807
32.4966
30.0969
22.3624
13.9299
0.0000
X : parts per Million : 13C

APPENDIX 73

^{1}H and ^{13}C-NMR spectra of 2-(4,6-bis((E)-2-(4-octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-ylidene)-4,6-bis((E)-2-(4-octylthiophen-2-yl)vinyl)thieno[3,4-*d*]-1,3-dithiole (80d)

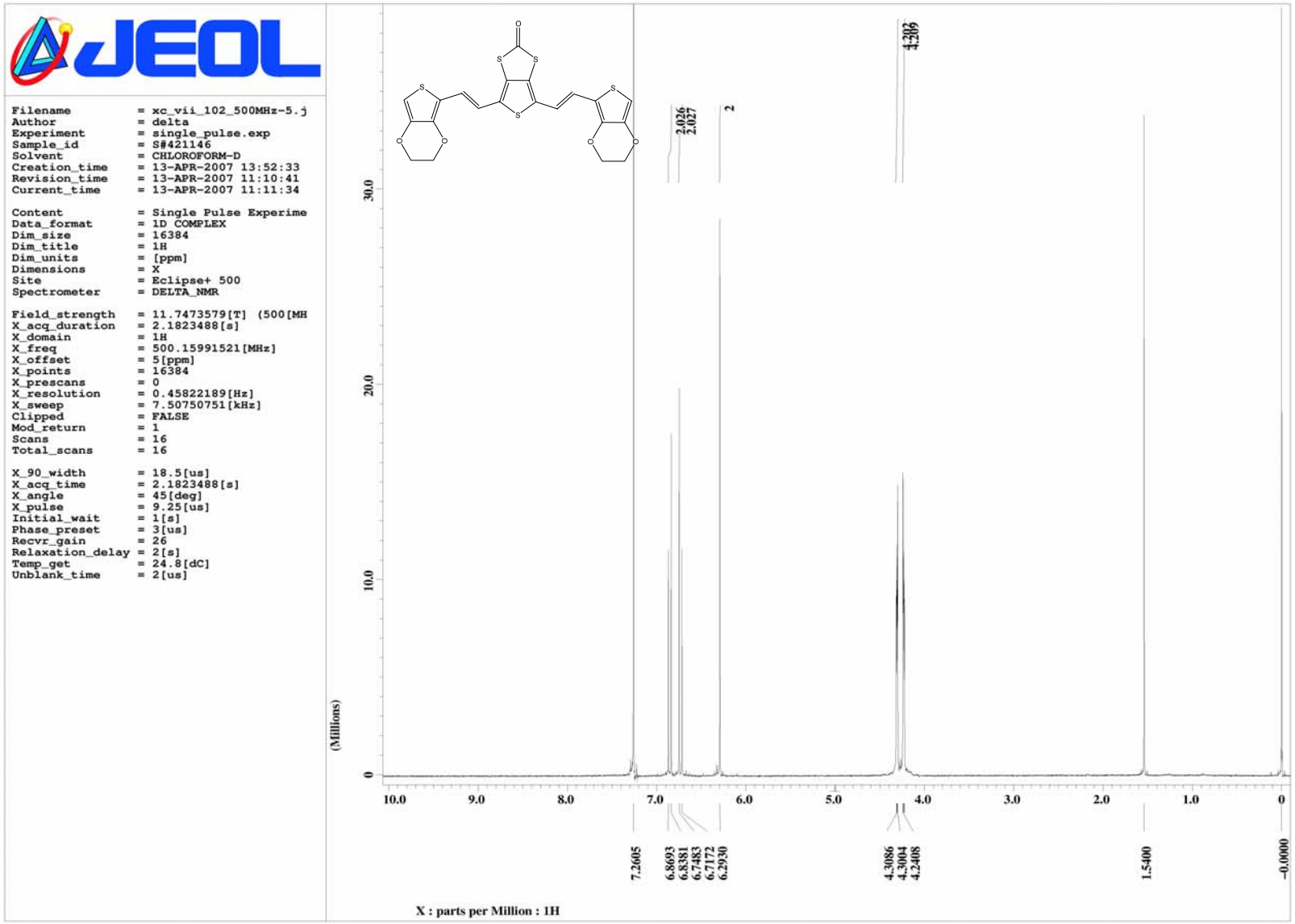

Filename = xc_vii_104-9.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#826643
Solvent = CHLOROFORM-D
Creation_time = 18-APR-2007 01:11:19
Revision_time = 23-APR-2007 01:42:37
Current_time = 23-APR-2007 01:43:16
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 18
Relaxation_delay = 2[s]
Temp_get = 24.8[dC]
Unblank_time = 2[us]
Octyl
Octyl
Octyl
Octyl
4.02
8.133
8.087
40.768
12.198
(Millions)
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2578
6.8455
6.7447
6.7172
6.6861
6.5798
6.5487
2.5231
2.5075
2.4919
1.5364
1.3156
1.3028
1.2927
1.2881
0.8969
0.8823
0.0000
X : parts per Million : 1H

(Millions)
0
1.0
2.0
3.0
4.0
5.0
6.0
X : parts per Million : 1H
6.8455
6.7447
6.7172
6.7017
6.6861
6.5798
6.5642
6.5487
15.58
15.58
Octyl
Octyl
Octyl
Octyl
S


Filename = xc_vii_104-4.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = S#828073
Solvent = CHLOROFORM-D
Creation_time = 18-APR-2007 14:45:15
Revision_time = 23-APR-2007 01:46:35
Current_time = 23-APR-2007 01:47:22
Content = single pulse decouple
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 = 8000
Total_scans = 8000
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]
Noe_time = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 3[s]
Temp_get = 26.4[dC]
Unblank_time = 2[us]
Octyl
Octyl
Octyl
Octyl
S
(Thousands)
400.0
300.0
200.0
100.0
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
0
143.9938
141.5405
132.8644
128.1792
126.2601
123.4100
119.9534
118.2174
118.0838
77.3056
77.0500
76.7943
31.9604
30.4686
30.3732
29.5224
29.4461
29.3583
22.7426
14.1810
X : parts per Million : 13C

APPENDIX 74

^{1}H and ^{13}C-NMR spectra of 4-((E)-2-(2,3-dihydrothieno[3,4-*b*]-1,4-dioxin-5-yl)vinyl)-6-((E)-2-(2,3-dihydrothieno[3,4-*b*]-1,4-dioxin-7-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (81a)


Filename = xc_vii_102_500MHz-5.j
Author = delta
Experiment = single_pulse.exp
Sample_id = S#421146
Solvent = CHLOROFORM-D
Creation_time = 13-APR-2007 13:52:33
Revision_time = 13-APR-2007 11:10:41
Current_time = 13-APR-2007 11:11:34
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0
X_resolution = 0.45822189[Hz]
X_sweep = 7.50750751[kHz]
Clipped = FALSE
Mod_return = 1
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 26
Relaxation_delay = 2[s]
Temp_get = 24.8[dC]
Unblank_time = 2[us]
(Millions)
30.0
20.0
10.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.026
2.027
2
4.202
4.209
7.2605
6.8693
6.8381
6.7483
6.7172
6.2930
4.3086
4.3004
4.2408
1.5400
-0.0000
X : parts per Million : 1H

Filename = xc_vii_102_300MHz-6.j
Author = delta
Experiment = single_pulse_dec
Sample_id = 1
Solvent = CHLOROFORM-D
Creation_time = 13-APR-2007 08:44:05
Revision_time = 13-APR-2007 11:19:48
Current_time = 13-APR-2007 11:20:22
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECX 300
Spectrometer = DELTA2_NMR
Field_strength = 7.05860131[T] (300[MHz
X_acq_duration = 1.38412032[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.72248054[Hz]
X_sweep = 23.67424242[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 7045
Total_scans = 7045
X_90_width = 9.75[us]
X_acq_time = 1.38412032[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 = 4[s]
Recvr_gain = 50
Relaxation_delay = 4[s]
Repetition_time = 5.38412032[s]
Temp_get = 23.5[dC]
(thousandths)
X : parts per Million : 13C
192.0066
142.0810
140.2358
130.5508
125.0152
120.4835
116.4107
115.9900
99.3640
77.4319
77.0113
76.5906
64.9553
64.6302
0.0003

APPENDIX 75

^{1}H-NMR Spectrum of
4,6-bis((E)-2-(5-bromo-2,3-dihydrothieno[3,4-*b*]-1,4-dioxin-7-yl)vinyl)thieno[3,4-*d*]-1,3-dithiol-2-one (81b)

Filename = xc_vii_108-9.jdf
Author = delta
Experiment = single_pulse.exp
Sample_id = S#828238
Solvent = CHLOROFORM-D
Creation_time = 19-APR-2007 01:14:23
Revision_time = 23-APR-2007 02:05:41
Current_time = 23-APR-2007 02:06:18
Content = Single Pulse Experime
Data_format = 1D COMPLEX
Dim_size = 16384
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 500
Spectrometer = DELTA_NMR
Field_strength = 11.7473579[T] (500[MH
X_acq_duration = 2.1823488[s]
X_domain = 1H
X_freq = 500.15991521[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 0.45822189[Hz]
X_resolution = 7.50750751[kHz]
X_sweep = FALSE
Clipped = 1
Mod_return = 16
Scans = 16
Total_scans = 16
X_90_width = 18.5[us]
X_acq_time = 2.1823488[s]
X_angle = 45[deg]
X_pulse = 9.25[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 25
Relaxation_delay = 2[s]
Temp_get = 25[dC]
Unblank_time = 2[us]
(Millions)
X : parts per Million : 1H
7.2614
6.6265
6.6036
6.3470
6.3251
4.2408
4.2216
4.2179
1.5391
0.0000
2.01
2
4.08

(Millions)
X : parts per Million : 1H
6.6265
6.6150
6.6036
6.3470
6.3361
6.3251
11.46
11.00

REFERENCES

1. Shirakawa, H. *Angew. Chem. Int. Ed.* **2001**, 40, 2575.

2. MacDiarmid, A. G. *Angew. Chem. Int. Ed.* **2001**, 40, 2581.

3. Heeger, A. J. *Angew. Chem. Int. Ed.* **2001**, 40, 2591.

4. Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc , Chem. Commun.* **1977**, 578.

5. Chiang, C. K.; Fincher, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, 39, 1098.

6. Ivory, D. M.; Miller, M. M.; Sowa, J. M.; Shacklette, L. W.; Chance, R. R.; Baughman, R. H. *J. Chem. Phys.,* **1979**, 71, 1506.

7. Chen, X.; Hou, C.; Chen, Y.; Wu, Q. *Plastics Industry* **1994,** 1, 53.

8. Lin, P.; Dudek, L. *J. Polym. Sci. Polym. Chem. Ed.* **1980**, 18, 2869.

9. Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc. Chem. Commun.* **1986**, 1346.

10. Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1979**, 635.

11. Yue, J.; Epstein, A. J.; MacDiarmid, A. G. *Mol. Cryst. Liq. Cryst*. **1990**, 189, 255.

12. Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun*. **1984**, 25, 327.

13. Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun*. **1987**, 28, 229.

14. Choi, S. K.; Gal, Y. S.; Jin, S. H.; Kim, H. K. *Chem. Rev.* **2000**, 100, 1645.

15. Bredas, J. L.; Themans, B.; Fripiat, J. G; Andre, J. M.; Chance, R. R. *Phys. Rev. B* **1984**, 29, 6761.

16. Van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Mater. Sci. Eng.* **2001**, *R*32, 1.

17. Boudreaux, D. S.; Chance, R. R.; Bredas, J. L.; Silbey, R. *Phys. Rev. B* **1983**, 28, 6927.

18. Bredas, J. L.; Themans, B.; Fripiat, J. G.; Andre, J. M.; Chance, R. R. *Synth. Met.* **1984**, 9, 265.

19. Chance, R. R.; Bredas, J. L.; Silbey, R. *Phys. Rev. B* **1984**, 29, 4491.

20. Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. ed. *Handbook of Conducting Polymers*, 2nd edition, Marcel Dekker Inc., New York, **1998.**

21. Nalwa, H. S. Ed. *Handbook of organic conductive molecules and polymers,* John Wiley & Sons, Chichester, England, **1997.**

22. Fichou, D. ed, *Handbook of Oligo- and Polythiophenes,* Wiley-VCH, Weinheim, Germany, **1999.**

23. Chan, H. S. O.; Ng, S. C. *Prog. Polym. Sci.* **1998**, 23, 1167.

24. Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc. Chem. Commun.* **1986**, 1346.

25. Elsenbaumer, R. L.; Jen, K. Y.; Oboodi, R. *Synth. Met.* **1986**, 15, 169.

26. De Paoli, M.; Gazotti, W. A. *Macromol. Symp.* **2002**, 189, 83.

27. Bredas J. L.; Silbey, R. ed. *Conjugated Polymers: the novel science and technology of highly conducting and nonlinear optically active materials,* Kluwer Academic Publishers, Dordrecht, **1991.**

28. Eckhardt, H.; Shacklette, L. W.; Jen, K. Y.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, 91, 1303.

29. Street, G. B.; Clarke, T. C.; Kroumbi, M. T.; Kanazawa, K. K.; Lee, V. Y.; Pfluger, P.; Scott, J. C.; Weiser, G. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 253.

30. Hotta, S.; Hosaka, T.; Shimotsuma, W. *Synth. Met.* **1983**, 6, 317.

31. Yamamoto, T.; Sanachika, K.; Yamamoto, A. *Bull. Chem. Soc. Jpn*. **1983**, 56, 1497.

32. Sichel, E. K.; Knowles, M.; Rubner, M.; Georges, J. *J. Phys. Rev.* **1982**, B25, 5574.

33. Chen, T.-A. and Rieke, R. D., *Synth. Met.* **1993**, 60, 175.

34. Leclerc, M.; Bergeron, J. Y. *Synth. Met.* **1993**, 55-57**,** 287.

35. Roux, C.; Bergeron, J. Y.; Leclerc, M. *Makromol. Chem.* **1993**, 194**,** 869.

36. Yoshino, K.; Yin, X. H.; Morita, S.; Kawai, T.; Zakhidov, A. A. *Solid State Commun.* **1993**, 85**,** 85.

37. Chen, S. A.; Hua, M. Y. *Macromolecules* **1993**, 26, 7108.

38. Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc*. **1987**, 109, 1858.

39. Ikenoue, Y.; Votani, N.; Patil, A. O.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1989**, 30, 305.

40. Lanzi, M.; Costa-Bizzarri, P.; Della-Casa, C.; Paganin, L.; Fraleoni, A. *Polymer* **2003**, 44, 535.

41. Daoust, G.; Leclerc, M. *Macromolecules* **1991**, 24, 455.

42. Lanzi, M.; Della-Casa, C.; Costa-Bizzarri, P.; Bertinelli, F. *Macromol. Chem. Phys.* **2001**, 202, 1917.

43. Bertinelli, F.; Costa-Bizzarri, P.; Della-Casa, C.; Lanzi, M. *Spectrochim Acta*, *Part A*, **2002**, 58, 585.

44. Wudl, F.; Kobiyashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, 49, 3382.

45. Jen, K. Y.; Elsenbaumer, R. L. *Synth. Met.* **1986,** 16, 379.

46. Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1984**, 82, 5717.

47. Ruhe, J.; Berlin, A.; Wegner, G. *Macromol. Chem. Phys.* **1995,** 196, 225.

48. Dietrich, M.; Heinze, J.; Heywang, G.; Jonas, F. *J. Electroanal. Chem.* **1994**, 369, 87.

49. Jonas, F.; Heywang, G. *Electrochim. Acta* **1994,** 39, 1345.

50. Kumar, A.; Reynolds, J. R. *Macromolecules* **1996,** 29, 7629.

51. Shiraishi, K.; Kanbara, T.; Yamamoto, T.; Groenendaal, L. *Polymer* **2001**, 42, 7229.

52. Wang, C.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1995**, 7, 58.

53. Pomerantz, M.; Chaloner-Gill, B.; Harding, L. O.; Tseng, J. J.; Pomerantz, W. J. *J. Chem. Soc., Chem. Commun*. **1992**, 22, 1672.

54. Pomerantz, M.; Chaloner-Gill, B.; Harding, L. O.; Tseng, J. J.; Pomerantz, W. J. *Synth. Met*. **1993**, 55, 960.

55. Ferraris, J. P.; Lambert, T. L. *J. Chem. Soc., Chem. Commun*. **1991**, 18, 1268.

56. Toussaint, J. M.; Bredas, J. L. *Synth. Met*. **1993**, 61, 103.

57. Gandhi, G.; Bakhshi, A. K. *Chem. Phys.* **2005**, 309, 143.

58. Turbiez, M.; Frere, P.; Leriche, P.; Mercier, N.; Roncali, J. *Chem. Commun*. **2005**, 1161.

59. Jonas, F.; Heywang, G.; Schmidtberg, W.; Heinze, J.; Dietrich, M. Bayer AG. *Eur. Pat. Appl*. **1989**, EP 0339340.

60. Jonas, F.; Schrader, L. *Synth. Met.* **1991**, 41, 831.

61. Jonas, F.; Krafft, W. *U.S. Pat. Appl. Publ*. **1994,** US 5300575.

62. Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000,** 12, 481.

63. Jen, K. Y.; Maxfield, M.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun*. **1987**, 309.

64. Bolognesi, A.; Catellani, M.; Porzio, W.; Speroni, F.; Galarini, R.; Musco, A.; Pontellini, R. *Polymer* **1993**, 34, 4150.

65. Jen, K. Y.; Eckhardt, H.; Jow, T. R.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun*. **1988**, 215.

66. Eckhardt, H.; ; Shacklette, L. W.; Jen, K. Y.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, 91, 1303.

67. Cheng, H.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun*. **1995**, 1451.

68. Van Dort, P. C.; Pickett, J. E.; Blohm, M. L. *Synth. Met.* **1991**, 42, 2305.

69. Blohm, M. L.; Pickett, J. E.; Van Dort, P. C. *Macromolecules* **1993**, 26, 2704.

70. D'Ilario, L.; Ettorre, A.; Ortaggi, G.; Sleiter, G. *J. Mater. Sci.* **1995**, 30**,** 4273.

71. Ng, S.; Ong, T.; Chan, H. S. O. *J. Mater. Chem*. **1998**, 8, 2663.

72. Jen, K. Y.; Jow, R.; Shacklette, L. W.; Maxfield, M.; Eckhardt, H.; Elsenbaumer, R. L. *Mol. Cryst. Liq. Cryst.* **1987**, 160, 69.

73. Jen, K. Y.; Han, C. C.; Elsenbaumer, R. L. *Mol. Cryst. Liq. Cryst.* **1990**, 186, 211.

74. Mao, H.; Xu, B.; Holdcroft; S. *Macromolecules* **1993,** 26, 1163.

75. Mao, H.; Holdcroft, S. *Macromolecules* **1992,** 25, 554.

76. Sato, M.; Morii, H. *Macromolecules* **1991**, 24, 1196.

77. Souto Maior, R. M.; Hinkelmann, K.; Eckert, H.; Wudl, F. *Macromolecules* **1990**, 23, 1268-1279**.**

78. McCullough, R. D.; Tristram-Nagle, S.; William, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, 115, 4910.

79. McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, 58, 904.

80. Chen, T.-A.; Wu, X.; Rieke, R. D**.** *J. Am. Chem. Soc*. **1995**,117, 233.

81. Chen, T.-A.; Rieke, R. D**.** *J. Am. Chem. Soc*. **1992**,114, l0087.

82. Chen, T.-A.; O'Brien, R. A.; Rieke, R. D. *Macromolecules* **1993**, 26, 3462.

83. McCullough, R. D.; William, S. P.; Tristram-Nagle, S.; Jayaraman, M.; Ewbank, P. C.; Miller, L. *Synth. Met.* **1995**, 69, 279.

84. McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70.

85. Kumada, M. *Pure Appl. Chem.* **1980**, 52, 669.

86. Negishi, E. *Organometallics in organic synthesis,* Wiley & Sons, New York, **1980.**

87. Stille , J. K. *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 508.

88. Iraqi, A.; Barker, G. W. *J. Mater. Chem.* **1998**, 8*,* 25.

89. Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Satoh, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, 111, 314.

90. Guillerez, S.; Bidan, G. *Synth. Met.* **1998**, 93, 123.

91. Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, 34, 4324.

92. Pomerantz, M.; Cheng, Y.; Kasim, R. K.; Elsenbaumer, R. L. *J. Mater. Chem.* **1999**, 9, 2155.

93. Maior, R. M. S.; Hinkelmann, K.; Eckert, H.; Wudl, F., *Macromolecules* **1990**, 23**,** 1268.

94. Pron, A.; Louarn, G.; Lapkowski, M.; Zagorska, M.; Glowczy-Zubek, J.; Lefrant, S. *Macromolecules* **1995**; 28, 4644.

95. Havinga, E. E.; Ten Hoeve, W.; Wynberg, H. *Polym. Bull.* **1992**, 29, 119.

96. Havinga, E. E.; Ten Hoeve, W.; Wynberg, H. *Synth. Met.* **1993**, 55-57, 299.

97. Dohler, G. *IEEE J. Quant. Electron.* **1986**, 22, 1682.

98. Brocks, G.; Tol, A. *J. Phys. Chem*. **1996,** 100, 1838.

99. Brocks, G.; Tol, A. *Synth. Met*. **1996,** 76, 213.

100. van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meije, E. W. *Chem. Eur. J.* **1998,** 4**,** 1235.

101. Gandhi, G.; Bakhshi, A. K. *Chem. Phys.* **2005**, 309, 143.

102. Joule, J. A.; Mills, K.; Smith, G. F. *Heterocyclic chemistry,* 3rd*,* Chapman & Hall, London, **1995.**

103. Lorcy, D.; Cava, M. P. *Adv. Mater.* **1992**, 4**,** 562.

104. Lakshmikantham, M. V.; Lorcy, D.; Scordilis-Kelley, C.; Wu, X.; Parakka, J. P.; Metzger, R. M.; Cava, M. P. *Adv. Mater.* **1993**, 5, 562.

105. Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, 8, 570.

106. King, G.; Higgins, S. J. *J. Mater. Chem.* **1995,** 5, 447.

107. Tanaka, S.; Yamashita, Y. *Synth. Met.* **1995,** 69, 599.

108. Karikomi, M.; Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Am. Chem. Soc*. **1995**, *117*, 6791.

109. Kitamura, C.; Tanaka, S.; Yamashita, Y.; *Chem. Mater.* **1996**, 8, 570.

110. Lu, H. F.; Chan, H. S. O.; Ng, S. C.; *Macromolecules* **2003,** 36, 1543.

111. Yamamoto, T.; Arai, M.; Kokubo, H.; Sasaki, S. *Macromolecules* **2003**, 36, 7986.

112. Yamamoto, T.; Zhou, Z. H.; Kanbara, T.; Shimura, M.; Kizu, K.; Maruyama, T.; Nakamura, Y.; Fukuda, T.; Lee, B. L.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K.; Sasaki, S.; *J. Am. Chem. Soc.* **1996***,*118*,* 10389.

113. Lee, B. L.; Yamamoto, T. *Macromolecules* **1999**, 32, 1375.

114. Huang, H.; Pickup, P. G. *Chem. Mater.* **1998,** 10, 2212.

115. Salzner, U. *J. Phys. Chem. B* **2002,**106, 9214.

116. Salzner, U.; Kose, M. E. *J. Phys. Chem. B* **2002,**106, 9221.

117. Braunling, H.; Becker, R.; Blochl, G. *Synth. Met*. **1991,** 41-43, 1539.

118. Braunling, H.; Becker, R.; Blochl, G. *Synth. Met*. **1993,** 55-57, 833.

119. Chen, W. C.; Jenehke, S.A. *Macromolecules* **1995,** 28, 465.

120. Yamamoto, T.; Abla, M. *Synth. Met.* **1999**, 100, 237.

121. Jonas, F.; Krafft, W.; Muys, B. *Macromol. Symp*. **1995,** 100, 169.

122. Cravino, A.; Zerza, G.; Maggini, M.; Bucella, S.; Svensson, M.; Anderson, M. R.; Neugebauer, H.; Brabec, C. J.; Sariciftci, N. S. *Monatshefte fur Chemie* **2003,** 134, 519.

123. Kim, D. Y.; Cho, H. N.; Kim, C. Y. *Prog. Polym. Sci*. **2000**, 25 1089.

124. J. W. Brown, G. J. Lambe, P. J. Foot, J. A. Clipson, *Macromol. Rapid Commun.* **2004**, 25, 1004.

125. Lopes, W. A.; Jaeger, H. M. *Nature* **2001**, 414, 735.

126. Saxena, V.; Malhotra, B. D. *Current Applied Physics* **2003**, 3, 293.

127. Whitesides, G. M.; B. Grzybowski, B. *Science* **2002**, 295, 2418.

128. Osterbacka, R.; An, C. P.; Jiang, X. M.; Vardeny, Z. V. *Science* **2000**, 287, 839.

129. Reitzel, N.; Greve, D. R.; Kjaer, K.; Howes, P. B.; Jayaraman, M.; Savoy, S.; McCullough, R. D.; McDevitt, J. T.; Bjornholm, T. *J. Am. Chem. Soc.* **2000,** 122*,* 5788.

130. Lee, S.; Kang, Y.; Lee, C. *Synth. Met.* **2001**, 117, 257.

131. McCullough, R. D.; Ewbank, P. C.; Loewe, R. S. *J. Am. Chem. Soc.* **1997**, 119, 633.

132. Sato, N.; Rikukawa, M.; Sanui, K.; Ogata, N. *Synth. Met.* **1999**, 101, 132.

133. Rep, D. B. A.; Roelfsema, R.; van Esch, J.; Schoonbeek, F. S.; Kellogg, R. M.; Feringa, B. L.; Palstra, T. T. M.; Klapwijk, T. M. *Adv. Mater.* **2000**, 12, 563.

134. Ewbank, P. C.; Loewe, R. S.; Zhai, L.; Reddinger, J.; Sauve, G.; McCullough, R. D. *Tetrahedron* **2004**, 60, 11269.

135. Hulvat, J. F.; Stupp, S. I. *Angew. Chem. Int. Ed.* **2003,** 42, 778.

136. Leclere, Ph.; Surin, M.; Viville, P.; Lazzaroni, R.; Kilbinger, A. F. M.; Henze, O.; Feast, W. J.; Cavallini, M.; Biscarini, F.; Schenning, A. P. H. J.; Meijer, E. W. *Chem. Mater.* **2004**, 16, 4452.

137. Ionescu-Zanetti, C.; Mechler, A.; Carter, S. A.; Lal, R. *Adv. Mater.* **2004,** 16, 385.

138. Boehme, J. L.; Mudigonda, D. S. K.; Ferraris, J. P. *Chem. Mater*. **2001**, 13, 4469.

139. Roberson, L. B.; Poggi, M. A.; Kowalik, J.; Smestad, G. P.; Bottomley, L. A.; Tolbert, L. M. *Coord. Chem. Rev.* **2004**, 248, 1491.

140. Hebestreit, N.; Hofmann, J.; Rammelt, U.; Plieth, W. *Electrochimi. Acta* **2003**, 48, 1779.

141. Macchi, G.; Meinardi, F.; Simonutti, R.; Sozzani, P.; Tubino, R. *Chem. Phys. Lett.* **2003**, 379, 126.

142. Vidya, V.; Ambily, S.; Narang, S. N.; Major S.; Talwar, S. S. *Colloids and Surf. A* **2002**, 198-200, 383.

143. Roncali, J. *Chem. Rev*. **1992**, 92, 731.

144. Isotalo, H.; Ahlskog, M.; Stubb, H.; Laakso, J.; Karna, T.; Jussila, M.; Osterholm, J. E. *Synth. Met.* **1993**, 57, 3581.

145. Gangopadhyay, R.; De, A. *Chem. Mater.* **2000**, 12, 608.

146. Arimoto, F. S.; Haven, A. C. Jr. *J. Am. Chem. Soc.* **1955,** 77, 6295.

147. Kingsborough, R. P.; Swager, T. M. *Prog. Inorg. Chem*. **1999**, 48, 123.

148. Wohrle, D.; Pomogailo, A. D. *Metal Complexes and Metals in Macromolecules, Synthesis, Structure and Properties,* Wiley-VCH, Weinheim, Germany, **2003.**

149. Abd-El-Aziz, A. S. et al. ed. *Macromolecules containing metal and metal-like elements,* John Wiley & Sons, Inc. Hoboken, New Jersey, **2003.**

150. Kingsborough, R.; Swager, T. M. *Prog. Inorg. Chem.* **1999,** 48, 123.

151. Abd-El-Aziz, A. S. et al. ed. *Frontiers in transition metal-containing polymers*, Wiley-Interscience, Hoboken, New Jersey, **2007.**

152. Holliday, B. J.; Swager, T. M. *Chem. Commun.* **2005**, 23.

153. Archer, R.D. *Inorganic and organometallic polymers*, Wiley-VCH, New York, **2001.**

154. Wolf, M. O. *Journal of Inorganic and Organometallic Polymers and Materials,* **2006**, 16, 189.

155. Barford, W. *Electronic and optical properties of conjugated polymers*, Clarendon Press, Oxford, UK, **2005.**

156. Moorlag, C.; Clot, O.; Zhu, Y.; Wolf, M. O. *Macromol. Symp.* **2004**, 209, 133.

157. Solomon, E. I.; Gorelsky, S. I.; Abhishek Dey, A. *Jouranl of Computational Chemistry* **2006**, 27, 1415.

158. Nakamura, A.; Ueyama, N.; Yamaguchi, K. ed. *Organometallic conjugation,* New York, Springer **2002.**

159. Fu, Y.; Cheng, H.; Elsenbaumer, R. L. *Chemistry of Materials* **1997**, 9, 1720.

160. Cheng, H.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1451.

161. Turbiez, M.; Frere, P.; Roncali, J. *Tetrahedron* **2005**, 61, 2045.

162. Wagner, P.; Ballantyne, A. M.; Jolley, K. W.; Officer, D. L. *Tetrahedron* **2006**, 62, 2190.

163. Kubo, M.; Takimoto, C.; Minami, Y.; Uno, T.; Itoh, T. *Macromolecules* **2005**, 38, 7314.

164. Bolognesi, A.; Catellani, M.; Porzio, W.; Speroni, F.; Galarini, R.; Musco, A.; Pontellini, R. *Polymer* **1993**, 34, 4150.

165. Galarini, R.; Musco, A.; Pontellini, R.; Bolognesi, A.; Catellani, M.; Destri, S.; Mascherpa, M.; Zhuo, G. J. *J. Chem. Soc., Chem. Commun*. **1991**, 364.

166. Hou, J.; Tan, Z.; He, Y.; Yang, C.; Li, Y. *Macromolecules* **2006**, 39, 4657.

167. Jen, K. Y.; Eckhardt, H.; Jow, T. R.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun*. **1988**, 215.

168. Blohm, M. L.; Pickett, J. E.; Van Dort, P. C. *Macromolecules* **1993**, 26, 2704.

169. Tsuie, B.; Wagener, K. B.; Reynolds, J. R. *Polymer Preprints* **1999**, 40, 790.

170. Iwatsuki, S.; Kubo, M.; Ito, Y. *Chem. Lett*. **1993**, 1085.

171. Zhou, G.; Li, J.; Ye, C. *Synth. Met*. **2003**, 135-136, 485.

172. Elandaloussi, E. H.; Frere, P.; Richomme, P.; Orduna, J.; Garin, J.; Roncali, J. *J. Am. Chem. Soc.* **1997**, 119, 10774.

173. Ono, N.; Okumura, H.; Murashima, T. *Heteroatom Chemistry* **2001**, 12, 414.

174. Hou, J.; Yang, C.; Qiao, J.; Li, Y. *Synth. Met.* **2005**, 150, 297.

175. Gilch, H. G.; Wheelwright, W. L. *J. Polym. Sci. Part A: Polym. Chem.* **1966**, 4, 1337.

176. Chiang, Y.; Shu, P.; Holt, D.; Cowan, D. *J. Org. Chem.* **1983**, 48, 4713.

177. Skabara, P. J.; Roberts, D. M.; Serebryakov, I. M.; Pozo-Gonzalo, C. *Chem. Commun.* **2000**, 1005.

178. Skabara, P. J.; Berridge, R.; Mcinnes, E. J. L.; West, D. P.; Coles, S. J.; Hursthouse, M. B.; Mullen, K. *J. Mater. Chem.* **2004**, 14, 1964.

179. Berridge, R.; Skabara, P. J.; Pozo-Gonzalo, C.; Kanibolotsky, A.; Lohr, J.; McDouall, J. J. W.; McInnes, E. J. L.; Wolowska, J.; Winder, C.; Serdar Sariciftci, N.; Harrington, R. W.; Clegg, W. *J. Phys. Chem. B* **2006**, 110, 3140.

180. Roncali, J. *J. Mater. Chem.* **1997**, 7, 2307.

181. Bricklebank, N.; Skabara, P. J.; Hibbs, D. E.; Hursthouse, M. B.; Abdul Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1999**, 3007.

182. Skabara, P. J.; Roberts, D. M.; Ray, A. K.; Umare, S. S.; Hassan, A. K.; Nabok, A. V.; Mullen, K. *Mat. Res. Soc. Symp. Proc.* **2002**, 665, 45.

183. Barker, J. M.; Huddleston, P. R.; Wood, M. L. *Synth. Commun.* **1975**, 5, 59.

184. Halfpenny, J.; Rooney, P. B.; Sloman, Z. S. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2595.

185. Tsuzuki, H.; Maeda, T.; Yonemitsu, T.; Mukumoto, M.; Mataka, S.; Tashiro, M.; *Kyushu Daigaku Sogorikogaku Kenkyuka Hokoku* **1993**, 15, 181.

186. Griffing, J. M.; Salisbury, L. F. *J. Am. Chem. Soc.* **1948**, 70, 3416.

187. Ozanne, A.; Pouysegu, L.; Depemet, D.; Francois, B.; Quideau, S. *Org. Lett*. **2003**, 5, 2903.

188. Corey, E. J.; Ensley, H. E.; Suggs, J. W. *J. Org. Chem.* **1976**, 41, 380.

189. Son, S.; Dadabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, 269, 376.

190. Lo, S. C.; Palsson, L. O.; Kalitziraki, M.; Burn, P. L.; Samuel, I. D. W. *J. Mater. Chem.* **2001**, 11, 2228.

191. Henckens, A.; Colladet, K.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Gelan, J.; Vanderzande, D. *Macromolecules* **2005**, 38, 19.

192. Gillissen, A.; Henckens, A.; Lutsen, L.; Vanderzande, D.; Gelan, J. *Synth. Met.* **2003**, 135-136, 255.

193. Ishiguro, T.; Yamaji, K.; Saito, G. ed. *Organic Superconductors, 2rd Ed*. Springer-Verlag, Berlin Heidelberg, **1998**.

194. Akoudad, S.; Frere, P.; Mercier, N.; Roncali, J. *J. Org. Chem*. **1999**, 64, 4267.

195. Brisset, H.; Thobie-Gautier, C.; Jubault, M.; Gorgues, A.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1994**, 1765.

196. Elandaloussi, E.; Frere, P.; Roncali, J.; Richomme, P.; Jubault, M.; Gorgues, A. *Adv. Mater.* **1995**, 7, 390.

197. Elandaloussi, E.; Frere, P.; Roncali, J. *Tetrahedron Lett.* **1996**, 37, 6121.

198. Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z.; Nakamura, Y.; Kanbara, T. *Macromolecules,* **1992**, 25, 1214.

199. Pomerantz, M.; Yang, C.; Kasim, R. K.; Elsenbaumer, R. L. *J. Mater. Chem.* **1999**, 9, 2155.

200. Bao, Z.; Chan, W.; Yu, L. *Chem. Mater.* **1993**, 5, 2

201. Bao, Z.; Chan, W.; Yu, L. *J. Am. Chem. Soc.* **1995**, 117, 12426

202. Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, 113, 8375

203. Amatore, C.; Jutand, A.; Suarez, A. *J. Am. Chem. Soc*. **1993**, 115, 9531.

204. Espinet, P.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2004**, 43, 4704

205. Cheng, H. *New precursors and polymerization route for the preparation of high molecular mass poly(3,4-dialkoxy-2,5-thienylene vinylene)s: low band gap conductive polymers*. The University of Texas of Arlington, **1995**.

206. Badudri, F.; Farinola, G. M.; Naso, F. *J. Mater. Chem*. **2004**, 14, 11.

207. Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, 34, 4324.

208. Zhu, Y.; Wolf, M. O. *J. Am. Chem. Soc*. **2000**, 41, 10121.

209. Silverstein, R. M.; Webster, F. X. *Spectrometric identification of organic compounds, 6th ed.* John Wiley and Sons, Inc. **1998**

210. Foster, C. M.; Kim, Y. H.; Uotani, N.; Heeger, A. J. *Synth. Met.* **1989**, 29, E135

211. W. G. Kofron, L. M. Baclawski, *J. of Org. Chem.* **1976**, 41, 1879

212. Janda, M.; Srogl, J.; Stibor, I.; Nemec, M.; Vopatrna, P. *Synthesis*, **1972**, 545

213. Weigert, F. J.; Roberts, J. D. *Inorg. Chem.* **1973**, 12, 313

BIOGRAPHICAL INFORMATION

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