
**The Effect of Alkyl Chain Parity on the In Situ Covalent
Modification of Carboxy Terminated Alkane Thiol SAMs**

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Abstract

This research investigated the covalent modification of self-assembled monolayers (SAMs) formed on gold substrates. Specifically, this work explored the esterification and amidification reactions of alkanethiol SAMs that contained even or odd number of methylene groups. The reactions were conducted using a common acid chloride intermediate that was generated in situ on the surface by treating the carboxy groups on the SAMs with oxalyl chloride. The reaction of aliphatic and aromatic alcohols and amines was explored to test the versatility of the reaction and the influence of the alkyl chain parity on the expected outcomes. The coupling reactions were monitored and analyzed using grazing angle FT-IR spectroscopy. It is shown that an activated acid monolayer surface is reactive to coupling with alcohols and amines.

The Effect of Alkyl Chain Parity on the In Situ Covalent Modification of Carboxy Terminated Alkane Thiol SAMs

1. Scope and Background

The goal of this research is to create self-assembled monolayers (SAMs) of ω -carboxy alkanethiols formed on gold and explore their reactivity toward alcohols and amines through an acid chloride intermediate. Specifically, this work tested four thiols that have either an even or an odd number of carbon atoms. This section gives a brief overview of self-assembly, SAMs, alkyl chain parity, the previous work in this area, and the common characterization techniques used in the monitoring of reaction chemistry.

1.1 Self-Assembly is the process by which multiple smaller constituent pieces assemble naturally and spontaneously to create a larger bulk material. Self-assembly can generate intricate and complicated structures from relatively simple components. Common instances of self-assembly are micelles¹, protein-binding², coiling double helix pairs³, molecular fabrication⁴, even the formation of crystals⁵. The elegance of self-assembling is that it uses weak interactions to fabricate robust structures which can be functionalized or modulated for specific applications.

1.2 Self-Assembled Monolayers are ultra-thin films with a single molecule thickness; these films are bonded covalently to a surface, and they display a high degree of

structural organization. The SAMs can be made from and deposited onto a variety of components and substrates, including monolayers of fatty acids on metal oxides⁶, silanes on oxidized glass, and alkane thiols⁷ on coinage and other metals. SAMs are used for a variety of applications including biomedical research⁸, nanoscale sensors⁹, organic solar cells¹⁰, and templated nucleation of polymorphic compounds¹¹. One of the major limitations of using self-assembled monolayers is that the terminal functional group may have a propensity to react with the surface-anchoring tail group. This limits the number of potential terminal head groups to be used, thus limiting the versatility of self-assembled monolayers in general.

1.3 Alkanethiol SAMs possess distinct advantages over other types of SAMs mentioned above. The primary advantage of SAMs based on alkanethiols is that they can be fabricated in a simple and reproducible manner. The fabrication involves the immersion of gold substrates into dilute solutions (~0.03 mM) of alkanethiols in ethanol. The thiol group bonds covalently to the gold atoms on the surface; the gold-bonded alkanethiol molecules move freely at the interface until the alkyl chains adopt a close packed structure

Thus, alkanethiols form monolayers in two steps, first rapid bonding to the surface followed by a slow organization period. Alkanethiols containing less than eight carbon atoms form disordered monolayers. Longer chain alkanethiols containing ten or more methylene units are known to form ordered monolayers despite a liquid-like packing of

the alkane chains.¹² Alkanethiols with greater than eleven methylene units adopt well ordered, crystalline monolayers with greater than 95% surface coverage (**Figure 1**).

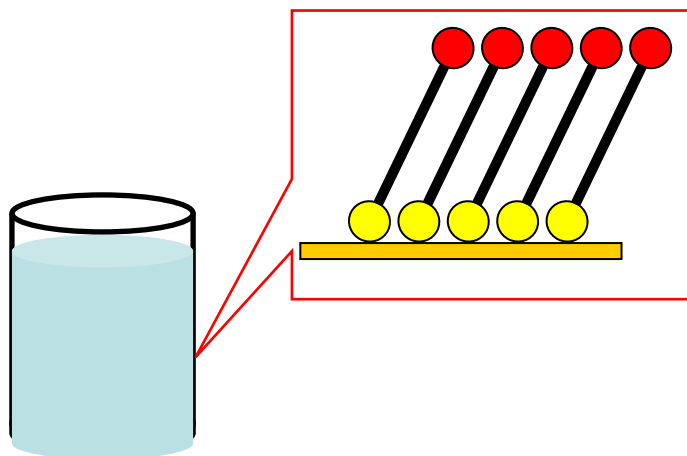


Figure 1. Alkanethiols pack into well ordered monolayers over a period of 2-16 hours when exposed to gold substrates placed in solution. The sulfur atom (yellow) is bonded to the gold surface; it is connected to the active head group (red) by a straight chain of methylene linkers.

1.4 Parity of Alkyl Chains refers to the even or odd number of carbon atoms contained within the chain^{13,14}. The tilt angle inherent in the well-packed monolayer does not differ between odd and even chains; however, if the terminal functional group is bound to an odd chain length it will have a different orientation to the surface normal compared to an even chain (**Figure 2**).

1.5 Common Characterization Techniques include measurement of the advancing and receding contact angles of common solvents on the monolayer using a goniometer. This method gives a measure of the polarity or hydrophobicity of the SAM/solvent interface.

The contact angle data can be used to deduce the chemical nature of the surface head groups, the interfacial free energy and, to a lesser extent, the coverage of the monolayer on the substrate.

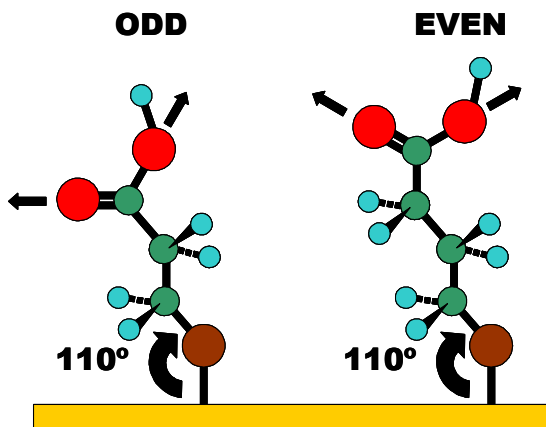


Figure 2. The effect of parity of an alkyl chain on the relative orientation of terminal groups.

Grazing incidence Fourier transform infrared spectroscopy (IR) provides more information about the functional groups of a monolayer. The specific vibrational frequencies of surface functional groups vary from their solid-state IR frequencies due to their well ordered orientation and a lack of hydrogen bonds. IR data of the compounds closer to the gold-sulfur bond of the monolayer are often not visible in the spectrum, due to insulation from functional groups on the surface of the well-packed SAM.

If the gold surface is submerged in a conducting solution, the electrical insulation of the monolayer can be measured through cyclic voltammetry (CV) experiments or impedance measurements. These techniques create a charge potential between the gold surface and

the conducting solution, which can provide information regarding the surface coverage of the SAM.

1.6 Previous Work on SAM fabrication was limited by reactivity of the head group with its own tail, in this case a thiol. This limitation of direct synthesis of the target molecule for deposition excludes complicated molecules, as the required organic synthesis and purification can prove to be tedious and time consuming before it is suitable for the formation of SAMs. The alternative method, examined here, is to create an alkane thiol with a head group that is susceptible to nucleophilic attack after deposition onto gold. This allows for functionalizing the monolayer surface after the organization has already taken place, making monolayers of thiol-reactive compounds or difficult target molecules possible.

There are multiple examples in the literature of on-board reactions¹⁵⁻²⁰, referring to in-situ functionalization of SAMs, with varying degrees of success. Amidification and esterification reactions are desired because of the facile manner in generating a variety of head groups using an acyl halide common intermediate that is readily generated in-situ. The first research of the reactivity of carboxylic acid terminated SAMs in 1992²¹ began by reacting monolayer surfaces with oxalyl chloride to create an acid-chloride terminated SAM. In that study, 11-mercaptoundecanoic acid (11-acid) was chosen as the thiol molecule because the liquid-like structure of the monolayer permits steric freedom of the carboxylic acid head group. This methodology produced successful ester and amide bond formation between desired head groups and the acid chloride.

Attempts to react the surface with oxalyl chloride in a dichloromethane solution were reported to strip the 11-acid monolayer off of the substrate, so the reaction was performed in the gas phase under reduced pressure (300-500 mTorr). The surfaces were activated with gaseous oxalyl chloride, which was assumed to produce the acid chloride derivative of the 11-acid surface, observed via a shift in the IR spectrum of the carboxyl peak from 1704 cm^{-1} to 1814 cm^{-1} . This activated surface then readily reacted with amines to produce an amide bond (**Figure 3**).

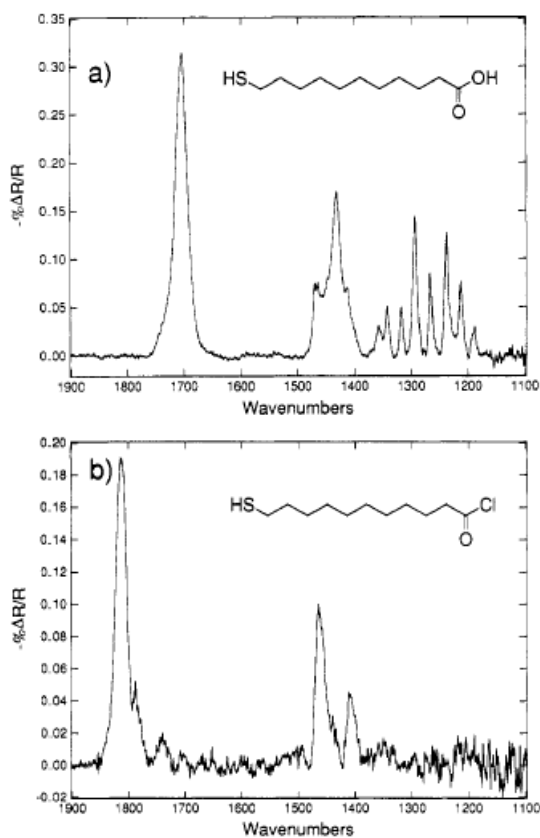


Figure 3. The mid range IR spectrum of a) the unreacted 11-acid monolayer, exhibiting a carbonyl stretching band at 1704 cm^{-1} , and b) the acid chloride derivative monolayer, with a blue-shifted carbonyl band at 1814 cm^{-1} . Reproduced from ref. 2.

The amines examined for surface coupling were n-hexylamine, benzylamine, and aniline. IR spectra of the reacted surfaces recorded characteristic amide I and II bonds at 1642 and 1550 cm^{-1} respectively. These peaks were broad, which was interpreted as hydrogen bonding at the surface of the monolayer. Further analysis with X-ray photoelectron spectrometry (XPS) data confirmed the decrease in the 1s peak of the oxygen atom after the formation of the amide bonds, due to shielding from the attached species.

Additional tests to create ester bonds were performed, first on ethanol qualitatively. Further investigation examined a ferrocene alcohol [(hydroxylmethyl)ferrocene], which was observed by IR spectroscopy to exhibit ester stretches at 1731 cm^{-1} and 1237 cm^{-1} . The XPS analysis and traces of the acid chloride peak in the IR spectrum suggested that an incomplete reaction with the ferrocene alcohol took place, which was attributed to the experimental methods and steric hindrance from the bulky ferrocene head group. As the ferrocene head group was electroactive, CV results further confirmed their conclusions.

An even shorter acid thiol monolayer was tested for reactivity, mercaptopropanoic acid.²² This compound was activated with di-*tert*-butyl carbodiimide to create a reactive acid derivative species, and the compound trifluoroethanol then readily reacted with the surface. This methodology took days to accomplish thereby limiting the ability to produce a variety of functionalized surfaces in a short time span. Later work on reacting acid terminated monolayers with amines was performed using cyanuric fluoride to create a reactive acid fluoride species on the surface.²³ The acid used to form the original monolayer was the longer 16-mercaptohexadecanoic acid (16-acid). The advantages of

the acid fluoride species was its stability in the presence of atmospheric water, allowing for less rigorous reaction methods. The IR characterization of the 16-acid monolayer observed two carbonyl stretches at 1742 and 1719 cm^{-1} , and the activated acid fluoride species produced a single 1837 cm^{-1} band (**Figure 4**).

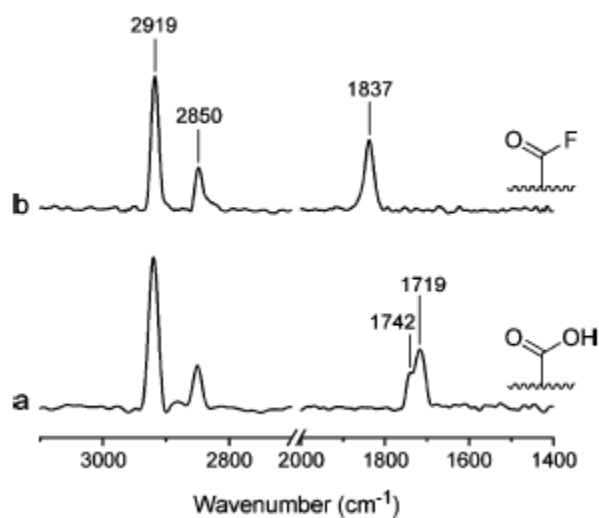


Figure 4. IR spectra of a) 16-acid SAM and b) acid fluoride derivative. Reproduced from Ref 4.

Three amines reacted with the activated acid fluoride surface, undecylamine, phenethylamine, and aniline. When reacted with undecylamine for about one hour, the acid fluoride peak completely disappeared from the IR spectrum, and was replaced with an amide II peak at 1552 cm^{-1} . No amide I peak was reported, assumed due to the parallel orientation of carbonyl groups. The phenethylamine reaction showed signs of residual acid fluoride bands in the IR spectrum after one hour of reaction, these bands disappeared after two hours.

When the secondary amine (diethylamine) was reacted with the activated surface, the acid fluoride peak remained even after 24 hours of reaction, this lack of reactivity attributed to incomplete coupling at the interface caused by steric hindrance. Further reactions between acid fluoride and alcohols did not yield the expected products (esters). An alcohol ferrocene derivative and an amine ferrocene derivative were run in parallel, which were characterized by CV and IR data. The amine reaction was interpreted to completely cover the monolayer surface, but the alcohol appeared to have no reaction.

1.7 Drawbacks of Previous Work included the difficult techniques adopted, such as performing gas or vapor phase reactions, or the reactivity of the surface that was unable to couple alcohols to the SAM via ester bond formation. The experiments outlined here suggest neat (liquid) oxalyl chloride will convert the carboxylic acid surface of a SAM into an acid chloride derivative, allowing further reactivity with alcohol and amines despite limited air exposure. The rapid, more robust method and notable exclusion of expensive equipment prove successful for a wide variety of head group couplings, drastically decreasing the time and money necessary to produce SAMs.

2. Results and Discussion

The goal of this research was to develop a wide variety of SAMs displaying multiple head groups, based on common, commercially available SAMs. Four chemicals for initial deposition were tested, identical with the exception of the length of the carbon chain linking the sulfur atom to the head group, in this case a carboxylic acid (**Figure 5**).

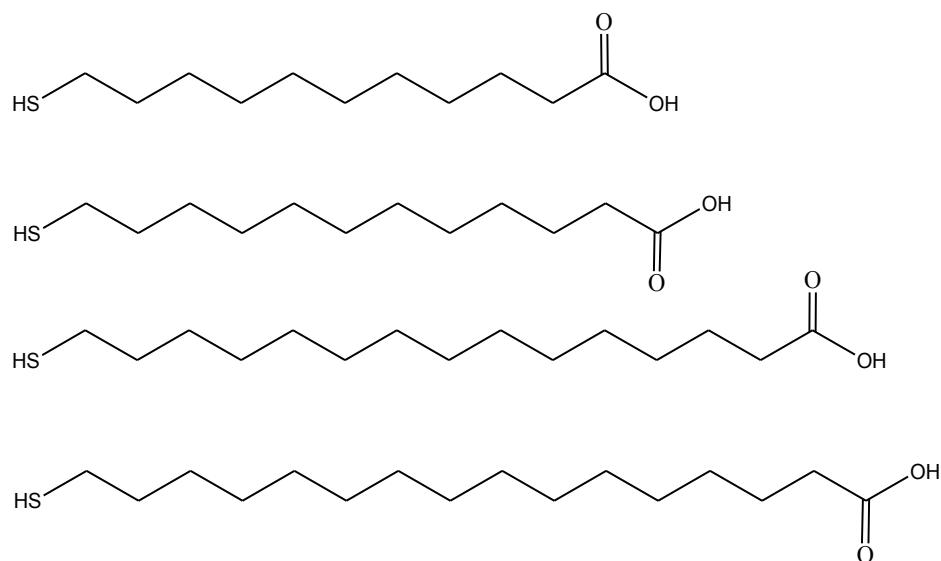


Figure 5. In descending order, 11-mercaptoundecanoic acid, 12-mercaptododecanoic acid, 15-mercaptopentadecanoic acid, and 16-mercaptohexadecanoic acid.

11-Mercaptoundecanoic acid (11-acid), 12-mercaptododecanoic acid (12-acid), 15-mercaptopentadecanoic acid (15-acid) and 16-mercaptohexadecanoic acid (16-acid) were deposited on gold surfaces and reacted with liquid oxalyl chloride. This acid chloride derivative is further reacted with amines and alcohols to form amides and esters. The acids were selected due to their increasing methylene chain length correlating to a more ordered crystal-like monolayer, and to analyze the effects of parity in the case of both a liquid-like and crystal-like monolayer.

2.1 Grazing-Incidence Infrared Spectroscopy was used as the primary method for characterizing the SAMs after formation. Although similar to conventional ATR spectroscopy in that it uses infrared radiation to measure absorbance for a spectrum of frequencies, grazing-incidence IR depends on reflecting the infrared laser off of the gold

slide on which the SAM is terminated. Using this method the absorbance of IR frequencies by the monolayer itself can be examined.

The position and orientation of head groups on the surface limit intermolecular interactions, for example removing the indicative broad $3500\text{-}2500\text{ cm}^{-1}$ carboxylic acid stretch corresponding to extensive hydrogen bonding seen in the solid state. Expected absorption bands for common moieties in bulk compounds were red or blue shifted on SAM surfaces, due to the specific and uniform orientation of the molecules in the monolayer and a lack of hydrogen bonding, thereby making IR the most useful and yet more involved characterization tool available for this research.

The symmetric and antisymmetric stretching vibrations of the methylene groups present between the sulfur atom and the functionalized head group appear at 2919 and 2850 cm^{-1} in a crystalline, well ordered monolayer. The methylene symmetric stretching of SAMs made of 11-acid and 12-acid occurs at 2929 cm^{-1} , suggesting a liquid-like monolayer with heavy disorder. The symmetric stretching of the methylene chains in the SAMs of 15-acid and 16-acid occurs at 2919 cm^{-1} , indicating ordered close-packing of the alkane chains of the surface.

The spectra of the four acids exhibited strong bands at around 1700 cm^{-1} , suggesting hydrogen bonding among the carboxylic acid head groupsⁱⁱ. As noted, the strong carboxylic acid band observed in bulk materials from $3500\text{-}2500\text{ cm}^{-1}$ was not present in the monolayer IR spectra.

2.2 Nucleophilic Substitution chemistry traditionally involves converting carboxylic acids to activated acid chlorides in the presence of oxalyl chloride (**Figure 6**). The expected carbonyl peak of an acid chloride species in a bulk material is $1815\text{-}1790\text{ cm}^{-1}$, but the acid chloride species on each monolayer surfaces consistently absorbed at 1730 cm^{-1} , due to the orientation of the species (**Figure 7**).

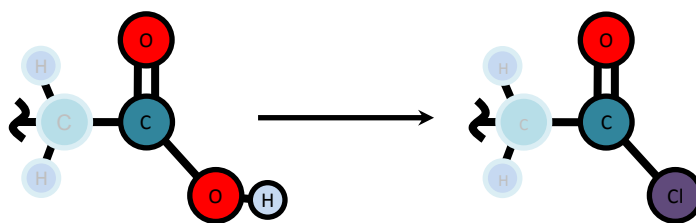


Figure 6. Carboxylic acids undergo nucleophilic substitution when exposed to oxalyl chloride, resulting in a highly unstable and moisture sensitive acid chloride. Acid chlorides rapidly hydrolyze to carboxylic acids when exposed to water.

2.3 The Coupling Reagents were chosen in order to test the effects of steric hinderance, aromaticity, amine/alcohol reactivity, of a variety of compounds. To form ester bonds, ethanol was reacted with the activated surface to create an ester linkage, and 3-nitrophenol and 4-nitrophenol were both tested with the activated surface for reactivity with identical results, representing conjugated esters.

2.4 The SAM of 11-Acid displayed antisymmetric stretching of the methylene units at 2928 cm^{-1} and the symmetric stretching at 2856 cm^{-1} indicating a liquid-like, disordered monolayer (**Figure 10b**). This is due to the short chain length exhibiting very weak van

der Waals forces to hold the methylenes in a solid structure. The subsequent reactions had no effect on the order of the monolayer. The carbonyl region of the base acid peaks at 1691 cm^{-1} and is broad, suggesting hydrogen bonding of the carboxylic acid head groups (**Figure 11b**). With the exception of the activated acid, no carbonyl shift is observed, indicating no successful reactions occurred.

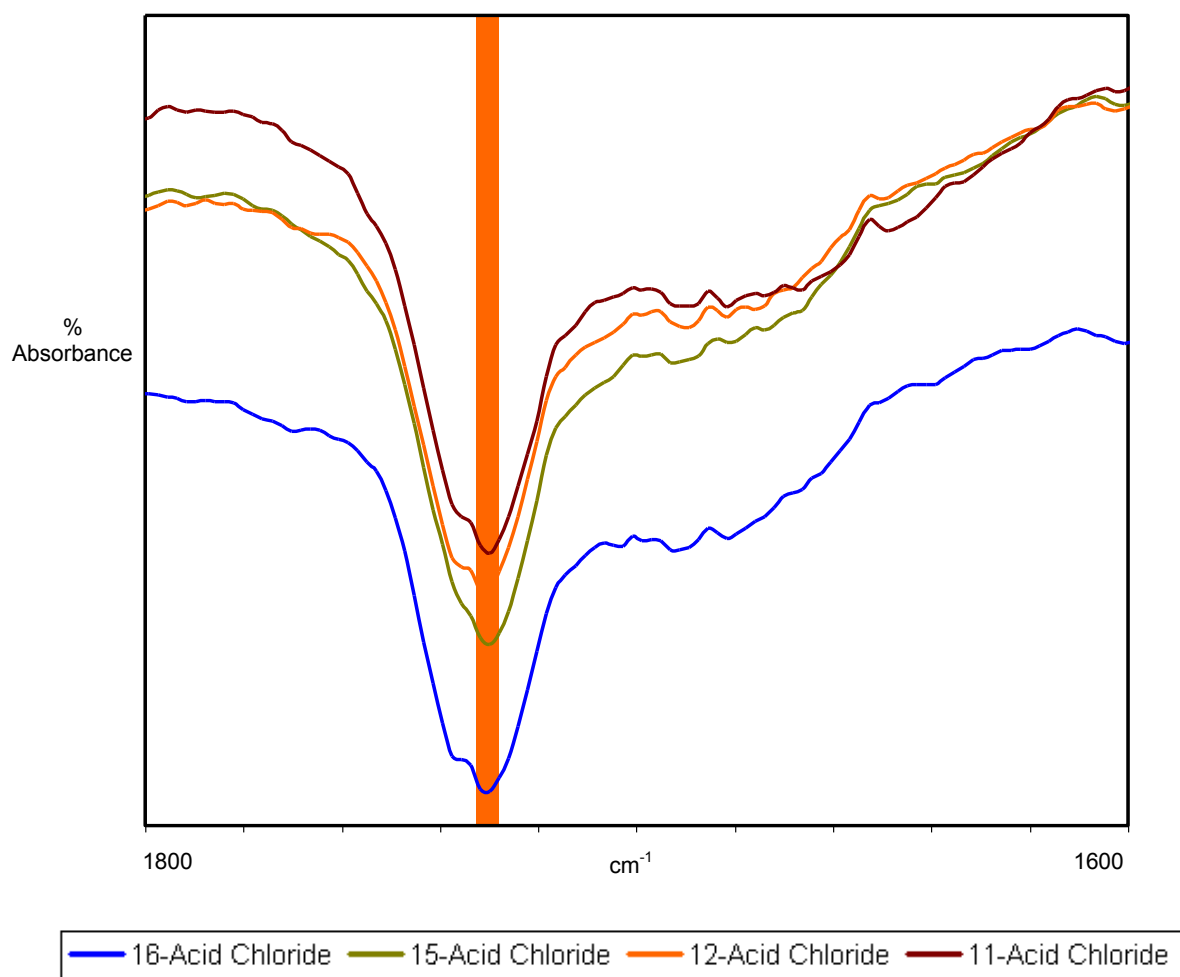


Figure 7. The acid chloride derivative exhibited a strong 1730 cm^{-1} band.

2.5 The SAM of 12-Acid exhibited the antisymmetric methylene stretching of the base acid at 2927 cm^{-1} , suggesting that the monolayer is relatively disordered, with similar results observed after the coupling reactions (**Figure 8b**). The carbonyl region of the carboxylic acid peak occurs at 1713 cm^{-1} and is broad, suggesting hydrogen bonding of the carboxylic acid head groups. The amine reactions of *n*-hexylamine and 4-nitroaniline shifted the carbonyl peak right to $\sim 1675\text{ cm}^{-1}$, indicating a successful amidification reaction. The ethanol reaction led to a blue-shifted carbonyl peak at 1741 cm^{-1} , which was mirrored by 4-nitrophenol, a peak suggesting ester formation was successful for both alcoholic compounds (**Figure 9b**).

2.6 The SAM of 15-Acid exhibited the antisymmetric stretching of the base acid at 2919 cm^{-1} and the symmetric stretching at 2850 cm^{-1} , which indicated a well ordered crystalline monolayer (**Figure 10a**). Any reaction attempts except for *n*-hexylamine indicate disorder in the monolayer by the left-shift of the symmetric and antisymmetric stretching. The carbonyl region of the base acid peaks at 1704 cm^{-1} and is broad, suggesting hydrogen bonding of the carboxylic acid head groups, but with the exception of the activated acid, no carbonyl shift is observed, indicating no successful reactions took place (**Figure 11a**).

2.7 The SAM of 16-Acid exhibited the antisymmetric methylene stretching band at 2919 cm^{-1} of the base acid indicating a well ordered monolayer, as did the 2850 cm^{-1} symmetric stretch. The shift in the methylene absorptions in the spectrum of the activated

SAM suggests disorder, which carried through to the nitrophenol and ethanol ester derivatives, as well as the nitroaniline derivative. When reacted with *n*-hexylamine, crystalline order of the monolayer was preserved (**Figure 8a**). The carbonyl stretching of the carboxylic acid is visible at approximately 1704 cm^{-1} , suggesting hydrogen bonding among the carboxylic acid groups. The amide derivative reactions uniformly right shifted the carbonyl peak to the $1690\text{-}1700\text{ cm}^{-1}$, whereas the ethanol ester derivative shifted the carbonyl peak to 1741 cm^{-1} , indicative of an ester. The nitrophenol is assumed to have not reacted with the terminal acid chloride head group (**Figure 9a**).

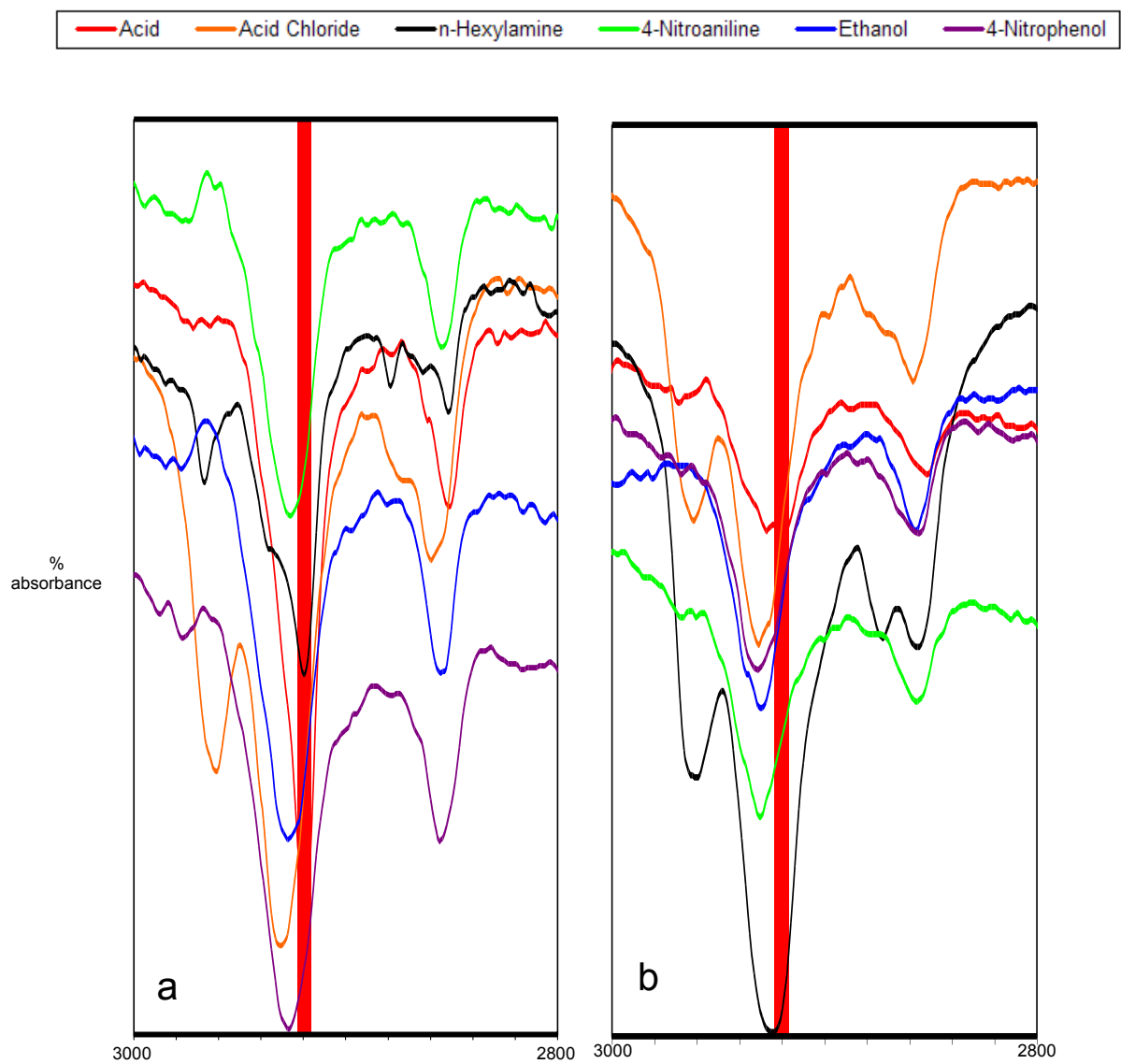


Figure 8. The aliphatic stretching region of the IR spectra for a)16-acid, and b)12-acid. The highlighted region is the 2919 cm^{-1} band indicating a well ordered monolayer.

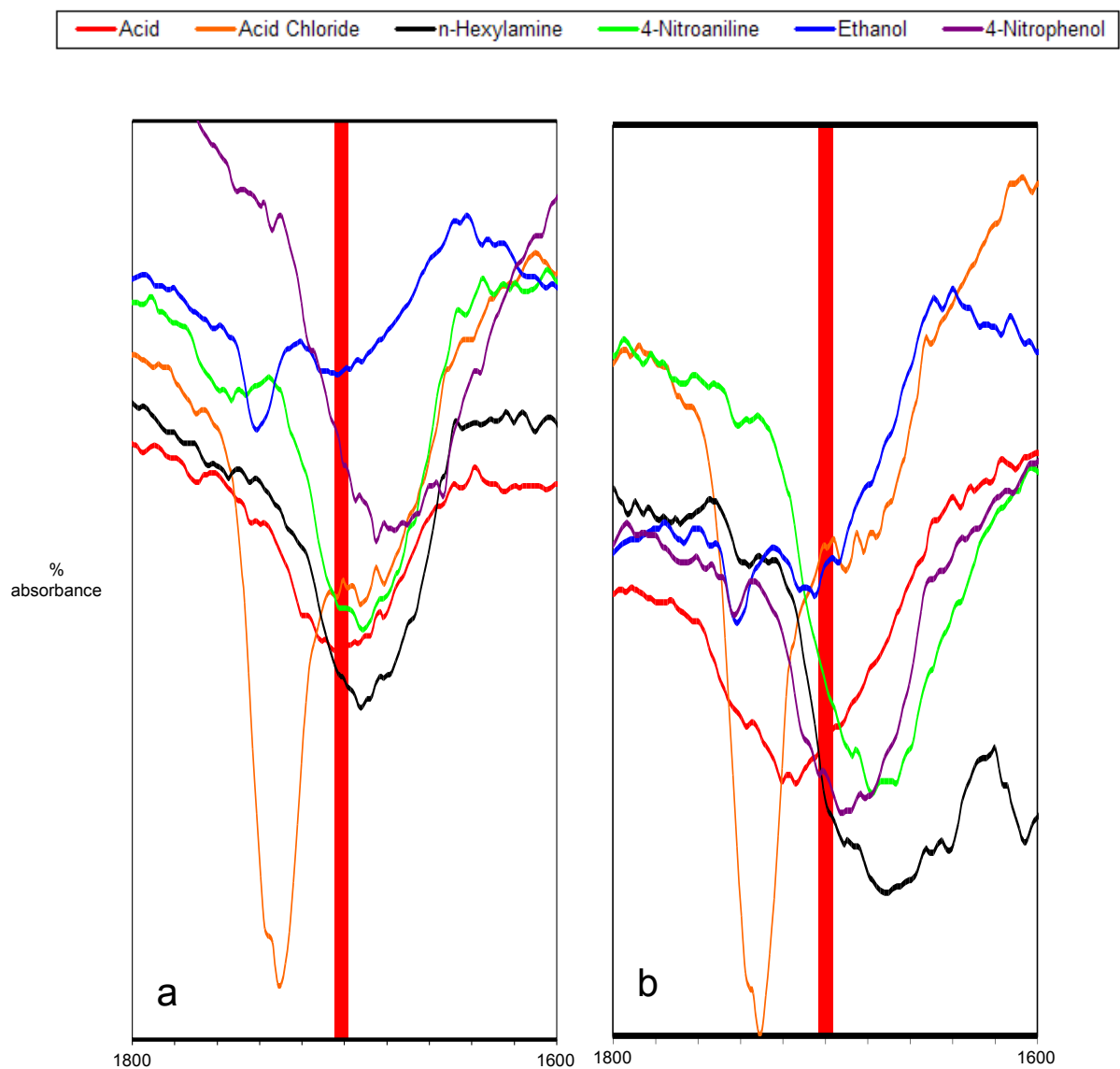


Figure 9. The carbonyl stretching region of the IR spectra for a)16-acid, and b)12-acid. The highlighted region is the 1700 cm⁻¹ band present in the original carboxylic acid terminated monolayers.

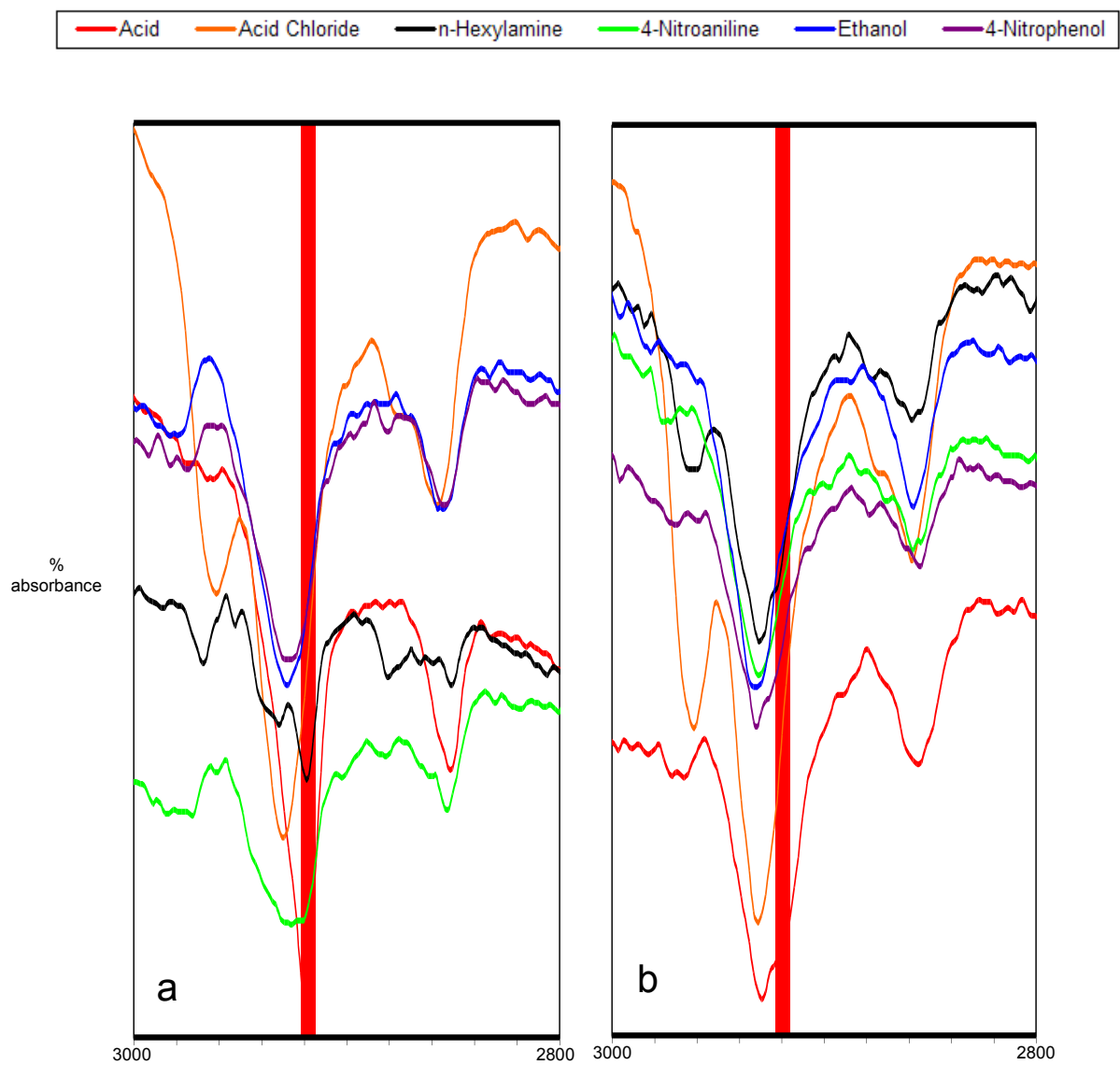


Figure 10. The aliphatic stretching region of the IR spectra for a)15-acid, and b)11-acid. The highlighted region is the 2919 cm^{-1} band indicative of a well ordered monolayer.

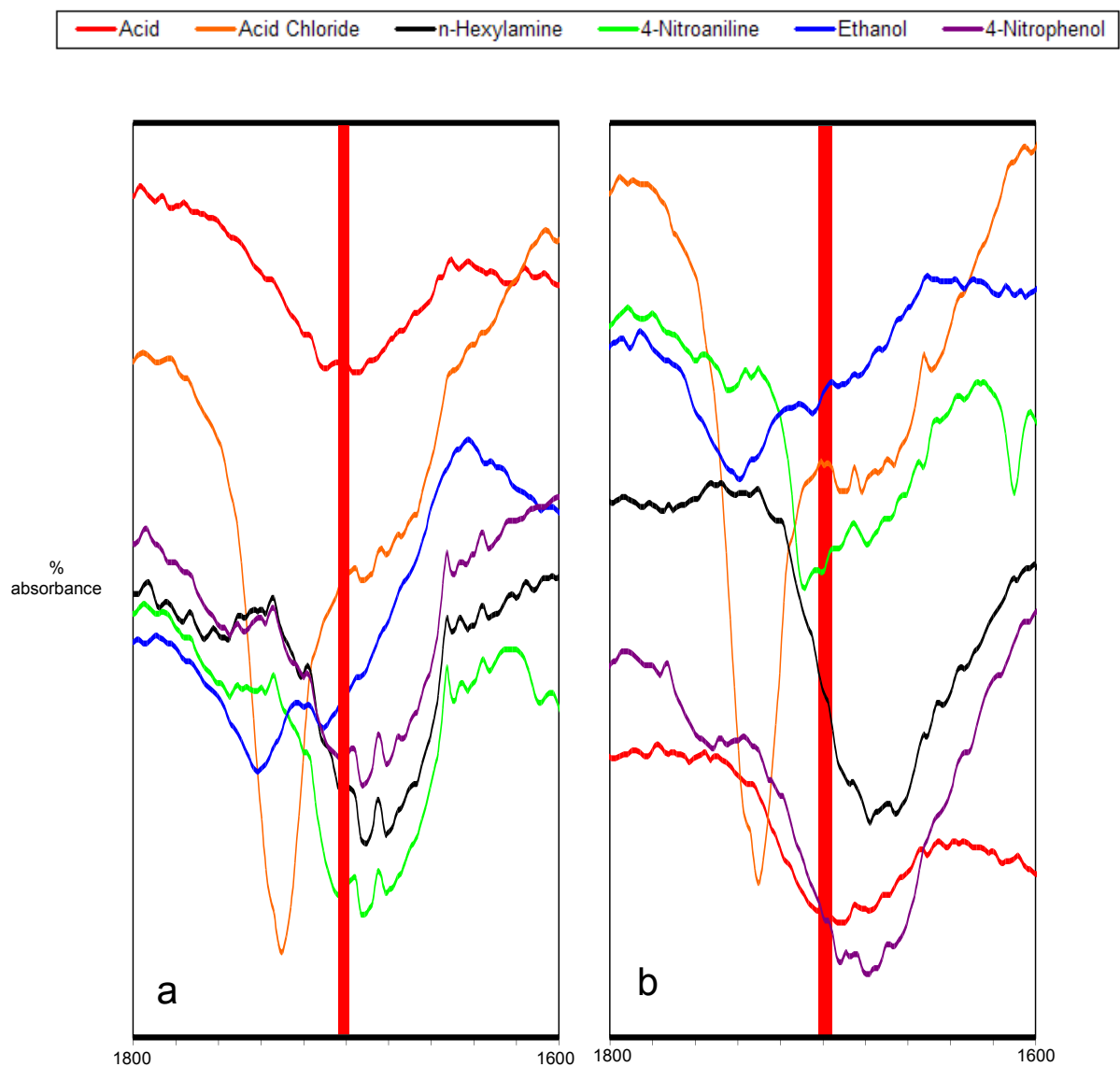


Figure 11. The carbonyl stretching region of the IR spectra for a)15-acid, and b)11-acid. The highlighted region is the 1700 cm⁻¹ band present in the original carboxylic acid terminated monolayers.

3. Experimental

3.1 Materials. All acid compounds and solvents were obtained from Aldrich and used without further purification. The reactant compounds 4-nitroaniline, 4-nitrophenol, and 3-nitrophenol were obtained from Alfa Aesar and used as received. *n*-Hexylamine and oxalyl chloride were received from TCI America and without further purification.

3.2 Preparation of Substrates. All gold slides were obtained from Evaporated Metal Films. Each slide has the dimensions 1" x 3" x .040", coated with 50 angstroms chromium, under 1000 angstroms of gold. The slides were cut as necessary to fit experimental needs. Slides were plasma cleaned for 30 seconds using a Plasma Prep II from SPI, and monolayers were immediately deposited thereafter.

3.3 Preparation of Alkane Thiol SAMs. Slides prepared in 3.2 were immersed in a 3mM solution of alkane thiol in ethanol in 20 mL scintillation vials, allowed to react in for 6 to 12 hours. After removal from the solution, the formed SAMs were rinsed thoroughly with ethanol and dried with nitrogen.

3.4 Onboard Reactions. Substrates prepared using procedure 3.3 were immersed in oxalyl chloride for 1-3 minutes, then quickly rinsed with nitrogen and submerged into a solution of 3 mM of reactant in dichloromethane. Alcohol reactants were allowed 40 minutes to react, amines 30 minutes. The slides were then rinsed with dichloromethane and dried with nitrogen.

3.5 Characterization of SAMs.

3.5.1 Grazing Incidence Infrared Spectroscopy. IR Spectra were obtained with a Nexus FT-IR spectrometer equipped with a ThermoNicolet grazing angle accessory and a liquid-nitrogen cooled MCTA detector. The IR beam was incident at 75° on the gold substrates. The optical path was purged with nitrogen gas before and during data acquisition. For each sample, 64 scans were collected with a 4 cm⁻¹ resolution. The scan range was from 4000 to 1000 cm⁻¹, the detector cut-off is around 800 cm⁻¹. A plasma cleaned gold substrate was used as a background before the acquisition of each sample's spectrum.

4. Conclusions

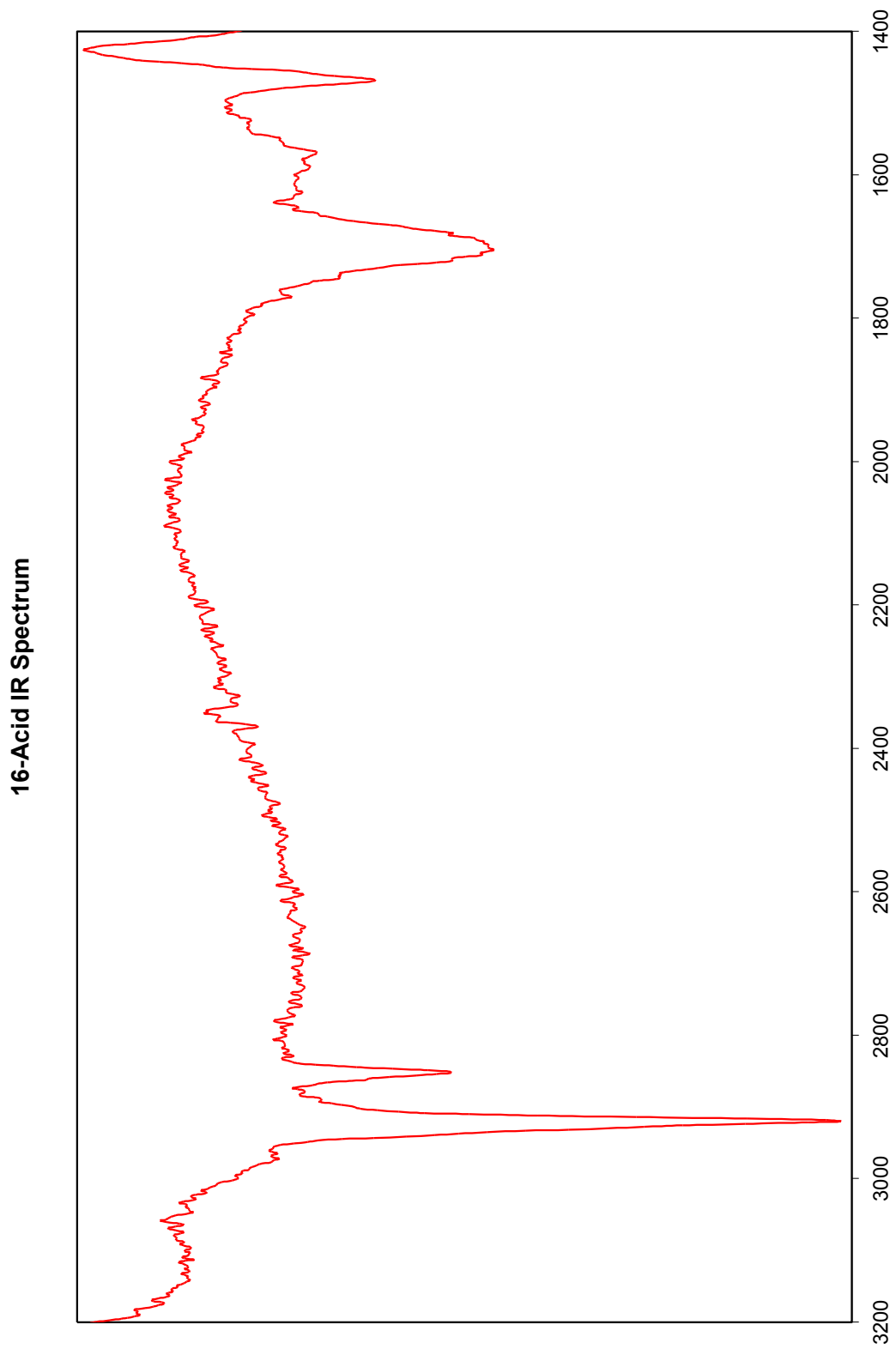
We have explored an onboard approach for the in situ synthesis of SAMs exhibiting different functional groups at the interface. Results from this work indicate that the functionalization of alkane thiols on gold is feasible, through ester and amide coupling with aliphatic and aromatic amines, and aliphatic alcohols. The effects of parity on the reactivity of a SAM surface do not appear to affect the coupling of shorter acid chains (12 and below), but odd-numbered methylene chains in longer, crystalline monolayers (15 and above) appear to exclude further reactions, where even-numbered long methylene chains will allow for ester and amide formation at the interface. Further investigation of the mechanism by which nucleophilic substitution is allowed or forbidden based on parity is planned, as well as the testing of additional reagents to couple to the surface for examination of steric hindrance, acidity, and reaction solvent.

5. References

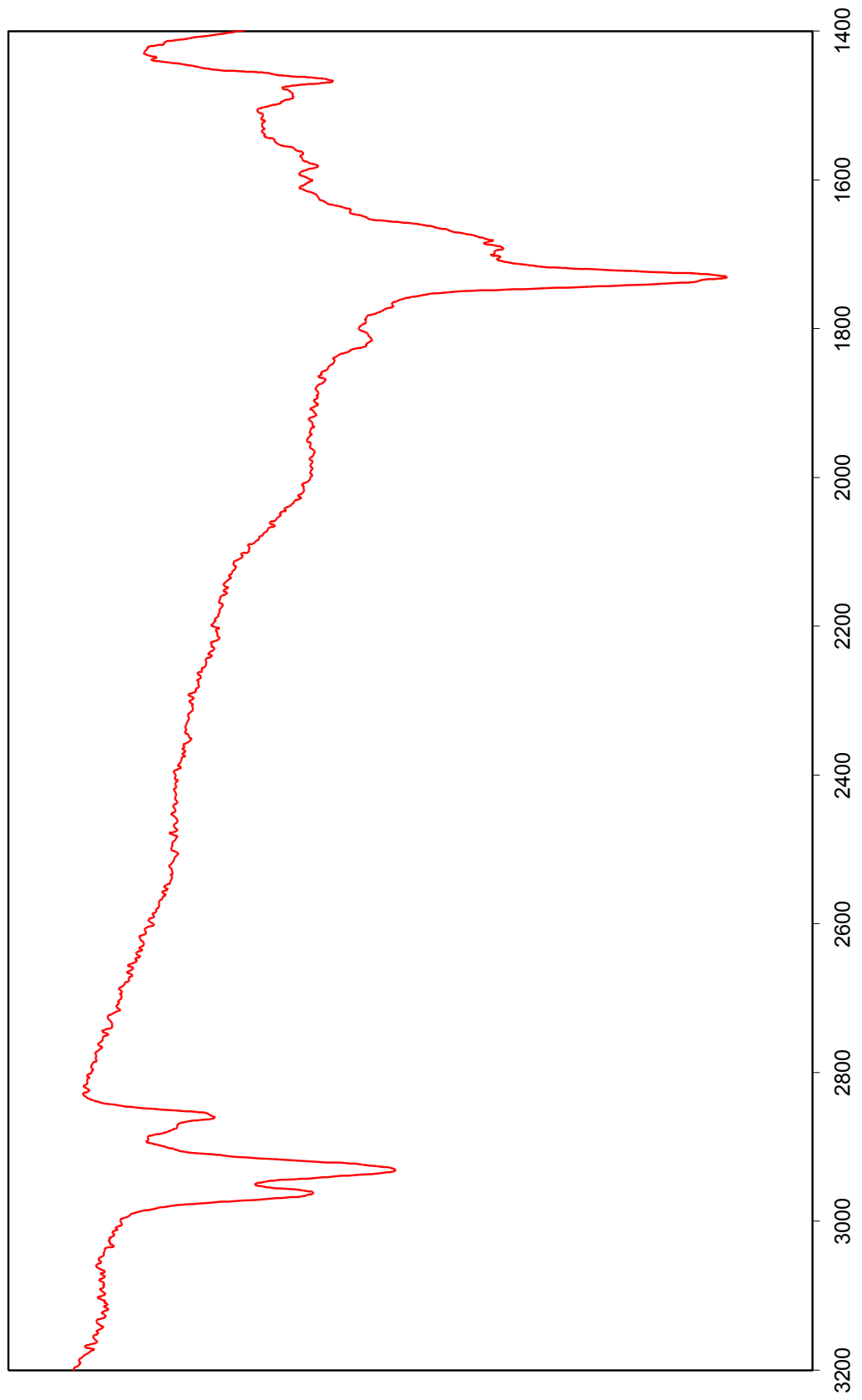
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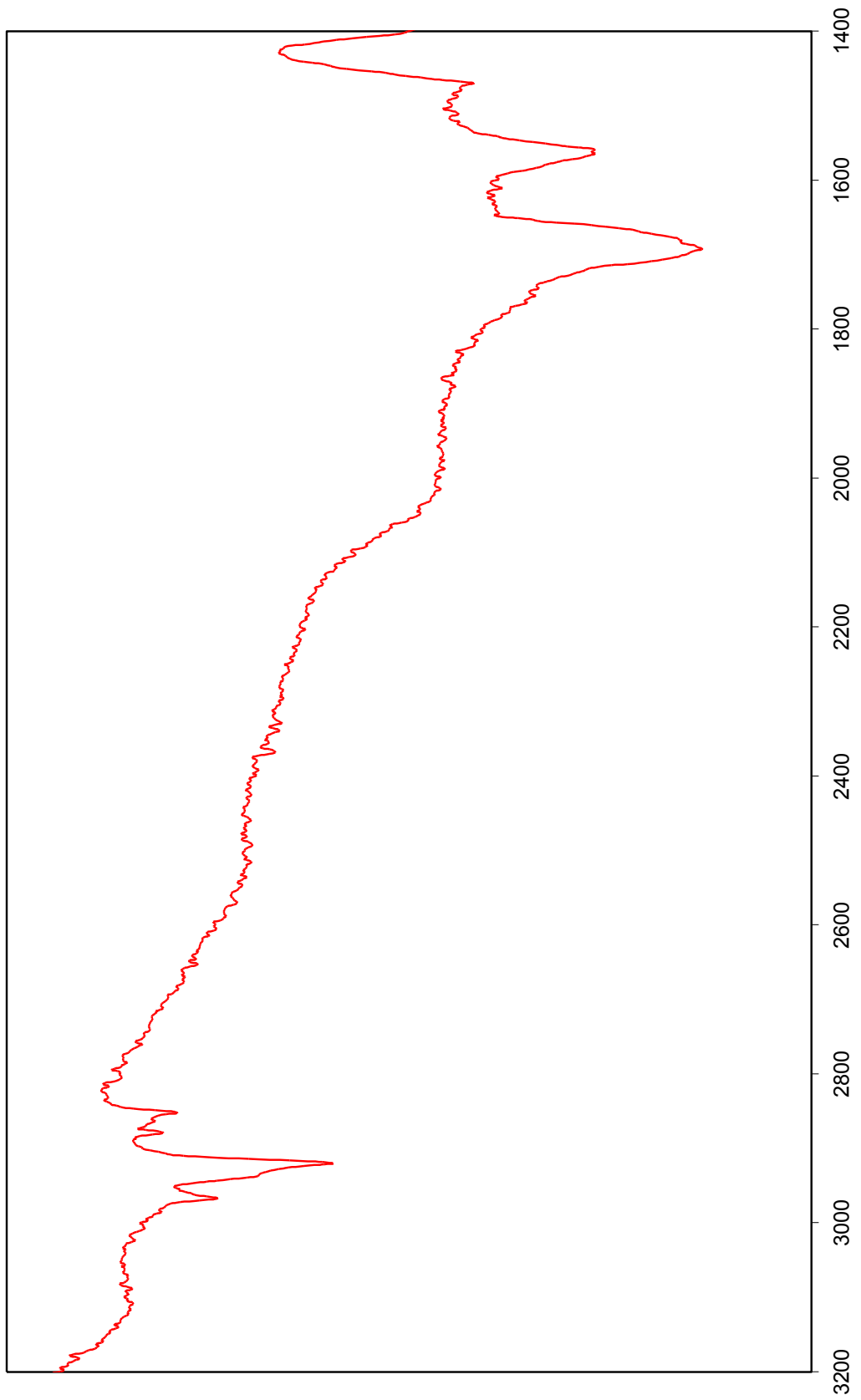
6. Appendix



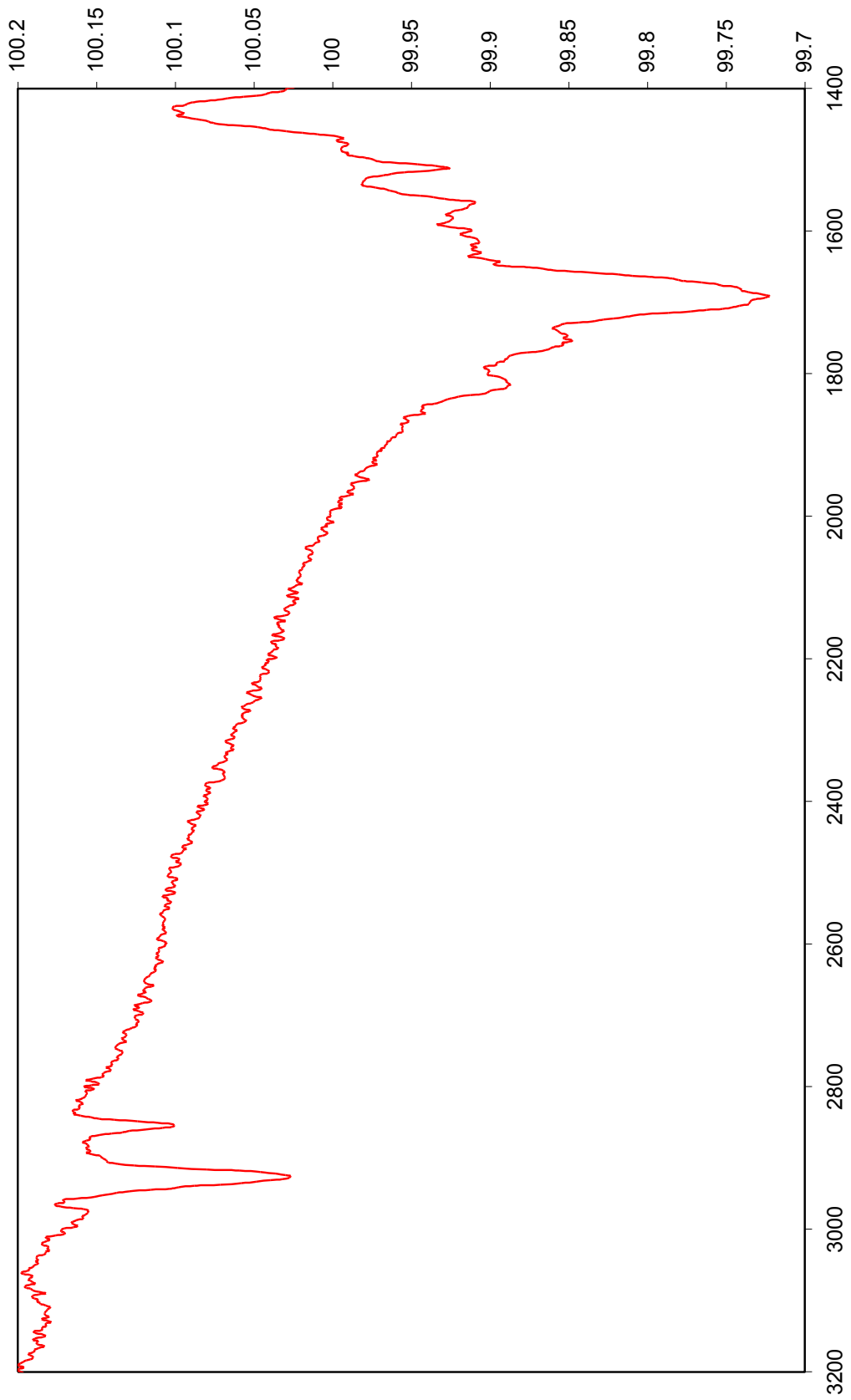
16-Acid Chloride Derivative IR Spectrum



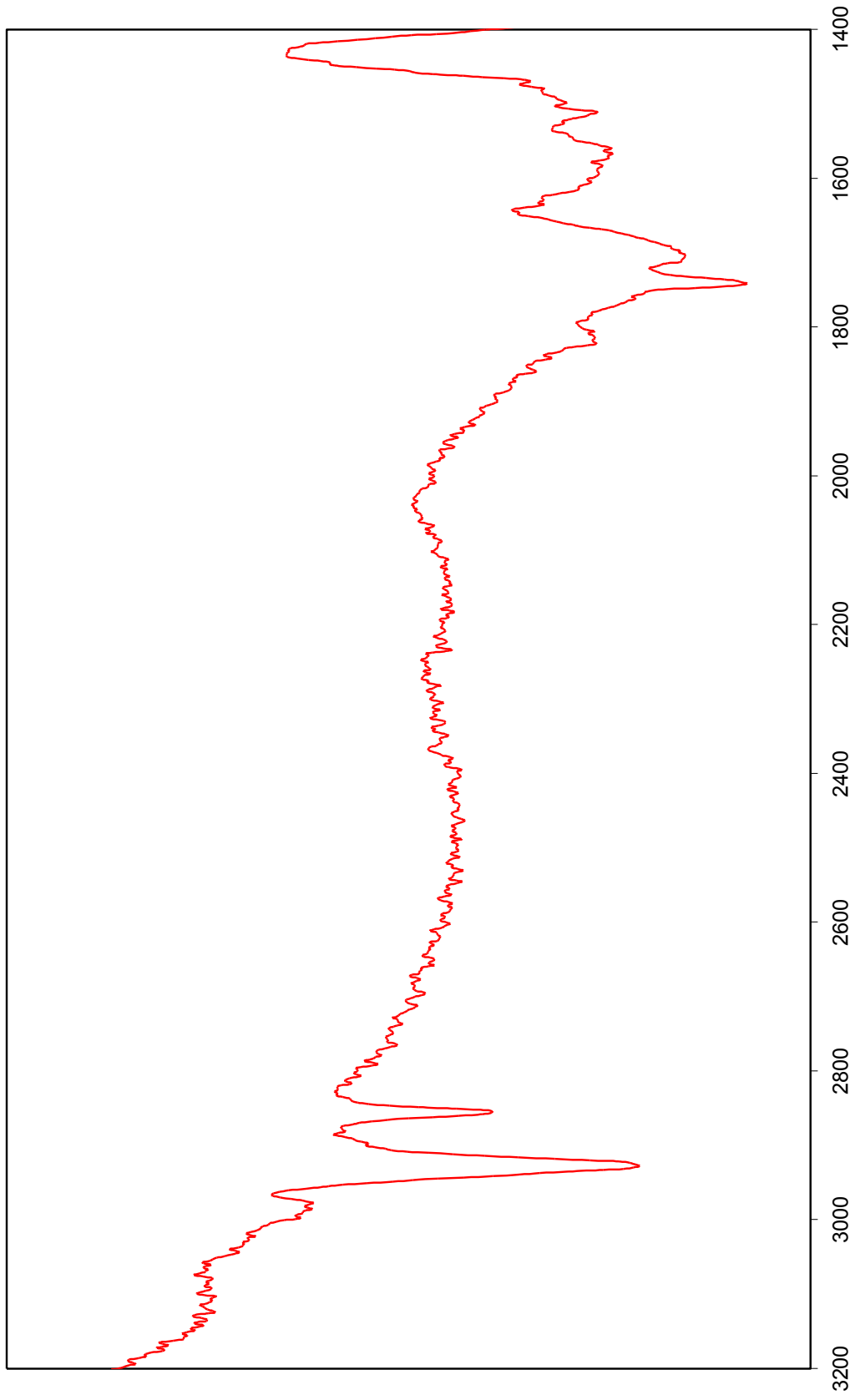
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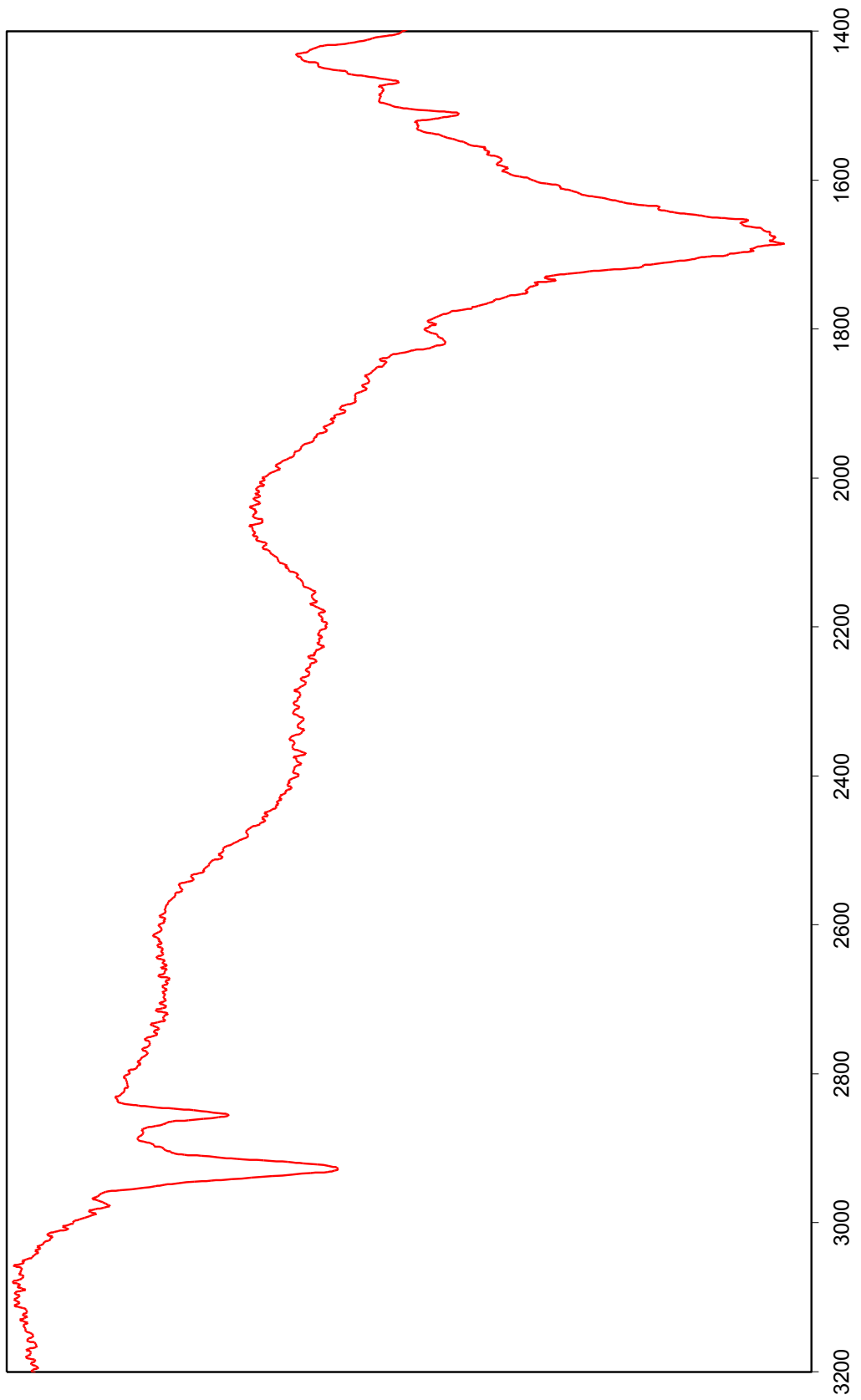
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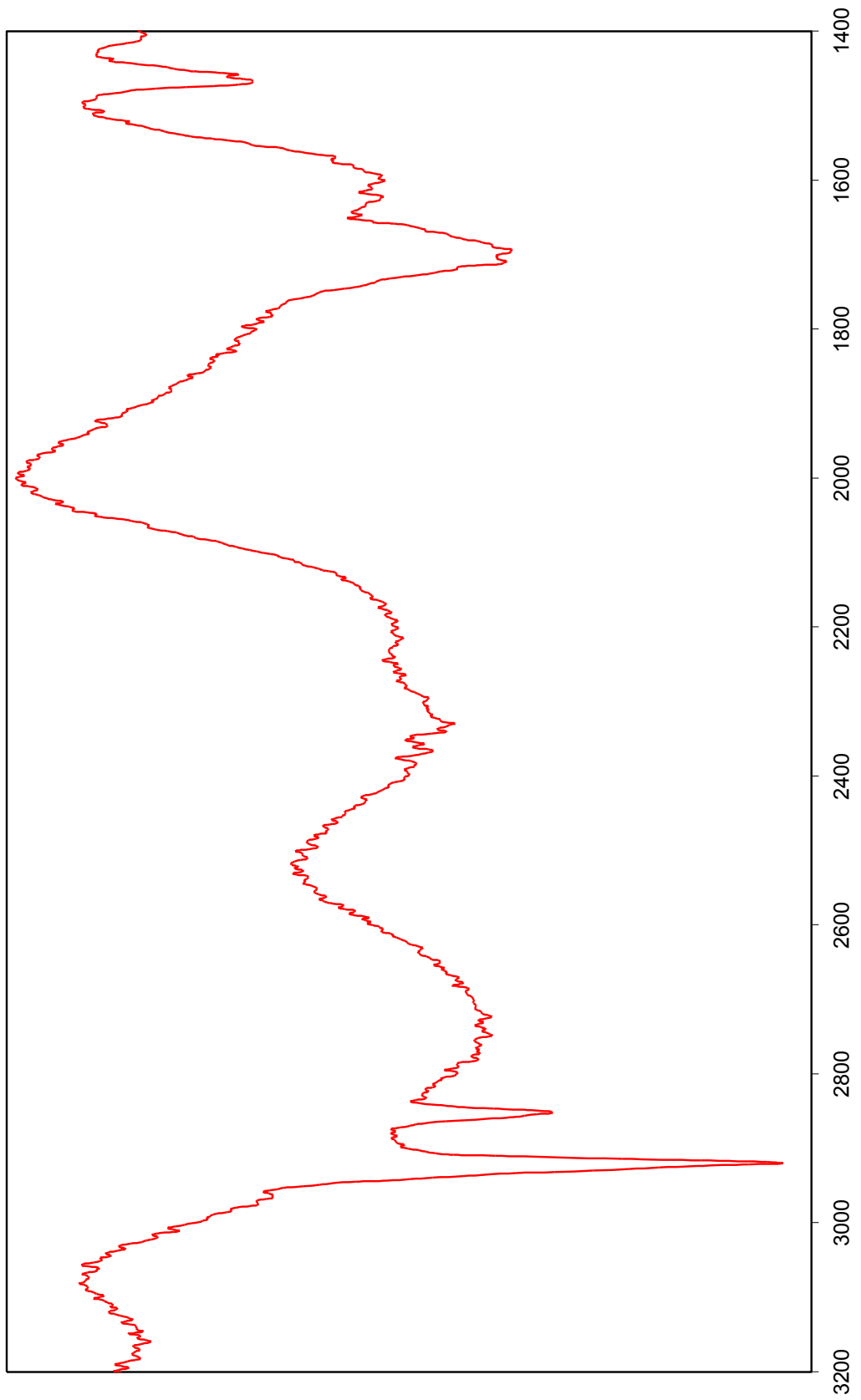
16-Acid Ethanol Amide IR Spectrum



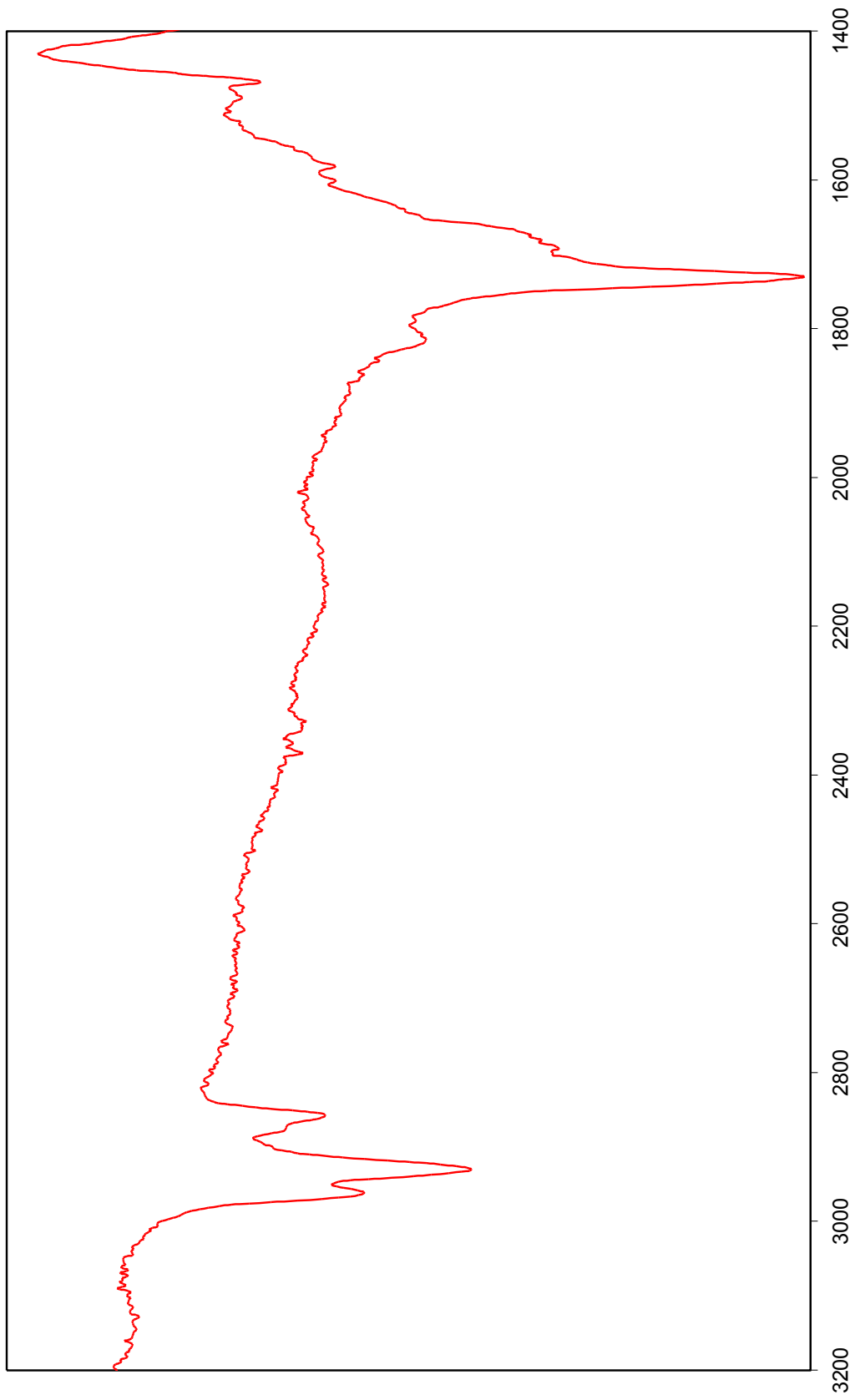
16-Acid 4-Nitrophenol Ester Spectrum



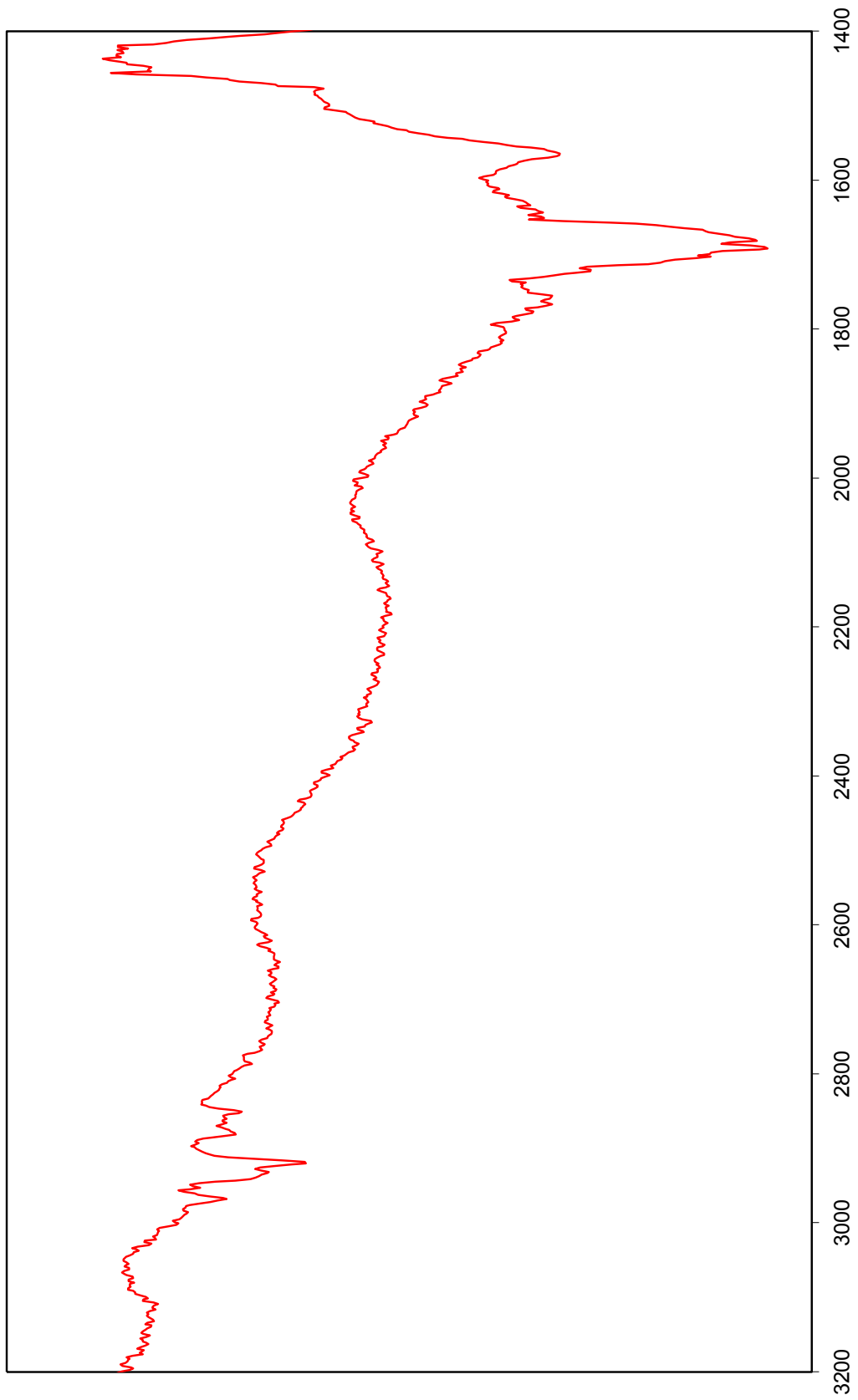
15-Acid IR Spectrum



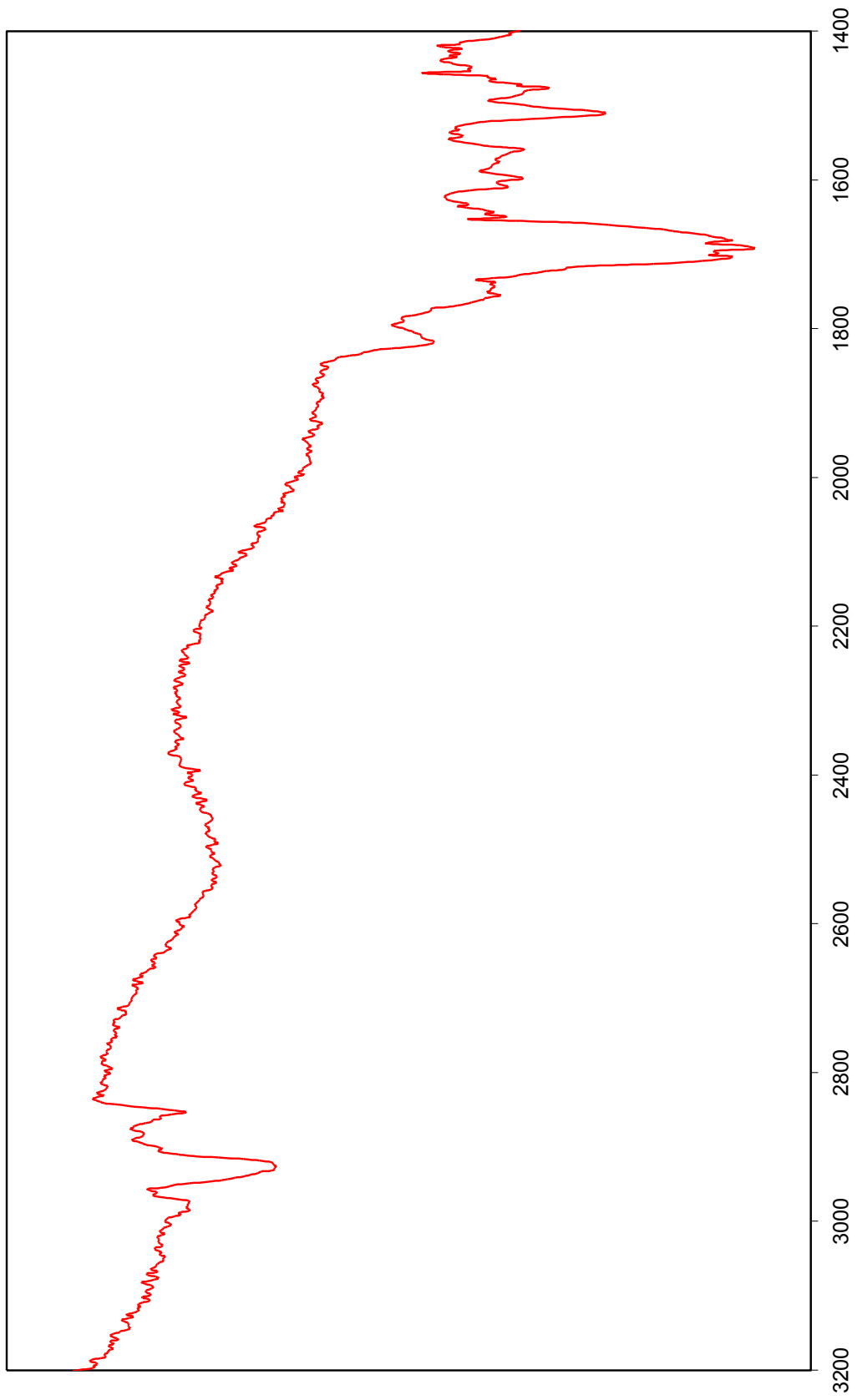
15-Acid Chloride Derivative IR Spectrum



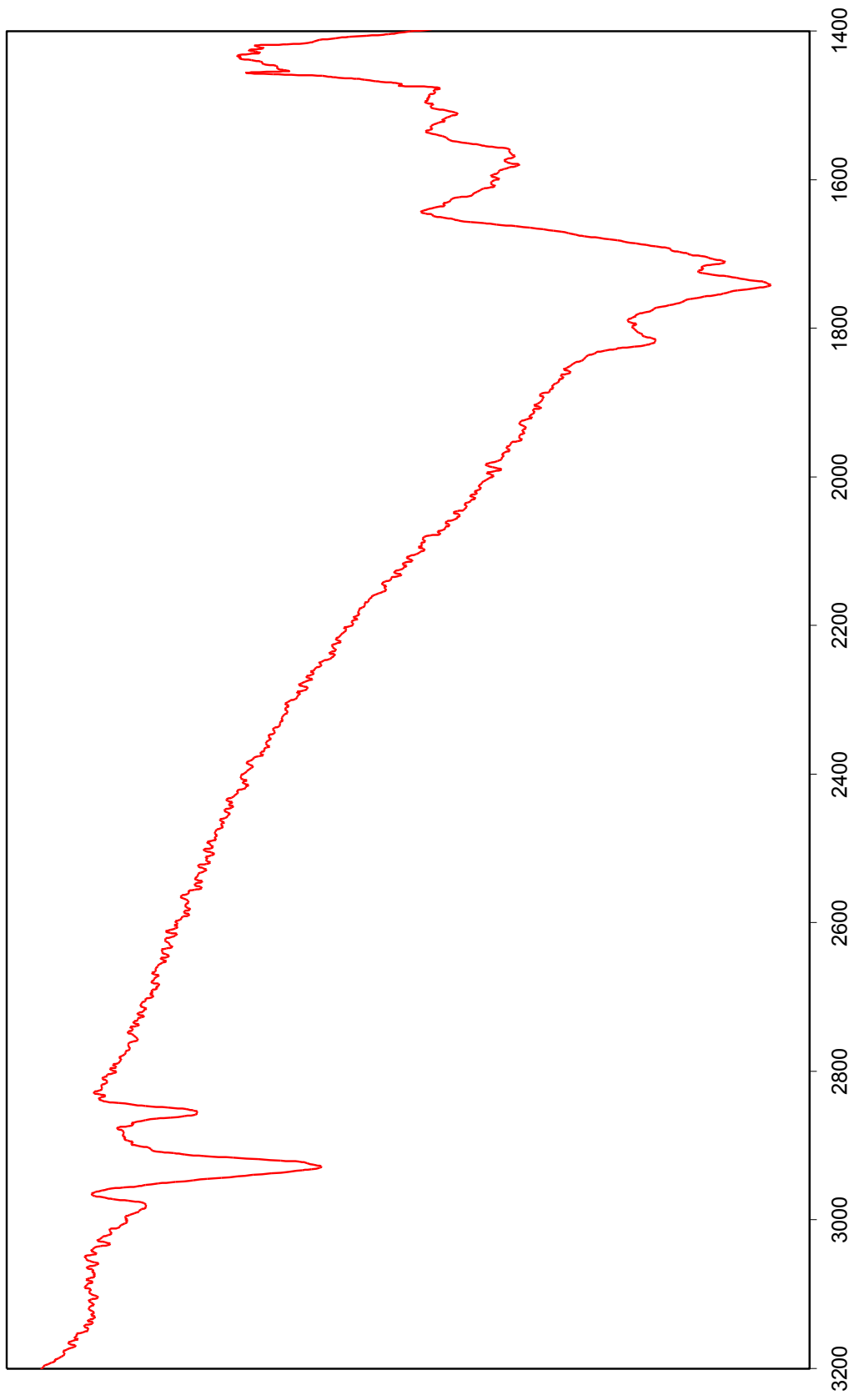
15-Acid n-Hexylamine Amide IR Spectrum



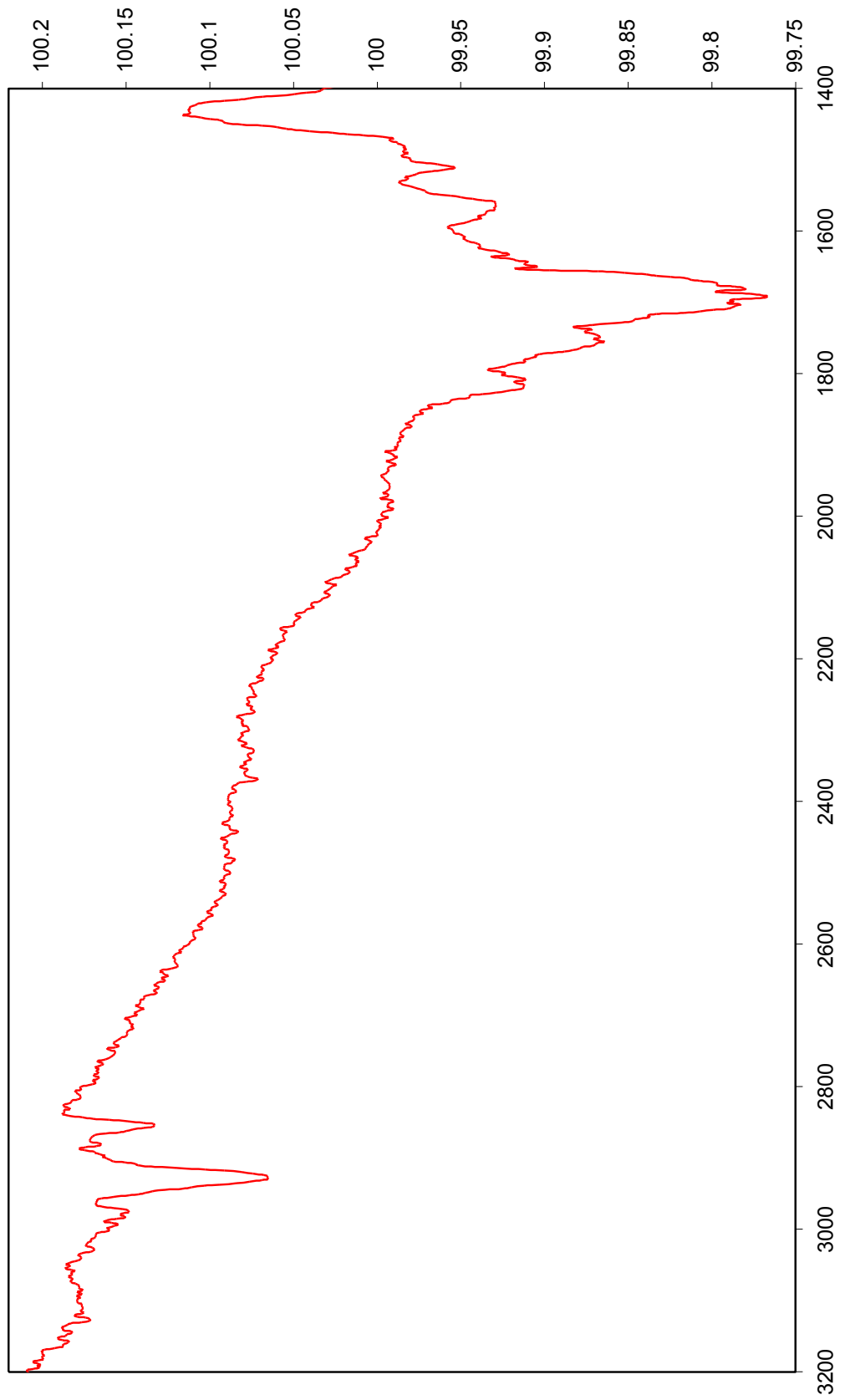
15-Acid 4-Nitroaniline Amide IR Spectrum



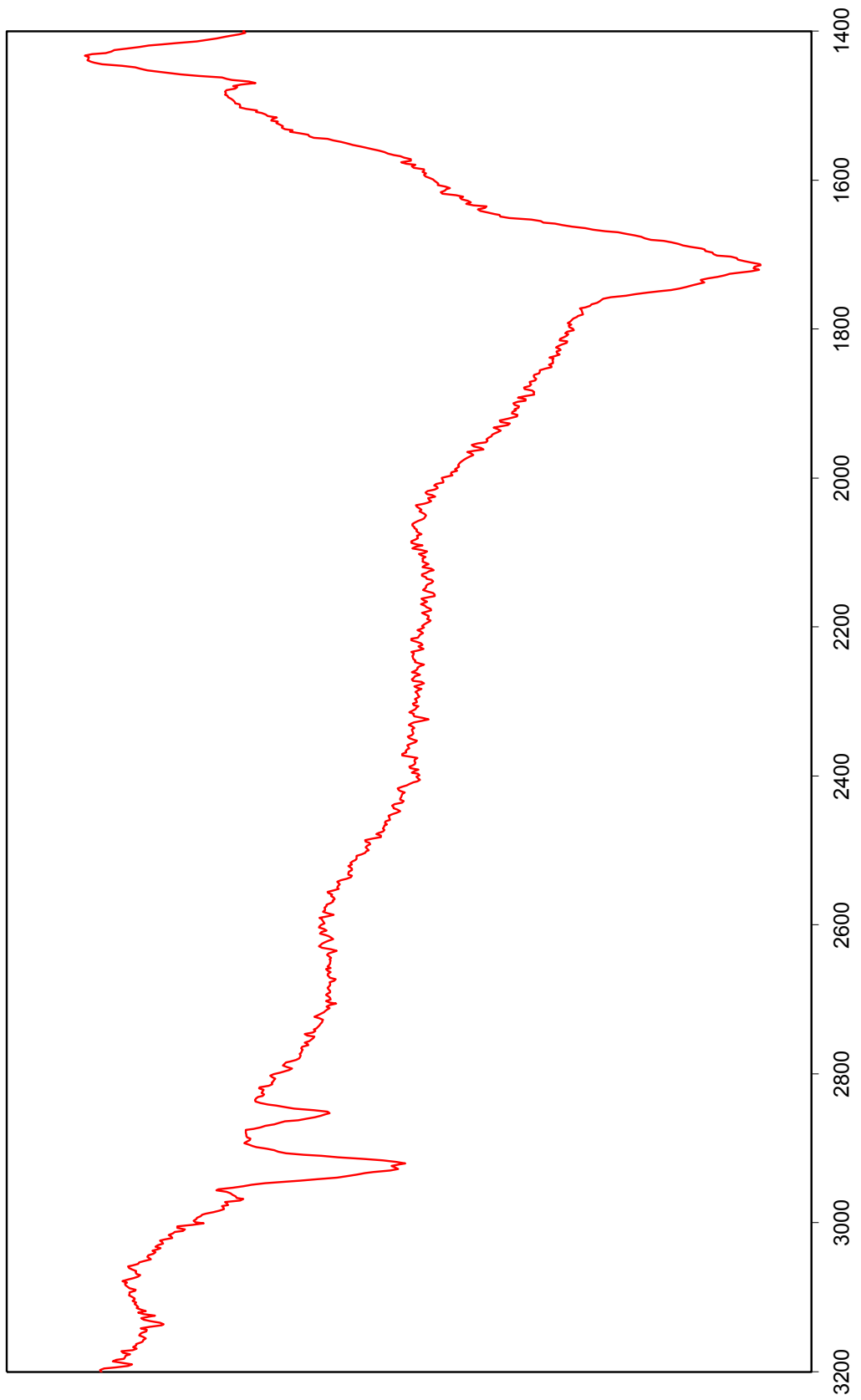
15-Acid Ethanol Ester IR Spectrum



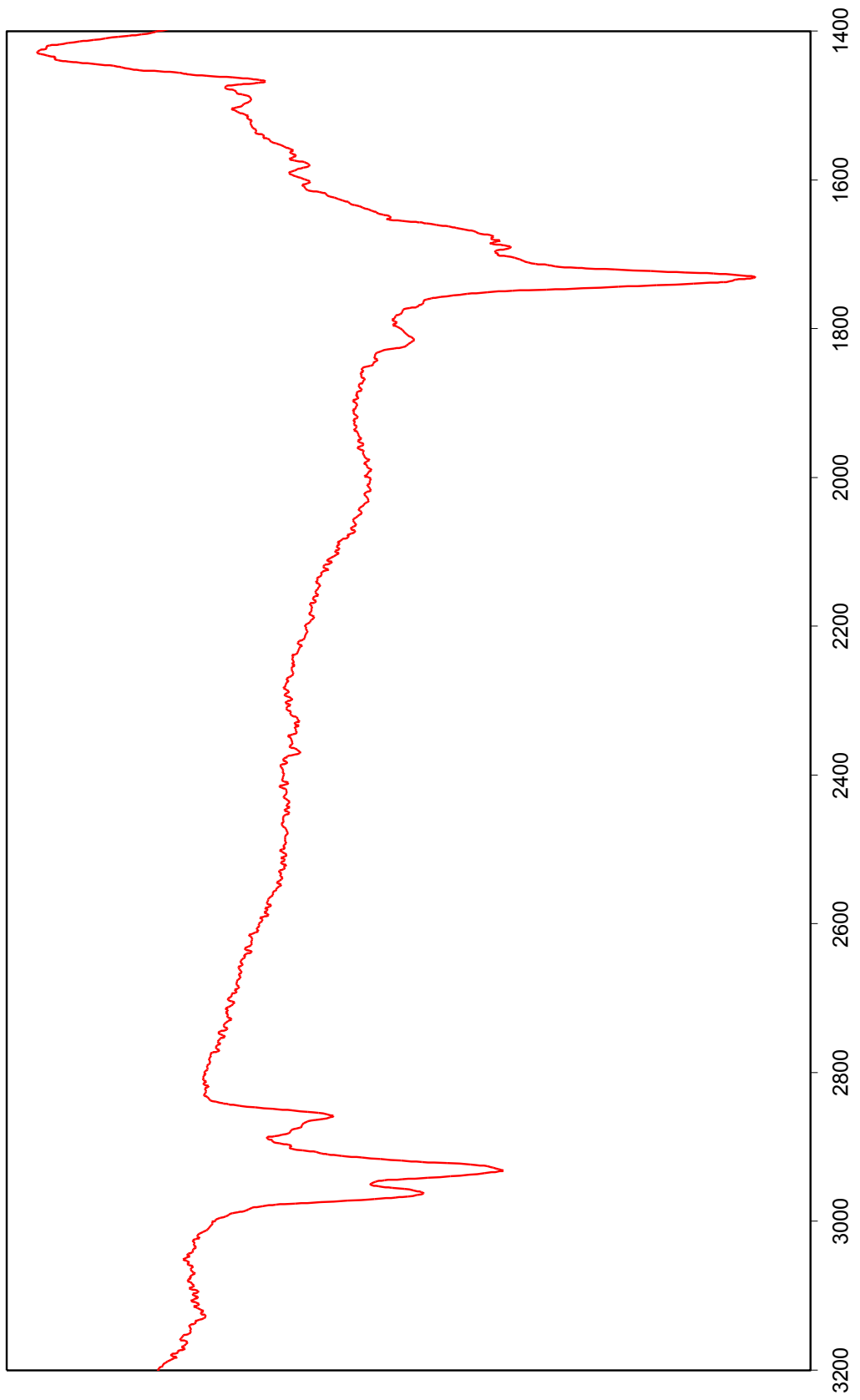
15-Acid 4-Nitrophenol Ester IR Spectrum



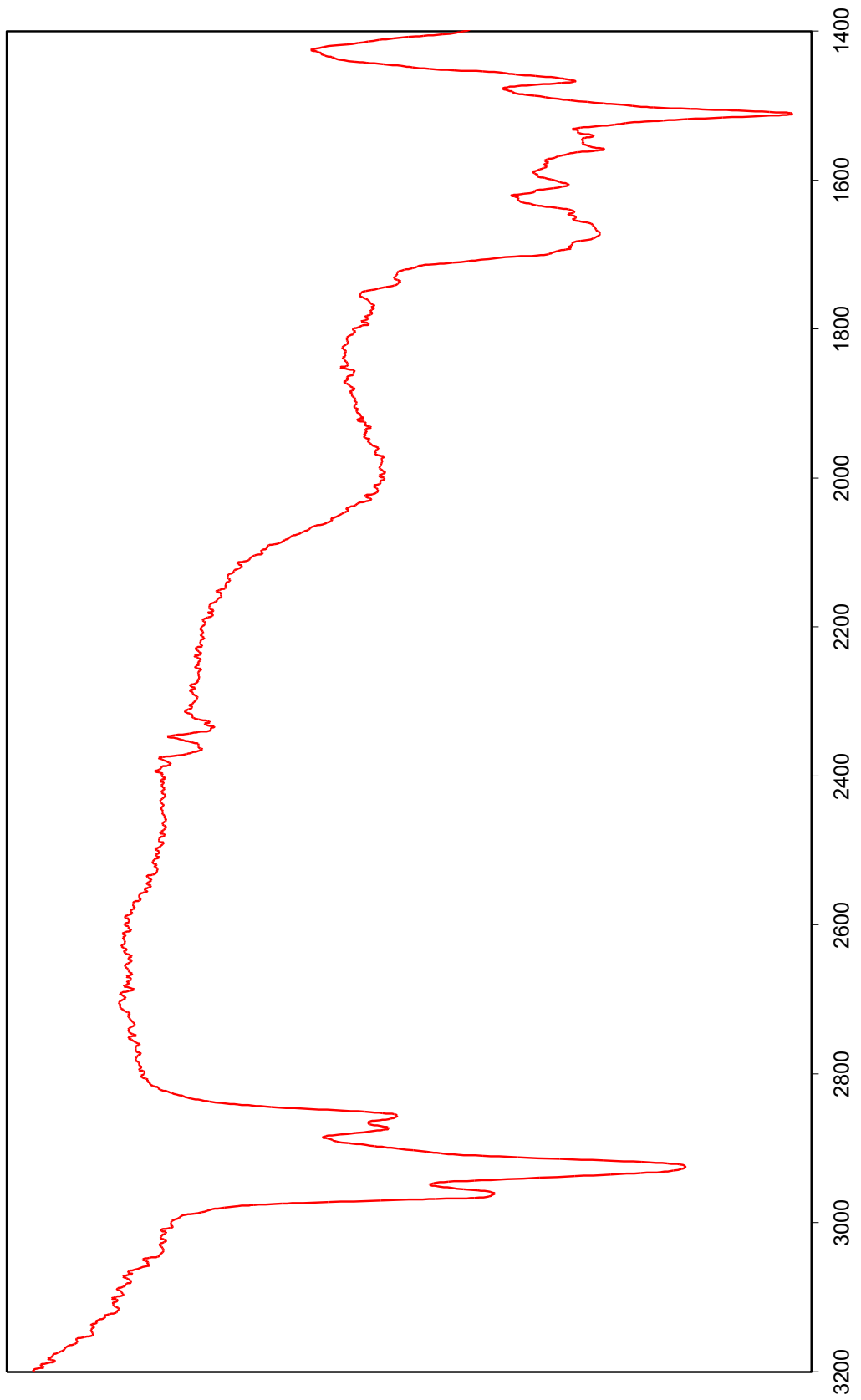
12-Acid IR Spectrum



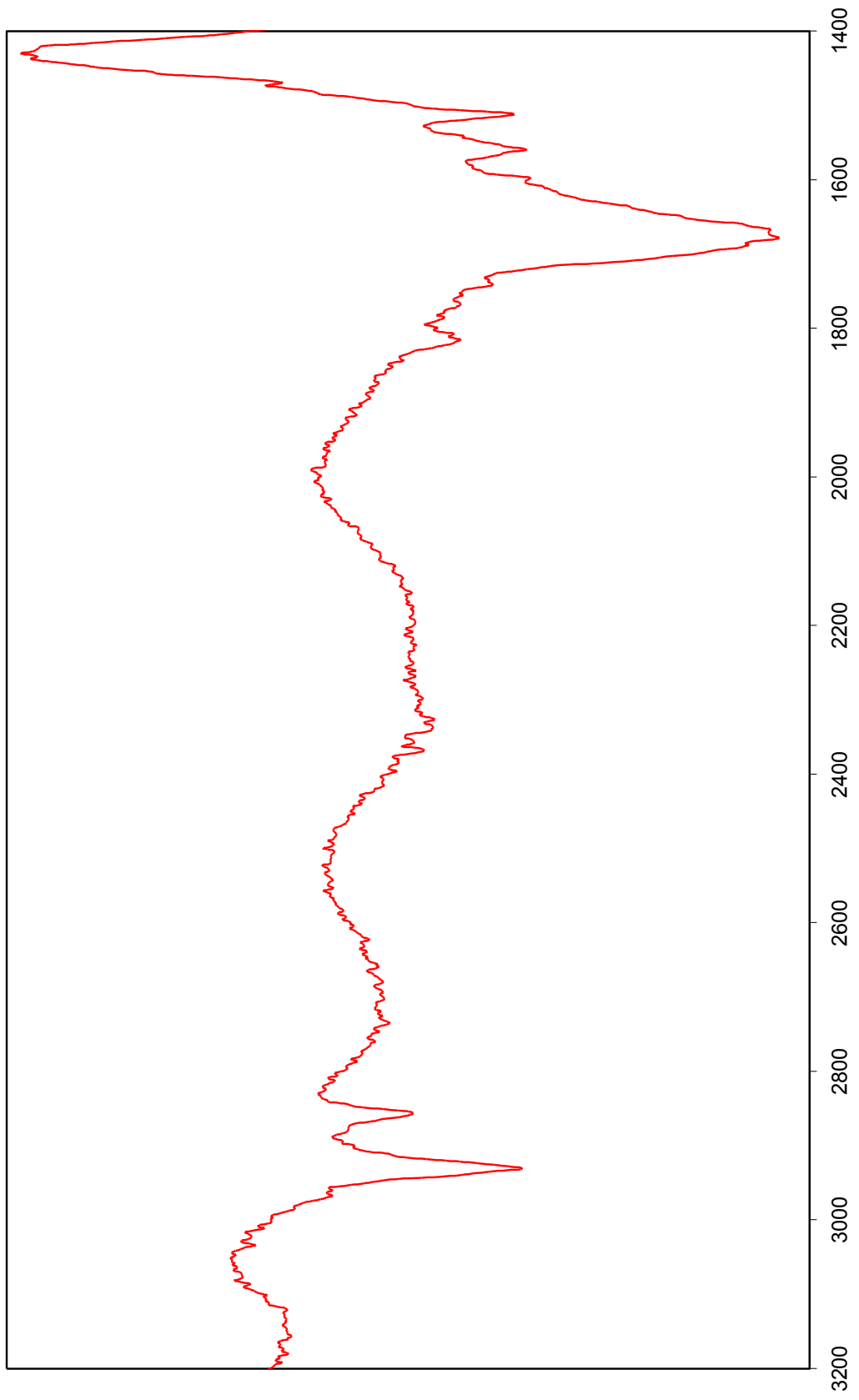
15-Acid Chloride Derivative IR Spectrum



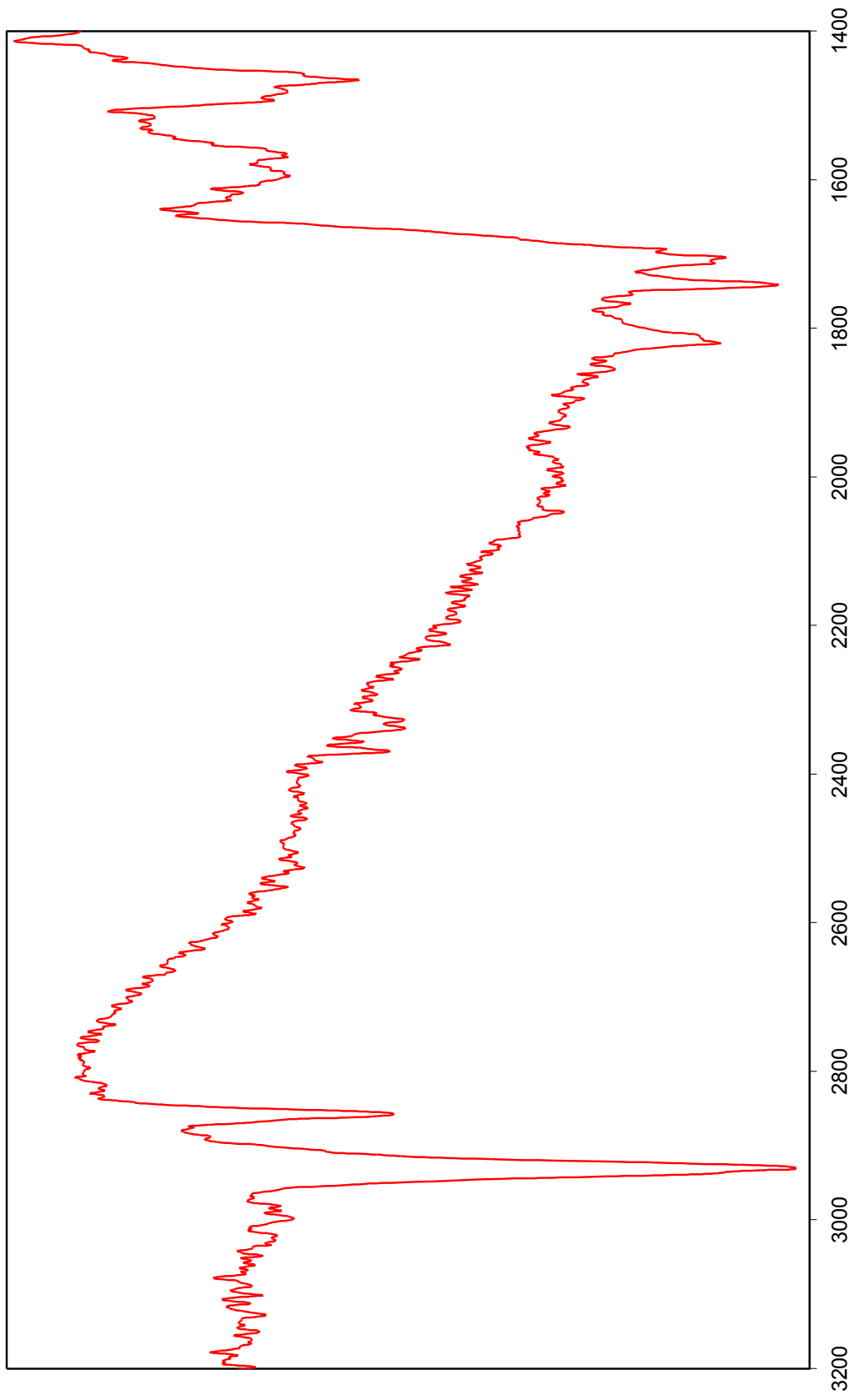
12-Acid n-Hexylamine Amide IR Spectrum



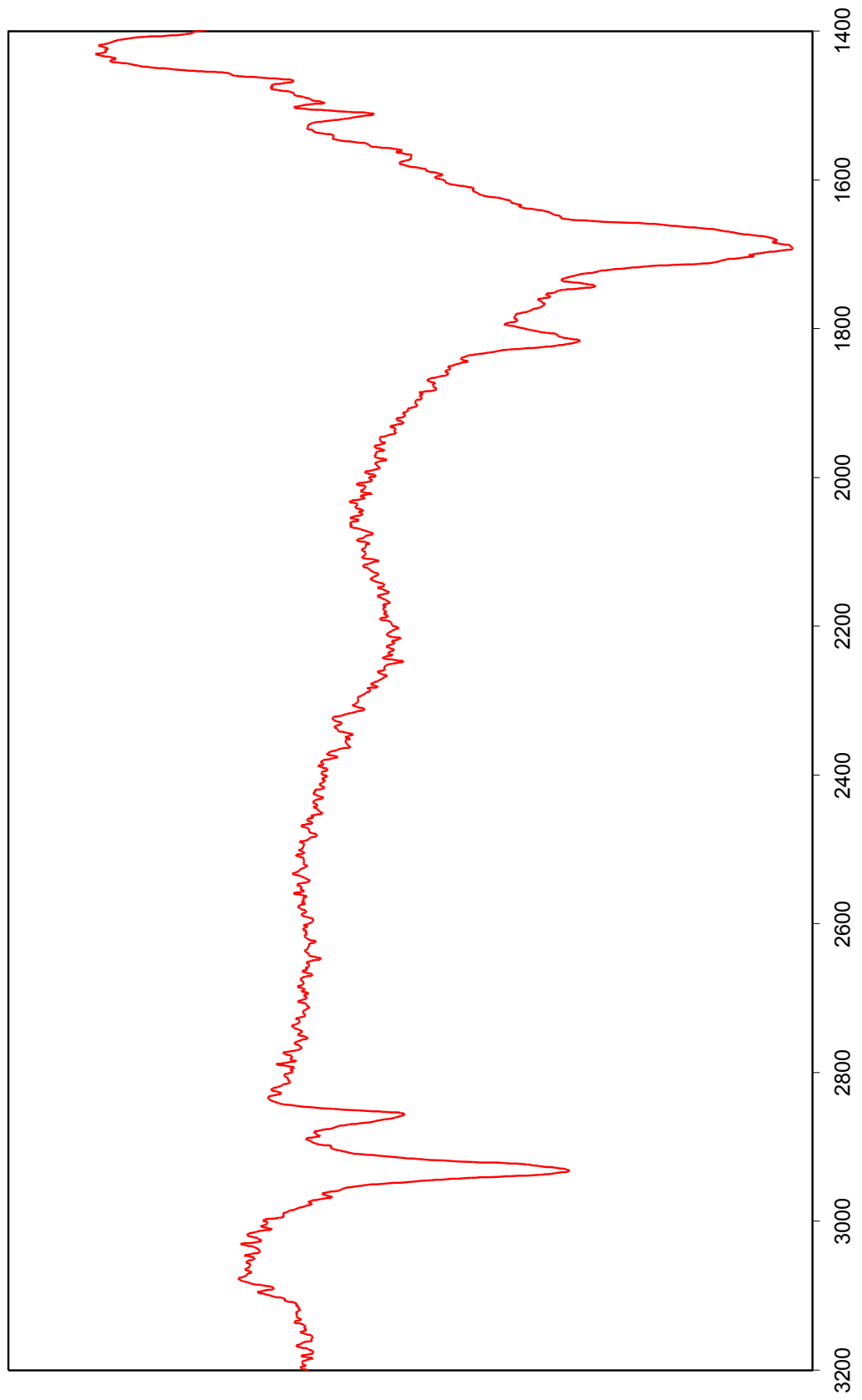
12-Acid 4-Nitroaniline Amide IR Spectrum



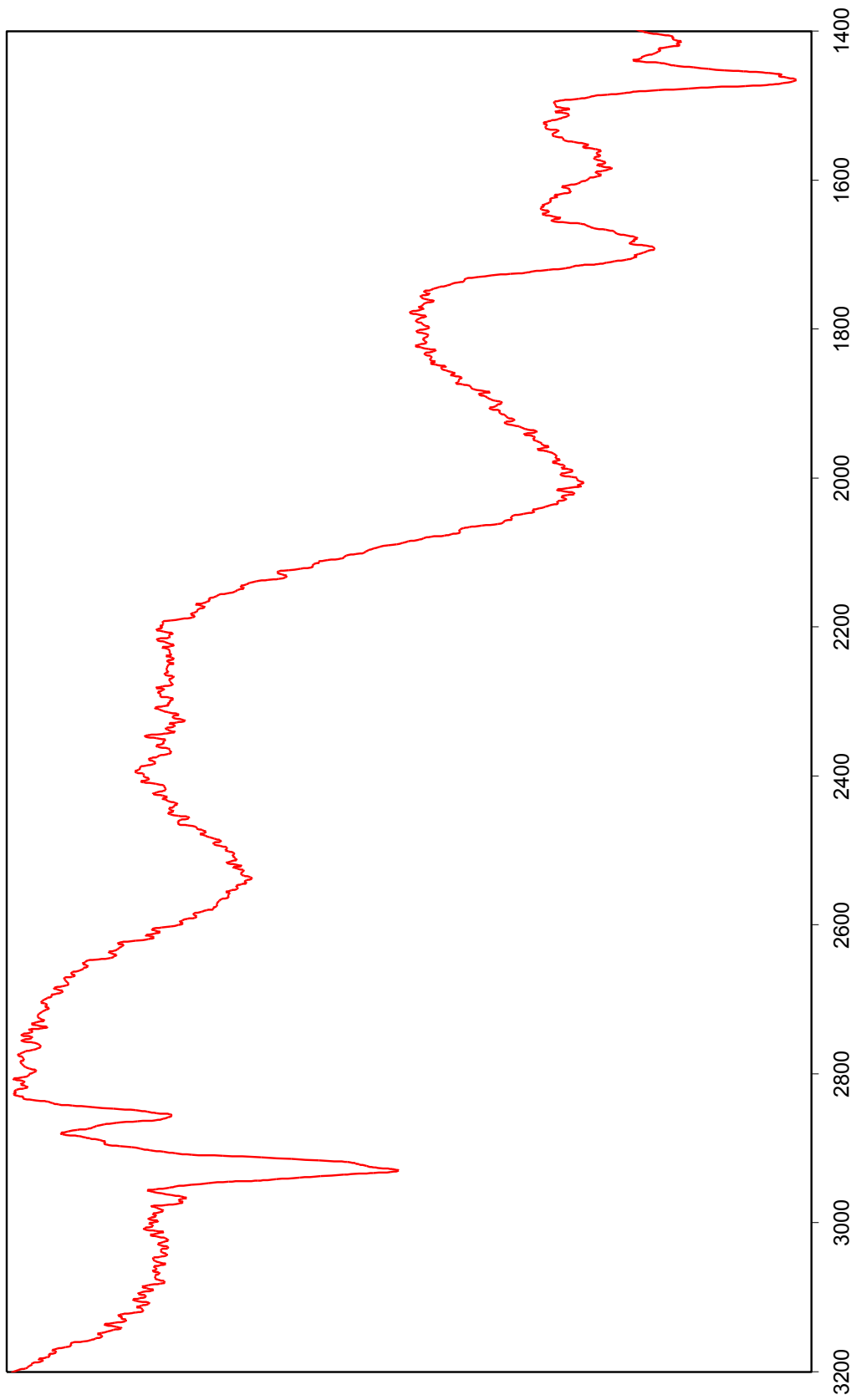
12-Acid Ethanol Ester IR Spectrum



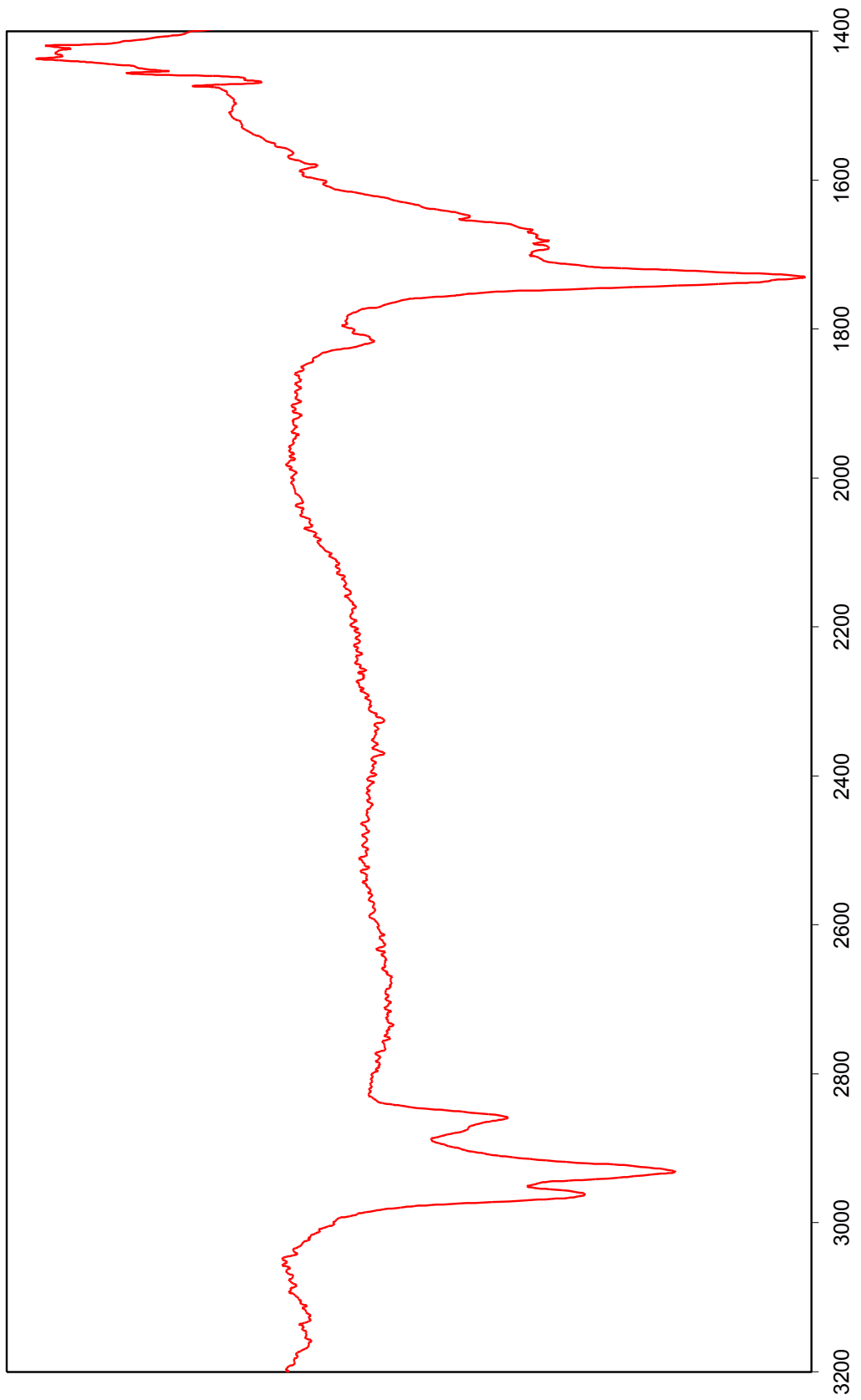
12-Acid 4-Nitrophenol Ester IR Spectrum



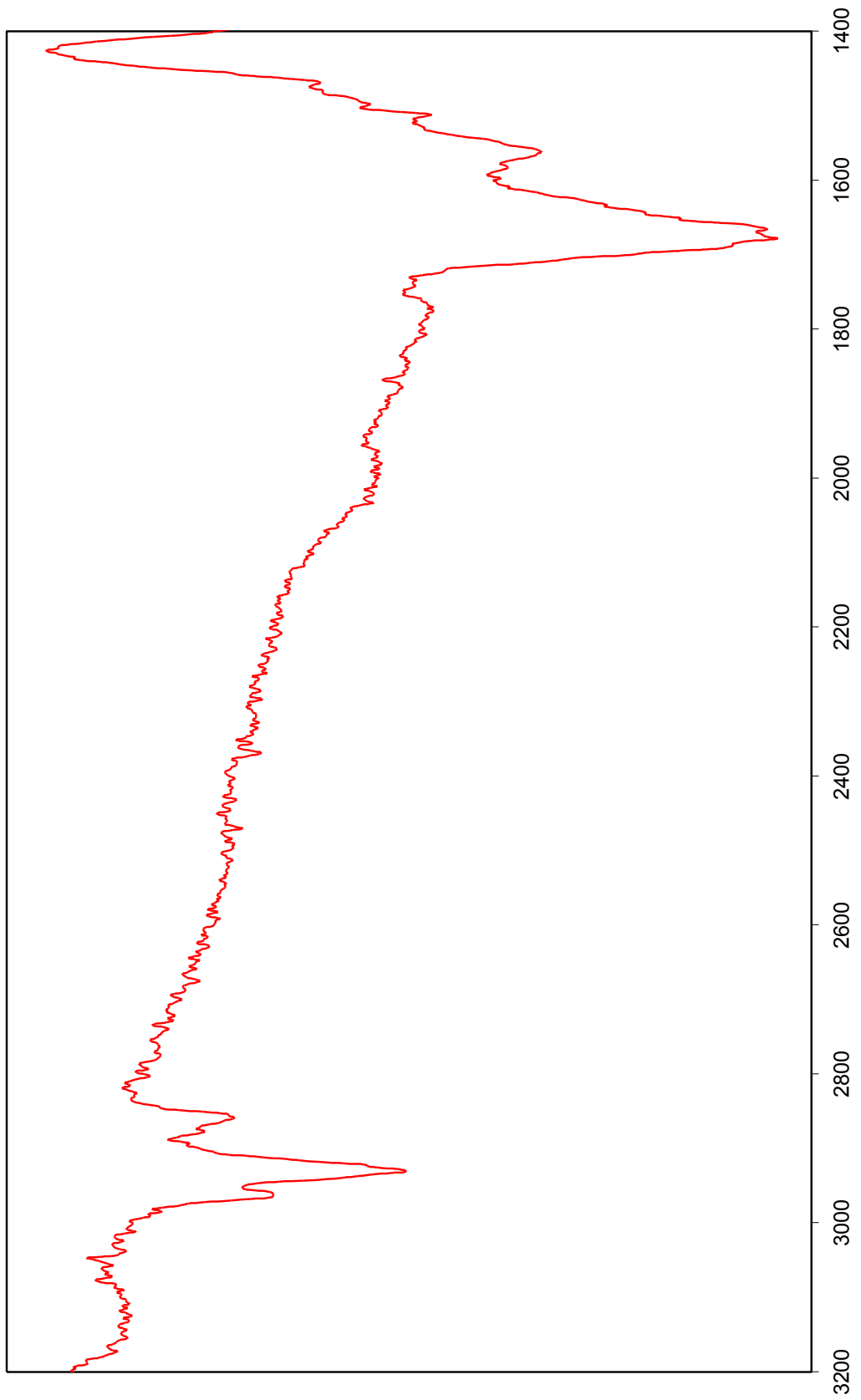
11-Acid IR Spectrum



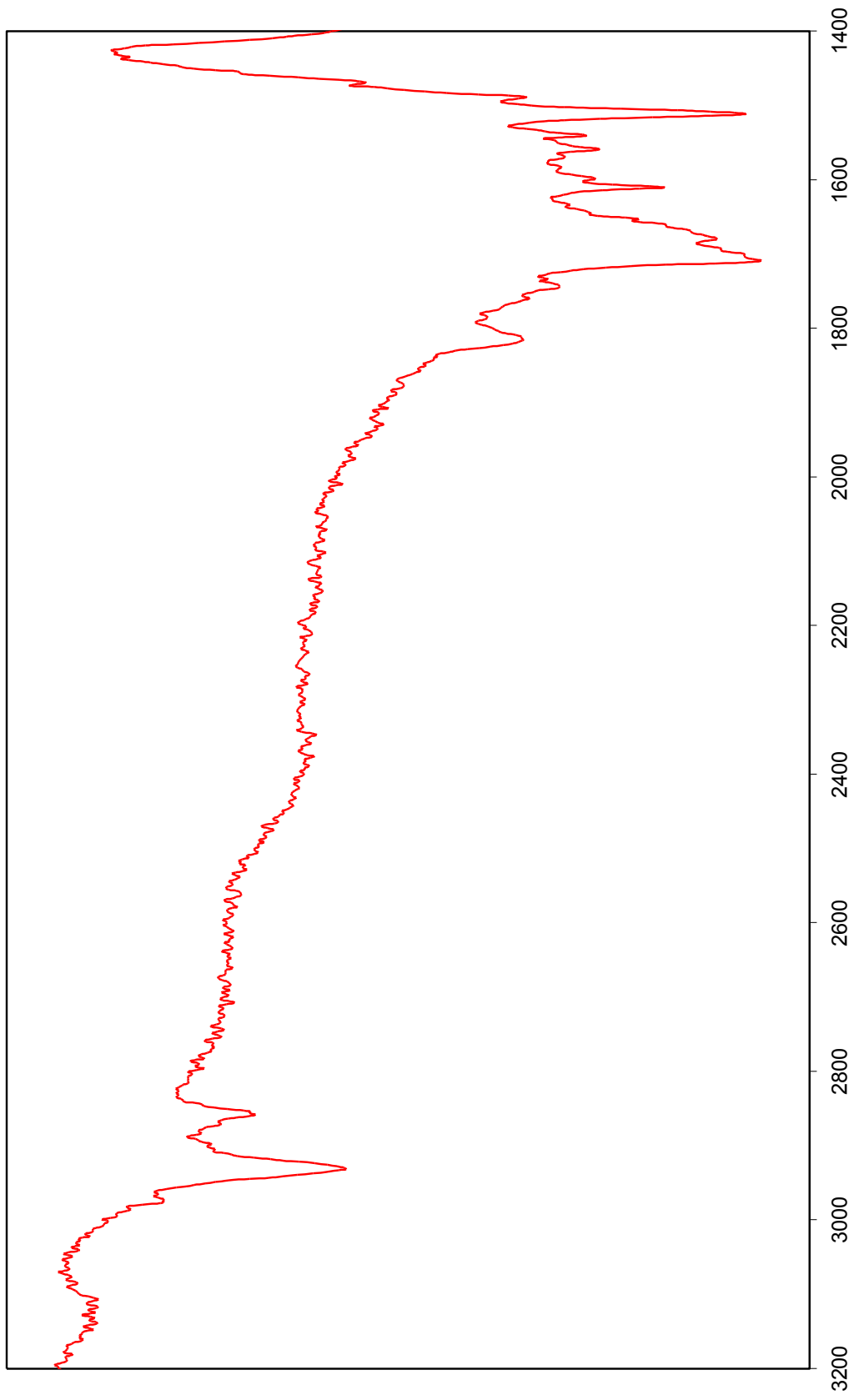
11-Acid Chloride Derivative IR Spectrum



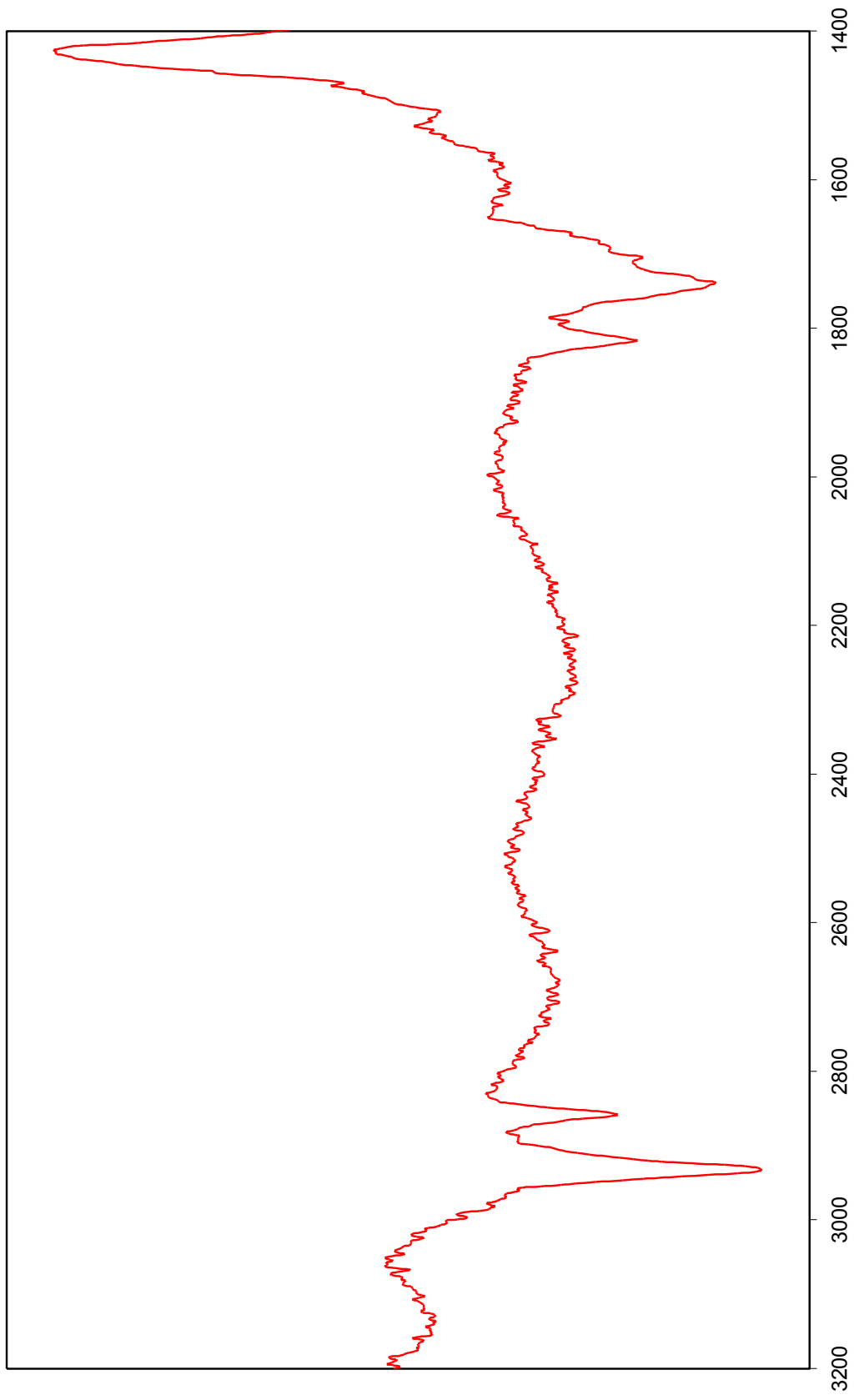
11-Acid IR n-Hexylamine Amide Spectrum



11-Acid 4-Nitroaniline Amide IR Spectrum



11-Acid Ethanol Ester IR Spectrum



11-Acid 4-Nitrophenol Ester IR Spectrum

