Fall 11-23-2021

SYNTHESIS AND STYRENE COPOLYMERIZATION OF OCTYL 2-CYANO-3-(R-PHENYL)-2-PROPENOATES

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Recommended Citation

Wasilewski, Martin S., "SYNTHESIS AND STYRENE COPOLYMERIZATION OF OCTYL 2-CYANO-3-(R-PHENYL)-2-PROPENOATES" (2021). *College of Science and Health Theses and Dissertations*. 407.
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SYNTHESIS AND STYRENE COPOLYMERIZATION OF OCTYL 2-CYANO-3-(R-PHENYL)-2-PROPENOATES

By

Martin S. Wasilewski

A Thesis
Submitted to the Department of Chemistry
DePaul University
In Partial Fulfillment of the Requirements
for the Degree of Master of Science
November 2021

Abstract

Novel alkyl ring-substituted octyl phenylcyanoacrylates (OPCA), $RPhCH=C(CN)CO_2CH_2(CH_2)_6CH_3$, where R is H, 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-propyl, 4-i-propyl, 4-butyl, 4-t-butyl, 4-i-butyl) were prepared and copolymerized with styrene. The ethylenes were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and octyl cyanoacetate, and characterized by CHN analysis, IR, ^1H and ^{13}C NMR. All the ethylenes were copolymerized with styrene in solution with radical initiation (ABCN) at 70°C. The compositions of the copolymers were calculated from nitrogen analysis. Compositions of ST-OPCA copolymers ranged from 18.6 % to 27.4% of the OPCA monomer. This composition was calculated via nitrogen elemental analysis with alternating sequences of styrene. The order of relative reactivity ($1/r_1$) with the radical end of the ST-polymer with OPCA was H (1.82) > 4-buytl (1.80) > 4-i-butyl (1.75) > 4-t-butyl (1.61) > 4-ethyl (1.46) > 3-methyl (1.44) > 4-methyl (1.31) > 4-i-propyl (1.20) > 2-methyl (1.1) > 4-propyl (1.04). The copolymers were characterized by nitrogen analysis, IR, DSC and TGA. The thermal decomposition of the copolymers occurred in two steps: the first step between 200 °C to 400 °C with a slow second-step decomposition from 400 °C to 800 °C and residue (1.8% to 6.5%).

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I. Introduction

Cyanoacrylates are a family of vinyl monomers renowned for their high reactivity, instant adhesive properties, and wide-ranging applications [1–3]. Trisubstituted ethylenes (TSE), ring–functionalized (R^1) alkyl (R^2) phenylcyanoacrylates, $R^1PhCH = C(CN)CO_2R^2$ (PCA) continue to attract attention as compounds with a variety of applications [4-11]. Thus, methoxy ring-substituted methyl phenylcyanoacrylate, MPCA was used in synthesis of pyridotriazines and triazolopyridines [4]. Dimethylamino ring-substituted MPCA was examined among other cyanovinyl heteroaromatics in relation to organic nonlinear optics [5]. There are a number of applications of ethyl phenylcyanoacrylate (EPCA) and its ring-substituted derivatives which include studies of catalysis [6] and potential antimicrobial and antioxidant agents [7]. 2,4-Dimethoxyphenyl EPCA was used in design, synthesis and study of anticancer activity of novel benzothiazole analogues [8], in synthesis of thiazacridine derivatives as anticancer agents against breast and hematopoietic neoplastic cells [9] and in DABCO-catalyzed Knoevenagel condensation using hydroxy ionic liquid as a promoter [10]. EPCA monomers were involved in the catalytic study of N,N'-dialkylimidazolium dimethyl phosphates [11], in synthesis and study of antimicrobial activity of some cyanoacrylates [12], as well as in synthesis of 2-aminobenzimidazole derivatives used for antiproliferative activity in the suppression of human cancer cell growth[13].

In regards to polymerization reactivity, previous studies showed that PCAs, as all TSE monomers containing vinyl substituents larger than fluorine, have very low reactivity in radical homopolymerization due to polar and steric reasons [14]. Although steric difficulties preclude homopolymerization of such monomers, their copolymerization with a monosubstituted alkenes makes it possible to overcome these steric problems. Thus, copolymerization of electrophilic TSE monomers having alkenes substituted with halo, cyano, and carbonyl groups and electron-rich monosubstituted ethylenes such as styrene, *N*-vinylcarbazole, and vinyl acetate [15-17] show a tendency toward the formation of alternating copolymers - suggesting a way of functionalization of commercial polymers via introduction of isolated monomer units in copolymers. Earlier we have reported synthesis and styrene copolymerization of a number of alkyl ring-substituted methyl [18, 19], ethyl [20, 21], propyl [22], isopropyl [23], butyl [24], isobutyl [25], and methoxyethyl [26] PCAs.

Our objectives in exploration of novel octyl phenylcyanoacrylates (OPCA) were twofold: (1) to utilize Knoevenagel condensation for synthesis of OPCA compounds with a variety of potentially reactive functional groups and (2) to explore feasibility of radical copolymerization with a commercial monomer styrene.

Thus, in continuation of our investigation of novel TSE compounds we have prepared octyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2(CH_2)_6CH_3$, where R is H, 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-propyl, 4-*i*-propyl, 4-butyl, 4-*t*-butyl, 4-*i*-butyl, and explored the feasibility of their copolymerization with styrene. To the best of our knowledge, there have been no reports on either synthesis of these compounds, nor their copolymerization with styrene [27].

II. Experimental

II.1. Materials

Benzaldehyde (≥ 99%), 2-methyl (≥ 96.5%), 3-methyl (≥ 97%), 4-methyl (≥ 97%), 4-ethyl (≥ 97%), 4-propyl (≥ 95%), 4-isopropyl (≥ 98%), 4-butyl (≥ 90%), 4-t-butyl (≥ 97%), and 4-i-butyl (≥ 97%) benzaldehydes, octyl cyanoacetate (≥ 98%), piperidine (≥ 99%), 1,1'-azobiscyclohexanecarbonitrile (ABCN), styrene (≥ 99%), and toluene (≥ 98%) were used as received from Sigma-Aldrich Co. with chloroform-d and dichloromethane used as solvents for analysis of the TSE and copolymers.

II.2. Instrumentation

Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), FTIR, Gel Permeation Chromatography (GPC), and proton and carbon NMR were the instrumentation analyses used for characterization of the TSE compounds.

DSC and TGA were used to obtain thermal data, with DSC used on both the monomer and polymer, and TGA only for polymers. TGA analysis was used to measure the thermal degradation of the TSE copolymers using the TA Instruments TGA Q50, where the sample is loaded on a platinum pan and placed in a furnace from room temperature to 700 °C at a heating rate of 20°C/min. DSC analysis was performed on the TA Instruments DSC Q10 to determine the melting point and glass transition temperature T_g in sealed aluminum pans. The only solid monomer characterized in this analysis was the non-functionalized phenyl ring TSE compound and all copolymers. The heating range was from 20°C to 300°C at a rate of 15°C/min. The T_g was determined from the thermogram.

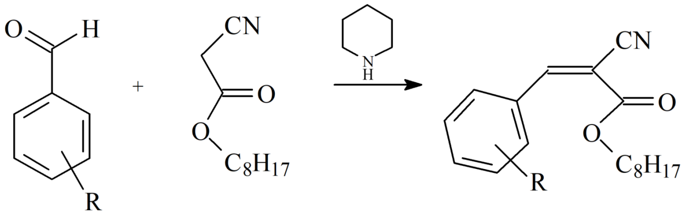
FTIR spectra were obtained with the ABB FTLA 2000 FT-IR spectrometer with the Horizon MB program and used to determine functional groups. Dichloromethane (Sigma Aldrich) was used to dissolve and transfer the monomer and copolymer onto the NaCl disk at 10% (w/v), and the solvent was allowed to evaporate.

The monomers were dissolved in chloroform-d (Sigma Aldridge) for ^{13}C and ^{1}H NMR at ambient temperature with a Bruker Avance 400 MHz spectrometer. Midwest Microlab, LLC provided CHN-elemental analyses of the TSE compounds and nitrogen analysis of the polymers.

III. Results and Discussion

III.1. Synthesis of Octyl Phenylcyanoacrylates

All octyl phenylcyanoacrylates (OPCA) compounds were prepared using the Knoevenagel condensation reaction [28] of appropriate benzaldehydes with octyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).

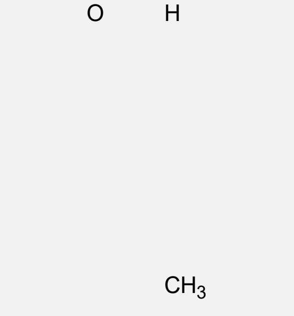
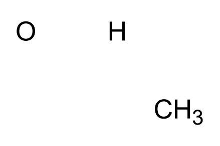
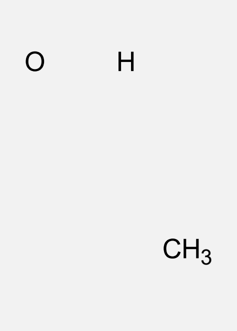
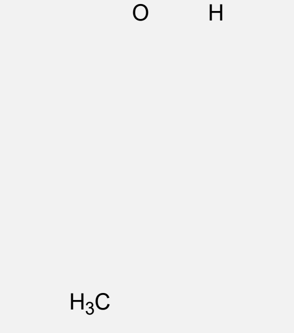
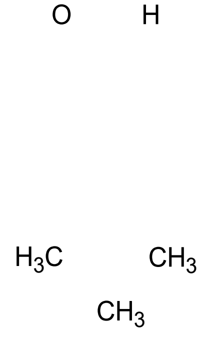


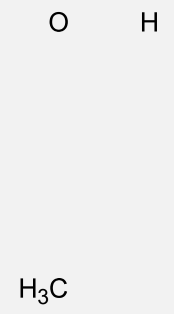
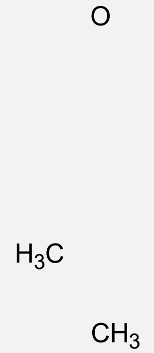
Scheme 1. Synthesis of octyl phenylcyanoacrylates where R is H, 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-propyl, 4-*i*-propyl, 4-butyl, 4-*t*-butyl, or 4-*i*-butyl.

The condensation of benzaldehydes with octyl cyanoacetates in a piperidine base yielded the octyl phenylcyanoacrylate compounds.

The standard synthesis began with mixing equimolar amounts of octyl cyanoacetate and the varying benzaldehyde in a 20 mL vial with 1-2 drops via pasteur pipette of piperidine while stirring. The octyl phenylcyanoacrylate compounds were filtered and purified via recrystallization in 2-proponal. There were no difficulties encountered throughout the condensation reaction and purification processes, giving the yields in Table 1.

Table 1. Alkyl Benzaldehyde R-groups for the synthesis of the OPCAs

TSE Group	R-Group	R-Group Structure	TSE Group	R-Group	R-Group Structure
M-0-20	H		**M-6-20**	4-propyl	
M-1-20	2-methyl		**M-7-20**	4-i-propyl	
M-2-20	3-methyl		**M-8-20**	4-butyl	
M-3-20	4-methyl		**M-9-20**	4-t-butyl	

M-5-20	4-ethyl		**M-10-20**	4-i-butyl	

With the structures of each of the TSE compounds highlighted above, Table 2 contains the percent yields of each functional group. It should be noted that no stereochemical analysis of the samples were performed due to no known configuration of stereoisomers (E/Z).

Table 2. Yield amounts for each R-Group on TSE structure

TSE Group	R-Group	Yield (wt%)
M-0-20	H	74
M-1-20	2-methyl	77
M-2-20	3-methyl	83
M-3-20	4-methyl	72
M-5-20	4-ethyl	71
M-6-20	4-propyl	79
M-7-20	4-i-propyl	87
M-8-20	4-butyl	88
M-9-20	4-t-butyl	75
M-10-20	4-i-butyl	81

III. 2. Characterization of OPCA

III. 2. 1. Physical Description

Table 3 lists the physical descriptions all TSE compounds, where all were liquids or pastes at room temperature.

Table 3. Octyl 2-cyano-3-phenyl-2-propenoate functional groups physical description

TSE Group	R-Group	Physical Description
M-0-20	H	Paste, Yellow
M-1-20	2-methyl	Paste, Yellow
M-2-20	3-methyl	Paste, Yellow
M-3-20	4-methyl	Paste, Yellow
M-5-20	4-ethyl	Liquid, Yellow
M-6-20	4-propyl	Liquid, Yellow
M-7-20	4-i-propyl	Paste, White
M-8-20	4-butyl	Liquid, Yellow
M-9-20	4-t-butyl	Paste, White
M-10-20	4-i-butyl	Liquid, Yellow

III. 2. 2. Elemental Composition

The composition and purity of the synthesized compounds were determined via Elemental Analysis (EA). This method would determine the mass fractions of carbon, hydrogen, and nitrogen (heteroatoms were not relevant to this study's compositions). Midwest Microlab, LLC, a commercial analytical lab, received 100 µg of each TSE monomer.

The theoretical calculated amounts for compositions were compared with the CHN composition of the commercial lab's findings to determine purity. A percent difference of less than 5% would indicate a relatively pure sample of the TSE monomer. The results of the calculated and found samples are presented in Table 4 below.

Table 4. Elemental Composition of Octyl Phenylcyanoacrylates between calculated and found samples.

TSE Number	R-Group	Calculated			Found		
		C	H	N	C	H	N
0	H	75.76	8.12	4.91	73.23	8.84	5.23
1	2-methyl	76.22	8.42	4.68	77.21	9.38	4.87
2	3-methyl	76.22	8.42	4.68	73.73	8.53	4.74
3	4-methyl	76.22	8.42	4.68	75.14	8.39	4.78

5	4-ethyl	76.64	8.68	4.47	73.53	8.00	4.47
6	4-propyl	77.02	8.93	4.28	76.42	9.29	4.71
7	4-i-propyl	77.02	8.93	4.28	66.27	7.86	4.07
8	4-butyl	77.38	9.15	4.1	76.42	9.67	4.2
9	4-t-butyl	77.38	9.15	4.1	76.32	9.55	4.62
10	4-i-butyl	77.38	9.15	4.1	75.75	8.90	4.08

While the calculated and found carbon compositions were within 5%, the H and N composition difference could be possible contamination from solvents. This also pertains to the carbon difference in composition.

In conclusion, the elemental analysis yielded relatively pure synthesized monomers.

III. 2. 3. IR Analysis

The presence of significant functional groups was determined via FTIR to distinguish differences in structure among similar compounds. Specifically for the TSE monomers, the presence of a nitrile, carbonyl, and C-H sp^3 peaks are among the functional groups characteristic to identifying TSE monomers.

The 4-i-propyl group FTIR of octyl phenylcyanoacrylate is presented below in Figure 1. Other monomer FTIR monomer data are in Appendix 1.

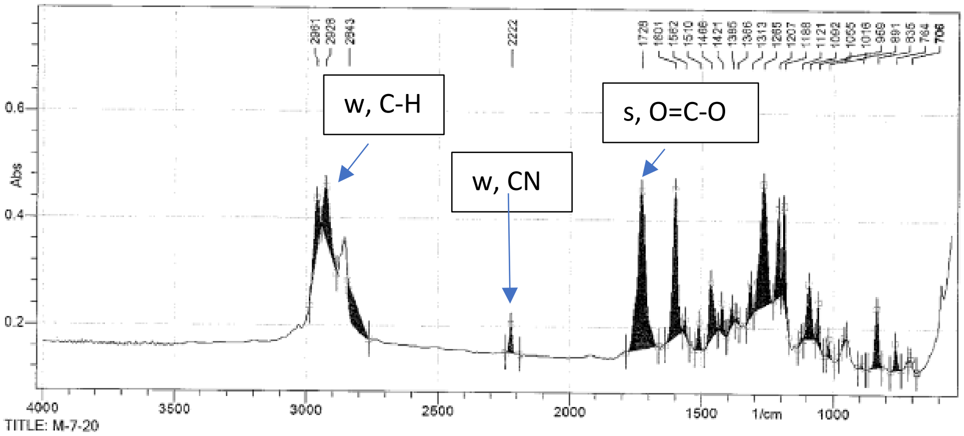


Figure 1. FTIR data for Octyl 2-cyano-3-(4-i-propyl-phenyl)-2 propenoates with characterizing functional groups.

Table 5. FTIR analysis data for Octyl 2-cyano-3-(R-phenyl)-2 propenoates

R-Group	Wave Number, cm^{-1} (intensity, bond/functional group assignment)
H	2924 (m, C-H), 6 2224 (m, CN), 1722 (s, C=O), 1265 (s, C-O-CH3), 771, 609 (s, C-H out of plane)
2-methyl	2926 (m, C-H), 2226 (m, CN), 1726 (s, C=O), 1593 (m, C=C), 1263 (s, C-OCH3), 814, 762, 725 (s, C-H out of plane)
3-methyl	2928 (m, C-H), 2224 (m, CN), 1728 (s, C=O), 1609 (m, C=C), 1230 (s, C-O-CH3), 881, 791, 762 (s, C-H out of plane)
4-methyl	2926 (m, C-H), 2222 (m, CN), 1726 (s, C=O), 1601 (m, C=C), 1207 (s, C-O-CH3), 816, 760 (s, C-H out of plane)
4-ethyl	2924 (m, C-H), 2222 (m, CN), 1728 (s, C=O), 1599 (C=C), 1267 (s, C-O-CH3), 835, 780 (s, C-H 8 out of plane)
4-propyl	2930 (m, C-H), 2222 (m, CN), 1728 (s, C=O), 1598 (C=C), 1265 (s, C-O-CH3), 841, 816, 762 (s, C-H out of plane)
4-i-propyl	2928 (m, C-H), 2222 (m, CN), 1728 (s, C=O), 1601 (C=C), 1265 (s, C-O-CH3), 835 (s, C-H out of plane)
4-butyl	3030-2813 (m, C-H), 2222 (m, CN), 1728 (s, C=O), 1599 (C=C), 1267 (s, C-O-CH3), 889, 762 (s, C-H out of plane)
4-t-butyl	2961, 2928 (m, C-H), 2224 (m, CN), 1726 (s, C=O), 1601 (C=C), 1223 (s, C-O-CH3), 835, 764 (s, C-H out of plane)
4-i-butyl	2928 (m, C-H), 2222 (m, CN), 1722 (s, C=O), 1599 (C=C), 1299 (s, C-O-CH3), 949, 847 (s, C-H out of plane)

As seen in Table 5, the key functional groups represented in the IR spectra include the nitrile (~2200 cm^{-1}), ester group (R-O-R, ~1200 cm^{-1})), and carbonyl stretch (~1725 cm^{-1}) from the acetate of the TSE monomers. The functional group stretches within each monomer IR spectrum were compared to an IR spectrum of cyanoacetate to confirm the presence of the relevant peaks.

The TSE monomer IR spectrum indicates success of synthesis via the presence of an alkene. The vinyl characteristics of each monomer were predicted. Regarding non-aromatic alkenes, the sp^3 and sp^2 hybridized C-H bonds were found between 2850 and 3000 cm^{-1} and between 3000-3100 cm^{-1}, respectively, while aromatic alkene C-H could be found between 3000-3100 cm^{-1}. FTIR made it possible to identify the synthesis of the alkene via the condensation mechanism to confirm the structure of the octyl phenylcyanoacrylates.

All IR spectra are presented in Appendix 1.

III. 2. 4. ^{1}H-NMR Analysis

The octyl phenylcyanoacrylates were also characterized via ^{1}H-NMR analysis, which is critical in identifying organic compounds via the positions of protons for structure determination. Figure 2 presents the crude spectrum for the 4-t-butyl group octyl phenylcyanoacrylate dissolved in chloroform-d.

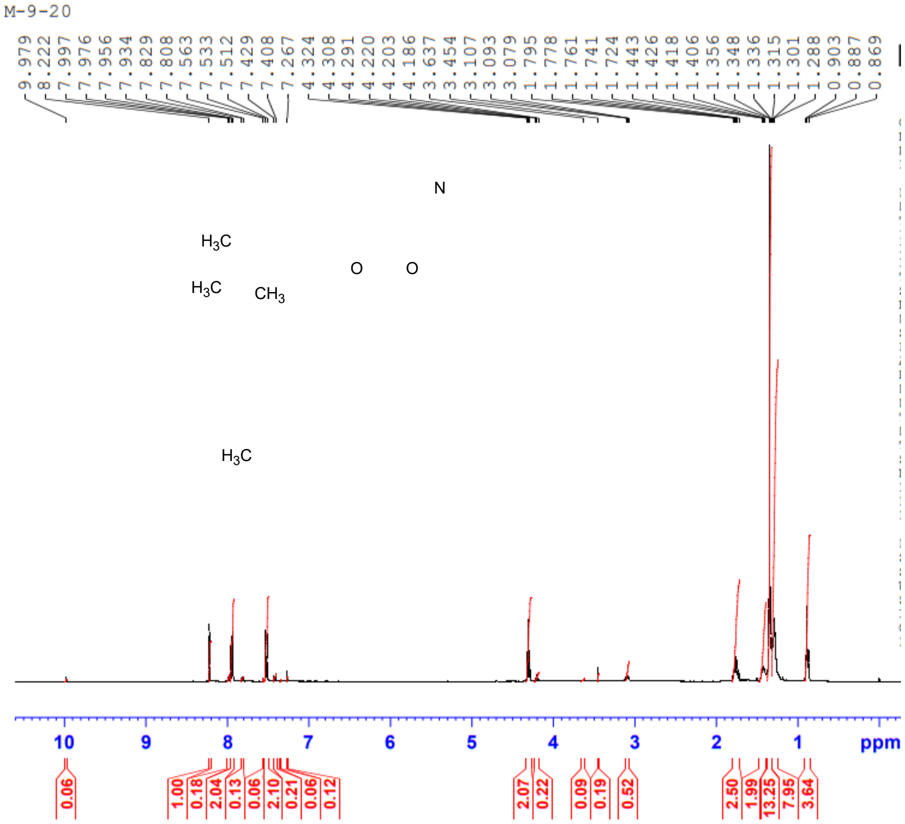


Figure 2. ^{1}H-NMR spectrum for Crude Octyl 2-cyano-3-(4-t-butyl-phenyl)-2 propenoate.

While the spectrum above shows the 4-t-butyl functional group monomer TSE, Table 6 presents the predicted functional groups of the crude samples with assignment, splitting, and integration.

Table 6. ^{1}H-NMR predicted data for Octyl 2-cyano-3-(R-phenyl)-2 propenoates of crude TSE samples

R-Group	Predicted Chemical shift, δ, ppm (splitting, integration, proton assignment)
H	8.3 (s, 1H, CH=), 8.2-7.3 (m, 5H, Ph), 4.3 (t, 2H, CO_2CH_2), 1.7- 1.8 (q, 2H, OCH_2CH_2), 1.6-1.5 (m, 6H, OCH_2CH_2 $(CH_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(CH_2)_2$), 0.9 (t, 3H, CH_3)
2-methyl	8.6 (s, 1H, CH=), 8.2-7.2 (m, 5H, Ph), 4.3 (t, 2H, CO_2CH_2), 2.5 (s, 3H, $PhCH_3$), 1.7-1.8 (q, 2H, OCH_2CH_2), 1.6-1.5 (m, 6H, $OCH_2CH_2(CH_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(CH_2)_2$), 0.9 (t, 3H, CH_3)
3-methyl	8.2 (s, 1H, CH=), 8.0-7.1 (m, 4H, Ph), 4.3 (t, 2H, CO_2CH_2), 2.4 ($PhCH_3$), 1.7-1.8 (q, 2H, OCH_2CH_2), 1.6-1.5 (m, 6H, $OCH_2CH_2(CH_2)_3$), 1.4-1.2 (m, 4H, $O(CH_2)_5(CH_2)_2$), 0.9 (t, 3H, CH_3)
4-methyl	8.2 (s, 1H, CH=), 8.0-7.2 (m, 4H, Ph), 4.3 (t, 2H, CO_2CH_2), 2.5 ($PhCH_3$), 1.9-1.7 (m, 2H, OCH_2CH_2), 1.5-1.3 (m, 8H, CH_2CH_2 $(CH_2)_4$), 0.9 (t, 3H, CH_3)
4-ethyl	8.2 (s, 1H, CH=), 8.0-7.3 (m, 4H, Ph), 4.3 (t, 2H, CO_2CH_2), 2.8 ($PhCH_2CH_3$), 1.8-1.7 (m, 2H, OCH_2CH_2), 1.5-1.3 (m, 8H, $C_2H_6(CH_2)_4$), 1.3-1.2 (t, 3H, $PhCH_2CH_3$), 0.9 (t, 3H, CH_3)
4-propyl	8.2 (s, 1H, CH=), 8.0-7.2 (m, 4H, Ph), 4.3 (t, 2H, $OCOCH_2$), 2.7-2.6 (t, 2H, $CH3CH_2CH_2Ph$), 1.8-1.7 (m, 2H, OCH_2CH_2), 1.7 (m, 2H, $CH_3CH_2CH_2Ph$), 1.5-1.3 (m, 8H, CH_2CH_2 $(CH_2)_4$), 1.0-0.8 (t, 3H, $CH_3CH_2CH_2Ph$; t, 3H, CH_3)
4-i-propyl	8.2 (s, 1H, CH=), 8.0-7.3 (m, 4H, Ph), 4.3 (t, 2H, $OCOCH_2$), 3.7 (m, 1H, CHPh), 1.8-1.7 (m, 2H, OCH_2CH_2), 1.5-1.3 (m, 8H, $O(CH_2)2(CH_2)_4$), 1.2 (d, 6H, $(CH_3)_2CH$), 0. (t, 3H, CH_3)
4-butyl	8.2 (s, 1H, CH=), 8.-7.2 (m, 4H, Ph), 4.3 (t, 2H, $OCOCH_2$), 2.7 (t, 2H, $C_3H_7CH_2Ph$), 1.8-1.7 (m, 2H, OCH_2CH_2), 1.7-1.6 (m, 2H, $C_2H_5CH_2CH_2Ph$), 1.5-1.3 (m, 8H, CH_2CH_2 $(CH_2)_4$), 1.0-0.8 (t, 3H, $CH_3(CH_2)_3Ph$),(t, 3H, CH_3)

4-t-butyl	δ 8.2 (s, 1H, CH=), 8.0-7.5 (s, 4H, Ph), 4.3 (t, 2H, $OCOCH_2$), 1.8- 1.7 (m, 2H, OCH_2CH_2), 1.5-1.3 (m, 8H, $O(CH_2)_2(CH_2)_4$), 1.3-1.2 (m, 9H, $(CH_3)_3C$-Ph), (m, 2H, $OC_6H_{12}CH_2$), 0.9 (t, 3H, CH_3)
4-i-butyl	8.2 (s, 1H, CH=), 8.0-7.2 (m, 4H, Ph), 4.3 (t, 2H, $OCOCH_2$), 2.5 (d, $(CH_3)_2CHCH_2$-Ph), 2.0-1.9 (m, (CH3)$_2$CHCH$_2$-Ph), 1.8-1.7 (m, 2H, OCH_2CH_2), 1.5- 1.2 (m, 8H, $O(CH_2)_2(CH_2)_4$), (m, 2H, $OC_6H_{12}CH_2$), 1.0-0.8 $(CH_3)_2CHCH_2$-Ph), $(CH_3)_2CHCH_2$-Ph), (t, 3H, CH_3)

Predicted peaks can be recognized in the spectral data of the crude samples. (Appendix 2).

III. 2. 5. ^{13}C-NMR Analysis

^{13}C-NMR spectral data were also essential in determining the structure of the octyl phenylcyanoacrylate monomers.

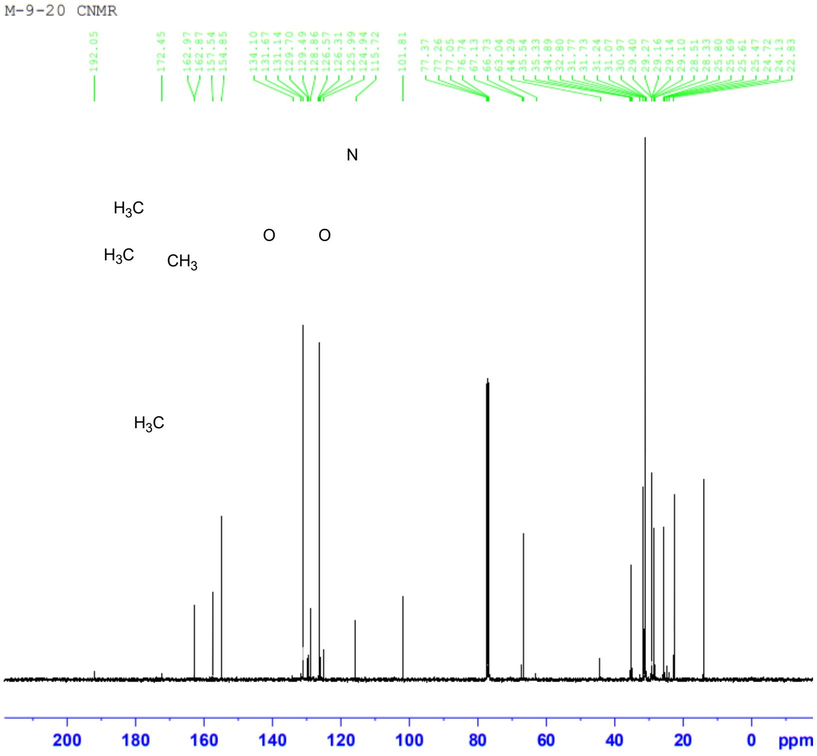


Figure 3. Crude ^{13}C-NMR data for Octyl 2-cyano-3-(4-t-butyl-phenyl)-2 propenoate with characterizing carbon shifts.

Figure 3 presents the Crude ^{13}C-NMR data for octyl 2-cyano-3-(4-t-butyl-phenyl)-2-propenoate. The ^{13}C chemical shifts and assignments are presented in Table 7 below.

Table 7. ^{13}C-NMR analysis data for Octyl 2-cyano-3-(R-phenyl)-2 propenoates

R-Group	Predicted Chemical shift, δ, ppm (splitting, integration, proton assignment)
H	164 (C=O), 153 (HC=), 135-128 (Ph), 116 (CN), 103 (C=), 67 (OCH_2), 32-22 ($OCH_2(CH_2)_6$), 14 (CH_3)
2-methyl	164 (C=O), 153 (HC=), 135-128 (Ph), 116 (CN), 103 (C=), 67 (OCH_2), 32-22 ($OCH_2\ (CH_2)_6$), 20 ($PhCH_3$), 14 (CH_3)
3-methyl	164 (C=O), 153 (HC=), 135-128 (Ph), 116 (CN), 103 (C=), 67 (OCH_2), 32-22 ($OCH_2(CH_2)_6$), 22 ($PhCH_3$), 13 (CH_3)
4-methyl	163 (C=O), 155 (HC=), 145, 130, 131, 129 (Ph), 116 (CN), 102 (C=), 67 (OCH_2), 32-23 ($OCH_2(CH_2)_6$), 22 ($PhCH_3$), 13 (CH_3)
4-ethyl	163 (C=O), 155 (HC=), 151, 132, 130, 129 (Ph), 116 (CN), 102 (C=), 67 (OCH_2), 32 ($OC_5H_{10}CH_2$), 29.5 ($OC_3H_6CH_2$), 28.5 ($PhCH_2$), 26 ($OC_2H_4CH_2$), 23 (CH_2CH_3), 15 ($PhCH_2CH_3$), 14 (CH_3)
4-propyl	163 (C=O), 155 (HC=), 132, 131, 130, 129, 128 (Ph), 116 (CN), 102 (C=), 67 ($OCOCH_2$), 38 ($CH_3CH_2CH_2Ph$), 32 ($O(CH_2)_5CH_2$), 30-26 ($OCH_2\ (CH_4$), 24 ($CH_3CH_2CH_2Ph$), 23 ($O(CH_2)_6CH_2$), 14.3 (CH_3), 13.8 ($Ph\text{-}CH_2CH_2CH_3$)
4-i-propyl	163 (C=O), 155 (HC=), 132, 130, 129, 128, 126 (Ph), 116 (CN), 102 (C=), 67 ($OCOCH_2$), 34 (CH_2Ph), 32 ($O(CH_2)_5CH_2$), 29 ($OCH_2(CH_2)_2$, 26 ($O(CH_2)_3CH_2$), 24 ($CH(CH_3)_2$), 23 ($O(CH_2)_6CH_2$), 14 (CH_3)
4-butyl	163 (C=O), 155 (HC=), 132, 131, 130, 129, 128 (Ph), 116 (CN), 102 (C=), 67 ($OCOCH_2$), 36 ($C_3H_7CH_2Ph$), 32 ($O(CH_2)_5CH_2$), 29 ($O(CH_2)_3(CH_2)_2$), 26 ($O(CH_2)_2CH_2$), 22.8 ($O(CH_2)_6CH_2$), 22.3 ($CH_2C_2H_4Ph$), 14.1 (CH_3), 13.9 ($Ph\text{-}C_3H_6CH_3$)
4-t-butyl	163 (C=O), 155 (HC=), 132, 130, 129, 128, 126 (Ph), 116 (CN), 102 (C=), 67 ($OCOCH_2$), 35 ($CH_3)_3C\text{-}Ph$), 31 ($CH_3)_3CPh$); 32 ($O(CH_2)_5CH_2$), 29 ($O(CH_2)_3(CH_2)_2$), 26 ($O(CH_2)_2CH_2$), 22.8 ($O(CH_2)_6CH_2$), 14.1 (CH_3)
4-i-butyl	163 (C=O), 155 (HC=), 149, 131, 130, 129 (Ph), 116 (CN), 101 (C=), 67 (OCH_2), 46 ($CH_3)_2CHCH_2\text{-}Ph$), 32 ($O(CH_2)_5CH_2$), 30 ($CH_3)_2CHCH_2\text{-}Ph$), 29

	$(O(CH_2)_3(CH_2)_2)$, 26 $(O(CH_2)_2CH_2)$, 22.8 $(O(CH_2)_6CH_2)$, 22 $(CH_3)_2CHCH_2$-Ph), 14.1 (CH_3)

Predicted peaks can be recognized in the spectral data of the crude samples. (Appendix 3). In conclusion, the combination of elemental analysis and crude spectral data may provide evidence for the octyl phenylcyanoacrylate structures.

III. 3. Copolymerization of OPCA and Styrene

III. 3. 1. OPCA-ST Copolymer Synthesis

Shown in Schemes 2 and 3 the OPCA monomers were copolymerized with styrene (ST) via the radical initiator 1,1'-azobiscyclohexanecarbonitrile (ABCN). The copolymers solubility was studied. The copolymers prepared in the present work were all soluble in ethyl acetate, THF, DMF and $CHCl_3$ and insoluble in methanol, ethyl ether, and petroleum ether. An attempted homopolymerization of OPCA yielded no polymer as indicated by the lack of precipitate in methanol. Steric difficulties are likely the reason for this lack of homopolymerization with the 1,1- and 1,2 disubstituted ethylenes. A copolymerization of styrene using the same procedure yielded 18.3% of polystyrene after 30 minutes of polymerization.

After it was discovered that the homopolymerization of OPCA-OPCA did not polymerize, ST-OPCA copolymerization was attempted. The polymers were prepared in 25 mL glass scintillation vials at ST/OPCA = 3 (mol) the monomer feed with 0.12 mol/L of ABCN. The overall monomer concentration was 2.44 mol/L in 10 milliliters of toluene. After the copolymerization was conducted at 70 °C, the mixture was cooled to room temperature and methanol was used to precipitate the copolymers in drop-wise fashion. Flaky, white precipitates formed as a result. The copolymers were dried in an oven set to 60 °C until the weight was constant.

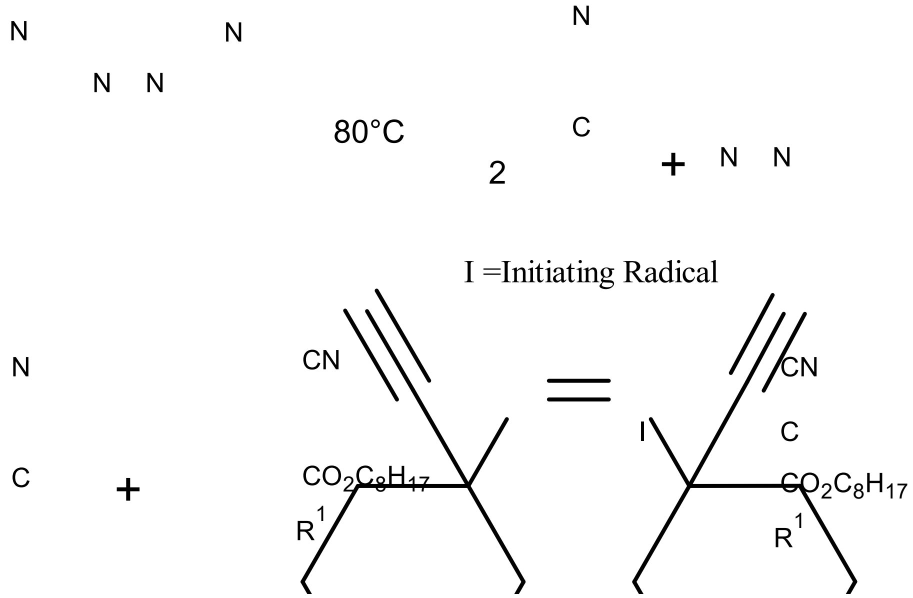
The cyano group in the OPCA was the key group for the nitrogen content analysis to determine the composition of the copolymers. Conversion was kept between 10% to 20%, minimizing compositional drift. Table 8 presents nitrogen content analysis results between OPCA and ST.

Table 8. Nitrogen content of OPCA-ST copolymer with yield.

TSE-ST Sample	R-Group	Yield (wt%)	Nitrogen Content (wt%)
P-0-20	H	11.6	2.50
P-1-20	2-methyl	10.5	2.02
P-2-20	3-methyl	13.2	2.26
P-3-20	4-methyl	16.9	2.18
P-5-20	4-ethyl	12.5	2.22
P-6-20	4-propyl	12.2	1.91
P-7-20	4-i-propyl	12.1	2.02
P-8-20	4-butyl	13.3	2.26
P-9-20	4-t-butyl	11.7	2.19
P-10-20	4-i-butyl	12.8	2.24

III. 3. 2. OPCA-ST Copolymerization Mechanism

The OPCA-ST copolymer was prepared using the steps of initiation, propagation, and termination. ABCN with a cleaved radical fragment at 80°C attacks the monomer alkene.

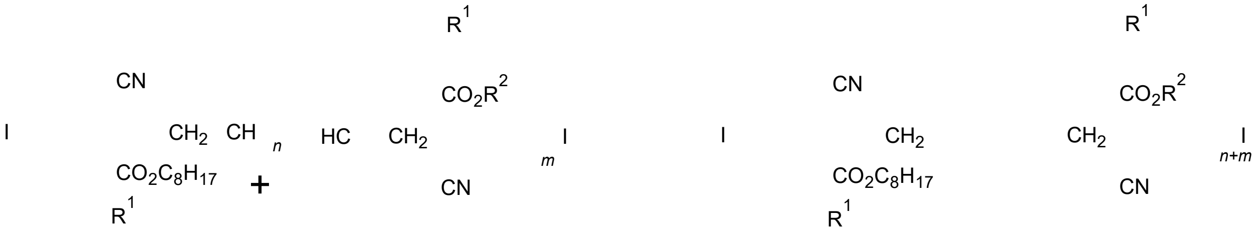


Scheme 8. Initiation of OPCA copolymerization

The initiating radical also begins propagation with the styrene monomer and propagation promotes the continual cleavage of alkenes on ST and OPCA, shown in Scheme 8 and 9.

Scheme 9. Propagation of OPCA copolymerization with styrene

Scheme 10 shows the final step of the copolymerization is the termination of the OPCA-ST copolymer via coupling of the two radicals.



Scheme 10. Termination of OPCA via coupling ST-OPCA radicals, where R^1 is the functional group on ring and R^2 is the octyl group, C_8H_{17}

III. 4. Characterization of OPCA-ST Copolymer

III. 4. 1. Composition Determination of the Copolymer

As mentioned previously, nitrogen content analysis is used to determine the ST-OPCA copolymer composition (Table 8). Monomer reactivity is responsible for the difference in ST and OPCA monomer units within the copolymer during the propagation.

The OPCA portion of the copolymer (**y**) is the only part containing nitrogen (within the nitrile), so the amount of nitrogen will determine the content of the TSE. Styrene's content is represented by **x**.

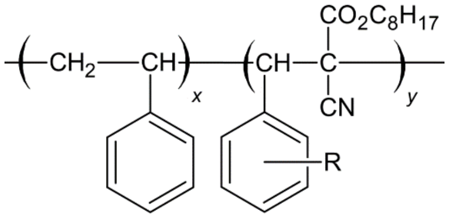


Table 9 presents the results of calculation to determine the mol% of ST and OPCA in the copolymer.

Table 9. Calculations from nitrogen content for determination of TSE and ST mole fraction %

R-Group	MW	N (g)	Mol N	TSE (g)	ST (g)	Mol ST	Mol fr TSE	TSE (mol %)	Mol fr ST	ST (mol %)
H	285	2.5	.18	50.9	49.1	.47	.274	27.4	.73	72.6
2-methyl	299	2.02	.14	43.1	56.9	.55	.209	20.9	.79	79.1
3-methyl	299	2.26	.16	48.3	51.7	.5	.245	24.5	.75	75.5
4-methyl	299	2.18	.16	46.6	53.4	.51	.233	23.3	.77	76.7
4-ethyl	313	2.22	.16	49.6	50.4	.48	.247	24.7	.75	75.3
4-propyl	328	1.914	.14	44.8	55.2	.53	.205	20.5	.8	79.5
4-i-propyl	328	2.022	.14	47.4	52.6	.51	.222	22.2	.78	77.8
4-butyl	342	2.26	.16	55.2	44.8	.43	.273	27.3	.73	72.7
4-t-butyl	342	2.19	.16	53.5	46.5	.45	.259	25.9	.74	74.1
4-i-butyl	342	2.24	.16	54.7	45.3	.44	.269	26.9	.73	73.1

Table 10. Mol % determination in ST and OPCA within copolymer

TSE-ST Sample	R-Group	ST mol %	OPCA mol%
P-0-20	H	72.6	27.4
P-1-20	2-methyl	79.1	20.9
P-2-20	3-methyl	75.5	24.5
P-3-20	4-methyl	76.7	23.3
P-5-20	4-ethyl	75.3	24.7
P-6-20	4-propyl	79.5	20.5
P-7-20	4-i-propyl	77.8	22.2
P-8-20	4-butyl	72.7	27.3
P-9-20	4-t-butyl	74.1	25.9

P-10-20	4-i-butyl	73.1	26.9

Nitrogen analysis in Table 10 showed that OPCA was present in 18.6 to 27.4 mol% of the copolymer prepared at ST-OPCA = 3 (mol), displaying high reactivity of between the styrene radical and OPCA monomer.

III. 4. 2. Monomer Reactivity within the Copolymer

Equimolar amounts of the monomer were used for the reaction to determine the composition of the copolymer. The TSE monomer's radical reactivity indicated that there was no polymerization occurring, so styrene's relative reactivity was examined. The copolymers synthesized would have alternating (i.e. R-ST-TSE-ST-TSE-R) and block (i.e. R-ST-ST-ST-R) arrangements because of styrene's own reactivity with other styrene monomers, as discussed previously. To minimize the composition drift, equimolar amounts were used.

The reactive centers, or radical chain ends, possible are ~ST• (M_1) and ~TSE• (M_2). The possible combinations of propagations of reactive centers are presented in Table 10.

Table 11. Four possible propagation reactions between the TSE and ST

Reaction Number, reaction constants	Radical Chain End	Monomer	New Radical Chain End
1, k_{11}	~ST•	ST	~ST-ST•
2, k_{12}	~ST•	TSE	~ST-TSE•
3, k_{21}	~TSE•	ST	~TSE-ST•
4, k_{22}	~TSE•	TSE	~TSE-TSE•

As labeled in the first column on Table 11, the reaction constants are presented for the self-propagation of ST (k_{11}), cross-propagation of TSE-ST (k_{21}), cross-propagation of ST-TSE (k_{12}), and self-propagation of TSE-TSE (k_{22}).

The copolymer composition data obtained at a 3:1 ratio of monomer feed were used to understand the monomer reactivities. With the rate constants not dependent on time, Equation 3 presents the total copolymer composition, with m_1 and m_2 being the mole fractions of ST and

TSE monomers, respectively. The concentrations of ST and TSE in the monomer feed are $[M_1]$ and $[M_2]$, respectively. The reactivity ratios r_1 and r_2 will represent rate constants used in self-propagation and cross-propagation. The reactivity ratios are presented below:

$$r_1 = \frac{k_{11}}{k_{12}} \tag{1}$$

$$r_2 = \frac{k_{22}}{k_{21}} \tag{2}$$

The copolymer composition equation including the following reactivity ratios will be presented below:

$$\frac{m_1}{m_2} = \frac{[M_1](r_1[M_1]+[M_2]}{[M_2]([M_1]+r_1[M_2]} \tag{3}$$

Due to the absence of self-propagation in the TSE monomer ($k_{22} = 0$), r_2 will be 0. In addition, it is known the monomer concentration feed will be a 3 to 1 ratio ($[M_1]/[M_2] = 3$). The addition of these knowns will yield the following equation.

$$r_1 = \left(\frac{\frac{m_1}{m_2}-1}{3}\right) \tag{4}$$

The relative reactivity of the ST-TSE monomer would be rearranged the following way:

$$1/r_1 = \left(\frac{3}{\frac{m_1}{m_2}-1}\right) \tag{5}$$

Using Equation 5 and the provided mol fractions from the Nitrogen composition analysis, Table 12 presents the relative reactivity for the TSE monomers synthesized.

Table 12. Copolymerization of ST-TSE Monomer relative reactivities

R-Group	**ST mol fraction, m_1**	**TSE mol fraction, m_2**	**r_1**	**$1/r_1$**
H	.726	.274	0.55	1.82
2-methyl	.791	.209	0.93	1.10
3-methyl	.755	.245	0.70	1.44
4-methyl	.767	.233	0.76	1.31

4-ethyl	.753	.247	0.68	1.46
4-propyl	.795	.205	0.96	1.04
4-i-propyl	.778	.222	0.83	1.20
4-butyl	.727	.273	0.55	1.80
4-t-butyl	.741	.259	0.62	1.61
4-i-butyl	.731	.269	0.57	1.75

Between the eight TSE monomers, the order of reactivity ($1/r_1$) was H (1.82) > 4-butyl (1.80) > 4-i-butyl (1.75) > 4-t-butyl (1.61) > 4-ethyl (1.46) > 3-methyl (1.44) > 4-methyl (1.31) > 4-i-propyl (1.20) > 2-methyl (1.1) > 4-propyl (1.04). It should be noted that 4-propyl could be an outlier given that the other 4-alkyl R-groups have a higher order of reactivity. This study did not investigate 4-propyl's lower order of reactivity. Minimal copolymer composition drift should be assumed from the 3:1 monomer feed. Because there are a few assumptions being made within the kinetic model, there can be high error in relative reactivity determination and need to be treated as rough estimates when used for commercial development.

III. 4. 3. Solubility

The copolymers prepared in the present work are all soluble in ethyl acetate, THF, DMF and $CHCl_3$ and insoluble in methanol, ethyl ether, and petroleum ether.

III. 4. 4. FTIR Analysis

The presence of significant functional groups was determined via FTIR to distinguish supporting evidence for the synthesis of the copolymer, monomer, and polystyrene. Similar to the IR spectra of the TSE monomer, the presence of the copolymer can be identified via the same functional groups. These functional groups include the cyano (CN), carbonyl from the octyl acetate, and ester.

The FTIR of H-group octyl phenylcyanoacrylate is presented below in Figure 4. Other TSE FTIR data appear in Appendix 4.

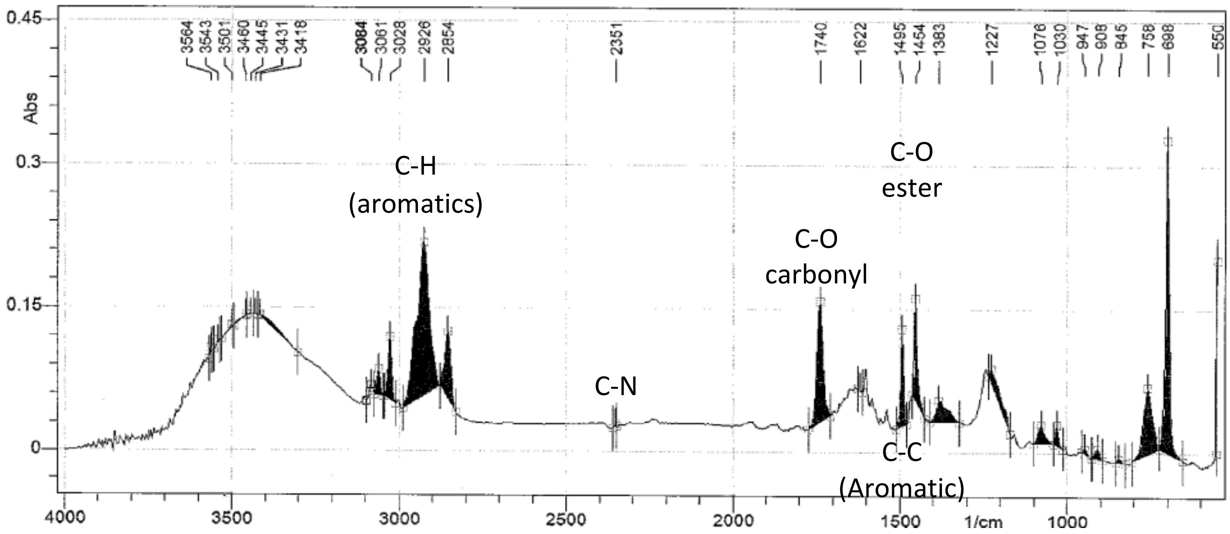


Figure 4. FTIR of the Octyl 2-cyano-3-(H-phenyl)-2 propenoate ST-TSE Copolymer

Table 13 below presents the three major functional group stretches between all R-Groups within this study. The H-group FTIR of ST-OPCA copolymer is presented in Figure 4. Other FTIR copolymer data are in Appendix 4.

Table 13. FTIR Major stretches within the ST-TSE Copolymer

R-Group	CN 2400-2100 (cm^{-1})	C-O, carbonyl 1850-1650 (cm^{-1})	C-O, ester 1320-900 (cm^{-1})
H	2351	1740	1227
2-methyl	2351	1738	1244-1227
3-methyl	2351	1740, 1715	1234-906
4-methyl	2349	1740	1227-1030
4-ethyl	2351	1740	1227-962
4-propyl	2351	1740	1225-1030
4-i-propyl	2351	1740	1259-1030
4-butyl	2351	1740	1227-1030
4-t-butyl	2241	1740	1227-1030
4-i-butyl	2351	1740	1259-1030

Among the three major functional groups present within the ST-TSE copolymer, carbonyls should be found around 1650 to 1850 cm^{-1}, esters from 900 to 1320 cm^{-1}, and nitriles from 2100 to 2400 cm^{-1}. From the data, the carbonyls were found around 1740 cm^{-1} and the esters were found between 962 and 1250 cm^{-1}. C-H stretches peaks were between 3000-3100 cm^{-1} indicating aromatics and aliphatic alkenes. Aliphatic alkanes were observed less than 2850-3000 cm^{-1}. C-H peaks for bending and rocking were observed in the regions 1300-1500 cm^{-1} and 600-920 cm^{-1}, respectively. C-C peaks can be found in the regions of 1220-800 cm^{-1} and 1600-1700 cm^{-1}. The aromatic rings for the copolymers were found in the regions of 3065-3030 cm^{-1} and 3103-3003 cm^{-1}. Cyano-groups can also be found around 2220 cm^{-1}, which the data reported as 2351 cm^{-1}.

III. 4. 5. Glass Transition

The thermal behavior of the copolymers is measured using DSC and TGA, with DSC specifically looking at the way the material's heat capacity differs with respect to temperature. The traces of transitions obtained from this graph can be melting temperatures, glass transitions, phase changes, and curing. For the purpose of this study, the glass transition temperature (T_g) of the copolymer is determined. Due to the monomer units being liquid or paste, the DSC data could not be obtained to determine the melting points. The H-group DSC of ST-OPCA copolymer is presented below in Figure 7. Other DSC copolymer data are in Appendix 5.

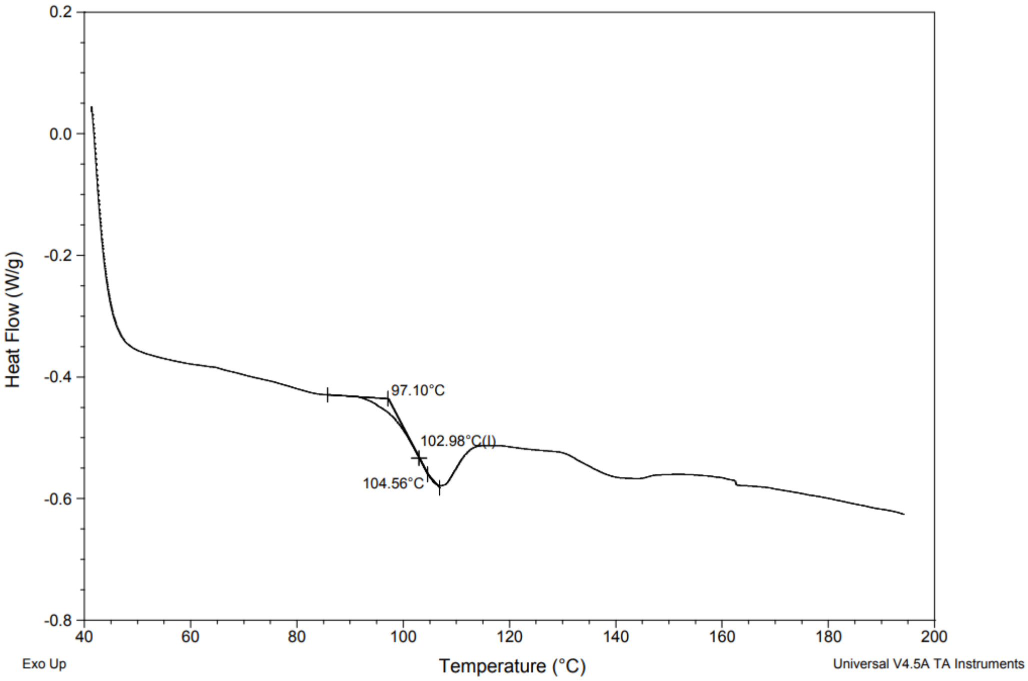


Figure 7. A DSC graph shows an example of the analysis of the Octyl 2-cyano-3-(H-phenyl)-2 propenoate copolymer

Table 14 shows the DSC data for each R-Group of the ST-OPCA copolymers.

Table 14. DSC data for ST-OPCA copolymers

TSE R-Group	Glass Transition Temp (°C)
H	102.98
2-methyl	95.81
3-methyl	116.99
4-methyl	102.27
4-ethyl	97.13
4-propyl	92.76
4-i-propyl	95.12
4-butyl	86.85
4-t-butyl	99.94
4-i-butyl	97.41

III. 4. 6. Thermal Stability

Another critical property measured is the thermal decomposition of the copolymer via TGA. The degradation of these copolymers occurs in two steps: a rapid decomposition from 200 °C to 400 °C with a slow decomposition from 400 °C to 800 °C which decomposes the leftover residue. The leftover residue is any remaining impurity or ash after the thermal degradation of the polymer, which could indicate any potential contaminate or not oxidized polymer after heating. Figure 8 shows a TGA plot of octyl 2-cyano-3-(H-phenyl)-2 propenoate. Onset decomposition temperature ranged from 128 °C to 198 °C, 10% wt loss from 279 °C to 294 °C, 50% wt loss from 325 °C to 334 °C, and finally, in the second decomposition, 1.8% to 6.4% residual mass remained. It should be noted that the residue formation mechanism was not investigated and due to this being a feasibility study, no additional experiments were performed to explore this.

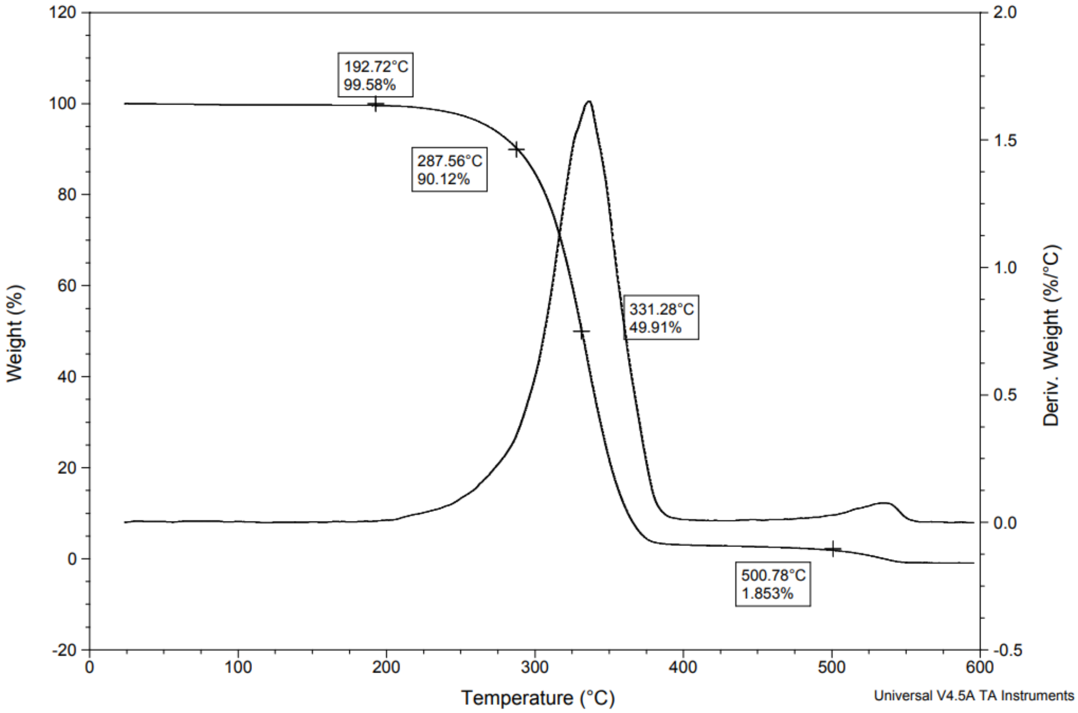


Figure 8. A TGA graph shows an example of the analysis of the Octyl 2-cyano-3-(H-phenyl)-2 propenoate copolymer

The H-group TGA of ST-OPCA copolymer is presented in Figure 8. Other TGA copolymer data are in Appendix 6.

Table 15. TGA data for ST-OPCA copolymers

TSE R-Group	Onset (°C)	90% (°C)	50% (°C)	Residue at 500 °C (%)
H	192.72	287.56	331.28	1.853
2-methyl	130.83	284.19	328.59	2.232
3-methyl	133.52	286.88	333.97	3.684
4-methyl	150.34	294.28	337.33	4.293
4-ethyl	128.14	276.79	325.22	4.355
4-propyl	177.25	280.16	327.24	4.613
4-i-propyl	198.10	284.87	328.59	6.375
4-butyl	156.74	280.02	328.11	5.688
4-t-butyl	157.42	283.41	328.11	4.705

4-i-butyl	169.61	272.57	325.4	6.496

As shown in Table 15, the onset temperature for the TGA averaged 158.34 °C. The temperatures at 90% decomposition of the copolymer averaged 284.24 °C. At 50% decomposition of the copolymer, the temperatures averaged 317.60 °C. The average leftover residue after the thermal decomposition at 500 °C was 4.20%.

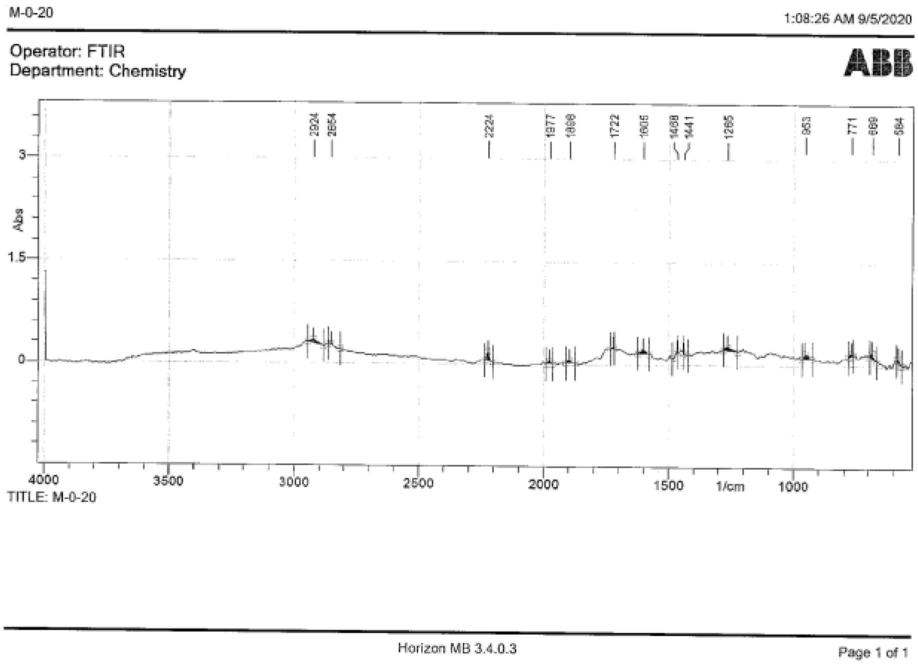
IV. Conclusions

Novel alkyl ring-substituted octyl phenylcyanoacrylates (OPCA), $RPhCH=C(CN)CO_2CH_2(CH_2)_6CH_3$, where R is H, 2-methyl, 3-methyl, 4-methyl, 4-ethyl, 4-propyl, 4-i-propyl, 4-butyl, 4-t-butyl, 4-i-butyl) were prepared via Knoevenagel condensation catalyzed by the base piperidine. The condensation between ring-substituted benzaldehydes and octyl cyanoacetates yielded the trisubstituted ethylene compound (TSE). The characterization of the compounds was conducted via elemental analysis, IR, ^{1}H-NMR, and ^{13}C-NMR. Compositions of ST-OPCA copolymers ranged from 18.6 % to 27.4% of the OPCA monomer. The order of relative reactivity ($1/r_1$) with the radical end of the ST-polymer with OPCA was H (1.82) > 4-buytl (1.80) > 4-i-butyl (1.75) > 4-t-butyl (1.61) > 4-ethyl (1.46) > 3-methyl (1.44) > 4-methyl (1.31) > 4-i-propyl (1.20) > 2-methyl (1.1) > 4-propyl (1.04). The copolymers were characterized by IR and thermal analysis. The thermal decomposition of the copolymers occurred in two steps: the first step yielded a residue (1.8% to 6.5% wt) at 500 °C, which later fully decomposed in the 500 °C to 800 °C range.

APPENDICES FOR SPECTROSCOPIC DATA

APPENDIX 1 TSE IR SPECTRA

Octyl 2-cyano-3-(H-phenyl)-2 propenoate



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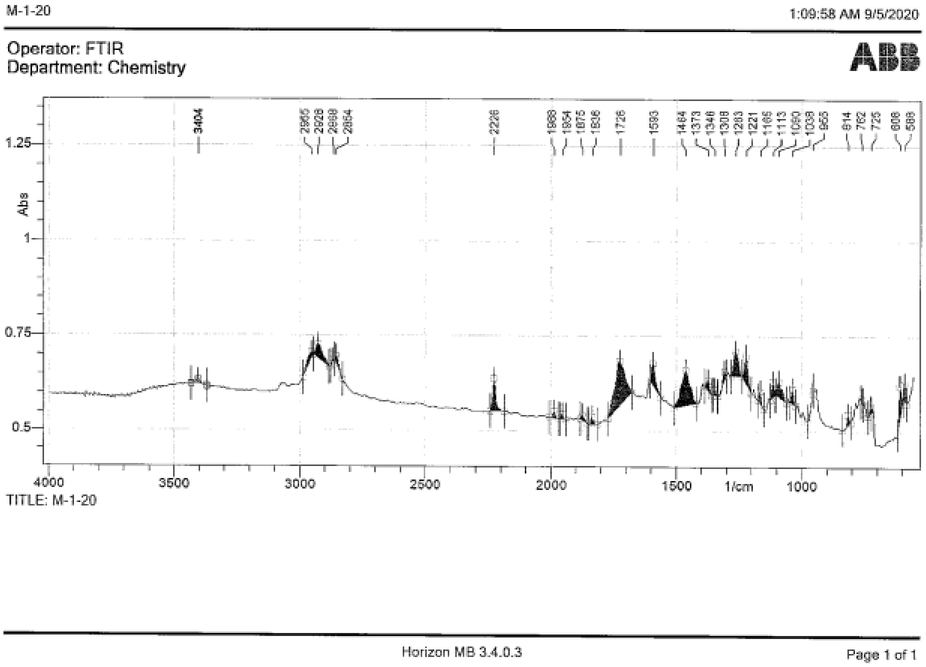
Horizon MB 3.4.0.3 Page 1 of 1

Octyl 2-cyano-3-(2-methyl-phenyl)-2 propenoate



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Department: Chemistry

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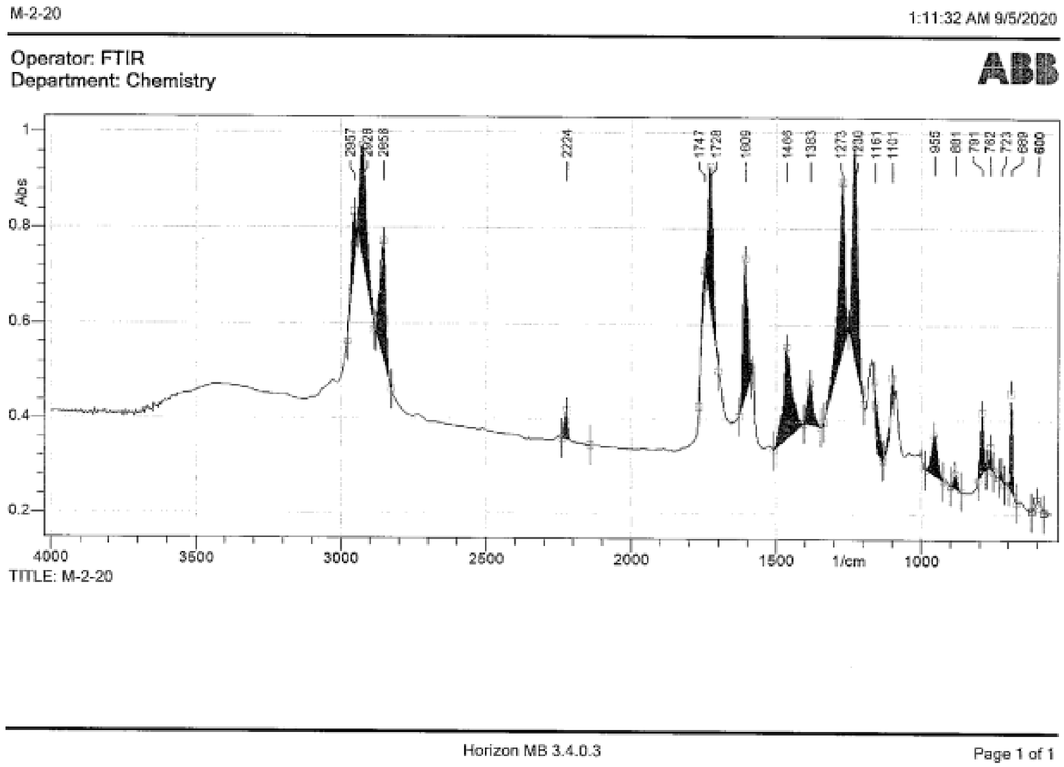
Horizon MB 3.4.0.3 Page 1 of 1

Octyl 2-cyano-3-(3-methyl-phenyl)-2 propenoate



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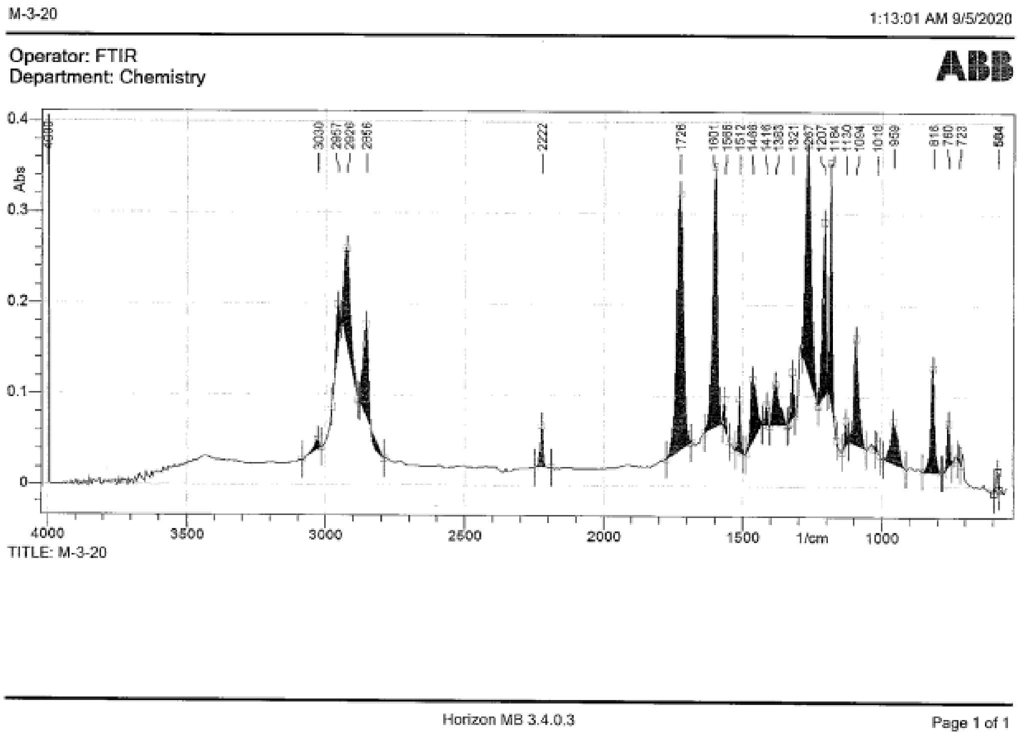
Octyl 2-cyano-3-(4-methyl-phenyl)-2 propenoate



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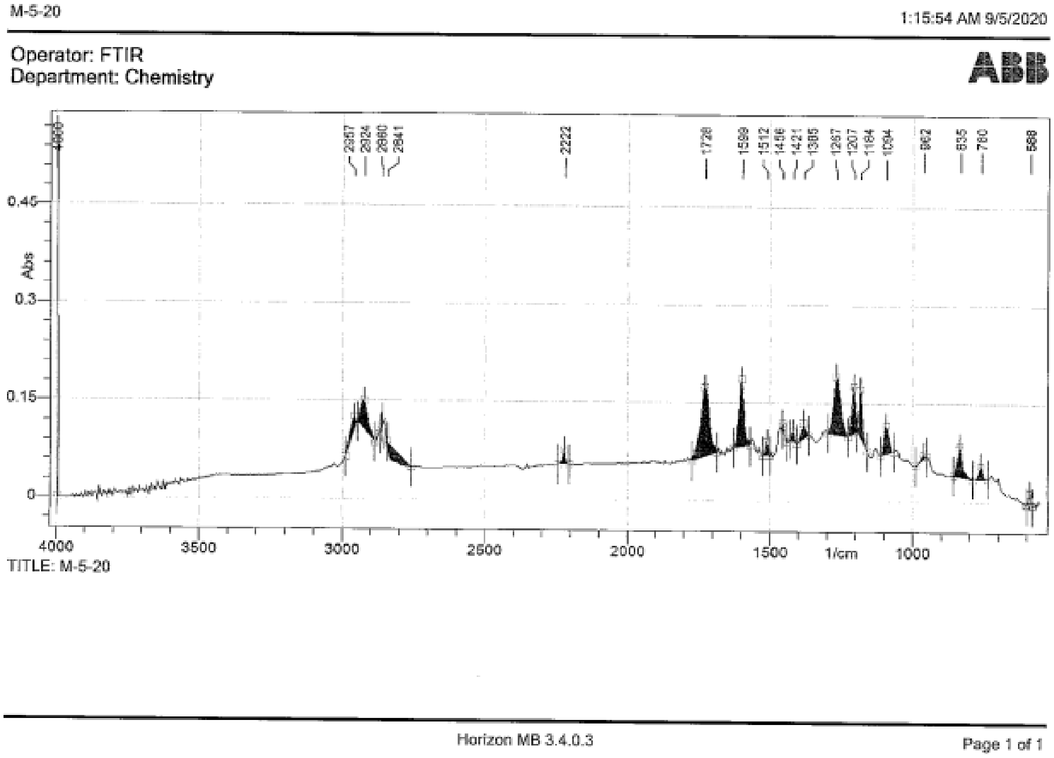
Octyl 2-cyano-3-(4-ethyl-phenyl)-2 propenoate



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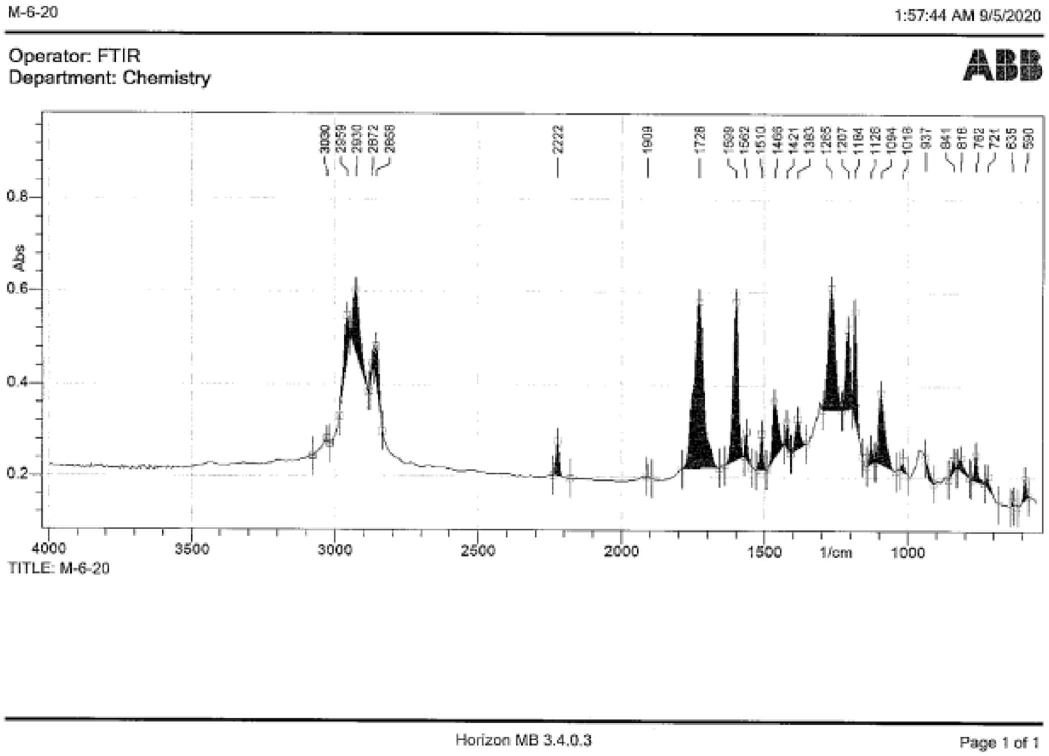
Octyl 2-cyano-3-(4-propyl-phenyl)-2 propenoate



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Department: Chemistry

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Octyl 2-cyano-3-(4-isopropyl-phenyl)-2 propenoate

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Department: Chemistry

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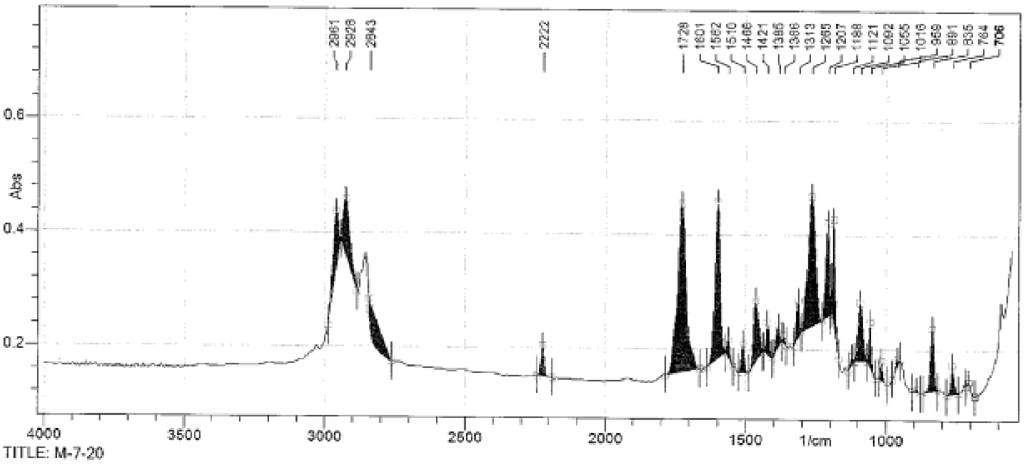

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Octyl 2-cyano-3-(4-butyl-phenyl)-2 propenoate

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Department: Chemistry

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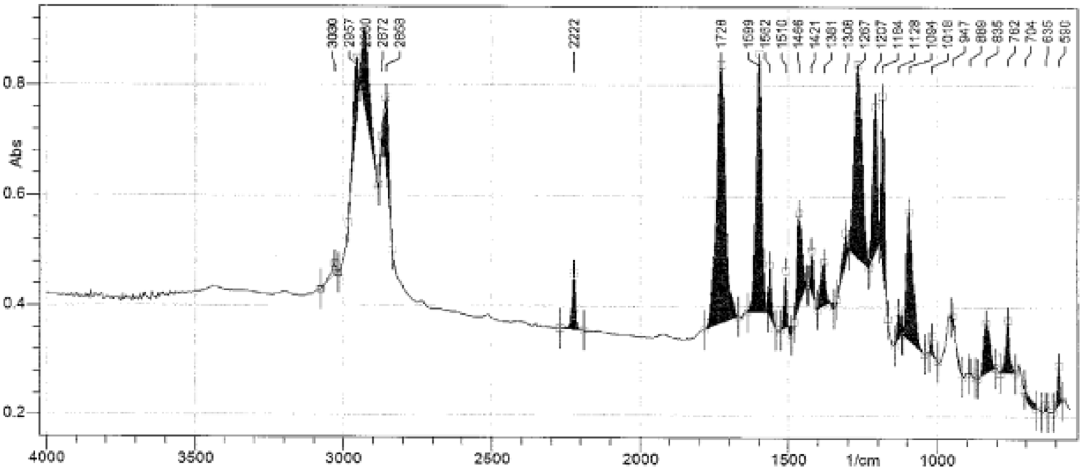

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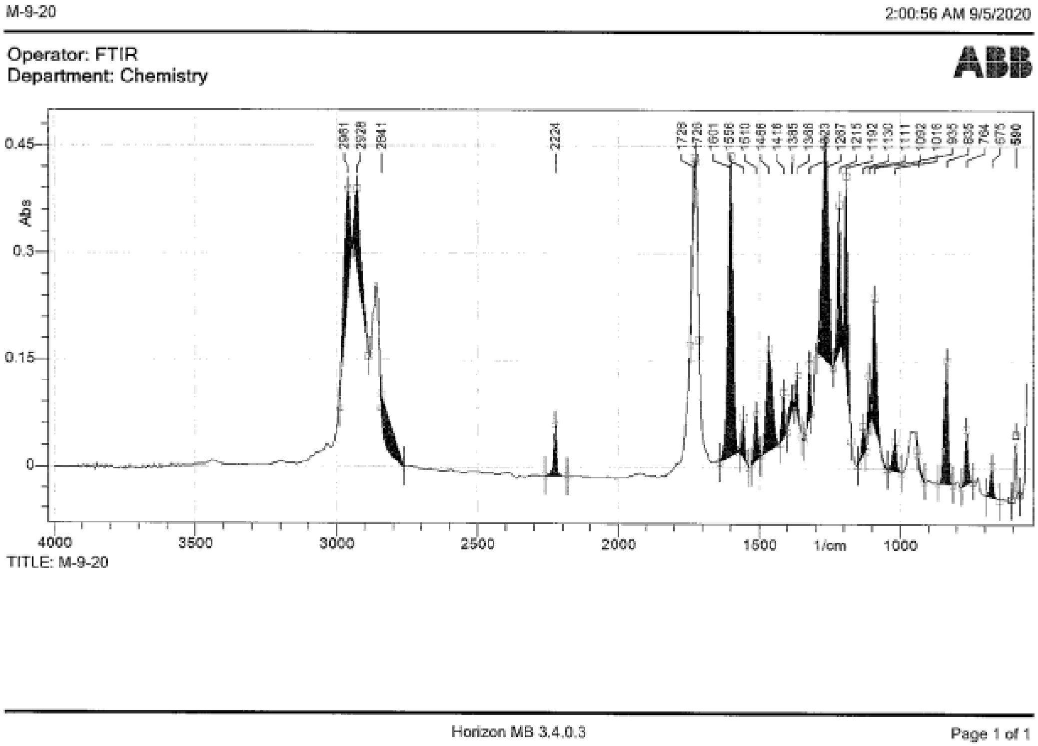
Horizon MB 3.4.0.3

Page 1 of 1

Octyl 2-cyano-3-(4-i-butyl-phenyl)-2 propenoate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Department: Chemistry

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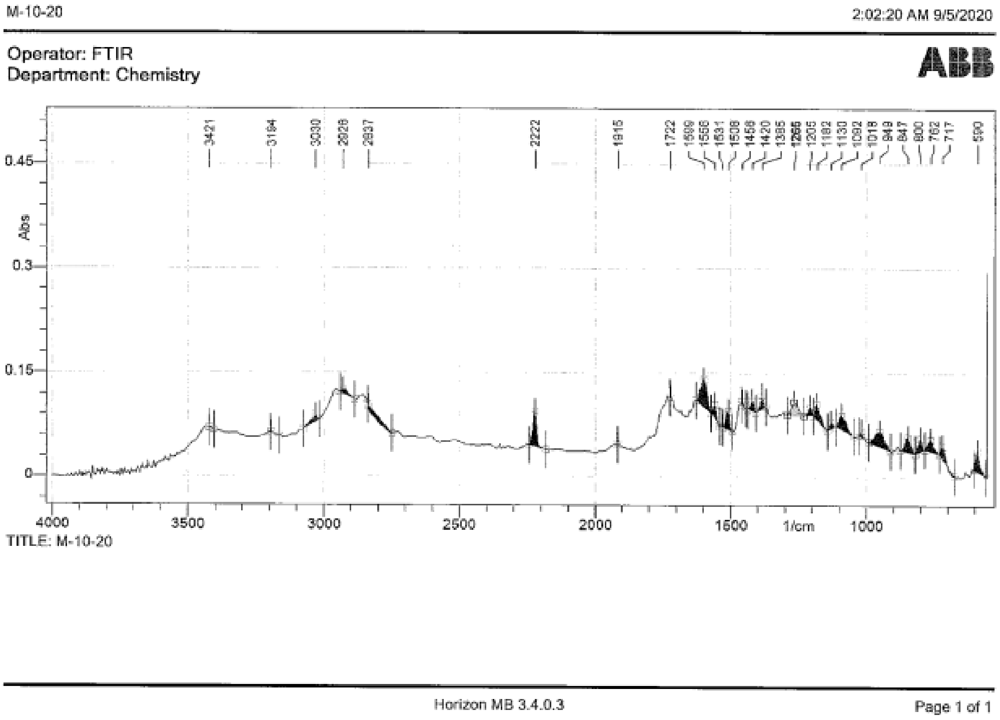
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Department: Chemistry

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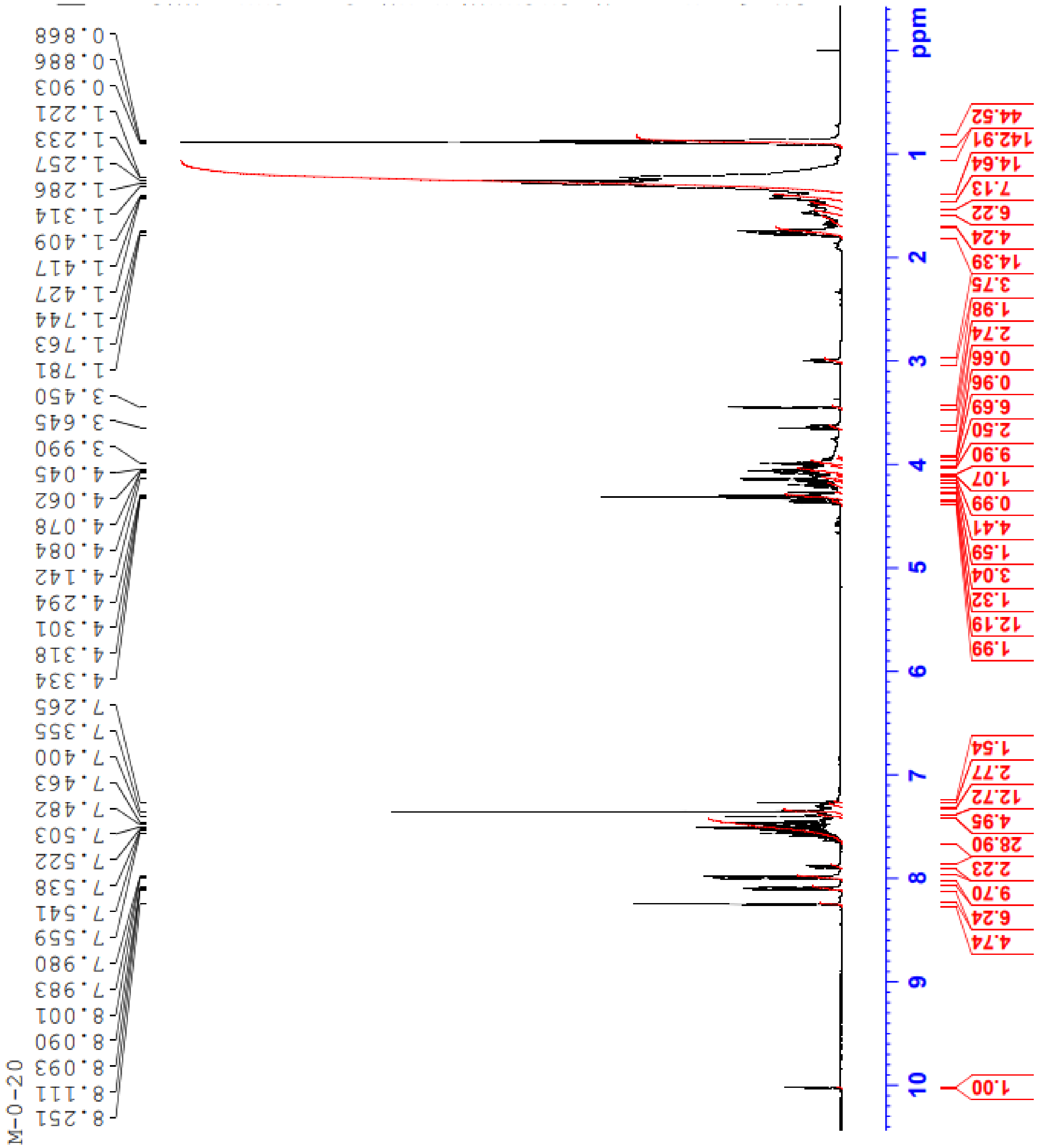
Horizon MB 3.4.0.3

Page 1 of 1

APPENDIX 2 ^{1}H-NMR SPECTRA

Octyl 2-cyano-3-(H-phenyl)-2 propenoate



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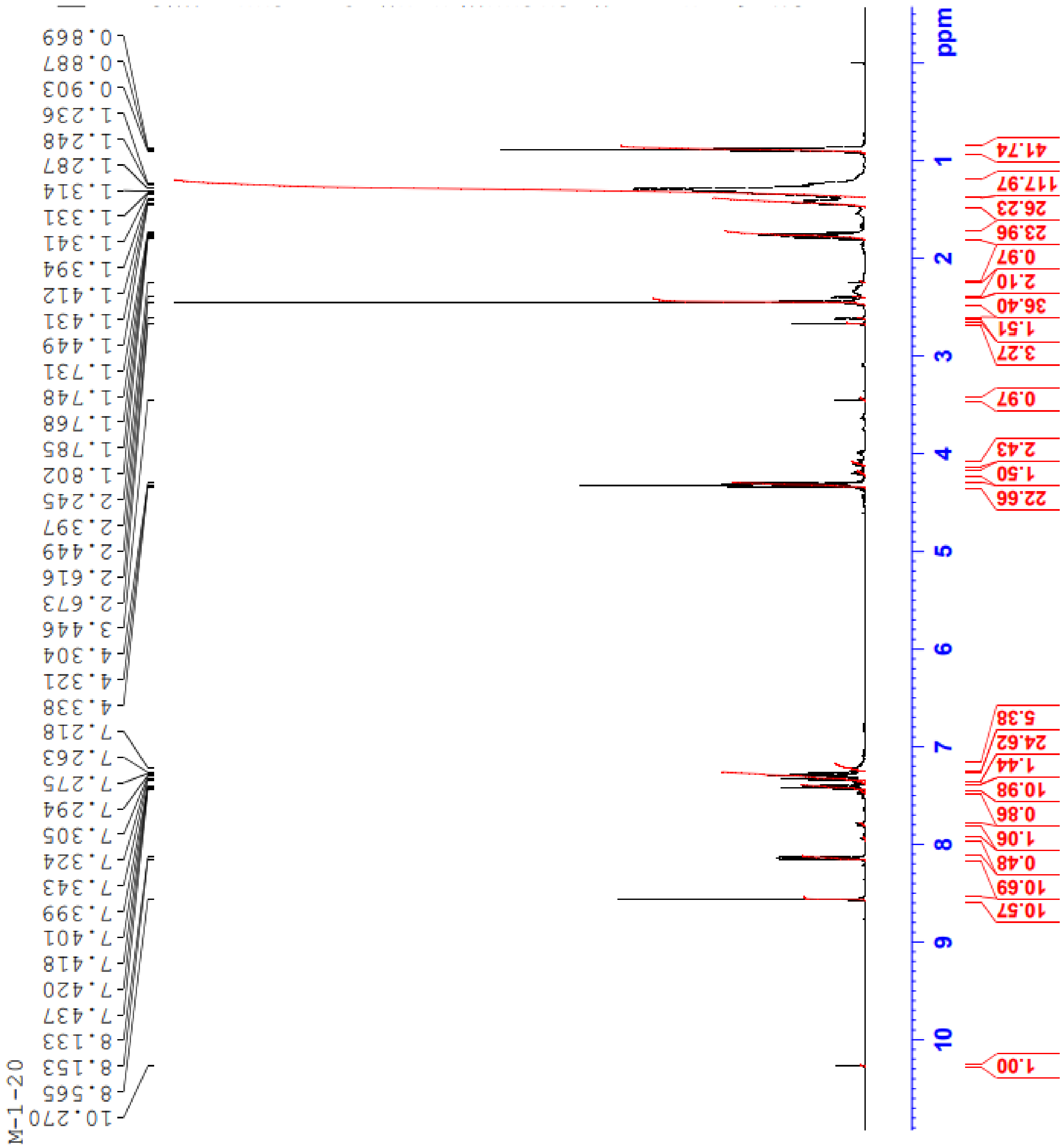

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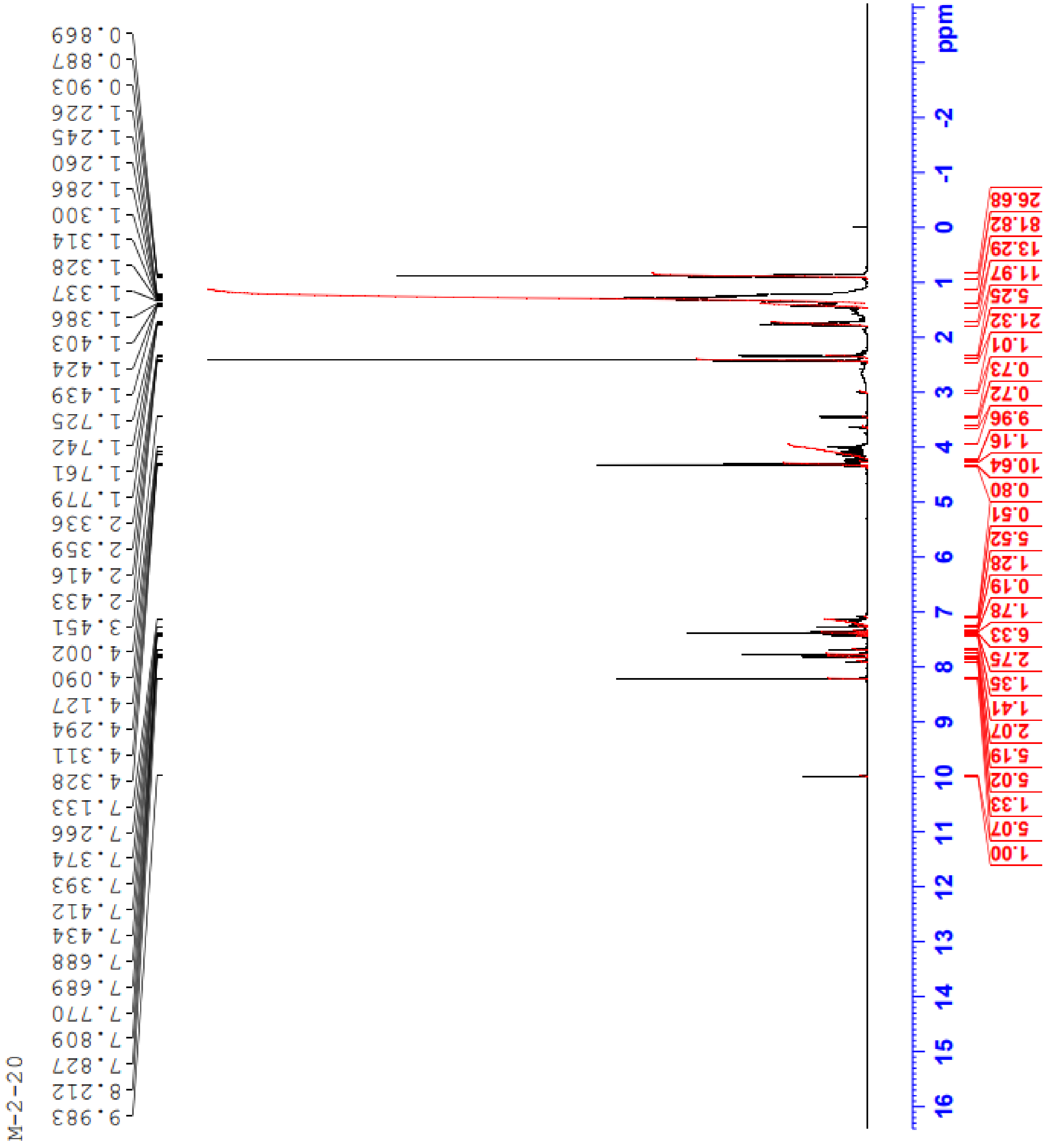

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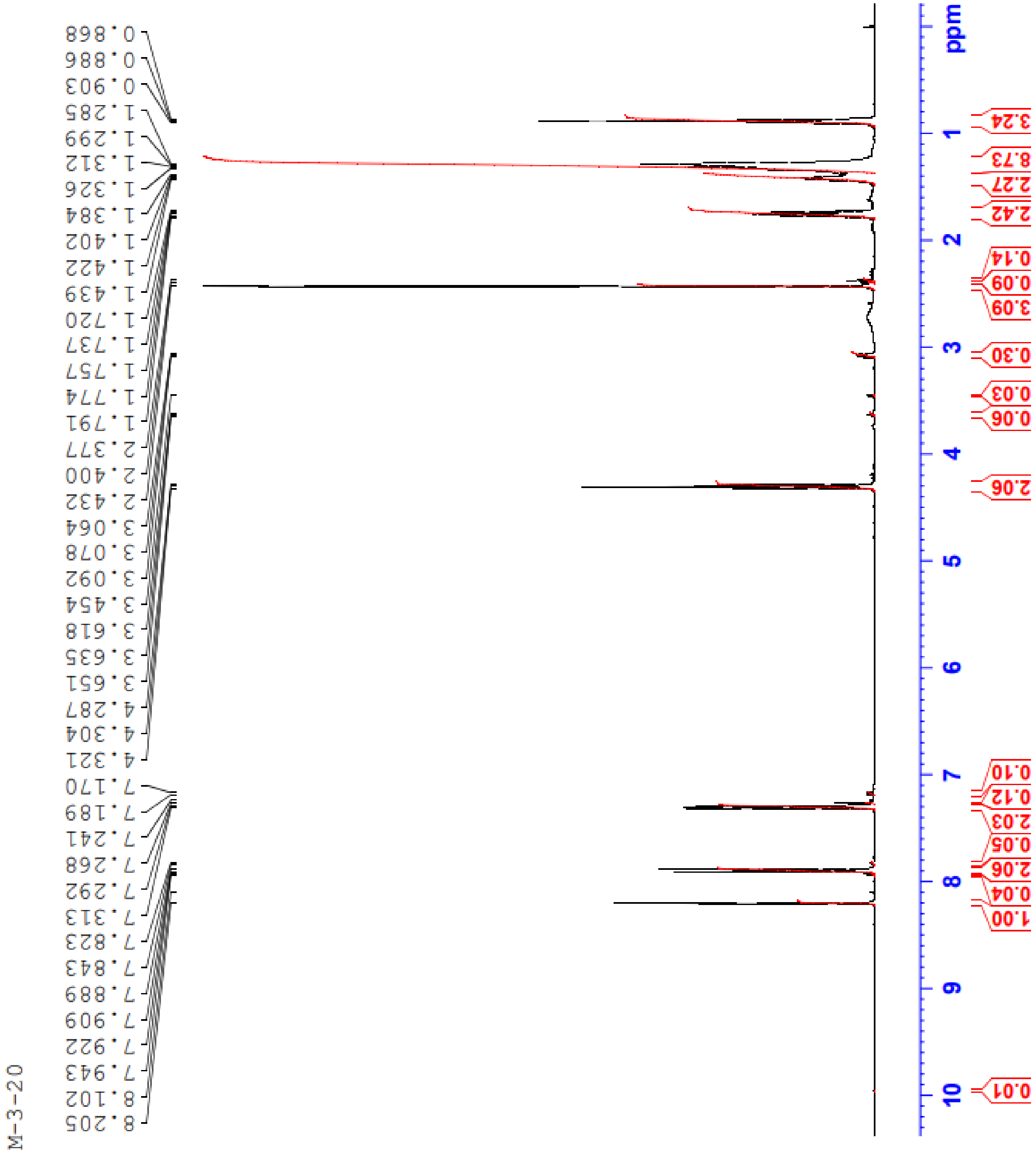

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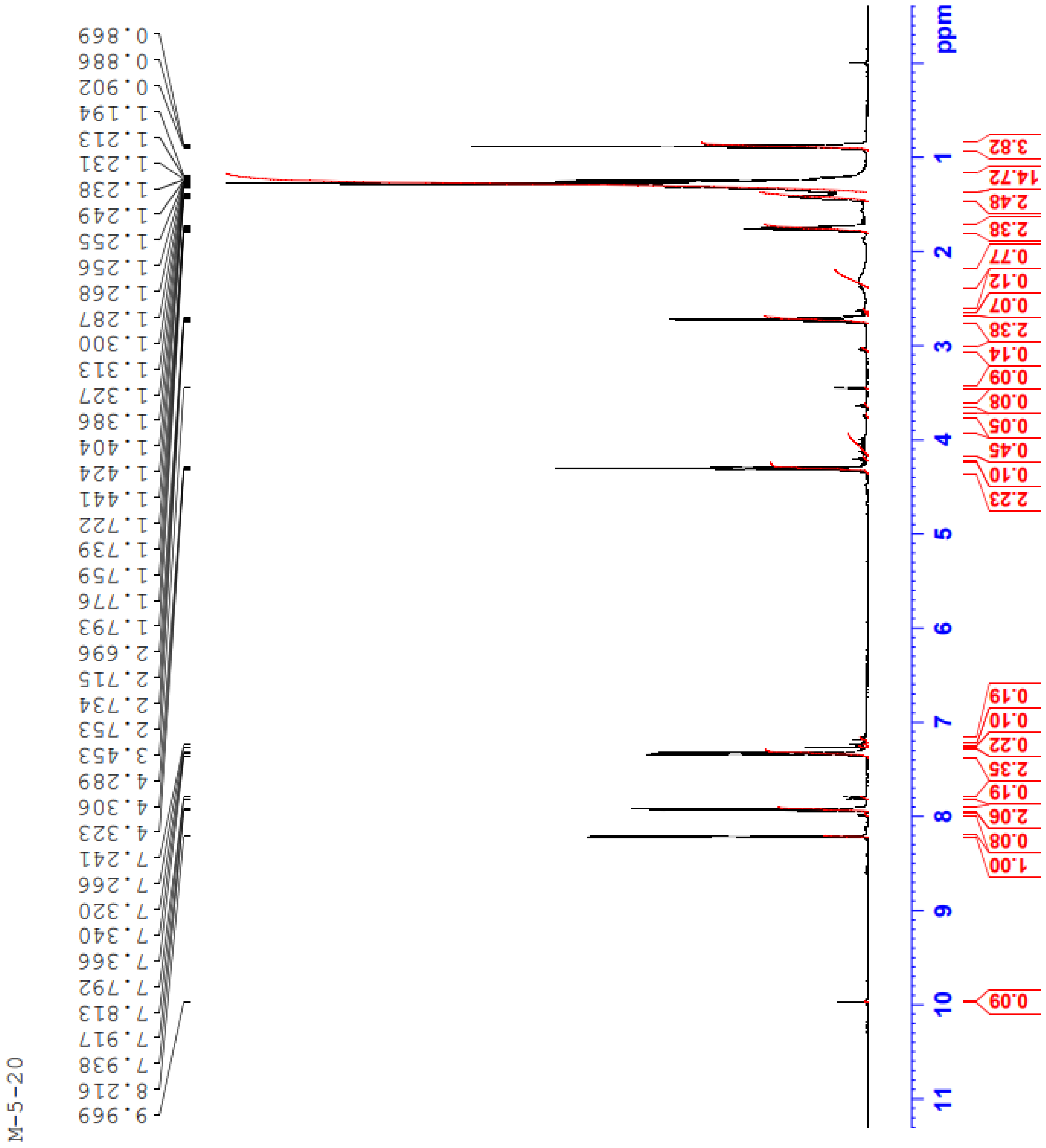

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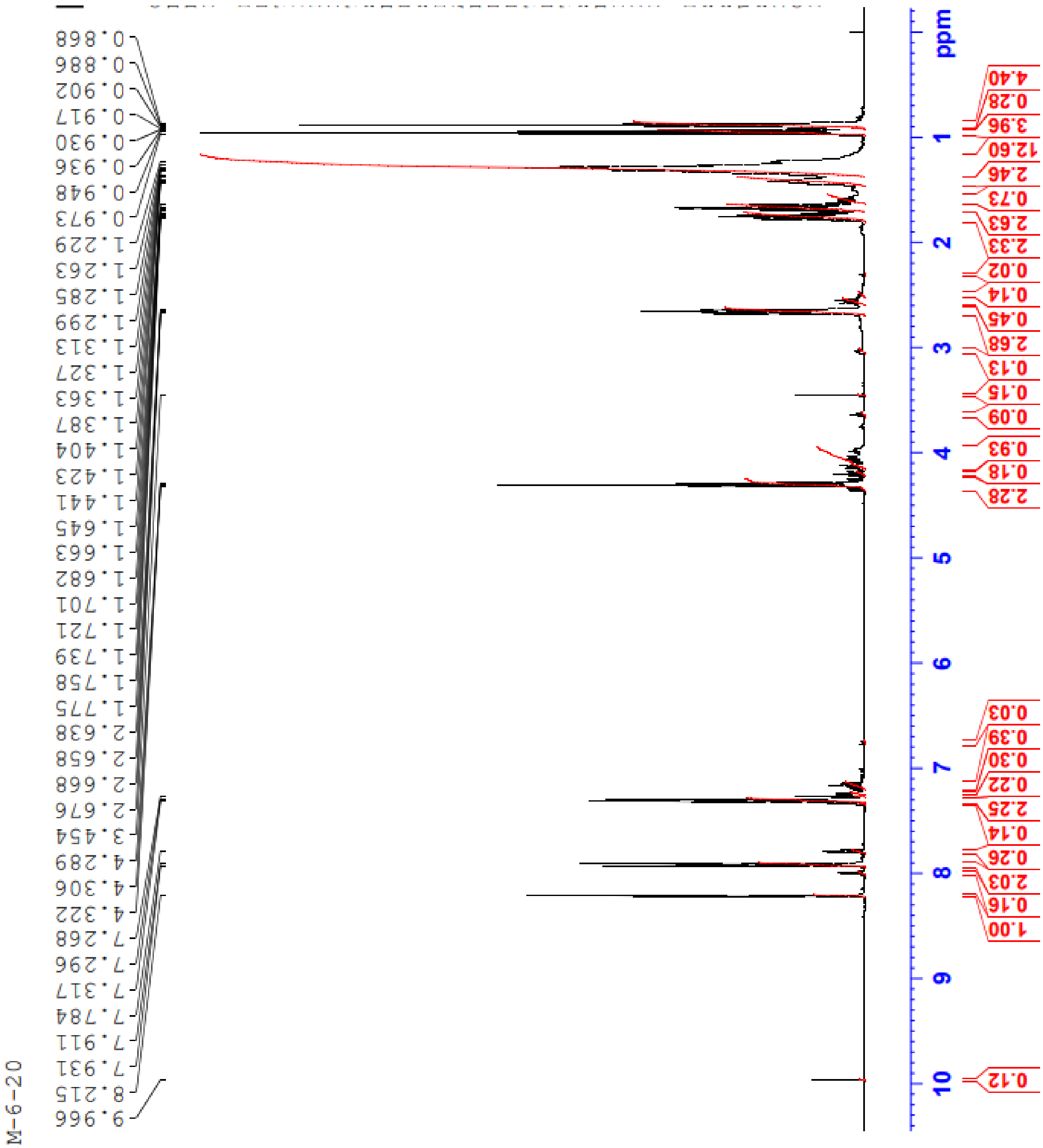

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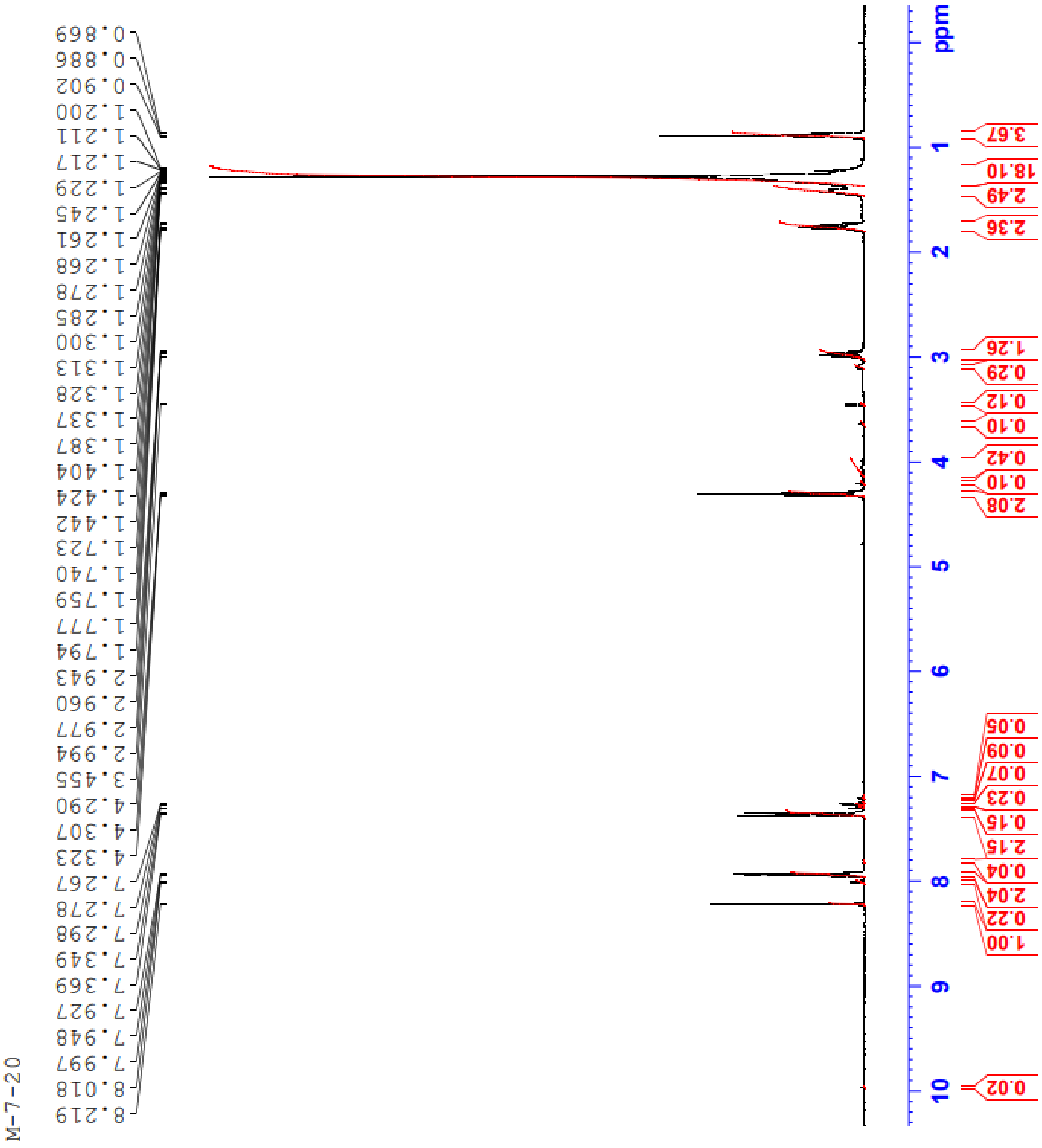

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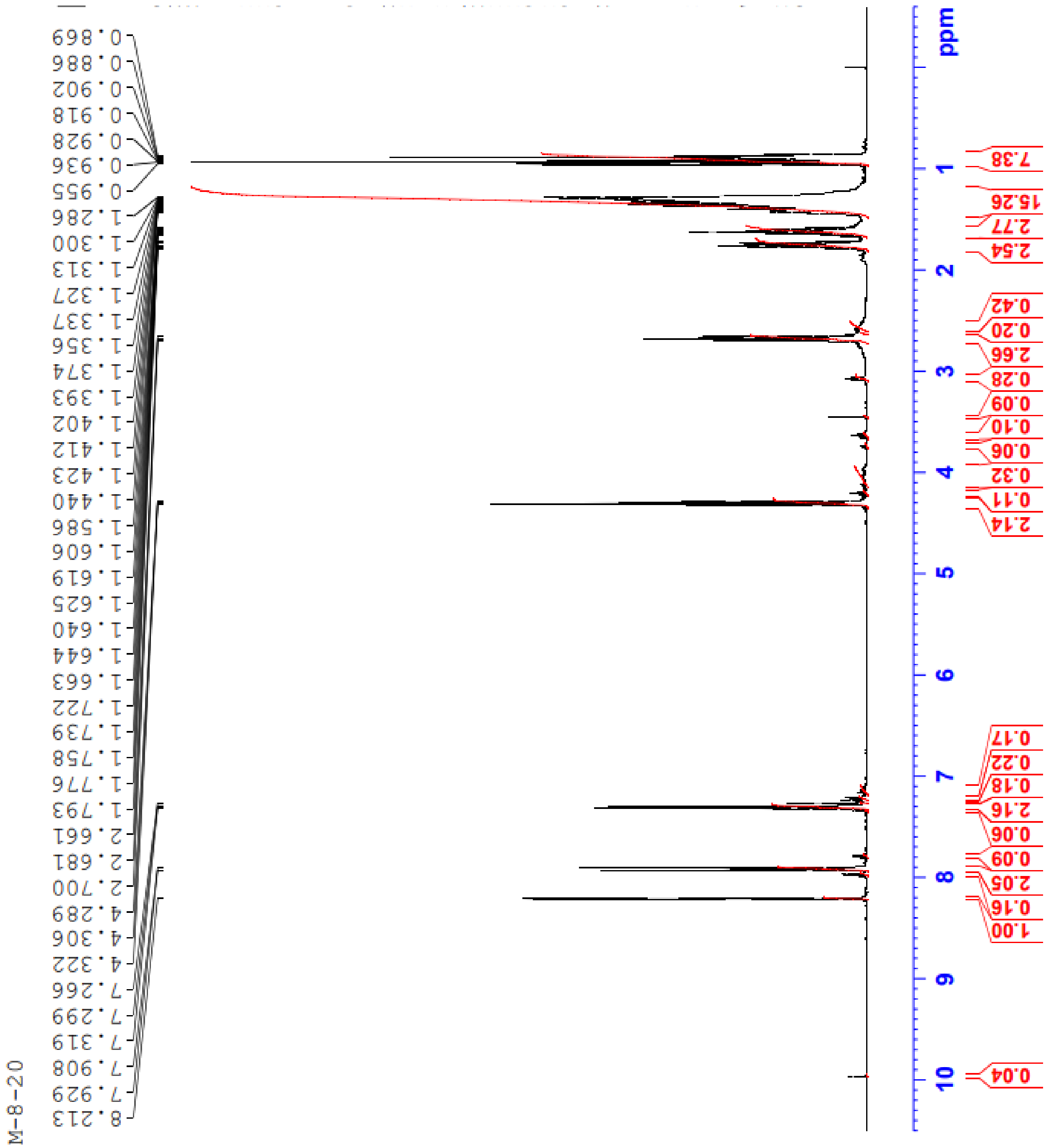

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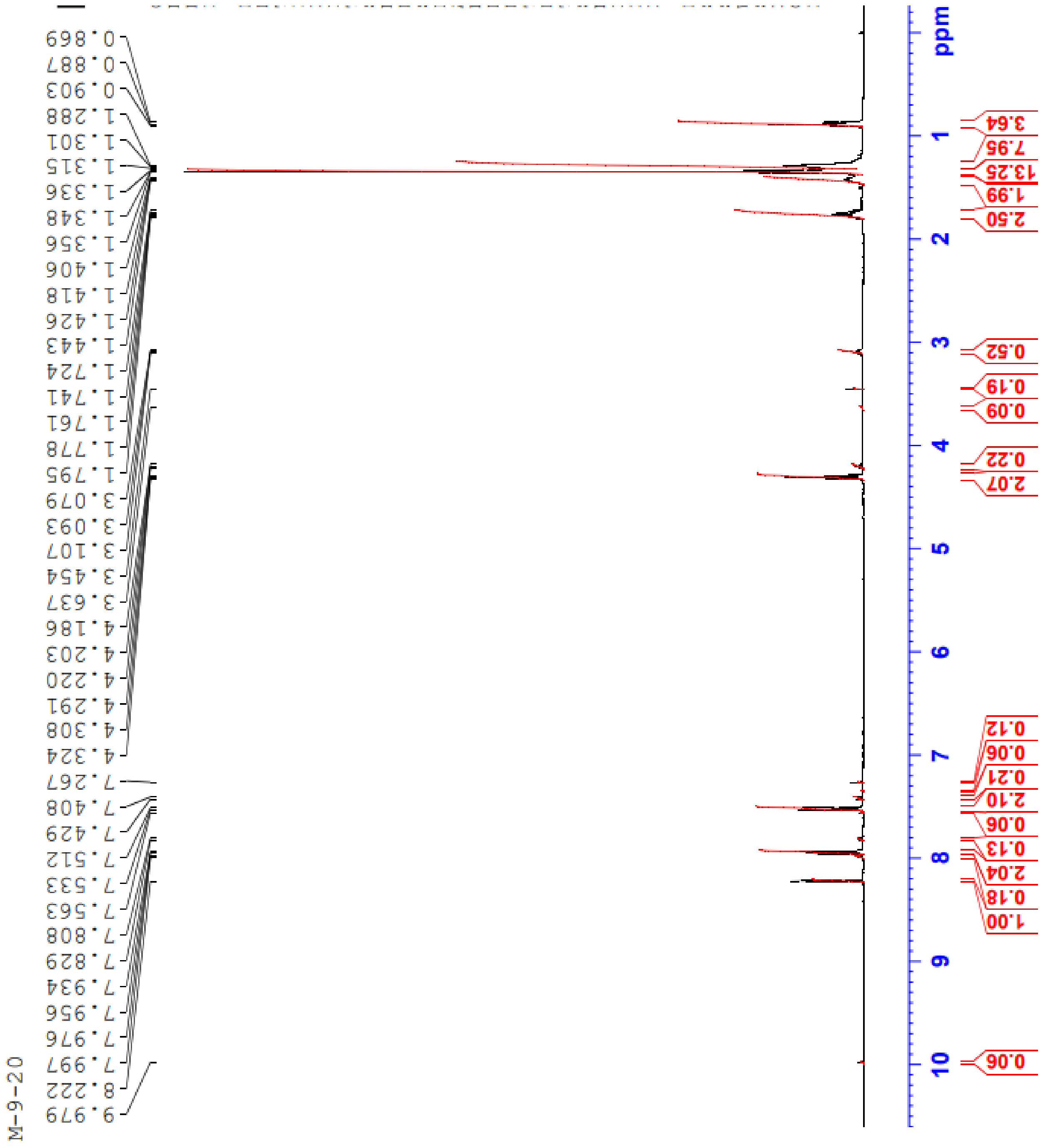

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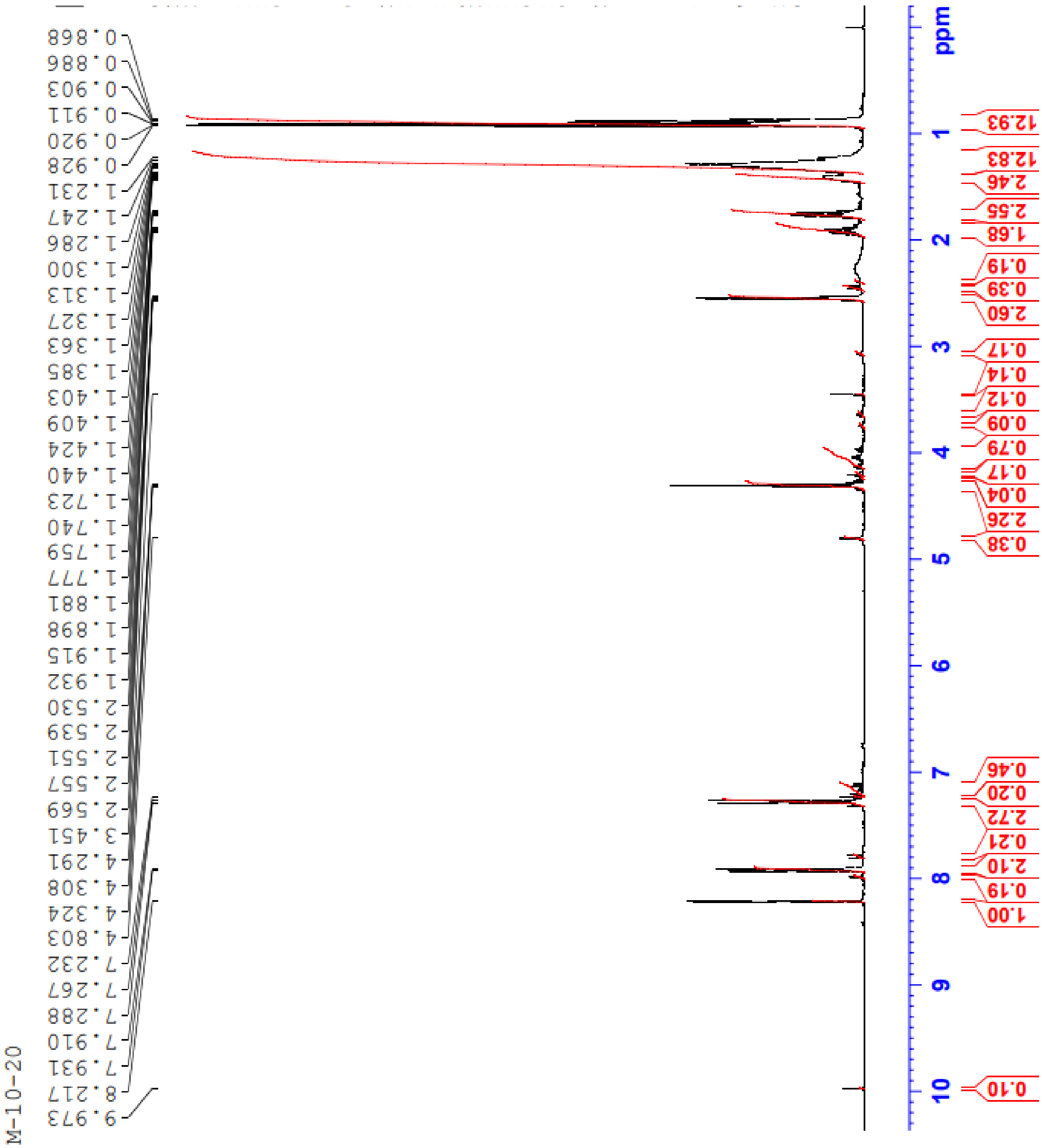

APPENDIX 3 ^{13}C-NMR SPECTRA

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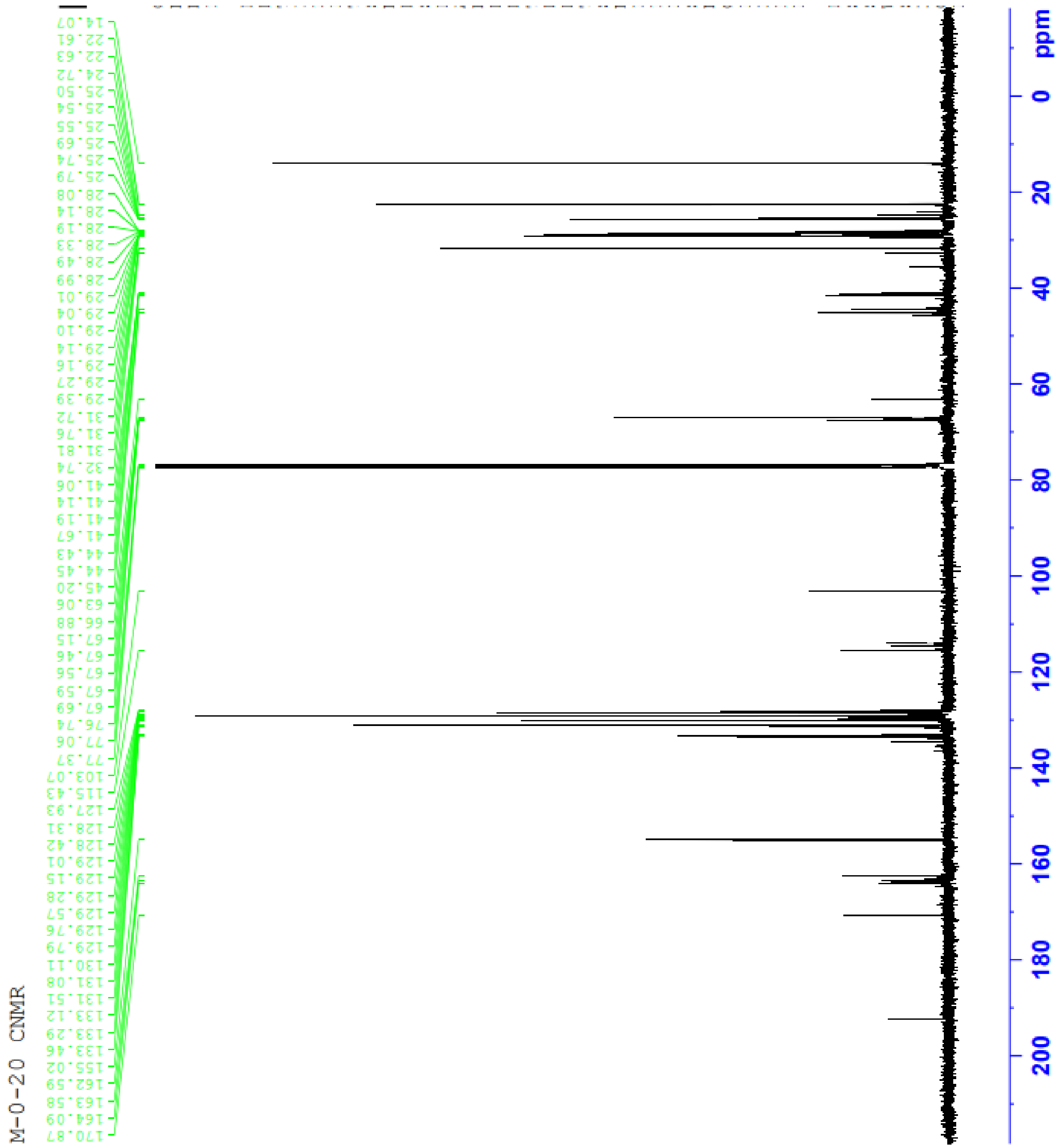

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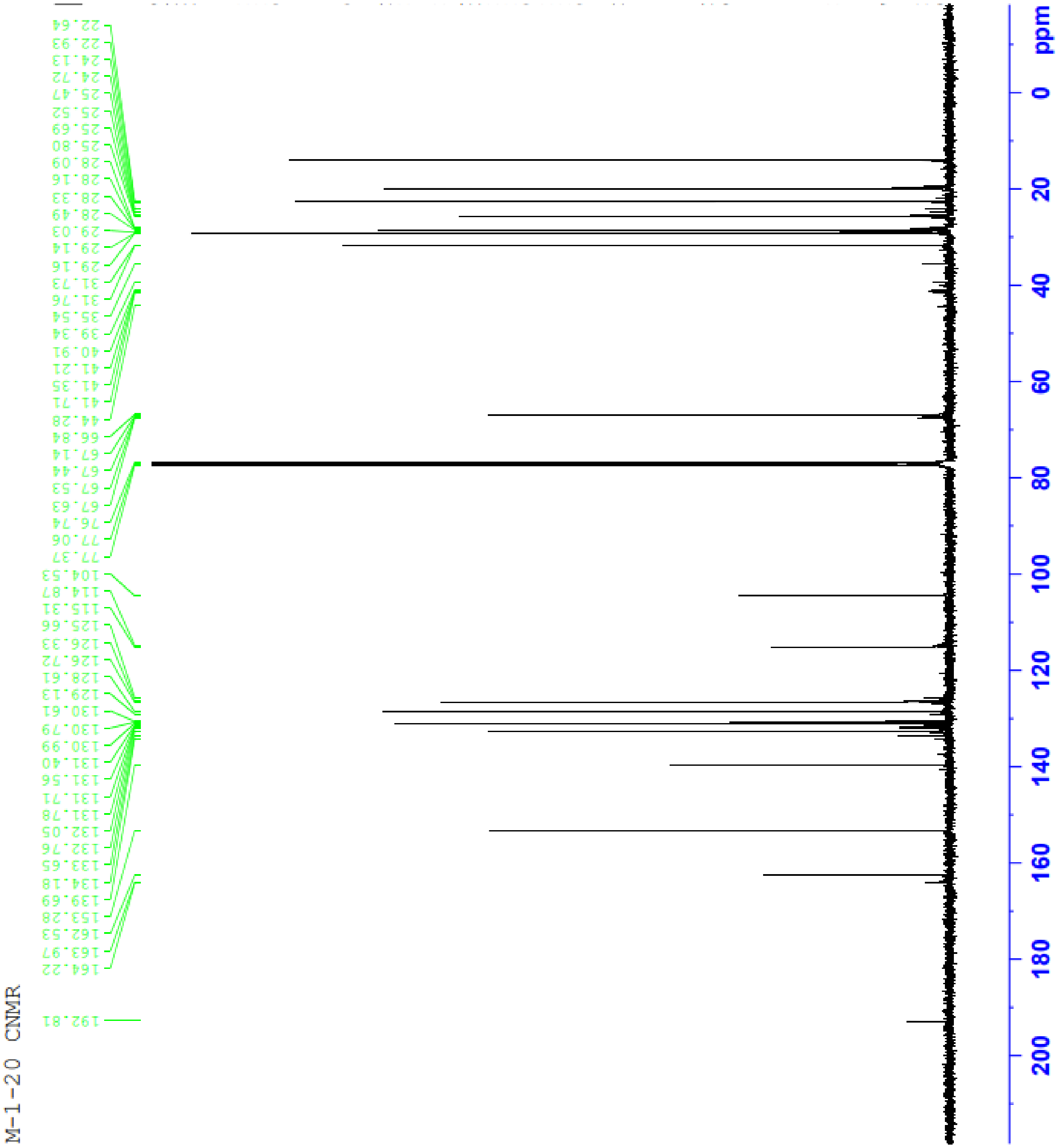

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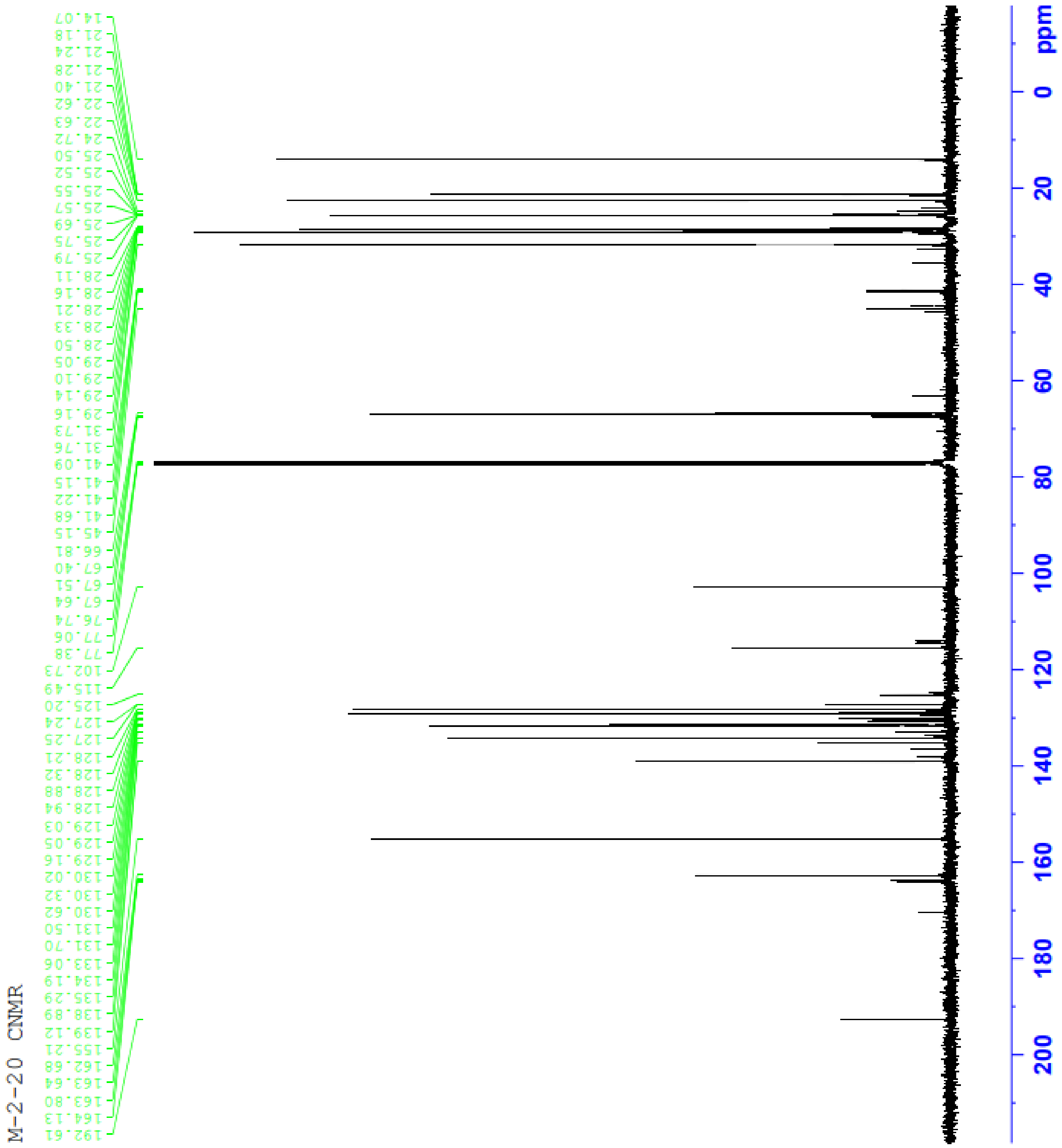

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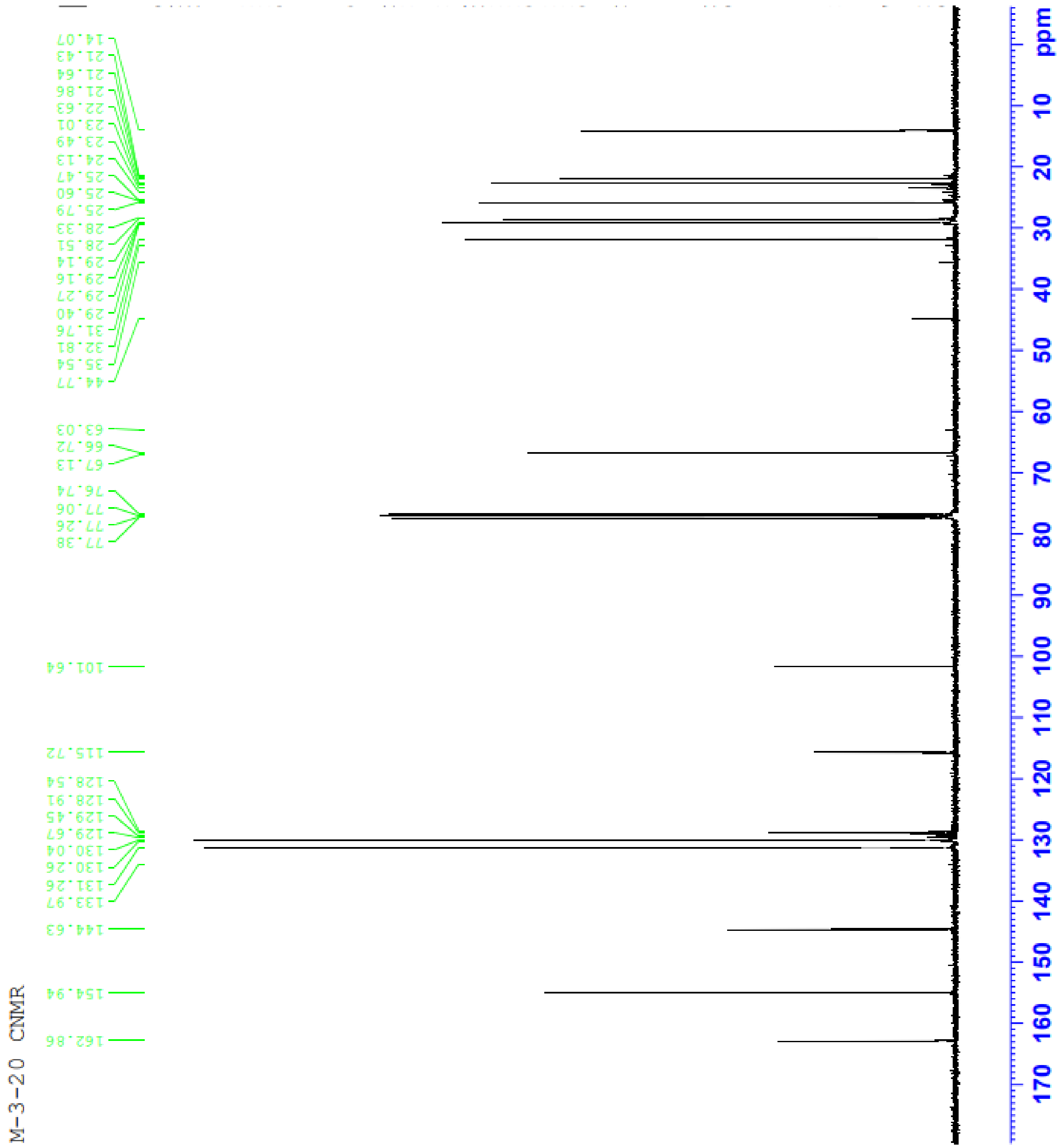

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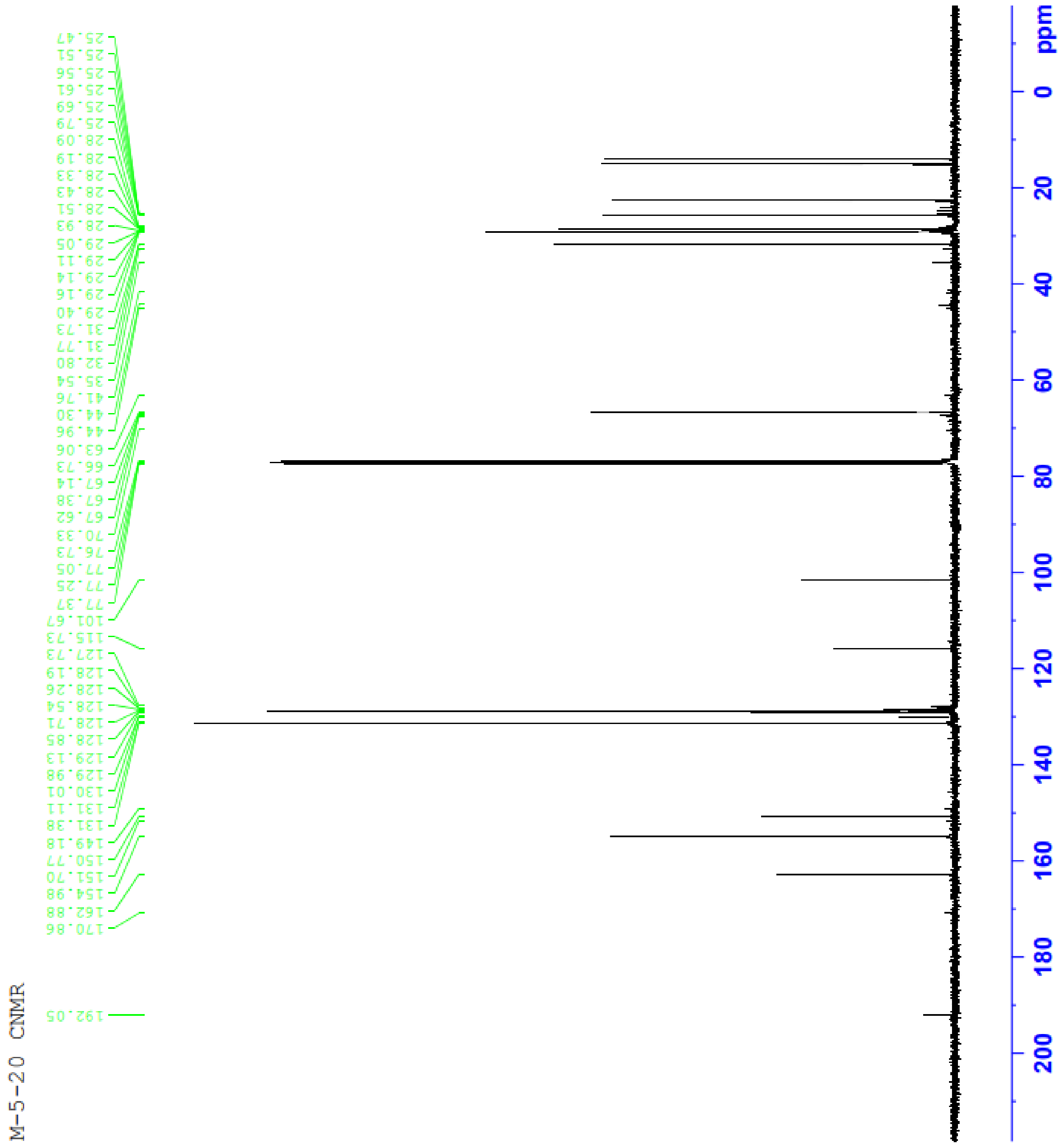

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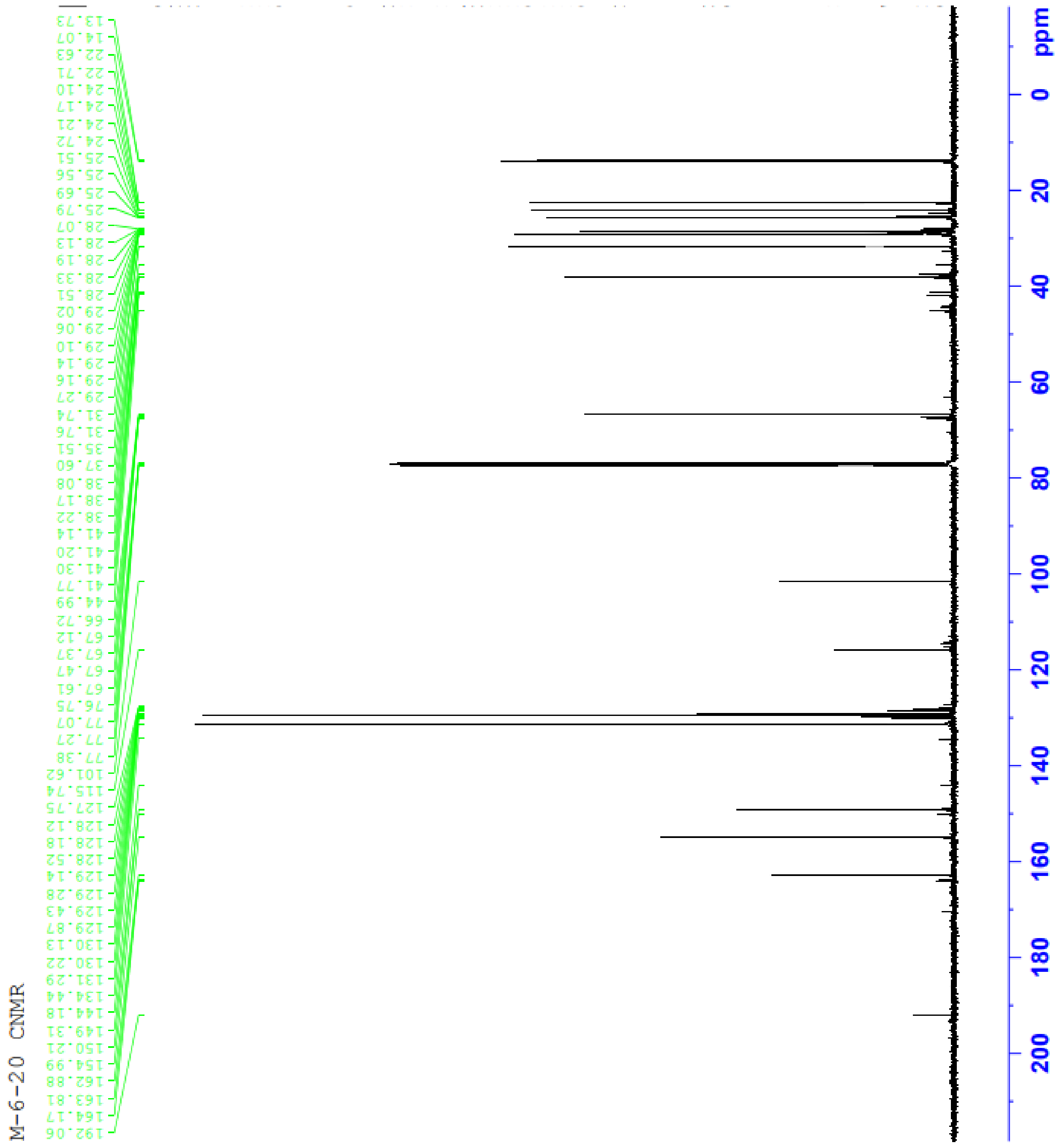

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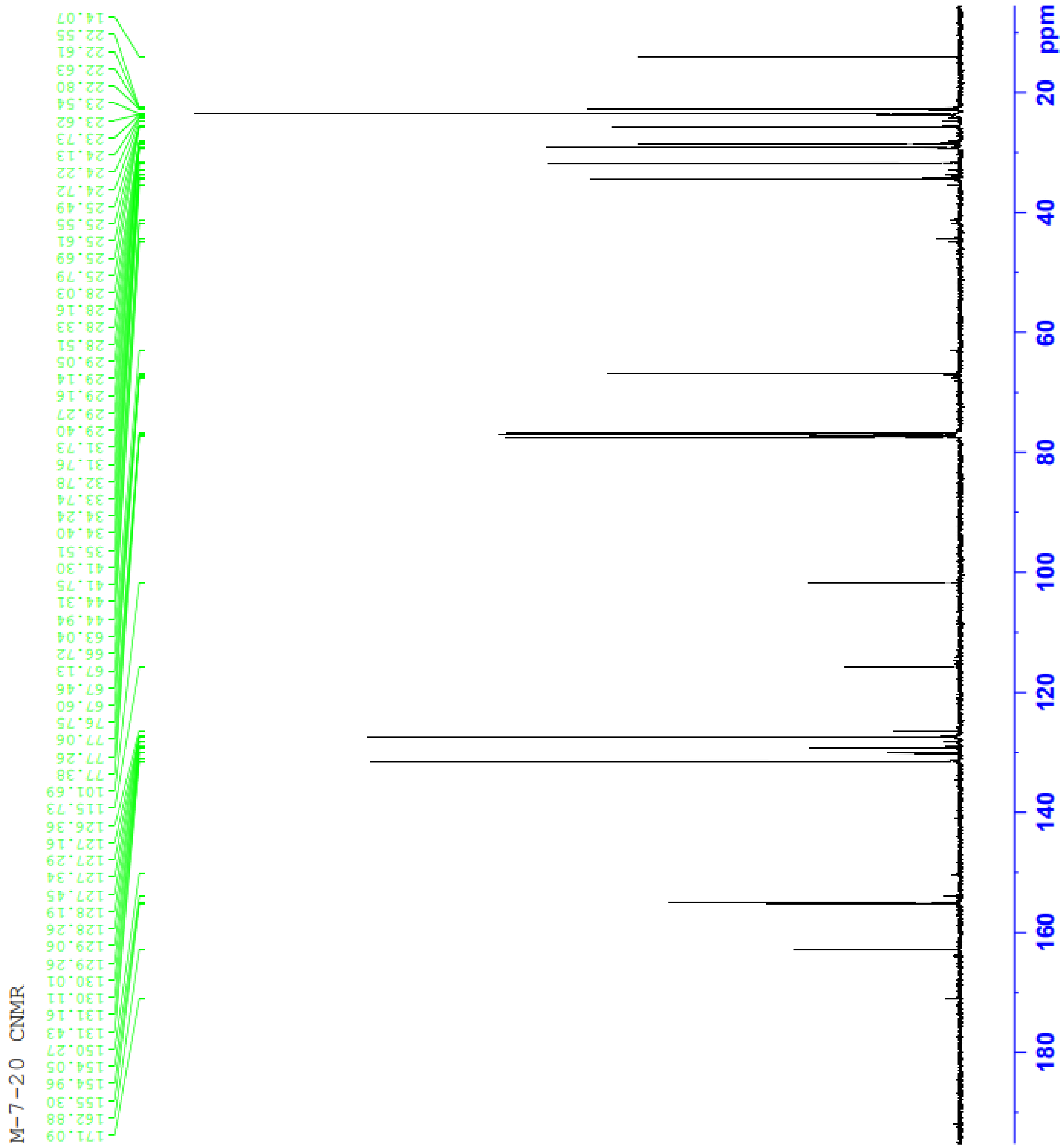

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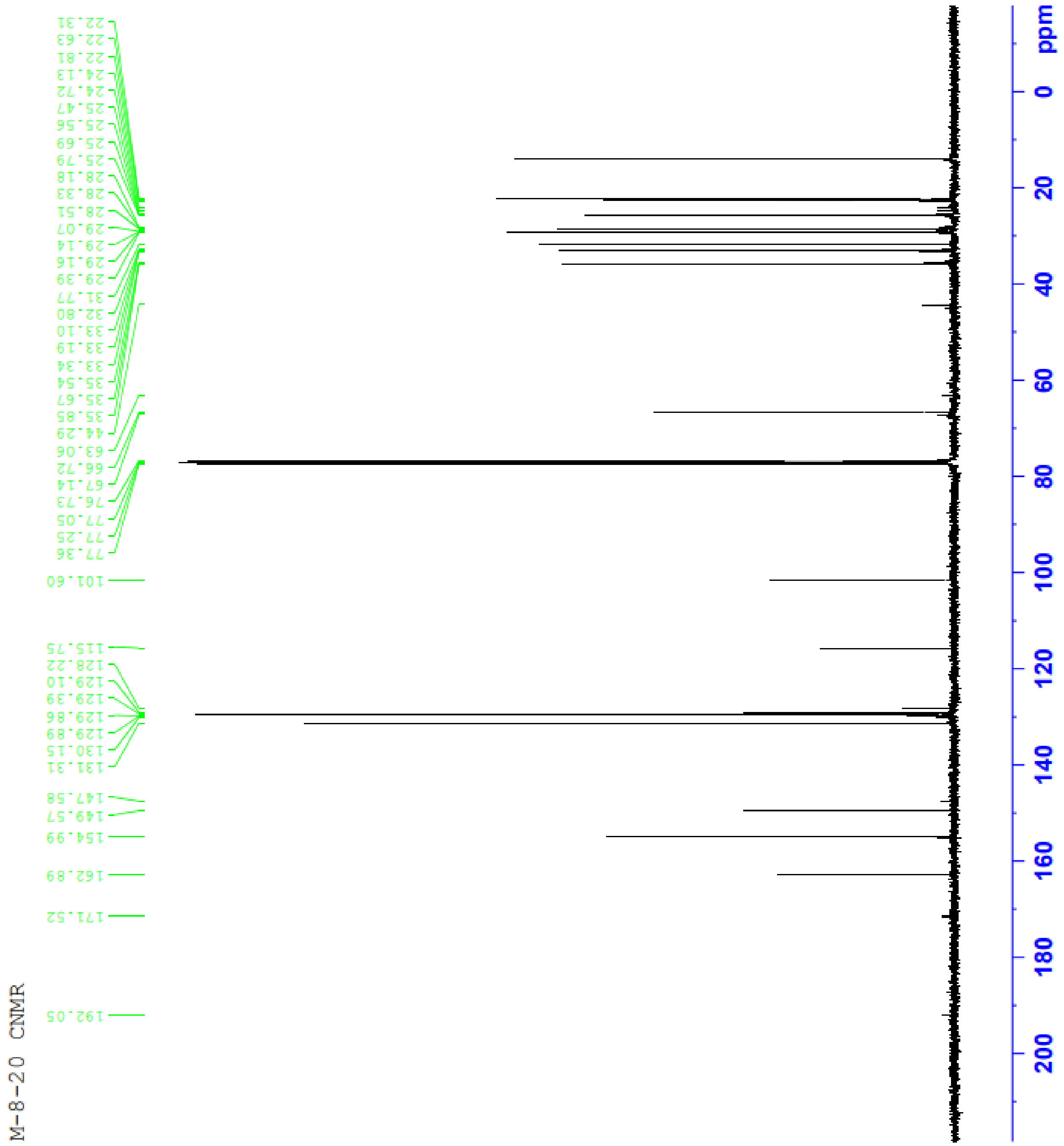

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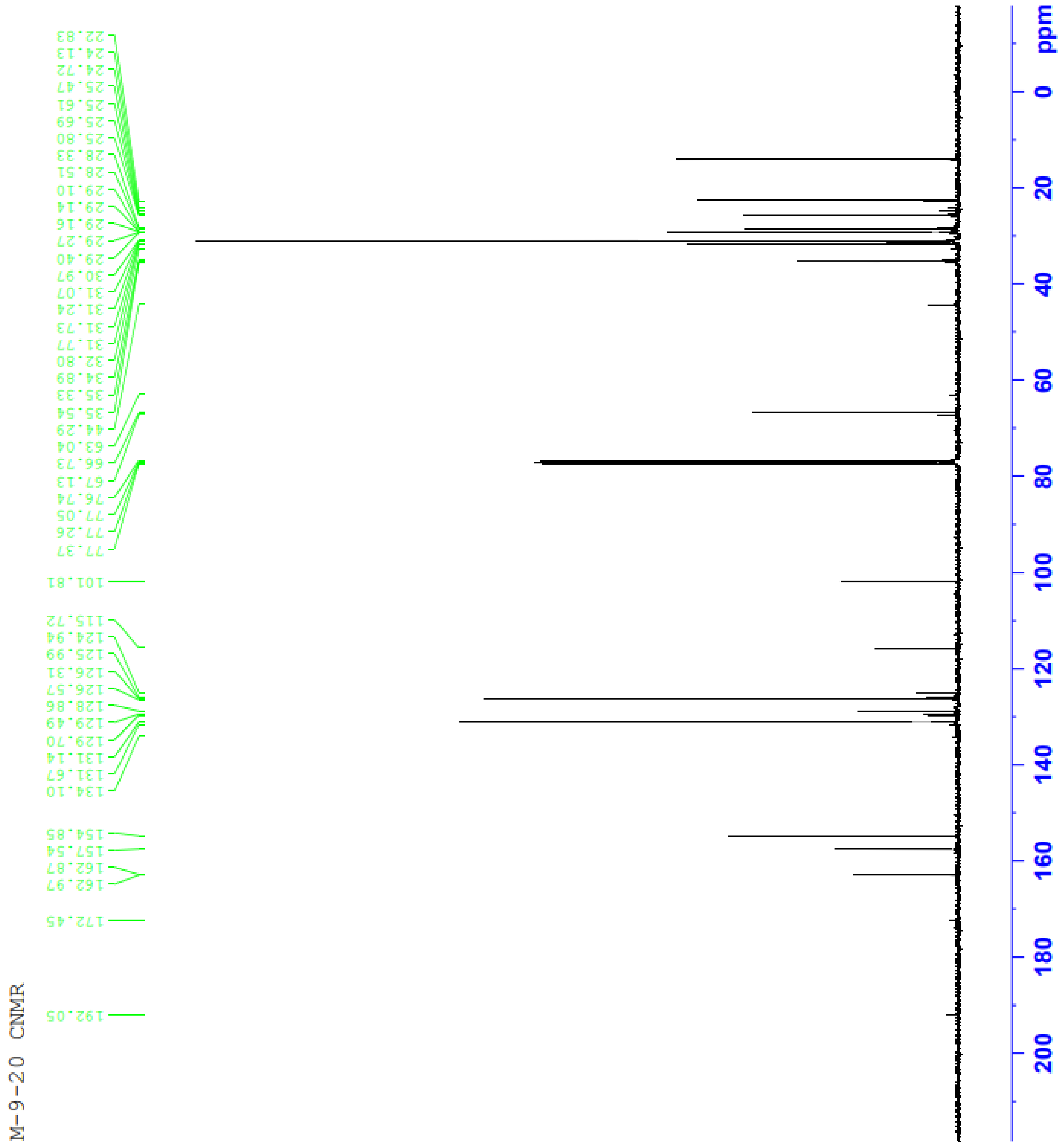

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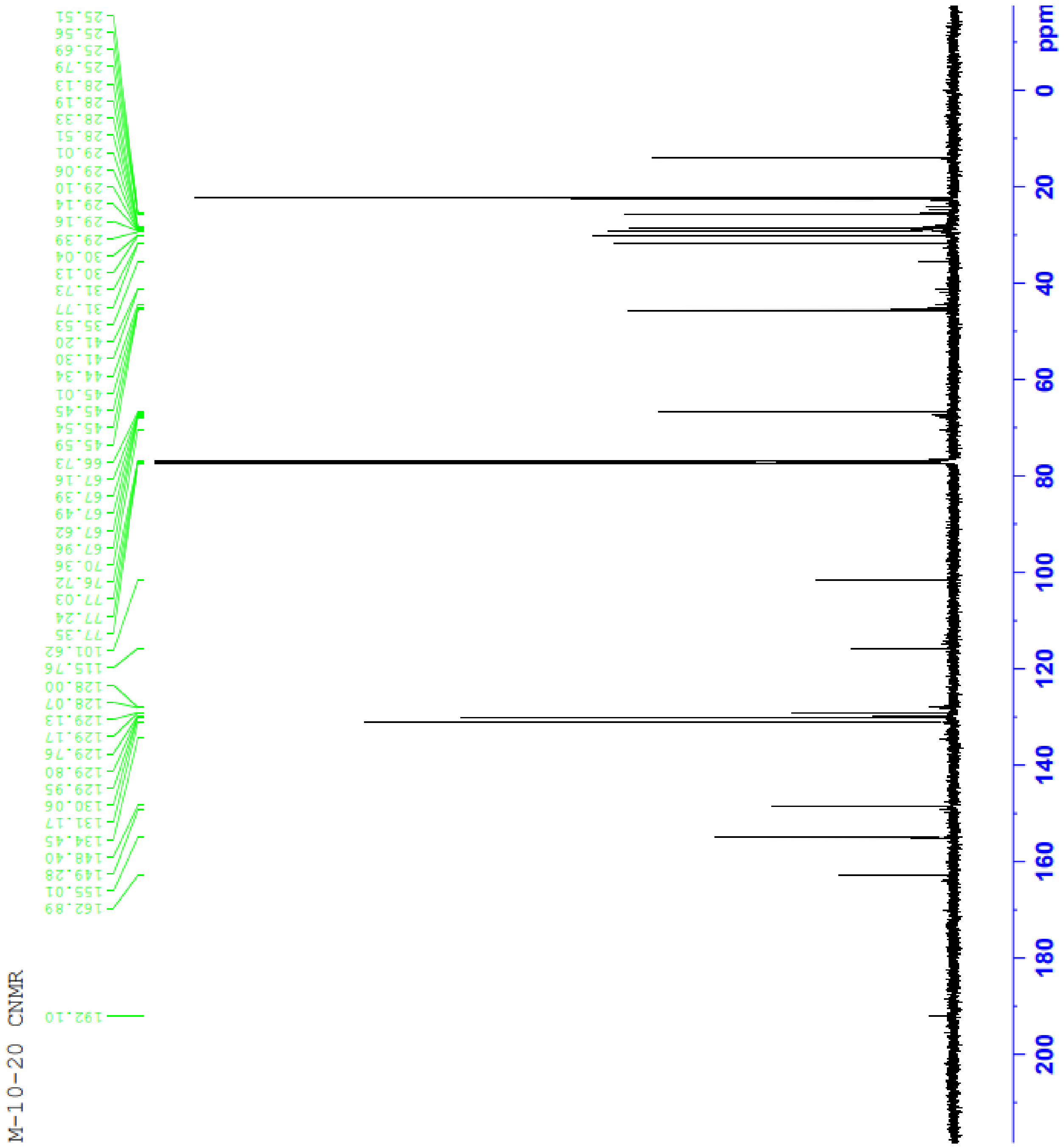
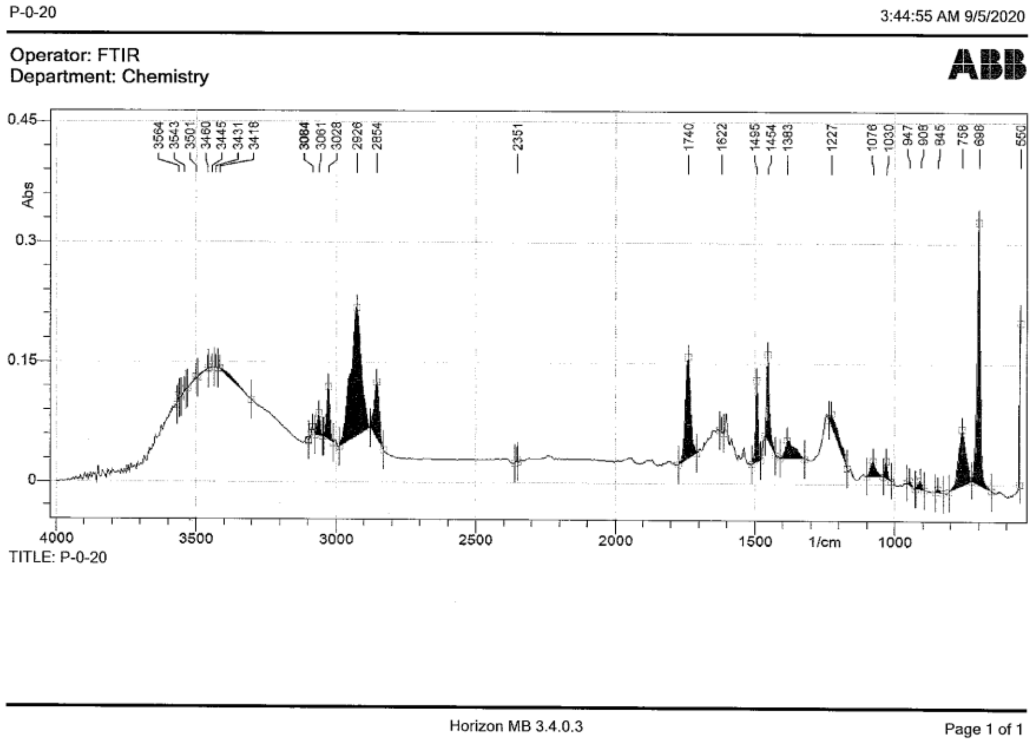


APPENDIX 4 COPOLYMER IR SPECTRA

Octyl 2-cyano-3-(H-phenyl)-2 propenoate – Styrene Copolymer



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Horizon MB 3.4.0.3

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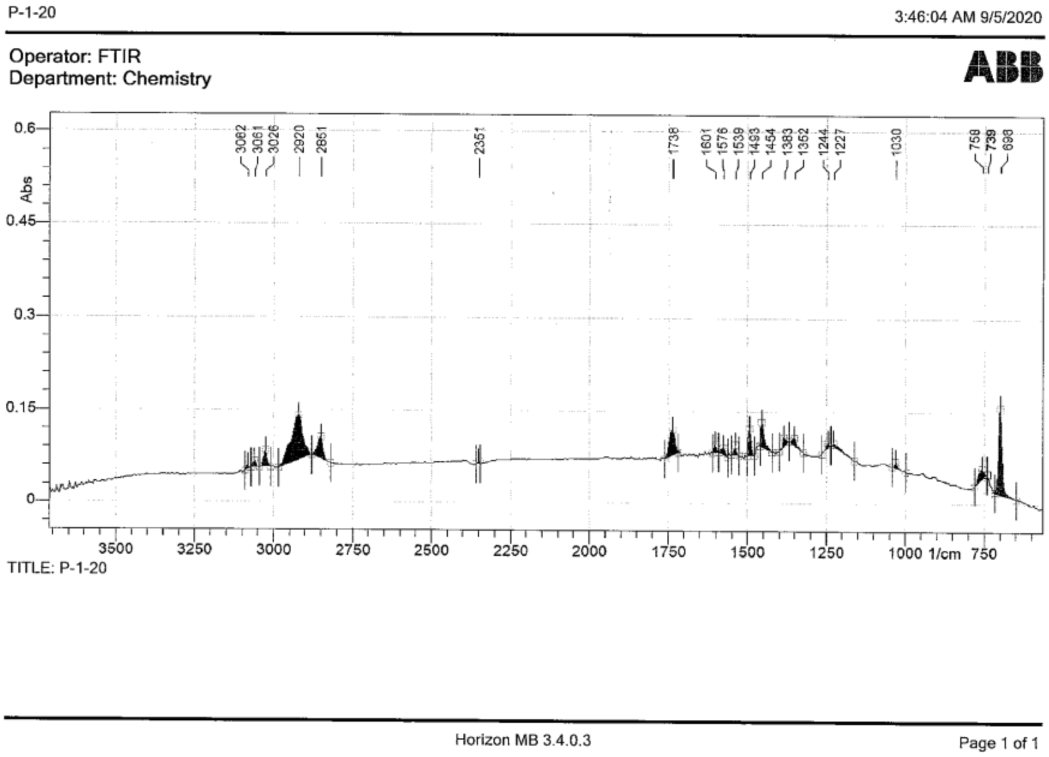
Octyl 2-cyano-3-(2-methyl-phenyl)-2 propenoate – Styrene Copolymer



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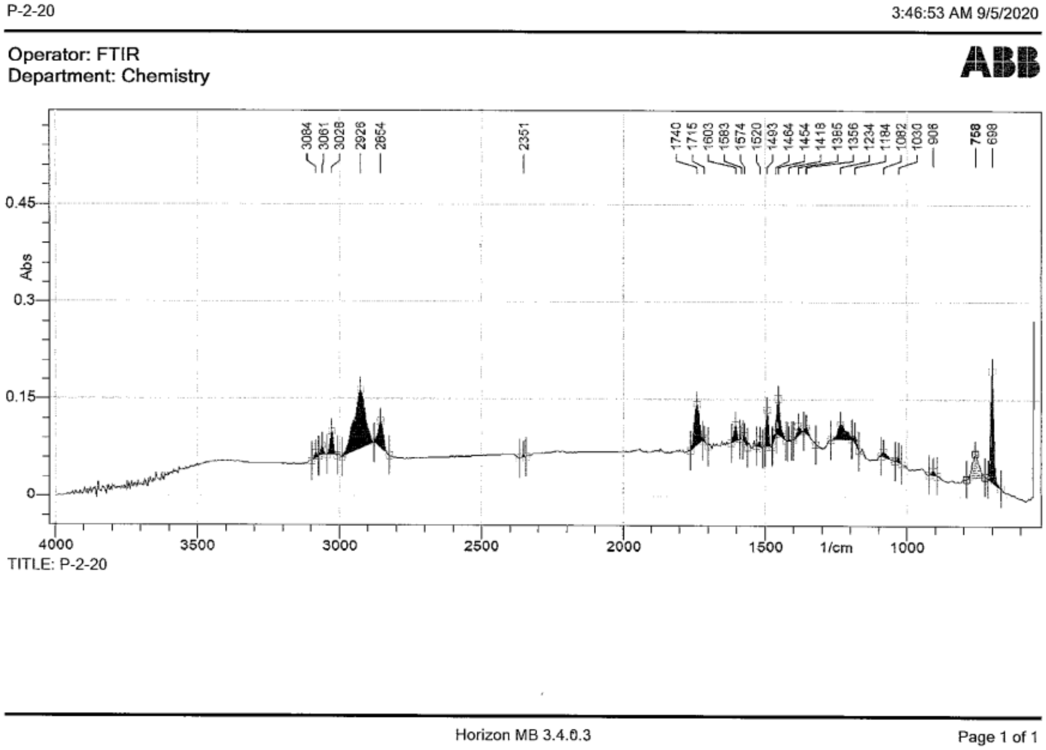
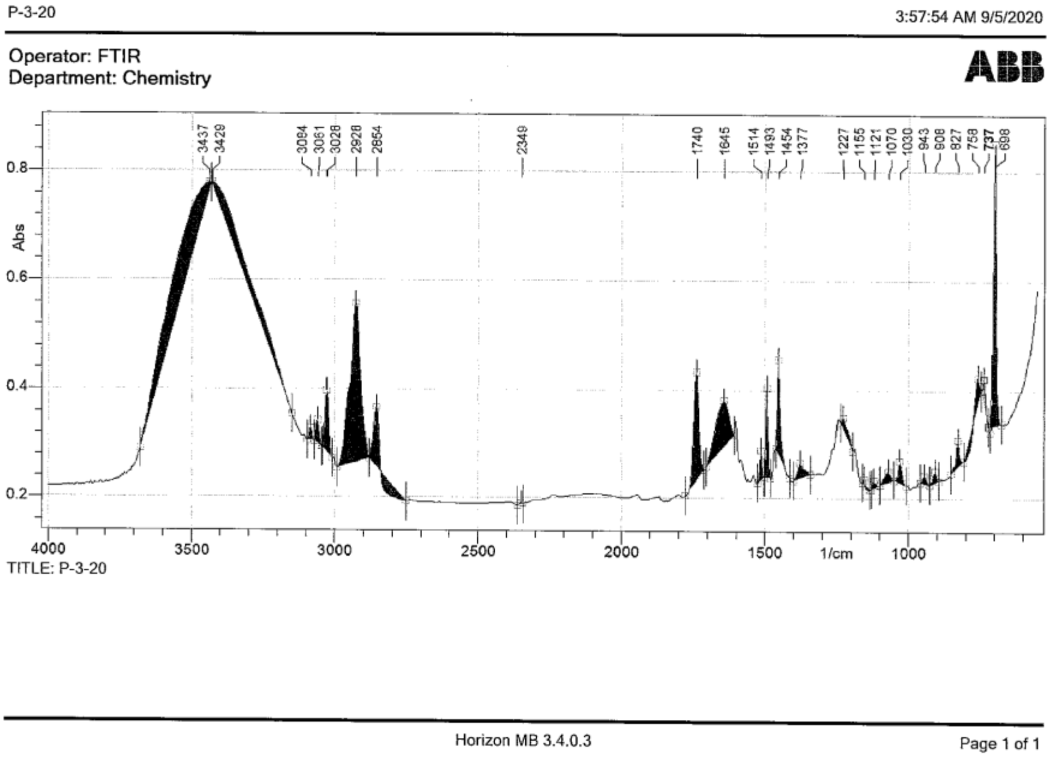
Horizon MB 3.4.0.3

Page 1 of 1

Octyl 2-cyano-3-(3-methyl-phenyl)-2 propenoate – Styrene Copolymer



Octyl 2-cyano-3-(4-methyl-phenyl)-2 propenoate – Styrene Copolymer



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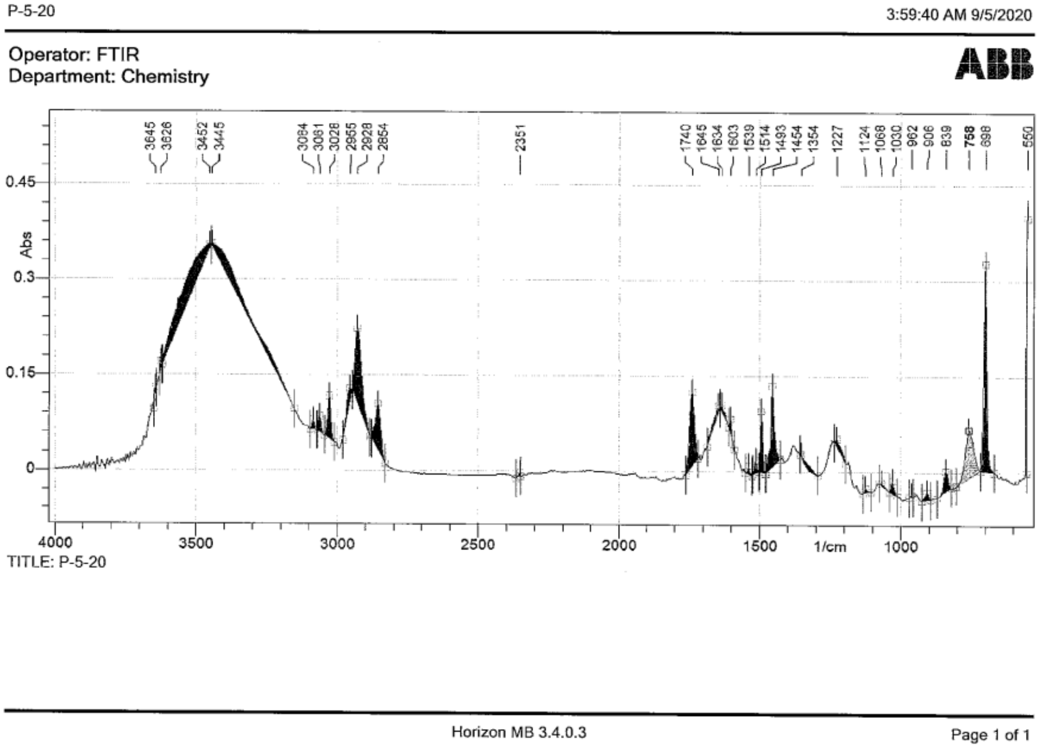

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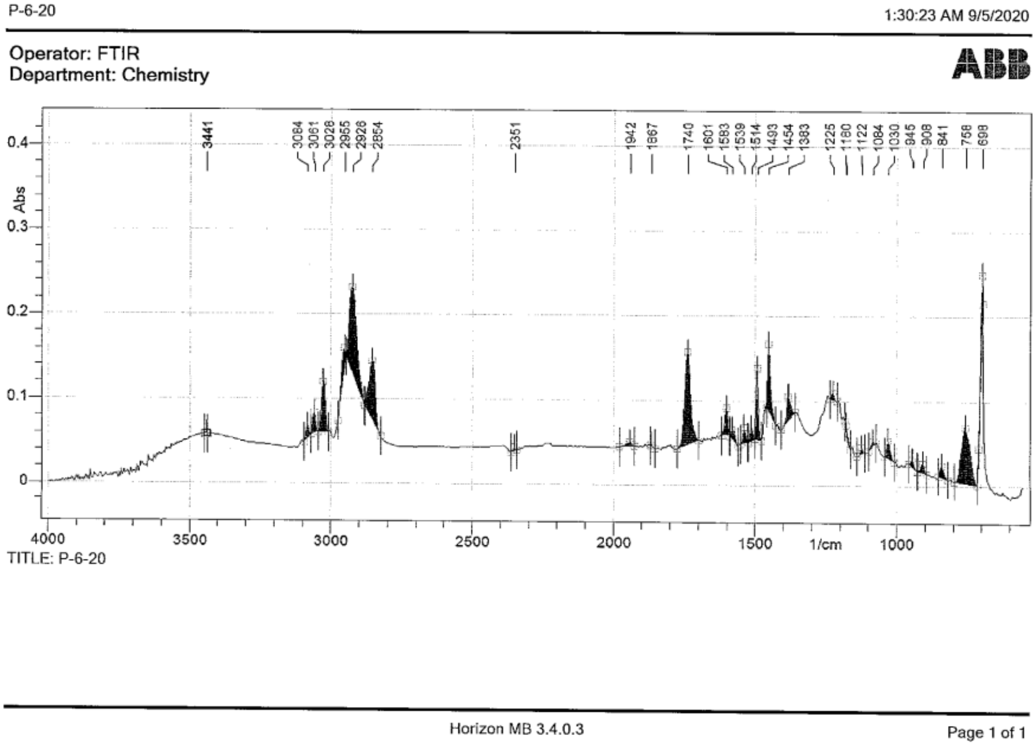
Horizon MB 3.4.0.3 Page 1 of 1

Octyl 2-cyano-3-(4-propyl-phenyl)-2 propenoate – Styrene Copolymer



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Horizon MB 3.4.0.3 Page 1 of 1

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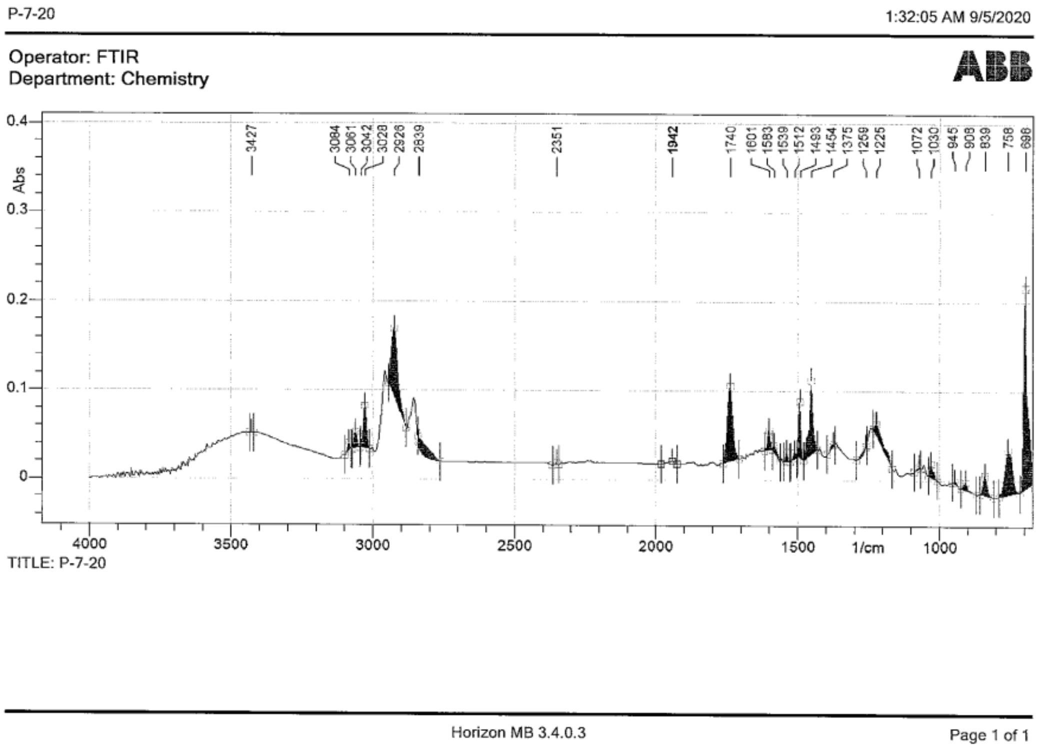
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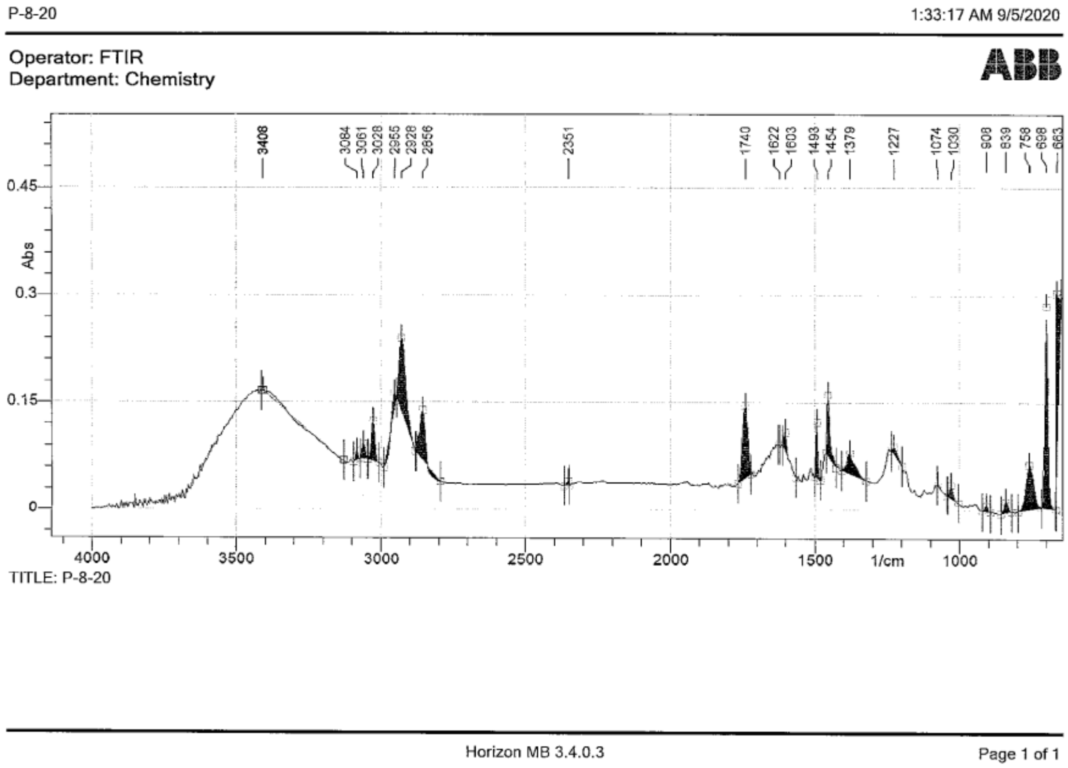
Horizon MB 3.4.0.3 Page 1 of 1

Octyl 2-cyano-3-(4-buty-phenyl)-2 propenoate – Styrene Copolymer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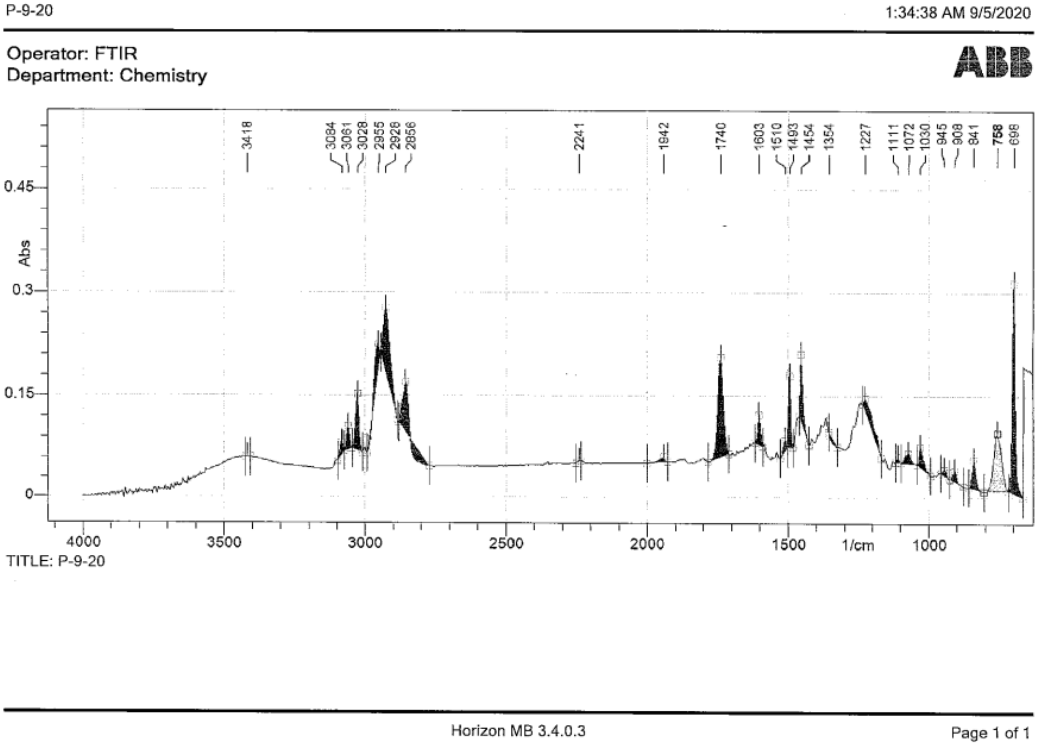
Horizon MB 3.4.0.3 Page 1 of 1

Octyl 2-cyano-3-(4-t-butyl-phenyl)-2 propenoate – Styrene Copolymer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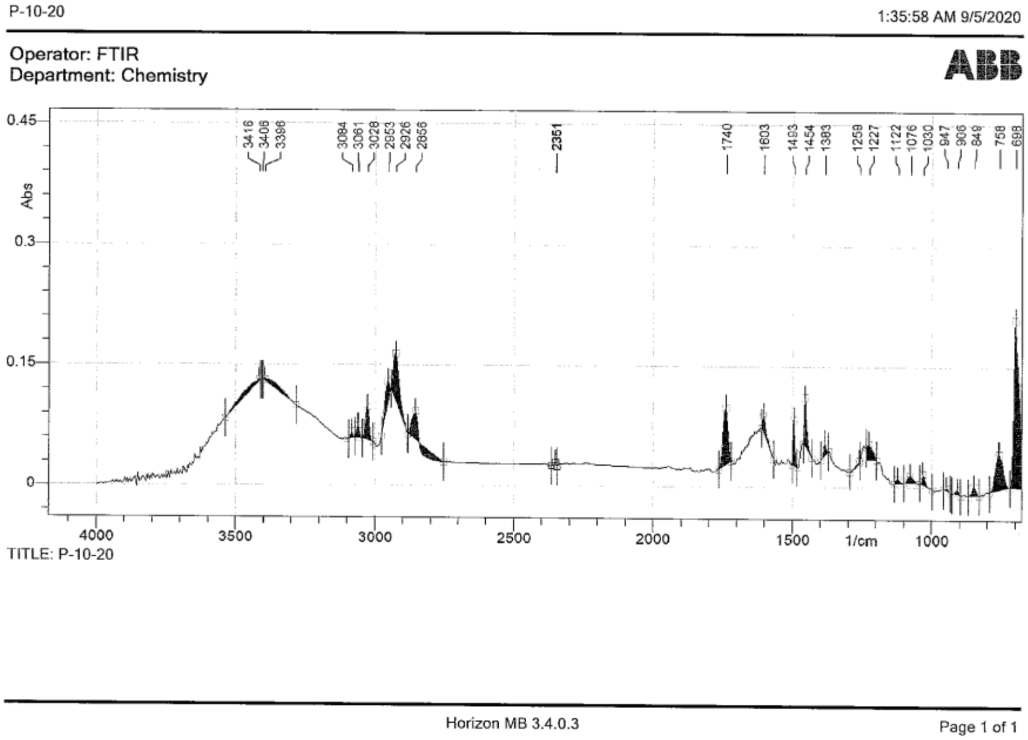
Octyl 2-cyano-3-(4-i-butyl-phenyl)-2 propenoate – Styrene Copolymer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Horizon MB 3.4.0.3
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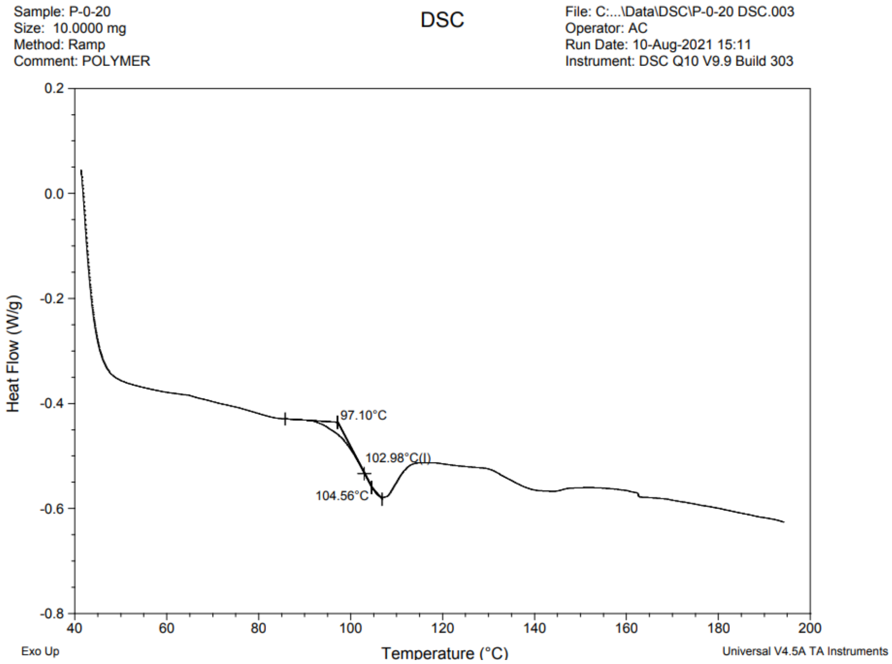
APPENDIX 5 COPOLYMER DSC

Octyl 2-cyano-3-(H-phenyl)-2 propenoate – Styrene Copolymer



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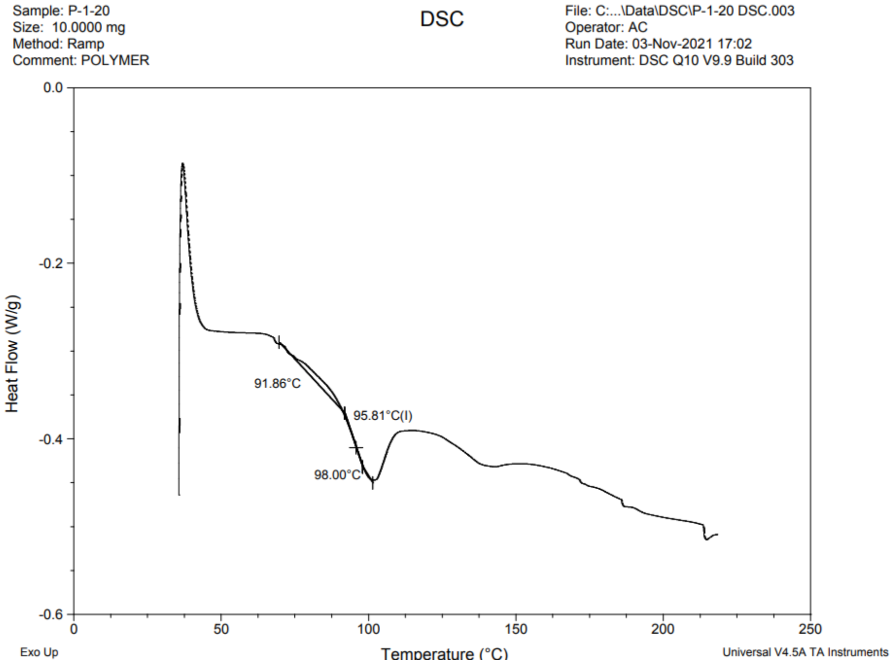

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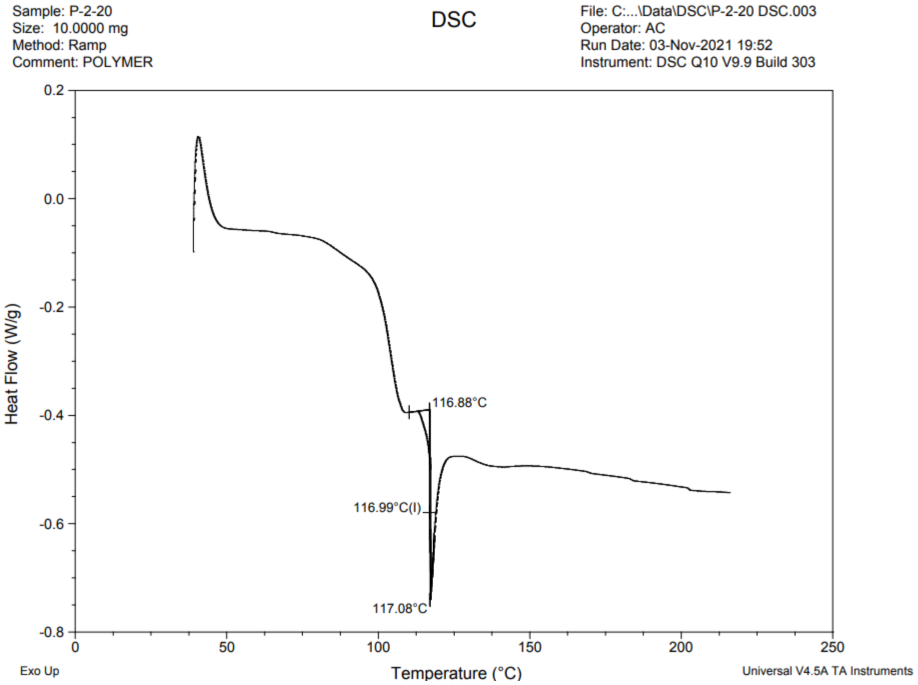

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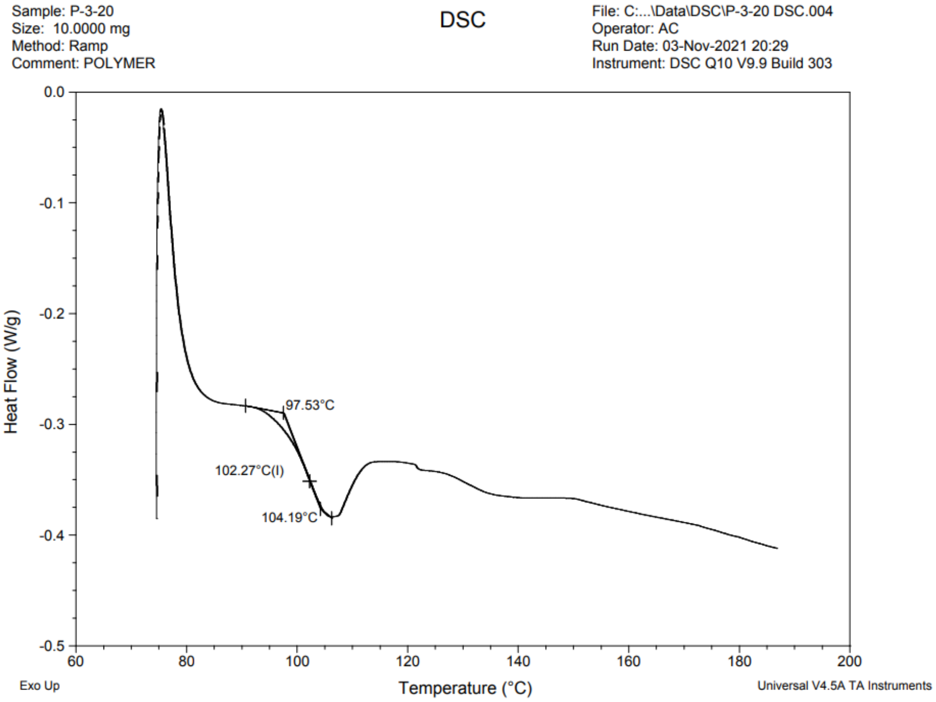

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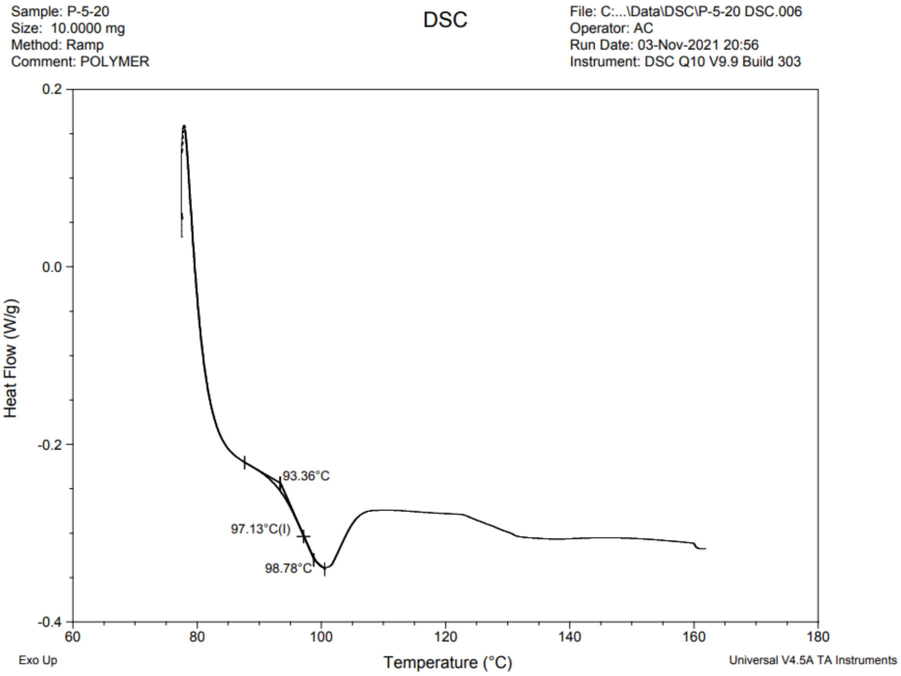

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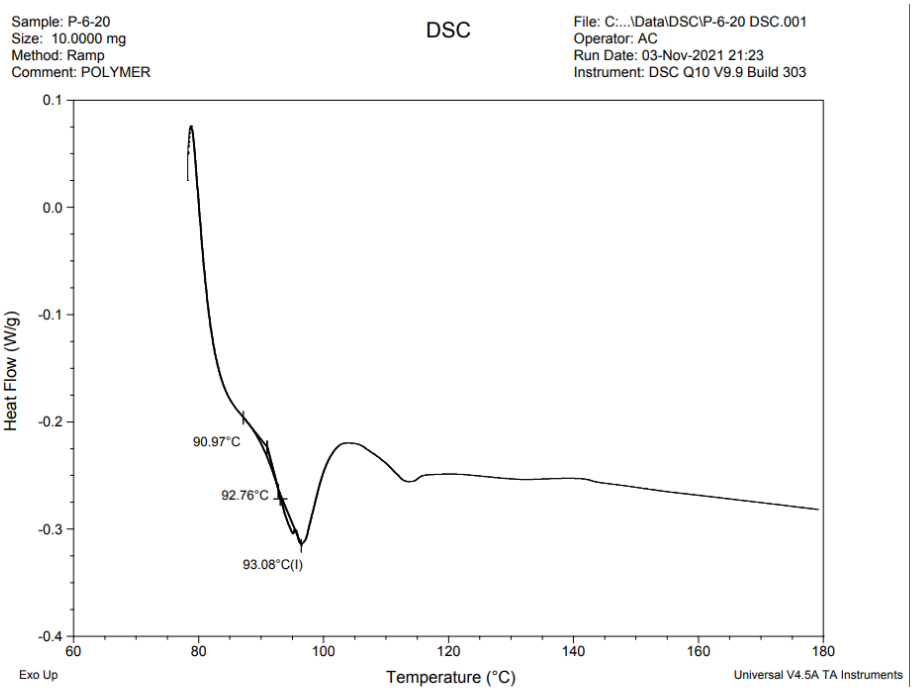

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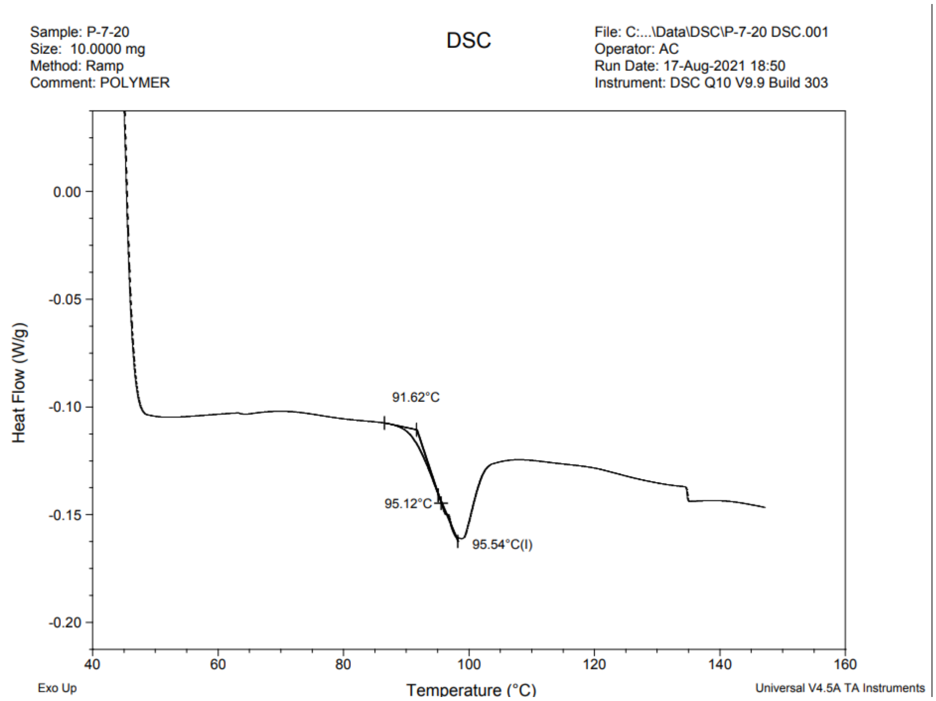

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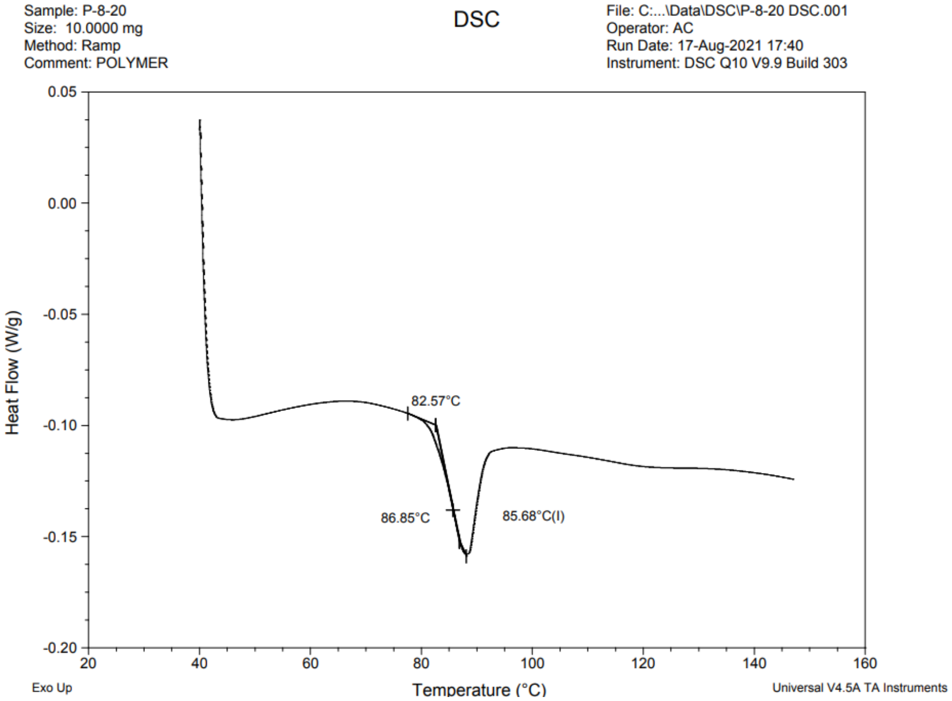

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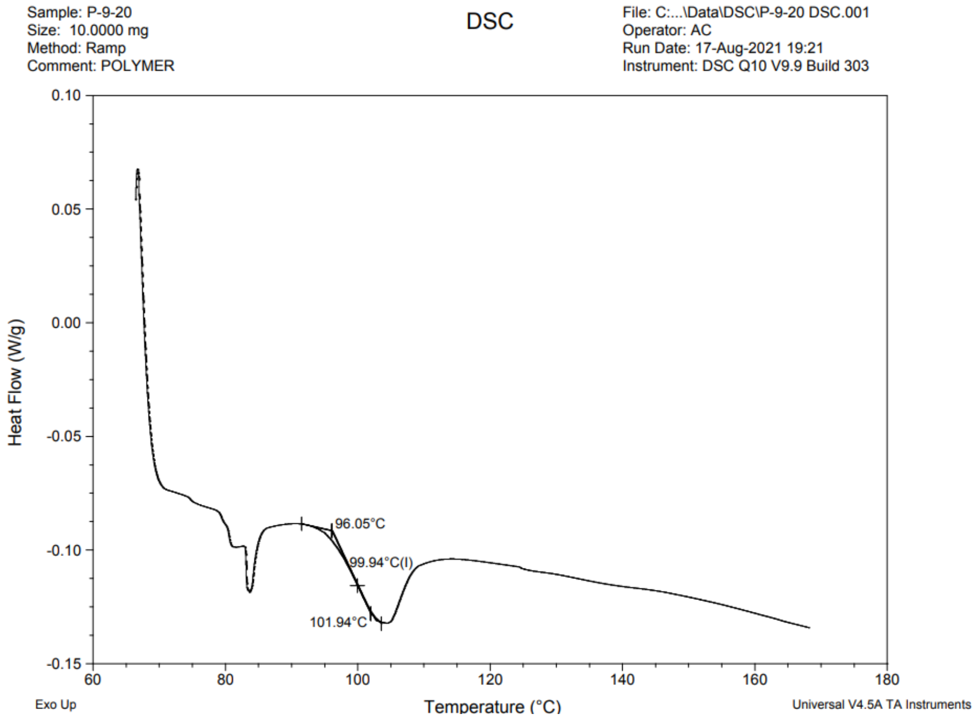

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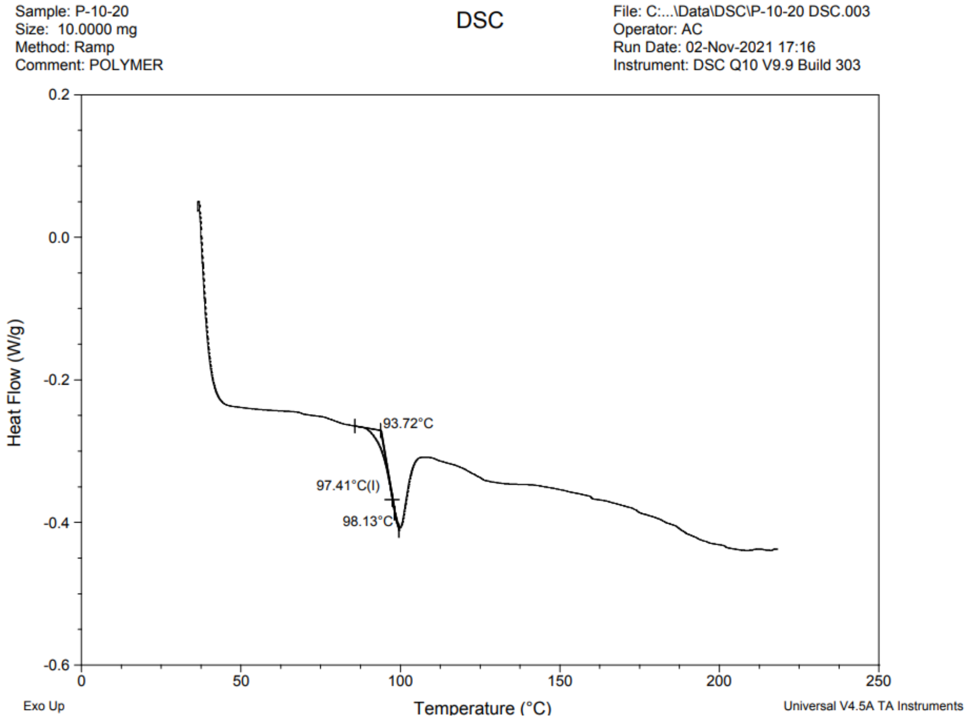
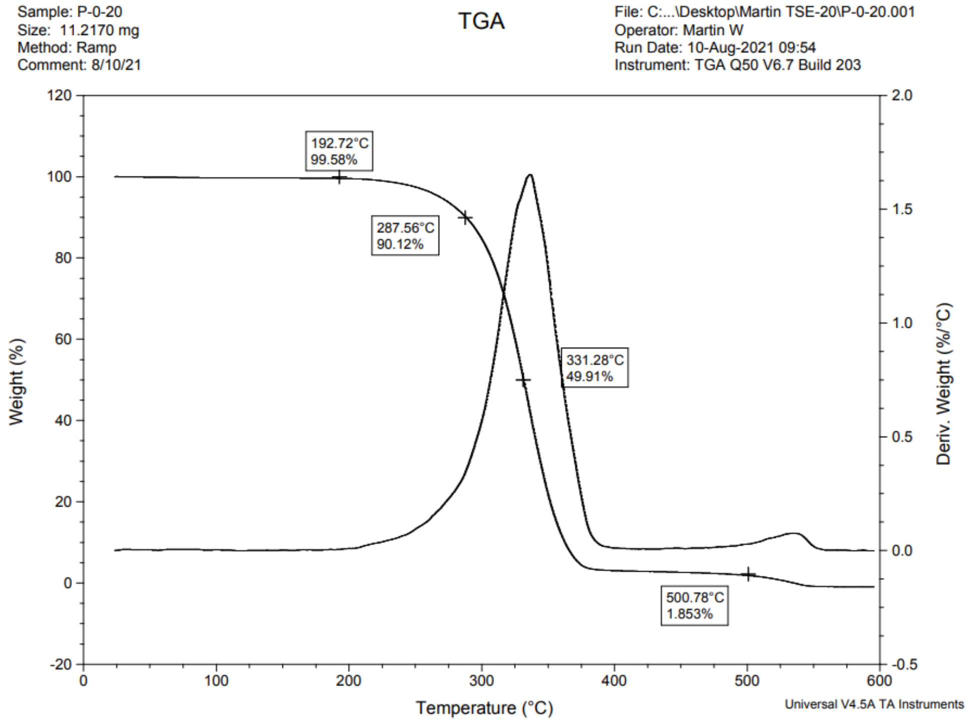


APPENDIX 6 COPOLYMER TGA

Octyl 2-cyano-3-(H-phenyl)-2 propenoate – Styrene Copolymer



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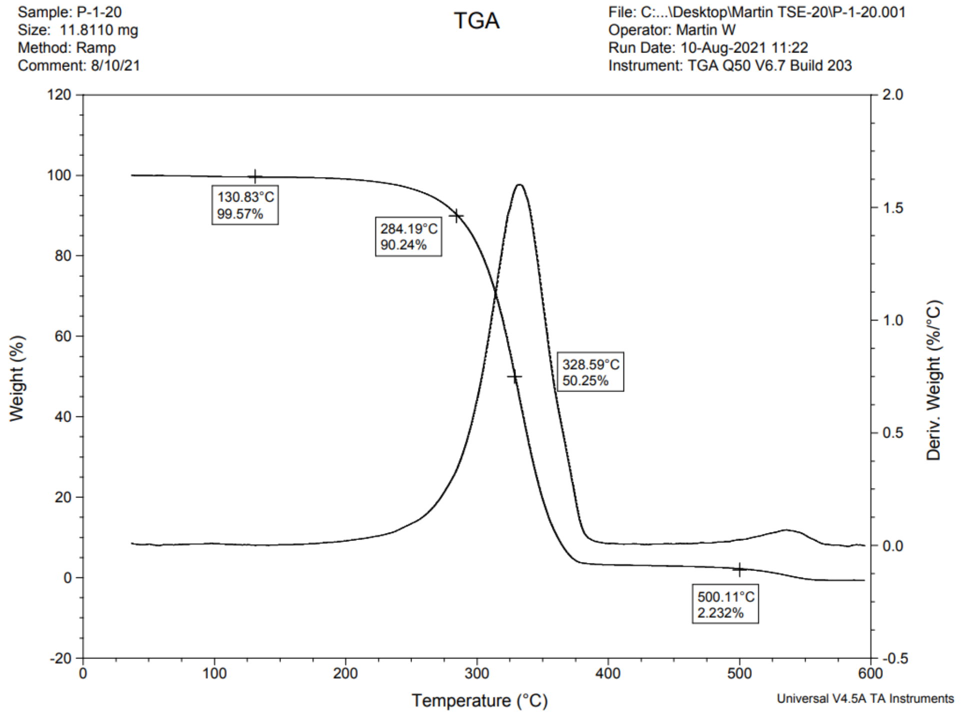

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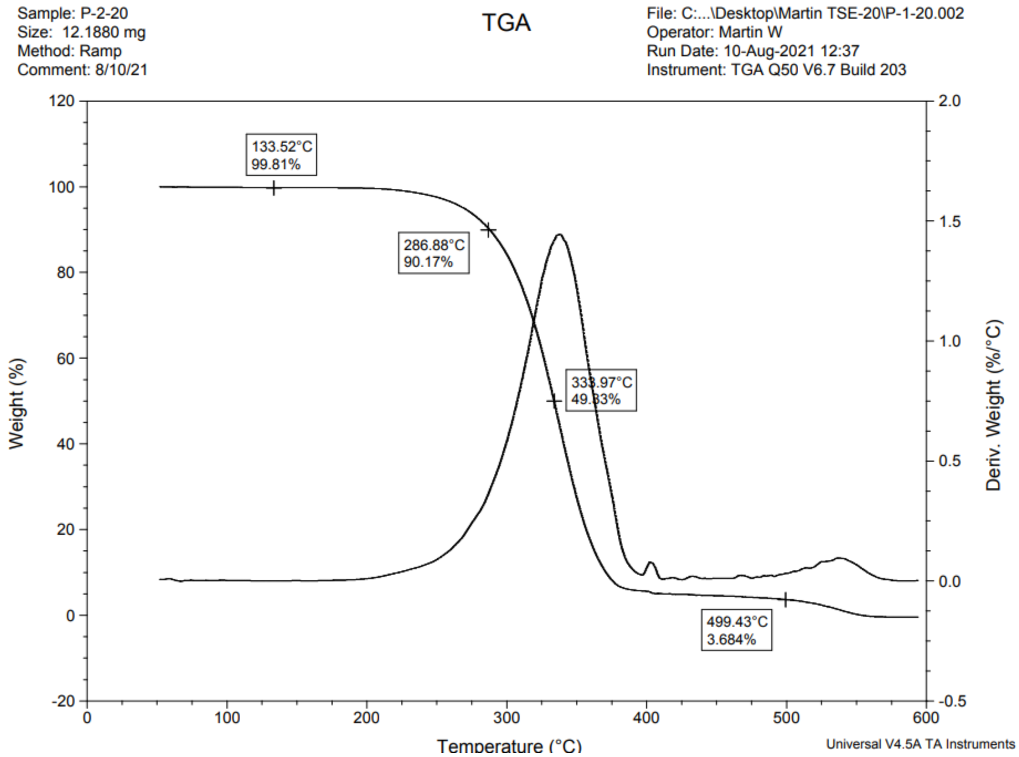

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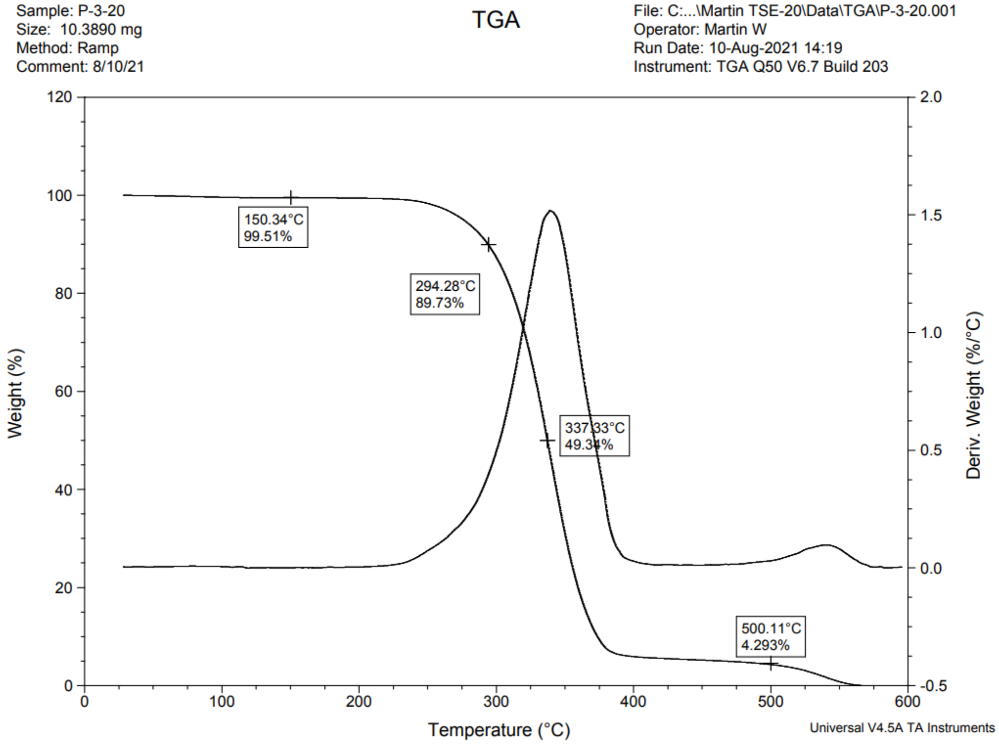

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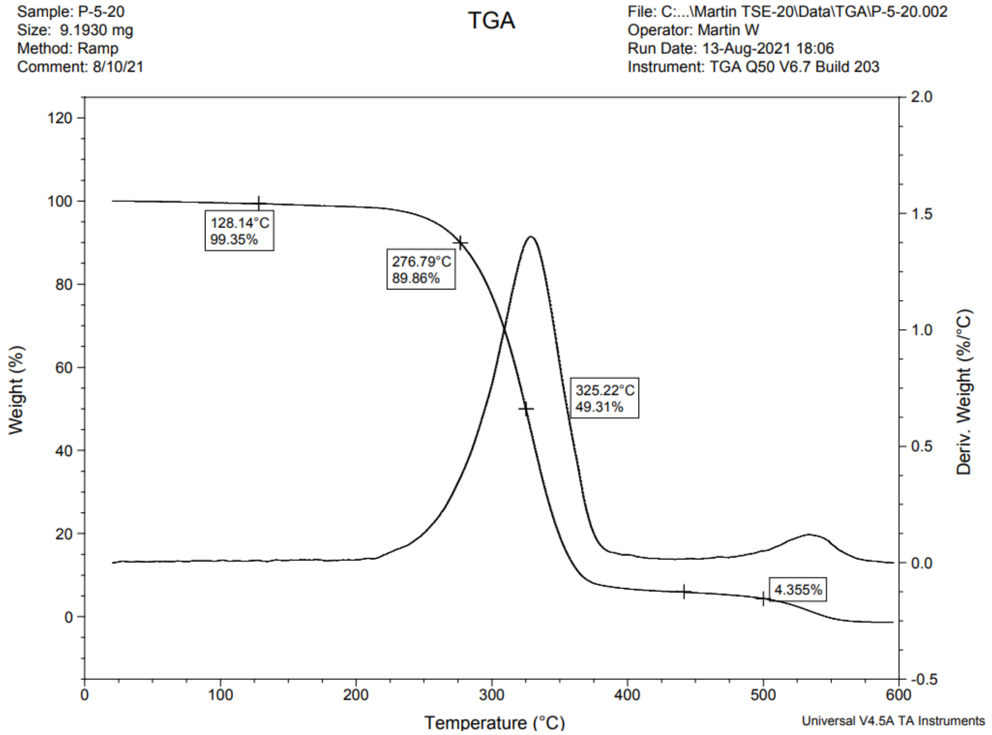

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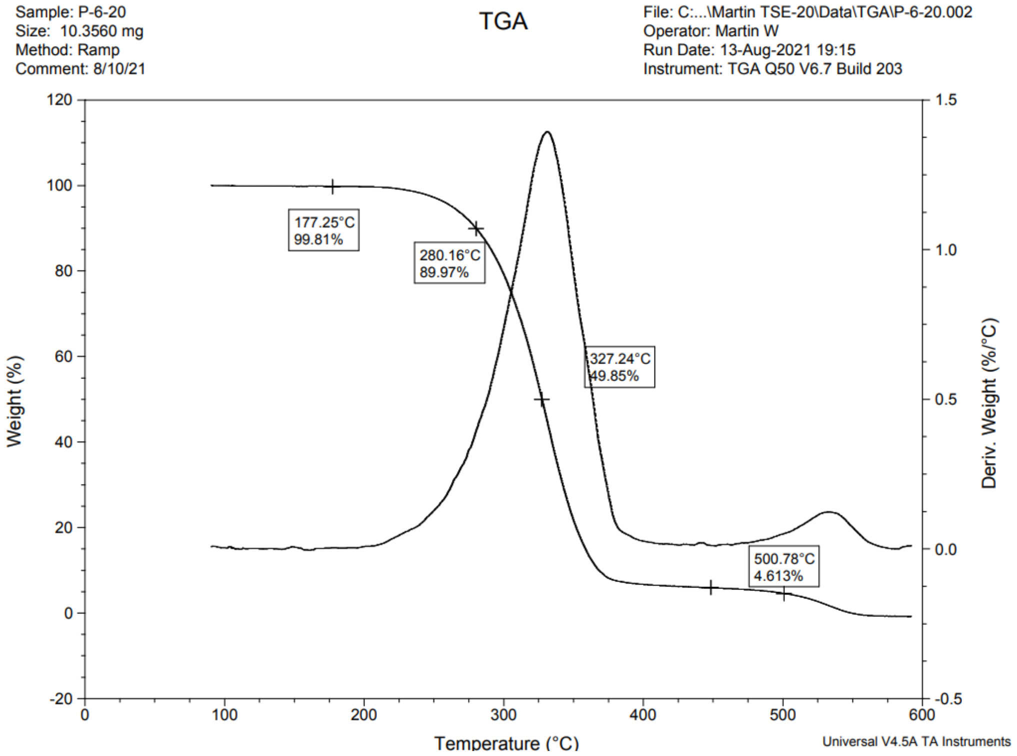

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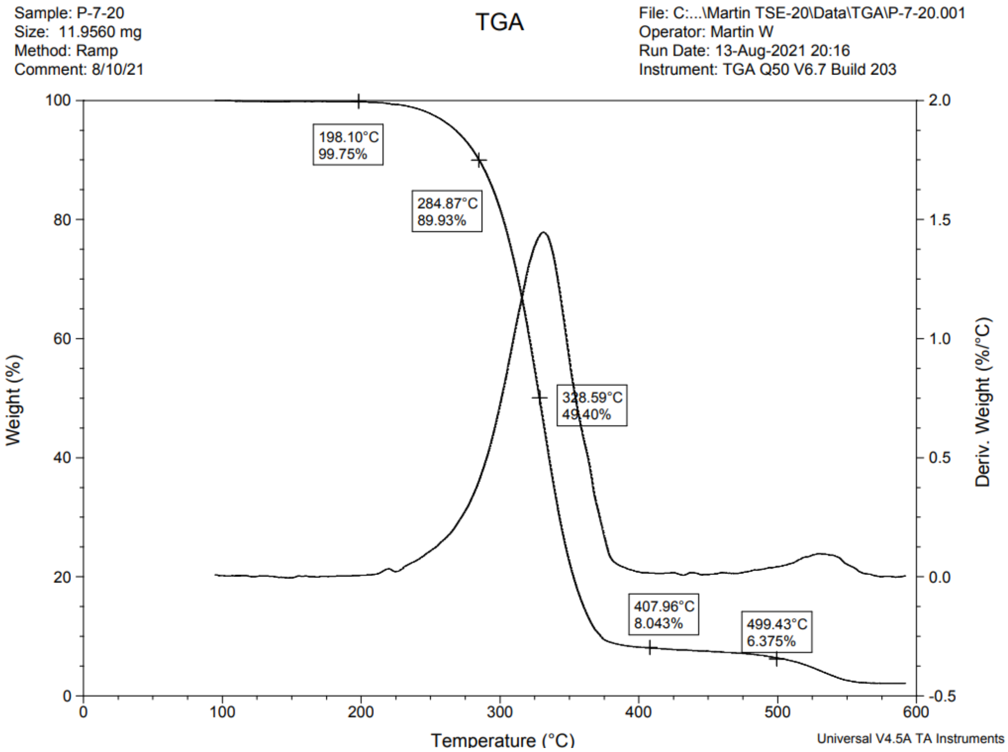

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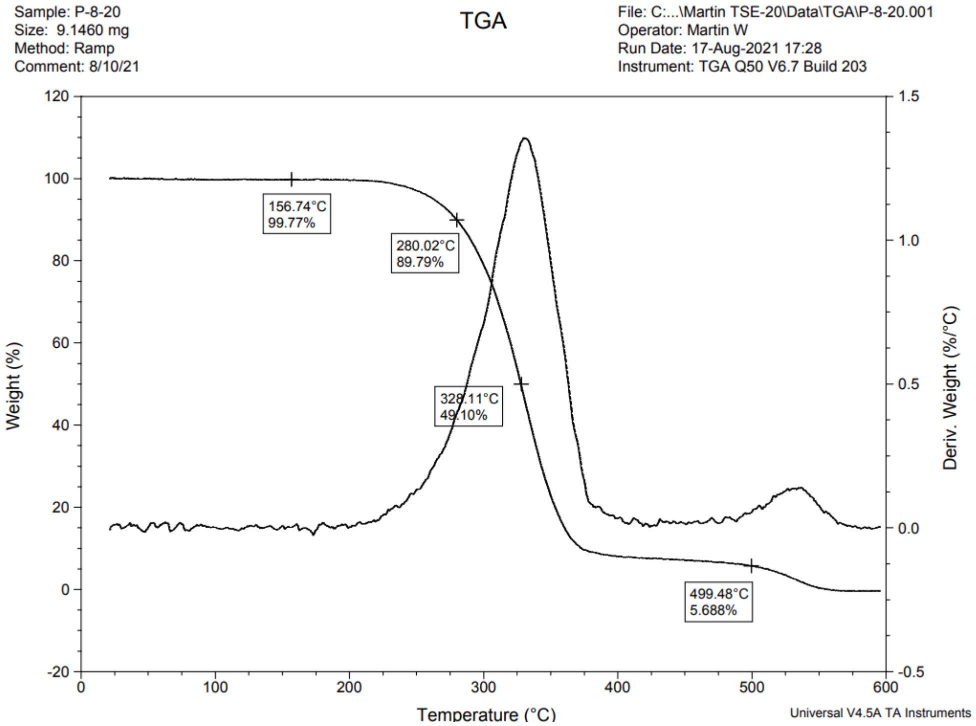

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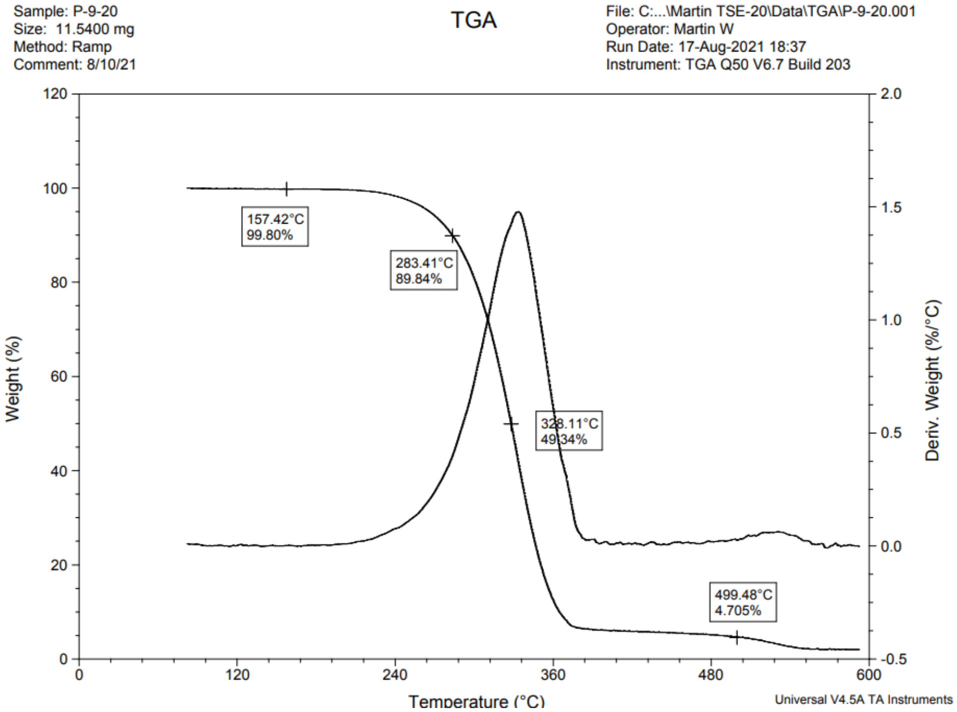

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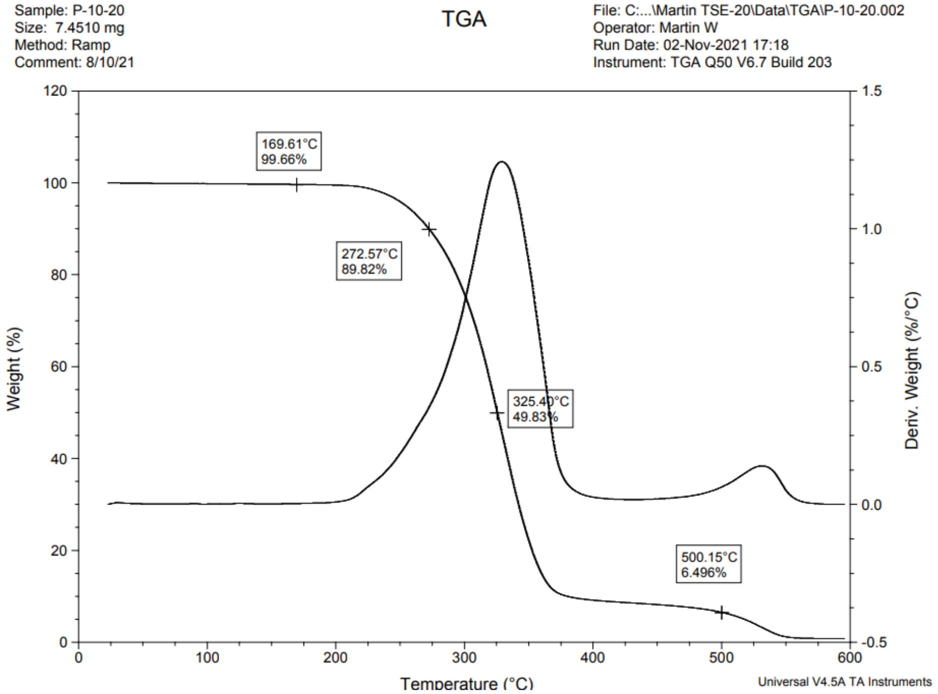

Acknowledgments

I would like to acknowledge that the project was partly supported by Chicago Society of Coating Technology (CSCT). I also thank the Chemistry department faculty, staff, and my advisor Dr. Gregory B. Kharas for their guidance in the pursuit of the completion of this thesis.

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