공학석사학위논문

Synthetic process development of laurolactam and C_{10}-ω-diamine as monomers for thermoplastic polyamide elastomers (TPAE)

열가소성 폴리아마이드 탄성체의 단량체로 사용되는 C_{10}−ω−diamine 과 laurolactam의 합성 공정 개발

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Abstract

Synthetic process development of laurolactam and C_{10}-ω-diamine as monomers for thermoplastic polyamide elastomers (TPAE)

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Engineering plastics (EP) are one of the most important materials in the world, because they have many advantages in properties. They remedied general plastic's critical shortcomings of thermal and physical properties. Among those EP, thermoplastic elastomer (TPE) has been the focus of the public attention since they have good elastomeric property and reusability through a good thermal stability. In the TPE, amide type of TPE, called thermoplastic amide elastomer (TPAE), has the best performance, which has excellent tear, weathering resistance, good elastic recovery, thermal stability, excellent chemical and hydrolytic resistance and so on.

In the domestic market, annual usage of TPAE is growing up gradually. However productions of TPAE's monomers are not fully developed. As reported our previous paper, we developed synthesis of C_9 to C_{11} monomers from biomass.

Herein, we try to introduce a synthetic methodologies C_{10} diamine and laurolactam based on biomass or petroleum as starting materials in the various reaction methods. We tried to synthesize C_{10} diamine from C_{10} or C_{12} diacid from biomass. C_{10} diacid was conducted in nitrile reduction process, and C_{12} diacid was used in Hofmann rearrangement and Curtius rearrangement methods. In the case of laurolactam, we tried to use cyclododecanone as starting materials. We obtained laurolactam via Beckmann rearrangement and Schmidt reaction. In Beckmann rearrangement, we tried to conduct one-pot process.

Finally, we fully developed the synthetic methods of C_{10} diamine and laurolactam. Especially, we conducted one-step processes, which were Curtius rearrangement and one-pot Beckmann rearrangement. One-step reaction reduced cost and reaction time and the yield was higher or similar compared to the other processes. In conclusion, the developed processes have quite meaningful and are applicable in the industry area.

Keywords: α, ω-diamine, EP, TPAE, Hofmann rearrangement, Nitrile reduction, Curtius rearrangement, Laurolactam, Beckmann rearrangement, Schmidt reaction

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LIST OF ABBREVIATIONS

AcOH	Acetic acid
Ar	Argon
aq.	Aqueous
br	Broad
C	Carbon
/C	Charcoal
calcd	Calculated
$CDCl_3$	Chloroform
CN	Nitriles
Conc.	Concentrated
δ	Chemical shift, ppm
d	Doublet
DMSO	Dimethyl sulfoxide
EI	Electron ionization
eq.	Equivalent
EtOAc	Ethyl acetate
g	Gram
GC	Gas chromatography
h	Hour
HCl	Hydrochloric acid
Hex	Hexane
HRMS	High resolution mass spectrometer
Hz	Hertz

J	Coupling constant(s)
lit.	Literature(value)
m	Multiplet
MC	Methylene chloride
MeOH	Methanol
mg	Milligram(s)
mL	Milliliter(s)
mmol	Mill mole(s)
mp	Melting point
MS	Mass spectrum
$NaHCO_3$	Sodium bicarbonate
NaN_3	Sodium azide
NaOMe	Sodium methoxide
NaOH	Sodium hydroxide
NH_2OH-HCl	Hydroxylamine hydrochloride
NMR	Nuclear magnetic resonance
s	Singlet
SiO_2	Silicon dioxide
t	Triplet
Temp.	Temperature
TLC	Thin-layer chromatography
TMS	Tetramethylsilane
TsCl	*p*-Toluenesulfonyl chloride
UV	Ultraviolet
wt%	Weight percent
$ZnCl_2$	Zinc dichloride

1. Introduction

1.1 Engineering plastic, EP

Nowadays, plastics are considered as one of the most important materials in the world. Compared to metal or ceramics, it has a poor thermal resistance and mechanical strength. However, it is widely used in the world because it has extremely light weight, a flexibility of design and shaping machinability.

Engineering plastic is developed to be grafted onto industry through overcoming those shortages. Engineering plastics (EP) are type of plastic materials that have better mechanical and thermal properties than the commonly used commodity plastics. There are 5 major EP in the industry.[1]

- Polyamide (1939, PA)
- Polyacetal (1956, POM)
- Polycarbonate (1958, PC)
- Modified Polyphenyl oxide (1966, M-PPO)
- Polybutylene terephthalate (1970, PBT)

Those plastics are replaced metal or wood in the commodity. For example, in the automotive industry, the plastics revolution was begun in 1950. The thermoplastics can be a usable price. It was started with ABS, and then progressively gotten on to polyamide, polycarbonate and polyacetal with an application of the mixture of various polymers. The development of advanced and nice performance polymers has dramatically grown because of their usage. Initially,

plastics were extraordinary because they offered good mechanical properties integrated with excellent appearance, including the capability of own coloring. In the automotive industry, the application of plastic components has been increasing. Furthermore, the plastics are mainly focused on making energy efficient on car by reducing weight, together with similar durability, weather resistance, flexibility of design, resiliency, toughness and nice performance with reasonable price. Because of those factors, the size of EP are going to be increased in the industry.[2]

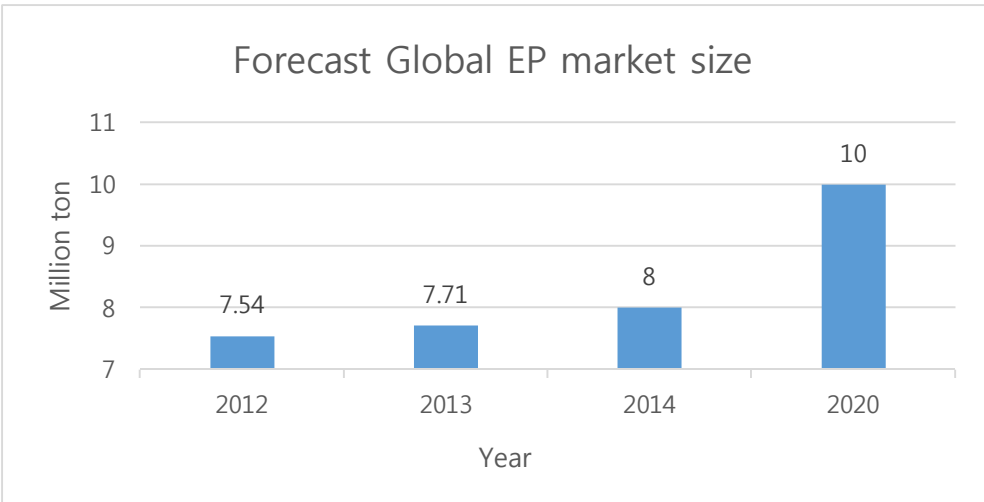


Figure 1. Forecasting annual global demands of EP in 2014-2020

1.2 Thermoplastic polyamide elastomer, TPAE

Among those EP, extensive research and development on thermoplastic elastomers (TPEs) have been conducted. Also global demand for TPEs through 2016 is forecast 5.5 percent at a year-on-year rate during the next five years, reaching 5.5 million ton in 2020, because TPEs are innovative materials which have advantages both thermoplastic and elastomeric properties.

Especially, thermoplastic polyamide-based elastomers (TPAE) as the newer additions to the class of the TPEs are considered good engineering plastics in terms of performance and cost.[3] TPAE have polyblock structure with replacing hard and soft segments.

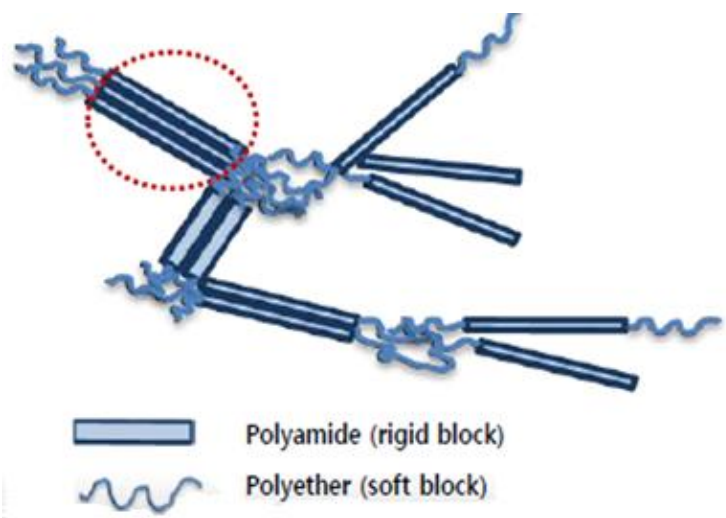


Figure 2. Schematic representation of polyamide thermoplastic elastomer

The hard segments are polyamides whilst the soft segments may be either polyether or polyester. The main characters of TPAE are shown below.[4]

- Excellent thermal stability (resistance to low -40 °C, high 190 °C)
- Excellent tear & weathering resistance
- Good formability to processing
- Good elastic recovery
- Excellent chemical & hydrolytic resistance
- Low specific gravity (fairly typical of so-called engineering TPEs)

For those reasons, there are increasing demands for production of TPAE with those good physical properties.

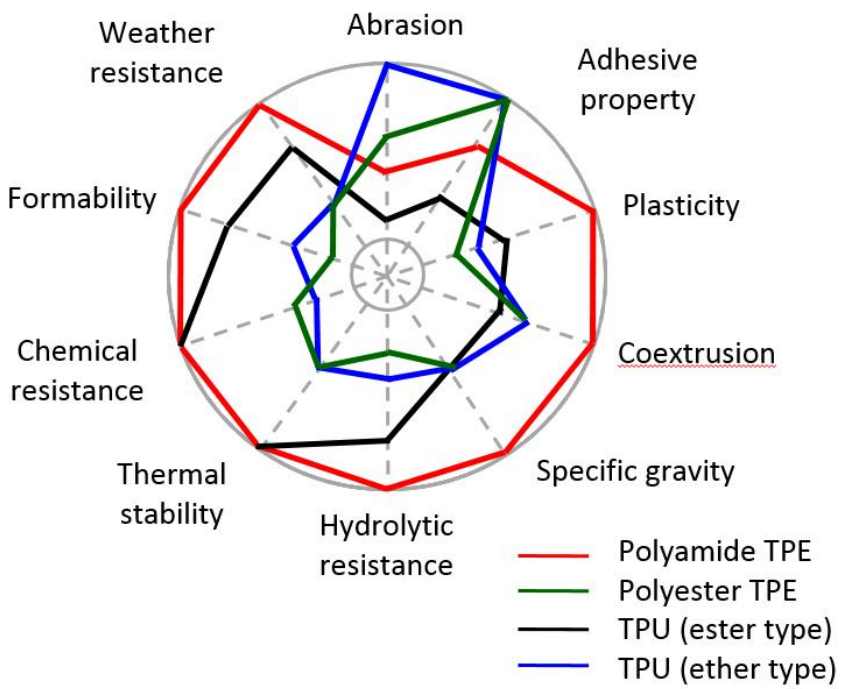


Figure 3. Comparison of physical properties of TPAE with other engineering TPE

1.3 Objective and Synthetic plan

As we discussed before this paper, a lot of efforts had been made to secure novel technologies for production of renewable resource-based polymer focus on Green chemistry with useful properties in our laboratory.[5,6]

In this paper, we have developed a concept to obtain the reasonable synthetic pathways of monomers for TPAE not only using natural oil but also petroleum as raw materials. The synthetic pathway is summarized below.

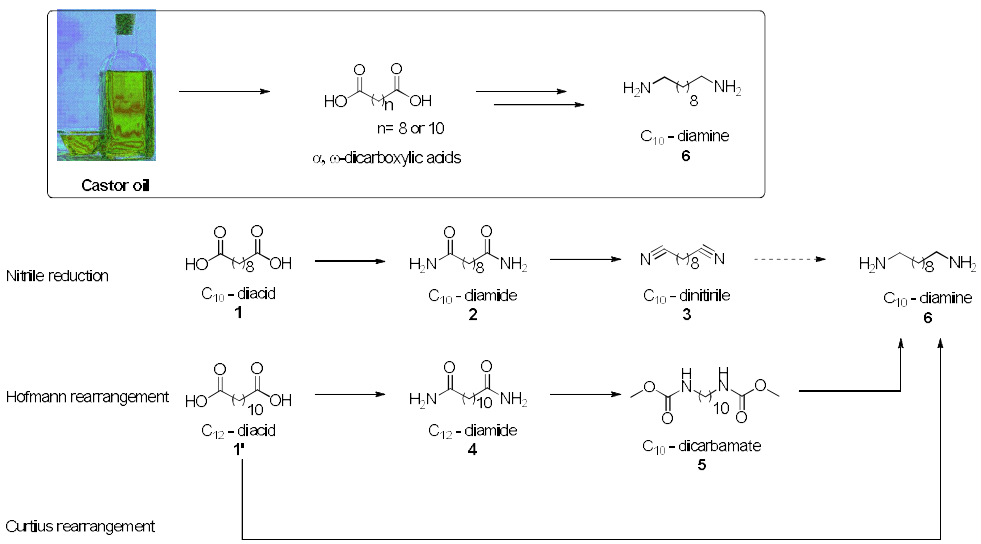


Figure 4. The divergent synthetic pathway of TPAE monomer from biomass

We have designed that the target compounds were C_{10} diamine and laurolactam. We already developed the synthesis of C_{10} or C_{12} diacid from biomass. However, diamine derivatives need to polymerize hard segments of TPAE with those diacid. In this aspect, we try to synthesize C_{10} diamine from C_{10} or C_{12} diacid which can be produced from renewable source. We have conducted three different reaction

methods which are nitrile reduction, Hofmann rearrangement and Curtius rearrangement in this paper.

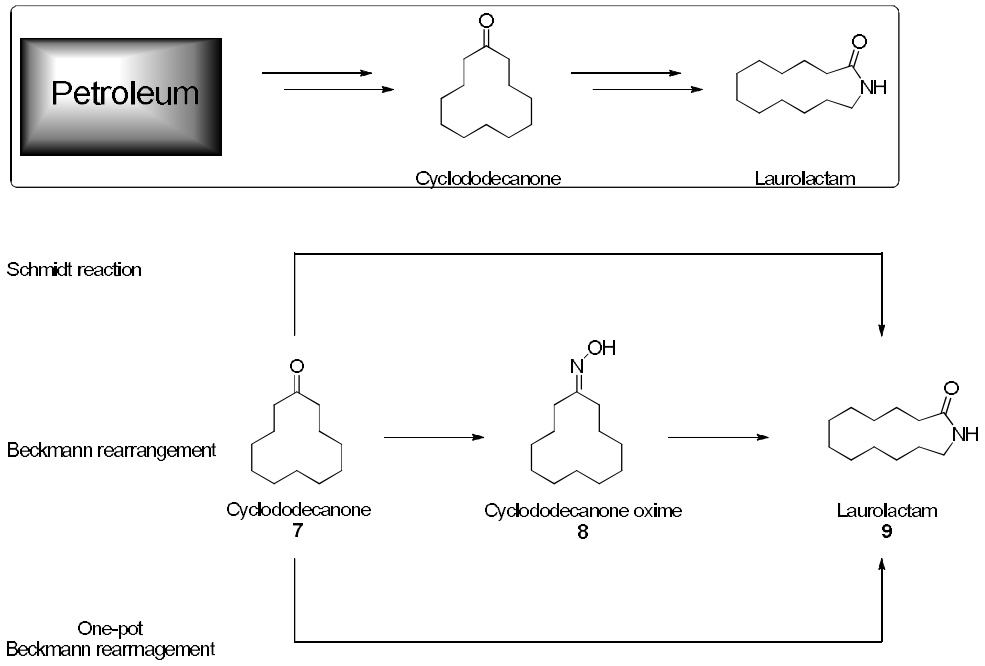


Figure 5. The divergent synthetic pathway of TPAE monomer from petroleum

In the case of α,ω amino acid, we already developed the procedure which come from a biomass. However, it has some shortages and inconvenient step in the purification. We try to design new methods and target compounds from traditional petroleum. We have conducted two different reaction methods which are Schmidt reaction and Beckmann rearrangement. In the case of Beckmann rearrangement, we have newly developed one-pot procedure without isolation of intermediate.

2. Result & Discussion

Herein, we report a divergent process for C_{10} and C_{12} polyamide monomers from a common starting materials, which come from petroleum and alternative sources such as vegetable oil, and optimize process.

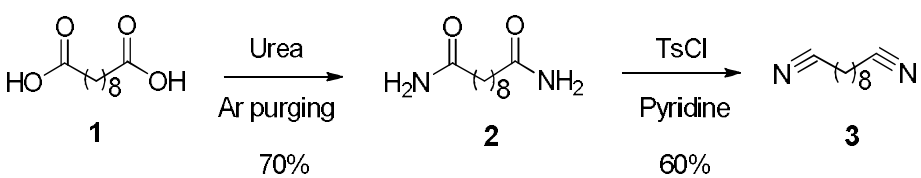
In case of synthesizing C_{10} diamine, there are used C_{10} and C_{12} dicarboxylic acid as starting materials. We can produce those monomers from castor oil and palm oil.[5,6] Even though we have C_{10} and C_{12} dicarboxylic acid, C_{10} diamine is an essential element to form the polymer. We apply many different synthetic pathways which are nitrile reduction, Hofmann rearrangement and Curtius rearrangement.

Laurolactam is synthesized from cyclododecanone which come from petroleum. We apply Azido-schmidt reaction and Beckmann rearrangement.

2-1 Synthesis of C_{10} – diamine

2-1-1 Nitrile reduction process

Preparation of C_{10} – dinitrile as a key intermediate is shown in scheme.



Scheme 1. Preparation of C_{10} dinitrile from C_{10} diacid

- C_{10} and C_{12} diamide formation

The preparation method of amide from carboxylic acid is very diverse. We investigated the method which is efficient and applicable to starting materials. Urea is quite good amine source and it can react without solvent.[7] Using urea condition, it show good reproducibility. However it has some problems which are quite disappointed yield and separation of impurity. To solve the problem, we focus on urea reaction mechanism.

Condition	^{1}H NMR ratio		
	SM	PRO	Impurity
130 °C, 1 h	91%	9%	0%
160 °C, 1 h	63%	32%	5%
160 °C, 2 h	58%	36%	5%
160 °C, 3 h	44%	49%	7%
160 °C, 4 h	38%	54%	9%
195 °C, 15 min	29%	65%	6%

Table 1. Conversion rate depending on the temperature and time

When the reaction temperature, urea decomposed and react with carboxylic acid, but urea react with itself in this condition. It formed biuret and cyanic acid.[8] Because of this reason, the reaction efficiency of urea decreased. To increase the reaction efficiency of urea, we eliminate or decompose biuret and cyanic acid. When the temperature is over than 190 °C, biuret decomposed and generate ammonia. Decomposition of urea is summarized in scheme. And the amide mechanism required heat energy.

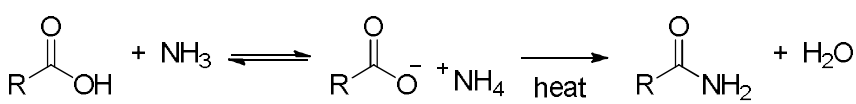
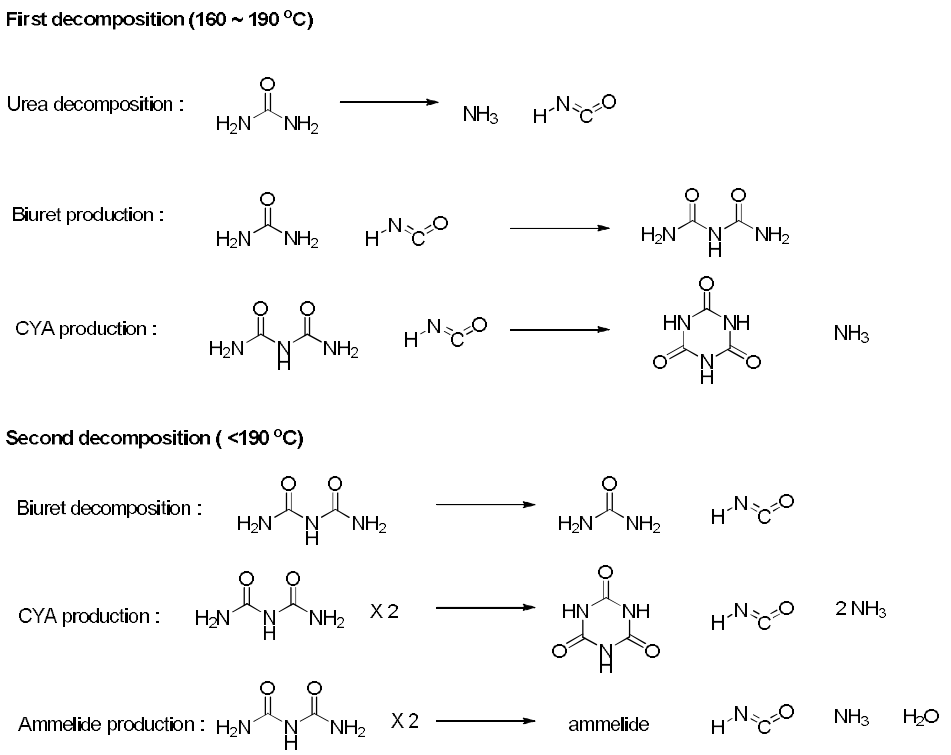


Figure 6. The amide formation mechanism from carboxylic acid



Scheme 2. Summarize urea decomposition depending on the temperature

In the crude product, starting material is still remained. We try to recrystallize crude in ethanol, but it still detected. We use the acid and base reaction mechanism. After then, we can eliminate the starting material. We apply those factors in our reaction. Finally, we can obtain the higher and purer yield than before.

- C_{10} dinitrile formation

Nitrile formation from amide is the very well-known reaction. $SOCl_2$ and $COCl_2$ are used in general procedure. However, we used TsCl and pyridine condition. In the reaction, $SOCl_2$ and $COCl_2$ generate SO_2 or CO_2 gas, but it does not generate any gas. Pyridine as a solvent and acid scavenger are used. It show good reproducibility with C_{10} diamide.

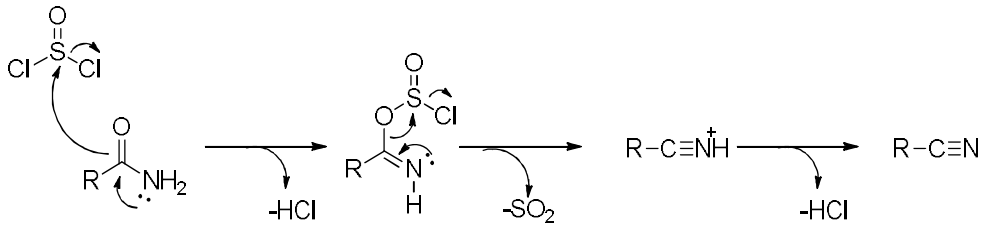
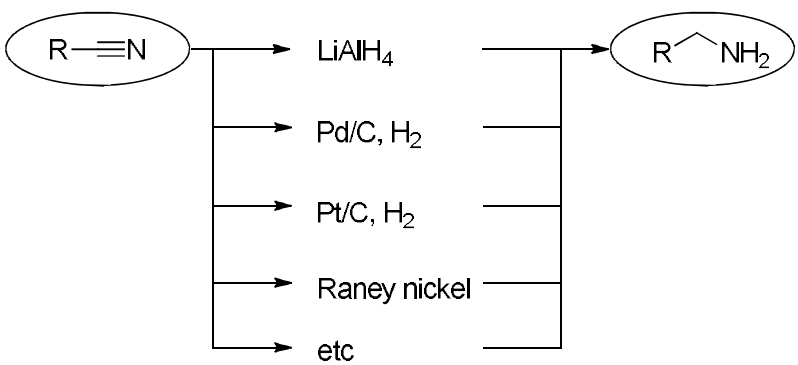


Figure 7. The nitrile formation mechanism from amide

- Reduction of nitrile

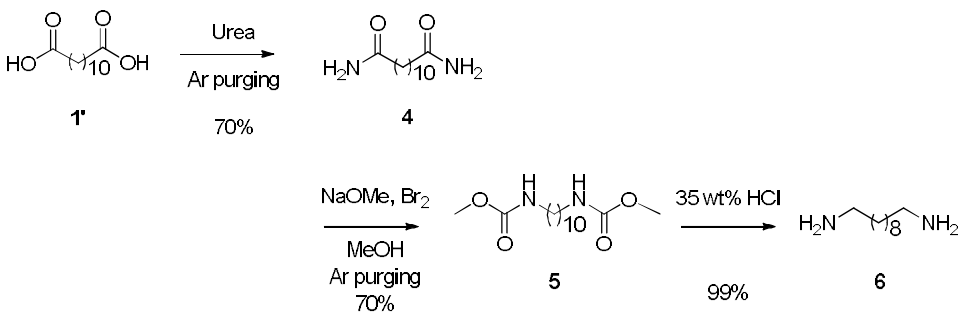
The reduction pathway of nitrile was already reported very many papers.[9,10] It is conducted via reduction through a catalyst and general reduction reagents. In the catalytic pathway, Raney nickel, palladium and platinum charcoal are used. In other cases, $LiAlH_4$ and BH_3 are used as general reduction reagents. We did not conduct the reduction of C_{10} dinitrile. We just proposed the potential of its reduction in this paper



Scheme 3. The various nitrile reduction pathways

2-1-2 Hofmann rearrangement

Preparation of C_{10} diamine from C_{12} diacid via Hofmann rearrangement is summarized in the scheme.



Scheme 4. Preparation of C_{10} diamine via Hofmann rearrangement

- Carbamate formation reaction

Hofmann rearrangement was first reported in 1881.[11] It is the reaction of an amide to a primary amine with degrading one carbon through the isocyanate intermediate by pathway of hypo-halite reaction mechanism. According to the standard procedure, the amide is dissolved in a cold solution of an alkali hypobromite or hypochlorite and the resulting solution is heated to 70-80 °C to bring about the rearrangement. It shown high yields in a wide variety of aliphatic and aromatic amides. However, the high yields for aliphatic amides are conducted when the starting material has shorter than 8 carbons.[12] Furthermore, C_{12} diamide has a terrible solubility in the various solvents. Because those reasons, general procedure shown a very disappointed result. To overcome the limitations, we used the formation of carbamate reaction. To form the carbamate group, methanol (MeOH) is used as a solvent. In the case of base, the solubility of KOH or NaOH decreased on MeOH. Therefore, sodium methoxide (NaOMe) are conducted

instead. When the reaction employ MeOH/NaOMe condition, the isocyanate intermediate react with MeOH. Finally, we can obtain the desired product with the reasonable yield which is 70%.

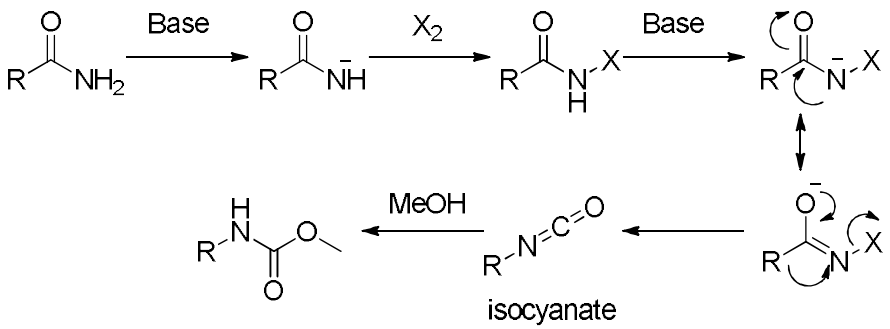


Figure 8. The formation mechanism of carbamate

Entry	Amides	Product	Condition	Yield
1	Capramide	Nonylamine	general procedure	25%
2	Undecylamide	Decylamine		5%
3	Lauramide	Undecylamine		Trace
4	Capramide	Methyl N-nonylcarbamate	modification	95%
5	Undecylamide	Methyl N-decylcarbamate		95%
6	Lauramide	Methyl N-undecylcarbamate		96%

Table 2. The tendency of Hofmann rearrangement with aliphatic amide[12]

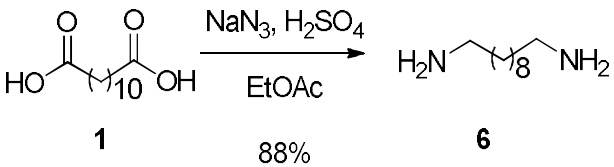
- Hydrolysis of carbamate

A carbamate is one of organic compound that derived from carbamic acid wich can be structurally and chemically interconverted carbamate group, carbamate ester and carbamic acids. A carbamate esters are also called as urethanes. In the reaction

of amino acid, we can identify it occasionally. It can be used as protective group for amino acid to minimize racemization in peptide synthesis. It has the quite strong stability in the basic condition, but it is easily deprotected in acid condition. We apply this fact to this reaction. In the basic condition, C_{10} dicarbamate show quiet stable. On the other hands, it became hydrolysis in the acid condition. We obtained 99% yield of hydrolysis product in acid condition.

2-1-3 Curtius rearrangement

Preparation of C_{10} diamine from C_{12} diacid via Curtius rearrangement is summarized in the scheme



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Scheme 5. Preparation of C_{10} diamine via Curtius rearrangement

This reaction was first reported by Curtius in 1890. [13] It is an organic reaction conducted to convert an acyl azide to an isocyanate with thermal conditions. The rearrangement is catalyzed by both protic and Lewis acids, and the decomposition temperature is significantly lowered compared to the uncatalyzed reaction.[14]

The mechanism consists of an alkyl shift from the carbonyl carbon to the next nitrogen with the release of nitrogen gas. The emitted gas drives the reaction forward and results in the isocyanate product which can potentially react further in the presence of nucleophiles as solution.[15]

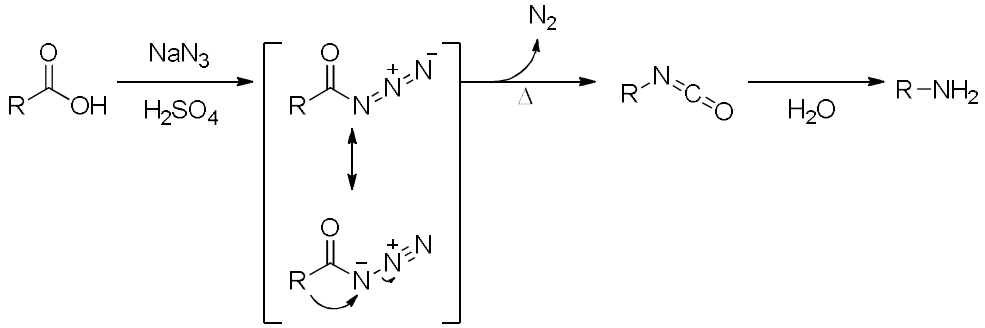


Figure 9. The summarized mechanism of Curtius rearrangement

It is a very general reaction and can be applied to carboxylic acids containing a wide range of functional groups. It is also possible to induce a Curtius rearrangement under photochemical conditions, but this reaction condition creates rise to several side-products except the desired isocyanate.[16]

We try to apply thermal and protic acid condition. When carboxylic acid change to acyl azide, it is the strong exothermic reaction. In the acid condition, sodium azide react with hydrogen cation and make a hydrazoic acid. It is unstable and very sensitive to temperature. If it is not under the room temperature, the reaction generate the eruptive nitrogen gas and heat energy. Because of this reason, we need to maintain the temperature until it is lower than the room temperature. Heat-up procedure is the same principles. The reaction temperature is insensibly raised. It slowly generate nitrogen gas. We try to do reaction in gram scale. It has the reproducibility in the large scale.

2-2 Synthesis of laurolactam

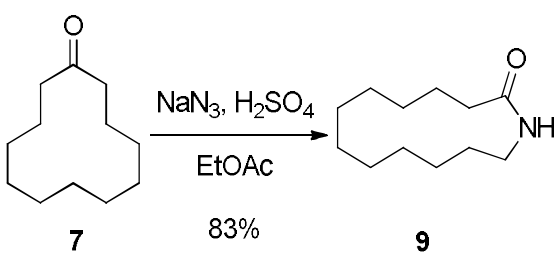
Before this paper, we already reported about TPAE monomer.[5,6] In this paper, we investigate the synthesis of C_9 to C_{12} amino acid from biomass as alternative sources. In the case of amino acid, it has the advantage that it does not need any

other monomer to form a polymer. However, it is very sensitive to an acidity, because carboxylic and amino group exist in the same molecule. To isolate the amino acid, we have to control the acidity of solution. Furthermore, the purified product is the salt formation. It has very inconvenient step and critical shortage. To overcome those problems, we investigate the target compound. In the case of C_{12} amino acid, it can be cyclized. It is referred laurolactam. It has a good property and stability. In the cyclized product, it has the primary amide bond. Even though an amide has a high polarity, it can be easily purified by column chromatograph and recrystallization. In the case of nylon 6, caprolactam is already mainly used instead of C_6 amino acid. Following those investigation, we establish the detail target compound and synthetic strategies.

Many different synthetic pathways are already reported. Beckmann rearrangement and Schmidt reaction are commonly mentioned in the cyclic amide bond formation reaction.[17] We developed and applied those name reactions to produce laurolactam in the reasonable method to employ industrial process.

2-2-1 Schmidt reaction

Preparation of laurolactam from cyclododecanone via Schmidt reaction is summarized in the scheme



Scheme 6. Preparation of laurolactam via Schmidt reaction

Schmidt reaction was reported in 1923. It is the reaction between a hydroazoic acid and a carbonyl group via a 1, 2-migration to form a molecule which contained nitrogen such as primary amide. It is very versatile and has the advantages of simplicity, readily available reactants, mild reaction conditions, and a certain level of functional group tolerance.[18] However, cyclododecanone is very simple cyclic ketone compound, we didn't need to investigate the tendency of migration of different alkyl or aryl groups. We only focused on the conversion and time of reaction.

In the resent paper, Silica sulfuric acid was used as an acid catalyst. It showed very good conversion and took a short reaction time without solvent.[19] We try to follow this paper, but cyclododecanone explosively react with silica sulfuric acid and burnt out. Therefore, we added an acetonitrile, which is polar aprotic, as a solvent. The product is isolated with a high yield, but disappointedly the reaction time took 48 h. it is too long and inefficient.

We try to change the catalyst as a Lewis acid. Using $FeCl_3$ as Lewis acid was already reported.[20] In this paper, they used TMS-N_3 instead of sodium azide. It is much more reactive than sodium azide. We follow up the procedure, but the isolated yield was only 42%. In addition, we tried to diversify the catalyst. It is summarized on the table.

Entry	**Catalyst**	**Solvent**	**Time (h)**	**Yield**
1	$FeCl_3$	DCE	4	42%
2	$FeCl_3$	Dry toluene	4	35%
3	$FeCl_3 \cdot 6H_2O$	MeCN	4	No Reaction
4	Fe^{3+}-Mont	MeCN	4	No Reaction
5	Silica sulfuric acid	MeCN	48	96%

6	Silica sulfuric acid	neat	-	-

Table 3. The catalyst screening of Schmidt reaction

Disappointedly, the catalytic acid condition was very disappointed. We realigned the reaction plan to using the equivalent amount acid. H_2SO_4 is used as the acid to covert sodium azide into hydroazoic acid. It was shorter reaction time and better yield than before. Moreover, it has a reproducibility in the large-scale reaction.

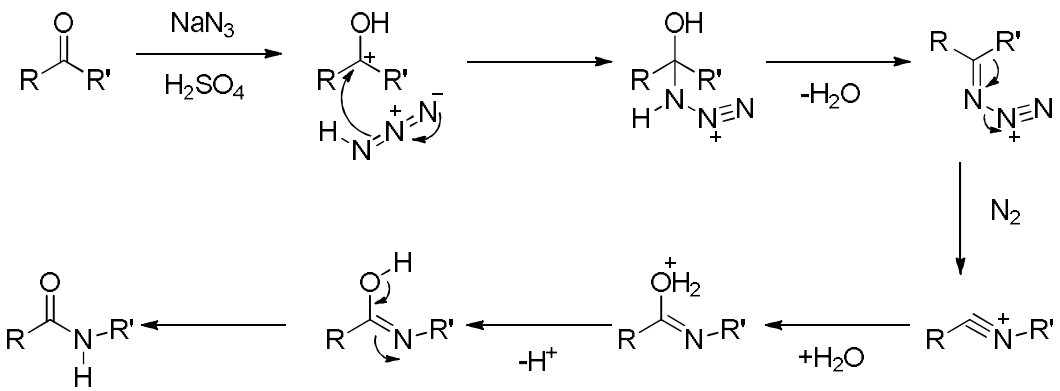
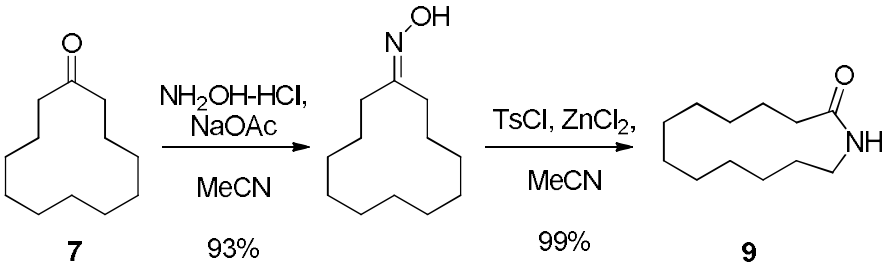


Figure 10. The summarized mechanism of Schmidt reaction

2-2-2 Beckmann rearrangement

Preparation of laurolactam from cyclododecanone via oxime intermediate and Beckmann rearrangement is shown in scheme.



Scheme 7. Preparation of laurolactam via Beckmann rearrangement

Beckmann rearrangement was firstly reported in 1886.[21] It is the rearrangement of oximes to its accordant amide in the presence of an acid. The oxime is formed by the reaction of a ketone with hydroxylamine.

The reaction is usually carried out very harsh conditions, which are high temperatures (above 130 °C) and over an equivalent amounts of strong Brönsted acids which it is not catalytic way. H_2SO_4, HCl, Ac_2O and AcOH are applied as Brönsted acids. It means that sensitive substrates cannot be tolerated in those conditions.

In the normal Beckmann rearrangement, It has a migrate attitude and produced different result for direction of OH group. The opposite alkyl group as the leaving group migrated on the nitrogen. When the oxime formation conducted under those reaction conditions, the two feasible amides are formed as a mixture. Because the hydrogen atom is immovable, this method can't be used for the synthesis of N-unsubstituted amides. However, those factor did not bother us because starting material is symmetric.

Especially, this reaction is important in the industry. It is the mechanism of caprolactam which is source of a monomer of a polyamide for the production of synthetic plastics. The synthesis process of caprolactam is very similar to laurolactam. We try to verify the reaction conditions, and apply the synthesis process of caprolactam to our reaction.

First, we tried to prepare the oxime formation of cyclododecanone. In this reaction, we verified the reaction solvent. Except of ethyl acetate, it represents the good result. In those solvents, acetonitrile showed the best yield. According to accrete the reaction time, the yield was slightly increased.

Entry	Solvent	Time	Condition	Yield
1	MeOH	2 h	Reflux	82%
2	MeCN			97%
3	Ethyl Acetate			No reaction
4	Toluene			89%
5	MeCN	6 h		96%

Table 4. The reaction screen of oxime formation

After the oxime of cyclododecanone was synthesized, Beckmann rearrangement was applied. We verified the reaction condition. We summarized the result on table

Entry	Solvent	Acid	Time	Condition	Yield (%)
1	MeCN	TFA	1 h	RT	SM recovered
2			12 h	RT	SM recovered
3				Reflux	73
4	MeOH				SM recovered
5	Toluene				41
6	Dry Toluene				65

7	MeCN	triflic acid			54
8	MeCN	TFAA			26
9	MeCN	TsOH			-

Table 5. The reaction screen of acid Beckmann rearrangement

The 3 equivalents of acids was used in this reaction. We changed the reaction time, heating condition and solvent. When the reaction was carried out in RT, SM was recovered. Even though the reaction time was accreted, product was not obtained. We try to conduct various conditions of solvents. MeOH, toluene, anhydrous toluene and MeCN are used. The water affect the reaction in toluene condtion. Anhydrous toluene condition showed better result than normal toluene condition, and MeCN showed the best yield. In addition, we changed the acid condition which are TFA, triflic acid, TFAA and TsOH. TFA condition showed the best yield.

However, the equivalents acids conditions have several shortages. If we used the equivalents of acids, we need to neutralize the reaction result. It consumed too many $NaHCO_3$ and also took a big-budget. In addition, the reaction time and yield are not reasonable. We need to find much more efficient and convenient method that is the catalytic condition. Recently, using organic-catalyst Beckmann rearrangement has been spotlight to researchers for usefulness in catalytic mechanism and easy to control during the reaction. TsCl as organic-catalyst was reported to be a highly convenient and useful catalyst.[22] On the other hand, cation-exchanged material, montmorillonite, is reported as an powerful heterogeneous catalyst.[23,24] We applied those results in the oxime of cyclododecanone.

Entry	**Solvent**	**Catalyst**	**Time**	**Condition**	**Conversion**	**Yield**

1	MeCN	Fe^{3+}-Mont	4 h	reflux	88%	-
2	PhCN	Fe^{3+}-Mont	4 h	90 °C	84%	-
3	MeCN	Ti^{4+}-Mont	4 h	reflux	82%	-
4	PhCN	Ti^{4+}-Mont	4 h	90 °C	76%	-
5	MeCN	TsCl & $ZnCl_2$	1 h	reflux	100%	99%
6	MeCN	TsOH & $ZnCl_2$	1 h	reflux	no reaction	-

Table 6. The reaction screen of catalytic Beckmann rearrangement

In this table, the cation exchanged montmorillonite, Fe^{3+} or Ti^{4+}, showed the good result. However, TsCl & $ZnCl_2$ reaction condition is the best outcome. The reason of this consequence is the intermediate of this reaction. In this reaction, TsCl reacted with the oxime and formed the reactive intermediate. It can be complicated with other oximes as a catalyst. It is summarized in Figure.

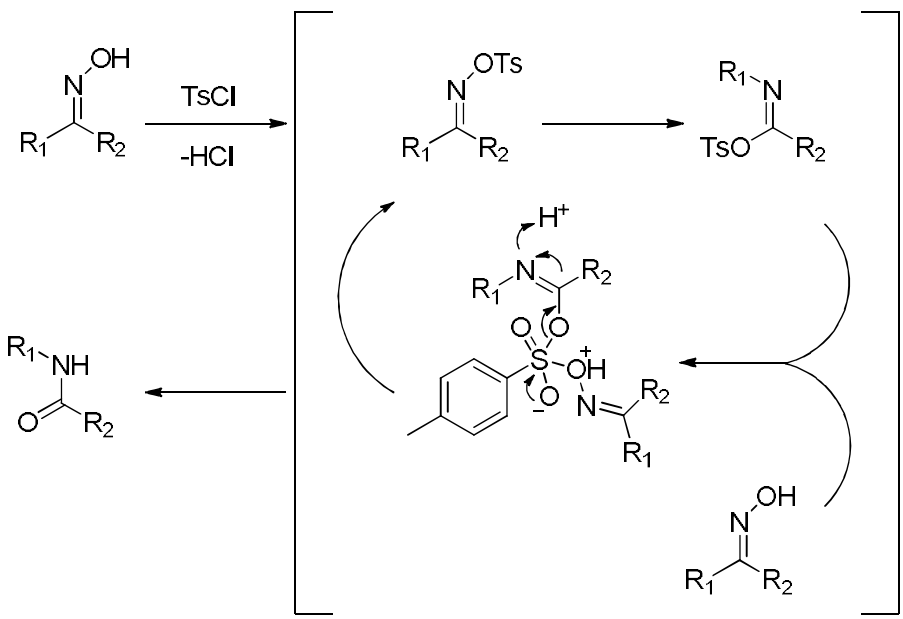
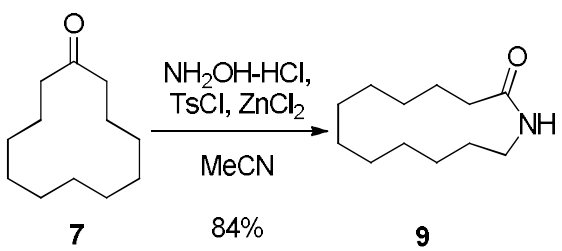


Figure 11. The summarized mechanism of TsCl catalyst pathway

In comparison with cation exchanged resin, TsCl & $ZnCl_2$ took short reaction time and represents a better yield. In addition, it has the reproducibility in the large scale reaction.

2-2-3 One-pot Beckmann rearrangement

Preparation of laurolactam from cyclododecanone via one-pot Beckmann rearrangement is shown in scheme.



Scheme 8. Preparation of laurolactam via one-pot Beckmann rearrangement

To react the Beckmann rearrangement, the reaction of oxime formation is previously accomplished. If this previous reaction is conducted with the Beckmann rearrangement in the same time, it can save the reactor occupation and the cost. In this light, the previous reaction have to be fused with the Beckmann rearrangement.

In the papers, they proposed one-pot reaction with catalytic amount of $FeCl_3 \cdot 6H_2O$.[25] We tried to apply this reaction in the cyclododecanone. However, it showed the disappointed result. To overcome this problem, we applied the reaction

of TsCl & $ZnCl_2$ as a catalyst with one-pot Beckmann rearrangement. At the first time, we added all reagents and solvent in one-pot and reflux. We checked the conversion by TLC. In the TLC, product did not stained as time goes on. Only the oxime was detected. We thought that some reagent react with the catalyst and deactivate the catalyst. When the reaction omitted NaOAc, product was detected in GCMS. The isolated yield is 80-84%. It is reasonable and reproducible. The reaction mechanism are same as two-step reaction. In the large scale reaction, it took longer time than small scale, but it still have the reproducibility.

It is a new one-pot Beckmann rearrangement pathway by using TsCl & $ZnCl_2$ as a catalyst. To confirm the reaction tendency, we tried to do various substrate. It showed a similar tendency which is two-step Beckmann rearrangement. Nitrogen of amide was formed at the side which stabilized a cationic character.

Entry	**Ketone**	**Product**	**Yield**
1	Cyclohexonone	Caprolactam, 10	40%
2	Cycloheptanone	Oenantholactam, 11	80%
3	Cyclooctanone	Capryllactam, 12	82%
4	Acetophenone	*N*-Phenylacetamide, 13	70%
5	4-Bromo acetophenone	*N*-(4-Bromophenyl)acetamide, 14	57%
6	4-Methyloxide acetophenone	*N*-(4-Methoxyphenyl)acetamide, 15	90%
7	2,5-Dimethyl acetophenone	*N*-(2,5-Dimethylphenyl)acetamide, 16	72%
8	4-Nitro acetophenone	N-(4-nitrophenyl)acetamide, 17	-
9	Cyclododexcanone	Laurolactam, 9	85%

Table 7. Scope of one-pot catalyzed Beckmann rearrangement

In the cyclic ketone, 6 member ring is shown disappointed result. In the acetophenone type materials, it is shown good result with the electron donating aromatic substrate. On the contrary to this, acetophenone with the electron withdrawing aromatic substrate has a very disappointed result.

3. Conclusion

Finally, we developed various methods to synthesize C_{10} diamine and laurolactam for the monomers of polyamide-based elastomers (TPAE) from biomass or petroleum.

C_{10} diamine was synthesized from C_{10} diacid or C_{12} diacid which were prepared from biomass. When the starting materials was C_{10} diacid, total yield of C_{10} diamine was disappointed. Even though, we overcame the many barriers to synthesize the product. Furthermore, total yield was unreasonable in Hofmann rearrangement pathway when the starting materials was C_{12} diacid. However, in Curtius rearrangement, not only the yield is reasonable, but also the synthesis process is very simple in one step. From an environmental point of view, it is quite meaningful method to substitute typical procedure.

Laurolactam was prepared from cyclododecanone. We applied three different reaction methods, which were Beckmann rearrangement, Schmidt reaction and one-pot Beckmann rearrangement, to synthesize the product. In case of Beckmann rearrangement, this method showed reasonable and effective results in the each step. However, the process need to isolate oxime formation as an intermediate. It is disadvantage to optimize the process. On the contrary, Schmidt reaction did not pass though those intermediate. Its yield is reasonable and efficient, but NaN_3 is 3 times expensive than NH_2OH-HCl and unstable. Finally, we newly developed one-pot process of Beckmann rearrangement to use organic catalyst. It did not need to isolate the intermediate. Furthermore, its yield was greatly similar other methods. It had reproducibility in the other ketones.

4. Experimental section

General procedure.

All materials were obtained from commercial sources and were used without further purification. Anhydrous acetonitrile solvent was treated by molecular sieve. Air or moisture sensitive reactions were conducted under nitrogen atmosphere using standard syringe/septa techniques. The reactions were monitored with SiO_2 TLC plates under UV light (254 nm) followed by visualization with a phosphomolybdic acid or a ninhydrin stain solution. Column chromatography was performed on silica gel 60 (70-230 mesh). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were measured at 400 MHz and 100 MHz, respectively, in deuterated chloroform ($CDCl_3$) or DMSO (DMSO-d_6) with Bruker Avance-400. The ^{1}H NMR spectroscopic data were reported as follows in ppm (δ) from the internal standard (TMS, 0.0 ppm) in $CDCl_3$ or DMSO-d_6

: Chemical shift (integration, multiplicity, coupling constant in Hz). The ^{13}C NMR spectra data were referenced with the 0.00 resonance of TMS or 77.16 resonance of $CDCl_3$. Low or high resolution mass spectra were measured by the EI ionization method.

Diamide synthesis

Diacid (1 eq., 9.89 mmol) and urea (2.2 eq., 22.76 mmol) were added at Argon condition. Temperature of this mixture was heated up until 130 ^{o}C and maintain 1 h. In this temperature, urea and SM became liquid. This mixture was heated up until 160 ^{o}C and maintain 4 h. After then, this mixture was heated up until 195 ^{o}C and maintain 15 min. This mixture was cooled down. White solid was formed. This solid was grinded and added in 1 N NaOH solution. This solution stirred 24 h in

room temperature. White solid was filtered out in this solution. This solid was dried 8 h in vacuum oven. The white solid (70%, 6.92 mmol) was product.

C_{10} diamide, 2

^{1}H NMR (DMSO, TMS): d 7.21 (s, 2H, NH), 6.66 (s, 2H, NH), 2.01 (t, 4H, *J* = 7.6 Hz), 1.46(t, 4H, *J* = 6.8 Hz), 1.23(s, 8H); ^{13}C NMR: d 174.77, 35.59, 29.18, 29.16, 25.56

C_{12} diamide, 4

MP 194 ^{o}C, ^{1}H NMR (DMSO, TMS): δ = 1.24(s, 12H), 1.46(t, 4H, *J* = 6.6 Hz), 2.01 (t, 4H, *J* = 7.6 Hz), 6.66 (s, 2H, NH), 7.20 (s, 2H, NH); ^{13}C NMR (DMSO, TMS): δ = 25.57, 29.18, 29.25, 29.38, 35.59 174.76; Anal. Calcd for $C_{12}H_{24}N_2O_2$ C, 63.65; H, 10.71; N, 12.37; C, 59.97; H, 10.07; N, 13.99;

C_{10} dinitrile, 3

TsCl (2.5 eq., 12.5 mmol) was added gradually to a stirred mixture of C_{10} diamide, 2 (1 eq., 5 mmol) and pyridine (50 eq., 250 mmol). The solution was refluxed overnight. This crude mixture was filtered with anhydrous diethyl ether. The mother liquid was extracted with brine solution and dried over anhydrous sodium sulfate. It was concentrated on rotary vacuum evaporator. The resulting crude product was purified by column chromatography (4:1 v/v, EtOAc: hexane) on silica gel. The product was clear liquid. : ^{1}H NMR ($CDCl_3$, TMS): δ = 1.35 (m, 4H) 1.46 (m, 4H), 1.66 (m, 4H), 2.34 (t, 4H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, TMS): δ = 17.13, 25.29, 28.49, 28.51, 119.70

C_{10} dicarbamateme, 5

Shredded Na (400mg, 8.86 mmol) was slightly added in 10 mL anhydrous MeOH at 0 ^{o}C in N_2 condition. When Na was totally dissolved, MeOH was concentrated on rotary vacuum evaporator and added anhydrous MeOH 10 mL again. C_{12} diamide (500 mg, 2.2 mmol) was added in MeOH/NaOMe solution. Reaction temperature slowly was raised at 60 ^{o}C in argon condition with reflux condenser. Br_2 (0.48 mL, 9.68 mmol) was slowly added in solution. The mixture was stirred and maintained temperature in 1 h. When the mixture was cooled down RT, 10 mL of saturated Na_2SO_3 was added to quench unreacted Br_2. And AcOH (0.4 mL, 7 mmol) was added to quench NaOMe. The mixture was concentrated on rotary vacuum evaporator to eliminate MeOH. The crude mixture was filtrated and washed with 10 ml water. The filter cake was crude product. The resulting crude product was purified by column chromatography (2:1 v/v, EtOAc: hexane) on silica gel. The white solid product (445 mg, 1.54mmol) was obtained. : ^{1}H NMR (DMSO): δ = 1.23 (s, 12H), 1.36 (t, 4H, J = 6.6 Hz), 2.96-2.91(q, 4H), 3.50(s, 6H), 7.06 (s, 2H, NH),; ^{13}C NMR ($CDCl_3$): δ = 26.68, 29.40, 29.40, 30.01, 41.11, 51.98, 175.10

Hydrolysis of C_{10} dicarbamateme

C_{10} dicarbamate (330 mg, 1.14 mmol) was added in 5 mL conc. HCl solution. The solution was refluxed 24 h. The completion of the reaction was monitored by TLC. The solution was washed by $CHCl_3$. After then, aqua layer was titrated with NaOH solution until pH 10-12. The aqua layer was extracted with $CHCl_3$. The organic layer was dried over anhydrous sodium sulfate, and concentrated on rotary vacuum evaporator. A resulting white solid (200 mg, 1.15 mmol) was C_{10} diamine, 6. It did not need to be purified in 100% yield

Curtius rearrangement

C_{12} diacid (1000 mg, 4.3 mmol) was added in $CHCl_3$ 7 mL and cooled down below 20^oC. H_2SO_4 (2.8mL, 52.52 mmol) was added dropwise in the solution. NaN_3 was slowly added in the solution. The temperature of solution was gradually raised until 55 ^oC. After 4 h, the completion of the reaction was monitored by TLC. When the solution was cooled down RT, saturated NaOH solution was added dropwise until pH 7-8. The solution was filtrated and extracted with $CHCl_3$. The organic layer was dried over anhydrous sodium sulfate, and concentrated on rotary vacuum evaporator. A resulting white solid (621 mg, 3.6 mmol) was C_{10} diamine. It did not need to be purified in 88% yield. : ^{1}H NMR ($CDCl_3$): δ =2.68 (t, 4H, *J* = 7.0 Hz) 1.45-1.40(m, 4H), 1.28(m, 12H); ^{13}C NMR ($CDCl_3$): δ = 42.30, 33.91, 29.57, 29.50, 26.90

Beckmann rearrangement

Cyclododecanone oxime, 8

Cyclododecanone 7 (2000 mg, 10.97 mmol), NH_2OH-HCl (1700 mg, 24.14 mmol) and NaOAc (1980 mg, 24.14 mmol) were added in 20 ml of normal MeCN. This solution was refluxed. After 2h completion of the reaction was monitored by TLC, the reaction was quenched with 50 mL saturated aqueous sodium hydrogen carbonate. The organic layer was extracted with ethyl acetate, dried over anhydrous sodium sulfate, and concentrated on rotary vacuum evaporator. A resulting white solid (2100 mg, 10.64 mmol) was cyclododecanone oxime, 8. It did not need to be purified in 97% yield. : Mp 134.7 ^oC; ^{1}H NMR ($CDCl_3$): δ = 1.34–1.27(m, 14H), 1.55–1.45 (m, 2H), 1.68–1.62 (m, 2H), 2.19–2.16 (m, 2H), 6.07 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ = 23.90, 24.61, 24.92, 25.20, 25.71, 26.17, 26.32, 26.73, 28.27, 36.82, 39.00, 173.57,

Azacyclotridecan-2-one, 9

A solution of cyclododecanone oxime 8 (395 mg, 2 mmol), TsCl (8 mg, 0.04 mmol) and $ZnCl_2$ (5 mg, 0.04 mmol) in 10 mL of dry MeCN was refluxed under a nitrogen or argon atmosphere. After 1h, completion of the reaction was monitored by TLC, the reaction was quenched with 5 mL saturated aqueous sodium hydrogen carbonate. The organic layer was extracted with ethyl acetate, dried over anhydrous sodium sulfate, and concentrated on rotary vacuum evaporator. A white solid was the product, 391 mg (1.98 mmol). It did not need to be purified. : Mp 151 ^{o}C (lit. mp 150–151 ^{o}C); ^{1}H NMR($CDCl_3$): δ = 1.34–1.27(m, 14H), 1.55–1.45 (m, 2H), 1.68–1.62 (m, 2H), 2.19–2.16 (m, 2H), 3.26 (dd, 2H), 6.07 (br s, 1H, NH); ^{13}C NMR($CDCl_3$): δ = 23.90, 24.61, 25.20, 24.92, 25.71, 26.17, 26.32, 26.73, 28.27, 36.82, 39.00, 173.57; HRMS m/z calcd for $C_{12}H_{23}NO$ 197.18; found 197.1780

Schmidt rearrangement

Cyclododecaone (1000 mg, 5.5 mmol) and NaN_3 (1000 mg, 9.9 mmol) were added in 7 mL ethyl acetate. The mixture was heated to reach 70-75 ^{o}C. H_2SO_4 (1 mL, 17 mmol) was added dropwise and maintained the reaction temperature in 3 h. The mixture was refluxed in 1h and cooled down. The crude mixture was extracted twice with 10mL of 2.5 M NaOH solution and 10 mL of saturated $NaHCO_3$. The organic layer was dried over anhydrous sodium sulfate, and concentrated on rotary vacuum evaporator. The white solid (901mg, 4.57mmol) was azacyclotridecan-2-one, 9. It did not need to be purified in 83% yield. : Mp 150 ^{o}C

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General procedure of One-pot Beckmann rearrangement

Ketone (2 mmol), NH_2OH-HCl (167 mg, 2.4 mmol), TsCl (19 mg, 0.1 mmol) and $ZnCl_2$ (14 mg, 0.1 mmol) were added in 10 ml of anhydrous MeCN and refluxed under a nitrogen or argon atmosphere. After 12h, completion of the reaction was monitored by TLC, the reaction was quenched with 5 mL saturated aqueous sodium carbonate. The organic layer was extracted with ethyl acetate, and dried over anhydrous sodium sulfate. It was concentrated on rotary vacuum evaporator. The resulting crude product was purified by column chromatography on silica gel to give the corresponding amide.

Caprolactam, 10

^{1}H NMR (400 MHz, CDCl3): δ = 1.78–1. 63 (m, 6H), 2.46 (t, 2H, *J* = 5.4 Hz), 3.23-3.19 (q, 2H), 6.35 (br, 1H, NH); ^{13}C NMR (100 MHz, CDCl3): δ =23.25, 29.81, 30.62, 36.70, 42.92, 179.04

Oenantholactam, 11

^{1}H NMR (400 MHz, CDCl3): δ = 1.65-1.53(m, 6H), 1.83-1.77(m, 2H), 2.42(t, 2H, *J* = 6.4 Hz), 3.36-3.33(m, 2H,), 6.99 (br, 1H, NH); ^{13}C NMR (100 MHz, CDCl3): δ = 24.45, 25.67, 27.96, 31.96, 32.15, 41.73, 178.21.

Capryllactam, 12

^{1}H NMR (400 MHz, CDCl3): δ = 1.62–1.55 (m, 8H), 1.86-1.80 (m, 2H), 2.43 (t, 2H, *J* = 6.4 Hz), 3.37-.334 (q, 2H), 6.29 (br, 1H, NH); ^{13}C NMR (100 MHz, CDCl3): δ = 22.99, 24.46, 25.37, 27.78, 30.00, 33.04, 43.30, 178.01,

***N*-Phenylacetamide, 13**

^{1}H NMR (400 MHz, CDCl3): δ = 2.18 (s, 3H), 7.11 (t, 2H, *J* = 7.4Hz), 7.32(t, 2H, *J* = 7.8Hz), 7.48 -7.50(d, 2H); ^{13}C NMR (100 MHz, CDCl3): δ = 24.78, 120.00, 124.48, 129.17, 138.04, 168.28

_N_-(4-Bromophenyl) acetamide, 14

^{1}H NMR (400 MHz, CDCl3): δ = 2.18 (s, 3H), 7.20 (br s, 1H), 7.44-7.39 (m, 4H); ^{13}C NMR (100 MHz, CDCl3): δ = 24.65, 116.87, 121.32, 131.98, 136.92, 168.19

_N_-(4-Methoxyphenyl) acetamide, 15

^{1}H NMR (400 MHz, CDCl3) : δ = 2.105 (s, 3H), 3.762 (s, 3H), 6.82 (m, 2H), 7.38 (m, 2H), 7.97 (s, 1H); ^{13}C NMR (100 MHz CDCl3) δ = 24.21, 55.46, 55.53, 114.13, 122.17, 131.26,156.46, 168.82.

_N_-(2,4-Dimethylphenyl) acetamide, 16

^{1} H (400 MHz CDCl3) δ = 2.20 (s, 3H), 2.22 (s, 3H), 2.32 (s, 3H), 6.89-6.89 (m, 1H), 7.06-7.08 (m, 1H), 7.60 (s, 1H); ^{13}C NMR (100 MHz CDCl3) δ = 17.48, 21.25, 24.50, 124.10, 126.16, 126.25, 130.41, 135.57, 136.72, 168.35

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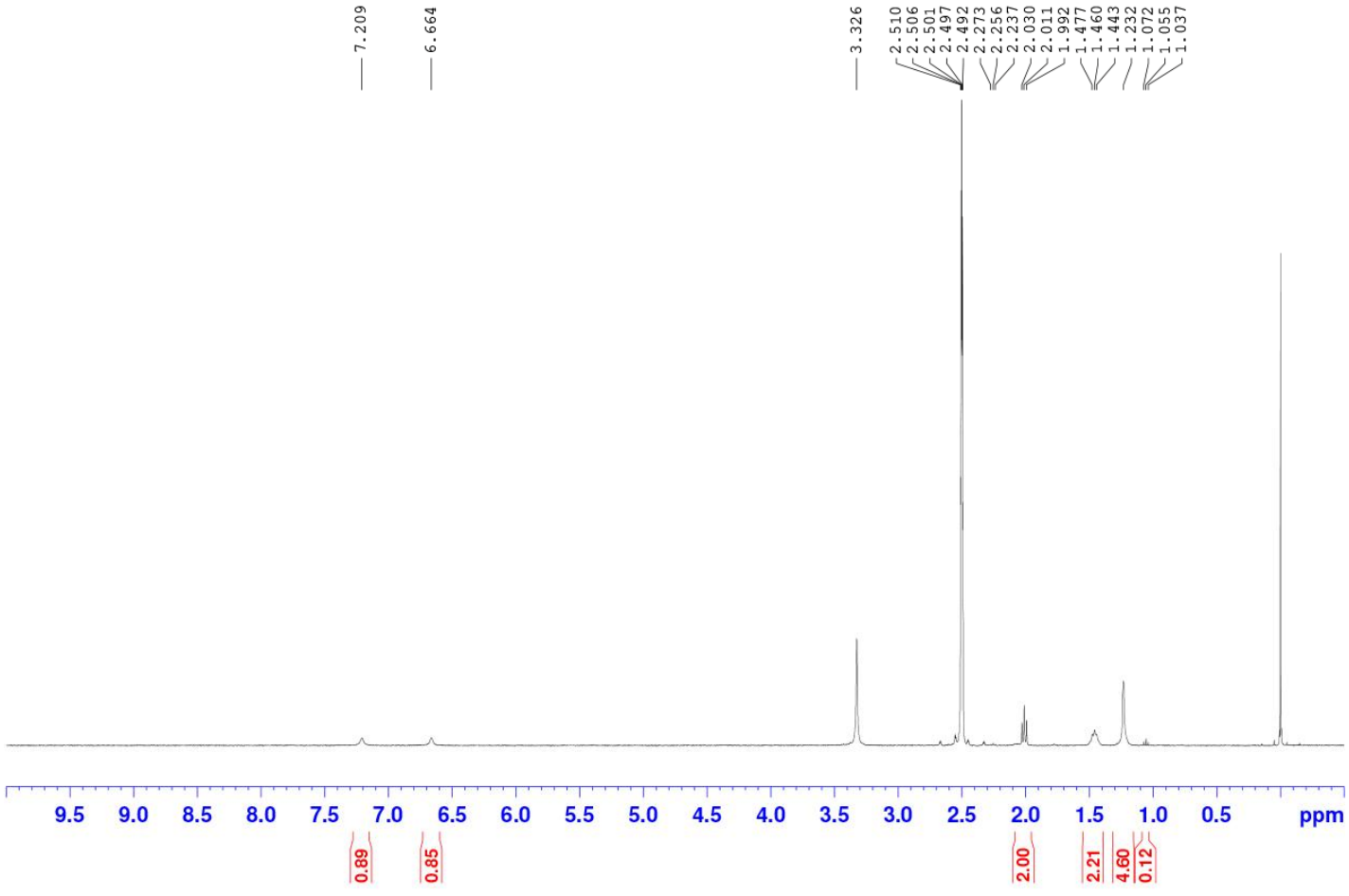
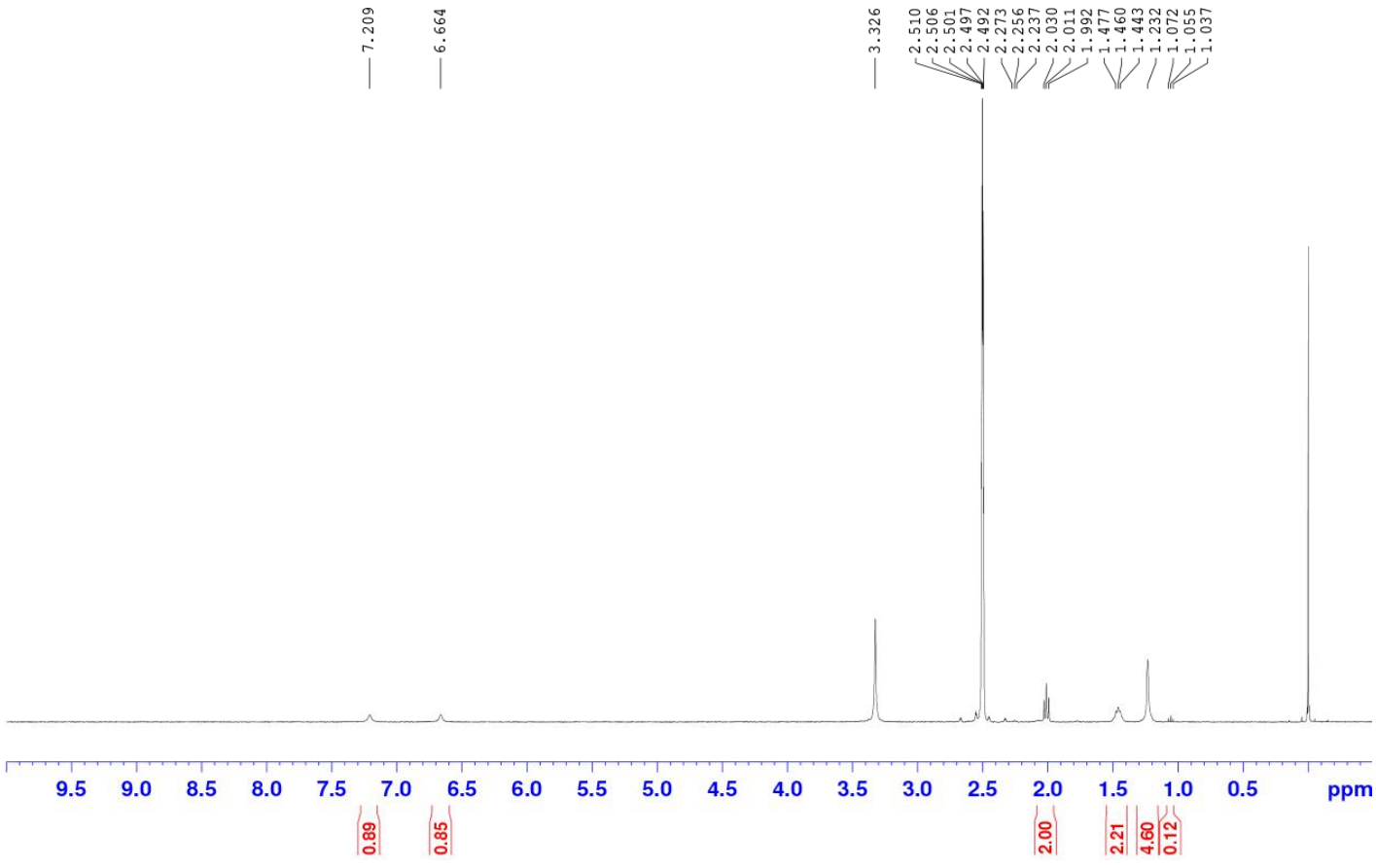
APPENDIX

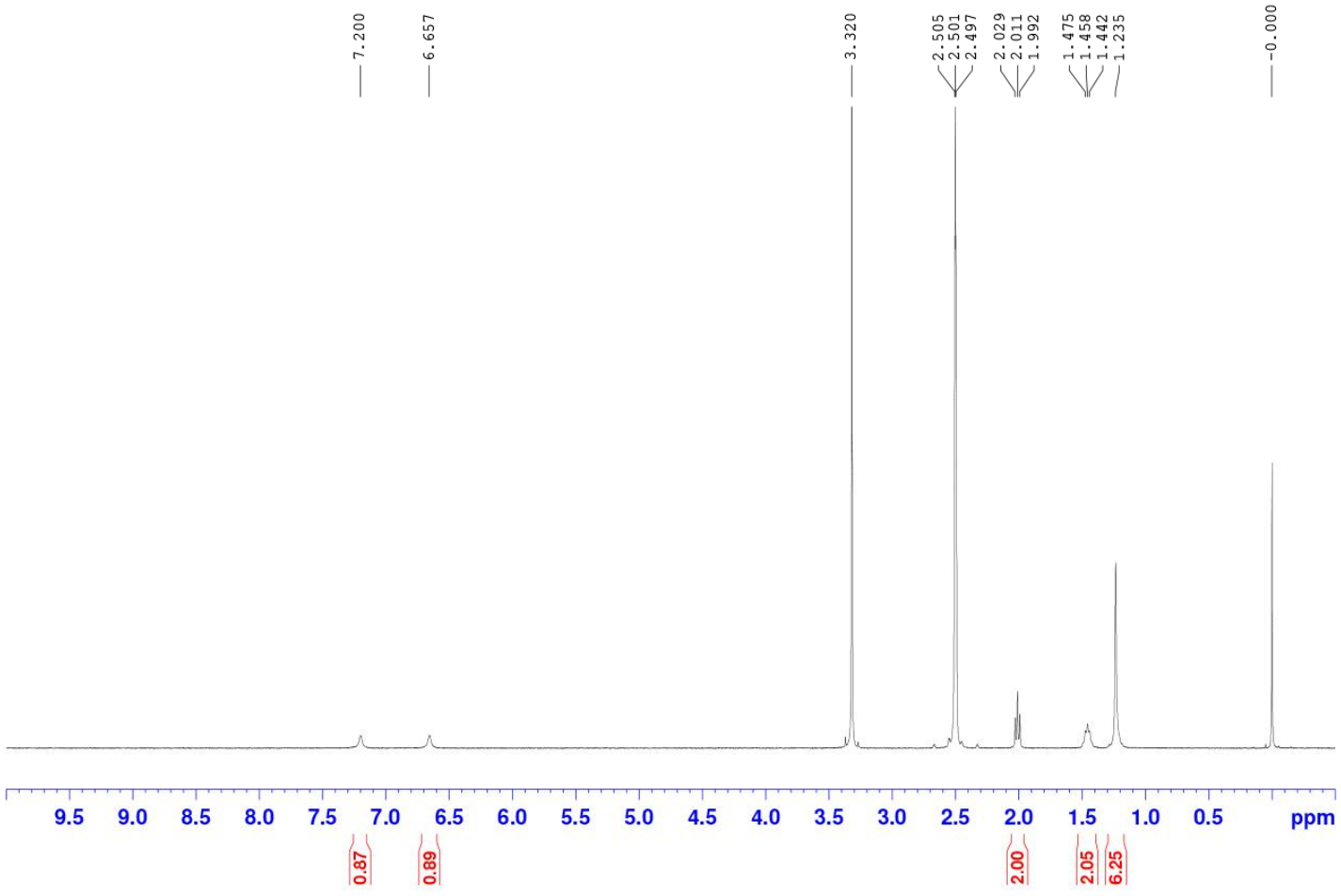
List of ^{1}H NMR Spectra of Selected Compounds



400 MHz ^{1}H NMR Spectrum (DMSO-d_6) of compound **2**



400 MHz ^{1}H NMR Spectrum ($CDCl_3$) of compound **3**



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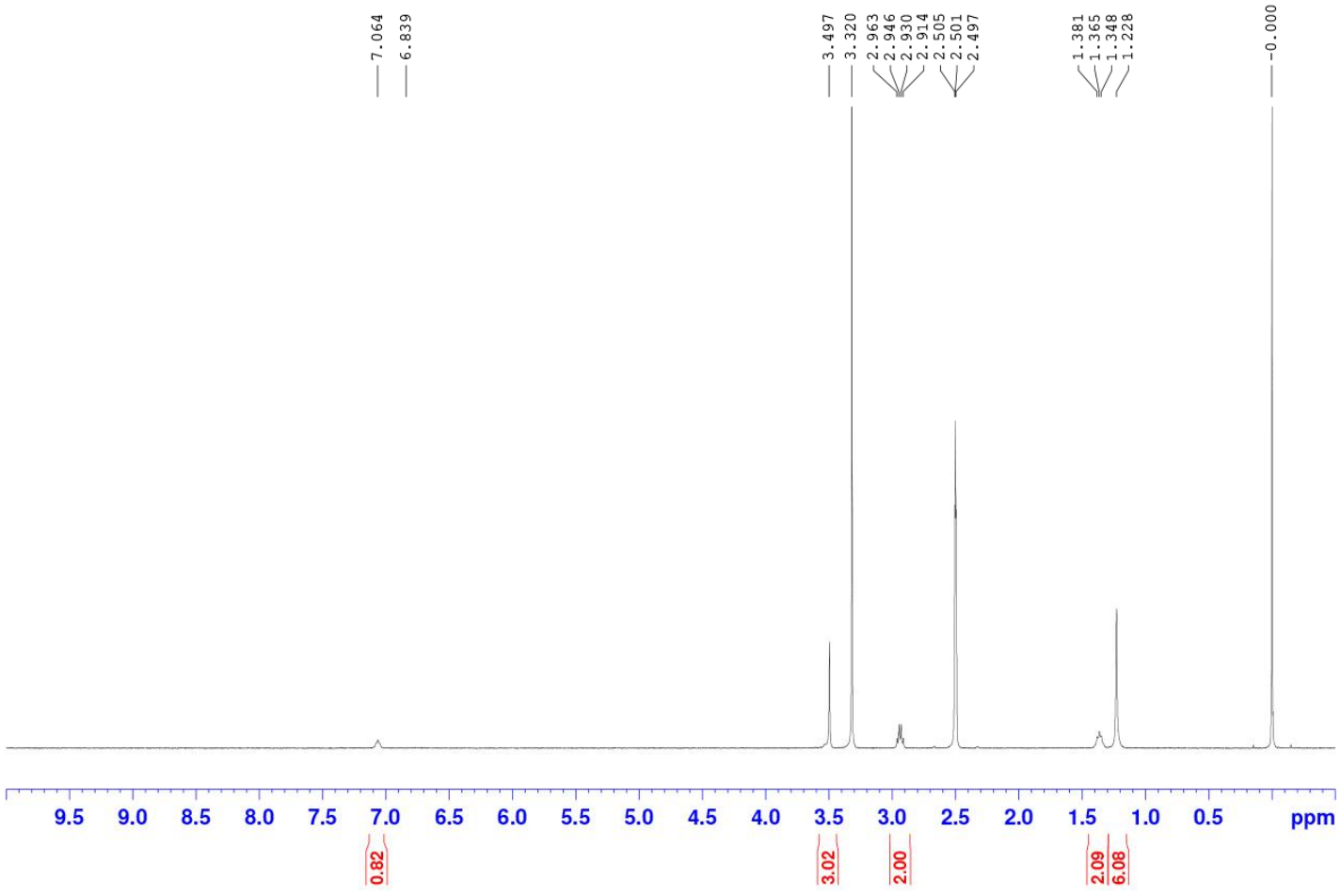
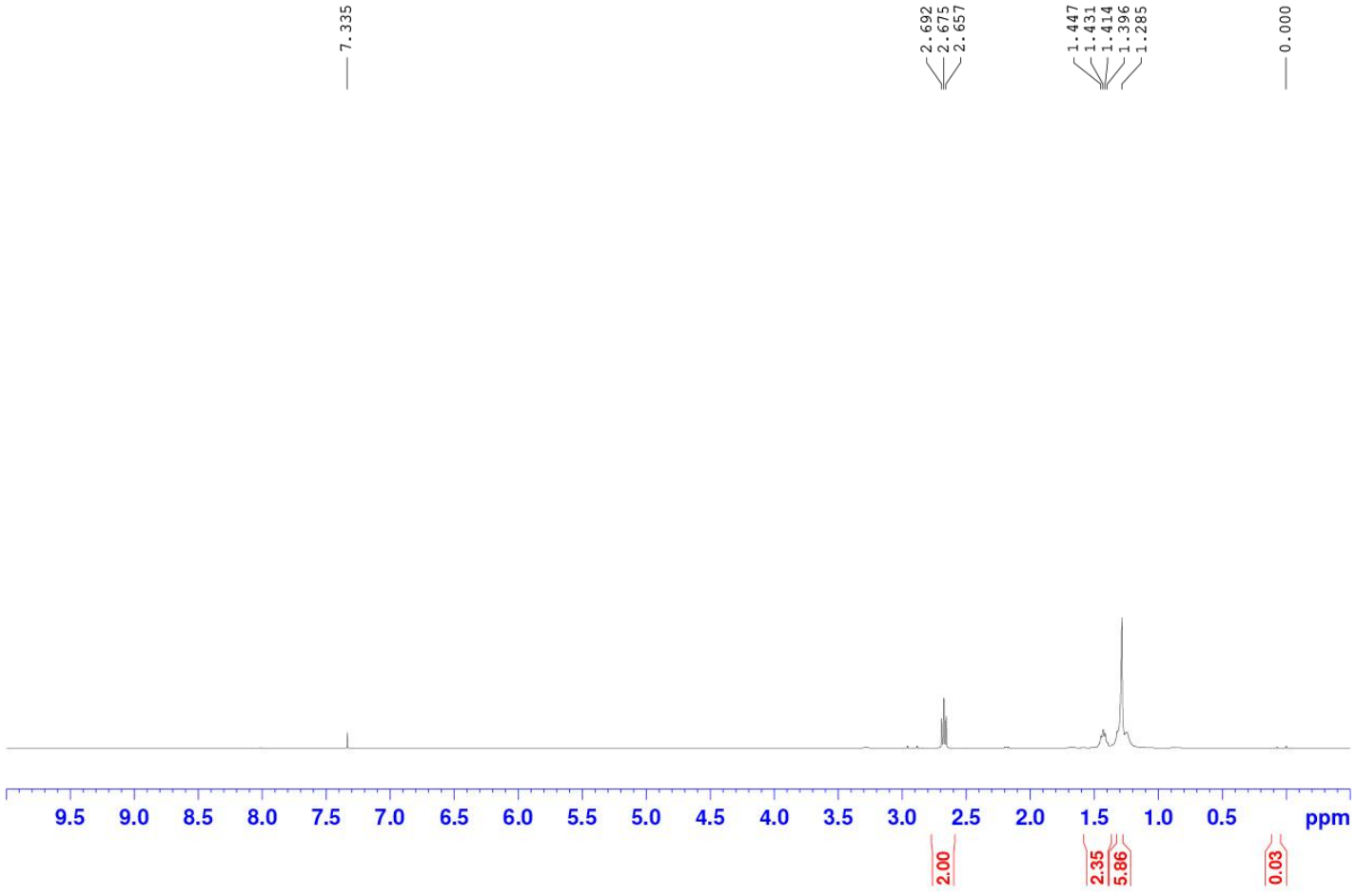
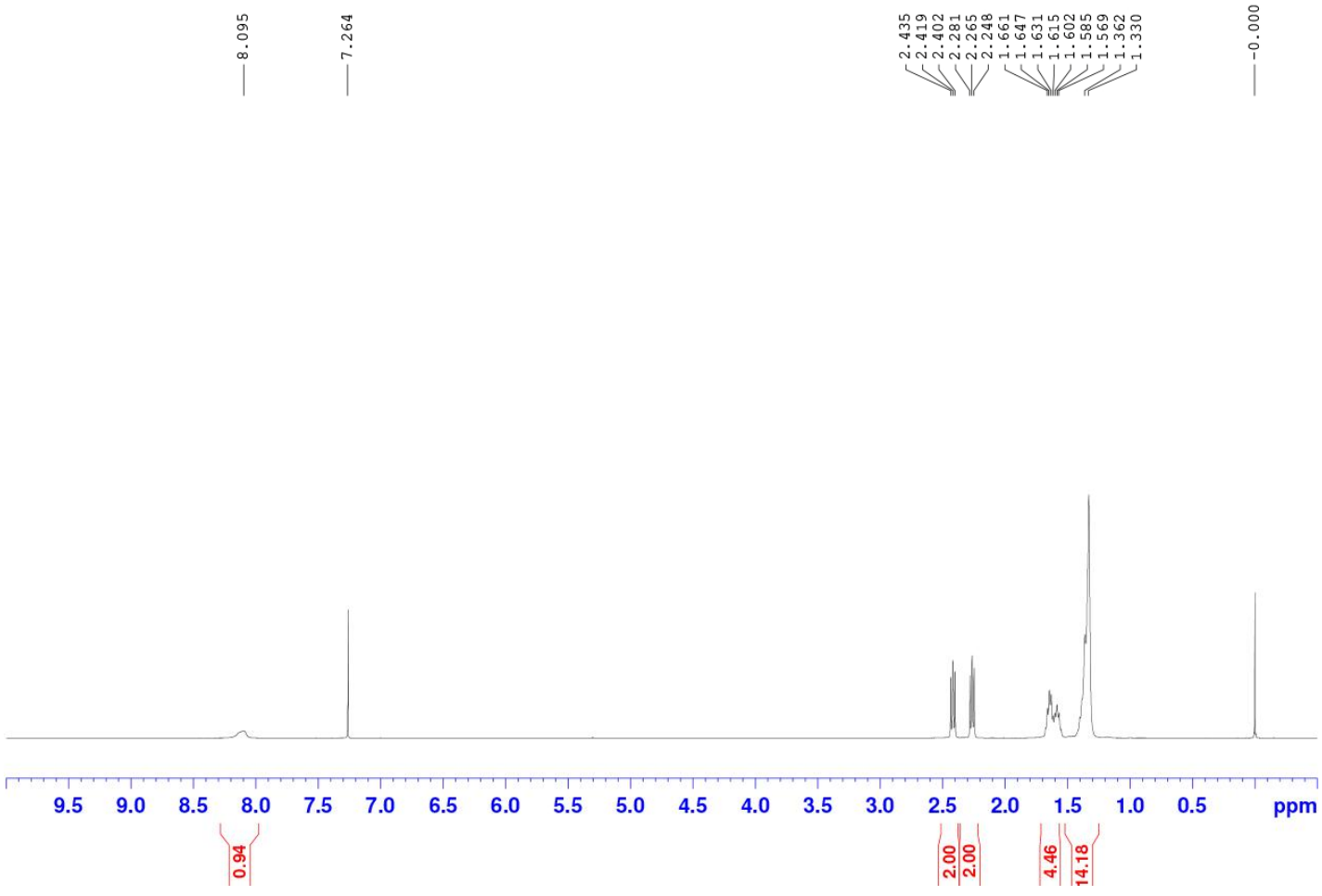


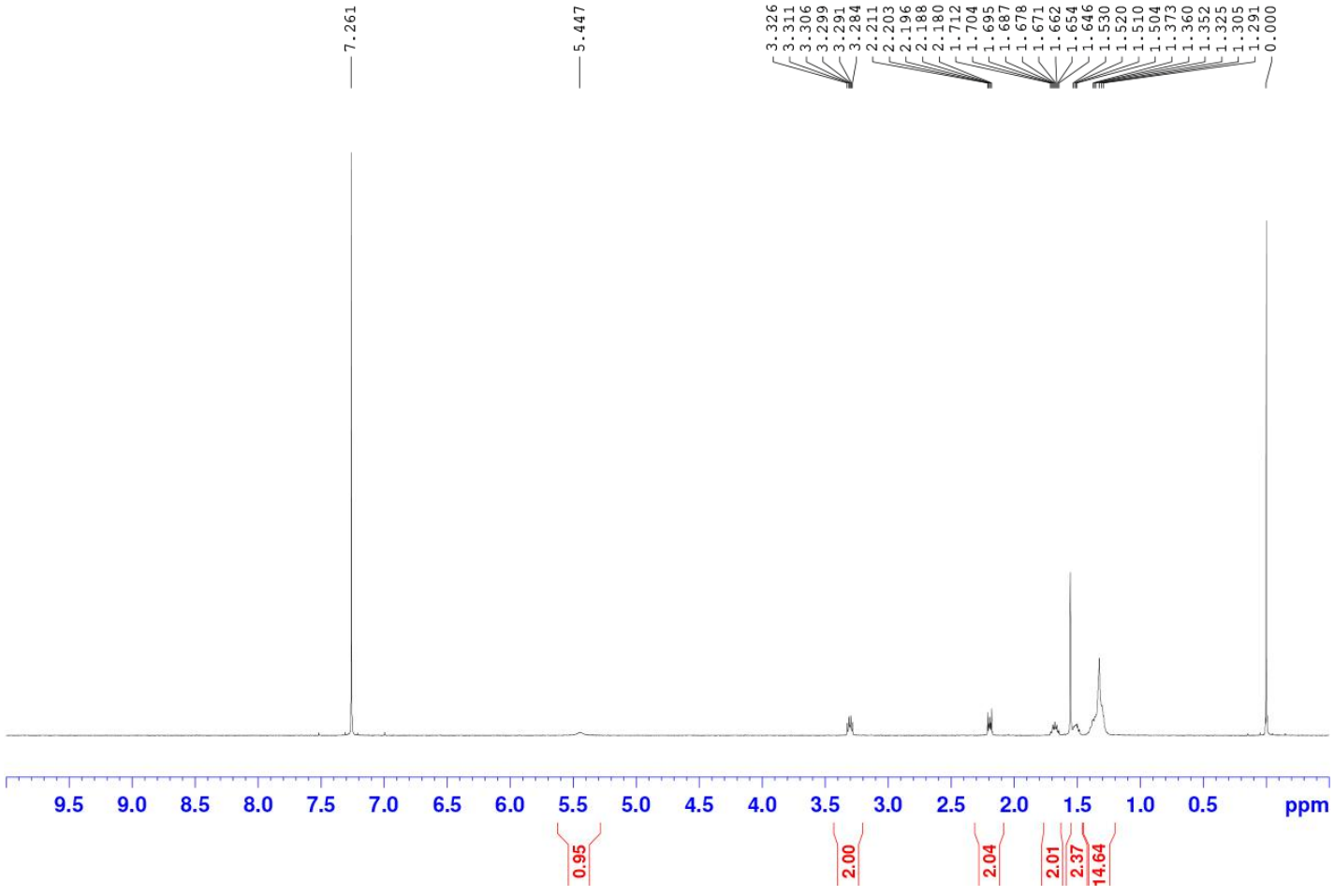
400 MHz ^{1}H NMR Spectrum (DMSO-d_6) of compound **5**



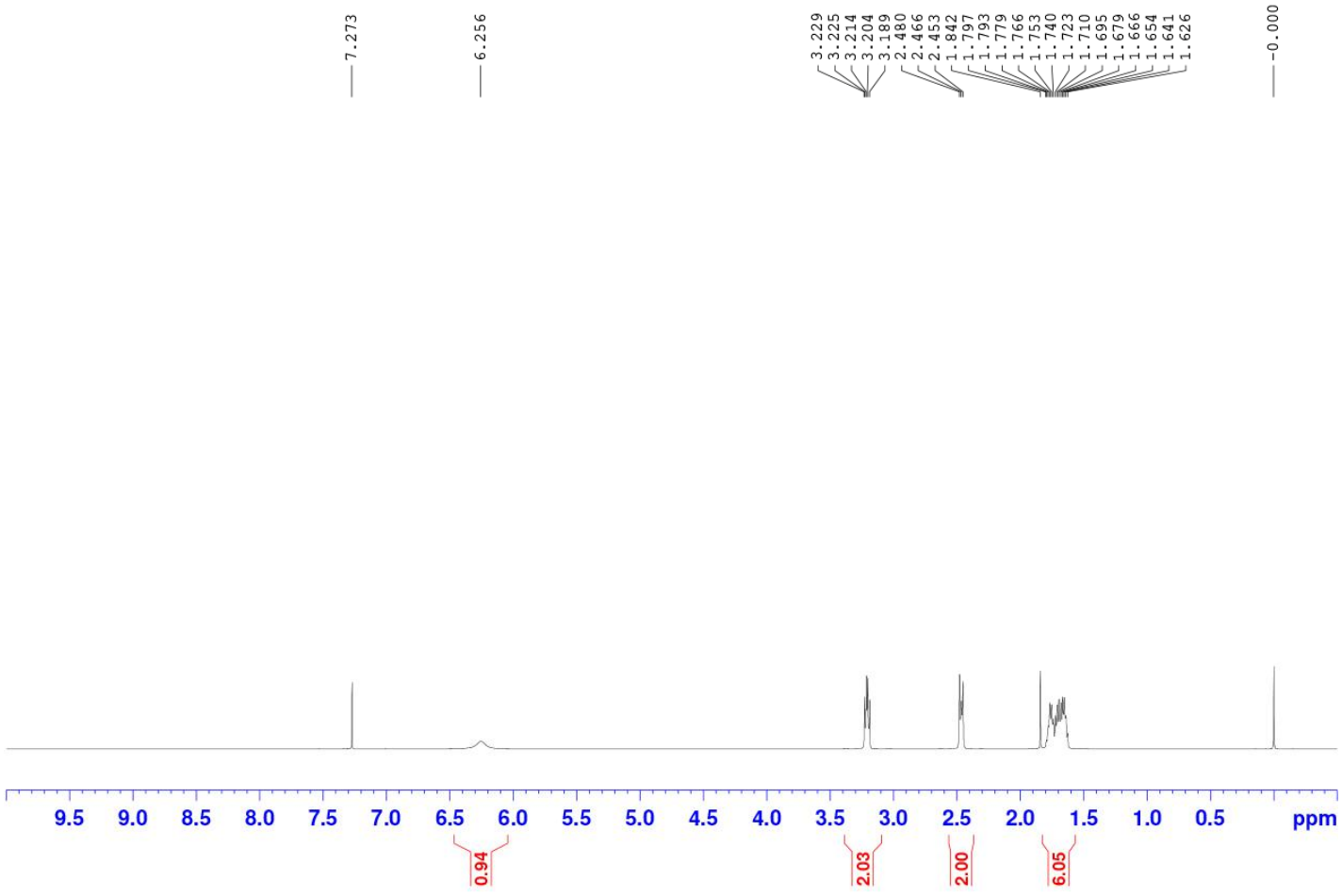
400 MHz ^{1}H NMR Spectrum ($CDCl_3$) of compound **6**



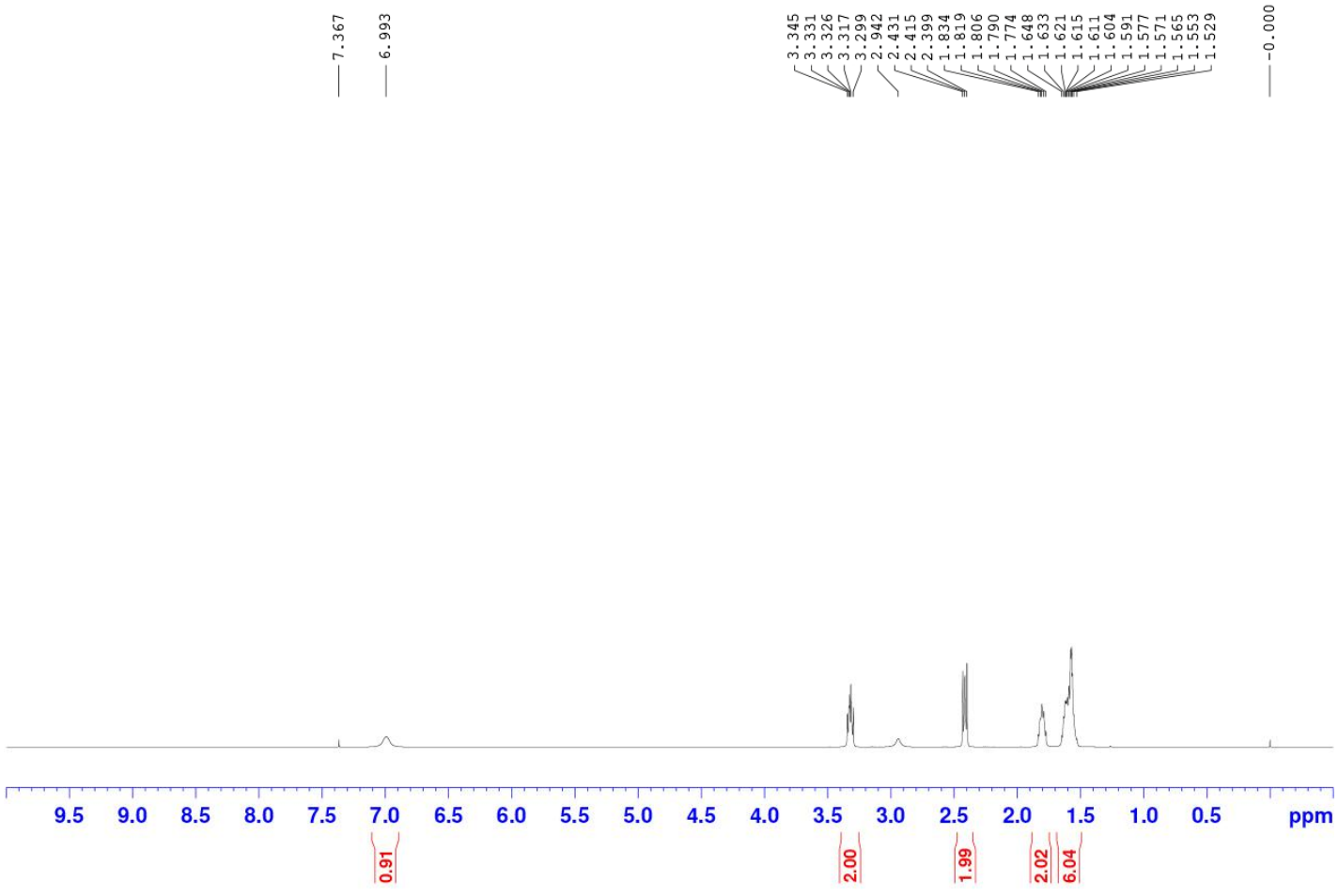
400 MHz ^{1}H NMR Spectrum ($CDCl_3$) of compound **8**



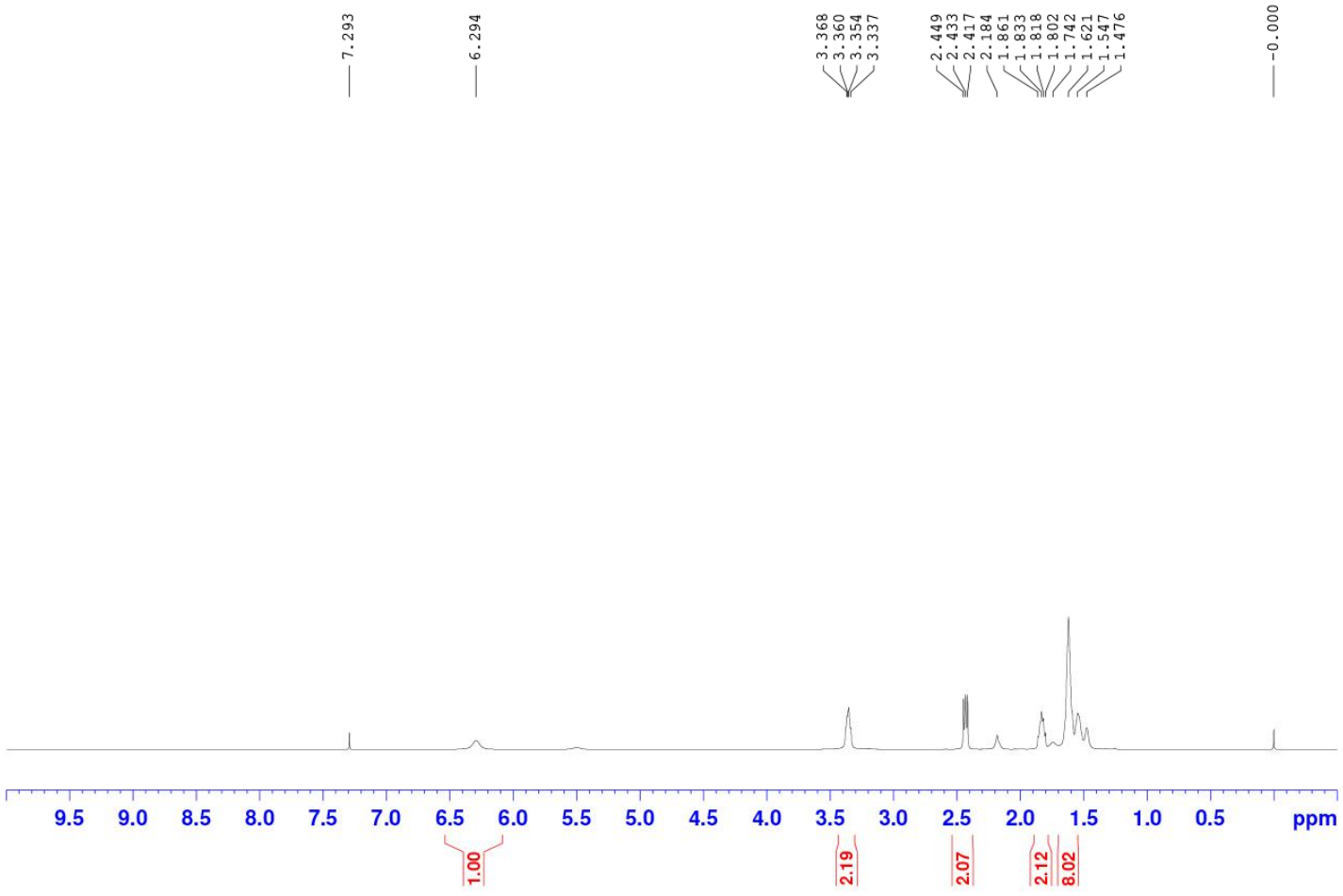
400 MHz ^{1}H NMR Spectrum ($CDCl_3$) of compound **9**



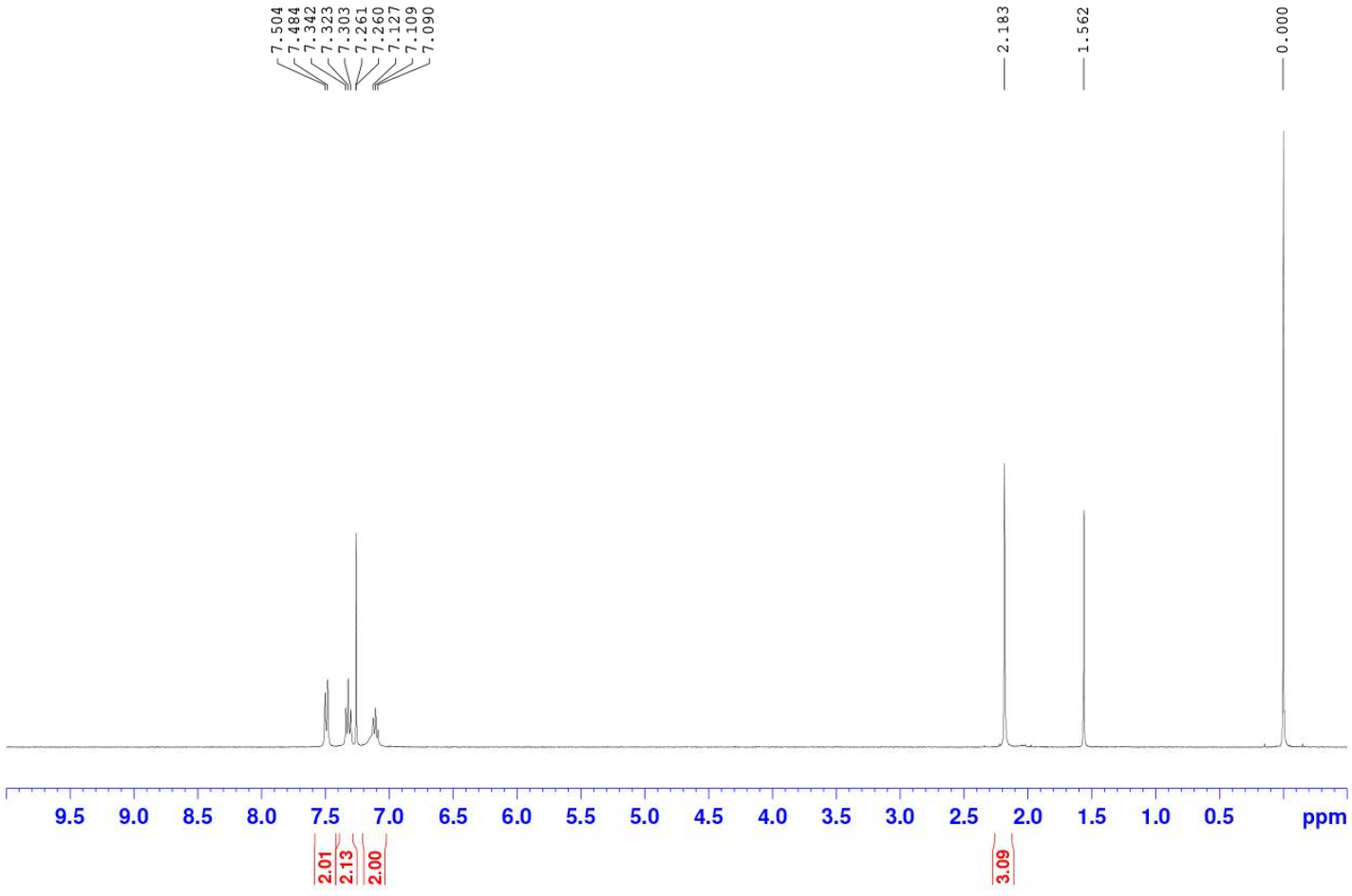
400 MHz ^{1}H NMR Spectrum ($CDCl_3$) of compound **10**



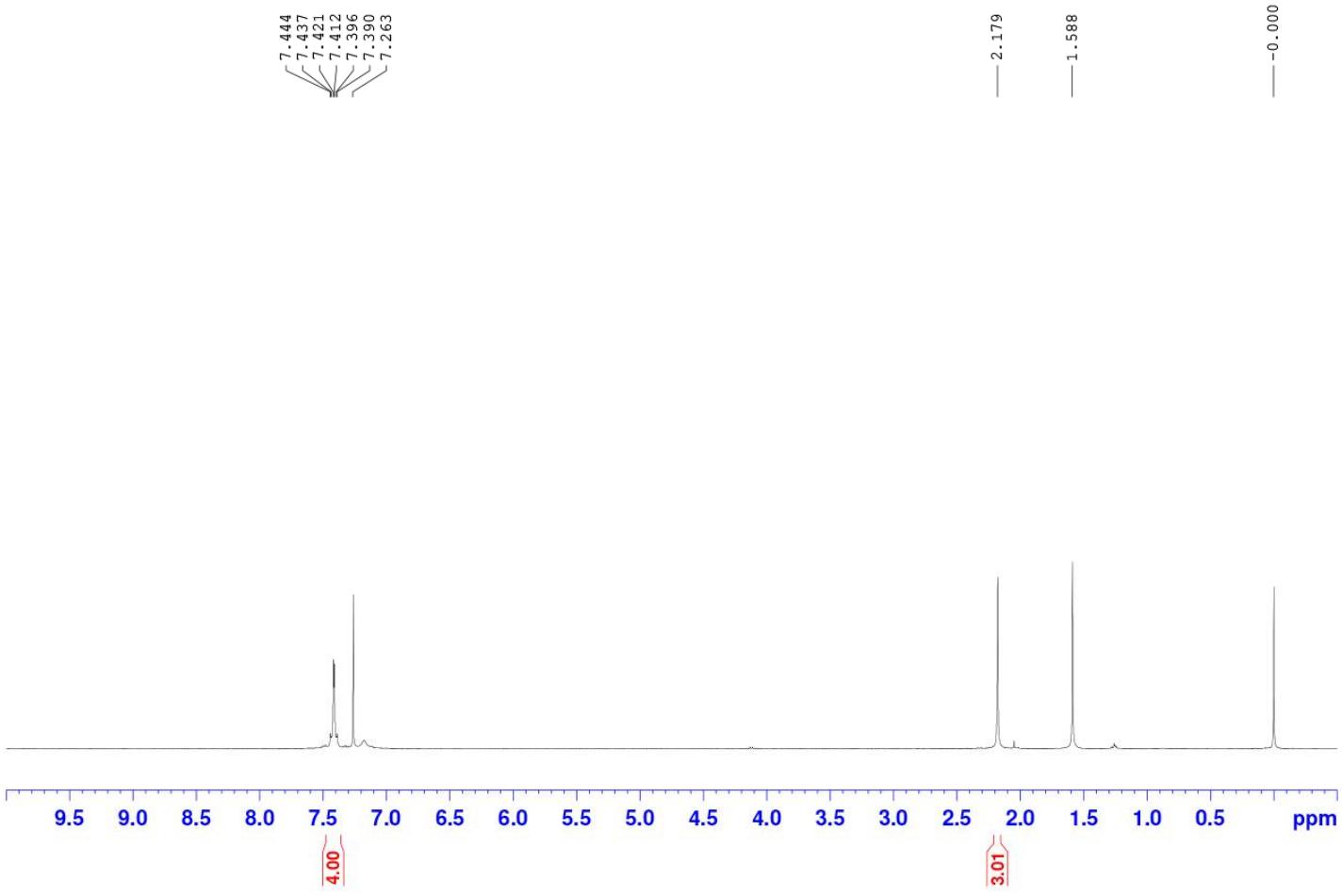
400 MHz ^{1}H NMR Spectrum ($CDCl_3$) of compound **11**



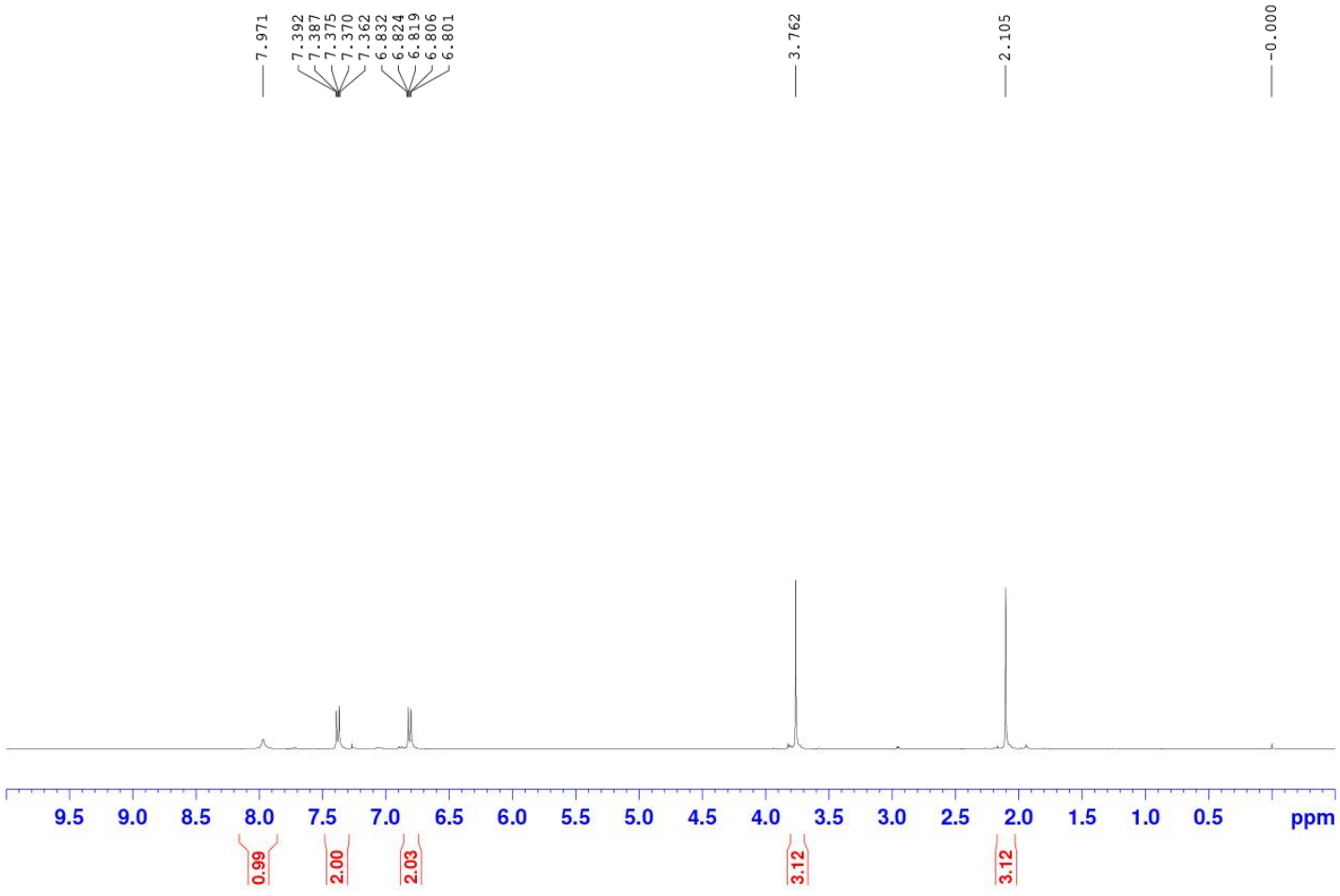
400 MHz ^{1}H NMR Spectrum ($CDCl_3$) of compound **12**



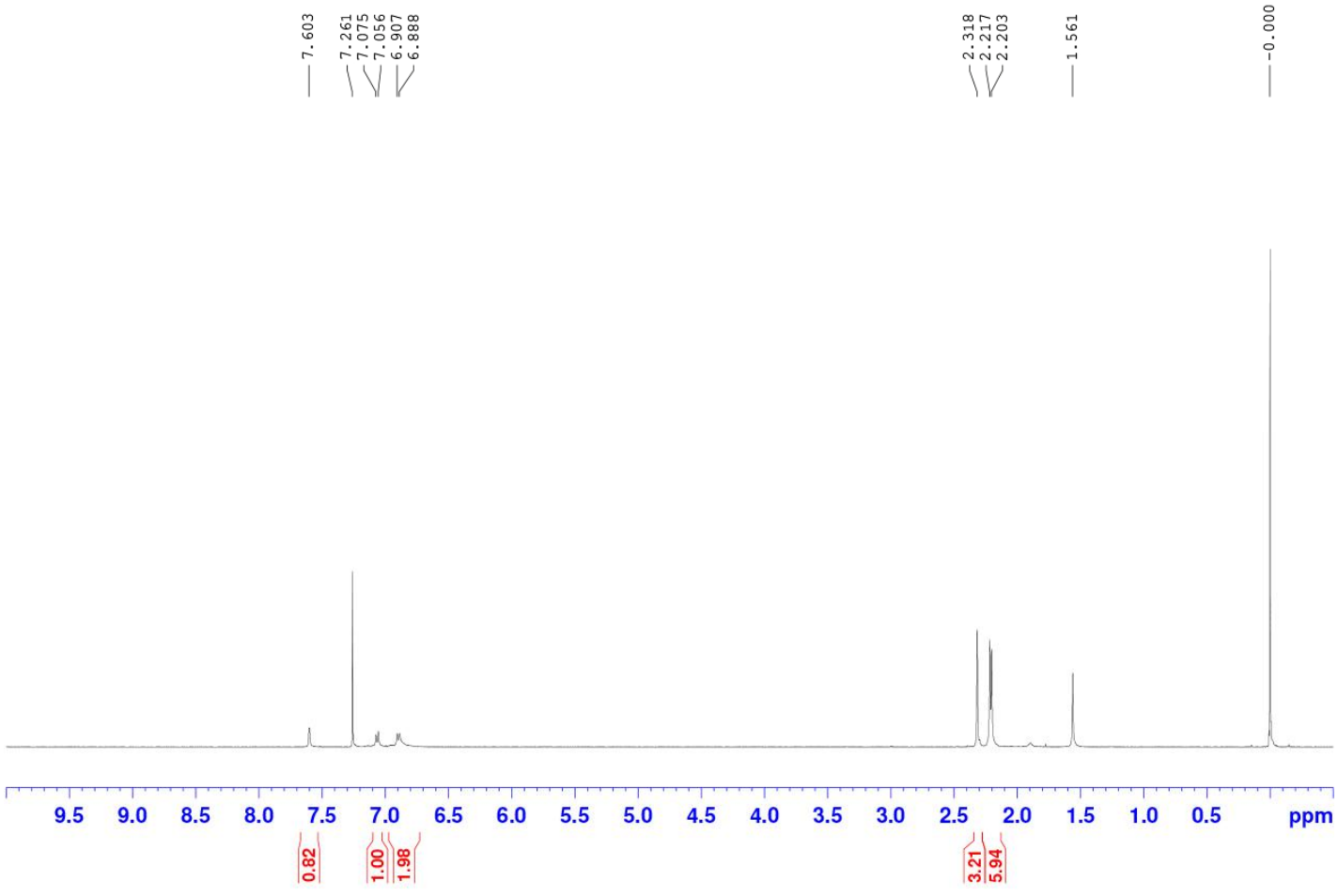
400 MHz ^{1}H NMR Spectrum ($CDCl_3$) of compound **13**



400 MHz ^{1}H NMR Spectrum ($CDCl_3$) of compound **14**

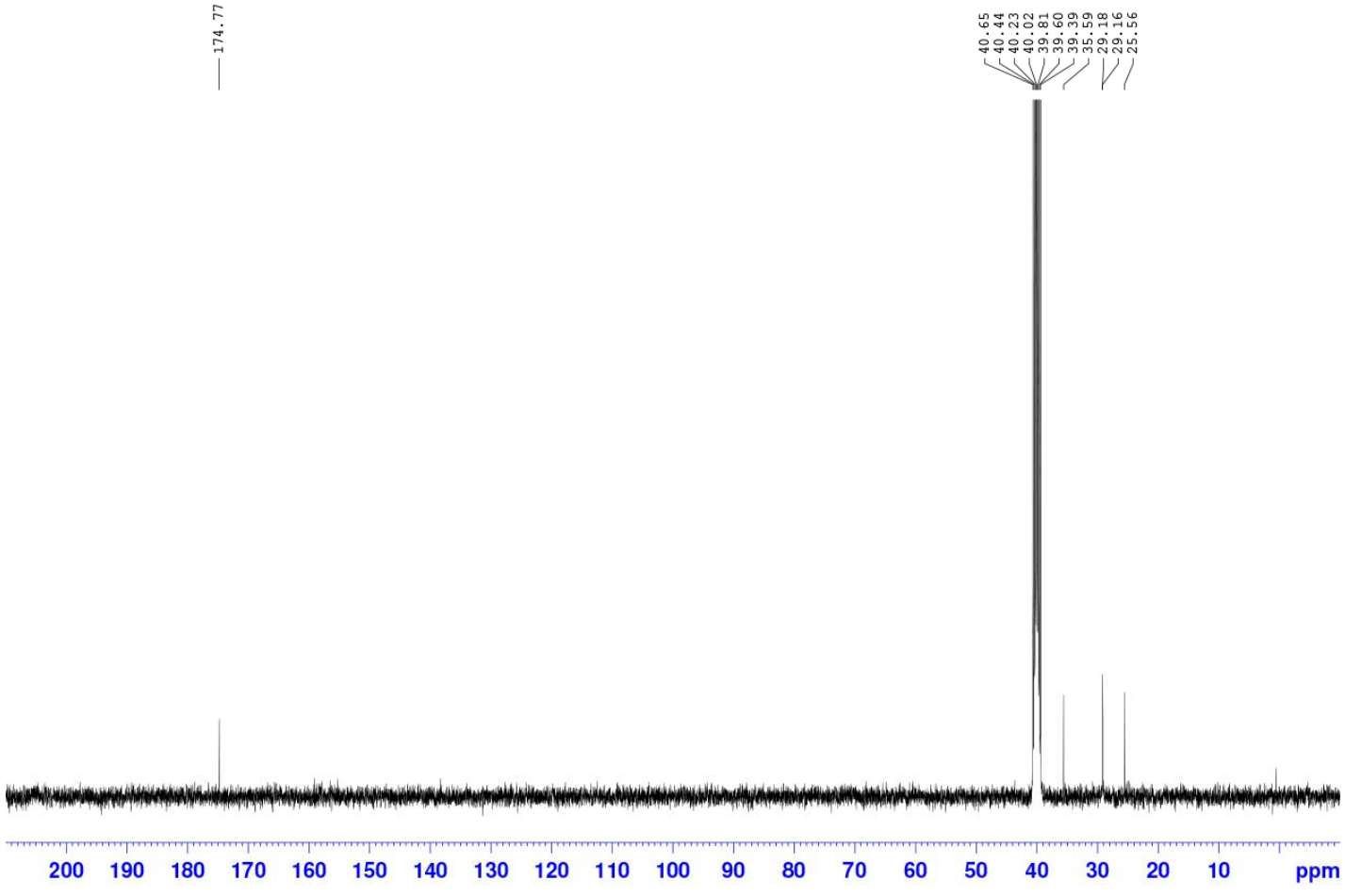


400 MHz ^{1}H NMR Spectrum ($CDCl_3$) of compound **15**

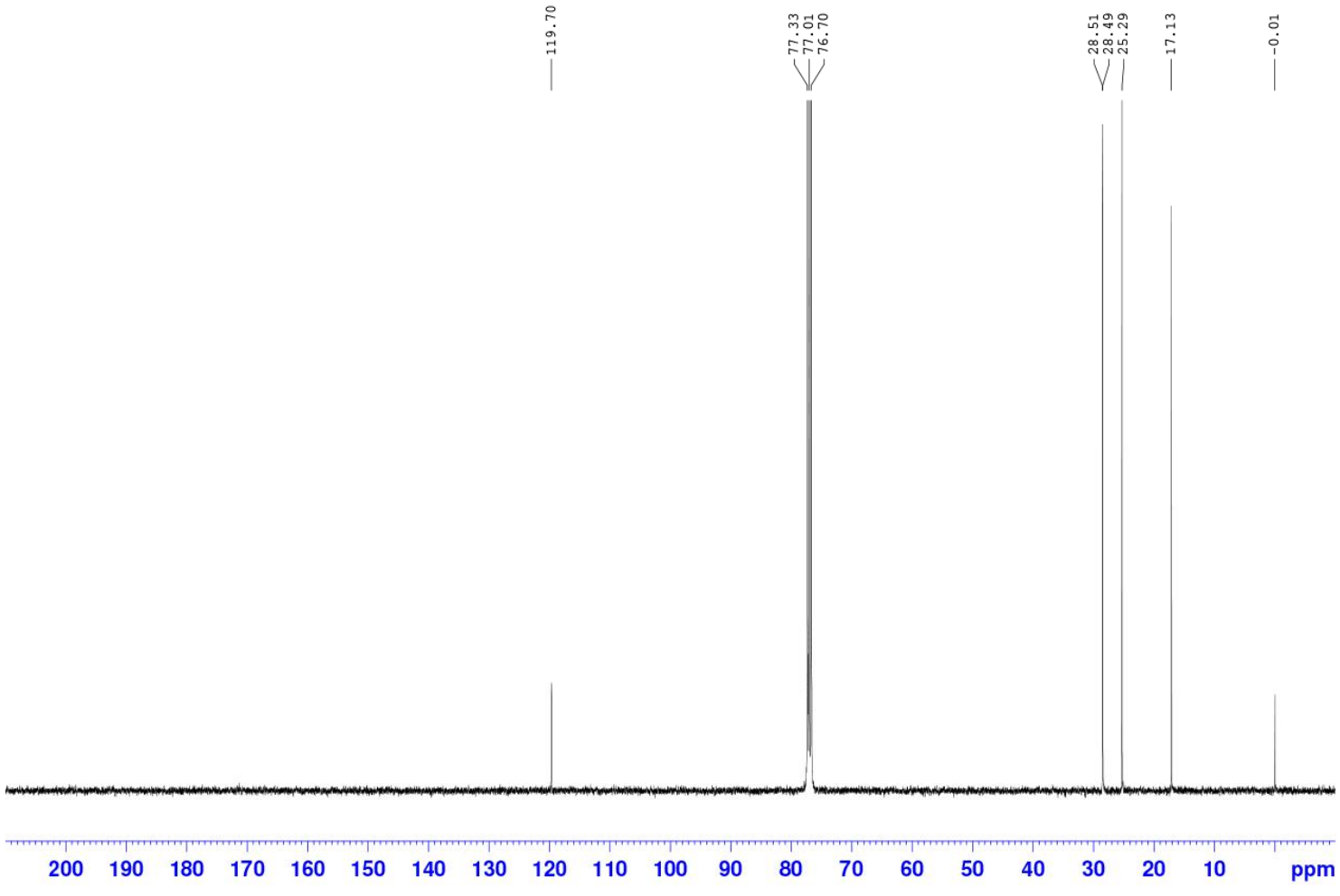


400 MHz ^{1}H NMR Spectrum ($CDCl_3$) of compound **16**

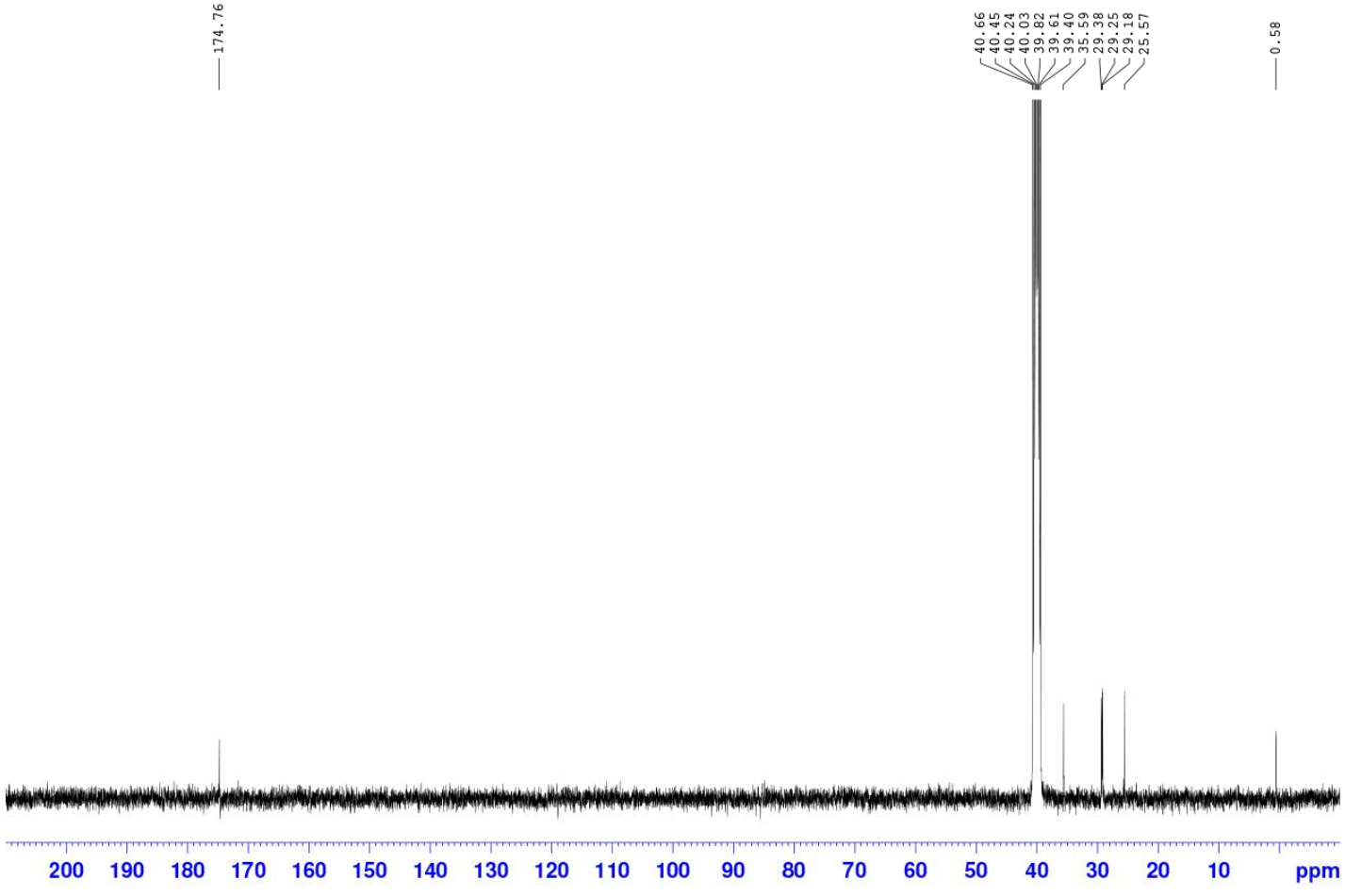
List of ^{1}H NMR Spectra of Selected Compounds



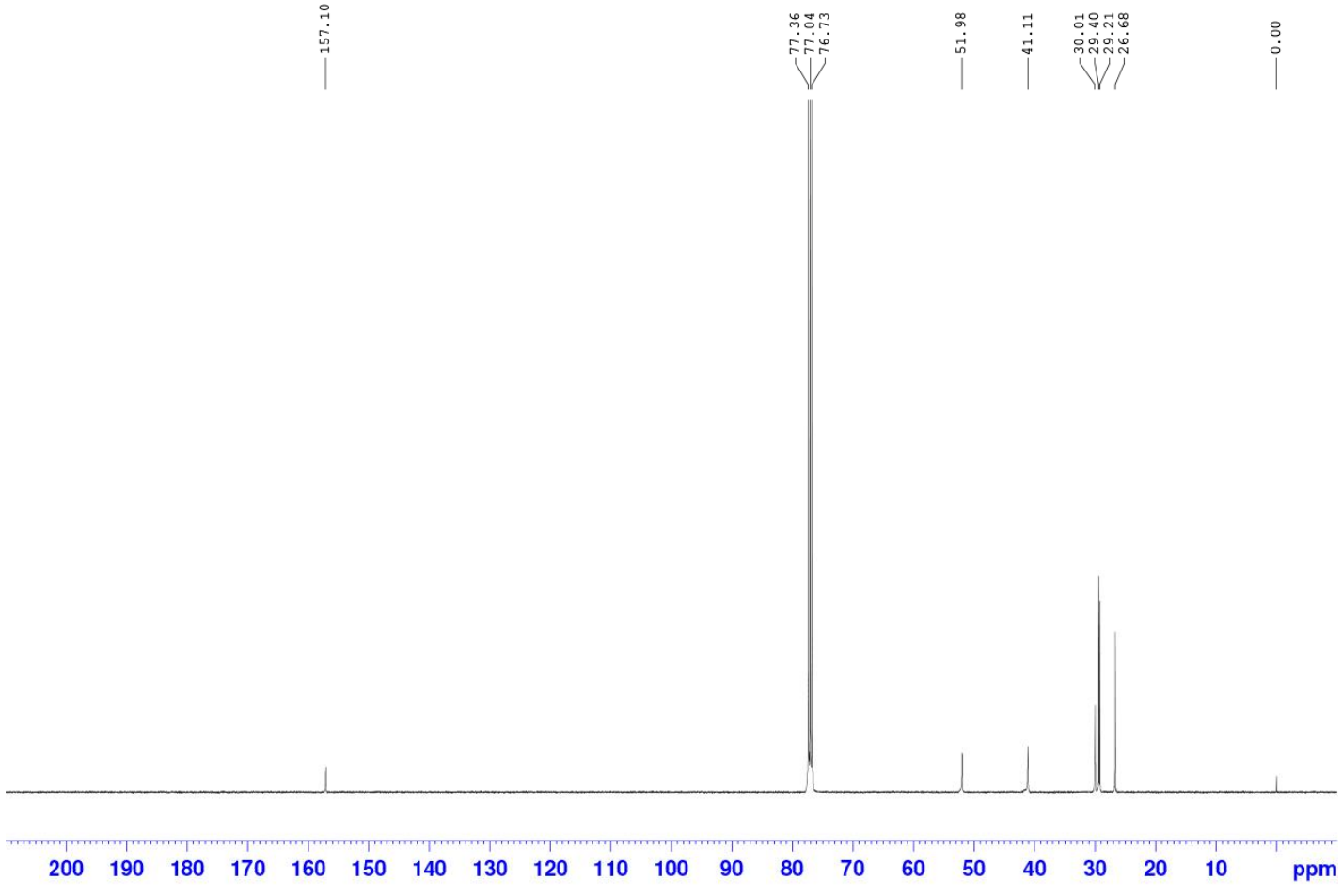
100 MHz ^{13}C NMR Spectrum (DMSO-d_6) of compound **2**



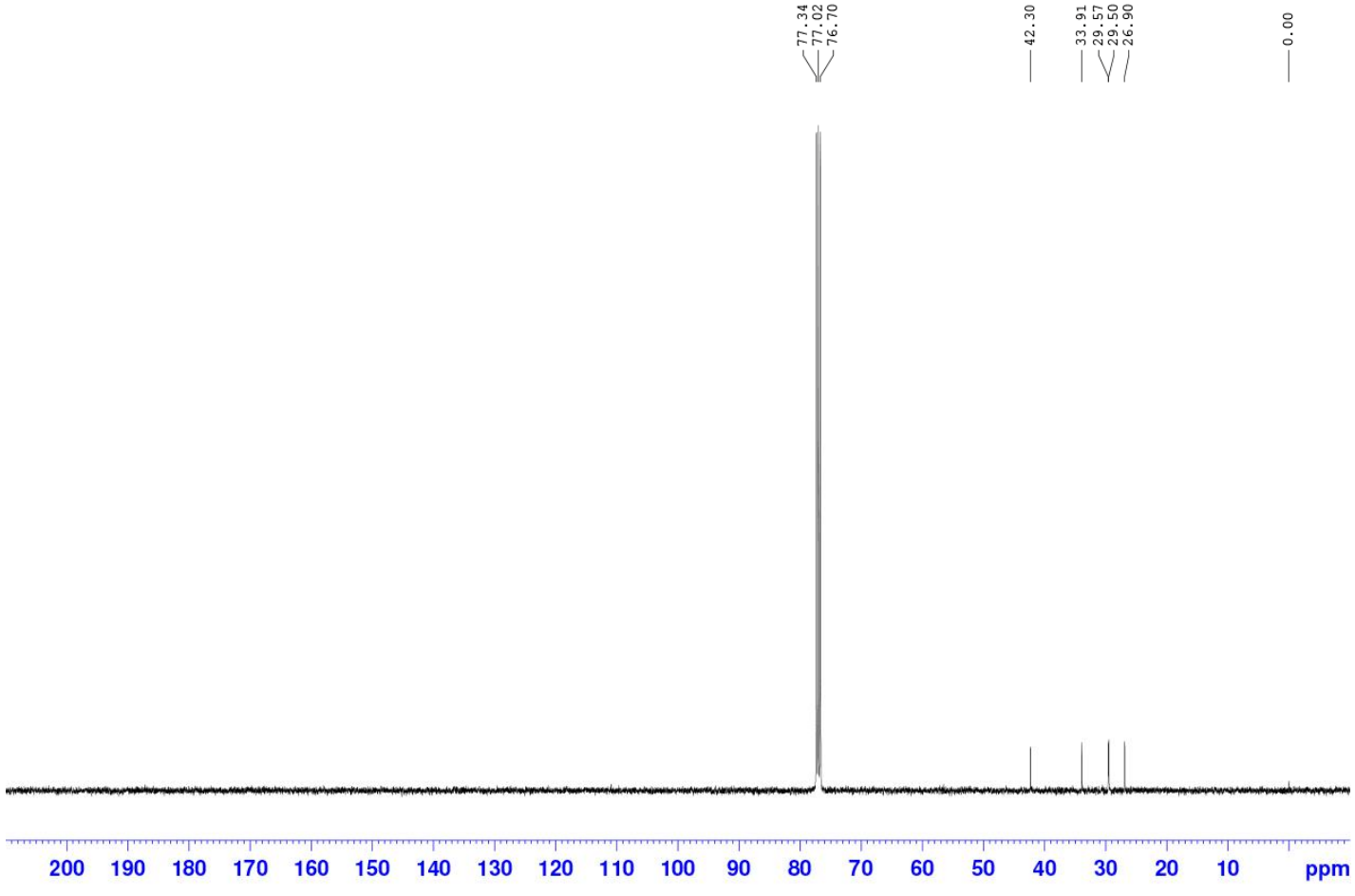
100 MHz ^{13}C NMR Spectrum ($CDCl_3$) of compound **3**



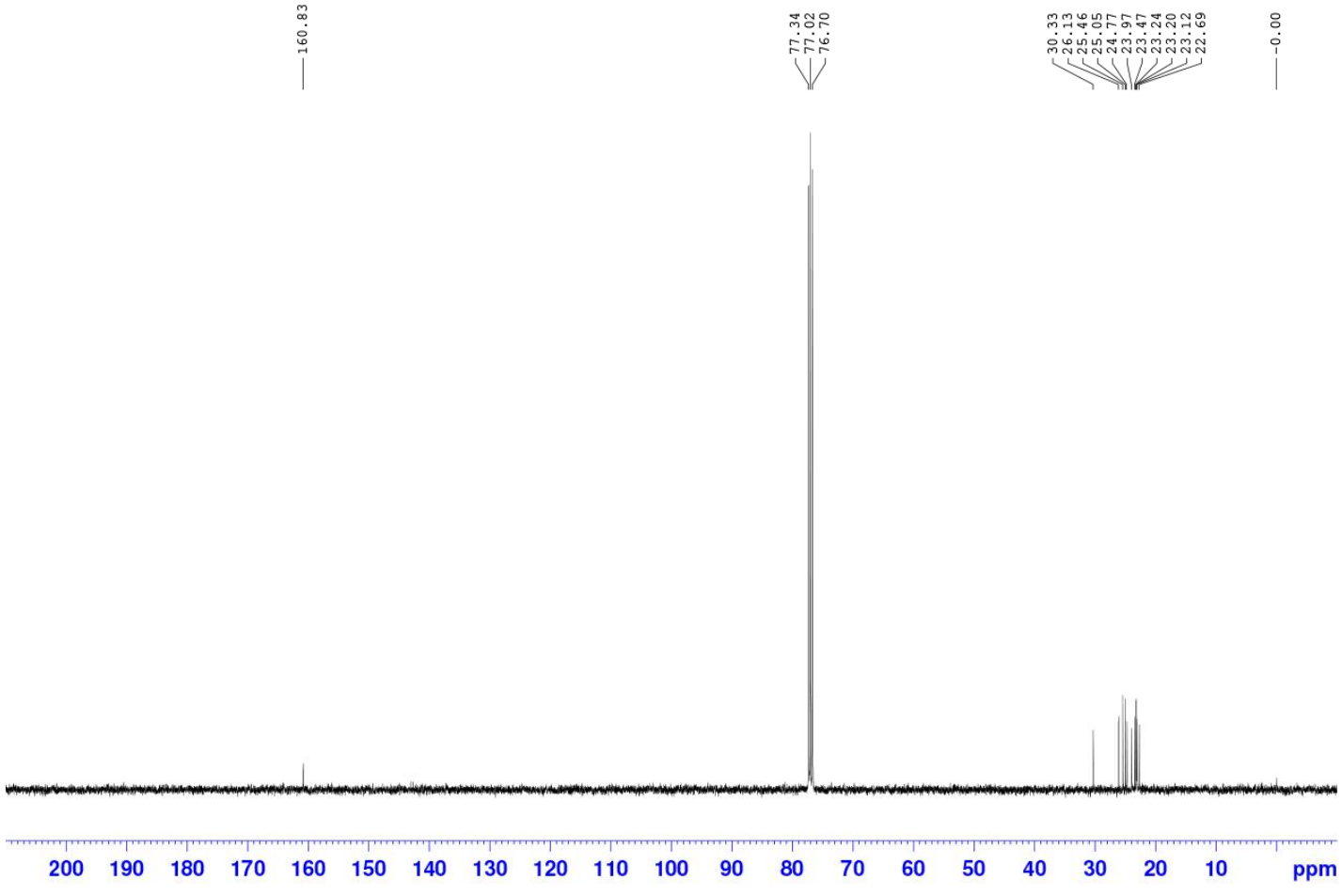
100 MHz ^{13}C NMR Spectrum (DMSO-d_6) of compound **4**



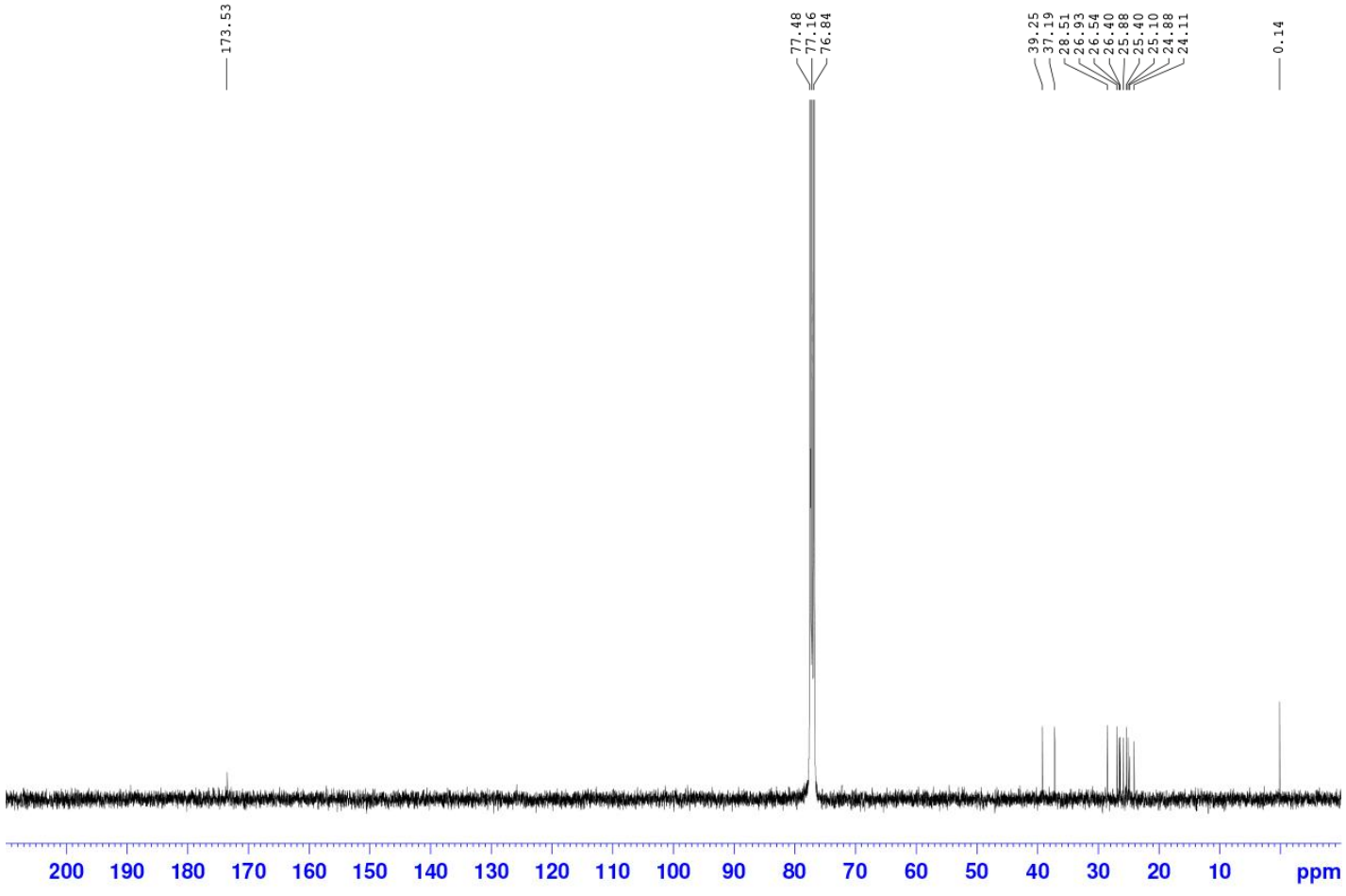
100 MHz ^{13}C NMR Spectrum ($CDCl_3$) of compound **5**



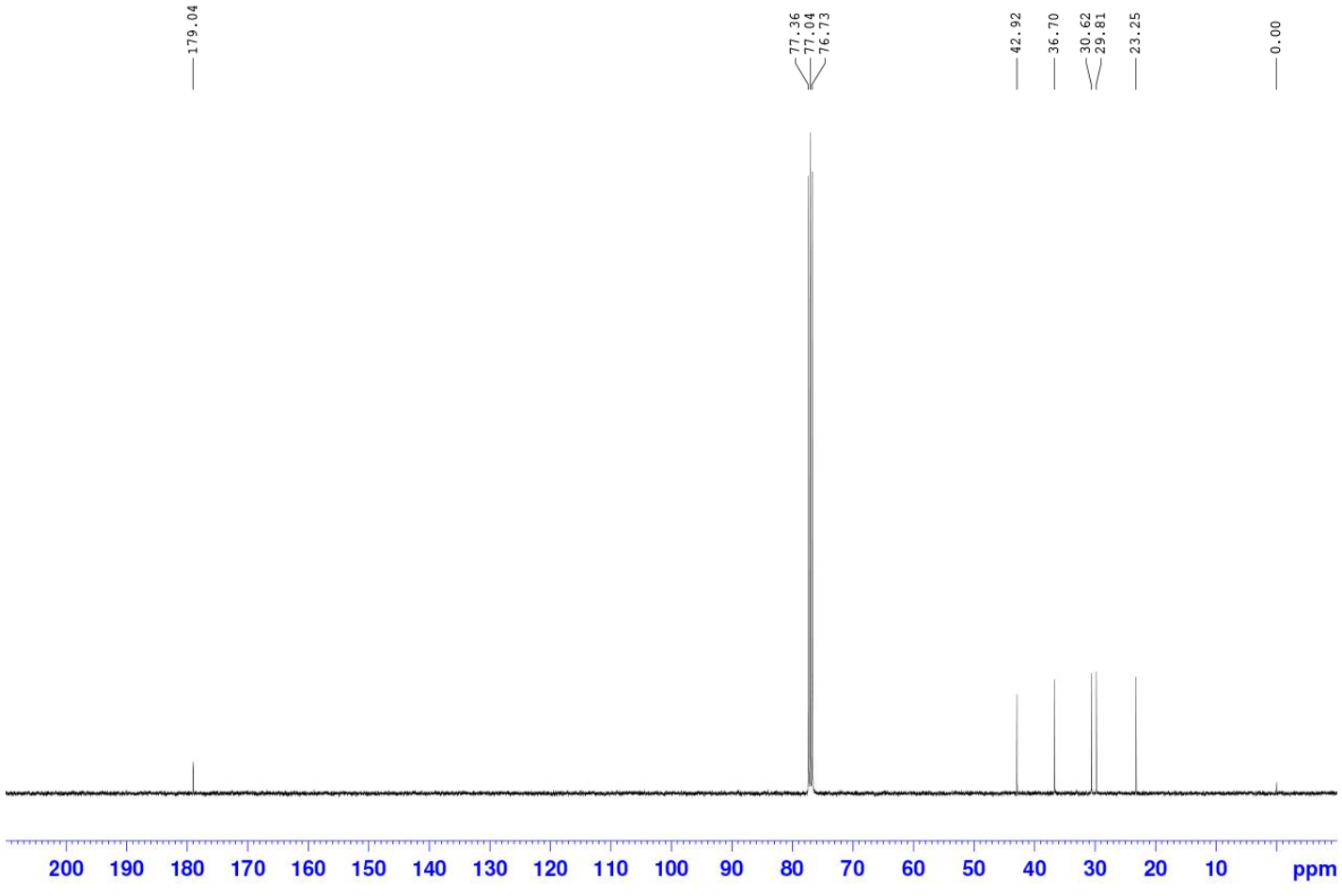
100 MHz ^{13}C NMR Spectrum ($CDCl_3$) of compound **6**



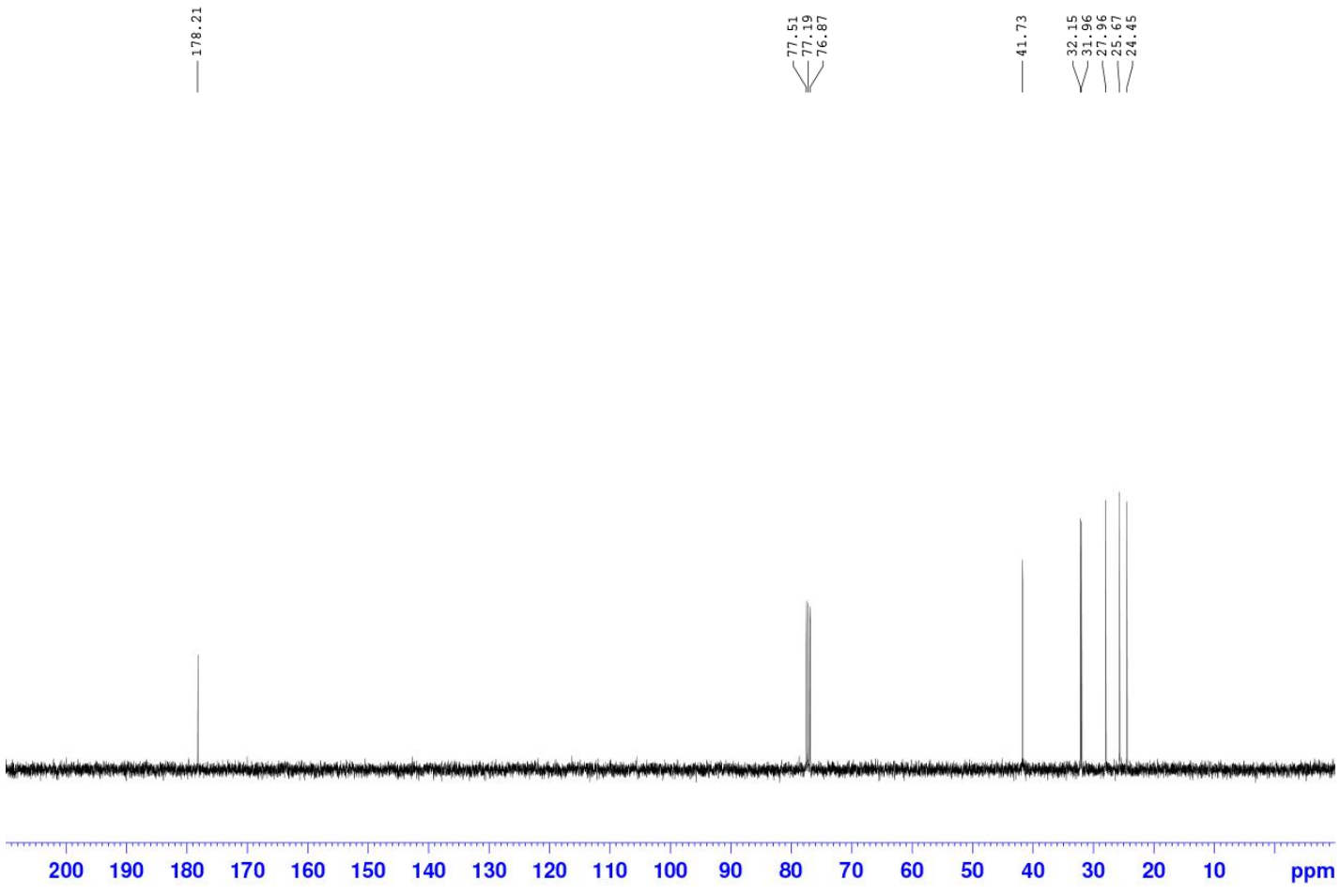
100 MHz ^{13}C NMR Spectrum ($CDCl_3$) of compound **8**



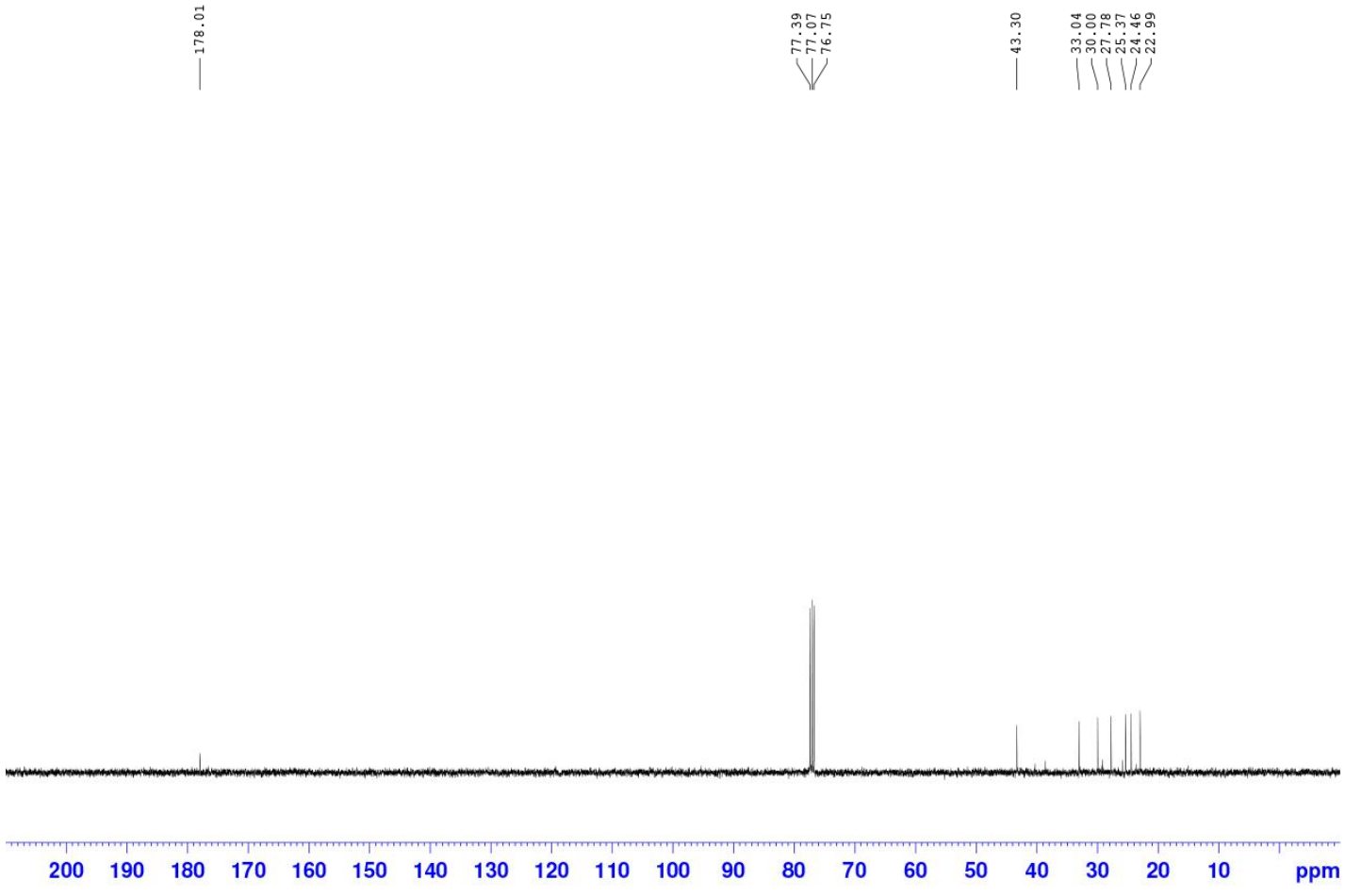
100 MHz ^{13}C NMR Spectrum ($CDCl_3$) of compound **9**



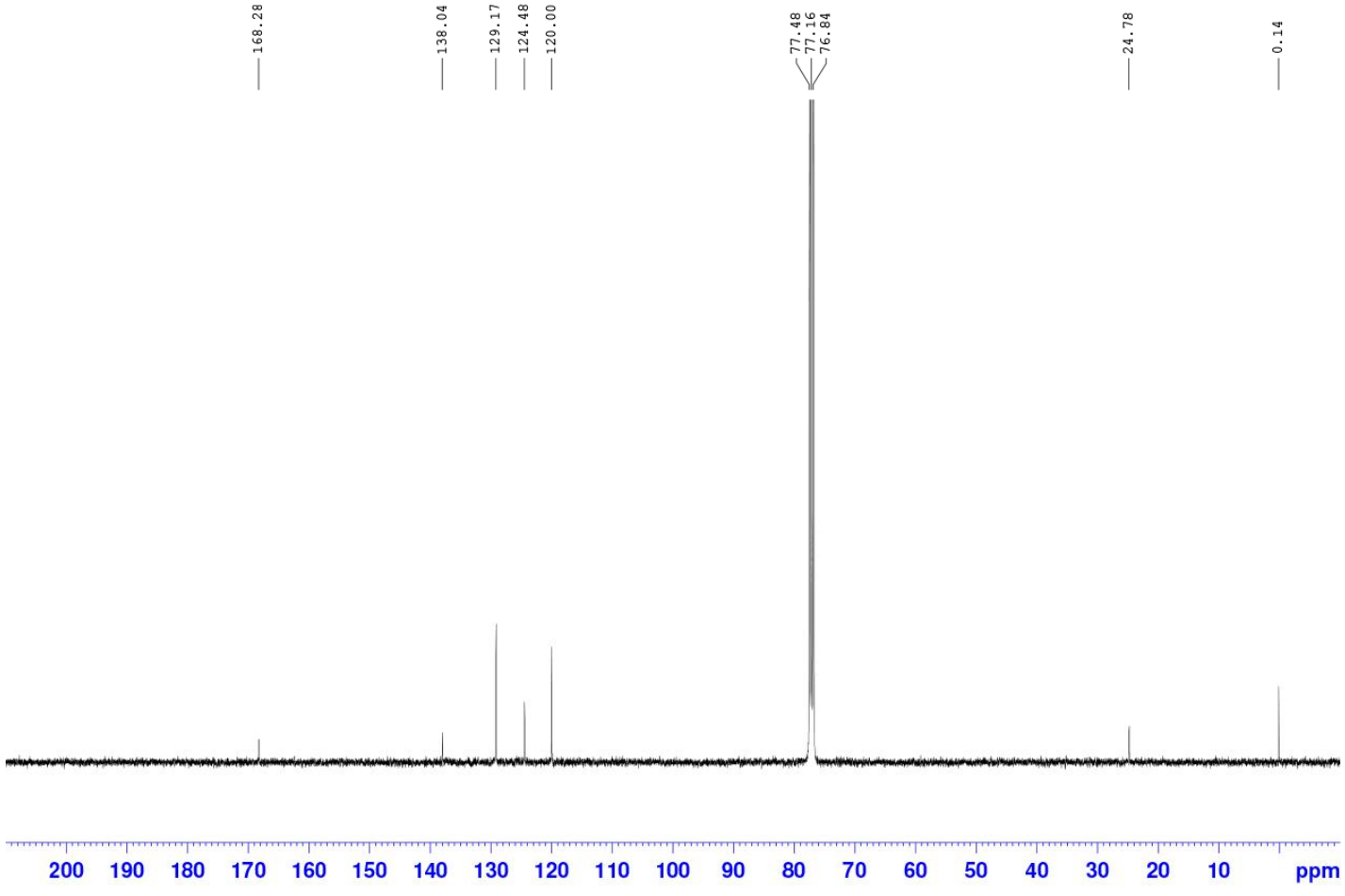
100 MHz ^{13}C NMR Spectrum ($CDCl_3$) of compound **10**



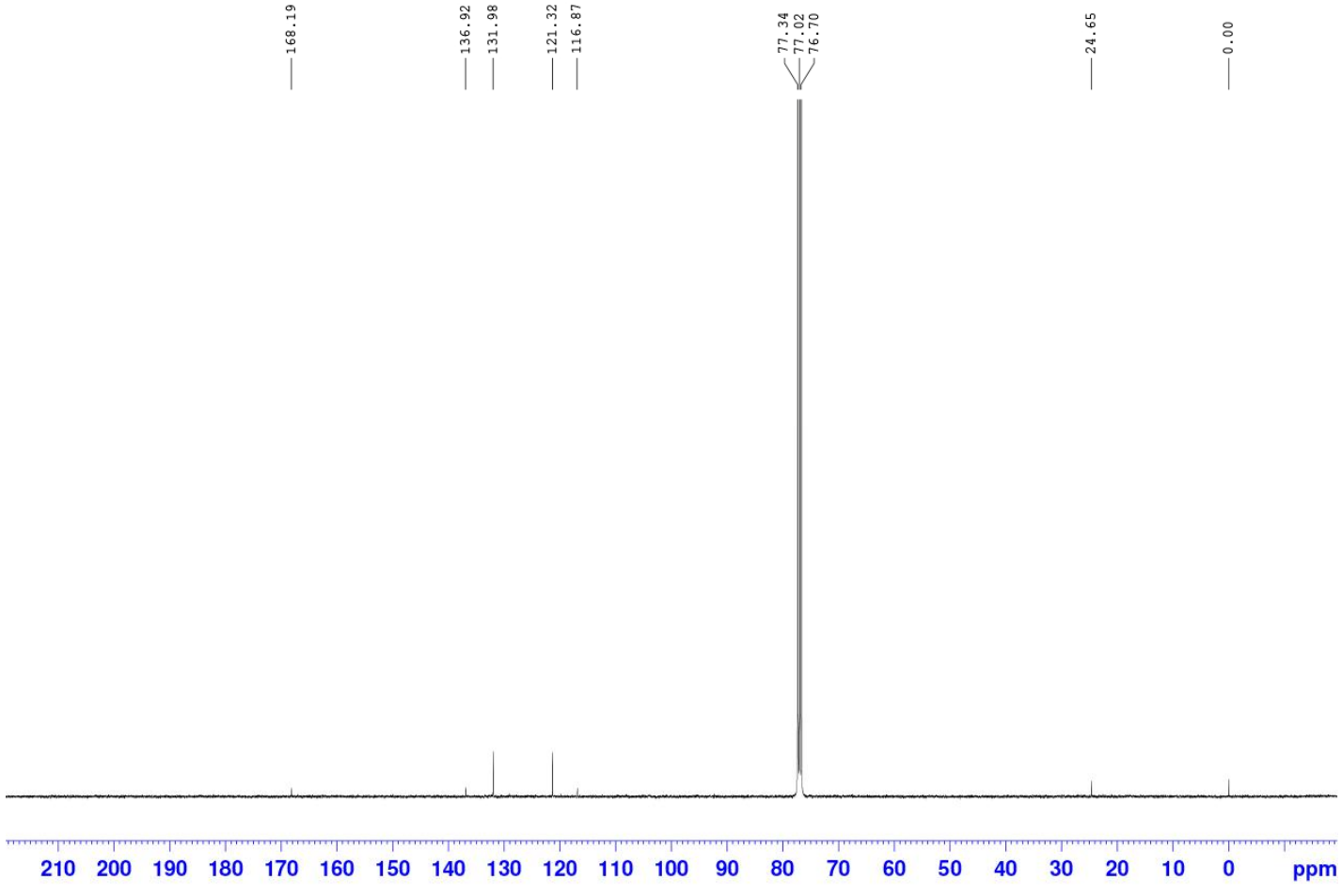
100 MHz ^{13}C NMR Spectrum ($CDCl_3$) of compound **11**



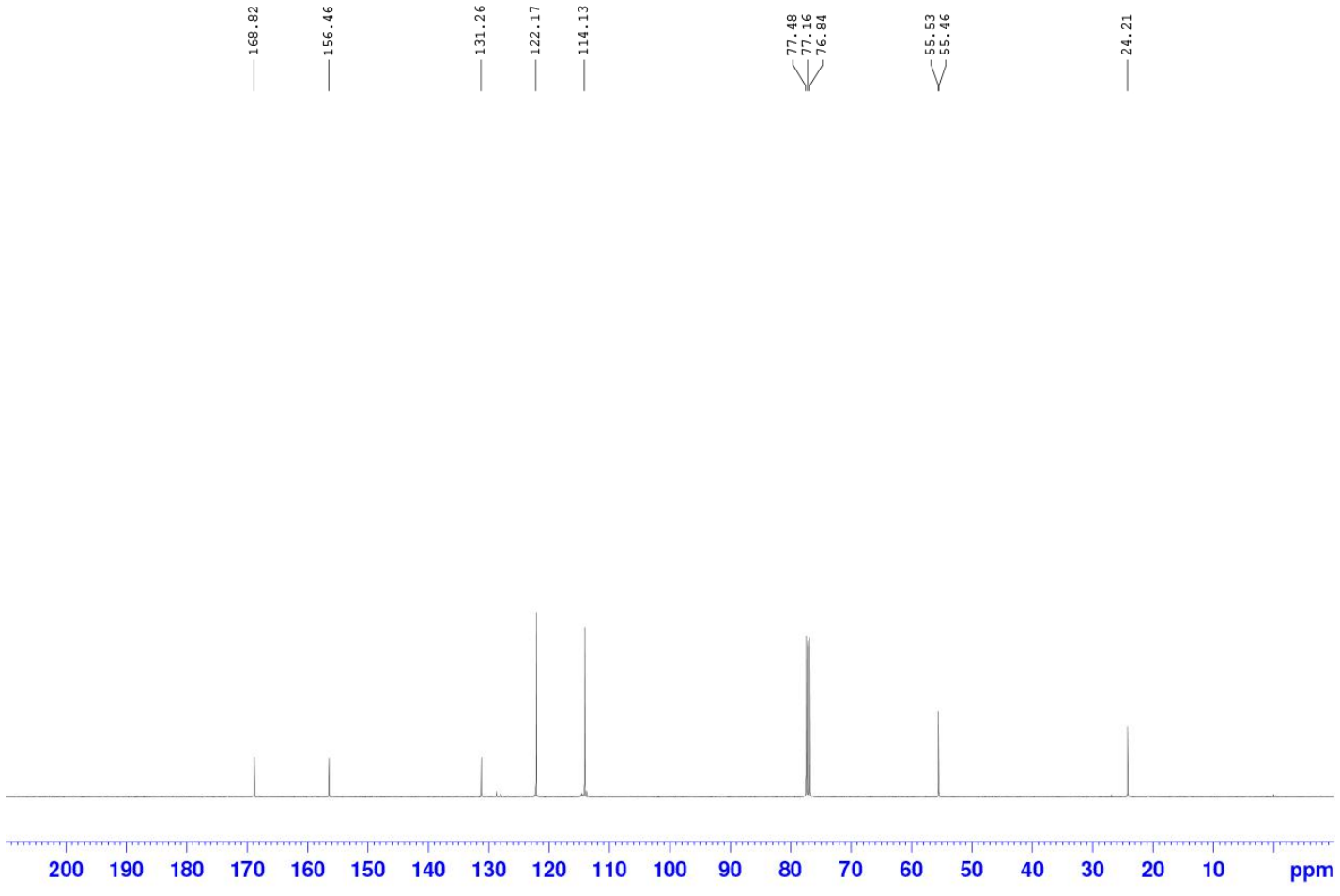
100 MHz ^{13}C NMR Spectrum ($CDCl_3$) of compound **12**



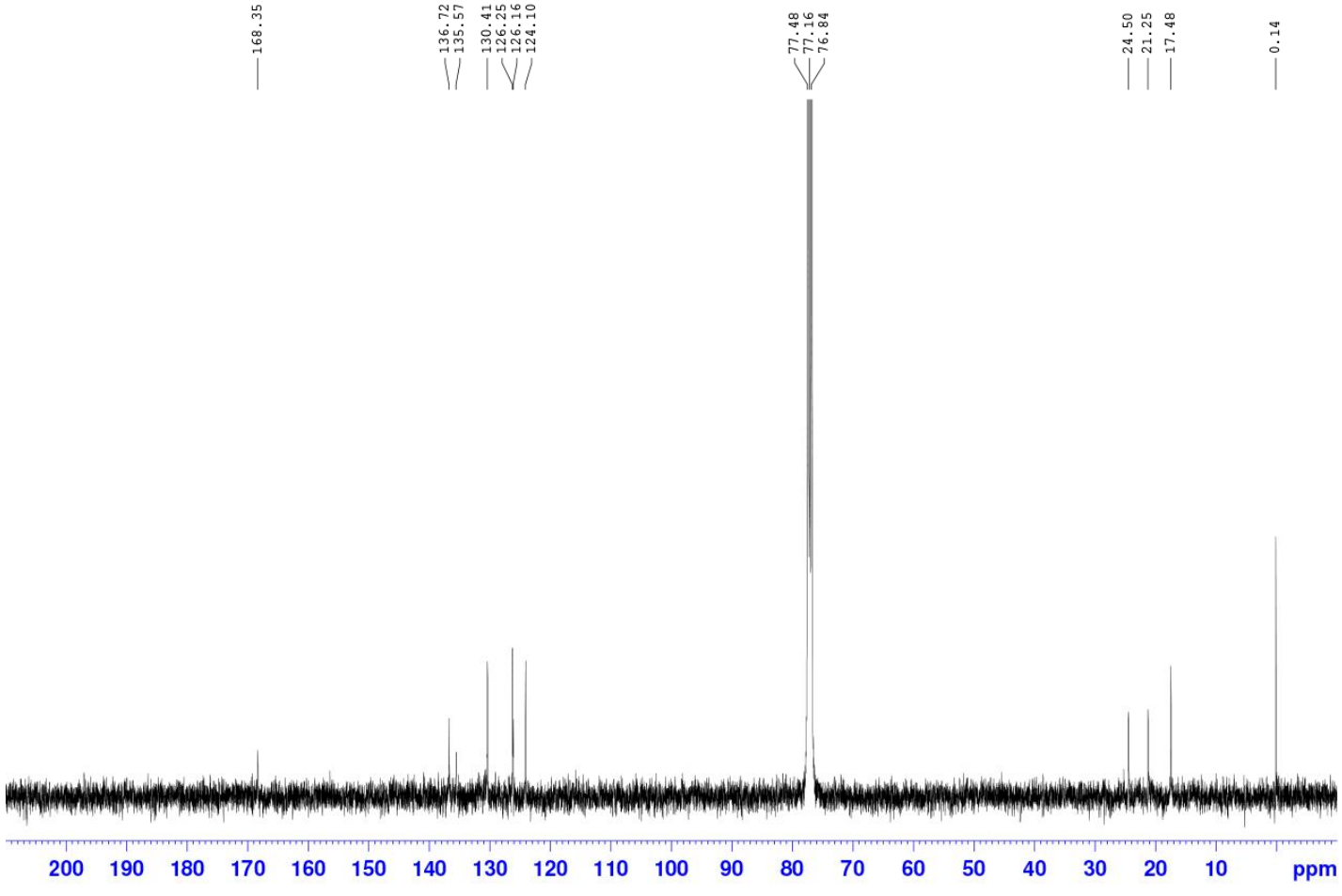
100 MHz ^{13}C NMR Spectrum ($CDCl_3$) of compound **13**



100 MHz ^{13}C NMR Spectrum ($CDCl_3$) of compound **14**



100 MHz ^{13}C NMR Spectrum ($CDCl_3$) of compound **15**



100 MHz ^{13}C NMR Spectrum ($CDCl_3$) of compound **16**

ABSTRACT IN KOREAN

열가소성 폴리아마이드 탄성체의 단량체로 사용되는 C_{10}-ω-diamine 과 laurolactam의 합성 공정 개발

김봉현

서울대학교 화학생물공학부 대학원

엔지니어링 플라스틱 (EP)은 많은 장점을 가지고 있기 때문에 산업에서 가장 중요한 소재 중 하나로 여겨진다. 이것은 일반 플라스틱이 가지는 치명적인 여러 물성적인 단점들을 보완하고 있다. 엔지니어링 플라스틱 중, 열가소성 탄성체(TPEs)는 아주 좋은 탄성체적 물성과 열 물성적 안정성을 통한 재사용 때문에 큰 이목을 끌고 있다. 열가소성 탄성체의 종류의 하나인 아마이드계 열가소성 탄성체(TPAE)가 다른 열가소성 탄성체들에 비해서 전체적인 성능이 뛰어나고 알려져 있다. 아마이트계 열가소성 탄성체의 경우 잘 찢어지지 않고, 날씨에 저항성이 크고, 탄성 복구율이 좋으며, 열적으로 상당히 안전하고, 내화학성 및 내수성이 매우 뛰어나다.

매해마다 국내 아마이드 계열의 열가소성 탄성체의 소모량은 늘어나고 있는 추세이다. 하지만 이러한 시장의 요구에도 불구하고 아마이드계 열가소성 탄성체를 이루는 단량체의 생성 공정은 국내에 요원한 상태이다. 이전 논문을 통해 우리는 탄소수가 9 개부터 11 개까지의 열가소성 아마이드계 탄성체의 단량체를 바이오 메스 기반으로 생산하는 것을 보고 하였다.

이번 논문에서는 바이오매스 혹은 석유 기반으로부터 탄소 10 개인 다이아민과 라우로락탐을 합성하는 다양한 방법을 소개한다. 탄소 10 개인 다이아민의 경우 탄소 10 개 혹은 12 개인 다이에시드로 출발하였다. 탄소 10 개 다이에시드는 나이트릴 환원 반응을, 탄소 12 개 의 경우는 호프만 재배열과 커티어스 재배열 반응을 진행하였다. 라우로락탐의 경우 배크만 재배열반응과 슈미츠 반응을 사용하였다. 배크만 반응의 경우 한반응기 배크만 반응을 진행하였다.

우리는 탄소 10 개 다이아민과 라우로락탐의 합성 방법을 완전하게 개발하였다. 특히 한 단계로 반응하는 경우, 반응에 들어가는 시간과 비용이 줄어드는 장점이 있고 수율 또한 이전 반응들과 비교하여 비슷하거나 높은 수율을 보여준다. 결론적으로 우리가 개발한 반응공정은 상당히 의미 있고 산업체에 적용이 가능할 것으로 판단된다.

주요어 : 알파, 오메가 다이아민, 엔지니어링 플라스틱, 열가소성 탄성체, 아마이드계 열가소성 탄성체, 호프만 재배열반응, 나이트릴 환원반응, 커티어스 재배열반응, 라우로락탐, 슈미츠 반응