工學博士 學位論文

Divergent Processes for the C_9 to C_{15} Monomers of Polyamide from Vegetable Oils and Synthesis of the Dissolution Inhibitors and the Negative Tone Photoresists for ArF Photolithography

식물성 오일 기반 폴리아미드 단량체의 다양한 합성 공정과 ArF 포토리소그래피용 용해억제제와 네거티브 포토레지스트의 합성

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Divergent Processes for the C_9 to C_{15} Monomers of Polyamide from Vegetable Oils and Synthesis of the Dissolution Inhibitors and the Negative Tone Photoresists for ArF Photolithography

By

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Abstract

This thesis is comprised of two chapters. Chapter 1 is “Divergent processes for the C_9 to C_{15} monomers of polyamide from vegetable oils”. Chapter 2 is the “Synthesis of the dissolution inhibitors and the negative tone photoresists for ArF photolithography” which is divided again into 2 subjects, “synthesis of the dissolution inhibitors” and “synthesis of the new conceptual negative tone photoresist”.

Chapter 1: In recent years, polymers from renewable resources have been attracting ever-increasing attention because of environmental concerns and depletion of petroleum resources. Since most of widely used polymers are generally based on fossil feedstocks, academic and industrial researchers have been increasingly concentrating their attention and efforts to the possible use of renewable feedstocks in order to keep global sustainability. Vegetable oils are one of the important renewable platform chemicals for producing polymeric materials. The main components of vegetable oils are esters of glycerol with three fatty acids, that is, triglycerides. Several reactive sites including double bonds and ester groups are present in tryglycerides. From this point of view, we developed a versatile and efficient process for the monomers of polyamide from vegetable oils as the renewable resources. We could obtain the C_9-C_{15} α,ω-dicarboxylic acids and ω-amino acids monomers from olive oil, castor oil and rapeseed oil, respectively. All of the monomers were obtained via the carbon homologation methods followed by the functional group transformations in good to excellent yields.

Chapter 2: The minimum size achievable by photolithography is already smaller than the wavelength of radiation, and the cost of improving its resolution is

increasing exponentially. But, unfortunately, current technology fails to meet the demand for the miniaturization of semiconductor. In order to break the barrier, several alternative technologies called next generation lithography (NGL) are currently being developed. First, we suggested the addition of dissolution inhibitor to enhance the contrast of ArF photoresists. Dissolution inhibitors (DIs) are a class of small molecules with acid-labile unit (ALUs). DIs decompose to disclose a base-soluble functional group and change the property of the DI molecules to be washed out rapidly by a developer. We have synthesized two dissolution inhibitors from calix[4]arene which was not applied to the ArF photoresists. Methoxymethyl (MOM) and tert-butyloxycarbonyl (t-Boc) protected calix[4]arene were obtained in 73% and 58% yields, respectively, in a single step. Second, negative tone photoresist (NTR) is suggested with a new concept. Conventional negative tone development (NTD) was embodied by using organic solvent as a developer or crosslinking reactions of negative tone resist. But organic developer is not freely available from overseas patents, and a limited number of negative tone resist for ArF are available in the market. From this point of view, we designed a negative tone resist which have not a hydrophilic functionality but also hydrophobic lactone when it exposed to ArF light, together. Several candidate monomers for photoresist were synthesized, but their physical properties were not enough to apply in practical process, yet. Although the desired result was not completely obtained, new approach to synthesize negative tone resist is worthy enough.

Key words: thermoplastic elastomer, polyamide, monomer, vegetable oil, dissolution inhibitor, calixarene, negative tone resist

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LIST OF ABBREVIATIONS

Ac	Acetyl
ALU	Acid labile unit
Bn	Benzyl
Boc	*tert*-Butyloxycarbonyl
CAN	Ceric ammonium nitrate
CAR	Chemical amplification resist
CDU	Critical dimension uniformity
CSI	Chlorosulfonyl isocyanate
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCC	*N*,*N'*-Dicyclohexylcarbodiimide
DCM	Dichloromethane
DI	Dissolution inhibitor
DMAP	4-Dimethylaminopyridine
DMF	*N*,*N*-Dimethylformamide
DMSO	Dimethyl sulfoxide
$\boldsymbol{E}_{\mathbf{a}}$	Activation energy
EE	Ethoxyethyl
EtOAc	Ethyl acetate

GC	Gas chromatography
HRMS	High resolution mass spectrometer
IR	Infrared
L/S	Line/Space
MEEF	Mask error enhancement factor
MEHQ	Monomethyl ether hydroquinone
MOM	Methoxymethyl
Mp	Melting point
Ms	Methanesulfonyl
MSD	Mass spectrometric detector
NMO	4-methylmorpholine N-oxide monohydrate
NMR	Nuclear magnetic resonance
NTD	Negative tone development
NTR or NTP	Negative tone photoresist
OA	Oleic acid
PA	Polyamide
PAG	Photoacid generator
PDI	Polydispersity index
PGMEA	Propylene glycol monomethyl ether acetate
PPTS	Pyridinium p-toluenesulfonate
PR	Photoresist

PTD	Positive tone development
PTR or PTP	Positive tone photoresist
Quant.	Quantitative
SEM	Scanning electron microscope
SRAM	Static random-access memory
TLC	Thin layer chromatography
TEA	Triethylamine
THF	Tetrahydrofuran
THP	Tetrahydropyran
TMAH	Tetramethylammonium hydroxide
TMS	Tetramethylsilane
TPAE	Thermoplastic polyamides
TPE	Thermoplastic elastomer
TPEE	Thoermoplastic copolyester
TPP	Triphenylphosphine
TPU	Thermoplastic polyurethane
pTsOH	para-Toluenesulfonic acid
UA	Undecylenic acid
UV	Ultraviolet

Part I. Divergent processes for the C_9 to C_{15} monomers of polyamide from vegetable oils

1. Introduction

Petrochemical industries have emitted huge amount of carbon dioxide and caused environmental problems such as climate change. In addition, fossil fuels are limited resource and they will be depleted in the near future as their demands increase. Thus, petroleum-based industries are facing challenges in technical, economic and environmental issues and the call for alternative carbon sources is growing. As a result, replacement of fossil fuel-based raw materials with renewable natural resources is a major concern from both economic and environmental perspectives. Biomass, which is biological material from living organisms such as corn starch, sugarcane and vegetable oil, has emerged as an important alternative resource because it has superior advantages over fossil fuel; it is economic, renewable, flexible and environmentally friendly.[1] Currently, about 3% of the global chemicals market sales are made up of "green chemicals" and the market share would grow to about 25% of global chemicals sales by 2025.[2] In addition, consumer interests in green products and public policy are accelerating the growth of green chemicals in the marketplace.

1.1 Thermoplastic elastomers (TPEs)

Among the green chemicals, bioplastics (green plastics) derived from sustainable biomass are predicted to show the highest growth rate due to their wide range of applications.[3] Especially, extensive research and development on thermoplastic elastomers (TPEs) have been conducted because TPEs typically

have advantages of both plastic and rubbery materials as well as their superior qualities to either rubbers or plastics. TPEs consist of linear segmented block copolymers composed of hard and soft segments with both thermoplastic and elastomeric properties. While most elastomers are thermosets, thermoplastics are in contrast relatively easy to use in manufacturing, for example, by injection molding. Thus, TPE materials have the potential to be recyclable, but they have typical elastic properties of rubbers which are not recyclable. TPE also require little or no compounding, with no need to add reinforcing agents, stabilizers or cure systems. Hence, batch-to-batch variations in weighting and metering components are absent, leading to improved consistency in both raw materials and fabricated articles. TPEs can be easily colored by most types of dyes. Besides that, it consumes less energy and closer and more economical control of product quality is possible.

TPEs are used where conventional elastomers cannot provide the range of physical properties needed in the product. These materials find large application in the automotive sector and in household appliances sector. Thus copolyester TPEs are used in snowmobile tracks where stiffness and abrasion resistance are at a premium. They are also widely used for catheters where nylon block copolymers offer a range of softness ideal for patients. Thermoplastic silicon and olefin blends are used for extrusion of glass run and dynamic weatherstripping car profiles. Styrene block copolymers are used in shoe soles for their ease of processing, and widely as adhesives. TPE is commonly used to make suspension bushings for automotive performance applications because of its greater resistance to deformation when compared to regular rubber bushings. TPE may also be used in medical devices and sex toys. TPE is also finding more and more uses as an electrical cable jacket/inner insulation. TPE is also

used in some headphone cables.

TPEs are categorized by their main structure of bond linkage. There are six generic classes of commercial TPEs.

- Styrenic block copolymers (TPE-s)
- Polyolefin blends (TPE-o)
- Elastomeric alloys (TPE-v or TPV)
- Thermoplastic polyurethanes (TPU)
- Thermoplastic copolyester (TPEE)
- Thermoplastic polyamides (TPAE)

TPEs have been applied to wide range of industry according to its structure (Figure 1).

Figure 1. Applications of TPEs.

Figure 2 depicted physical properties of four types of TPEs. Among them,

polyamide TPE shows a remarkable physical properties than other engineering plastics. Thus, demands for polyamide TPE (TPAE) is increasing around the world.

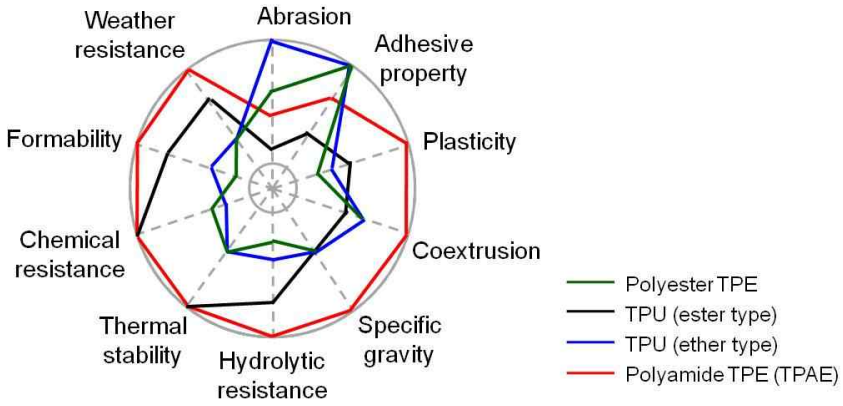


Figure 2. Physical properties of TPEs.

1.1.1 Polyamide-type thermoplastic elastomers (TPAE)

As mentioned above, polyamide TPE (TPAE) among the TPEs have been utilized in engineering plastics and the demands for the production are increasing due to their high strength, toughness, and thermal stability.[4] Polyamides have also great potentials for other functional applications, particularly in biomedical fields as they show good biocompatibility and degradability.[5]

TPAE have a polyamide part as a hard segment (Figure 3). Polyamide group bring about thermoplastic characteristics. Elastomeric unit is consist of polyether or polyester functionality. Polyethylene glycol (PEG), polypropylene glycol (PPG), polytetramethylene glycol (PTMG) and polytetrahydrofuran (PTHF) are well-known soft segment units.

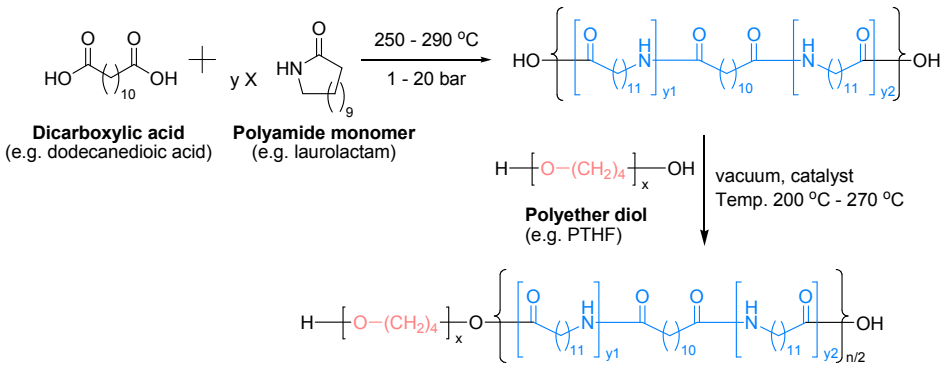


Figure 3. Typical preparation of TPAE.

The price of engineering plastics is closely related to its performance (Figure 4). According to Figure 4, TPAE is a reasonable choice from a price and performance prospective.

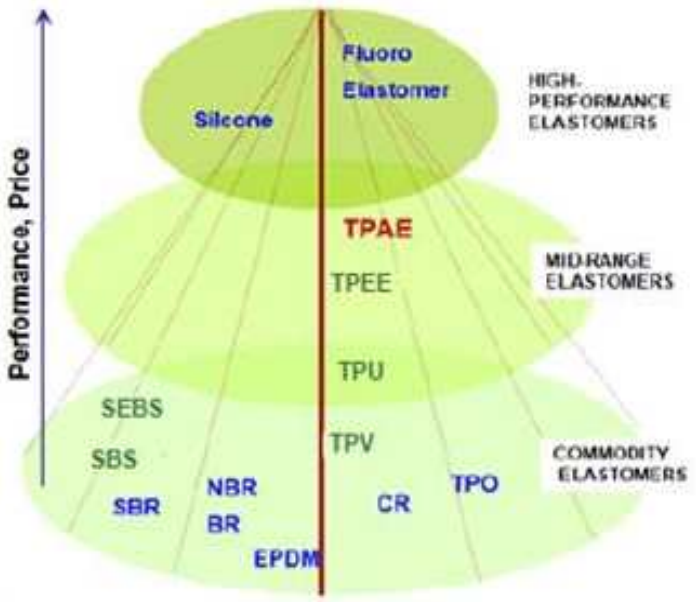


Figure 4. Comparisons of various types of thermoplastic elastomers.

1.1.2 Vegetable oils as a renewable resources

Since most of TPAE monomers have been obtained from non-renewable resources such as natural gas and petroleum, a lot of research has been conducted to obtain their monomers from alternative sources such as vegetable oil. Vegetable oil can be an ideal alternative source because it is abundant throughout the world, and moreover, can be easily modified to the polymer precursors due to its active chemical sites such as double bonds and esters.[6]

In 1996, 96.6 million ton oils and fats were produced worldwide.[7] Most of them were used in food applications such as salad and cooking oils. About 13.5 million ton (14%) were used for the production of oleochemicals. The main field for the oleochemical industry is the preparation of soaps, which are based on fatty acids or triglycerides, and other kinds of surfactants. The use of oleochemical products as a part of the polymer backbone is a minor application field for oleochemical products because of the lack of di- or multifunctionality in most oils. However, some oleochemical derivatives overcome this limitation by having special application properties which allow them to find a market in the polymer field. They do not have the economic competitiveness based on petrochemicals. Therefore, they are applied in niche markets, where advantages in application compensate for the higher price level.

The consumption of polymers at 153 million ton world-wide is much bigger than the production of oils and fats. A single raw material for polyesters, terephthalic acid that are used for oleochemical purpose. For cost reasons, oleochemical building blocks must deliever specific properties to be able to compete with commodities based on petrochemicals.

Castor oil, a triglyceride, has found applications as a polymer backbone. It has a unique composition with 90% of the fatty acids being ricinoleic acid. The

composition of castor oil is determined by nature and is very specific. The ring-opening reaction can be done with alcohols or acids which themselves both can be mono- or polyfunctional molecules. Hence, it is possible to prepare polyols based on oils that fit well to the application. These polyols can be cured with multifunctional isocyanates to produce cross-linked polyurethanes for casting or flooring.

Sebacic acid can be obtained from caustic oxidation of castor oil, too. This diacid has a chain length of 10 C-atoms and leads to more flexible polyesters than adipic acid does. It competes with azelaic acid which is manufactured by ozonolysis of oleic acid.

The dimer acids could obtain by dimerisation of unsaturated acids from tall oil, soybean oil, or technical oleic acid at 230–260 °C with a montmorillonite clay as a catalyst. The linkage of the fatty acid chains consists of cyclic and non cyclic structures as well as of aromatic structures. Some double bonds also exist in dimer acids and they are in many different positions.

Again dimerization and hydrogenation are involved. Starting from distilled dimer acid, a methyl ester is prepared and the hydrogenation is carried out with a typical hydrogenation catalyst as it is used for the production of saturated fatty alcohols. Under these conditions the double bonds are mainly removed. This route to dimer alcohol was commercialized at the beginning of the nineties.

1.1.3 Previous research

Various aliphatic monomers for polyamide are commercially available, but there are a few processes were known that prepared from biomass. And in a conventional process, only a few monomer could be obtained from one biomass

source. Current processes require various sources of biomass for the production of the polyamide monomers having different chain length.

1.1.3.1 Linear fatty α,ω-dicarboxylic acids

Middle- to to long-chain linear diacids derived from natural oils and fats are valuable renewable monomers for polyesters, polyamides, and polyurethanes (Table 1).[8]

Table 1. Unsaturated fatty acids and esters for the synthesis of linear diacids.

Entry	Substrate	Synthesis	# of C atoms of diacid
1	Oleic acid	ozonolysis	9
2		microbial oxidation	18
3		methoxycarbonylation	19
4	Oleic acid methyl ester	cross-metathesis with methyl acrylate ; hydrogenation	11
5		cross-metathesis with 2-butene ; methoxycarbonylation ; hydrogenation	12
6		self-metathesis ; hydrogenation	18
7	Erucic acid	ozonolysis	13
8	Erucic acid methyl ester	cross-metathesis with methyl acrylate ; hydrogenation	15

9		cross-metathesis with 2-butene ; methoxycarbonylation	16
10		methoxycarbonylation	23
11		self-metathesis ; hydrogenation	26
12	Ricinoleic acid	splitting with caustic soda	10
13	Petroselinic acid	ozonolysis	6
14	Petroselinic acid methyl ester	cross-metathesis with methyl acrylate ; hydrogenation	8
15	5-Eicosenoic acid methyl ester	cross-metathesis with methyl acrylate ; hydrogenation	7
16		methoxycarbonylation	21
17	10-Undecenoic acid methyl ester	cross-metathesis with methyl acrylate ; hydrogenation	12
18		cross-metathesis with 2-butene ; methoxycarbonylation	14
19		self-metathesis ; hydrogenation	20
20	9-Decenoic acid methyl ester	self-metathesis ; hydrogenation	18
21	13-Tetradecenoic acid methyl ester	cross-metathesis with 1-butene ; methoxycarbonylation	17
22		self-metathesis ; hydrogenation	26

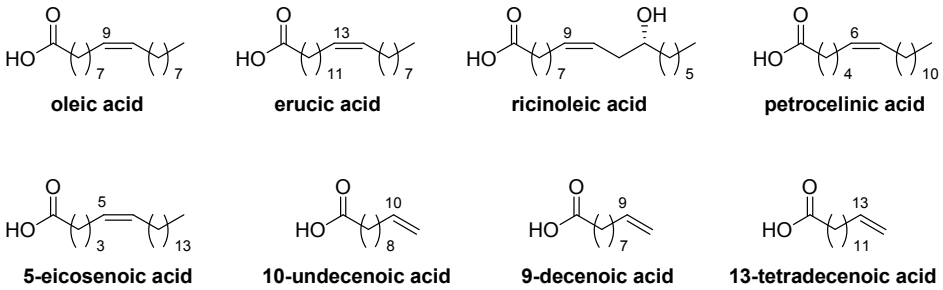


Figure 5. Unsaturated fatty acids for synthesis of diacids.

Azelaic acid (nonanedioic acid) (Table 1, entry 1) and brassylic acid (tridecanedioic acid) (Table 1, entry 7) can be produced by ozonolysis of oleic acid and erucic acid, respectively, giving both nonanoic acid as by-product. Presently, about 20,000 t/a of oleic acid are reacted to azelaic acid. Adipic acid (hexanedioic acid) and the by-product lauric acid (dodecanoic acid) may be obtained analogously from petroselinic acid (Table 1, entry 13). Because ozone is very expensive and the industrial ozonolysis presents some difficulties, an alternative process is required. The direct catalytic cleavage with H_2O_2 as oxidant was investigated extensively. A catalytic process using peracetic acid and ruthenium catalysts or catalysts based on H_2O_2 and Mo, W, or Re was reported, yielding only 50–60% diacids. Obviously, a highly efficient catalytic process using oxygen from the air has to be developed. Such a process would open the door for the production of dibasic acids of different chain length from plant oils. Sebacic acid (decanedioic acid) can be produced by splitting of ricinoleic acid with caustic soda using a ratio of 2 : 1 at 250–275 ^{o}C (Table 1, entry 12).

Cole-Hamilton reported quite recently on the methoxycarbonylation of unsaturated fatty esters and acids to α,ω-diesters with very high selectivity using

palladium catalysts with bulky bis(ditertiarybutylphosphinomethyl) benzene (DTBPMB) as ligand. The double bond is isomerized to the o-position, which is methoxycarbonylated. Most importantly, dimethyl nonadecanedioate was obtained not only from oleic acid but also from linoleic and linolenic acid. Thus, all unsaturated C18 fatty acids being present in the fatty acid mixture are reacted to the same saturated diacid (Table 1, entry 3).

Linear diacids were also synthesized by metathesis reaction of unsaturated fatty acids. Methyl 10-undecenoate gives, by self-metathesis after hydrogenation, dimethyl eicosanedioate (Table 1, entry 19). Self-metathesis of methyl 9-decenoate (Table 1, entry 20) and methyl 13-tetradecenoate (Table 1, entry 22) gives, after hydrogenation, dimethyl octadecanedioate and dimethyl hexaeicosanedioate, respectively, which can also be obtained by self-metathesis of methyl oleate (Table 1, entry 6) and methyl erucate (Table 1, entry 11), respectively. Quite recently, Meier and coworkers reported on the crossmetathesis of methyl oleate and methyl acrylate using second-generation ruthenium-based Hoveyda–Grubbs catalysts in a solvent-free reaction with high conversion and a catalyst load of only 0.2%, giving dimethyl 2-undecendioate and methyl 2-undecenoate (Table 1, entry 4). Methyl erucate yields analogously dimethyl pentadecanedioate (Table 1, entry 8), methyl petroselinate dimethyl octanedioate (Table 1, entry 14), and methyl 5-eicoseneoate dimethyl heptanedioate (Table 1, entry 15). Hydrogenation gives quantitatively the respective saturated acids. Metathesis is really a versatile tool in oleochemistry.

The spectrum of diacids obtainable from unsaturated fatty acids was enlarged by combination of the metathesis reaction with o-methoxycarbonylation in a one-pot reaction. For example, methyl oleate was cross-metathesized with 2-butene using second-generation Hoveyda–Grubbs

catalyst, giving methyl 9-undecenoate and 2-undecene. The unreacted 2-butene was then evaporated and, without workup, the ω-methoxycarbonylation was performed, giving very high conversion of methyl 9-undecenoate and 2-undecene to dimethyl dodecanedioate and methyl dodecanoate, respectively, after hydrogenation (Table 1, entry 5).

Microbial ω-oxidation of fatty acids, which leads via ω-hydroxy fatty acids to diacids, is of great interest. Cognis developed a metabolically engineered strain of *Candida tropicalis* to oxidize a terminal methyl group of an alkyl chain. The reaction of oleic acid gives, *via* the respective unsaturated ω-hydroxyoctadecanoic acid, octadecanedioic acid (Table 1, entry 2). Another way to long-chain fatty diesters is the Kolbe electrolysis of half esters of fatty diacids.

Finally, it may be mentioned that succinic acid being petrochemically produced by hydrogenation of maleic anhydride will become available biotechnologically from glucose.

The linear diacids that are produced or can be produced from natural unsaturated fatty acids are compiled in Table. It seems to be most remarkable that the complete series of linear diacids from C6 up to C20 and higher becomes easily available. Moreover, the diacids can be converted by standard industrial processes to the respective diols and diamines, thus offering opportunities for the production of established and also of new polyesters and polyamides completely from renewable feedstock. Polyesters derived from long-chain diacids and diols (>C18) seem to be most interesting, having properties similar to polyethene and being biodegradable.

1.1.3.2 ω-Amino fatty acids

11-Aminoundecanoic acid is the monomer of Nylon-11 and is produced in two steps from 10-undecenoic acid.[9] Quite analogously, 10-aminodecanoic acid and 14-aminotetradecanoic acid can be obtained from 9-decenoic and 13-tetradecenoic acid, respectively. Unfortunately, the direct addition of ammonia to the C=C double bond has not yet been invented. The rhodium-catalyzed hydroaminomethylation of the double bond has been described, unfortunately not with ammonia but with primary and secondary amines. Quite recently, cross-metathesis of methyl oleate and allylchloride reportedly gave methyl 11-chloro-2-undecenoate, which after hydrogenation and amination opens a new access to 11-aminoundecanoic acid.[10] The cross-metathesis of methyl 10-undecenoate and acrylonitrile using Hoyveda–Grubbs second-generation catalysts was reported to give methyl 11-cyano-10-undecenoate, which could be hydrogenated with the same catalyst to give the saturated methyl 11-cyanoundecanoate.[11] The same product was also obtained by radical addition of iodoacetonitrile to methyl 10-undecenoate followed by hydrogenation to remove the iodine.[12] The selective hydrogenation of the cyano group would give a new access to 12-aminododecanoic acid. Ayorinde et al reported the syntheses of 12-Aminododecanoic acid and 11-aminoundecanoic acid, monomer precursors for nylon-12 and nylon-11, respectively, from vernolic acid (cis-12,13-epoxy-cis-9-octadecenoic acid) via a reaction sequence that includes the formation of 12-oxododecanoic acid oxime (Figure 6).

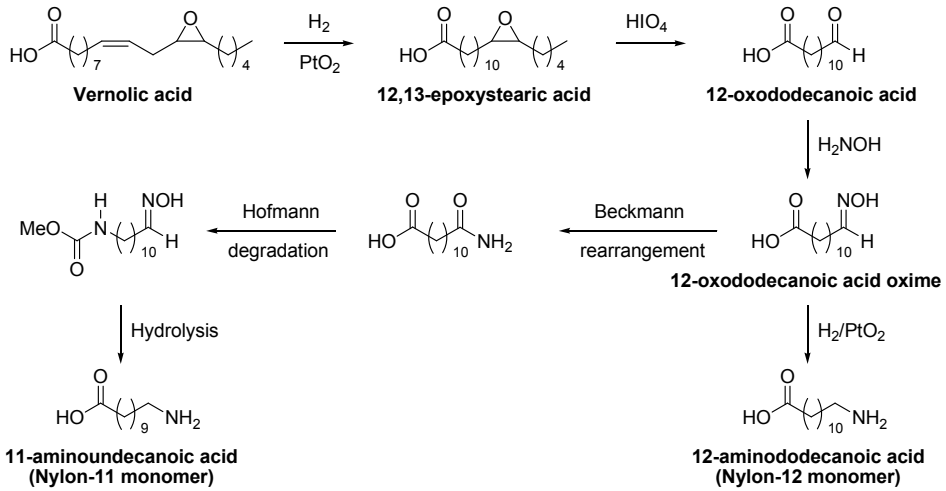


Figure 6. 12-Amino acid and 11-amino acid from vernolic acid.

1.1.3.3 Commercialized polyamide TPEs

Polyamide TPEs were first commercialized under the trade name "Pebax" by Atofina, currently Arkema chemical, in 1983. Since then polyamide-b-polyether which have a polyamide-12 as a hard segment was developed as a commercial name of "Vestamid" by Evonik Degussa GmbH in Germany. And Switzerland's EMS-Grivory AG launched "Grilamide" which have nylon-6 and nylon-12 as hard segments. In 2004, Ube industry (Japan) developed "Ubesta XPA", which soft segment is consist of polyether or polyester, based on synthetic techniques of polyamide. Recently Arkema chemical developed the biomass-based TPAE which has nylon-11 as a hard segment from castor oil, the trade name is "Pebax renew". Major makers over the world and chemical structure of TPAE are summarized in Table 2.[13]

Table 2. Major makers and chemical structure of TPAE

Maker	Trade name	Hard segment	Soft segment
Arkema	Pebax	PA12, PA11, PA6, Copolyamide	PTMO, PEO
Evonik Degussa	Vestamid	PA12	PTMO
Ube Industry	Ubesta XPA	PA12	PTMO
EMS-Grivory AG	Grilamide ELY	PA12	PTMO

2. Results and discussion

2.1 Synthesis of C_{10}-C_{12} monomers from castor oil

2.1.1 Undecylenic acid from castor oil

Castor oil is derived from the bean of the castor plant *Ricinus communi* of the family Euphorbiaceae. Castor plants grow in practically all tropical and subtropical countries of the world, such as India and Brazil.[1b] Crude castor oil is used in many nonfood applications such as polyurethane polymers, plasticizers and lubricants, pharmaceuticals and cosmetics, soaps, inks and paints, and others.[14] Recently BASF has relaunched a polyamide 6,10 polymer derived from sebacic acid produced from castor oil. Owing to the presence of ricine, a toxic protein, castor oil possesses laxative and vomitive properties and cannot be used as a food oil. Therefore, the refining process comprises a detoxification step that uses $Ca(OH)_2$, NaOH, and NaOCl. Castor oil contains up to 90%

ricinoleic acid, a mono-unsaturated, 18-carbon fatty acid with a hydroxyl function at position 12, which is prone to cleavage upon heating. Undecylenic acid (UA) is thus obtained from castor oil by pyrolysis of either the crude oil or the ricinoleic acid methyl esters. The former method is less favorable because of the formation of side products and an ensuing difficult product recovery. Different catalysts have been used, including various metals (Al, Tl, Ti, Ce, Th, W, and Mo), glass, polymers (PVC), and free-radical initiators. Several mechanisms have been proposed for the conversion of ricinoleic acid methyl esters to heptaldehyde and methyl undecenoate, which, after hydrolysis, yields UA; a McLafferty-like rearrangement (Figure 7), a concerted mechanism, and a free-radical mechanism.[15]

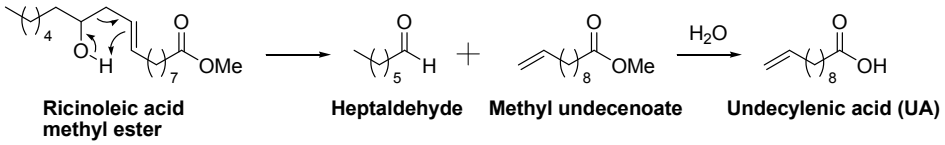


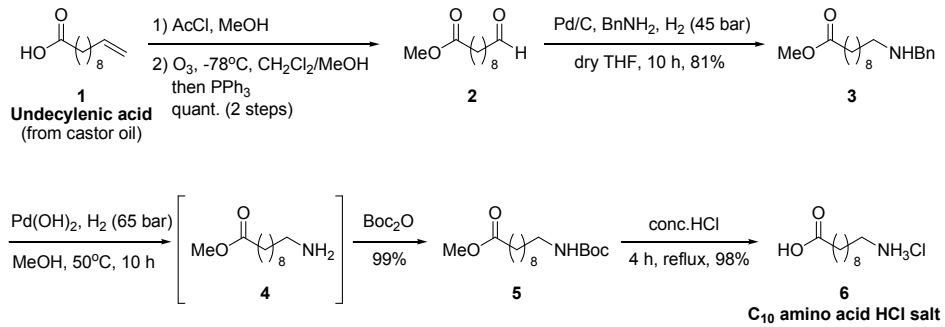
Figure 7. McLafferty-type rearrangement of methyl ricinoleate

Optimized parameters for the pyrolysis are an ester flow rate of 40–70 g/h and temperatures of 400–500 ^{o}C. Mixing of the ester stream with steam is not necessary but minimizes carbon deposition on the reactor walls and prevents charring of the products.[16]

2.1.2 Synthesis of C_{10} α,ω-dicarboxylic acid and ω-amino acid

We designed to introduce the aldehyde functional group by oznoloysis of unsaturated fatty acids. Aldehyde is a suitable intermediate to give desired functionality.

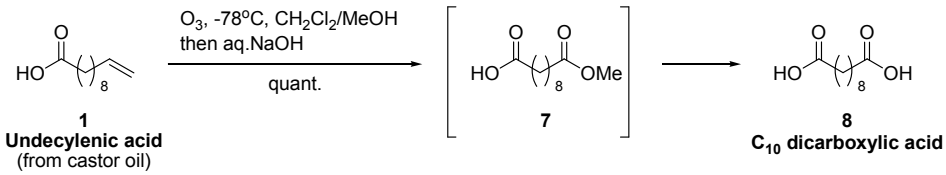
Preparation of the C_{10} monomers from undecylenic acid **1** is shown in Scheme 1. For the production of C_{10} ω-amino acid, we first prepared the key aldehyde intermediate **2** from ozonolysis of methyl ester of **1**. Because aldehyde **2** was labile to autoxidation, it was immediately used after column purification for the next reactions.[17] Catalytic reductive amination of **2** with benzylamine under 45 bar of H_2 gas afforded C_{10} ω-benzylamino ester **3**. Initially, we tried the reductive amination of **2** with ammonia, but considerable by-products of dialkylated and trialkylated amines were obtained.[18] A debenzylated intermediate **4** was protected with Boc_2O to afford **5** in excellent yield. Without the protection, the debenzylation reaction of **3** yielded some unidentified by-products together with the corresponding free amine **4**, presumably due to the instability of the free amine when exposed to the air during the isolation. The following simple acidic hydrolysis of **5** gave the desired C_{10} ω-amino acid **6** as its hydrochloride salt. Thus, the C_{10} ω-amino acid monomer **6** was obtained in 79% yield over six steps starting from **1** (Scheme 1).



Scheme 1. Synthesis of C_{10} ω-amino acid from undecylenic acid

Ozonolysis of **1** provided C_{10} α,ω-dicarboxylic acid **8** via its monoester precursor **7** in quantitative yield after work-up with aq. NaOH.[19] The work-up

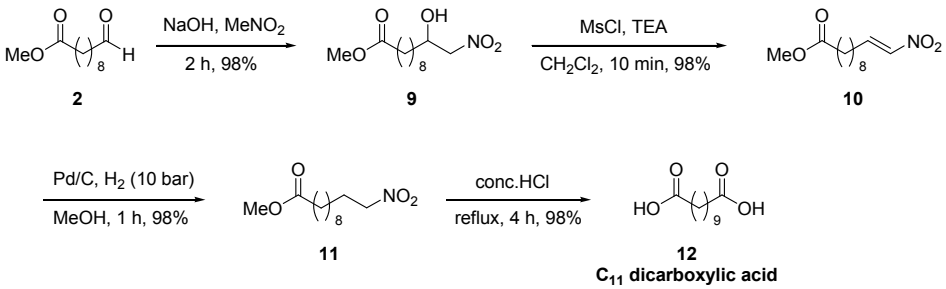
of the ozonolysis reaction with H_2O_2 gave the similar results for diacid **3** (Scheme 2).[20]



Scheme 2. Synthesis of C_{10} dicarboxylic acid from undecylenic acid

2.1.3 Synthesis of C_{11} α,ω-dicarboxylic acid and ω-amino acid

For the synthesis of C_{11} ω-amino acid and α,ω-dicarboxylic acid from the C_{10} key intermediate **2**, a nitromethyl group was employed to introduce the desired functional groups as well as one more carbon (Scheme 3).

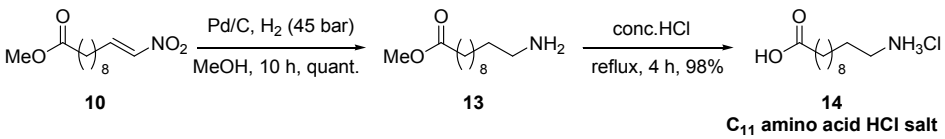


Scheme 3. Synthesis of C_{11} dicarboxylic acid from undecylenic acid

A nitromethyl group is such a versatile functional group that it can be transformed into either an aminomethyl or a carboxyl group. The desired nitroolefin **10** was produced in excellent yield from **2** in two steps by a sequence of a nitro-aldol reaction (Henry reaction)[21] followed by dehydration with methanesulfonyl chloride (MsCl). The more effective Henry reaction was achieved with excess nitromethane in the presence of stoichiometric amount of

NaOH in less than 2 h. A catalytic version of the Henry reaction did not go to completion and use of weaker bases such as K_2CO_3 required longer reaction time (more than 12 h).

We then investigated selective reduction procedures for either partial reduction of only the carbon-carbon double bond in the presence of the nitro group or complete reduction of both functional groups. Thus, catalytic hydrogenation of **10** under low pressure of H_2 (10 bar) was efficient enough for selective partial reduction and avoiding further reduction of the nitro group. The partial reduction was complete within 1 h and provided desired nitroalkane **11** in excellent yield, which was successfully converted into the desired C_{11} α,ω-dicarboxylic acid **12** under acidic hydrolysis conditions (Nef reaction).[22] The selective partial reduction of nitroolefin **10** was also possible with sodium borohydride ($NaBH_4$), which does not seem suitable for an industrial process. Catalytic hydrogenation of **10** under higher pressure of H_2 (45 bar) yielded the fully reduced amino ester in 10 h, which was hydrolysed under acidic conditions into the desired C_{11} ω-amino acid **14** as a hydrochloride salt (Scheme 4).



10 **13** **14**

C_{11} amino acid HCl salt

Scheme 4. Synthesis of C_{11} ω-amino acid from undecylenic acid

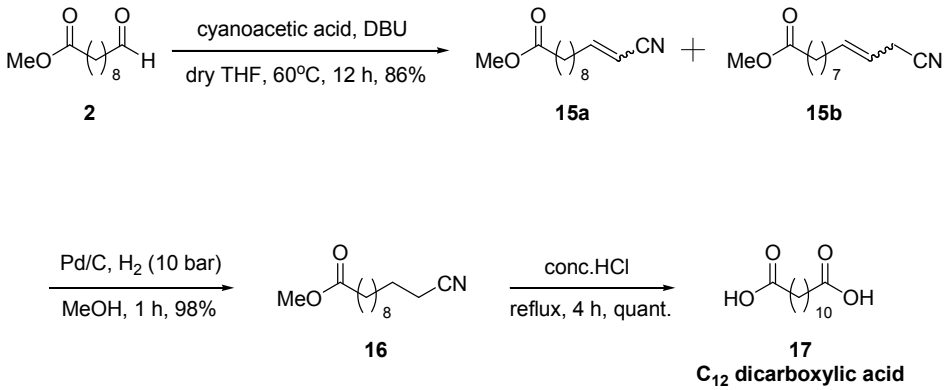
Alternatively, **14** could be obtained by further reduction of **11** and the following acidic hydrolysis. Thus, the C_{11} α,ω-dicarboxylic acid monomer **12** and the C_{11} ω-amino acid monomer **14** were obtained in 74% and 94% yields,

respectively, over six steps starting from **1**.

2.1.4 Synthesis of C_{12} α,ω-dicarboxylic acid and ω-amino acid

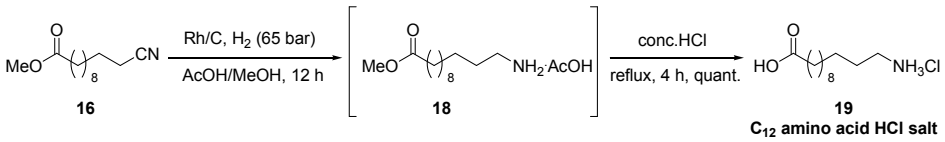
Finally, a two-carbon extension from the C_{10} intermediate **2** for the synthesis of the C_{12} α,ω-dicarboxylic acid and ω-amino acid monomers was possible with cyanoacetic acid (Knoevenagel condensation, Scheme 2).[23]

The in-situ decarboxylative condensation of cyanoacetic acid with **2** gave conjugated nitrile **15a** as a mixture of *E* and *Z* isomers along with a non-conjugated isomeric mixture of nitrile **15b**. We found that 4 equiv. of DBU was best at 60 ^{o}C for the modified Knoevenagel condensation. Other bases such as ^{t}BuOK, $^{i}Pr_2NEt$, and piperidine didn't work at all and most of the staring material was recovered. Although a mixture of four olefinic isomers was obtained, it was not important because they were eventually transformed into the same compound **16** via partial hydrogenation. Selective partial catalytic hydrogenation of **15** (**15a** and **15b**) with Pd/C at low pressure of H_2 (10 bar) gave **16** with the saturated alkyl chain in excellent yield, the key intermediate for both C_{12} α,ω-dicarboxylic acid and C_{12} ω-amino acid. The following hydrolysis of **16** under acidic conditions produced the desired C_{12} α,ω-dicarboxylic acid **17** in quantitative yield (Scheme 5).



Scheme 5. Synthesis of C_{12} dicarboxylic acid from undecylenic acid

Further reduction of **16** into **18** was carried out by catalytic hydrogenation with Rh/C at higher pressure (65 bar). The reduction did not proceed at all with other catalysts such as Pt/C or PtO_2 and the starting material was fully recovered. The catalytic reduction with Pd/C or $Pd(OH)_2$ seemed working but the yield was low and some unknown by-products were observed. The Rh-catalysed reduction was successful in the presence of various acids such as acetic acid, trifluoroacetic acid, and formic acid to give the rather stable product as its ammonium salt. Indeed, we had difficulty in isolating the completely reduced compound as a free amino acid form due to its instability. Among others, the co-solvent system of AcOH and MeOH gave the best yield and purity. Although the complete reduction of **15** into **18** worked well, a stepwise reduction process via **16** was adopted because the direct reduction of **15** was less efficient than the stepwise reduction in terms of the yield and purity. Acidic hydrolysis of **18** then afforded C_{12} ω-amino acid **19** as its hydrochloride salt (Scheme 6).



16 18 19

C_{12} amino acid HCl salt

Scheme 6. Synthesis of C_{12} ω-amino acid from undecylenic acid

Thus, the C_{12} α,ω-dicarboxylic acid monomer **17** and the C_{12} ω-amino acid monomer **19** were obtained in 84% yield over five steps and 83% yield over six steps, respectively, starting from **1**.

2.2 Synthesis of C_9-C_{11} monomers from olive oil

2.2.1 Oleic acid from olive oil

Oleic acid is a C18 fatty acid containing a carbon-carbon double bond at the ninth position that can be found in several natural oils such as olive oil (55-83%), pecan oil (59-75%), peanut oil (36-67%), canola oil (61%), macadamia oil (60%), sunflower oil (42%) and palm oil (39%). The biosynthesis of oleic acid involves the action of the enzyme stearoyl-CoA 9-desaturase acting on stearoyl-CoA. In effect, stearic acid is dehydrogenated to give the monounsaturated derivative oleic acid.[24] Oleic acid undergoes the reactions of carboxylic acids and alkenes. It is soluble in aqueous base to give soaps called oleates. Hydrogenation of the double bond yields the saturated derivative stearic acid. Oxidation at the double bond occurs slowly in air and reduction of the carboxylic acid group yields oleyl alcohol. Ozonolysis of oleic acid is an important route to azelaic acid. The by-product is nonanoic acid. Esters of azelaic acid find applications in lubrication and plasticizers.

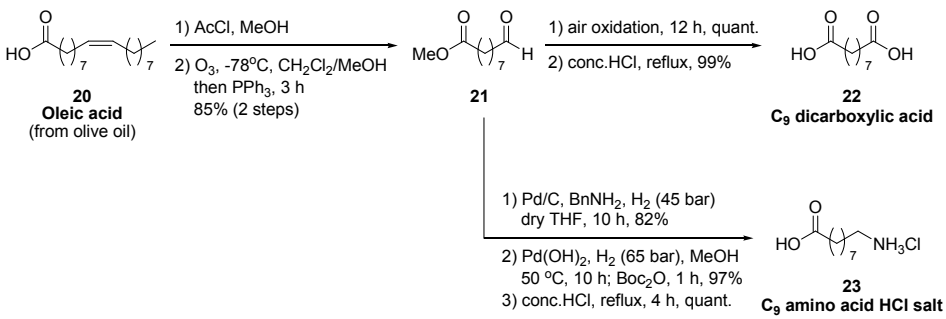
Oleic acid as its sodium salt is a major component of soap as an

emulsifying agent. It is also used as emollient. Small amounts of oleic acid are used as an excipient in pharmaceuticals, oleic acid is used as an emulsifying or solubilizing agent in aerosol products. Oleic acid is also used to induce lung damage in certain types of animals, for the purpose of testing new drugs and other means to treat lung diseases. Specifically in sheep, intravenous administration of oleic acid causes acute lung injury with corresponding pulmonary edema. This sort of research has been of particular benefit to premature newborns, for whom treatment for underdeveloped lungs (and associated complications) often is a matter of life and death.

2.2.2 Synthesis of C_9-C_{11} monomers from oleic acid

Our developed process with undecylenic acid can be applied to preparations of C_9-C_{11} monomers from oleic acid. When this process was conducted with oleic acid, number of carbon in aldehyde was the only difference. With a versatile aldehyde in hand, C_9-C_{11} dicarboxylic acid and ω-amino acid were synthesized in good yield with high purity.

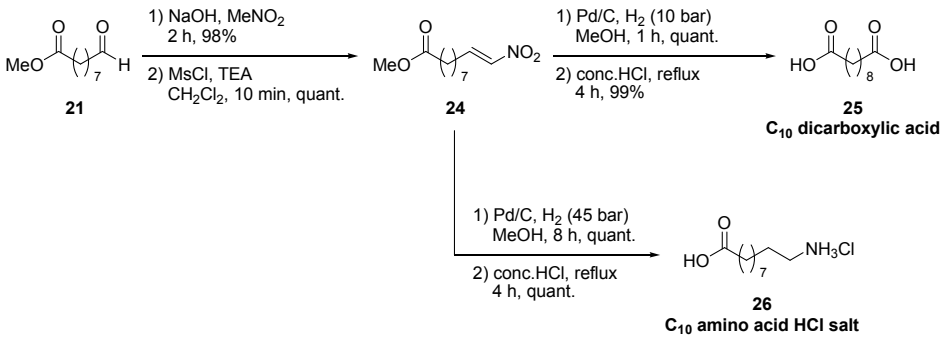
Preparation of the C_9 monomers from oleic acid **20** is shown in Scheme 7.



Scheme 7. Synthesis of C_9 monomers from oleic acid

Although the yield is relatively lower than undecylenic acid, C_9 aldehyde was obtained in good yield. The reason why lower yield is that is difficult to separate nonanol which is by-product of ozonolysis of oleic acid. When the ozonolysis reaction was scaled up, distillation was effective to remove nonanal first. As mentioned before, resulting aldehyde was labile to autoxidation. In the case of synthesis of C_9 dicarboxylic acid, conversion of aldehyde into carboxylic acid was conducted in the air atmosphere at room temperature. After full conversion of aldehyde into carboxylic acid, hydrolysis with conc.HCl under reflux condition gave a desired C_9 dicarboxylic acid **22** in 84% yield in 4 steps. Catalytic reductive amination of **21** with benzylamine under 45 bar of H_2 gas afforded C_9 ω-benzylamino ester. Following debenzylation and subsequent protection reaction afforded Boc-protected amino ester. After acidic hydrolysis gave the desired C_9 ω-amino acid **23** as its hydrochloride salt. Thus, the C_9 ω-amino acid monomer **23** was obtained in 68% yield over five steps starting from **20**.

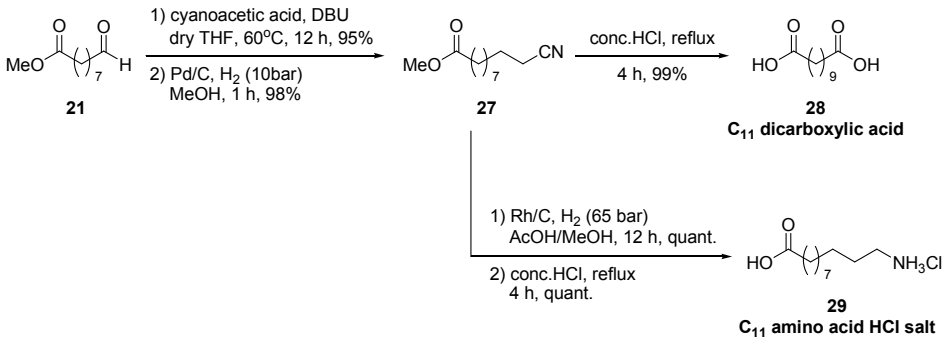
For the synthesis of C_{10} ω-amino acid and α,ω-dicarboxylic acid from the C_9 key intermediate **21**, Henry reaction was employed to introduce the desired functional groups as well as one more carbon (Scheme 8).



Scheme 8. Synthesis of C_{10} monomers from oleic acid

The desired nitroolefin **24** was produced in excellent yield from **21** in two steps by a sequence of a nitro-aldol reaction (Henry reaction) followed by dehydration with methanesufonyl chloride (MsCl). The partial reduction was complete within 1 h and provided desired nitroalkane in excellent yield, which was successfully converted into the desired C_{10} α,ω-dicarboxylic acid **25** under acidic hydrolysis conditions (Nef reaction). Catalytic hydrogenation of **24** under higher pressure of H_2 (45 bar) yielded the fully reduced amino ester in 8 h, which was hydrolysed under acidic conditions into the desired C_{10} ω-amino acid **26** as a hydrochloride salt. The C_{10} α,ω-dicarboxylic acid monomer **25** and the C_{10} ω-amino acid monomer **26** were obtained in 82% and 83% yields, respectively, over six steps starting from **20**.

Finally, a two-carbon extension from the C_9 intermediate **21** for the synthesis of the C_{11} α,ω-dicarboxylic acid and ω-amino acid monomers was possible with cyanoacetic acid (Knoevenagel condensation, Scheme 9).



Scheme 9. Synthesis of C_{11} monomers from oleic acid

The in-situ decarboxylative condensation of cyanoacetic acid with **21**

gave conjugated nitrile along with a non-conjugated isomeric mixture. Although a mixture of four olefinic isomers was obtained, it was not important because they were eventually transformed into the same compound **27** via partial hydrogenation. The following hydrolysis of **27** under acidic conditions produced the desired C_{11} α,ω-dicarboxylic acid **28** in 99% yield. Further reduction of **27** was carried out by catalytic hydrogenation with Rh/C at higher pressure (65 bar). The following acidic hydrolysis afforded C_{11} ω-amino acid **29** as its hydrochloride salt. Thus, the C_{11} α,ω-dicarboxylic acid monomer **28** and the C_{11} ω-amino acid monomer **29** were obtained in 78% yield over five steps and 79% yield over six steps, respectively, starting from **20**.

2.3 Synthesis of C_{13}-C_{15} monomers from rapeseed oil

2.3.1 Erucic acid from rapeseed oil

Since summer and winter forms of rapeseed (*B. napus*) are available, they can be planted as oil plant in climatically different regions of the world. A further advantage of rapeseed over other cultivated species is in its accessibility to biotechnological methods and, in particular, in its capability for transformation and regeneration.

Rapeseed oil is very rich in erucic acid, a widely sought raw material for many nonfood uses. In the context of improvement in nutritional oil quality, the low erucic acid varieties-named zero and double zero or canola types, which exhibit about 60% oleic acid – were developed by classical breeding methods, The breeding of linoleic acid deficient (<3%) or high oleic acid (>80%) rapeseed forms has been achieved both by induced mutation and genetically by inhibition of the inherent 12- or 15-desaturase genes. Anti-sense inhibition of

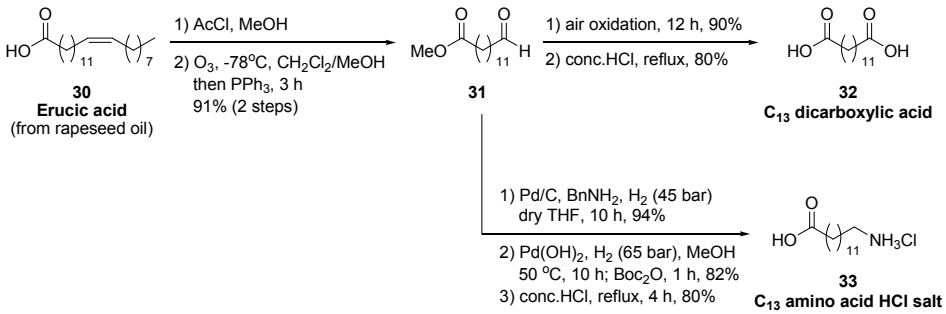
the desaturation step in *Brassica rapa* (a close relative of *B. napus*) yields up to 40% stearic acid in the seed oil and has been already tested under field conditions.

There is a constant demand for high erucic acid rapeseed oil for industrial use. Here, breeding is devoted to increasing the fraction of this very long chain fatty acid well above the current maximum of 55-60%. It has been known for a long time that, because of the nonoccupation of the middle of the three triacylglycerol positions by erucic acid, a (thereoretical) maximum of 67% cannot be exceeded. However, partial success was achieved recently when transgenic rape forms were developed with varying contents of trierucin (trierucoglycerol) in the seed oil by transfer of the gene for sn-2-acyltransferase (lyophosphatidic acid acyltransferase, LPAAT) from different *Limnanthes* species (meadow-foam) and by inhibition of the inherent LPAAT of rapeseed.[25]

2.3.2 Synthesis of C_{13}-C_{15} monomers from erucic acid

Our developed process can be also applied to preparations of C_{13}-C_{15} monomers from erucic acid. C_{13}-C_{15} dicarboxylic acids and ω-amino acids were not commercially available yet, except for C_{14} and C_{15} dicarboxylic acid. Since there are few researches about synthesis of long-chain aliphatic monomers for polyamide, it is worthy and useful. Although only a difference in number of carbon, C_{13}-C_{15} monomers show a quite different physical properties. Previous purification method could not applied to these monomers. Though all of monomers were prepared, further study for enhancement of purity should be conducted.

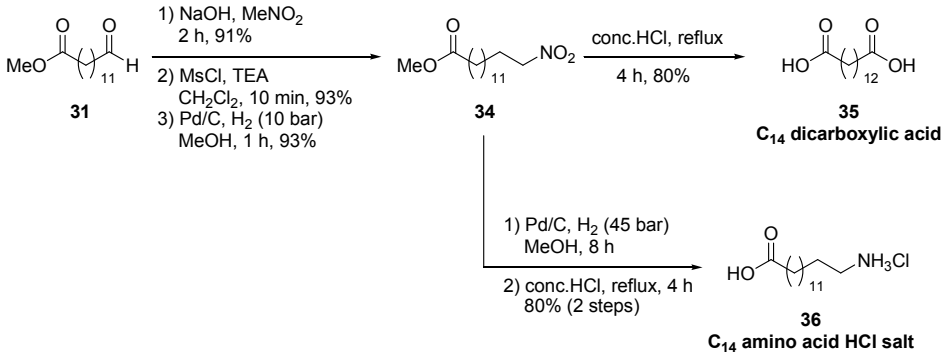
Preparation of the C_{13} monomers from erucic acid **30** is shown in Scheme 10.



Scheme 10. Synthesis of C_{13} monomers from erucic acid

For the preparation of C_{13} dicarboxylic acid and ω-amino acid, we first prepared the key aldehyde intermediate **31** from ozonolysis of methyl ester **30**. Resulting aldehyde was converted into carboxylic acid and hydrolyzed under acidic condition to give a C_{13} dicarboxylic acid **32** in 66% yield over 4 steps. Catalytic reductive amination of **31** with benzylamine under 45 bar of H_2 gas afforded C_{13} ω-benzylamino ester. Following debenzylation and subsequent protection reaction afforded Boc-protected amino ester. After acidic hydrolysis gave the desired C_{13} ω-amino acid **33** as its hydrochloride salt. Thus, the C_{13} ω-amino acid monomer **33** was obtained in 56% yield over five steps starting from **20**.

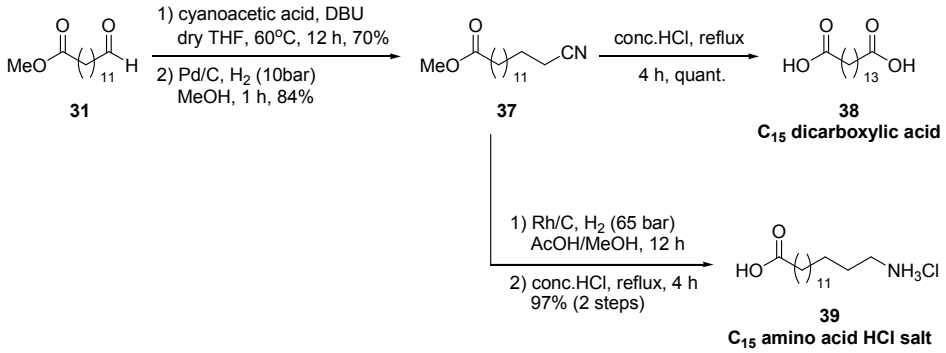
For the synthesis of C_{14} ω-amino acid and α,ω-dicarboxylic acid from the C_{13} key intermediate **31**, Henry reaction was employed to introduce the desired functional groups as well as one more carbon (Scheme 11).



Scheme 11. Synthesis of C_{14} monomers from erucic acid

The desired nitroolefin **34** was produced in high yield from **31** in two steps by a sequence of a nitro-aldol reaction (Henry reaction)[21] followed by dehydration with methanesufonyl chloride (MsCl). The partial reduction was complete within 1 h and provided desired nitroalkane **34** in 93% yield, which was successfully converted into the desired C_{14} α,ω-dicarboxylic acid **35** under acidic hydrolysis conditions (Nef reaction).[22] Catalytic hydrogenation of **34** under higher pressure of H_2 (45 bar) yielded the fully reduced amino ester in 8 h, which was hydrolysed under acidic conditions into the desired C_{14} ω-amino acid **36** as a hydrochloride salt. The C_{14} α,ω-dicarboxylic acid monomer **35** and the C_{14} ω-amino acid monomer **36** were obtained in 57% yield over six steps and 57% yield over seven steps, respectively, starting from **30**.

Finally, a two-carbon extension from the C_{13} intermediate **31** for the synthesis of the C_{15} α,ω-dicarboxylic acid and ω-amino acid monomers was possible with cyanoacetic acid (Knoevenagel condensation, Scheme 12).[23]



Scheme 12. Synthesis of C_{15} monomers from erucic acid

The in-situ decarboxylative condensation of cyanoacetic acid with **31** gave conjugated nitrile along with a non-conjugated isomeric mixture. Although a mixture of four olefinic isomers was obtained, it was not important because they were eventually transformed into the same compound **37** via partial hydrogenation. The following hydrolysis of **37** under acidic conditions produced the desired C_{15} α,ω-dicarboxylic acid **38** in quantitative yield. Further reduction of **37** was carried out by catalytic hydrogenation with Rh/C at higher pressure (65 bar). The following acidic hydrolysis afforded C_{15} ω-amino acid **39** as its hydrochloride salt. Thus, the C_{15} α,ω-dicarboxylic acid monomer **28** and the C_{15} ω-amino acid monomer **29** were obtained in 54% yield over five steps and 52% yield over six steps, respectively, starting from **30**.

2.4 Process improvement studies

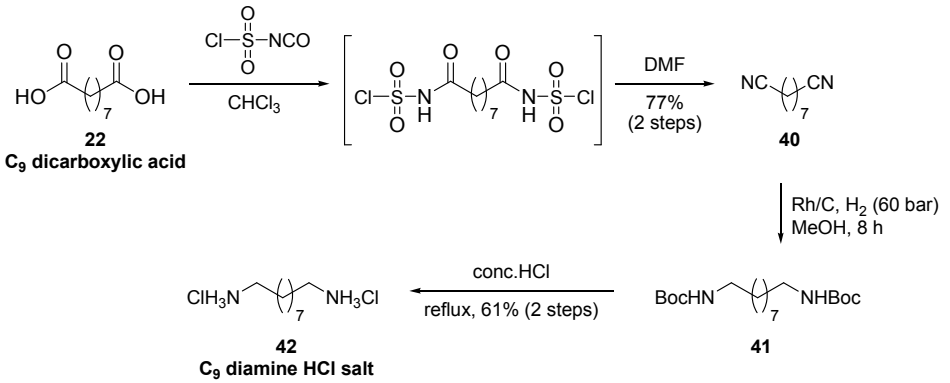
2.4.1 Synthesis of α,ω-diamine from α,ω-dicarboxylic acid

α,ω-Diamine is a essential monomer for the synthesis of Nylon. For example, hexamethylene diamine is an important monomer for the preparation

of Nylon-6,6 or Nylon-6,10. A successful and economical process for commercial preparations of substantially pure hexamethylene diamine is by continuous catalytic hydrogenation of adiponitrile in the presence of ammonia and a suitable catalyst, such as a nickel or cobalt catalyst, followed by purification of the hydrogenation product. Conventionally, the purification is accomplished by passing crude hexamethylene diamine through a series of distillation stills. A lot of efforts have been made to improve the overall economics of the process. But most of commercially available diamine was obtained from the petrochemicals. From this point of view, process development of diamine synthesis from renewable resources had received attention over the world. We had developed a process for the synthesis of α,ω-dicarboxylic acid from the natural oils. This process can overcome the limit of petrochemical-based monomer from the environmentally friendly viewpoint.

Synthesis of α,ω-diamine was conducted with azelaic acid **22** (nonaedioic acid) (Scheme 13). Carboxylic acid was converted into nitrile by 2 step sequence. We employed chlorosulfonyl isocyanate (CSI) for the conversion of carboxylic acid into the corresponding nitrile. CSI is known as a versatile reagent in organic synthesis which could be prepared by treating cyanogen chloride with sulfur trioxide. CSI has been employed for the preparation of β–lactams, some of which are medicinally important. And it can also be applied to cycloaddition to alkynes, conversion of primary alcohols to carbamates and preparation of N,N-disubstituted sulfamides. Resulting chlorosulfonyl intermediate stirred in DMF at room temperature until starting material was disappeared in thin-layer chromatography (TLC) and purified by column chromatography. Catalytic hydrogenation of dinitrile **40** under 60 bar of H_2 gas afforded crude diamine and subsequent Boc protection reaction afforded Boc-

protected diamine **41**. After acidic hydrolysis with concentrated hydrochloride gave the desired nonanediamine as a hydrochloride salt **42**.



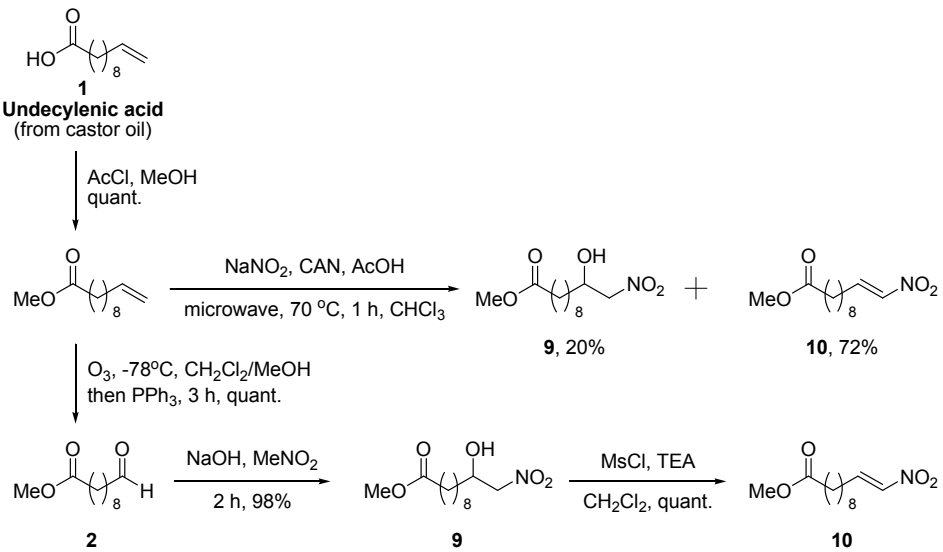
Scheme 13. Synthesis of nonanediamine from nonanedioic acid

If this process was applied to any other α,ω-dicarboxylic acid, desired α,ω-diamine could be easily obtained. In other words, to obtain desired α,ω-diamine, α,ω-dicarboxylic acid which have same number of carbons is all that's needed.

2.4.2 Microwave-assisted direct nitration

Amine moiety is a very important functionality in the chemistry of polyamide. Conventional introduction of the amine moiety was conducted by hydrogenation of nitrile or nitro group. There are a lot of attempts to give amine equivalent to alkene in a single step, but efficient result for the industry was not successful, yet. The hydroamination reaction was considered, but this reaction naturally occurred with a Markovnikov's product. So, synthetic approaches by using radical intermediate was studied. In 1996, efficient nitration process with

sodium nitrite ($NaNO_2$) and ceric ammonium nitrate (CAN) was reported.[26] According to their reported results, direct nitration of methyl undecylenate was conducted (Scheme 14). For the introduction of nitration, methyl undecylenate was used as a starting material. CAN generated a nitro radical from $NaNO_2$, and resulting radical was introduced to terminal alkene. The radical mechanism allows of the anti-Markovnikov reaction. Desired nitroolefin **10** was obtained in 72% yield, and the by-product **9** which can be easily converted to **10** was obtained in 20% yield at the same time. Though previous process including 4 steps shows a good efficiency (98%, 4 steps), newly developed direct nitration is no less efficient than previous one considering by-product can easily converted to desired product.



Scheme 14. Microwave-assisted direct nitration

2.5 Economic analysis of synthetic monomers

For TPEs and its monomers, Korea depends entirely on imports. The

technology of synthesis and production technologies are not exist in this country. The ultimate purpose of this project is concentrated on this problem. And the global issues on the green chemicals make this project as an important challenge. We developed a versatile and efficient process for the synthesis of monomers for TPEs. For securing the global competitiveness, economic analysis of the developed process is essential. Although industrial obtainable prices could not find, the prices from commercial suppliers in the laboratory are shown in Figure 8.

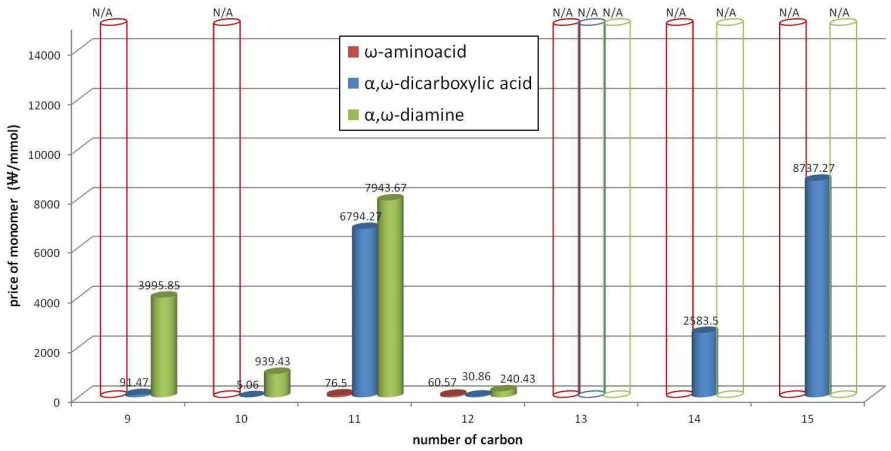


Figure 8. Prices of commercially available monomers for polyamides

The prices are investigated using the website of major commercial suppliers. Among the investigated prices, the lowest price per mmol is chosen and recorded at the top of the graph. C_{12} monomers are the cheapest monomers. While C_9 and C_{10} α,ω-dicarboxylic acid have very low price, same number of carbons of ω-amino acid are not commercially available. The odd number of carbons of α,ω-diamine shows a relatively high prices than the even number

carbon having α,ω-diamines. C_{13}-C_{15} α,ω-diamines and ω-amino acids are not available, therefore, it is obvious that our developed process have a global competitiveness. Although the process based on renewable resources are not efficient and economical in comparison with the petrochemical-based process, the potential of the eco-friendly process is worthy enough.

3. Summary and conclusions

We have developed a versatile and efficient process for three C_{10} to C_{12} α,ω-dicarboxylic acid monomers and three C_{10} to C_{12} ω-amino acid monomers of polyamides from one common starting material, undecylenic acid **1**, which can be easily obtained from castor oil. All of the C_{10} to C_{12} monomers were successfully synthesized in good to excellent yields. The C_{10} α,ω-dicarboxylic acid and ω-amino acid monomers, **8** and **6**, were obtained from the ozonolysis of **1** followed by appropriate transformations of the functional groups. The one-carbon extended nitroolefin **10**, produced from **1** in four steps and excellent yield, was the common precursor for both C_{11} α,ω-dicarboxylic acid and ω-amino acid monomers, **12** and **14**. The two-carbon extended C_{12} α,ω-dicarboxylic acid and ω-amino acid monomers, **17** and **19**, were resulted from the common precursor **16** that was produced from **1** in five steps and high yield. When this process was applied to oleic acid **20**, which is contained in most of vegetable oil, C_9 to C_{11} α,ω-dicarboxylic acids and ω-amino acids monomers could be obtained in good to excellent yields. In the case of erucic acid from rapeseed oil, C_{13} to C_{15} α,ω-dicarboxylic acids and ω-amino acids monomers could be obtained. Although high purity of C_{13} to C_{15} monomers were not obtained yet, availability of this process is fully proved (Table 3).

Table 3. Synthesis of monomer for polyamide from vegetable oils

	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}
Undecylenic acid		[a]quant. [b]79%	[a]74% [b]94%	[a]84% [b]83%			
Oleic acid	[a]84% [b]68%	[a]82% [b]83%	[a]78% [b]79%				
Erucic acid					[a]66% [b]56%	[a]57% [b]57%	[a]54% [b]52%

[a] overall yield of α,ω-dicarboxylic acids monomers

[b] overall yield of ω-amino acids monomers

It is also noteworthy that most of the reagents and the reaction conditions used in the present study are readily available and adjustable for an industrial development. And we expect that this versatile process would be another solution for the era of green chemistry.

4. Experimental details

Materials and methods. Materials were obtained from commercial suppliers and were used without further purification. 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). Infrared (IR) spectra were recorded on a JASCO FT-IR 200. Films for IR were spin-coated on silicon wafers. ^{1}H NMR spectra were measured on JEOL 300 MHz or Bruker 400 MHz while ^{13}C NMR spectra were measured on JEOL 75 MHz or Bruker 100 MHz. Tetramethylsilane was used as an internal reference (0.0 ppm): chemical shift (multiplicity, coupling constant in Hz, integration). Melting points were determined with an open capillary melting point apparatus and were uncorrected. High resolution mass spectra were obtained with a JEOL JMS-AX505WA mass spectrometer.

Decanedioic acid (8). A solution of undecylenic acid **1** (3.0 mL, 14.8 mmol) in dichloromethane (100 mL) and methanol (50 mL) was cooled to -78 ^{o}C, and a stream of ozone was bubbled into the reaction mixture until a light blue color became evident. Argon was then bubbled through the reaction mixture until the blue color disappeared and then was added 1 N aqueous NaOH solution (44.4 mL, 44.4 mmol). The reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated and washed with diethyl ether (50 mL x 2). The aqueous layer was acidified by conc. aqueous hydrochloric acid (7.5 mL) and extracted with ethyl acetate (50 mL x 3). The organic layers were dried over

$MgSO_4$, filtered and concentrated *in vacuo*. Decanedioic acid **8** (3.00 g, quantitative) was obtained as a white solid. Mp 131 ^oC [lit. 131-132 ^oC][27]; IR (KBr) 1696 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.99 (br s, 2 H), 2.19-2.17 (m, 4 H), 1.50-1.46 (m, 4 H), 1.31-1.20 (m, 8 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.9, 34.1, 29.1, 29.0, 24.9; HRMS (CI) calcd for $C_{10}H_{19}O_4$ $[M + H]^+$ 203.1283, found 203.1281.

Methyl 10-oxodecanoate (2). A solution of undecylenic acid **1** (10 mL, 49.4 mmol) in methanol (50 mL) was cooled to 0 ^oC and acetyl chloride (4.2 mL, 59.3 mmol) was added slowly. The reaction mixture was stirred at room temperature for 6 h, and the solvent was evaporated *in vacuo*. The mixture was diluted with ethyl acetate (75 mL) and washed with an aqueous solution of $NaHCO_3$ (75 mL x 2), and then with brine (75 mL x 2). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (1:8 v/v, EtOAc:hexane) afforded methyl undecylenate (9.79 g, quantitative) as a colorless liquid: IR (KBr) 3077, 1742, 1640 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.88-5.74 (m, 1 H), 5.02-4.91 (m, 2 H), 3.67 (s, 3 H), 2.30 (t, J = 7.5, 2 H), 2.07-2.00 (m, 2 H), 1.64-1.57 (m, 2 H), 1.39-1.28 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 139.2, 114.2, 51.5, 34.1, 33.8, 29.3, 29.2, 29.1, 29.1, 28.9, 25.0; HRMS (CI) calcd for $C_{12}H_{23}O_2$ $[M + H]^+$ 199.1698, found 199.1701.

A solution of methyl undecylenate (5.00 g, 25.2 mmol) obtained from the above in dichloromethane (100 mL) and methanol (50 mL) was cooled to -78 ^oC, and a stream of ozone was bubbled into the reaction mixture until a light blue color became evident. Argon was then bubbled through the reaction mixture until the blue color disappeared and then triphenylphosphine (7.28 g, 27.7 mmol) was

added. The reaction mixture was stirred at room temperature for 3 h. The solvent was evaporated, and the crude product was purified by silica gel column chromatography (1:8 v/v, EtOAc:hexane) to give methyl 10-oxodecanoate **2** (5.05 g, quantitative) as a colorless liquid: IR (KBr) 1738 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.77 (t, J = 1.8, 1 H), 3.68 (s, 3 H), 2.43 (dt, J = 1.8 and 7.3, 2 H), 2.31 (t, J = 7.5, 2 H), 1.62 (br s, 4 H), 1.36-1.26 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.0, 174.3, 51.5, 43.9, 34.0, 29.1, 29.1, 29.0, 24.9, 22.0; HRMS (CI) calcd for $C_{11}H_{21}O_3$ $[M + H]^+$ 201.1491, found 201.1492.

Methyl 10-(benzylamino)decanoate (3). To a solution of aldehyde **2** (355 mg, 1.77 mmol) in dry tetrahydrofuran (10 mL) was added benzylamine (1.0 mL, 9.14 mmol) under nitrogen atmosphere and the reaction mixture was stirred for 4 h at room temperature. To the reaction mixture was added 10 wt% palladium on carbon (18.0 mg, 0.018 mmol). The reaction mixture was stirred for 10 h under 45 bar of hydrogen atmosphere and the resulting mixture was filtered through a celite pad with excess methanol. The filtrate was concentrated *in vacuo*. Purification by silica gel column chromatography (1:20 v/v, MeOH:CH_2Cl_2) afforded methyl 10-(benzylamino)decanoate **3** (414 mg, 81%) as a colorless liquid. IR (coated on silicon wafer) 3325, 1738, 1199, 1172 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.25 (m, 5 H), 3.78 (s, 2 H), 3.66 (s, 3 H), 2.62 (t, J = 7.3, 2 H), 2.29 (t, J = 7.6, 2 H), 1.64-1.55 (m, 2 H), 1.53-1.42 (m, 2 H), 1.35-1.24 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 140.4, 128.4, 128.1, 126.9, 54.0, 51.4, 49.4, 34.1, 30.0, 29.4, 29.4, 29.2, 29.1, 27.3, 24.9; HRMS (CI) calcd for $C_{18}H_{30}NO_2$ $[M + H]^+$ 292.2277, found 292.2279.

Methyl 10-(tert-butoxycarbonylamino)decanoate (5). To a solution of **3** (520

mg, 1.78 mmol) in methanol (25 mL) was added 20 wt% palladium hydroxide on carbon (52.0 mg, 0.074 mmol). The reaction mixture was stirred for 10 h at 50 ^{o}C under 65 bar of hydrogen atmosphere and then filtered through a celite pad with excess methanol. The filtrate was concentrated *in vacuo* to give the free amine as a crude product. Di-tert-butyl dicarbonate (0.46 mL, 2.14 mmol) was added to a solution of the crude free amine in methanol (5.0 mL) and the reaction mixture was stirred for 1 h and concentrated *in vacuo*. Purification by silica gel column chromatography (1:4 v/v, EtOAc:hexane) afforded methyl 10-(tert-butoxycarbonylamino)decanoate **5** (529 mg, 99%) as a white solid. Mp 44 ^{o}C; IR (coated on silicon wafer) 3385, 1732, 1690, 1516, 1168 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49 (br s, 1 H), 3.67 (s, 3 H), 3.09 (app. q, J = 6.4, 2 H), 2.30 (t, J = 7.6, 2 H), 1.63-1.58 (m, 2 H), 1.50-1.40 (m, 11 H), 1.26-1.34 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 156.0, 85.2, 51.4, 40.6, 34.1, 30.0, 29.3, 29.2, 29.1, 29.1, 28.4, 26.8, 24.9; HRMS (CI) calcd for $C_{16}H_{32}NO_4$ $[M + H]^+$ 302.2331, found 302.2332.

10-Aminodecanoic acid hydrochloride salt (6). A mixture of conc. aqueous hydrochloric acid (5.0 mL) and the Boc-protected amino ester **5** (474 mg, 1.57 mmol) was heated under reflux for 4 h. The resulting reaction mixture was diluted with water (20 mL) and washed by dichloromethane (20 mL x 2) and ethyl acetate (20mL). The aqueous layer was concentrated *in vacuo*. The crude product was purified by recrystallization in water/acetone to give 10-aminodecanoic acid hydrochloride salt **6** (344 mg, 98%) as a white solid. Mp 157 ^{o}C [lit. 157-159 ^{o}C][28]; IR (coated on silicon wafer) 3206-2974 (br), 1726, 1583 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.99 (br s, 1 H), 7.84 (br s, 3 H), 2.80-2.70 (m, 2 H), 2.19 (t, J = 7.4, 2 H), 1.58-1.44 (m, 4 H), 1.34-1.22 (m, 10

H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.9, 39.2, 34.1, 29.1, 29.1, 29.0, 28.9, 27.3, 26.3, 24.9; HRMS (CI) calcd for $C_{10}H_{22}NO_2$ $[M - Cl]^+$ 188.1651, found 188.1647.

Methyl 11-nitroundec-10-enoate (10). A mixture of nitromethane (4.0 mL, 73.8 mmol) and aldehyde **2** (1.08 g, 5.39 mmol) was stirred at 0 ^oC. Sodium hydroxide (237 mg, 5.93 mmol) was added slowly. The reaction mixture was stirred at room temperature for 2 h. The mixture was diluted with diethylether (30 mL) and washed with an aqueous solution of saturated NH_4Cl (30 mL x 3), and brine (30 mL x 2). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (1:4 v/v, EtOAc:hexane) afforded the nitroalcohol intermediate **9** (1.38 g, 98%) as a white solid. Mp 56-57 ^oC: IR (coated on silicon wafer) 3426, 2925, 1722, 1557, 1357 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.46-4.31 (m, 3 H), 3.67 (s, 3 H), 2.55-2.52 (m, 1 H), 2.31 (t, J = 7.5, 2 H), 1.64-1.58 (m, 2 H), 1.51-1.47 (m, 2 H), 1.39-1.31 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 80.6, 68.6, 51.5, 34.1, 33.6, 29.2, 29.1, 29.0, 25.1, 24.9; HRMS (CI) calcd for $C_{12}H_{24}NO_5$ $[M + H]^+$ 262.1654, found 262.1656.

To a solution of the nitroalcohol intermediate **9** (1.19 g, 4.55 mmol) in dichloromethane (10 mL) was added triethylamine (0.46 mL, 5.92 mmol) at 0 ^oC, and then methanesulfonyl chloride (1.6 mL, 11.4 mmol) was added dropwise. The resulting mixture was stirred for 10 min at room temperature and then was diluted with diethylether (50 mL) and washed with an aqueous solution of saturated $NaHCO_3$ (60 mL x 2), and then with brine (60 mL x 2). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (1:4 v/v, EtOAc:hexane)

afforded nitroolefin **10** (1.09 g, 98%) as a pale yellow liquid: IR (coated on silicon wafer) 1738, 1649, 1525, 1353 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33-7.23 (m, 1 H), 6.98 (d, J = 13.4, 1 H), 3.67 (s, 3 H), 2.31 (t, J = 7.6, 2 H), 2.28-2.23 (m, 2 H), 1.64-1.59 (m, 2 H), 1.53-1.46 (m, 2 H), 1.31 (br s, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 142.8, 139.6, 51.5, 34.0, 29.1, 29.1, 29.0, 29.0, 28.4, 27.7, 24.9; HRMS (CI) calcd for $C_{12}H_{22}NO_4$ $[M + H]^+$ 244.1549, found 244.1548.

Methyl 11-nitroundecanoate (11). To a solution of nitroolefin **10** (213 mg, 0.88 mmol) in methanol (5 mL) was added 10 wt% palladium on carbon (10.7 mg, 0.010 mmol). The reaction mixture was stirred at room temperature for 1 h under 10 bar of hydrogen atmosphere and filtered through a celite pad with excess methanol. The combined filtrates were concentrated *in vacuo*. Purification by silica gel column chromatography (1:2 v/v, EtOAc:hexane) afforded nitroalkane **11** (210 mg, 98%) as a colorless liquid: IR (coated on silicon wafer) 1738, 1554, 1377 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.38 (t, J = 7.1, 2 H), 3.67 (s, 3H), 2.30 (t, J = 7.5, 2H), 2.05-1.96 (m, 2 H), 1.64-1.59 (m, 2 H), 1.34-1.28 (m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 75.7, 51.5, 34.1, 29.2, 29.1, 29.1, 28.8, 27.4, 26.2, 24.9; HRMS (CI) calcd for $C_{12}H_{24}NO_4$ $[M + H]^+$ 246.1705, found 246.1703.

Undecanedioic acid (12). A solution of nitroalkane **11** (66.0 mg, 0.27 mmol) in conc. aqueous hydrochloric acid (10 mL) was heated under reflux for 4 h and then concentration of the reaction mixture *in vacuo* afforded undecanedioic acid **12** (46.0 mg, 79%) as a white solid after recrystallization in water. Mp 99-102 ^oC [lit. 131-132 ^oC][29]; IR (coated on silicon wafer) 1696 cm^{-1}; ^1H NMR (400

MHz, DMSO-d_6) δ 11.99 (br s, 2 H), 2.19 (t, J = 7.4, 4 H), 1.50-1.46 (m, 4 H), 1.29-1.22 (m, 10 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.8, 33.3, 28.6, 28.6, 28.4, 24.6; HRMS (CI) calcd for $C_{11}H_{21}O_4$ $[M + H]^+$ 217.1440, found 217.1443.

11-Aminoundecanoic acid hydrochloride salt (14). To a solution of nitroolefin **10** (680 mg, 2.78 mmol) in methanol (5 mL) was added 10 wt% palladium on carbon (68.0 mg, 0.063 mmol). The reaction mixture was stirred for 10 h at room temperature under 45 bar of hydrogen atmosphere and then filtered through a celite pad with excess methanol. The combined filtrates were concentrated *in vacuo* and the resulting crude oil was refluxed with conc. aqueous hydrochloric acid (20 mL) for 2.5 h. The resulting reaction mixture was concentrated *in vacuo*. The crude product was purified by recrystallization in water/acetone to give 11-aminoundecanoicacid hydrochloride salt **14** (650 mg, 98%) as a white solid. Mp 144-145 ^{o}C [lit. 144-145 ^{o}C][30]; IR (coated on silicon wafer) 3206-2975 (br), 1725, 1584 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.0 (br s, 1 H), 7.91 (br s, 3 H), 2.76-2.73 (m, 2 H), 2.19 (t, J = 7.4, 2 H), 1.53-1.46 (m, 4 H), 1.31-1.22 (m, 12 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.9, 39.2, 34.2, 29.2, 29.2, 29.0, 29.0, 27.4, 26.3, 25.0; HRMS (CI) calcd for $C_{11}H_{24}NO_2$ $[M - Cl]^+$ 202.1807, found 202.1804.

Methyl 11-cyanoundec-10-enoate (15a) / Methyl 11-cyanoundec-9-enoate (15b). To a solution of aldehyde **2** (1.50 g, 7.49 mmol) and cyanoacetic acid (960 mg, 11.2 mmol) in tetrahydrofuran (15 ml) under nitrogen atmosphere was added DBU (4.56 g, 30.0 mmol). The reaction mixture was heated at 60 ^{o}C for 12 h and then was extracted with ethyl acetate (60 mL x 2) and distilled water (60 mL x 2). The combined organic extracts were dried over $MgSO_4$, filtered

and concentrated *in vacuo*. Purification by silica gel column chromatography (1:8 v/v, EtOAc:hexane) afforded a mixture of nitriles **15a** and **15b** (1.44 g, 86%, **15a**:**15b** = 86:14 by GC/MSD) as colorless liquid. IR (coated on silicon wafer) 2224, 1739, 1629 cm^{-1}; HRMS (CI) calcd for $C_{13}H_{22}NO_2$ $[M + H]^+$ 224.1651, found 224.1647.

Methyl 11-cyanoundecanoate (16). To a solution of methyl 11-cyanoundecenoate **15** (**15a** and **15b**, 2.93 g, 12.6 mmol) in methanol (6 mL) was added 10 wt% palladium on carbon (29.3 mg, 0.028 mmol). The reaction mixture was stirred for 1 h at room temperature under 10 bar of hydrogen atmosphere and then filtered through a celite pad with excess methanol. The combined organic filtrates were concentrated *in vacuo*. Purification by silica gel column chromatography (1:4 v/v, EtOAc:hexane) afforded methyl 11-cyanoundecanoate **16** (2.78 g, 98%) as a colorless liquid. IR (coated on silicon wafer) 2246, 1738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 3 H), 2.34 (t, J = 7.2, 2 H), 2.30 (t, J = 7.6, 2 H), 1.69-1.60 (m, 4 H), 1.46-1.40 (m, 2 H), 1.33-1.26 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 119.8, 51.4, 34.0, 29.2, 29.2, 29.1, 29.1, 28.7, 28.6, 25.3, 24.9, 17.1; HRMS (CI) calcd for $C_{13}H_{24}NO_2$ $[M + H]^+$ 206.1807, found 206.1807.

Dodecanedioic acid (17). Methyl 11-cyanoundecanoate **16** (177 mg, 0.76 mmol) was heated under reflux with conc. aqueous hydrochloric acid (10 mL) for 4 h and the resulting mixture was concentrated *in vacuo*. The residue was purified by recrystallization in water/MeOH to give dodecanedioic acid **17** (175 mg, quantitative) as a white solid. Mp 126-127 ^oC [lit. 127-128 ^oC][31]; IR (KBr) 1693 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.97 (br s, 2 H), 2.16 (t, J = 7.4, 4 H),

1.47-1.44 (m, 4 H), 1.32-1.21 (m, 12 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.5, 33.7, 28.9, 28.8, 28.6, 24.5; HRMS (CI) calcd for $C_{12}H_{23}O_4$ $[M + H]^+$ 231.1596, found 231.1596.

12-Aminododecanoic acid hydrochloride salt (19). To a solution of methyl 11-cyanoundecanoate **16** (300 mg, 1.29 mmol) in methanol (6 mL) and acetic acid (6 mL) was added 5 wt% Rhodium on carbon (60 mg, 0.029 mmol). The reaction mixture was stirred for 12 h at room temperature under 65 bar of hydrogen atmosphere and then filtered through a celite pad with excess methanol. The combined filtrates were concentrated to afford methyl 12-aminododecanoate acetic acid salt **18** as a white solid. The crude product **18** was used for the next reaction without further purification. Mp 79-80 ^{o}C; IR (coated on silicon wafer) 1732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (br s, 3 H), 3.66 (s, 3 H), 2.77 (t, J = 7.6, 2 H), 2.30 (t, J = 7.4, 2 H), 1.93 (s, 3 H), 1.63-1.58 (m, 4 H), 1.35-1.23 (m, 14 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 174.3, 51.4, 39.6, 34.1, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 28.3, 26.7, 25.0, 24.6; HRMS (CI) calcd for $C_{13}H_{28}NO_2$ $[M - C_2H_3O_2]^+$ 230.2120, found 230.2114.

Methyl 12-aminododecanoate acetic acid salt **18** from the above was heated under reflux with conc. aqueous hydrochloric acid (10 mL) for 2.5 h. Concentration *in vacuo* afforded 12-aminoundodecanoic acid hydrochloride salt **19** (277 mg, 86%) as a white solid. Mp 162 ^{o}C [lit. 163-164 ^{o}C][32]; IR (coated on silicon wafer) 3212-2991 (br), 1726, 1584 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.00 (br s, 1 H), 8.05 (br s, 3 H), 2.77-2.69 (m, 2 H), 2.19 (t, J = 7.2, 2 H), 1.56-1.46 (m, 4 H), 1.31-1.21 (m, 14 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.4, 38.6, 33.6, 28.8, 28.8, 28.7, 28.5, 26.8, 25.8, 24.4; HRMS (CI) calcd for $C_{12}H_{26}NO_2$ $[M - Cl]^+$ 216.1964, found 216.1960.

Nonanedioic acid (22). Mp 107-108 °C [lit. 106-107 °C][33]; IR (KBr) 1705 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 2.18 (t, J = 7.3, 4 H), 1.47 (q, 4 H), 1.23-1.27 (m, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.9, 34.0, 28.9, 28.8, 24.9; HRMS (CI) calcd for $C_9H_{17}O_4$ $[M + H]^+$ 189.1127, found 189.1125.

9-Aminononanoic acid hydrochloride salt (23). Mp 133-135 °C [lit. 132-133 °C][34]; IR (KBr) 3434, 1725, 1585 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 2.74 (t, J = 7.6, 2 H), 2.19 (t, J = 7.4, 2 H), 1.46-1.54 (m, 4 H), 1.24-1.27 (m, 8 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.9, 39.1, 34.1, 28.9, 28.8 (2C), 27.3, 26.2, 24.9; HRMS (CI) calcd for $C_9H_{20}NO_2$ $[M - Cl]^+$ 174.1494, found 174.1494.

Tridecanedioic acid (32). ^1H NMR (400 MHz, DMSO-d_6) δ 11.97 (br s, 2 H), 2.20-2.18 (m, 4 H), 1.48-1.40 (m, 4 H), 1.24 (br s, 14 H).

13-Aminotridecanoic acid hydrochloride salt (33). ^1H NMR (400 MHz, DMSO-d_6) δ 2.80-2.70 (m, 2 H), 2.19 (t, J = 7.4, 2 H), 1.58-1.44 (m, 4 H), 1.34-1.22 (m, 16 H).

Tetradecanedioic acid (35). ^1H NMR (400 MHz, DMSO-d_6) δ 2.18 (t, J = 7.8, 4 H), 1.48 (m, J = 6.8, 4 H), 1.19 (s, 16 H).

14-Aminotetradecanoic acid hydrochloride salt (36). ^1H NMR (400 MHz, DMSO-d_6) δ 2.75 (t, J = 7.6, 2 H), 2.18 (t, J = 7.8, 2 H), 1.53-1.48 (m, 4 H), 1.24 (br s, 18 H).

Pentadecanedioic acid (38). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.96 (br s, 2 H), 2.18 (t, J = 7.4, 4 H), 1.48 (t, J = 6.8, 4 H), 1.24 (m, 18 H).

15-Aminopentadecanoic acid hydrochloride salt (39). ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.75 (t, J = 6.6, 2 H), 2.18 (t, J = 7.4, 2 H), 1.58-1.44 (t, J = 7.6, 4 H), 1.24 (m, 20 H).

Part II. Synthesis of the dissolution inhibitors and the negative tone photoresists for ArF photolithography

1. Introduction

A remarkable advancement on a semiconductor through photolithography has contributed to wide range of industry, such as computer, mobile equipment and display. The most important categories of the semiconductor technology are miniaturization and large scale integration. Smartphone is the representative product of the cutting edge technology with semiconductor. Photolithography plays a very important role in the development of semiconductor. The word "lithography" comes from the Greek *lithos*, meaning stones, and *graphia*, meaning to write. It means quite literally writing on stones. In the case of semiconductor lithography (also called photolithography), "stones" are "silicon wafers" and "patterns" are "written with a light sensitive polymer, photoresist". To build the complex structures that make up a transistor and the many wires that connect the millions of transistors of a circuit, lithography and etch pattern transfer steps are repeated at least 10 times, but more typically are done 20 to 30 times to make one circuit. Each pattern being transferred on the wafer is aligned to the previously formed patterns and slowly the conductors, insulators, and selectively doped regions are built up to form the final device.

Until recently, the semiconductor technology has quickly developed along with Moore's law which is the observation that the number of transistors in a dense integrated circuit doubles approximately every 18 months. But, the speed of semiconductor's development has markedly slowed after the appearance of sub-20nm transistor. In spite of significant development of light-source

equipment, the technological gap between practical process and cutting edge technology still remains a critical problem.

From this point of view, we suggest two strategies which can be overcome the resolution limit of current photolithography with ArF light without a considerable change in the practical process. First one is the addition of novel calixarene-based dissolution inhibitors. Although dissolution inhibitor is the well-known additives to photoresists which can efficiently enhance the contrast, it has not applied to the ArF photoresists So we designed two novel dissolution inhibitors from calixarene, which is studied in the molecular photoresists in KrF, and evaluated the lithographic performances. And another is design of the unprecedented negative tone photoresist. Conventional negative tone image on wafer was embodied by negative tone photoresist which formed the crosslink bond after irradiation. Or organic developer can make the negative tone image, but it is already dominated by overseas patent. So we designed a new conceptual photoresists which can make a negative tone with a practical process. We thought that organic synthetic technology can be a good alternative to overcome the resolution limit of the current photolithography.

2. Synthesis of the dissolution inhibitors

2.1 Introduction

2.1.1 Dissolution inhibitor

The resolution limit of photolithography has been overcome by the introduction of pattern multiplication processes. However, selection of a photoresist is still one of the key factors as minimum resolution is primarily defined by the first photo-pattern itself. To achieve the required performance, commercial ArF photoresists have complex formulations comprising multiple resins with various monomers, photoacid generators (PAGs), and even a couple of photo-decomposable quenchers.[35]

ArF photoresists basically use acrylate resins with various pendant groups.[36] Among the pendant groups, acid-labile units (ALUs) act as a polarity switcher to separate patterns between exposed and unexposed areas.[37] The contrast of the photoresist is influenced by the activation energy (E_a) of ALUs.[38] In KrF photoresists, one of the most used ALUs is an acetal functionality that has a low E_a.[39] However, ArF photoresists cannot use an ALU with low E_a due to its chemical instability. To overcome this limitation, PAGs with stronger acidity have been developed for a wide range of applications in ArF photoresists.

Addition of dissolution inhibitors (DIs) to photoresists can also help enhance the contrast. DIs are a class of small molecules with ALUs. Various functional groups have been used in DIs such as carbonates or acetals of phenols, and esters or orthoesters of carboxylic acids.[40] They tend to exist in free volume between the polymer chains of the base resin and form stable

intermolecular interaction with the base resin to enforce the film density of the photoresist film.[41] When the photoresist is exposed to a light source, the DIs with an ALU decompose to disclose a base-soluble functional group and change the physical property of the DI molecules to be washed out rapidly by a developer such as TMAH.[42] Since Reichmanis *et al.* had introduced a novel two component photoresist containing DIs,[43] several reports about DIs have been published (Figures 9 and 10).[44]

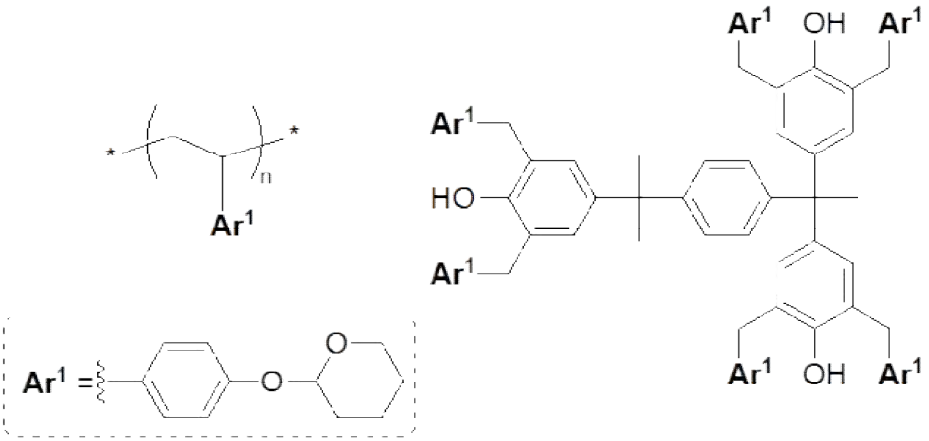


Figure 9. Dissolution inhibitors for KrF (248 nm).

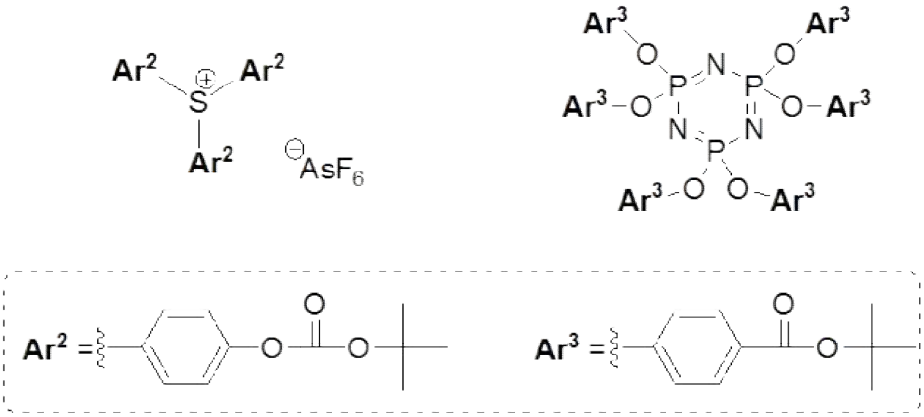


Figure 10. Dissolution inhibitors for E-beam.

Researchers at Toshiba reported the significant improvement of sensitivity from 50-60 mJ/cm^2 to 28 mJ/cm^2 when the photoresists containing a DI were exposed to 193 nm light.[45] They used an adamantane-based compound or a naphthol novolac-based polymer as the DI but more than 20 wt% of the DI was needed (Figure 11).

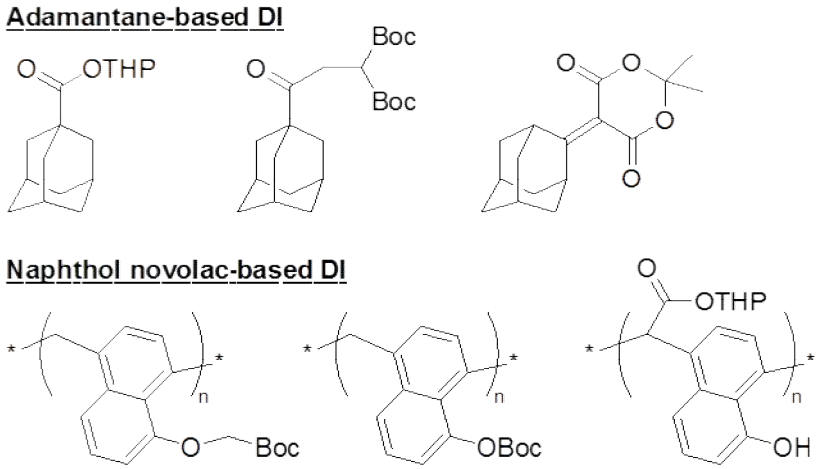


Figure 11. Dissolution inhibitors for ArF (193 nm) by Toshiba.

Calixarenes and their derivatives have been studied as macromolecular photoresists for g-line (436 nm),[46] i-line (365 nm),[47] KrF (248 nm),[48] EUV (13.5 nm)[49] and E-beam,[50] except for ArF (193 nm). We thought that some advantageous properties of the calixarenes as photoresists could be utilized as DIs with an ALU of low E_a to enhance the resolution of the photoresists. To the best of our knowledge, they have been used as DIs in KrF photoresists[24] but not in ArF photoresists. Herein, we wish to report convenient syntheses of two novel calixarene-based DIs and their applications to efficiently improve the contrast of ArF photoresists.

2.1.2 Calixarenes in photolithography

Calixarene is a macrocycle or cyclic oligomer based on a hydroxyl alkylation product of phenols and aldehydes. Calixarenes have hydrophobic cavities that can hold smaller molecules or ions and belong to the class of cavitands known as host-guest chemistry. In 1940s, Zinke & Ziegler discovered base-induced reaction of p-alkylphenols with formaldehyde, which yields cyclic oligomers. Then, synthesis of cyclic oligomers was reported. Calixarenes can be used as ion sensitive electrodes or sensors, optical sensors, chiral recognition devices for solid phase exraction, as a stationary phase and modifiers. Several books and reviews covered synthesis, properties and applications of calixarenes.[51]

In the case of photolithography, the calixarenes were initially used as a molecular resist. While negative tone solvent-developed calix[6]arene and calix[7]arene resists were demonstrated by NEC researchers to produce high-resolution patterns (at a very high electron beam dose), the use of polyphenolic calix[4]resocinarenes as molecular glass chemical amplification resists was pioneered by Ueda and co-workers. Calix[4]resorcinarenes, which are produced by the condensation of resorcinol with aldehydes, have eight phenolic hydroxyl groups, which could be protected with acid-labile groups. Initially, Ito's group was interested in calix[4]resocinarenes as a platform for molecular glass resists, but because their film-forming property was not high enough, they have decided to evaluate protected calixarenes as dissolution inhibitors in phenolic resists.[52]

2.2 Results and discussion

2.2.1 Preparations of dissolution inhibitors

In this study, two DIs have been prepared by using calix[4]arene (Figure 12). **DI-1** is a MOM-protected calix[4]arene with an ALU of low E_a. **DI-2** has an ALU of medium E_a (t-Boc). The activation energy for MOM deprotection was reported to be 13.2 kcal/mol, while that for t-Boc deprotection was 28.6 kcal/mol.[53]

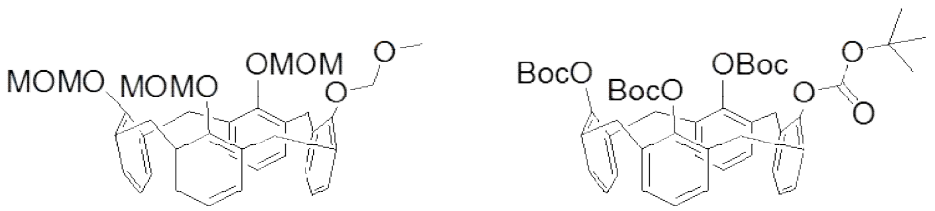
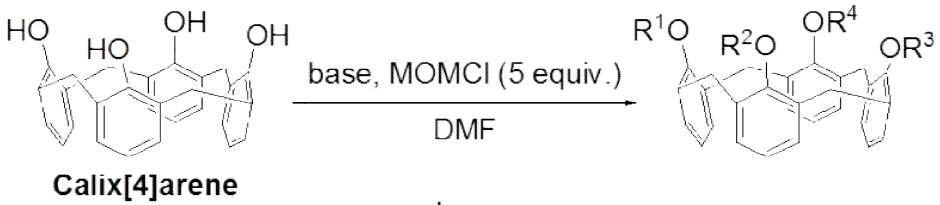


Figure 12. The DIs prepared in the present study, **DI-1** and **DI-2**.

Even though the MOM protection of a hydroxy group is a well-established reaction,[54] finding the proper reaction conditions to protect all the four hydroxy groups in one pot was necessary in the case of calix[4]arene (Scheme 15). While a poor yield of mono-*O*-MOM-calix[4]arene **DI-3** was obtained in DMF as a solvent with 5 equiv. of K_2CO_3 (Table 4, entry 1), di-*O*-MOM-calix[4]arene **DI-4** was produced in moderate yields with a large excess of K_2CO_3 (>10 equiv.) (entries 2 and 3). Although tetra-*O*-MOM-calix[4]arene **DI-1** could not be obtained with K_2CO_3, it was prepared by using an excess of stronger base, NaH, in DMF (entry 4). **DI-1** was obtained in a 73% yield as a

white solid after recrystallization in EtOAc and hexane.



Calix[4]arene

	R^1	R^2	R^3	R^4
DI-1	MOM	MOM	MOM	MOM
DI-3	MOM	H	H	H
DI-4	MOM	H	MOM	H

Scheme 15. Preparation of MOM-protected calix[4]arenes.

Table 4. The MOM protection of calix[4]arene.

Entry	Base	Equiv.	Product	Yield[a]
1	K_2CO_3	5	**DI-3**	8%
2	K_2CO_3	10	**DI-4**	45%
3	K_2CO_3	20	**DI-4**	48%
4	NaH	10	**DI-1**	73%

[a] Yield of purified product after recrystallization

Tetra-*O*-Boc-protected calix[4]arene **DI-2** was synthesized under the same reaction conditions as those for **DI-1** in a 58% yield after purification. Boc protecting group is the most widely used functionality in the chemical amplification resist (CAR). And it also used in designing acid-labile dissolution inhibitors for positive type resists. With the synthesized two DIs in hand, lithographic evaluation was conducted in 193 nm photolithography.

2.2.2 Lithographic evaluations

First, to observe the effect of the DIs on the sensitivity and the contrast of ArF photoresists, **DI-1** and **DI-2** were added to a commercial ArF photoresist. The quantity of the **DI-1** and **DI-2** were controlled to be 1, 2 and 3 wt% of the resin. Regardless of the DIs used, the contrast curves of all the photoresists with a DI were similar to that of the photoresist without a DI (Figure 13). However, both the sensitivity and the contrast ratio of the photoresists with a DI were substantially improved when even a small amount of any DI was added. Contrast ratio, γ, is the slope the line at the steepest part of the curve and defined as:

$$\gamma = 1/[\log_{10}(D_f/D_0)]$$

Where D_0 is the minimum exposure required for the photoresist reacting to light and D_f, also called a sensitivity, is the exposure *E* dose for complete removal of photoresist. The photoresist without a DI exhibited the sensitivity of 24 mJ/cm^2 with the contrast ratio of 17 after exposure to 193 nm light and PEB treatment at 110 ^{o}C. When 1 wt% of **DI-1** was added to the photoresist, the sensitivity of 19 mJ/cm^2 and the contrast ratio of 21 were measured. The photoresists with more than 2 wt% of **DI-1** gave the higher contrast ratio of 38 and the sensitivity of 17 mJ/cm^2. In the case of **DI-2**, the similar performance could be obtained by using more than 3 wt% of **DI-2**. Therefore, the sensitivity of the photoresists was increased by 21-29% with addition of a small amount of **DI-1** or **DI-2** (1 to 3 wt%) to the commercial ArF photoresist. In addition, **DI-1** with low E_a of the ALU makes the photoresists more sensitive to the exposure energy and could improve the efficiency of the lithography process itself. As mentioned before, one of the limitations of ArF photoresists is that the use of

low E_a resins is difficult due to the instability issues. The use of **DI-1** and **DI-2** as an additive to ArF photoresists shows a way to overcome the weakness.

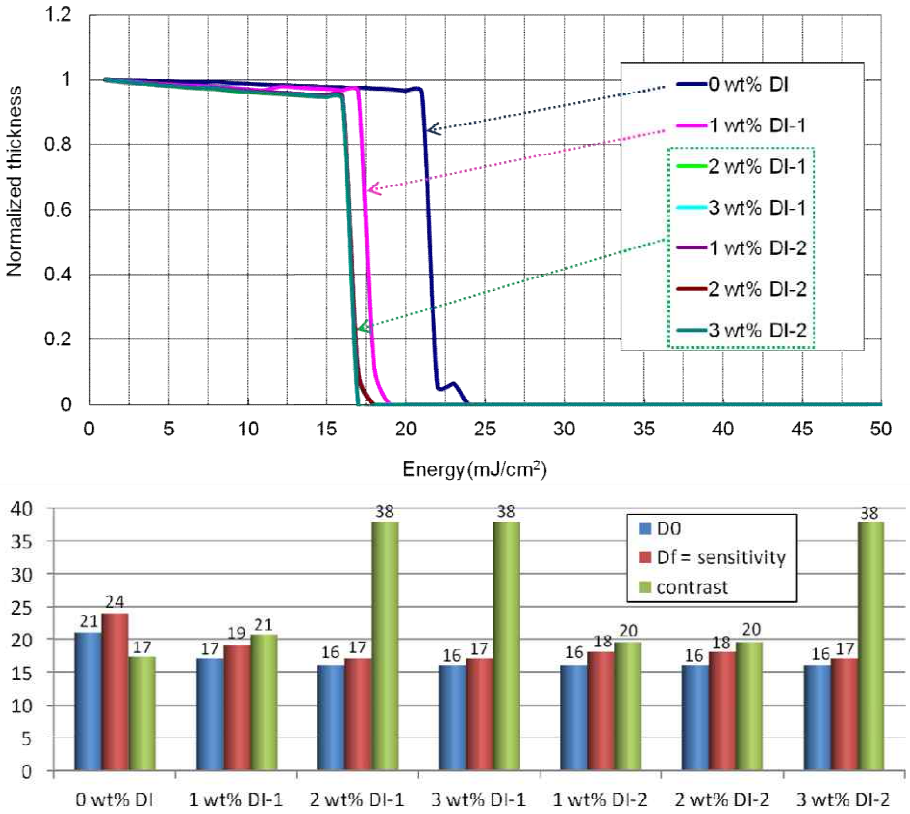


Figure 13. Contrast curves of the photoresists with **DI-1** and **DI-2**.

Overall lithographic performance of the photoresists was observed on both 200 nm dense and iso line/space (L/S) patterns. On the dense L/S pattern, no significant difference was observed as optimal light dose and focus was retained. However, on the iso L/S pattern, the reference photoresist showed broad focus shift whereas DI added samples showed narrower focus shift. This indicates that the addition of the DIs was effective on the improvement of the

dark-bright field bias of the photoresist (Figure 14).

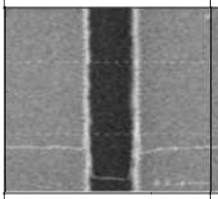
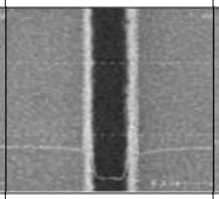
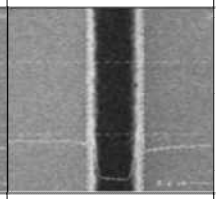
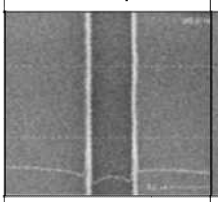
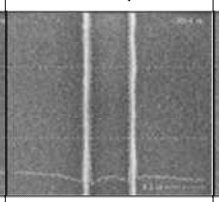
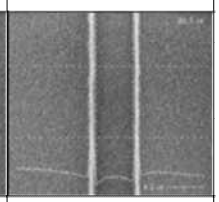
0 wt% DI (48 mJ)	2 wt% **DI-1** (48 mJ)	2 wt% **DI-2** (48 mJ)
+ 0.1 μm	+ 0.1 μm	0
		
204.5 nm	199.2 nm	202.9 nm
- 0.2 μm	+ 0.1 μm	0
		
202.0 nm	203.4 nm	201.5 nm

Figure 14. SEM images for dark-bright field focus shift of the photoresist.

Also, the remarkable effect of DIs was shown on the minimum resolution of the photoresist (Figure 15). In the case of Toshiba's result, 10% of resolution enhancement was obtained by using naphthol novolak backbone DI. The resolution enhancement of the photoresist is also related to the quantity of the DI applied. The application of the **DI-1** with an ALU of low E_a improved the minimum resolution up to 36%. Unfortunately, further application of the 1 wt% of **DI-2** could not be measured due to the unexpected pattern defects. The application of **DI-2** also showed an improvement of the minimum resolution, though the effect was less than that of **DI-1**. This could be due to the lower E_a of

ALU on the **DI-1** than **DI-2**.

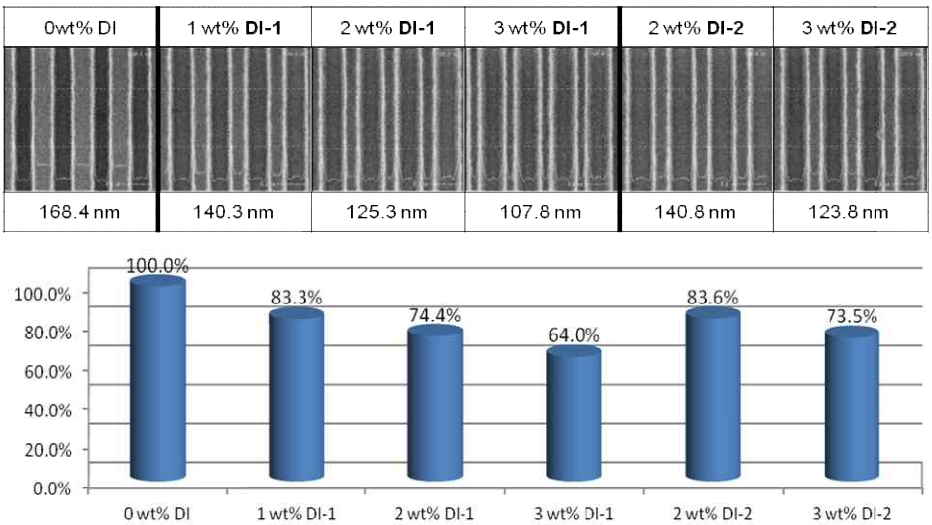


Figure 15. SEM images for minimum resolution of the photoresist.

2.3 Conclusion

In the present study, two novel calix[4]arene-based DIs, **DI-1** and **DI-2**, were efficiently synthesized from calix[4]arene and inceptively evaluated for the lithographic characteristics of the photoresist under ArF exposure. Although calix[4]arene has not been used as DIs in ArF photoresist so far, we expected that some advantageous properties of the calixarenes as photoresists could improve the contrast of ArF photoresists. MOM and t-Boc, which are well-known for acid-labile protecting group, protected calixarenes were prepared in 73% and 58% yields, respectively. While 20 wt% of DI was needed in the previous result, an outstanding improvement of sensitivity (21-29%) was obtained by addition of a small amount of calixarene-based DIs (1 to 3 wt%), **DI-1** and **DI-2**, to the commercial photoresists. Contrast ratio was also

enhanced along with sensitivity and the dark-bright field bias was efficiently revised, too. When applied to the commercial photoresist, the minimum resolution was improved up to 36% whereas 10% of resolution enhancement was observed in the previous result. A simple and efficient way to surpass the resolution limit of the ready-made photoresist under ArF exposure is suggested.

2.4 Experimental details

Materials and methods. Materials were obtained from commercial suppliers and were used without further purification. The reactions were monitored with SiO_2 TLC plates under UV light (254 nm) followed by visualization with a phosphomolybdic acid stain solution. Infrared (IR) spectra were recorded on a JASCO FT-IR 200. ^{1}H NMR spectra were measured on a Bruker 400 MHz spectrometer while ^{13}C NMR spectra were measured on Bruker 100 MHz. Tetramethylsilane was used as an internal reference (0.0 ppm): chemical shift (multiplicity, coupling constant in Hz, integration). Melting points were determined with an open capillary melting point apparatus and were uncorrected. High resolution mass spectra were obtained with a JEOL JMS-AX505WA mass spectrometer.

25,26,27,28-Tetra-*O*-MOM-calix[4]arene (DI-1). A mixture of calix[4]arene (700 mg, 1.65 mmol) and sodium hydride (55% in mineral oil, 720 mg, 16.5 mmol) in *N*,*N*-dimethylformaldehyde (DMF, 10 mL) was stirred for 1.5 h under nitrogen atmosphere at room temperature. To the reaction mixture was added chloromethyl methyl ether (MOMCl, 0.63 mL, 8.25 mmol) and the resulting mixture was stirred for 2 h at room temperature. The mixture was diluted with diethyl ether (30 mL). The resulting solution was washed with water (50 mL x 2), and then with an aqueous solution of sodium bicarbonate (50 mL x 1). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by recrystallization in EtOAc/hexane to give 25,26,27,28-tetra-*O*-MOM-calix[4]arene **DI-1** (721 mg, 73%) as a white solid. Mp 208-209 ^{o}C; IR (KBr) 1455, 1154 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65-

6.63 (m, 12H), 5.10 (s, 8H), 4.47 (d, J = 13.6, 4H), 3.62 (s, 12H), 3.24 (d, J = 13.6, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 134.9, 128.4, 122.9, 100.4, 57.9, 31.6; HRMS (CI) calcd for $C_{36}H_{39}O_8$ $[M-H]^+$ 599.2645, found 599.2647.

25,26,27,28-Tetra-*O*-Boc-calix[4]arene (DI-2). A mixture of calix[4]arene (1,00 g, 2.36 mmol) and sodium hydride (55% in mineral oil, 1.03 g, 23.6 mmol) in *N*,*N*-dimethylformaldehyde (DMF, 50 mL) was stirred for 1.5 h under nitrogen atmosphere at room temperature. To the reaction mixture was added di-tert-butyl dicarbonate (Boc_2O, 5.41 mL, 23.6 mmol) and was stirred for 2 h at room temperature. The mixture was diluted with diethyl ether (80 mL) and washed with an aqueous solution of sodium bicarbonate (100 mL x 3). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by recrystallization in EtOAc/hexane to give 25,26,27,28-tetra-*O*-Boc-calix[4]arene **DI-2** (1.13 g, 58%) as a white solid. Mp 219.3 ^oC; IR (KBr) 1783, 1457 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81-6.75 (m, 12H), 4.03 (d, J = 13.6, 4H), 3.28 (d, J = 13.6, 4H), 1.57-1.53 (br s, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 147.3, 134.0, 128.2, 124.7, 81.9, 30.2, 27.8; HRMS (FAB) calcd for $C_{48}H_{56}O_{12}Na$ $[M + Na]^+$ 847.3669, found 847.3657.

Method for lithography test. Synthesized DIs were added to a methacrylate-based commercial ArF photoresist, and filtered through a syringe filter with pore size of 0.04 μm. The prepared samples were spin-coated on silicon wafers and soft baked (SOB) on hot plates at 100 ^oC for 60 seconds. The coated wafers were exposed in an ASML ArF scanner and washed with aqueous tetramethylammonium hydroxide (TMAH) solution on a TEL track. The

patterned wafers were examined on a Hitachi S9000 series SEM. The contrast curve was obtained by exposing the wafers with different light dose, and measuring the film thickness on an ellipsometer.

3. Synthesis of the new conceptual negative tone photoresists

3.1 Introduction

Nano-scale photolithography is the technology which applied to transfer integrated circuit onto silicon wafer. Especially, imaging of patterns in mask and miniaturization are achieved by high-performance exposure equipment. Continuous development of photolithography technology for nano-scale semiconductor made it possible to decrease the line width of pattern about 30 % every two years. But there are still remain the technological gap between lithography development and economical optimization of practical synthesis. Thus, various technologies suggested to overcome the technological barrier. Negative tone development is one of the leading candidates. In general, negative tone photoresist is well-known for better than positive tone photoresist in micro-patterning. Thus, it is valuable to study about the negative tone photoresists. Although negative tone image can be formed by hydrophobic developer, it was already dominated by overseas patents. Thus, synthetic studies of new conceptual photoresists which can be formed negative tone without a considerable change of practical process will be discussed.

3.1.1 Negative tone photoresist (NTR or NTP)

Unlike positive tone photoresist (PTR or PTP), negative tone photoresists make a pattern at the exposed area. A negative tone imaging process, including a negative tone photoresist (NTR or NTP) process and a negative tone development (NTD) process, can offer substantially better process windows than a positive tone imaging process for certain lithographic features.[55]

Conventional negative tone image can be achieved by using negative tone photoresist, organic developer, or bright-field mask (Figure 16). Most of negative tone photoresists are polyisoprene type. When they exposed to the excimer laser, it becomes cross-linked polymer. And unexposed area will be dissolved in the development solution. Cross-linked polymer shows higher chemical etch resistance. But resulting polymer can absorb the development solvent and shows poor resolution due to the swelling of PR. And environmental and safety issues still remains. Organic developer can be a great solution for achieving the negative tone image with a practical process. If organic developer was used, negative tone image will be easily obtained without any changes of process. It seems that the cheapest process, but infringement of patent with overseas companies is inevitable. Although bright-field mask is one of the well-known processes for negative tone, the production cost of new mask is relatively higher than other processes.

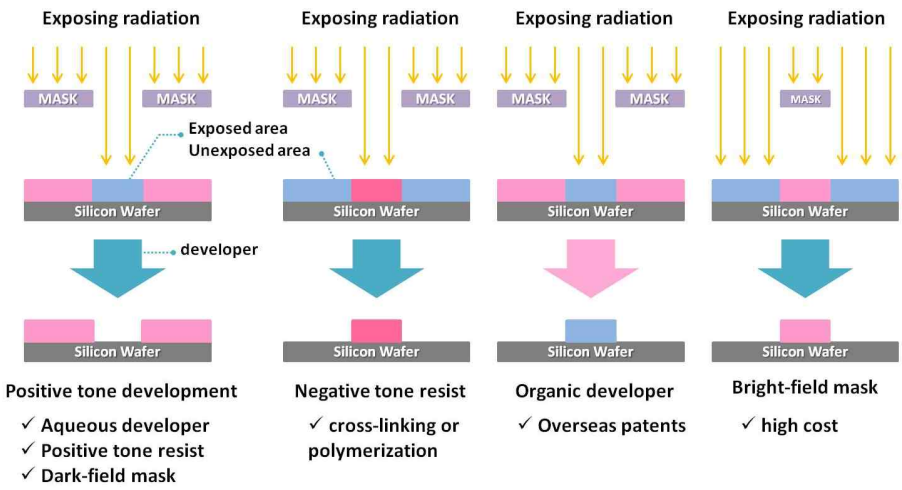


Figure 16. Types of negative tone process.

3.1.2 Previous research

The development of chemically amplified NTR in 248 nm lithography required no major changes in the polymer backbone and a deprotected form of 248 nm resist polymers, poly(hydroxyl styrene), was used as a matrix polymer along with a crosslinker, methoxymethylmelamin. Benefits with 248 nm NTR process were found in the control of the resist bottom profiles in a dual damascene process and in the improvement of the optical proximity effect and depth of focus when combined with off-axis illumination and attenuated phase-shift masks. While the 248 nm NTR process was implemented in the semiconductor manufacturing without dramatic changes in the 248 nm resist backbone chemistry, the development of 193 nm NTR process has been rather challenging due to the difficulties in the development of mature 193 nm NTR. Although there are many reports for various 193 nm NTR chemistries, none of these 193 nm NTR chemistries fully demonstrated the lithographic benefits of the negative tone imaging process in 193 nm lithography.

Tarutani *et al.* demonstrated benefits of the negative tone imaging in 193 nm lithography using the NTD process of 193 nm positive tone resists where unexposed areas of resists are removed by a solvent developer. It was reported that the NTD process can give better line width roughness for narrow trenches than a positive tone development (PTD) process.

When combined with a cross-line double exposure process, NTD process could further extend contact hole printing down to $k1$ of 0.28 to print 40 nm half-pitch contact holes with good process window, CDU and MEEF. Both simulation and lithographic data demonstrated that NTD is a superior imaging process to PTD to print sub-100 nm pitch dense contact holes due to superior aerial images originated from the bright field masks. In addition to dense

regular contact arrays, 193 nm immersion NTD process was demonstrated to give superior imaging performance for trenches, 2D SRAM core patterns and 2D logic patterns.

3.2 Our strategy

Conventional process make a negative tone by using crosslinked type polymer resist or organic developers. The photoresist which brings about negative tone is referred to as a negative tone photoresist (NTR or NTP). And the process that showed a negative type pattern by using change of developer or mask is known as a negative tone development (NTD). NTD with an organic developer is well-known process to achieve a negative tone image. By using organic developers, conventional positive tone resist could be used without any manipulations to the structure or composition. This method is very facile and efficient, but confliction with the prior patent is an inevitable problem.

From this point of view, we designed a negative tone resist which not avoid range of prior patent but also utilize the conventional positive tone imaging process. While conventional NTD use the solubility reversal of photoresist to the developer, we suggest the polarity reversal of photoresist. When the positive photoresist is exposed to a light source, the acid-labile protection group decomposes to result in a hydrophilic functional group and change the solubility of the photoresist to be washed out rapidly with a developer such as aqueous tetramethylammonium hydroxide (TMAH) solution (Figure 17).

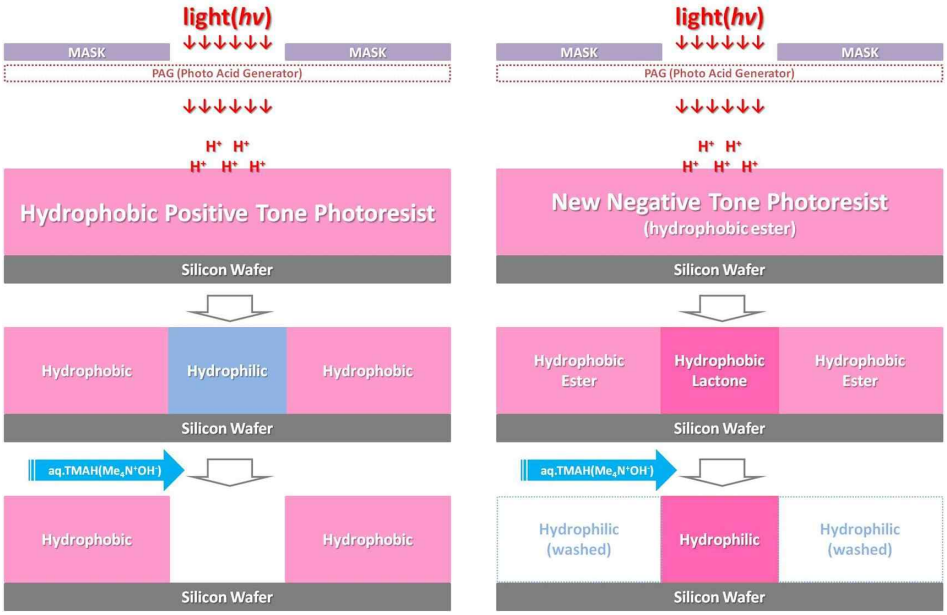


Figure 17. New conceptual photoresist for negative tone.

In our research, photoresist is designed as it has a hydrophilic functionality such as hydroxyl and carboxylic acid group (Figure 18). Because the unexposed photoresist should be washed by TMAH, alkyl ester which can be hydrolyzed by TMAH could alternate the carboxylic acid group. The protecting group located within 5 or 6 carbon chain, thus they can be easily cyclized by acid from photo acid generator (PAG) after exposure. As a result, hydrophobic lactone could be obtained. In short, hydrophilic photoresist could be converted into hydrophobic photoresist and gave an insoluble product in TMAH after exposure. While the resolution limit of KrF could resolved by ArF, resolution limit between ArF and extreme ultraviolet still remains a challenging subject to photolithography. So, we decided to study synthesis of a new conceptual monomer of negative tone photoresist under ArF excimer laser.

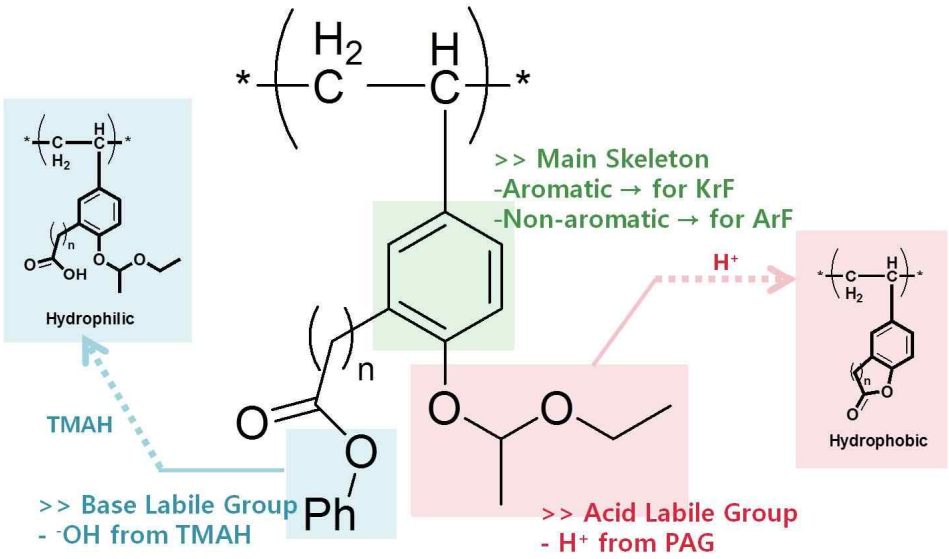


Figure 18. Synthetic strategies for new conceptual photoresist for negative tone.

3.3 Results and discussion

First, we designed a synthetic route which have a cyclic olefin as a polymerizable site (Figure 19). Cis-1,2,3,6-tetrahydrophthalic anhydride and cis-5-norornene-endo-2,3-dicarboxylic anhydride were selected as a starting material. This strategy was expected that give a 5-memebered lactone ring after exposure, if synthesis of desired monomer had been successful. Anhydride was converted into dicarboxylic acid ester under lewis acid condition with alcohol, but selective reduction of ester was not successful. But since the cyclic olefin was not enough to polymerize according to previous literature, further study to find a suitable condition for reduction was not conducted any more.

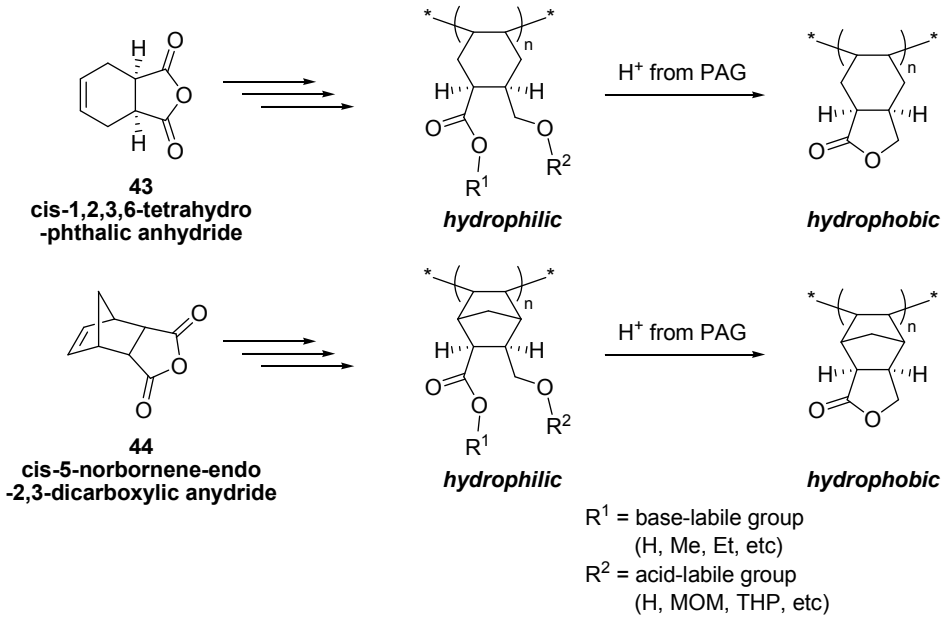


Figure 19. Synthetic strategies from cyclic olefin.

Because the cyclic olefin was not suitable for polymerization, design of

new strategy was essential. In polymerization, styrene derivatives are well-known for that have very fast rate of polymerization. But, since the aromatic ring can not apply to the photoresist for ArF due to its excessive absorption, we considered a methacrylate structure as a candidate for ArF photoresist. Methacrylate structure has already been used in the photoresist under ArF. We selected a α-methylene-γ-butyrolactone as a starting material (Figure 20). If desired polymer was successfully synthesized, then hydrophobic γ-lactone could be obtained.

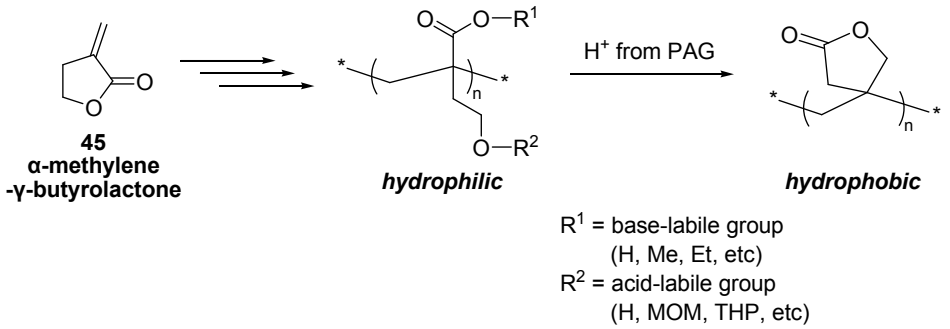
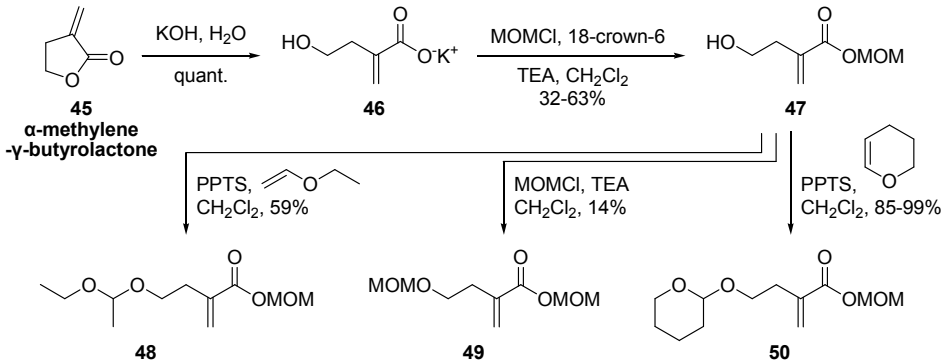


Figure 20. Synthetic strategy from methacrylate-like structure.

Ring opening reaction was conducted by aqueous KOH solution (Scheme 16). Other metal salt, such as cesium (Cs) and sodium (Na), or ammonium salt (NMe_4) was also easily obtained. Resulting potassium carboxylate salt **46** was not soluble in any organic solvents without 18-crown-6. Although the salt was soluble in alcohol, esterfication reaction was occurred all. Methoxymethyl (MOM) protection of **46** with 18-crown-6 and triethylamine (TEA) afforded desired ester **47** in moderate yield. Protection reaction of free hydroxyl group with acid-labile group was conducted and 3 types of target monomer were obtained. Ethoxyethyl (EE) protected monomer **48** was obtained in 59% yield,

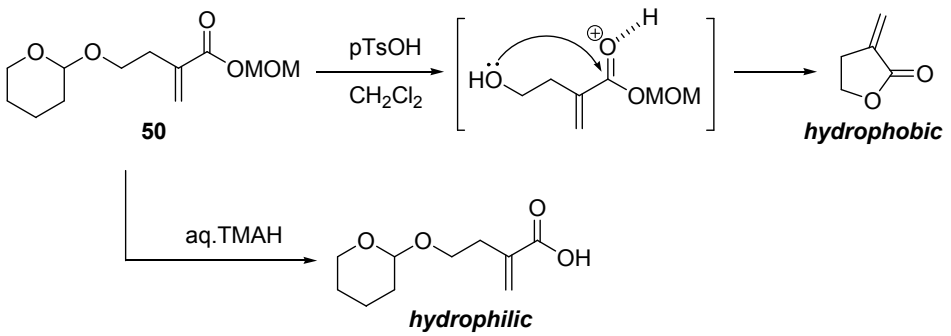
but it shows many impurities in ^{1}H NMR. Although purification was conducted by silica gel column chromatography, impurities were not completely removed. MOM protected monomer **49** also has impurities but purification was not successful. Since MOM and EE group are easy to deprotect by small amount of acid, they seemed unstable in silica gel column chromatography. Although tetrahydropyran (THP) has a acetal moiety which is acid-labile functionality, ring strain of THP makes the monomer more stable than other monomers. Moreover, the product **50** could be obtained in excellent yield with high purity.



Scheme 16. Synthesis of methacrylate-based monomer for NTR.

Resulting monomer **50** was subjected to feasibility test as a negative tone resist (Scheme 17). When the monomer was treated with catalytic amount of p-toluenesulfonic acid (pTsOH) at room temperature for 30 min, cyclized product was obtained in excellent yield. Although not exactly same with practical process, it is confirmed that deprotection and sequential cyclization can be occurred under acidic condition. Since the unexposed photoresist should be hydrolyzed by TMAH solution in a very short time, hydrolysis of 50 was conducted in separatory funnel. A mixture of **50** in ethyl acetate (EtOAc) was

washed by 1N aq.TMAH twice. After removal of aqueous layer, organic extracts were concentrated and checked by ^{1}H NMR as a crude mixture. As we expected, hydrophobic monomer was hydrolyzed and converted into hydrophilic product, so there are not any compound in organic layer. According to this feasibility test, it is shown that our synthesized monomer can act as a negative tone resist.



Scheme 17. Feasibility test for negative tone resist.

Based on the result of feasibility test, lithography test was conducted by Dongjin semichem. Photoresist was prepared by co-polymerization of **50** with other monomers which show desired physical properties for photoresist. But lithographic test was progressed any more. The critical reason is the poor polymerizability of our monomer 50. Although 50 has a methacrylate structure, it is seems that acid-labile MOM ester would interrupt the polymerization. When homo-polymerization of 50, it is obvious that has a low polymerizability (Mn = 1,064; Mw = 1,410; PDI = 1.325). As a result, we found that methacrylate based monomer could not apply to a negative resist.

Therefore, modification of target molecule was inevitable. Because protecting group which induced negative tone interrupt polymerization, we tried

to isolate the negative working and polymerization ability (Figure 21). For the isolation of two functionality, dihydroxylation reaction was employed.

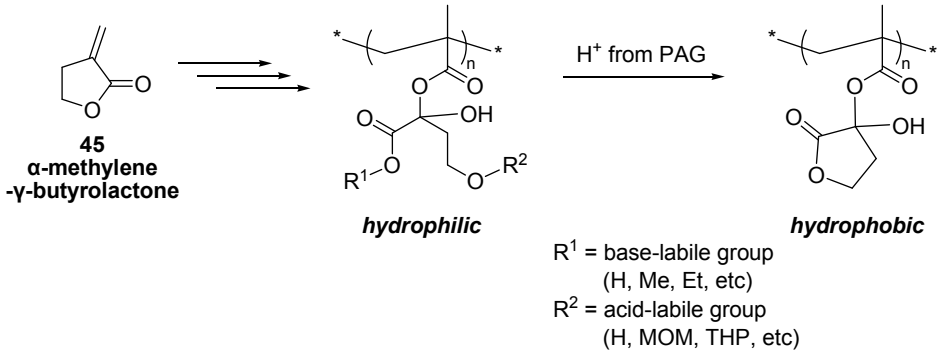
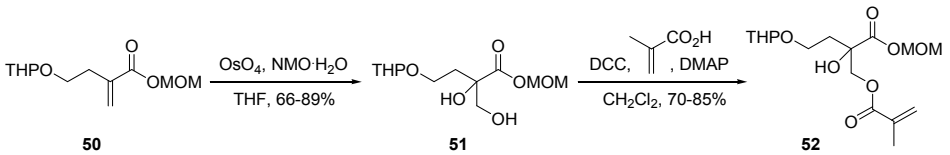


Figure 21. Modifed synthetic strategy from methacrylate-like structure.

Dihydroxylation of **50** afforded diol **51** with a good yield. Resulting diol was coupled with methacrylic acid in the presence of DCC and DMAP (Scheme 18). When the modified target left in room temperature as a crude product, it quickly turned into amorphous gel which is insoluble in any other solvents. The instability of MOM ester and high polymerizability of methacrylate make them as an unidentifiable compound. So, retention time at crude mixture should shorten as possible. Since methacrylate part of the purified product **52** can be polymerized by oxygen in air, monomethyl ether hydroquinone (MEHQ) must be included in monomer as a polymerization inhibitor. The monomer **52** passed the feasibility test and polymerization as a homopolymer was successful, too (Mn = 610,340; Mw = 687,896; PDI = 1.127).



50 51 52

Scheme 18. Synthesis of modified methacrylate-based monomer.

Despite of modification of target molecule, the lithographic test was not successful. It showed a good polymerizability, but didn't work as a negative tone resist. While the photoresist showed a low activity as a negative tone resist when it was co-polymer, homopolymer was not soluble in commercial solvent, such as PGMEA (propylene glycol monomethyl ether acetate). When the protecting group changed, the results were not different, too. Thus, new route from new starting material was essential to solve the problem.

Terminal alkenoic acids were chosen as a starting material for a new synthetic route (Figure 22). 3-Butenoic acid, 4-pentenoic acid and 5-hexenoic acid were employed in practice. In our strategy, the key strategy is a high tendency to form the five- or six-membered lactone. When 3-butenoic acid was employed, resulting diol can be cyclized 4- or 5-membered lactone. Because the formation of 4-membered ring is very strained, it is designed that precursor for cyclization of γ-lactone. So terminal hydroxyl group was designed to protect with acid-labile protecting group, and polymerizable site (methacrylic acid) was planned to introduce in internal hydroxyl group. Otherwise, internal hydroxyl group was used as a nucleophile to form δ–lactone in the case of 5-hexenoic acid. In that case, since 7-membered lactone has a low reactivity to cyclize, terminal alcohol was counted for the polymerization. In case of 4-pentenoic acid, the structure of resulting lactone can have a 4- or 5-membered ring. Thus, 2 types of choice were possible in terms of efficiency of synthesis.

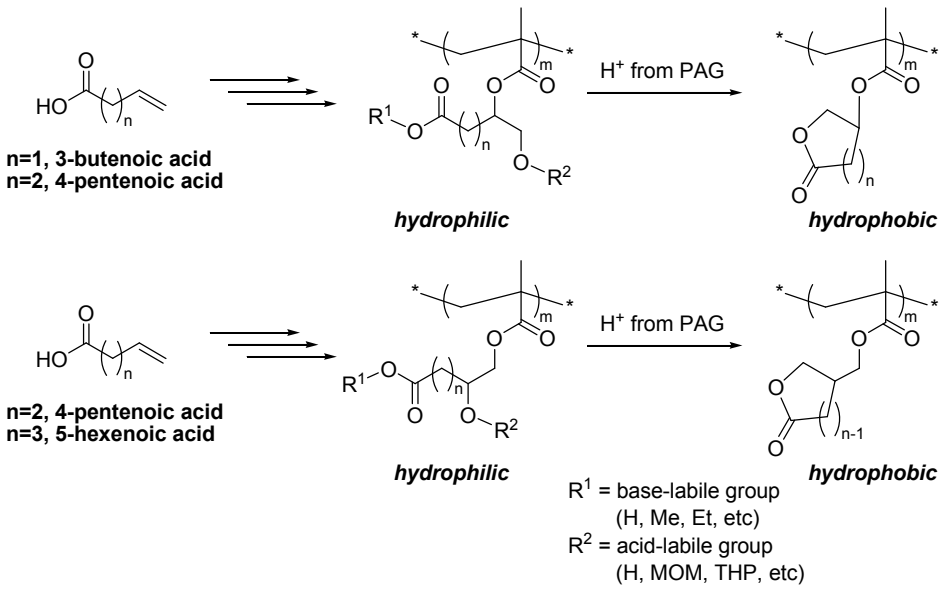
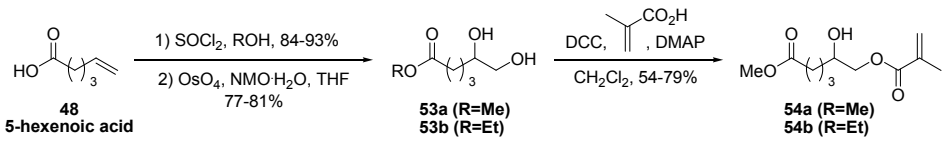


Figure 22. Synthetic strategy from alkenoic acid.

When practical synthesis of target monomers, desired monomers were obtained with a moderate yield (Scheme 19). The monomers were proved as a negative tone resist by previous feasibility test. But their homopolymers still showed a very low solubility in commercial solvents. Thus, co-polymerization with other monomers which can enhance the solubility of polymer has been an inevitable choice. Since various combinations for the preparation of photoresist is in progress, it is expected that problem will be solved in the near future. The lithographic test of the synthesized monomer will be conducted after completion of preparations of photoresist.



Scheme 19. Synthesis of monomer for NTR from alkenoic acid.

3.4 Conclusion

Various synthetic strategies were designed and conducted for the synthesis of new conceptual negative tone photoresist. The key concept of our research is a polarity reversal by structural modification of monomer for photoresist in the solubility perspectives. Hydrophilic characteristic of photoresist was designed to convert into hydrophobic structure after exposure to ArF excimer laser. While carboxylic acid and hydroxyl functionality were used as an hydrophilic functional group, formation of 5- or 6- membered lactone was expected that insoluble in aqueous developer. Cyclic olefin, α-methylene-γ-butyrolactone and alkenoic acid were used as a starting material for the preparations of negative tone photoresist. Although desired monomers were obtained and passed the simple feasibility test, their physical properties were not enough to apply in practical process. Thus, various combination for co-polymerization and modifications of synthetic strategies will be studied. And the lithographic test will be also conducted after preparations of photoresist.

3.5 Experimental details

Materials and methods. Materials were obtained from commercial suppliers and were used without further purification. 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 NMR spectra were measured on Bruker 400 MHz while ^{13}C NMR spectra were measured on Bruker 100 MHz. Tetramethylsilane was used as an internal reference (0.0 ppm): chemical shift (multiplicity, coupling constant in Hz, integration).

Potassium 4-hydroxy-2-methylenebutanoate (46). To a solution of α-methylene-γ-butyrolactone **45** (1.0 mL, 11.40 mmol) in water (20 mL) was added potassium hydroxide (633 mg, 11.29 mmol) and the reaction mixture was stirred for 2 h at room temperature. The resulting mixture was washed with diethyl ether (30 mL x 2) and concentrated *in vacuo* to afford potassium 4-hydroxy-2-methylenebutanoate 46 (1.76 g, quant.) as a white solid. ^{1}H NMR (400 MHz, D_2O) δ 5.66 (s, 1 H), 5.26 (s, 1 H), 3.56 (t, J = 6.6, 2 H), 2.39 (dt, J = 0.8, 6.2, 2 H).

Methoxymethyl 4-hydroxy-2-methylenebutanoate (47). To a solution of 4-hydroxy-2-methylenebutanoate **46** (1.78 g, 11.56 mmol) in dichloromethane (30 mL) was added 18-crown-6 (3.05 g, 11.56 mmol) and stirred for 30 min at room temperature. To the reaction mixture was added triethylamine (3.5 mL, 25.42 mmol), and then chloromethyl methyl ether (1.0 mL, 12.71 mmol) was added dropwise. The resulting mixture was stirred for 2 h at room temperature and

then was washed by brine (30 mL x 2). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel chromatography afforded methoxymethyl 4-hydroxy-2-methylenebutanoate **47** (1.17 g, 63%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (s, 1 H), 5.75 (s, 1 H), 5.33 (s, 2 H), 3.79 (t, J = 6.0, 2 H), 3.50 (s, 3 H), 2.61 (t, J = 6.2, 2 H).

Methoxymethyl 2-methylene-4-(tetrahydro-*2H*-pyran-2-yloxy)butanoate (50). To a solution of methoxymethyl 4-hydroxy-2-methylenebutanoate **47** (2.26 g, 14.14 mmol) in dichloromethane (30 mL) was added pyridinium p-toluenesulfonate (178 mg, 0.71 mmol). To the reaction mixure was added 3,4-dihydro-*2H*-pyran (1.3 mL, 14.14 mmol) was added and stirred for 8 h at room temperature. The resulting mixture was washed by brine (30mL x 1). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel chromatography afforded methoxymethyl 2-methylene-4-(tetrahydro-*2H*-pyran-2-yloxy)butanoate **50** (1.17 g, 63%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (s, 1 H), 5.73 (s, 1 H), 5.32 (s, 2 H), 4.60 (m, 1 H), 3.91-3.83 (m, 2 H), 3.59-3.52 (m, 2 H), 3.49 (s, 3 H), 2.64 (t, J = 6.8, 2 H), 1.84-1.51 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 137.4, 127.3, 98.7, 90.8, 65.8, 62.3, 57.6, 32.0, 30.6, 25.4, 19.5.

Methoxymethyl 2-hydroxy-2-(hydroxymethyl)-4-(tetrahydro-*2H*-pyran-2-yloxy)butanoate (51). To a solution of Methoxymethyl 2-methylene-4-(tetrahydro-*2H*-pyran-2-yloxy)butanoate **50** (1.48 g, 6.06 mmol) in tetrahydrofuran (15 mL) was added 4-methylmorpholine N-oxide monohydrate (983mg, 7.27 mmol). To the reaction mixure was added osmium tetroxide (15

mg, 0.06 mmol) was added and stirred for 12 h at room temperature. The resulting mixture was quenched by saturated sodium sulfite solution (5 mL) and extracted by diethyl ether (30mL x 5). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel chromatography afforded Methoxymethyl 2-hydroxy-2-(hydroxymethyl)-4-(tetrahydro-*2H*-pyran-2-yloxy)butanoate **51** (1.50 g, 89%) as a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39-5.26 (m, 2 H), 4.57-4.51 (m, 1 H), 3.99-3.81 (m, 4 H), 3.69-3.48 (m, 6 H), 2.45 (br s, 1 H), 2.17-2.10 (m, 1 H), 1.96-1.86 (m, 1 H), 1.76-1.50 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 99.5, 91.8, 77.3, 68.3, 62.5, 62.3, 57.8, 34.3, 30.4, 25.3, 19.3.

Methoxymethyl 2-hydroxy-2-(methacryloyloxymethyl)-4-(tetrahydro-*2H*-pyran-2-yloxy)butanoate (52). To a solution of methoxymethyl 2-hydroxy-2-(hydroxymethyl)-4-(tetrahydro-*2H*-pyran-2-yloxy)butanoate **51** (1.48 g, 6.06 mmol) in tetrahydrofuran (15 mL) was added 4-methylmorpholine N-oxide monohydrate (983 mg, 7.27 mmol). To the reaction mixure was added osmium tetroxide (15 mg, 0.06 mmol) was added and stirred for 12 h at room temperature. The resulting mixture was quenched by saturated sodium sulfite solution (5 mL) and extracted by diethyl ether (30 mL x 5). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel chromatography afforded methoxymethyl 2-hydroxy-2-(hydroxymethyl)-4-(tetrahydro-*2H*-pyran-2-yloxy)butanoate **51** (1.50 g, 89%) as a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (s, 1 H), 5.58 (s, 1 H), 5.41-5.17 (m, 2 H), 4.57-4.52 (m, 1 H), 4.34 (s, 2 H), 4.00-3.89 (m, 1 H), 3.84-3.73 (m, 1 H), 3.62-3.48 (m, 2 H), 3.44 (s, 3 H), 2.26-2.18 (m, 1 H), 2.04-1.91 (m, 4 H), 1.77-1.49 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 166.7, 135.7, 126.2, 99.5,

91.9, .75.2, 69.4, 62.4, 62.1, 57.8, 34.6, 30.8, 19.1, 18.1.

Methyl 5,6-dihydroxyhexanoate (53a). A solution of 5-hexenoic acid **48** (0.6 mL, 5.01 mmol) in methanol (10 mL) was cooled to 0 ^{o}C and thionyl chloride (0.4 mL, 5.01 mmol) was added slowly. The reaction mixture was stirred at room temperature for 6 h. The mixture was diluted with ethyl acetate (30 mL) and washed with brine (30 mL x 2). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo* afforded methyl hex-5-enoate (597 mg, 93%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83-5.73 (m, 1 H), 5.06-4.97 (m, 2 H), 3.67 (s, 3 H), 2.33 (t, J = 7.6, 2 H), 2.07 (q, J = 7.1, 2 H), 1.74 (q, J = 7.6, 2 H).

To a solution of methyl hex-5-enoate (652 mg, 5.09 mmol) in tetrahydrofuran (15 mL) was added 4-methylmorpholine N-oxide monohydrate (825 mg, 6.10 mmol). To the reaction mixure was added osmium tetroxide (13 mg, 0.05 mmol) was added and stirred for 12 h at room temperature. The resulting mixture was quenched by saturated sodium sulfite solution (5 mL) and extracted by diethyl ether (30mL x 5). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by silica gel chromatography afforded methyl 5,6-dihydroxyhexanoate **53a** (668 mg, 81%) as a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72-3.64 (m, 5 H), 3.49-3.43 (m, 1 H), 2.62-2.59 (m, 1 H), 2.37 (t, J = 7.2, 2 H), 1.84-1.68 (m, 2 H), 1.50-1.45 (m, 2 H).

Methyl 5-hydroxy-6-(methacryloyloxy)hexanoate (54a). A solution of methyl 5,6-dihydroxyhexanoate **53a** (663 mg, 4.09 mmol) was dissolved in dichloromethane (30 mL) followed by addition of dicyclohexylcarbodiimide (843 mg, 4.09 mmol) and 4-(dimethylamino)pyridine (50 mg, 0.41 mmol). To

the reaction mixture was added methacrylic acid (0.4 mL, 4.09 mmol) and stirred at room temperature at 6 h, and then was evaporated and the residual mixture was filtered through a celite pad in vacuo. Purification by silica gel chromatography afforded methyl 5-hydroxy-6-(methacryloyloxy)hexanoate **54a** (744 mg, 79%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (s, 1 H), 5.61 (s, 1 H), 4.23-4.05 (m, 2 H), 3.89 (m, 1 H), 3.68 (s, 3 H), 2.38 (t, J = 7.2, 2 H), 2.24 (m, 1 H), 1.96 (s, 3 H), 1.89-1.69 (m, 2 H), 1.57-1.56 (m, 2 H).

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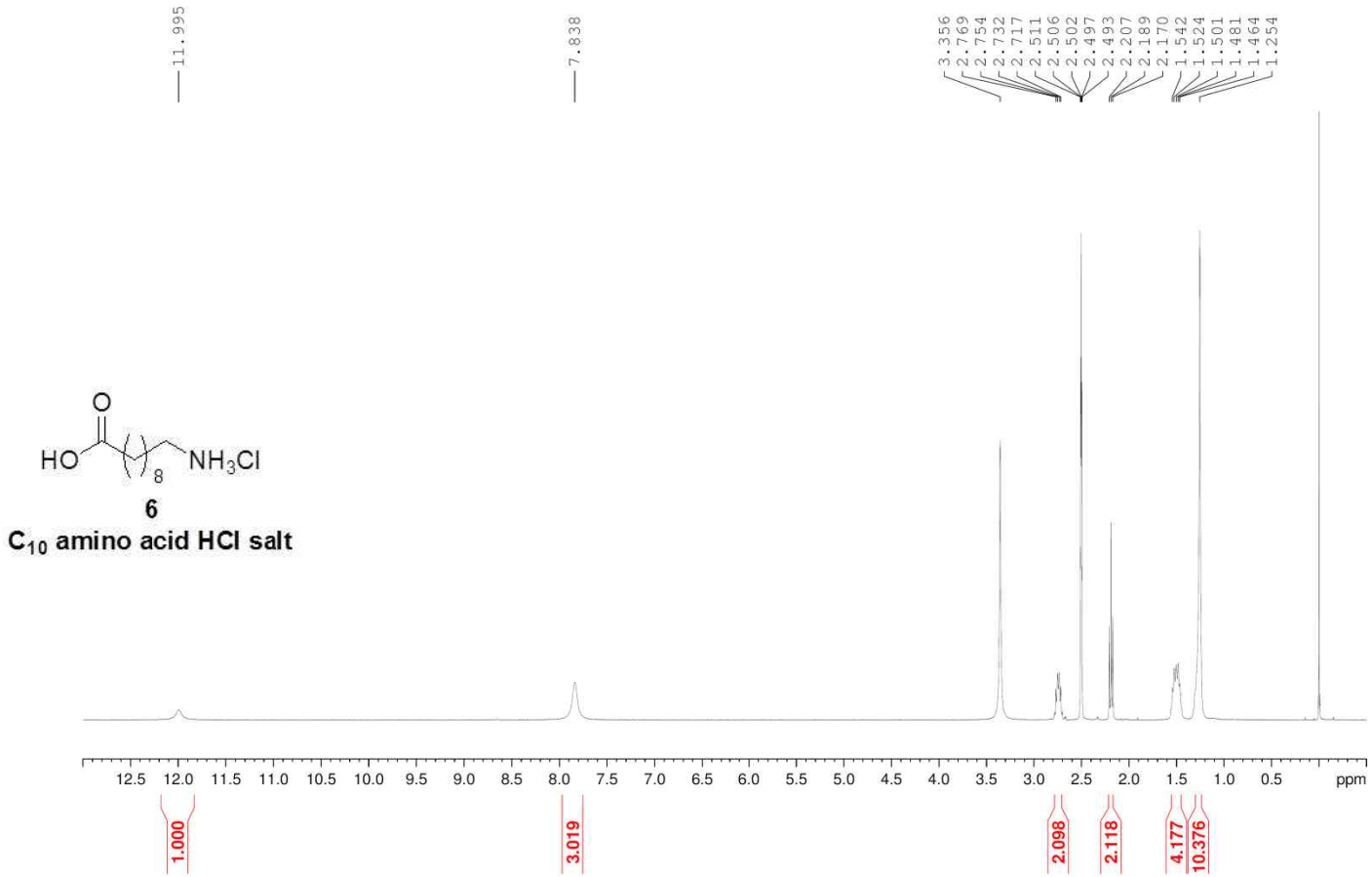
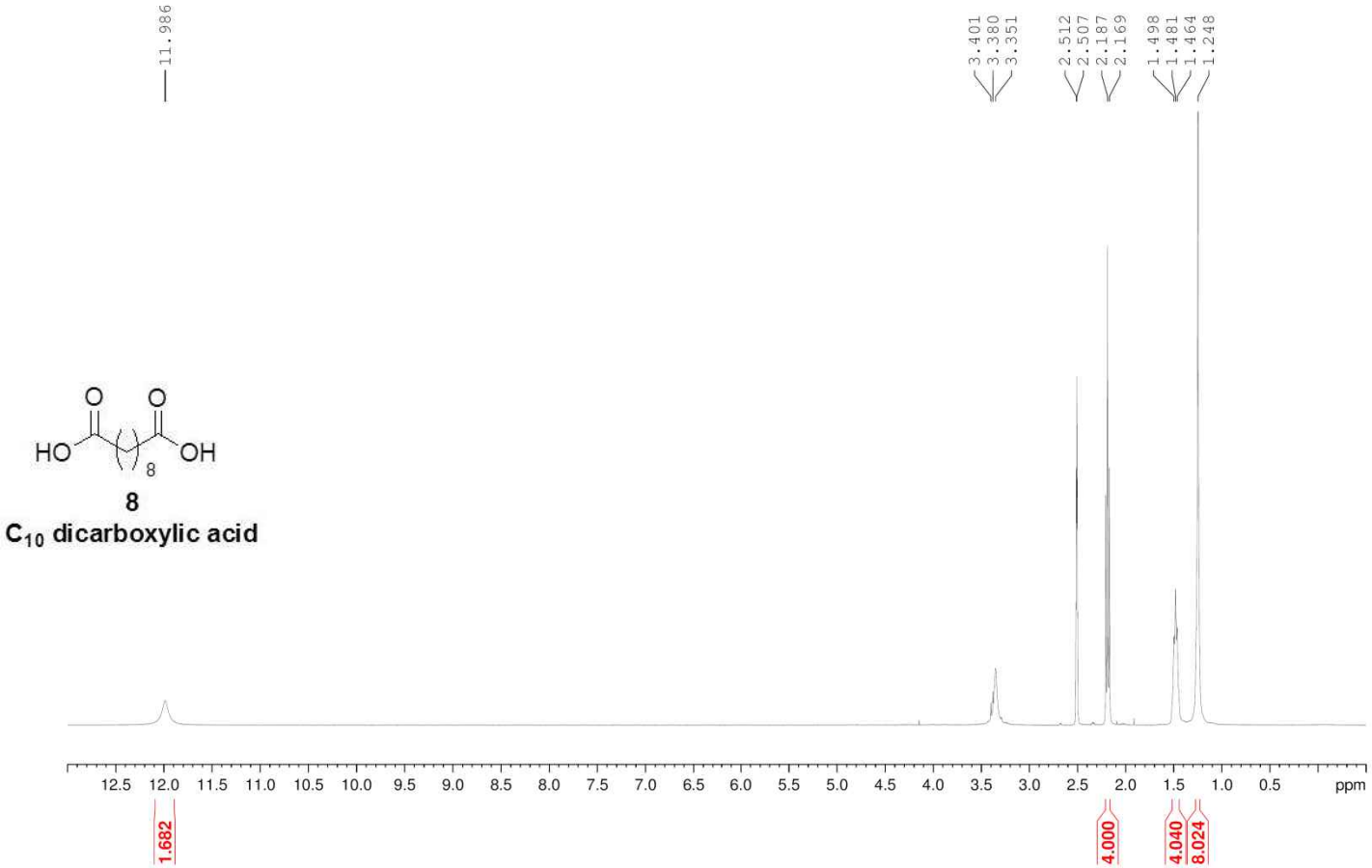
APPENDICES

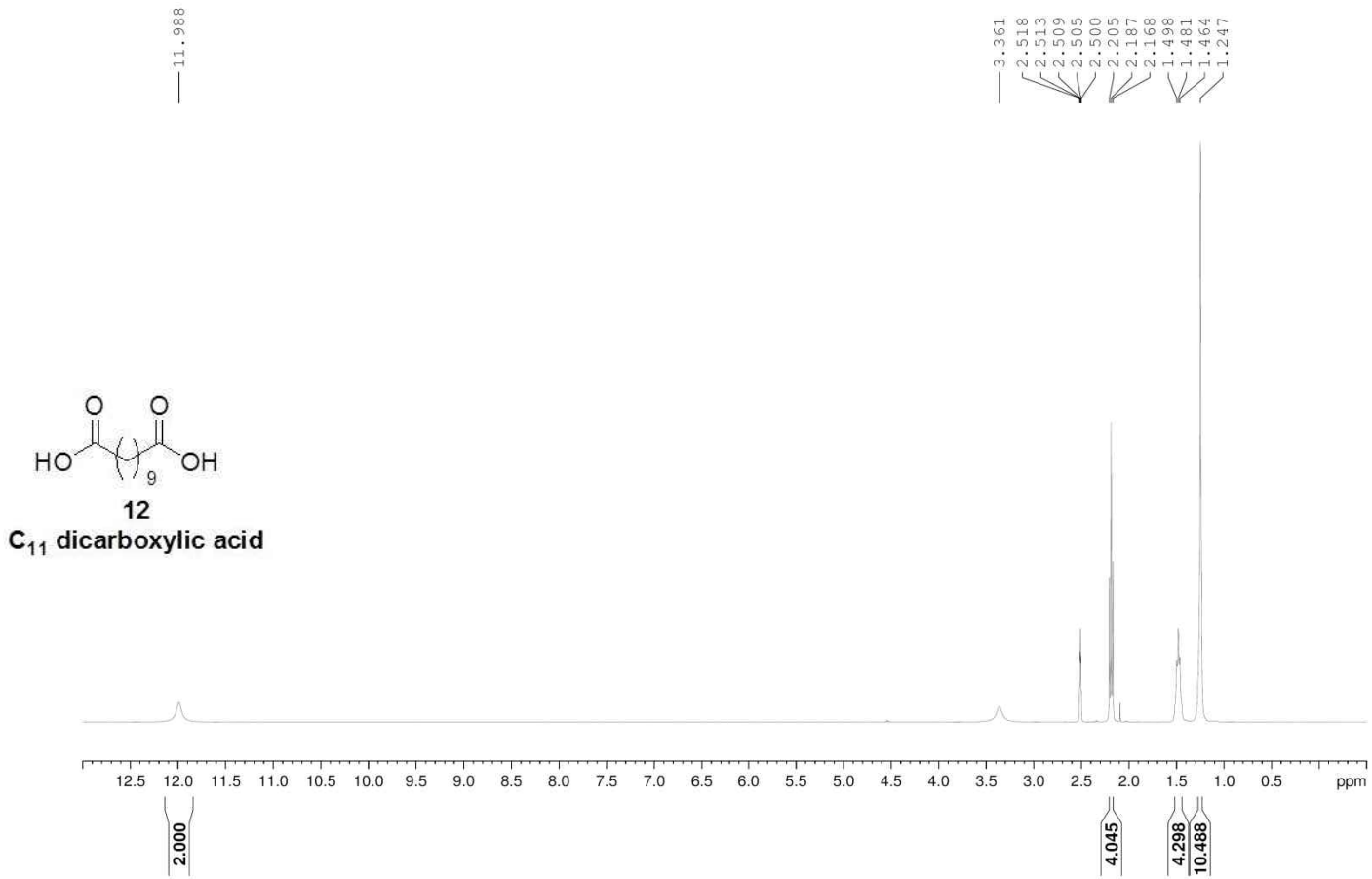
List of ^{1}H-NMR Spectra of Selected Compounds



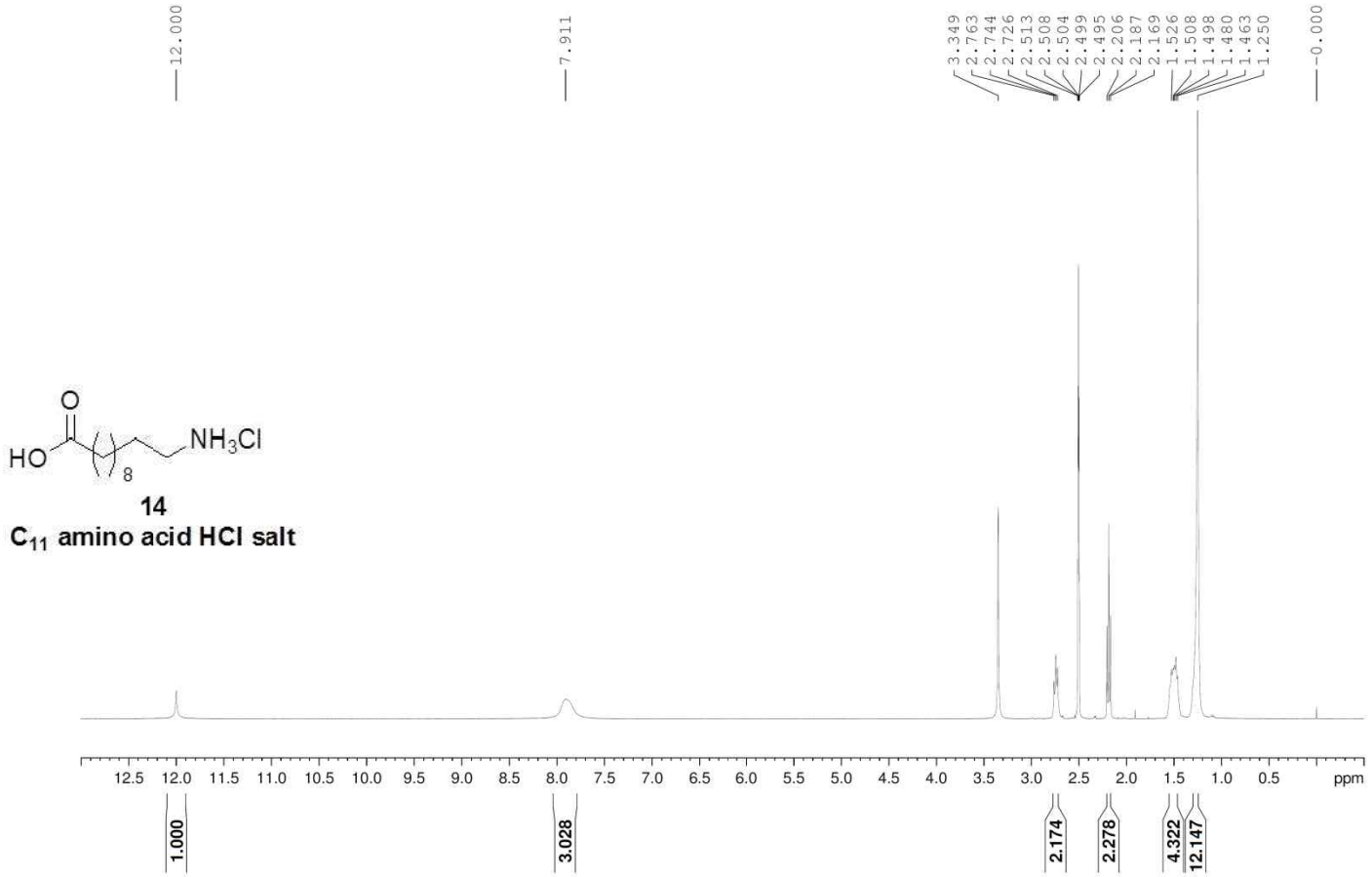
400 MHz ^{1}H-NMR spectrum (DMSO-d_6) of compound **6**



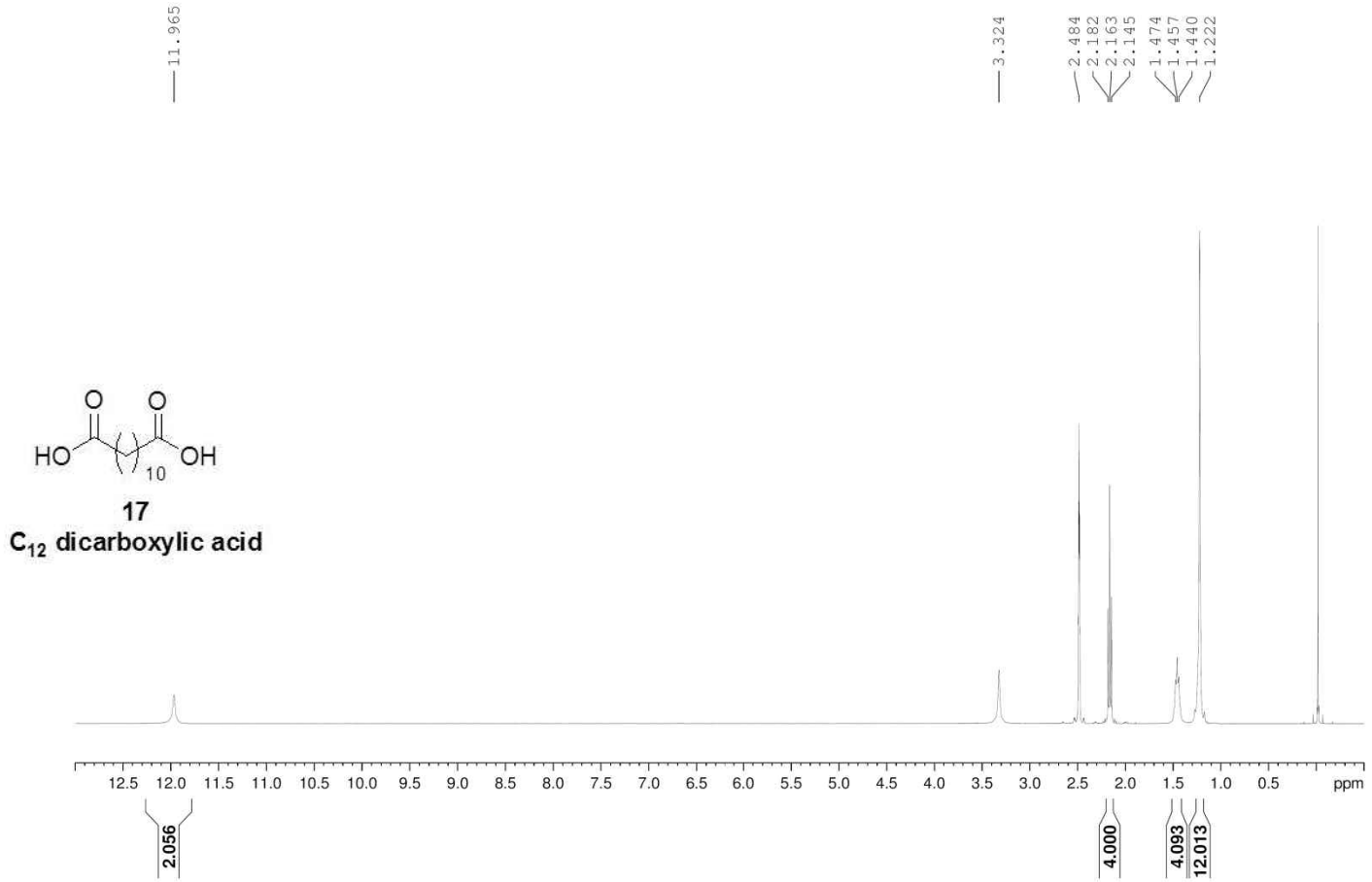
400 MHz ^{1}H-NMR spectrum (DMSO-d_6) of compound **8**



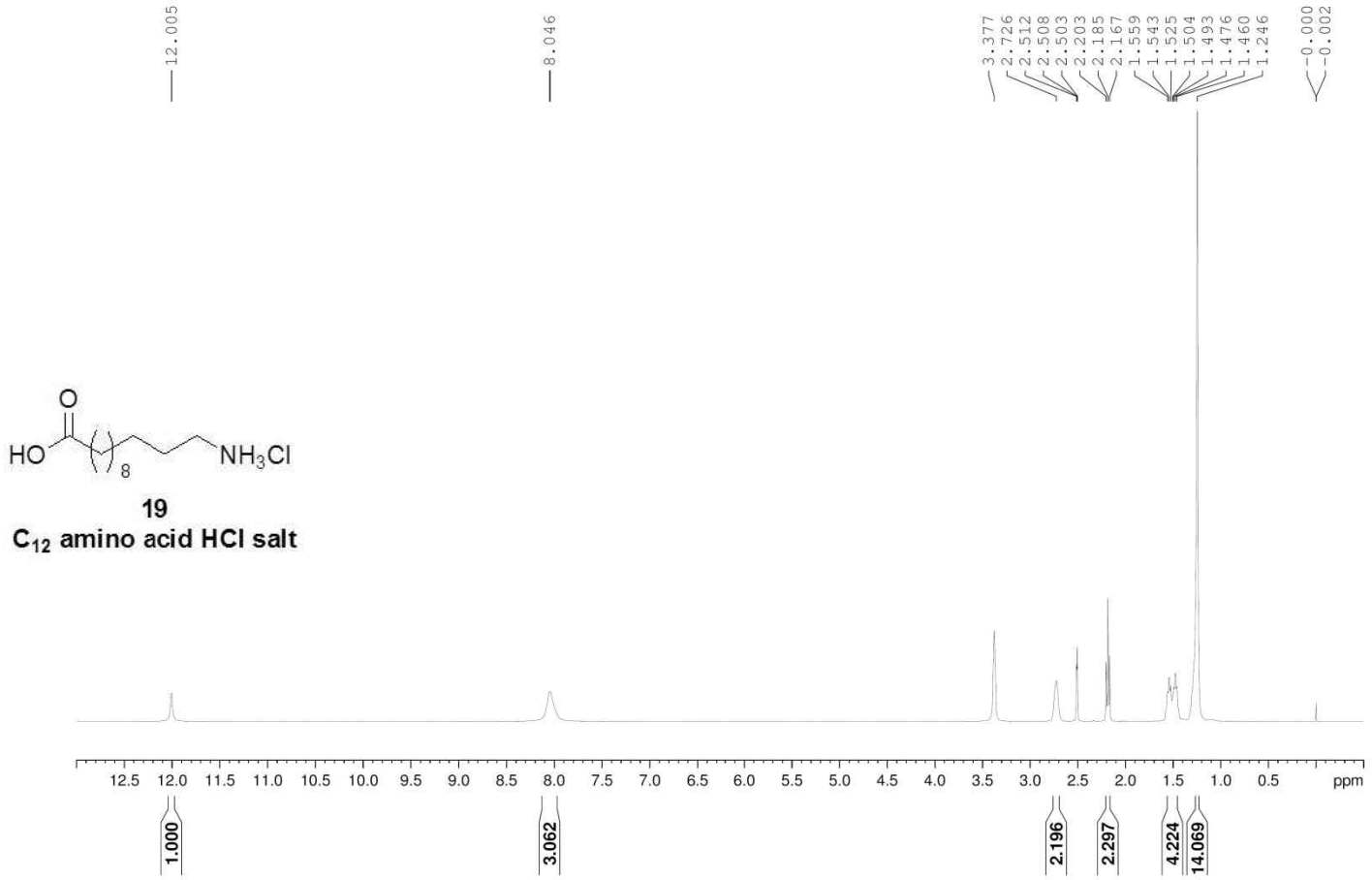
400 MHz ^{1}H-NMR spectrum (DMSO-d_6) of compound **12**



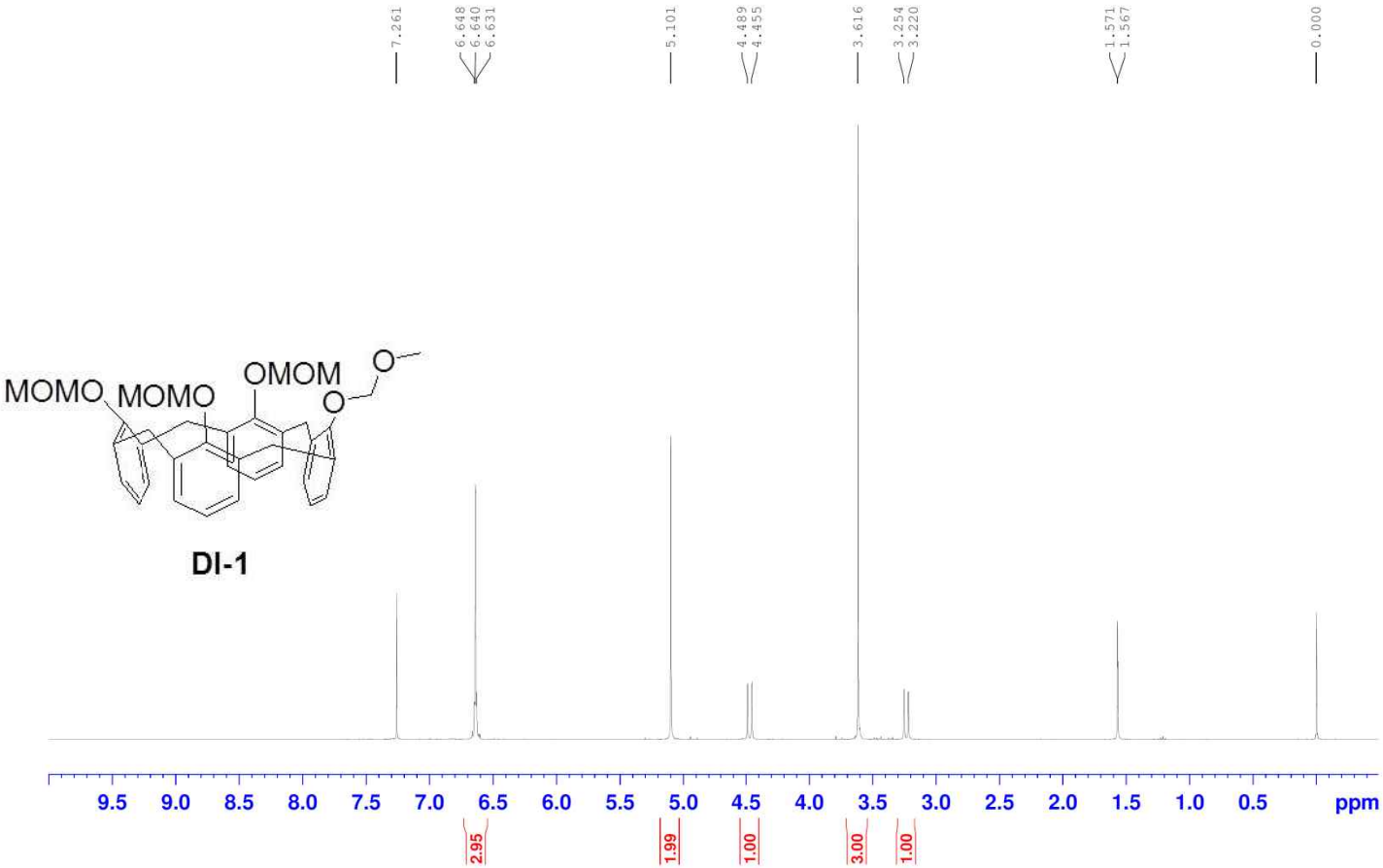
400 MHz ^{1}H-NMR spectrum (DMSO-d_6) of compound **14**



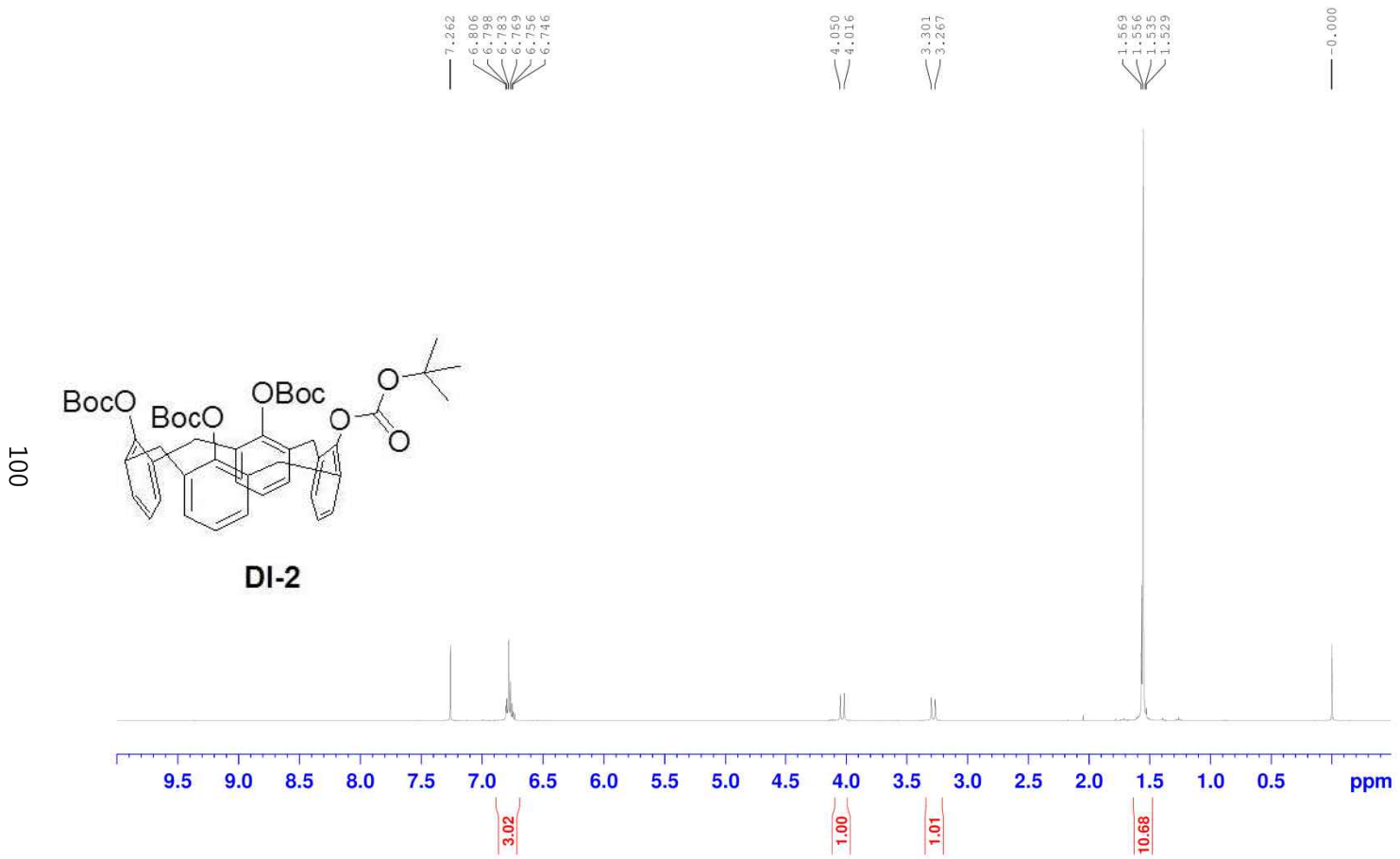
400 MHz ^{1}H-NMR spectrum (DMSO-d_6) of compound **17**



400 MHz ^{1}H-NMR spectrum (DMSO-d_6) of compound **19**

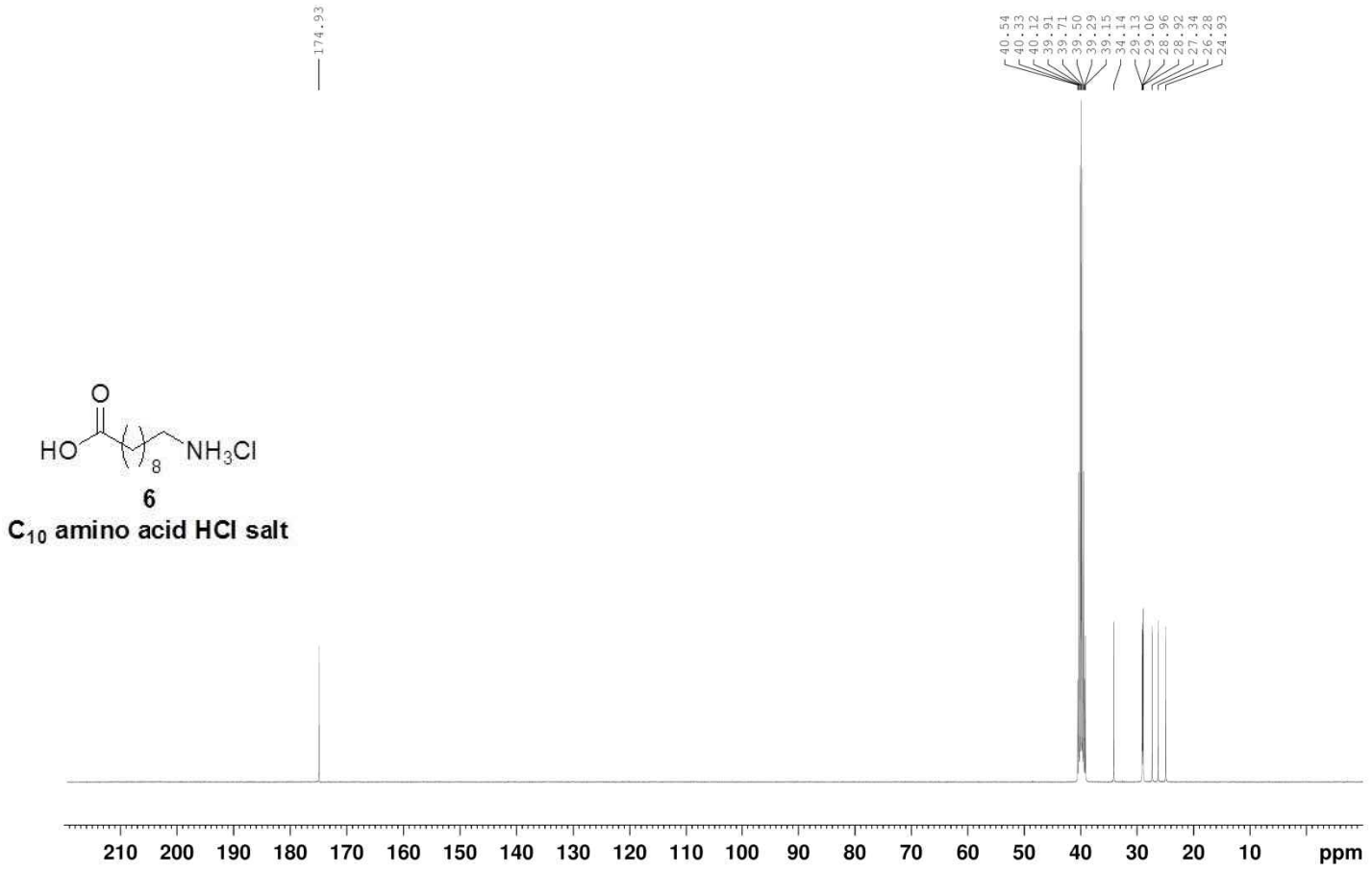


400 MHz ^{1}H-NMR spectrum ($CDCl_3$) of compound **DI-1**

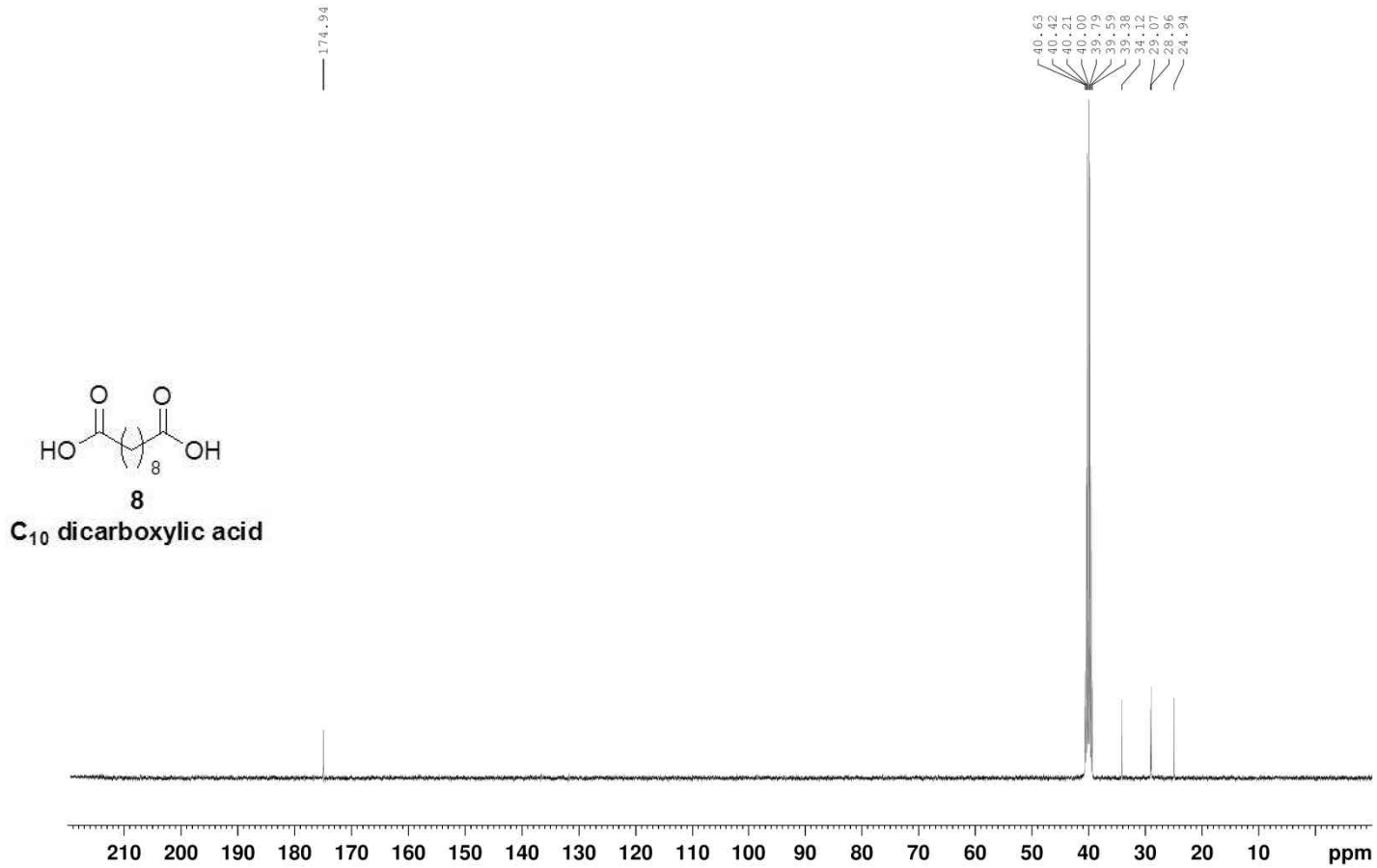


400 MHz ^{1}H-NMR spectrum ($CDCl_3$) of compound **DI-2**

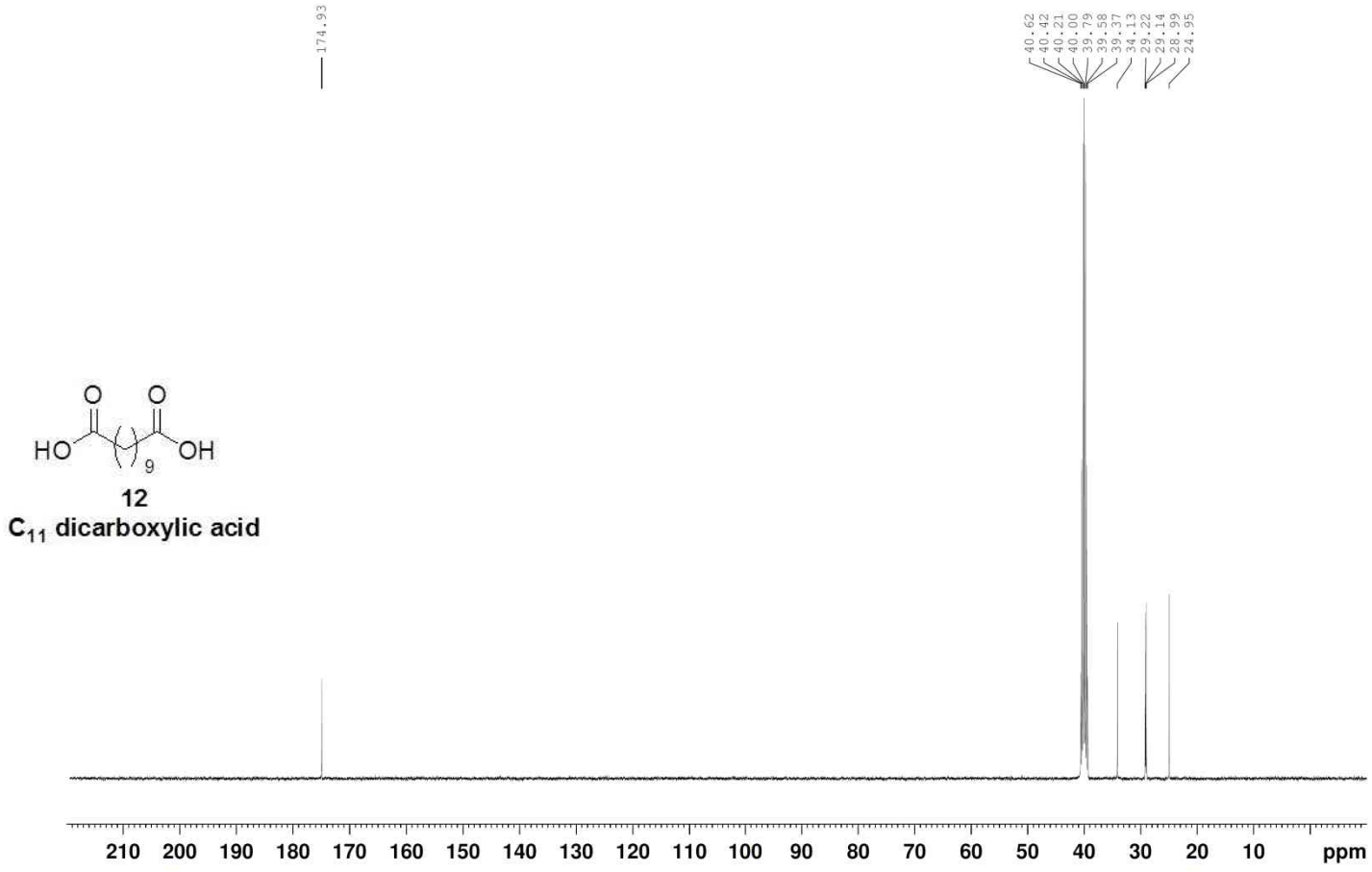
List of ^{13}C-NMR Spectra of Selected Compounds



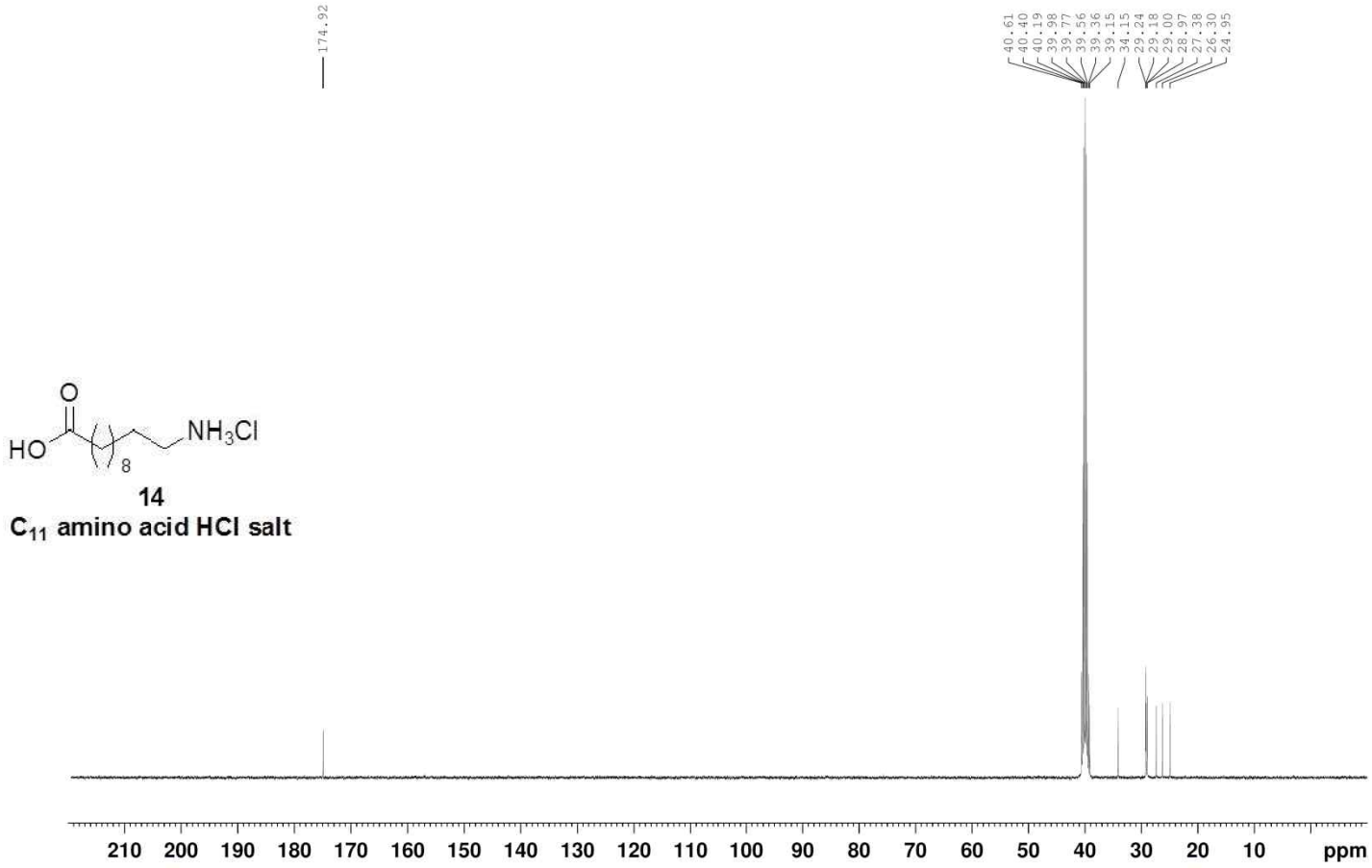
100 MHz ^{13}C-NMR spectrum (DMSO-d_6) of compound **6**



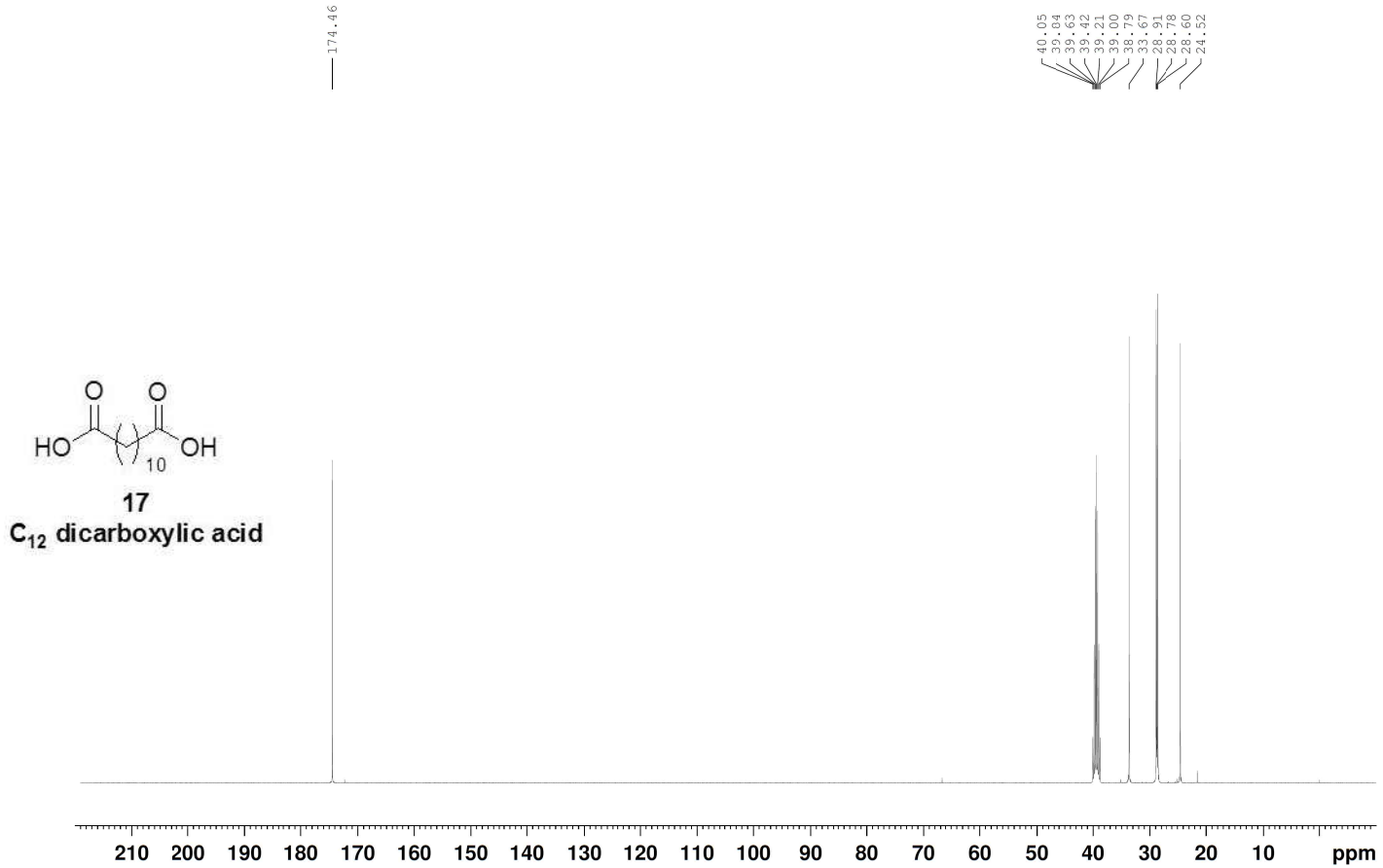
100 MHz ^{13}C-NMR spectrum (DMSO-d_6) of compound **8**



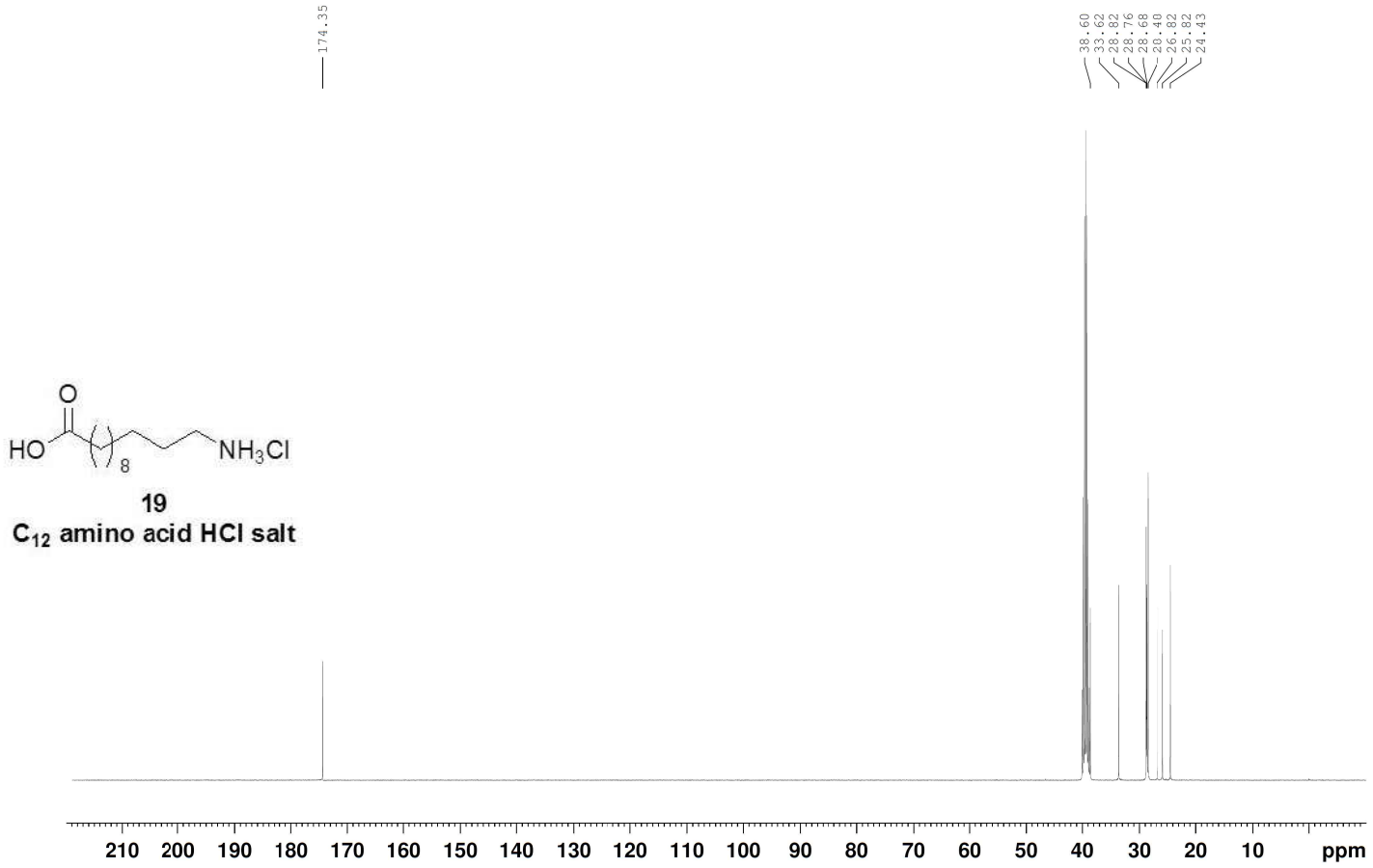
100 MHz ^{13}C-NMR spectrum (DMSO-d_6) of compound **12**



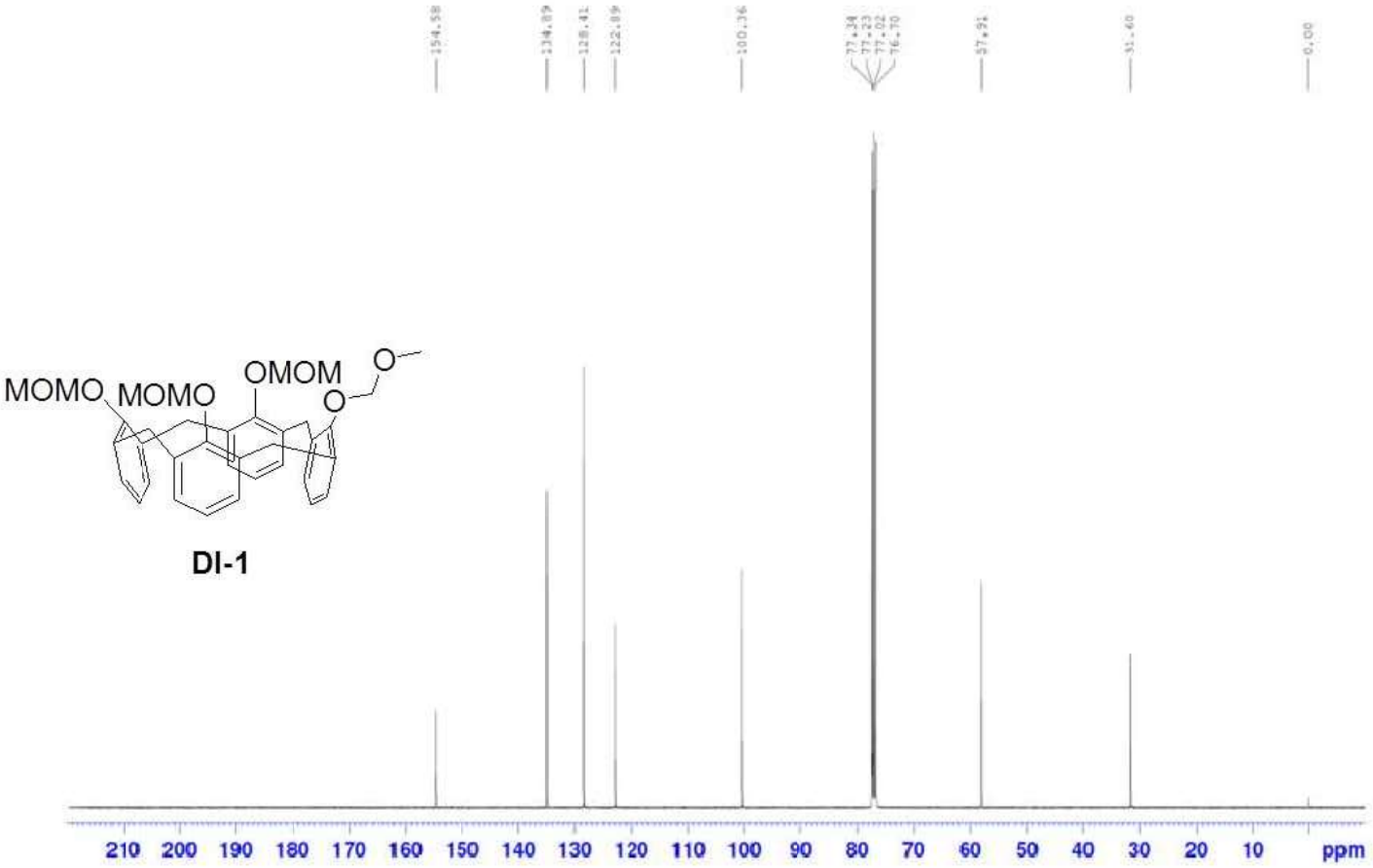
100 MHz ^{13}C-NMR spectrum (DMSO-d_6) of compound **14**



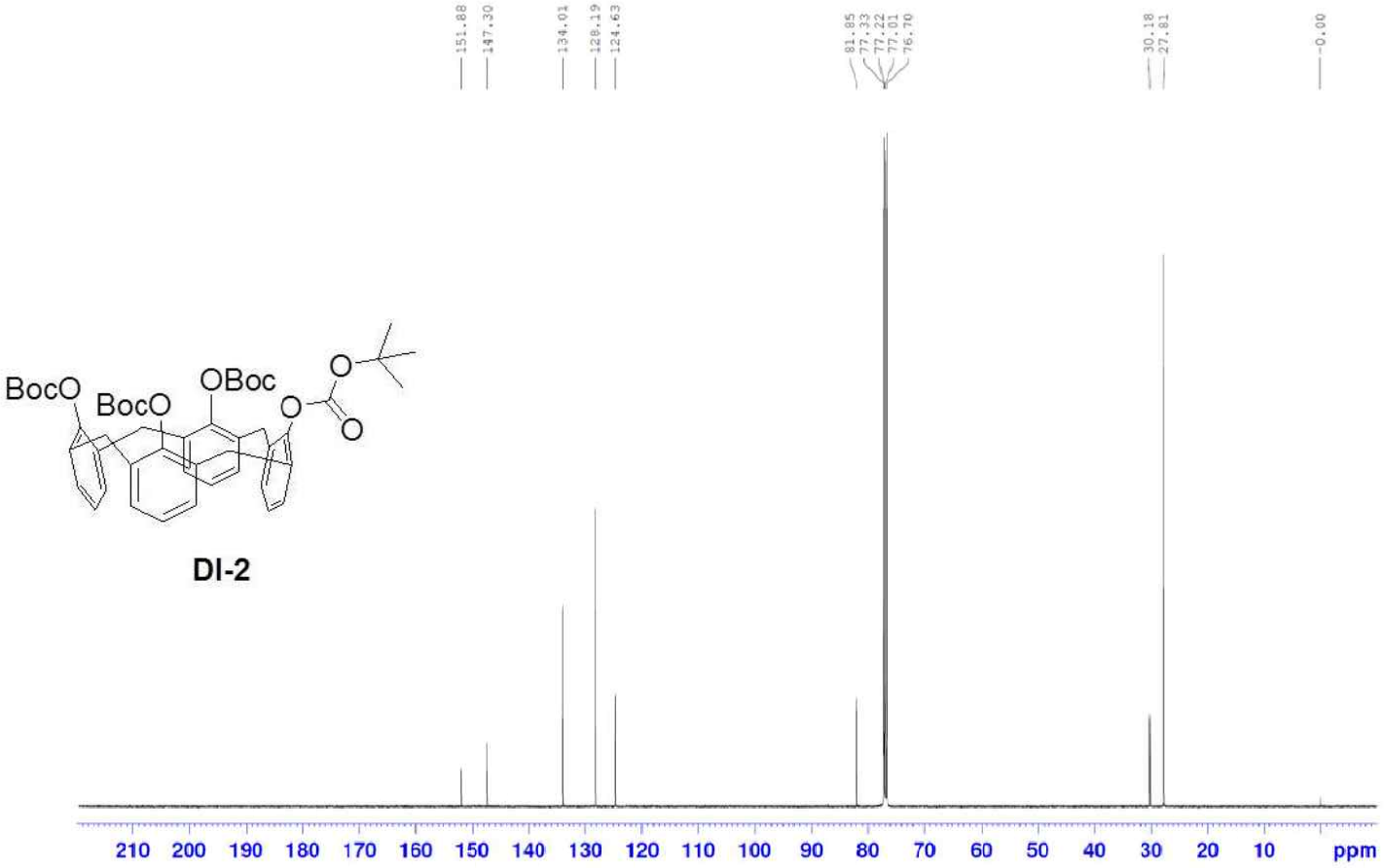
100 MHz ^{13}C-NMR spectrum (DMSO-d_6) of compound **17**



100 MHz ^{13}C-NMR spectrum (DMSO-d_6) of compound **19**



100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of compound **DI-1**



100 MHz ^{13}C-NMR spectrum ($CDCl_3$) of compound **DI-2**

국 문 초 록

유용한 엔지니어링 플라스틱으로 잘 알려진 열가소성 탄성체 중에서 폴리아미드를 경질부로 하는 폴리아미드계 열가소성 탄성체는 뛰어난 물리적 특성으로 인해 다양한 분야에 활용이 되고 있다. 석유를 기반으로 한 화학 산업이 가진 한계로 인해 재생 가능한 자원에 대한 관심이 증대되기 시작하였고, 이러한 연구의 일환으로 식물성 오일을 출발물질로 하여 폴리아미드 단량체를 합성하는 친환경적 기술에 대한 연구를 진행하게 되었다. 작용기 변환 반응과 탄소 신장 반응 등을 활용하여 피마자유를 기반으로 한 운데실렌산으로부터 탄소수가 10 개~12 개인 디카르복실산과 아미노산 단량체 6 종을 좋은 수율과 높은 순도로 합성할 수 있었다. 올리브유를 비롯한 대부분의 식물성 오일에 다량 포함된 올레익산과 유채씨유로부터 추출할 수 있는 에루식산에 이 공정을 적용한 결과, 탄소수가 각각 9 개~11 개, 13 개~15 개인 디카르복실산과 아미노산 단량체 12 종을 얻을 수 있었다. 하나의 식물성 오일 기반 출발물질로부터 유용한 6 종의 단량체를 합성할 수 있는 효율적인 공정을 개발하여 친환경적 기술을 확보할 수 있게 되었다.

반도체 메모리의 고집적화는 미세 패턴을 형성하기 위한 광원 기술의 개발과 더불어 발전해 왔으나, 새로운 기술을 실제 공정에

적용하기까지는 막대한 투자비용과 효율성 문제가 발생한다. 따라서 기존 공정을 활용하면서 공정의 효율성을 증가시키기 위한 방법으로 용해억제제와 네거티브 포토레지스트의 합성 연구를 진행하였다. 감광성 물질로 잘 알려진 칼릭사렌을 출발물질로 하여 산성 조건에서 쉽게 제거가 가능한 MOM 과 t-Boc 을 보호기로 도입하여 각각 73%, 58%의 좋은 수율로 2 종의 용해억제제를 합성하였다. 2 종의 용해억제제는 상용화된 포토레지스트에 첨가하여 포토리소그래피 성능을 평가하였고, 포토레지스트의 감도와 대비의 향상으로 인한 해상도 증가, 초점 심도와 최소 선폭의 개선 효과를 확인할 수 있었다. 현재 공정에서 네거티브 이미지를 구현하기 위해 유기 용매를 현상액으로 사용하는 공정이 가장 효과적으로 사용되고 있으나, 이미 외국 기업에 의한 기술 선점이 이루어져 있기 때문에 이를 우회하기 위해 새로운 개념의 네거티브 포토레지스트를 제안하였다. 단량체 수준에서 원하는 물성을 구현하기 위해 다양한 구조의 목표 화합물을 설계하였고 실제 합성을 진행하였으나, 아직까지 원하는 결과를 얻지는 못하였다. 본 연구를 통해 공정의 개선을 위해 유기합성적인 관점에서 접근하는 것에 대한 가능성을 확인할 수 있었다.

주요어 : 열가소성 탄성체, 폴리아미드, 단량체, 식물성 오일, 용해 억제제, 네거티브 포토레지스트

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