Olefin Metathesis Assisted Synthesis of Biodegradable Polymers Using Algae Phospholipid Renewable Resources

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KM2: 117986 final report

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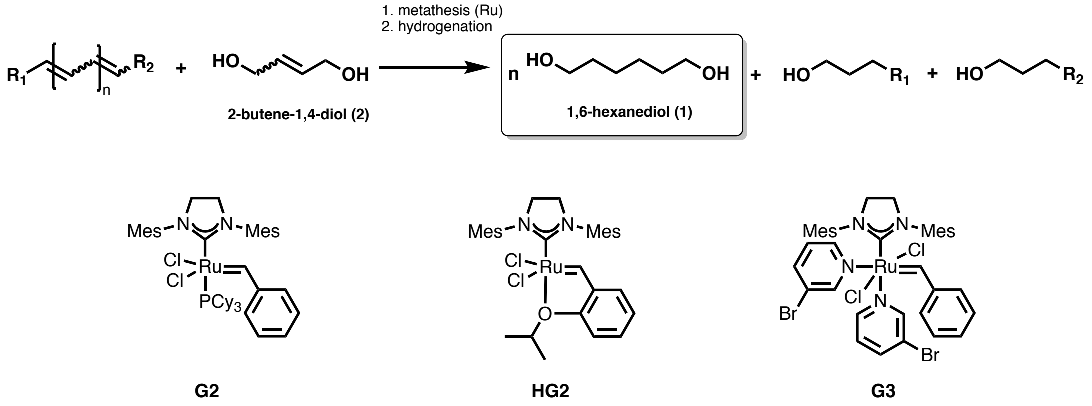
2. Introduction

"Green chemistry" is a central issue in both in academia and industry with regard to chemical synthesis in the 21st century.[1] Fossil fuels increase greenhouse gas emissions in the atmosphere resulting in serious climate changes. Moreover, as they are constantly diminishing, development of CO_2-neutral fuels and raw materials is one of the most urgent challenges facing our society. Therefore, there is an urgent need for CO_2-neutral and sustainable resources to replace fossil raw materials in the upcoming decades. Following the industrial trends, more emphasis has been placed upon materials (preferably degradable) from renewable resources.[2] Polymers such as polyamides and polyesters are produced on a vast scale. These are one of the most popular plastics in use today and they are considered as petroleum-based polymers. This area of research is undoubtedly under constant strain, where advances and interest concerning the applicability of new and novel environmentally benign materials are required.[3] Therefore, development of robust, sustainable and green synthetic procedures for the production of value-added chemicals and materials from renewable resources is of great industrial interest.

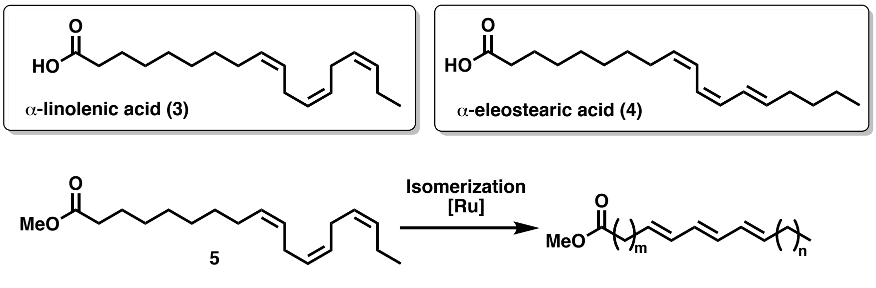
An emerging commodity chemical is the 1,6-hexanediol, which is used as intermediate in polyurethanes (PUR), acrylates, polyesters (e.g. PET), polyols (for example, in reaction with propylene oxide), coatings and plasticizers represent a large slice of the present plastic slate of the world.[4] The market of 1,6-hexanediol is estimated at USD 730 million in 2016 and is projected to grow over 1 billion USD by 2021. The 1,6-hexanediol is not only a high-value building block in the above mentioned commercial polymers, but it can also be used as precursor for adipic acid production via aerobic oxidation using heterogeneous Pt, Au and Pd based catalyst systems.[5]

Tentatively it was supposed that 1,6-hexanediol (**1**) can alternatively be synthetized via the cross metathesis of conjugated polyunsaturated materials including polyunsaturated fatty acids with *cis*/*trans* butene diol (**2**) using commercially available olefin metathesis catalysts (Scheme 1). **2** can be readily synthesized from allyl alcohol via olefin metathesis. Allyl alcohol is considered as a renewable material as it can be obtained from glycerol.[6]



Scheme 1. Top: Main concept for the synthesis of 1,6-hexanediol (**1**) via the cross-metathesis of conjugated feedstock and 2-butene-1,4-diol (**2**). Bottom: commercially available Ru olefin metathesis catalysts

Microalgae oil is a potential renewable source for biobased-material production.[7] It has a great capability to accumulate significantly higher amounts of lipids[8] than conventional oil crops like sunflower or palm (80% vs 5% of dry weight).[9] Moreover, the algae phospholipids which are formed during algae oil production on vast scale are side products and are considered as low-value materials, which does not have any utilization yet. Similarly to algae oils the phospholipids also contain a wide range of fatty acids with comparable chain length extractable from all feedstock, however they contain considerably higher amount of polyunsaturated chains (16:0; 18:1; 18:3; 18:4; 20:5).[10] These highly unsaturated fatty acids are ideal green stock material for the synthesis of sustainable chemicals via metathesis such as innovative polymers, fine chemicals and pharmaceutical ingredients. Polyunsaturated fatty acids can also be found in a wide range of seed oils including linseed (flax) and tung oil. The main component of linseed oil is α-linolenic acid (**3**) (55%), containing three isolated double bonds. As thermodynamically preferred, the isolated double bonds of the polyunsaturated materials can be readily converted to conjugated ones via ruthenium catalyzed isomerization reactions (Scheme 2). The major component of tung oil is the α-eleostearic acid (**4**) (82%), containing three conjugated double bonds.

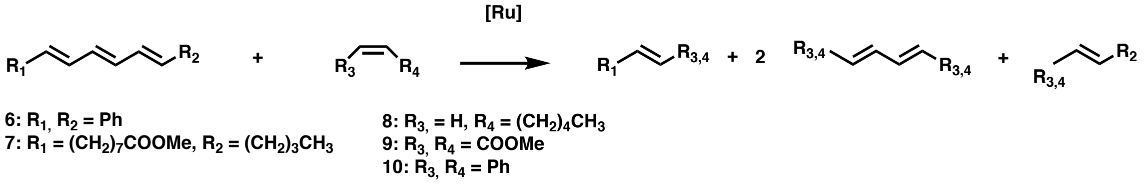


Scheme 2. Top: α-linolenic (**3**) and α-eleostearic acid (**4**). Bottom: isomerization of α-linolenic acid methyl ester

3. Investigation of the metathesis of conjugated feedstock[11]

At the beginning of the project the background literature was worked up and a review article was written containing olefin metathesis reactions using conjugated substrates.[12] As it was learned, the olefin metathesis catalytic reactions were not optimized for conjugated feedstocks and their reaction mechanism was not studied in detail yet. Therefore, some model reactions and theoretical calculations were carried out to investigate the feasibility of the conversion of conjugated polyunsaturated olefins via olefin metathesis using commercially available catalyst systems.

Cross-metathesis (**CM**) of conjugated polyenes, such as 1,6-diphenyl-1,3,5-hexatriene (**6**) and α-eleostearic acid methyl ester (**7**) with several olefins, including 1-hexene (**8**), dimethyl maleate (**9**) and *cis*-stilbene (**10**) as model compounds was carried out using Hoveyda-Grubbs 2nd generation, **HG2** catalyst. The feasibility of these reactions was demonstrated by the observed high conversions and reasonable yields. Thus, regardless of the relatively low electron density, =CH–CH= conjugated units of molecules, including **7** as a sustainable, non-foodstuff source, can be utilized as building blocks for the synthesis of various value-added chemicals via olefin metathesis. DFT-studies and the product spectrum of the self-metathesis of **6** suggest that a Ru η^2-allylidene complex is the active species in the reaction.

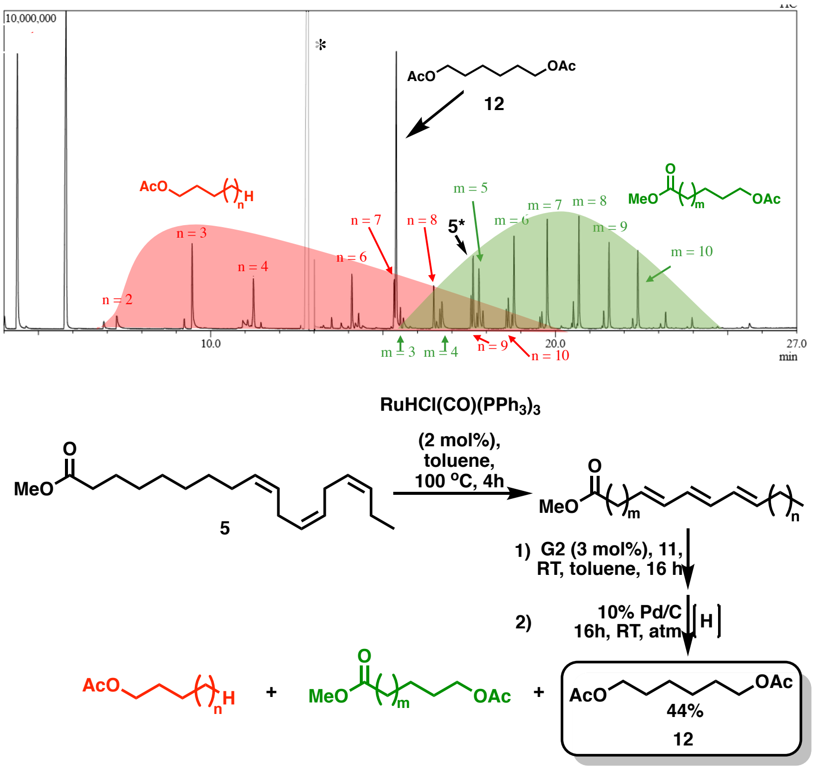


Scheme 3. Model cross-metathesis (CM) reactions of conjugated feedstocks

4. Synthesis of 1,6-hexanediol from renewable resources via isomerization metathesis[13]

Cross metatheses of tung oil, a non-edible vegetable oil and α–eleostearic acid ((9*Z*,11*E*,13*E*)-octadeca-9,11,13-trienoic acid, ESA) methyl ester (**7**), obtained from tung oil containing the same highly unsaturated, conjugated double bonds, have been carried out with *cis*-1,4-diacetoxy-2-butene (**11**) using Hoveyda-Grubbs (**HG2**), Grubbs second or third generation catalysts (**G2** or **G3**). The reactions followed by Pd/C-catalyzed hydrogenation, give methyl 11-acetoxyundecanoate as a polyester raw material, 1,6-diacetoxy-hexane (**12**) as a precursor of 1,6-hexanediol (**1**) polyurethane monomer and heptyl acetate as a flagrance in 53-99% yields after Pd/C-catalyzed hydrogenation. The above-mentioned promising results prompted us to extend the investigations of the synthesis of 1,6-hexanediol (**1**) via isomerization metathesis of isolated double bond containing renewable feedstocks. The one-pot isomerization metathesis of α–linolenic acid ((9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrienoic acid, ALA) methyl ester (**5**) using **11** as cross coupling agent, $RuHCl(CO)(PPh_3)_3$ as isomerization and **G2** as metathesis catalyst followed by Pd/C catalyzed hydrogenation also leads to the formation of **12** and the homologs of 11-acetoxyundecanoate and heptyl acetate in reasonable yield. Thus, in the latter approach, the key step of the synthesis of **12** is the one-pot isomerization of the isolated double bonds of **5** into conjugated ones along the fatty acid chain in combination with a subsequent cross-metathesis by using cross-coupling agent **11**.

It has been shown that the synthesis of some commercially available so far petrochemical based chemicals is feasible from renewable feedstocks. This chemical procedure makes the synthesis of polyurethane and polyester monomers possible using a wide range of polyunsaturated fatty acids of different origin containing conjugated or isolated double bonds. The combination of one-pot isomerization and cross-metathesis reactions of polyunsaturated fatty acid feedstocks (either vegetable oil or algae oil based) provides new alternatives for the replacement of fossil-based materials into carbon dioxide neutral, sustainable ones.



Scheme 4. Synthesis of 1,6-hexanediol via isomerization metathesis of α-linolenic acid (top: TIC diagram of the reaction mixture)

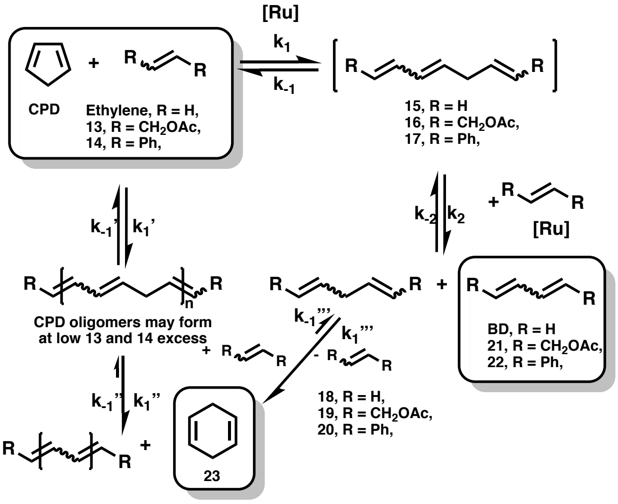
5. Synthesis of 1,6-hexanediol from petrochemical by-products[14]

As an additional idea, the above-mentioned concept was extended to petrochemical by-products including the low-value cyclopentadiene (**CPD**) and cyclopentene.

The petrochemical industry continues to face enormous challenges from product development and diversification, and nowadays also from sustainability. For example, three decades ago the plastic production was based on ethylene, propylene and the aromatic BTX-fractions almost solely. Thus, refineries were optimized for the production of these compounds.[15] C4 and C5 olefin and diene streams or components were considered as low-value intermediates and were typically recycled in steam-crackers in order to increase the yields of the light olefins. The unusual chemical properties and low commercial value of **CPD** have prompted us to investigate its activity in olefin metathesis reactions.

The metathesis of dicyclopentadiene (**DCPD**) with ruthenium metathesis catalysts is well-known and has been investigated in detail.[16] However, the reported metathesis reactions of **CPD** and other compounds containing conjugated double bonds are rare.[17] This is not surprising as **CPD** is relatively unstable, it can spontaneously dimerize to **DCPD** via Diels-Alder (DA) reaction.[18,19] In addition, the conjugated electron system is expected to reduce activity in metathesis reactions via the formation of less or non-reactive η^4-allylidene(vinylcarbene) species.[12,20,21] Despite the relative instability of neat **CPD** at room temperature, it was supposed that the DA reaction can be hindered using low temperature and/or diluted solutions.[22] Considering the mediocre ring strain, it was presumed that the ring opening cross-metathesis (ROCM) of **CPD** should be feasible in diluted solution (5 V%) using an excess of electron rich cross-coupling agents (such as ethylene, *cis*-butenediol diacetate (**13**) or *cis*-stilbene (**14**)) and highly active metathesis catalysts systems (**G2, HG2** and **G3**) (Scheme 1).

A novel tandem reaction of **CPD** leading to value-added linear polyolefins has been demonstrated. It has been shown that **CPD** can be readily converted to high-value chemicals such as 1,6-hexanediol (**1**) polyurethane monomer and 1,3-butadiene (**BD**) in reasonable yields via ruthenium-catalyzed tandem ring opening cross-metathesis (**ROCM**) and cross-metathesis (**CM**) reactions at low catalyst loading and ambient reaction conditions (TON up to 1180). The reaction product composition strongly depends on the applied reaction time and the excess of the cross-coupling agents. When the tandem **ROCM/CM** of **CPD** is carried out in the presence of stoichiometric amount or slight excess of cross coupling agents (**Ethylene**, **13** or **14**) at extended reaction time **CPD** oligomerization (giving a non-soluble solid), some secondary metathesis products and 1,4-cyclohexadiene (**23**) formation occur. When relatively short reaction time (3h) and high excess of cross-coupling agents applied the target, secondary metathesis products (e.g. **21** and **19**) form in reasonable yield (up to 68%). The primary metathesis products (**15**, **16**, or **17**) could always be detected, however the secondary metathesis products are always the major components of the reaction mixture. Theoretical calculations indicated that the relatively high yields for the secondary metathesis products (**19**, **21** and **20**, **22**) are most apparently due to the relative high K_2 (>> K_1) equilibrium constants (Scheme 5).



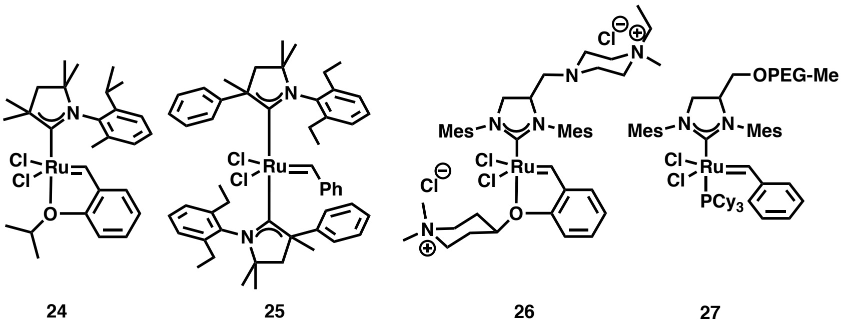
Scheme 5. Synthesis of 1,6-hexanediol (**1**) derivative, 1,4-diphenylbuta-1,3-diene and butadiene via ring opening cross metathesis (ROCM) of cyclopentadiene

6. Development of Highly Efficient Olefin Metathesis Catalysts in Protic Media

The chemical industrial processes comprise in more or less all cases at least one enabling catalytic step to provide chemicals to many other industries.[23] Olefin metathesis is fundamentally one of the novel organometallics catalyzed reactions discovered in the last fifty years that initiated new industrial technology avenues leading to innovative materials, petrochemicals and pharmaceuticals.[24,25] Nevertheless, the current “state of the art” ruthenium catalyst systems render exceptional activity, their applications in environmental benign, protic media are often limited.[26] The “green” solvents imply such reaction media, which have low environmental impact. Alcohols including methanol, ethanol, propanol or their alcohol-water mixtures are generally considered as a green-solvents and their use in high scale industrial applications are strongly recommended.[27]

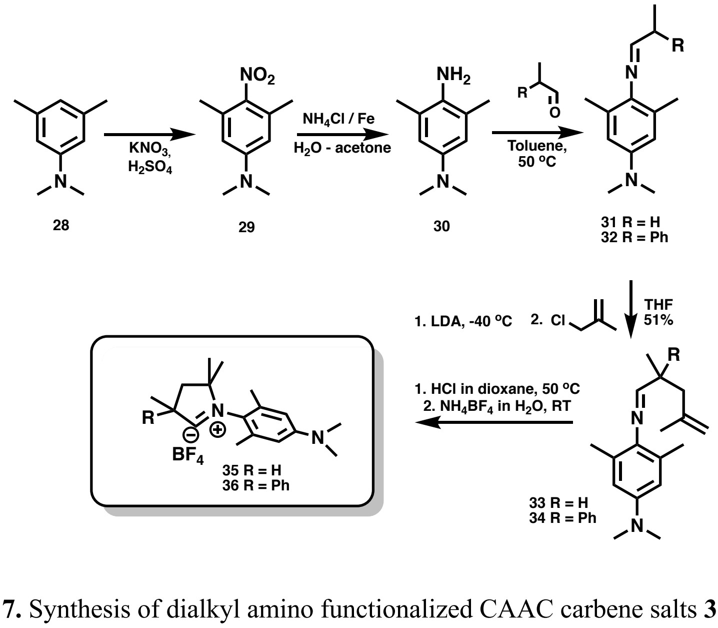
The recent olefin metathesis catalytic processes require 2-5 mol% catalyst loadings to achieve reasonable substrate conversions using environmental benign, protic media.[28] Nevertheless, catalyst turn over numbers (TONs) 50.000 (0,002 mol% catalyst loading) are considered as a minimum threshold in commodity chemicals’ manufacturing.[29]

It has recently been reported that replacing the NHC ligand of the **HG2** catalyst by cyclic alkyl amino carbene (CAAC) (**24**) ones render superior olefin metathesis catalytic activity even at 3 ppm catalyst loading level (TON > 100000).[30,31] Skowerski has also reported a highly active bis(CAAC)-Ru indenylidene complex (**25**) showing exceptional, as high as 315000 TON (Scheme 6).[32] This outstanding activity could be explained by the improved stability of the 14 electron, catalytically active species. It was envisioned that the development of polar, phase labelled protic solvent and/or water-soluble CAAC coordinated ruthenium olefin metathesis catalysts would open the way to highly efficient, green and sustainable chemical processes. Considering the synthesis of highly polar water and protic solvents soluble catalyst systems in general two main approaches are applied: (1) grafting the catalyst to water-soluble polymers such as polyethylene glycol (PEG, **27**)[33] and (2) synthesis of catalysts containing highly polar, small tags such as quaternary ammonium salts or sulfonyl groups (**26**) (Scheme 6).[33]



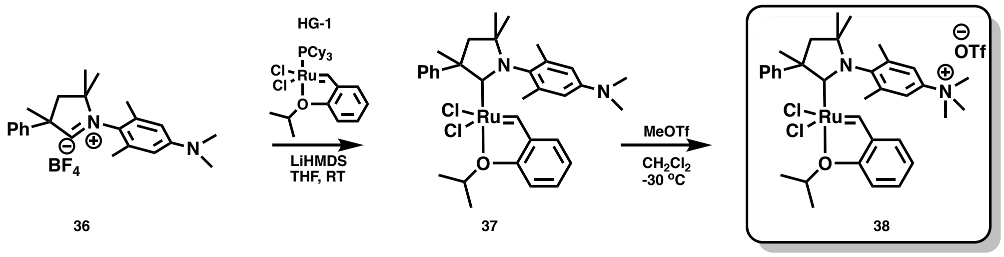
Scheme 6. Cyclic Alkyl Amino Carbene (CAAC) and bis(Cyclic Alkyl Amino Carbene) ruthenium complexes showing exceptional activity in olefin metathesis reactions

Experiments were carried out to investigate the introduction of dimethyl amino group on the N-aromatic ring of the CAAC ligand. It turned out that the synthesis of **35** and **36** carbene precursor salts are straightforward and the reaction can easily be scaled up to multigram scale. Some tests were also carried out to investigate the feasibility of the introduction of additional ammonium ion salts in the *R* position. The compound **36** can be synthetized on multigram scale (Scheme 7, overall yield 12%).



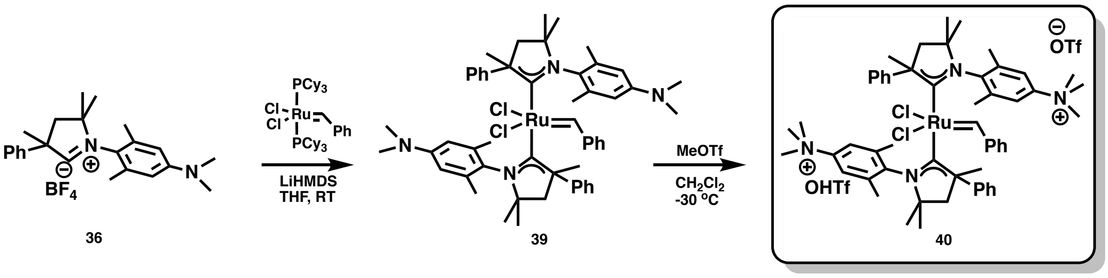
Scheme 7. Synthesis of dialkyl amino functionalized CAAC carbene salts **35** and **36**.

The Hoveyda-Grubbs type CAAC-Ru complex **38** can be synthesized by the reaction of deprotonated **36** with **HG1** complex. Quaternization of CAAC complexes **37** was completed by the reaction of its DCM solution with MeOTf in an inert atmosphere at -30 °C giving the target complex (**38**) as green microcrystals (Scheme 8, overall yield 40%).



Scheme 8. Synthesis of quaternary ammonium ion tagged HG2 type CAAC ruthenium metathesis catalysts (**38**).

The *bis*(CAAC)-Ru complex can be synthetized via the reaction of deprotonated CAAC salt **14** and first generation Grubbs catalyst (**G1**). Quaternization of CAAC complexes **23** was completed by the reaction of a DCM solution of **23** and MeOTf in an inert atmosphere at -30 °C giving the target complex **24** as yellow needle crystals in reasonable yield (48%).



Scheme 9. Synthesis of quaternary ammonium ion tagged ***bis*(CAAC)-Ru** type CAAC ruthenium metathesis catalysts (**40**).

After methylation, the complexes **38** and **40** could even be filtered on air, so their stability are remarkably better than that of the older generation ruthenium-based metathesis catalysts. Complexes **37** and **39** could be crystallized from hexane.

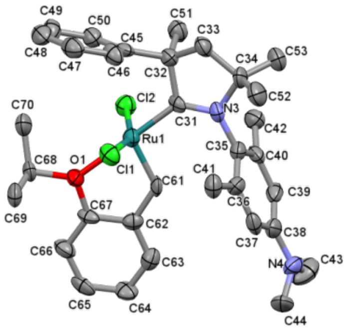


Figure 1. X-Ray structure of complex **37**.

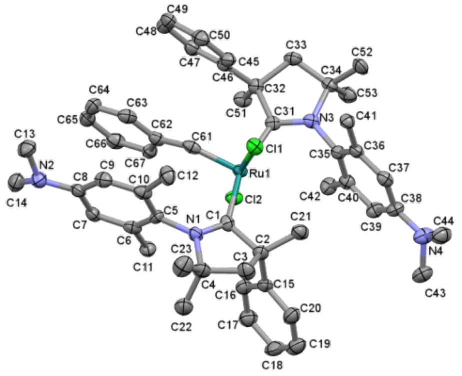


Figure 2. X-Ray structure of complex **39**

Some experiments have been carried out to investigate the catalytic activity of the synthetized “prototype” olefin metathesis catalysts **37** – **40**. Preliminary ring closing metathesis (RCM) and ring opening metathesis polymerization (ROMP) reactions have been carried out either in methanol, isopropanol or methanol/water solvent mixture. It was observed that the non-quaternerized complexes were not soluble in methanol, they formed suspension even at low catalyst loadings at room temperature. However, the complex **38** and **40** showed reasonable solubility and stability in methanol. The half-lifes of **38** and **40** was around one week at room temperature in methanol under exposure to air.

The NMR-spectra of complexes **37** and **39** are rather complex as in solution several rotational and diastereomeric isomers can be observed. The spectra of both complexes indicated fluxional behavior. Complex **37** exhibited one major and one minor broad peak for benzylidene proton, meanwhile complex **39** showed four peaks for the benzylidene proton. By examining the structure of this complex, it appeared that the CAAC ligands rotate in the way that the dimethylamino groups are placed on the opposite sites of the molecule. The signal of the benzylidene hydrogen atom is the most characteristic in the ^{1}H spectra. It has an extremely high chemical shift (about 18 ppm), and all the isomers (rotational diastereomers) gave shifts with different intensity – depending on their chemical environment. Interestingly, upon quaternarization the spectra become much simpler, only one signal for the benzylidene proton could be observed in each case.

The kinetic investigation of the ring closing metathesis (**RCM**) of diallyl malonate (**41**, Scheme 10) was selected as model reaction to compare the catalytic activity of **HG2**, **37** and **38** complexes at similar reaction condition (30 °C, acetone-d_6). The investigations revealed that complexes **37** and **38** render similar activity in RCM reaction of **41**.

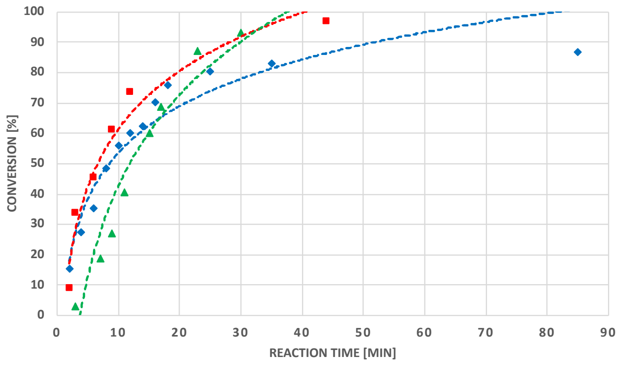
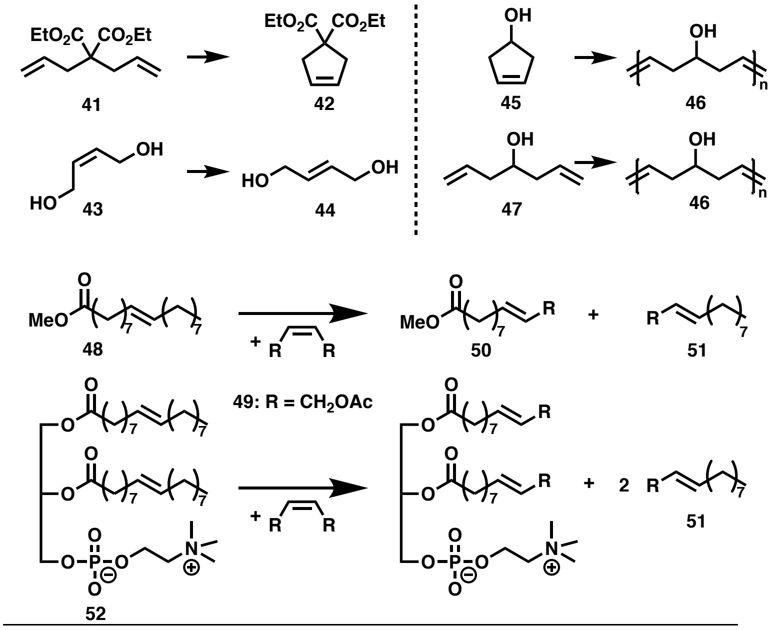


Figure 3. Reaction kinetic investigation of the formation of **42** using catalyst **HG2** (blue), **37** (red) and **38** (green). ([**41**] = 120 mM; [**Cat**] = 0.06 mM; 30 °C, acetone-d_6).

However, based on the repeated experiments a slightly prolonged initiation period could be observed when **38** was used. Nevertheless, 90% yield could be obtained with both **37** and **38** complexes after 30 minutes reaction time. The **HG2** revealed slightly lower activity (80% yield). It can be concluded that the investigated complexes render similar activity and most probably catalysts **37** and **38** decompose slower than the **HG2** catalyst.

The catalytic activity of the complex **38-40** in protic solvents including MeOH, MeOH/water mixture and isopropanol (IPA) or in neat were investigated. Complex **37** is not soluble in methanol meanwhile complex **39** show slight solubility at elevated temperature. The reactions were carried out at 0.05 – 5 mol% catalyst loading range. The isomerization of *cis*-butenediol (**13**) was carried out with catalyst **38** in methanol and isopropanol (IPA) solutions. When IPA was used significantly higher conversion (56% vs. 36%) was observed.

Table 1. Result of olefin metathesis reactions



Entry	substrate	Product	Cat.	Mol%	Temp (°C)	Time (h)	Yield (%)	TON
1	41	42	38	0.05	RT	3	29	580
2	41	42	40	0.05	65	3	64	1280
4	43	44	38	0.05	RT	3	36	780
5	43	44	38	0.05	RT	3	56	1120[f]
6	43	44	40	0.05	65	3	30	-[a]
7	45	46	38	0.05	RT	3	65	1300
8	45	46	38	0.05	RT	24	79	1580
9	45	46	38	0.05	RT	24	32	640[b]
10	45	46	39	0.05	65	3	32	640[c]
11	45	46	40	0.05	65	3	50	1000[c]
12	47	46	38	0.50	RT	3	39	78[d]
13	47	46	40	0.50	65	3	50	100[d]
14	48	51	38	0.05	RT	24	NR[e]	NR[e]
15	48	51	39	0.05	65	3	99	1980[c]
16	48	51	30	0.05	65	3	41	820
20	52	51	38	0.50	RT	24	57	114
21	52	51	39	4.2	65	3	NR[e]	NR[e]
22	52	51	40	4.2	65	3	80	19

[a] a mass formed; [b] Reaction carried out in 50% MeOH/50% H_2O mixture; [c] Reaction carried out in neat;
[d] mixture of 26% **46**, 13% **45**; [e] NR: no reaction; [f] reaction carried out in isopropyl alcohol (IPA)

The ring closing metathesis (**RCM**) reaction of diallyl-malonate (**41**) model compound was carried out in methanol solution using catalyst **38** at RT and **40** at 65 ºC at 0.1 and 0.05 mol% catalyst loading. It was found that **RCM** reaction took place in 94% yield when catalyst **40** was used at 0.1 mol% loading (TON: 940, 65 ºC). Repeating the reaction at 0.05 mol% catalyst loading 64% (TON: 1280) RCM product (**42**) formation was observed. Catalyst **38** was already active at room temperature. After three-hour reaction time at 0.05 mol% catalyst loading the formation of **42** was observed in 29% yield (TON: 580).

The ring opening metathesis polymerization of 3-Cyclopenten-1-ol (**45**) was carried out in methanol using catalyst **38** and **40** at 0.05 mol% loadings. When the reaction was carried out using catalyst **40** at 65 ºC the polymer **46** formed in 50% yield, (TON: 1000). The polymerization of **45** with catalyst **38** at room temperature resulted in the formation of the polymer in 79% yield (TON: 1580). Repeating the experiment in methanol/water 1:1 mixture at the same condition revealed the formation of the polymer in 32% (TON: 640).

7. Summary

Development of environmentally benign chemical processes and technologies are central issues to both academia and industry. The use of fossil fuel based raw materials increase greenhouse gas emissions in the atmosphere resulting in serious climate changes. The development of CO_2 neutral fuels and materials is one of the most urgent challenges facing our society. Olefin metathesis is a powerful and versatile environmentally benign method in synthetic organic and polymer chemistry. Most of the reactions take place at ambient condition and the atom economy of these synthetic procedures is high (often 100%), indicating that most of the starting materials are incorporated into the end products. Nature is abundant in polyunsaturated bio-based materials. Low value added conjugated olefins can also be found in vast amount in petrochemical by-products. These chemicals often render an underutilized feedstock.

In the frame of this project exploratory studies were carried out on the metathesis of polyenes including a renewable material. It could be concluded that conjugated polyenes containing three olefinic bonds undergo metathesis reaction despite the relatively low electron density of the double bonds. Thus, a sustainable, non-foodstuff material such as α-eleostearic acid can be converted into high-value chemicals. It was shown that the synthesis of some commercially available so far petrochemical based chemicals is feasible from renewable feedstocks. The combination of one-pot isomerization and cross-metathesis reactions of polyunsaturated fatty acid feedstocks (either vegetable oil or algae oil based) provides new alternatives for the replacement of fossil based materials into carbon dioxide neutral, sustainable ones. These chemical processes make the synthesis of polyurethane and polyester monomers feasible using a wide range of polyunsaturated fatty acids of different origin containing either conjugated or isolated double bonds.

A novel tandem reaction of low-value cyclopentadiene (**CPD**), petrochemical side product leading to value added linear polyolefins was demonstrated. It was shown that **CPD** could be readily converted to high value chemicals such as 1,6-hexanediol polyurethane monomer and 1,3-butadiene (**BD**) in reasonable yields via ruthenium-catalyzed tandem ring opening cross-metathesis (**ROCM**) and cross-metathesis (**CM**) reactions at low catalyst loading and ambient reaction conditions. An alternative utilization of low-value cyclopentene was also elaborated including the development of recyclable polypentenamer derivatives.

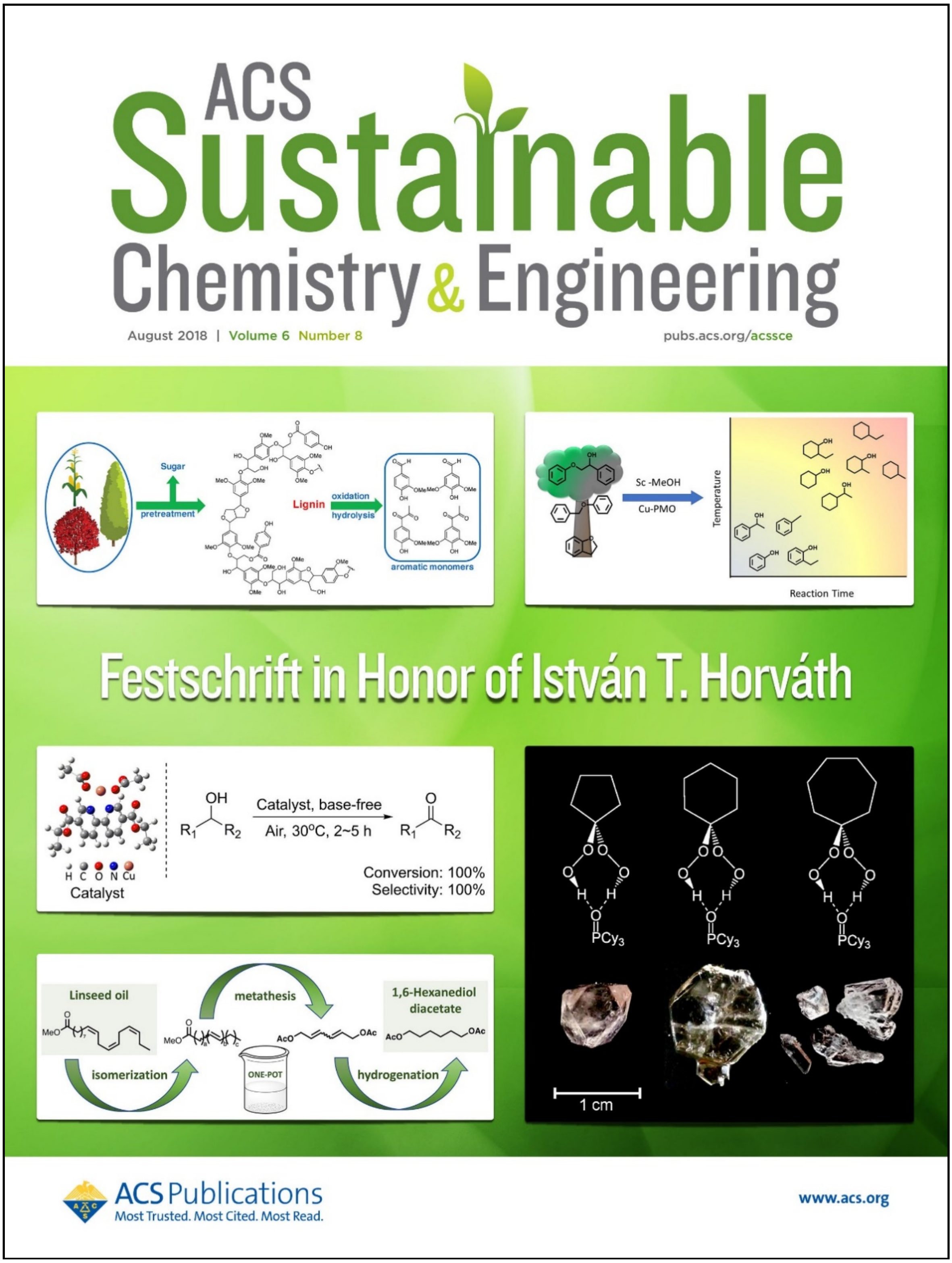
New generation, protic solvent soluble cyclic alkyl amino carbene (CAAC) ligand coordinated ruthenium complexes were synthetized. Their catalytic activity were investigated on different model reactions in methanol, isopropanol and methanol/water mixture rendering exceptional activity. The ultimate goal is the development of such chemical processes where the conversion of low-value renewable materials can be carried out in environmental benign media at moderate reaction condition and low catalyst loading. The feasibiliy of the synthesis of biopesticides from renewable materials has recently been reviewed which may also be a follow-up chemistry of this project.

In the frame of this project six papers have been published (∑ IF: 30), two of them are cover featured. One additional manuscript is still in preparation. The authors were pleased to take part in this project and are highly appreciate for the generous support.

Cover Feature:

Kovács, E.; Turczel, G.; Szabó, L.; Varga, R.; Tóth, I.; Anastas, P. T.; **Tuba, R.**
“Synthesis of 1,6-Hexandiol, Polyurethane Monomer Derivatives via Isomerization Metathesis of Methyl Linolenate”

ACS Sustainable Chem. Eng., **2017**, *5, 11215.*



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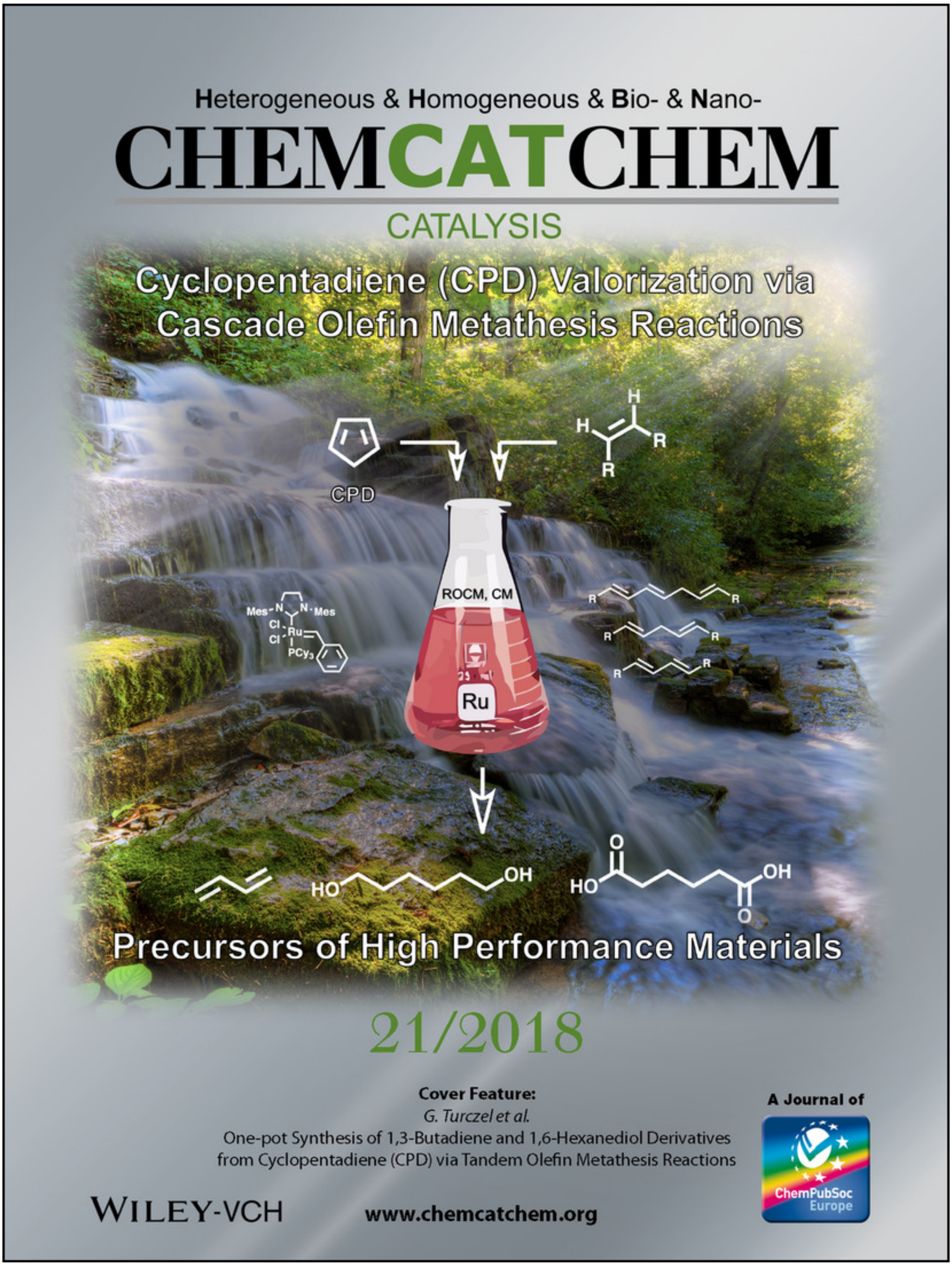
"One-pot Synthesis of 1,3-Butadiene and 1,6-Hexanediol Derivatives from Cyclopentadiene (CPD) via Tandem Olefin Metathesis Reactions"

ChemCatChem. **2018**, *10*, 4884.



8. References

(1) Anastas, P.; Warner, J. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1980.

(2) Khemani, K.; Scholz, C. *Degradable Polymers and Materials: Principles and Practice (2nd Edition)*; Khemani, K., Scholz, C., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 2012; Vol. 1114.

(3) Rydz, J.; Sikorska, W.; Kyulavska, M.; Christova, D. Polyester-Based (Bio)Degradable Polymers as Environmentally Friendly Materials for Sustainable Development. *Int. J. Mol. Sci.* **2014**, *16* (1), 564–596.

(4) Geyer, R.; Jambeck, J. R.; Law, K. L. Production, Uses, and Fate of All Plastics Ever Made. *Sci. Adv.* **2017**, *3* (7), 5.

(5) Mounguengui-Diallo, M.; Vermersch, F.; Perret, N.; Pinel, C.; Besson, M. Base Free Oxidation of 1,6-Hexanediol to Adipic Acid over Supported Noble Metal Mono- and Bimetallic Catalysts. *Appl. Catal. A Gen.* **2018**, *551*, 88–97.

(6) Sun, D.; Yamada, Y.; Sato, S.; Ueda, W. Glycerol Hydrogenolysis into Useful C3 Chemicals. *Appl. Catal. B Environ.* **2016**, *193*, 75–92.

(7) Bellou, S.; Baeshen, M. N.; Elazzazy, A. M.; Aggeli, D.; Sayegh, F.; Aggelis, G. Microalgal Lipids Biochemistry and Biotechnological Perspectives. *Biotechnol. Adv.* **2014**, *32* (8), 1476–1493.

(8) Schenk, P. M.; Thomas-Hall, S. R.; Stephens, E.; Marx, U. C.; Mussgnug, J. H.; Posten, C.; Kruse, O.; Hankamer, B. Second Generation Biofuels: High-Efficiency Microalgae for Biodiesel Production. *BioEnergy Res.* **2008**, *1* (1), 20–43.

(9) Amaro, H. M.; Guedes, A. C.; Malcata, F. X. Advances and Perspectives in Using Microalgae to Produce Biodiesel. *Appl. Energy* **2011**, *88* (10), 3402–3410.

(10) Dembitsky, V. M.; Rozentsvet, O. A.; Pechenkina, E. E. Glycolipids, Phospholipids and Fatty Acids of Brown Algae Species. *Phytochemistry* **1990**, *29* (11), 3417–3421.

(11) Kovács, E.; Sághy, P.; Turczel, G.; Tóth, I.; Lendvay, G.; Domján, A.; Anastas, P. T.; Tuba, R. Metathesis of Renewable Polyene Feedstocks – Indirect Evidences of the Formation of Catalytically Active Ruthenium Allylidene Species. *J. Organomet. Chem.* **2017**, *847*, 213–217.

(12) Balla, Á.; Al-Hashimi, M.; Hlil, A.; Bazzi, H. S.; Tuba, R. Ruthenium-Catalyzed Metathesis of Conjugated Polyenes. *ChemCatChem* **2016**, *8*, 2865–2875.

(13) Kovács, E.; Turczel, G.; Szabó, L.; Varga, R.; Tóth, I.; Anastas, P. T.; Tuba, R. Synthesis of 1,6-Hexandiol, Polyurethane Monomer Derivatives via Isomerization Metathesis of Methyl Linolenate. *ACS Sustain. Chem. Eng.* **2017**, *5* (12), 11215–11220.

(14) Turczel, G.; Kovács, E.; Csizmadia, E.; Nagy, T.; Tóth, I.; Tuba, R. One-Pot Synthesis of 1,3-Butadiene and 1,6-Hexandiol Derivatives from Cyclopentadiene (CPD) via Tandem Olefin Metathesis Reactions. *ChemCatChem* **2018**, *10*, 4884–4891.

(15) Ren, T.; Patel, M.; Blok, K. Olefins from Conventional and Heavy Feedstocks: Energy Use in Steam Cracking and Alternative Processes. *Energy* **2006**, *31* (4), 425–451.

(16) Chen, J.; Burns, F. P.; Moffitt, M. G.; Wulff, J. E. Thermally Crosslinked Functionalized Polydicyclopentadiene with a High Tgand Tunable Surface Energy. *ACS Omega* **2016**, *1* (4), 532–540.

(17) Ellis, J. M.; King, S. B. Ring-Opening Cross Metathesis of 1,3-Cyclopentadiene-Heterodienophile Cycloadducts to Produce Cyclic Hydrazines and Hydroxylamines. *Tetrahedron Lett.* **2002**, *43* (33), 5833–5835.

(18) Krupka, J. Kinectics of Thermal Dimerization of Cyclopentadiene and Methylcyclopentadiene and Their Codimerization. *Pet. Coal* **2010**, *52* (4), 290–306.

(19) Moffett, R. B. Cyclopentadiene and 3-Chlorocyclopentene. *Org. Synth.* **1952**, *32* (September), 41.

(20) Funk, T. W.; Efskind, J.; Grubbs, R. H. Chemoselective Construction of Substituted Conjugated Dienes Using an Olefin Cross-Metathesis Protocol. *Org. Lett.* **2005**, *7*, 187–190.

(21) Kovács, E.; Sághy, P.; Turczel, G.; Tóth, I.; Lendvay, G.; Domján, A.; Anastas, P. T.; Tuba, R. Metathesis of Renewable Polyene Feedstocks – Indirect Evidences of the Formation of Catalytically Active Ruthenium Allylidene Species. *J. Organomet. Chem.* **2017**, *847*, 213–217.

(22) CLaus, M.; Claus, E.; CLaus, P.; Hönicke, D.; Födisch, R.; Olson, M. Cyclopentadiene and Cyclopentene. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2016; pp 1–13.

(23) Schmidt, F. *Basic Principles in Applied Catalysis*; Baerns, M., Ed.; Springer Berlin Heidelberg: Berlin, 2004.

(24) Hoveyda, A. H.; Zhugralin, A. R. The Remarkable Metal-Catalysed Olefin Metathesis Reaction. *Nature* **2007**, *450* (7167), 243–251.

(25) Mol, J. C. Industrial Applications of Olefin Metathesis. *J. Mol. Catal. A Chem.* **2004**, *213* (1), 39–45.

(26) Allen, D. P. OlefinMetathesis in Nontraditional Media. In *Handbook of Metathesis Volume 1: Catalyst Development and Mechanism*; Grubbs, R. H., G.Wenzel, A., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2015.

(27) Prat, D.; Wells, A.; Hayler, J.; Sneddon, H.; McElroy, C. R.; Abou-Shehada, S.; Dunn, P. J. CHEM21 Selection Guide of Classical- and Less Classical-Solvents. *Green Chem.* **2015**, *18* (1), 288–296.

(28) Connon, S. J.; Rivard, M.; Zaja, M.; Blechert, S. Practical Olefin Metathesis in Protic Media under an Air Atmosphere. *Adv. Synth. Catal.* **2003**, *345* (5), 572–575.

(29) Burdett, K. A.; Harris, L. D.; Margl, P.; Maughon, B. R.; Mokhtar-Zadeh, T.; Saucier, P. C.; Wasserman, E. P. Renewable Monomer Feedstocks via Olefin Metathesis: Fundamental Mechanistic Studies of Methyl Oleate Ethenolysis with the First-Generation Grubbs Catalyst. *Organometallics* **2004**, *23*, 2027–2047.

(30) Anderson, D. R.; Lavallo, V.; O'Leary, D. J.; Bertrand, G.; Grubbs, R. H. Synthesis and Reactivity of Olefin Metathesis Catalysts Bearing Cyclic (Alkyl)(Amino)Carbenes. *Angew. Chemie - Int. Ed.* **2007**, *46*, 7262–7265.

(31) Wyrebek, P.; Maecki, P.; Sytniczuk, A.; Kośnik, W.; Gawin, A.; Kostrzewa, J.; Kajetanowicz, A.; Grela, K. Looking for the Noncyclic(Amino)(Alkyl)Carbene Ruthenium Catalyst for Ethenolysis of Ethyl Oleate: Selectivity Is on Target. *ACS Omega* **2018**, *3* (12), 18481–18488.

(32) Gawin, R.; Kozakiewicz, A.; Guńka, P. A.; Dąbrowski, P.; Skowerski, K. Bis(Cyclic Alkyl Amino Carbene) Ruthenium Complexes: A Versatile, Highly Efficient Tool for Olefin Metathesis. *Angew. Chemie - Int. Ed.* **2017**, *56*, 981–986.

(33) Jordan, J. P. The Development of Water-Soluble Olefin Metathesis Catalysts Containing an N-Heterocyclic Carbene Ligand. **2008**, *2008*.