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Synthesis of novel porphyrins cardanol based *via* cross metathesis

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ABSTRACT

Cardanol – an alternative, sustainable, low-cost, largely available natural resource and obtained as by-product of the cashew industry – is used in this work as the starting material for the preparation of new molecular arrays containing porphyrin–cardanol hybrids through ruthenium catalyzed olefin cross metathesis reactions.

Different Grubbs' catalysts were used to perform the metathesis reactions but only one of the second generation of catalyst – the Ru-carbene catalyst **C627** – was the most efficient for the preparation of new cardanol derivatives by simple olefin homo-cross-metathesis (HCM). Also, new class of porphyrin–cardanol hybrids obtained *via* HCM or *via* ring closing metathesis (RCM), in which one or two rings are in the same molecule, were also prepared.

1. Introduction

The production of fine chemicals and new materials from waste is not a new concept. In fact, "*from waste to value*" is a well-known phrase, following the basic idea to make new molecules using secondary materials and by-products from industry.

For this reason, the preparation of fine chemicals from waste, that is from natural and renewable organic raw materials, is becoming an attractive topic of research especially when purpose is also the recycling of huge amounts of agro-industrial wastes through environmentally sustainable catalytic processes and possibly through concise route to produce novel compounds that possessed interesting structures or physical properties for potential applications, just starting from inexpensive starting materials and/or renewable resources.

In this context, cardanol, obtained as by-product of the cashew industry, cheap and renewable material, is obtained by vacuum distillation of cashew nut shell liquid (CNSL) [1]. In addition, cardanol can be considered a starting material unique natural source because of its unsaturated long-chain attached to the phenolic ring.

Cardanol, the main component of CNSL, is indeed a mixture of 3-*n*-pentadecyl phenol, 3-(pentadeca-8-enyl) phenol, 3-(pentadeca-8,11-dienyl) phenol, and 3-(pentadeca-8,11,14-trienyl) phenol (Fig. 1); it is important to remark that both *E* and *Z* isomers of each components are present in the mixture; but usually the *Z* components are the major one.

Actually, cardanol and cardanol derivatives, due to their unique characteristic, over the last few years have interested scientists for their potential use in resins, friction lining materials, surface coatings, and organic synthesis [2] and recently some works have focused on molecular hybrid systems, in which cardanol is involved [3].

Since the development of well-defined single component molybdenum and ruthenium carbene catalysts, the olefin metathesis has already commercially utilized in the processing of fine chemicals. For instance, with the use of Grubbs ruthenium-based catalyst olefin metathesis enables vegetable oils to be efficiently processed into compounds that can serve as renewable sources of petroleum product alternatives [4] as well as in the industrially attractive synthesis of a variety of fine chemicals, vitamins and nutraceuticals [5].

The olefin metathesis has become a very important reaction for constructing carbon–carbon double bonds, especially in complex molecules [6].

On the other hand, porphyrins are considered recently to be very attractive compounds due to their extensive application in many areas of new materials as chemical technology, ecology, medicine, and electronics. In addition, there is nowadays growing interest also in the development of a new class of multiporphyrin architectures and arrays due to the easy formation of molecular wires, molecular recognition system, energy transduction, and so on [7].

In the last years, they have also received increasing attention because of their implications for many photocatalytic reactions [8].

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Fig. 1. The structure and composition of cardanol.

For this reason, the development of hybrid systems containing natural products such as cardanol and macrocycles such as porphyrins are well developed and recently, many porphyrin–porphyrin coupled molecules and mixed metal system containing pendant functional groups have been prepared successfully using different techniques.

Olefin metathesis and cross metathesis (CM) have seldom been applied to porphyrin substrates [9]; only more recently they have been used in porphyrin modifications using Grubbs' catalysts (first and second generation) [10].

Langford et al. have shown that the CM reaction is suitable as a construction protocol for porphyrinic arrays which exhibit a high degree of *E*/*Z* selectivity in the products [11]. So that, CM reaction can be considered a useful coupling technique due to its mild reaction conditions and exceptional tolerance toward a variety of functional groups.

Continuing our work in the preparation of porphyrin–cardanol hybrids, we like to report here the synthesis of new molecular arrays porphyrin–cardanol based some of which contain a ring system in the same molecule. The synthetic utility of the method is demonstrated through the preparation of metalated (Zn) porphyrins.

2. Experimental

All starting materials were purchased from Aldrich Chemical Co. and used as received. Silica gel(Merck) was used in the chromatographic separations. FT-IR spectra were recorded on a JASCO FT-IR 430 spectrometer. UV–vis spectra were recorded on a Cary 100scan UV–visible spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 at room temperature and chemical shifts are reported relative to tetramethylsilane.

Mass spectrometry analyses were carried out on a matrix assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF MS, Krato Analytical Company of Shimadzu Biotech, Manchester, Britain). 1 μL of sample solution of CH_2Cl_2 was spotted into wells of the MALDI sample plate, and air-dried. The samples were analyzed in the linear ion mode with CHCA as matrix. External calibration was achieved using a standard peptide and protein mix from Sigma.

Meso-phenyldipyrrolmethane was synthesized with the standard procedure in the literature [12].

5,10,15-triphenyl-20-mono-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy]phenyl porphyrin **5** and 5,15 – diphenyl -10,20- di-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy] phenyl porphyrin **6** and 5,10,15,20-tetra- [4-(2-(3- pentadec-8-enyl)phenoxy)-ethoxy] phenyl porphyrin **7** used as the starting materials were synthesized according to slightly modified procedures already reported in the literature [13].

2.1. General procedure for metathesis reaction of metal-free porphyrins

0.032 mmol of cardanol based porphyrins (**5–7**) were dissolved in 20 mL of dichloromethane. Then, 10 μL of $Ti(O^iPr)_4$ (1 equivalents, 0.032 mmol) were added and the solution was refluxing. After 1 h a solution of catalyst **C627** (0.5 mg in 1.5 mL of CH_2Cl_2, 0.025 equivalents) was added and the resulting mixture was stirred for 64 h. The mixture was cooled to room temperature and concentrated in vacuum. The crude product was purified by silica gel chromatography (methylene chloride) to give product (**5a–7a**).

Selected data for **6a** as a brownish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.77 (br s, 2H), 1.27–1.35 (m, 18 H), 1.62–1.69 (m, 4H), 1.94–2.06 (m, 4H), 2.61–2.65 (m, 4H), 4.52–4.54 (m, 4H), 4.62–4.65 (m, 4H), 5.33–5.42 (m, 2H), 6.84–6.99 (m, 6H), 7.25–7.29 (m, 2H), 7.33(s, 2H), 7.35(s, 2H), 7.73–7.78(m, 6H), 8.12–8.14 (m, 4H), 8.20–8.22(m, 4H), 8.82–8.91 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 145.3, 135.6, 135.4, 131.3, 130.6, 130.4, 130.3, 129.7, 121.9, 119.0, 114.8, 112.3, 112.7, 111.7, 67.1, 36.5, 33.6, 32.2, 30.1, 29.8, 29.5, 22.8. FTIR (neat), ν (cm^{-1}): 3461, 3006, 2984, 2909, 1740, 1465, 1447, 1372, 1233, 1097, 1047, 938, 918, 847. UV–vis (CH_2Cl_2) λ_{max}, nm: 419, 516, 552, 590, 647. MALDI-TOF MS *m*/*z*:1107 $(M+H)^+$ amu. Anal. Calc. for $C_{76}H_{74}N_4O_4$: C 81.00; H 9.12; N 3.50. Found: C 82.46; H 6.69; N 5.06.

2.2. General procedure for metathesis reaction of Zn-porphyrins

0.029 mmol of zinc porphyrins [**(Zn)5-(Zn)7**] were dissolved in 20 mL of dichloromethane. A solution of catalyst **C627** (0.45 mg in 1.5 mL of CH_2Cl_2, 0.025 equivalents) was added and the resulting mixture was stirred for 64 h under N_2 atmosphere.

The mixture was cooled to room temperature and concentrated in vacuum. The crude product was purified by silica gel chromatography (methylene chloride) to give products [**(Zn)5a-(Zn)7a**]..

3. Results and discussion

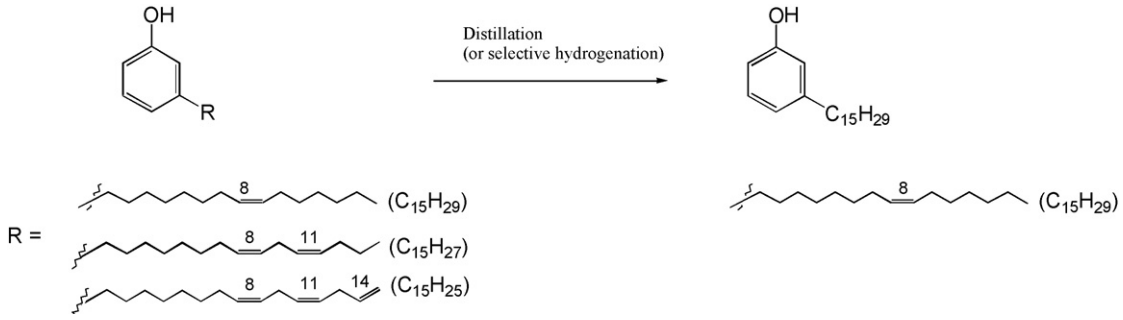
As shown in Fig. 1, cardanol is a mixture of 3-*n*-pentadecyl phenol, 3-(pentadeca-8-enyl) phenol, 3-(pentadeca-8,11-dienyl) phenol, and 3-(pentadeca-8,11,14-trienyl) phenol in 80%, 2% and 5%, respectively. However, the composition of the mixture strongly depends on the processes of extraction and purification. In fact, after further re-distillation of CNSL it is possible to obtain a mixture that contains, in almost 90%, the monoolefinic and diolefinic components, averagely and minor amounts of the tri olefinic and 3-*n*-pentadecyl phenol compounds.

The mixture can be successively purified by distillation/chromatography obtaining the monoolefinic component almost pure. It must be pointed out that, catalytic hydrogenation reactions, already used for the selective transformation of unsaturated fatty acids [14], have real perspectives in the production of the monoolefinic component having homogeneous chemical composition (Scheme 1) as useful starting material for metathesis reactions. So, for convenience, in this work cardanol is referred to as the monoolefinic component the other ones being present in small amount.

3.1. Homo-cross metathesis reactions of cardanol based compounds

Metathesis catalysts were initially screened in the homo-cross metathesis (HCM) reaction of cardanol derivatives **1–4** by using different Ru-catalysts (**C627**, **C823**, **C801** and **C848**) which, for convenience, are identified by their molecular weights (Fig. 2).

In this way, the optimized condition for HCM resulted by using 2.0 mmol of starting material in CH_2Cl_2 (1.2 ml) treated with 5 mol% of catalyst **C627** in dichloromethane at 40 °C for 45–87 h under N_2 atmosphere [15].



Scheme 1. Selective hydrogenation of the cardanol mixture.

In all cases, the conversion of the substrates **1–4** could not reach 100%, which should attribute to the reaction's reversibility [16]. In particular, the HCM reaction/reactions of cardanol and three of its derivatives worked very well under the optimized conditions affording the biscardanol derivatives **1a–4a** in 42–65% isolated yields. All products were formed as a mixture of *Z*- and *E*-isomers, in which *Z*-isomers were dominant.

3.2. Synthesis and metathesis of cardanol based porphyrins

Recently, we have reported the synthesis characterization of lipophilic porphyrins cardanol based using as the starting materials pure 3-*n*-pentadecylphenol, obtained by exhaustive hydrogenation of the double bond(s) in the cardanol side-chain, as well as some derivatives obtained by alkylation reaction of the aromatic ring group according to procedures already reported in the literature [13].

The possibility to manipulate cardanolic derivatives having homogeneous chemical composition and molecular features *ad hoc* for metathesis reactions focused our attention on the preparation of novel porphyrins containing unsaturated chains deriving from cardanol oil (Scheme 2).

The mono unsaturated compound, 3-*n*-pentadeca-8-enylphenol, **1** was treated with 1,2-dibromo-ethane under solvent-free reaction conditions in the presence of anhydrous potassium hydroxide at 70 °C for 6 h to give **2** in 92% yield. Successively, **2** was converted into **3** by reaction with 4-hydroxybenzaldehyde, as shown in Scheme 3.

Compound **3** was successively reacted as starting material using different protocols of reaction in order to obtain the cardanol based porphyrins **5–7** used for the metathesis reactions.

The cardanol-based porphyrin 5,10,15-triphenyl-20-mono-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy]phenylporphyrin **5** and 5,15-diphenyl- 10,20-di-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy]phenylporphyrin **6** were synthesized by acid-catalyzed condensation of 4-[2-(3-(pentadeca-8-enyl) phenoxy)-ethoxy]-benzaldehyde **3** by statistic reaction with pyrrol and benzaldehyde (*method* 1) or *meso*-phenyldipyrrolmethane (*method* 2), respectively.

The cardanol-based porphyrin **7** was obtained by reaction of compound **3** with pyrrol, as shown in Scheme 4 (*method 3*).

Methods 1–3 can be considered as different approaches performed in accordance with the Lindsey procedure opportunely modified by us for the convenient synthesis of the target precursor [17].

Compounds **5–7** were successively used in metalation reactions with $Zn(OAc)_2$ for the preparation of the corresponding *meso*-tetraarylporphyrin zinc complexes (**Zn)5**–**(Zn)7** shown in Fig. 3 in nearly quantitative yields.

The most efficient Ru catalyst – **C627** – used for the preparation of the bis cardanol derivatives by HCM was also used to perform the preparation of the porphyrin–cardanol hybrids. However, the reaction conditions employed in the synthesis of novel based porphyrins – reported in Section 2 – were slightly different from that used for the preparation of the simple biscardanol derivatives reported in the previous section.

In the case of the metathesis involving cardanol based, the best condition for metathesis reaction resulted by using 0.030 mmol of starting material in CH_2Cl_2 (20 ml) treated with 10 mol% of catalyst **C627** in dichloromethane refluxed for 64 h.

However, the metal free porphyrins **5–7**, differently by their zinc complexes, produced minor amounts of the corresponding metathesis products. For this reason, according to previous finding [18], the addition of $Ti(OPr^i)_4$ to the reaction system improves the metathesis reaction.

As shown in Scheme 5, cardanol based porphyrin **5** produced **5a** in 15% isolated yield by addition of $Ti(OPr^i)_4$ minor amounts of side products that are under investigation. Interestingly, the zinc pophyrin **Zn-5**, under the same reaction condition and without addition of $Ti(OPr^i)_4$, produced the corresponding HCM product in better yield compared with the metal-free derivative.

NMR and MALDI-TOF spectra of **5a** and **Zn-5a** were consistent with the proposed structure. For example, the ^1H NMR spectrum of **5a** shows the disappearing of the signal corresponding to methyl

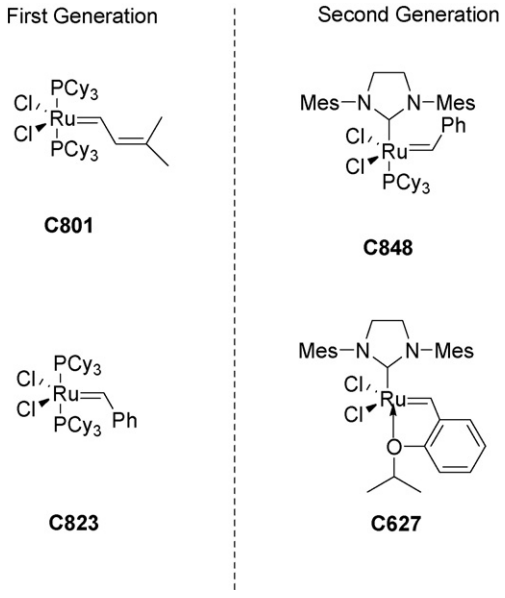
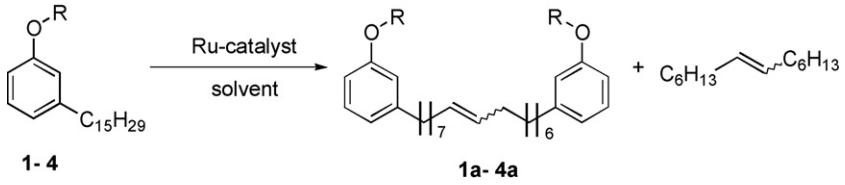


Fig. 2. Ruthenium (First and Second Generation) catalysts.



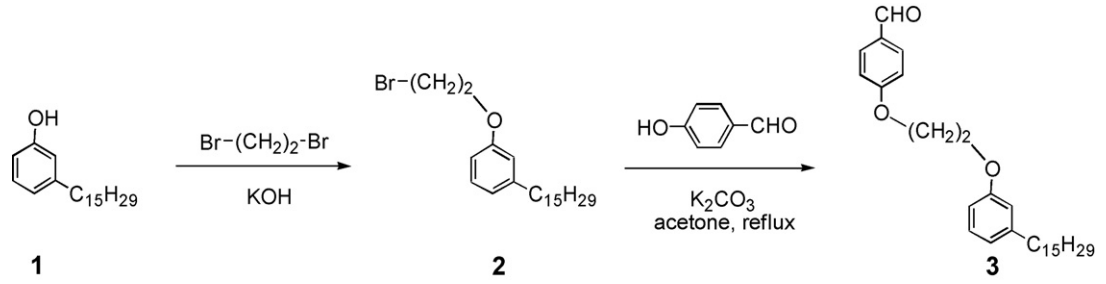
1,1a: R = H;

2, 2a: R = -CH_2CH_2Br;

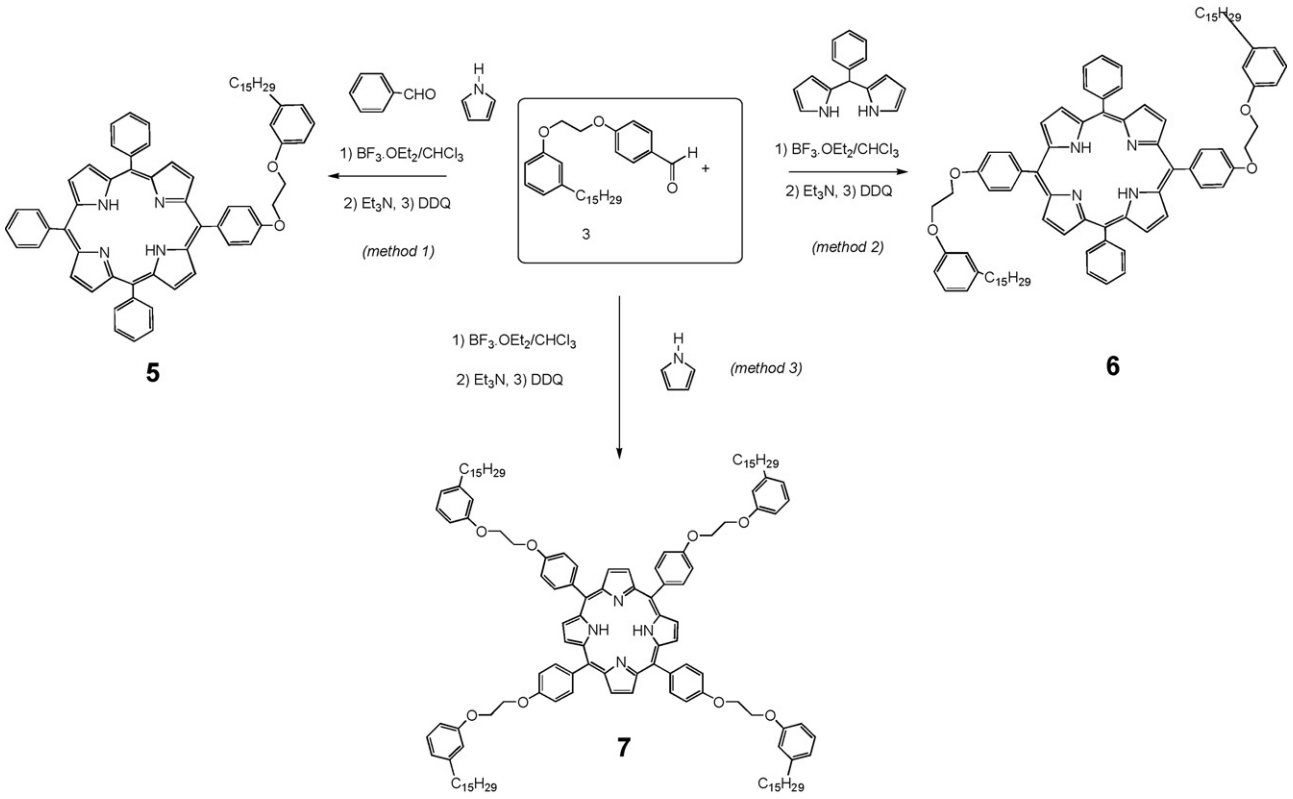
3, 3a: R = -CH_2CH_2O-(C$_6$H$_4$)-CHO

4, 4a: R = (C$_6$H$_4$)-(CN)$_2$

Scheme 2.



Scheme 3.



Scheme 4.

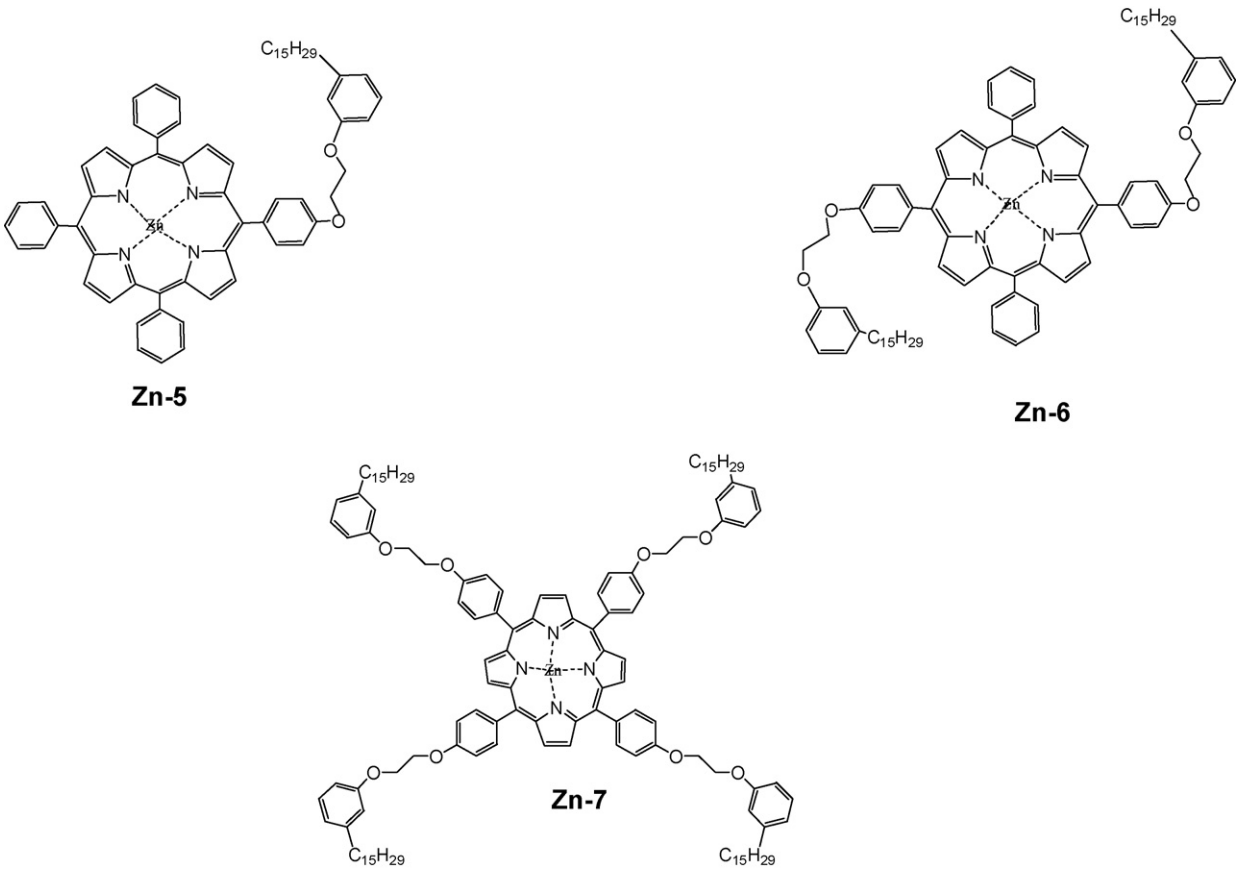
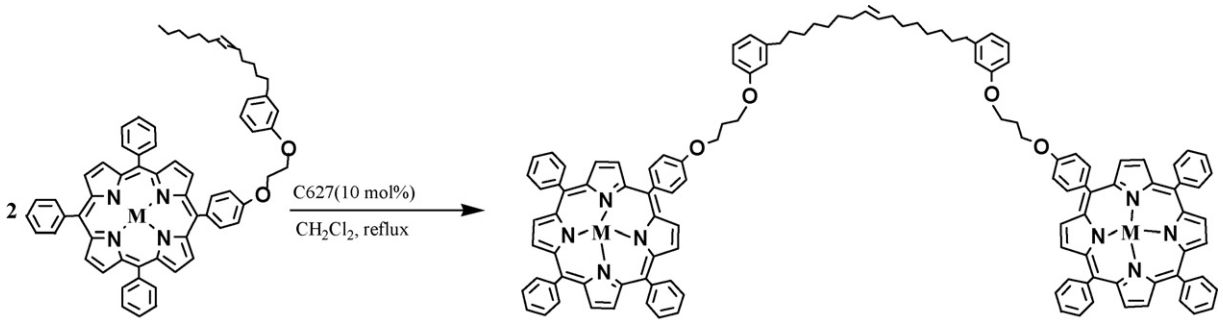


Fig. 3. Structure of the porphyrin-cardanol based zinc complexes **(Zn)5-(Zn)7**.



Scheme 5.

group at 0.9 ppm. The mass spectrum of **5a** exhibits a cluster of signals centered at *m*/*z* 1723 $[M+H]^+$ (Fig. 4).

Interesting, ring-closing metathesis (RCM) product formation was observed when porphyrins **6**, **7** – as well as their zinc complexes – were used as the starting materials. Analogously to that observed for the porphyrin **5**, treatment of **6** and **7** with **C627** under dilute conditions give the corresponding RCM product by addition of stoichiometric amount of $Ti(OPr^i)_4$ to the reaction system.

We believe that the strong coordination function of porphyrins plays a crucial role both in HCM as well as in this RCM reaction and the coordination between the porphyrins and a ruthenium species may turn down the expected RCM reaction of **6** and **7** [19]. Also in these cases, solution of **6** or **7** in dichloromethane, $Ti(OPr^i)_4$ and the catalyst **C627** were added and then the solution refluxed for 64 h. As expected, the target product was formed (Scheme 6, Scheme 7).

Also in this case the presence of Zn improves the yields of the RCM product.

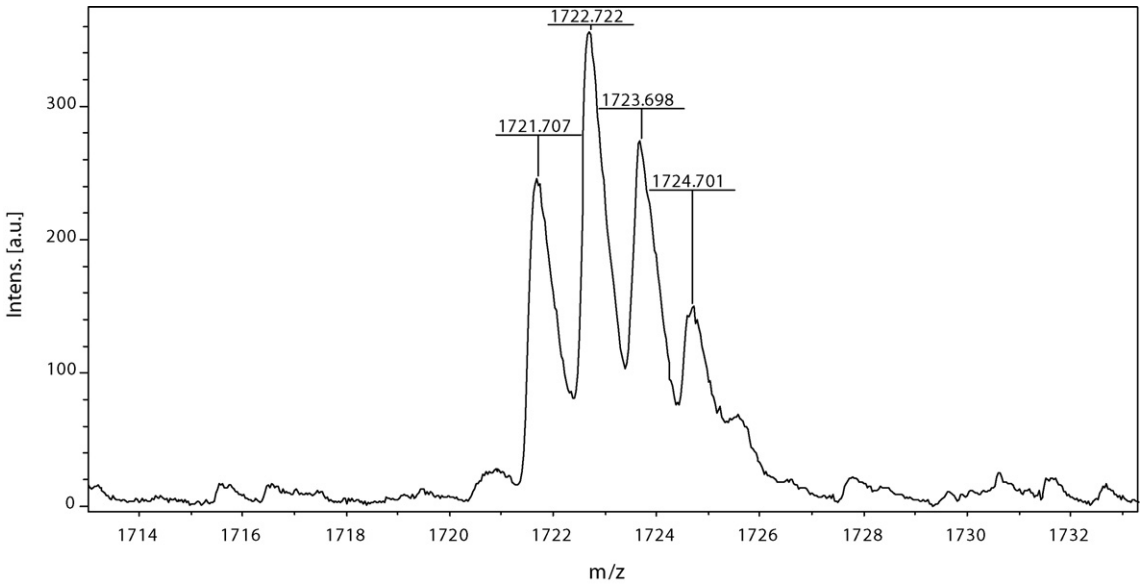
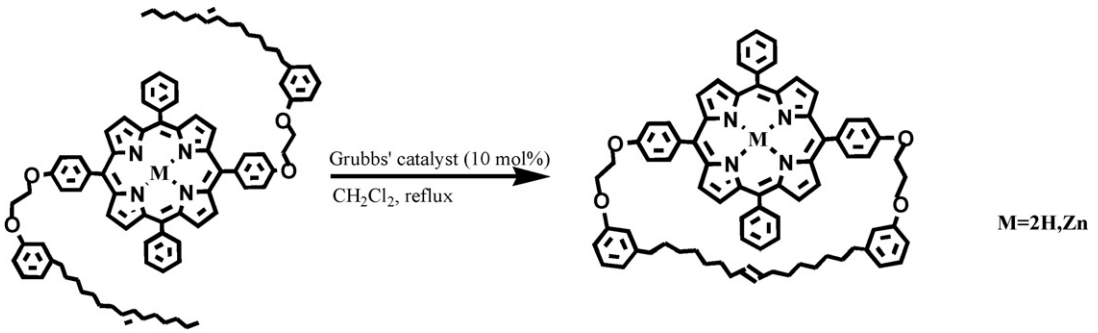


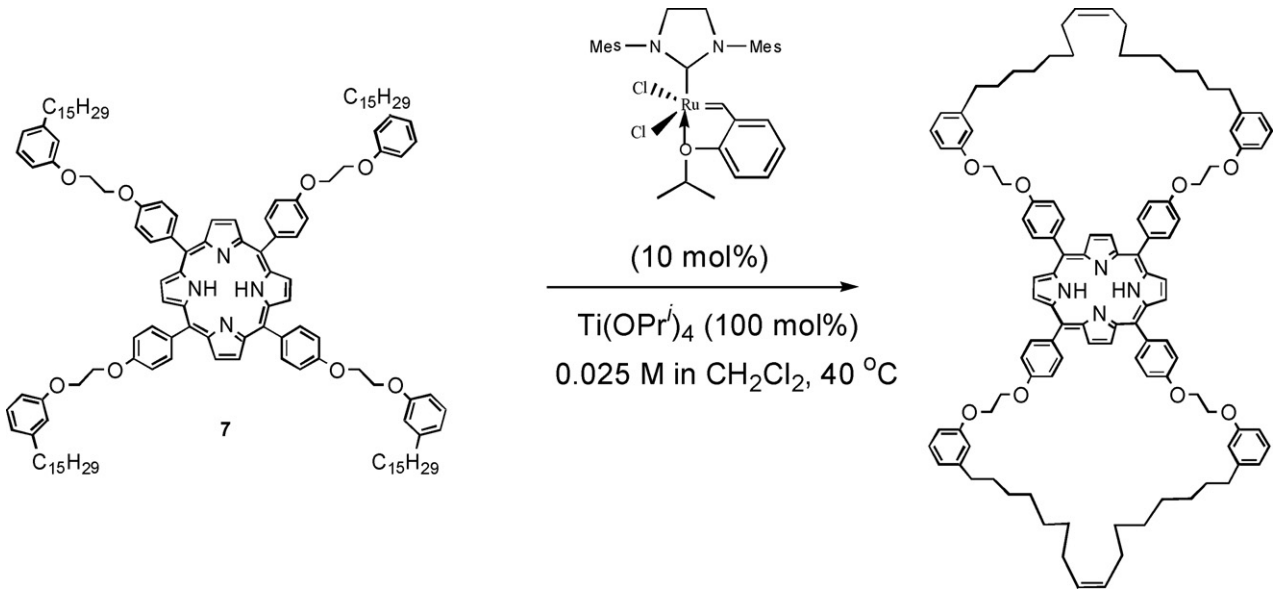
Fig. 4. Mass spectrum of **5a**.



6 **6a** (20%)

(30%)

Scheme 6.



Scheme 7.

4. Conclusion

Cardanol a well-known by-product of the cashew industry has been successfully used as the starting material to perform olefin cross metathesis reactions by using different generations of Grubbs' catalysts.

In particular, the Ru-carbene catalyst **C627** resulted the most efficient to perform homo-cross-metathesis (HCM) both using simple cardanol based olefin as well as new porphyrin–cardanol/cardanol based. These latter gave HCM or ring closing metathesis (RCM) forming one or two rings in the same molecule depending on the kind of mono, bis or tetra-meso substitution.

References

[1] J.H.P. Tyman, Synthetic and Natural Phenols, Elsevier, Amsterdam, 1996;
P.P. Kumar, R. Paramashivappa, P.J. Vithayathil, P.V.S. Rao, A.S. Rao, J. Agric. Food Chem. 50 (2002) 4705.

[2] A.R.R. Menon, C.K.S. Pillai, J.D. Sudha, A.G. Mathew, J. Sci. Ind. Res. 44 (1985) 324;
M.C. Lubi, E.B. Thachill, Des. Monomers Polym. 3 (2000) 123;
F.H.A. Rodrigues, J.P.A. Feitosa, N.M.P.S. Ricardo, F.C.F. de Franca, J.O.B. Carioca, J. Braz. Chem. Soc. 17 (2006) 265;
Y.H. Kim, K. Won, J.M. Kwon, H.S. Jeong, S.Y. Park, E.S. An, B.K. Song, J. Mol. Catal. Enzymatic 34 (2005) 33.

[3] O.A. Attanasi, G. Ciccarella, P. Filippone, G. Mele, J. Spadavecchia, G. Vasapollo, J. Porphyrins Phthalocyanines 7 (2003) 52;
O.A. Attanasi, R. Del Sole, P. Filippone, R. Ianne, S.E. Mazzetto, G. Mele, G. Vasapollo, Synlett 5 (2004) 799;
J.M. Bakker, S.J. Langford, M.J. Latter, K.A. Lee, C.P. Woodward, Aust. J. Chem. 58 (2005) 757;
A. Maffezzoli, E. Calò, S. Zurlo, G. Mele, A. Tarzia, C. Stifani, Composites Sci. Technol. 64 (2004) 839.

[4] J. Patel, S. Mujcinovic, W.R. Jackson, A.J. Robinson, A.K. Serelis, C. Such, Green Chem. 8 (2006) 450;
J.C. Mol, Green Chem. 4 (2002) 5;
R.H.A. Bosma, F. Van Den Aardweg, J.C. Mol, J. Chem. Soc., Chem. Commun. (1981) 1132;
Frost & Sullivan's Industrial Bioprocessing Alert, September 9, 2005.

[5] W. Bonrath, M. Eggersdorfer, T. Netscher, Catal. Today 121 (2007) 45;
T. Netscher, G. Malaise, W. Bonrath, M. Breuninger, Catal. Today 121 (2007) 71.

[6] For recent reviews on olefin metathesis reactions, see:
Y. Chauvin, Angew. Chem. Int. Ed. 45 (2006) 3741;
R.R. Schrock, Angew. Chem. Int. Ed. 45 (2006) 3748;
R.H. Grubbs, Angew. Chem. Int. Ed. 45 (2006) 3760;
R.H. Grubbs (Ed.), Handbook of Metathesis, vol. 1–3, Wiley-VCH, Weinheim, 2003 ;
A. Furstner, Angew. Chem. Int. Ed. 39 (2000) 3012.

[7] Some recent topical reviews include: H. Imahori, J. Phys. Chem. B 108 (2004) 6130.
C.M. Drain, J.T. Hupp, K.S. Suslick, M.R. Wasielewski, J. Porph. Phthal. 6 (2002) 243;
H. Imahori, Org. Biomol. Chem. 2 (2004) 1425;
A. Satake, Y. Kobuke, Tetrahedron 61 (2005) 13.

[8] G. Mele, R. Del Sole, G. Vasapollo, E. García-López, L. Palmisano, M. Schiavello, J. Catal. 217 (2003) 334;
G. Mele, R. Del Sole, G. Vasapollo, E. Garcìa-Lòpez, L. Palmisano, S.E. Mazzetto, O.A. Attanasi, P. Filippone, Green Chem. 6 (2004) 604;
G. Mele, R. Del Sole, G. Vasapollo, G. Marcì, E. Garcìa-Lòpez, L. Palmisano, J.M. Coronado, M.D. Hernández-Alonso, C. Malitesta, R. Guascito, J. Phys. Chem. B 109 (2005) 12347;
G. Mele, R. Del Sole, G. Vasapollo, E. García-López, L. Palmisano, J. Li, R. Słota, G. Dyrda, Res. Chem. Intermed. 33 (2007) 433;
C. Wang, J. Li, G. Mele, G.M. Yang, F.-X. Zhang, L. Palmisano, G. Vasapollo, Appl. Cat. B: Environmental 76 (2007) 218.

[9] X. Liu, E. Sternberg, D. Dolphin, Chem. Commun. (2004) 852.

[10] A. Furstner, Angew. Chem., Int. Ed. 39 (2000) 3013;
T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18;
R.H. Grubbs, S. Chang, Tetrahedron 54 (1998) 4413.

[11] S.J. Langford, M.J. Latter, C.P. Woodward, Org. Lett. 8 (2006) 2595.

[12] J.K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise, J.S. Lindsey, Org. Process Res. Dev. 7 (2003) 799.

[13] O.A. Attanasi, R. Del Sole, P. Filippone, S.E. Mazzetto, G. Mele, G. Vasapollo, J. Porphyrins Phthalocyanines 8 (2004) 1276 (and unpublished results).

[14] N. Ravasio, F. Zaccheria, M. Gargano, S. Recchia, A. Fusi, N. Poli, R. Psaro, Appl. Cat. A-General 233 (2002) 1.

[15] Y.C. Guo, G. Mele, F. Martina, E. Margapoti, G. Vasapollo, W.J. Xiao, J. Organomet. Chem. 691 (2006) 5383.

[16] Y.C. Guo, W.J. Xiao, Chin. J. Org. Chem. 11 (2005) 1334.

[17] C.H. Lee, J.S. Lindsey, Tetrahedron 50 (1994) 11427.

[18] Q. Yang, W.-J. Xiao, Z. Yu, Org. Lett. 7 (2005) 871;
Q. yang, X.-Y. Li, H. Wu, W.-J. Xiao, Tetrahedron Lett. 47 (2006) 3893.

[19] A. Camara-Campos, C.A. Hunter, S. Tomas, Proc. Nat. Acad. Sci. U.S.A. 103 (2006) 3034;
F. D'Souza, M.E. El-Khouly, S. Gadde, M.E. Zandler, A.L. McCarty, Y. Araki, O. Ito, Tetrahedron 62 (2006) 1967 (and references cited therein).