# Synthesis of bifunctional monomers *via* palladium catalyzed carbonylation of cardanol and its derivatives.

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Dedication ((optional))

**Abstract:** A 1,2-bis(ditertiarybutylphosphinomethyl)benzene modified palladium catalyst have been used to synthesize bifunctional monomers of different chain lengths from cardanol **(1)**. Short chain derivatives of cardanol such as (E)-3-(dodec-8-enyl)phenol; HOPhC12-ene **(2)**, (E)-3-(undec-8-enyl)phenol; HOPhC11-ene **(3)**, (E)-3-(dec-8-enyl)phenol; HOPhC10-ene **(4)** and 3-(non-8-enyl)phenol; HOPhC9-ene **(5)** were synthesized by metathesis reactions of cardanol with symmetrical internal alkenes. These derivatives were methoxycarbonylated to produce different chain length monomers such as methyl-16-(3-hydroxyphenyl)hexadecanoate; HOPhC15COOMe **(6)**, methyl-13-(3-hydroxyphenyl)tridecanoate; HOPhC12COOMe **(7)**, methyl 12-(3-hydroxyphenyl)dodecanoate; HOPhC11COOMe **(8)**, methyl-11-(3-hydroxyphenyl)undecanoate; HOPhC10COOMe **(9)**, and methyl-10-(3-hydroxyphenyl)decanoate; HOPhC9COOMe **(10)** respectively. Polymerization of the synthesized monomers produced oligomers consisting of up to 7 monomer units as confirmed by MALDITOF MS analysis. Lactone formation was also observed in some cases under polymerisation conditions.

## Introduction

Replacement of non-renewable raw materials by renewable materials is inevitable for sustainable industrial development. Non-renewable materials are subject to depletion which means that overdependence on such materials is indeed a risk. The polymer industry is one of the sectors that relies on non-renewable resources such as petroleum and natural gas for its raw materials. For example, polyethylene is made by polymerising ethylene using free radical reactions,[1] or catalysts such as Ziegler catalysts,[2] and single site metallocene catalysts.[3] The major source of ethylene is petroleum, which means the threat of oil depletion is also a threat to the polymer industry. Renewable resources such as bioethylene, plant oils and agricultural wastes are potential replacements for non-renewable raw materials.[4] However these types of biomass usually contain a mixture of compounds, which means

conversion of these materials needs catalysts that are very selective to the desired products. A methoxycarbonylation palladium catalyst modified by a bulky ligand; 1,2-bis(ditertiarybutylphosphinomethyl)benzene (DTBPMB), has been reported to be very selective for conversion of plant oils into desired linear polymer precursors.[5] Plant oils contain compounds with double bonds located deep in the chain. For complete utilization of these oils to make polymers, the internal double bonds must be isomerized to the least thermodynamically favored terminal position before introducing the desired functional group for polymerization. DTBPMB modified palladium is an efficient catalyst that can isomerize the internal double bonds of plant oils in high yields and selectivity. Carbonylation of these oils using this catalyst produces linear diesters in extremely high selectivity (>95%).[5a-i, 5k-n] These diesters are reduced into dialcohols[5c, 5f, 5k, 5n] which are co-polymerized with diesters to produce polymers with properties more or less similar to those of polyethylene.[5a, 5b, 5f-j, 5l, 5m]

One of the main problems of polymers is that they are organic materials which often burn with an intense heat. For many applications especially in fibers and furniture, they must be treated with fire retardants, most of which contain substantial amounts of bromine.[6] There is considerable concern about the release of bromine into the environment,[7] so polymers which themselves are fire retardant are extremely attractive goals. One potential way to manufacture halogen free fire-retardant polymers is to incorporate significant amounts of aromatic groups into the polymer backbone.[8] However, all-aromatic polymers are difficult to process, so linking them with oligomethylene chains and /or ester functions could offer fire retardancy and processability.[9]
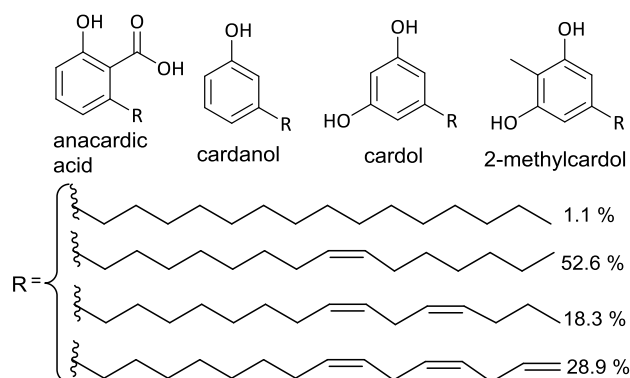
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**Figure 1.** Components of cashew nut shell liquid.

Cardanol is a major component (up to 85 % depending on the extraction method) of technical cashew nut shell liquid (CNSL); a by-product of cashew processing factories, which is not suitable as a food oil (Figure 1).[10] Cardanol is a phenol substituted in the 3 position with a linear $C_{15}$ chain with various degrees of unsaturation. We have carried out a range of catalytic reactions[11] aimed at synthesizing useful chemicals such as detergents and tsetse fly attractants from cardanol and we reasoned that methoxycarbonylation should give a 3-alkylphenol bearing an ω-ester function.

An important potential advantage of the products from these reactions is that they have an alcoholic function at one end and an ester function at the other so they may undergo polymerization without the need for a second monomer. They also have a phenyl group embedded in them, which may offer fire retardancy properties. The alkyl chain may afford .

processability to the polymer. Since incorporation of aromatic groups in a polymer backbone offers fire-retardancy, it seems likely that having fewer methylene groups per phenyl may improve the fire-retardancy still further.

In this paper we describe a series of monomers derived from cardanol. We have used metathesis reactions to vary the chain length attached to the aromatic ring. The monounsaturated 3-alkenylphenols so formed were subjected to isomerizing methoxycarbonylation to form the desired monomers with a phenol at one end and an ester group at the other. Finally, preliminary tests were carried out on polymerization of the monomers using a standard condensation polymerization catalyst, [Ti(OBu)$_4$]. In some cases polymers were formed, whilst in others the main products appeared to be macrolactones .
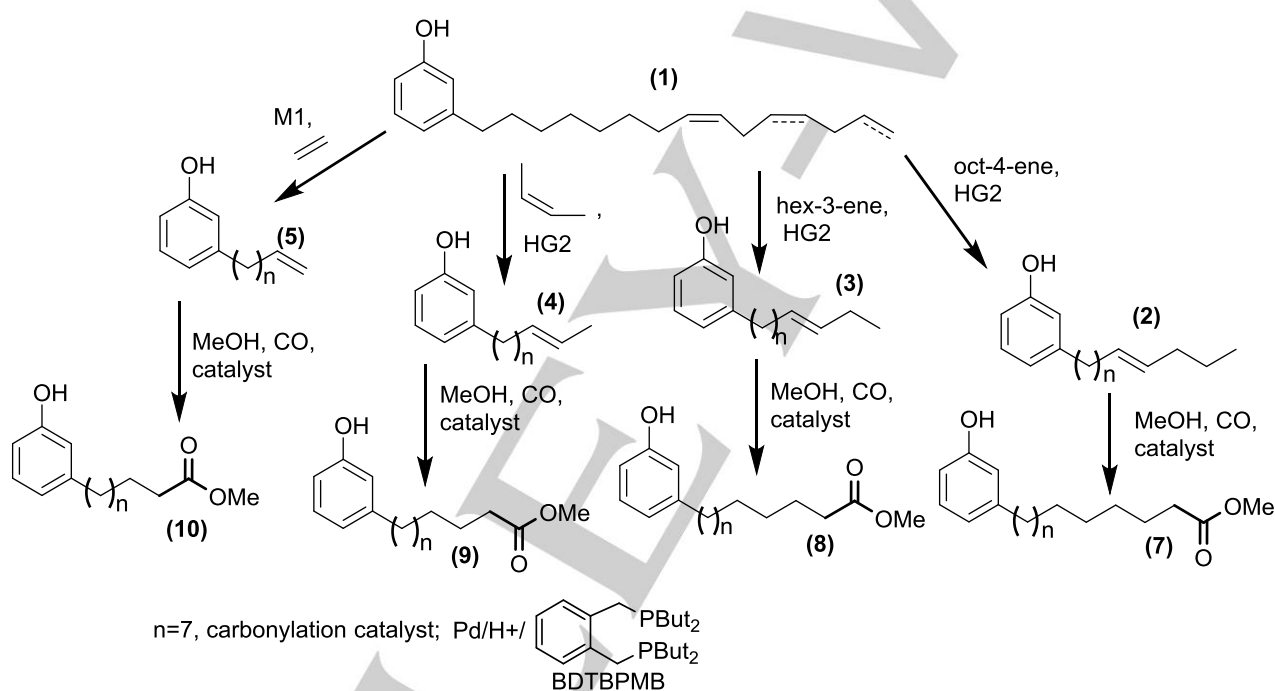


**Scheme 1.** Synthesis of short chain monomers from cardanoland their methoxycarbonylatioin.M1 is a First generation Grubbs type catalyst containing indenylidene. HG2 is Hoveyda Grubbs second generation catalyst M1

## Results and Discussion

### Shorter chain 3-alkenylphenols derived from cardanol

The idea that incorporation of aromatic groups in the polymer chain might improve fire-retardancy may mean that shorter chain monomers (Scheme 1) might be preferred because of the higher density of phenyl rings provided by them.

With this idea in mind, we carried out metathesis reactions of cardanol with different alkenes to produce shorter chain length derivatives of cardanol. Screening of suitable catalysts for ethenolysis and but-2-enolysis reactions of cardanol has been

reported elsewhere.[11a, 11b, 11d] The Hoveyda Grubb's 2nd generation catalyst (HG2) which has been reported to be effective for the but-2-enolysis reaction was found effective for hex-3-enolysis and oct-4-enolysis reactions reported for the first time in this work, whilst a first generation catalyst is preferred for ethenolysis.[11b] In this way we were able to prepare 3-alkenyl phenols in which the chain has 9, 10, 11 or 12 C atoms, as well as the having available the parent cardanol with 15 C atoms in the chain. In all cases except that of the 3-nonenyl phenol, the double bond is not in the terminal position, but this was not seen to be a problem because it was anticipated that isomerizing methoxycarbonylation would always introduce the ester group onto the desired terminal position.
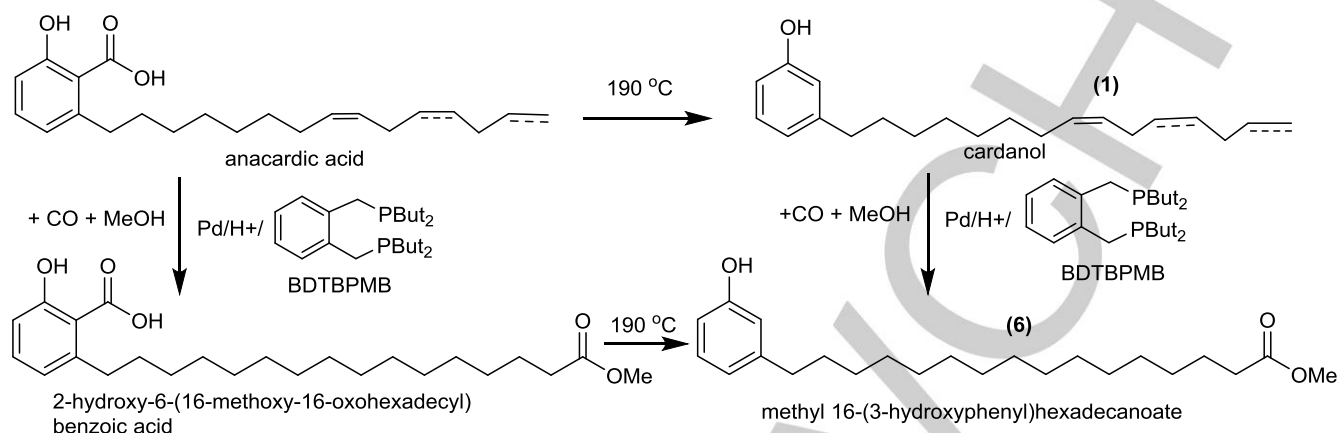
**Scheme 2**. Synthesis of methyl16-(3-hydroxyphenyl)hexadecanoate from anachardic acid or cardanol.

## Methoxycarbonylation of cardanol

The methoxycarbonylation reaction of cardanol (monoene 52.6 %, diene 18.3 %, triene 28.9 %, and saturated 1.1 %) using a palladium catalyst modified by the bulky ligand, DTBPMB[5e, 12] proceeds in a satisfactory yield (50.6 %, 96 % based on monoene fraction) to linear monomer; methyl16-(3-hydroxyphenyl)hexadecanoate, which was isolated and fully characterised by X-ray crystallography (Scheme 2, Figure 1). The yield increased to 64 % when pure monoene cardanol, obtained by selective transfer hydrogenation of natural cardanol with 2-propanol,[13] was employed in the reaction.
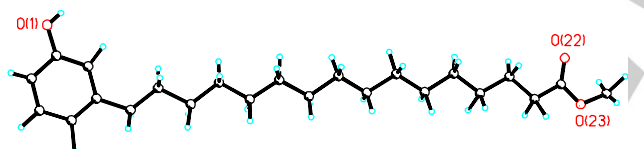


**Figure 2.** Crystal structure of methyl16-(3-hydroxyphenyl)hexadecanoate); HOPhC15COOMe.

The selectivity to linear monomer is due to the use of a bulky ligand, DTBPMB.[5e, 12] During carbonylation of cardanol, the internal double bond is isomerized within the chain and is most stable in the position conjugated to the aromatic ring. Despite this, the double bond is only trapped by carbonylation when it reaches the terminal end of the molecule; the ω position relative to the phenol group, thus promoting selectivity to produce the linear monomer.[5e, 12] The optimum temperature for this catalytic system is 80 °C. This is particularly important because the carbonylation reaction of cardanol at temperatures higher than 80 °C proceeds with formation of undesired polymeric materials which affect the yield of the desired monomer.

The same monomer could be synthesized by methoxycarbonylation of monoene anacardic acid, obtained from transfer hydrogenation of anacardic acid,[11c] as starting material in similar yield (65 %). The methoxycarbonylated anacardic acid must be then be decarboxylated to produce the desired monomer (58 % overall yield, Scheme 2). Decarboxylation of the methoxycarbonylated anacardic acid leads to formation of chars which makes the final product impure and also affects the yield. We consider, therefore, that methoxycarbonylation of cardanol is a preferred route to synthesis of methyl16-(3- hydroxyphenyl)hexadecanoate.

Shorter chain bifunctional monomers could be easily synthesized by methoxycarbonylation of the prepared shorter chain 3-alkenylphenols (Scheme 1). The same catalyst, DTBPMB modified palladium was used to effect the reactions. Interestingly, carbonylation reactions of short chain cardanol derivatives resulted in better isolated yields (80-83 %) compared to cardanol (64 %) and anacardic acid (65 %) under similar reaction conditions. The high yield of short chain derivatives could be due to the fact that, short chain derivatives have short alkyl chain with the single double bond located near or to the terminal end of the molecule compared to cardanol which has a long alkyl chain with the double bond closest to the aromatic ring located deep in the chain.

The fact that monomers derived from carbonylation of cardanol possess phenol and carbomethoxy functionalities within the same molecule is particularly interesting (Figure 2). Methoxycarbonylation of plant oils using palladium catalysts modified by DTBPMB usually produces linear α,ω- diesters which must be reduced to dialcohols before they are co-polymerized.[5c, 5f, 5k, 5n] Cardanol derived monomers having a hydroxyl group at one end and carbomethoxy group at the other end of the molecule do not require a reduction step, and can, in principle, be polymerized by direct heating of the monomers in

the presence of a condensation polymerization catalyst such as tetrabutoxytitanium (IV).[10]

### Polymerisation of cardanol derived bifunctional monomers

The synthesized monomers were heated at different temperatures: 100, 120, 130, 150 and 200 °C) in the presence of tetrabutoxytitanium (IV) to confirm the idea that these single bifunctional monomers can form polymers directly. Heating **6** at lower temperatures (100, 120 and 130 °C) did not show any sign of reaction. At 150 °C oligomers up to 7 monomer units, were formed as revealed by MALDI-TOF mass spectrometry analyses (Figure 3), although the insolubility and intractability of the solid products suggests it consists mainly of longer chain polymers. When the temperature was raised to 200 °C, char formation was observed. This is common for phenolic polymers which are known to be fire retardants due to their ability to form chars when they are exposed to intense heat.[8] A catalyst loading of 5-10 % gave ~50 % polymer with the rest being lactone contaminated with a small amount of starting material. At 15 % catalyst loading, only a brittle intractable polymer as formed, Some shorter chain monomers such as C-9-$CO_2$Me and C-11-$CO_2$Me gave highly brittle, insoluble polymers without lactones. On the other hand, C-10-$CO_2$Me and C-12-$CO_2$Me preferred the formation of lactones over polymers; very little, if any, polymer was formed in these cases.
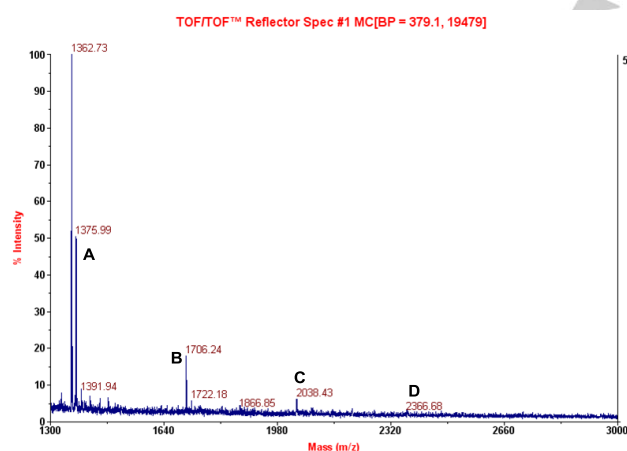


**Figure 3**. MALDI-TOF MS spectrum of oligomers from condensation reaction of methyl-16-(3-hydroxyphenyl) hexadecanoate. The peaks A, B, C and D correspond to oligomers consisting of four, five, six and seven monomer units respectively.

### Lactone Formation

Although polymerisation of **6** gave some brown insoluble polymer and some oligomers, there was also a significant amount of a liquid product which could be solidified to a white powder by reprecipitation on cooling a hot hexane solution. Unfortunately, we could never get this compound completely free from **6** itself. The GCMS of this product showed it to have a shorter retention time than that of **6** and to have an $M_r$ of 330 (32 less than that of **6**). This mass, together with the loss of the

methoxy and hydroxyl signals in the $^1$H NMR spectrum suggests that methanol has been lost and that the 20 membered macrolactone has surprisingly formed.[14] This product was found to be highly sensitive and was unable to be isolated cleanly or pushed through to complete reaction (with yields < 50%).

We also found that lactones were formed with some of the shorter chain monomers. To our surprise we found that these shorter chain monomers gave either the lactone or the polymer but never both when heated in the presence of 5% [Ti(OBu)$_4$]. C-10-$CO_2$Me and C-12-$CO_2$Me always led to lactone formation of 14- and 16-membered ring sizes respectively (although once again, these could not be isolated completely pure), whereas with an uneven number of methylene groups in the chain, C-9-$CO_2$Me and C-11-$CO_2$Me, only highly brittle, insoluble polymers were observed. In contrast, (6) gave both polymer and lactone formation (19-membered ring).
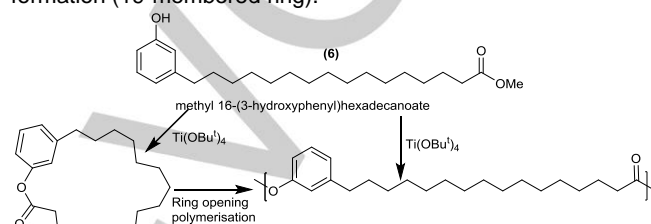


**Scheme 3**. Polymerization of methyl 16-(3-hydroxyphenyl)hexadecanoate and formation of a 20 membered ring lactone and its proposed use in ring opening polymerisation reactions

Modeling has shown that ring stability is dependent on a number of factors, especially its size that can allow for stable conformations to be taken up, and so certain macro lactones are favorable over others.[15] Clearly in the case of these very rare and precious phenolic lactones more modeling is required to understand the driving force of their formation. Similar trends have also been seen previously, where even numbered ring sizes are favored.[16]

Table 1. Summary of Lactone Formation

| Monomer | Mwt. of monomer | Lactone formation | Mwt. of lactone |
|---|---|---|---|
| HOPhC15COOMe | 362 | Form | 330 |
| HOPhC12COOMe | 320 | Form | 288 |
| HOPhC11COOMe | 306 | Doesn't form | 274 |
| HOPhC10COOMe | 292 | Form | 260 |
| HOPhC9COOMe | 278 | Doesn't form | 246 |

Reaction conditions; Tetrabutoxytitanium (IV) catalyst (5 wt %), under vacuum, 150 °C

Further work will be undertaken to understand the formation of these lactones and to increase yields as they hold the possibility to of being used as highly reactive monomers for ring-opening rather than condensation polymerization reactions.

## Conclusions

Metathesis with symmetrical alkenes allows the formation of 3-alkenylphenols with the alkenyl chain having 9, 10, 11 or 12 C atoms. Methoxycarbonylation reactions using a palladium catalyst modified by a bulk ligand DTBPMB have proven to be efficient in converting cardanol and its derivatives into polymerisable bifunctional monomers. The reaction proceeds in a satisfactory yield (65 % for cardanol and 83-84 % for short chain derivatives).

The bifunctional monomers synthesized either produce intractable upon heating in the presence of tetrabutoxytitanium (IV) catalyst or, in some cases, macrolactones appear to form. The monomer derived from cardanol produces both polymer and lactone.

# Experimental

### Materials and instruments

All reagents and solvents were purchased from sigma Aldrich and used as received. Cashew nut shell liquid was obtained from the shells by the solvent extraction method.[10] Anacardic acid,[17] cardanol (**1**),[11d] monoene cardanol,[13] monoene anacardic acid[11c] and 3-(non-8-enyl)phenol; HOPhC9-ene (**5**)[11b] were obtained by previously reported methods. All reactions were carried out using standard Schlenk line and glove box techniques. GC-MS analyses were performed using a Hewlett-Packard 6890 series gas chromatograph instrument equipped with a flame ionization detector for quantitative analysis and a Hewlett-Packard 5973 series mass selective detector fitted with hp1 film for mass spectral identification of products. Helium was used as the carrier gas with initial flow of 1 mL/min. The temperature program used was 50 °C (4 min), 20 °C min$^{-1}$ to 130 °C (2 min), 20°C min$^{-1}$ to 220 °C (15.5 min). $^1$H and $^{13}$C NMR spectra were recorded at 298 K on Bruker 300 MHz or 400 MHz and 75 MHz or 100 MHz spectrometers for $^1$H NMR and $^{13}$C NMR respectively. Samples for NMR analysis were dissolved in deuterated solvents, the peaks of which were used to reference the spectra to tetramethylsilane at δ 0 ppm. The IR spectra were recorded on Perkin Elmer Spectrum GX FT-IR spectrometer using KBr discs.

### Synthesis of different chain length 3-alkenylphenols

### (E)-3-(dodec-8-enyl)phenol; HOPhC12-ene (2)

Cardanol (1 g, 3.31 mmol) and oct-4-ene (3 mL, 24.13 mmol) were placed into Schlenk tubes and bubbled with nitrogen for 10 minutes. In the glove box, Hoveyda-Grubbs 2$^{nd}$ generation catalyst, [1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(o-isopropoxyphenylmethylene)ruthenium) (0.02 g, 0.032 mmol) was weighed into a round bottomed flask. The flask was connected to a Schlenk line under nitrogen. The mixture of cardanol and oct-4-ene was transferred into the round bottomed flask containing the catalyst. The mixture was stirred under nitrogen for 24 hours at 25 °C. The reaction was quenched by adding vinylethylether (0.2 mL) to the reaction mixture. Purification of the product was by fractional distillation at low pressure (0.01 mbar) at 125 °C using a kugelrohl. MS [*m/z* (%)]: 260 (6) [*M*$^+$-H], 147 (6), 133 (8), 120 (26), 108 (100), 91 (5), 77 (16), 55 (21), 41 (23). $^1$H NMR (400 Hz; CDCl$_3$): δ 0.81 (t, $^3J$(H,H)=6.4 Hz, 3H; -CH$_3$), 1.12-1.36 (m, 11.3H; -CH$_2$-, alkyl chain), 1.41-1.57 (m, 2H; -CH$_2$-), 1.82-2.01 (m, 3.8H; -CH$_2$-), 2.46 (t, $^3J$(H,H)=7.5, 2H; -CH$_2$-), 4.91 (s, 1H; -OH), 5.23-5.39 (m, 2H; -CH-), 6.53-6.61 (m, 2H; Ar-H), 6.67 (d, $^3J$(H,H)=7.8, 1H; Ar-H), 7.05 (t, $^3J$(H,H) =7.8, 1H; Ar-H). $^{13}$C NMR (100 Hz; CDCl$_3$): δ 14.4 (CH$_3$), 23.4, 30.0, 31.8, 33.3, 35.1, 36.3 (-CH$_2$-), 113.1 (Ar-CH-), 116.1

(Ar-CH-), 121.5 (Ar-CH-), 129.8 (-CH-), 130.6 (Ar-CH-), 131.2 (-CH-), 145.5 (Ar-C-R), 155.9 (Ar-C-OH).

### (E)-3-(undec-8-enyl)phenol; HOPhC11-ene (3)

The synthesis of (E)-3-(undec-8-enyl)phenol was carried out as for (E)-3-(dodec-8-enyl)phenol using hex-3-ene in place of oct-4-ene (3 mL). MS [*m/z* (%)]: 246 (15) [*M*$^+$-H], 161 (3), 147 (7), 133 (8), 120 (26), 108 (100), 91 (7), 77 (16), 69 (5), 55 (13), 41 (21). $^1$H NMR (400 Hz; CDCl$_3$): δ 0.99 (t, $^3J$(H,H)=7.4, 3H -CH$_3$), 1.25-1.44 (m, 9H; -CH$_2$-, alkyl chain), 1.56-1.69 (m, 2H; -CH$_2$-), 1.95-2.12 (m, 4H; -CH$_2$-), 2.59 (t, $^3J$(H,H) =7.4, 2H; -CH$_2$-), 4.86 (s, 1H; -OH), 5.31-5.54 (m, 2H; -CH-), 6.63-6.73 (m, 2H; Ar-H), 6.79 (d, $^3J$(H,H)=7.7, 1H; Ar-H), 7.18 (t, $^3J$(H,H)=7.7, 1H; Ar-H). $^{13}$C NMR (100 Hz; CDCl$_3$): δ 14.5 (-CH$_3$), 26.0, 29.7, 31.7, 32.9, 36.3 (--CH$_2$-), 112.9 (Ar-CH-), 115.7 (Ar-CH-), 121.7 (Ar-CH-), 129.7 (-CH-), 132.5 (-CH-), 145.6 (Ar-C-R), 155.9 (Ar-C-OH).

### (E)-3-(dec-8-enyl)phenol; HOPhC10-ene (4)

Cardanol (2 g, 6.62 mmol) was dissolved in dichloromethane (5 mL) in a Schlenk tube. The cardanol solution was bubbled with nitrogen for 10 minutes. In the glove box, Hoveyda-Grubbs catalyst 2$^{nd}$ generation, [1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(o-isopropoxyphenylmethylene)ruthenium) (0.02 g, 0.032 mmol) was put in the autoclave charged with magnetic stirrer. Cardanol solution was transferred by means of a 20 mL syringe to the autoclave under nitrogen followed by addition of cis-2-butene (6 mL). The reaction was left under stirring at room temperature for 24 hours. Purification of the product was by distillation under vacuum. MS [*m/z* (%)]: 232 (13) [*M*$^+$-H], 161 (3), 147 (6), 133 (6), 120 (25), 108 (100), 91 (6), 77 (22), 55 (22), 41 (16). $^1$H NMR (400 Hz; CDCl$_3$): δ 1.23-1.47 (m, 9H; -CH$_2$-, alkyl chain), 1.54-1.73 (m, 4.9H; -CH$_2$-, -CH$_3$), 1.94-2.11 (m, 2H; -CH$_2$-), 2.59 (t, $^3J$(H,H)=7.2, 2H; -CH$_2$-), 4.83 (s, 1H; -OH), 5.36-5.52 (m, 2H; -CH-), 6.63-6.71 (m, 2H; Ar-H), 6.79 (d, $^3J$(H,H)=7.4, 1H; Ar-H), 7.18 (t, $^3J$(H,H) =8.1, 1H; Ar-H). $^{13}$C NMR (100 Hz; CDCl$_3$): δ 18.4 (-CH$_3$), 27.1, 29.7, 31.5, 32.9, 36.3 (-CH$_2$-), 113.2 (Ar-CH-), 115.7 (Ar-CH-), 121.7 (Ar-CH-), 125.1 (-CH-), 129.9 (Ar-CH-), 132.2 (-CH-), 145.6 (Ar-C-R), 155.9 (Ar-C-OH).

### Synthesis of methyl-16-(3-hydroxyphenyl)hexadecanoate; HOPhC15COOMe (6)

**Method 1:** Unsaturated cardanol (2 g, 6.6 mmol) was dissolved in methanol (10 mL) in a schlenk tube. The Schlenk tube containing unsaturated cardanol solution was connected to the Schlenk lines and left under nitrogen bubbling for 10 minutes. In the glove box, DTBPMB (0.592 g, 1.5 mmol) and Pd$_2$(dba)$_3$ (0.137 g, 0.15 mmol) were put into the autoclave charged with magnetic stirrer. The autoclave was connected to the Schlenk line where it was degassed three times. The unsaturated cardanol solution was transferred into the autoclave using a 20 mL syringe. Methane sulfonic acid (0.2 mL) was added to the solution in the autoclave. The solution was flushed with carbon monoxide three times before it was pressurised to 30 bar. The reaction was left to proceed at 80 °C for 24 hours. After venting the carbon monoxide, the obtained solution was filtered through a celite bed and concentrated under vacuum. The product was purified by chromatography using hexane / ethyl acetate (90/10). The fraction containing the desired product was concentrated to yield a white powder (1.21 g, 50.6 %). Methoxycarbonylation of monoene cardanol using similar procedure proceeded in 64 % yield. Crystals for crystal structure determination was obtained by layering a dichloromethane solution with hexane and slow diffusion. Elemental analysis: calcd (%) for C$_{23}$H$_{38}$O$_3$ (362.28): C 76.20, H 10.56; found: C 76.09, H 10.63. MS [*m/z* (%)]: 362 (8) [*M*$^+$-H], 330 (13), 161 (2), 147 (6), 135 (8), 121 (21), 108 (100), 98 (27), 91 (8), 77 (16), 69 (11), 55 (21), 41 (19). $^1$H NMR (400 Hz; CDCl$_3$): δ 1.13-1.29 (m, 22H; -

CH$_2$- alkyl chain), 1.44-1.61 (m, 4H; -CH$_2$-), 2.34 (t, $^3J$(H,H)=7.5, 1.9H; CH$_2$), 2.57 (t, $^3J$(H,H)=7.8, 2H; -CH$_2$-), 3.61 (s, 3H; -OCH$_3$), 5.16 (s, 0.9H; Ar-OH), 6.54-6.61 (m, 2H; Ar-H), 6.68 (d, $^3J$(H,H) =7.9, 1H; Ar-H), 7.01 (t, $^3J$(H,H) =7.8, 1H; Ar-H). $^{13}$C NMR (100 Hz; CDCl$_3$): δ 25.4, 30.0, 31.6, 34.8, 36.5 (-CH$_2$-), 52.0 (-OCH$_3$), 113.1 (Ar-CH-), 115.9 (Ar-CH-), 121.3 (Ar-CH-), 129.9 (Ar-CH-), 145.1 (Ar-C-R), 156.3 (Ar-C-OH), 173.0 (R-COOMe).

**Method 2:** Methoxycarbonylation of monoene anacardic acid[11c] was carried out as for methoxycarbonylation of cardanol to yield 2-hydroxy-6-(16-methoxy-16-oxohexadecyl)benzoic acid in 66 % isolated yield. Elemental analysis: calcd (%) for C$_{24}$H$_{38}$O$_5$ (406.27): C 70.90, H 9.42; found: C 70.77, H 9.54; $^1$H NMR (400 Hz; CDCl$_3$): δ 1.07-1.49 (m, 22H; -CH$_2$-, alkyl chain), 1.54-1.73 (m, 4H; -CH$_2$-), 2.33 (t, $^3J$(H,H) =8.1, 2H; -CH$_2$-), 3.01 (t, $^3J$(H,H) =8.2, 2H; -CH$_2$-), 3.70 (s, 3H; -OCH$_3$), 6.80 (d, $^3J$(H,H) =7.5, 1H; Ar-H), 6.90 (d, $^3J$(H,H) =8.98, 1H; Ar-H), 7.38 (t, $^3J$(H,H)=8.98, 1H; Ar-H), 11.11 (s, 1H; -COOH). $^{13}$C NMR (100 Hz; CDCl$_3$): δ 25.3, 29.8, 32.4, 34.9, 37.0 (-CH$_2$-), 52.0 (-OCH$_3$), 116.4 (Ar-CH-), 123.1 (Ar-CH-), 136.0 (Ar-CH-), 148.0 (Ar-C-R), 163.9 (Ar-C-OH), 175.9 (R-COOMe). In a 10 mL Schlenk tube, 2-hydroxy-6-(16-methoxy-16-oxohexadecyl)benzoic acid (1 g) was heated at 190 °C in a graphite bath for 3 hours to produce methyl-16-(3-hydroxyphenyl)hexadecanoate (0.8 g, 90 %). MS [$m/z$ (%)]: 362 (8) [$M^+$-H], 330 (13), 161 (2), 147 (6), 135 (8), 121 (21), 108 (100), 98 (27), 91 (8), 77 (16), 69 (11), 55 (21), 41 (19). $^1$H NMR (400 Hz; CDCl$_3$): δ 1.09-1.47 (m, 22H; -CH$_2$- alkyl chain), 1.53-1.78 (m, 4H; -CH$_2$-), 2.34 (t, $^3J$(H,H)=7.7, 1.9H; CH$_2$), 2.58 (t, $^3J$(H,H)=7.7, 2H; -CH$_2$-), 3.70 (s, 3H; -OCH$_3$), 5.16 (s, 0.8H; Ar-OH), 6.63-6.70 (m, 2H; Ar-H), 6.77 (d, $^3J$(H,H) =7.6, 1H; Ar-H), 7.16 (t, $^3J$(H,H) =7.6, 1H; Ar-H). $^{13}$C NMR (100 Hz; CDCl$_3$): δ 25.0, 29.4, 31.3, 34.2, 35.3 (-CH$_2$-), 52.0 (-OCH$_3$), 112.6 (Ar-CH-), 115.3 (Ar-CH-), 120.6 (Ar-CH-), 129.3 (Ar-CH-), 144.9 (Ar-C-R), 155.7 (Ar-C-OH), 174.7 (R-COOMe).

### Synthesis of short chain bifunctional monomers

Methoxycarbonylation reactions of short chain cardanol derivatives were as for the methoxycarbonylation of cardanol to yield short chain monomers of different chain lengths. The yield of the short chain monomers ranged from 80 to 83%.

**Methyl 13-(3-hydroxyphenyl)tridecanoate; HOPhC12COOMe (7);** From **2**; elemental analysis: calcd (%) for C$_{20}$H$_{32}$O$_3$ (320.24): C 74.96, H 10.06; found: C 74.93, H 9.10.15. MS [$m/z$ (%)]: 320 (12) [$M^+$-H], 288 (10), 147 (6), 133 (8), 121 (25), 108 (100), 91 (8), 77 (19), 69 (8), 55 (23), 41 (19). $^1$H NMR (400 Hz; CDCl$_3$): δ 1.20-1.42 (m, 16.8H; -CH$_2$- alkyl chain), 1.54-1.76 (m, 5H; -CH$_2$-), 2.34 (t, $^3J$(H,H) =7.2, 2H; -CH$_2$-), 2.57 (t, $^3J$(H,H) =7.7, 2H; -CH$_2$-), 3.70 (s, 3H; -OCH$_3$), 5.19 (s, 1H; Ar-OH), 6.63-6.71 (m, 2H; Ar-H), 6.77 (d, $^3J$(H,H) =7.7, 1H; Ar-H), 7.16 (t, $^3J$(H,H) =7.7, 1H; Ar-H). $^{13}$C NMR (100 Hz; CDCl$_3$): δ 25.5, 29.7, 31.7, 34.7, 36.3 (-CH$_2$-), 52.2 (-OCH$_3$), 112.9 (AR-CH-), 115.7 (Ar-CH-), 121.2 (Ar-CH-), 129.7 (Ar-CH-), 145.1 (Ar-C-R), 155.9 (Ar-C-OH), 175.0 (R-COOMe).

**Methyl 12-(3-hydroxyphenyl)dodecanoate; HOPhC11COOMe (8);** From **3**; MS [$m/z$ (%)]: 306 (12) [$M^+$-H], 274 (10), 176 (2), 162 (2), 147 (10), 134 (13), 121 (26), 108 (100), 91 (35), 77 (29), 55 (28), 41 (24). $^1$H NMR (400 Hz; CDCl$_3$): δ 1.21-1.37 (m, 13H; -CH$_2$-, alkyl chain), 1.54-1.69 (m, 3.5H; -CH$_2$-), 2.33 (t, $^3J$(H,H) =7.35, 2H; -CH$_2$-), 2.56 (t, $^3J$(H,H) =7.4, 1.8H; -CH$_2$-), 3.70 (s, 3H; -OCH$_3$), 6.65-6.71 (m, 1.7H; Ar-H), 6.76 (d, $^3J$(H,H) =7.5, 0.9H; Ar-H), 7.15 (t, $^3J$(H,H) =7.5, 1H; Ar-H). $^{13}$C NMR (100 Hz; CDCl$_3$): δ 23.2, 25.3, 30.1, 31.7, 34.5, 36.3 (-CH$_2$-), 52.0 (-OCH$_3$), 113.2 (Ar-CH-), 115.9 (Ar-CH-), 121.0 (Ar-CH-), 129.5 (Ar-CH-), 145.1 (Ar-C-R), 155.9 (Ar-C-OH). GC analysis of this product showed that it contained significant amounts of impurity.

**Methyl 11-(3-hydroxyphenyl)undecanoate; HOPhC10COOMe (9);** From **4**; Elemental analysis: calcd (%) for C$_{18}$H$_{28}$O$_3$ (292.41): C 73.93, H 9.65 %.; found: C 73.80, H 9.53. MS [$m/z$ (%)]: 292 (10) [$M^+$-H], 261 (6), 162 (8), 147 (8), 133 (10), 120 (10), 108 (100), 98 (37), 91 (10), 84 (5), 77 (24), 69 (6), 55 (21), 41 (18). $^1$H NMR (400 Hz; CDCl$_3$): δ 1.21-1.41 (m, 12.7H; -CH$_2$-, alkyl chain), 1.55-1.71 (m, 4.8H; -CH$_2$), 2.35 (t, J=7.2, 2H; -CH$_2$-), 2.57 (t, $^3J$(H,H) =7.2, 2H; -CH$_2$-), 3.7 (s, 3H; -OCH$_3$), 5.76-5.90 (s, 1H; Ar-OH), 6.65-6.72 (m, 1.7H; Ar-H), 6.76 (d, $^3J$(H,H) =8.0, 1H; Ar-H), 7.15 (t, $^3J$(H,H) =8.0, 1H; Ar-H). $^{13}$C NMR (100 Hz; CDCl$_3$): δ 25.3, 29.7, 31.7, 34.7, 36.3 (-CH$_2$-), 52.0 (-OCH$_3$), 113.0 (Ar-CH-), 115.7 (Ar-CH-), 121.2 (Ar-CH-), 129.7 (Ar-CH-), 145.1 (Ar-C-R), 155.9 (Ar-C-OH), 175.5 (R-COOMe).

**Methyl 10-(3-hydroxyphenyl)decanoate; HOPhC9COOMe (10);** From **5**;[11b] Elemental analysis: calcd (%) for C$_{17}$H$_{26}$O$_3$ (292.41): C 73.35, H 9.41.; found: C 76.40, H 9.93. MS [$m/z$ (%)]: 278 (1.4) [$M^+$-H], 247 (10), 148 (16), 133 (11), 121 (26), 108 (100), 98 (42), 87 (3), 77 (1.5), 69 (0.4), 55 (1.2), 41 (16). $^1$H NMR (400 Hz; CDCl$_3$): δ 1.23-1.40 (m, 11H; -CH$_2$-, alkyl chain), 1.48-1.75 (m, 4H; -CH$_2$-), 2.36 (t, $^3J$(H,H) =7.6, 1.8H; -CH$_2$-), 2.56 (t, $^3J$(H,H) =7.6, 1.9H; -CH$_2$-), 3.70 (s, 3H; -OCH$_3$), 5.39 (s, 1H; Ar-OH), 6.65-6.72 (m, 2H; Ar-H), 6.77 (d, $^3J$(H,H)=7.5, 1H; Ar-H), 7.14 (t, $^3J$(H,H) =7.9, 1H, Ar-H). $^{13}$C NMR (100 Hz; CDCl$_3$): δ 25.5, 27.6, 29.9, 31.5, 34.5, 36.3 (-CH$_2$-), 51.7 (-OCH$_3$), 113.0 (Ar-CH-), 115.7 (Ar-CH-), 120.7 (Ar-CH-), 129.5 (Ar-CH-), 145.1 (Ar-C-R), 156.6 (Ar-C-OH), 174.9 (R-COOMe).

**Attempted polymerization of methyl 16-(3-hydroxyphenyl)hexadecanoate.** In a 10 ml Schlenk tube, methyl 16-(3-hydroxyphenyl)hexadecanoate (1 g, 2.8 mmol) and [Ti(OBu)$_4$] (0.0573 g, 0.2 mmol) were heated at 150 °C under dynamic vacuum over 24 hours. The product was cooled followed by addition of dichloromethane (10 mL) to dissolve any unreacted monomers and or soluble products. After filtration, a brown solid (0.6 g), insoluble in all solvents tested, was obtained and analyzed by MALDI-TOF mass spectrometry which indicated the presence of up to seven monomer units in the volkatile fraction. MALDI-TOF MS [m/z]; m=monomer units in an oligomer: 715.42 (m=2), 1045.76 (m=3), 1375.99 (m=4), 1706.24 (m=5), 2038.43 (m=6), 2366.68 (m=7). The dichloromethane extract was analsed by, GC-MS which in addition to the monomer's peak (362 g/mol), showed another peak with molecular mass of 330 g /mol (a loss of methanol; 32 g/mol) which corresponds to loss of methanol. Attempts at purification included column chromatography using hexane/ethyl acetate (90/10) and recrystallizing from hot hexane, but the white solid could not be obtained completely free from starting material (**6**). MS [$m/z$ (%)]: 330 (34) [$M^+$-H], 161 (2), 147 (13), 135 (13), 121 (30), 108 (100), 98 (48), 91 (23), 77 (23), 69 (15), 55 (63), 41 (56). $^1$H NMR (400 Hz; CDCl$_3$): δ 1.06-1.39 (m, 26.5H; -CH$_2$-, alkyl chain), 1.43-1.60 (m, 6H; -CH$_2$-), 1.61-1.74 (m, 2H; -CH$_2$-), 2.24 (t, $^3J$(H,H)=8.0, 0.8H; -CH$_2$-), 2.41-2.58 (m, 4.3H; -CH$_2$-), 3.60 (s,0.9H; -OCH$_3$), 4.76 (s, 0.3H; ArOH), 6.78-6.87 (m, 2H; Ar-H), 6.96 (d, $^3J$(H,H) =7.6, 1H; Ar-H), 7.19 (t, Ar-H). $^{13}$C NMR (100 Hz; CDCl$_3$): δ 25.3, 29.7, 31.7, 35.0, 36.1 (-CH$_2$-), 113.0 (Ar-CH-), 115.7 (Ar-CH-), 119.1 (Ar-CH-), 121.7 (Ar-CH-), 126.3 (Ar-CH-), 129.7 (Ar-CH-), 145.1 (Ar-C-R).

**Attempted polymerization of shorter chain alkenyl phenols.** Polymerisation of short chain monomers was attempted using tetrabutoxytitanium (IV) under similar conditions with molecular masses corresponding to a loss of methanol from particular monomers. HOPhC9COOMe and HOPhC11COOMe gave insoluble polymeric materials whilst HOPhC10COOMe and HOPhC12COOMe gave liquid products for which GCMS studies showed apparent loss of methanol. The isolation of these products was carried out by column chromatography using hexane/ethyl acetate (90/10), although the apparent lactones were always contaminated with starting materials.

**Cyclisation of HOPhC12COOMe;** MS [$m/z$ (%)]: 288 (37) [$M^+$-H], 190 (6), 161 (5), 147 (12), 133 (14), 121 (34), 108 (100), 98 (53), 77 (31), 67 (12), 55 (64), 41 (54). $^1$H NMR (400 Hz; CDCl$_3$): δ 1.11-1.51 (m, 23H; -CH$_2$- alkylchain), 1.43-1.59 (m, 3.8H; -CH$_2$-), 1.60-1.79 (m, 2.8H; -CH$_2$-), 2.25-2.40 (m, 1H; -CH$_2$-), 2.49-2.72 (m, 4.3H; -CH$_2$-), 3.70 (s, 1.5H; -OCH$_3$), 4.84 (s, 0.4H; ArOH), 6.68-6.97 (m, 1.8H; Ar-H), 7.60 (d, $^3J$(H,H)=7.5, 1H; Ar-H), 7.19 (t, Ar-H). $^{13}$C NMR (100 Hz; CDCl$_3$): δ 25.3, 31.1, 35.0, 36.9 (-CH$_2$-, alkyl chain), 119.1 (Ar-CH-), 121.9 (Ar-CH-), 126.5 (Ar-CH-), 129.7 (Ar-CH-), 145.1 (Ar-C-R), 151 (Ar-C-O-R).

**Cyclisation of HOPhC10COOMe;** MS [$m/z$ (%)]: 260 (37) [$M^+$-H], 162 (11), 146 (18), 133 (18), 120 (33), 108 (100), 91 (37), 77 (37), 55 (55), 41 (50). $^1$H NMR (400 Hz; CDCl$_3$): δ 1.21-1.48 (m, 16.4H; -CH$_2$-), 1.53-1.69 (m, 5.6H; -CH$_2$-), 1.70-1.83 (m, 2H; -CH$_2$-), 2.27-2.37 (m, 1H; -CH$_2$-), 2.52-2.68 (m, 4.4H; -CH$_2$-), 3.69 (s, 0.9H; -OCH$_3$), 4.85 (s,0.5H; ArOH), 6.87-6.95 (m, 2H; Ar-H), 7.06 (d, $^3J$(H,H) =7.4, 1H; Ar-H), , 7.28 (t, Ar-H). $^{13}$C NMR (100 Hz; CDCl$_3$): δ 25.3, 29.9, 31.7, 35.0, 36.1 (-CH$_2$-), 119.1 (Ar-CH-), 121.9 (Ar-CH-), 126.5 (Ar-CH-), 129.7 (Ar-CH-).

## Acknowledgements

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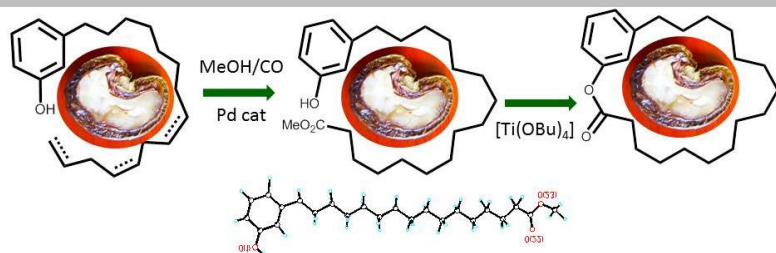
Cardanol derived from cashew nut shell liquid and shorter chain derivatives obtained by metathesis can be methoxycarbonylated to bifunctional ester phenols; reaction with [Ti(OBu)₄] then gives polymers or macrolactones

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**Synthesis of bifunctional monomers via palladium catalyzed carbonylation of cardanol and its derivatives**