Bull. Chem. Soc. Ethiop. **2022**, 36(1), 173-186.
© 2022 Chemical Society of Ethiopia and The Authors
DOI: https://dx.doi.org/10.4314/bcse.v36i1.14

ISSN 1011-3924
Printed in Ethiopia
Online ISSN 1726-801X

CATALYTIC HYDROGENATION OF CARDANOL DERIVED BIFUNCTIONAL MONOMERS FOR POLYMERIZATION WITH DIESTERS

James E. Mgaya*

Dar es Salaam University College of Education (DUCE), University of Dar es Salaam, Tanzania

(Received November 16, 2021; Revised February 21, 2022; Accepted February 23, 2022)

ABSTRACT. Cardanol extracted from cashew nut shell liquid (agro-waste) was used to synthesize a bifunctional monomer; methyl 16-(3-hydroxyphenyl)hexadecanoate using DTBPMB modified palladium catalyst. Hydrogenation of this monomer using a Ru(acac)$_3$/triphos/MSA catalytic system in aqueous dioxane and ammonia solution gave 3-(16-hydroxyhexadecyl)phenol (75% yield) and 3-(16-aminohexadecyl)phenol (37% yield) respectively. Polymerization of 3-(16-aminohexadecyl)phenol and 3-(16-hydroxyhexadecyl)phenol with dimethyl nonadecanedioate (a di-ester obtained from methoxycarbonylation of methyl oleate) resulted into oligomers consisting of up to nine condensed monomer units (in the volatile fraction) as was revealed by MALDI-TOF MS.

KEY WORDS: Cardanol, Bifunctional monomers, Catalytic hydrogenation, Polymerization

INTRODUCTION

Cashew nut shell liquid; a by-product of cashew nut processing factories is a promising source of environmentally friendly starting materials for production of various valuable materials. The liquid is rich in phenolic compounds having functional groups such as double bonds, carboxylic group and alcohol group which make them suitable starting materials for various reactions [1–5]. The phenolic components of cashew nut shell liquid are also potential compounds for making fire retardant polymers due to the presence of aromatic ring in their structures [6–8]. Natural cashew nut shell liquid (which is obtained by cold extraction methods) contains anacardic acid as a major component (60–65%). On the other hand, technical cashew nut shell liquid (extracted from cashew nut shells at higher temperatures) contains cardanol up to 85%. Other components of cashew nut shell liquid are cardol (15–20%) and traces of 2-methylcardol (Figure 1) [9].

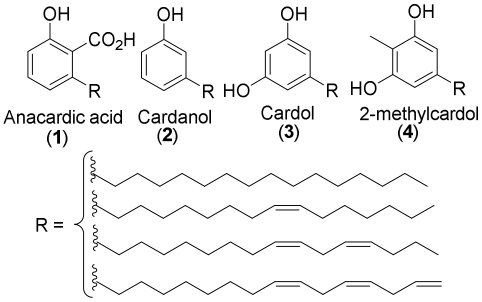


Figure 1. Components of cashew nut shell liquid.

In recent years, various research groups have shown great interest in investigating the possibility of replacing non-renewable by renewable materials in synthesizing materials of interest

---

*Corresponding author. E-mail: james.mgaya@duce.ac.tz ; jamesmgaya@yahoo.com

[10–16]. The major reason is that non-renewable materials are subject to depletion, which means that overdependence on such materials is a risk. Cashew nut shell liquid is one of the bio-based resources that have been extensively investigated for its use in preparation of useful fine chemicals and materials [17–22]. One of the areas that cashew nut shell liquid has been investigated is in the synthesis of bifunctional monomers for making fire resistant polymers. Successful synthesis of bifunctional monomers by the palladium catalyzed methoxycarbonylation of cardanol component of cashew nut shell liquid with good yield have been reported [23]. Combination of metathesis and carbonylation techniques were used to make bifunctional monomers of various chain lengths from cardanol. The fact that these monomers derived from cardanol have both alcohol and ester groups (Figure 2) means that they could be polymerized by simply heating in the presence of appropriate catalyst without the need of a second monomer.

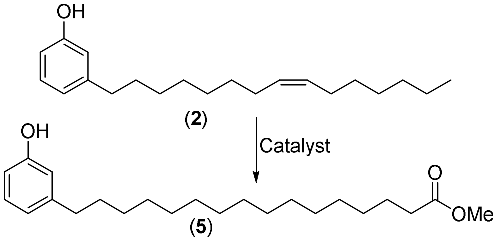


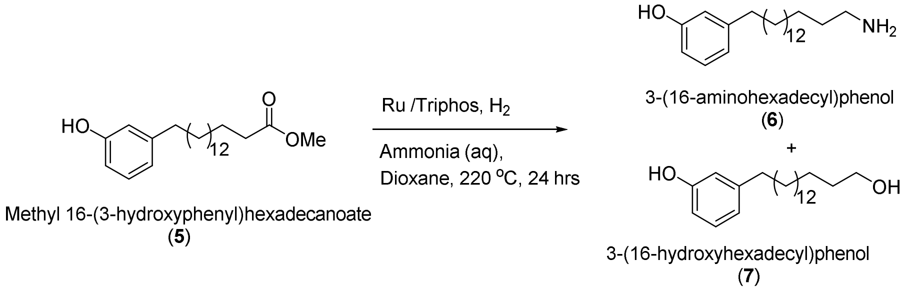
Figure 2. Structures of cardanol (**2**) and cardanol derived bifunctional monomer (**5**) [23].

However, the polymerization reaction of these monomers using a standard $Ti(OBu)_4$ condensation catalyst produced either brittle polymers, or lactones contaminated with bifunctional monomers [23]. Brittle polymers are difficulty to process. Purification of lactones (formed by cyclization reaction of bifunctional monomers) was unsuccessful. This paper therefore focusses on improving the method of polymerization of cardanol derived bifunctional monomers. A discussion on the catalytic hydrogenation of methyl 16-(3-hydroxyphenyl)hexadecanoate to produce 3-(16-aminohexadecyl)phenol and 3-(16-hydroxyhexadecyl)phenol is presented. The results obtained from polymerization of 3-(16-aminohexadecyl)phenol and 3-(16-hydroxyhexadecyl)phenol with dimethyl 1,19-nonadecanedioate (a di-ester obtained from a methoxycarbonylation reaction of methyl oleate) are also presented.

RESULTS AND DISCUSSION

Hydrogenation of methyl 16-(3-hydroxyphenyl)hexadecanoate in aqueous ammonia

The hydrogenation reaction of methyl 16-(3-hydroxyphenyl)hexadecanoate (**5**) in aqueous ammonia using a $Ru(acac)_3$/triphos/MSA catalytic system (Scheme 1) produced 3-(16-aminohexadecyl)phenol (**6**). The reaction proceeded in >99% conversion; however, the desired compound, (3-(16-aminohexadecyl)phenol) was isolated in 37% yield only. Among other factors, the low yield of the desired compound could be attributed to two major factors. First factor; the reaction was performed in aqueous conditions, which led to the formation of the desired compound and another hydrogenation product; 3-(16-hydroxyhexadecyl)phenol (**7**) (Scheme 1).



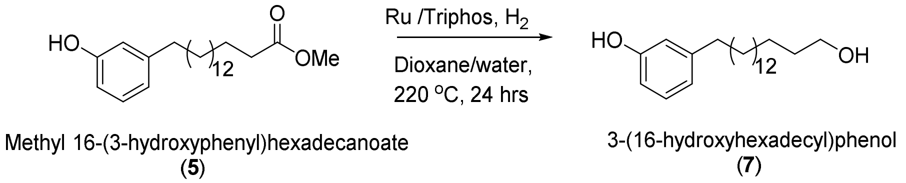
Scheme 1. Hydrogenation of methyl 16-(3-hydroxyphenyl)hexadecanoate in aqueous ammonia.

Second factor; formation of insoluble polymeric solids which were possibly polyamides/polyesters formed from a reaction of 3-(16-aminohexadecyl)phenol (**6**) with methyl 16-(3-hydroxyphenyl) hexadecanoate (**5**). However, interpretation of MALDI-TOF MS spectra of these polymeric solids was unsuccessful.

Both ^{1}H NMR and ^{13}C NMR data (shown in the experimental section) agree well with the structure of compound **6**. In the ^{1}H NMR spectral data, the disappearance of peaks at δ 3.7 ($\text{-OC}\underline{\text{H}_3}$) and δ 2.3 ($\text{-C}\underline{\text{H}_2}\text{-COOMe}$) as well as the appearance of a peak at δ 2.7 ($\text{-C}\underline{\text{H}_2}\text{-NH}_2$) confirm that compound **5** has been hydrogenated to form compound **6**. In ^{13}C NMR spectral data, the disappearance of the methoxy ($\text{O}\underline{\text{C}}\text{H}_3$) peak at δ 60 and carbonyl ($\underline{\text{C}}\text{=O}$) peak at δ176 with the appearance of a peak at δ 47 ($\text{-}\underline{\text{C}}\text{H}_2\text{-NH}_2$) further confirm the formation of compound **6**.

Hydrogenation of methyl 16-(3-hydroxyphenyl)hexadecanoate in dioxane/water solution

The hydrogenation reaction of methoxycarbonylated cardanol in dioxane/water solution using the Ru(acac)_3/triphos/MSA catalytic system produced 3-(16-hydroxyhexadecyl)phenol (**7**). In this reaction (Scheme 2), the desired product (**7**) was the major product (75% isolated yield) with only negligibly small amount of insoluble polymeric solids being formed.



Scheme 2. Hydrogenation of methyl 16-(3-hydroxyphenyl)hexadecanoate in aqueous dioxane.

The fact that the desired compound **7** was the major product of the reaction explains the big difference in the yield of 3-(16-hydroxyhexadecyl)phenol (75%) when compared to the yield of 3-(16-aminohexadecyl)phenol (37%).

Both ^{1}H NMR and ^{13}C NMR spectral data agree well with the structure of compound **7**. In the ^{1}H NMR spectral data, the disappearance of peaks at δ 3.7 ($\text{-OC}\underline{\text{H}_3}$) and δ 2.3 ($\text{-C}\underline{\text{H}_2}\text{-COOMe}$) as well as the appearance of a peak at δ 3.6 ($\text{-C}\underline{\text{H}_2}\text{-OH}$) confirm that compound **5** has been hydrogenated to form compound **7**. In the ^{13}C NMR spectral data, the disappearance of the methoxy ($\text{O}\underline{\text{C}}\text{H}_3$) peak at δ 60 and carbonyl ($\underline{\text{C}}\text{=O}$) peak at δ 176 together with the appearance of a peak at δ 65 ($\text{-}\underline{\text{C}}\text{H}_2\text{-OH}$) further confirm the formation of compound **7**.

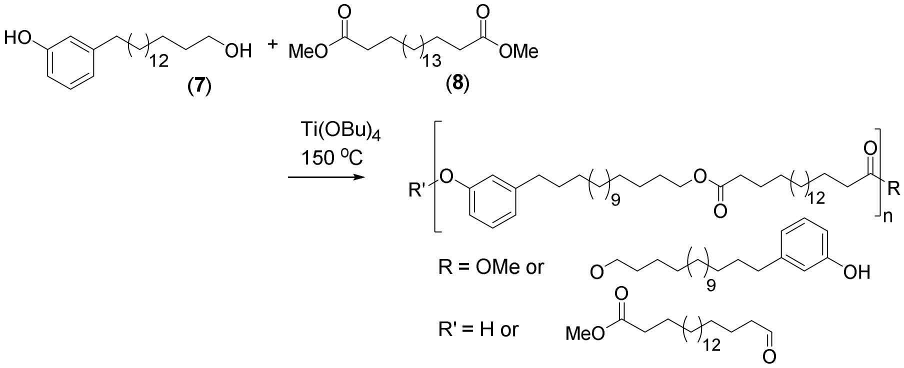
Methoxycarbonylation of olive oil

Natural oils differ in the amounts of methyl oleate they contain. For instance, olive, rapeseed, and sunflower oils from supermarket contain 73%, 64%, and 38% of methyl oleate, respectively.

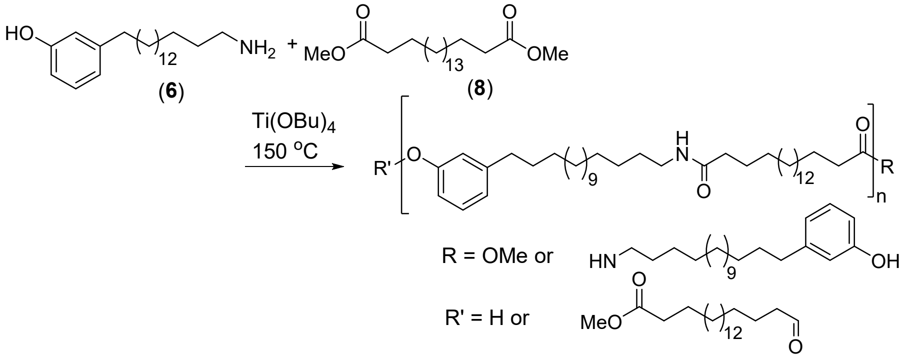
Furst *et al.* [11] investigated the methoxycabonylation reaction of these oils to synthesize dimethyl 1,19-nonadecanedioate (**8**). The authors found that the amount of dimethyl 1,19-nonadecanedioate (**8**) produced from methoxycarbonylation reaction of natural oils differed depending on the percentage of methyl oleate they contain [11]. Olive oil which contains 73% methyl oleate gave highest yield compared to rapeseed and sunflower oils. Methoxycarbonylation reaction of 10 mL of each of the oils yielded 6.93 g (74.7%), 6.44 g (69.3%), and 3.36 g (36.8%) for olive, rapeseed and sunflower oils respectively. Thus in this paper, olive oil was used as a starting material for the synthesis of dimethyl 1,19-nonadecanedioate (**8**) to be used in the polymerization reaction with cardanol derived monomers. The methoxycarbonylation reaction of olive oil was achieved using the Pd/DTBPMB/H^+ catalytic system to give dimethyl 1,19-nonadecanedioate (**8**) in 74.3% yield. The spectral data (shown in the experimental section) agree well with literature data [11, 24], as well as the chemdraw prediction for the structure of the compound.

Polymerization of 3-(16-aminohexadecyl)phenol (**6**) *and 3-(16-hydroxyhexadecyl)phenol* (**7**) *with dimethyl nonadecanedioate* (**8**)

Schemes 3 and 4 show the polymerization reactions of monomers (**6**) and (**7**) with dimethyl 1,19-nonadecanedioate (**8**). It was previously reported [23], that the polymerization reaction of methoxylated cardanol and its derivatives had two main challenges. One was; the formation of a mixture of oligomers and a lactone in a single polymerization reaction. Oligomers were easily isolated from the product mixture, but for the lactones, it was impossible to isolate them from the starting materials. The second challenge; the formed polymers were very brittle. Interestingly, polymerization reaction of monomers **6** and **7** with dimethyl 1,19-nonadecanedioate reported in this paper (Schemes 3 and 4) produced oligomers that are not brittle. This could be due to the increased number of methylene groups between aromatic groups as a result of including dimethyl nonadecanedioate in the polymerization reaction.



Scheme 3. Polymerization reaction of 3-(16-hydroxyhexadecyl)phenol (**7**) with dimethyl 1,19-nonadecanedioate (**8**).



Scheme 4. Polymerization reaction of 3-(16-aminohexadecyl)phenol (**6**) with dimethyl 1,19-nonadecanedioate (**8**).

Monomer **6** contains hydroxyl group at one end and amine at the other end of the molecule. Likewise, monomer **7** contains hydroxyl group on both ends of the molecule. Thus there is no chance of formation of both, an olygomer and a lactone in the single polymerization reaction.

MALDI-TOF MS spectra of the polymerization product of 3-(16-hydroxyhexadecyl)phenol with dimethyl nonadecanedioate revealed formation of oligomers consisting of up to nine monomer units. The spectra are reported in the experimental section (Figures 3–6).

Zooming the MALDI-TOF MS spectra further reveal that, for the odd numbered oligomers both two forms are formed; $[A_2B+Na]^+$ and $[AB_2+Na]^+$ (A; stands for 3-(16-hydroxyhexadecyl)phenol, B; stands for dimethyl 1,19-nonadecanedioate). For example, in the three monomer units oligomer; $[A_2B+Na]^+$ has an M_r = 983.8, whilst $[AB_2+Na]^+$ has M_r = 1005.82, as seen in the zoomed spectra. For five monomer units oligomer; $[A_3B_2+Na]^+$ has an M_r = 1610.33, whilst $[A_2B_3+Na]^+$ has M_r = 1632.35. The same appears in the seven monomer units oligomer; $[A_4B_3+Na]^+$ has an M_r = 2236.87, whilst $[A_3B_4+Na]^+$ has M_r = 2259.87.

Comparing the ^{1}H NMR spectral data of 3-(16-hydroxyhexadecyl)phenol monomer (**7**) with that of an oligomer (shown in an experimental section), it can be observed that the peak for $C\underline{H_2}OH$ appears at δ 3.5 (for compound **7**) while in an oligomer there is no any resonance at δ 3.5 but appears at δ 4.1 which corresponds to $-C\underline{H_2}O(CO)R$. This agrees well with the chemdraw predictions for the structure of an oligomer.

Zooming the aromatic region in the ^{1}H NMR of an oligomer (Figure 8) in the experimental section; two different kinds of aromatic rings are observed: terminal ones, which should appear very similar to those in the monomer (**7**), and the one on the middle of AB_2, where the aromatic ring is expected to be significantly different from the terminal ones, but similar as those in any oligomers where the monomer is incorporated through the phenolic OH group. The aromatic ring of the cardanol derived monomer is expected to have 4 signals. If the OH in the aromatic ring of the monomer is defined as being in position 1 and the alkyl chain in position 3, then the H atoms should resonate: in positions 2 (s), 4 (d), 5 (t) and 6 (d). Comparing with the spectral data of the cardanol derived monomer (**7**) it is evident that t, x, y and z arise from terminal aromatic ring of cardanol derived units whilst s, u, v and w arise from the in chain cardanol units. Thus, the spectrum in figure 8 indicates that there are two kinds of aromatc rings, as it should be expected for any linear chain cardanol derived oligomers.

On the other hand, polymerization reaction of 3-(16-aminohexadecyl)phenol with dimethyl 1,19-nonadecanedioate resulted into formation of trimers as revealed by MALDI-TOF MS spectrum (Figure 7). In this case too, both forms of trimers such as AB_2 and A_2B are observed (where A stands for 3-(16-aminohexadecyl)phenol and B stands for dimethyl 1,19-nonadecanedioate). In Figure 7, $[A_2B+Na]^+$ has an *Mr* = 980.8 whereas $[AB_2+Na]$ has an *Mr* =1002.9. The other ion peaks in the spectrum do not relate with any oligomer fragments. They may possibly come from matrix clusters.

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 [25]. Cardanol and methoxylated cardanol; methyl 16-(3-hydroxyphenyl) hexadecanoate were synthesized using methods reported previously [3, 23]. Standard Schlenk line and glove box techniques were employed to carry out all hydrogenation reactions reported in this paper. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at 298 K by using Bruker 300 or 400 MHz and 75 or 100 MHz spectrometers for ^{1}H and ^{13}C NMR, respectively. Samples for NMR analysis were dissolved in deuterated chloroform as solvent. The chemical shifts of both ^{1}H NMR and ^{13}C NMR spectra were reported relative to tetramethylsilane.

Synthesis of 3-(16-aminohexadecyl)phenol (**6**)

Dioxane (5 mL) and ammonia solution (5 mL) were placed in a Schlenk tube and bubbled with argon (in the Schlenk line) for 10 min. In the glove box, methyl 16-(3-hydroxyphenyl)hexadecanoate (600 mg), Ru(acac)$_3$ (8 mg) and 1,1,1-tris(diphenylphosphino-methyl)ethane, Triphos (28 mg) were measured and added into an autoclave previously charged with magnetic stirrer. The autoclave was degassed three times using the Schlenk line. Dioxane (5 mL) and ammonia solution (5 mL) in the Schlenk tube were transferred into the autoclave using a 20 mL syringe. The solution in the autoclave was flushed with hydrogen three times, and pressurized to 40 bar. The reaction was left to proceed at 220 °C for 24 h. After venting hydrogen, and concentrating the solution (under vacuum), the yellowish solid product (565 mg) was obtained. The product was dissolved in chloroform (10 mL). Some insoluble solids (95 mg) were observed and removed from the solution by filtration. The yellowish solid (obtained after concentrating the solution containing soluble products) was dissolved in dichloromethane (5 mL) and recrystallized by addition of methanol to give white solids; 3-(16-aminohexadecyl)phenol (208 mg, 37%). ^{1}H-NMR (400 Hz, $CDCl_3$): δ = 1.11-1.41 (m, 24H; -alkyl chain), 1.45-1.70 (m, 4H; -CH_2), 2.56 (t, $^3J_{H,H}$ = 7.7 Hz, 2H; -CH_2), 2.66 (t, $^3J_{H,H}$ = 7.3 Hz, 2H; -CH_2), 6.59-6.70 (m, 2H; Ar-H), 6.73 (d, $^3J_{H,H}$ = 7.5 Hz, 1H; Ar-H), 7.14 (t, $^3J_{H,H}$ = 7.2 Hz, 1H; Ar-H). ^{13}C-NMR (100 Hz, $CDCl_3$): δ = 27.2, 29.3, 31.3, 35.9 (-CH_2), 49.8 (-R-C-NH_2), 112.7 (Ar-CH), 115.5 (Ar-CH), 120.3 (Ar-CH), 129.3 (Ar-CH). Elemental analysis calcd (%) for $C_{22}H_{39}NO$: C, 79.22; H, 11.79; N, 4.20. Found: C, 78.99; H, 11.70; N, 4.00.

Synthesis of 3-(16-hydroxyhexadecyl)phenol (**7**)

Dioxane (10 mL) and water (1 mL) were placed in a Schlenk tube and bubbled with argon (in the Schlenk line) for 10 min. In the glove box, methyl 16-(3-hydroxyphenyl) hexadecanoate (400 mg), Ru(acac)$_3$ (8 mg) and 1,1,1-tris(diphenylphosphinomethyl)ethane, Triphos (28 mg) were measured and added into an autoclave previously charged with magnetic stirrer. The autoclave was degassed three times using the Schlenk line. Dioxane (10 mL) and water (1 mL) in the Schlenk tube were transferred into the autoclave using a 20 ml syringe. The solution in the autoclave was flushed with hydrogen three times, and pressurized to 40 bar. The reaction was left to proceed at 220 °C for 24 h. After venting hydrogen, and concentrating the solution (under vacuum), the yellowish solid product obtained was dissolved in dichloromethane and recrystallized by addition of hexane to give a white solid; 3-(16-hydroxyhexadecyl)phenol (275 mg; 75%). ^{1}H-NMR (400 Hz, $CDCl_3$): δ = 1.04-1.47 (m, 24H; -alkyl chain), 1.50-1.69 (m, 4H; -CH_2-), 2.57 (t, $^3J_{H,H}$ = 7.8 Hz, 2H; -CH_2-), 3.68 (t, $^3J_{H,H}$ = 6.3 Hz, 2H; -CH_2-), 6.60-6.72 (m, 1.8H; Ar-H), 6.77 (d, $^3J_{H,H}$ = 7.2 Hz, 1H; Ar-H), 7.16 (t, $^3J_{H,H}$=7.5 Hz, 1H; Ar-H). ^{13}C-NMR (100 Hz, $CDCl_3$): δ = 25.7, 29.2, 31.4, 32.9, 35.9 (-CH_2), 63.1 (-R-C-OH), 112.5 (Ar-CH), 115.3 (Ar-CH), 120.8 (Ar-CH), 129.4 (Ar-CH), 144.9 (Ar-C-R), 155.6 (Ar-C-OH). Elemental analysis calcd (%) for $C_{22}H_{38}O_2$: C, 78.99; H, 11.45. Found: C, 77.30; H, 10.26.

Synthesis of dimethyl 1,19-nonadecanedioate (**8**).

Olive oil (10 mL) was dissolved in methanol (10 mL) in a Schlenk tube and bubbled with argon for 10 min. In the glovebox, [$Pd_2(dba)_3$] (dba = 1,3-dibenzylideneacetone) (0.549 g) and 1,2-bis(ditertbutylphosphinomethyl)benzene (DTBPMB) (2.367 g) were placed into the steel autoclave along with a magnetic stirrer. The autoclave was connected to the Schlenk line and it was degassed three times. The olive oil solution was transferred into the autoclave by means of a 20 mL syringe. Methane sulfonic acid (0.78 mL) was added to the solution in the autoclave. The autoclave was purged with CO before it was pressurized to 30 bar. The reaction progressed at 80 °C for 24 h. After cooling, the CO was vented, and the obtained yellow powder was dissolved by adding dichloromethane (20 mL). The resulting yellow solution was filtered through a Celite bed, and concentrated under vacuum until a white precipitate appeared. Cold methanol (0 °C) was added and the mixture was stirred in an ice bath for 20 min before filtration. The desired product was obtained as a white powder (6.89 g, 74.3%). ^{1}H-NMR (400 MHz; $CDCl_3$): δ = 1.18-1.37 (m, 26H; -alkyl chain), 1.53-1.71 (m, 4H; -CH_2-), 2.29 (t,$^3J_{H,H}$ = 7.6 Hz, 4H; -CH_2-), 3.67 (s, 6H; -O-CH_3). ^{13}C-NMR (100 Hz, $CDCl_3$): δ = 25.01, 29.7, 31.4, 32.9, 34.01 (-CH_2), 51.38 (-OCH_3), 174.24 (-CO-). Elemental analysis calcd (%) for $C_{21}H_{40}O_4$: C, 70.74; H, 11.31. Found: C, 71.10; H, 11.21.

Polymerization of 3-(16-hydroxyhexadecyl)phenol (**7**) *with dimethyl 1,19-nonadecanedioate* (**8**)

3-(16-Hydroxyhexadecyl)phenol (315 mg) and dimethyl 1,19-nonadecanedioate (335 mg) were placed in a 10 mL Schlenk tube followed by addition of $Ti(OBu)_4$ (0.24 mg) catalyst. The mixture was heated at 150 °C under reduced pressure (0.01 mbar) in the course of 24 h. The resulting solids were analyzed by MALDI-TOF MS which revealed the formation of oligomers from condensation of up to nine monomers. MALDI-TOF MS (A; stands for 3-(16-hydroxyhexadecyl) phenol, B; stands for dimethyl 1,19-nonadecanedioate): *Mr* = 983.8; $[A_2B+Na]^+$, *Mr* = 1005.82; $[AB_2+Na]^+$, *Mr* = 1308.09; $[A_2B_2+Na]^+$, *Mr* = 1610.33; $[A_3B_2+Na]^+$, *Mr* = 1632.35; $[A_2B_3+Na]^+$, *Mr* = 1934.62; $[A_3B_3+Na]^+$, *Mr* = 2236.87; $[A_4B_3+Na]^+$, *Mr* = 2259.87; $[A_3B_4+Na]^+$, *Mr* = 2864.39; $[A_5B_4+Na]^+$. ^{1}H-NMR (400 Hz, $CDCl_3$): δ = 0.99-1.48 (m, 66.7H; -alkyl chain), 1.51-1.70 (m, 9.6H; -CH_2-), 1.72-1.81 (m, 1.5H; -CH_2-), 2.20-2.40 (m, 4.5H; -CH_2CO-), 2.46-2.68 (m, 3.4 H; $ArCH_2$-), 3.69 (s, 3H; -OCH_3), 4.08 (t, $^3J_{H,H}$ = 6.6 Hz, 2H; -CO_2CH_2-), 6.61-6.71 (m, 1H; Ar-H), 6.75 (d, $^3J_{H,H}$ = 6.9 Hz, 0.8H; Ar-H), 6.90 (s, 1.4H, Ar-H), 7.04 (d, $^3J_{H,H}$ = 6.9 Hz, 0.9H; Ar-H), 7.15 (t, $^3J_{H,H}$ = 7.6 Hz, 1H; Ar-H). ^{13}C-NMR (100 Hz, $CDCl_3$): δ = 25.1, 25.9, 29.6, 31.2, 32.9, 34.5, 35.8 (-CH_2), 51.6 (-OCH_3), 64.5 (-CH_2OCOR), 112.4, 113.8, 115.4, 118.6, 120.7, 121.5, 125.8, 129.0 (Ar-CH), 150.7 (Ar-CO-COR).

Polymerization of 3-(16-aminohexadecyl)phenol (**6**) *with dimethyl 1,19-nonadecanedioate* (**8**)

3-(16-Aminohexadecyl)phenol (315 mg) and dimethyl 1,19-nonadecanedioate (335 mg) were placed in a 10 mL Schlenk tube followed by addition of $Ti(OBu)_4$ (0.24 mg) catalyst. The mixture was heated at 150 °C under reduced pressure (0.01 mbar) over the course of 24 h. The resulting solids were analyzed by MALDI-TOF MS which revealed the formation of dimers and trimers. MALDI-TOF MS (A; stands for 3-(16-aminohexadecyl)phenol and B; stands for dimethyl 1,19-nonadecanedioate): *Mr* = 980.8; $[A_2B+Na]^+$, *Mr* = 1002.9; $[AB_2+Na]$. ^{1}H-NMR (400 Hz, $CDCl_3$): δ = 1.06-1.42 (m, 61.7H; -alkyl chain), 1.47-1.72 (m, 10.4H; $-CH_2-$), 2.13(t, $^3J_{H,H}$ = 6.9 Hz, 1.7H; $-CH_2CONH-$), 2.31 (t, $^3J_{H,H}$ = 6.9 Hz, 4H; $-CH_2CO_2Me$), 2.5 (t, $^3J_{H,H}$ = 6.9, 4H; Ar-CH_2-), 3.15-3.51 (m, 4.2H; $-CH_2NHCO-$), 3.70 (s, 3H; $-OCH_3$), 6.51-7.24 (m, 6.8H; Ar-H). ^{13}C-NMR (100 Hz, $CDCl_3$): δ = 25.0, 29.6, 31.2, 32.9, 35.8 ($-CH_2$), 51.6 (OCH_3), 112.5, 114.04, 115.01, 121.4, 129.2 (Ar-CH), 173.78 (R-CO-N-).

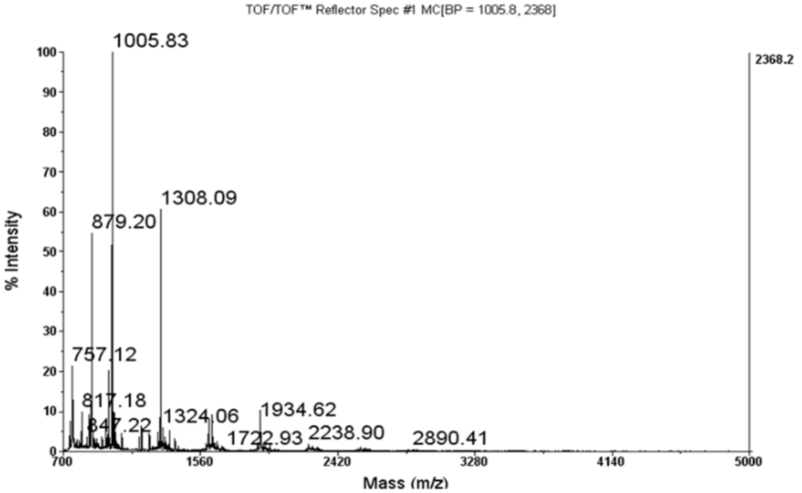


Figure 3. MALDI-TOF MS spectra of oligomers from the polymerization reaction of 3-(16-hydroxyhexadecyl)phenol with dimethyl 1,19-nonadecanedioate.

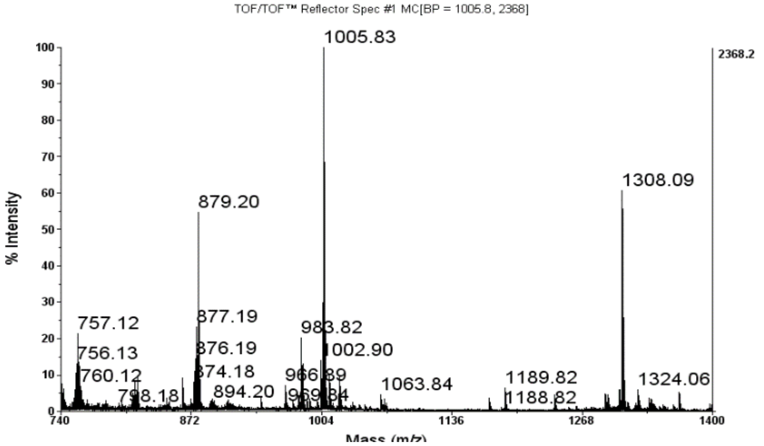


Figure 4. MALDI-TOF MS spectra (zoom 1) of oligomers from the polymerization reaction of 3-(16-hydroxyhexadecyl)phenol with dimethyl 1,19-nonadecanedioate .

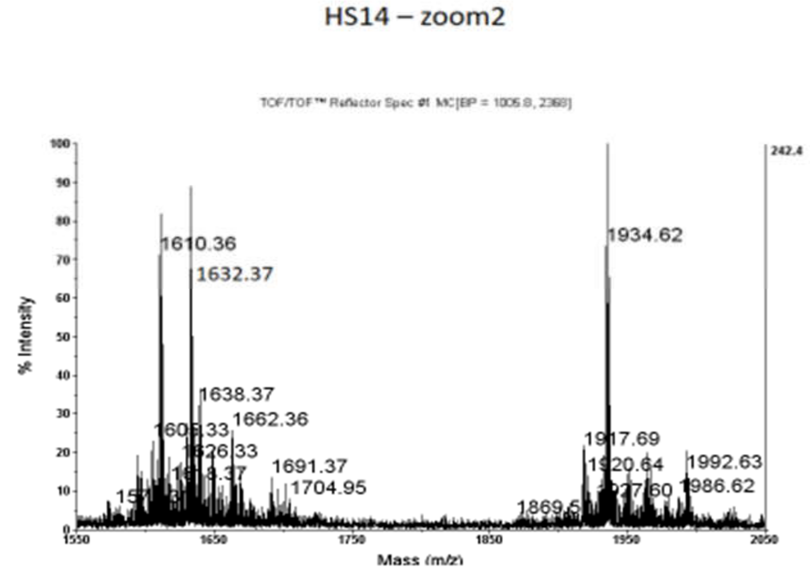


Figure 5. MALDI-TOF MS spectra (zoom 2) of oligomers from the polymerization reaction of 3-(16-hydroxyhexadecyl)phenol with dimethyl 1,19-nonadecanedioate.

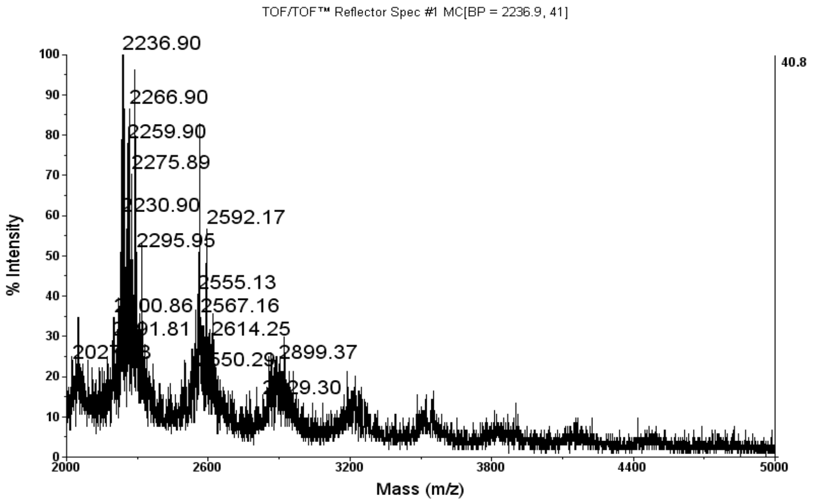


Figure 6. MALDI-TOF MS spectra (zoom 3) of oligomers from the polymerization reaction of 3-(16-hydroxyhexadecyl)phenol with dimethyl 1,19-nonadecanedioate.

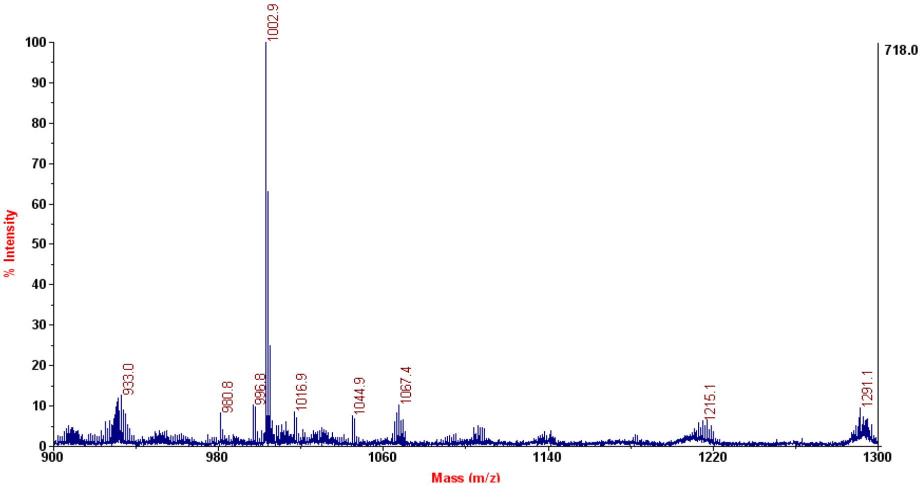


Figure 7. MALDI-TOF MS analysis spectrum of oligomer from a condensation reaction of 3-(16-aminohexadecyl)phenol with dimethyl 1,19-nonadecanedioate.

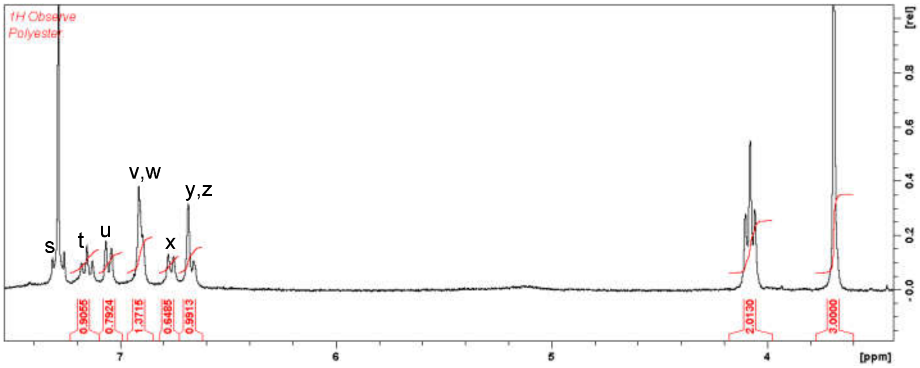


Figure 8. Zoomed ^{1}H NMR spectrum of oligomers from the polymerization reaction of dimethyl nonadecanedioate with3-(16-hydroxyhexadecyl)phenol for analysis of aromatic region.

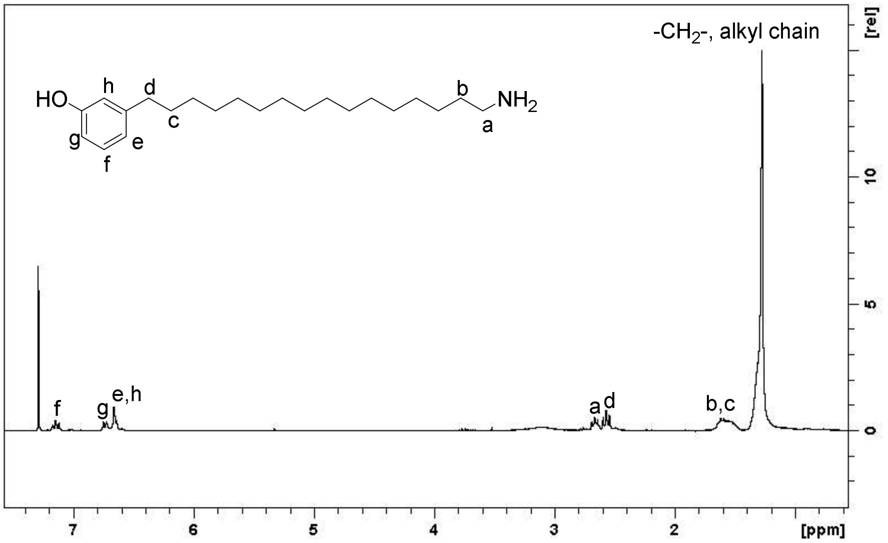


Figure 9 (a). ^{1}H NMR spectrum of 3-(16-aminohexadecyl)phenol (**6**) with peak assignments.

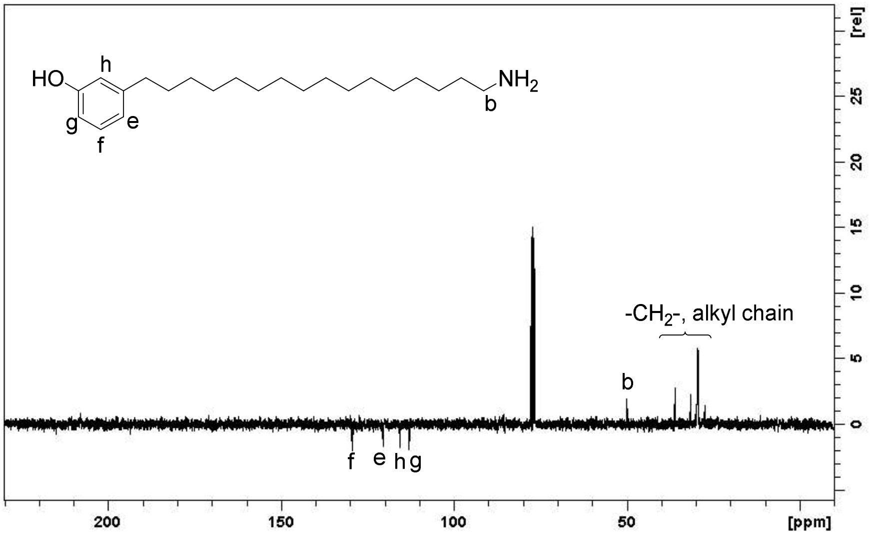


Figure 9 (b). ^{13}C NMR spectrum of 3-(16-aminohexadecyl)phenol (**6**) with peak assignments.

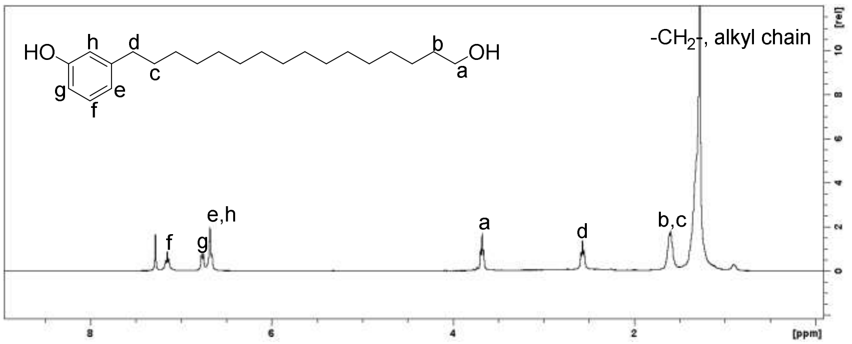


Figure 10 (a). ^{1}H NMR spectrum of 3-(16-hydroxyhexadecyl)phenol (**7**) with peak assignments.

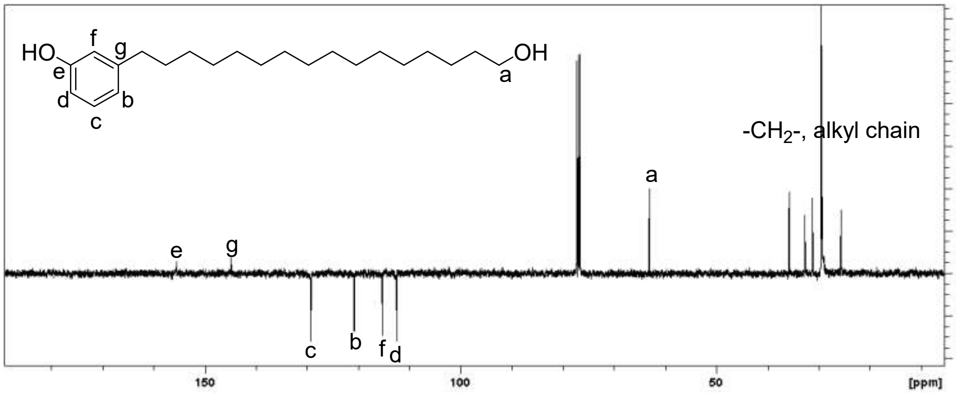


Figure 10 (b). ^{13}C NMR spectrum of 3-(16-hydroxyhexadecyl)phenol (**7**) with peak assignments.

CONCLUSION

The hydrogenation reaction of methoxycarbonylated cardanol has been successively achieved. A big difference in the yield of 3-(16-hydroxyhexadecyl)phenol (75%) and 3-(16-aminohexadecyl)phenol (37%) was observed. The low yield of 3-(16-aminohexadecyl)phenol was due to formation of other products such as 3-(16-hydroxyhexadecyl)phenol and insoluble polymeric solids during the course of the reaction. Polymerization reaction of 3-(16-hydroxyhexadecyl)phenol and 3-(16-aminohexadecyl)phenol with dimethyl nonadecanedioate produced oligomers from condensation of up to 9 monomers as was revealed by MALDI -TOF MS.

ACKNOWLEDGEMENTS

This work is dedicated to the late Professor Egid B. Mubofu who was an outstanding reseacher and my great academic supervisor. Professor David Cole Hamilton is acknowledged for partial funding and providing Lab space. Royal Society of Chemistry for a Research Mobility Grant is also acknowledged for funding this work.

REFERENCES

1. Graham, M.B.; Tyman, J.H.P. Ozonization of phenols from *Anacardium occidentale* (cashew). *JAOC* **2002**, 79, 725–732.
2. Vasapollo, G.; Mele, G.; Del Sole, R. Cardanol-based materials as natural precursors for olefin metathesis. *Molecules* **2011**, 16, 6871–6882.
3. Mmongoyo, J.A.; Mgani, Q.A.; Mdachi, S.J.M.; Pogorzelec, P.J.; Cole-Hamilton, D.J. Synthesis of a kairomone and other chemicals from cardanol: A renewable resource. *Eur. J. Lipid Sci. Technol.* **2012**, 114, 1183–1192.
4. Mgaya, J.E.; Mubofu, E.B.; Mgani, Q.A.; Cordes, D.B.; Slawin, A.M.; Cole-Hamilton, D.J. Isomerization of anacardic acid: A possible route to the synthesis of an unsaturated benzolactone and a kairomne. *Eur. J. Lipid Sci. Technol.* **2015**, 117, 190–199.
5. Deutsch, J.; Köckritz, A. Synthesis of novel chemicals from cardanol as a product of cashew nutshell processing. *Food Sci. Nutr.* **2020**, 8, 3081–3088.
6. Neuse, E.W. Polymers for potential use as charring ablators under hyperthermal re-entry conditions: A review of recent developments. *Mater. Sci. Eng.* **1973**, 11, 121–150.
7. Morgan, A.B.; Gilman, J.W. An Overview of flame retardancy of polymeric materials: Application, technology, and future directions. *Fire Mater.* **2013**, 37, 259–279.
8. Markwart, J.C.; Battig, A.; Velencoso, M.M.; Pollok, D.; Schartel, B.; Wurm, F.R. Aromatic vs. aliphatic hyperbranched polyphosphoesters as flame retardants in epoxy resin. *Molecules* **2019**, 24, 390.
9. Kumar, P.P.; Paramashivappa, R.; Vithayathil, P.J. Process for isolation of cardanol from technical cashew (*Anacardium occidentale L.*) nut shell liquid. *J. Agric. Food Chem.* **2002**, 50, 4705–4708.
10. Quinzler, D.; Mecking, S. Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization. *Angew. Chemie. Int. Ed.* **2010**, 49, 4306–4308.
11. Furst, M.R.L.; Le Goff, R.; Quinzler, D.; Mecking, S.; Botting, C.H.; Cole-Hamilton, D. Polymer precursors from catalytic reactions of natural oils. *J. Green Chem.* **2012**, 14, 472–477.
12. Julis, J.; Bartlett, S.A.; Baader, S.; Beresford, N.; Routledge, E.J.; Cazin, C.S.J.; Cole-Hamilton, D.J. Selective ethenolysis and oestrogenicity of compounds from cashew nut shell liquid. *Green Chem.* **2014**, 16, 2846–2856.
13. Andrew, M.; Mubofu, E.B. Catalytic efficiency of palladium(II) supported on castor oil based micelle templated silica for peroxide promoted catalytic wet oxidation of phenols. *IRJPAC* **2017**, 15, 1-12.
14. Mubofu, E.B.; Mlowe, S.; Revaprasadu, N. Cashew nut shells as source of chemicals for preparation of chalcogenide nanoparticles. *Nanosyst. Phys. Chem. Math.* **2016**, 7, 724–727.
15. Mensah, M.B.; Awudza, J.A.M.; O'Brien, P. Castor oil: A suitable green source of capping agent for nanoparticle syntheses and facile surface functionalization. *Royal Soc. Open Sci.* **2018**, 5, 180824.
16. Shi, X.; Ye, X, Zhong, H.; Wang, T.; Jin, F. Sustainable nitrogen-containing chemicals and materials from natural marine resources chitin and microalgae. *Mol. Catal.* **2021**, 505, 111517.
17. Mlowe, S.; Nejo, A.A.; Pullabhotla, V.R.; Mubofu, E.B.; Ngassapa, F.N.; O'Brien, P.; Revaprasadu, N. Lead chalcogenides stabilized by anacardic acid. *Mater. Sci. Semicond. Process.* **2013**, 16, 263–268.
18. Mlowe, S.; Pullabhotla, R.; Mubofu, E.B.; Ngassapa, F.; Revaprasadu, N. Low temperature synthesis of anacardic-acid-capped cadmium chalcogenide nanoparticle. *Int. Nano Lett.* **2014**, 4, 4–9.

19. Mubofu, E.B.; Mgaya, J.E.; Chemical valorization of cashew nut shell waste. *Top. Curr. Chem.* **2018**, 376, 1–15.
20. Pius, G.; Mgani, Q.A. Synthesis of semiochemicals and related fine chemicals from cashew nut shell liquid. *Tanz. J. Sci.* **2019**, 45, 297–306.
21. Ike, D.C.; Ibezim-Ezeani, M.U.; Akaranta, O. Cashew nut shell liquid and its derivatives in oil field applications: an update. *Green Chem. Lett. Rev.* **2021**, 14, 618–631.
22. Sahin, C.; Magomedova, L.; Ferreira, T.A.M.; Liu, J.; Tiefenbach, J.; Alves, P.S.; Queiroz, F.J.G.; de Oliveira, A.S.; Bhattacharyya, M.; Grouleff, J.; Nogueira, P.C.N.; Silveira, E.R.; Moreira, D.C.; Leite, J.R.S.; Brand, G.D.; Uehling, D.; Poda, G.; Krause, H.; Cummins, C.L.; Romeiro, L.A.S. Phenolic lipids derived from cashew nut shell liquid to treat metabolic diseases. *J. Med. Chem.* **2022**, 65, 1961−1978.
23. Mgaya, J.E.; Bartlett, S.A.; Mubofu, E.B.; Mgani, Q.A.; Slawin, A.M.Z.; Pogorzelec, P.J.; Cole-Hamilton, D.J. Synthesis of bifunctional monomers by the palladium-catalyzed carbonylation of cardanol and its derivative. *ChemCatChem* **2016**, 8, 751–757.
24. Stempfle, F.; Quinzler, D.; Heckler, I.; Mecking, S. Long-chain linear C 19 and C 23 monomers and polycondensates from unsaturated fatty acid esters. *Macromolecules* **2011**, 44, 4159–4166.
25. Gandhi. T.; Patel, M.; Dholakiya, B.K. Studies on effect of various solvents on extraction of cashew nut shell liquid (CNSL) and isolation of major phenolic constituents from extracted CNSL. *J. Nat. Prod. Plant Resour.* **2012**, 2, 135–142.