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Valorisation of Cashew Nut Shell Liquid Phenolics in the Synthesis of UV Absorbers

Kennedy J. Ngwira, [a] Jonas Kühlborn, [b] Quintino A. Mgani, [c] Charles B. de Koning, [a]* and Till Opatz [b]*

Abstract: With current concerns over the use of fossil resources for chemical synthesis of functional molecules and the effect of current UV absorbers in sunscreens have on the ecosystem, we describe a xylochemical synthesis of different classes of aromatic UV absorbers utilising cashew nut shell liquid as a non-edible bio-renewable carbon source. Hydroxybenzophenones, xanthones, triazines and flavones were synthesized starting from cardanol or anacardic acid. Several compounds exhibited favorable UVA and UVB absorption characteristics.

Introduction

Biomass is defined as a renewable resource derived from the agricultural or forestry sector. It has been estimated to provide about 25% of global energy requirements.[1] In recent times there has been significant interest in developing strategies for the use of non-edible biomass as a sustainable alternative to petroleum and petroleum based products.[2] This paradigm shift is necessitated by diminishing petroleum reserves, the rise of oil prices, the negative effects of petroleum on the environment and the advantages of using fast-growing non-edible biomass as a sustainable resource.[3] The advantages of using biomass rather than petroleum to manufacture chemicals include opportunities for reducing the environmental burden, net CO_2 neutral production and possibly even economic benefits.[4] While bio-derived chemical products *a priori* have no better biodegradability than their petrochemical antetypes, the redesign of the chemical compounds and the way they are produced can provide opportunities for a change to the better in this respect.

Although biomass and other renewable resources are primarily utilized for energy production, their use as starting materials in the pharmaceutical, chemical and cosmetic industries has been demonstrated.[5] This has led to a number of research activities within the academic sector.[6] For example, the groups of Opatz and Arduengo have developed synthetic procedures in which all carbon atoms are derived from wood-based chemicals, an approach for which the term "xylochemistry" was coined.[6a]

As a second example, a great deal of attention has been given to Cashew Nut Shell Liquid (CNSL) as a non-edible biomass-derived chemical feedstock. CNSL is a product of little commercial value but with high technological potential due to abundant, readily extractable phenolic constituents as well as biological activities of the constituents, including antimicrobial, anti-inflammatory, antitumor, antioxidant and insecticidal properties.[6b] However, the use of CNSL biomass for chemical synthesis requires its valorisation for the production of novel platform chemicals.[2] CNSL through its main phenolic constituents, namely anacardic acid, cardol and cardanol, fit this profile. These phenolic platform compounds can readily be isolated from CNSL through extraction. Their transformation into useful functional molecules and materials is an active area of research, including the use of a number recently developed catalytic approaches.[6c]

The protection of polymers, coatings, and even human skin against solar UV radiation is an important task. The damaging effects of UV rays are responsible for the discoloration of dyes and pigments, weathering, yellowing of plastics, loss of gloss and mechanical properties. Sunburnt skin, premature aging and even the development of potentially lethal melanomas must be prevented in livestock as well as in the human population.[7] To mitigate UV damage, both organic and inorganic compounds have been used as UV filters. Ideal organic UV filters display a high UV absorption in the region ranging from 315–400 nm (UVA) and 280–315 nm (UVB).[8] One important family of UV-absorber molecules are derived from phenols of which whose hydroxyl group plays an important role in the dissipation of the absorbed energy. These UV absorbers feature intramolecular O–H···O bridges. Prominent examples include salicylates, 2-hydroxybenzophenones, 2,2'-dihydroxybenzophenones, 3-hydroxyflavones and xanthones. Also important are those that form intramolecular O–H···N bridges, such as 2-(2-hydroxyphenyl)benzotriazoles and 2-(2-hydroxyphenyl)-1,3,5-triazines and 2-(5-aryl-1,3,4-oxadiazol-2-yl)- phenols.[9] These compounds also exhibit outstanding photo-stabilities and small quantum yields of photo-decomposition in the range of 10^{-7} to 10^{-6}.[10] They dissipate UV radiation through an efficient radiationless deactivation process by means of rapid tautomerization *via* the excited-state intramolecular proton transfer (ESIPT) mechanism.[11] Some of the mentioned types of absorbers have been used in human sunscreens. For example, 2-hydroxy-4-methoxybenzophenone, also known as oxobenzone is a common ingredient that has also been added to plastics to limit UV degradation.[12] Apart from their petrochemical origin, a major drawback of current UV protection agents is their negative effect on aquatic ecosystems[13] associated with a poor

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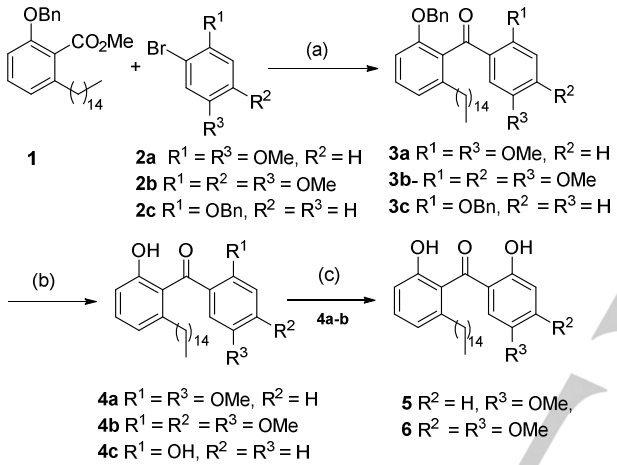
Supporting information for this article is given via a link at the end of the document.

biodegradability. As a result, there is growing attention from regulatory bodies and hence stricter regulations are being enforced.[14] To this end, there is a need to develop new, efficient, less toxic, and eco-friendly UV filters, ideally in a sustainable fashion. More importantly, a broad spectrum of UV filters capable of absorbing both UVA and UVB are required.

Here, we report the synthesis of a number of important classes of organic UV filters using "xylochemical" strategies, and by employing CNSL-derived phenolics as key starting materials. Finally, the synthesized compounds were evaluated as potential UV absorbers using UV spectroscopy.

Results and Discussion



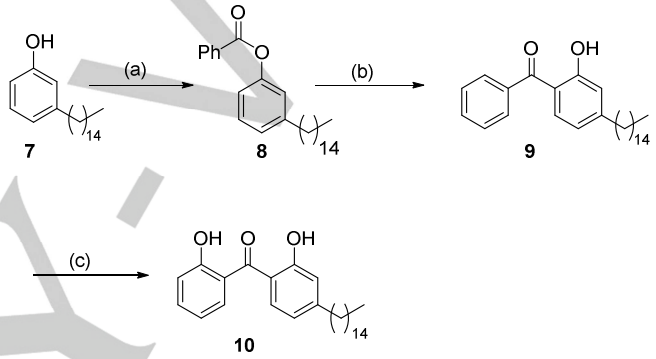
Scheme 1. *Reagents and conditions: (a) n*-BuLi, THF, -78 °C to rt, 2-24 h, **3a-c** 10-47%; (b) Pd/C, H_2, MeOH, EtOAc, rt, 24 h, **4a-c,** 84-99%; (c) For **4a**: $AlCl_3$, pyridine, PhMe, reflux, 4 d, 58%; For **4b**: BCl_3, CH_2Cl_2, -78 °C to rt, 4 d, 69%.

Initially, CNSL-derived cardanol and anacardic acid were used as starting materials, and a range of classes of potential UV absorbers were prepared in short synthetic sequences. Hydrogen-bonding of the phenolic hydroxyl group to a C=X (X= O or N)-moiety of the chromophore was a central design feature to ensure an efficient ESIPT. As a starting point, benzophenones and xanthones with neighbouring hydrogen-bonded hydroxyl substituents were synthesized.

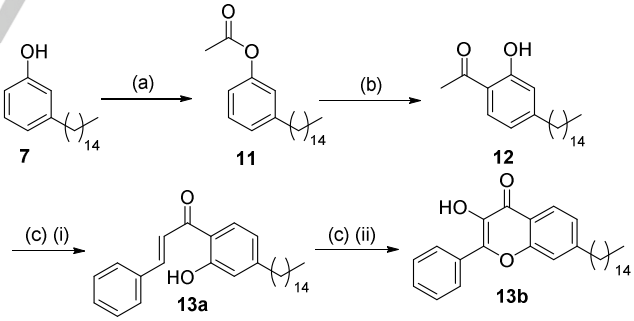
Synthesis of hydroxybenzophenones 4c, 5 and 6

Starting from CNSL-derived anacardic acid, the benzyl protected methyl ester **1** was prepared using known procedures (see experimental). Halogen/lithium exchange on substituted bromobenzenes **2a-c** accessible from xylochemicals[15a-c] followed by the addition of the ester **1** (as shown in Scheme 1) led to the formation of protected benzophenones **3a-c** in moderate to poor yields. Hydrogenolytic *O*-debenzylation of **3a-c** furnished benzophenones **4a-c** in excellent yields. Benzophenone **4c** contained the desired two hydrogen-bonded phenols. Exposure of **4a** to $AlCl_3$ afforded the second desired compound **5**, while the third hydrogen-bonded 2,2'-dihydroxybenzophenones **6** was obtained by treatment of **4b** with BCl_3.

One further benzophenone possessing two hydrogen bonded phenols was synthesized utilising the CNSL derived cardanol **7** as a starting material. Esterification of **7** with benzoyl chloride in the green solvent 2-Me-THF gave the ester **8** in excellent yields. This was followed by a microwave-promoted Fries rearrangement of **8** in the presence of $AlCl_3$ to furnish benzophenone **9**. A ruthenium-mediated C–H oxygenation of **9** gave 2,2'-dihydroxybenzophenone **10** in 61% yield (Scheme 2).[16]



Scheme 2. *Reagents and conditions*: (a) PhCOCl, DMAP, Et_3N, 2-Me-THF, 0° C to rt, 2 h, 95%; (b) $AlCl_3$, PhCl, Mw (160 °C, 150 W, 30 min), 78%; (c) $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol %), $K_2S_2O_8$, TFA/TFAA, 80 °C, 14 h, 72%.



Scheme 3. *Reagents and conditions:* (a) CH_3COCl, DMAP, Et_3N, 2-Me-THF, 0 °C to rt, 2 h, 96%; (b) $AlCl_3$, PhCl, Mw (160 °C, 150 W, 30 min), quant; (c) (i) NaOH, PhCHO, MeOH, 3 h, 67% (ii) 0.5N aq. NaOH, H_2O_2, rt, 4 h, 88%.

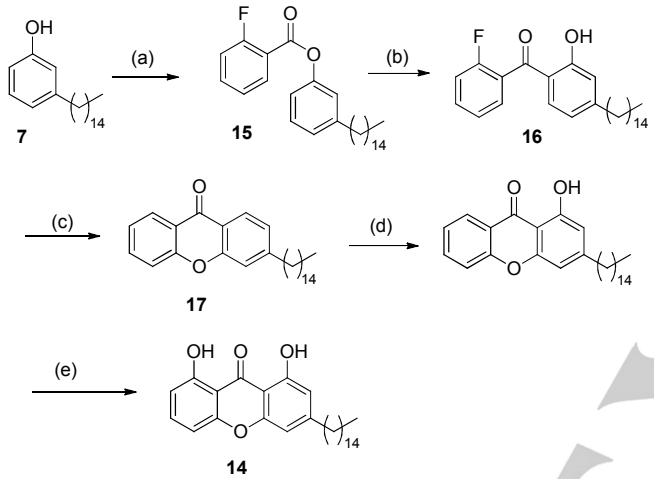
Synthesis of 3-hydroxyflavone 13b

Another class of potential UV absorbers possessing a hydroxyl group hydrogen bonded to a carbonyl are the 3-hydroxyflavones. Utilizing CNSL derived cardanol **7** the first step was accomplished in a similar manner to Scheme 2 by initial *O*-acetylation of cardanol **7** to furnish **11**. Again, a microwave assisted Fries rearrangement of **11** under $AlCl_3$ catalysis afforded the 1-(2-hydroxyphenyl)ethanone **12** in an excellent overall yield. Aldol condensation of **12** with benzaldehyde,

afforded the chalcone intermediate **13a**. *In-situ* oxidation of **13a** with hydrogen peroxide, the desired 3-hydroxyflavone **13b**, was obtained in a 67% yield over the two steps (Scheme 3)**.** Since acetic acid and benzaldehyde are xylochemicals, *i. e.* they can be derived from wood and related types of biomass, the entire molecular skeleton of **13a** and **13b** is derived from renewable carbon.

Synthesis of 1, 8-dihydroxyxanthone 14

The next class of compounds investigated as potential UV-absorbers were hydrogen-bonded xanthones. As an example, the 1,8-dihydroxyxanthone **14** was synthesized from cardanol.

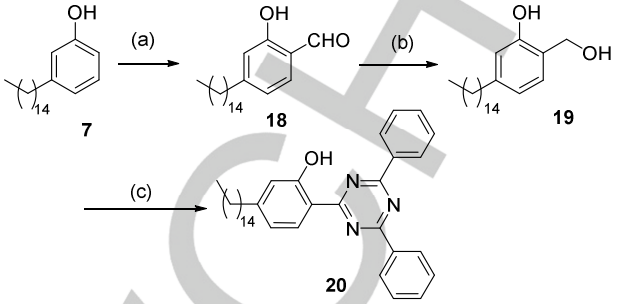


Scheme 4. *Reagents and conditions:* (a) 2-Flourobenzoyl chloride, DMAP, Et_3N, 2-Me-THF, 0 °C to rt, 2 h, quant.; (b) $AlCl_3$, PhCl, Mw (160 °C, 150 W), 30 min, 84%; (c) K_2CO_3, Me_2CO, reflux, 6 h, 86%; (d) $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol %), $K_2S_2O_8$, TFA/TFAA, 80 °C, 12 h, 71%; (e) $[Ru(p\text{-cymene})Cl_2]_2$ (2.5 mol %), $K_2S_2O_8$, TFA/TFAA, 80 °C, 12 h, 64%.

Using the methodology previously described, the Fries rearrangement of **15** provided benzophenone **16** (Scheme 4) in 84% over two steps. Refluxing of **16** with potassium carbonate in acetone yielded the xanthone **17**. A ruthenium catalysed C–H oxygenation of **16** furnished the desired 1,8-dihydroxyxathone **14** over two steps in 54% yield.[16] Since 2-fluorobenzoic acid can be derived from the natural product anthranilic acid,[15d] the entire molecular skeleton of **14** is formally derivable through xylochemistry.

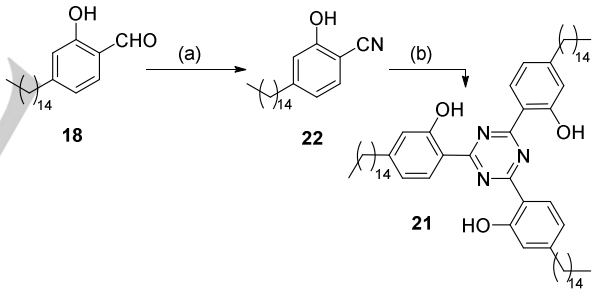
Synthesis of triazines 20 and 21

Nitrogen containing compounds such as 2-hydroxytriazines have also been reported to be suitable UV absorbers owing to intramolecular O–H···N hydrogen bonding. For our purposes, 2-(4,6-diphenyl-1,3,5-triazin-2-yl)phenol **20** was synthesized from CNSL derived cardanol in three steps. The $SnCl_4$-mediated formylation of cardanol **7** gave benzaldehyde **18** in excellent yield, which was followed by $LiAlH_4$-reduction of the aldehyde **18** to afford benzyl alcohol **19** (Scheme 5)**.** Exposure of the alcohol **19** to benzamidine under $Cu(OAc)_2$ catalysis afforded the 2-(4,6-diphenyl-1,3,5-triazin-2-yl)phenol **20** in 62% yield.



Scheme 5. *Reagents and conditions:* (a) $SnCl_4$, Bu_3N, $(CH_2O)_n$, PhMe, 100 °C, 18 h, 77%; (b) $LiAlH_4$, THF, rt, 6 h, 81%; Benzamidine hydrochloride, $Cu(OAc)_2$, Na_2CO_3, PhMe, 110 °C, 12 h, 62%.

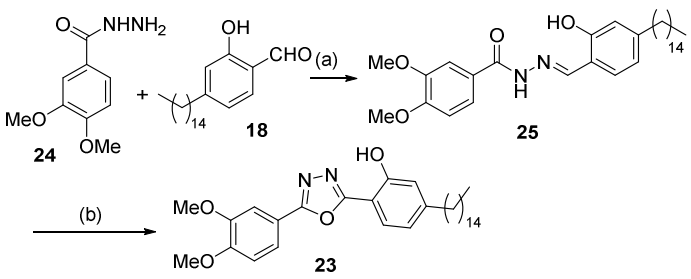
Since the second organic building block, benzamidine can be prepared from benzoic acid or benzaldehyde this strategy is compatible with xylochemical principles. In order to assess the effect of increasing the number of intramolecular hydrogen bonded N atoms on the UV absorbance, 2,2',2''-(1,3,5-triazine-2,4,6-triyl)triphenol **21** was also prepared. It was envisioned that this could be obtained from the formylated cardanol **18** (Scheme 6)**.** Reacting aldehyde **18** with hydroxylamine hydrochloride and $FeCl_3$ in DMF under reflux conditions yielded nitrile **22** which could be trimerized through microwave irradiation to furnish the fully symmetrical *s*-triazine **21** in 73% yield.



Scheme 6. *Reagents and conditions:* (a) $NH_2OH{\cdot}HCl$, $FeCl_3$, DMF, reflux, 18 h, 80%; (b) Mw: 220 °C, 200 W, 1.5 h, neat, 73%.

Synthesis of oxadiazole 23

A final compound which should also display N···H hydrogen bonding and hence be a possible UV filter was the oxadiazole **23**. Exposure of the aldehyde **18** to the hydrazide of veratric acid (**24**, synthesized from veratraldehyde by known methods[17]) afforded **25**. Oxidative oxadiazole ring formation yielded **23** in an overall yield of 39% over two steps (Scheme 7). Since veratraldehyde is derived from xylochemicals, the entire carbon skeleton of **23** can be constructed from biomass without petrochemical input.



Scheme 7. *Reagents and conditions:* ((a) Et_2O, MeOH, rt, 18 h, 82%; (b) $PhI(OAc)_2$, Me_2CO, rt, 5 h, 47%.

Analysis of UV profiles of the synthesized compounds

The synthesized compounds **4c**, **5**, **6**, **9**, **10**, **13a**, **13b**, **14**, **20**, **21**, and **23**, were analysed for their UV absorbances and their molar absorptivity coefficients (**ε**) were determined. Analysis of UV absorbance was done in order to establish whether the compounds exhibited **ε** values in the UV-B and UV-A regions of the UV spectra commensurate with those for commercial UV absorbers.

The 2,2'-dihydroxybenzophenone **4c** synthesized from anacardic acid showed reasonable UV absorbance in the UVA region with the experimental ε values of 10,538 L mol^{-1} cm^{-1} at 335 nm and a high absorbance of 36,366 L mol^{-1} cm^{-1} at 261 nm albeit outside both UVA and UVB region (Figure 1). The benzophenone **5** exhibited **ε** values of 8,785 L mol^{-1} cm^{-1} at 374 nm and 18,439 L mol^{-1} cm^{-1} at 265 nm. Benzophenone **6** showed excellent UVA absorbance with **ε** values 25,014 L mol^{-1} cm^{-1} at 358 nm and 34,096 L mol^{-1} cm^{-1} at 287 nm.

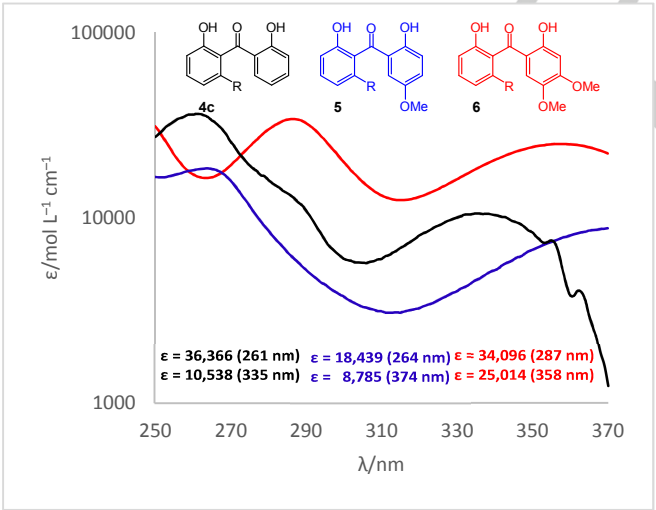


Figure 1: UV absorbance profiles of benzophenones **4c, 5** and **6** derived from anacardic acid.

In comparison, the benzophenones **9**[18a] and **10** derived from cardanol showed excellent absorption at the edge of the UVB region with experimental **ε** values of 47,909 L mol^{-1} cm^{-1} and 31,659 L mol^{-1} cm^{-1} at 279 nm and 282 nm for mono- and dihydroxy- benzophenones respectively as shown in **Figure 2**.

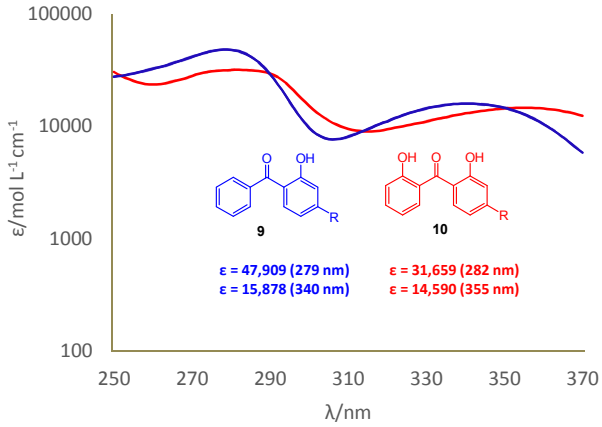


Figure 2: UV absorbance profiles of benzophenones **9** and **10** derived from cardanol.

3-Hydroxyflavone **13b** displayed an excellent absorption profile in the UVA region with experimental **ε** values of 39,870 L mol^{-1} cm^{-1} at 314 nm and 44,979 L mol^{-1} cm^{-1} at 345 nm as shown in Figure 3. The intermediate phenylpropenone **13a** showed an experimental **ε** value of 20,403 L mol^{-1} cm^{-1} at 314 nm and 10, 250 L mol^{-1} cm^{-1} at 347 nm. Dihydroxy xanthone **14** exhibited a good UV absorption profile with **ε** value of 23,765 L mol^{-1} cm^{-1} at 254 nm (Figure 3). However, UVC is less relevant at sea level due to the filtering function of the atmospheric ozone layer.

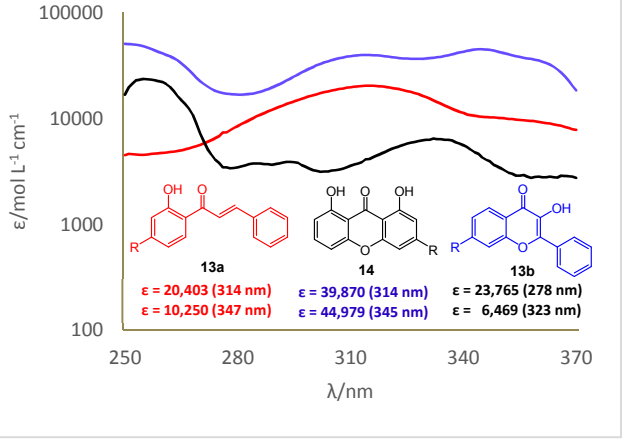


Figure 3: UV profiles of chalcone **13a**, flavone **13b** and xanthone **14**.

The *s*-triazine **21** showed the best UV absorbance in both the UVA and UVB region with experimental **ε** value of 21,452 L mol^{-1} cm^{-1} at 300 nm and 12,515 L mol^{-1} cm^{-1} at 364 nm. These results suggest **21** to be classified as a broad spectrum UV filtering agent as it showed excellent results in both relevant UV regions. The 2-(4,6-diphenyl-1,3,5-triazin-2-yl)phenol **20** on the

other hand exhibited excellent UV absorbance at the beginning of the UVB region with an ε value of 29,252 L mol^{-1} cm^{-1} at 278 nm (Figure 4).

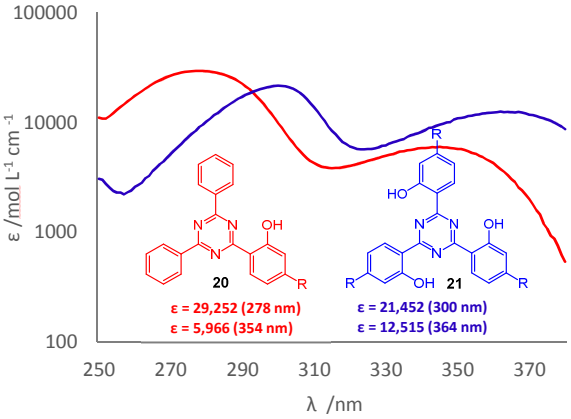


Figure 4: UV profiles of triazines **20** and **21**.

The oxadiazole **23** displayed moderate UV absorbance in the UVA region with experimental ε values of 6,367 L mol^{-1} cm^{-1} at 326 nm and 3,373 L mol^{-1} cm^{-1}at 293 nm as shown in Figure 5.

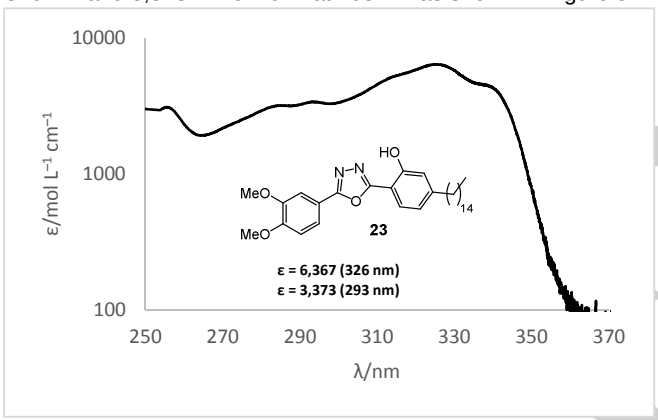


Figure 5: UV profile of oxadiazole **23**.

Commercially available sunscreen protectants oxybenzone (OB), 2-ethylhexyl 4-methoxycinnamate (OMC) and avobenzone) were reported to show experimental molar absorption coefficients of 15,150 L mol^{-1} cm^{-1} at 287 nm, 39,470 L mol^{-1} cm^{-1} at 356 nm and 31,670 L mol^{-1} cm^{-1} at 310 nm, respectively.[19a] Most of our hydrogen-bonded aromatic compounds display similar UV absorptions and the molecules may well possess emulsion-stabilizing properties due to their amphiphilic nature. However, newly proposed US-FDA legislation for sunscreens entails a provision that would require broad-spectrum UVA and UVB protection in sunscreens.[19b] Therefore, the results of this research suggest that benzophenones **6**, **9** and **10**, as well as, the *s*-triazine **21** might be suitable candidates for further development.

Conclusions

Representatives of various classes of UV absorbers have been synthesized using CNSL as a non-edible, bio-renewable chemical feedstock. In addition, wherever possible, the principles of xylochemistry were utilized. As the properties of the synthesized materials were to be investigated first, the employed reaction conditions need further improvement so as to minimize their environmental burden. For example, dichloromethane was employed as an inert solvent for the bromination using NBS as well as for the dealkylation reactions since a commercial solution of BCl_3 in CH_2Cl_2 was used in the latter. However, CH_2Cl_2 is considered to be a less desirable solvent.[20] Moreover, reactions involving organolithium reagents should be replaced by Grignard procedures when upscaling is to be considered. Another attractive point for further investigations will be the role of biocatalysis in facilitating several of the presented transformations (e.g. the esterification reactions).[21]

The UV profiles of the synthesized aromatic hydrogen-bonded compounds (especially *s*-triazine **21**) and their lipophilic or amphiphilic character are promising for potential use as sunscreens, in paints, coatings or polymers and other related applications.[22] However, in particular if these compounds are to be used as sunscreen investigations into their toxicity to human health still need to be conducted.

Experimental Section

For general experimental procedures please consult the supplementary information.

Methyl 2-benzyloxy-6-pentadecylbenzoate 1

A suspension of calcium anacardate (20.0 g, ca. 52.3 mmol) in aqueous HCl (10%, 100 mL) was stirred for 3 h at rt. Afterwards, EtOAc (100 mL) was added and the mixture was stirred for 1 h and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 50 mL) and the combined organic extracts were washed with brine (30 mL). After drying over $MgSO_4$ and evaporation of the solvent the anacardic acids were obtained as a brown oil (13.7 g, ca. 39.9 mmol, 76%). **IR** ($\tilde{\nu}$/cm^{-1}): 2923, 2853, 1644, 1607, 1447, 1245, 1207, 1166, 910, 822, 783; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.01 (s, 1H), 9.62 (s, 2H), 7.35 (dd, *J* = 8.3, 7.5 Hz, 1H), 6.86 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.76 (dd, *J* = 7.5, 1.2 Hz, 1H), 5.81 (ddt, *J* = 17.3, 10.1, 6.2 Hz, 0.4H), 5.51–5.24 (m, 4H), 5.04 (dq, *J* = 17.1, 1.8 Hz, 0.4H), 4.97 (dq, *J* = 10.1, 1.6 Hz, 0.4H), 3.05–2.94 (m, 2H), 2.87–2.68 (m, 2H), 2.04–1.94 (m, 3H), 1.69–1.53 (m, 2H), 1.44–1.19 (m, 21H), 0.99–0.83 (m, 3H); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 176.0, 163.5, 147.7, 136.8, 135.3, 130.4, 130.1, 129.9, 129.8, 129.3, 128.1, 128.0, 127.6, 126.8, 122.7, 115.8, 114.7, 110.5, 36.4, 32.0, 31.8, 31.5, 29.7, 29.4, 29.23, 29.0, 27.2, 25.6, 22.8, 22.6, 14.1; **MS** (ESI+): *m/z* (%) = 343.5 (100) $[M_{3DB}+H]^+$, 345.5 (97) $[M_{2DB}+H]^+$, 347.4 (100) $[M_{1DB}+H]^+$, 365.5 (26) $[M_{3DB}+Na]^+$, 367.4 (35) $[M_{2DB}+Na]^+$, 369.4 (39) $[M_{1DB}+Na]^+$. The index "DB" denotes the number of double bonds present. The analytical data are in accordance with the literature.[23]

Palladium on activated charcoal (10 wt%, 600 mg, 0.56 mmol) was added to a solution of anacardic acids (10.2 g, 29.6 mmol) in MeOH (125 mL) under an atmosphere of nitrogen. The flask was purged with

hydrogen and the suspension was stirred for 60 h at rt under an atmosphere of hydrogen. Afterwards, the flask was purged with nitrogen and the reaction mixture was filtered through Celite®. After rinsing with MeOH (300 mL), the solvent was evaporated and 2-hydroxy-6-pentadecylbenzoic acid was obtained as a brownish solid (10.0 g, 28.8 mmol, 97%). **Mp**. 87–88 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2916, 2850, 1651, 1604, 1445, 1248, 1218, 815, 724, 707; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.36 (t, *J* = 7.9 Hz, 1H, H4), 6.87 (d, *J* = 8.3 Hz, 1H, H3), 6.77 (dd, *J* = 7.5, 1.2 Hz, 1H, H5), 2.98 (dd, *J* =9.1, 6.4 Hz, 2H, H1'), 1.65–1.55 (m, 2H, H2'), 1.39–1.25 (m, 24H, H3'–H14'), 0.88 (t, *J* = 6.3 Hz, 3H, H15'); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 176.0 (CO_2H), 163.6 (C2), 147.8 (C6), 135.4 (C4), 122.7 (C5), 115.8 (C3), 110.4 (C1), 36.5 (C1'), 32.0 (C13'), 31.9 (C2'), 29.8, 29.7 (6C), 29.6, 29.5, 29.4, 22.7 (C14'), 14.1 (C15'); **MS** (ESI–): *m/z* (%) = 347.3 (100) $[M–H]^-$, 717.6 (12) $[2M+Na–2H]^-$; **HRMS** (ESI–): Found $(M–H)^-$ 347.2592, $C_{22}H_{35}O_3$ $(M–H)^-$ requires 347.2592. The analytical data are in accordance with the literature.[24]

Conc. sulfuric acid (2.50 mL, 139 µmol) was carefully added to a stirred solution of 2-hydroxy-6-pentadecylbenzoic acid (2.00 g, 5.74 mmol) in MeOH (50 mL). The resulting mixture was stirred at reflux overnight and then cooled to rt. The solvent was evaporated and an aqueous saturated $NaHCO_3$ solution (30 mL) was added to the residue. After extraction with EtOAc (3 x 25 mL), the combined organic extracts were subsequently washed with water and brine (20 mL each) and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by column chromatography on silica gel (20% EtOAc/hexane) affording methyl 2-hydroxy-6-pentadecylbenzoate as a pale brown solid (1.67 g, 4.71 mmol, 82%). **Mp**. 41.5–43 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2914, 2850, 1662, 1578, 1441, 1315, 1201, 1120, 946, 817, 742; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.10 (s, 1H, O*H*), 7.28 (dd, $^3J_{4,3}$ = 8.4 Hz, $^3J_{4,5}$ = 7.5 Hz, 1H, H4), 6.83 (dd, *J* = 7.5, 1.3 Hz, 1H, H3), 6.71 (dd, *J* = 7.5, 1.3 Hz, 1H, H5), 3.95 (s, 3H, CO_2CH_3), 2.88 (dd, *J* =8.8, 6.8 Hz, 2H, H1'), 1.56–1.47 (m, 2H, H2'), 1.36–1.24 (m, 24H, H3'–H14'), 0.88 (t, *J* = 7.0 Hz, 3H, H15'); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 171.9 (CO_2CH_3), 162.6 (C2), 146.2 (C6), 134.1 (C4), 122.4 (C5), 115.6 (C3), 111.8 (C1), 52.0 (CO_2CH_3), 36.6 (C1'), 32.1 (C13'), 31.9 (C2'), 29.9, 29.7–29.6 (7C), 29.5, 29.3, 22.7 (C14'), 14.1 (C15'); **MS** (ESI–): *m/z* (%) = 361.4 (100) $[M–H]^-$; **HRMS** (ESI+): Found $(M+H)^+$ 363.2889, $C_{23}H_{39}O_3$ $(M+H)^+$ requires 363.2894. The analytical data are in accordance with the literature.[24]

A suspension of methyl 2-hydroxy-6-pentadecylbenzoate (1.20 g, 3.31 mmol) and K_2CO_3 (915 mg, 6.62 mmol) in acetone (20 mL) was stirred under reflux for 10 min. After cooling to rt, benzyl bromide (591 µL, 4.97 mmol) was carefully added and the mixture was stirred for 8 h under reflux under an atmosphere of nitrogen. The mixture was cooled to rt, filtered through Celite® and rinsed with acetone (100 mL). After evaporating the solvent, the crude product was purified by column chromatography on silica gel (5% EtOAc/hexane) to obtain methyl 2-benzyloxy-6-pentadecylbenzoate **1** as a colourless solid (1.25 g, 2.76 mmol, 83%). **Mp**. 29–31 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2922, 2852, 1732, 1583, 1453, 1264, 1109, 1066, 734; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.42–7.29 (m, 5H, Bn-H2–Bn-H6), 7.23 (dd, *J* = 8.4, *J*7.7 Hz, 1H, H4), 6.83 (d, *J* = 7.5 Hz, 1H, H5), 6.78 (dd, *J* = 7.7, 1.0 Hz, 1H, H3), 5.10 (s, 2H, Bn-CH_2), 3.89 (s, 3H, CO_2CH_3), 2.59–2.53 (m, 2H, H1'), 1.63–1.54 (m, 2H, H2'), 1.33–1.23 (m, 24H, H3'–H14'), 0.88 (t, *J* = 6.5 Hz, 3H, H15'); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 168.8 (CO_2CH_3), 155.4 (C2), 141.5 (C6), 136.9 (Bn-C1), 130.1 (C4), 128.4 (2C, Bn-C3, Bn-C5), 127.7 (Bn-C4), 126.8 (2C, Bn-C2, Bn-C6), 124.1 (C1), 121.8 (C5), 110.0 (C3), 70.4 (Bn-CH_2), 52.0 (CO_2CH_3), 33.5 (C1'), 31.9 (C13'), 31.1 (C2'), 29.7 (6C), 29.5 (2C), 29.4, 29.3, 22.7 (C14'), 14.1 (C15'); **MS** (ESI+): *m/z* (%) = 21.5 (98) $[M–OMe+H]^+$, 453.5 (100) $[M+H]^+$, 475.4 (54) $[M+Na]^+$; **HRMS** (ESI+): Found $(M+H)^+$ 453.3358, $C_{30}H_{45}O_3$ $(M+H)^+$ requires 453.3363.

General procedure for the synthesis of benzophenones 3a–c

The respective bromobenzene **2a-c** (1.05 mmol) was added to a flame dried 50 mL Schlenk flask and the flask was subsequently evacuated and filled with nitrogen three times. Dry THF (5 mL) was added and the solution was cooled to –83 °C while stirring. A solution of *n*-butyllithium in hexane (1.39 m, 752 µL, 1.05 mmol) was added during 15 min. The resulting mixture was left stirring at –83 °C for 1 h and a solution of methyl 2-benzyloxy-6-pentadecylbenzoate **1** (430 mg, 0.95 mmol) in dry THF (5 mL) was added during 15 min. After stirring for 1 h at –83°C the solution was slowly brought to rt and stirred further. The mixture was quenched with a saturated NH_4Cl solution (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography on silica gel (EtOAc/hexane).

[2-(Benzyloxy)-6-pentadecylphenyl](2,5-dimethoxyphenyl)methanone 3a

The title compound was synthesized following the general procedure from 2,5-dimethoxybromobenzene **2a** (157 µL, 1.05 mmol) and methyl 2-benzyloxy-6-pentadecylbenzoate **1** (430 mg, 0.95 mmol). The resulting solution was stirred over night at rt and the crude product was purified by column chromatography on silica gel (5–10% EtOAc/hexane) to yield [2-(benzyloxy)-6-pentadecylphenyl](2,5-dimethoxyphenyl)methanone **3a** as colourless solid (245 mg, 438 µmol, 46%). **Mp**. 53.5–54.5 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2923, 2853, 1656, 1579, 1495, 1464, 1281, 1221, 1048, 745; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.26–7.18 (m, 5H, H6, H4', Bn-H3, Bn-H4, Bn-H5), 7.04–6.97 (m, 3H, H4, Bn-H2, Bn-H6), 6.86 (d, *J* = 7.9 Hz, 1H, H5'), 6.84 (d, *J* = 8.9 Hz, 1H, H3), 6.75 (dd, *J* = 8.3, 0.9 Hz, 1H, H3'), 4.91 (s, 2H, Bn-CH_2), 3.72 (s, 3H, C5-OCH_3), 3.52 (s, 3H, C2-OCH_3), 2.57–2.51 (m, 2H, H1''), 1.57–1.50 (m, 2H, H2''), 1.33–1.20 (m, 24H, H3''-H14''), 0.88 (t, *J* = 7.0 Hz, 3H, H15''); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 196.5 (C=O), 155.6 (C2'), 153.8 (C2), 153.3 (C5), 141.6 (C6'), 136.8 (Bn-C1), 132.0 (C1'), 129.6 (C1), 129.4 (C4'), 128.1 (2C, Bn-C3, Bn-C5), 127.4 (Bn-C4), 126.8 (2C, Bn-C2, Bn-C6), 122.1 (C5'), 120.0 (C4), 115.2 (C6), 114.0 (C3), 109.3 (C3'), 56.4 (C2-OCH_3), 55.7 (C5-OCH_3), 33.1 (C1''), 31.9 (C13''), 31.2 (C2''), 29.7 (6C), 29.6 (2C), 29.4 (2C), 22.7 (C14''), 14.1 (C15''); **MS** (ESI+): *m/z* (%) = 559.5 (100) $[M+H]^+$, 581.5 (12) $[M+Na]^+$; **HRMS** (ESI+): Found $(M+H)^+$ 559.3776, $C_{37}H_{51}O_4$ $(M+H)^+$ requires 559.3782.

[2-(Benzyloxy)-6-pentadecylphenyl](2,4,5-trimethoxyphenyl)methanone 3b

NBS (2.12 g, 11.9 mmol) was added to a solution of 1,2,4-trimethoxybenzene (2.00 g, 11.9 mmol) in dry CH_2Cl_2 (20 mL) under an atmosphere of nitrogen. The resulting solution was heated to reflux and stirred overnight. After cooling to rt, the solution was washed with an aqueous saturated $Na_2S_2O_3$ solution (15 mL) before the aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL). The combined organic extracts were dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography on silica gel (10% EtOAc/hexane) to obtain 2,4,5-trimethoxybromobenzene **2b** as a colourless solid (2.61 g, 10.6 mmol, 89%). **Mp**. 56–58 °C; **IR** ($\tilde{\nu}$/cm^{-1}): = 2999, 2942, 2843, 1505, 1451, 1378, 1204, 1166, 1022, 838, 799; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.02 (s, 1H, H6), 6.55 (s, 1H, H3), 3.87 (s, 3H, C4-OCH_3), 3.85 (s, 3H, C2-OCH_3), 3.82 (s, 3H, C5-OCH_3); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 150.3 (C2), 149.2 (C4), 143.8 (C5), 116.5 (C6), 101.1 (C1), 99.0 (C3), 57.2 (C2-OCH_3), 56.7 (C5-OCH_3), 56.3 (C4-OCH_3); **MS** (ESI+): *m/z* (%) = 246.1 (100) $[M(Br^{79})+H]^+$, 248.1 (98) $[M(Br^{81})+H]^+$. The analytical data are in accordance with the literature.[25]

The title compound was synthesized following the general procedure from 2,4,5-trimethoxybromobenzene **2b** (258 mg, 1.05 mmol) and methyl 2-benzyloxy-6-pentadecylbenzoate **1** (430 mg, 0.95 mmol). The resulting

solution was stirred for 1 h at rt and the crude product was purified by column chromatography on silica gel (10–50% EtOAc/hexane) to yield [2-(benzyloxy)-6-pentadecylphenyl](2,4,5-trimethoxyphenyl)methanone **3b** as yellowish solid (264 mg, 448 µmol, 47%). **Mp**. 53.5–55 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2923, 2852, 1599, 1579, 1511, 1464, 1272, 1213, 1029, 739; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.38 (s, 1H, H6), 7.22–7.16 (m, 4H, H4', Bn-H3, Bn-H4, Bn-H5), 7.07–7.02 (m, 2H, Bn-H2, Bn-H6), 6.86 (dd, *J* = 7.7, 0.9 Hz, 1H, H5'), 6.75 (dd, *J* = 8.3, 0.9 Hz, 1H, H3'), 6.41 (s, 1H, H3), 4.96 (s, 2H, Bn-CH_2), 3.92 (s, 3H, C2-OCH_3/C4-OCH_3), 3.82 (s, 3H, C5-OCH_3), 3.49 (s, 3H, C2-OCH_3/C4-OCH_3), 2.55–2.48 (m, 2H, H1''), 1.54–1.48 (m, 2H, H2''), 1.27–1.19 (m, 24H, H3''–H14''), 0.88 (t, *J* = 7.0 Hz, 3H, H15''); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 194.4 (C=O), 156.0 (C2/C4), 155.2 (C2'), 154.1 (C2/C4), 143.1 (C5), 140.9 (C6'), 137.1 (Bn-C1), 133.1 (C1'), 128.8 (C4'), 128.1 (2C, Bn-C3, Bn-C5), 127.4 (Bn-C4), 126.7 (2C, Bn-C2, Bn-C6), 122.0 (C5'), 120.7 (C1), 113.8 (C6), 109.3 (C3'), 97.3 (C3), 70.0 (Bn-CH_2), 56.5 (C2-OCH_3/C4-OCH_3), 56.3 (C5-OCH_3), 56.0 (C2-OCH_3/C4-OCH_3), 33.0 (C1''), 31.9 (C13''), 31.0 (C2''), 29.7 (6C), 29.6, 29.5, 29.4, 29.3, 22.7 (C14''), 14.1 (C15''); **MS** (ESI+): *m/z* (%) = 555.5 (100) [M–OMe+H]$^+$, 587.7 (29) [M+H]$^+$; **HRMS** (ESI+): Found (M+H)$^+$ 589.3882, $C_{38}H_{53}O_5$ (M+H)$^+$ requires 589.3888.

[2-(Benzyloxy)-6-pentadecylphenyl](2-benzyloxyphenyl)methanone 3c

A suspension of 2-bromophenol (611 µL, 5.78 mmol) and K_2CO_3 (1.20 g, 8.70 mmol) in acetone (10 mL) was stirred at reflux under an atmosphere of nitrogen for 10 min. Benzyl bromide (1.03 mL, 8.70 mmol) was then added dropwise and the mixture was stirred for 17 h at reflux. After cooling to rt, the solvent was evaporated and the residue was dissolved in water and EtOAc (30 mL each). After separation of the layers, the organic layer was washed with water and brine (15 mL each), dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography on silica gel (0–30% EtOAc/cyclohexane) to obtain 2-benzyloxybromobenzene **2c** as a colourless oil (1.38 g, 5.26 mmol, 91%). **IR** ($\tilde{\nu}$/cm^{-1}): 3064, 2870, 1586, 1476, 1441, 1379, 1276, 1051, 1029, 742; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.9, 1.6 Hz, 1H, H6), 7.49–7.46 (m, 2H, Bn-H2, Bn-H6), 7.41–7.35 (m, 2H, Bn-H3, Bn-H5), 7.34–7.31 (m, 1H, Bn-H4), 7.22 (ddd, *J* = 8.2, 7.4, 1.6 Hz, 1H, H4), 6.92 (dd, *J* = 8.3, 1.4 Hz, 1H, H3), 6.85 (td, *J* = 7.9, 1.4 Hz, 1H, H5), 5.15 (s, 2H, Bn-CH_2); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 155.0 (C2), 136.5 (Bn-C1), 133.4 (C6), 128.5 (2C, Bn-C3, Bn-C5), 128.4 (C4), 127.9 (Bn-C4), 127.0 (2C, Bn-C2, Bn-C6), 122.1 (C5), 113.9 (C3), 112.5 (C1), 70.8 (Bn-CH_2); **MS** (ESI+): *m/z* (%) = 277.0 (100) [M(Br^{79})+NH$_4$]$^+$, 279.0 (78) [M(Br^{81})+NH$_4$]$^+$. The analytical data are in accordance with the literature.[26]

Utilizing the synthesized 2-benzyloxybromobenzene **2c**, the title compound was synthesized following the general procedure from 2-benzyloxybromobenzene **2c** (275 mg, 1.05 mmol) and methyl 2-benzyloxy-6-pentadecylbenzoate **1** (430 mg, 0.95 mmol). The resulting solution was stirred for 48 h at rt and the crude product was purified by column chromatography on silica gel (2.5–5% EtOAc/hexane) to yield [2-(benzyloxy)-6-pentadecylphenyl](2-benzyloxyphenyl)methanone **3c** as colourless oil (57.5 mg, 94.5 µmol, 10%). **IR** (v/cm^{-1}): 2923, 2853, 1653, 1595, 1580, 1450, 1379, 1297, 1052, 925, 750; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.7 Hz, 1H, H6), 7.42 (t, *J* = 7.9 Hz, 1H, H4), 7.25–7.21 (m, 3H, Bn-H3, Bn-H5, Bn'-4), 7.17–7.13 (m, 4H, H4', Bn-4, Bn'-3, Bn'-5), 7.03–7.01 (m, 3H, H5, Bn-H2, Bn-H6), 6.98–6.93 (m, 3H, H3, Bn'-H2, Bn'-H6), 6.77 (d, *J* = 7.9 Hz, 1H, H5'), 6.67 (d, *J* = 7.9 Hz, 1H, H3'), 4.86 (s, 2H, Bn-CH_2), 4.84 (s, 2H, Bn'-CH_2), 2.49 (dd, *J* = 9.2, 7.3 Hz, 2H, H1''), 1.46 (p, *J* = 7.3 Hz, 2H, H2''), 1.28–1.16 (m, 24H, H3''–H14''), 0.88 (t, *J* = 6.9 Hz, 3H, H15''); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 196.7 (C=O), 158.2 (C2), 155.6 (C2'), 141.8 (C6), 136.9 (Bn'-C1), 136.2 (Bn-C1), 133.5 (C4), 132.1 (C1'), 131.6 (C6), 129.6 (C1), 129.4 (C4'), 128.2 (2C, Bn-C3, Bn-C5), 128.1 (2C, Bn'-C3, Bn'-C5), 127.5 (Bn-C4), 127.4 (Bn'-C4), 127.1 (2C, Bn-C2, Bn-C6), 126.8 (2C, Bn'-C2, Bn'-C6), 122.2 (C5'), 120.6 (C5), 113.0 (C3), 109.4 (C3'), 70.3 (Bn-CH_2), 69.9 (Bn'-CH_2), 33.1 (C1''), 31.9 (C13''), 31.2 (C2''), 29.7 (6C), 29.6, 29.5, 29.4, 29.3, 22.7 (C14''), 14.1 (C15''); **MS** (ESI+): *m/z* (%) = 605.5 (100) [M+H]$^+$, 627.5 (53) [M+Na]$^+$; **HRMS** (ESI+): Found (M+H)$^+$ 605.3976, $C_{42}H_{53}O_3$ (M+H)$^+$ requires 605.3989.

General procedure for the synthesis of Hydroxybenzophenones 4a–c

Palladium on activated charcoal (10 wt%) was added to a solution of the respective benzophenone **3a-c** dissolved in a mixture of MeOH/EtOAc (10/1) under an atmosphere of nitrogen. The flask was purged with hydrogen and the suspension was stirred over night at rt. After filtration through Celite® the residue was rinsed with MeOH and EtOAc (50 mL each) and the solvents were evaporated to afford the desired products **4a-c**.

(2-Pentadecyl-6-hydroxyphenyl)(2,5-dimethoxyphenyl)methanone 4a

The title compound was synthesized following the general procedure starting from [2-(benzyloxy)-6-pentadecylphenyl](2,5-dimethoxyphenyl)methanone **3a** (217 mg, 384 µmol) using Pd/C (10 wt%, 22.0 mg, 20.1 µmol) and MeOH/EtOAc (10/1, 15 mL). The product **4a** was obtained as a brownish solid (181 mg, 380 µmol, 99%). **Mp**. 45–47 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 3362, 2922, 2852, 1606, 1582, 1494, 1463, 1278, 1223, 1046, 813, 722; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 9.32 (s, 1H, O*H*), 7.30 (dd, *J* = 7.5, 8.3 Hz, 1H, H4'), 7.01 (dd, *J* = 9.0, 3.1 Hz, 1H, H4), 6.91–6.85 (m, 3H, H3, H6, H5'), 6.69 (dd, *J* = 7.5, 1.2 Hz, 1H, H3'), 3.74 (s, 3H, C5-OCH_3), 3.70 (s, 3H, C2-OCH_3), 2.26 (dd, *J* = 9.8, 6.3 Hz, 2H, H1''), 1.34–1.14 (m, 26H, H2''–H14''), 0.88 (t, *J* = 6.5 Hz, 3H, H15''); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 200.9 (C=O), 160.3 (C6'), 153.4 (C5), 151.5 (C2), 145.0 (C2'), 134.0 (C4'), 131.2 (C1), 122.6 (C1'), 121.6 (C3'), 118.2 (C4), 115.4 (C5'), 114.4 (C6), 113.2 (C3), 56.4 (C2-OCH_3), 55.8 (C5-OCH_3), 34.7 (C1''), 32.4 (C2''), 31.9 (C13''), 29.7 (6C), 29.6, 29.5, 29.4, 29.3, 22.7 (C14''), 14.1 (C15''); **MS** (ESI+): *m/z* (%) = 469.4 (100) [M+H]$^+$, 491.4 (16) [M+Na]$^+$; **HRMS** (ESI+): Found (M+H)$^+$ 469.3303, $C_{30}H_{45}O_4$ (M+H)$^+$ requires 469.3312.

(2-Pentadecyl-6-hydroxyphenyl)(2,4,5-trimethoxyphenyl)methanone 4b

The title compound was synthesized following the general procedure starting from [2-(benzyloxy)-6-pentadecylphenyl](2,4,5-trimethoxyphenyl)methanone **3b** (243 mg, 413 µmol) using Pd/C (10 wt%, 25.0 mg, 23.5 µmol) and MeOH/EtOAc (10/1, 20 mL). The product **4b** was obtained as a brownish solid (190 mg, 381 µmol, 92%). **Mp**. 78–81 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 3314, 2922, 2852, 1581, 1513, 1462, 1354, 1270, 1212, 1025, 807; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 9.18 (s, 1H, O*H*), 7.25 (t, *J* = 7.9 Hz, 1H, H4'), 7.02 (s, 1H, H6), 6.84 (dd, *J* = 8.2, 1.1 Hz, 1H, H5'), 6.71 (dd, *J* = 7.6 1.1 Hz, 1H, H3'), 6.49 (s, 1H, H3), 3.96 (s, 3H, C2-OCH_3/C4-OCH_3), 3.82 (s, 3H, C5-OCH_3), 3.68 (s, 3H, C2-OCH_3/C4-OCH_3), 2.36–2.30 (m, 2H, H1''), 1.36–1.12 (m, 26H, H2''–H14''), 0.88 (t, *J* = 7.0 Hz, 3H, H15'') ppm; **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 198.7 (C=O), 158.1 (C6'), 154.1 (C2/C4), 153.7 (C2/C4), 143.9 (C2'), 143.2 (C5), 132.8 (C4'), 124.6 (C1'), 121.4 (C3'), 121.4 (C1), 114.9 (C5'), 113.1 (C6), 97.2 (C3), 56.6 (C2-OCH_3/C4-OCH_3), 56.5 (C5-OCH_3), 56.1 (C2-OCH_3/C4-OCH_3), 34.4 (C1''), 32.2 (C2''), 31.9 (C13''), 29.7 (6C), 29.5 (2C), 29.3 (2C), 22.7 (C14''), 14.1 (C15''); **MS** (ESI+): *m/z* (%) = 499.5 (100) [M+H]$^+$, 521.4 (6) [M+Na]$^+$; **HRMS** (ESI+): Found (M+H)$^+$ 499.3409, $C_{31}H_{47}O_5$ (M+H)$^+$ requires 499.3418.

[2-(Hydroxy)-6-pentadecylphenyl](2-hydroxyphenyl)methanone 4c

The title compound was synthesized following the general procedure starting from [2-(benzyloxy)-6-pentadecylphenyl](2-benzyloxyphenyl)methanone **3c** (44.6 mg, 74.0 µmol) using Pd/C (10 wt%, 5.00 mg, 4.70 µmol) and MeOH/EtOAc (10/1, 4 mL). The product **4c** was obtained as a yellowish oil (26.3 mg, 61.9 µmol, 84%). **IR** ($\tilde{\nu}$/cm^{-1}): 3392, 2923, 2853, 1625, 1583, 1463, 1307, 1283, 1110, 939, 756; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 12.07 (s, 1H, C2-O*H*), 7.48 (ddd, *J* = 8.5, 7.2, 1.7 Hz, 1H, H4), 7.31 (dd, *J* = 8.0, 1.7 Hz, 1H, H6), 7.25 (t, *J* = 7.9 Hz, 1H, H4'), 7.03 (dd, *J* = 8.5, 1.1 Hz, 1H, H3), 6.87 (d, *J* = 7.7 Hz, 1H, H3), 6.83–6.79 (m, 1H, H5), 6.73 (dd, *J* = 8.2, 1.0 Hz, 1H, H3'), 5.69 (s, 1H, C2'-O*H*), 2.42 (dd, *J* = 9.0, 6.7 Hz, 2H, H1''), 1.45 (p, *J* = 6.8 Hz, 2H, H2''), 1.33–1.14 (m, 24H, H3''–H14''), 0.86 (t, *J* = 6.7 Hz, 3H, H15''); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 203.8 (C=O), 162.7 (C2), 152.8 (C2'), 142.0 (C6'), 137.0 (C4), 133.2 (C6), 131.0 (C4'), 125.1 (C1'), 121.8 (C5'), 120.7 (C1), 119.2 (C5), 118.2 (C3), 113.8 (C3'), 33.5 (C1''), 31.9 (C13''), 31.1 (C2''), 29.7 (3C), 29.6 (3C), 29.4, 29.3, 29.2 (2C), 22.7 (C14''), 14.1 (C15''); **MS** (ESI–): *m/z* (%) = 423.4 (100) [M–H]$^-$; **HRMS** (ESI+): Found (M+H)$^+$ 425.3047, $C_{28}H_{41}O_3$ (M+H)$^+$ requires 425.3050.

(2-Hydroxy-5-methoxyphenyl)(2-hydroxy-6-pentadecylphenyl)methanone 5

$AlCl_3$ (9.05 mg, 67.9 µmol) and pyridine (16.4 µL, 203.6 µmol) were added to a solution of (2-pentadecyl-6-hydroxyphenyl)(2,5-dimethoxyphenyl)methanone (15.9 mg, 33.9 µmol) in dry toluene (1 mL) at room temperature under an atmosphere of nitrogen. The resulting solution was stirred for 5 d under reflux and each day $AlCl_3$ (9.05 mg, 67.9 µmol) and pyridine (16.4 µL, 203.6 µmol) were added. The mixture was cooled to room temperature afterwards. Aqueous HCl (2 m, 5 mL) was added and the mixture was extracted with diethyl ether (3 x 5 mL). The combined organic extracts were dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography on silica gel (17% EtOAc/cyclohexane) to obtain the product as a brown oil **5** (8.60 mg, 18.9 µmol, 56%). **IR** ($\tilde{\nu}$/cm^{-1}): 3377, 2922, 2853, 1612, 1484, 1463, 1284, 1040, 791; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.68 (s, 1H, C2'-O*H*), 7.27 (t_{app}, J_{app} = 7.9 Hz, 1H, H4), 7.13 (dd, *J* = 9.1, 3.0 Hz, 1H, H4'), 7.00 (d, *J* = 9.1 Hz, 1H, H3'), 6.88 (d, *J* = 7.5 Hz, 1H, H5), 6.76 (m, 2H, H3, H6'), 5.59 (s, br, 1H, C2-O*H*), 3.63 (s, 3H, C5'-OCH_3), 2.46–2.43 (m, 2H, H1''), 1.49–1.44 (m, 2H, H2''), 1.25–1.15 (m, 24H, H3''–H14''), 0.88 (t, *J* = 6.7 Hz, 3H, H15''); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 203.3 (C=O), 157.2 (C2'), 152.9 (C2), 151.9 (C5'), 142.1 (C6), 131.2 (C4), 124.9 (2C, C1, C4'), 121.9 (C5), 120.3 (C1'), 119.2 (C3'), 115.4 (C6'), 113.9 (C3), 55.8 (C5'-OCH_3), 33.6 (C1''), 31.9 (C13''), 31.2 (C2''), 29.7 (4C), 29.6 (2C), 29.4 (2C), 29.2 (2C), 22.7 (C14''), 14.1 (C15''); **MS** (ESI+): *m/z* (%) = 455.4 (100) [M+H]$^+$, 477.3 (37) [M+Na]$^+$; **HRMS** (ESI+): Found (M+H)$^+$ 455.3159, $C_{29}H_{43}O_4$ (M+H)$^+$ requires 455.3156.

(2-Pentadecyl-6-hydroxyphenyl)(2-hydroxy-4,5-dimethoxyphenyl)methanone 6

A solution of BCl_3 in CH_2Cl_2 (1 m, 29.0 µL, 29.0 µmol) was added to a solution of (2-pentadecyl-6-hydroxyphenyl)(2,4,5-trimethoxyphenyl)methanone **4b** (13.3 mg, 26.7 µmol) in dry CH_2Cl_2 at –78 °C under an atmosphere of nitrogen while stirring. The solution was kept at this temperature for 8 h and then brought to rt overnight. Stirring was continued for 4 d at rt and each day BCl_3 in CH_2Cl_2 (1 M, 29.0 µL, 29.0 µmol) was added. Aqueous NaOH (1 m, 1 mL) was added and the mixture was stirred for 1 h. Then aqueous HCl (2 m, 1 mL) was added and the mixture was extracted with CH_2Cl_2 (2 x 3 mL). The combined organic extracts were dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography on silica gel (25% EtOAc/cyclohexane) to obtain (2-pentadecyl-6-hydroxyphenyl)(2-hydroxy-4,5-dimethoxyphenyl)methanone as a yellow solid **6** (8.90 mg, 18.3 µmol, 69%). **Mp**. 86.3–88 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 3439, 2922, 2852, 1626, 1441, 1238, 1204, 1164, 1126, 800; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 12.58 (s, 1H, C2-O*H*), 7.27 (t_{app}, J_{app} = 7.9 Hz, 1H, H4'), 6.88 (dd, *J* = 7.7, 1.0 Hz, 1H, H3'), 6.79 (dd, *J* = 8.1, 1.0 Hz, 1H, H5'), 6.65 (s, 1H, H6), 6.52(s, 1H, H3), 5.78 (s, br, 1H, C6'-O*H*), 3.94 (s, 3H, C4-OCH_3), 3.62 (s, 3H, C5-OCH_3), 2.47 (t, *J* = 7.8 Hz, 2H, H1''), 1.50–1.42 (m, 2H, H2''), 1.30–1.16 (m, 24H, H3''–H14''), 0.86 (t, *J* = 6.9 Hz, 3H, H15''); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 200.8 (C=O), 161.0 (C2), 157.6 (C4), 153.0 (C6'), 142.2 (C5), 141.8 (C2'), 131.1 (C4'), 125.0 (C1'), 121.8 (C3'), 114.0 (C5'), 113.4 (C6), 112.8 (C1), 100.5 (C3), 56.4 (C5-OCH_3), 56.3 (C4-OCH_3), 33.6 (C1''), 31.9 (C13''), 31.3 (C2''), 29.7 (5C), 29.6 (2C), 29.5, 29.4, 29.3, 22.7 (C14''), 14.1 (C15''); **MS** (ESI+): *m/z* (%) = 485.4 (100) [M+H]$^+$, 507.3 (22) [M+Na]$^+$; **HRMS** (ESI+): Found (M+H)$^+$ 485.3258, $C_{30}H_{45}O_5$ (M+H)$^+$ requires 485.3262.

3-Pentadecylphenyl benzoate 8

To a stirred solution of 3-pentadecylphenol **7** (5.00 g, 16.42 mmol) in 2-Methyl-THF (60 mL), triethylamine (4.58 mL, 32.84 mmol) and 4-dimethylaminopyridine (0.200 g, 1.64 mmol) was added and the mixture cooled to 0 °C. To this cooled mixture, benzoyl chloride (2.54 g, 2.10 mL, 18.06 mmol) dissolved in 2-Methyl-THF (20 mL) was slowly added and the reaction mixture was warmed to rt and stirred for 2 h. Upon completion, the reaction was quenched with water (50 mL) and the mixture extracted with EtOAc (3 × 100 mL). The combined organic extracts were washed with aq. $NaHCO_3$ (100 mL) followed by brine (100 mL) and then dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel (10 % EtOAc/cyclohexane) to afford the 3-pentadecylphenyl benzoate **8** as a white crystalline solid (6.36 g, 95%). **Mp**. 52.1-53.9 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2918, 2846, 1731, 1585, 1238, 1144, 1079, 710; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.25 (dd, *J* = 8.3, 1.4 Hz, 2H, H2'), 7.69–7.64 (m, 1H, H4'), 7.55 (dd, *J* = 8.3, 7.0 Hz, 2H, H3'), 7.36 (td, *J* = 7.6, 1.5 Hz, 1H, H5), 7.13 (dd, *J* = 7.7, 1.3 Hz, 1H, H4), 7.10–7.05 (m, 2H, H2, H6), 2.68 (t, *J* = 7.7 Hz, 2H, H1''), 1.75–1.63 (m, 2H, H2''), 1.30 (m, 24H, H3''-H14''), 0.92 (t, *J* = 5.7 Hz, 3H, H15''); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.2 (C=O), 151.0 (C1), 144.8 (C3), 133.5 (C4'), 130.2 (C2'), 129.7 (C1'), 129.2 (C5), 128.5 (C3'), 126.0 (C4), 121.6 (C2), 118.8 (C5), 35.8 (C1''), 32.0 (C13''), 31.3 (C2''), 29.7 (6C), 29.6 (1C), 29.5 (1C), 29.4 (1C), 29.3 (1C), 22.7 (C14''), 14.2 (C15''); **HRMS** (ESI+): Found (M+H)$^+$ 409.3107, $C_{28}H_{41}O_2$ (M+H)$^+$ requires 409.3101.

(2-Hydroxy-4-pentadecylphenyl)(phenyl)methanone 9

3-Pentadecylphenyl benzoate **8** (0.20 g, 0.49 mmol) was dissolved in chlorobenzene (3 mL) in a microwave reactor tube. To this solution, $AlCl_3$ (0.16 g, 1.23 mmol) was added. The tube was sealed and the reaction mixture was subjected to microwave irradiation (150 W, 160 °C) for 30 min. After cooling to rt, the crude product was purified by column chromatography (5% EtOAc/cyclohexane) to afford (2-hydroxy-4-pentadecylphenyl)(phenyl)methanone **9** as an off-white solid (0.16 g, 78%). **Mp**. 40.8-42.6 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2912, 2848, 1626, 1600, 1470, 1334, 1223, 915, 765, 700; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 12.19 (s, 1H, C2-OH), 7.72–7.67 (m, 2H, H2'), 7.62–7.56 (m, 1H, H4'), 7.54–7.50 (m, 3H, H3' and H6), 6.93 (d, *J* = 1.6 Hz, 1H, H3), 6.72 (dd, *J* = 8.2, 1.7 Hz, 1H, H5), 2.65 (t, 2H, H1''), 1.73–1.60 (m, 2H, H2''), 1.30 (m, 24H, H3''-H14''), 0.91 (t, *J* = 5.6 Hz, 3H, H15''); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 201.1 (C=O), 163.5 (C2), 153.0 (C4), 138.2 (C1'), 133.5 (C6), 131.7 (C4'), 129.1 (C2'), 128.3 (C3'), 119.3 (C5), 117.8 (C3), 117.1 (C1), 36.3 (C1''), 32.0 (C13''), 30.7 (C2''), 29.7 (6C), 29.6 (1C), 29.5 (1C), 29.4 (1C), 29.3 (1C), 22.7 (C14''), 14.2 (C15''); **HRMS** (ESI+): Found (M+H)$^+$ 409.3096, $C_{28}H_{41}O_2$ (M+H)$^+$ requires 409.3101. The analytical data are in accordance with the literature.[18]

(2-hydroxy-4-pentadecylphenyl)(2-hydroxyphenyl)methanone 10

To a 15 mL scintillation vial were added (2-hydroxy-4-pentadecylphenyl)(phenyl)methanone **9** (0.30 g, 0.73 mmol), $K_2S_2O_8$ (0.40 g, 1.47 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (11 mg, 0.018 mmol), TFAA (5.0 mL) and TFA (2.0 mL). The vessel was sealed with a Teflon-lined cap and the mixture was heated at 80 °C under TLC monitoring. After completion, EtOAc was added to dilute the reaction mixture and saturated aqueous $NaHCO_3$ was added to neutralize TFA and TFAA. Then the organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Finally, the residue was purified by silica gel column chromatography (5% EtOAc/hexane) to give (2-hydroxy-4-pentadecylphenyl)(2-hydroxyphenyl)methanone **10** as a white crystalline solid (220 mg, 72%). **Mp**. 31.4-32.6 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 3403, 2921, 2852, 1599, 1573, 1337, 1229, 755, 699; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.86 (s, 1H, C2-OH), 10.52 (s, 1H, C2'-OH), 7.61 (dd, *J* = 8.0, 1.8 Hz, 1H, H6'), 7.56–7.41 (m, 2H, H4' and H6), 7.07 (d, *J* = 8.4 Hz, 1H, H3'), 6.93 (d, *J* = 7.7 Hz, 1H, H5'), 6.89 (s, 1H, H3), 6.74 (dd, *J* = 8.3, 1.8 Hz, 1H, H5), 2.62 (t, 2H, H1''), 1.67-1.61 (m, 2H, H2''), 1.26 (m, 24H, H3''-H14''), 0.87 (t, *J* = 5.7 Hz, 3H, H15''); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 201.8 (C=O), 162.3 (C2), 161.4 (C2'), 152.8 (C4), 135.5 (C4'), 133.1 (C6), 132.9 (C6'), 120.1 (C1'), 119.5 (C5), 118.7 (C5'), 118.5 (C3'), 118.0 (C3), 117.5 (C1), 36.2 (C1''), 31.9 (C13''), 30.6 (C2''), 29.7 (6C), 29.6 (1C), 29.5 (1C), 29.4 (1C), 29.3 (1C), 22.7 (C14''), 14.1 (C15''); **HRMS** (ESI+): Found (M+H)$^+$ 425.3058, $C_{28}H_{41}O_3$ (M+H)$^+$ requires 425.3050.

3-Pentadecylphenyl acetate 11

To a stirred solution of 3-pentadecylphenol **7** (2.03g, 6.57 mmol) in 2-Methyl-THF (20 mL), triethylamine (1.83 mL, 13.14 mmol) and 4-dimethylaminopyridine (0.08g, 0.66 mmol) was added and the mixture cooled to 0 °C. To this cooled mixture, acetyl chloride (0.62g, 0.56 mL, 7.88 mmol) dissolved in 2-methyl-THF (5 mL) was slowly added and the reaction mixture was slowly warmed to rt and stirred at rt for 2 h. The reaction was quenched with water (20 mL) and the mixture extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with aq. $NaHCO_3$ (50 mL) followed by brine (50 mL) and then dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel (10 % EtOAc/cyclohexane) to afford the 3-pentadecylphenyl acetate **11** as a low melting white solid (2.22 g, 96%). **Mp**. 36.9-37.5 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2914, 2848, 1757, 1612, 1587, 1204, 1142, 1015, 952, 694; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 1H, H5), 7.09 (d, *J* = 7.7 Hz, 1H, H4), 6.96 (d, *J* = 1.3 Hz, 1H, H2), 6.97–6.93 (m, 1H, H6), 2.66 (t, 2H, H1''), 2.32 (s, 3H, H1'), 1.73 – 1.60 (m, 2H, H2''), 1.32 (m, 24H, H3''-H14''), 0.94 (t, *J* = 5.7 Hz, 3H, H15''); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.5 (C=O), 150.7 (C1), 144.7 (C3), 129.1 (C5), 125.9 (C4), 121.4 (C2), 118.7 (C6), 35.8 (C1''), 32.0 (C13''), 31.3 (C2''), 29.8 (5C) 29.7 (1C), 29.6 (1C), 29.5 (1C), 29.4(1C), 29.3 (1C), 22.8 (C14''), 21.1 (C1'), 14.2 (C15''); **HRMS** (ESI+): Found (M+Na)$^+$ 369.2761, $C_{23}H_{38}O_2Na$ (M+Na)$^+$ requires 369.2764.

1-(2-Hydroxy-4-pentadecylphenyl)ethanone 12

3-Pentadecylphenyl acetate **11** (0.40 g, 1.16 mmol) was dissolved in chlorobenzene (6 mL) in a microwave reaction vial. To this solution, $AlCl_3$ (0.38 g, 2.88 mmol) was added. The vial was sealed and the reaction mixture was subjected to microwave irradiation (150 W, 160 °C) for 30 min. After cooling, the crude product was purified by column chromatography (10% EtOAc/cyclohexane) to afford 1-(2-hydroxy-4-pentadecylphenyl)ethanone **12** as a light brown solid (0.39 g, 99%). **Mp**. 49.1-50.5 °C; **IR** ($\tilde{\nu}$/cm^{-1}):2915, 2848, 1636, 1573, 1471, 1365, 1249, 799, 717; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 12.31 (s, C2'-OH), 7.65 (d, *J* = 8.2 Hz, 1H, H6'), 6.81 (d, *J* = 1.6 Hz, 1H, H3'), 6.74 (dd, *J* = 8.2, 1.7 Hz, 1H, H5'), 2.67 – 2.54 (m, 5H, H1 and H1''), 1.70 – 1.57 (m, 2H, H2''), 1.40 – 1.20 (m, 24H, H3''-H14''), 0.89 (t, *J* = 5.5 Hz, 3H, H15''); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 203.8 (C=O), 162.5 (C2'), 153.0 (C4'), 130.6 (C6'), 119.6 (C5'), 117.7 (C3'), 36.2 (C1''), 31.9 (C13''), 30.7 (C2''), 29.7(6C), 29.6 (1C), 29.5 (1C), 29.4 (1C), 29.3 (1C), 26.5 (C1), 22.7 (C14''), 14.1 (C15''); **HRMS** (ESI+): Found (M+H)$^+$ 347.2942, $C_{23}H_{39}O_2$ (M+H)$^+$ requires 347.2945. The data is consistent with what has been reported in literature.[27]

(*E*)-1-(2-hydroxy-4-pentadecylphenyl)-3-phenylprop-2-en-1-one 13a

To a round-bottom flask (10 mL), equipped with a magnetic stir bar were added 1-(2-hydroxy-4-pentadecylphenyl)ethanone **12** (0.097 g, 0.28 mmol), benzaldehyde (28 µL, 30 mg, 0.28 mmol), sodium hydroxide (34 mg, 0.85 mmol) and methanol (2 mL). The pale yellow mixture was refluxed until the colour was turned into orange (about 4 h). The mixture was poured into ice-water and extracted with ethyl acetate (3 × 10 mL). The organic layer was dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. The crude product was subjected to column chromatography (5% EtOAc/cyclohexane) to furnish ((*E*)-1-(2-hydroxy-4-pentadecylphenyl)-3-phenylprop-2-en-1-one **13a** as a bright yellow solid (0.085 g, 67%). **Mp**. 54.7-56.4 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2915, 2849, 1640, 1618, 1350, 1204, 1148, 788, 738; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 12.91 (s, 1H, C2''-OH), 7.93 (d, *J* = 15.5 Hz, 1H, H3), 7.85 (d, *J* = 8.3 Hz, 1H, H6''), 7.71 – 7.63 (m, 3H, H2 and H2'), 7.50 – 7.43 (m, 3H, H3' and H4'), 6.87 (d, *J* = 1.5 Hz, 1H, H3''), 6.79 (dd, *J* = 8.2, 1.7 Hz, 1H, H5''), 2.64 (t, 2H, H1'''), 1.90 – 1.47 (m, 2H, H2'''), 1.28 (m, 24H, H3'''-H14'''), 0.90 (t, *J* = 5.7, 3H, H15'''); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 193.1 (C=O), 163.8 (C2''), 153.1 (C4''), 144.9 (C3), 134.7 (C1'), 130.8 (C4'), 129.5 (C6''), 129.0 (C3'), 128.6 (C2'), 120.3 (C2), 119.5 (C5''), 118.0 (C3''), 36.3 (C1'''), 31.9 (C13'''), 30.7(C2'''), 29.7 (6C), 29.6 (1C), 29.5 (1C), 29.4 (1C), 29.3 (1C), 22.7 (C14'''), 14.1 (C15'''); **HRMS** (ESI+): Found (M+H)$^+$ 435.3259, $C_{30}H_{43}O_2$ (M+H)$^+$ requires 435.3258.

3-Hydroxy-7-pentadecyl-2-phenyl-4*H*-chromen-4-one 13b

((*E*)-1-(2-hydroxy-4-pentadecylphenyl)-3-phenylprop-2-en-1-one (0.156 g, 0.36 mmol) was dissolved in methanol (10 mL) in a 50 mL round-bottom flask. To the stirred solution, sodium hydroxide (0.5 N, 2.7 mL) and hydrogen peroxide (30%, 220 µL) were added and the mixture was stirred at rt for 2 h upon which its colour changed to orange. The mixture was acidified with aqueous HCl (15 mL) and extracted with ethyl acetate (3 × 20 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was subjected to column chromatography (10% EtOAc/hexane) to give 3-hydroxy-7-pentadecyl-2-phenyl-4*H*-chromen-4-one **13b** as a yellow solid (0.141 g, 88%). **Mp**. 81.2-83.7 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 3406, 2918, 2841, 1643, 1612, 1363, 1203, 1149, 747; **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.26 (dd, *J* = 8.8, 1.5 Hz, 2H, H2'), 8.15 (d, *J* = 8.1 Hz, 1H, H5), 7.54 (t, *J* = 7.6, Hz, 2H, H3'), 7.50–7.44 (m, 1H, H4'), 7.40 (d, *J* = 1.4 Hz, 1H, H8), 7.28–7.22 (m, 2H, H6 and C3-O*H*), 2.76 (t, *J* = 7.7, Hz, 2H, H1''), 1.75–1.65 (m, 2H, H2''), 1.41–1.20 (m, 24H, H3''-H14''), 0.88 (t, *J* = 6.9, Hz, 3H, H15''); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 173.4 (C=O), 155.7 (C8a), 150.1 (C7), 144.5 (C2), 138.3 (C3), 131.3 (C1'), 130.0 (C4'), 128.6 (C3'), 127.7 (C2'), 125.6 (C6), 125.2 (C5), 118.6 (C4a), 117.3 (C8), 36.2 (C1''), 31.9 (C13''), 30.9 (C2''), 29.7 (5C), 29.6 (1C), 29.5 (2C), 29.4 (1C), 29.2 (1C), 22.7 (C14''), 14.1 (C15''); **HRMS** (ESI+): Found (M+H)$^+$ 449.3054, $C_{30}H_{41}O_3$ (M+H)$^+$ requires 449.3050.

3-Pentadecylphenyl-2-fluorobenzoate 15

To a stirred solution of 3-pentadecylphenol **7** (2.07g, 6.69 mmol) in 2-methyl-THF (20 mL), triethylamine (1.37 g, 1.89 mL, 13.58 mmol) and 4-

dimethylaminopyridine (0.083 g, 0.68 mmol) was added and the mixture cooled to 0 °C. To this cooled mixture, 2-fluorobenzoyl chloride (1.19 g, 0.89 mL, 7.48 mmol) dissolved in 2-methyl-THF (5 mL) was slowly added and the reaction mixture was slowly warmed to rt and stirred at rt for 2 h. The reaction was quenched with water (20 mL) and the mixture extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with aq. $NaHCO_3$ (50 mL) followed by brine (500 mL) and then dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel (10% EtOAc/cyclohexane) to afford the 3-pentadecylphenyl-2-flurobenzoate **15** as a white crystalline solid (2.78 g, 98%). **Mp**. 57.2-58.9 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2932, 2813, 1702, 1596, 1214, 1130, 1081, 747, 712; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (td, *J* = 7.5, 7.5, 1.8 Hz, 1H, H6'), 7.68–7.57 (m, 1H, H4'), 7.36 (td, *J* = 7.4, 7.4, 1.3 Hz, 1H, H5), 7.35–7.26 (m, 1H, H5'), 7.24 (ddd, *J* = 10.8, 8.3, 1.1 Hz, 1H, H3'), 7.13 (dd, *J* = 7.7, 1.3 Hz, 1H, H4), 7.10 (d, *J* = 1.3 Hz, 1H, H2), 7.09–7.06 (m, 1H, H6), 2.68 (t, 2H, H1''), 1.73–1.62 (m, 2H, H2''), 1.31 (m, 24H, H3''-H14''), 0.92 (t, *J* = 5.7 Hz, 3H, H15''); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.6 (C=O), 162.9 (C2'), 162.8 (C2'), 161.0 (C2'), 150.6 (C1), 144.8 (C3), 135.1 (C4'), 132.5 (C6'), 129.2 (C5), 126.1 (C4), 124.1 (C5'), 124.1, 121.5 (C2), 118.8 (C6), 117.3 (C1'), 117.1 (C3'), 35.8 (C1''), 32.0 (C13''), 31.3 (C2''), 29.7 (6C), 29.6 (1C), 29.5 (1C), 29.4 (1C), 29.3 (1C), 22.8 (C14''), 14.2 (C15''); **HRMS** (ESI+): Found $(M+Na)^+$ 449.2881, $C_{28}H_{39}FNaO_2$ $(M+Na)^+$ requires 449.2886.

(2-Fluorophenyl)(2-hydroxy-4-pentadecylphenyl)methanone 16

3-Pentadecylphenyl-2-flurobenzoate **15** (0.101 g, 2.37 mmol) was dissolved in chlorobenzene (12 mL) in a microwave reaction vial. To this solution, $AlCl_3$ (0.79 g, 5.92 mmol) was added. The vial was sealed and the reaction mixture was subjected to microwave irradiation (150 W, 160 °C) for 30 min. After cooling, the crude product was purified by column chromatography (5% EtOAc/cyclohexane) to afford (2-fluorophenyl)(2-hydroxy-4-pentadecylphenyl)methanone **16** as an off-white solid (0.85 g, 84%). **Mp**. 41.4-43.2 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2916, 2846, 1614, 1454, 1333, 1217, 1162, 914, 759; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 12.09 (s, OH, C2-OH), 7.58–7.43 (m, 2H, H4' and H6'), 7.38–7.25 (m, 2H, H3' and H6), 7.21 (ddd, *J* = 9.5, 8.3, 1.0 Hz, 1H, H5'), 6.91 (d, *J* = 1.6 Hz, 1H, H3), 6.71 (dd, *J* = 8.3, 1.7 Hz, 1H, H5), 2.64 (t, 2H, H1''), 1.74–1.59 (m, 2H, H2''), 1.30 (m, 24H, H3''-H14''), 0.91 (t, *J* = 5.8 Hz, 3H, H15''); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.8 (C=O), 163.3 (C2-OH), 160.3 (C2'), 157.8 (C1'), 153.8 (C4), 133.3 (C6), 132.7 (C6'), 129.8 (C4'), 128.6 (C1), 124.4 (C3'), 119.7 (C4), 117.7 (C3), 116.1 (C5'), 36.4 (C1''), 32.0 (C13''), 30.6 (C2''), 29.8 (6C), 29.6 (1C), 29.5 (1C), 29.4 (1C), 29.3 (1C), 22.7 (C14''), 14.2 (C15''); **HRMS** (ESI+): Found $(M+H)^+$ 427.3002, $C_{28}H_{40}FO_2$ $(M+H)^+$ requires 427.3007.

3-Pentadecyl-9*H*-xanthen-9-one 17

To a 25 mL round bottom flask were added (2-fluorophenyl)(2-hydroxyphenyl)methanone **16** (0.225 g, 0.53 mmol), K_2CO_3 (0.146 g, 1.05 mmol) and 5 mL of acetone at rt. The reaction mixture was heated to 50 °C for 4 h. The resulting mixture was allowed to cool to rt, the filtered and then extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was concentrated *in vacuo*. Finally, the residue was purified by silica gel column chromatography (5% EtOAc/cyclohexane) to give the desired 3-pentadecyl-9*H*-xanthen-9-one **17** as a white solid (0.183 g, 86%). **Mp**. 75.2-76.4 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2915, 2848, 1663, 1606, 1463, 1431, 1344, 1179, 1149, 1109, 959, 758, 727; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.34 (dd, *J* = 7.9, 1.7 Hz, 1H, H8), 8.24 (d, *J* = 8.2 Hz, 1H, H1), 7.70 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 1H, H6), 7.47 (dd, *J* = 8.5, 1.0 Hz, 1H, H5), 7.36 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H, H7), 7.28 (d, *J* = 1.3 Hz, 1H, H4), 7.20 (dd, *J* = 8.2, 1.6 Hz, 1H, H2), 2.75 (t, 2H, H1'), 1.76-1.64 (m, 2H, H2'), 1.40–1.19 (m, 24H, H3'-H14'), 0.88 (t, *J* = 5.8 Hz, 3H, H15') ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.0 (C=O), 156.3 (C4a), 156.1 (C10a), 151.3 (C3), 134.5 (C6), 126.7 (C8), 126.5 (C1), 124.8 (C2), 123.7 (C7), 121.9 (C8a), 119.8 (C9a), 117.9 (C5), 117.0 (C4), 36.2 (C1'), 31.9 (C13'), 30.9 (C2'), 29.7 (6C), 29.6 (1C), 29.5 (1C), 29.4 (1C), 29.3 (1C), 22.7 (C14'), 14.1 (C15') ppm; **HRMS** (ESI+): Found $(M+H)^+$ 407.2940, $C_{28}H_{39}O_2$ $(M+H)^+$ requires 407.2945.

1,8-Dihydroxy-3-pentadecyl-9*H*-xanthen-9-one 14

To a 25 mL scintillation vial were added 3-pentadecyl-9*H*-xanthen-9-one **16** (0.54 g, 1.32 mmol), $K_2S_2O_8$ (1.44 g, 5.31 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (11 mg, 20.2 mmol), TFAA (10.5 mL) and TFA (4.5 mL). The reaction vessel was sealed with a Teflon-lined cap and the mixture was heated to 80 °C under TLC-monitoring. After completion, EtOAc was added to dilute the reaction mixture and saturated aqueous $NaHCO_3$ was added to neutralize TFA and TFAA. Then the organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Finally, the residue was purified by silica gel column chromatography (5% EtOAc/hexane) to give 1-hydroxy-3-pentadecyl-9*H*-xanthen-9-one as a white crystalline solid (395 mg, 71%). **Mp**. 93.7-95.9 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 3401, 2914, 2849, 1630 1597, 1498, 1319, 1239, 1077, 1057, 831, 749, 736; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 12.56 (s, 1H, C1-OH), 8.27 (dd, *J* = 8.0, 1.7 Hz, 1H, H8), 7.73 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H, H6), 7.45 (dd, *J* = 7.5, 1.0 Hz, 1H, H5), 7.38 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H, H7), 6.77 (d, *J* = 1.4 Hz, 1H, H2), 6.65 (d, *J* = 1.4 Hz, 1H, H4), 2.67 (t, *J* = 7.7, Hz, 2H, H1'), 1.77–1.56 (m, 2H, H2'), 1.31-1.19 (m, 24H, H3'-H14'), 0.88 (t, *J* = 6.3 Hz, 3H, H15') ppm; **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 181.8 (C=O), 161.6 (C1), 156.2 (C4a), 156.2 (C10a), 154.0 (C3), 135.3 (C6), 126.0 (C8), 123.9 (C7), 120.7 (C8a), 117.8 (C5), 110.6 (C4), 107.2 (C9a), 106.8 (C2), 36.8 (C1'), 31.9 (C13'), 30.6 (C2'), 29.7 (6C), 29.5 (1C), 29.5 (1C), 29.4 (1C), 29.2 (1C), 22.7 (C14'), 14.1 (C15') ppm; **HRMS** (ESI+): Found $(M+H)^+$ 423.2894, $C_{28}H_{39}O_3$ $(M+H)^+$ requires 423.2894. To a 15 mL scintillation vial was added a portion of the 1-hydroxy-3-pentadecyl-9*H*-xanthen-9-one (0.18 g, 0.43 mmol), $K_2S_2O_8$ (0.46 g, 1.70 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (13.1 mg, 0.022 mmol), TFAA (5.0 mL) and TFA (2.0 mL). The reaction vessel was sealed with a Teflon-lined cap the mixture was heated to 80 °C under TLC-monitoring. After completion, EtOAc was added to dilute the reaction mixture and saturated aqueous $NaHCO_3$ was added to neutralize TFA and TFAA. Then the organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Finally, the residue was purified by silica gel column chromatography (5% EtOAc/hexane) to furnish 1,8-dihydroxy-3-pentadecyl-9*H*-xanthen-9-one **14** as off-white solid (121 mg ,64%). **Mp**. 92.3-93.2 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2915, 2849, 1633, 1595, 1490, 1471, 1316, 1233, 1079, 1055, 831, 747, 732; **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 11.92 (s, 1H, C8-OH), 11.75 (s, 1H, C1-OH), δ 7.61 (t, J = 8.4, 8.4 Hz, 1H, H6), 6.91 (dd, J = 8.4, 0.9 Hz, 1H, H5), 6.80 (dd, J = 8.3, 0.9 Hz, 1H, H7), 6.77 (d, J = 1.4 Hz, 1H, H4), 6.66 (d, J = 1.4 Hz, 1H, H2), 2.69 (t, 2H, H1'), 1.75–1.64 (m, 2H, H2'), 1.39–1.24 (m, 24H, H3'-H14'), 0.89 (t, *J* = 5.9 Hz, 3H, H15'); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 185.7 (C=O), 161.3 (C8), 161.0 (C1), 156.3 (C10a), 156.2 (C4a), 154.9 (C3), 137.2 (C6), 111.0 (C2), 110.7 (C7), 107.8 (C8a), 107.1 (C4), 107.1 (C5), 106.0 (C9a), 36.8 (C1'), 31.9 (C13'), 30.6 (C2'), 29.7 (5C), 29.6 (1C), 29.5 (1C), 29.4 (1C), 29.2 (1C), 26.9 (1C), 22.7 (C14'), 14.2 (C15'); **HRMS** (ESI+): Found $(M+H)^+$ 439.2861, $C_{28}H_{39}O_4$ $(M+H)^+$ requires 439.2843.

2-Hydroxy-4-pentadecylbenzaldehyde 18

To a stirred mixture of 3-pentadecylphenol **7** (3.04 9, 9.85 mmol), tri-*n*-butylamine ((0.4 M), and tin tetrachloride (0.26 g, 0.115 mL, 0.96 mmol) in toluene (50 mL), at ambient temperature, paraformaldehyde (0.65 g, 21.67 mmol) was added and after 30 min the yellow solution was heated at 100 °C for 8 h. Then reaction mixture was then cooled and then poured into water acidified with 2 m HCl and extracted with diethyl ether.

The ether extract, was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (5 % EtOAc/cyclohexane) to furnish 2-hydroxy-4-pentadecylbenzaldehyde **18** as a white solid (2.45 g, 77%). **Mp**. 50.6-51.8 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2914, 2848, 1667, 1626, 1470, 1306, 1191, 1128, 797, 735; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 11.06 (s, 1H, C2-OH), 9.85 (s, 1H, CHO), 7.46 (d, *J* = 7.8 Hz, 1H, H6), 6.85 (dd, *J* = 7.9, 1.5 Hz, 1H, H5), 6.82 (d, *J* = 1.4 Hz, 1H, H3), 2.63 (t, 2H, H1'), 1.76–1.48 (m, 2H, H2'), 1.40-1.18 (m, 24H, H3'-H14'), 0.89 (t, *J* = 5.7 Hz, 3H, H15'); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 195.8 (CHO), 161.8 (C2-OH), 153.8 (C4), 133.6 (C6), 120.5 (C5), 118.8 (C1), 117.1 (C3), 36.4 (C1'), 31.9 (C13'), 30.7 (C2'), 29.7 (6C), 29.6 (1C), 29.5 (1C), 29.4 (1C), 29.3 (1C), 22.7 (C14'), 14.1 (C15'); **HRMS** (ESI+): Found $(M+H)^+$ 333.2786, $C_{22}H_{37}O_2$ $(M+H)^+$ requires 333.2788. This data is consistent with that reported in the literature.[28]

2-(Hydroxymethyl)-5-pentadecylphenol 19

2-Hydroxy-4-pentadecylbenzaldehyde **18** (0.48 g, 1.44 mmol) was dissolved in 15 mL of freshly distilled dry THF under inert conditions in a 25 mL round bottom flask. The reaction was cooled 0 °C and $LiAlH_4$ (0.22 g, 5.78 mmol) was carefully added. The reaction mixture was slowly warmed to rt and was stirred for 2 h. Upon completion, the mixture was cooled again to 0 °C and a 2% aq. NaOH (10 mL) was added dropwise to quench the unreacted $LiAlH_4$ followed by dilution with ice-cold water (25 mL). The organic material was the extracted with EtOAc (3 × 320 mL) and combined organic phases were washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed *in vacuo* to obtain a crude product which was then subjected to column chromatography (20% EtOAc/cyclohexane) to obtain 2-(hydroxymethyl)-5-pentadecylphenol **19** as a white crystalline solid (0.39 g, 81%). **Mp**. 94.6-95.9 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 3442, 3165, 2915, 2847, 1624, 1592, 1463, 1440, 1284, 1125, 992, 826, 753; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.13 (s, 1H, C2-O*H*), 6.93 (d, *J* = 7.6 Hz, 1H, H6), 6.73 (d, *J* = 1.6 Hz, 1H, H3), 6.67 (dd, *J* = 7.6, 1.6 Hz, 1H, H5), 4.83 (s, 2H, C*H*$_2$OH), 2.54 (t, 2H, H1'), 2.13 (br, s, 1H,), 1.68–1.49 (m, 2H, H2'), 1.42-1.17 (m, 24H, H3'-H14'), 0.87 (t, *J* = 5.6 Hz, 3H, H15'); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.0 (C2), 145.0 (C4), 127.6 (C6), 121.9 (C1), 120.2 (C5), 116.5 (C3), 64.6 (-*C*H$_2$OH), 35.7 (C1'), 31.9 (C13'), 31.3 (C2)', 29.7 (6C), 29.6 (1C), 29.5 (1C), 29.4 (1C), 29.3 (1C), 22.7 (C14'), 14.1 (C15'); **HRMS** (ESI+): Found $(M+Na)^+$ 357.2770, $C_{22}H_{38}NaO_2$ $(M+Na)^+$ requires 357.2764. This data was consistent with that reported in the literature.[29]

2-(4,6-Diphenyl-1,3,5-triazin-2-yl)-5-pentadecylphenol 20

A mixture of 2-(hydroxymethyl)-5-pentadecylphenol **19** (0.19 g, 0.57 mmol), benzamidine hydrochloride (0.15 g, 0.97 mmol), Na_2CO_3 (0.10 g, 0.97 mmol) and $Cu(OAc)_2$ (10 mol%) was stirred in toluene (3.5 mL) at 110 °C for 24 h. The resulting mixture was cooled to rt and then extracted with EtOAc (3 × 10 mL) followed by a brine wash. The organic phases were combined and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (5% EtOAc/cyclohexane) to give 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-pentadecylphenol **20** as a white crystalline solid (0.16 g, 62%). **Mp**. 117.6-119.4 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2915, 2849, 1587, 1509, 1470, 1394, 1365, 1352, 1314, 1232, 753, 689; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 13.27 (s, 1H, C1-OH), 8.66 (dd, *J* = 11.2, 7.8 Hz, 6H, H2'' and H4''), 7.77 – 7.49 (m, 5H, H3'' and H3), 6.93 (d, *J* = 1.6 Hz, 1H, H6)), 6.89 (dd, *J* = 8.2, 1.7 Hz, 1H, H4), 2.68 (t, 2H, H1'''), 1.77–1.66 (m, 2H, H2'''), 1.41–1.22 (m, 24H, H3'''-H14''') (0.90 (t, *J* = 5.8, 3H, H15'''); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.9 (C2' and C6', 162.2 (C1), 151.5 (C5), 135.3 (C1''), 133.0 (C2''), 129.8 (C3), 129.0 (C3''), 128.8 (C4''), 120.1 (C4), 117.7 (C6), 115.2 (C2), 36.2 (C1'''), 31.9 (C13'''), 30.9 (C2'''), 29.7 (6C), 29.6 (1C), 29.5 (1C), 29.4 (1C), 29.3 (1C), 22.7 (C14'''), 14.1 (C15'''); **HRMS** (ESI+): Found $(M+H)^+$ 536.3643, $C_{36}H_{46}N_3O$ $(M+H)^+$ requires 536.3636.

2-Hydroxy-4-pentadecylbenzonitrile 22

2-Hydroxy-4-pentadecylbenzaldehyde **18** (1.05 g, 3.15 mmol) and hydroxylamine hydrochloride (0.29 g, 4.10 mmol) were added successively to a solution of anhydrous ferric chloride (0.26 g, 1.58 mmol) in 20 mL dry DMF. The mixture was refluxed for 16 h. After completion of the reaction, the solution was poured into 200 mL water and extract with EtOAc (3 × 50 mL) and washed several times with water. The combined organic mixture was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (20% EtOAc/cyclohexane) to furnish 2-hydroxy-4-pentadecylbenzonitrile **22** as a white solid (0.82 g, 80%). **Mp**. 71.4-72.9 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 3273, 2957, 2915, 2851, 2229, 1615, 1585, 1470, 1439, 1310, 949, 874, 796; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.9 Hz, 1H, H6), 6.85 (d, *J* = 1.4 Hz, 1H, H3), 6.82 (dd, *J* = 7.9, 1.4 Hz, 1H, H5), 6.64 (s, 1H, C2-O*H*), 2.61 (t, 3H, H1'), 1.67–1.56 (m, 2H, H2'), 1.35–1.23 (m, 24H, H3'-H14'), 0.89 (t, *J* = 5.6 Hz, 3H, H15'); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.7 (C2), 151.3 (C4), 132.6 (C6), 121.4 (C5), 116.8 (C1'), 116.4 (C3), 96.5 (C1), 36.2 (C1''), 31.9 (C13''), 30.8 (C2''), 29.7 (6C), 29.6 (1C), 29.4 (1C), 29.4 (1C), 29.2 (1C), 22.7 (C14''), 14.1 (C15''); **HRMS**: Found $(M+Na)^+$ 352.2605, $C_{22}H_{35}NNaO$ $(M+Na)^+$ requires 352.2611.

6,6',6''-(1,3,5-Triazine-2,4,6-triyl)tris(3-pentadecylphenol) 21

2-Hydroxy-4-pentadecylbenzonitrile **22** (0.37g, 1.12 mmol) was placed in a microwave vial. The vial was sealed and then subjected to microwave irradiation (200 W, 220 °C) for 3 h. After cooling, the crude product was purified by column chromatography (5% EtOAc/cyclohexane) to afford 6,6',6''-(1,3,5-triazine-2,4,6-triyl)tris(3-pentadecylphenol) **21** as a light yellowish crystalline solid (0.133g, 73%). **Mp**. 75.8-77.7 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2916, 2848, 1630, 1584, 1535, 1494, 1386, 1361, 1310, 1228, 1161, 799; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 12.98 (s, 1H, C1-O*H*), 8.04 (d, *J* = 8.2 Hz, 1H, H5), 6.90 (s, 1H, H2), 6.85 (dd, *J* = 8.4, 1.5 Hz, 1H, H4), 2.64 (t, *J* = 7.7 Hz, 2H, H1''), 1.73–1.61 (m, 2H, H2''), 1.40–1.20 (m, 24H, H3''-H14''), 0.89 (t, *J* = 5.6 Hz, 3H, H15''); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.2 (C2'), 162.8 (C1), 152.9 (C3), 128.7 (C5), 120.7 (C4), 118.1 (C2), 113.4 (C6), 36.2 (C1''), 31.9 (C13''), 30.7 (C2''), 29.7 (6C), 29.6 (1C), 29.5 (1C), 29.4 (1C), 29.4 (1C), 22.7 (C14''), 14.1 (C15''); **HRMS**: Found $(M+H)^+$ 988.8235, $C_{66}H_{106}N_3O_3$ $(M+H)^+$ requires 988.8229.

3,4-dimethoxybenzohydrazide 24

Palladium on activated charcoal (10 wt%, 645 mg, 0.61 mmol) was added at rt to a stirred suspension of veratraldehyde (2.00 g, 12.0 mmol) and NaOH (1.07 g, 26.4 mmol) in water (48 mL). The mixture was stirred for 20 h at 80 °C and under a reduced pressure of 800 mbar. After cooling to rt, the mixture was filtered through Celite® and poured onto 1 n H_2SO_4 (60 mL). The resulting precipitate was collected by filtration and washed with water (120 mL). The filtrate was extracted with EtOAc (3 x 20 mL) and the combined organic extracts were dried over Na_2SO_4. After evaporation of the solvent, the resulting solid was combined with the residue of filtration and dried under reduced pressure in order to obtain 3,4-dimethoxybenzoic acid as a colourless solid (1.92 g, 10.5 mmol, 87%). **Mp**. 178.3–180.1 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2964, 2836, 1671, 1516, 1298, 1266, 1232, 1023, 917, 758; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.39 (s, 1H, CO_2H), 7.79 (dd, *J* = 8.4, 2.0 Hz, 1H, H6), 7.60 (d, *J* = 2.0 Hz, 1H, H2), 6.92 (d, *J* = 8.5 Hz, 1H, H5), 3.96 (s, 3H, C4-OCH_3), 3.95 (s, 3H, C3-OCH_3); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 172.0 (CO_2H), 153.7 (C4) 148.7 (C3), 124.6 (C6), 121.7 (C1), 112.3 (C2), 110.3 (C5), 56.1 (C4-

OCH_3), 56.0 (C3-OCH_3); **MS** (ESI+): *m/z* (%) = 181.1 (100) $[M–H]^-$. The analytical data are in accordance with the literature.[30] A solution of 3,4-dimethoxybenzoic acid (800 mg, 4.39 mmol) and conc. H_2SO_4 (90.0 µL, 1.62 mmol) in EtOH (5 mL) was stirred for 18 h under reflux. After cooling to rt the solvent was evaporated and the residue was dissolved in diethyl ether (15 mL). After washing with saturated aq $NaHCO_3$ (5 mL) and drying over Na_2SO_4 the solvent was evaporated in order to obtain ethyl 3,4-dimethoxybenzoate as a colourless oil (868 mg, 4.13 mmol, 94%). **IR** ($\tilde{\nu}$/cm^{-1}): 2979, 2839, 1708, 1514, 1345, 1290, 1269, 1177, 1025, 763; **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 8.4, 2.0 Hz, 1H, H6), 7.55 (d, *J* = 2.0 Hz, 1H, H2), 6.88 (d, *J* = 8.4 Hz, 1H, H5), 4.36 (q, *J* = 7.1 Hz, 2H, CH_2CH_3), 3.93 (s, 6H, C3-OCH_3 ,C4-OCH_3), 1.39 (t, *J* = 7.1 Hz, 3H, CH_2CH_3); **^{13}C NMR** (76 MHz, Chloroform-*d*) δ 166.4 (CO_2Et), 152.8 (C4) 148.5 (C3), 123.4 (C6), 123.0 (C1), 111.9 (C2), 110.2 (C5), 60.8 (CH_2CH_3), 56.0 (2C, C3-OCH_3, C4-OCH_3), 14.4 (CH_2CH_3); **MS** (ESI+): *m/z* (%) = 211.1 (100) $[M+H]^+$, 233.1 (5) $[M+Na]^+$. The analytical data are in accordance with the literature.[31] A solution of ethyl 3,4-dimethoxybenzoate (868 mg, 4.13 mmol.) and hydrazine hydrate (64 wt%, 600 µL, 12.4 mmol) in EtOH (0.3 mL) was refluxed for 18 h while stirring. After cooling to rt, the solvent was evaporated and the residue was dissolved in water (10 mL). The resulting solution was extracted with EtOAc (10 x 10 mL) and the combined organic extracts were dried over Na_2SO_4 and evaporated in order to obtain 3,4-dimethoxybenzohydrazide **24** as a colourless solid (770 mg, 3.92 mmol, 95%). **Mp**. 132.8–134.4 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 3307, 2939, 2845, 1626, 1500, 1275, 1148, 1073, 957, 635; **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.62 (s, 1H, N*H*NH_2), 7.44 (dd, *J* = 8.2, 1.2 Hz, 1H, H6), 7.42 (d, *J* = 2.0 Hz, 1H, H2), 6.99 (d, *J* = 8.2 Hz, 1H, H5), 4.42 (s, 2H, NHNH_2), 3.79 (s, 6H, C3-OCH_3, C4-OCH_3); **^{13}C NMR** (76 MHz, DMSO-d_6) δ 165.5 (CO_2NHNH_2), 151.0 (C4) 148.1 (C3), 125.4 (C1), 120.0 (C6), 110.8 (C5), 110.1 (C2), 55.5 (C3-OCH_3/C4-OCH_3), 55.4 (C3-OCH_3/C4-OCH_3); **MS** (ESI+): *m/z* (%) = 197.4 (100) $[M+H]^+$, 219.3 (22) $[M+Na]^+$. The analytical data are in accordance with the literature.[17]

2-[5-(3,4-dimethoxyphenyl)-1,3,4-oxadiazol-2-yl]-5-pentadecylphenol 25

To a stirred solution of 2-hydroxy-4-pentadecylbenzaldehyde (500 mg, 1.51 mmol) in diethyl ether (3.5 mL) and MeOH (3.5 mL) was added 3,4-dimethoxybenzohydrazide **24** (325 mg, 1.66 mmol). The resulting mixture was stirred over night at rt. During that time a colorless solid precipitated which was collected by filtration, washed with cyclohexane/EtOAc = 10/1 (30 mL) and dried under reduced pressure. Thus *N*'-[(2-hydroxy-4-pentadecylphenyl)methylidene]-3,4-dimethoxybenzohydrazide **25** was obtained as a colorless solid (623 mg, 1.22 mmol, 82%). **Mp**. 123.7–125.0 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 3225, 2918, 2849, 1639, 1415, 1271, 1194, 1132, 1022, 771; **^{1}H NMR** (600 MHz, acetone-d_6) δ 11.64 (s, 1H, OH), 11.21 (s, 1H, NH), 8.51 (s, 1H, C*H*N), 7.61 (dd, *J* = 8.3, 2.0 Hz, 1H, H6), 7.57 (d, *J* = 2.0 Hz, 1H, H2), 7.23 (d, *J* = 7.7 Hz, 1H, H6'), 7.06 (d, *J* = 8.4 Hz, 1H, H5), 6.79 (s, 1H, H3'), 6.77 (d, *J* = 7.7 Hz, 1H, H5'), 3.88 (s, 6H, C3-OCH_3, C4-OCH_3), 2.59 (t, *J* = 7.8 Hz, 2H, H1''), 1.62 (q, *J* = 7.8 Hz, 2H, H2''), 1.34–1.23 (m, 24H, H3''–H14''), 0.87 (t, *J* = 6.9 Hz, 3H, H15'') ppm; **^{13}C NMR** (151 MHz, acetone-d_6) δ 162.2 (*C*ONH), 158.6 (C2'), 152.6 (C4), 149.2 (C3), 149.1 (*C*HN), 146.9 (C4'), 130.7 (C6'), 125.2 (C1), 120.7 (C6), 119.5 (C5'), 116.5 (C3'), 115.9 (C1'), 110.9 (C5), 110.8 (C2), 55.2 (2C, C3-OCH_3, C4-OCH_3), 35.6 (C1''), 31.8 (C13''), 31.0 (C2''), 29.5 (6C), 29.4, 29.3, 29.2 (2C), 22.5 (C14''), 13.5 (C15'') ppm; **MS** (ESI+): *m/z* (%) 511.7 (100) $[M+H]^+$; **HRMS** (ESI+): Found $(M+H)^+$ 511.3514, $C_{31}H_{47}N_2O_4$ $(M+H)^+$ requires 511.3536.

2-[5-(3,4-Dimethoxyphenyl)-1,3,4-oxadiazol-2-yl]-5-pentadecylphenol 23

To a stirred solution of *N*'-[(2-hydroxy-4-pentadecylphenyl)methylidene]-3,4-dimethoxybenzohydrazide **25** (100 mg, 196 µmol) in dry acetone (4 mL) was added PIDA (126 mg, 392 µmol) under an atmosphere of argon. The resulting mixture was stirred for 2.5 h at rt and another portion of PIDA (63.1 mg, 196 µmol) was added. After stirring for a further 2.5 h, the solvent was evaporated and the residue was purified by column chromatography on silica gel (5–70% EtOAc/cyclohexane) in order to obtain 2-[5-(3,4-dimethoxyphenyl)-1,3,4-oxadiazol-2-yl]-5-pentadecylphenol **23** as a yellowish solid (46.3 mg, 91.0 µmol, 47%). **Mp**. 106.5–107.9 °C; **IR** ($\tilde{\nu}$/cm^{-1}): 2955, 2919, 2850, 1609, 1583, 1503, 1469, 1284, 1229, 1098, 721; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.12 (s, 1H, O*H*), 7.75 (d, *J* = 8.0 Hz, 1H, H3), 7.71 (dd, *J* = 8.4, 2.0 Hz, 1H, H6'), 7.64 (d, *J* = 2.0 Hz, 1H, H2'), 7.00 (d, *J* = 8.4 Hz, 1H, H5'), 6.97 (d, *J* = 1.4 Hz, 1H, H6), 6.86 (dd, *J* = 8.0, 1.6 Hz, 1H, H4), 4.01 (s, 3H, C3'-OCH_3), 3.98 (s, 3H, C4'-OCH_3), 2.64 (t, *J* = 7.5 Hz, 2H, H1''), 1.63 (q, *J* = 7.3 Hz, 2H, H2''), 1.33–1.23 (m, 24H, H3''–H14''), 0.88 (t, *J* = 6.8 Hz, 3H, H15'') ppm; **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.0 (oxadiazole-C2), 163.0 (oxadiazole-C5), 157.6 (C1), 152.3 (C4'), 149.7 (C5), 149.4 (C3'), 128.6 (C6'), 126.2 (C3), 120.4 (C4), 117.2 (C6), 115.9 (C1'), 111.1 (C5'), 109.4 (C2'), 105.8 (C2), 56.2 (C3'-OCH_3), 56.1 (C4'-OCH_3), 36.1 (C1''), 31.9 (C13''), 30.9 (C2''), 29.7 (6C), 29.6, 29.5, 29.4, 29.2, 22.7 (C14''), 14.1 (C15''); **MS** (ESI+): *m/z* (%) = 509.6 (100) $[M+H]^+$; **HRMS** (ESI+): Found $(M+H)^+$ 509.3372, $C_{31}H_{45}N_2O_4$ $(M+H)^+$ requires 509.3379.

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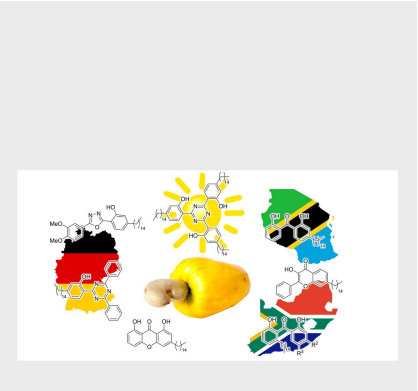
FULL PAPER

The synthesis of aromatic UV absorbers from the bio-renewables, cardanol and anacardic acid is described



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Key topic: Cashew Nut Shell Liquid, UV absorbers

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Title Valorisation of Cashew Nut Shell Liquid Phenolics in the Synthesis of UV Absorbers