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Highly efficient synthesis of sustainable bisphenols from hydroxycinnamic acids

Hydroxycinnamic acids, which can be derived from abundant lignocellulosic biomass, were converted to stilbene-based bisphenols by a two-step process consisting of catalyst-free thermal decarboxylation followed by [Ru]-catalyzed olefin metathesis. Yields of > 90% were achieved starting from the carboxylic acids. The bisphenols have applications as components of sustainable polymers, coatings, and thermosetting resins.

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Highly efficient synthesis of sustainable bisphenols from hydroxycinnamic acids†

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Three stilbene based bisphenols: (*E*)-4,4′-(ethene-1,2-diyl)diphenol (**1**), (*E*)-4,4′-(ethene-1,2-diyl)bis(2-methoxyphenol) (**2**), and (*E*)-4,4′-(ethene-1,2-diyl)bis(2,6-dimethoxyphenol) (**3**) were synthesized from *p*-coumaric, ferulic, and sinapic acid, respectively. This was accomplished with a high-yielding two-step approach, which combined catalyst-free thermal decarboxylation of the cinnamic acids followed by olefin metathesis. The thermal decarboxylation proceeded in quantitative yield merely by refluxing the cinnamic acids in DMF under a nitrogen atmosphere. The resulting vinyl phenols were briefly isolated and then immediately subjected to olefin metathesis with a Grubbs−Hoveyda 2nd generation catalyst, which resulted in direct precipitation of the bisphenols from the reaction mixture. Overall yields of **1**, **2**, and **3** were 92, 88, and 85%, respectively, starting from the cinnamic acids. The compounds were isolated as pure solids without the need for crystallization or column chromatography. Bisphenol **1** was isomerized to the *cis*-isomer by irradiation with UV light. The resulting 80 : 20 *cis* : *trans* mixture exhibited a glass transition at low temperatures and a decreased melting temperature. To further expand the suite of bisphenols that can be produced from cinnamic acids, *p*-coumaric acid was directly converted into a 4-vinylphenol dimer by thermal decarboxylation/dimerization in a biphasic aqueous base/toluene solution to yield (*E*)-4,4′-(but-1-ene-1,3-diyl)diphenol (**4**). The ability to efficiently produce bisphenols from abundant, low-cost, and easily sourced bio-based substrates holds great promise for the development of more sustainable polymers.

Sustainability spotlight

Bisphenol A (BPA) is an important industrial chemical building block for polycarbonates, coatings, and structural composite materials. However, the derivation of this molecule from petrochemical sources and the negative health impacts of BPA necessitate a transition to more sustainable and less toxic molecules that can be derived from biomass substrates using efficient synthetic methods. To accomplish this goal, we developed an atom economic process for the conversion of hydroxycinnamic acids (readily obtained from lignin) to bisphenols through a two-step method consisting of catalyst-free decarboxylation followed by olefin metathesis. This work aligns with several UN sustainable development goals including: health/well-being (SDG 3), sustainable industrialization (SDG 9), responsible production (SDG 12), climate change (SDG 13) and sustainable terrestrial ecosystems (SDG 14).

Introduction

Bisphenols, such as bisphenol A (BPA; 2,2-bis(4-hydroxyphenyl) propane), are commodity chemicals used in the synthesis of polyethers, polycarbonates, and epoxy resins.[1,2] However, most bisphenol-based polymers are made from petroleum sources and not widely recycled, which leads to significant negative impacts on the environment.[3,4] Further, the synthesis of BPA-like bisphenols results in the formation of isomeric and oligomeric products and requires several equivalents of phenol.[5,6] This unsustainable and low atom-economy synthetic route, along with the documented health risks of BPA and similar bisphenols,[7–9] has inspired the study of lower toxicity, sustainable alternatives that can be derived from biomass feedstocks in an efficient manner.[2,10]

Processing biomass to access platform chemicals is a key strategy for producing sustainable materials. Important feedstocks such as fatty acids, phenols, and hydrocarbons can be produced through the valorization or fermentation of biomass substrates and used for the preparation of fuels, polymers, and composite materials.[11–13] A number of studies have demonstrated that bio-based bisphenols are useful synthons for the production of sustainable thermoplastics and thermosetting resins.[14–17] This previous work includes studies on cyanate ester resins and polycarbonates based on bisphenols derived from

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vanillin, eugenol, and resveratrol.[16,18–23] Recently, several groups have reported bio-based bisphenols with little to no estrogenic effects when compared to BPA.[24–29] The presence of sterically hindering functional groups (*e.g.* methoxy) *ortho* to the phenolic –OH groups appears to reduce estrogenic effects by preventing binding at the active sites of estrogen receptors.[26]

Hydroxycinnamic acids such as *p*-coumaric, ferulic, and sinapic acid are phenolic compounds that can be isolated from lignin and used as valuable synthons for the preparation of bisphenols and polymeric materials.[30–32] These α,β-unsaturated carboxylic acid functionalized phenols are ubiquitous components of the cell walls of plants and have previously been utilized to generate polymers with remarkable thermal properties,[33,34] biodegradability,[35,36] and liquid crystallinity.[36–38] Hydroxycinnamic acids can be efficiently extracted from woody biomass with purities of up to 99%. Extraction can be conducted through alkaline[39–42] or enzymatic hydrolysis[43,44] followed by solvent extraction,[45,46] adsorption onto nanomaterials or membranes,[47,48] or counter-current chromatography (Fig. 1).[49,50] Decarboxylation of these hydroxycinnamic acids followed by dimerization of the subsequent vinyl phenols is an intriguing approach for the formation of sustainable bisphenols. However, procedures for synthesizing bisphenols from hydroxycinnamic acid bio-feedstocks typically require metal catalysts[51,52] or enzymes[53–56] for the initial decarboxylation step. Few examples of catalyst-free thermal decarboxylation of cinnamic acids exist. However, recently, Yang and coworkers synthesized various functionalized 4-vinylphenols from hydroxycinnamic acids by heating dilute solutions of the acids in *N,N*-dimethylformamide (DMF), above the boiling point, in sealed reactors.[57] This approach eliminated the need for catalysts or other additives, but may be difficult to scale-up due to the use of low concentrations and elevated pressures.

Dimerization of 4-vinylphenols to yield bisphenols can be accomplished through Ru-catalyzed olefin metathesis.[56,58] Our group has previously employed this approach for the synthesis of high-performance renewable thermosets and thermoplastics from eugenol.[16] Recently, Baraibar and coworkers developed a one-pot cascade reaction to synthesize bisphenols directly from hydroxycinnamic acids. The decarboxylation step was accomplished with a phenolic acid decarboxylase derived from *Bacillus subtilis*.[56] The Ru-catalyst loading for the dimerization

step was quite high (5%), which would ultimately limit sustainability and scalability due to the cost and scarcity of ruthenium. The scalability of the reported approach was further hindered by the need for flash chromatography to purify the bisphenol products. Finally, the enzymatic approach failed to catalyze the decarboxylation of the highly-substituted sinapic acid.

To develop an efficient and sustainable pathway for the synthesis of bisphenols from naturally abundant hydroxycinnamic acid feedstocks, this work describes the catalyst-free thermal decarboxylation of the acids followed by Ru-catalyzed olefin metathesis to afford bisphenol compounds in outstanding yields (Scheme 1a). In addition, a second thermal dimerization route was studied for *p*-coumaric acid that eliminated the need for a metal catalyst (Scheme 1b). To further
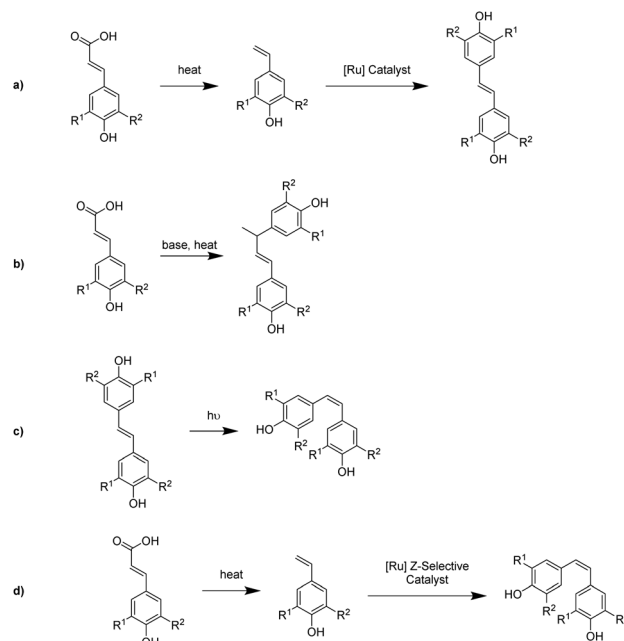
Scheme 1 Synthesis of bio-based bisphenols from hydroxycinnamic acids through (a) catalyst-free decarboxylation and Ru-catalysis, (b) thermal dimerization, (c) photoisomerization of *trans*-bisphenols to *cis*-isomers, and (d) direct conversion of vinyl phenols to *cis*-isomers using a *Z*-selective catalyst.
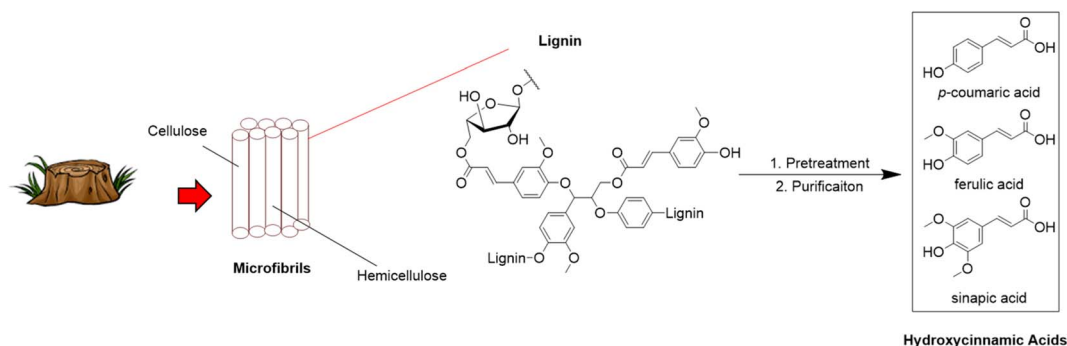

Fig. 1 Extraction of hydroxycinnamic acids from biomass-derived lignin.

diversify the products obtainable from hydroxcinnamic acids, we studied the photochemical isomerization of the *trans*-stilbene isomer derived from *p*-coumaric acid to generate the *cis*-isomer (Scheme 1c). We also attempted the direct synthesis of the *cis*-isomer from 4-vinylphenol using a *Z*-selective olefin metathesis catalyst (Scheme 1d).

Experimental details

General considerations

Unless otherwise noted, all reagents were purchased and used as received from the manufacturer without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL 400 MHz spectrometer. All NMR chemical shifts are reported in ppm downfield from tetramethylsilane and are referenced relative to the NMR solvent according to the literature values: ^{1}H NMR ($CDCl_3$ = 7.26 ppm, DMSO-d_6 = 2.50 ppm, $(CD_3)_2CO$ = 2.05 ppm); ^{13}C NMR ($CDCl_3$ = 77.16 ppm, DMSO-d_6 = 39.52 ppm, $(CD_3)_2CO$ = 29.84 ppm). Olefin metathesis reactions were prepared and performed under an inert atmosphere of N_2 using either a Schlenk line or glovebox.

Synthesis of (*E*)-4,4′-(ethene-1,2-diyl)diphenol from *p*-coumaric acid (1)

In a 250 mL round bottom flask, *p*-coumaric acid (50 g, 0.3 mol) was dissolved in 100 mL of DMF. The flask was fitted with a condenser and heated to reflux with vigorous stirring for 6 h. The flask was then cooled to ambient temperature and the solution poured into water (1 L). This mixture was then extracted with 3 × 200 mL EtOAc and washed with water (100 mL) followed by a 5% LiCl solution (2 × 200 mL) to remove excess DMF. The organic layer was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to yield a yellow solid. In a nitrogen-filled glovebox, Hoveyda–Grubbs Catalyst® M720 (1.91 g, 1 mol%) and toluene (160 mL) were added to the residue. The resulting dark red solution was then transferred to a Schlenk line and stirred at 80 °C for 18 h. The product rapidly started precipitating out of solution. After the reaction was complete, the solid was collected on a frit, rinsed with hexanes, and dried under reduced pressure to afford a tan powder (29.70 g, 0.140 mol, 92% yield). The NMR data were consistent with literature reports.[59] mp. 284–290 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.46 (s, 2H, Ar-O*H*), 7.34 (d, *J* = 8.6 Hz, 4H, Ar-*H*), 6.86 (s, 2H, C(sp^2)-*H*), 6.74 (d, *J* = 8.6 Hz, 4H, Ar-*H*), ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.3, 129.1, 127.9, 125.7, 116.0.

Synthesis of (*E*)-4,4′-(ethene-1,2-diyl)bis(2-methoxyphenol) (2) from ferulic acid

In a similar manner to the procedure described above, ferulic acid (5 g, 0.026 mol) was decarboxylated in DMF to yield a yellow oil. In an N_2 filled glovebox, Hoveyda–Grubbs Catalyst® M720 (0.161 g, 1 mol%) and toluene (30 mL) were added to the residue. The metathesis reaction was conducted as described above to afford 3.08 g of product (88%) as a tan solid. The NMR data were consistent with literature reports.[60] mp. 217–220 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.03 (s, 2H, Ar-O*H*), 7.14 (s, 2H, Ar-*H*), 6.93 (d, *J* = 9.5 Hz, 4H, Ar-*H*), 6.75 (d, *J* = 7.7 Hz, 2H, 2× C(sp^2)-*H*), 3.82 (s, 6H, OC*H*$_3$), ^{13}C NMR (100 MHz, DMSO-d_6) 146.8, 145.4, 130.3, 126.6, 120.2, 114.6, 108.1, 56.0.

Synthesis of (*E*)-4,4′-(ethene-1,2-diyl)bis(2,6-dimethoxyphenol) (3) from sinapic acid

In similar manner to the procedure described above, sinapic acid (5 g, 0.022 mol) was decarboxylated in refluxing DMF (20 mL). After the standard workup, the resulting vinylphenol was isolated as a yellow oil. In an N_2-filled glovebox, Hoveyda–Grubbs Catalyst® M720 (0.140 g, 1 mol%) and toluene (30 mL) were added to the residue. The metathesis reaction was conducted as described above to yield 3.15 g of the product (85%) as a tan solid. The NMR data were consistent with literature reports.[61] mp. 256–261 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.40 (s, 2H, Ar-O*H*), 6.99 (s, 2H, C(sp^2)-*H*), 6.84 (s, 4H, Ar-*H*), 3.81 (s, 12H, -OC*H*$_3$), ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.3, 134.6, 133.4, 128.1, 103.6, 79.8, 77.4, 59.2, 55.9.

Synthesis of (*E*)-4,4′-(but-1-ene-1,3-diyl)diphenol (4)

To a 250 mL round-bottomed flask equipped with a reflux condenser, 4-hydroxycinnamic acid (4.92 g, 0.03 mol), toluene (75 mL), and NaOH (1.26 g, 0.0315 mol) in DI water (45 mL) were added under nitrogen. The bilayered solution was stirred vigorously and refluxed for 24 hours. After allowing the mixture to cool, the aqueous phase was neutralized and extracted with ethyl acetate (3 × 100 mL). The organic phase was collected, dried with anhydrous $MgSO_4$, filtered, and the solvent removed under reduced pressure to obtain a viscous oil containing the 4-hydroxystyrene dimer along with some oligomeric material (1.95 g, 54% yield). The crude material was then purified *via* column chromatography (R_f: 0.48, 1 : 1 EA : Hex) to afford the product as a white solid. The NMR data were consistent with literature reports.[62] mp. 210–214 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.24 (s, 1H, O*H*), 8.04 (s, 1H, O*H*), 7.21 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.06 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 6.73 (dd, *J* = 8.5, 3.3 Hz, 4H, Ar-*H*), 6.31–6.15 (m, 2H, C(sp^2)-*H*), 3.48 (m, 1H, C*H*), 1.32 (d, *J* = 7.3 Hz, 3H, C*H*$_3$) ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.1, 156.0, 136.5, 133.0, 130.4, 128.7, 128.3, 127.7, 127.6, 115.8, 115.6, 44.5, 22.2.

Photochemical isomerization of 1

500 mg of **1** were added to a 100 mL quartz flat-bottom flask. Dry MeCN (50 mL) was then added and the mixture sparged with N_2 for 45 min. The flask was then placed in a Luzchem® LZC-4V photoreactor fitted with fourteen 355 nm, 8 W fluorescent lamps and irradiated with stirring for 2 h. The reaction mixture was then filtered and the filtrate concentrated under reduced pressure to yield a viscous oil. Approximately 3 mL of MeCN were added to the residual oil, which resulted in dissolution of most of the product along with precipitation of **1** as a tan solid. The solid was collected on a fine fritted funnel and the filtrate was then concentrated under reduced pressure to yield an 8 : 2 mixture of *cis* : *trans* **1** as a viscous brown oil (455 mg, 91% yield). mp. 256–259 °C. ^{1}H NMR of the *cis*-isomer (400 MHz,

$(CD_3)_2CO)$ δ 8.35 (s, 2H, Ar-OH), 7.08 (d, $J = 8.54$ Hz, 4H, Ar-H), 6.69 (d, $J = 8.5$ Hz, 4H, Ar-H), 6.35 (s, 2H, C(sp^2)-H).

Results and discussion

We began our study with *p*-coumaric acid, an unsubstituted hydroxycinnamic acid, as a model substrate for optimization of reaction conditions. Unlike previous work, the decarboxylation of *p*-coumaric acid was not conducted in a sealed tube but instead was conducted under atmospheric pressure in a round-bottom flask equipped with a condenser.[57] *p*-Coumaric acid was dissolved in DMF and heated to reflux. After one hour, we observed a 41% conversion of the hydroxycinnamic acid. Running the reaction for 4 hours resulted in a 56% conversion and 6 hours yielded full conversion of the starting material.

After a standard workup, crude 4-vinylphenol was obtained as an off-white solid contaminated with residual DMF. Uninhibited 4-vinylphenol partially polymerized overnight, even at reduced temperature (4 °C), which greatly reduced the yield for the subsequent homometathesis step (Table 1, entry 1). To remedy this issue, the vinyl phenol was immediately allowed to react with Grubbs 2nd generation catalyst M204 (1 mol%) in toluene at 80 °C to obtain the desired bisphenol [(*E*)-4,4′-(ethene-1,2-diyl)diphenol] (**1**) in 29% yield. The product directly precipitated from the reaction solution and could be isolated in high purity without recrystallizing the product or subjecting it to column chromatography (Table 1, entry 2). Scale-up of the reaction to 50 g of *p*-coumaric acid resulted in a similar (30%) yield of the bisphenol (Table 1, entry 3). These initial results were promising, but the modest yield of the bisphenol was of concern due to the low carbon efficiency and sustainability of the process.
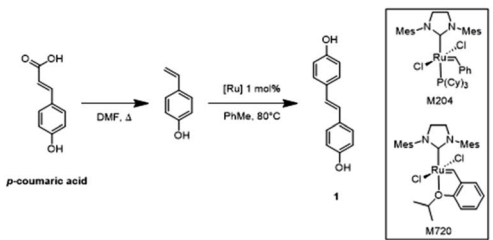
Several studies have shown that DMF, even in small quantities, can be problematic for [Ru]-catalyzed olefin metathesis due to coordination of DMF to the metal center and subsequent inhibition of the catalyst.[63] To mitigate this issue, the organic layer from the decarboxylation step was carefully washed with a 5% aqueous LiCl solution to drive off any residual DMF. To further enhance the yield of the product, the second generation Hoveyda–Grubbs Catalyst® M720 (1 mol%), a more stable catalyst, was used for the metathesis reaction. This allowed us to obtain a 92% overall yield of **1** (from *p*-coumaric acid) at the 50 g scale (Table 1, entry 4). In a similar fashion to the initial reactions, the product readily precipitated from the reaction mixture and was isolated simply by filtration followed by solvent washing. Reducing the catalyst loading to 0.1% resulted in a 65% yield of bisphenol (Table 1, entry 5), representing a minimum turnover number (TON) of 650. Previous work has shown that catalyst loadings as low as 0.009 mol%, an order-of-magnitude lower than demonstrated here, are effective for the synthesis of *trans*-stilbene from styrene.[64,65] In the current case, the presence of acidic phenolic groups and the purity of the substrate limit the TON. Protection of the phenolic groups and/or purification of the vinyl phenol through column chromatography would likely allow for an increased TON, but at the expense of additional synthetic complexity as well as increased solvent, reagent, and energy use, which would dramatically reduce the sustainability of our approach.

Application of the optimized reaction conditions to ferulic acid resulted in an 88% yield of (*E*)-4,4′-(ethene-1,2-diyl)bis(2-methoxyphenol) (**2**) (Scheme 2). These conditions were also effective for the decarboxylation/metathesis of the stubborn sinapic acid, affording an 85% overall yield of (*E*)-4,4′-(ethene-1,2-diyl)bis(2,6-dimethoxyphenol) (**3**) (Scheme 2). Suitable crystals for X-ray analysis of **3** were obtained *via* slow evaporation of dichloromethane. The X-ray structure (Fig. 2) confirmed a planar molecule with the expected *trans* orientation. Close non-bonded interactions designated as non-classical hydrogen bonds (C–H–π) were observed between alkene and phenyl hydrogens and the oxygens of the hydroxyl and methoxy groups of a neighboring molecule (Fig. S7†).

Differential Scanning Calorimetry (DSC) analysis of the bisphenols revealed melting points of 280 °C, 215 °C, and 250 °C for compounds **1**, **2**, and **3** respectively (Fig. S1–S3†). These melting points were confirmed using a Mel-Temp apparatus. High melting points of bisphenols can be detrimental to the processability of derivative thermosetting resins. One way to decrease the melting point is through isomerization of the *trans*-stilbene moiety to the *cis*-isomer.[66] This can be

Table 1 Optimization of reaction conditions for the synthesis of bisphenols from hydroxycinnamic acids

Entry	Scale of *p*-coumaric acid	5% LiCl (aq) wash	Ru-catalyst	Catalyst loading (%)	Yield of **1**
1^a	5 g	No	M204	1	Trace
2	5 g	No	M204	1	29%
3	50 g	No	M204	1	30%
4	50 g	Yes	M720	1	92%
5	5 g	Yes	M720	0.1	65%

^{a} Vinylphenol left overnight in the solid phase.
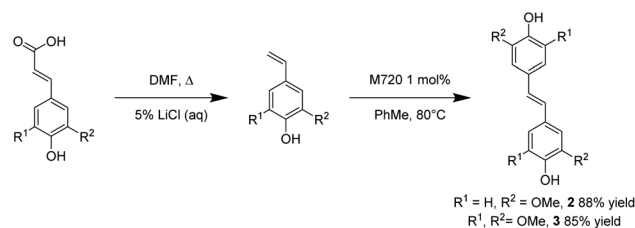
Scheme 2 Synthesis of bisphenols from sinapic and ferulic acid using optimized reaction conditions.
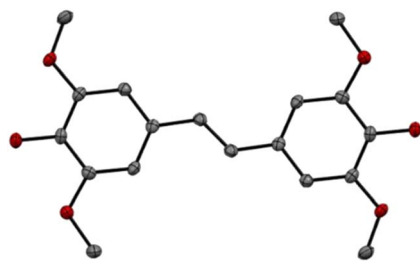
Fig. 2 X-ray structure of **3** with thermal ellipsoids at 50% probability.

accomplished through irradiation of the compound with UV light.[67,68] To this end, we subjected **1** in dry, degassed MeOH to 355 nm light in a photoreactor for 24 h to obtain a mixture of the *cis*- and *trans*-bisphenol. Under these conditions, several diastereomeric dimers were formed by [2 + 2]-cycloaddition (Scheme 3) and observed as a series of doublets in the ^{1}H NMR spectrum of the mixture (Fig. S18†). It has previously been reported that cyclobutanes and phenanthrenes can be made from stilbenes when irradiated in methanol for long periods of time.[69,70] To avoid these side reactions, acetonitrile was used as the solvent and the photochemical reaction was limited to two hours. This resulted in an 8 : 2 *cis* : *trans* mixture (Scheme 3) with no detectable formation of cyclobutane-containing products. Thermal analysis of this material revealed a complex DSC with an apparent glass transition at 3 °C and a depressed melting point compared to **1** (Fig. S5†). It's unclear how this difference will impact the properties of derivative polymers, but one would expect it to have a positive effect on processability. Efforts to obtain a pure *cis* isomer from the 8 : 2 product mixture *via* column chromatography or fractional crystallization were unsuccessful. In an effort to establish a more direct route to the *cis*-isomer, we attempted the metathesis reaction of 4-vinylphenol with a *Z*-selective Grubbs catalyst, M2001. Unfortunately, the catalyst decomposed under the standard reaction conditions and none of the *cis*-isomer was produced. This result was attributed to catalyst sensitivity to the hydroxyl groups of the vinyl phenol.

To further expand on the suite of bisphenols accessible from hydroxycinnamic acids, we explored a catalyst-free pathway utilizing thermal decarboxylation/dimerization to generate (*E*)-4,4′-(but-1-ene-1,3-diyl)diphenol (**4**) from *p*-coumaric acid (Scheme 1b), R[1] = R[2] = H. Initially, an overnight neat thermal dimerization at 120 °C in the presence of a radical inhibitor was attempted from pure 4-vinylphenol isolated as described above. However, the vinyl phenol underwent spontaneous polymerization to generate poly(4-vinylphenol) (PVP) (Scheme 4, Fig. S16 and S17†),[71,72] which plays an important role in the electronics
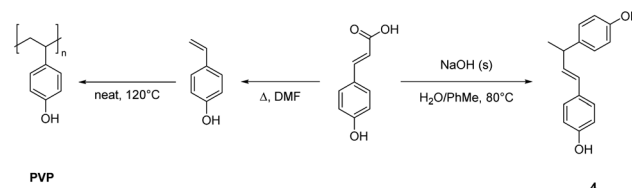

Scheme 4 Thermal dimerization of *p*-coumaric acid.

industry and is utilized in dielectric, photoresist, and energy storage based applications.[73] DSC of the PVP showed a T_g of 170 °C while gel permeation chromatography (GPC) indicated an M_w of 16 570 with a dispersity index (M_w/M_n) of 2.0. In an attempt to increase the selectivity to dimer, a modified metal-free regioselective dimerization procedure was then attempted utilizing a catalytic amount of a Brønsted acid in a ketone-based solvent system.[62] 4-Vinylphenol generated from *p*-coumaric acid was dissolved in either 3-pentanone or cyclopentanone (1 : 1) with a catalytic amount of *p*-toluene sulfonic acid (PTSA) (1 : 12). The reaction was conducted at various times and temperatures ranging from 1–24 hours and room temperature to 120 °C, but consistently yielded a polymerized product upon workup.

Previous studies by Hosoda *et al.* demonstrated decarboxylative coupling of 4-hydroxycinnamic acids in the presence of base catalysts, using a biphasic (water/toluene) solvent system.[74] Using a similar approach, *p*-coumaric acid was heated overnight in a biphasic aqueous sodium hydroxide/toluene mixture to yield the dimer as a white solid (Scheme 4). This coupling can be accomplished in a single step under moderate reaction conditions, but suffers from a modest yield and the need to purify the product by either column chromatography or crystallization. The three-carbon bridge between the aromatic rings could reduce the T_g of derivative thermosetting resins, but the greater flexibility of the linkage may allow for the isolation of more processable monomers.

Conclusions

This work describes efficient methods for the conversion of hydroxycinnamic acids to a family of bisphenols. The ability to derive the starting materials from abundant biomass sources opens the door to large scale production of sustainable building blocks that can be used for a variety of applications including coatings, structural composites, electronic devices, food packaging and optical devices. In addition to the sustainability of the approach, bisphenols derived from ferulic and sinapic acid are expected to have reduced estrogenic effects due to the methoxy groups *ortho* to the phenolic –OH groups. Future work on these materials should include the synthesis and characterization of various thermosetting resins and thermoplastic polymers generated from the bisphenols as well as efforts to reduce catalyst loadings for bisphenol synthesis and/or the exploration of metathesis catalysts based on cheaper and more abundant transition metals. To further enhance the sustainability of our approach, it would be interesting to explore alternatives to DMF and toluene for the synthesis of the bisphenols. In particular,
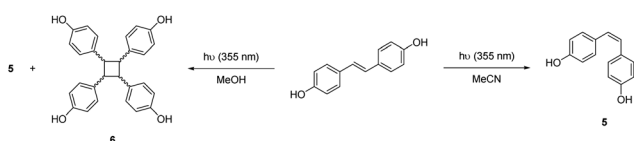
Scheme 3 Photoisomerization of **1** to *cis* isomer **5**.

the use of a bio-based solvent (*e.g.* 2-methyltetrahydrofuran) for the metathesis reactions would be a simple approach to reduce the carbon intensity of the process. Other topics may include the study of more efficient, catalyst-free routes to the thermal dimer as well as hydrogenated bisphenols derived from bisphenols 1–4. Studies along these lines are ongoing in our laboratory.

Author contributions

Cristian Zavala: investigation, methodology, writing-original draft. Natalie Vest: investigation. Joshua Baca: investigation, writing-review and editing. Derek Zhang: investigation. Randall McClain: investigation. Benjamin Harvey: conceptualization, supervision, writing-review and editing.

Conflicts of interest

There are no conflicts to declare.

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